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Ru(II) POLYPYRIDINE COMPLEXES: PHOTOPHYSICS, PHOTOCHEMISTRY, ELECTROCHEMISTRY, AND CHEMILUMINESCENCE

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CONTENTS

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A. INTRODUCTION

(i) Scope and limitations

$Ru(bpy)_3^{2+}$ has certainly been one of the molecules most extensively studied and most widely used in research laboratories during the last ten years. A unique combination of chemical stability, redox properties, excited state reactivity, luminescence emission, and excited state lifetime has attracted the attention of many research workers first on this molecule and then on some several hundred of its derivatives. The great interest generated by the studying of this class of complexes has stimulated the growth of several branches of pure and applied chemistry. In particular, the Ru(II) polypyridine complexes have played and are still playing a key role in the development of photochemistry, photophysics, photocatalysis, electrochemistry, photoelectrochemistry, chemi- and electrochemi-luminescence, and electron and energy transfer.

The aims of this review are (i) to collect data concerning the absorption and emission spectra and the electrochemical, photochemical, and photophysical properties of the Ru(II) polypyridine complexes in solution, and (ii) to discuss briefly some selected topics related to the excited state properties of these complexes. In an introductory section we have illustrated some fundamental concepts which are needed in order to understand the scope of the material reviewed. The literature coverage concerning the electrochemical, photochemical and photophysical data has been quite extensive and much effort has been made to provide tables where the available data can be easily found.

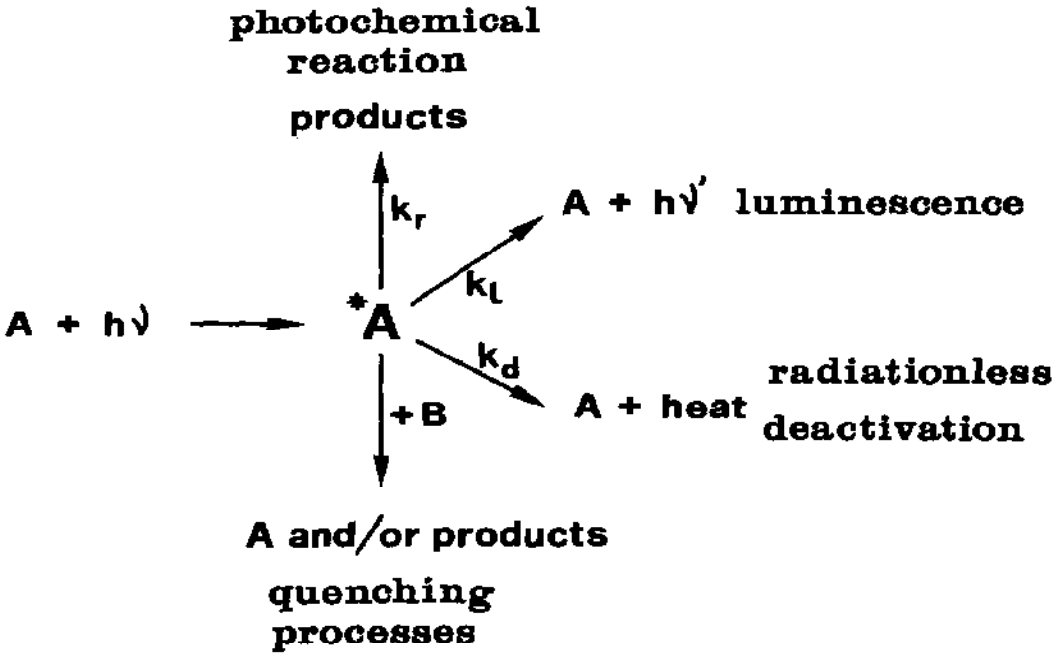

Fig. 1. Schematic representation of excited state deactivation processes.

(ii) Photochemical and photophysical processes

The first act of any photochemical and photophysical process is the absorption of a photon by a molecule. The excited state that is formed in this way is a high energy, unstable species which must undergo some type of deactivation. As shown in Fig. 1, excited state deactivation can occur via (i) disappearance of the original molecule (photochemical reaction), (ii) emission of light (luminescence), (iii) degradation of the excess energy into heat (radiationless deactivation), and (iv) some type of interaction with other species present in the solution (quenching process).

As is well known from electronic spectroscopy [1–5], the probability of light absorption (and thus the intensity of the correspondent absorption band) is related to the characteristics of the states involved and particularly to their spin quantum number. Transitions from the ground state to excited states having the same spin value are allowed and give rise to intense bands, whereas transitions to excited states of different spin value are forbidden and can hardly be observed in the absorption spectra. In most molecules the ground state is a singlet and the lowest excited state is a triplet that cannot be directly populated by light absorption but can be obtained from the

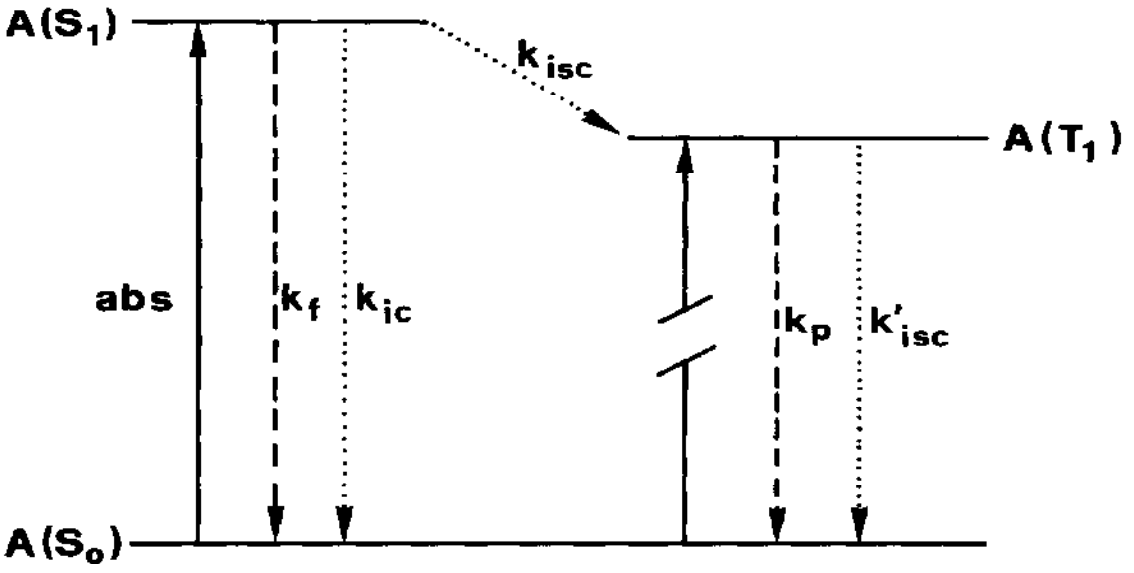

Fig. 2. Schematic Jablonski diagram showing the various deactivation processes. k_g, k_{ic}, k_{isc}, k_p, and k'_{isc} are the unimolecular rate constants for fluorescence, internal conversion, $S_1 \rightarrow T_1$ intersystem crossing, phosphorescence, and $T_1 \rightarrow S_0$ intersystem crossing, respectively.

deactivation of upper excited states. For this reason, at least three states (e.g., ground state singlet and excited singlet and triplet) are involved in a photochemical process, as is shown in the Jablonski diagram of Fig. 2. Emission of light (luminescence) is called fluorescence or phosphorescence depending on whether the excited state has the same or different spin compared to the ground state. In the same way, radiationless deactivation is called internal conversion when it occurs between states of the same spin and intersystem crossing when it occurs between states of different spin. Fluorescence and internal conversion are spin-allowed steps, whereas phosphorescence and intersystem crossing are spin-forbidden steps. Each intramolecular decay step is characterized by its own rate constant (Fig. 2) and each excited state is characterized by its lifetime, given by

$$\tau = 1/\sum_i k_i \tag{1}$$

where k_i is the first order rate constant for a generic unimolecular process that causes the disappearance of the excited state [3,4,6,7]. For each process one can define the quantum yield, which is the ratio between the number of moles of species (photons or molecules) produced and the number of

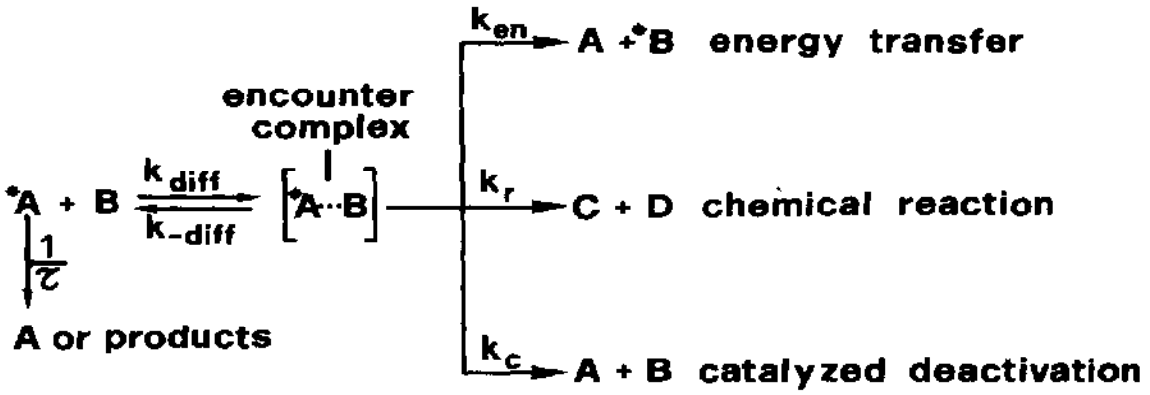

Fig. 3. Schematic representation of bimolecular processes that may take place following an encounter between an excited state and another chemical species.

einsteins that have been absorbed. A particularly important quantity is the quantum yield of emission from the lowest spin-forbidden excited state (phosphorescence quantum yield, Φ_p) which, making reference to Fig. 2, can be expressed by the following equation

$$\Phi_p = \eta_{isc} k_p \tau_{T_1} \tag{2}$$

In this equation, η_{isc} is the efficiency of population of the emitting excited state from the state populated by light absorption:

$$\eta_{isc} = k_{isc}/(k_{isc} + k_f + k_{ic}) \tag{3}$$

and τ_{T_1} is the lifetime of the emitting excited state

$$\tau_{T_1} = 1/(k_p + k'_{isc}) \tag{4}$$

When the intramolecular deactivation steps are not too fast, i.e. when the lifetime of the excited state (eqn. 1) is sufficiently long, the excited molecule may have a chance to encounter a molecule of another solute, B (Fig. 1). In such a case, some specific interaction may occur (Fig. 3) and the process taking place is called a bimolecular process [6–9]. Simple kinetic arguments show that only those excited states that live longer than $\sim 10^{-9}$ s may have a chance to be involved in encounters with other solute molecules. For transition metal complexes, only the lowest spin-forbidden excited state satisfies this requirement.

The most important bimolecular processes are energy transfer [4,7,9,10] and electron transfer [4,7–9,11]; the latter process may involve either the oxidation or the reduction of the excited state

$$*A + B \xrightarrow{k_{en}} A + *B \qquad \text{energy transfer} \tag{5}$$

$$^*A + B \xrightarrow{k_{ox}} A^+ + B^- \qquad \text{oxidative electron transfer} \qquad (6)$$

$$^*A + B \xrightarrow{k_{red}} A^- + B^+ \qquad \text{reductive electron transfer} \qquad (7)$$

The ability of an excited state to intervene in energy transfer processes is related to its zero–zero spectroscopic energy, E^{0-0}. For the electron transfer processes, the relevant thermodynamic parameters are the oxidation (eqn. 6) and reduction (eqn. 7) potentials of the $^*A/A^+$ and $^*A/A^-$ couples. Because of its higher energy content, an excited state is both a stronger reductant and a stronger oxidant than the corresponding ground state. To a first approximation, the redox potentials for the excited state couples may be calculated from the potentials of the ground state couples and the zero–zero excitation energy E^{0-0}:

$$E(A^+/^*A) = E(A^+/A) - E^{0-0} \qquad (8)$$

$$E(^*A/A^-) = E(A/A^-) + E^{0-0} \qquad (9)$$

Figure 4 shows schematically some quantities that characterize an excited state from the point of view of energy and electron transfer processes. Kinetic parameters (i.e., intrinsic barrier and electronic transmission coefficient) can also play an important role in energy and electron transfer processes, as is discussed in detail in the next Section.

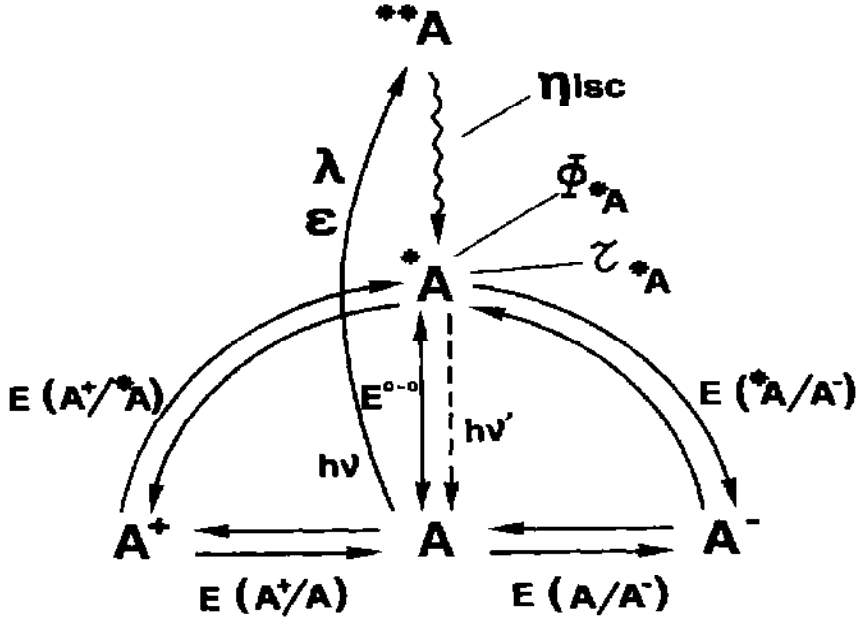

Fig. 4. Schematic diagram showing the molecular quantities relevant for energy and electron transfer processes.

(iii) Kinetics of energy and electron transfer processes

Ru(II) polypyridine complexes are extensively used in energy and electron transfer processes [8,9,11–16]. An important aim of these studies is the elucidation of the factors that govern the reaction rates.

Outer-sphere electron transfer (regardless of the ground or excited state nature of the reactants) [8,9,17–20] and exchange energy transfer [9,10] are closely related processes that can be dealt with by the same formalism [21]. Using an excited state electron transfer reaction as an example [18]

$$^*D + A \xrightarrow{k_{exp}} D^+ + A^- \tag{10}$$

the reaction rate can be discussed on the basis of the mechanism shown in the scheme of Fig. 5, where k_d, k_{-d}, k'_d, and k'_{-d} are rate constants for formation and dissociation of the outer-sphere encounter complex, k_e and k_{-e} are unimolecular rate constants for the electron transfer step involving the excited state, and $k_e(g)$ and $k_{-e}(g)$ are the corresponding rate constants for the ground state electron transfer step. A simple steady state treatment shows that the experimental rate constant of eqn. (10) can be expressed as a function of the rate constants of the various steps

$$k_{exp} = \frac{k_d}{1 + \frac{k_{-d}}{k_e} + \frac{k_{-d}}{k_x}\frac{k_{-e}}{k_e}} \tag{11}$$

where k_x may often be replaced by k'_{-d} (for more details, see ref. 18). Using a classical approach, k_{-e}/k_e is given by $\exp(\Delta G/RT)$, where ΔG is the free energy change of the electron transfer step. The key step of the process is, of course, the electron transfer step and the essence of the problem is the fact that the equilibrium nuclear configuration of a species changes when it gains or loses an electron (or electronic energy) [19]. For transition metal complexes in fluid solution this configuration change may involve changes in metal–ligand bond and intraligand bond lengths and angles and, at least in

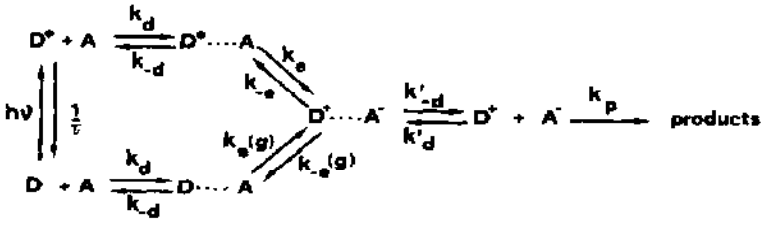

Fig. 5. Detailed mechanism for an electron transfer process involving an excited state reactant (see text).

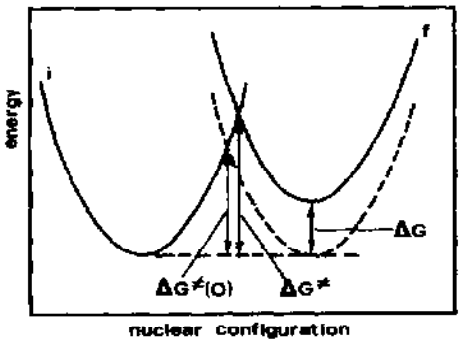

Fig. 6. Representation of an outer-sphere electron transfer process using energy curves: curves i and f correspond to the precursor ($D^* \cdots A$) and successor ($D^+ \cdots A^-$) complexes of Fig. 5. For more details, see text.

the case of electron transfer, changes in the vibrations and rotations of solvent dipoles. Since electronic motions are much faster than nuclear motions (Franck–Condon principle), in a classical approach an adjustment of the nuclear configuration prior to electron (or energy) transfer is required. This gives rise to an activation barrier, $\Delta G^{\neq}$, as shown in Fig. 6. Once a suitable nuclear configuration has been reached, whether or not electron (or energy) transfer occurs is a matter of electronic factors (adiabaticity problem [19,22]).

Using a classical approach, the rate constant of electron transfer can be given by

$$k_e = \kappa \nu_n \exp(-\Delta G^{\neq}/RT) \tag{12}$$

where κ is the electronic transmission coefficient, ν_n is an effective frequency for nuclear motion, and $\Delta G^{\neq}$ is the free activation energy, which may be expressed by a free energy relationship like the classical Marcus quadratic equation [19,23]

$$\Delta G^{\neq} = \Delta G^{\neq}(0)\{1 + [\Delta G/4\Delta G^{\neq}(0)]\}^2 \tag{13}$$

or empirical equations like [18,24,25]

$$\Delta G^{\neq} = \Delta G + \frac{\Delta G^{\neq}(0)}{\ln 2}\left[1 + \exp\left(-\frac{\Delta G \ln 2}{\Delta G^{\neq}(0)}\right)\right] \tag{14}$$

where $\Delta G^{\neq}(0)$ is the so-called intrinsic nuclear barrier (Fig. 6). For a homogeneous series of reactions [18,26,27], such as those between the same reductant $^*D$ and a series of structurally related oxidants A_1, A_2, A_3... (or vice versa) that have variable redox potential but the same size, shape, electronic structure and electric charge, one can assume that throughout the series the reaction parameters k_d, k_{-d}, k'_{-d} in eqn. (11), κ and ν_n in eqn.

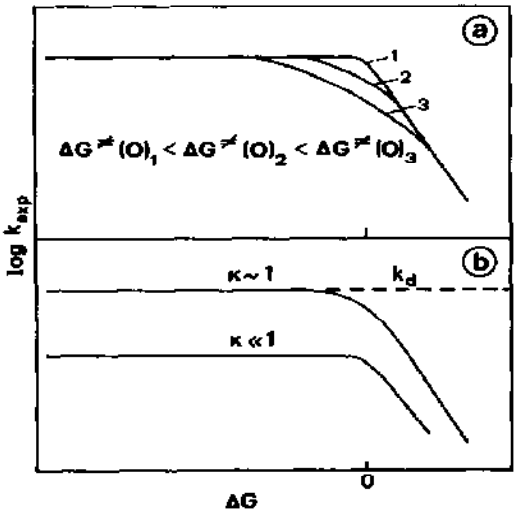

Fig. 7. Expected log k_{exp} vs. ΔG plots for a homogeneous series of outer-sphere electron transfer reactions, according to eqns. (11), (12), and (14). (a) Effect of the intrinsic barrier $\Delta G^{\neq}(0)$; (b) effect of the transmission coefficient κ.

(12) and $\Delta G^{\neq}(0)$ in eqn. (14) are constant. Under these assumptions, k_{exp} (eqn. 11) is only a function of ΔG and a log k_{exp} vs. ΔG plot will exhibit the following features (Fig. 7): (i) an Arrhenius type linear region for sufficiently endergonic reactions; (ii) a more or less wide intermediate region (depending on $\Delta G^{\neq}(0)$) in which log k_{exp} increases in a complex but monotonic way as ΔG decreases, and (iii) a plateau region for sufficiently exergonic reactions when the free energy correlation given by eqn. (14) is used (use of eqn. 13 would predict a decrease of the reaction rate at high exergonicity usually not observed for reactions in fluid solution at room temperature [7,18,28–33]). As shown in Fig. 7, the values of the intrinsic barrier $\Delta G^{\neq}(0)$ strongly influence the values of the rate constant in the intermediate non-linear region, while a lower than diffusion controlled value of the plateau at high exergonicity is related to a low value of the transmission coefficient κ (non-adiabatic behavior). These free energy relationships are extensively used to establish whether a series of quenching reactions take place via energy transfer, reductive electron transfer, or oxidative electron transfer (Section B (vi)). Furthermore, when the values of the other parameters are known, a two-parameter fit of the log k_{exp} vs. ΔG plot to eqns. (11), (12), and (14) may allow, in principle, estimation of the values of $\Delta G^{\neq}(0)$ and κ of the homogeneous series of reactions. When either $\Delta G^{\neq}(0)$ or κ is known from other experimental results (or can be estimated from reasonable assumptions), a more reliable one-parameter fit can be used to estimate the unknown quantity. The model can also be further elaborated [18,22,27,34–37] in an attempt to obtain parameters related to the individual reactants.

(iv) Light as a reactant and light as a product

The class of chemical reactions that plays the most important role in the connection between chemistry and light is that of electron transfer reactions. Ru(II) polypyridine complexes have given a determinant contribution to the recent development of this class of reactions.

When light is used as a reactant (photochemical reaction, eqns. (15) and (16)),

$$A + h\nu \rightarrow {}^*A \tag{15}$$

$${}^*A + B \rightarrow A^+ + B^- \tag{16}$$

there are two possible energetic situations for electron transfer reactions, schematically represented in Fig. 8. The scheme of Fig. 8(a) corresponds to an exergonic dark reaction which is slow for kinetic reasons (high activation energy). Upon light excitation, the reductant A is transformed into the much stronger reductant *A (vide supra), so that the reaction between *A and B is much more exergonic that the reaction between A and B. Since the activation energy generally decreases with increasing exergonicity, the reaction involving the excited state will be much faster than that involving the ground state. In a system of this kind light is simply used to overcome a kinetic barrier and plays the role of a catalyst. The scheme shown in Fig. 8(b) corresponds to the case of a $A + B \rightarrow A^+ + B^-$ dark reaction that cannot take place because of thermodynamic reasons. Light excitation causes the formation of *A which is a reductant much stronger than A, so that the reaction $^*A + B \rightarrow A^+ + B^-$ is thermodynamically allowed. Light

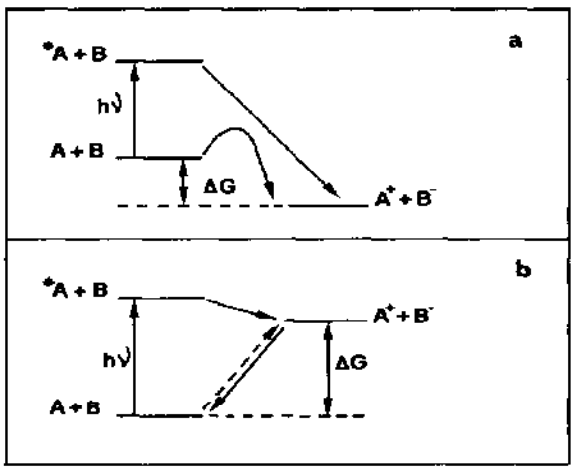

Fig. 8. Schematic representation of the two possible energetic situations for electron transfer reactions involving an excited state reactant. For details see text.

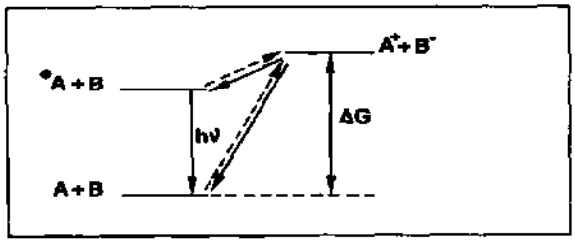

Fig. 9. Schematic representation of the energetic situation needed for generation of an excited state from an electron transfer reaction.

can thus drive A + B to $A^+ + B^-$ via *A + B, and in such a process a fraction of the light energy is converted into chemical energy of the products. The converted energy is released when A^+ and B^- undergo the back electron transfer reaction leading to A + B.

In electron transfer reactions, light can also be involved as a product (chemiluminescent reactions):

$$A^+ + B^- \rightarrow {}^*A + B \tag{17}$$

$$^*A \rightarrow A + h\nu \tag{18}$$

This process can be schematically represented as in Fig. 9, which differs from those shown in Fig. 8 because the energy content of $A^+ + B^-$ is not only higher than that of A + B, but also than that of *A + B. In such a case the reaction from A + B to $A^+ + B^-$ can be driven neither thermally nor photochemically. When A^+ and B^- can be prepared in some other way (e.g., electrochemically) and are mixed together, their electron transfer reaction can lead either to A + B, with complete dissipation of the excess free energy into heat, or to *A + B, with dissipation of a smaller amount of energy. In the latter case, *A can undergo radiative deactivation (luminescence) so that in this reaction a fraction of the available chemical energy is converted into light energy.

From this discussion it is clear that a chemiluminescent process can be considered as the reverse of a photochemical process

$$\underset{\text{photochemistry}}{A + B + h\nu \rightleftarrows {}^*A + B \rightleftarrows A^+ + B^-} \tag{19}$$
$$\text{chemiluminescence}$$

and that the equilibrium represented by eqn. (19) is displaced from left to right or from right to left depending on whether the energetic situation is that depicted in Fig. 8 or in Fig. 9. The availability of a class of compounds (such as those of the Ru(II) polypyridine family) which cover a wide range of redox potentials and excited state energies (Tables 1 and 3) is of course fundamental to the investigation of these processes.

(v) Light absorption and light emission sensitizers

Ru(II) polypyridine compounds are extensively used not only as primary reactants in electron transfer processes involving light (Section A (iv)), but also as mediators of potential photochemical and chemiluminescent processes [38,39].

There are "potential" photochemical reactions that do not occur because the reactants are not able to absorb light and/or because their excited states are too short lived. Consider, for example, a chemical reaction

$$A + B \not\rightarrow A^+ + B^- \tag{20}$$

that cannot occur in the dark because it is endoergonic by, say, 1 eV. In principle, excitation with visible light would made the process thermodynamically allowed (Fig. 8(b)). However, if neither A nor B are able to absorb the exciting light, the reaction cannot occur

$$A + B + h\nu \rightarrow A^+ + B^- \tag{21}$$

This "potential" photochemical reaction can be induced (or sensitized) by a species which possesses specific redox, spectroscopic, and excited state properties. Such species can be called light absorption sensitizers (LAS) [38] and must perform as shown schematically in Fig. 10: (i) it must absorb light so as to give an excited state; (ii) this excited state must be able to oxidize (or reduce) one of the reactants of eqn. (21); (iii) the reduced (or oxidized) form of the photosensitizer must be able to reduce (or oxidize) the other reactant in order to complete the redox process indicated by eqn. (21) and to

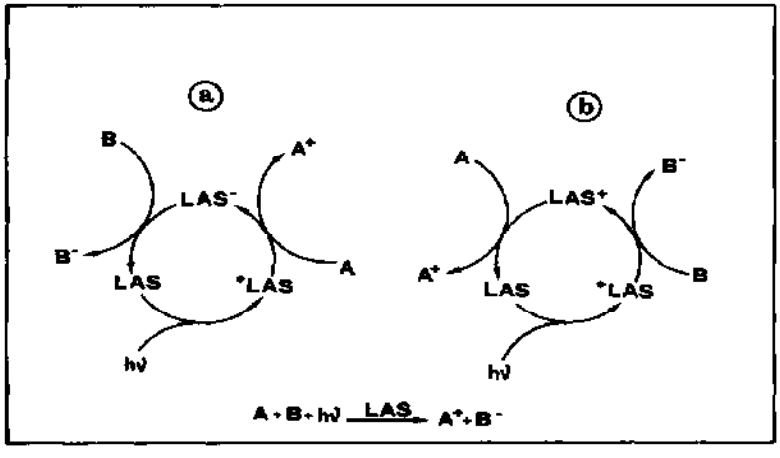

Fig. 10. Schematic representation of a photosensitized electron transfer reaction. LAS = light absorption sensitizer.

regenerate the LAS. Looking at the schemes of Figs. 4 and 10, it is possible to make the following list of requirements for an ideal LAS [40,41]: (1) reversible redox behavior; (2) suitable ground and excited state potentials; (3) stability towards thermal and photochemical decomposition; (4) intense absorption in a suitable spectral region; (5) small energy gap between relevant excited states; (6) high efficiency of population of the reactive excited state; (7) suitable lifetime of the reactive excited state; (8) high energy content of the reactive excited state; (9) good kinetic factors for outer sphere electron transfer reactions. LAS can carry on a variety of useful processes [38]. Their development will hopefully make possible the conversion of simple molecules like H_2O and CO_2 (which do not absorb solar energy) into fuels (H_2, CH_4) by means of non-biological photosynthetic processes [42–45].

"Potential" chemiluminescent reactions are reactions sufficiently exergonic to generate light but producing only heat because no excited state (or, better, no emitting excited state) is formed

$$A^+ + B^- \not\rightarrow A + B + h\nu \qquad (22)$$

In the same way as "potential" photochemical reactions can be induced by LAS, "potential" chemiluminescent reactions can be induced by suitable species that can be called light emission sensitizers (LES) [38]. As shown in Fig. 11, a LES must perform in the following way: (i) it must be oxidized (or reduced) by one of the reactants of eqn. (22); (ii) its oxidized (or reduced) form so obtained must then oxidize (or reduce) the other reactant to yield an excited state, *LES; (iii) such an excited state must undergo radiative deactivation (luminescence), regenerating the ground state LES. In this way,

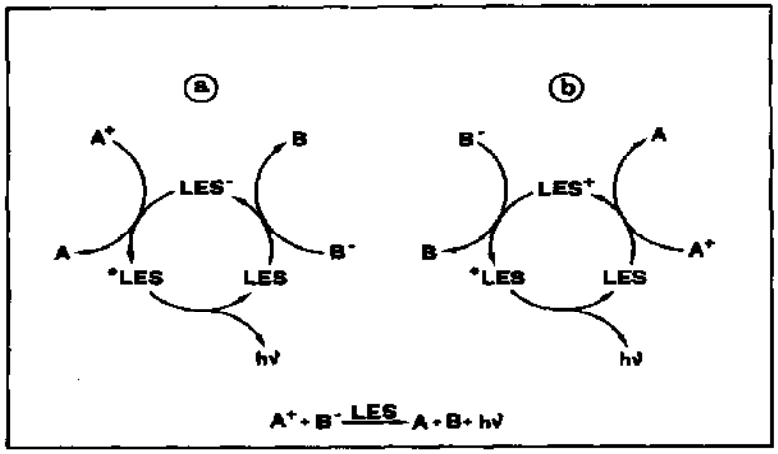

Fig. 11. Schematic representation of a sensitized chemiluminescent electron transfer reaction. LES = light emission sensitizer.

part of the exergonicity of the electron transfer reaction between A^+ and B^- is channelled to light generation. LES are less known than LAS, but they are presently the object of much research because they may have several applications (e.g., in the field of display devices [46, 47]). From the schemes shown in Figs. 4 and 11, the requirements for an ideal LES must be as follows [40]: (1) reversible redox behavior; (2) suitable ground and excited state potentials; (3) stability towards thermal and photochemical decomposition reactions; (4) suitable excited state energy; (5) strong luminescence emission (high efficiency for the radiative deactivation of the excited state); (6) good kinetic factors for outer sphere electron transfer reactions.

As can be seen from the above lists, the stability and redox requirements are the same for LAS and LES. From a spectroscopic point of view, the requirements are somewhat different (e.g., a LES does not need to have intense absorption bands and a LAS does not need to exhibit luminescence), but slow radiationless deactivation of the excited state is a fundamental requirement in both cases because a LAS must have a long excited state lifetime and a LES must have a high emission efficiency. Thus, it is not surprising that a compound which can play a role of LAS can also play a role of LES. Ru(II) polypyridine complexes, because of their redox and excited state properties, satisfy most of the requirements needed for LAS and LES.

(vi) Structure, bonding, and excited states of Ru(II) polypyridine complexes

Ru^{2+} is a d^6 system and the polypyridine ligands are usually colorless molecules possessing σ-donor orbitals localized on the nitrogen atoms and π donor and π^* acceptor orbitals more or less delocalized on aromatic rings. Following a single-configuration one-electron description of the excited state in octahedral symmetry (Fig. 12(a)), promotion of an electron from a π_M metal orbital to the π_L^* ligand orbitals gives rise to metal-to-ligand charge transfer (MLCT) excited states, whereas promotion of an electron from π_M to σ_M^* orbitals gives rise to metal centered (MC) excited states. Ligand centered (LC) excited states can be obtained by promoting an electron from π_L to π_L^*. All these excited states may have singlet or triplet multiplicity, although spin–orbit coupling causes singlet–triplet mixing in the MC and MLCT excited states [48–51]. Actually $Ru(bpy)_3^{2+}$, as well as the other $Ru(LL)_3^{2+}$ complexes (LL = bidentate polypyridine ligand), exhibits a D_3 symmetry (Fig. 13) [52]. Following Orgel's notation [53], the π^* orbitals may be symmetrical (χ) or antisymmetrical (ψ) with respect to rotation around the C_2 axis retained by each Ru(bpy) unit. A more detailed picture of the highest occupied and lowest empty orbital is shown in Fig. 12(b) [14,15,54]. The highest filled molecular orbitals are $\pi_M a_1(d)$ and $\pi_M e(d)$, which are

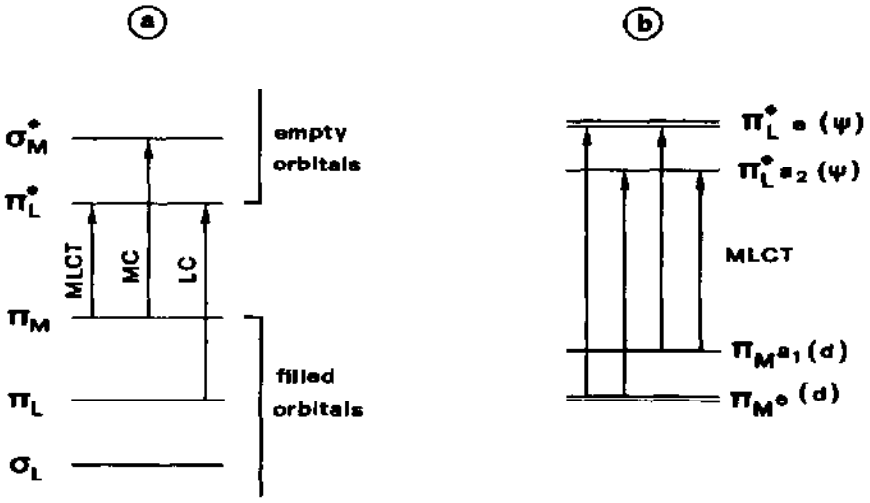

Fig. 12. (a). Simplified molecular orbital diagram for $Ru(LL)_3^{2+}$ complexes in octahedral symmetry showing the three types of electronic transitions occurring at low energies; (b) detailed representation of the MLCT transition in D_3 symmetry.

predominantly localized on the metal; the lowest empty molecular orbitals are $\pi_L^* a_2(\psi)$ and $\pi_L^* e(\psi)$, which are predominantly localized on the ligands. The ground state of the complex is a singlet, derived from the $\pi_M e(d)^4 \pi_M a_1(d)^2$ electronic configuration.

The high energy excited states of transition metal complexes undergo fast radiationless deactivation [55]. Thus, only the lowest excited state and the upper states that can be populated on the basis of the Boltzmann equi-

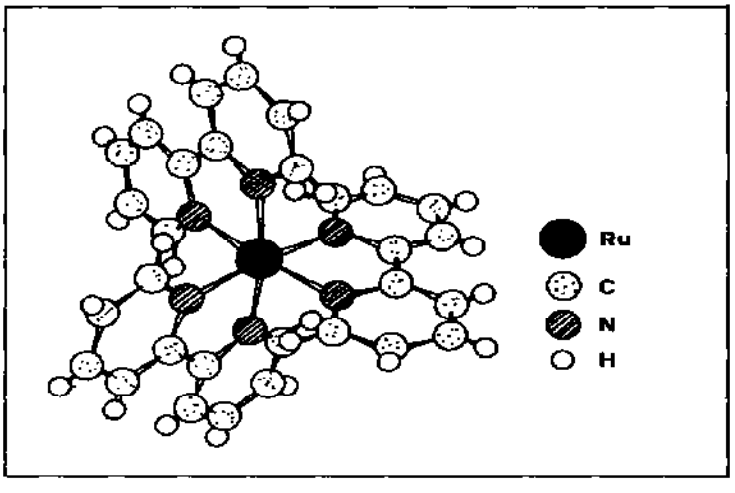

Fig. 13. Structure of $Ru(bpy)_3^{2+}$ [52].

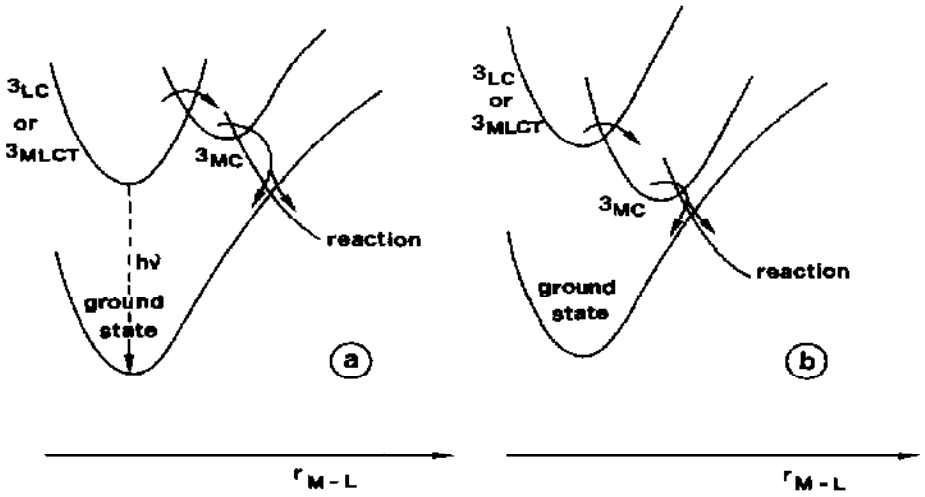

Fig. 14. Schematic representation of two limiting cases for the relative positions of ^{3}MC and ^{3}LC (or ^{3}MLCT) excited states.

librium law may play a role in the luminescence emission and in bimolecular processes.

The MC excited states of d^6 octahedral complexes are strongly displaced with respect to the ground state geometry along metal–ligand vibration coordinates [2,56]. When the lowest excited state is MC, it undergoes fast radiationless deactivation to the ground state and/or ligand dissociation reactions (Fig. 14(b)). As a consequence, at room temperature the excited state lifetime is very short, no luminescence emission can be observed [57] and no bimolecular reaction can take place. LC and MLCT excited states are usually not strongly displaced compared to the ground state geometry. Thus, when the lowest excited state is LC or MLCT (Fig. 14(a)) it does not undergo fast radiationless decay to the ground state and luminescence can usually be observed, except at high temperature when thermally activated radiationless deactivation via upper lying MC excited states can occur. The radiative deactivation rate constant is somewhat higher for ^{3}MLCT than for ^{3}LC because of the larger spin–orbit coupling effect. For this reason, the ^{3}LC excited states are longer lived at low temperature in rigid matrix and the ^{3}MLCT excited states are more likely to exhibit luminescence at room temperature in fluid solution where the lifetime of ^{3}LC and ^{3}MLCT is shortened by activated surface crossing to short lived MC excited states or by bimolecular quenching processes.

From this discussion it is clear that the luminescent properties of a complex as well as its ability to play the role of excited state reactant, (eqn. 16), excited state product (eqn. (17)), LAS (Fig. 10), or LES (Fig. 11) are

related to the energy ordering of its low energy excited states and, particularly, to the orbital nature of its lowest excited state. The energy positions of the MC, MLCT, and LC excited states depend on the ligand field strength, the redox properties of metal and ligands, and intrinsic properties of the ligands, respectively [2]. Thus, in a series of complexes of the same metal ion the energy ordering of the various excited states, and particularly the orbital nature of the lowest excited state, can be controlled by a judicious choice of the ligands [40,48,58]. In this way, it is possible to design complexes having, at least to a certain degree, the desired properties (Section C). For most Ru(II) polypyridine complexes, the lowest excited state is a ^{3}MLCT which undergoes relatively slow radiationless transitions and thus exhibits long lifetime and intense luminescence emission.

(vii) Redox properties of Ru(II) polypyridine complexes in the ground state

As mentioned above, the complexes of the Ru(II) polypyridine family are particularly interesting as excited state reactants or products in electron transfer processes and as mediators (LAS or LES) of electron transfer reactions involving light. A fundamental requirement for playing these roles is the stability of the oxidized and/or reduced forms, i.e. the reversibility of the oxidation and/or reduction processes in the ground state. A wealth of information is available on the electrochemical behavior of ruthenium–polypyridine complexes. The most widely used electrochemical method has been cyclic voltammetry (CV) in non-aqueous aprotic solvents. Following the pioneering work on $Ru(bpy)_3^{2+}$ [59], many measurements on similar complexes were performed (Table 3). The feature of CVs of many complexes of the Ru(II)–polypyridine family is the possibility of localizing with a high degree of certainty the donor or the acceptor orbital of the one electron transfer reaction.

Oxidation of Ru(II) polypyridine complexes usually involves a metal centered (parent $\pi_M(t_{2g})$ in octahedral symmetry) orbital, with formation of genuine Ru(III) complexes (low spin $4d^5$ configuration) which are inert to ligand substitution [59]

$$\left[Ru^{2+}(LL)_3\right]^{2+} \rightleftarrows \left[Ru^{3+}(LL)_3\right]^{3+} + e^- \qquad (23)$$

Normally, only a one-electron oxidation is obtained in the potential range available. It is not always feasible to compare potentials reported in the literature on an absolute scale. It can be stated, however, that the Ru(II)/Ru(III) potentials in the complexes where the ligands are exclusively true polypyridine molecules, fall in a rather narrow range around +1.25 V with respect to NHE. Substitution of one or more polypyridine ligands by another base can drastically change these potentials. The substitution of one

bpy in $Ru(bpy)_3^{2+}$ with two Cl^- ions to give $Ru(bpy)_2Cl_2$ lowers the potential to about +0.35 V, whereas the strong π^*-acceptor CO causes an increase above +1.9 V in $Ru(bpy)_2(CO)_2^{2+}$ (Table 3).

Reduction of Ru(II) polypyridine complexes may in principle involve either a metal-centered or a ligand-centered orbital, depending on the relative energy ordering. When the ligand field is sufficiently strong and/or the ligands can be easily reduced, reduction takes place on a ligand π_L^* orbital. This is the commonly observed behavior of Ru(II)–polypyridine complexes [60,61,65] (Table 3). The reduced form, keeping its low-spin $4d^6$ configuration, is usually quite inert and the reduction process is reversible:

$$[Ru^{2+}(LL)_3]^{2+} + e^- \rightleftarrows [Ru^{2+}(LL)_2(LL^-)]^+ \tag{24}$$

As discussed in Sections A (viii) and D (iii), the added electron appears to be localized on a single ligand. Several reduction steps can often be observed in the potential range accessible. This range has been considerably enlarged through the measurement of CV at low temperature [62,63]. Up to six electrons can be pumped into $Ru(bpy)_3^{2+}$ in this way [62], yielding a highly reduced complex which can be formulated as $[Ru^{2+}(bpy^{2-})_3]^{4-}$. The localization of the acceptor orbitals in the reduction processes is often particularly clear in mixed ligand complexes involving polypyridine ligands with different energies of the π^* orbitals. In such cases, the first and subsequent reduction steps can be attributed to the various ligands in the complex.

When the ligand field is weak and/or the ligands cannot be easily reduced, the lowest empty orbital in the reduction process could be metal centered (parent $\pi_M^*(e_g)$ in octahedral symmetry). In such a case, reduction would lead to an unstable low spin d^7 system, which should give rise to a fast ligand dissociation making the process electrochemically irreversible

$$[Ru^{2+}(LL)_3]^{2+} + e^- \rightarrow [Ru^{+}(LL)_3]^{+} \rightarrow [Ru^{+}(LL)_2]^{+} + LL \tag{25}$$

Such behavior has been reported for iridium complexes [64], but has never been clearly observed in the case of ruthenium.

It is important to note that, if the Koopmans theorem is valid for the starting t_{2g}^6 system and for the one-electron reduced species, the π_L^* or σ_M^* orbitals that can be involved in the reduction processes (redox orbitals) are the same orbitals which are involved in the MLCT and MC transition, respectively (spectroscopic orbitals). Thus, reversibility of the first reduction step, indicating a ligand centered LUMO, also implies (to a first approximation) that the lowest excited state is MLCT. More generally, there are correlations between the electrochemical and spectroscopic data, as will be discussed in Section D (ii).

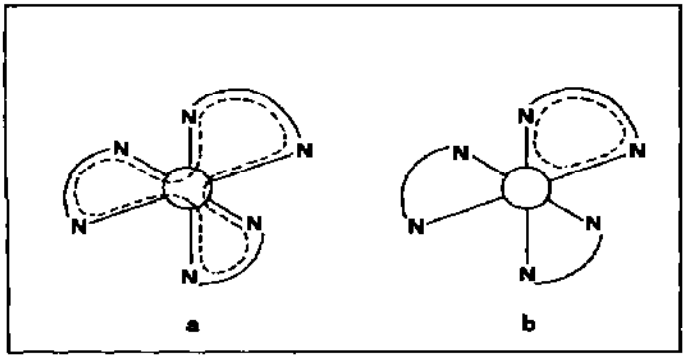

Fig. 15. Pictorial description of the electron promoted to the π_L^* orbital: (a) multichelate ring delocalized orbital; (b) single chelate ring localized orbital [65].

(viii) Localization and delocalization problems

For most complexes of the Ru(II) polypyridine family the excited state responsible for luminescence emission and bimolecular excited state reactions is a ^{3}MLCT (or a cluster [48] of closely spaced ^{3}MLCT levels), i.e. a state obtained promoting a metal π_M orbital to a ligand π_L^* orbital (Fig. 12). As mentioned before, the same π_L^* orbital is involved in the one-electron reduction process. Even if we leave aside a detailed spin and symmetry description of the ^{3}MLCT state, the problem arises whether the spectroscopic and redox orbital is best described as a multichelate ring delocalized orbital (Fig. 15(a)) or a single chelate ring localized orbital with a small amount of interligand interaction (Fig. 15(b)) [65]. This problem has been tackled with a variety of techniques both on reduced and excited complexes. Compelling evidence for "spatially isolated" [66] redox orbitals has been obtained from low temperature cyclic voltammetry [62,63], electron spin resonance [67–69], electronic absorption spectra [70–72], nuclear magnetic resonance [73], and resonance Raman spectra [74]. A more detailed discussion of the localization problem will be given in Section D (iii).

B. $Ru(bpy)_3^{2+}$: THE PROTOTYPE

(i) Ground state properties

The ground state structure of $Ru(bpy)_3^{2+}$ in its hexafluorophosphate salt has been determined by X-ray crystallography [52]. The complex possesses D_3 symmetry (Fig. 13) and the Ru–N bond length of 205.6 pm is somewhat shorter than the 210.4 pm value in $Ru(NH_3)_6^{3+}$ [75], indicating a significant backbonding between Ru(II) and the π^* orbitals of bpy. A five line ^{13}C

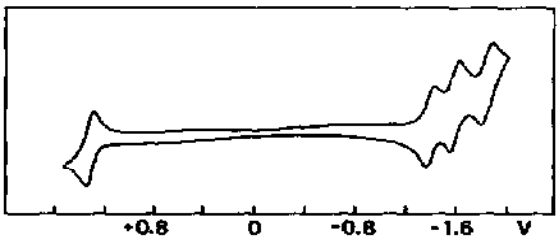

Fig. 16. Cyclic voltammogram of $Ru(bpy)_3^{2+}$ in acetonitrile.

NMR spectrum is observed for the solvated species [54] and the ^1H NMR spectrum [76] can be interpreted in terms of four coupled spins in each six equivalent pyridine rings. The solution NMR data are therefore consistent with retention of D_3 symmetry for the solvated species. Resolution of the enantiomers can be achieved [77], and these are found to be thermally stable with respect to racemization [78].

The $Ru(bpy)_3^{2+}$ cation shows remarkable chemical stability. For example it can be stored in aqueous solutions for months [79] and is reported to be unaffected by boiling concentrated HCl or 50% aqueous sodium hydroxide solutions [80].

The cyclic voltammogram of $Ru(bpy)_3^{2+}$ in AN (potentials vs. Ag electrode) is shown in Fig. 16. One oxidation and three reduction processes, all monoelectronic and reversible, can be observed. The redox potentials are independent of solvent (for AN, DMSO, DMF, and propylene carbonate) [81]. The oxidized form, $Ru(bpy)_3^{3+}$, can be easily obtained by chemical oxidation of $Ru(bpy)_3^{2+}$ with nitric acid [80], dichlorine [82] or lead dioxide [83]. The absorption spectrum of $Ru(bpy)_3^{3+}$ shows a weak band at ~ 420 nm ($\epsilon_{max} = 3.3 \times 10^3\ M^{-1}\,cm^{-1}$) and a broad and weak absorption at longer wavelengths [14]. $Ru(bpy)_3^{3+}$ is reduced by water, but the reaction mechanism is very complicated and governed by the pH of the solution and the presence of catalysts, even at impurity levels [84–90]. Under most experimental conditions the amount of O_2 generated is much less than that expected on the basis of a simple reduction of $Ru(bpy)_3^{3+}$ to $Ru(bpy)_3^{2+}$. The reduction of aqueous $Ru(bpy)_3^{2+}$ by pulse radiolysis via the CH_2O^- and $(CH_3)_2CO^-$ radicals at pH 11–13 yields $Ru(bpy)_3^{+}$ [91] which can also be prepared by extensive electrolysis of $Ru(bpy)_3^{2+}$ in non-aqueous solvents [71,72,92,93]. The absorption spectrum of $Ru(bpy)_3^{+}$ shows a broad and intense ($\epsilon_{max} \sim 10^4\ M^{-1}\,cm^{-1}$) band in the visible with maximum at ~ 510 nm. Compelling evidence for reduction taking place on a single chelate ring localized orbital (spatially isolated orbital, Sections A (viii) and D (iii)) has been obtained, so that the reduced form is best described as a Ru(II) complex containing a coordinated bpy^- ligand radical, $[Ru^{2+}(bpy)_2(bpy^-)]^+$.

$Ru(bpy)_3^+$ does not reduce water under neutral or alkaline conditions [91,94].

(ii) Absorption spectrum

The absorption spectrum of $Ru(bpy)_3^{2+}$ is shown in Fig. 17 along with the proposed assignments [8,14,15,48,54,95]. The bands at 185 nm (not shown in the Figure) and 285 nm have been assigned to LC $\pi \rightarrow \pi^*$ transitions by comparison with the spectrum of protonated bipyridine [96]. The two remaining intense bands at 240 and 450 nm have been assigned to MLCT $d \rightarrow \pi^*$ transitions. The shoulders at 322 and 344 nm might be MC transitions. In the long wavelength tail of the absorption spectrum a shoulder is present at about 550 nm ($\epsilon \sim 600$) when the absorption measurement is made on $Ru(bpy)_3^{2+}$ in an ethanol–methanol glass at 77 K [97]. This absorption feature is thought to correspond to the lowest ^{3}MLCT excited state(s).

In spite of the presence of the heavy Ru atom, it has been established that it is reasonable to assign the electronic transitions of $Ru(bpy)_3^{2+}$ as being to "singlet" or "triplet" states. In particular, a singlet character $\leqslant 10\%$ has been estimated [50] for the lower-lying excited states of $Ru(bpy)_3^{2+}$. The maximum of the ^{1}MLCT band at ~ 450 nm is slightly sensitive to solvent, suggesting an instantaneous sensing of the formation of the dipolar excited state $[Ru^{3+}(bpy)_2(bpy^-)]^{2+}$ [98] (see Section D (iii)).

(iii) Deactivation of upper excited states

As mentioned in the introduction (Section A (ii)) the upper excited states of transition metal complexes undergo either chemical reaction or radiation-

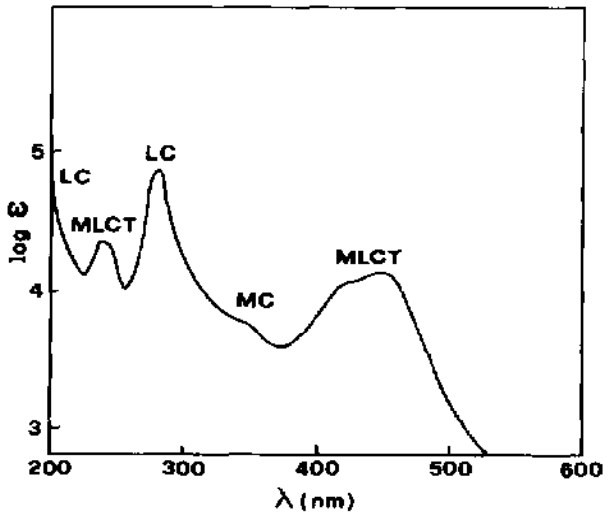

Fig. 17. Electronic absorption spectrum of $Ru(bpy)_3^{2+}$.

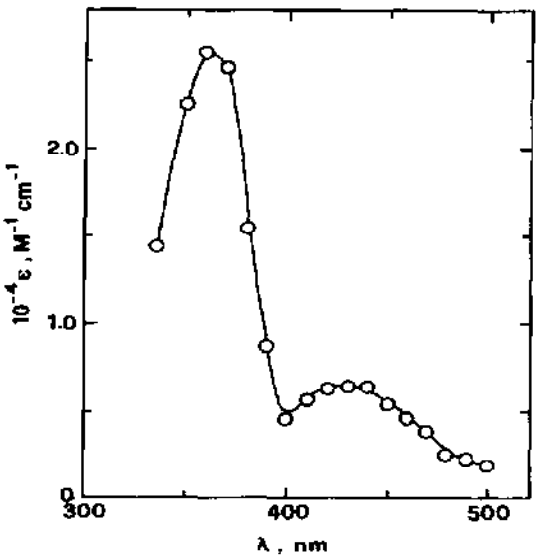

Fig. 18. Electronic absorption spectrum of the lowest excited state of $Ru(bpy)_3^{2+}$ [101].

less deactivation to the lowest excited state. For $Ru(bpy)_3^{2+}$ the lowest excited state (or, better, the cluster of lowest excited states) is relatively long lived and its formation and disappearance can be easily monitored by flash spectroscopy and luminescence decay. The absorption spectrum of the lowest excited state is shown in Fig. 18 [99–101]. The risetime of the lowest excited state upon excitation of spin allowed excited states was estimated to be $\ll 1$ ns for $Ru(bpy)_3^{2+}$ [102,103], indicating that the conversion of the upper excited states to the lowest one is indeed very fast. The quantum yield of formation of the lowest excited state $\Phi_{^3MLCT}$ (and thus, the efficiency of intersystem crossing from the upper singlets obtained by excitation to the lowest triplet, η_{isc}) is essentially unity [99,104–106]. Interestingly, $\Phi_{^3MLCT}$ has also been evaluated by a photochemical technique, based on the ability of $(^3CT)Ru(bpy)_3^{2+}$ to function as a reductant (Section B (vi)) [106]. This method, which may be useful also for other complexes, works in the following way. The reaction of $(^3CT)Ru(bpy)_3^{2+}$ with $S_2O_8^{2-}$ yields $Ru(bpy)_3^{3+}$, SO_4^{2-} and the strongly oxidizing SO_4^- radical. Once formed, this radical reacts with ground state $Ru(bpy)_3^{2+}$ to yield a second $Ru(bpy)_3^{3+}$ complex ion. Experimentally, the quantum yield for disappearance of $Ru(bpy)_3^{2+}$, $\Phi_{-Ru^{2+}}$, was followed by monitoring the 450 nm absorption band of $Ru(bpy)_3^{2+}$, and the measurements were made as a function of $[S_2O_8^{2-}]$. From a plot of $1/\Phi_{-Ru^{2+}}$ versus $1/[S_2O_8^{2-}]$, the limiting value of $\Phi_{-Ru^{2+}}$ for infinite $S_2O_8^{2-}$ concentration was found to be 2.0 ± 0.2. This value can only occur if all the $Ru(bpy)_3^{2+}$ excited states which are formed

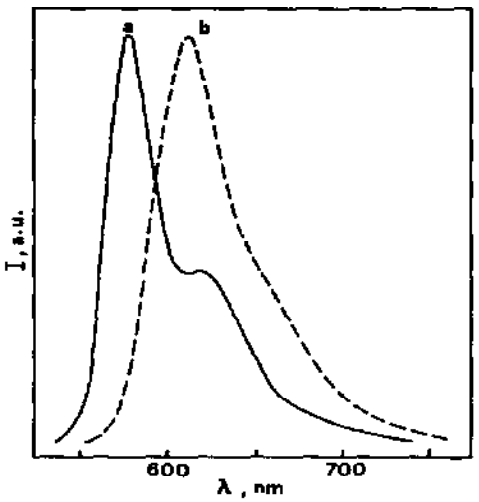

Fig. 19. Emission spectrum of $*Ru(bpy)_3^{2+}$ in alcoholic solution: (a) at 77 K; (b) at room temperature.

upon light absorption react to yield $Ru(bpy)_3^{3+}$ and SO_4^-, and all of the SO_4^- goes on to react with $Ru(bpy)_3^{2+}$ to form a stoichiometric amount of $Ru(bpy)_3^{3+}$.

(iv) Emission properties

Excitation of $Ru(bpy)_3^{2+}$ in any of its absorption bands leads to a luminescence emission (Fig. 19) whose intensity, lifetime, and energy position are more or less temperature dependent. Detailed studies on the temperature dependence [48,107–111] of the luminescence lifetime and quantum yield in the temperature range 2–70 K showed that luminescence originates from a set of three closely spaced levels (ΔE 10 and 61 cm^{-1}) in thermal equilibrium. The theoretical description of the luminescent levels continues to be a matter of debate. There is no doubt about their MLCT nature, whereas different opinions exist on whether these levels can be described by a spin quantum number and whether the promoted electron resides in a single bpy ligand or in a delocalized π^* orbital. Recent results suggest that the best description is that which assumes a substantial triplet character and a single ligand localized excitation (Section D (iii)). This cluster of luminescent, closely spaced excited states will be indicated in the following by $*Ru(bpy)_3^{2+}$.

In rigid alcoholic glass at 77 K the emission lifetime of $*Ru(bpy)_3^{2+}$ is ~ 5 μs and the emission quantum yield is ~ 0.4 (Table 1). Taken together with the unitary intersystem crossing efficiency, these figures yield (see eqn.

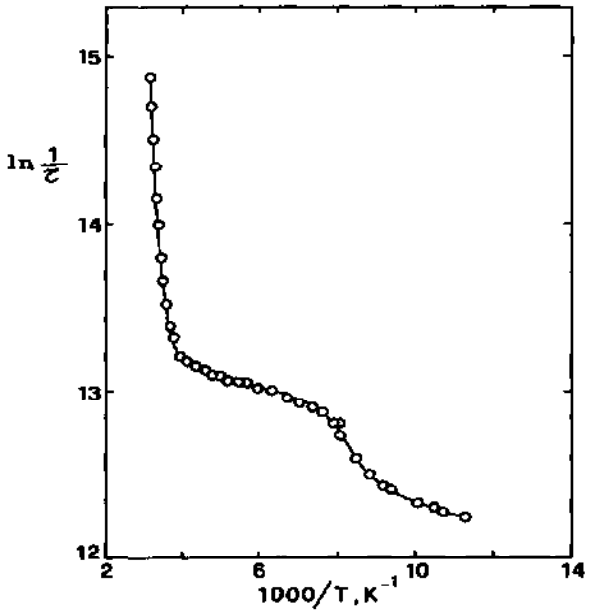

Fig. 20. Temperature dependence of the emission lifetime of * $Ru(bpy)_3^{2+}$ in nitrile solution [13].

2) a value of ~ 13 μs for the radiative lifetime. Values of this order of magnitude have been found for MLCT excited states of other transition metal complexes [112–114]. Ligand centered excited states exhibit radiative lifetimes in the ms range [111–113,115–118].

With increasing temperature, the emission lifetime (Fig. 20) and quantum yield decrease [48,95,96,119–137]. This behavior may be accounted for (see Section D (i)) by a stepwise term and two Arrhenius terms:

$$1/\tau = k_0 + \frac{B}{1 + \exp[C(1/T - 1/T_B)]} + A_1 e^{-\Delta E_1/RT} + A_2 e^{-\Delta E_2/RT} \qquad (26)$$

The value of the various parameters are somewhat dependent on the nature of the solvent. In propionitrile–butyronitrile (4 : 5 v/v) the values are as follows [131,132]: $k_0 = 2 \times 10^5\ s^{-1}$; $B = 2.1 \times 10^5\ s^{-1}$; $A_1 = 5.6 \times 10^5\ s^{-1}$; $\Delta E_1 = 90\ cm^{-1}$; $A_2 = 1.3 \times 10^{14}\ s^{-1}$; $\Delta E_2 = 3960\ cm^{-1}$. Included in k_0 are the radiative k_0^r and nonradiative k_0^{nr} rate constants at 84 K. The stepwise term B is due to the melting of the matrix (100–150 K) and is thought to correspond to the coming into play of vibrations capable of facilitating radiationless deactivation [132]. In the same temperature interval a red shift of ~ 1000 cm^{-1} is observed in the maximum of the emission band [132]. The Arrhenius term with $A_1 = 5.6 \times 10^5\ s^{-1}$ and $\Delta E_1 = 90\ cm^{-1}$ is thought to correspond to the thermal equilibration with a level lying at slightly

higher energy and having the same electronic nature. The second Arrhenius term is thought to correspond to a thermally activated surface crossing to an upper-lying ^{3}MC level which undergoes fast deactivation (Section D (i)). Identification of this higher level as a ^{3}MC state is based upon the observed photosubstitution behavior at elevated temperatures [119], consistent with established photoreactivity patterns for d^6 metal complexes [2]. Experiments carried out with $Ru(bpy)_3^{2+}$ and $Ru(bpy\text{-}d_8)_3^{2+}$ in H_2O and D_2O [119,130,138] indicate that k_0^{nr} is sensitive to deuteration, as expected for a weak-coupled radiationless process [139–142]. By contrast, A_2 is insensitive to deuteration, suggesting a strong-coupled (surface crossing) deactivation pathway, which may be related to the observed photosensitivity. It should be noted that the decrease in lifetime on melting has also been explained on the basis of the energy gap law because of the correspondent red shift in the emission band [142].

(v) Photosubstitution and photoracemization processes

Although $Ru(bpy)_3^{2+}$ is normally considered as photochemically inert towards ligand substitution, there is increasing evidence that this is not so [14,15,142]. In aqueous solution the quantum yield of $Ru(bpy)_3^{2+}$ disappearance is in the range 10^{-5}–10^{-3}, depending on the pH of the solution and temperature. The exact nature of the reaction products has not been elucidated [119,124]. In chlorinated solvents such as CH_2Cl_2 the photochemistry of $[Ru(bpy)_3]X_2$ ($X = Cl^-$, Br^-, NCS^-) is well behaved [124,143], giving rise to $Ru(bpy)_2X_2$ as final product. The quantum yields are in the range 10^{-1}–10^{-2}. The PF_6^- salt is photoinert. A substantial difference between aqueous and CH_2Cl_2 solutions is that salts of $Ru(bpy)_3^{2+}$ are completely ion-paired in the latter medium.

A detailed mechanism for the ligand photosubstitution reaction for $Ru(bpy)_3^{2+}$ has been proposed [124] (Fig. 21). According to this mechanism, thermally activated formation of a ^{3}MC excited state (vide supra) leads to the cleavage of a Ru–N bond, with formation of a five-coordinate square pyramidal species. In the absence of coordinating ions, as with the PF_6^- salt, this square pyramidal species returns to $Ru(bpy)_3^{2+}$. When coordinating anions are present, as in the Cl^- salt, a hexacoordinated monodentate bpy intermediate is formed. Once formed, this monodentate bpy species can undergo loss of bpy and formation of $Ru(bpy)_2X_2$, or a "self-annealing" process (chelate ring closure), with reformation of $Ru(bpy)_3^{2+}$. The "self-annealing" protective step is favored in aqueous solution, presumably because of stabilization of the cationic $Ru(bpy)_3^{2+}$ species, whereas formation of neutral $Ru(bpy)_2X_2$ complexes is favored in low polarity solvents. Photoracemization of $Ru(bpy)_3^{2+}$ [144] also occurs with low quantum yield ($2.9 \times$

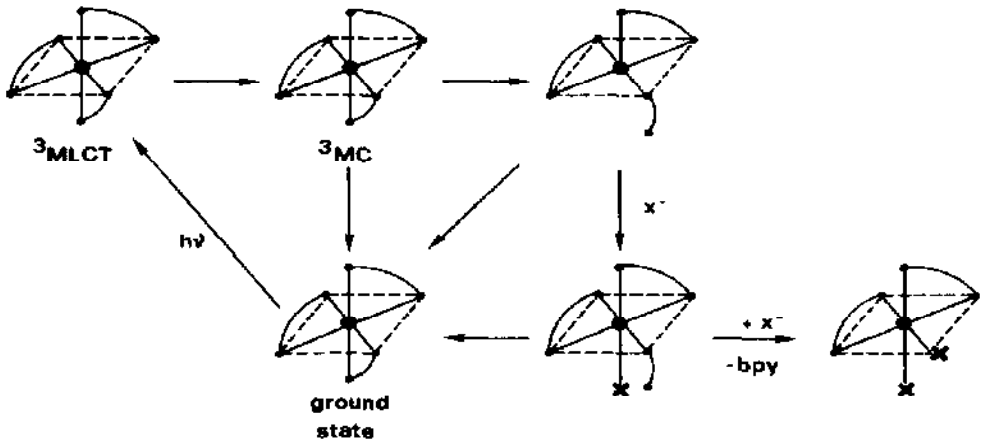

Fig. 21. Schematic representation of the proposed mechanism of ligand photosubstitution reactions of $Ru(bpy)_3^{2+}$ [124].

10^{-4} in water at 25 °C). This process can be accounted for by a rearrangement of the square pyramidal primary photoproduct (Fig. 21) into a trigonal bipyramidal intermediate which can lead back to either the Δ or the Λ isomer [124].

Ligand photodissociation is, of course, a major drawback for the use of $Ru(bpy)_3^{2+}$ as LAS or LES (Sections B (viii) and (ix)). From the above discussion, it follows that to avoid ligand photodissociation the population of ^{3}MC and/or ligand dissociation from ^{3}MC should be prevented. Population of ^{3}MC can be prevented or at least reduced by: (a) addition of sufficient quencher to capture ^{3}MLCT before surface crossing to ^{3}MC can occur; (b) working at low temperature (Section D (i)); (c) increasing the energy gap between ^{3}MLCT and ^{3}MC; (d) increasing pressure [145,146]. On the other hand, ligand dissociation from ^{3}MC can be reduced (e) avoiding coordinating anions in solvent of low dielectric constant and (f) linking together the three bpy ligands so as to form a single caging ligand which encapsulates the metal ion. Points (c) and (f) are particularly interesting and much effort is presently devoted to research along such directions. The tuning of excited state energy by changing ligands (point (c) above) will be discussed in detail in Section C. Caging Ru^{2+} into a single polypyridine type ligand (point (f)) poses severe synthetic problems. A first step in this direction has been the synthesis [147] of the polypyridine cage-type ligands shown in Fig. 22. The Ru(II) complexes of such ligands, however, have not yet been prepared. Furthermore, there might be subtle problems related to the shape and size of the cage. If the Ru–N bonds are too long and/or the bite angles are unfavorable, the ligand field strength would be small and the consequent decrease in energy of the lowest ^{3}MC level would compromise

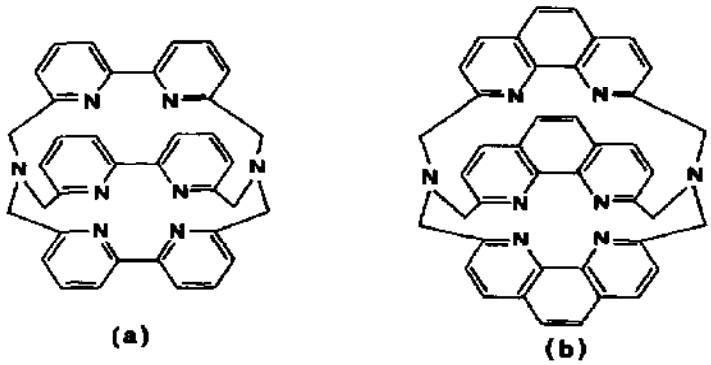

Fig. 22. Cage-type polypyridine ligands [147].

the lifetime of ^{3}MLCT, since caging is not expected to slow down the physical radiationless deactivation of ^{3}MC [148]. The short lifetime of ^{3}MLCT at room temperature for $Ru(trpy)_2^{2+}$ (less than 5 ns [149,150]) is likely due to fast radiationless decay via a low lying ^{3}MC level.

(vi) Quenching of the ^{3}MLCT excited state: energy and electron transfer processes

As discussed in Section A (ii), an excited state which is sufficiently long lived may be involved in energy and electron transfer processes in fluid solution. The lowest ^{3}MLCT excited state of $Ru(bpy)_3^{2+}$ lives long enough (Table 1) to encounter other solute molecules (even when these are present at relatively low concentration) and possesses suitable properties to play the role of energy donor, electron donor, or electron acceptor. As is also shown in Fig. 23, the energy available to $^*Ru(bpy)_3^{2+}$ for energy transfer processes is 2.12 eV and its reduction and oxidation potentials are +0.84 and −0.86 V (in water). It follows that $^*Ru(bpy)_3^{2+}$ is at the same time a good energy donor (eqn. 27), a good electron acceptor (eqn. 28), and a good electron donor (eqn. 29):

$$^*Ru(bpy)_3^{2+} + Q \rightarrow Ru(bpy)_3^{2+} + {}^*Q \quad \text{energy transfer} \tag{27}$$

$$^*Ru(bpy)_3^{2+} + Q \rightarrow Ru(bpy)_3^{3+} + Q^- \quad \text{oxidative quenching} \tag{28}$$

$$^*Ru(bpy)_3^{2+} + Q \rightarrow Ru(bpy)_3^{+} + Q^+ \quad \text{reductive quenching} \tag{29}$$

The direct observation of redox products in flash photolysis experiments represents the strongest evidence to support the occurrence of oxidative and reductive quenching mechanisms. These observations can be performed in a few cases with continuous irradiation [106,151] and more often in flash

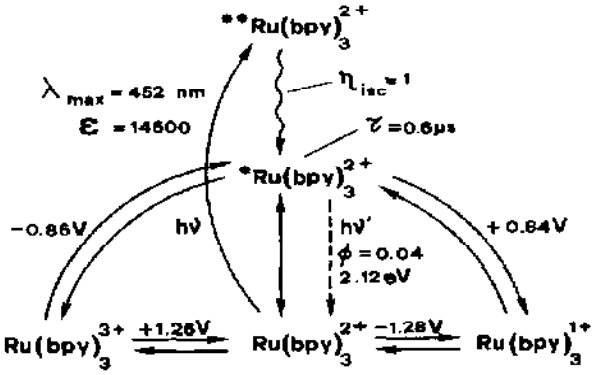

Fig. 23. Molecular quantities of $Ru(bpy)_3^{2+}$ relevant for energy and electron transfer processes. ** $Ru(bpy)_3^{2+}$ indicates spin-allowed excited states and * $Ru(bpy)_3^{2+}$ indicates the lowest spin-forbidden excited state (^{3}MLCT) $Ru(bpy)_3^{2+}$.

photolysis experiments because usually the redox products decay rapidly either by back electron transfer reactions to reform the starting materials or by secondary reactions to form other products. In practice, the possibility to observe transient absorptions is related to the changes in the optical density of the solution caused by the photoreaction. Bleaching and recovering of the $Ru(bpy)_3^{2+}$ spectrum can often be used for kinetic measurements. The absorption band at 680 nm of $Ru(bpy)_3^{3+}$ (Section B (i)) is too weak to detect small $Ru(bpy)_3^{3+}$ concentrations, so that in oxidative quenching processes one is forced to use the absorption spectrum of Q^- to monitor product formation. By contrast, $Ru(bpy)_3^{+}$ exhibits a strong absorption band at 510 nm (Section B (i)), which is particularly useful to investigate reductive quenching reactions.

Following some pioneering work [151–155], literally hundreds of bimolecular excited state reactions of $Ru(bpy)_3^{2+}$ and of its derivatives have been studied in the last 15 years. An accurate compilation of rate constants of electron transfer processes will soon be available [16], so that we do not review this field in detail. We only wish to illustrate a few examples to show that these excited state reactions can be used for mechanistic studies as well as for potential applications of the greatest interest.

The early interest in $Ru(bpy)_3^{2+}$ photochemistry arose from the possibility of using its long-lived excited state as energy donor in energy transfer processes. Although several sensitized reactions attributed to energy transfer processes (see, e.g. refs. 156, 157) were later shown to proceed via electron transfer [155], there are a few, very interesting cases in which energy transfer quenching of $*Ru(bpy)_3^{2+}$ has been firmly demonstrated. A clear example is the quenching of $*Ru(bpy)_3^{2+}$ by $Cr(CN)_6^{3-}$, where sensitized phosphores-

cence of the chromium complex has been observed both in fluid solution [158–162] and in the solid state [163–165]:

$$*Ru(bpy)_3^{2+} + Cr(CN)_6^{3-} \rightarrow Ru(bpy)_3^{2+} + ({}^2E_g)Cr(CN)_6^{3-} \quad (30)$$

$$({}^2E_g)Cr(CN)_6^{3-} \rightarrow Cr(CN)_6^{3-} + h\nu \quad (31)$$

Energy transfer from $*Ru(bpy)_3^{2+}$ to $Cr(CN)_6^{3-}$ was also used to demonstrate that the photosolvation reaction observed upon direct excitation of $Cr(CN)_6^{3-}$ does not originate from the luminescent ^2E_g state of the chromium complex [158,166].

It should be pointed out that both reductive and oxidative $*Ru(bpy)_3^{2+}$ electron transfer quenchings by $Cr(CN)_6^{3-}$ are thermodynamically forbidden because it is very difficult to reduce or oxidize $Cr(CN)_6^{3-}$ [162]. $Cr(bpy)_3^{3+}$, by contrast, can be very easily reduced and with this quencher oxidative electron transfer prevails over energy transfer

$$*Ru(bpy)_3^{2+} + Cr(bpy)_3^{3+} \xrightarrow{k = 3.3 \times 10^9 M^{-1}s^{-1}} Ru(bpy)_3^{3+} + Cr(bpy)_3^{2+} \quad (32)$$

as is shown by the appearance of the $Cr(bpy)_3^{2+}$ absorption spectrum in flash photolysis experiments [167]. Reaction (32) converts 71% of the spectroscopic energy (2.12 eV) of the excited state reactant into chemical energy of the products. As usually happens in these simple homogeneous systems, the converted energy cannot be stored but is immediately dissipated into heat by the back electron transfer reaction:

$$Ru(bpy)_3^{3+} + Cr(bpy)_3^{2+} \xrightarrow{k = 2 \times 10^9 M^{-1}s^{-1}} Ru(bpy)_3^{2+} + Cr(bpy)_3^{3+} \quad (33)$$

A carefully studied example of reductive electron transfer quenching (reaction 34) is that involving Eu_{aq}^{2+} as a quencher [168,169]:

$$*Ru(bpy)_3^{2+} + Eu_{aq}^{2+} \xrightarrow{k = 2.8 \times 10^7 M^{-1}s^{-1}} Ru(bpy)_3^{+} + Eu_{aq}^{3+} \quad (34)$$

The difference spectrum obtained by flash photolysis after a 30 ns light pulse shows a bleaching in the region around 430 nm due to depletion of $Ru(bpy)_3^{2+}$ and an increased absorption around 500 nm due to the formation of $Ru(bpy)_3^{+}$ (note that both Eu_{aq}^{2+} and Eu_{aq}^{3+} are transparent in this spectral region). Clear kinetic evidence for reductive quenching comes from the observation that the growth of the absorption at 500 nm occurs at a rate equal to the rate of decay of the luminescence emission of $*Ru(bpy)_3^{2+}$. As it may happen in excited state reactions (Fig. 8(b)) the products of reaction (34) have a high energy content and thus they give rise to a back electron transfer reaction

$$Ru(bpy)_3^{+} + Eu_{aq}^{3+} \xrightarrow{k = 2.7 \times 10^7 M^{-1}s^{-1}} Ru(bpy)_3^{2+} + Eu_{aq}^{2+} \quad (35)$$

that can be monitored (on a longer time scale) through the recovering of the 430 nm absorption or the disappearance of the 500 nm absorption.

In several cases direct evidence for energy transfer quenching (i.e., sensitized luminescence or absorption spectrum of the excited acceptor) or electron transfer quenching (i.e., absorption spectrum of redox products) is difficult or even impossible to obtain. In such cases, free energy correlations of rate constants are quite useful to elucidate the reaction mechanism [12,162,170–172].

(vii) Chemical generation of the ^{3}MLCT excited state: chemiluminescence and electrochemiluminescence processes

As mentioned in Section A (iv), excited states can be generated in very exergonic electron transfer reactions (Fig. 9). Formation of excited states can be easily demonstrated when the excited states are luminescent species. Because of its stability in the reduced and oxidized forms and of the strong luminescence of $^*Ru(bpy)_3^{2+}$, $Ru(bpy)_3^{2+}$ is an extremely versatile base reactant for a variety of chemiluminescent processes [38,39,83,173–175].

In principle, there are two ways to generate the luminescent $^*Ru(bpy)_3^{2+}$ excited state in chemical reactions. One way (see eqn. (36)) is to oxidize $Ru(bpy)_3^+$ with a species X having reduction potential $E^0(X/X^-)$ more positive than 0.84 V, and another way (eqn. 37) is to reduce $Ru(bpy)_3^{3+}$ with a species Y^- whose potential $E^0(Y/Y^-)$ is more negative than -0.86 V (see also Fig. 23).

$$Ru(bpy)_3^+ + X \rightarrow {}^*Ru(bpy)_3^{2+} + X^- \quad (36)$$

$$Ru(bpy)_3^{3+} + Y^- \rightarrow {}^*Ru(bpy)_3^{2+} + Y \quad (37)$$

$$^*Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + h\nu \quad (38)$$

A variety of oxidants (e.g. $S_2O_8^{2-}$ [176,177]) and reductants (e.g., e_{aq}^- [178,179], N_2H_4 [180], oxalate ion [181,182], OH^- [180]) have been found to be active in these chemiluminescence processes. In some cases (e.g., with OH^-), the reaction mechanism cannot be a simple outer sphere electron transfer reaction and the emitting species could be a slightly modified (on the ligands) complex. It should also be pointed out that minor amounts of oxidizing and reducing impurities are sufficient to produce luminescence in chemiluminescence and electrochemiluminescence experiments [183].

The most elegant way [59] to obtain chemiluminescence from $Ru(bpy)_3^{2+}$ solutions is to produce the oxidized and/or reduced form of the complex "in situ" by electrochemical methods. Three classical experiments of this type can be performed.

(a) To pulse the potential applied to a working electrode between the oxidation and reduction potentials of $Ru(bpy)_3^{2+}$ in a suitable solvent [59,184]. In such a way the reduced and oxidized form produced in the same region of space can undergo a comproportionation reaction where enough energy is available to produce an excited state and a ground state (see also Fig. 23):

$$Ru(bpy)_3^{2+} + e^- \rightarrow Ru(bpy)_3^{+} \quad (39)$$

$$Ru(bpy)_3^{2+} - e^- \rightarrow Ru(bpy)_3^{3+} \quad (40)$$

$$Ru(bpy)_3^{+} + Ru(bpy)_3^{3+} \rightarrow {}^*Ru(bpy)_3^{2+} + Ru(bpy)_3^{2+} \quad (41)$$

(b) To reduce $Ru(bpy)_3^{2+}$ in the presence of a strong oxidant (reductive oxidation). For example, luminescence is obtained upon continuous reduction of $Ru(bpy)_3^{2+}$ at a working electrode in the presence of $S_2O_8^{2-}$ [176,177]. This oxidant in a first one-electron oxidation reaction generates the very powerful oxidant SO_4^- that either can oxidize $Ru(bpy)_3^{+}$ to $^*Ru(bpy)_3^{2+}$ (eqn. 43) or $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ (eqn. 44) which then reacts with $Ru(bpy)_3^{+}$ (eqn. 41) to yield the luminescent excited state

$$Ru(bpy)_3^{2+} + e^- \rightarrow Ru(bpy)_3^{+} \quad (39)$$

$$Ru(bpy)_3^{+} + S_2O_8^{2-} \rightarrow Ru(bpy)_3^{2+} + SO_4^- + SO_4^{2-} \quad (42)$$

$$Ru(bpy)_3^{+} + SO_4^- \rightarrow {}^*Ru(bpy)_3^{2+} + SO_4^{2-} \quad (43)$$

$$Ru(bpy)_3^{2+} + SO_4^- \rightarrow Ru(bpy)_3^{3+} + SO_4^{2-} \quad (44)$$

$$Ru(bpy)_3^{+} + Ru(bpy)_3^{3+} \rightarrow {}^*Ru(bpy)_3^{2+} + Ru(bpy)_3^{2+} \quad (41)$$

(c) To oxidize $Ru(bpy)_3^{2+}$ in the presence of a strong reductant (oxidative reduction). For example, light is generated upon continuous oxidation of $Ru(bpy)_3^{2+}$ at a working electrode in the presence of $C_2O_4^{2-}$ [181,182]. This reductant in a first one-electron reaction generates the strongly reducing CO_2^- radical that can reduce $Ru(bpy)_3^{3+}$ to the excited $^*Ru(bpy)_3^{2+}$:

$$Ru(bpy)_3^{2+} - e^- \rightarrow Ru(bpy)_3^{3+} \quad (40)$$

$$Ru(bpy)_3^{3+} + C_2O_4^{2-} \rightarrow Ru(bpy)_3^{2+} + CO_2 + CO_2^- \quad (45)$$

$$Ru(bpy)_3^{3+} + CO_2^- \rightarrow {}^*Ru(bpy)_3^{2+} + CO_2 \quad (46)$$

$Ru(bpy)_3^{3+} + \underline{Ru}(bpy)_3^{+}$ branches to:

- $\rightarrow Ru(bpy)_3^{2+} + Ru(bpy)_3^{2+}$ -2.54 eV (47)
- $\rightarrow {}^*Ru(bpy)_3^{2+} + \underline{Ru}(bpy)_3^{2+}$ (41a)
- $\rightarrow Ru(bpy)_3^{2+} + {}^*\underline{Ru}(bpy)_3^{2+}$ (41b)

-0.42 eV (41)

- $\not\rightarrow {}^*Ru(bpy)_3^{2+} + {}^*Ru(bpy)_3^{2+}$ $+1.70$ eV (48)

Scheme 1

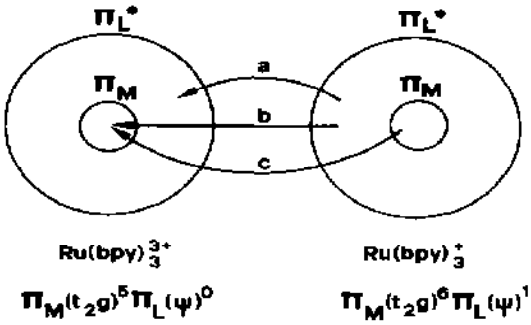

Fig. 24. Pictorial representation of the three possible electronic transitions in the comproportionation reaction between $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^{+}$; for details see text.

These chemiluminescent electron transfer reactions are quite interesting from an applicative [46,47,185] as well as from a theoretical viewpoint. In particular, the comproportionation reaction (41) poses subtle mechanistic problems that we will now discuss briefly. As shown in Scheme 1, the comproportionation reaction in principle can lead to two ground states (eqn. 47), one ground state and one excited state (eqn. 41), or two excited states (eqn. 48). Furthermore, in the case in which one ground state and one excited state are formed, the excited state can originate either from the oxidized (eqn. 41(a)) or reduced (eqn. 41(b)) parent. Formation of two excited states (eqn. 48) can clearly be ruled out for energetic reasons. Which one of the three remaining processes takes place (and why) is a matter of great theoretical interest. Reaction (47) is so exergonic as to fall in the "inverted region" predicted by the Marcus electron transfer theory [23,186,187], and the occurrence of chemiluminescence from the comproportionation reaction with an efficiency for reaction (41) near 100% [188,189] has indeed been taken as evidence [14,188] in favour of this inverted region. Although excess exergonicity is certainly a limiting factor in the reaction rates [17,19,20,31] it should be noticed [190] that reactions (47), (41a), and (41b), differ from one another because different orbitals are involved. As shown in Fig. 24, formation of two ground state molecules (eqn. (47)) involves electron transfer from a ligand orbital of the reduced species to a metal orbital of the oxidized species. Formation of an excited state deriving from the oxidized species (eqn. 41(a)) involves a ligand-to-ligand electron transfer, whereas formation of an excited state from the reduced parent (eqn. 41(b)) requires a metal-to-metal electron transfer. Simple orbital overlap arguments suggest that the electronic interaction between the two reaction partners decreases in the electron transfer series $L \rightarrow L > L \rightarrow M > M \rightarrow M$. It follows that reaction (41) is favored over reaction (47) not only for nuclear reasons (Marcus inverted region), but also because of a more

favorable electronic factor via the reaction path (41a). In other words, when the two reactants of eqns. (47) and (41) approach each other, reaction (41) is expected to prevail because it can take place over larger separation distances. This simple orbital overlap argument also suggests that reactions (41a) and (41b), which are exactly identical from a thermodynamic viewpoint and also exhibit the same nuclear intrinsic barrier, may nevertheless occur with different rates. Unfortunately, there is no simple way to "label" the reactants and products of the comproportionation reaction and to obtain experimental data relevant to this subtle mechanistic alternative. Another interesting chemiluminescent reaction dealing with the Marcus inverted region has been reported recently [175].

(viii) $Ru(bpy)_3^{2+}$ as a light absorption sensitizer

As mentioned in Section A (v), there are potential photochemical reactions which do not occur because the reactants are not able to absorb light. Such reactions can be photosensitized by suitable chemical species that have been called LAS (light absorption sensitizers) [38]. In the same section we have also seen that a molecule must satisfy a number of kinetic, thermodynamic, spectroscopic and excited state requirements to play the role of LAS. It may also be seen from the above discussion (see also Fig. 23), that $Ru(bpy)_3^{2+}$ satisfies to a noticeable degree most of such requirements and is therefore widely used as a light absorption sensitizer [8,13,14,31,38,41,54,191]. Among the great variety of "potential" photochemical reactions that can be sensitized by $Ru(bpy)_3^{2+}$, an interesting example is that of the reduction of methylviologen (1,1′-dimethyl-4,4′-bipyridinium dication, MV^{2+}) by triphenylamine (NPh_3) [192]:

$$MV^{2+} + NPh_3 \not\longmapsto MV^{+} + NPH_3^{+} \quad \Delta G = +1.45 \text{ eV} \tag{49}$$

This process is strongly endergonic as a dark reaction but it could be driven by visible light (i.e., by photons having an energy content higher than 1.45 eV). However, neither MV^{2+} nor NPh_3 are able to absorb visible light, so that such a "potential" photochemical reaction cannot take place by direct irradiation:

$$MV^{2+} + NPh_3 + h\nu \not\longmapsto MV^{+} + NPh_3^{+} \quad \Delta G < 0 \tag{50}$$

When $Ru(bpy)_3^{2+}$ is present in the solution, it can be excited by visible light and its excited state is able to reduce MV^{2+} to MV^{+}:

$$Ru(bpy)_3^{2+} + h\nu \rightarrow {}^{*}Ru(bpy)_3^{2+} \tag{51}$$

$$^{*}Ru(bpy)_3^{2+} + MV^{2+} \rightarrow Ru(bpy)_3^{3+} + MV^{+} \tag{52}$$

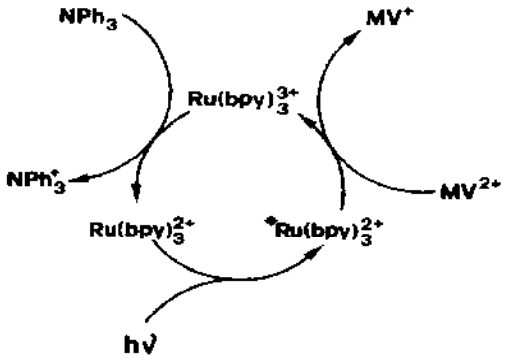

Fig. 25. An example of the use of $Ru(bpy)_3^{2+}$ as light absorption sensitizer (LAS): light energy is converted into chemical energy [192].

Using high concentrations of NPh_3, the reaction

$$Ru(bpy)_3^{3+} + NPh_3 \rightarrow Ru(bpy)_3^{2+} + NPh_3^+ \qquad (53)$$

prevails over the back electron transfer reaction of $Ru(bpy)_3^{3+}$ with MV^+ and the net result of the experiment is the occurrence of the potential photochemical reaction represented by eqn. 50, driven by the light absorbed by $Ru(bpy)_3^{2+}$ (Fig. 25) [192,193].

Much more important for practical applications is the splitting of water into hydrogen and oxygen by visible light

$$1/2\ H_2O + h\nu \not\rightarrow 1/2\ H_2 + 1/4\ O_4 \quad \Delta G = +1.23\ eV \qquad (54)$$

This reaction, which in the dark is endergonic by 1.23 eV, could be driven by visible photons which, however, are not absorbed by water. In principle, $Ru(bpy)_3^{2+}$ can play the role of LAS even in this case. At pH 7, the energetics of the relevant steps are as follows:

$$*Ru(bpy)_3^{2+} + H^+ \rightarrow Ru(bpy)_3^{3+} + 1/2\ H_2 \quad \Delta G = -0.44\ eV \qquad (55)$$

$$Ru(bpy)_3^{3+} + 1/2\ H_2O \rightarrow Ru(bpy)_3^{2+} + 1/4\ O_2 + H^+ \quad \Delta G = -0.45\ eV \qquad (56)$$

In practice, however, reaction 55 is too slow to compete with the excited state decay. The great number of studies on the problem of the photoinduced water splitting reactions have been reviewed recently by several authors [13–15,42–45,194–198] and will not be discussed any further here.

The conversion of light energy into electrical energy (via intermediate conversion to chemical energy) is also possible using $Ru(bpy)_3^{2+}$ as LAS. Consider, for example, a cell consisting of two identical compartments separated by a sintered glass disk and containing a Pt electrode and an

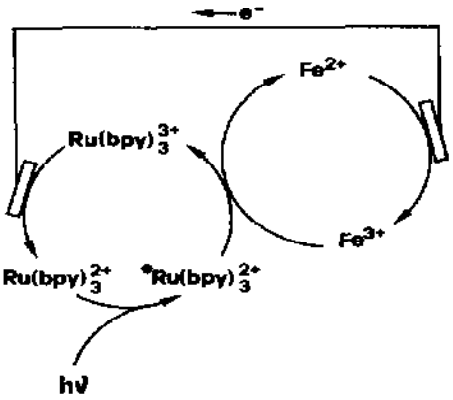

Fig. 26. An example of the use of $Ru(bpy)_3^{2+}$ as LAS: light energy is converted into electrical energy (photogalvanic effect) [199].

aqueous solution of $Ru(bpy)_3^{2+}$ and Fe^{3+} [199]. If one compartment is illuminated and the other is kept in the dark, an electrical potential is generated which depends on the incident light intensity (photogalvanic effect [200]). This potential is due to the difference in the composition of the solutions in the dark and illuminated compartments caused by the following reactions (Fig. 26):

$$Ru(bpy)_3^{2+} + h\nu \rightarrow {}^*Ru(bpy)_3^{2+} \quad (51)$$

$${}^*Ru(bpy)_3^{2+} + Fe^{3+} \rightarrow Ru(bpy)_3^{3+} + Fe^{2+} \quad (57)$$

$Ru(bpy)_3^{2+}$ can also be used to convert light into electrical energy and, at the same time, to carry on a net redox process. For example, photocurrents can be obtained from a cell where the net reaction involves the photochemical oxidation of water by $Co(C_2O_4)_3^{3-}$. The reaction mechanism is as follows [201] (Fig. 27):

Cathodic compartment

$$Ru(bpy)_3^{2+} + h\nu \rightarrow {}^*Ru(bpy)_3^{2+} \quad (51)$$

$${}^*Ru(bpy)_3^{2+} + Co(C_2O_4)_3^{3-} \rightarrow Ru(bpy)_3^{3+} + Co^{2+} + 3C_2O_4^{2-} \quad (58)$$

$$Ru(bpy)_3^{3+} + e^- \rightarrow Ru(bpy)_3^{2+} \quad (59)$$

Anodic compartment

$$OH^- - e^- \rightarrow 1/2\ H_2O_2 \quad (60)$$

(ix) $Ru(bpy)_3^{2+}$ as a light emission sensitizer

As shown in Section A (v), potential chemiluminescent reactions can be transformed into effective chemiluminescent reactions by species called light

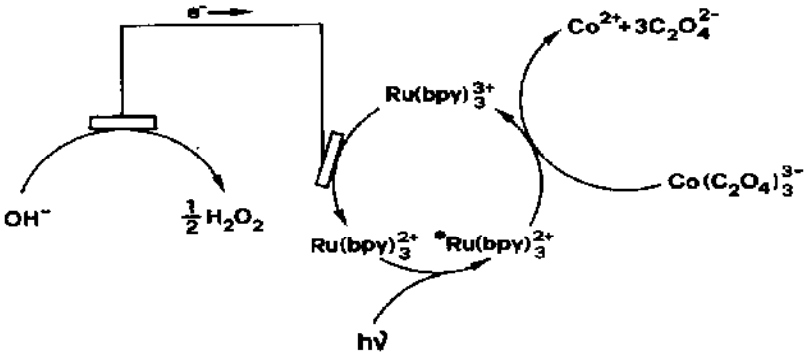

Fig. 27. An example of the use of $Ru(bpy)_3^{2+}$ as LAS: light is used to generate electrical energy and to carry on a net redox process [201].

emission sensitizers (LES) that have appropriate kinetic, thermodynamic, spectroscopic, and excited state properties [38]. $Ru(bpy)_3^{2+}$ possesses such properties to a noticeable degree and is extensively used as LES.

A very interesting example of this type of reaction is that concerning the well known reduction of lead dioxide by oxalate ions in acid medium

$$1/2\ PbO_2 + 1/2\ C_2O_4^{2-} + 2H^+ \rightarrow 1/2\ Pb^{2+} + CO_2 + H_2O \quad \Delta G \sim -2\ eV \tag{61}$$

which would be sufficiently exergonic to produce visible light. In fact, this reaction produces only heat. However, when the reaction is carried out in the presence of $Ru(bpy)_3^{2+}$, light emission is clearly observed [181]. The most likely reaction mechanism involves first the oxidation of $Ru(bpy)_3^{2+}$ by PbO_2 and then the reduction of $Ru(bpy)_3^{3+}$ by $C_2O_4^{2-}$ already discussed to yield the luminescent $^*Ru(bpy)_3^{2+}$ excited state (Fig. 28).

$$Ru(bpy)_3^{2+} + 1/2\ PbO_2 + 2H^+ \rightarrow Ru(bpy)_3^{3+} + 1/2\ Pb^{++} + H_2O \tag{62}$$

$$Ru(bpy)_3^{3+} + C_2O_4^{2-} \rightarrow Ru(bpy)_3^{2+} + CO_2 + CO_2^- \tag{45}$$

$$Ru(bpy)_3^{3+} + CO_2^- \rightarrow {}^*Ru(bpy)_3^{2+} + CO_2 \tag{46}$$

$$^*Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + h\nu \tag{38}$$

In the previously discussed (Section B (vii)) electrochemiluminescent reactions involving $Ru(bpy)_3^{2+}$ and $S_2O_8^{2-}$, $Ru(bpy)_3^{2+}$ and $C_2O_4^{2-}$, and $Ru(bpy)_3^{2+}$ alone, $Ru(bpy)_3^{2+}$ actually plays the role of LES, as can be better seen from Figs. 29–31. In particular, the electrogenerated chemiluminescence process shown in Fig. 31 is to some extent the reverse of the photogalvanic effect previously seen (Fig. 26) and the processes in which chemiluminescence is generated by a combined use of chemical and electri-

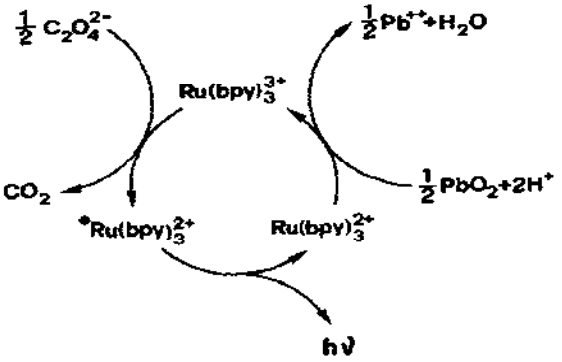

Fig. 28. An example of the use of $Ru(bpy)_3^{2+}$ as light emission sensitizer (LES): chemical energy is converted into light energy [181].

cal energy (Figs. 29 and 30) are to some extent the reverse of the process in which light carries on a chemical reaction generating a photocurrent (Fig. 27).

The most curious reaction in which $Ru(bpy)_3^{2+}$ plays the role of LES is in the oscillating Belousov–Zhabotinskii reaction. This very complicated reaction essentially consists of the oxidation of carboxylic acids by bromate ions (eqn. 63) catalyzed by one-electron redox couples such as $Ru(bpy)_3^{3+/2+}$:

$$3BrO_3^- + 5CH_2(COOH)_2 + 3H^+ \xrightarrow{Ru(bpy)_3^{3+/2+}} 4CO_2 + 3BrCH(COOH)_2 + 2HCOOH + 5H_2O \qquad (63)$$

This reaction proceeds through periodic rate fluctuations (oscillating reaction) which also cause a fluctuation in the concentration of $Ru(bpy)_3^{3+}$. When it was recognized that $Ru(bpy)_3^{3+}$ can be reduced by carboxylic acids thus emitting light (see, e.g., eqns. 45 and 46), it was thought [202] that because of the fluctuation of the $Ru(bpy)_3^{3+}$ concentration and the presence of carboxylic acid an oscillating chemiluminescence emission should be

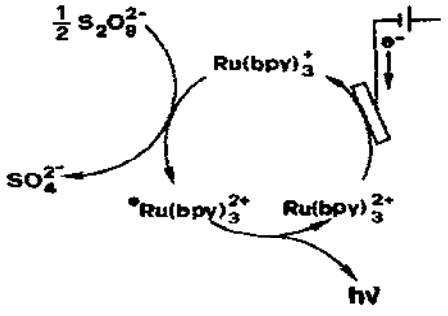

Fig. 29. An example of the use of $Ru(bpy)_3^{2+}$ as LES: electrical energy and chemical energy are converted into light energy in a reductive oxidation process [176,177].

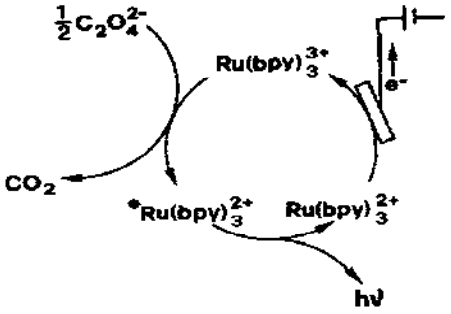

Fig. 30. An example of the use of $Ru(bpy)_3^{2+}$ as LES: electrical energy and chemical energy are converted into light energy in an oxidative reduction process [181,182].

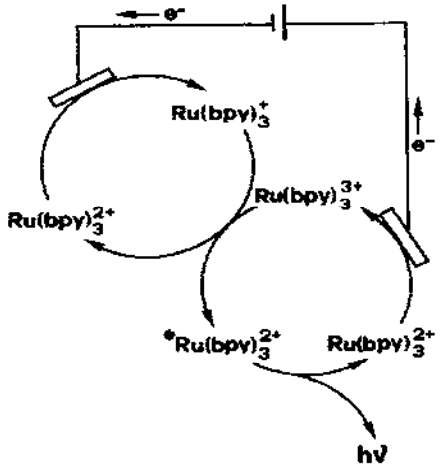

Fig. 31. An example of the use of $Ru(bpy)_3^{2+}$ as LES: electrical energy is converted into light energy [59].

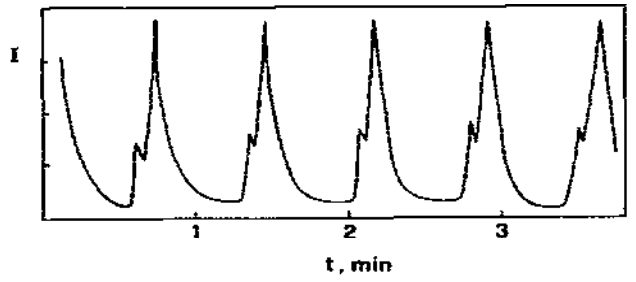

Fig. 32. Oscillating chemiluminescence observed using $Ru(bpy)_3^{2+}$ as LES in the Belousov–Zhabotinskii reaction [202] (see text).

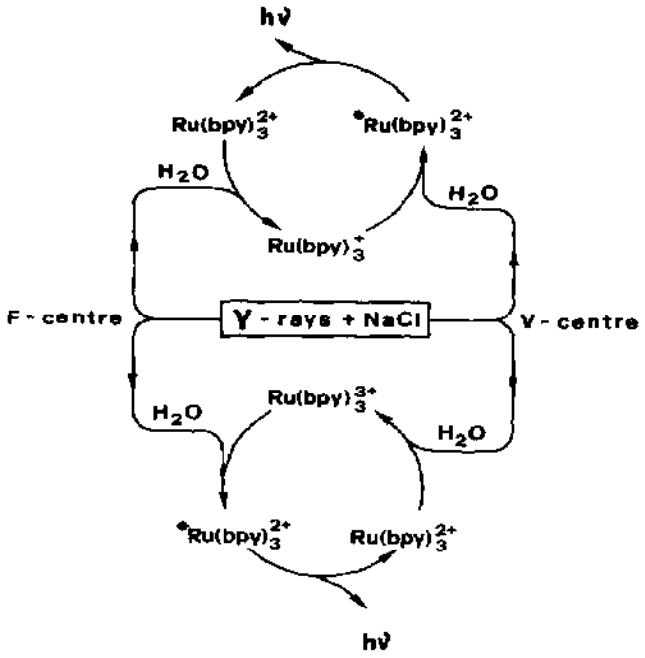

Fig. 33. An example of the use of $Ru(bpy)_3^{2+}$ as LES: chemical energy stored into γ-irradiated solids is converted into light (sensitized lyoluminescence) [203].

produced by the Belousov–Zhabotinskii reaction. This expectation was fulfilled as shown in Fig. 32 which reports the time dependence of the chemiluminescent signal generated by the reaction. This chemical system can be considered as an artificial firefly.

Finally, it has been recently shown [203] that dissolution of γ-irradiated NaCl in aqueous solutions containing $Ru(bpy)_3^{2+}$ causes generation of the characteristic $*Ru(bpy)_3^{2+}$ luminescence. The reaction mechanism of this process, where $Ru(bpy)_3^{2+}$ mediates the conversion into light of the chemical energy stored into γ-irradiated solids (sensitized lyoluminescence), involves a complicated sequence of redox reactions initiated by the dissolution in water of the *F*- and *V*-centres of the irradiated NaCl crystals. First $Ru(bpy)_3^{2+}$ is reduced to $Ru(bpy)_3^{+}$ or oxidized to $Ru(bpy)_3^{3+}$. Then, oxidation of $Ru(bpy)_3^{+}$ (eqn. 36) or reduction of $Ru(bpy)_3^{3+}$ (eqn. 37) or the comproportionation reaction (eqn. 41) can yield $*Ru(bpy)_3^{2+}$. This unusual process where $Ru(bpy)_3^{2+}$ is again involved as LES is schematically shown in Fig. 33.

C. TUNING OF EXCITED STATE PROPERTIES IN THE Ru(II)–POLYPYRIDINE FAMILY

The Ru(II)–polypyridine complexes find their most extensive and interesting applications as (i) photoluminescent compounds (see, e.g., refs.

204–206), (ii) excited state reactants in electron and energy transfer processes (Section B (vi)), and (iii) excited state products in electron transfer chemiluminescence and electrochemiluminescence processes (Section B (vii)). In this section we will deal with the possibility of changing gradually (i.e., "to tune") the excited state properties that are relevant to the above processes. This tuning can be performed by judicious choice and combination of the ligands. In this report more than 200 bidentate polypyridine-type ligands (LL) are contained. In principle, from a group of 200 bidentate ligands, 200 homoleptic complexes $Ru(LL)_3^{2+}$, 39,800 bis-heteroleptic complexes $Ru(LL)_{3-n}(LL')_n^{2+}$, and 1,313,400 tris-heteroleptic complexes $Ru(LL)(LL')(LL'')^{2+}$ could be prepared. The synthetic accessibility of the first (homoleptic) and the second (bis-heteroleptic), and in some cases even of the third group [207] is another feature of Ru(II) chemistry, which makes extensive studies in chemically related series possible.

(i) Orbital nature of the lowest excited state

As we have seen in Section A (ii), for transition metal complexes only the lowest excited state (or the lowest manifold of thermally equilibrated excited states) has a chance to emit luminescence and/or to live long enough to participate in bimolecular processes in fluid solution. In d^6 transition metal complexes the MC excited states are strongly distorted compared with the ground state geometry; this causes fast radiationless deactivation which prevents luminescence from occurring and precludes the participation of the excited state in bimolecular processes. LMCT excited states behave in the same way. By contrast, LC and MLCT excited states, being relatively undistorted, undergo slow radiationless decay processes so that they can give rise to luminescence and can be involved in bimolecular reactions. It follows that the ability to determine the orbital nature of the lowest excited state is a key step toward the design of useful compounds.

The orbital nature of the lowest excited state can be revealed by examination of the luminescence behavior [48,58,208]. Luminescence arising from a ^{3}MC excited state appears as a gaussian-shaped emission band that is devoid of structure and considerably red-shifted compared with the lowest energy absorption bands. The excited state lifetime is relatively long in rigid matrix at 77 K but decreases rapidly with increasing temperature as does the luminescence intensity, so that ^{3}MC emission usually cannot be observed in fluid solution at room temperature. The radiative lifetime is of the order of 10^{-3}–10^{-5} s, indicating that the triplet character is attenuated by spin–orbit coupling, as expected for compounds containing a (heavy) metal ion.

Luminescence from ^{3}LMCT excited states is rare [209] and not well characterized. It can be expected, however, that ^{3}LMCT emission for d^6

transition metal complexes gives rise to a broad unstructured band exhibiting a large Stokes shift because of the large distortion caused by the presence of an electron in the σ_M^* orbitals [2].

Luminescence from a ^{3}MLCT excited state is generally highly structured at low temperature, with a prominent vibrational progression [48,58,112–114,208,210–214]. The lifetime at 77 K is in the 1–10 μs range and the radiative lifetime is only ~ 10 times longer, indicating that the triplet character of MLCT excited states is also strongly attenuated by the metal ion. On increasing temperature, the luminescence intensity and lifetime decrease more or less slowly. Generally, ^{3}MLCT emission is easily observable in fluid solution at room temperature, with lifetimes of the order of 10–1000 ns.

Luminescence originating from a ^{3}LC excited state is usually structured at low temperature as is the luminescence originating from ^{3}MLCT states. Usually it is possible to distinguish the two types of emissions on energy and lifetime grounds [48,58,112,115,117,118,214,215]. ^{3}LC emission occurs quite close to (usually, ~ 1000 cm^{-1} red-shifted from) the emission of the free ligand, whereas ^{3}MLCT emission can occur, of course, at much lower energies. Furthermore, the ^{3}LC emission is less influenced by the (heavy) metal ion, so that it maintains its spin-forbidden character to a larger degree than the ^{3}MLCT emission. Thus, the radiative lifetime of ^{3}LC emission is usually $> 10^{-4}$ s. This relatively slow radiative decay can compete with the slow radiationless decay at low temperature in rigid media, as shown by the appearance of ^{3}LC emission bands in rigid matrix at 77 K. In fluid solution at room temperature, however, ^{3}LC emission can seldom be observed because of the occurrence of faster (thermally activated) unimolecular decay processes and/or bimolecular quenching processes.

It has been known for a long time [48,49,58] that in a series of complexes of the same metal ion one can determine the orbital nature of the lowest excited state by a suitable choice of ligands. The energy of the MC excited states depends on the ligand field strength, which in its turn depends on the σ-donor and π-acceptor properties of the ligands, the steric crowding around the metal (that can preclude a sufficiently close approach between metal and ligand) [40], and the bite angle of the polydentate ligands (which in some cases cannot be optimized because of molecular constraints (see, e.g., ref. 216)). The energy of the MLCT excited states depends on the reduction potential of the ligand involved in the MLCT transition, the oxidation potential of the metal in the complex (which is affected by the electron donor and acceptor properties of all the ligands), and by the charge separation caused by the transition. The energy of the LC excited states depends on intrinsic properties of the ligands, such as the HOMO–LUMO energy gap and the singlet–triplet splitting.

The luminescence of $Ru(bpy)_3^{2+}$ is a typical ^{3}MLCT emission [48]: (i) it occurs at much lower energy ($\nu_{max} = 17\,200\ cm^{-1}$) than the phosphorescence of free bpy ($\nu_{max} = 23\,100\ cm^{-1}$); (ii) the luminescence spectrum is structured at low temperature; (iii) the radiative lifetime is $\sim 13\ \mu s$. Most of the known Ru(II)–polypyridine complexes (Table 1) exhibit a luminescent behavior quite similar to that of $Ru(bpy)_3^{2+}$, indicating that the lowest excited state is a ^{3}MLCT state. By an appropriate choice of the ligands, however, it has been possible to change the orbital nature of the lowest excited state. ^{3}MC emission can be obtained decreasing the ligand field strength, e.g. replacing one or two polypyridine ligands by Cl^- ions [217]. It should be noted, however, that the π-donor ability of the Cl^- ligand also lowers the energy of the MLCT excited states by increasing the negative charge on the metal. Thus, when the $Ru(LL)_3^{2+}$ compound has a ^{3}MLCT excited state at very low energy (as is the case for LL = biq or DMCH), substitution of LL by $2Cl^-$ does not cause an inversion on the excited state energy ordering. A case in which a clean ^{3}MC emission can be observed is $Ru(i\text{-}biq)_2Cl_2$ [217].

^{3}LC emission can be obtained using polypyridine ligands which satisfy the following requirements: (i) presence of a relatively low-lying ^{3}LC level; (ii) sufficiently high ligand field strength to keep ^{3}MC at high energy; (iii) sufficiently negative reduction potential to keep ^{3}MLCT at high energy. The i-biq ligand apparently satisfies these requirements [215]. A clear example of tuning of the excited state orbital nature is shown in Fig. 34. For $Ru(i\text{-}biq)_3^{2+}$, emission is clearly ^{3}LC in nature, as shown by: (i) the shape of the luminescence spectrum, which is identical to that of the free i-biq ligand; (ii) the energy of the emission maximum, which is less than $1000\ cm^{-1}$ red shifted compared with that of the free ligand; (iii) the relatively long emission lifetime at 77 K (96 μs). When an i-biq ligand is replaced by bpy, which has a higher ^{3}LC, a similar ligand field strength, and is easier to

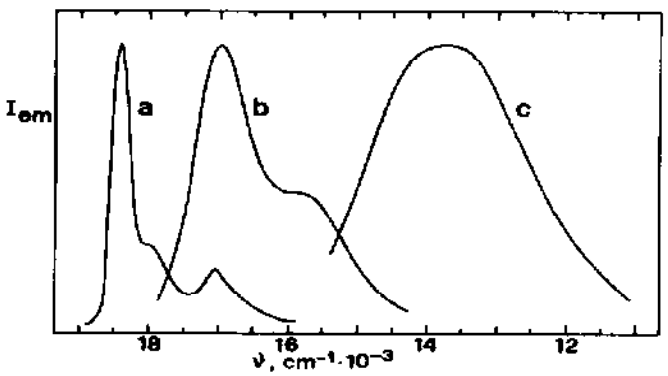

Fig. 34. Emission spectra of $Ru(i\text{-}biq)_3^{2+}$ (a), $Ru(i\text{-}biq)_2(bpy)^{2+}$ (b), and $Ru(i\text{-}biq)_2Cl_2$ (c) [217].

reduce, the emission (Fig. 34) moves to the red, exhibits a different structure and a shorter lifetime at 77 K (5 μs), maintaining a high intensity in fluid solution at room temperature, as expected for a ^{3}MLCT (specifically, Ru → bpy) emitting level [128]. When an i-biq ligand is replaced by two Cl^- ligands, the emission moves further to the red, becomes broad, unstructured, shorter lived (2.2 μs), and can no longer be observed at room temperature as expected for a ^{3}MC emission [217].

Interestingly, a tuning between ^{3}LC and ^{3}MLCT can also be obtained by changing the acidity of the solution [218,219]. This happens for the $Ru(LL)_2(CN)_2$ complexes (LL = bpy,phen,i-biq) [218–220] where the CN^- ligands can be protonated at their nitrogen end. The unprotonated forms of the complexes exhibit the usual ^{3}MLCT emission. Protonation withdraws negative charge from the metal, thus moving the MLCT (Ru → LL) levels to higher energy, leaving the LC levels unaffected. For the diprotonated species, the emission clearly exhibits ^{3}LC character as shown, for example, by the extremely long lifetime (8800 μs) of $Ru(i\text{-}biq)_2(CNH)_2^{2+}$ in H_2SO_4 at 77 K [220].

Another interesting case of tuning of the orbital nature of the lowest excited state by changing the pH of the solution occurs in the complexes of 2,2′-dipyridylamine (HDPA) and its deprotonated form (DPA^-) [209]. For the complexes of the deprotonated ligand the lowest excited state appears to be, quite unusually, a ^{3}LMCT level.

(ii) Excited state energy

As mentioned above (see also Table 1), in the great majority of Ru(II)–polypyridine complexes the lowest (luminescent) excited state is a ^{3}MLCT level (or a cluster of ^{3}MLCT levels). For a systematic use of these complexes in luminescence and chemiluminescence experiments and in energy transfer processes it is important to have a series of complexes covering a broad range of excited state energies. This can be done by (i) changing the type of ligand involved in the formation of the MLCT excited state, (ii) controlling the amount of negative charge on the metal by changing the nature of the ligands, and (iii) changing the solvent interaction. The parameters to be taken into consideration are the reduction potential of the free ligand, the σ-donor ability of the ligand (which is related to the pK_a of the free ligand), π-donor and acceptor properties of the ligand, the charge separation in the excited state (since the coulombic interaction between the hole on the metal and the electron on the ligand decreases with increasing separation distance), and solvent parameters which govern the complex–solvent interaction (dielectric constant, donor and acceptor numbers, etc.).

Big changes in the excited state energy can be obtained on changing the ligand involved in the MLCT (e.g., compare $Ru(bpy)_3^{2+}$ with $Ru(bpy)_2(biq)^{2+}$ (Table 1)), while substitution on the ligand aromatic rings offers the opportunity to carry on a fine tuning (e.g., $Ru(bpy)_3^{2+}$ vs. $Ru(4,4'\text{-dm-bpy})_3^{2+}$). Considerable changes in the excited state energy can also be obtained upon substitution of the ligand not involved in the MLCT transition (e.g., $Ru(bpy)(i\text{-biq})_2^{2+}$ vs. $Ru(i\text{-biq})_2Cl_2$), and on changing the solvent when a mixed ligand complex undergoes a strong solvent interaction (e.g., $Ru(bpy)_2(CN)_2$ [221] and $Ru(bpy)(CN)_4^{2-}$ [222]). For complexes containing only one type of ligand (e.g., $Ru(bpy)_3^{2+}$) the solvent effect is very small [98, 223].

(iii) Excited state redox properties

As we have seen in Section A (ii) the excited state redox potentials are given, to a first approximation, by eqns. 8 and 9 and thus they can be tuned by changing the ground state redox potentials and/or the excited state energy. It should also be noted that, with a few exceptions, the redox and spectroscopic orbitals are the same for each Ru(II)–polypyridine complex [65], so that ground state redox potentials and excited state energy are quantities related to one another (see Section D (ii)). Since reduction usually takes place on a ligand, the ground state reduction potential will be roughly related to the reduction potential of the free ligand (compare, e.g., the first reduction potentials of $Ru(bpy)_3^{2+}$ and $Ru(biq)_3^{2+}$, Table 3, with those of the free ligands: $E^0(bpy/bpy^-) = -2.22$ V; $E^0(biq/biq^-) = -1.75$ V). However, the ability of a coordinated ligand to accept an electron also depends on the amount of charge transferred to the metal or received from the metal via the σ and π bonding by the other ligands. It should also be recalled that the changes in the reduction potential of the ground state do not cause an equal change in the reduction potential of the excited state because the energy of the ^{3}MLCT level decreases as the ligand becomes easier to be reduced.

Oxidation of Ru(II)–polypyridine complexes usually consists in the removal of an electron from a $\pi_M(d)$ metal orbital. The oxidation potential, however, is affected by the nature of the ligands because the amount of electric charge localized on the metal (and thus, the tendency to lose an electron) is governed by the σ and π properties of the ligands. For ligands of the same series, the presence of electron withdrawing groups increases the oxidation potential while the opposite occurs, of course, for electron donating substituents. Linear correlations between the reduction potential of the complexes and the Hammet σ constants of the free ligands have been obtained for 4,4′- and 5,5′-disubstituted bpy [224]. A change in the oxidation potential of the ground state causes a change in the excited state

oxidation potential. The relationship between spectroscopic and redox quantities will be discussed in more detail in Section D (ii).

In conclusion, the factors which govern the excited state redox potentials are known and can be manipulated by changing the structure of the ligands. Hundreds of Ru(II)–polypyridine complexes having variable redox potentials in the excited state (and, of course, in the ground state) are now available (Table 3). This is particularly useful for systematic studies where homogeneous series of powerful oxidants or reductants are needed (Section A (iii)).

D. OTHER SELECTED TOPICS

(i) Emission lifetime and its temperature dependence

As we have seen in Section A (ii), the decay of an excited state takes place by competitive radiative and non-radiative processes. This can be expressed by the following equation

$$1/\tau = k^{r} + k^{nr} \tag{64}$$

where τ is the excited state lifetime and k^{r} and k^{nr} are the radiative and non-radiative rate constants.

The temperature dependence of the emission lifetime of several Ru(II)–polypyridine complexes in the temperature range 1.8–77 K in polymethylmethacrylate matrices has been carefully investigated [107–111,123]. The luminescence was found to originate from a cluster of three closely lying levels (ΔE 10–100 cm^{-1}) which are in Boltzmann equilibrium, each having its own radiative and non-radiative temperature independent rate constant.

In this review, we are more interested to examine the temperature dependence of the luminescence lifetime for temperatures from 77 K to room temperature. For this purpose, the two levels separated by 10 cm^{-1} can be dealt with as a single level and their radiative and non-radiative rate constants account for most of the temperature independent lifetime at 77 K. While the rate of the radiative transition is essentially governed by spin and symmetry factors [48], the radiationless rate constant generally increases with decreasing excited state energy, as expected on the basis of the energy gap law [142]. As the temperature increases, the luminescence lifetime is found to decrease with a behavior which is different from complex to complex. Significant examples are shown in Figs. 20 and 35. To account for such behavior, $1/\tau$ can be expressed as a sum of a temperature independent and several temperature dependent terms:

$$1/\tau = k_0 + \sum_i k_i^{nr}(T) \tag{65}$$

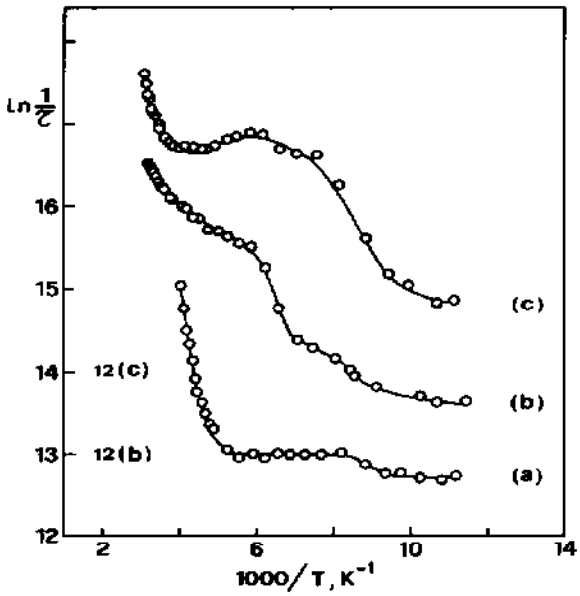

Fig. 35. Temperature dependence of the emission lifetime of $Ru(biq)_3^{2+}$ (a), $Ru(bpy)_2(CN)_2$ (b), and $Ru(taphen)_3^{2+}$ (c). Curves (b) and (c) are shifted along the ordinate axis as indicated.

The temperature dependent terms can be associated, in a schematic way, either to (a) an activated surface crossing to another excited state, described by the Arrhenius equation

$$k_i^{nr} = A_i e^{-\Delta E/RT} \tag{66}$$

or (b) to the coming into play of vibrational modes that can favour the radiationless decay and that are prevented at low temperature because of the frozen molecular environment; this second type of thermally activated process can be dealt with by the following equation

$$k_i^{nr} = \frac{B_i}{1 + \exp\left[C_i\left(1/T - 1/T_{B_i}\right)\right]} \tag{67}$$

which describes stepwise behavior centered at a certain temperature T_{B_i}. In eqn. (67), C_i is temperature-related to the smoothness of the step and B_i is the value attained by k_i at $T \gg T_{B_i}$. A way in which eqn. (67) can be derived from arguments based on dielectric relaxation processes has been reported [137]. This equation is particularly useful for describing the behavior of a system in the glass–fluid transition region of a solvent matrix.

The $1/\tau$ vs. $1/T$ plots (Figs. 20 and 35) can usually be fitted by using eqn. 65, with an appropriate number of terms given by eqns. (66) and (67). For $Ru(biq)_3^{2+}$ (Fig. 35), only one term of the type of eqn. (66) and one term

of the type of eqn. (67) are necessary to account for the behavior observed [128]. For $Ru(bpy)_3^{2+}$ (Fig. 20), two eqn. (66) terms and one eqn. (67) term are needed [131]. For $Ru(bpy)_2(CN)_2$ (Fig. 35), two eqn. (66) and two eqn. (67) terms are required [137]. For $Ru(taphen)_3^{2+}$ (Fig. 35), the behavior is extremely complicated and cannot be fitted with a reasonably simple mathematical equation [136]. When a narrow temperature range concerning fluid solutions is examined, eqn. (67) terms, of course, are not required.

There is general agreement [95,119,121,124,129,137,210,225] in the literature that the Arrhenius type term

$$k_e = A_e \, e^{-\Delta E_e/RT} \tag{68}$$

which accounts for the temperature dependence of the luminescence lifetime at high temperature ($T > 250$ K) is related to an activated surface crossing from the ^{3}MLCT manifold to a ^{3}MC level (eqn. 69) which undergoes photochemical and/or photophysical deactivation (eqn. 70)

$$3_{MLCT} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} 3_{MC} \tag{69}$$

$$3_{MC} \xrightarrow{k_c} \text{ground state and/or photoproducts} \tag{70}$$

Note that k_c represents the sum of all the rate constants of the processes that deactivate ^{3}MC, with the exception of the back surface crossing to ^{3}MLCT. The experimental deactivation rate constant that comes into play at high temperature (eqn. 68) can be expressed as follows on the basis of eqns. (69) and (70):

$$k_e = k_a [k_c/(k_b + k_c)] \tag{71}$$

Eqn. (71) can give rise to two limiting cases (Fig. 36).

(i) When $k_c \gg k_b$, the decay of ^{3}MC is rapid and eqn. (71) becomes

$$k_e = k_a \tag{72}$$

It follows that

$$A_e \exp(-\Delta E_e/RT) = A_a \exp(-\Delta E_a/RT) \tag{73}$$

In this limit, the A_e and ΔE_e parameters obtained from the fitting correspond to the pre-exponential factor and activation energy for the ^{3}MLCT $\rightarrow$ ^{3}MC surface crossing (Fig. 36(a)). It follows that for complexes whose ^{3}MC excited state undergoes a very fast decay, the only way to maintain a long excited state lifetime in fluid solution at room temperature is to have a large activation energy for the ^{3}MLCT $\rightarrow$ ^{3}MC surface crossing. The energy barrier for this surface crossing is presumably related to the energy gap between the zero–zero energies of the two states. Thus, in principle, this

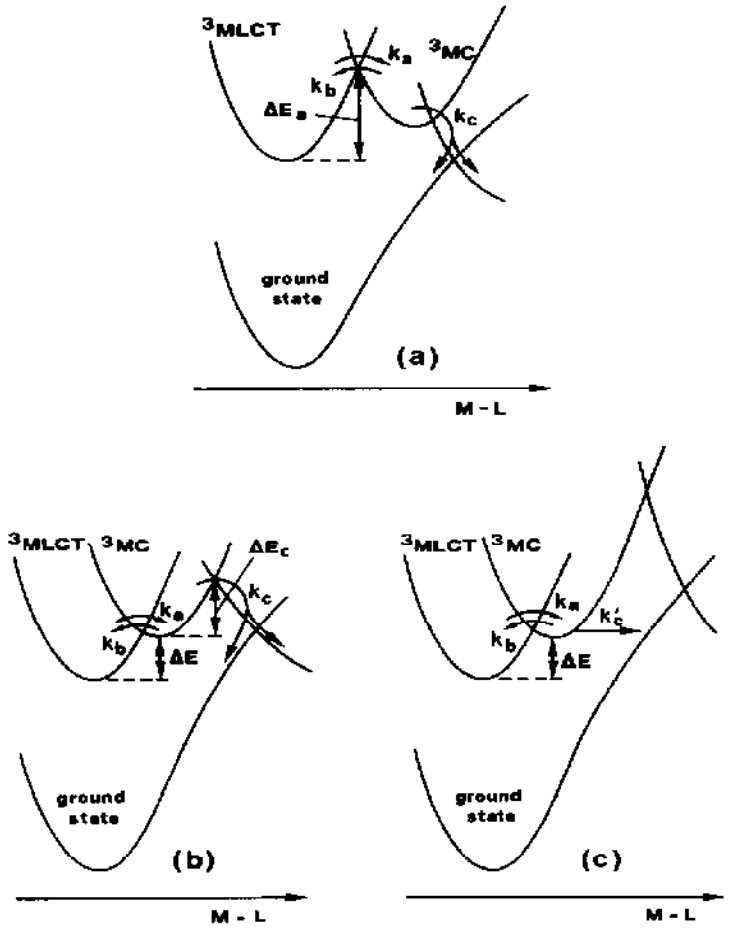

Fig. 36. Schematic representation of the situation of the potential energy surfaces for the three limiting cases described in the text [137].

activation energy can be tuned by tuning the energy of the ^{3}MLCT and ^{3}MC excited states as described in Section C (ii).

(ii) When $k_b \gg k_c$, the decay of ^{3}MC is slow compared to the back surface crossing to ^{3}MLCT. In such a case, the two states are in equilibrium and eqn. (71) becomes

$$k_e = (k_a/k_b)k_c \tag{74}$$

Since $k_a/k_b = K = \exp(-\Delta E/RT)\exp(\Delta S/R)$, where ΔE and ΔS are the internal energy and entropy differences between ^{3}MLCT and ^{3}MC, it follows that

$$A_e \exp(-\Delta E_e/RT) = k_c \exp[-\Delta E/RT] \exp[\Delta S/R] \tag{75}$$

Neglecting the entropic difference between the two states, which is expected to be small, eqn. (75) can be re-written as

$$A_e \exp[-\Delta E_e/RT] = k_c \exp[-\Delta E/RT] \quad (76)$$

The meaning of the experimental quantities A_e and ΔE_e depends on the nature of the processes that contribute to k_c. The following limiting cases are of interest.

(ii-a) When the major contribution to k_c comes from a chemical reaction or a deactivation process that can be described by an Arrhenius-type equation, eqn. (76) can be written as

$$A_e \exp[-\Delta E_e/RT] = A_c \exp[-(\Delta E_c + \Delta E)/RT] \quad (77)$$

In such a case, the A_e and ΔE_e parameters obtained from the fitting of the $1/\tau$ vs. $1/T$ plot correspond to the pre-exponential factor of the decay process of ^{3}MC and to the sum of the ^{3}MC–^{3}MLCT energy gap and the activation energy of the decay process of ^{3}MC (Fig. 36(b)).

(ii-b) When the main contribution to k_c comes from a non-activated process k_c', from eqn. (76) it follows that the pre-exponential parameter A_e corresponds to the rate of the non-activated ^{3}MC decay, k_c', and the activation energy ΔE_e corresponds to the ^{3}MC–^{3}MLCT energy gap, ΔE (Fig. 36(c)). Thus, even in cases (ii-a) and (ii-b) the lifetime at room temperature can be tuned by an appropriate tuning of the energies of the ^{3}MLCT and ^{3}MC levels via the choice of suitable ligands (Section C (ii)).

The meaning of A_e and ΔE_e in the three limiting cases described above is as follows (see also Fig. 36). In principle it can be expected that A_a and A_c are high frequency (10^{13}–10^{14} s^{-1}) vibrations whose activation leads to the surface crossing region (Fig. 36(a) and (b)). By contrast, k_c' can be much smaller because it represents the rate constant of radiationless transition having a poor Franck–Condon factor (Fig. 36(c)). $Ru(bpy)_3^{2+}$ ($A_e \sim 10^{13}$–10^{14} s^{-1}, $\Delta E_e \sim 4000$ cm^{-1}) [128,129] is thought to belong to case (i) [124,129,210,225]. However, on the basis of the values of A_e and ΔE_e it is not possible to distinguish between case (i) and case (ii-a). Several other Ru(II) polypyridine complexes [131,133,135,210,225], exhibit comparable A_e and ΔE_e values and are also considered to belong to the same (i) limit. The A_e and ΔE_e values for $Ru(bpy)_2(CN)_2$, however, are quite different ($A_e \sim 3 \times 10^{10}$ s^{-1}, $\Delta E_e = 2400$ cm^{-1}) [137]. In particular, the value for A_e is too low to correspond to the frequency factor of a surface crossing process. This suggests that $Ru(bpy)_2(CN)_2$ represents a limiting case (ii-b).

(ii) Correlations between spectroscopy and electrochemistry

The ruthenium polypyridine complexes are well suited for the study of correlations between electrochemical and spectroscopic properties [226–240]

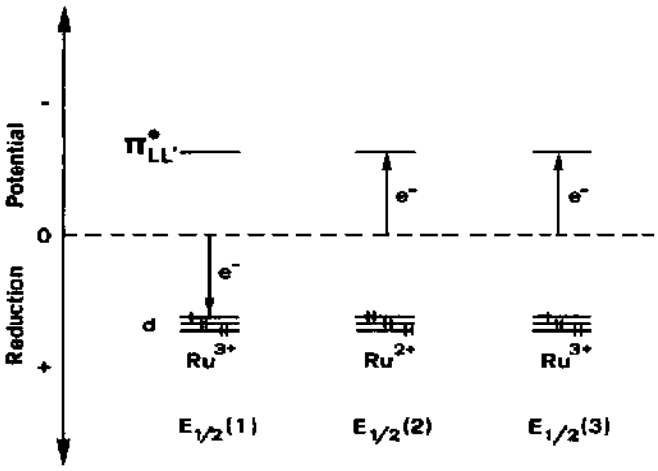

Fig. 37. Schematic diagram showing pictorially the three reduction processes relevant to a discusssion of the correlation between spectroscopic and electrochemical properties in a Ru(LL′) unit.

because a large number of such complexes can be reduced and oxidized in reversible one-electron steps (Table 3) and a wealth of information is available on absorption and emission spectra (Table 1). Relations of this type have been studied in both homoleptic and heteroleptic Ru(II)–polypyridine complexes. In the latter a very simple assignment of the absorption bands and of the reduction waves is often possible. When two polypyridine ligands which are sufficiently different in their redox behavior, such as biq and bpy, are present, generally dual MLCT absorption is observed, and the successive reduction waves can be assigned to a "localized" reduction in a single ligand (see, e.g., ref. 239).

For $Ru(LL)_2(LL')^{2+}$ complexes, where LL′ is the ligand easier to reduce, the relevant reduction potentials to establish the correlation between spectroscopy and electrochemistry are $E_{1/2}(1)$, $E_{1/2}(2)$, and $E_{1/2}(3)$ [233], which correspond to the following processes (Fig. 37)

$$E_{1/2}(1) \quad \left[Ru^{3+}(LL)_2(LL')\right]^{3+} + e^- \rightarrow \left[Ru^{2+}(LL)_2(LL')\right]^{2+} \tag{78}$$

$$E_{1/2}(2) \quad \left[Ru^{2+}(LL)_2(LL')\right]^{2+} + e^- \rightarrow \left[Ru^{2+}(LL)_2(LL'^-)\right]^{1+} \tag{79}$$

$$E_{1/2}(3) \quad \left[Ru^{3+}(LL)_2(LL')\right]^{3+} + e^- \rightarrow \left[Ru^{3+}(LL)_2(LL'^-)\right]^{2+} \tag{80}$$

The values for $E_{1/2}(1)$ and $E_{1/2}(2)$ can usually be obtained, whereas $E_{1/2}(3)$, which corresponds to reduction of LL′ in the Ru^{3+} field, is a quantity not directly measurable (for $Ru(bpy)_3^{2+}$, it is estimated to be -0.8 V vs. SCE in acetonitrile [233]). If the lowest lying triplet excited state is formed by a single configuration $d \rightarrow \pi^*(LL')$ transition occurring between

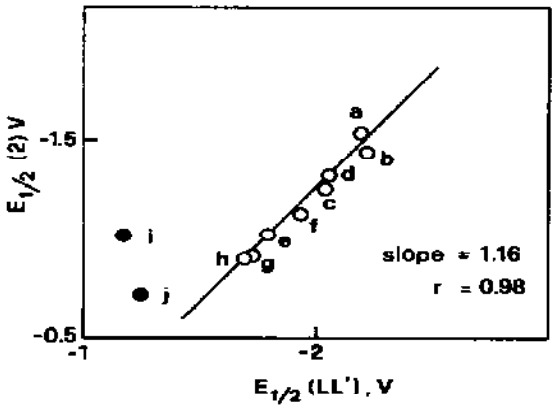

Fig. 38. Correlation between the first reduction potential $E_{1/2}(2)$ of some selected $Ru(LL')_3^{2+}$ or $Ru(LL)_2(LL')^{2+}$ complexes and the reduction potential $E_{1/2}(LL')$ of the free LL' ligand. $Ru(i\text{-}biq)_3^{2+}$ (a); $Ru(i\text{-}biq)_2(bpy)^{2+}$ (b); $Ru(phen)_3^{2+}$ (c); $Ru(bpy)_2(4,4'\text{-}dph\text{-}bpy)^{2+}$ (d); $Ru(bpy)_2(bpym)^{2+}$ (e); $Ru(bpy)_2(pq)^{2+}$ (f); $Ru(bpy)_2(biq)^{2+}$ (g); $Ru(bpy)_2(bpz)^{2+}$ (h); $Ru(bpy)_2(DP)^{2+}$ (i); and $Ru(bpy)_2(taphen)^{2+}$ (j). The regression has been performed using only the open circle data [240].

the same orbitals that are involved in the electrochemical processes and the entropy difference between ground and excited state is negligible, the 0–0 triplet excited state energy is given by

$$h\nu_{00}(T) = e\left[E_{1/2}(1) - E_{1/2}(3)\right] + X_T \tag{81}$$

where X_T is the triplet charge transfer interaction energy.

The structure of LL' largely determines the electrochemical and spectroscopic properties of Ru–polypyridine complexes. Figure 38, for example, reports the first reduction potential, $E_{1/2}(2)$, of some $Ru(LL')_3^{2+}$ or $Ru(LL)_2(LL')^{2+}$ complexes compared with that of the free ligand, $E_{1/2}(LL')$ [240]. The good correlation (with the exception of two complexes, vide infra) indicates that the reduction of the complexes involves a "spatially isolated" $\pi^*(LL')$ ligand orbital (Section D (iii)) which largely resembles the free ligand orbital. Furthermore, σ-donor and π^*-acceptor properties of the ligands are expected to affect the oxidation process (removal of an electron from a metal *d* orbital). Stronger σ-donor ability (higher pK_a) results in lower formal charge of Ru^{2+} and consequently in a lower oxidation potential of the complex [224,230,232,234,241]. On the other hand, d–π^* interaction causes a certain amount of *d*-orbital stabilization (and π^* orbital destabilization) which may lead to a higher oxidation potential. Substituent effects on the oxidation potential of $Ru(bpy)_3^{2+}$ derivatives have been systematically investigated [224].

$E_{1/2}(3)$ is related to $E_{1/2}(2)$ by the following equation:

$$E_{1/2}(3) = E_{1/2}(2) + (\alpha' - S') \tag{82}$$

where α' and S' are potential terms which take into account the energy changes due to changes in charge repulsion (α) and solvation (S) on passing from Ru^{3+} to Ru^{2+} fields. Substitution of eqn. (82) into eqn. (81) yields

$$h\nu_{00}(T) = \Delta E_{1/2} - (\alpha - S) + X_T \tag{83}$$

where $\Delta E_{1/2}$ is the so called "redox energy", given by

$$\Delta E_{1/2} = e\left[E_{1/2}(1) - E_{1/2}(2)\right] \tag{84}$$

The term $(\alpha - S)$ is estimated to be 0.5 eV in $Ru(bpy)_3^{2+}$ [233].

Equation (83) gives rise to eqn. (85)

$$h\nu_{max}^{em}(T) = \Delta E_{1/2} - (\alpha - S) + X_T - \Delta(h\nu)_T \tag{85}$$

where $\Delta(h\nu)_T$ takes into account the distortion energy for the triplet state. As can be seen, the linearity between $h\nu_{max}^{em}$ and $\Delta E_{1/2}$ depends on the constancy of $(\alpha - S)$, X_T and $\Delta(h\nu)_T$ along a Ru–polypyridine series. For the lowest excited singlet state

$$h\nu_{00}(S) - h\nu_{00}(T) = 2K + X_S - X_T \tag{86}$$

where K is the exchange energy and X_S is the singlet interaction energy. Equation (87) then follows, where $\Delta(h\nu)_S$ takes into account the distortion energy for the singlet state:

$$h\nu_{max}^{abs} = \Delta E_{1/2} - (\alpha - S) + 2K + X_S - X_T + \Delta(h\nu)_S \tag{87}$$

Typical values for $Ru(bpy)_{3-n}(LL)_n^{2+}$ complexes are: $\Delta(h\nu)_S = \Delta(h\nu)_T = 0.1$ eV; $K = 0.1$ eV; $X_S = 0.3$ eV [233].

A different approach [236,237,242], based on the use of a free energy diagram relating optical (absorption) energies and electrochemical quantities, leads to eqn. (88):

$$h\nu_{max}^{abs} = \Delta E_{1/2} + Q + \Delta\Delta G_S + \Delta(sol) + \chi_i + \chi_o \tag{88}$$

where χ_i and χ_o are the inner (vibrational) and outer (solvation) reorganization energies in going from the ground to the excited state related to $\Delta(h\nu)_S$, Q is the energy required for the gas phase process $M(LL)^{3+} + M(LL)^{+} \rightarrow M(LL)^{2+} + {}^{*}M(LL)^{2+}$, $\Delta\Delta G_S$ includes the free energy changes due to the different solvation of the ground state compared to its oxidized and reduced forms, and $\Delta(sol)$ includes the solvation free energy of the ground and excited state species. Equation (88) has been used to obtain values of χ_o for $Ru \rightarrow LL$ and $Ru \rightarrow LL'$ transitions in the $Ru(bpy)_2(LL')^{2+}$ and $Ru(bpy)(LL')_2^{2+}$ series [236].

Equations (87) and (88) and eqn. (85) can be written as eqns. (89) and

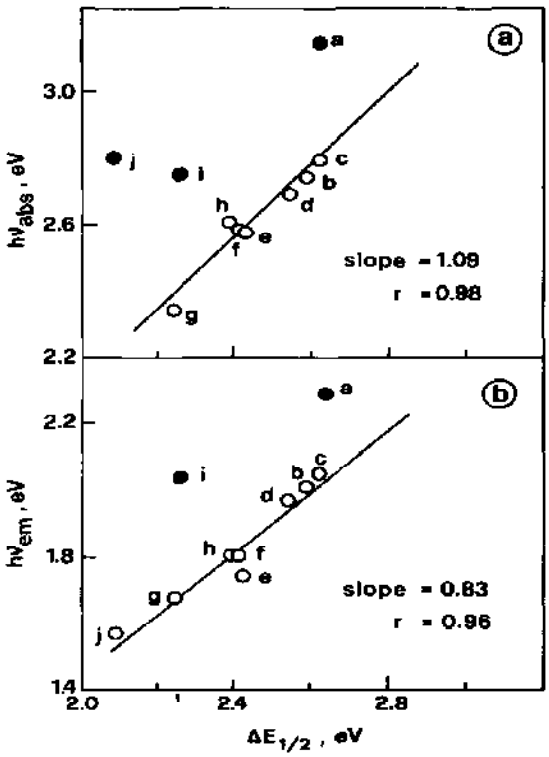

Fig. 39. Correlation between absorption (a) and emission (b) energies and redox energy $\Delta E_{1/2}$ for the same complexes of Fig. 38 [240].

(90) for the absorption and emission maxima, respectively, with $a = b = 1$ and $A \neq B$.

$$h\nu_{abs} = a\ \Delta E_{1/2} + A \tag{89}$$

$$h\nu_{em} = b\ \Delta E_{1/2} + B \tag{90}$$

Figure 39 shows the correlations between optical energies and $\Delta E_{1/2}$ for some representative Ru–polypyridine complexes [240]. The coefficients are: $a = 1.09$, $A = -0.05$ eV; $b = 0.83$, $B = -0.18$ eV. Generally, b is found to be significantly lower than unity [232,238], which may be taken as an indication that the $d \rightarrow \pi^*$ single configuration description is an approximation not fully valid for the case of emission.

As discussed above, the correlation between spectroscopy and electrochemistry lies on the assumption that the "spatially isolated" π^* acceptor orbital is the same both for the reduction process and the CT transition resulting in the ligand localized excited state. Furthermore, correlations can also be expected between the reduction potentials of the coordinated and free ligand, because the same π^* lowest unoccupied molecular orbital

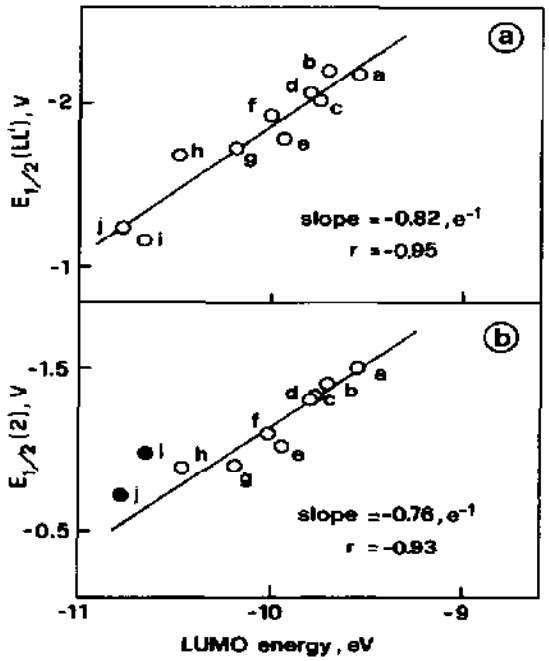

Fig. 40. Correlations of the reduction potential of the free ligand (a) and of the correspondent ruthenium complex (b) with the LUMO energy of the free ligand [240]. For identification of complexes, see caption of Fig. 38.

(LUMO) is involved. Extended Huckel (EH) MO calculations on a series of unsubstituted ligands have been performed [240] with the aim of studying the effect of increasing conjugation on the spectroscopic and electrochemical properties. Figure 40(a) shows that $E_{1/2}(LL')$ is correlated, as expected, with the calculated ligand LUMO energy. As seen above, the plot of $E_{1/2}(2)$ vs. $E_{1/2}(LL')$ also results in a linear relation (Fig. 38) except for complexes containing the ligands taphen [136] and DP [243]. Similarly, the plot of $E_{1/2}(2)$ vs. E_{LUMO} (Fig. 40(b)) exhibits deviations for complexes containing taphen and DP. Explanation for these deviations have recently been discussed [240].

(iii) Localization and delocalization problems

The problem of the localization or delocalization of the excitation is concerned with the description of the excited state $^*Ru(LL)_3^{2+}$ as $[Ru^{3+}(LL)_2(LL^-)]^{2+}$ or as $[Ru^{3+}(LL^{-1/3})_3]^{2+}$. The former case corresponds to a situation in which the promoted electron resides for a certain amount of time on a single ligand (Fig. 15(b)). The latter case describes a situation in which either the electron is completely shared by the three

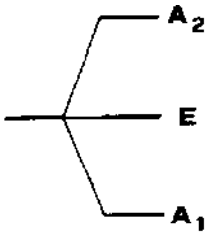

Fig. 41. Energy level scheme (D_3 symmetry) in the e.i.c. model [111] for the MLCT states responsible for the emission of $Ru(LL)_3^{2+}$ complexes. The energy separation between the A_1 and E and A_1 and A_2 states is of the order of 10 cm^{-1} and 50 cm^{-1}, respectively, in $Ru(bpy)_3^{2+}$.

ligands or it undergoes hopping from ligand to ligand faster than the resolution time of the monitoring technique (Fig. 15(a)).

Models concerned with the excited state structure of Ru(II)–polypyridine complexes have to take into account a very large body of literature [50,65–67,69,71–74,93,98,99,102,107–111,123,141,211,244–314].

The reference model of delocalization, as derived from studies of luminescence, is the electron-ion coupling (e.i.c.) model [107–111,123]. This model leads to a description of the lowest energy $d \rightarrow \pi^*$ configurations as a set of three levels. The promoted electron resides in an orbital (a_2 in D_3 symmetry) based on the lowest antibonding orbitals, ψ_i, of each ligand and encompassing the three ligands:

$$\Psi(a_2) = 1/\sqrt{3}\,(\psi_1 + \psi_2 + \psi_3) \tag{92}$$

In this model the ligand–ligand overlap is explicitly disregarded and the exchange interaction between the excited electron and the electrons remaining in the d^5 core is held responsible for the splitting among the energy levels (scheme shown in Fig. 41). Infinite separation of the promoted electron and the metal core would result in a fourfold degenerate state. The e.i.c. model was also proposed to describe mixed-ligand chelates like $Ru(bpy)_n(phen)_{3-n}^{2+}$ [111] by assuming an electronic symmetry (D_3) higher than that of the molecular structure.

The localized description assumes C_{2v} symmetry for the hypothetical Ru–LL unit [245,263] (Fig. 42). Complete localization, i.e. excitation localized on decoupled ligands throughout the lifetime of the emitting species, seems unlikely because in this case both the emission spectrum and lifetime of mixed ligand complexes should exhibit dual behavior [257,268], as found for $Rh(bpy)_n(phen)_{3-n}^{2+}$ complexes [111,249], that is not actually observed for the Ru complexes [274,275,315].

A simple treatment for the charge transfer transition intensities can be based on the localized fragment of Fig. 42. Here, the interaction between the

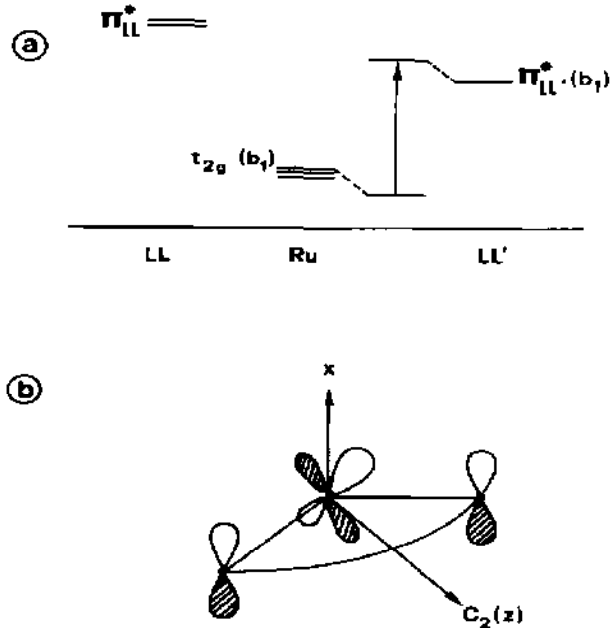

Fig. 42. Localized Ru-LL′ fragment under C_{2v} symmetry: (a) orbital interaction scheme; (b) ligand antibonding and metal orbitals of b_1 symmetry.

$b_1^0(t_{2g})$ metal orbital and the $b_1^0(\psi)$ ligand orbital leads to a bonding combination $b_1(t_{2g})$ mainly centered on the metal and to an antibonding combination $b_1(\psi)$ mainly centered on the ligand

$$b_1(t_{2g}) = b_1^0(t_{2g}) + cb_1^0(\psi) \tag{93}$$

$$b_1(\psi) = b_1^0(\psi) - cb_1^0(t_{2g}) \tag{94}$$

where c is the first order mixing coefficient. From group theoretical considerations the $d \rightarrow \pi^*$ transition for the localized fragment is polarized along the C_2 axis, that is in the direction of the charge transfer from the metal to the ligand. In this case, the transition moment $\vec{\mu}$ is mainly due to the transfer term [245,263]

$$\vec{\mu} = cq\vec{\mathbf{S}} \tag{95}$$

where q is the electronic charge and $\vec{\mathbf{R}}$ is the position vector of the ligand center. On these grounds, for a $Ru(LL)_3^{2+}$ complex (D_3 symmetry) one should expect that transitions polarized along the individual C_2 axes do not provide intensity parallel to the C_3 axis. This is only partly consistent with the absorption spectrum of $Ru(bpy)_3^{2+}$ observed in host single crystals at 8 K [259] which is mainly polarized in the direction perpendicular to the C_3 axis but is also entangled by a weaker component polarized parallel to C_3.

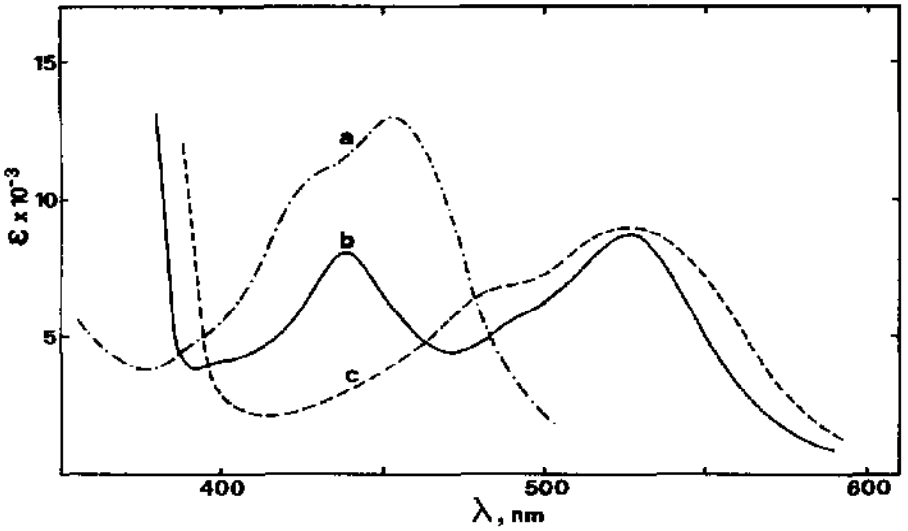

Fig. 43. Absorption spectra in alcoholic solution at room temperature of $Ru(bpy)_3^{2+}$ (a), $Ru(bpy)_2(biq)^{2+}$ (b), and $Ru(biq)_3^{2+}$ (c) [128].

The prediction of separate charge transfer bands based on the localized model is verified for the charge transfer absorption spectra of complexes containing non-equivalent ligands. For example, in $Ru(bpy)_n(biq)_{3-n}^{2+}$ and other mixed ligand complexes ([128,274], Fig. 43) two well separated MLCT bands have been observed, the lower energy one corresponding to promotion of the electron to the ligand easier to reduce. However, even a delocalized model including weak interligand coupling [263] predicts that the MLCT absorption in trischelated complexes should indeed be characterized by two distinct absorption bands.

The electronic spectrum of $Ru(bpy)_3^{2+}$ in host single crystals at 8 K has been interpreted according to D_3 symmetry [259]. Two spin-allowed transitions perpendicular to the C_3 axis were described as involving ligand orbitals of ψ and χ origin. Polarized emission of $[Ru(bpy)_3](PF_6)_2$ single crystals was observed in the temperature range 243–343 K by exciting at 488 nm with $\vec{E} \parallel c$ (C_3 axis) [282]. The emission was found to occur mainly with $\vec{E} \perp c$, but a red-shifted activated emission ($E = 650$ cm^{-1}) with $\vec{E} \parallel c$ was also found. In the frame of D_3 symmetry the main emission was ascribed to E states while the red-shifted emission was ascribed to an A_2 state. Similar results were obtained extending the explored temperature to the 1.6 – 300 K range [286]. On the basis of the temperature dependence studies of the polarized emission spectrum an energy ordering for the lowest energy excited states (D_3 symmetry) was proposed that includes up to five states in a 800 cm^{-1} range.

The analogy between the singly-reduced species, which has been observed by spectro-electrochemical measurements and described as $[Ru^{2+}(bpy)_2(bpy^-)]^+$ (Section A (vii)) [71,72,93,289] and the excited species $[*Ru^{3+}(bpy)_2(bpy^-)]^{2+}$ helps in modeling the excited state potential curves for the localized case [65,66]. One gross feature should be the presence of potential barriers for the transfer of the electron from ligand to ligand. A model based on Franck–Condon overlap between the trigonal ground state and the three equivalent asymmetric excited states has led to three minima as in the case of the reduced complex [289]. Therefore, the excited state potential energy profile could be used for the same parameters found for the singly-reduced species by temperature dependent ESR studies, i.e. the electron hopping should experience a barrier of about 700–1000 cm^{-1} depending on the solvent employed [67,69].

Concerning the spin properties, on the basis of the high efficiency of energy transfer from the luminescent $*Ru(bpy)_3^{2+}$ excited state to dyes with formation of excited singlet dyes it has been suggested that $*Ru(bpy)_3^{2+}$ has a great deal of singlet character [51]. However, the singlet character of each of the three low-lying MLCT levels should not exceed 10% according to a recent electronic model [50] for the interpretation of absorption spectra of $M(bpy)_3^{2+}$ complexes (M = Fe, Ru, Os).

In an attempt to establish a symmetry labelling and energy ordering of the lowest excited states, both D_3 and C_2 symmetry sites have been examined [316]. Four states can be predicted to lie at low energy in a localized MLCT configuration for Ru and Os complexes, three of them being closely spaced (< 200 cm^{-1}) and the fourth occurring several hundred cm^{-1} to higher energy [284]. Molecular orbital calculations performed for $Ru(LL)_3^{2+}$ complexes in the frame of trigonal symmetry and using multiple scattering $X\alpha$ and EH models satisfactorily compare with the known low-temperature single crystal absorption spectrum of $Ru(bpy)_3^{2+}$ [264]. The assignment of the MLCT transitions occurring at 21 500 and 23 400 cm^{-1} was based on the involvement of the lowest antibonding ψ orbital of the ligands, since the ligand χ orbital lies at much higher energy (see Section A (vi)). Interpretation of the CD spectrum of $Ru(bpy)_3^{2+}$ as resolved into many components based on the lowest energy ψ orbital has led to the same conclusions [262].

Photoselection studies on $Ru(bpy)_3^{2+}$ and related complexes indicate that the emitting state is localized on a single ring [255,269] and temperature dependent data suggest that both intermolecular (solvent–solute) and intramolecular mechanisms are active in single ligand localization of the excitation for $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ [290,314].

Other studies basically employing absorption or luminescence spectroscopy [271,272,294,295,304] have tried to elucidate the localization prob-

lem, also with special emphasis on viscosity dependent relaxation effects [132,293,303,305,306,310,311].

Studies based on resonance Raman spectroscopy have provided evidence for localization of the excitation both in mixed ligand complexes and in complexes containing equivalent ligands [74,102,253,299,307]. Time resolved resonance Raman (TR^3) studies of $Ru(bpy)_3^{2+}$ and related complexes have given evidence for a single ligand localized excited state on the time scale of molecular vibrations. It was argued that the localized species is present in solution within a maximum of 1 ns after the excitation [102]. Similar conclusions were reached by means of resonance Raman spectroscopy of mixed ligand complexes. It was found that on the time scale of the laser pulse (18 ns) the excited electron is localized on the ligand which is easier to reduce [307].

Detailed structural information can be obtained by the TR^3 technique. Indeed high precision determination of an average equilibrium bond length displacement (of the order of 10 to 30 thousands of an ångstrom unit) between the ground and excited states for the bpy ligand in Os and Ru complexes has been reported [211]. These results are in a very good agreement with those obtained from Franck–Condon analysis of the vibrational progression observed in absorption and emission spectra.

Evidence for localization also comes from shifts in absorption spectra as a function of the solvent polarity, which have been interpreted as due to instantaneous sensing of the formation of the dipolar excited state $[M^{3+}(bpy)_2(bpy^-)]^{2+}$ [98], and from excited state absorption spectra [99–101].

As can be seen, the available experimental results indicate that, in fluid solution and on the time scale of vibration relaxation, the emitting excited state of $Ru(bpy)_3^{2+}$ and related complexes is best described as based on a single chelate ring localized orbital (Fig. 15(b)). A small amount of inter-ligand interaction provides delocalization of the excitation on longer time scales. Upper limit value for the rate of transfer of the excitation can be estimated as follows. According to Foerster [244] an electronic interaction, β, can be classified as very strong if the resulting transfer rate, $w(t)$, between equivalent electronic systems (i.e., ligands) is faster than the rate of vibrational relaxation. In this case eqn. (96) holds

$$w(t) = 4\beta/h \tag{96}$$

As the rate constant for vibrational relaxation is about 10^{13} s^{-1}, a value of β slightly higher than 200 cm^{-1} induces strong coupling behavior. In such a case, different emission spectra for complexes containing the $Ru(bpy)^{2+}$ and $Ru(bpy)_2^{2+}$ emitting units should be observed. As the same spectra have been found for the series of mixed-ligand $Ru(bpy)_n(i\text{-}biq)_{3-n}^{2+}$ complexes

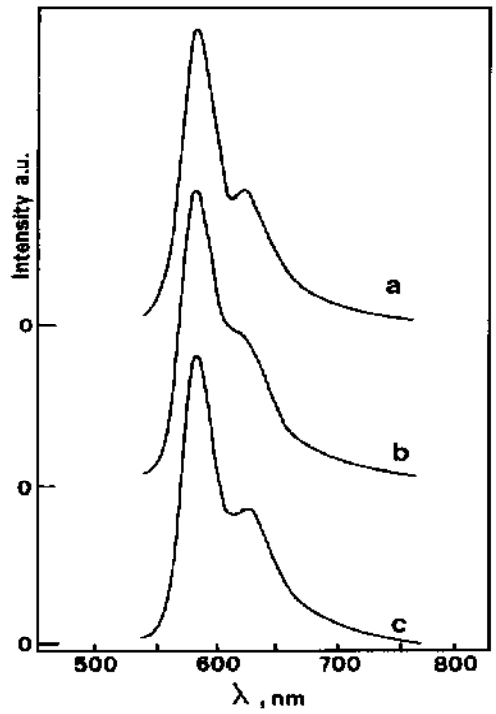

Fig. 44. Emission spectra in nitrile solution at 84 K of $Ru(bpy)_3^{2+}$ (a), $Ru(bpy)_2(i\text{-}biq)^{2+}$ (b), and $Ru(bpy)(i\text{-}biq)_2^{2+}$ (c) [131].

containing the spectator i-biq ligand (Fig. 44) [131], it must be concluded that $w(t) < 10^{13}\ s^{-1}$ and that thermal equilibrium, i.e. vibrational relaxation inside the Ru(bpy) unit, is established before the transfer of excitation occurs.

It is interesting to note that, in the case of strong interaction between non-equivalent electronic systems (i.e. ligands), the transfer rate is given by eqn. (97) [247]

$$w(t) = (4\beta/h)/(1 + \Delta^2/4\beta^2)^{1/2} \tag{97}$$

where Δ can be taken as the energy separation between the accepting orbitals of the two ligands. When $\Delta \gg \beta$, the transfer rate of excitation is strongly reduced compared to the case of eqn. (96) for equivalent ligands. It is therefore expected that complexes of the type $Ru(LL)_n(LL')_{3-n}^{2+}$ will exhibit a "weaker" behavior with respect to $Ru(LL)_3^{2+}$ or $Ru(LL')_3^{2+}$ complexes.

The nature of the electronic interaction responsible for the interligand transfer of the excitation is still not well defined. A through bond interaction requires involvement of metal *d* orbitals as for the e.i.c. model. A through space interaction [248] should not be disregarded when large size ligands

that exhibit reciprocal steric hindrance (i.e., that 'touch' each other) are present. Thus, it has been suggested that in complexes containing biq and DMCH ligands the interligand interaction may produce detectable effects on the emission spectra [128,132].

E. COLLECTION OF SPECTROSCOPIC, REDOX, PHOTOCHEMICAL, AND PHOTOPHYSICAL DATA

In this Section we have collected data on ground and excited state properties of Ru(II)–polypyridine complexes. Table 1 summarizes the spectroscopic and photophysical data, Table 2 the photochemical properties, and Table 3 the electrochemical data.

Abbreviations and structural formulae of the ligands are shown in the Appendix. For the sake of convenience, all the polypyridine and polypyridine-like ligands and some other ligands have been numbered. In the Tables, the first four columns contain these numbers or abbreviations to facilitate a search based on the coordination sphere. One example of a proper use of the Tables is as follows. To find the complexes containing the 4,4′-dimethyl-2,2′-bipyridine ligand, one should first look at the structural formulae in Table A2, where number 15 is assigned to this ligand. Scanning the first columns of the Tables this number is easily found. The abbreviations for solvents, electrodes, etc., are explained in Table A3. The figures given in the Tables are usually those reported in the original papers. Such data should be used with caution because, as in our experience, the experimental errors in quantum yields, lifetimes, and redox potentials are seldom smaller than 20%, 10% and 10 mV, respectively.

ACKNOWLEDGMENTS

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TABLE 1

Spectroscopic and photophysical data. This Table lists the lowest energy absorption maximum (and its extinction coefficient ϵ) at room temperature, the emission maximum, the emission lifetime, and the emission quantum yield at 77 K and at room temperature (RT). Lifetime and quantum yield values are for de-aerated solutions unless otherwise noted. Wavelengths are in nm and lifetimes in μs. Unless otherwise noted, emission occurs from ^{3}MLCT or from an unassigned level (most likely ^{3}MLCT)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
1	CN	CN	CN	$Ru(bpy)(CN)_4^{2-}$	DMF	562	610	2.0		813	~ 0.004		222
1	CN	CN	CN	$Ru(bpy)(CN)_4^{2-}$	EtOH	457	568	2.2		671	0.025		222
1	CN	CN	CN	$Ru(bpy)(CN)_4^{2-}$	H_2O	400	521	6.8		602	0.101	0.0068	222
1	en	en		$Ru(bpy)(en)_2^{2+}$		510	722				0.064		317
1	1	AN	AN	$Ru(bpy)_2(AN)_2^{2+}$	CH_2Cl_2	426							318
1	1	AN	AN	$Ru(bpy)_2(AN)_2^{2+}$	MeOH/EtOH		542						318
1	1	AN	Cl	$Ru(bpy)_2(AN)Cl^+$	CH_2Cl_2	481							318
1	1	AN	Cl	$Ru(bpy)_2(AN)Cl^+$	MeOH/EtOH		627						318
1	1	Cl	Cl	$Ru(bpy)_2Cl_2$	DMF	553 (8910)							319
1	1	Cl	Cl	$Ru(bpy)_2Cl_2$	MeOH/EtOH		705	0.69					97,320
1	1	Cl	Cl	$Ru(bpy)_2Cl_2$	MF	538 (9890)	752	0.17 [a]					217
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	AN	445 (9000)					0.34		321
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	AN	494				675			221
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	$CHCl_3$	495				652	0.54	0.072	221
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	D_2O						0.456		322
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	DMF						0.22		323
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	DMF	505	680	0.205					324
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	DMF	505				680	0.205		325
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	DMF	506 (8350)	620	3.5		683	0.22	0.020	221
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	H_2O	431 (5900)				635	0.27		323
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	H_2O						0.26		326
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	H_2O						0.254		322
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	H_2O	428				620	0.250		325
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	$HClO_4$ 1M						0.36		321
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	MeOH	457 (8400)				653	0.40		323

1	1	CN	CN	$Ru(bpy)_2(CN)_2$	MeOH						0.40		327
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	MeOH		578						219 [b]
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	MeOH	458		3.9		636	0.39	0.038	221
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	MeOH/EtOH		592						97
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	MeOH/EtOH			3.96	0.269				104
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	MeOH/EtOH			4.0	0.27				107
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	MeOH/EtOH		584						323
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	MeOH/EtOH		580	3.8					40
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	$MeOH/H_2O$		566						323
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	MF	467				648			221
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	PMM			3.96					328
1	1	CO	CO	$Ru(bpy)_2(CO)_2^{2+}$	CH_2Cl_2	305							318
1	1	CO	CO	$Ru(bpy)_2(CO)_2^{2+}$	MeOH/EtOH		443						318
1	1	dia	dia	$Ru(bpy)_2(diars)^{2+}$	MeOH/EtOH		551						210
1	1	dmp	dmp	$Ru(bpy)_2(dmpe)^{2+}$	MeOH/EtOH		557						210
1	1	EDP		$Ru(bpy)_2(EDP)^{2+}$	MeOH/EtOH		518						210
1	1	en		$Ru(bpy)_2(en)^{2+}$		487	624				0.070		317
1	1	en		$Ru(bpy)_2(en)^{2+}$	MeOH/EtOH		683	0.71					97,320
1	1	en		$Ru(bpy)_2(en)^{2+}$	MeOH/EtOH			0.96	0.0222				104
1	1	MPP		$Ru(bpy)_2(MPP)_2^{2+}$	CH_2Cl_2	429							318
1	1	MPP		*cis*-$Ru(bpy)_2(MPP)_2^{2+}$	MeOH/EtOH		540						210
1	1	MPP		$Ru(bpy)_2(MPP)_2^{2+}$	MeOH/EtOH		547						318
1	1	MPP		*trans*-$Ru(bpy)_2(MPP)_2^{2+}$	MeOH/EtOH		549						210
1	1	NH_3	NH_3	$Ru(bpy)_2(NH_3)_2^{2+}$		488	734				0.033		317
1	1	ox		$Ru(bpy)_2(ox)$	MeOH/EtOH		714	0.60					97,320
1	1	ox		$Ru(bpy)_2(ox)$	MeOH/EtOH			0.61	0.0124				104
1	1	1		$Ru(bpy)_3^{2+}$	1-decanol	454				630		0.056	223
1	1	1		$Ru(bpy)_3^{2+}$	1-octanol	454				628		0.061	223
1	1	1		$Ru(bpy)_3^{2+}$	1-pentanol	452				610		0.059	223
1	1	1		$Ru(bpy)_3^{2+}$	2-propanol						0.87		155
1	1	1		$Ru(bpy)_3^{2+}$	Ac. anh.	451				611		0.075	223
1	1	1		$Ru(bpy)_3^{2+}$	AN						0.850		321

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
1	1	1	$Ru(bpy)_3^{2+}$	AN	452 (13000)				615	1.10		329
1	1	1	$Ru(bpy)_3^{2+}$	AN	450				611	0.89	0.059	223
1	1	1	$Ru(bpy)_3^{2+}$	AN							0.062	126
1	1	1	$Ru(bpy)_3^{2+}$	AN					609	0.87		330
1	1	1	$Ru(bpy)_3^{2+}$	AN	451				620	0.86	0.086	232
1	1	1	$Ru(bpy)_3^{2+}$	BN	454				609	0.92	0.073	223
1	1	1	$Ru(bpy)_3^{2+}$	BzOH	454				610		0.078	223
1	1	1	$Ru(bpy)_3^{2+}$	CD_3OH						0.72		330
1	1	1	$Ru(bpy)_3^{2+}$	CH_3COOH	451				619	0.85	0.065	223
1	1	1	$Ru(bpy)_3^{2+}$	CH_3OD						0.76		330
1	1	1	$Ru(bpy)_3^{2+}$	D_2O						1.02	0.070	138
1	1	1	$Ru(bpy)_3^{2+}$	D_2O						0.936		322
1	1	1	$Ru(bpy)_3^{2+}$	D_2O						1.00		330
1	1	1	$Ru(bpy)_3^{2+}$	D_2O						0.980		146
1	1	1	$Ru(bpy\text{-}d_8)_3^{2+}$	D_2O						1.25	0.079	138
1	1	1	$Ru(bpy)_3^{2+}$	DMF	453				628	0.93	0.068	223
1	1	1	$Ru(bpy)_3^{2+}$	DMF						0.92	0.11	232
1	1	1	$Ru(bpy)_3^{2+}$	DMSO	454				630	0.96	0.077	223
1	1	1	$Ru(bpy)_3^{2+}$	eglyc	452				611		0.070	223
1	1	1	$Ru(bpy)_3^{2+}$	EPA		580	5.92					331
1	1	1	$Ru(bpy)_3^{2+}$	EPA			3.75	0.746		0.926	0.270	96
1	1	1	$Ru(bpy)_3^{2+}$	EPA	446				601	0.945	0.130	332
1	1	1	$Ru(bpy)_3^{2+}$	EtOH	449				603	0.900	0.078	332
1	1	1	$Ru(bpy)_3^{2+}$	EtOH					588	0.79		333
1	1	1	$Ru(bpy)_3^{2+}$	EtOH						0.90	0.060	334
1	1	1	$Ru(bpy)_3^{2+}$	EtOH	450				608	0.74	0.052	223
1	1	1	$Ru(bpy)_3^{2+}$	EtOH						0.68	0.07	232
1	1	1	$Ru(bpy)_3^{2+}$	glycerol						1.2 [c]		335
1	1	1	$Ru(bpy)_3^{2+}$	H_2O	450				580			336

1	1	1	$Ru(bpy)_3^{2+}$	H_2O						0.66		153
1	1	1	$Ru(bpy)_3^{2+}$	H_2O						0.58	0.042	138
1	1	1	$Ru(bpy)_3^{2+}$	H_2O	452 (14600)				607	0.60		149
1	1	1	$Ru(bpy)_3^{2+}$	H_2O						0.600		337
1	1	1	$Ru(bpy)_3^{2+}$	H_2O						0.665		99
1	1	1	$Ru(bpy)_3^{2+}$	H_2O	453				608	0.685	0.055	332
1	1	1	$Ru(bpy)_3^{2+}$	H_2O	450					0.60		12
1	1	1	$Ru(bpy)_3^{2+}$	H_2O						0.64	0.042	334
1	1	1	$Ru(bpy)_3^{2+}$	H_2O	452				628	0.65	0.042	223
1	1	1	$Ru(bpy)_3^{2+}$	H_2O	452 (14000)				628		0.042	338
1	1	1	$Ru(bpy)_3^{2+}$	H_2O							0.028 [c]	338
1	1	1	$Ru(bpy)_3^{2+}$	H_2O						0.576		322
1	1	1	$Ru(bpy)_3^{2+}$	H_2O	452				607	0.580	0.042	299
1	1	1	$Ru(bpy)_3^{2+}$	H_2O					609	0.61		330
1	1	1	$Ru(bpy)_3^{2+}$	H_2O						0.600		146
1	1	1	$Ru(bpy)_3^{2+}$	H_2O					627	0.63	0.053	339
1	1	1	$Ru(bpy)_3^{2+}$	H_2O						0.67	0.053	232
1	1	1	$Ru(bpy\text{-}d_8)_3^{2+}$	H_2O						0.69	0.047	138
1	1	1	$Ru(bpy\text{-}d_8)_3^{2+}$	H_2O						0.69		12
1	1	1	$Ru(bpy)_3^{2+}$	HCl 1.5M						0.53		340
1	1	1	$Ru(bpy)_3^{2+}$	$HClO_4$ 1M						0.62		321
1	1	1	$Ru(bpy)_3^{2+}$	MeOH						0.765		337
1	1	1	$Ru(bpy)_3^{2+}$	MeOH	453 (14650)				620	0.75		341
1	1	1	$Ru(bpy)_3^{2+}$	MeOH	449				609	0.72	0.045	223
1	1	1	$Ru(bpy)_3^{2+}$	MeOH						0.72		330
1	1	1	$Ru(bpy)_3^{2+}$	MeOH/EtOH			5.1					331
1	1	1	$Ru(bpy)_3^{2+}$	MeOH/EtOH			5.21	0.376				104
1	1	1	$Ru(bpy)_3^{2+}$	MeOH/EtOH			5.21	0.376				342
1	1	1	$Ru(bpy)_3^{2+}$	MeOH/EtOH			5.7	0.38				107
1	1	1	$Ru(bpy)_3^{2+}$	MeOH/EtOH		581						337
1	1	1	$Ru(bpy)_3^{2+}$	MeOH/EtOH		578	5.2	0.35				111
1	1	1	$Ru(bpy)_3^{2+}$	MeOH/EtOH		582	5.0					217, 329
1	1	1	$Ru(bpy)_3^{2+}$	MeOH/EtOH		582	5.1	0.328				338
1	1	1	$Ru(bpy)_3^{2+}$	MeOH/EtOH	450 (14300)				630	1.15	0.089	205

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
1	1	1		$Ru(bpy)_3^{2+}$	MeOH/ EtOH							0.029 [c]	205
1	1	1		$Ru(bpy)_3^{2+}$	MeOH/ EtOH	450 (14300)				630		0.089	204
1	1	1		$Ru(bpy)_3^{2+}$	MeOH/ EtOH		580						232
1	1	1		$Ru(bpy\text{-}d_8)_3^{2+}$	MeOH/ EtOH			6.1					138
1	1	1		$Ru(bpy\text{-}d_8)_3^{2+}$	MeOH/ EtOH	448				630		0.096	205
1	1	1		$Ru(bpy\text{-}d_8)_3^{2+}$	MeOH/ EtOH							0.031 [c]	205
1	1	1		$Ru(bpy)_3^{2+}$	PC							0.071	126
1	1	1		$Ru(bpy)_3^{2+}$	PC					620	0.850	0.04	229
1	1	1		$Ru(bpy)_3^{2+}$	PC					622	0.87	0.071	225
1	1	1		$Ru(bpy)_3^{2+}$	py	454				619	0.92	0.087	223
1	1	1	Cl	$Ru(bpy)_2$ (-bpy)Cl^+	HCl 1M	495	680						343
1	1	1	OH	$Ru(bpy)_2$ (-bpy)OH^+	$NaHCO_3$	510	705						343
1	1	7		$Ru(bpy)_2$ $(4\text{-n-bpy})^{2+}$	AN	493 (11100)				625	0.78		344
1	1	7		$Ru(bpy)_2$ $(4\text{-n-bpy})^{2+}$	MeOH/ EtOH		655	3.1					315
1	1	11		$Ru(bpy)_2$ $(6\text{-sty-bpy})^{2+}$	acetone	450 (13800)				616			345
1	1	12		$Ru(bpy)_2$ $(6\text{-tol-bpy})^{2+}$	acetone	450 (13500)				618			345

1	1	13	$Ru(bpy)_2$ $(3,3'\text{-dm-bpy})^{2+}$	AN	448 (11500)				620	0.74		329
1	1	13	$Ru(bpy)_2$ $(3,3'\text{-dm-bpy})^{2+}$	AN						0.59		338
1	1	13	$Ru(bpy)_2$ $(3,3'\text{-dm-bpy})^{2+}$	EtOH						0.39		338
1	1	13	$Ru(bpy)_2$ $(3,3'\text{-dm-bpy})^{2+}$	H_2O	453 (12600)				630	0.41	0.00036	338
1	1	13	$Ru(bpy)_2$ $(3,3'\text{-dm-bpy})^{2+}$	H_2O							0.00030 [c]	338
1	1	13	$Ru(bpy)_2$ $(3,3'\text{-dm-bpy})^{2+}$	MeOH						0.44		338
1	1	13	$Ru(bpy)_2$ $(3,3'\text{-dm-bpy})^{2+}$	MeOH/ EtOH		595	5.3					40, 329
1	1	13	$Ru(bpy)_2$ $(3,3'\text{-dm-bpy})^{2+}$	MeOH/ EtOH		588	5.2	0.252				338
1	1	13	$Ru(bpy)_2$ $(3,3'\text{-dm-bpy})^{2+}$	py						0.63		338
1	1	15	$Ru(bpy)_2$ $(4,4'\text{-dm-bpy})^{2+}$	AN	445 (16000)				615			307
1	1	15	$Ru(bpy)_2$ $(4,4'\text{-dm-bpy})^{2+}$	H_2O						0.49		326
1	1	15	$Ru(bpy)_2$ $(4,4'\text{-dm-bpy})^{2+}$	H_2O	457 (11000)				~ 630			346
1	1	15	$Ru(bpy)_2$ $(4,4'\text{-dm-bpy})^{2+}$	H_2O	454				620	0.470	0.025	299
1	1	15	$Ru(bpy)_2$ $(4,4'\text{-dm-bpy})^{2+}$	MeOH/ EtOH		586	5.2	0.35				123
1	1	16	$Ru(bpy)_2$ $(4,4'\text{-dCl-bpy})^{2+}$	AN	448 (12600)				645	0.42		344
1	1	16	$Ru(bpy)_2$ $(4,4'\text{-dCl-bpy})^{2+}$	MeOH/ EtOH		608	2.6					344
1	1	17	$Ru(bpy)_2$ $(4,4'\text{-dBr-bpy})^{2+}$	AN	450 (14000)				647			307

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
1	1	18	$Ru(bpy)_2$ $(4,4'\text{-dn-bpy})^{2+}$	AN	514 (10300)				752			40
1	1	18	$Ru(bpy)_2$ $(4,4'\text{-dn-bpy})^{2+}$	MeOH/ EtOH		700	2.5					40
1	1	26	$Ru(bpy)_2$ $(4,4'\text{-dph-bpy})^{2+}$	AN	458				628			233
1	1	26	$Ru(bpy)_2$ $(4,4'\text{-dph-bpy})^{2+}$	MeOH/ EtOH		593	5.6	0.46				123
1	1	26	$Ru(bpy)_2$ $(4,4'\text{-dph-bpy})^{2+}$	MeOH/ EtOH	457 (19700)				630	1.92	0.197	205
1	1	26	$Ru(bpy)_2$ $(4,4'\text{-dph-bpy})^{2+}$	MeOH/ EtOH							0.041 [c]	205
1	1	29	$Ru(bpy)_2$ $(4,4'\text{-dc-bpy})^{2+}$	D_2O					686	0.572	0.012	130 [b]
1	1	29	$Ru(bpy)_2$ $(4,4'\text{-dc-bpy})^{2+}$	H_2O	460				655	0.32 [c]		347 [b]
1	1	29	$Ru(bpy)^2$ $(4,4'\text{-dc-bpy})^{2+}$	H_2O					686	0.299	0.006	130 [b]
1	1	29	$Ru(bpy)_2$ $(4,4'\text{-dc-bpy})^{2+}$	H_2O					705	0.190 [c,d]	0.013 [c]	348 [b]
1	1	29	$Ru(bpy)_2$ $(4,4'\text{-dc-bpy})^{2+}$	H_2O					615	0.46		349 [b]
1	1	29	$Ru(bpy)_2$ $(4,4'\text{-dc-bpy})^{2+}$	H_2O						0.50 [c]		134
1	1	29	$Ru(bpy)_2$ $(4,4'\text{-dc-bpy})^{2+}$	H_2O					686	0.29	0.006	339
1	1	29	$Ru(bpy)_2$ $(4,4'\text{-dc-bpy})^{2+}$	HCl 0.1M						0.26		326 [b]

1	1	30	$Ru(bpy)_2$ (4,4′-DTB -bpy)$^{2+}$	AN	450 (14500)				625	1.17		329
1	1	30	$Ru(bpy)_2$ (4,4′-DTB-bpy)$^{2+}$	MeOH/ EtOH		590	4.6					40, 329
1	1	31	$Ru(bpy)_2$ (4,4′-dnd-bpy)$^{2+}$	$CHCl_3$	459 (12000)				630			346
1	1	31	$Ru(bpy)_2$ (4,4′-dnd-bpy)$^{2+}$	$CHCl_3$	458 (13200)				610			350
1	1	31	$Ru(bpy)_2$ (4,4′-dnd-bpy)$^{2+}$	$CHCl_3$	457				620			351
1	1	32	$Ru(bpy)_2$ (4,4′-dst-bpy)$^{2+}$	$CHCl_3$	482				668	0.900	0.180	332
1	1	32	$Ru(bpy)_2$ (4,4′-dst-bpy)$^{2+}$	$CHCl_3$	482 (18200)				674			350
1	1	32	$Ru(bpy)_2$ (4,4′-dst-bpy)$^{2+}$	$CHCl_3$	485				665			351
1	1	34	$Ru(bpy)_2$ (4,4′-DCM-bpy)$^{2+}$	H_2O	475				660	0.615	0.045	332
1	1	35	$Ru(bpy)_2$ (Cl2B)$^{2+}$	AN					646	1.26		330
1	1	35	$Ru(bpy)_2$ (Cl2B)$^{2+}$	CD_3OH						0.84		330
1	1	35	$Ru(bpy)_2$ (Cl2B)$^{2+}$	CH_3OD						0.98		330
1	1	35	$Ru(bpy)_2$ (Cl2B)$^{2+}$	D_2O						0.61		330
1	1	35	$Ru(bpy)_2$ (Cl2B)$^{2+}$	H_2O					663	0.42		330
1	1	35	$Ru(bpy)_2$ (Cl2B)$^{2+}$	MeOH						0.85		330

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
1	1	36		$Ru(bpy)_2(Cl6B)^{2+}$	$CHCl_3$	460				615			352
1	1	36		$Ru(bpy)_2(Cl6B)^{2+}$	H_2O	480				660			352
1	1	37		$Ru(bpy)_2$(4,4′-DCE-bpy)$^{2+}$	EtOH						1.03	0.074	334
1	1	37		$Ru(bpy)_2$(4,4′-DCE-bpy)$^{2+}$	H_2O						0.37	0.027	334
1	1	38		$Ru(bpy)_2$(4,4′-DCI-bpy)$^{2+}$	MeOH	420					0.700		353
1	1	43		$Ru(bpy)_2$(4,4′-DHC-bpy)$^{2+}$	iBN/AN					660	2.00		354
1	1	45		$Ru(bpy)_2$(4,4′-cm-bpy)$^{2+}$	H_2O					~ 720	0.082 [c,d]	~ 0.006 [c]	348 [b]
1	1	48		$Ru(bpy)_2[P(St\text{-}Vbpy)]^{2+}$	DMF	446				625			355
1	1	48		$Ru(bpy)_2[P(St\text{-}Vbpy)]^{2+}$	DMF/H_2O						0.434 [c]		355
1	1	49		$Ru(bpy)_2(bpyCOOH)^{2+}$	H_2O	476				632	0.287		356 [b]
1	1	57	Cl	$Ru(bpy)_2$(4,4′-bpy)Cl^+	AN	490 (10800)							358
1	1	57	Cl	$Ru(bpy)_2$(4,4′-bpy)Cl^+	CH_2Cl_2/AN					698		$<10^{-3}$	358, 359

1	1	57	57	$Ru(bpy)_2(4,4'\text{-}bpy)_2^{2+}$	CH_2Cl_2	447						318
1	1	57	57	$Ru(bpy)_2(4,4'\text{-}bpy)_2^{2+}$	MeOH				601			357 [b]
1	1	57	57	$Ru(bpy)_2(4,4'\text{-}bpy)_2^{2+}$	MeOH/EtOH		577					318
1	1	58	58	*cis*-$Ru(bpy)_2(m\text{-}4,4'\text{-}bpy)_2^{4+}$	AN	450 (23900)			680	0.104 [c]	$\sim 10^{-4}$ [c]	357
1	1	58	58	*cis*-$Ru(bpy)_2(m\text{-}4,4'\text{-}bpy)_2^{4+}$	eglyc				612, 675 [e]	0.805 [c]	~ 0.0004 [c]	357
1	1	58	58	*cis*-$Ru(bpy)_2(m\text{-}4,4'\text{-}bpy)_4^{4+}$	MeOH		580	7.59	690			357
1	1	59		$Ru(bpy)_2(bpz)^{2+}$	AN	473 (9900)						229
1	1	59		$Ru(bpy)_2(bpz)^{2+}$	AN	471 (9600)			690			40
1	1	59		$Ru(bpy)_2(bpz)^{2+}$	AN	474			686			233
1	1	59		$Ru(bpy)_2(bpz)^{2+}$	MeOH/EtOH		639	3.4				40
1	1	59		$Ru(bpy)_2(bpz)^{2+}$	PC				710	0.376	0.019	229
1	1	59		$Ru(bpy)_2(bpz)^{2+}$	PC				710	0.38	0.019	225
1	1	61		$Ru(bpy)_2(bpym)^{2+}$	AN	420 (10500)			600			360
1	1	61		$Ru(bpy)_2(bpym)^{2+}$	AN	480 [f]						227
1	1	61		$Ru(bpy)_2(bpym)^{2+}$	H_2O	475 [f]			680			361
1	1	61		$Ru(bpy)_2(bpym)^{2+}$	PC				710	0.076	0.0036	229
1	1	61		$Ru(bpy)_2(bpym)^{2+}$	PC				710	0.08	0.004	225
1	1	62		$Ru(bpy)_2(4,4'\text{-dm-bpym})^{2+}$	AN	442 (10900)			598			360

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
1	1	67	$Ru(bpy)_2$ $(h\text{-}phen)^{2+}$	AN	451 (13900)				612			40
1	1	67	$Ru(bpy)_2$ $(h\text{-}phen)^{2+}$	MeOH/ EtOH		585	4.9					40
1	1	68	$Ru(bpy)_2$ $(phen)^{2+}$	CH_2Cl_2					601	0.31	0.033	210
1	1	68	$Ru(bpy)_2$ $(phen)^{2+}$	H_2O						0.684		275
1	1	68	$Ru(bpy)_2$ $(phen)^{2+}$	MeOH/ EtOH		575	6.6	0.44				111, 123
1	1	68	$Ru(bpy)_2$ $(phen)^{2+}$	MeOH/ EtOH		580						210
1	1	81	$Ru(bpy)_2$ $(5\text{-}n\text{-}phen)^{2+}$	H_2O						$\leqslant 0.007$		275
1	1	82	$Ru(bpy)_2$ $(5\text{-}a\text{-}phen)^{2+}$	AN	452 (15900)							362
1	1	82	$Ru(bpy)_2$ $(5\text{-}a\text{-}phen)^{2+}$	CH_2Cl_2						1.151		362
1	1	85	$Ru(bpy)_2$ $(2,9\text{-}dm\text{-}phen)^{2+}$	AN	452 (13600)				588			360
1	1	86	$Ru(bpy)_2$ $(4,7\text{-}dm\text{-}phen)^{2+}$	MeOH/ EtOH		583	5.6	0.38				123
1	1	88	$Ru(bpy)_2$ $(4,7\text{-}Ph_2\text{-}phen)^{2+}$	H_2O						1.591		275
1	1	88	$Ru(bpy)_2$ $(4,7\text{-}Ph_2\text{-}phen)^{2+}$	MeOH/ EtOH		589	9.4	0.54				123
1	1	94	$Ru(bpy)_2$ $(4,7\text{-}dhy\text{-}phen)^{2+}$	D_2O					652	0.800	0.02 [c]	363 [b]

1	1	94		$Ru(bpy)_2(4,7\text{-dhy-phen})^{2+}$	EtOH		597	3.9	0.27				363 [b]
1	1	94		$Ru(bpy)_2(4,7\text{-dhy-phen})^{2+}$	H_2O	460 (12600)				652	0.455	0.01 [c]	363 [b]
1	1	99		$Ru(bpy)_2(5,6\text{-dm-phen})^{2+}$	MeOH/ EtOH		577	6.1	0.42				123
1	1	107		$Ru(bpy)_2(DIAF)^{2+}$	H_2O							0.0008	216, 339
1	1	107		$Ru(bpy)_2(DIAF)^{2+}$	MeOH/ EtOH		574	5.9	0.56				216, 339
1	1	107		$Ru(bpy)_2(DIAF)^{2+}$	MeOH/ EtOH						0.00007		133
1	1	108		$Ru(bpy)_2(DIAFO)^{2+}$	AN	440 (14100)				658			40
1	1	108		$Ru(bpy)_2(DIAFO)^{2+}$	H_2O						0.137	0.0056	216, 339
1	1	108		$Ru(bpy)_2(DIAFO)^{2+}$	MeOH/ EtOH		609	4.3	0.23				216, 339
1	1	108		$Ru(bpy)_2(DIAFO)^{2+}$	MeOH/ EtOH		574	5.9					40
1	1	109		$Ru(bpy)_2(taphen)^{2+}$	AN	440 (14000)				788	0.05	0.004	238
1	1	109		$Ru(bpy)_2(taphen)^{2+}$	MeOH/ EtOH		660	1.8					238
1	1	111	Cl	$Ru(bpy)_2(py)Cl^{+}$	CH_2Cl_2	505							318
1	1	111	Cl	$Ru(bpy)_2(py)Cl^{+}$	MeOH/ EtOH		660						318
1	1	111	CN	$Ru(bpy)_2(py)(CN)^{+}$	AN	469							364
1	1	111	CN	$Ru(bpy)_2(py)(CN)^{+}$	H_2O					620			364
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	acetone					615			319

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
1	1	111	111	*cis*-Ru(bpy)$_2$ (py)$_2^{2+}$	AN	450 (7900)							365
1	1	111	111	Ru(bpy)$_2$(py)$_2^{2+}$	AN	457				606	0.500	2.33×10^{-4}	126
1	1	111	111	Ru(bpy)$_2$(py)$_2^{2+}$	AN	455				606			364
1	1	111	111	Ru(bpy)$_2$(py)$_2^{2+}$	AN	455 (8130)							319
1	1	111	111	*trans*-Ru(bpy)$_2$ (py)$_2^{2+}$	AN	474 (8600)							365
1	1	111	111	Ru(bpy)$_2$(py)$_2^{2+}$	CH_2Cl_2						0.50		124
1	1	111	111	Ru(bpy)$_2$(py)$_2^{2+}$	CH_2Cl_2					609	0.47	0.0042	210
1	1	111	111	Ru(bpy)$_2$(py)$_2^{2+}$	CH_2Cl_2	454							318
1	1	111	111	*cis*-Ru(bpy)$_2$ (py)$_2^{2+}$	eglyc		581	11.4					251
1	1	111	111	*trans*-Ru(bpy)$_2$ (py)$_2^{2+}$	eglyc		585	10.6					251
1	1	111	111	Ru(bpy)$_2$(py)$_2^{2+}$	MeOH/ EtOH		588	5.25					97, 320
1	1	111	111	Ru(bpy)$_2$(py)$_2^{2+}$	MeOH/ EtOH		589						210
1	1	111	111	Ru(bpy)$_2$(py)$_2^{2+}$	MeOH/ EtOH		585						318
1	1	111	111	Ru(bpy)$_2$(py)$_2^{2+}$	MeOH/ EtOH						0.0027		133
1	1	111	111	Ru(bpy)$_2$(py)$_2^{2+}$	PC	457				608		2.28×10^{-4}	126
1	1	115	115	Ru(bpy)$_2$ (3-I-py)$_2^{2+}$	CH_2Cl_2	442							318
1	1	115	115	Ru(bpy)$_2$ (3-I-py)$_2^{2+}$	MeOH/ EtOH		575						318
1	1	116		Ru(bpy)$_2$ (3-AEP)$^{2+}$	CH_2Cl_2					645	0.12	0.0066	210

1	1	116		$Ru(bpy)_2(3\text{-}AEP)^{2+}$	MeOH/EtOH		637						210
1	1	118	118	$Ru(bpy)_2(pic)_2^{2+}$	MeOH/EtOH		592	5.6	0.41				366
1	1	119	Cl	$Ru(bpy)_2$(4-acetyl-py)Cl^+	CH_2Cl_2	495							318
1	1	119	Cl	$Ru(bpy)_2$(4-acetyl-py)Cl^+	MeOH/EtOH		653						318
1	1	119	119	$Ru(bpy)_2(4\text{-acetyl-py})_2^{2+}$	CH_2Cl_2	442							318
1	1	119	119	$Ru(bpy)_2(4\text{-acetyl-py})_2^{2+}$	MeOH/EtOH		576						318
1	1	124	CN	$Ru(bpy)_2(PVP)(CN)^+$	AN	469							364
1	1	124	CN	$Ru(bpy)_2(PVP)(CN)^+$	H_2O					610			364
1	1	124	124	$Ru(bpy)_2(PVP)_{2/20}^{2+}$	AN	460				609	0.020	0.0019	126
1	1	124	124	$Ru(bpy)_2(PVP)_{2/5}^{2+}$	AN	460				611	0.020	0.0011	126
1	1	124	124	$Ru(bpy)_2(PVP)_2^{2+}$	AN	460				611			364
1	1	124	124	$Ru(bpy)_2(PVP)_{2/20}^{2+}$	MeOH/EtOH		595						126
1	1	124	124	$Ru(bpy)_2(PVP)_{2/20}^{2+}$	PC	460				612	0.044	0.0018	126
1	1	124	124	$Ru(bpy)_2(PVP)_{2/5}^{2+}$	PC	460				613	0.068	0.0020	126
1	1	137	137	$Ru(bpy)_2(pyd)_2^{2+}$	CH_2Cl_2					610	0.31	2.7×10^{-4}	210
1	1	137	137	$Ru(bpy)_2(pyd)_2^{2+}$	CH_2Cl_2	440							318
1	1	137	137	$Ru(bpy)_2(pyd)_2^{2+}$	MeOH/EtOH		574						210
1	1	137	137	$Ru(bpy)_2(pyd)_2^{2+}$	MeOH/EtOH		572						318
1	1	144	144	$Ru(bpy)_2(pz)_2$	DMF	581 (4570)							319

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
1	1	144	145	$Ru(bpy)_2(pz)(pzH)^+$	AN	510 (4890)				722		10^{-5}	367
1	1	145	145	$Ru(bpy)_2(pzH)_2^{2+}$	acetone					627			319
1	1	145	145	$Ru(bpy)_2(pzH)_2^{2+}$	AN	470 (5180)				627	0.350	$\sim 10^{-4}$	367
1	1	145	145	$Ru(bpy)_2(pzH)_2^{2+}$	AN	470 (5130)							319
1	1	145	145	$Ru(bpy)_2(pzH)_2^{2+}$	DMF					661			319
1	1	146	146	$Ru(bpy)_2(imid)_2^{2+}$	CH_2Cl_2	489							318
1	1	146	146	$Ru(bpy)_2(imid)_2^{2+}$	MeOH/EtOH		628						318
1	1	147	147	$Ru(bpy)_2(NMI)_2^{2+}$	CH_2Cl_2					682	0.31	0.034	210
1	1	147	147	$Ru(bpy)_2(NMI)_2^{2+}$	CH_2Cl_2	483							318
1	1	147	147	$Ru(bpy)_2(NMI)_2^{2+}$	MeOH/EtOH		633						210
1	1	147	147	$Ru(bpy)_2(NMI)_2^{2+}$	MeOH/EtOH		642						318
1	1	151	151	$Ru(bpy)_2(trz)_2$	DMF	544 (8130)							319
1	1	152	152	$Ru(bpy)_2(m\text{-}trz)_2^{2+}$	acetone					660			319
1	1	152	152	$Ru(bpy)_2(m\text{-}trz)_2^{2+}$	AN	473 (8910)							319
1	1	153	153	$Ru(bpy)_2(Ph\text{-}trz)_2^{2+}$	acetone					645			319
1	1	153	153	$Ru(bpy)_2(Ph\text{-}trz)_2^{2+}$	AN	468 (8710)							319
1	1	154	154	$Ru(bpy)_2(All\text{-}trz)_2^{2+}$	acetone					660			319
1	1	154	154	$Ru(bpy)_2(All\text{-}trz)_2^{2+}$	AN	472 (9330)							319
1	1	155	155	$Ru(bpy)_2(Htrz)_2^{2+}$	acetone					660			319

1	1	155	155	$Ru(bpy)_2(Htrz)_2^{2+}$	AN	470 (8710)						319
1	1	157		$Ru(bpy)_2(DPM)^{2+}$	MeOH/EtOH		584	7.2	0.56			366
1	1	158		$Ru(bpy)_2(DPE)^{2+}$	MeOH/EtOH		605	7.5	0.11			366
1	1	159	Cl	$Ru(bpy)_2(BPA)Cl^{+}$	CH_2Cl_2/AN					707	$<10^{-3}$	358, 359
1	1	160	Cl	$Ru(bpy)_2(BPE)Cl^{+}$	CH_2Cl_2/AN					697	$<10^{-3}$	358, 359
1	1	163		$Ru(bpy)_2(DPAH)^{2+}$	AN	453 (7200)	645					235
1	1	163		$Ru(bpy)_2(DPAH)^{2+}$	MeOH/EtOH		600					235
1	1	171		$Ru(bpy)_2(PimH)^{2+}$	AN	460 (10500)						368
1	1	171		$Ru(bpy)_2(PimH)^{2+}$	MeOH/EtOH		596	4.450		625	0.160	368
1	1	171		$Ru(bpy)_2(PimH)^{2+}$	MeOH/H_2O					633	0.224	368 [b]
1	1	173		$Ru(bpy)_2(PBzimH)^{2+}$	AN	458 (25700)						368
1	1	173		$Ru(bpy)_2(PBzimH)^{2+}$	MeOH/EtOH		600	4.240		622	0.418	368
1	1	173		$Ru(bpy)_2(PBzimH)^{2+}$	MeOH/H_2O					630	0.262	368 [b]
1	1	176		$Ru(bpy)_2(biimH_2)^{2+}$	AN					595		360
1	1	176		$Ru(bpy)_2(biimH_2)^{2+}$	AN	473 (9330)						368
1	1	176		$Ru(bpy)_2(biimH_2)^{2+}$	$HClO_4$	448 (9500)						360
1	1	176		$Ru(bpy)_2(biimH_2)^{2+}$	MeOH/EtOH		620	3.25		651	0.150	368

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
1	1	176	$Ru(bpy)_2$ $(biimH_2)^{2+}$	$MeOH/H_2O$					656	0.092		368
1	1	179	$Ru(bpy)_2$ $(BiBzimH_2)^{2+}$	AN	463 (11800)							368
1	1	179	$Ru(bpy)_2$ $(BiBzimH_2)^{2+}$	MeOH/ EtOH		616	3.000		640	0.120		368
1	1	179	$Ru(bpy)_2$ $(BiBzimH_2)^{2+}$	MeOH/ H_2O					640	0.111		368 [b]
1	1	180	$Ru(bpy)_2$ $(pydipy)^{2+}$	AN	450 (10800)				602		0.004 [c]	369
1	1	184	$Ru(bpy)_2(thpy)^{2+}$	H_2O	453				671	0.32	0.029	370
1	1	203	$Ru(bpy)_2(NPP)^{+}$	MeOH	495							371
1	1	203	$Ru(bpy)_2(NPP)^{+}$	MeOH/ EtOH		682	0.898	0.038				371
1	1	244	$Ru(bpy)_2(piq)^{2+}$	AN	483 (10200)				720			40
1	1	244	$Ru(bpy)_2(piq)^{2+}$	MeOH/ EtOH		662	1.7					40
1	1	245	$Ru(bpy)_2(hpiq)^{2+}$	AN	480 (14600)							40
1	1	245	$Ru(bpy)_2(hpiq)^{2+}$	MeOH/ EtOH		658	2.3					40
1	1	246	$Ru(bpy)_2(pq)^{2+}$	AN	478 (10800)				700			40
1	1	246	$Ru(bpy)_2(pq)^{2+}$	AN	445				687			233
1	1	246	$Ru(bpy)_2(pq)^{2+}$	EtCN					720			351
1	1	246	$Ru(bpy)_2(pq)^{2+}$	EtOH	480 [f]							351
1	1	246	$Ru(bpy)_2(pq)^{2+}$	MeOH	476 [f]							274
1	1	246	$Ru(bpy)_2(pq)^{2+}$	MeOH/ EtOH		667	3.5					274
1	1	246	$Ru(bpy)_2(pq)^{2+}$	MeOH/ EtOH		654	2.6					315
1	1	251	$Ru(bpy)_2$ $(DMCH)^{2+}$	AN	528 (9410)				736	0.38		329

1	1	251	$Ru(bpy)_2(DMCH)^{2+}$	MeOH/EtOH		720	1.5					40, 329
1	1	255	$Ru(bpy)_2(OMCH)^{2+}$	AN	562 (8540)				755			40
1	1	255	$Ru(bpy)_2(OMCH)^{2+}$	MeOH/EtOH		742	2.6					40
1	1	257	$Ru(bpy)_2(biq)^{2+}$	AN	526 (8710)				742	0.27		344
1	1	257	$Ru(bpy)_2(biq)^{2+}$	MeOH	527 (8190)							274
1	1	257	$Ru(bpy)_2(biq)^{2+}$	MeOH/EtOH		728	1.4					344
1	1	257	$Ru(bpy)_2(biq)^{2+}$	MeOH/EtOH		736	1.9					274
1	1	259	$Ru(bpy)_2(i\text{-}biq)^{2+}$	AN	450 (11900) [f]				610	1.1		131
1	1	259	$Ru(bpy)_2(i\text{-}biq)^{2+}$	nitrile		586	4.7					131
1	1	261	$Ru(bpy)_2(DP)^{2+}$	EtOH	448 (15700)				610		0.027	243
1	1	267	$Ru(bpy)_2(dpp)^{2+}$	H_2O	430 (12000)				675	0.135	0.049	103
1	1	270	$Ru(bpy)_2(BL3)^{2+}$	AN	525 (8490)				770	$\leqslant$ 0.060 [c]	6×10^{-6} [c]	372
1	1	271	$Ru(bpy)_2(BL4)^{2+}$	H_2O			4.560		610	0.356 [c]	0.052 [c]	373
1	1	272	$Ru(bpy)_2(BL5)^{2+}$	H_2O			4.090		610	0.390 [c]	0.048 [c]	373
1	1	273	$Ru(bpy)_2(BL6)^{2+}$	H_2O			4.020		613	0.389 [c]	0.048 [c]	373
1	1	274	$Ru(bpy)_2(BL7)^{2+}$	H_2O			4.070		610	0.360 [c]	0.048 [c]	373
1	13	13	$Ru(bpy)(3,3'\text{-dm-bpy})_2^{2+}$	AN	453 (12200)				625	0.72		329
1	13	13	$Ru(bpy)(3,3'\text{-dm-bpy})_2^{2+}$	H_2O	454 (12300)						1.3×10^{-5}	338
1	13	13	$Ru(bpy)(3,3'\text{-dm-bpy})_2^{2+}$	H_2O							8×10^{-6} [c]	338
1	13	13	$Ru(bpy)(3,3'\text{-dm-bpy})_2^{2+}$	MeOH/EtOH		590	4.9					40, 329
1	13	13	$Ru(bpy)(3,3'\text{-dm-bpy})_2^{2+}$	MeOH/EtOH		597	5.4	0.192				338
1	15	15	$Ru(bpy)(4,4'\text{-dm-bpy})_2^{2+}$	AN	449 (14000)				625			307

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
1	15	15		Ru(bpy)(4,4′-dm-bpy)$_2^{2+}$	H_2O	456				631	0.385	0.014	299
1	17	17		Ru(bpy)(4,4′-dBr-bpy)$_2^{2+}$	AN	456 (10000)				636			307
1	26	26		Ru(bpy)(4,4′-dph-bpy)$_2^{2+}$	AN	467				631			233
1	26	26		Ru(bpy)(4,4′-dph-bpy)$_2^{2+}$	MeOH/EtOH	465 (14700)				635	2.12	0.098	205
1	26	26		Ru(bpy)(4,4′-dph-bpy)$_2^{2+}$	MeOH/EtOH							0.025 [c]	205
1	29	29		Ru(bpy)(4,4′-dc-bpy)$_2^{2-}$	H_2O						0.54 [c]		134
1	30	30		Ru(bpy)(4,4′-DTB-bpy)$_2^{2+}$	AN	454 (15300)				630	1.07		329
1	30	30		Ru(bpy)(4,4′-DTB-bpy)$_2^{2+}$	MeOH/EtOH		590	4.8					40, 329
1	31	CN	CN	Ru(bpy)(4,4′-dnd-bpy)$(CN)_2$	$CHCl_3$	502				655			351
1	43	43		Ru(bpy)(4,4′-DHC-bpy)$_2^{2+}$	iBN/AN					644	2.10		354
1	59	59		Ru(bpy)(bpz)$_2^{2+}$	AN	463 (12000)							229
1	59	59		Ru(bpy)(bpz)$_2^{2+}$	AN	465				645			233
1	59	59		Ru(bpy)(bpz)$_2^{2+}$	PC					654	1.099	0.079	229
1	59	59		Ru(bpy)(bpz)$_2^{2+}$	PC					654	1.13	0.079	225
1	59	61		Ru(bpy)(bpz)(bpym)$^{2+}$	PC					684	0.70	0.049	225
1	61	61		Ru(bpy)(bpym)$_2^{2+}$	AN	460 [f]							229
1	61	61		Ru(bpy)(bpym)$_2^{2+}$	PC					670	0.182	0.011	229

1	61	61		$Ru(bpy)(bpym)_2^{2+}$	PC					670	0.18	0.011	225
1	67	67		$Ru(bpy)(h\text{-}phen)_2^{2+}$	AN	450 (14800)				612			40
1	67	67		$Ru(bpy)(h\text{-}phen)_2^{2+}$	MeOH/ EtOH		585	4.9					40
1	68	68		$Ru(bpy)(phen)_2^{2+}$	AN	442 (18000)							365
1	68	68		$Ru(bpy)(phen)_2^{2+}$	eglyc		575	15.8					251
1	68	68		$Ru(bpy)(phen)_2^{2+}$	H_2O						0.784		275
1	68	68		$Ru(bpy)(phen)_2^{2+}$	MeOH/ EtOH		569	9.1	0.56				111, 123
1	68	111	111	*cis*-$Ru(bpy)(phen)(py)_2^{2+}$	AN	448 (9600)							365
1	68	111	111	*trans*-$Ru(bpy)(phen)(py)_2^{2+}$	AN	476 (11000)							365
1	68	111	111	*cis*-$Ru(bpy)(phen)(py)_2^{2+}$	eglyc		578	14.8					251
1	68	111	111	*trans*-$Ru(bpy)(phen)(py)_2^{2+}$	eglyc		588	8.0					251
1	81	81		$Ru(bpy)(5\text{-}n\text{-}phen)_2^{2+}$	H_2O						$\leqslant 0.007$		275
1	88	88		$Ru(bpy)(4,7\text{-}Ph_2\text{-}phen)_2^{2+}$	H_2O						2.646		275
1	108	108		$Ru(bpy)(DIAFO)_2^{2+}$	AN	446 (11300)				608			40
1	108	108		$Ru(bpy)(DIAFO)_2^{2+}$	MeOH/ EtOH		573	5.2					40
1	109	109		$Ru(bpy)(taphen)_2^{2+}$	AN	438 (13200)				750	0.13	0.012	238
1	109	109		$Ru(bpy)(taphen)_2^{2+}$	MeOH/ EtOH		650	2.0					238
1	111	111	en	$Ru(bpy)(py)_2(en)^{2+}$	AN	476 (4000)							365
1	111	111	en	$Ru(bpy)(py)_2(en)^{2+}$	eglyc		581	10.9					251
1	111	111	NH_3	$Ru(bpy)(py)_2(NH_3)_2^{2+}$	eglyc		625						251

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
1	111	111	111	$Ru(bpy)(py)_4^{2+}$	AN	457 (5500)							365
1	111	111	111	$Ru(bpy)(py)_3Cl^+$	eglyc		581	10.5					251
1	111	111	111	$Ru(bpy)(py)_4^{2+}$	eglyc		585	10.9					251
1	111	111	112	$Ru(bpy)(py)_2$ $(PMA)^{2+}$	AN	465 (6000)							365
1	111	111	112	$Ru(bpy)(py)_2$ $(PMA)^{2+}$	eglyc		581	10.6					251
1	111	111	113	$Ru(bpy)(py)_2$ $(2\text{-}AEP)^{2+}$	AN	455 (5500)							365
1	111	111	113	$Ru(bpy)(py)_2$ $(2\text{-}AEP)^{2+}$	eglyc		581	11.3					251
1	111	281		$Ru(bpy)$ $(py)(trpy)^{2+}$	AN	468				636			374
1	112	112		$Ru(bpy)(PMA)_2^{2+}$	AN	478 (6500)							365
1	112	112		$Ru(bpy)(PMA)_2^{2+}$	eglyc		616	9.0					251
1	163	163		$Ru(bpy)$ $(DPAH)_2^{2+}$	AN	458 (5400)	700						235
1	163	163		$Ru(bpy)$ $(DPAH)_2^{2+}$	MeOH/ EtOH		625						235
1	180	180		$Ru(bpy)$ $(pydipy)_2^{2+}$	AN	435 (12200)				604		< 0.001 [c]	369
1	181	181		$Ru(bpy)(Azpy)_2^{2+}$	CH_2Cl_2	517 (11600)	829 [g]						375
1	181	181		$Ru(bpy)(Azpy)_2^{2+}$	H_2O					854			376
1	184	184		$Ru(bpy)(thpy)_2^{2+}$	H_2O	458				670	0.30	0.028	370
1	246	246		$Ru(bpy)(pq)_2^{2+}$	AN	479				685			233
1	246	246		$Ru(bpy)(pq)_2^{2+}$	EtCN					718			351
1	246	246		$Ru(bpy)(pq)_2^{2+}$	EtOH	475							351
1	246	246		$Ru(bpy)(pq)_2^{2+}$	MeOH	480 (11100)							274

1	246	246	$Ru(bpy)(pq)_2^{2+}$	MeOH/ EtOH			666	3.1				274
1	251	251	$Ru(bpy)(DMCH)_2^{2+}$	AN	559	(9640)			742	0.39		329
1	251	251	$Ru(bpy)(DMCH)_2^{2+}$	MeOH/ EtOH			737	1.9				40, 329
1	257	257	$Ru(bpy)(biq)_2^{2+}$	AN	547	(8550)			742	0.20		344
1	257	257	$Ru(bpy)(biq)_2^{2+}$	MeOH	546	(7250)						274
1	257	257	$Ru(bpy)(biq)_2^{2+}$	MeOH/ EtOH			733	1.8				344
1	257	257	$Ru(bpy)(biq)_2^{2+}$	MeOH/ EtOH			741	2.1				274
1	259	259	$Ru(bpy)(i\text{-}biq)_2^{2+}$	AN	450	(11600) [f]			615	1.0		131
1	259	259	$Ru(bpy)(i\text{-}biq)_2^{2+}$	nitrile			586	5.0				131
1	281	Cl	$Ru(bpy)(trpy)Cl^+$	AN	506	(7800)			729			40
1	281	Cl	$Ru(bpy)(trpy)Cl^+$	MeOH/ EtOH			692	2.4				40
1	281	CN	$Ru(bpy)(trpy)(CN)^+$	AN	487	(9950)			664			40, 221
1	281	CN	$Ru(bpy)(trpy)(CN)^+$	$CHCl_3$	484				657		< 0.001	221
1	281	CN	$Ru(bpy)(trpy)(CN)^+$	DMF	487	(9950)	639	5.3	666		0.001	221
1	281	CN	$Ru(bpy)(trpy)(CN)^+$	MeOH	472			5.1	664		< 0.001	221
1	281	CN	$Ru(bpy)(trpy)(CN)^+$	MeOH/ EtOH			626	4.6				40
1	281	CN	$Ru(bpy)(trpy)(CN)^+$	MF	480				654			221
1	281	MPZ	$Ru(bpy)(trpy)(MPZ)^{2+}$	H_2O					608		3.8×10^{-4}	377
1	281	NH_3	$Ru(bpy)(trpy)(NH_3)^{2+}$	AN	462	(8800)						321

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
1	281	NH_3	Ru(bpy)(trpy) $(NH_3)^{2+}$	glycerol						2.0 [c]		335
1	281	NH_3	Ru(bpy)(trpy) $(NH_3)^{2+}$	$HClO_4$ 1M						0.43		321
1	281	156	Ru(bpy)(trpy) $(PTZ)^{2+}$	H_2O	450				608	0.480	0.0005	377
2	2	2	$Ru(4\text{-Cl-bpy})_3^{2+}$	MeOH/ EtOH	454 (13500)				640	0.67	0.030	205
2	2	2	$Ru(4\text{-Cl-bpy})_3^{2+}$	MeOH/ EtOH							0.014 [c]	205
3	3	3	$Ru(4\text{-Br-bpy})_3^{2+}$	MeOH/ EtOH	457 (14000)				640	0.82	0.052	205
3	3	3	$Ru(4\text{-Br-bpy})_3^{2+}$	MeOH/ EtOH							0.018 [c]	205
4	4	4	$Ru(4\text{-a-bpy})_3^{2+}$	MeOH/ EtOH	472 (12100)				675	0.35	0.021	205
4	4	4	$Ru(4\text{-a-bpy})_3^{2+}$	MeOH/ EtOH							0.006 [c]	205
5	5	5	$Ru(4\text{-dma-bpy})_3^{2+}$	MeOH/ EtOH	475 (15000)				680	0.35	0.023	205
5	5	5	$Ru(4\text{-dma-bpy})_3^{2+}$	MeOH/ EtOH							0.006 [c]	205
6	6	6	$Ru(4\text{-mo-bpy})_3^{2+}$	MeOH/ EtOH	461 (14100)				660	0.67	0.039	205
6	6	6	$Ru(4\text{-mo-bpy})_3^{2+}$	MeOH/ EtOH							0.014 [c]	205

7	7	7	$Ru(4\text{-}n\text{-}bpy)_3^{2+}$	AN	480 (20400)				700	0.12		344
7	7	7	$Ru(4\text{-}n\text{-}bpy)_3^{2+}$	MeOH/ EtOH		643	3.8					344
8	8	8	$Ru(4\text{-}bo\text{-}bpy)_3^{2+}$	MeOH/ EtOH	460 (14800)				650	0.60	0.053	205
8	8	8	$Ru(4\text{-}bo\text{-}bpy)_3^{2+}$	MeOH/ EtOH							0.017 [c]	205
9	9	9	$Ru(4\text{-}tep\text{-}bpy)_3^{5+}$	H_2O	466 (18300)				638	0.760		378
9	9	9	$Ru(4\text{-}tep\text{-}bpy)_3^{5+}$	MeOH/ EtOH		628						378
10	10	10	$Ru(6\text{-}m\text{-}bpy)_3^{2+}$	MeOH	448 (11000)							379
10	10	10	$Ru(6\text{-}m\text{-}bpy)_3^{2+}$	MeOH/ EtOH		585	4.1	0.0968				379
13	13	13	$Ru(3,3'\text{-}dm\text{-}bpy)_3^{2+}$	AN	456 (10800)				625	0.21		329
13	13	13	$Ru(3,3'\text{-}dm\text{-}bpy)_3^{2+}$	H_2O	456 (11600)							338
13	13	13	$Ru(3,3'\text{-}dm\text{-}bpy)_3^{2+}$	MeOH/ EtOH		595	6.4					40, 329
13	13	13	$Ru(3,3'\text{-}dm\text{-}bpy)_3^{2+}$	MeOH/ EtOH		601	6.4	0.113				338
13	13	68	$Ru(3,3'\text{-}dm\text{-}bpy)_2(phen)^{2+}$	H_2O	451 (14000)						6×10^{-6}	338
13	13	68	$Ru(3,3'\text{-}dm\text{-}bpy)_2(phen)^{2+}$	H_2O							5×10^{-6} [c]	328
13	13	68	$Ru(3,3'\text{-}dm\text{-}bpy)_2(phen)^{2+}$	MeOH/ EtOH		591	9.3	0.281				338
13	68	68	$Ru(3,3'\text{-}dm\text{-}bpy)(phen)_2^{2+}$	H_2O	450 (15200)				611		4.0×10^{-5}	338
13	68	68	$Ru(3,3'\text{-}dm\text{-}bpy)(phen)_2^{2+}$	H_2O							4.6×10^{-5} [c]	338
13	68	68	$Ru(3,3'\text{-}dm\text{-}bpy)(phen)_2^{2+}$	MeOH/ EtOH		576	9.4	0.422				338

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
14	14	14	$Ru(3,3'\text{-DCI-bpy})_3^{2+}$	AN	505				670			380
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	AN	450 (17000)				618			307
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	AN	458				634			232
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	CH_2Cl_2	459	593			618	0.931	0.12	135
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	D_2O						0.607		322
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	EtOH					590			333
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	glycerol						0.90 [c]		335
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	H_2O	450				589			336
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	H_2O	460 (14300)				628	0.33		149
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	H_2O						0.33		12
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	H_2O						0.330		101
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	H_2O	459 (14900)				642		0.026	338
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	H_2O							0.021 [c]	338
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	H_2O						0.342		322
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	H_2O						0.34		381
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	H_2O	459				631	0.335	0.014	299
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	H_2O						0.35		232
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	MeOH/EtOH		593	4.6	0.283				338
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	MeOH/EtOH							0.027 [c]	205
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	MeOH/EtOH	455 (17000)				640	0.95	0.086	204, 205
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	MeOH/EtOH		593						232
15	15	15	$Ru(4,4'\text{-dm-bpy})_3^{2+}$	NaLS						0.56		382
15	15	17	$Ru(4,4'\text{-dm-bpy})_2(4,4'\text{-dBr-bpy})^{2+}$	AN	455 (13000)				661			307

15	15	37	$Ru(4,4'\text{-dm-bpy})_2(4,4'\text{-DCE-bpy})^{2+}$	CH_2Cl_2	493	642			695	0.853	0.07	135
15	15	94	$Ru(4,4'\text{-dm-bpy})_2(4,7\text{-dhy-phen})^{2+}$	D_2O					658	0.610	0.02 [c]	363 [b]
15	15	94	$Ru(4,4'\text{-dm-bpy})_2(4,7\text{-dhy-phen})^{2+}$	EtOH		595	10.50	0.15				363 [b]
15	15	94	$Ru(4,4'\text{-dm-bpy})_2(4,7\text{-dhy-phen})^{2+}$	H_2O	460 (13550)				658	0.340	0.01 [c]	363 [b]
15	17	17	$Ru(4,4'\text{-dm-bpy})(4,4'\text{-dBr-bpy})_2^{2+}$	AN	452 (11000)				647			307
15	37	37	$Ru(4,4'\text{-dm-bpy})(4,4'\text{-DCE-bpy})_2^{2+}$	CH_2Cl_2	483	632			658	1.415	0.10	135
16	16	16	$Ru(4,4'\text{-dCl-bpy})_3^{2+}$	AN	462 (17000)				632	0.48		344
16	16	16	$Ru(4,4'\text{-dCl-bpy})_3^{2+}$	MeOH/EtOH		600	2.9					344
16	16	16	$Ru(4,4'\text{-dCl-bpy})_3^{2+}$	MeOH/EtOH	665 (15500)				670	0.40	0.036	205
16	16	16	$Ru(4,4'\text{-dCl-bpy})_3^{2+}$	MeOH/EtOH							0.020 [c]	205
17	17	17	$Ru(4,4'\text{-dBr-bpy})_3^{2+}$	AN	456 (19000)				624			307
17	17	17	$Ru(4,4'\text{-dBr-bpy})_3^{2+}$	MeOH/EtOH							0.028 [c]	205
17	17	17	$Ru(4,4'\text{-dBr-bpy})_3^{2+}$	MeOH/EtOH	465 (17300)				660	0.52	0.060	204, 205
18	18	18	$Ru(4,4'\text{-dn-bpy})_3^{2+}$	MeOH/EtOH	473				700	0.25	0.02	205
18	18	18	$Ru(4,4'\text{-dn-bpy})_3^{2+}$	MeOH/EtOH							0.001 [c]	205
19	19	19	$Ru(4,4'\text{-da-bpy})_3^{2+}$	MeOH/EtOH							0.002 [c]	205
19	19	19	$Ru(4,4'\text{-da-bpy})_3^{2+}$	MeOH/EtOH	504 (10500)				705	0.10	0.004	204, 205
20	20	20	$Ru(4,4'\text{-ds-bpy})_3^{4-}$	D_2O						0.99 [c]		134
20	20	20	$Ru(4,4'\text{-ds-bpy})_3^{4-}$	H_2O						0.48 [c]		134
20	20	20	$Ru(4,4'\text{-ds-bpy})_3^{4-}$	MeOH						0.87 [c]		134

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
21	21	21	$Ru(4,4'\text{-DEA-bpy})_3^{2+}$	MeOH/EtOH	518 (14500)				700	0.13	0.010	205
21	21	21	$Ru(4,4'\text{-DEA-bpy})_3^{2+}$	MeOH/EtOH							0.005 [c]	205
22	22	22	$Ru(4,4'\text{-BAA-bpy})_3^{2+}$	MeOH/EtOH	479 (15000)				670	0.41	0.027	205
22	22	22	$Ru(4,4'\text{-BAA-bpy})_3^{2+}$	MeOH/EtOH							0.014 [c]	205
23	23	23	$Ru(4,4'\text{-DEO-bpy})_3^{2+}$	MeOH/EtOH							0.009 [c]	205
23	23	23	$Ru(4,4'\text{-DEO-bpy})_3^{2+}$	MeOH/EtOH	477 (13000)				675	0.30	0.020	204, 205
24	24	24	$Ru(4,4'\text{-DPO-bpy})_3^{2+}$	MeOH/EtOH	479 (13400)				670	0.35	0.038	205
24	24	24	$Ru(4,4'\text{-DPO-bpy})_3^{2+}$	MeOH/EtOH							0.018 [c]	205
25	25	25	$Ru(4,4'\text{-DBO-bpy})_3^{2+}$	MeOH/EtOH	476 (13500)				670	0.31	0.032	205
25	25	25	$Ru(4,4'\text{-DBO-bpy})_3^{2+}$	MeOH/EtOH							0.015 [c]	205
26	26	26	$Ru(4,4'\text{-dph-bpy})_3^{2+}$			610						383
26	26	26	$Ru(4,4'\text{-dph-bpy})_3^{2+}$	AN	474				638			233
26	26	26	$Ru(4,4'\text{-dph-bpy})_3^{2+}$	H_2O	474 (32700)				632	0.67		149
26	26	26	$Ru(4,4'\text{-dph-bpy})_3^{2+}$	MeOH/EtOH			4.68	0.573				342
26	26	26	$Ru(4,4'\text{-dph-bpy})_3^{2+}$	MeOH/EtOH			4.9	0.57				107
26	26	26	$Ru(4,4'\text{-dph-bpy})_3^{2+}$	MeOH/EtOH							0.058 [c]	205
26	26	26	$Ru(4,4'\text{-dph-bpy})_3^{2+}$	MeOH/EtOH	473 (28000)				635	1.95	0.306	204, 205

27	27	27	$Ru(4,4'\text{-dbz-bpy})_3^{2+}$	MeOH/ EtOH	460 (16100)			640	1.25	0.098	205
27	27	27	$Ru(4,4'\text{-dbz-bpy})_3^{2+}$	MeOH/ EtOH						0.030 [c]	205
28	28	28	$Ru(4,4'\text{-dsty-bpy})_3^{2+}$	MeOH/ EtOH	487 (33000)			680	0.72	0.030	205
28	28	28	$Ru(4,4'\text{-dsty-bpy})_3^{2+}$	MeOH/ EtOH						0.009 [c]	205
29	29	29	$Ru(4,4'\text{-dc-bpy})_3^{4-}$	H_2O					0.62 [c]		134
29	29	31	$Ru(4,4'\text{-dc-bpy})_2$ $(4,4'\text{-dnd-bpy})^{2+}$	$CHCl_3$				677			346
29	29	31	$Ru(4,4'\text{-dc-bpy})_2$ $(4,4'\text{-dnd-bpy})^{2+}$	H_2O/ THF	478 (13000)			643			346 [b]
29	29	31	$Ru(4,4'\text{-dc-bpy})_2$ $(4,4'\text{-dnd-bpy})^{2+}$	H_2O/THF	484			660			351 [b]
30	30	30	$Ru(4,4'\text{-DTB-bpy})_3^{2+}$	AN	456 (16800)			625	1.15		329
30	30	30	$Ru(4,4'\text{-DTB-bpy})_3^{2+}$	MeOH/ EtOH		575	5.3				40, 329
31	33	33	$Ru(4,4'\text{-dnd-bpy})$ $(4,4'\text{-poeg-bpy})_2^{2+}$	H_2O	455 (7000)				0.43	0.008	384
34	34	34	$Ru(4,4'\text{-DCM-bpy})_3^{2+}$	H_2O					0.89 [c]		134
37	37	37	$Ru(4,4'\text{-DCE-bpy})_3^{2+}$	CH_2Cl_2	467	607		629	2.230	0.30	135
37	37	37	$Ru(4,4'\text{-DCE-bpy})_3^{2+}$	MeOH/ EtOH						0.076 [c]	205
37	37	37	$Ru(4,4'\text{-DCE-bpy})_3^{2+}$	MeOH/ EtOH	464 (23300)			655	1.65	0.200	204, 205
38	38	38	$Ru(4,4'\text{-DCI-bpy})_3^{2+}$	AN				629	2.39		354
38	38	38	$Ru(4,4'\text{-DCI-bpy})_3^{2+}$	AN	468			625			380
39	39	39	$Ru(4,4'\text{-DCC-bpy})_3^{2+}$	AN				630	2.21		354

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
40	40	40	Ru(4,4′-DCB-bpy)$_3^{2+}$	AN					636	1.93		354
41	41	41	Ru(4,4′-DCNE-bpy)$_3^{2+}$	AN					631	2.19		354
42	42	42	Ru(4,4′-DCNY-bpy)$_3^{2+}$	AN					632	2.21		354
43	43	43	Ru(4,4′-DHC-bpy)$_3^{2+}$	iBN/AN					638	2.14		354
50	50	50	Ru(5,5′-dm-bpy)$_3^{2+}$	MeOH/EtOH	440 (14700)				620	0.35	0.037	205
50	50	50	Ru(5,5′-dm-bpy)$_3^{2+}$	MeOH/EtOH							0.015 [c]	205
51	51	51	Ru(5,5′-DCE-bpy)$_3^{2+}$	MeOH/EtOH							0.003 [c]	205
51	51	51	Ru(5,5′-DCE-bpy)$_3^{2+}$	MeOH/EtOH	495 (9900)				720	0.23	0.004	204, 205
52	52	52	Ru(5,5′-BAA-bpy)$_3^{2+}$	MeOH/EtOH	445 (14900)				630	2.40	0.126	205
52	52	52	Ru(5,5′-BAA-bpy)$_3^{2+}$	MeOH/EtOH							0.021 [c]	205
54	54	54	Ru(6,6′-dm-bpy)$_3^{2+}$	MeOH	446 (7440)							379
54	54	54	Ru(6,6′-dm-bpy)$_3^{2+}$	MeOH/EtOH		589	2.5	0.0176				379
59	59	59	Ru(bpz)$_3^{2+}$	AN	443 (15100)							382
59	59	59	Ru(bpz)$_3^{2+}$	AN	435				585			386
59	59	59	Ru(bpz)$_3^{2+}$	AN	440 (13000)							229
59	59	59	Ru(bpz)$_3^{2+}$	AN	443				591	0.740		387 [b]
59	59	59	Ru(bpz)$_3^{2+}$	AN	439				627	0.72	0.024	232
59	59	59	Ru(bpz)$_3^{2+}$	AN	440				603			233

59	59	59	$Ru(bpz)_3^{2+}$	AN	442		605	0.84		388
59	59	59	$Ru(bpz)_3^{2+}$	DMF				1.1	0.11	232
59	59	59	$Ru(bpz)_3^{2+}$	EtOH				0.76	0.060	232
59	59	59	$Ru(bpz)_3^{2+}$	H_2O	443 (15000)		603	1.04		389
59	59	59	$Ru(bpz)_3^{2+}$	H_2O			595	0.90 [c]		278
59	59	59	$Ru(bpz)_3^{2+}$	H_2O	441		595	0.920		387 [b]
59	59	59	$Ru(bpz)_3^{2+}$	H_2O			603	0.75	0.043	390
59	59	59	$Ru(bpz)_3^{2+}$	H_2O				0.94	0.075	232
59	59	59	$Ru(bpz)_3^{2+}$	MeOH/ EtOH		573				232
59	59	59	$Ru(bpz)_3^{2+}$	PC			610	0.795	0.074	229
59	59	59	$Ru(bpz)_3^{2+}$	PC			610	0.82	0.074	225
59	59	61	$Ru(bpz)_2(bpym)^{2+}$	PC			633	1.06	0.074	225
59	61	61	$Ru(bpz)(bpym)_2^{2+}$	PC			655	0.95	0.077	225
61	61	61	$Ru(bpym)_3^{2+}$	AN	454 (8600)					229
61	61	61	$Ru(bpym)_3^{2+}$	AN	450		635			232
61	61	61	$Ru(bpym)_3^{2+}$	H_2O	452 (7400)		644	0.064	0.09	361
61	61	61	$Ru(bpym)_3^{2+}$	H_2O			639	0.19	0.002	390
61	61	61	$Ru(bpym)_3^{2+}$	H_2O				0.06		232
61	61	61	$Ru(bpym)_3^{2+}$	MeOH/ EtOH		588				232
61	61	61	$Ru(bpym)_3^{2+}$	PC			639	0.131	0.011	229
61	61	61	$Ru(bpym)_3^{2+}$	PC			639	0.12	0.011	225
62	62	62	$Ru(4,4'\text{-dm-bpym})_3^{2+}$	AN	449		725			232
62	62	62	$Ru(4,4'\text{-dm-bpym})_3^{2+}$	MeOH/ EtOH		662				232
63	63	63	$Ru(6,6'\text{-dm-bpym})_3^{2+}$	H_2O	503 (10700)		705			241
63	63	63	$Ru(6,6'\text{-dm-bpym})_3^{2+}$	MeOH/ EtOH		662				241

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
64	64	64	$Ru(bprid)_3^{2+}$	AN	449				652	1.0	0.059	232
64	64	64	$Ru(bprid)_3^{2+}$	DMF						0.89	0.048	232
64	64	64	$Ru(bprid)_3^{2+}$	EtOH						0.95	0.055	232
64	64	64	$Ru(bprid)_3^{2+}$	H_2O	444 (11500)				636	0.700		241
64	64	64	$Ru(bprid)_3^{2+}$	H_2O					622	0.58	0.014	390
64	64	64	$Ru(bprid)_3^{2+}$	H_2O						0.59	0.028	232
64	64	64	$Ru(bprid)_3^{2+}$	MeOH/ EtOH		601						241
64	64	64	$Ru(bprid)_3^{2+}$	MeOH/ EtOH		601						232
65	65	65	$Ru(4\text{-py-prim})_3^{2+}$	AN	451				634	0.41	0.012	232
65	65	65	$Ru(4\text{-py-prim})_3^{2+}$	DMF						0.45	0.017	232
65	65	65	$Ru(4\text{-py-prim})_3^{2+}$	EtOH						0.37	0.012	232
65	65	65	$Ru(4\text{-py-prim})_3^{2+}$	H_2O							0.008	390
65	65	65	$Ru(4\text{-py-prim})_3^{2+}$	H_2O						0.22	0.0070	232
65	65	65	$Ru(4\text{-py-prim})_3^{2+}$	MeOH/ EtOH		594						232
66	66	66	$Ru(6\text{-py-prim})_3^{2+}$	AN	476				670			232
66	66	66	$Ru(6\text{-py-prim})_3^{2+}$	H_2O	452 (10200)				633	0.190		241
66	66	66	$Ru(6\text{-py-prim})_3^{2+}$	H_2O						0.11		232
66	66	66	$Ru(6\text{-py-prim})_3^{2+}$	MeOH/ EtOH		589						241
66	66	66	$Ru(6\text{-py-prim})_3^{2+}$	MeOH/ EtOH		625						232
67	67	67	$Ru(h\text{-phen})_3^{2+}$	AN	453 (14700)				610			40
67	67	67	$Ru(h\text{-phen})_3^{2+}$	MeOH/ EtOH		582	5.5					40

68	en	en		$Ru(phen)(en)_2^{2+}$		469	716			0.154		317
68	68	CN	CN	$Ru(phen)_2(CN)_2$	D_2O					0.825		322
68	68	CN	CN	$Ru(phen)_2(CN)_2$	DMF					1.09		323
68	68	CN	CN	$Ru(phen)_2(CN)_2$	EtOH				605			391
68	68	CN	CN	$Ru(phen)_2(CN)_2$	H_2O	421 (9500)			626	0.71		323
68	68	CN	CN	$Ru(phen)_2(CN)_2$	H_2O					0.654		322
68	68	CN	CN	$Ru(phen)_2(CN)_2$	MeOH	448 (10400)			638	1.58		323
68	68	CN	CN	$Ru(phen)_2(CN)_2$	MeOH					1.58		327
68	68	CN	CN	$Ru(phen)_2(CN)_2$	MeOH		562					219 [b]
68	68	CN	CN	$Ru(phen)_2(CN)_2$	MeOH/ EtOH		584					323
68	68	CN	CN	$Ru(phen)_2(CN)_2$	MeOH/ H_2O		567					323
68	68	CN	CN	$Ru(phen)_2(CN)_2$	MeOH/ H_2O	431	570	5.1				219
68	68	en	en	$Ru(phen)_2(en)^{2+}$		478	702			0.250		317
68	68	NH_3	NH_3	$Ru(phen)_2(NH_3)_2^{2+}$		477	759			0.144		317
68	68	ox		$Ru(phen)_2(ox)$	MeOH/ EtOH		702					97
68	68	68		$Ru(phen)_3^{2+}$		447	608			0.870		317
68	68	68		$Ru(phen)_3^{2+}$	AN	477 (18400)				0.50		321
68	68	68		$Ru(phen)_3^{2+}$	AN	442			604	0.46	0.028	232
68	68	68		$Ru(phen)_3^{2+}$	CH_2Cl_2					0.15		124
68	68	68		$Ru(phen)_3^{2+}$	D_2O					1.09		322
68	68	68		$Ru(phen)_3^{2+}$	D_2O					1.1		392
68	68	68		$Ru(phen)_3^{2+}$	D_2O				1.080		146	
68	68	68		$Ru(phen)_3^{2+}$	DMF					0.68	0.063	232
68	68	68		$Ru(phen)_3^{2+}$	EPA		565	9.93				331
68	68	68		$Ru(phen)_3^{2+}$	EtOH					0.29	0.019	232
68	68	68		$Ru(phen)_3^{2+}$	H_2O	450			577			336
68	68	68		$Ru(phen)_3^{2+}$	H_2O	447 (19000)			593	0.92		149

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
68	68	68	$Ru(phen)_3^{2+}$	H_2O						1.08		337
68	68	68	$Ru(phen)_3^{2+}$	H_2O						0.92		12
68	68	68	$Ru(phen)_3^{2+}$	H_2O						1.06		393
68	68	68	$Ru(phen)_3^{2+}$	H_2O	447 (18100)				604		0.058	338
68	68	68	$Ru(phen)_3^{2+}$	H_2O							0.032 [c]	338
68	68	68	$Ru(phen)_3^{2+}$	H_2O						0.921		275
68	68	68	$Ru(phen)_3^{2+}$	H_2O						0.908		322
68	68	68	$Ru(phen)_3^{2+}$	H_2O						1.11		381
68	68	68	$Ru(phen)_3^{2+}$	H_2O					603	0.962		392
68	68	68	$Ru(phen)_3^{2+}$	H_2O						0.459 [c]		394
68	68	68	$Ru(phen)_3^{2+}$	H_2O						0.960		146
68	68	68	$Ru(phen)_3^{2+}$	H_2O						0.96	0.072	232
68	68	68	$Ru(phen)_3^{2+}$	HCl, 1.5 M						0.72		340
68	68	68	$Ru(phen)_3^{2+}$	$HClO_4$, 1 M						0.81		321
68	68	68	$Ru(phen)_3^{2+}$	MeOH						0.313		337
68	68	68	$Ru(phen)_3^{2+}$	MeOH	446 (19000)							379
68	68	68	$Ru(phen)_3^{2+}$	MeOH/ EtOH			9.79	0.584				104
68	68	68	$Ru(phen)_3^{2+}$	MeOH/ EtOH			9.79	0.584				342
68	68	68	$Ru(phen)_3^{2+}$	MeOH/ EtOH		565						337
68	68	68	$Ru(phen)_3^{2+}$	MeOH/ EtOH		567	9.8	0.58				111, 123
68	68	68	$Ru(phen)_3^{2+}$	MeOH/ EtOH		589	9.8	0.600				379

68	68	68	$Ru(phen)_3^{2+}$	MeOH/ EtOH	447	565	10.1					268
68	68	68	$Ru(phen)_3^{2+}$	MeOH/ EtOH		566	9.9	0.578				338
68	68	68	$Ru(phen)_3^{2+}$	MeOH/ EtOH	445 (20000)				595	0.45	0.019	204, 206
68	68	68	$Ru(phen)_3^{2+}$	MeOH/ EtOH		564						232
68	68	68	$Ru(phen)_3^{2+}$	NaLS						1.82		382
68	68	68	$Ru(phen)_3^{2+}$	PMM		573						109
68	68	79	$Ru(phen)^{2+}$ $(5\text{-Cl-phen})^{2+}$	MeOH						0.947		327
68	68	80	$Ru(phen)_2$ $(5\text{-Br-phen})^{2+}$	MeOH						0.989		327
68	68	84	$Ru(phen)_2$ $(5\text{-Ph-phen})^{2+}$	H_2O						0.488 [c]		394
68	68	86	$Ru(phen)_2$ $(4,7\text{-dm-phen})^{2+}$	D_2O						1.94		392
68	68	86	$Ru(phen)_2$ $(4,7\text{-dm-phen})^{2+}$	H_2O					611	1.389		392
68	68	88	$Ru(phen)_2$ $(4,7\text{-Ph}_2\text{-phen})^{2+}$	D_2O						4.22		322
68	68	88	$Ru(phen)_2$ $(4,7\text{-Ph}_2\text{-phen})^{2+}$	H_2O						3.07		322
68	68	88	$Ru(phen)_2$ $(4,7\text{-Ph}_2\text{-phen})^{2+}$	MeOH						2.56		327
68	68	92	$Ru(phen)_2$ (4,7-dsph-phen)	D_2O						5.25		322
68	68	92	$Ru(phen)_2$ (4,7-dsph-phen)	H_2O						3.46		322
68	68	92	$Ru(phen)_2$ (4,7-dsph-phen)	H_2O						0.920 [c]		394

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
68	68	92	$Ru(phen)_2$ (4,7-dsph-phen)	MeOH						3.98		327
68	68	94	$Ru(phen)_2$ $(4,7\text{-dhy-phen})^{2+}$	D_2O					635	2.10	0.07 [c]	363 [b]
68	68	94	$Ru(phen)_2$ $(4,7\text{-dhy-phen})^{2+}$	EtOH		590	3.0	0.38				383 [b]
68	68	94	$Ru(phen)_2$ $(4,7\text{-dhy-phen})^{2+}$	H_2O	455 (15000)				635	1.25	0.04 [c]	363 [b]
68	68	105	$Ru(phen)_2$ (BDCMP)	AN	463 (43600)				610	1.4		395 [b]
68	68	106	$Ru(phen)_2$ $(BDCMPH2)^{2+}$	HCl 12 M	465 (10700) [f]				632			395 [b]
68	68	246	$Ru(phen)_2(pq)^{2+}$	AN	483 (9200)				690			40
68	68	246	$Ru(phen)(pq)^{2+}$	MeOH	476 [f]							274
68	68	246	$Ru(phen)_2(pq)^{2+}$	MeOH/ EtOH		664	3.8					274
68	68	246	$Ru(phen)_2(pq)^{2+}$	MeOH/ EtOH		653	3.1					315
68	68	251	$Ru(phen)_2$ $(DMCH)^{2+}$	AN	522 (10600)				728			40
68	68	251	$Ru(phen)_2$ $(DMCH)^{2+}$	MeOH/ EtOH		710	2.0					315
68	68	257	$Ru(phen)_2(biq)^{2+}$	AN	522 (9300)				741			40
68	68	257	$Ru(phen)_2(biq)^{2+}$	MeOH	523 (9480)							274
68	68	257	$Ru(phen)_2(biq)^{2+}$	MeOH/ EtOH		729	2.1					274
68	68	257	$Ru(phen)_2(biq)^{2+}$	MeOH/ EtOH		711	1.8					315

68	68	262	$Ru(phen)_2(9\text{-}PDP)^{3+}$	AN	440 (19000) [f]				600	0.53		395
68	84	84	$Ru(phen)(5\text{-}Ph\text{-}phen)_2^{2+}$	H_2O						0.770 [c]		394
68	86	86	$Ru(phen)(4,7\text{-}dm\text{-}phen)_2^{2+}$	D_2O						2.201		392
68	86	86	$Ru(phen)(4,7\text{-}dm\text{-}phen)_3^{2+}$	H_2O					643	1.243		392
68	246	246	$Ru(phen)(pq)_2^{2+}$	MeOH	480 [f]							274
68	246	246	$Ru(phen)(pq)_2^{2+}$	MeOH/EtOH		675	3.8					274
68	257	257	$Ru(phen)(biq)_2^{2+}$	MeOH	551 (8690)							274
68	257	257	$Ru(phen)(biq)_2^{2+}$	MeOH/EtOH		738	2.3					274
68	69	69	$Ru(2\text{-}m\text{-}phen)_3^{2+}$	MeOH	446 (14400)							379
69	69	69	$Ru(2\text{-}m\text{-}phen)_3^{2+}$	MeOH/EtOH		576	5.9	0.172				379
72	72	72	$Ru(4\text{-}Cl\text{-}phen)_3^{2+}$	MeOH/EtOH	450 (18100)				630	1.78	0.037	206
73	73	73	$Ru(4\text{-}m\text{-}phen)_3^{2+}$	MeOH/EtOH	445 (22000)				602	0.80	0.054	206
74	74	74	$Ru(4\text{-}Ph\text{-}phen)_3^{2+}$	MeOH/EtOH	450 (22100)				605	4.00	0.109	206
75	75	75	$Ru(4\text{-}tol\text{-}phen)_3^{2+}$	MeOH/EtOH	453 (23600)				605	3.50	0.117	206
76	76	76	$Ru(4\text{-}bph\text{-}phen)_3^{2+}$	MeOH/EtOH	454 (28700)				612	4.9	0.184	206
77	77	77	$Ru(4\text{-}BrPh\text{-}phen)_3^{2+}$	MeOH/EtOH	452 (25300)				615	4.1	0.136	206
78	78	78	$Ru(4\text{-}MoPh\text{-}phen)_3^{2+}$	MeOH/EtOH	452 (25300)				615	3.25	0.130	206

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
79	79	79	$Ru(5\text{-Cl-phen})_3^{2+}$	D_2O						1.09		322
79	79	79	$Ru(5\text{-Cl-phen})_3^{2+}$	glycerol						3.0 [c]		335
79	79	79	$Ru(5\text{-Cl-phen})_3^{2+}$	H_2O	447 (18400)				593	0.94		149
79	79	79	$Ru(5\text{-Cl-phen})_3^{2+}$	H_2O						0.94		12
79	79	79	$Ru(5\text{-Cl-phen})_3^{2+}$	H_2O	447				605	0.94		101
79	79	79	$Ru(5\text{-Cl-phen})_3^{2+}$	H_2O						0.962		322
79	79	79	$Ru(5\text{-Cl-phen})_3^{2+}$	H_2O						1.23		381
79	79	79	$Ru(5\text{-Cl-phen})_3^{2+}$	HCl, 1.5 M						0.72		340
79	79	79	$Ru(5\text{-Cl-phen})_3^{2+}$	MeOH/ EtOH	446 (17900)				604	0.67	0.035	206
79	79	79	$Ru(5\text{-Cl-phen})_3^{2+}$	NaLS						2.08		382
80	80	80	$Ru(5\text{-Br-phen})_3^{2+}$	D_2O						1.50		322
80	80	80	$Ru(5\text{-Br-phen})_3^{2+}$	H_2O	448 (18800)				593	1.04		149
80	80	80	$Ru(5\text{-Br-phen})_3^{2+}$	H_2O						0.94		393
80	80	80	$Ru(5\text{-Br-phen})_3^{2+}$	H_2O						1.21		322
80	80	80	$Ru(5\text{-Br-phen})_3^{2+}$	H_2O						1.25		381
80	80	80	$Ru(5\text{-Br-phen})_3^{2+}$	NaLS						2.16		382
81	81	81	$Ru(5\text{-n-phen})_3^{2+}$	H_2O	449 (20000)				~ 595	< 0.005		149
81	81	81	$Ru(5\text{-n-phen})_3^{2+}$	H_2O						< 0.005		12
81	81	81	$Ru(5\text{-n-phen})_3^{2+}$	H_2O	449				606			101
81	81	81	$Ru(5\text{-n-phen})_3^{2+}$	H_2O						< 0.005		275
83	83	83	$Ru(5\text{-m-phen})_3^{2+}$	D_2O						1.71		322
83	83	83	$Ru(5\text{-m-phen})_3^{2+}$	D_2O						2.71		392
83	83	83	$Ru(5\text{-m-phen})_3^{2+}$	H_2O	450				575			336
83	83	83	$Ru(5\text{-m-phen})_3^{2+}$	H_2O	450 (19400)				597	1.33		149
83	83	83	$Ru(5\text{-m-phen})_3^{2+}$	H_2O						1.33		12
83	83	83	$Ru(5\text{-m-phen})_3^{2+}$	H_2O						1.330		101
83	83	83	$Ru(5\text{-m-phen})_3^{2+}$	H_2O						1.33		322

83	83	83	$Ru(5\text{-m-phen})_3^{2+}$	H_2O						1.35		381
83	83	83	$Ru(5\text{-m-phen})_3^{2+}$	H_2O					607	1.32		392
83	83	83	$Ru(5\text{-m-phen})_3^{2+}$	H_2O						0.500 [c]		394
83	83	83	$Ru(5\text{-m-phen})_3^{2+}$	MeOH/ EtOH	445 (21000)				597	0.85	0.061	206
83	83	83	$Ru(5\text{-m-phen})_3^{2+}$	NaLS						2.26		382
84	84	84	$Ru(5\text{-Ph-phen})_3^{2+}$	D_2O						2.02		322
84	84	84	$Ru(5\text{-Ph-phen})_3^{2+}$	H_2O	448 (24600)				595	1.29		149
84	84	84	$Ru(5\text{-Ph-phen})_3^{2+}$	H_2O						1.63		322
84	84	84	$Ru(5\text{-Ph-phen})_3^{2+}$	MeOH/ EtOH	448 (21700)				597	1.15	0.033	206
85	85	85	$Ru(2,9\text{-dm-phen})_3^{2+}$	MeOH	501 (2580)							379
85	85	85	$Ru(2,9\text{-dm-phen})_3^{2+}$	MeOH/ EtOH		588	2.3	0.0479				379
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	D_2O						2.22		393
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	D_2O						2.29		322
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	D_2O						2.19		392
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	H_2O	445 (25300)				607	1.74		149
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	H_2O						1.58		393
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	H_2O	445				613	1.740		101
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	H_2O						1.65		322
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	H_2O						1.87		381
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	H_2O					612	1.68		392
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	H_2O						0.490 [c]		394
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	HCl, 1.5 M						1.27		340
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	MeOH						0.846		396
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	MeOH/ EtOH				0.65				109
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	MeOH/ EtOH	448 (22700)				600	0.85	0.059	206
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	NaLS						3.30		382
86	86	86	$Ru(4,7\text{-dm-phen})_3^{2+}$	PMM		615						109

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
87	87	87	$Ru(4,7\text{-}Cl_2\text{-}phen)_3^{2+}$	MeOH/ EtOH	456 (20600)				668	1.55	0.028	204, 206
88	88	88	$Ru(4,7\text{-}Ph_2\text{-}phen)_3^{2+}$	D_2O						5.83		322
88	88	88	$Ru(4,7\text{-}Ph_2\text{-}phen)_3^{2+}$	D_2O						4.56		392
88	88	88	$Ru(4,7\text{-}Ph_2\text{-}phen)_3^{2+}$	H_2O	460 (29500)				610	4.68		149
88	88	88	$Ru(4,7\text{-}Ph_2\text{-}phen)_3^{2+}$	H_2O						4.680		275
88	88	88	$Ru(4,7\text{-}Ph_2\text{-}phen)_3^{2+}$	H_2O						3.58		322
88	88	88	$Ru(4,7\text{-}Ph_2\text{-}phen)_3^{2+}$	H_2O					635	3.30		392
88	88	88	$Ru(4,7\text{-}Ph_2\text{-}phen)_3^{2+}$	MeOH						5.34		327
88	88	88	$Ru(4,7\text{-}Ph_2\text{-}phen)_3^{2+}$	MeOH/ EtOH		595						383
88	88	88	$Ru(4,7\text{-}Ph_2\text{-}phen)_3^{2+}$	MeOH/ EtOH			9.58	0.682				342
88	88	88	$Ru(4,7\text{-}Ph_2\text{-}phen)_3^{2+}$	MeOH/ EtOH	463 (28600)				618	6.40	0.366	204, 206
88	88	88	$Ru(4,7\text{-}Ph_2\text{-}phen)_3^{2+}$	PMM		602						109
89	89	89	$Ru(4,7\text{-}bbr\text{-}phen)_3^{2+}$	MeOH/ EtOH	464 (33000)				623	5.95	0.403	206
90	90	90	$Ru(4,7\text{-}bmo\text{-}phen)_3^{2+}$	MeOH/ EtOH	468 (37900)				615	6.10	0.387	206
91	91	91	$Ru(4,7\text{-}bph_2\text{-}phen)_3^{2+}$	MeOH/ EtOH	465 (36300)				620	7.20	0.360	206
92	92	92	$Ru(4,7\text{-}dsph\text{-}phen)_3^{4-}$	D_2O						5.84		322
92	92	92	$Ru(4,7\text{-}dsph\text{-}phen)_3^{4-}$	H_2O						3.73		322
92	92	92	$Ru(4,7\text{-}dsph\text{-}phen)_3^{4-}$	H_2O						3.860		101
93	93	93	$Ru(4,7\text{-}dtol\text{-}phen)_3^{2+}$	MeOH/ EtOH	464 (27400)				618	6.43	0.280	206

94	100	100	Ru(4,7-dhy-phen)(tm1-phen)$_2^{2+}$	D_2O					629	2.250	0.05 [c]	363 [b]
94	100	100	Ru(4,7-dhy-phen)(tm1-phen)$_2^{2+}$	EtOH		590	11.0	0.39				363 [b]
94	100	100	Ru(4,7-dhy-phen)(tm1-phen)$_2^{2+}$	H_2O	450 (16700)				629	1.250	0.03 [c]	363 [b]
95	95	95	Ru(4,7-bpbr-phen)$_3^{2+}$	MeOH/EtOH	465 (31000)				623	6.00	0.310	206
96	96	96	Ru(4,7-bpmo-phen)$_3^{2+}$	MeOH/EtOH	468 (34800)				620	6.05	0.305	206
97	97	97	Ru(4,7-bpph-phen)$_3^{2+}$	MeOH/EtOH	465 (33700)				618	6.10	0.330	206
98	98	98	Ru(4,7-brmo-phen)$_3^{2+}$	MeOH/EtOH	464 (25500)				625	5.95	0.237	206
99	99	99	Ru(5,6-dm-phen)$_3^{2+}$	D_2O						2.80		322
99	99	99	Ru(5,6-dm-phen)$_3^{2+}$	D_2O						2.77		392
99	99	99	Ru(5,6-dm-phen)$_2^{2+}$	H_2O	450				583			336
99	99	99	Ru(5,6-dm-phen)$_3^{2+}$	H_2O	453 (20400)				602	1.81		149
99	99	99	Ru(5,6-dm-phen)$_3^{2+}$	H_2O						1.81		12
99	99	99	Ru(5,6-dm-phen)$_3^{2+}$	H_2O						1.810		101
99	99	99	Ru(5,6-dm-phen)$_3^{2+}$	H_2O						1.91		322, 381
99	99	99	Ru(5,6-dm-phen)$_3^{2+}$	H_2O					612	1.79		392
99	99	99	Ru(5,6-dm-phen)$_3^{2+}$	H_2O						0.513 [c]		394
99	99	99	Ru(5,6-dm-phen)$_3^{2+}$	MeOH						1.404		396
99	99	99	Ru(5,6-dm-phen)$_3^{2+}$	MeOH/EtOH				0.56				109
99	99	99	Ru(5,6-dm-phen)$_3^{2+}$	MeOH/EtOH	450 (19800)				598	2.50	0.143	206
99	99	99	Ru(5,6-dm-phen)$_3^{2+}$	NaLS						3.08		382
99	99	99	Ru(5,6-dm-phen)$_3^{2+}$	PMM		585						109

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
100	100	100	$Ru(tm1\text{-}phen)_3^{2+}$	D_2O						2.03		322
100	100	100	$Ru(tm1\text{-}phen)_3^{2+}$	D_2O						2.14		392
100	100	100	$Ru(tm1\text{-}phen)_3^{2+}$	glycerol						3.2 [c]		335
100	100	100	$Ru(tm1\text{-}phen)_3^{2+}$	H_2O	438 (24500)				597	1.39		149
100	100	100	$Ru(tm1\text{-}phen)_3^{2+}$	H_2O						1.52		393
100	100	100	$Ru(tm1\text{-}phen)_3^{2+}$	H_2O						1.75		322
100	100	100	$Ru(tm1\text{-}phen)_3^{2+}$	H_2O						2.28		381
100	100	100	$Ru(tm1\text{-}phen)_3^{2+}$	H_2O					608	1.81		392
100	100	100	$Ru(tm1\text{-}phen)_3^{2+}$	H_2O						0.507 [c]		394
100	100	100	$Ru(tm1\text{-}phen)_3^{2+}$	HCl 1.5 M						1.0		340
100	100	100	$Ru(tm1\text{-}phen)_3^{2+}$	MeOH/ EtOH	439 (23300)				595	0.48	0.032	206
100	100	100	$Ru(tm1\text{-}phen)_3^{2+}$	NaLS						1.85		382
101	101	101	$Ru(tm2\text{-}phen)_3^{2+}$	H_2O	450				574			336
101	101	101	$Ru(tm2\text{-}phen)_3^{2+}$	H_2O	440 (19800)				594	2.22		149
101	101	101	$Ru(tm2\text{-}phen)_3^{2+}$	H_2SO_4 0.5 M						2.08		149
103	103	103	$Ru(TAP)_3^{2+}$	H_2O	435 (16000)				580	0.200		397
104	104	104	$Ru(2,7\text{-}dm\text{-}TAP)_3^{2+}$	H_2O	424 (16700)				575	0.090 [c]		398
105	105	105	$Ru(BDCMP)_3^{4-}$	AN	502 (50100)				683	1.4		395
107	107	107	$Ru(DIAF)_3^{2+}$	H_2O	440							216
107	107	107	$Ru(DIAF)_3^{2+}$	MeOH/ EtOH		585		low				216
108	108	108	$Ru(DIAFO)_3^{2+}$	AN	422 (14900)				~ 700			40
108	108	108	$Ru(DIAFO)_3^{2+}$	MeOH/ EtOH		600						40
109	109	109	$Ru(taphen)_3^{2+}$	AN	436 (15700)				705	0.33	0.034	238
109	109	109	$Ru(taphen)_3^{2+}$	MeOH/ EtOH		630	3.1					238

162	162	162		$Ru(DPA)_3^-$	MeOH/ EtOH		603 [h]	5.9					209
162	162	162		$Ru(DPA)_3 \cdot H_2O^-$	MeOH/ EtOH		644 [h]	1.8					209
162	162	163		$Ru(DPA)_2$ (DPAH)	MeOH/EtOH		650 [h]						209
162	163	163		$Ru(DPA)(DPAH)_2^+$	MeOH/ EtOH		603 [h]	6					209
163	163	163		$Ru(DPAH)_3^{2+}$	AN	375 [f]							235
163	163	163		$Ru(DPAH)_3^{2+}$	MeOH/ EtOH		730 [a]						209 [b]
163	163	163		$Ru(DPAH)_3^{2+}$	MeOH/ H_2O		730 [a]	2.0					209
181	181	aca		$Ru(Azpy)_2(acac)^{2+}$	H_2O					⩾ 870			376
181	181	CN	CN	$Ru(Azpy)_2(CN)_2$	H_2O					⩾ 870			376
181	181	en		$Ru(Azpy)_2(en)^{2+}$	H_2O					⩾ 870			376
181	181	NO_2	NO_2	$Ru(Azpy)_2(NO_2)_2$	H_2O					⩾ 870			376
181	181	181		$Ru(Azpy)_3^{2+}$	acetone					835			376
181	181	181		$Ru(Azpy)_3^{2+}$	CH_2Cl_2	498 (13500)	764 [g]						375
181	181	181		$Ru(Azpy)_3^{2+}$	H_2O					784			376
181	181	181		$Ru(Azpy)_3^{2+}$	MeOH/ EtOH		763	~ 0.01					399
181	181	186		$Ru(Azpy)_2(Btz)^{2+}$	CH_2Cl_2	515	755 [g]						375
181	181	186		$Ru(Azpy)_2(Btz)^{2+}$	H_2O					766			376
183	183	183		$Ru(NA)_3^{2+}$	AN	505 (14000)							399
183	183	183		$Ru(NA)_3^{2+}$	MeOH/ EtOH		798	~ 0.01					399
184	184	184		$Ru(thpy)_3^{2+}$	H_2O	463				668	0.22	0.026	370
187	187	187		$Ru(bt)_3^{2+}$	MeOH/ EtOH	515 (16600)	782	0.080	0.0003				400
188	188	188		$Ru(PTPI)_3^{2+}$	AN	552 (7200)				400			360

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
245	245	245		$Ru(hpiq)_3^{2+}$	AN	494 (19500)							40
245	245	245		$Ru(hpiq)_3^{2+}$	MeOH/ EtOH		733	1.1					40
246	246	246		$Ru(pq)_3^{2+}$	AN	484				687			233
246	246	246		$Ru(pq)_3^{2+}$	EtCN					718			351
246	246	246		$Ru(pq)_3^{2+}$	EtOH	484							351
246	246	246		$Ru(pq)_3^{2+}$	MeOH	483							401
246	246	246		$Ru(pq)_3^{2+}$	MeOH/ EtOH		658						401
246	246	246		$Ru(pq)_3^{2+}$	MeOH/ EtOH	488	670	3.4					268
246	246	257		$Ru(pq)_2(biq)^{2+}$	MeOH	530 (7350)							274
246	246	257		$Ru(pq)_2(biq)^{2+}$	MeOH/ EtOH		722	2.4					274
246	257	257		$Ru(pq)(biq)_2^{2+}$	MeOH	533 (7640)							274
246	257	257		$Ru(pq)(biq)_2^{2+}$	MeOH/ EtOH		731	2.0					274
247	247	247		$Ru(pynapy)_3^{2+}$	AN	526 (12500)							402
247	247	247		$Ru(pynapy)_3^{2+}$	MeOH/ EtOH		735	0.50					402
251	251	Cl	Cl	$Ru(DMCH)_2Cl_2$	MF	636 (12000)	865	0.72					217
251	251	CN	CN	$Ru(DMCH)_2(CN)_2$	AN	625				830			221
251	251	CN	CN	$Ru(DMCH)_2(CN)_2$	$CHCl_3$	618				824	0.18	0.017	221
251	251	CN	CN	$Ru(DMCH)_2(CN)_2$	DMF	640 (9800)	772	1.2		839	0.14	0.007	221
251	251	CN	CN	$Ru(DMCH)_2(CN)_2$	MeOH	575		1.1		785	0.18	0.012	221
251	251	CN	CN	$Ru(DMCH)_2(CN)_2$	MeOH/ EtOH		732	1.2					40
251	251	CN	CN	$Ru(DMCH)_2(CN)_2$	MF	588				797			221

251	251	251		$Ru(DMCH)_3^{2+}$	AN	540 (10550)			~ 740 [i]			329
251	251	251		$Ru(DMCH)_3^{2+}$	MeOH/ EtOH		732	1.8				40, 329
256	256	256		$Ru(dinapy)_3^{2+}$	AN	585 (9900)						402
256	256	256		$Ru(dinapy)_3^{2+}$	MeOH/ EtOH		840	0.18				402
257	257	Cl	Cl	$Ru(biq)_2Cl_2$	MF	623 (12200)	855	0.46				217
257	257	CN	CN	$Ru(biq)_2(CN)_2$	AN	625			834			221
257	257	CN	CN	$Ru(biq)_2(CN)_2$	$CHCl_3$	620			825	0.16	0.016	221
257	257	CN	CN	$Ru(biq)_2(CN)_2$	DMF	635 (8900)	780	0.8	842	0.11	0.007	221
257	257	CN	CN	$Ru(biq)_2(CN)_2$	MeOH	580		0.93	790	0.17	0.009	221
257	257	CN	CN	$Ru(biq)_2(CN)_2$	MeOH/ EtOH		736	0.91				40
257	257	CN	CN	$Ru(biq)_2(CN)_2$	MF	593			804			221
257	257	257		$Ru(biq)_3^{2+}$	AN	524 (9000)			705 [i]			344
257	257	257		$Ru(biq)_3^{2+}$	MeOH	524						401
257	257	257		$Ru(biq)_3^{2+}$	MeOH/ EtOH		719					401
257	257	257		$Ru(biq)_3^{2+}$	MeOH/ EtOH		718	2.6				344
259	259	Cl	Cl	$Ru(i\text{-}biq)_2Cl_2$	MF	436 (15900)	730 [a]	2.2				217
259	259	CN	CN	$Ru(i\text{-}biq)_2(CN)_2$	$CHCl_3$	425			594	0.21	0.011	221
259	259	CN	CN	$Ru(i\text{-}biq)_2(CN)_2$	DMF	437 (17600)	577	40	632	0.45	0.023	221
259	259	CN	CN	$Ru(i\text{-}biq)_2(CN)_2$	MeOH	404		240	582	0.05	< 0.001	221
259	259	CN	CN	$Ru(i\text{-}biq)_2(CN)_2$	MeOH/ EtOH		542	250 [j]				40
259	259	CN	CN	$Ru(i\text{-}biq)_2(CN)_2$	MF	412			602			221
259	259	259		$Ru(i\text{-}biq)_3^{2+}$	AN	392 (24100)			555	0.045		215
259	259	259		$Ru(i\text{-}biq)_3^{2+}$	AN	392 (24100)			543	0.25 [k]		131
259	259	259		$Ru(i\text{-}biq)_3^{2+}$	nitrile		540	96.0				131
261	261	261		$Ru(DP)_3^{2+}$	AN	455 (22400)			615	0.73		395
267	267	267		$Ru(dpp)_3^{2+}$	H_2O	455			636	0.27		403
281	281			$Ru(trpy)_2^{2+}$	AN	474 (14600)						40
281	281			$Ru(trpy)_2^{2+}$	H_2O	473 (16200)			~ 620	< 0.005		149

TABLE 1 (continued)

(a) Mononuclear complexes

Ligands		Complex	Solvent	Abs (ϵ)	Em. (77 K)	τ (77 K)	ϕ (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
281	281	$Ru(trpy)_3^{2+}$	H_2O	473				628	< 0.005		101
281	281	$Ru(trpy)_2^{2+}$	$HClO_4$						> 0.0012		404
281	281	$Ru(trpy)_2^{2+}$	MeOH	475 (15100)							405
281	281	$Ru(trpy)_2^{2+}$	MeOH	470 (16100)							406
281	281	$Ru(trpy)_2^{2+}$	MeOH/ EtOH		600	11					407
281	281	$Ru(trpy)_2^{2+}$	MeOH/ EtOH		596	10.82					97, 320
281	281	$Ru(trpy)_2^{2+}$	MeOH/ EtOH			10.66	0.479				104
281	281	$Ru(trpy)_2^{2+}$	MeOH/ EtOH		599	11.0	0.48				406
281	281	$Ru(trpy)_2^{2+}$	MeOH/ EtOH		600						127
281	281	$Ru(trpy)_2^{2+}$	MeOH/ EtOH		596	10					40
282	282	$Ru(tro)_2^{2+}$	MeOH	560 (8200)							406
282	282	$Ru(tro)_2^{2+}$	MeOH/ EtOH		629	12.3	0.45				406
282	282	$Ru(tro)_2^{2+}$	MeOH/ EtOH		628						127
283	283	$Ru(tsite)_2^{2+}$	MeOH	500 (38400)							406
283	283	$Ru(tsite)_2^{2+}$	MeOH/ EtOH		633	7.8	0.57				406
283	283	$Ru(tsite)_2^{2+}$	MeOH/ EtOH		632						127
284	284	$Ru(dqp)_2^{2+}$	MeOH	517 (8880)							405
284	284	$Ru(dqp)_2^{2+}$	MeOH	610 (2200)							406
284	284	$Ru(dqp)_2^{2+}$	MeOH/ EtOH		685	4.77					405
284	284	$Ru(dqp)_2^{2+}$	MeOH/ EtOH		680	5.6	0.05				406
286	286	$Ru(TPTZ)_2^{2+}$	H_2O	501 (19200)				~ 600	< 0.005		149
286	286	$Ru(TPTZ)_2^{2+}$	H_2O	501				605			101

(b) Polynuclear complexes

Ligands							Complex	Solvent	Abs. (ϵ)	Em. (77 K)	Em. (RT)	τ (RT)	ϕ (RT)	Ref.
1	1	1	1	61			$[(bpy)_2Ru(bpym)Ru(bpy)_2]^{4+}$	H_2O	606 (7600)	769 [gl]				361
1	1	1	1	267			$[(bpy)_2Ru(dpp)Ru(bpy)_2]^{4+}$	EtOH	525 (21000)		755		2.7×10^{-3}	103
1	1	1	1	267			$[(bpy)_2Ru(dpp)Ru(bpy)_2]^{4+}$	H_2O				0.054		103
1	1	1	1	270			$[(bpy)_2Ru(BL3)Ru(bpy)_2]^{4+}$	AN	528 (16300)		780	0.060	6×10^{-6}	372
1	1	57	Cl	NH_3	NH_3	NH_3	$[(NH_3)_5Ru(4,4'\text{-bpy})RuCl(bpy)_2]^{3+}$	CH_2Cl_2/AN			700			358
1	1	57	Cl	NH_3	NH_3	NH_3	$[(NH_3)_5Ru^{III}(4,4'\text{-bpy})RuCl(bpy)_2]^{4+}$	CH_2Cl_2/AN			700			358
1	1	57	2SC	2SC	Cl	Cl	$[(2SC)_2ClRu(4,4'\text{-bpy})RuCl(bpy)_2]^{2+}$	AN	468 (16000)					358
1	1	57	2SC	2SC	Cl	Cl	$[(2SC)_2ClRu(4,4'\text{-bpy})RuCl(bpy)_2]^{2+}$	CH_2Cl_2/AN			706		10^{-3}	358, 359
1	1	57	2SC	2SC	Cl	Cl	$[(2SC)_2ClRu(4,4'\text{-bpy})Ru^{III}Cl(bpy)_2]^{3+}$	AN	412 (8900)					358
1	1	57	2SC	2SC	Cl	Cl	$[(2SC)_2ClRu(4,4'\text{-bpy})Ru^{III}Cl(bpy)_2]^{3+}$	CH_2Cl_2/AN			708		10^{-3}	358, 359
1	1	159	Cl	NH_3	NH_3	NH_3	$[(NH_3)_5Ru(BPA)RuCl(bpy)_2]^{3+}$	CH_2Cl_2/AN			711		10^{-3}	358, 359
1	1	159	Cl	NH_3	NH_3	NH_3	$[(NH_3)_5Ru^{III}(BPA)RuCl(bpy)_2]^{4+}$	CH_2Cl_2/AN			713		10^{-3}	358, 359
1	1	159	2SC	2SC	Cl	Cl	$[(2SC)_2ClRu(BPA)RuCl(bpy)_2]^{2+}$	CH_2Cl_2/AN			706		10^{-3}	358, 359
1	1	159	2SC	2SC	Cl	Cl	$[(2SC)_2ClRu(BPA)Ru^{III}Cl(bpy)_2]^{3+}$	CH_2Cl_2/AN			704		10^{-3}	358, 359
1	1	160	Cl	NH_3	NH_3	NH_3	$[(NH_3)_5Ru(BPE)RuCl(bpy)_2]^{3+}$	CH_2Cl_2/AN			700			358
1	1	160	Cl	NH_3	NH_3	NH_3	$[(NH_3)_5Ru^{III}(BPE)RuCl(bpy)_2]^{4+}$	CH_2Cl_2/AN			700			358
1	1	160	2SC	2SC	Cl	Cl	$[(2SC)_2ClRu(BPE)RuCl(bpy)_2]^{2+}$	CH_2Cl_2/AN			700		10^{-3}	358, 359
1	1	160	2SC	2SC	Cl	Cl	$[(2SC)_2ClRu(BPE)Ru^{III}Cl(bpy)_2]^{3+}$	CH_2Cl_2/AN			704		10^{-3}	358, 359

[a] MC emission. [b] pH dependence. [c] Air equilibrated solution. [d] $t_{1/2}$. [e] Double emission. [f] Shoulder. [g] Solid sample. [h] LMCT emission. [i] Not measurable. [j] LC emission. [k] At 250 K. [l] At 15 K.

TABLE 2

Photochemical properties

Ligands				Complex	Solvent	ϕ	Type of reaction	Ref.
1	1	AN	AN	$Ru(bpy)_2(AN)_2^{2+}$	CH_2Cl_2,Cl^-	0.31	$\rightarrow Ru(bpy)_2(AN)Cl^+$	318
1	1	AN	AN	$Ru(bpy)_2(AN)_2^{2+}$	CH_2Cl_2,Cl^-	0.32	$\rightarrow Ru(bpy)_2(AN)Cl^+$	409
1	1	AN	AN	$Ru(bpy)_2(AN)_2^{2+}$	H_2SO_4 1M	0.44	Photoaquation	318
1	1	AN	Cl	$Ru(bpy)_2(AN)Cl^+$	CH_2Cl_2,Cl^-	0.12	$\rightarrow Ru(bpy)_2Cl_2$	318
1	1	AN	CO	$Ru(bpy)_2(AN)(CO)^{2+}$	AN		CO photosubstitution	410
1	1	Cl	CO	*cis*-$Ru(bpy)_2(CO)Cl^+$	AN		CO photosubstitution	411
1	1	Cl	CO	$Ru(bpy)_2(CO)Cl^+$	AN	0.09	CO photosubstitution	410
1	1	Cl	CO	$Ru(bpy)_2(CO)Cl^+$	CH_2Cl_2,Cl^-	0.045	$\rightarrow Ru(bpy)_2Cl_2$	318
1	1	Cl	CO	$Ru(bpy)_2(CO)Cl^+$	H_2O		CO photosubstitution	412
1	1	Cl	CO	*cis*-$Ru(bpy)_2(CO)Cl^+$	MeOH		Co photosubstitution	411
1	1	Cl	CO	$Ru(bpy)_2(CO)Cl^+$	MeOH		CO photosubstitution	410
1	1	Cl	CO	*cis*-$Ru(bpy)_2(CO)Cl^+$	py		CO photosubstitution	411
1	1	Cl	CO	$Ru(bpy)_2(CO)Cl^+$	py		CO photosubstitution	410
1	1	Cl	H2	$Ru(bpy)_2(H_2)Cl^+$	H_2O		H_2 photosubstitution	412
1	1	Cl	NO	$Ru(bpy)_2(NO)Cl^{2+}$	AN		$\rightarrow Ru(bpy)_2(AN)Cl^{2+}$	413
1	1	CO	CO	$Ru(bpy)_2(CO)_2^{2+}$	CH_2Cl_2,Cl^-	0.05	$\rightarrow Ru(bpy)_2(CO)Cl^+$	318
1	1	CO	CO	$Ru(bpy)_2(CO)_2^{2+}$	MeOH		CO photosubstitution	410
1	1	CO	H	$Ru(bpy)_2(CO)H^+$	MeOH	< 0.001	Disappearance	410, 414
1	1	H	PPP	$Ru(bpy)_2(PPP)H^+$	AN		$\rightarrow Ru(bpy)_2(AN)_2^{2+}$	414
1	1	H_2O	H_2O	*trans*-$Ru(bpy)_2(H_2O)_2^{2+}$	H_2SO_4 1 M	0.026	Photoaquation	318
1	1	H_2O	H_2O	*cis*-$Ru(bpy)_2(H_2O)_2^{2+}$	H_2SO_4 1 M	0.045	Photoaquation	318
1	1	H_2O	H_2O	*cis*-$Ru(bpy)_2(H_2O)_2^{2+}$	H_2SO_4 1 N	0.04	Photoisomerization	415
1	1	H_2O	H_2O	*trans*-$Ru(bpy)_2(H_2O)_2^{2+}$	H_2SO_4 1 N	0.025	Photoisomerization	415
1	1	MPP	MPP	$Ru(bpy)_2(MPP)_2^{2+}$	CH_2Cl_2,Cl^-	~ 0	Photoanation	318
1	1	N_3	N_3	$Ru(bpy)_2(N_3)^{2+}$	AN		$\rightarrow Ru(bpy)_2(AN)(N_3)^+$	416
1	1	N_3	N_3	$Ru(bpy)_2(N_3)^{2+}$	AN		Decomposition or photosolvation	416
1	1	SCN	SCN	$Ru(bpy)_2(SCN)_2$	DMF		Photosolvation	426

1	1	1		$Ru(bpy)_3^{2+}$	AN,Cl^-	0.01	Photoanation	387
1	1	1		$Ru(bpy)_3^{2+}$	AN,Cl^-	0.003	Photoanation	366
1	1	1		$Ru(bpy)_3^{2+}$	AN	< 0.0003	→ $Ru(bpy)_2(AN)_2^{2+}$	417
1	1	1		$Ru(bpy)_3^{2+}$	AN	0.029	Ligand loss	225
1	1	1		$Ru(bpy)_3^{2+}$	CH_2Cl_2,Cl^-	0.04	Photoanation	366
1	1	1		$Ru(bpy)_3(NCS)_2$	CH_2Cl_2,Cl^-	0.068	Photoanation	124
1	1	1		$Ru(bpy)_3Cl_2$	CH_2Cl_2,Cl^-	0.100	Photoanation	124
1	1	1		$Ru(bpy)_3^{2+}$	CH_2Cl_2,Cl^-	0.030	Photoanation	409
1	1	1		$Ru(bpy)_3^{2+}$	DCl 1 M	0.00036	→ $Ru(bpy)_2(\text{-bpy})Cl^+$	121
1	1	1		$Ru(bpy)_3^{2+}$	DMF,Br^-	0.0003	→ $Ru(bpy)_2(DMF)Br^+$ + $Ru(bpy)_2Br_2$	418
1	1	1		Δ-$Ru(bpy)_3^{2+}$	H_2O	0.00029	Racemization	144
1	1	1		$Ru(bpy)_3^{2+}$	H_2SO_4 1 N	< 0.0001	Photoanation	366
1	1	1		$Ru(bpy)_3^{2+}$	HCl 12 M	> 0.0015	→ $Ru(bpy)_2(\text{-bpy})Cl^+$	121
1	1	1		$Ru(bpy)_3^{2+}$	HCl 1 M	0.00019	→ $Ru(bpy)_2(\text{-bpy})Cl^+$	121
1	1	1		$Ru(bpy)_3^{2+}$	HCl 1 M		→ $Ru(bpy)_2(\text{-bpy})Cl^+$	343
1	1	1		$Ru(bpy)_3^{2+}$	HCl 2 M		Disappearance	419
1	1	1		$Ru(bpy)_3^{2+}$	$NaHCO_3$		→ $Ru(bpy)_2(\text{-bpy})(OH)^+$	343
1	1	1		$Ru(bpy)_3^{2+}$	NaOH 0.3 M	0.00033	Disappearance	420
1	1	11		$Ru(bpy)_2(6\text{-sty-bpy})^{2+}$	AN	0.0008	Photosolvation	345
1	1	57	57	$Ru(bpy)_2(4,4'\text{-bpy})_2^{2+}$	CH_2Cl_2,Cl^-	0.20	→ $Ru(bpy)_2(4,4'\text{-bpy})Cl^+$	318
1	1	59		$Ru(bpy)_2(bpz)^{2+}$	AN	< 0.0001	Ligand loss	225
1	1	61		$Ru(bpy)_2(bpym)^{2+}$	AN	< 0.0001	Ligand loss	225
1	1	107		$Ru(bpy)_2(DIAF)^{2+}$	AN	0.004	Photosubstitution	421
1	1	107		$Ru(bpy)_2(DIAF)^{2+}$	CH_2Cl_2	0.043 [a]	Photosubstitution	421
1	1	111	Cl	$Ru(bpy)_2(py)Cl^+$	CH_2Cl_2,Cl^-	0.04	→ $Ru(bpy)_2Cl_2$	318
1	1	111	Cl	$Ru(bpy)_2(py)Cl^+$	MeOH		Cl^- photosubstitution	422
1	1	111	NCS	$Ru(bpy)_2(py)(NCS)^+$	CH_2Cl_2,Cl^-		→ $Ru(bpy)_2(NCS)Cl$	423
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	AN	0.036	Photosubstitution	421
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	CH_2Cl_2	0.211	Photosubstitution	421
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	CH_2Cl_2,X^-	0.18	→ $Ru(bpy)_2(py)X^+$	423
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	CH_2Cl_2,Cl^-	0.20	→ $Ru(bpy)_2(py)Cl^+$	318

TABLE 2 (continued)

Ligands				Complex	Solvent	ϕ	Type of reaction	Ref.
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	CH_2Cl_2,Cl^-	0.22	$\rightarrow Ru(bpy)_2(py)Cl^+$	409
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	H_2O	0.170	Photosubstitution	421
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	H_2SO_4 1 M	0.26	Photoaquation	318
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	MeOH		Photosubstitution	422
1	1	115	115	$Ru(bpy)_2(3\text{-I-py})_2^{2+}$	CH_2Cl_2,Cl^-	0.20	$\rightarrow Ru(bpy)_2(3\text{-I-py})Cl^+$	318
1	1	118	CO	$Ru(bpy)_2(pic)(CO)^{2+}$	MeOH		CO photosubstitution	410
1	1	118	CO	$Ru(bpy)_2(pic)(CO)^{2+}$	py		CO photosubstitution	410
1	1	118	118	$Ru(bpy)_2(pic)_2^{2+}$	AN,Cl^-	0.21	Photoanation	366
1	1	118	118	$Ru(bpy)_2(pic)_2^{2+}$	CH_2Cl_2,Cl^-	0.17	Photoanation	366
1	1	118	118	$Ru(bpy)_2(pic)_2^{2+}$	H_2SO_4 1 N	0.24	Photoanation	366
1	1	119	Cl	$Ru(bpy)_2(4\text{-acetyl-py})Cl^+$	CH_2Cl_2,Cl^-	0.07	$\rightarrow Ru(bpy)_2Cl_2$	318
1	1	119	119	$Ru(bpy)_2(4\text{-acetyl-py})_2^{2+}$	CH_2Cl_2,Cl^-	0.29	$\rightarrow Ru(bpy)(4\text{-acetyl-py})Cl^+$	318
1	1	124	Cl	$Ru(bpy)_2(PVP)(Cl)^+$	MeOH		Cl^- photosubstitution	422
1	1	124	CO	$Ru(bpy)_2(PVP)(CO)^{2+}$	MeOH		CO photosubstitution	410
1	1	124	CO	$Ru(bpy)_2(PVP)(CO)^{2+}$	py		CO photosubstitution	410
1	1	124	124	$Ru(bpy)_2(PVP)_{2/20}^{2+}$	AN	0.087	Ligand loss	126
1	1	124	124	$Ru(bpy)_2(PVP)_2^{2+}$	MeOH		Photosubstitution	422
1	1	125	Cl	$Ru(bpy)_2(t\text{-stylb})Cl^+$	BN	0.09	Ligand isomerization	424, 425
1	1	125	125	$Ru(bpy)_2(t\text{-stylb})_2^{2+}$	BN	0.15	Ligand isomerization	424, 425
1	1	126	Cl	$Ru(bpy)_2(c\text{-stylb})Cl^+$	BN	0.12	Ligand isomerization	424, 425
1	1	125	126	$Ru(bpy)_2(c\text{-stylb})_2^{2+}$	BN	0.16	Ligand isomerization	424, 425
1	1	137	137	$Ru(bpy)_2(pyd)_2^{2+}$	CH_2Cl_2,Cl^-	0.06	$\rightarrow Ru(bpy)_2(pyd)Cl^+$	318
1	1	145	145	$Ru(bpy)_2(pzH)_2^{2+}$	H_2SO_4 1 M	0.20	Photoaquation	318
1	1	146	146	$Ru(bpy)_2(imid)_2^{2+}$	CH_2Cl_2,Cl^-	< 0.001	$\rightarrow Ru(bpy)_2(imid)Cl^+$	318
1	1	147	147	$Ru(bpy)_2(NMI)_2^{2+}$	CH_2Cl_2,Cl^-	< 0.001	$\rightarrow Ru(bpy)_2(NMI)Cl^+$	318
1	1	157		$Ru(bpy)_2(DPM)^{2+}$	AN,Cl^-	0.24	Photoanation	366
1	1	157		$Ru(bpy)_2(DPM)^{2+}$	CH_2Cl_2,Cl^-	0.21	Photoanation	366

1	1	157		$Ru(bpy)_2(DPM)^{2+}$	H_2SO_4 1 N	0.04	Photoanation	366
1	1	158		$Ru(bpy)_2(DPE)^{2+}$	AN,Cl^-	0.18	Photoanation	366
1	1	158		$Ru(bpy)_2(DPE)^{2+}$	CH_2Cl_2,Cl^-	0.58	Photoanation	366
1	1	158		$Ru(bpy)_2(DPE)^{2+}$	H_2SO_4 1 N	< 0.3	Photoanation	366
1	59	59		$Ru(bpy)(bpz)_2^{2+}$	AN	0.035	Ligand loss	225
1	61	61		$Ru(bpy)(bpym)_2^{2+}$	AN	< 0.001	Ligand loss	225
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	CH_2Cl_2,Cl^-	0.005	Photoanation	135
15	15	37		$Ru(4,4'\text{-dm-bpy})_2(4,4'\text{-DCE-bpy})^{2+}$	CH_2Cl_2,Cl^-	< 0.001	Photoanation	135
15	37	37		$Ru(4,4'\text{-dm-bpy})(4,4'\text{-DCE-bpy})_2^{2+}$	CH_2Cl_2,Cl^-	< 0.001	Photoanation	135
37	37	37		$Ru(4,4'\text{-DCE-bpy})_3^{2+}$	CH_2Cl_2,Cl^-	0.012	Photoanation	135
54	54	AN	AN	$Ru(6,6'\text{-dm-bpy})_2(AN)_2^{2+}$	CH_2Cl_2,Cl^-		Photoanation	427
59	59	AN	Cl	$Ru(bpz)_2(AN)Cl^+$	AN	0.001	→ $Ru(bpz)_2Cl_2$	382
59	59	AN	Cl	$Ru(bpz)_2(AN)Cl^+$	AN	< 0.001	→ $Ru(bpz)_2Cl_2$	388
59	59	59		$Ru(bpz)_3^{2+}$	AN	0.37	→ $Ru(bpz)_2(AN)Cl^+$	382
59	59	59		$Ru(bpz)_3^{2+}$	AN,Cl^-	0.37	Photoanation	387
59	59	59		$Ru(bpz)_3^{2+}$	AN	0.45	Ligand loss	225
59	59	59		$Ru(bpz)_3^{2+}$	AN,Cl^-	0.37	Photoanation	387
59	59	59		$Ru(bpz)_3^{2+}$	AN,Cl^-		Photoanation	388
61	NH_3	NH_3	NH_3	$[Ru(NH_3)_4]_2(bpym)^{4+}$	H_2O	< 0.0005	Decomposition	428
68	68	AN	AN	*trans*-$Ru(phen)_2(AN)_2^{2+}$	AN		Photoisomerization	429
68	68	AN	H_2O	*trans*-$Ru(phen)_2(H_2O)(AN)^{2+}$	H_2O		Photoisomerization	429
68	68	H_2O	H_2O	*cis*-$Ru(phen)_2(H_2O)_2^{2+}$	H_2O		Photoisomerization	429
68	68	68		$Ru(phen)_3^{2+}$	CH_2Cl_2,Cl^-	0.020	Photoanation	124
68	68	68		$Ru(phen)_3^{2+}$	CH_2Cl_2,Cl^-	0.014	Photoanation	124
68	68	111	111	*trans*-$Ru(phen)_2(py)_2^{2+}$	AN		Photoisomerization	429
103	103	103		$Ru(TAP)_3^{2+}$	H_2O	< 0.001	Dechelation	398
180	180	180		$Ru(pydipy)_3^{2+}$	AN		Photosolvation	369
285	285			$Ru(dpt)_2^{2+}$	CH_2Cl_2,X^-	0.0040	Photoanation ($X^- = Br^-$, SCN^-)	150

[a] Under 100 atm O_2.

TABLE 3

Ground and excited state redox properties. This Table lists the first oxidation and the first reduction potential in the ground state (E_{ox} and E_{red}) and in the lowest excited state ($^*E_{ox}$ and $^*E_{red}$, calculated according to eqn. (8) and (9)), the reference and the standard electrodes, and the energy of the lowest lying excited state, in cases where the 0–0 excitation energy is known. All potentials are given in mV; the precision should be taken from the original literature

(a) Mononuclear complexes

Ligands			Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE(H_2O)	SCE		−1350			840	–	169
1	1	1	$Ru(bpy)_3^{2+}$	H_2O	SCE	NHE	1260			−840		–	149
1	1	1	$Ru(bpy)_3^{2+}$	DMF	SCE	SCE	1240	−1270				–	270
1	1	1	$Ru(bpy)_3^{2+}$	DMF		Fc+/0		−1760				−54°C, $E_{red}1 = -2540$	63
1	1	1	$Ru(bpy)_3^{2+}$	H_2O	SCE	SCE	1270	−1310		−800	800	–	443
1	1	1	$Ru(bpy)_3^{2+}$	AN and DMF	SCE	SCE	1240	−1270	2030	−790	760	E_{ox} = AN, E_{red} = DMF	444
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1290	−1330				–	243
1	1	1	$Ru(bpy)_3^{2+}$	DMF		Fc+/0		−1760				at −54°C	62
1	1	1	$Ru(bpy)_3^{2+}$	AN	SSCE	SSCE	1270	−1310				–	229
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1260					–	369
1	1	1	$Ru(bpy)_3^{2+}$	DMF	SSCE	SSCE		−1250				–	69
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1290					–	378
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1290	−1400				–	431
1	1	1	$Ru(bpy)_3^{2+}$	SO_2	AgRE	AgRE	1000					Ag_{RE} = ~ 300 mV v SCE	433
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1354	−1332				–	385
1	1	1	$Ru(bpy)_3^{2+}$	AN	AgRE	AgRE	1665	−1060				–	437
1	1	1	$Ru(bpy)_3^{2+}$	acetone	Ag/AgCl	s ref	1490	−1100				E/p f. diff. pulse-p.	451
1	1	1	$Ru(bpy)_3^{2+}$	AN	SSCE	SSCE	1290					Diss. D.J. Salmon, 1977	457
1	1	1	$Ru(bpy)_3^{2+}$	AN	SSCE	SSCE	1290					–	458
1	1	1	$Ru(bpy)_3^{2+}$	AN	$Ag/AgNO_3$	s ref		−1810				–	465
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1290			−830		–	467
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1263	−1338				–	469
1	1	1	$Ru(bpy)_3^{2+}$	DMF		Fc+/0		−1760				–	470
1	1	1	$Ru(bpy)_3^{2+}$	H_2O		NHE	1260	−1280		−840	840	–	12
1	1	1	$Ru(bpy)_3^{2+}$	DMF		Fc+/0		−1760				at −54°C	473
1	1	1	$Ru(bpy)_3^{2+}$	AN	SSCE	SSCE	1234	−1355				–	473

1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1270	−1340			760	–	232
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1270	−1350				–	474
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1268	−1350				–	477
1	1	1	$Ru(bpy)_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1260	−1350				–	131
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1290	−1330		−810	770	–	482
1	1	1	$Ru(bpy)_3^{2+}$	H_2O		NHE	1260	−1260		−840	840	–	482
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1354	−1332				Peak potentials	4
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1290	−1330		−810	770	–	387
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1270	−1340	2100	−830	760	–	487
1	1	1	$Ru(bpy)_3^{2+}$	AN	SSCE	SSCE	1290					–	489
1	1	1	$Ru(bpy)_3^{2+}$	AN	SSCE	SSCE	1240	−1340				–	402
1	1	1	$Ru(bpy)_3^{2+}$	H_2O		NHE	1260	−1280	2120			–	176
1	1	1	$Ru(bpy)_3^{2+}$	AN		Fc+/0	850	−1760				−40 °C, $E_{red} = E/p,c$	235
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1354	−1332				–	397
1	1	1	$Ru(bpy)_3^{2+}$	AN	Ag/AgCl	NHE	1402					–	103
1	1	1	$Ru(bpy)_3^{2+}$	AN	SSCE	SSCE	1220	−1360		−900	760	–	210
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE		−1320				–	380
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1290	−1320				–	354
1	1	1	$Ru(bpy)_3^{2+}$	DMF	SCE	SCE		−1250				–	60
1	1	1	$Ru(bpy)_3^{2+}$	AN	SSCE	SSCE	1290					–	497
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1290	−1230				–	501
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1260	−1350				–	403
1	1	1	$Ru(bpy)_3^{2+}$	0.5 M H_2SO_4	SCE	SCE	1010					–	509
1	1	1	$Ru(bpy)_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1260	−1350	2130	−870	780	–	329
1	1	1	$Ru(bpy)_3^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1260	−1350	2130	−870	780	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	1	$Ru(bpy)_3^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1260	−1345				* $Ru(bpy)_3^{2+}$/ +1260 mV	512
1	1	1	$Ru(bpy)_3^{2+}$	AN	SCE	SCE	1190					–	360
1	1	1	$Ru(bpy)_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1280			−830		–	224
1	1	1	$Ru(bpy)_3^{2+}$	H_2O						−840		–	393
1	1	1	$Ru(bpy)_3^{2+}$	AN			1280	−1320				–	135
1	1	1	$Ru(bpy)_3^{2+}$	AN	Ag/Ag^+	s ref	970	−1650				–	307
1	1	7	$Ru(bpy)_2$ (4-n-bpy)$^{2+}$	AN	$Ag/AgNO_3$	NHE	1365	−560				–	239

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
1	1	7	$Ru(bpy)_2$ $(4\text{-n-bpy})^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1370	−560	1890	−520	1330	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	7	$Ru(bpy)_2$ $(4\text{-n-bpy})^{2+}$	AN			1370	−560	1890	−520	1330	-	344
1	1	11	$Ru(bpy)_2$ $(6\text{-sty-bpy})^{2+}$	acetone	Ag/AgCl	s ref	1530	−1120				-	345
1	1	12	$Ru(bpy)_2$ $(6\text{-tol-bpy})^{2+}$	acetone	Ag/AgCl	s ref	1490	−1110				-	345
1	1	13	$Ru(bpy)_2$ $(3,3'\text{-dm-bpy})^{2+}$	AN	$Ag/AgNO_3$	NHE	1220	−1370	2080	−860	710	-	329
1	1	13	$Ru(bpy)_2$ $(3,3'\text{-dm-bpy})^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1220	−1370	2080	−860	710	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	15	$Ru(bpy)_2$ $(4,4'\text{-dm-bpy})^{2+}$	AN	Ag/Ag^+	s ref	930	−1680				-	307
1	1	16	$Ru(bpy)_2$ $(4,4'\text{-dCl-bpy})^{2+}$	AN	$Ag/AgNO_3$	NHE	1300	−1140				-	239
1	1	16	$Ru(bpy)_2$ $(4,4'\text{-dCl-bpy})^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1300	−1140	2040	−740	900	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	16	$Ru(bpy)_2$ $(4,4'\text{-dCl-bpy})^{2+}$	AN			1300	−1140	2040	−740	900	-	344
1	1	17	$Ru(bpy)_2$ $(4,4'\text{-dBr-bpy})^{2+}$	AN	Ag/Ag^+	s ref	1020					E_{red} = irr.	307
1	1	18	$Ru(bpy)_2$ $(4,4'\text{-dn-bpy})^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1480	−510	1770	−290	1260	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	26	$Ru(bpy)_2$ $(4,4'\text{-dph-bpy})^{2+}$	AN	$Ag/AgNO_3$	NHE	1240			−870		-	224
1	1	26	$Ru(bpy)_2$ $(4,4'\text{-dph-bpy})^{2+}$	DMF		Fc+/0		−1720				at −54° C	473
1	1	26	$Ru(bpy)_2$ $(4,4'\text{-dph-bpy})^{2+}$	AN	SSCE	SSCE	1233	−1308				-	473
1	1	30	$Ru(bpy)_2$ $(4,4'\text{-DTB-bpy})^{2+}$	AN	$Ag/AgNO_3$	NHE	1210	−1365				-	239
1	1	30	$Ru(bpy)_2$ $(4,4'\text{-DTB-bpy})^{2+}$	AN	$Ag/AgNO_3$	NHE	1210	−1370	2100	−890	730	-	329
1	1	30	$Ru(bpy)_2$ $(4,4'\text{-DTB-bpy})^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1210	−1370	2100	−890	730	* $Ru(bpy)_3^{2+}$/ +1260 mV	40

1	1	38		$Ru(bpy)_2$ $(4,4'\text{-DCl-bpy})^{2+}$	CH_2Cl_2	Ag/AgCl	NHE		−550				–	447
1	1	43		$Ru(bpy)_2$ $(4,4'\text{-DHC-bpy})^{2+}$	iBN/AN	SCE	SCE	1350	−990				–	354
1	1	44		$Ru(bpy)_2$ $(4,4'\text{-DCA-bpy})^{2+}$	DMF	SCE	SCE	1380	−930				–	270
1	1	54		$Ru(bpy)_2$ $(6,6'\text{-dm-bpy})^{2+}$	AN	$Ag/AgNO_3$	NHE	1285	−1330				–	514
1	1	56		$Ru(bpy)_2$ $(H4\text{-bpy})^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1238	−1317				* $Ru(bpy)_3^{2+}$/ +1260 mV	511
1	1	57	57	$Ru(bpy)_2$ $(4,4'\text{-bpy})_2^{2+}$	AN	SSCE	SSCE	1320					–	318
1	1	57	57	$Ru(bpy)_2$ $(4,4'\text{-bpy})_2^{2+}$	AN	SSCE	SSCE	1320					–	459
1	1	57	Cl	$Ru(bpy)_2$ $(4,4'\text{-bpy})(Cl)^{+}$	AN	SCE	SCE	790					–	358
1	1	57	Cl	$Ru(bpy)_2$ $(4,4'\text{-bpy})(Cl)^{+}$	AN	SSCE	SSCE	790					–	510
1	1	58	58	$Ru(bpy)_2$ $(m\text{-}4,4'\text{-bpy})_2^{4+}$	AN	SCE	SCE	1340	−760				–	357
1	1	59		$Ru(bpy)_2$ $(bpz)^{2+}$	AN	SSCE	SSCE	1490	−910				–	229
1	1	59		$Ru(bpy)_2$ $(bpz)^{2+}$	DMF		Fc+/0		−1340				at −54 °C	473
1	1	59		$Ru(bpy)_2$ $(bpz)^{2+}$	AN	SSCE	SSCE	1485	−910				–	473
1	1	59		$Ru(bpy)_2$ $(bpz)^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1500	−890	1940	−440	1050	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	60		$Ru(bpy)_2$ $(bpzH)^{3+}$	AN	SCE	SCE	2270	−280		550	1440	*E* values are calculated	387
1	1	61		$Ru(bpy)_2$ $(bpym)^{2+}$	AN	SSCE	SSCE	1400	−1020				–	229
1	1	61		$Ru(bpy)_2$ $(bpym)^{2+}$	AN	SSCE	SSCE	1360	−1010				–	454
1	1	61		$Ru(bpy)_2$ $(bpym)^{2+}$	AN	SCE	SCE	1290					–	360
1	1	61		$Ru(bpy)_2$ $(bpym)^{2+}$	AN	$Ag/AgNO_3$	s ref		−1510				–	465
1	1	61		$Ru(bpy)_2$ $(bpym)^{2+}$	AN	$Ru(bpy)_3^{2+}$	NHE	1370					reference =1260 mV	361
1	1	61		$Ru(bpy)_2$ $(bpym)^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1385	−1025				* $Ru(bpy)_3^{2+}$/ +1260 mV	512

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
1	1	62		$Ru(bpy)_2(4,4'\text{-dm-bpym})^{2+}$	AN	SCE	SCE	1250					–	360
1	1	67		$Ru(bpy)_2(h\text{-phen})^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1240	−1360	2120	−880	760	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	68		$Ru(bpy)_2(phen)^{2+}$	AN	SSCE	SSCE	1290					–	458
1	1	68		$Ru(bpy)_2(phen)^{2+}$	AN	SSCE	SSCE	1230	−1360		−910	780	–	210
1	1	70		$Ru(bpy)_2(2\text{-meo-phen})^{2+}$	acetone	Ag/AgCl	s ref	1440	−1130				E_p f. diff. pulse-p.	451
1	1	71		$Ru(bpy)_2(Pc\text{-phen})^{2+}$	acetone	Ag/AgCl	s ref	1520	−1030				E_p f. diff. pulse-p.	451
1	1	85		$Ru(bpy)_2(2,9\text{-dm-phen})^{2+}$	AN	SCE	SCE	1180					–	360
1	1	88		$Ru(bpy)_2(4,7\text{-Ph2-phen})^{2+}$	AN	$Ag/AgNO_3$	NHE	1245	−1320				–	239
1	1	AN	AN	$Ru(bpy)_2(AN)_2^{2+}$	AN	SSCE	SSCE	1440					–	318
1	1	AN	AN	$Ru(bpy)_2(AN)_2^{2+}$	AN	SCE	SCE	1440					–	369
1	1	AN	AN	*cis*-$Ru(bpy)_2(AN)_2^{2+}$	AN	SSCE	SSCE	1440					E_{ox}-*trans* 1440 mV	450
1	1	AN	AN	$Ru(bpy)_2(AN)_2^{2+}$	AN	SSCE	SSCE	1410					–	455
1	1	AN	AN	$Ru(bpy)_2(AN)_2^{2+}$	AN	SSCE	SSCE	1300					Diss. D.J. Salmon, 1977	462
1	1	AN	AN	$Ru(bpy)_2(AN)_2^{2+}$	AN	SSCE	SSCE	1440					–	476
1	1	AN	AN	$Ru(bpy)_2(AN)_2^{2+}$	AN	SSCE	SSCE	1470					–	489
1	1	AN	Cl	$Ru(bpy)_2(AN)(Cl)^+$	AN	SSCE	SSCE	860					–	318
1	1	AN	Cl	$Ru(bpy)_2(AN)(Cl)^+$	AN	SSCE	SSCE	840					–	385
1	1	AN	N_3	$Ru(bpy)_2(AN)(N_3)^+$	AN	SSCE	SSCE	650					–	476

1	1	AN	NO	$Ru(bpy)_2(AN)(NO)^{3+}$	AN	SSCE	SSCE	560	−350				–	441
1	1	AN	NO	$Ru(bpy)_2(AN)(NO)^{3+}$	AN	SSCE	SSCE	560					–	464
1	1	AN	NO	$Ru(bpy)_2(AN)(NO)^{3+}$	AN	SSCE	SSCE	560	−350				–	488
1	1	AN	H_2O	*cis*-$Ru(bpy)_2(AN)(H_2O)^{2+}$	AN	SSCE	SSCE						E_{ox}-*trans* 1150 mV	450
1	1	AN	NO_2	$Ru(bpy)_2(AN)(NO_2)^{+}$	AN	SSCE	SSCE	1170					$E_{ox} = E/p$,a	464
1	1	AN	NO_3	$Ru(bpy)_2(AN)(NO_3)^{+}$	AN	SSCE	SSCE	1020					–	464
1	1	BA	BA	$Ru(bpy)_2(BA)_2^{2+}$	AN	SSCE	SSCE	1030					–	492
1	1	BA	PRC	$Ru(bpy)_2(BA)(PRC)^{2+}$	AN	SSCE	SSCE	1240					–	492
1	1	Br	Br	$Ru(bpy)_2(Br)_2$	AN	SSCE	SSCE	370					–	489
1	1	Br	SEE	*cis*-$Ru(bpy)_2(Br)(SEE)^{+}$	AN	SSCE	SSCE	920	−1470				–	486
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	DMF	SCE	SCE	730	−1680	2050	−1320	370	–	325
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	AN	SCE	SCE	800	−1633				–	469
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	DMF		Fc+/0	360	−2020				–	470
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	DMF	SCE	SCE	896	−1572				$E = E/p$,a and E/p,c	471
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	AN	SCE	SCE	805	−1605				–	477
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	DMF	SCE	SCE	850	−1540	2150			–	176
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	0.5 M H_2SO_4	SCE	SCE	930					–	509
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	DMF	$Ag/AgNO_3$	*	840	−1560		−1160	440	* $Ru(bpy)_3^{2+}$/ +1260 mV	221
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	DMF	$Ag/AgNO_3$	*	840	−1560	2140	−1300	580	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	AN	$Ag/AgNO_3$	*	810	−1640				* $Ru(bpy)_3^{2+}$/ +1260 mV	221
1	1	CN	CN	$Ru(bpy)_2(CN)_2$	DMF	$Ag/AgNO_3$	*	830	−1590				* $Ru(bpy)_3^{2+}$/ +1260 mV	221

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
1	1	CN	CN *	$Ru(bpy)_2(CN)((CN)Pt(dien))^{2+}$	DMF	SCE	SCE	1030	−1620	2190	−1160	570	CN * is (CN) Pt(dien)	325
1	1	CO	H	*cis*-$Ru(bpy)_2(CO)(H)^+$	AN	SCE	SCE	1140					–	449
1	1	CO	H	$Ru(bpy)_2(CO)(H)^+$	AN	SSCE	SSCE	1140	−1450				$E_{ox} = E/p$,a	483
1	1	CO	AN	$Ru(bpy)_2(CO)(AN)^{2+}$	AN	SCE	SCE	2140	−1150				–	479
1	1	CO	CO	$Ru(bpy)_2(CO)_2^{2+}$	AN	SSCE	SSCE	>1900					–	318
1	1	CO	Cl	$Ru(bpy)_2(CO)(Cl)^+$	AN	SSCE	SSCE	1550					–	318
1	1	CO	Cl	*cis*-$Ru(bpy)_2(CO)(Cl)^+$	AN	SCE	SCE	1500					–	449
1	1	CO	Cl	$Ru(bpy)_2(CO)(Cl)^+$	AN	SSCE	SSCE	1500	−1320				–	483
1	1	CO	Cl	$Ru(bpy)_2(CO)(Cl)^+$	AN	SCE	SCE	1500	−1320				–	479
1	1	CO	Cl	$Ru(bpy)_2(CO)(Cl)^+$	AN	SSCE	SSCE	1460	−1300				–	210
1	1	CO	For	$Ru(bpy)_2(CO)(For)^+$	AN	SSCE	SSCE	1470	−1320				–	483
1	1	Cl	Cl	$Ru(bpy)_2(Cl)_2$	AN	SCE	SCE	320					–	222
1	1	Cl	Cl	$Ru(bpy)_2(Cl)_2$	AN	SCE	SCE	350					–	431
1	1	Cl	Cl	$Ru(bpy)_2(Cl)_2$	AN	SSCE	SSCE	310					–	385
1	1	Cl	Cl	$Ru(bpy)_2(Cl)_2$	AN	SSCE	SSCE	300					Diss. D.J. Salmon, 1977	457
1	1	Cl	Cl	$Ru(bpy)_2(Cl)_2$	AN	SCE	SCE	310			−1700		–	467
1	1	Cl	Cl	$Ru(bpy)_2(Cl)_2$	AN	SCE	SCE	308					–	469
1	1	Cl	Cl	$Ru(bpy)_2(Cl)_2$	DMF		Fc+/0	3	−1950				–	470
1	1	Cl	Cl	$Ru(bpy)_2(Cl)_2$	AN	SCE	SCE	320	−1610				–	479

1	1	Cl	Cl	$Ru(bpy)_2(Cl)_2$	AN	SSCE	SSCE	320	−1670				$E_{red} = E/p,c$	367
1	1	Cl	Cl	$Ru(bpy)_2(Cl)_2$	AN	SSCE	SSCE	310					–	489
1	1	Cl	Cl	$Ru(bpy)_2(Cl)_2$	CH_2Cl_2	Ag/Ag NO_3	s ref	50	−2110				–	505
1	1	Cl	Cl	$Ru(bpy)_2(Cl)_2$	DMF	Ag/Ag NO_3	*	310	−1670	1650	−1340	−20	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	Cl	NO	$Ru(bpy)_2(Cl)(NO)^{2+}$	AN	SSCE	SSCE	190	−600				–	441
1	1	Cl	NO	$Ru(bpy)_2(Cl)(NO)^{2+}$	AN	SSCE	SSCE	190					–	464
1	1	Cl	NO	$Ru(bpy)_2(Cl)(NO)^{2+}$	AN	SSCE	SSCE	200	−600				$E_{red} = E/p,c$	488
1	1	Cl	NO	$Ru(bpy)_2(Cl)(NO)^{2+}$	Acetone	SSCE	SSCE	290					–	488
1	1	Cl	NO	$Ru(bpy)_2(Cl)(NO)^{2+}$	H_2O	SSCE	SSCE	40					–	488
1	1	Cl	NCS	$Ru(bpy)_2(Cl)(NCS)$	AN	SSCE	SSCE	500					–	489
1	1	Cl	NO_2	$Ru(bpy)_2(Cl)(NO_2)$	AN	SSCE	SSCE	570					–	464
1	1	Cl	NO_3	$Ru(bpy)_2(Cl)(NO_3)$	AN	SSCE	SSCE	450					–	464
1	1	N_3	N_3	$Ru(bpy)_2(N_3)_2$	AN	SSCE	SSCE	170					–	476
1	1	N_3	N_3	$Ru(bpy)_2(N_3)_2$	AN	Ag/Ag NO_3 *	NHE	190	−1590				* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	N_3	NO	$Ru(bpy)_2(N_3)(NO)^{2+}$	AN	SSCE	SSCE	170	−630				–	441
1	1	N_3	NO	$Ru(bpy)_2(N_3)(NO)^{2+}$	AN	SSCE	SSCE	180	−630				$E_{red} = E/p,c$	488
1	1	SF	SF	$Ru(bpy)_2(SF)_2$	AN	SSCE	SSCE	120					–	486
1	1	SP	SP	$Ru(bpy)_2(SP)_2$	AN	SSCE	SSCE	−280					–	486
1	1	TN		$Ru(bpy)_2(TN)^{2+}$	AN	SSCE	SSCE	−980					–	495
1	1	en		$Ru(bpy)_2(en)^{2+}$	AN	SCE	SCE	950			−970		–	467
1	1	en		$Ru(bpy)_2(en)^{2+}$	AN	SCE	SCE	933	−1485				–	469

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
1	1	en		$Ru(bpy)_2(en)^{2+}$	DMF		Fc+/0	450	−1910				$E_{ox} = E/p,a$	470
1	1	en		$Ru(bpy)_2(en)^{2+}$	AN	SCE	SCE	980	−1498				–	477
1	1	en		$Ru(bpy)_2(en)^{2+}$	AN	SSCE	SSCE	960					–	495
1	1	en		$Ru(bpy)_2(en)^{2+}$	H_2O	Ag/Ag^+	s ref	620					–	317
1	1	ox		$Ru(bpy)_2(ox)$	AN	SCE	SCE	450	−1598				–	469
1	1	ox		$Ru(bpy)_2(ox)$	DMF		Fc+/0	20	−1980				–	470
1	1	108		$Ru(bpy)_2(DIAFO)^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1360	−670	2160	−800	1490	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	109		$Ru(bpy)_2(taphen)^{2+}$	AN	$Ag/AgNO_3$	NHE	1370	−720				–	238
1	1	109		$Ru(bpy)_2(taphen)^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1370	−720	1870	−500	1150	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	110		$Ru(bpy)_2(phen\text{-}dione)^{2+}$	AN	SSCE	SSCE	1350	−65				–	480
1	1	111	AN	$Ru(bpy)_2(py)(AN)^{2+}$	AN	SSCE	SSCE	1280					–	364
1	1	111	AN	$Ru(bpy)_2(py)(AN)^{2+}$	AN	SSCE	SSCE	1360					–	455
1	1	111	AN	$Ru(bpy)_2(py)(AN)^{2+}$	AN	SSCE	SSCE	1360					–	476
1	1	111	AN	$Ru(bpy)_2(py)(AN)^{2+}$	AN	SSCE	SSCE	1350					–	489
1	1	111	CN	$Ru(bpy)_2(py)(CN)^+$	AN	SSCE	SSCE	1040					–	364
1	1	111	CN	$Ru(bpy)_2(py)(CN)^+$	AN	SCE	SCE	1040	−1480				–	479
1	1	111	Cl	$Ru(bpy)_2(py)(Cl)^+$	AN	SSCE	SSCE	800					–	364
1	1	111	Cl	$Ru(bpy)_2(py)(Cl)^+$	AN	SSCE	SSCE	790					–	318

1	1	111	Cl	$Ru(bpy)_2(py)(Cl)^+$	AN	SSCE	SSCE	777			466
1	1	111	Cl	$Ru(bpy)_2(py)(Cl)^+$	AN	SCE	SCE	790	−1510	-	479
1	1	111	Cl	$Ru(bpy)_2(py)(Cl)^+$	AN	SSCE	SSCE	770	−1500	-	367
1	1	111	Cl	$Ru(bpy)_2(py)(Cl)^+$	AN	SSCE	SSCE	760		-	489
1	1	111	Cl	$Ru(bpy)_2(py)(Cl)^+$	AN	SSCE	SSCE	790		-	510
1	1	111	N_3	$Ru(bpy)_2(py)(N_3)^+$	AN	SSCE	SSCE	580		-	364
1	1	111	N_3	$Ru(bpy)_2(py)(N_3)^+$	AN	SSCE	SSCE	580		-	476
1	1	111	NO	$Ru(bpy)_2(py)(NO)^{3+}$	AN	SSCE	SSCE	530		-	364
1	1	111	NO	$Ru(bpy)_2(py)(NO)^{3+}$	AN	SSCE	SSCE	530	−370	-	441
1	1	111	NO	$Ru(bpy)_2(py)(NO)^{3+}$	AN	SSCE	SSCE	530		-	455
1	1	111	NO	$Ru(bpy)_2(py)(NO)^{3+}$	AN	SSCE	SSCE	530		-	464
1	1	111	NO	$Ru(bpy)_2(py)(NO)^{3+}$	AN	SSCE	SSCE	530	−370	$E_{red} = E/p,c$	488
1	1	111	OH	$Ru(bpy)_2(py)(OH)^+$	H_2O	SSCE	SSCE	230		-	364
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	AN	SSCE	SSCE	1240		-	364
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	AN	SSCE	SSCE	1300		-	318
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	AN	SCE	SCE	1300	−1320	-	222
1	1	111	111	*cis*-$Ru(bpy)_2(py)_2^{2+}$	AN	SSCE	SSCE	1300		E_{ox}-*trans* 1280 mV	450
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	AN	SSCE	SSCE	1280		Diss. D.J. Salmon, 1977	462
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	AN	SCE	SCE	1270	−1383	-	469
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	DMF		Fc+/0	760	−1790	-	470
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	AN	SCE	SCE	1265	−1365	-	477

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	AN	SSCE	SSCE	1300	−1320				–	367
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	AN	SSCE	SSCE	1290					–	489
1	1	111	111	$Ru(bpy)_2(py)_2^{2+}$	AN	SSCE	SSCE	1250	−1350		−860	760	–	210
1	1	111	ClO	$Ru(bpy)_2(py)(ClO_4)^+$	AN	SSCE	SSCE	1090					–	489
1	1	111	H_2O	$Ru(bpy)_2(py)(H_2O)^{2+}$	AN	SSCE	SSCE	710					–	364
1	1	111	H_2O	$Ru(bpy)_2(py)(H_2O)^{2+}$	1 M H_2SO_4	SCE	SCE	780					–	463
1	1	111	H_2O	$Ru(bpy)_2(py)(H_2O)^{2+}$	1 M $HClO_4$	SCE	SCE	790					–	463
1	1	111	NCS	$Ru(bpy)_2(py)(NCS)^+$	AN	SSCE	SSCE	850					–	489
1	1	111	NO_2	$Ru(bpy)_2(py)(NO_2)^+$	AN	SSCE	SSCE	1060					–	364
1	1	111	NO_2	$Ru(bpy)_2(py)(NO_2)^+$	AN	SSCE	SSCE	1060					$E_{ox} = E/p$,a	464
1	1	111	NO_2	$Ru(bpy)_2(py)(NO_2)^+$	AN	SCE	SCE	1060	−1460				–	479
1	1	111	NO_2	$Ru(bpy)_2(py)(NO_2)^+$	AN	SSCE	SSCE	1060					$E_{ox} = E/p$,a	489
1	1	111	NO_3	$Ru(bpy)_2(py)(NO_3)^+$	AN	SSCE	SSCE	910					–	364
1	1	111	NO_3	$Ru(bpy)_2(py)(NO_3)^+$	AN	SSCE	SSCE	960					–	455
1	1	111	NO_3	$Ru(bpy)_2(py)(NO_3)^+$	AN	SSCE	SSCE	910					–	464
1	1	111	NO_3	$Ru(bpy)_2(py)(NO_3)^+$	AN	SSCE	SSCE	910					–	489
1	1	111	ON1	$Ru(bpy)_2(py)(ON1)^{2+}$	AN	SSCE	SSCE	1760					$E_{ox} = E/p$,a	461
1	1	111	ON2	$Ru(bpy)_2(py)(ON2)^{2+}$	AN	SSCE	SSCE	1750					$E_{ox} = E/p$,a	461
1	1	111	ON3	$Ru(bpy)_2(py)(ON3)^{2+}$	AN	SSCE	SSCE	1730					–	461

1	1	111	ON4	$Ru(bpy)_2(py)(ON4)^{2+}$	AN	SSCE	SSCE	1770				$E_{ox} = E/p$,a	461
1	1	111	PTS	$Ru(bpy)_2(py)(PTS)^{+}$	AN	SSCE	SSCE	900				-	489
1	1	111	TFA	$Ru(bpy)_2(py)(TFA)^{+}$	AN	SSCE	SSCE	890				-	489
1	1	112		$Ru(bpy)_2(PMA)^{2+}$	PC	SSCE	SSCE	1330				-	494
1	1	112		$Ru(bpy)_2(PMA)^{2+}$	1 M H_2SO_4	SSCE	SSCE	970				-	494
1	1	112		$Ru(bpy)_2(PMA)^{2+}$	AN	SSCE	SSCE	1120				-	495
1	1	113		$Ru(bpy)_2(2\text{-}AEP)^{2+}$	AN	SSCE	SSCE	1120				-	495
1	1	115	115	$Ru(bpy)_2(3\text{-}I\text{-}py)_2^{2+}$	AN	SSCE	SSCE	1360				-	318
1	1	116		$Ru(bpy)_2(3\text{-}AEP)^{2+}$	AN	SSCE	SSCE	1020	−1440	−930	510	-	210
1	1	117	117	$Ru(bpy)_2(3pyr\text{-}py)_2^{2+}$	AN		?	990				ref + stand not ind.	446
1	1	119	Cl	$Ru(bpy)_2(4\text{-}acetyl\text{-}py)(Cl)^{+}$	AN	SSCE	SSCE	820				-	318
1	1	119	119	$Ru(bpy)_2(4\text{-}acetyl\text{-}py)_2^{2+}$	AN	SSCE	SSCE	1450				-	318
1	1	122	122	$Ru(bpy)_2(t\text{-}bupy)_2^{2+}$	AN	SSCE	SSCE	1230				-	489
1	1	122	H_2O	$Ru(bpy)_2(t\text{-}bupy)(H_2O)^{2+}$	CH_2Cl_2	SSCE	SSCE	1180				-	489
1	1	122	NO_3	$Ru(bpy)_2(t\text{-}bupy)(NO_3)^{+}$	AN	SSCE	SSCE	880				-	489
1	1	123	AN	$Ru(bpy)_2(4\text{-}vpy)(AN)^{2+}$	AN	SSCE	SSCE	1290				polymer film	455
1	1	123	Cl	$Ru(bpy)_2(4\text{-}vpy)(Cl)^{+}$	AN	SSCE	SSCE	760	−1500			-	448
1	1	123	Cl	$Ru(bpy)_2(4\text{-}vpy)(Cl)^{+}$	AN	SSCE	SSCE	760	−1490			-	455
1	1	123	NO	$Ru(bpy)_2(4\text{-}vpy)(NO)^{3+}$	AN	SSCE	SSCE	470				polymer film	455
1	1	123	123	$Ru(bpy)_2(4\text{-}vpy)_2^{2+}$	AN	SSCE	SSCE	1250	−1360			-	448

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
1	1	123	123	$Ru(bpy)_2(4\text{-vpy})_2^{2+}$	AN	SSCE	SSCE	1240	−1355				–	455
1	1	123	123	$Ru(bpy)_2(4\text{-vpy})_2^{2+}$	1 M $HClO_4$	SSCE	SSCE	1045					polymer film	455
1	1	123	123	$Ru(bpy)_2(4\text{-vpy})_2^{2+}$	AN	SSCE	SSCE	1250	−1360				–	478
1	1	123	123	$Ru(bpy)_2(4\text{-vpy})_2^{2+}$	AN	SSCE	SSCE	1220					E_{ox} surf.	478
1	1	123	123	$Ru(bpy)_2(4\text{-vpy})_2^{2+}$	AN	SSCE	SSCE	1225	−1360				polymer film	455
1	1	123	NO_2	$Ru(bpy)_2(4\text{-vpy})(NO_2)^+$	AN	SSCE	SSCE	1035	−1455				$E_{ox} = E/p$,a	455
1	1	123	NO_2	$Ru(bpy)_2(4\text{-vpy})(NO_2)^+$	AN	SSCE	SSCE	1030					polymer film, $E_{ox} = E/p$,a	455
1	1	123	NO_3	$Ru(bpy)_2(4\text{-vpy})(NO_3)^+$	AN	SSCE	SSCE	910					polymer film	455
1	1	123	Cl	$Ru(bpy)_2(PVP)(Cl)^+$	AN	SSCE	SSCE	760	−1480				polymer film	455
1	1	124	124	$Ru(bpy)_2(PVP)_2^{2+}$	AN	SCE	SCE	1240	−1390	2030	−790	640	–	126
1	1	124	AN	$Ru(bpy)_2(PVP)(AN)^{2+}$	H_2O	SSCE	SSCE	1240					–	364
1	1	124	AN	$Ru(bpy)_2(PVP)(AN)^{2+}$	AN	SCE	SCE	1135					–	453
1	1	124	CN	$Ru(bpy)_2(PVP)(CN)^+$	CH_2Cl_2	SSCE	SSCE	990					–	364
1	1	124	Cl	$Ru(bpy)_2(PVP)(Cl)^+$	AN	SSCE	SSCE	760					–	364
1	1	124	Cl	$Ru(bpy)_2(PVP)(Cl)^+$	AN	SCE	SCE	640					–	453
1	1	124	Cl	$Ru(bpy)_2(PVP)(Cl)^+$	1M H_2SO_4	SCE	SCE	700						475
1	1	124	N_3	$Ru(bpy)_2(PVP)(N_3)^+$	AN	SSCE	SSCE	570					–	364
1	1	124	OH	$Ru(bpy)_2(PVP)(OH)^+$	H_2O	SSCE	SSCE	240					–	364
1	1	124	124	$Ru(bpy)_2(PVP)_2^{2+}$	AN	SSCE	SSCE	1240					–	364
1	1	124	ClO	$Ru(bpy)_2(PVP)(ClO_4)^+$	AN	SCE	SCE	945					–	453

1	1	124	H_2O	$Ru(bpy)_2(PVP)(H_2O)^{2+}$	AN	SSCE	SSCE	730				–	364
1	1	124	NO_2	$Ru(bpy)_2(PVP)(NO_2)^{+}$	AN	SSCE	SSCE	1050				–	364
1	1	124	NO_3	$Ru(bpy)_2(PVP)(NO_3)^{+}$	AN	SSCE	SSCE	900				–	364
1	1	125	125	$Ru(bpy)_2(t\text{-stylb})_2^{2+}$	AN	SSCE	SSCE	1230	−1360			–	448
1	1	127	127	$Ru(bpy)_2(4'\text{-Cl-stylb})_2^{2+}$	AN	SSCE	SSCE	1220	−1380			–	448
1	1	128	128	$Ru(bpy)_2(4'\text{-OMe-stylb})_2^{2+}$	AN	SSCE	SSCE	1190	−1390			–	448
1	1	129	129	$Ru(bpy)_2(4'\text{-CN-stylb})_2^{2+}$	AN	SSCE	SSCE	1250	−1400			Pot. py-bound isomer	448
1	1	130	130	$Ru(bpy)_2(p\text{-cinn})_2^{2+}$	AN	SSCE	SSCE	1190	−1390				448
1	1	131	131	$Ru(bpy)_2(m\text{-cinn})_2^{2+}$	AN	SSCE	SSCE	1280	−1380			–	448
1	1	132	Cl	$Ru(bpy)_2(4\text{-vpy})(Cl)^{+}$	AN	SSCE	SSCE	760	−1480			polymer film	455
1	1	132	132	$Ru(bpy)_2(p\text{-CH2-cinn})_2^{2+}$	AN	SSCE	SSCE	1260	−1390			–	448
1	1	133	133	$Ru(bpy)_2(p\text{-fum})_2^{2+}$	AN	SSCE	SSCE	1220	−1400			–	448
1	1	134	134	$Ru(bpy)_2(N\text{-Me-py})_2^{4+}$	AN	SSCE	SSCE	1220	−1390			–	448
1	1	135	Cl	$Ru(bpy)_2(pym)(Cl)^{+}$	AN	SSCE	SSCE	840				–	490
1	1	136	Cl	$Ru(bpy)_2(pymH)(Cl)^{2+}$	AN	SSCE	SSCE	970				–	490
1	1	137	137	$Ru(bpy)_2(pyd)_2^{2+}$	AN	SSCE	SSCE	1420				–	318
1	1	137	137	$Ru(bpy)_2(pyd)_2^{2+}$	AN	SSCE	SSCE	1240	−1380	−920	780	–	210
1	1	138	Cl	$Ru(bpy)_2(pyr)(Cl)^{+}$	AN	SSCE	SSCE	880				–	510
1	1	138	NO	$Ru(bpy)_2(pyr)(NO)^{3+}$	AN	SSCE	SSCE	570				–	464
1	1	138	138	$Ru(bpy)_2(pyr)_2^{2+}$	AN	SSCE	SSCE	1510				–	459
1	1	138	NO_2	$Ru(bpy)_2(pyr)(NO_2)^{+}$	AN	SSCE	SSCE	1140				$E_{ox} = E/p$,a	464
1	1	138	NO_3	$Ru(bpy)_2(pyr)(NO_3)^{+}$	AN	SSCE	SSCE	1000				–	464

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
1	1	140		$Ru(bpy)_2(napy)^{2+}$	AN	SSCE	SSCE	1260					–	458
1	1	141		$Ru(bpy)_2(ppyz)^{2+}$	AN	SSCE	SSCE	1320					–	458
1	1	142		$Ru(bpy)_2(2\text{-m-napy})^{2+}$	AN	SSCE	SSCE	1250					–	458
1	1	143		$Ru(bpy)_2(2,7\text{-dmnapy})^{2+}$	AN	SSCE	SSCE	1320					–	458
1	1	144	144	$Ru(bpy)_2(pz)_2$	AN	SCE	SCE	300					–	222
1	1	144	144	$Ru(bpy)_2(pz)_2$	AN	SSCE	SSCE	300					–	367
1	1	144	145	$Ru(bpy)_2(pz)(pzH)^+$	AN	SSCE	SSCE	690	−1500				–	367
1	1	145	145	$Ru(bpy)_2(pzH)_2^{2+}$	AN	SCE	SCE	1180	−1520				–	222
1	1	145	145	*cis*-$Ru(bpy)_2(pzH)_2^{2+}$	AN	SSCE	SSCE	1180					E_{ox}-*trans* 1110 mV	450
1	1	145	145	$Ru(bpy)_2(pzH)_2^{2+}$	AN	SSCE	SSCE	1180	−1520				–	367
1	1	146	146	$Ru(bpy)_2(imid)_2^{2+}$	AN	SSCE	SSCE	1020					–	318
1	1	147	147	$Ru(bpy)_2(NMI)_2^{2+}$	AN	SSCE	SSCE	940	−1480		−1020	480	–	210
1	1	147	147	$Ru(bpy)_2(NMI)_2^{2+}$	AN	SSCE	SSCE	940					–	318
1	1	148	Cl	$Ru(bpy)_2(viz)(Cl)^+$	AN	SCE	SCE	680					–	472
1	1	148	148	$Ru(bpy)_2(viz)_2^{2+}$	AN	SCE	SCE	1050					–	472
1	1	149	Cl	$Ru(bpy)_2(PVI)(Cl)^+$	AN	SCE	SCE	670					–	472
1	1	149	149	$Ru(bpy)_2(PVI)_2^{2+}$	AN	SCE	SCE	1000					–	472
1	1	150	150	$Ru(bpy)_2(trza)_2$	AN	SCE	SCE	450	−1650				E_{red} in DMSO	222
1	1	151	151	$Ru(bpy)_2(trz)_2^{2+}$	AN	SCE	SCE	1130	−1490				E_{red} in DMSO	222

1	1	152	152	$Ru(bpy)_2(m\text{-}trz)_2^{2+}$	AN	SCE	SCE	1000	−1460	-	222
1	1	153	153	$Ru(bpy)_2(Ph\text{-}trz)_2^{2+}$	AN	SCE	SCE	1050	−1480	-	222
1	1	154	154	$Ru(bpy)_2(All\text{-}trz)_2^{2+}$	AN	SCE	SCE	1010	−1470	-	222
1	1	159	Cl	$Ru(bpy)_2(BPA)(Cl)^{+}$	AN	SCE	SCE	770		-	358
1	1	159	Cl	$Ru(bpy)_2(BPA)(Cl)^{+}$	AN	SSCE	SSCE	770		-	510
1	1	159	159	$Ru(bpy)_2(BPA)_2^{2+}$	AN	SSCE	SSCE	1290		-	459
1	1	160	Cl	$Ru(bpy)_2(BPE)(Cl)^{+}$	AN	SCE	SCE	780		-	358
1	1	160	Cl	$Ru(bpy)_2(BPE)(Cl)^{+}$	AN	SSCE	SSCE	780		-	510
1	1	160	160	$Ru(bpy)_2(BPE)_2^{2+}$	AN	SSCE	SSCE	1300	−1350	-	448
1	1	160	160	$Ru(bpy)_2(BPE)_2^{2+}$	AN	SSCE	SSCE	1310		-	459
1	1	160	160	$Ru(bpy)_2(BPE)_2^{2+}$	AN	SSCE	SSCE	1290	−1360	-	478
1	1	160	160	$Ru(bpy)_2(BPE)_2^{2+}$	AN	SSCE	SSCE	1240		E_{ox} surf.	478
1	1	161	161	$Ru(bpy)_2(PC2)_2^{2+}$	AN	SSCE	SSCE	1330	−1300	-	478
1	1	161	161	$Ru(bpy)_2(PC2)_2^{2+}$	AN	SSCE	SSCE	1320		E_{ox} surf.	478
1	1	162		$Ru(bpy)_2(DPA)^{+}$	AN		Fc+/0	30	−1890	−40 °C, $E_{red} = E/p,c$	235
1	1	163		$Ru(bpy)_2(DPAH)^{2+}$	AN		Fc+/0	720	−1780	−40 °C, $E_{red} = E/p,c$	235
1	1	165		$Ru(bpy)_2(opdi)^{2+}$	AN	Ag/Ag NO_3 *	NHE	irr.	−500	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	166		$Ru(bpy)_2(phedi)^{2+}$	AN	Ag/Ag NO_3 *	NHE	1250	−680	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	169		$Ru(bpy)_2(pymi)^{2+}$	AN	Ag/Ag NO_3 *	NHE	1280	−1250	-	239
1	1	171		$Ru(bpy)_2(PimH)^{2+}$	AN	SCE	SCE	1140	−1520	-	368
1	1	173		$Ru(bpy)_2(PBzimH)^{2+}$	AN	SCE	SCE	1170	−1490	-	368

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
1	1	176	$Ru(bpy)_2(biimH2)^{2+}$	AN/ $HClO_4$	SCE	SCE	930					-	360
1	1	176	$Ru(bpy)_2(biimH2)^{2+}$	AN	SCE	SCE	1040	−1660				-	368
1	1	179	$Ru(bpy)_2(BiBzimH2)^{2+}$	AN	SCE	SCE	1110					-	485
1	1	179	$Ru(bpy)_2(BiBzimH2)^{2+}$	AN	SCE	SCE	1120	−1600				-	368
1	1	180	$Ru(bpy)_2(pydipy)^{2+}$	AN	SCE	SCE	1220					-	369
1	1	181	$Ru(bpy)_2(Azpy)^{2+}$	AN	SCE(H_2O)	SCE	1600	−520				-	432
1	1	181	$Ru(bpy)_2(Azpy)^{2+}$	AN	SCE	SCE	1603	−520				-	452
1	1	182	$Ru(bpy)_2(MeAzpy)^{2+}$	AN	SCE(H_2O)	SCE	1600	−520				-	432
1	1	182	$Ru(bpy)_2(MeAzpy)^{2+}$	AN	SCE	SCE	1600	−525				-	452
1	1	184	$Ru(bpy)_2(thpy)^{2+}$	1 M HNO_3	SCE	NHE	1260		2010	−750		-	370
1	1	185	$Ru(bpy)_2(pmth)^{2+}$	AN	$Ag/AgNO_3$	NHE	1282	−1266				-	514
1	1	203	$Ru(bpy)_2(NPP)^+$	CH_2Cl_2	SCE	SCE	766					-	371
1	1	205	$Ru(bpy)_2(OBzimH)^+$	AN	SCE	SCE	390	−1670				-	368
1	1	206	$Ru(bpy)_2(EtTROMe)^+$	AN	SCE	SCE	160					-	439
1	1	207	$Ru(bpy)_2(EtTROH)^+$	AN	SCE	SCE	220					-	439
1	1	208	$Ru(bpy)_2(EtTROCl)^+$	AN	SCE	SCE	250					-	439
1	1	209	$Ru(bpy)_2(EtTROCO2Et)^+$	AN	SCE	SCE	280					-	439
1	1	210	$Ru(bpy)_2(EtTRONO2)^+$	AN	SCE	SCE	360					-	439

1	1	211	$Ru(bpy)_2$ $(PhenTROMe)^+$	AN	SCE	SCE	250		–	439
1	1	212	$Ru(bpy)_2$ $(PhenTROH)^+$	AN	SCE	SCE	290		–	439
1	1	213	$Ru(bpy)_2$ $(PhenTROCl)^+$	AN	SCE	SCE	320		–	439
1	1	214	$Ru(bpy)_2$ $(PhenTROCO2Et)^+$	AN	SCE	SCE	410		–	439
1	1	215	$Ru(bpy)_2$ $(PhenTRONO2)^+$	AN	SCE	SCE	440		–	439
1	1	216	$Ru(bpy)_2$ $(HHyamOMe)^+$	AN	SCE	SCE	350	−1630	–	442
1	1	217	$Ru(bpy)_2$ $(HHyamMe)^+$	AN	SCE	SCE	350	−1610	–	442
1	1	218	$Ru(bpy)_2$ $(HHyamH)^+$	AN	SCE	SCE	370	−1620	–	442
1	1	219	$Ru(bpy)_2$ $(HHyamCl)^+$	AN	SCE	SCE	390	−1620	–	442
1	1	220	$Ru(bpy)_2$ $(HHyamNO2)^+$	AN	SCE	SCE	450	−1630	–	442
1	1	221	$Ru(bpy)_2$ $(MeHyamOMe)^+$	AN	SCE	SCE	330	−1590	–	442
1	1	222	$Ru(bpy)_2$ $(MeHyamMe)^+$	AN	SCE	SCE	340	−1590	–	442
1	1	223	$Ru(bpy)_2$ $(MeHyamH)^+$	AN	SCE	SCE	350	−1500	–	442
1	1	224	$Ru(bpy)_2$ $(MeHyamCl)^+$	AN	SCE	SCE	370	−1590	–	442
1	1	225	$Ru(bpy)_2$ $(MeHyamNO2)^+$	AN	SCE	SCE	420	−1590	–	442
1	1	226	$Ru(bpy)_2$ $(HyamOMe)^{2+}$	AN	SCE	SCE	−300	−1650	–	442
1	1	227	$Ru(bpy)_2$ $(HyamH)^{2+}$	AN	SCE	SCE	−270	−1650	–	442
1	1	228	$Ru(bpy)_2$ $(HyamNO2)^{2+}$	AN	SCE	SCE	−210	−1640	–	442
1	1	229	$Ru(bpy)_2$ $(el)^+$	AN	SCE	SCE	900	−1400	–	434
1	1	230	$Ru(bpy)_2$ $(Hel)^{2+}$	AN	SCE	SCE	990		–	434
1	1	231	$Ru(bpy)_2$ $(e2)^+$	AN	SCE	SCE	830	−1440	$E_{red} = E/p,c$	434

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
1	1	232	$Ru(bpy)_2(He2)^{2+}$	AN	SCE	SCE	960					-	434
1	1	233	$Ru(bpy)_2(e3)^{+}$	AN	SCE	SCE	930	−1640				$E_{red} = E/p$,c	434
1	1	234	$Ru(bpy)_2(He3)^{2+}$	AN	SCE	SCE	980					-	434
1	1	235	$Ru(bpy)_2(e4)^{+}$	AN	SCE	SCE	820	−1540				-	434
1	1	236	$Ru(bpy)_2(He4)^{2+}$	AN	SCE	SCE	1030					-	434
1	1	237	$Ru(bpy)_2(e5)^{+}$	AN	SCE	SCE	850	−1570				$E_{red} = E/p$,c	434
1	1	238	$Ru(bpy)_2(He5)^{2+}$	AN	SCE	SCE	1010					-	434
1	1	239	$Ru(bpy)_2(e6)^{+}$	AN	SCE	SCE	840	−1600				$E_{red} = E/p$,c	434
1	1	240	$Ru(bpy)_2(He6)^{2+}$	AN	SCE	SCE	960					-	434
1	1	241	$Ru(bpy)_2(e7)^{+}$	AN	SCE	SCE	830	−1580				$E_{red} = E/p$,c	434
1	1	242	$Ru(bpy)_2(e8)^{+}$	AN	SCE	SCE	1050					-	434
1	1	244	$Ru(bpy)_2(piq)^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1270	Irr.	1870	−600		* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	245	$Ru(bpy)_2(hpiq)^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1250	−1170	1880	−630	710	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	246	$Ru(bpy)_2(pq)^{2+}$	DMF		Fc+/0		−1530				at −54°C	473
1	1	246	$Ru(bpy)_2(pq)^{2+}$	AN	SSCE	SSCE	1270	−1135				-	473
1	1	246	$Ru(bpy)_2(pq)^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1300	−1110	1900	−600	790	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	248	$Ru(bpy)_2(MMCH)^{2+}$	AN	$Ag/AgNO_3$	NHE	1260	−1030				-	239
1	1	249	$Ru(bpy)_2(MPCH)^{2+}$	AN	$Ag/AgNO_3$	NHE	1295	−895				-	239
1	1	250	$Ru(bpy)_2(DHCH)^{2+}$	AN	$Ag/AgNO_3$	NHE	1310	−910				-	239
1	1	251	$Ru(bpy)_2(DMCH)^{2+}$	AN	$Ag/AgNO_3$	HNE	1255	−1000				-	239

1	1	251	$Ru(bpy)_2(DMCH)^{2+}$	AN	$Ag/AgNO_3$	NHE	1250	−1000	1720	−470	720		329
1	1	251	$Ru(bpy)_2(DMCH)^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1250	−1000	1720	−470	720	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	252	$Ru(bpy)_2(DPCH)^{2+}$	AN	$Ag/AgNO_3$	NHE	1300	−905				–	239
1	1	253	$Ru(bpy)_2(TMCH)^{2+}$	AN	$Ag/AgNO_3$	NHE	1240	−1080				–	239
1	1	254	$Ru(bpy)_2(TPCH)^{2+}$	AN	$Ag/AgNO_3$	NHE	1290	−990				–	239
1	1	255	$Ru(bpy)_2(OMCH)^{2+}$	AN	$Ag/AgNO_3$	NHE	1275	−1645				–	239
1	1	255	$Ru(bpy)_2(OMCH)^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1270	−1650	1670	−400	20	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	256	$Ru(bpy)_2(dinapy)^{2+}$	AN	$Ag/AgNO_3$	NHE	1220	−710				–	514
1	1	257	$Ru(bpy)_2(biq)^{2+}$	AN	$Ag/AgNO_3$	NHE	1330	−905				–	239
1	1	257	$Ru(bpy)_2(biq)^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1330	−910	1700	−370	790	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	257	$Ru(bpy)_2(biq)^{2+}$	AN			1330	−910	1700	−370	790	–	344
1	1	259	$Ru(bpy)_2(i\text{-}biq)^{2+}$	AN	$Ag/AgNO_3$	NHE	1220	−1380				–	131
1	1	259	$Ru(bpy)_2(i\text{-}biq)^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1220	−1380	2120	−900	740	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	1	260	$Ru(bpy)_2(H2por)^{2+}$	DMF	SCE	SCE	1160	−1510				–	491
1	1	261	$Ru(bpy)_2(DP)^{2+}$	AN	SCE	SCE	1240	−1020				–	243
1	1	265	$Ru(bpy)_2$(Mebpy-2DQ +2)$^{4+}$	AN and DMF	SCE	SCE	1240	−1290				E_{ox} = AN, E_{red} = DMF	444
1	1	266	$Ru(bpy)_2$(Mebpy-3DQ+2)$^{4+}$	AN and DMF	SCE	SCE	1240	−1290				E_{ox} = AN, E_{red} = DMF	444
1	1	266	$Ru(bpy)_2$(Me-bpy-3DQ +2)$^{4+}$	DMF	SCE	SCE	1240	−1290				–	506
1	1	267	$Ru(bpy)_2(dpp)^{2+}$	AN	Ag/AgCl	NHE	1580					–	103
1	1	267	$Ru(bpy)_2(dpp)^{2+}$	AN	SCE	SCE	1310	−1060				–	403

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
1	1	268		$Ru(bpy)_2(BL1)^{2+}$	AN	SSCE	SSCE	1410	−780				–	454
1	1	269		$Ru(bpy)_2(BL2)^{2+}$	AN	SSCE	SSCE	1420	−420				–	454
1	1	270		$Ru(bpy)_2(BL3)^{2+}$	AN	SSCE	SSCE	1410	−720				–	372
1	1	275		$Ru(bpy)_2(diffn)^{2+}$	AN	$Ag/AgNO_3$	NHE	1430	−595				–	514
1	1	2SA		$Ru(bpy)_2(2SA)^{2+}$	AN	SSCE	SSCE	1430	−1280				–	486
1	1	2SB		$Ru(bpy)_2(2SB)^{2+}$	AN	SSCE	SSCE	1410	−1280				–	486
1	1	2SC		$Ru(bpy)_2(2SC)^{2+}$	AN	SSCE	SSCE	1500	−1280				–	486
1	1	2SD		$Ru(bpy)_2(2SD)^{2+}$	AN	SSCE	SSCE	1540	−1250				–	486
1	1	ADP	Cl	$Ru(bpy)_2(ADP)(Cl)^+$	AN	SSCE	SSCE	1010	−1330				E_{red} = irr.	456
1	1	BBB	Cl	$Ru(bpy)_2(BBB)(Cl)^+$	AN	SSCE	SSCE	810	−1320				E_{red} = irr.	456
1	1	Bic		$Ru(bpy)_2(Bic)^{2+}$	AN	SSCE	SSCE	1900					–	462
1	1	CN *	CN *	$Ru(bpy)_2((CN)Pt(dien))_2^{2+}$	DMF	SCE	SCE	860	−1500	2310	−1450	810	CN * is(CN) Pt(dien)	325
1	1	DAC		$Ru(bpy)_2(DAC)^{2+}$	AN	SSCE	SSCE	960					–	495
1	1	DAM		$Ru(bpy)_2(DAM)^{2+}$	AN	SSCE	SSCE	990					–	495
1	1	ECN	ECN	$Ru(bpy)_2(ECN)_2^{2+}$	AN	SSCE	SSCE	1530					–	492
1	1	EDP		$Ru(bpy)_2(EDP)^{2+}$	AN	SSCE	SSCE	1750	−1280				–	456
1	1	EDP		$Ru(bpy)_2(EDP)^{2+}$	AN	SSCE	SSCE	1750					–	457
1	1	EDP		$Ru(bpy)_2(EDP)^{2+}$	AN	SSCE	SSCE	1740					–	462

1	1	EDP		$Ru(bpy)_2(EDP)^{2+}$	AN	SSCE	SSCE	1750	−1280	−640	1110	–	210
1	1	For	CO	$Ru(bpy)_2(For)(CO)^{+}$	AN	SCE	SCE	1440	−1320			–	479
1	1	H_2O	H_2O	*cis*-$Ru(bpy)_2(H_2O)_2^{2+}$	H_2O	SCE	SCE	630				E_{ox}-*trans* 460 mV	450
1	1	MDP		$Ru(bpy)_2(MDP)^{2+}$	AN	SSCE	SSCE	1630	−1290			–	456
1	1	MDP		$Ru(bpy)_2(MDP)^{2+}$	AN	SCE	SCE	1630	−1290			–	479
1	1	MMP	MMP	*cis*-$Ru(bpy)_2(MMP)_2^{2+}$	AN	SSCE	SSCE	1450				E_{ox}-*trans* 1330 mV	450
1	1	MPP	Cl	$Ru(bpy)_2(MPP)(Cl)^{+}$	AN	SSCE	SSCE	910	−1330			E_{red} = irr.	456
1	1	MPP	MPP	$Ru(bpy)_2(MPP)_2^{2+}$	AN	SSCE	SSCE	1520				–	318
1	1	MPP	MPP	*cis*-$Ru(bpy)_2(MPP)_2^{2+}$	AN	SSCE	SSCE	1520				E_{ox}-*trans* 1390 mV	450
1	1	MPP	MPP	$Ru(bpy)_2(MPP)_2^{2+}$	AN	SSCE	SSCE	1500	−1330			–	456
1	1	MPP	MPP	*trans*-$Ru(bpy)_2(MPP)_2^{2+}$	AN	SSCE	SSCE	1460	−1300	−800	960	–	210
1	1	MPP	MPP	*cis*-$Ru(bpy)_2(MPP)_2^{2+}$	AN	SSCE	SSCE	1550	−1280	−750	1020	–	210
1	1	MeP	Cl	$Ru(bpy)_2(MeP)(Cl)^{+}$	AN	SSCE	SSCE	940	−1320			–	456
1	1	MeP	MeP	$Ru(bpy)_2(MeP)_2^{2+}$	AN	SSCE	SSCE	1510	−1340			–	456
1	1	Mpc		$Ru(bpy)_2(Mpc)^{2+}$	AN	SSCE	SSCE	1980				–	462
1	1	NCS	NCS	$Ru(bpy)_2(NCS)_2$	AN	SSCE	SSCE	670				–	489
1	1	NH_3	NO	$Ru(bpy)_2(NH_3)(NO)^{3+}$	AN	SSCE	SSCE	360	−480			$E_{red} = E/p$,c	488
1	1	NH_3	NO	$Ru(bpy)_2(NH_3)(NO)^{3+}$	AN	SSCE	SSCE	360	−480			–	441
1	1	NH_3	NO	$Ru(bpy)_2(NH_3)(NO)^{3+}$	AN	SSCE	SSCE	300				–	464
1	1	NH_3	NH_3	$Ru(bpy)_2(NH_3)_2^{2+}$	AN	SCE	SCE	1268	−1350			–	469
1	1	NH_3	NH_3	$Ru(bpy)_2(NH_3)_2^{2+}$	DMF		Fc+/0	270	−1930			–	470

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
1	1	NH_3	NH_3	$Ru(bpy)_2(NH_3)_2^{2+}$	AN	SCE	SCE	1280	−1340				-	474
1	1	NH_3	NH_3	$Ru(bpy)_2(NH_3)_2^{2+}$	AN	SCE	SCE	1255	−1353				-	477
1	1	NH_3	NH_3	$Ru(bpy)_2(NH_3)_2^{2+}$	AN	SSCE	SSCE	920					-	495
1	1	NH_3	NH_3	$Ru(bpy)_2(NH_3)_2^{2+}$	AN	SCE	SCE	910	−1480				-	501
1	1	NH_3	NH_3	$Ru(bpy)_2(NH_3)_2^{2+}$	H_2O	Ag/Ag^+	s ref	580					-	317
1	1	NH_3	NO_2	$Ru(bpy)_2(NH_3)(NO_2)^+$	AN	SSCE	SSCE	850					$E_{ox} = E/p$,a	464
1	1	NH_3	NO_3	$Ru(bpy)_2(NH_3)(NO_3)^+$	AN	SSCE	SSCE	700					-	464
1	1	NO_2	NO	$Ru(bpy)_2(NO_2)(NO)^{2+}$	AN	SSCE	SSCE	330	−560				$E_{red} = E/p$,c	488
1	1	NO_2	NO	$Ru(bpy)_2(NO_2)(NO)^{2+}$	AN	SSCE	SSCE	330	−560				-	441
1	1	NO_2	NO_2	$Ru(bpy)_2(NO_2)_2$	AN	SCE	SCE	1258	−1355				-	469
1	1	ON2	Cl	$Ru(bpy)_2(ON2)(Cl)^+$	AN	SSCE	SSCE	1240					$E_{ox} = E/p$,a	461
1	1	ON4	Cl	$Ru(bpy)_2(ON4)(Cl)^+$	AN	SSCE	SSCE	1230					$E_{ox} = E/p$,a	461
1	1	PAs	Cl	$Ru(bpy)_2(PAs)(Cl)^+$	AN	SSCE	SSCE	930	−1350				E_{red} = irr.	456
1	1	PCN	PCN	$Ru(bpy)_2(PCN)_2^{2+}$	AN	SSCE	SSCE	1520					-	492
1	1	PDA	Cl	$Ru(bpy)_2(PDA)(Cl)^+$	AN	SSCE	SSCE	900	−1290				E_{red} = irr.	456
1	1	PDP		$Ru(bpy)_2(PDP)^{2+}$	AN	SSCE	SSCE	1620	−1300				-	456
1	1	PDP	Cl	$Ru(bpy)_2(PDP)(Cl)^+$	AN	SSCE	SSCE	910	−1310				E_{red} = irr.	456
1	1	PEA	ECN	$Ru(bpy)_2(PEA)(ECN)^{2+}$	AN	SSCE	SSCE	1260					-	492
1	1	PEA	PEA	$Ru(bpy)_2(PEA)_2^{2+}$	AN	SSCE	SSCE	1040						492

1	1	PMA	PCN	$Ru(bpy)_2(PMA)(PCN)^{2+}$	AN	SSCE	SSCE	1290		–	492
1	1	PMA	PMA	$Ru(bpy)_2(PMA)_2^{2+}$	AN	SSCE	SSCE	1040		–	492
1	1	PPP	Cl	$Ru(bpy)_2(PPP)(Cl)^{+}$	AN	SSCE	SSCE	940	−1290	–	456
1	1	PPP	Cl	$Ru(bpy)_2(PPP)(Cl)^{+}$	AN	SCE	SCE	940	−1460	–	479
1	1	PPP	NO	$Ru(bpy)_2(PPP)(NO)^{3+}$	AN	SSCE	SSCE	560		–	464
1	1	PPP	NO_2	$Ru(bpy)_2(PPP)(NO_2)^{+}$	AN	SSCE	SSCE	1250		$E_{ox} = E/p$,a	464
1	1	PPP	NO_3	$Ru(bpy)_2(PPP)(NO_3)^{+}$	AN	SSCE	SSCE	1070		–	464
1	1	PPP	PPP	$Ru(bpy)_2(PPP)_2^{2+}$	AN	SSCE	SSCE	1540		Diss. D.J. Salmon, 1977	462
1	1	PPP	SEE	*cis*-$Ru(bpy)_2(PPP)(SEE)^{2+}$	AN	SSCE	SSCE	1550	−1280	–	486
1	1	PRC	PRC	$Ru(bpy)_2(PRC)_2^{2+}$	AN	SSCE	SSCE	1480		–	492
1	1	PSb	Cl	$Ru(bpy)_2(PSb)(Cl)^{+}$	AN	SSCE	SSCE	930	−1370	E_{red} = irr.	456
1	1	SEE	Cl	*cis*-$Ru(bpy)_2(SEE)(Cl)^{+}$	AN	SSCE	SSCE	880	−1490	–	486
1	1	SMM	SMM	*cis*-$Ru(bpy)_2(SMM)_2^{2+}$	PC	SSCE	SSCE	1420	−1310	–	486
1	1	SMM	SMM	*trans*-$Ru(bpy)_2(SMM)_2^{2+}$	PC	SSCE	SSCE	1370		–	486
1	1	SMP	Cl	*cis*-$Ru(bpy)_2(SMP)(Cl)^{+}$	AN	SSCE	SSCE	880	−1500	–	486
1	1	SNA		$Ru(bpy)_2(SNA)^{2+}$	AN	SSCE	SSCE		−1360	–	486
1	1	SNB		$Ru(bpy)_2(SNB)^{2+}$	AN	SSCE	SSCE		−1340	–	486
1	1	SNC		$Ru(bpy)_2(SNC)^{2+}$	AN	SSCE	SSCE		−1380	–	486
1	1	SND		$Ru(bpy)_2(SND)^{2+}$	AN	SSCE	SSCE	1380	−1280	–	486
1	1	SNE		$Ru(bpy)_2(SNE)^{+}$	AN	SSCE	SSCE	300	−1490	–	486
1	1	SNO		$Ru(bpy)_2(SNO)^{2+}$	AN	SSCE	SSCE		−1250	–	486
1	1	SSB		$Ru(bpy)_2(SSB)^{+}$	AN	SSCE	SSCE	540	−1530	–	486

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
1	1	SSE	$Ru(bpy)_2(SSE)^+$	AN	SSCE	SSCE	550	−1520				–	486
1	1	SSM	$Ru(bpy)_2(SSM)^+$	AN	SSCE	SSCE	540	−1530				–	486
1	1	SSO	$Ru(bpy)_2(SSO)^+$	AN	SSCE	SSCE	740	−1480				–	486
1	1	aca	$Ru(bpy)_2(aca)^+$	AN	SCE	SCE	610			−1070		–	467
1	1	aca	$Ru(bpy)_2(aca)^+$	AN	SCE	SCE	603	−1563				–	469
1	1	aca	$Ru(bpy)_2(aca)^+$	AN	SCE	SCE	620	−1550				–	477
1	1	dia	$Ru(bpy)_2(dia)^{2+}$	AN	SSCE	SSCE	1450	−1360		−800	890	–	210
1	1	dmp	$Ru(bpy)_2(dmp)^{2+}$	AN	SSCE	SSCE	1400	−1380		−830	850	–	210
1	1	gly	$Ru(bpy)_2(gly)^+$	AN	SCE	SCE	673	−1530				–	469
1	1	ipp	$Ru(bpy)_2(ipp)^+$	AN	SCE	SCE	800					–	468
1	1	nor	$Ru(bpy)_2(nor)^{2+}$	AN	SSCE	SSCE	1700					–	462
1	1	nor	*cis*-$Ru(bpy)_2(nor)^{2+}$	AN	SSCE	SSCE	1700					E_{ox} = E/p,a	497
1	13	13	$Ru(bpy)(3,3'\text{-dm-bpy})_2^{2+}$	AN	Ag/Ag NO_3	NHE	1180	−1410	2100	−920	690	–	329
1	13	13	$Ru(bpy)(3,3'\text{-dm-bpy})_2^{2+}$	AN	Ag/Ag NO_3 *	NHE	1180	−1410	2100	−920	690	* Ru $(bpy)_3^{2+}$ /+1260 mV	40
1	15	15	$Ru(bpy)(4,4'\text{-dm-bpy})_2^{2+}$	AN	Ag/Ag^+	s ref	900	−1690				–	307
1	17	17	$Ru(bpy)(4,4'\text{-dBr-bpy})_2^{2+}$	AN	Ag/Ag^+	s ref	1080					E_{red} = irr.	307
1	26	26	$Ru(bpy)(4,4'\text{-dph-bpy})_2^{2+}$	AN	Ag/Ag NO_3	NHE	1220			−870		–	224

1	26	26			Ru(bpy)(4,4′-dph-bpy)$_2^{2+}$	DMF		Fc+/0		−1710				at −54°C	473
1	26	26			Ru(bpy)(4,4′-dph-bpy)$_2^{2+}$	AN	SSCE	SSCE	1203	−1298				–	473
1	30	30			Ru(bpy)(4,4′-DTB-bpy)$_2^{2+}$	AN	Ag/Ag NO_3	NHE	1160	−1390	2100	−940	710	–	329
1	30	30			Ru(bpy)(4,4′-DTB-bpy)$_2^{2+}$	AN	Ag/Ag NO_3 *	NHE	1160	−1390	2100	−940	710	* Ru(bpy)$_3^{2+}$ /+1260 mV	40
1	38	38			Ru(bpy)(4,4′-DCI-bpy)$_2^{2+}$	CH_2Cl_2	Ag/Ag Cl	NHE		−480				–	447
1	54	54			Ru(bpy)(6,6′-dm-bpy)$_2^{2+}$	AN	Ag/Ag NO_3	NHE	1185	−1400				–	514
1	59	59			Ru(bpy)(bpz)$_2^{2+}$	AN	SSCE	SSCE	1720	−790				–	229
1	59	59			Ru(bpy)(bpz)$_2^{2+}$	DMF		Fc+/0		−1270				at −54°C	473
1	59	59			Ru(bpy)(bpz)$_2^{2+}$	AN	SSCE	SSCE	1713	−805				–	473
1	61	61			Ru(bpy)(bpym)$_2^{2+}$	AN	SSCE	SSCE	1550	−950				–	229
1	67	67			Ru(bpy)(h-phen)$_2^{2+}$	AN	Ag/Ag NO_3 *	NHE	1210	−1370	2120	−910	750	* Ru(bpy)$_3^{2+}$ /+1260 mV	40
1	68	68			Ru(bpy)(phen)$_2^{2+}$	AN	SSCE	SSCE	1300					–	458
1	CN	CN	CN	CN	Ru(bpy)(CN)$_4^{2-}$	H_2O	SCE	SCE	780					–	222
1	CN	CN	CN	CN	Ru(bpy)(CN)$_4^{2-}$	DMF	SCE	SCE	200	−1950				–	222
1	en	en			Ru(bpy)(en)$_2^{2+}$	H_2O	Ag/Ag^+	s ref	260					–	317
1	108	108			Ru(bpy)(DIAFO)$_2^{2+}$	AN	Ag/Ag NO_3 *	NHE	1310	−680i	2160	−850	~1500	* Ru(bpy)$_3^{2+}$ /+1260 mV	40

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
1	109	109	Ru(bpy)(taphen)$_2^{2+}$	AN	$Ag/AgNO_3$	NHE	1480	−740				–	238
1	109	109	Ru(bpy)(taphen)$_2^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1480	−740	1930	−450	1190	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
1	110	110	Ru(bpy)$_2$(phen-dione)$_2^{2+}$	AN	SSCE	SSCE	1430	−160				–	480
1	111	281	Ru(bpy)(py)(trpy)$^{2+}$	AN	SSCE	SSCE	1210	−1260	1950			–	374
1	120	281	Ru(bpy)(4-vpy)(trpy)$^{2+}$	AN	SSCE	SSCE	1210	−1260				–	448
1	124	281	Ru(bpy)(PVP)(trpy)$^{2+}$	1,2-dme	SSCE	SSCE	1210					–	374
1	124	281	Ru(bpy)(PVP)(trpy)$^{2+}$	CH_2Cl_2	SSCE	SSCE	1300					Diss. D.J. Salmon, 1977	374
1	127	281	Ru(bpy)(4′-Cl-stylb)(trpy)$^{2+}$	AN	SSCE	SSCE	1210	−1350				–	448
1	156	281	Ru(bpy)(PTZ)(trpy)$^{2+}$	AN	SSCE	SSCE	1190					–	377
1	160	281	Ru(bpy)(BPE)(trpy)$^{2+}$	AN	SSCE	SSCE	1210	−1260				–	448
1	162	162	Ru(bpy)(DPA)$_2$	AN		Fc+/0	−410	−2060				−40 °C, $E_{red} = E/p$,c	235
1	163	163	Ru(bpy)(DPAH)$_2^{2+}$	AN		Fc+/0	510	−1820	1770			−40 °C, $E_{red} = E/p$,c	235
1	164	281	Ru(bpy)(ipa)(trpy)$^{+}$	AN	SSCE	SSCE	720					–	503
1	180	180	Ru(bpy)(pydipy)$_2^{2+}$	AN	SCE	SCE	1210					–	369
1	181	181	Ru(bpy)(Azpy)$_2^{2+}$	AN	$SCE(H_2O)$	SCE	1880	−210				*trans/cis*	432
1	181	181	Ru(bpy)(Azpy)$_2^{2+}$	CH_2Cl_2	$Ru(bpy)_3^{2+}$	SCE		−70				–	375
1	181	181	Ru(bpy)(Azpy)$_2^{2+}$	H_2O			170					–	376
1	182	182	Ru(bpy)(MeAzpy)$_2^{2+}$	AN	$SCE(H_2O)$	SCE	1890	−210				*trans/cis*	432

1	182	182	Ru(bpy)$_2$(MeAzpy)$_2^{2+}$	AN	SCE(H$_2$O)	SCE	1920	−230				*cis/cis*	432
1	184	184	Ru(bpy)$_2$(thpy)$_2^{2+}$	1 M HNO$_3$	SCE	NHE	1270		2010	−740		–	370
1	185	185	Ru(bpy)$_2$(pmth)$_2^{2+}$	AN	Ag/AgNO$_3$	NHE	1298	−1254				–	514
1	246	246	Ru(bpy)$_2$(pq)$_2^{2+}$	DMF		Fc+/0		−1490				at −54°C	473
1	246	246	Ru(bpy)$_2$(pq)$_2^{2+}$	AN	SSCE	SSCE	1300	−1075				–	473
1	251	251	Ru(bpy)$_2$(DMCH)$_2^{2+}$	AN	Ag/AgNO$_3$	NHE	1255	−920				–	239
1	251	251	Ru(bpy)$_2$(DMCH)$_2^{2+}$	AN	Ag/AgNO$_3$	NHE	1250	−920	1680	−430	760	–	329
1	251	251	Ru(bpy)$_2$(DMCH)$_2^{2+}$	AN	Ag/AgNO$_3$ *	NHE	1250	−920	1680	−430	760	* Ru(bpy)$_3^{2+}$/ +1260 mV	40
1	256	256	Ru(bpy)$_2$(dinapy)$_2^{2+}$	AN	Ag/AgNO$_3$	NHE	1130	−640				–	514
1	257	257	Ru(bpy)$_2$(biq)$_2^{2+}$	AN	Ag/AgNO$_3$	NHE	1395	−820				–	239
1	257	257	Ru(bpy)$_2$(biq)$_2^{2+}$	AN	Ag/AgNO$_3$ *	NHE	1400	−820	1690	−290	870	* Ru(bpy)$_3^{2+}$/ +1260 mV	40
1	257	257	Ru(bpy)$_2$(biq)$_2^{2+}$	AN			1400	−820	1690	−290	870	–	344
1	259	259	Ru(bpy)$_2$(i-biq)$_2^{2+}$	AN	Ag/AgNO$_3$	NHE	1170	−1420				–	131
1	259	259	Ru(bpy)$_2$(i-biq)$_2^{2+}$	AN	Ag/AgNO$_3$ *	NHE	1170	−1420	2120	−950	700	* Ru(bpy)$_3^{2+}$/ +1260 mV	40
1	281	AN	Ru(bpy)$_2$(trpy)(AN)$^{2+}$	AN	SSCE	SSCE	1310					–	377
1	281	CN	Ru(bpy)$_2$(trpy)(CN)$^{+}$	DMF	Ag/AgNO$_3$	*	1080	−1330		−860	610	* Ru(bpy)$_3^{2+}$/ +1260 mV	221
1	281	CN	Ru(bpy)$_2$(trpy)(CN)$^{+}$	AN	Ag/AgNO$_3$ *	NHE	1080	−1330	1980	−900	650	* Ru(bpy)$_3^{2+}$/ +1260 mV	40
1	281	CN	Ru(bpy)$_2$(trpy)(CN)$^{+}$	AN	Ag/AgNO$_3$	*	1030	−1440				* Ru(bpy)$_3^{2+}$/ +1260 mV	221
1	281	CN	Ru(bpy)$_2$(trpy)(CN)$^{+}$	DMF	Ag/AgNO$_3$	*	1050	−1390				* Ru(bpy)$_3^{2+}$/ +1260 mV	221
1	281	Cl	Ru(bpy)$_2$(trpy)(Cl)$^{+}$	AN	Ag/AgNO$_3$ *	NHE	810	−1350	1790	−980	440	* Ru(bpy)$_3^{2+}$/ +1260 mV	40
1	281	NO	Ru(bpy)$_2$(trpy)(NO)$^{3+}$	AN	SSCE	SSCE	450	−200				–	441

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands					Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
1	281	NO			Ru(bpy)(trpy)$(NO)^{3+}$	H_2O pH 4.68	SSCE	SSCE		190				–	253
1	281	IPA			Ru(bpy)(trpy)$(IPA)^{2+}$	AN	SSCE	SSCE	720					–	493
1	281	IPA			Ru(bpy)(trpy)$(IPA)^{2+}$	AN	SSCE	SSCE	1080					–	503
1	281	NH_3			Ru(bpy)(trpy)$(NH_3)^{2+}$	AN	SCE	SCE	1170	−1230				–	501
1	Hed				Ru(bpy)(Hed)	H_2O	SCE	SCE	330	−600				–	481
1	NH_3	NH_3	NH_3	NH_3	Ru(bpy)$(NH_3)_4^{2+}$	AN	SCE	SCE	510	−1710				–	501
1	nor	Cl	Cl		Ru(bpy)(nor)$(Cl)_2$	AN	SSCE	SSCE	1040					–	497
2	2	2			Ru(4-Cl-bpy)$_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1330			−750		–	224
3	3	3			Ru(4-Br-bpy)$_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1340			−740		–	224
7	7	7			Ru(4-n-bpy)$_3^{2+}$	AN	SCE(H_2O)	SCE	1540	−630		−420		$E_{red} = E_p$ = irr.	378
7	7	7			Ru(4-n-bpy)$_3^{2+}$	AN	SCE	SCE	1540					–	378
7	7	7			Ru(4-n-bpy)$_3^{2+}$	AN	SCE	SCE	1540	−630				E_{red} = irr.	431
7	7	7			Ru(4-n-bpy)$_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1550	−545				–	239
7	7	7			Ru(4-n-bpy)$_3^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1550	−550	1930	−380	1138	$^*Ru(bpy)_3^{2+}$/ +1260 mV	40
7	7	Cl	Cl		*cis*-Ru(4-n-bpy)$_2$ $(Cl)_2$	AN	SCE	SCE	850					–	431

9	9	9		$Ru(4\text{-tep-bpy})_3^{5+}$	AN	$SCE(H_2O)$	SCE	1520	−960		−480		$E_{oxex} = 5+/6+$	378
9	9	9		$Ru(4\text{-tep-bpy})_3^{5+}$	AN	SCE	SCE	1520					–	378
9	9	9		$Ru(4\text{-tep-bpy})_3^{5+}$	AN	SCE	SCE	1520	−960				–	431
9	9	Cl	Cl	$Ru(4\text{-tep-bpy})_2(Cl)_2^{2+}$	AN	SCE	SCE	750					–	431
13	13	13		$Ru(3,3'\text{-dm-bpy})_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1150	−1460	2080	−930	620	–	329
13	13	13		$Ru(3,3'\text{-dm-bpy})_3^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1150	−1460	2080	−930	620	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	AN	$SCE(H_2O)$	SCE	1140			−940		–	149
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1110			−950		–	224
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	AN and DMF	SCE	SCE	1130	−1370	1980	−850	670	E_{ox} = AN, E_{red} = DMF	444
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	DMF	SSCE	SSCE	1165	−1336				–	69
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	AN	$Ag/AgNO_3$	s ref		−1940				–	465
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	AN	SCE	SCE	1093	−1470				–	469
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	H_2O		NHE	1100	−1370	2040	−940	690	–	12
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	AN	SCE	SCE	1100	−1450			640	–	232
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	H_2O		NHE	1100	−1370	2040			–	176
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	DMF	SCE	SCE		−1340				–	60
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	0.5 M H_2SO_4	SCE	SCE	850					–	509
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	AN	$SCE(H_2O)$	SCE		−1440			690	–	169
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	EtOH					2270			–	515
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	CH_2Cl_2			1100	−1460				–	135
15	15	15		$Ru(4,4'\text{-dm-bpy})_3^{2+}$	AN	Ag/Ag^+	s ref	810	−1760				–	307

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands			Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
15	15	15	Ru(4,4′-dm-bpy)$_3^{2+}$	DMF	SCE	SCE	1130	−1370				–	270
15	15	17	Ru(4,4′-dm-bpy)$_2$(4,4′-dBr-bpy)$^{2+}$	AN	Ag/Ag$^+$	s ref	930					E_{red} = irr.	307
15	15	37	Ru(4,4′-dm-bpy)$_2$(4,4′-DCE-bpy)$^{2+}$	CH_2Cl_2			1300	−1030				–	135
15	15	61	Ru(4,4′-dm-bpy)$_2$(bpym)$^{2+}$	AN	Ag/AgNO$_3$	s ref		−1520				–	465
15	15	266	Ru(4,4′-dm-bpy)$_2$(Mebpy-3DQ+2)$^{4+}$	AN and DMF	SCE	SCE	1120	−1350				E_{ox} = AN, E_{red} = DMF	444
15	17	17	Ru(4,4′-dm-bpy)(4,4′-dBr-bpy)$_2^{2+}$	AN	Ag/Ag$^+$	s ref	1030					E_{red} = irr.	307
15	37	37	Ru(4,4′-dm-bpy)(4,4′-DCE-bpy)$_2^{2+}$	AN and DMF	SCE	SCE	1440	−880	1890	−440	1010	E_{ox} = AN, E_{red} = DMF	444
16	16	16	Ru(4,4′-dCl-bpy)$_3^{2+}$	AN	Ag/AgNO$_3$	NHE	1440			−550		–	224
16	16	16	Ru(4,4′-dCl-bpy)$_3^{2+}$	AN	Ag/AgNO$_3$	NHE	1425	−1060				–	239
16	16	16	Ru(4,4′-dCl-bpy)$_3^{2+}$	AN	Ag/AgNO$_3$ *	NHE	1420	−1060	2070	−650	1010	* Ru(bpy)$_3^{2+}$/ +1260 mV	40
16	16	16	Ru(4,4′-dCl-bpy)$_3^{2+}$	AN			1420	−1060	2070	−650	1010	–	344
17	17	17	Ru(4,4′-dBr-bpy)$_3^{2+}$	AN	Ag/AgNO$_3$	NHE	1440			−580		–	224
17	17	17	Ru(4,4′-dBr-bpy)$_3^{2+}$	AN	Ag/Ag$^+$	s ref	1140					E_{red} = irr.	307
21	21	21	Ru(4,4′-DEA-bpy)$_3^{2+}$	AN	Ag/AgNO$_3$	NHE	610			−1300		–	224
22	22	22	Ru(4,4′-BAA-bpy)$_3^{2+}$	AN	Ag/AgNO$_3$	NHE	970			−1060		–	224
23	23	23	Ru(4,4′-DEO-bpy)$_3^{2+}$	AN	Ag/AgNO$_3$	NHE	900			−1090		–	224

24	24	24	$Ru(4,4'\text{-DPO-bpy})_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1050			−940		–	224
25	25	25	$Ru(4,4'\text{-DBO-bpy})_3^{2+}$	AN	$Ag/AgNO_3$	NHE	950			−1070		–	224
26	26	26	$Ru(4,4'\text{-dph-bpy})_3^{2+}$	AN	$SCE(H_2O)$	SCE	1200			−850		–	149
26	26	26	$Ru(4,4'\text{-dph-bpy})_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1200			−880		–	224
26	26	26	$Ru(4,4'\text{-dph-bpy})_3^{2+}$	DMF		Fc+/0		−1690				At −54°C	473
26	26	26	$Ru(4,4'\text{-dph-bpy})_3^{2+}$	AN	SSCE	SSCE	1188	−1273				–	473
28	28	28	$Ru(4,4'\text{-dsty-bpy})_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1140			−820		–	224
29	29	29	$Ru(4,4'\text{-dc-bpy})_3^{2+}$	0.85M H_2SO_4		NHE	1560					–	504
30	30	30	$Ru(4,4'\text{-DTB-bpy})_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1110	−1335				$E_{red} = E/p,c$	239
30	30	30	$Ru(4,4'\text{-DTB-bpy})_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1110	−1440	2160	−1050	720	–	329
30	30	30	$Ru(4,4'\text{-DTB-bpy})_3^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1110	−1440	2160	−1050	720	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
31	33	33	$Ru(4,4'\text{-dnd-bpy})(4,4'\text{-poeg-bpy})_2^{2+}$	AN	SCE	SCE	1040	−1500		−1080	620	–	384
37	37	37	$Ru(4,4'\text{-DCE-bpy})_3^{2+}$	DMF	SCE	SCE	1540	−890				–	270
37	37	37	$Ru(4,4'\text{-DCE-bpy})_3^{2+}$	DMF		Fc+/0		−1340				−54°C, E_{red} 37 = −2050	63
37	37	37	$Ru(4,4'\text{-DCE-bpy})_3^{2+}$	AN and DMF	SCE	SCE	1540	−890	1960	−420	1070	E_{ox} = AN, E_{red} = DMF	444
37	37	37	$Ru(4,4'\text{-DCE-bpy})_3^{2+}$	DMF		Fc+/0		−1340				At −54°C	62
37	37	37	$Ru(4,4'\text{-DCE-bpy})_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1560			−470		–	224
37	37	37	$Ru(4,4'\text{-DCE-bpy})_3^{2+}$	CH_2Cl_2			1550	−910				–	135
37	37	266	$Ru(4,4'\text{-DCE-bpy})_2(\text{Mebpy-3DQ+2})^{4+}$	AN and DMF	SCE	SCE	1430	−860				E_{ox} = AN, E_{red} = DMF	444
38	38	38	$Ru(4,4'\text{-DCl-bpy})_3^{2+}$	CH_2Cl_2	Ag/AgCl	NHE		−460				–	447

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
38	38	38		$Ru(4,4'\text{-DCI-bpy})_3^{2+}$	AN	SCE	SCE		−900				–	380
38	38	38		$Ru(4,4'\text{-DCI-bpy})_3^{2+}$	AN	SCE	SCE	1590	−900				–	354
38	38	130	130	$Ru(4,4'\text{-DCI-bpy})_2(p\text{-cinn})_2^{2+}$	AN	SSCE	SSCE	1460	−960				–	448
39	39	39		$Ru(4,4'\text{-DOC-bpy})_3^{2+}$	AN	SCE	SCE	1560	−910				–	354
40	40	40		$Ru(4,4'\text{-DCB-bpy})_3^{2+}$	AN	SCE	SCE	1560	−950				–	354
43	43	43		$Ru(4,4'\text{-DHC-bpy})_3^{2+}$	AN/iBN	SCE	SCE	1350	−990				–	354
44	44	44		$Ru(4,4'\text{-DCA-bpy})_3^{2+}$	DMF	SCE	SCE	1280	−1120				–	270
46	46	46		$Ru(v\text{-bpy})_3^{2+}$	AN	SSCE	SSCE	1160	−1430				–	455
46	46	46		$Ru(v\text{-bpy})_3^{2+}$	1 M $HClO_4$	SSCE	SSCE	925					Polymer film	455
46	46	46		$Ru(v\text{-bpy})_3^{2+}$	AN	SSCE	SSCE	1160	−1430				Polymer film	455
46	46	AN	AN	$Ru(v\text{-bpy})_2(AN)_2^{2+}$	AN	SSCE	SSCE	1350					Polymer film	455
46	46	Cl	Cl	$Ru(v\text{-bpy})_2(Cl)_2$	AN	SSCE	SSCE	300					–	455
46	46	Cl	Cl	$Ru(v\text{-bpy})_2(Cl)_2$	AN	SSCE	SSCE	360					Polymer film	455
47	47	47		$Ru(VB)_3^{2+}$	AN	SSCE	SSCE	1130	−1410				–	502
50	50	50		$Ru(5,5'\text{-dm-bpy})_3^{2+}$	AN	Ag/Ag NO_3	NHE	1160			−980		–	224
50	50	50		$Ru(5,5'\text{-dm-bpy})_3^{2+}$	AN	Ag/Ag NO_3	s ref		−1980				–	465
50	50	50		$Ru(5,5'\text{-dm-bpy})_3^{2+}$	DMF	SCE	SCE		−1390				–	60
50	50	50		$Ru(5,5'\text{-dm-bpy})_3^{2+}$	0.5 M H_2SO_4	SCE	SCE	920					–	509
50	50	50		$Ru(5,5'\text{-dm-bpy})_3^{2+}$	DMF	SCE	SCE	1150	−1410				–	270
50	50	61		$Ru(5,5'\text{-dm-bpy})_2(bpym)^{2+}$	AN	Ag/Ag NO_3	s ref		−1530				–	465
51	51	51		$Ru(5,5'\text{-DCE-bpy})_3^{2+}$	DMF		Fc+/0		−1140				−54 °C, E_{red} 51 = −1770	63

51	51	51		$Ru(5,5'\text{-DCE-bpy})_3^{2+}$	AN	SCE	SCE	1630	−650		−280	1240	–	516
51	51	51		$Ru(5,5'\text{-DCE-bpy})_3^{2+}$	DMF	SCE	SCE	1530	−660				–	270
52	52	52		$Ru(5,5'\text{-BAA-bpy})_3^{2+}$	AN	Ag/Ag NO_3	NHE	1210			−900		–	224
53	53	53		$Ru(5,5'\text{-DCI-bpy})_3^{2+}$	AN	SCE	SCE		−720				–	380
54	54	54		$Ru(6,6'\text{-dm-bpy})_3^{2+}$	AN	Ag/Ag NO_3	NHE	1365	−1330				–	514
55	55	55		$Ru(tm\text{-bpy})_3^{2+}$	AN and DMF	SCE	SCE	1060	−1490	2050	−990	560	E_{ox} = AN, E_{red} = DMF	444
55	55	266		$Ru(tm\text{-bpy})_2$ (Mebpy -3DQ + 2)$^{4+}$	AN and DMF	SCE	SCE	1060	−1390				E_{ox} = AN, E_{red} = DMF	444
56	56	56		$Ru(H4\text{-bpy})_3^{2+}$	AN	Ag/Ag NO_3 *	NHE	1175					* $Ru(bpy)_3^{2+}$ / +1260 mV	511
59	59	I	I	$Ru(bpz)_2(I)_2$	AN	SCE	SCE	800	−1050				E_{ox} = irr., E_{red} = p.rev.	436
59	59	59		$Ru(bpz)_3^{2+}$	AN	AgRE	SCE	1895	−765				–	386
59	59	59		$Ru(bpz)_3^{2+}$	H_2O	SCE	SCE	1980	−680		−100	1400	–	443
59	59	59		$Ru(bpz)_3^{2+}$	AN	SSCE	SSCE	1980	−680				–	229
59	59	59		$Ru(bpz)_3^{2+}$	AN	SCE	SCE	1860	−800				–	385
59	59	59		$Ru(bpz)_3^{2+}$	DMF		Fc+/0		−1210				At −54° C	473
59	59	59		$Ru(bpz)_3^{2+}$	AN	SSCE	SSCE	1930	−743				–	473
59	59	59		$Ru(bpz)_3^{2+}$	AN	SCE	SCE	1860	−800			1360	–	232
59	59	59		$Ru(bpz)_3^{2+}$	AN	SCE	SCE	1860	−800		−260	1450	Same res. for H_2O	387
59	59	59		$Ru(bpz)_3^{2+}$	AN	SCE	SCE		−860				–	389
59	59	59		$Ru(bpz)_3^{2+}$	AN	SCE	SCE	1860	−800				–	397
59	59	60		$Ru(bpz)_2$ $(bpzH)^{3+}$	H_2O	SCE	SCE	2270	−280		550	1440	–	387
59	59	AN	Cl	$Ru(bpz)_2$ $(AN)(Cl)^+$	AN	SCE	SCE	1320	−990				–	385
59	59	Br	Br	$Ru(bpz)_2$ $(Br)_2$	AN	SCE	SCE	790	−1090				E_{red} = part. revers.	436
59	59	Cl	Cl	$Ru(bpz)_2$ $(Cl)_2$	AN	SCE	SCE	800	−1040				E_{red} = part. revers.	385
59	59	Cl	Cl	$Ru(bpz)_2$ $(Cl)_2$	AN	SCE	SCE	800	−1040				E_{red} = part. revers.	436

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands					Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
59	59	NCS	NCS		$Ru(bpz)_2(NCS)_2$	AN	SCE	SCE	940	−930				E_{ox} = irr.	436
59	59	NO_2	NO_2		$Ru(bpz)_2(NO_2)_2$	AN	SCE	SCE	1180					E_{ox} = part. revers.	436
61	61	61			$Ru(bpym)_3^{2+}$	AN	SSCE	SSCE	1690	−910				–	229
61	61	61			$Ru(bpym)_3^{2+}$	AN	$Ag/AgNO_3$	s ref		−1400				–	465
61	61	61			$Ru(bpym)_3^{2+}$	AN	$Ru(bpy)_3^{2+}$	NHE	1640					Reference = 1260 mV	361
61	61	61			$Ru(bpym)_3^{2+}$	AN	SCE	SCE	1690	−910			1200	–	232
61	257	257			$Ru(bpym)(biq)_2^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1515	−750				* $Ru(bpy)_3^{2+}$ / +1260 mV	512
61	261	261			$Ru(bpym)(DP)_2^{2+}$	AN	SCE	*	1452	−980				* $Ru(bpy)_3^{2+}$ / +1260 mV	513
61	NH_3	NH_3	NH_3	NH_3	$Ru(bpym)(NH_3)_4^{2+}$	H_2O		NHE	756					–	460
63	63	63			$Ru(6,6'\text{-dm-bpym})_3^{2+}$	AN	SCE	SCE	1490	−780			1090	–	232
63	63	63			$Ru(6,6'\text{-dm-bpym})_3^{2+}$	AN	SCE	SCE	1490	−780	1870	−380	1090	–	487
64	64	64			$Ru(bprid)_3^{2+}$	AN	SCE	SCE	1580	−1000			1060	–	232
64	64	64			$Ru(bprid)_3^{2+}$	AN	SCE	SCE	1580	−1000	2060	−480	1060	–	487
65	65	65			$Ru(4\text{-py-prim})_3^{2+}$	AN	SCE	SCE	1380	−1180			910	–	232
65	65	65			$Ru(4\text{-py-prim})_3^{2+}$	AN	SCE	SCE	1380	−1180	2110	−730	930	–	487
66	66	66			$Ru(4\text{-py-prim})_3^{2+}$	AN	SCE	SCE	1380	−1040			940	–	232
67	67	67			$Ru(h\text{-phen})_3^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1200	−1390	2130	−930	740	* $Ru(bpy)_3^{2+}$ / +1260 mV	40
68	68	68			$Ru(phen)_3^{2+}$	H_2O		NHE	1260			−870		–	149
68	68	68			$Ru(phen)_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1270			−940		–	224
68	68	68			$Ru(phen)_3^{2+}$	AN	Ag/AgCl	s ref	1400	−1200				–	445
68	68	68			$Ru(phen)_3^{2+}$	CH_2Cl_2	Ag/AgCl	NHE		−1010				–	447
68	68	68			$Ru(phen)_3^{2+}$	SO_2	AgRE	AgRE	1030					–	438
68	68	68			$Ru(phen)_3^{2+}$	AN	SSCE	SSCE	1300					–	458
68	68	68			$Ru(phen)_3^{2+}$	H_2O		NHE	1260	−1360	2130	−870	790	–	12
68	68	68			$Ru(phen)_3^{2+}$	AN	SCE	SCE	1270	−1350			850	–	232
68	68	68			$Ru(phen)_3^{2+}$	AN	SCE	SCE	1400	−1410				Peak potentials	4

68	68	68		$Ru(phen)_3^{2+}$	H_2O		NHE	1260	−1360	2180			–	176
68	68	68		$Ru(phen)_3^{2+}$	AN	SCE	SCE	1400	−1410				–	397
68	68	68		$Ru(phen)_3^{2+}$	AN	SCE	SCE		−1430			790	–	169
68	68	68		$Ru(phen)_3^{2+}$	H_2O						−870		–	393
68	68	87		$Ru(phen)_2$ (4,7-C12-phen)$^{2+}$	AN	AgRE	SCE	1290	−1220				–	395
68	68	AN	AN	*cis*-Ru (phen)$_2$ $(AN)_2^{2+}$	AN	SSCE	SSCE	1440					–	484
68	68	AN	AN	*trans*-Ru (phen)$_2$ $(AN)_2^{2+}$	AN	SSCE	SSCE	1450					–	484
68	68	AN	H_2O	*trans*-Ru (phen)$_2$ (AN) $(H_2O)^{2+}$	AN	SSCE	SSCE	1080					–	484
68	68	CN	CN	$Ru(phen)_2$ $(CN)_2$	DMF	SCE	SCE	884	−1598				$E = E/p$,a and E/p,c	471
68	68	CN	CN	$Ru(phen)_2$ $(CN)_2$	DMF	SCE	SCE	880	−1550	2190			–	176
68	68	en		$Ru(phen)_2$ $(en)^{2+}$	6 M H_2SO_4	SCE	SCE	800					–	496
68	68	en		$Ru(phen)_2$ $(en)^{2+}$	1.5 M HCl	SCE	SCE	870					–	496
68	68	en		$Ru(phen)_2$ $(en)^{2+}$	H_2O	Ag/Ag^+	s ref	610					–	317
68	68	105		$Ru(phen)_2$ (BDCMP)	AN	AgRE	SCE	1430	−1520				–	395
68	68	111	I	$Ru(phen)_2$ $(py)(I)^+$	AN	Ag/AgCl	s ref	930	−1340				E_{ox} vs. NHE/ Fc+/0 = 790	445
68	68	111	Br	$Ru(phen)_2$ $(py)(Br)^+$	AN	Ag/AgCl	s ref	940	−1370				E_{ox} vs. NHE/ Fc+/0 = 800	445
68	68	111	CN	$Ru(phen)_2$ $(py)(CN)^+$	AN	Ag/AgCl	s ref	960	−1340				E_{ox} vs. NHE/ Fc+/0 = 820	445
68	68	111	Cl	$Ru(phen)_2$ $(py)(Cl)^+$	AN	Ag/AgCl	s ref	920	−1390				E_{ox} vs. NHE/ Fc+/0 = 780	445
68	68	111	Cl	$Ru(phen)_2$ $(py)(Cl)^+$	AN	SSCE	SSCE	782					$T = 20.0$ °C	466
68	68	111	N_3	$Ru(phen)_2$ $(py)(N_3)^+$	AN	Ag/AgCl	s ref	730	−1380				E_{ox} vs/ NHE/ Fc+/0 = 590	445
68	68	111	111	$Ru(phen)_2$ $(py)_2^{2+}$	AN	Ag/AgCl	s ref	1440	−1350				E_{ox} vs. NHE/ Fc+/0 = 1290	445

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
68	68	111	111	*cis*-Ru(phen)$_2$ (py)$_2^{2+}$	AN	SSCE	SSCE	1290					–	484
68	68	111	111	*trans*-Ru(phen)$_2$ (py)$_2^{2+}$	AN	SSCE	SSCE	1260					–	484
68	68	111	NH_3	Ru(phen)$_2$ (py)(NH_3)$^{2+}$	AN	Ag/AgCl	s ref	1020	−1330				E_{ox} vs. NHE/ Fc+/0 = 880	445
68	68	111	NO_2	Ru(phen)$_2$ (py)(NO_2)$^+$	AN	Ag/AgCl	s ref	~1200	−1340				E_{ox} vs. NHE/ Fc+/0 = 950	445
68	68	111	SCN	Ru(phen)$_2$ (py)(SCN)$^+$	AN	Ag/AgCl	s ref	~1050	−1320				E_{ox} vs. NHE/ Fc+/0 = 900	445
68	68	123	123	Ru(phen)$_2$ (4-vpy)$_2^{2+}$	AN	SSCE	SSCE	1250	−1370				–	448
68	68	138	Cl	Ru(phen)$_2$ (pyr)(Cl)$^+$	AN	SSCE	SSCE	860					–	430
68	68	140		Ru(phen)$_2$ (napy)$^{2+}$	AN	SSCE	SSCE	1270					–	458
68	68	141		Ru(phen)$_2$ (ppyz)$^{2+}$	AN	SSCE	SSCE	1330					–	458
68	68	142		Ru(phen)$_2$ (2-m-napy)$^{2+}$	AN	SSCE	SSCE	1260					–	458
68	68	143		Ru(phen)$_2$ (2,7-dmnapy)$^{2+}$	AN	SSCE	SSCE	1330					–	458
68	68	168		Ru(phen)$_2$ (diim)$^{2+}$	6 M H_2SO_4	SCE	SCE	1300					–	496
68	68	246		Ru(phen)$_2$ (pq)$^{2+}$	AN	Ag/Ag NO_3 *	NHE	1290	−1140	1900	−610	760	* Ru(bpy)$_3^{2+}$/ +1260 mV	40
68	68	251		Ru(phen)$_2$ (DMCH)$^{2+}$	AN	Ag/Ag NO_3 *	NHE	1290	−1000	1750	−460	750	* Ru(bpy)$_3^{2+}$/ +1260 mV	40
68	68	257		Ru(phen)$_2$ (biq)$^{2+}$	AN	Ag/Ag NO_3 *	NHE	1360	−910	1740	−380	830	* Ru(bpy)$_3^{2+}$/ +1260 mV	40
68	68	262		Ru(phen)$_2$ (9-PDP)$^{2+}$	AN	AgRE	SCE	1360	−500				–	395
68	68	NH_3	NH_3	Ru(phen)$_2$ (NH_3)$_2^{2+}$	H_2O	Ag/Ag$^+$	s ref	570					–	317
68	en	en		Ru(phen)(en)$_2^{2+}$	1.5 M HCl	SCE	SCE	550					–	496
68	en	en		Ru(phen)(en)$_2^{2+}$	H_2O	Ag/Ag$^+$	s ref	290					–	317

68	Hed			Ru(phen)(Hed)	H_2O	SCE	SCE	310	−600				–	481
79	79	79		$Ru(5\text{-Cl-phen})_3^{2+}$	AN	$SCE(H_2O)$	SCE		−1220			1000	–	169
79	79	79		$Ru(5\text{-Cl-phen})_3^{2+}$	AN	$SCE(H_2O)$	SCE	1390			−770		–	149
79	79	79		$Ru(5\text{-Cl-phen})_3^{2+}$	CH_2Cl_2	Ag/AgCl	NHE		−850				–	447
79	79	79		$Ru(5\text{-Cl-phen})_3^{2+}$	H_2O		NHE	1360	−1150	2130	−770	1000	–	12
79	79	79		$Ru(5\text{-Cl-phen})_3^{2+}$	H_2O		NHE	1360	−1150	2150			–	176
80	80	80		$Ru(5\text{-Br-phen})_3^{2+}$	AN	$SCE(H_2O)$	SCE	1400			−760		–	149
80	80	80		$Ru(5\text{-Br-phen})_3^{2+}$	H_2O						−760		–	393
81	81	81		$Ru(5\text{-n-phen})_3^{2+}$	AN	$SCE(H_2O)$	SCE	1490			−670		–	149
81	81	138	Cl	$Ru(5\text{-n-phen})_2(pyr)(Cl)^+$	AN	SSCE	SSCE	990					–	430
83	83	83		$Ru(5\text{-m-phen})_3^{2+}$	AN	$SCE(H_2O)$	SCE	1260			−900		–	149
83	83	83		$Ru(5\text{-m-phen})_3^{2+}$	H_2O		NHE	1230	−1310	2130	−900	890	–	12
84	84	84		$Ru(5\text{-Ph-phen})_3^{2+}$	AN	$SCE(H_2O)$	SCE	1290			−870		–	149
86	86	86		$Ru(4,7\text{-dm-phen})_3^{2+}$	AN	$SCE(H_2O)$	SCE		−1520			670	–	169
86	86	86		$Ru(4,7\text{-dm-phen})_3^{2+}$	AN	$SCE(H_2O)$	SCE	1120			−1010		–	149
86	86	86		$Ru(4,7\text{-dm-phen})_3^{2+}$	CH_2Cl_2	Ag/AgCl	NHE		~ −1210				–	447
86	86	86		$Ru(4,7\text{-dm-phen})_3^{2+}$	H_2O		NHE	1090	−1470	2120			–	176
86	86	86		$Ru(4,7\text{-dm-phen})_3^{2+}$	H_2O		NHE	1070	−1280	2080	−1010	670	–	12
86	86	86		$Ru(4,7\text{-dm-phen})_3^{2+}$	H_2O						−1010		–	393
86	86	86		$Ru(4,7\text{-dm-phen})_3^{2+}$	AN	SCE	SCE	810					–	396
86	86	138	Cl	$Ru(4,7\text{-dm-phen})_2(pyr)(Cl)^+$	AN	SSCE	SSCE	770					–	430
87	87	87		$Ru(4,7\text{-C12-phen})_3^{2+}$	AN	AgRE	SCE	1370	−1160				–	395
88	88	88		$Ru(4,7\text{-Ph2-phen})_3^{2+}$	AN	$SCE(H_2O)$	SCE	1230			−900		E_{red} = irr.	149
88	88	88		$Ru(4,7\text{-Ph2-phen})_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1220			−960		–	224
88	88	88		$Ru(4,7\text{-Ph2-phen})_3^{2+}$	H_2O		NHE	1090	−1470		−1010	670	–	12
93	93	93		$Ru(4,7\text{-dtol-phen})_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1190			−990		–	47
99	99	99		$Ru(5,6\text{-dm-phen})_3^{2+}$	AN	$SCE(H_2O)$	SCE	1230			−930		–	149

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
99	99	99		Ru(5,6-dm-phen)$_3^{2+}$	DMF	SSCE	SSCE	1266	−1288				–	69
99	99	99		Ru(5,6-dm-phen)$_3^{2+}$	H_2O		NHE	1200	−1340	2130	−930	860	–	12
99	99	99		Ru(5,6-dm-phen)$_3^{2+}$	H_2O		NHE	1200	−1340	2140			–	176
99	99	99		Ru(5,6-dm-phen)$_3^{2+}$	AN	SCE	SCE	790					–	396
100	100	100		Ru(tm1-phen)$_3^{2+}$	AN	SCE(H_2O)	SCE	1050			−1110		–	149
100	100	100		Ru(tm1-phen)$_3^{2+}$	CH_2Cl_2	Ag/AgCl	NHE		~ −1330				–	447
100	100	100		Ru(tm1-phen)$_3^{2+}$	H_2O						−1110		–	393
100	100	138	Cl	Ru(tml-phen)$_2$ (pyr)(Cl)$^+$	AN	SSCE	SSCE	730					–	430
101	101	101		Ru(tm2-phen)$_3^{2+}$	AN	SCE(H_2O)	SCE	1120			−1040		–	149
103	103	103		Ru(TAP)$_3^{2+}$	AN	SCE	SCE	1930	−760		< −210	>1380	–	397
104	104	104		Ru(2,7-dm-TAP)$_3^{2+}$	AN	SCE	SCE	1800	−840		< −360	>1320	–	393
108	108	108		Ru(DIAFO)$_3^{2+}$	AN	Ag/$AgNO_3$ *	NHE	1580	−710i				* Ru(bpy)$_3^{2+}$/ +1260 mV	40
109	109	109		Ru(taphen)$_3^{2+}$	AN	Ag/$AgNO_3$	NHE	1600	−700				–	238
109	109	109		Ru(taphen)$_3^{2+}$	AN	Ag/$AgNO_3$ *	NHE	1600	−700	1990	−390	1290	* Ru(bpy)$_3^{2+}$/ +1260 mV	40
110	110	110		Ru(phen-dione)$_3^{2+}$	AN	SSCE	SSCE	1400	−130				–	480
111	181	181	H_2O	tc-Ru(py)(Azpy)$_2$ (H_2O)$^{2+}$	AN	SCE	SCE	1880	−320				–	435
118	181	181	H_2O	tc-Ru(pic)(Azpy)$_2$ (H_2O)$^{2+}$	AN	SCE	SCE	1880	−280				pic = 3-pico-line	435
123	123	123	276	Ru(4-vpy)$_3$ (HCpz3)$^{2+}$	AN	SSCE	SSCE	1170	−1580				–	448
123	123	123	281	Ru(4-vpy)$_3$ (trpy)$^{2+}$	AN	SSCE	SSCE	1230	−1240				–	448
123	123	123	281	Ru(4-vpy)$_3$ (trpy)$^{2+}$	AN	SSCE	SSCE	1230	−1240				–	478
123	123	123	281	Ru(4-vpy)$_3$ (trpy)$^{2+}$	AN	SSCE	SSCE	1210					E_{ox} surf.	478
125	125	125	281	Ru(t-stylb)$_3$ (trpy)$^{2+}$	AN	SSCE	SSCE	1200	−1250				–	448

125	125	281	Cl	$Ru(t\text{-stylb})_2(trpy)(Cl)^+$	AN	SSCE	SSCE	770	−1380	–	448
127	127	127	281	$Ru(4'\text{-Cl-stylb})_3(trpy)^{2+}$	AN	SSCE	SSCE	1200	−1250	–	448
143	143	143		$Ru(2,7\text{-dmnapy})_3^{2+}$	AN	SSCE	SSCE	1370	−1240	$E_{red} = E/p,c$	517
160	160	160	281	$Ru(BPE)_3(trpy)^{2+}$	AN	SSCE	SSCE	1230	−1260	–	448
160	160	160	281	$Ru(BPE)_3(trpy)^{2+}$	AN	SSCE	SSCE	1260	−1220	–	478
160	160	160	281	$Ru(BPE)_3(trpy)^{2+}$	AN	SSCE	SSCE	1240		E_{ox} surf.	478
161	161	161	281	$Ru(PC2)_3(trpy)^{2+}$	AN	SSCE	SSCE	1320	−1220	–	478
161	161	161	281	$Ru(PC2)_3(trpy)^{2+}$	AN	SSCE	SSCE	1320		E_{ox} surf.	478
163	163	163		$Ru(DPAH)_3^{2+}$	AN		Fc+/0	530	−2600	−40 °C, $E_{red} = E/p,c$	235
168	en	en		$Ru(diim)(en)_2^{2+}$	4 M H_2SO_4	SCE	SCE	740		–	496
176	176	176		$Ru(biimH2)_3^{2+}$	AN		NHE	440		–	507
180	180	AN	AN	$Ru(pydipy)_2(AN)_2^{2+}$	AN	SCE	SCE	1360		Deuterated AN	369
180	180	180		$Ru(pydipy)_3^{2+}$	AN	SCE	SCE	1170		–	369
181	181	I	I	$Ru(Azpy)_2(I)_2$	AN	SCE	SCE	853		–	452
181	181	I	I	$Ru(Azpy)_2(I)_2$	CH_2Cl_2	SCE	SCE	910		–	452
181	181	Br	Br	$Ru(Azpy)_2(Br)_2$	AN	SCE	SCE	950		–	452
181	181	Br	Br	$Ru(Azpy)_2(Br)_2$	CH_2Cl_2	SCE	SCE	985		–	452
181	181	Br	Br	$Ru(Azpy)_2(Br)_2$	CH_2Cl_2	$Ru(bpy)_3^{2+}$	SCE	1190	−540	–	375
181	181	CN	CN	$Ru(Azpy)_2(CN)_2$	H_2O				−240	–	376
181	181	CN	CN	$Ru(Azpy)_2(CN)_2$	CH_2Cl_2	$Ru(bpy)_3^{2+}$	SCE		−480	–	375
181	181	Cl	Cl	$Ru(Azpy)_2(Cl)_2$	AN	SCE	SCE	925		–	452
181	181	Cl	Cl	$Ru(Azpy)_2(Cl)_2$	CH_2Cl_2	SCE	SCE	965		–	452
181	181	Cl	Cl	$\alpha\text{-}Ru(Azpy)_2(Cl)_2$	CH_2Cl_2	SCE	SCE	1210		–	500
181	181	Cl	Cl	$\beta\text{-}Ru(Azpy)_2(Cl)_2$	CH_2Cl_2	SCE	SCE	1150		–	500
181	181	Cl	Cl	$\gamma\text{-}Ru(Azpy)_2(Cl)_2$	CH_2Cl_2	SCE	SCE	1000		–	500
181	181	Cl	Cl	$Ru(Azpy)_2(Cl)_2$	AN			1110		–	399
181	181	N_3	N_3	$Ru(Azpy)_2(N_3)_2$	CH_2Cl_2	$Ru(bpy)_3^{2+}$	SCE	960	−520	–	375
181	181	OH	OH	$tc\text{-}Ru(Azpy)_2(OH)_2$	CH_2Cl_2	SCE	SCE	1070	−580	–	435
181	181	en		$Ru(Azpy)_2(en)^{2+}$	AN	$Ru(bpy)_3^{2+}$	SCE		−310	–	375
181	181	en		$Ru(Azpy)_2(en)^{2+}$	H_2O				−70	–	376
181	181	tu	tu	$Ru(Azpy)_2(tu)_2^{2+}$	AN	$Ru(bpy)_3^{2+}$	SCE	1140	−320	–	375
181	181	181		$Ru(Azpy)_3^{2+}$	AN	SCE(H_2O)	SCE	2100	−130	*mer*	432
181	181	181		$Ru(Azpy)_3^{2+}$	CH_2Cl_2	$Ru(bpy)_3^{2+}$	SCE		60	–	375
181	181	181		$Ru(Azpy)_3^{2+}$	AN	$Ru(bpy)_3^{2+}$	SCE		−90	–	375
181	181	181		$Ru(Azpy)_3^{2+}$	AN				−116	–	399
181	181	181		$Ru(Azpy)_3^{2+}$	H_2O				300	–	376
181	181	182		$Ru(Azpy)_2(MeAzpy)^{2+}$	AN	SCE(H_2O)	SCE	2140	−110	*mer*	432

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
181	181	186		$Ru(Azpy)_2(Btz)^{2+}$	AN	$Ru(bpy)_3^{2+}$	SCE	1800	−430				–	375
181	181	186		$Ru(Azpy)_2(Btz)^{2+}$	H_2O			2000	−190				–	376
181	181	H_2O	OH	tc-$Ru(Azpy)_2(H_2O)(OH)^+$	AN	SCE	SCE	1180	−580				–	435
181	181	H_2O	H_2O	tc-$Ru(Azpy)_2(H_2O)_2^{2+}$	AN	SCE	SCE		−360				–	435
181	181	NO_2	NO_2	$Ru(Azpy)_2(NO_2)_2$	CH_2Cl_2	$Ru(bpy)_3^{2+}$	SCE		−460				–	375
181	181	aca		$Ru(Azpy)_2(aca)^+$	CH_2Cl_2	$Ru(bpy)_3^{2+}$	SCE	1540	−380				–	375
181	181	aca		$Ru(Azpy)_2(aca)^+$	H_2O			1780	−140				–	376
181	182	182		$Ru(Azpy)(MeAzpy)_2^{2+}$	AN	SCE(H_2O)	SCE	2190	−80				*mer*	432
182	182	I	I	$Ru(MeAzpy)_2(I)_2$	AN	SCE	SCE	907	−730				–	452
182	182	Br	Br	$Ru(MeAzpy)_2(Br)_2$	AN	SCE	SCE	897	−720				–	452
182	182	Cl	Cl	$Ru(MeAzpy)_2(Cl)_2$	AN	SCE	SCE	907	−730				–	452
182	182	182		$Ru(MeAzpy)_3^{2+}$	AN	SCE(H_2O)	SCE	2230	−100				*mer*	432
182	182	H_2O	H_2O	tc-$Ru(MeAzpy)_2(H_2O)_2^{2+}$	AN	SCE	SCE		−360				–	435
182	182	H_2O	H_2O	cc-$Ru(MeAzpy)_2(H_2O)_2^{2+}$	AN	SCE	SCE		−370				–	435
183	183	Cl	Cl	$Ru(NA)_2(Cl)_2$	AN			1270					–	399
183	183	183		$Ru(NA)_3^{2+}$	AN				15				–	399
184	184	184		$Ru(thpy)_3^{2+}$	1 M HNO_3	SCE	NHE	1280		2010	−730		–	370
185	185	185		$Ru(pmth)_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1310	−1215				–	514
187	187	187		$Ru(bt)_3^{2+}$	AN	$Ag/AgNO_3$	NHE	1248	−954				–	514
188	188	188		$Ru(PTPI)_3^{2+}$	AN	SCE	SCE	1170					E_{ox} from polarogramm	360
189	190	Br	Br	$Ru(L1)(HL1)(Br)_2$	AN	SCE	SCE	420	−850				$E_{red} = E/p$,c	499
189	190	Br	Br	$Ru(L1)(HL1)(Br)_2$	CH_2Cl_2	SCE	SCE	330					–	499
189	190	Cl	Cl	$Ru(L1)(HL1)(Cl)_2$	AN	SCE	SCE	390	−830				$E_{red} = E/p$,c	499
189	190	Cl	Cl	$Ru(L1)(HL1)(Cl)_2$	CH_2Cl_2	SCE	SCE	310					–	499
191	192	Br	Br	$Ru(L2)(HL2)(Br)_2$	AN	SCE	SCE	520	−730				$E_{red} = E/p$,c	499

191	192	Br	Br	$Ru(L2)(HL2)(Br)_2$	CH_2Cl_2	SCE	SCE	420					–	499
191	192	Cl	Cl	$Ru(L2)(HL2)(Cl)_2$	AN	SCE	SCE	480	−780				$E_{red} = E/p$,c	499
191	192	Cl	Cl	$Ru(L2)(HL2)(Cl)_2$	CH_2Cl_2	SCE	SCE	410					–	499
193	194	Br	Br	$Ru(L3)(HL3)(Br)_2$	AN	SCE	SCE	470	−880				$E_{red} = E/p$,c	499
193	194	Br	Br	$Ru(L3)(HL3)(Br)_2$	CH_2Cl_2	SCE	SCE	380					–	499
193	194	Cl	Cl	$Ru(L3)(HL3)(Cl)_2$	AN	SCE	SCE	450	−810				$E_{red} = E/p$,c	499
193	194	Cl	Cl	$Ru(L3)(HL3)(Cl)_2$	CH_2Cl_2	SCE	SCE	360					–	499
195	196	Br	Br	$Ru(L4)(HL4)(Br)_2$	AN	SCE	SCE	460	−850				$E_{red} = E/p$,c	499
195	196	Br	Br	$Ru(L4)(HL4)(Br)_2$	CH_2Cl_2	SCE	SCE	400					–	499
195	196	Cl	Cl	$Ru(L4)(HL4)(Cl)_2$	AN	SCE	SCE	440	−830				$E_{red} = E/p$,c	499
195	196	Cl	Cl	$Ru(L4)(HL4)(Cl)_2$	CH_2Cl_2	SCE	SCE	370					–	499
197	197	Cl	Cl	*trans*-$Ru(mpp)_2(Cl)_2$	CH_2Cl_2	$Ag/AgNO_3$	s ref	−60	−1670				–	505
197	197	Cl	Cl	*cis*-$Ru(mpp)_2(Cl)_2$	CH_2Cl_2	$Ag/AgNO_3$	s ref	220	−1750				–	505
198	198	Cl	Cl	*trans*-$Ru(mtt)_2(Cl)_2$	CH_2Cl_2	$Ag/AgnO_3$	s ref	−100	−1710				–	505
198	198	Cl	Cl	*trans*-$Ru(mtt)_2(Cl)_2$	AN	$Ag/AgNO_3$	s ref	−190	−1640				–	505
198	198	Cl	Cl	*cis*-$Ru(mtt)_2(Cl)_2$	CH_2Cl_2	$Ag/AgNO_3$	s ref	130	−1810				–	505
198	198	Cl	Cl	*cis*-$Ru(mtt)_2(Cl)_2$	AN	$Ag/AgNO_3$	s ref	90	−1710				–	505
199	199	Cl	Cl	*trans*-$Ru(mdm)_2(Cl)_2$	CH_2Cl_2	$Ag/AgNO_3$	s ref	−150	−1770				–	505
199	199	Cl	Cl	*trans*-$Ru(mdm)_2(Cl)_2$	AN	$Ag/AgNO_3$	s ref	−190	−1650				–	505
199	199	Cl	Cl	*cis*-$Ru(mdm)_2(Cl)_2$	CH_2Cl_2	$Ag/AgNO_3$	s ref	160	−1880				–	505
199	199	Cl	Cl	*cis*-$Ru(mdm)_2(Cl)_2$	AN	$Ag/AgNO_3$	s ref	100	−1750				–	505
200	200	Cl	Cl	*trans*-$Ru(mmd)_2(Cl)_2$	CH_2Cl_2	$Ag/AgNO_3$	s ref	−60	−1690				–	505
201	201	Cl	Cl	*trans*-$Ru(hmd)_2(Cl)_2$	CH_2Cl_2	$Ag/AgNO_3$	s ref	190	−1290				–	505
202	202	Cl	Cl	*trans*-$Ru(htt)_2(Cl)_2$	CH_2Cl_2	$Ag/AgNO_3$	s ref	200	−1110				–	505
202	202	Cl	Cl	*cis*-$Ru(htt)_2(Cl)_2$	CH_2Cl_2	$Ag/AgNO_3$	s ref	410	−1200				–	505
202	202	Cl	Cl	*cis*-$Ru(htt)_2(Cl)_2$	AN	$Ag/AgNO_3$	s ref	330	−1280				–	505
243	243			$Ru(4'\text{-MeL})_2$	DMF		NHE	278	−1381				–	498
243	263			Ru(4′-MeL)(L-LH)	DMF		NHE	324					–	498
245	245	245		$Ru(B\text{-bpy-H2})_3^{2+}$	AN	$Ag/AgNO_3$ *	NHE	1230	−1070	1690	−460	620	* $Ru(bpy)_3^{2+}$ / +1260 mV	40

TABLE 3 (continued)

(a) Mononuclear complexes

Ligands				Complex	Solvent	Ref.	Stand.	E_{ox}	E_{red}	E^{0-0}	$^*E_{ox}$	$^*E_{red}$	Notes	Ref.
246	246	246		$Ru(pq)_3^{2+}$	DMF		Fc+/0		−1460				at −54°C	473
246	246	246		$Ru(pq)_3^{2+}$	AN	SSCE	SSCE	1333	−1058				–	473
247	247	247		$Ru(pynapy)_3^{2+}$	AN	SSCE	SSCE	1080	−990	1690	−610	700	–	402
250	250	250		$Ru(DHCH)_3^{2+}$	AN	Ag/Ag NO_3	NHE	1425	−755				–	239
251	251	CN	CN	$Ru(DMCH)_2(CN)_2$	DMF	Ag/Ag NO_3	*	830	−1130		−780	480	* $Ru(bpy)_3^{2+}$/ +1260 mV	221
251	251	CN	CN	$Ru(DMCH)_2(CN)_2$	DMF	Ag/Ag NO_3	*	830	−1130	1690	−860	560	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
251	251	CN	CN	$Ru(DMCH)_2(CN)_2$	AN	Ag/Ag NO_3	*	770	−1230				* $Ru(bpy)_3^{2+}$/ +1260 mV	221
251	251	CN	CN	$Ru(DMCH)_2(CN)_2$	DMF	Ag/Ag NO_3	*	890	−1120				* $Ru(bpy)_3^{2+}$/ +1260 mV	221
251	251	Cl	Cl	$Ru(DMCH)_2(Cl)_2$	DMF	Ag/ $AgNO_3$	*	460	−1010	1430	−970	420	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
251	251	251		$Ru(DMCH)_3^{2+}$	AN	Ag/Ag NO_3	NHE	1260	−895				–	239
251	251	251		$Ru(DMCH)_3^{2+}$	AN	Ag/Ag NO_3	NHE	1260	−900	1690	−430	790	–	329
251	251	251		$Ru(DMCH)_3^{2+}$	AN	Ag/Ag NO_3 *	NHE	1260	−900	1690	−430	790	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
252	252	252		$Ru(DPCH)_3^{2+}$	AN	Ag/Ag NO_3	NHE	1420	−900				–	239
256	256	256		$Ru(dinapy)_3^{2+}$	AN	SSCE	SSCE	970	−830	1480	−510	650	–	402
256	256	256		$Ru(dinapy)_3^{2+}$	AN	Ag/Ag NO_3	NHE	980	−840				–	514
257	257	CN	CN	$Ru(biq)_2(CN)_2$	DMF	Ag/Ag NO_3	*	940	−980		−650	610	* $Ru(bpy)_3^{2+}$/ +1260 mV	221
257	257	CN	CN	$Ru(biq)_2(CN)_2$	DMF	Ag/Ag NO_3	*	940	−980	1680	−740	700	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
257	257	CN	CN	$Ru(biq)_2(CN)_2$	AN	Ag/Ag NO_3	*	900	−1040				* $Ru(bpy)_3^{2+}$/ 1260 mV	221

257	257	CN	CN	$Ru(biq)_2(CN)_2$	DMF	Ag/Ag NO_3	*	1010	−970				* $Ru(bpy)_3^{2+}$/ 1260 mV	221
257	257	Cl	Cl	$Ru(biq)_2(Cl)_2$	DMF	Ag/Ag NO_3	*	610	−900	1450	−840	550	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
257	257	257		$Ru(biq)_3^{2+}$	AN	Ag/Ag NO_3 *	NHE	1470	−730	1730	−260	830	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
257	257	257		$Ru(biq)_3^{2+}$	AN			1470	−730	1730	−260	830	–	344
259	259	CN	CN	$Ru(i\text{-}biq)_2(CN)_2$	DMF	Ag/Ag NO_3	*	730	−1640i		−1420	510	* $Ru(bpy)_3^{2+}$/ +1260 mV	221
259	259	CN	CN	$Ru(i\text{-}biq)_2(CN)_2$	DMF	Ag/Ag NO_3	*	730	−1500	2290	−1560	800	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
259	259	CN	CN	$Ru(i\text{-}biq)_2(CN)_2$	DMF	Ag/Ag NO_3	*	740	−1640i				* $Ru(bpy)_3^{2+}$/ +1260 mV	221
259	259	Cl	Cl	$Ru(i\text{-}biq)_2(Cl)_2$	DMF	Ag/Ag NO_3	*	380	−1460	1700	−1320	240	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
259	259	259		$Ru(i\text{-}biq)_3^{2+}$	AN	Ag/Ag NO_3	NHE	1120	−1510				E_{red} = irr., E/p,c	131
259	259	259		$Ru(i\text{-}biq)_3^{2+}$	AN	Ag/Ag NO_3 *	NHE	1120	−1510i	2300	−1180	~800	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
261	261	261		$Ru(DP)_3^{2+}$	AN	AgRE	SCE	1370	−1000				–	395
261	261	261		$Ru(DP)_3^{2+}$	AN	SCE	*	1385	−916				* $Ru(bpy)_3^{2+}$/ +1260 mV	513
266	266	266		$Ru(Mebpy\text{-}3DQ+2)_3^{8+}$	AN and DMF	SCE	SCE	1150	−1370				E_{ox} = AN, E_{red} = DMF	444
267	267	267		$Ru(dpp)_3^{2+}$	AN	SCE	SCE	1680	−950				–	403
267	267	267		$Ru(dpp)_3^{2+}$	AN	SCE	SCE	1680	−950		−400	1130	–	403
281	281			$Ru(trpy)_2^{2+}$	DMF	SSCE	SSCE	1264	−1266				–	69
281	281			$Ru(trpy)_2^{2+}$	AN	SCE	SCE	1280	−1430				Peak potentials	4
281	281			$Ru(trpy)_2^{2+}$	AN	Ag/Ag NO_3 *	NHE	1260	−1290	2080	−810	790	* $Ru(bpy)_3^{2+}$/ +1260 mV	40
281	281			$Ru(trpy)_2^{2+}$	H_2O		NHE	1250	−1360				–	12
281	NH_3	NH_3	NH_3	$Ru(trpy)(NH_3)_3^{2+}$	AN	SCE	SCE	740	−1530				–	501
286	286			$Ru(TPTZ)_2^{2+}$	AN	SCE	SCE	1520	−840				Peak potentials	4
286	286			$Ru(TPTZ)_2^{2+}$	H_2O		NHE	1490	−770				–	12

TABLE 3 (continued)

(b) Polynuclear complexes

Ligands							Complex	Solvent	Reference	Standard	E_{ox1}	E_{ox2}	E_{red}	Notes	Ref.
1	1	1	1	1	1	102	$(Ru(bpy)_2)_3(NOphen)^{6+}$	Acetone	Ag/AgCl	Ag/AgCl	1480		−1110	-	451
1	1	1	1	1	1	270	$(Ru(bpy)_2)_3(BL3)^{6+}$	AN	SSCE	SSCE	1630	1460	−310	-	372
1	1	1	1	1	$(I)_3$	270	$(Ru(bpy)_2)_4(BL3)^{8+}$	AN	SSCE	SSCE	1640	1460	−220	-	372
1	1	1	1	57	Cl	Cl	$Ru(bpy)_2(Cl)(4,4'\text{-bpy})(Cl)(bpy)_2Ru^{2+}$	AN	SSCE	SSCE	850	800		Differential pulse polarography	440
1	1	1	1	57	Cl	Cl	$Ru(bpy)_2(Cl)(4,4'\text{-bpy})(Cl)(bpy)_2Os^{2+}$	AN	SSCE	SSCE	830	410		Differential pulse polarography	440
1	1	1	1	61			$Ru(bpy)_2(bpym)(bpy)_2Ru^{4+}$	AN	$Ag/AgNO_3$	NHE	1705	1520	−425	-	511
1	1	1	1	61			$Ru(bpy)_2(bpym)(bpy)_2Ru^{4+}$	AN	SSCE	SSCE	1770	1610		Differential pulse polarography, E_{ox1} = irr.	440
1	1	1	1	61			$Ru(bpy)_2(bpym)(bpy)_2Os^{4+}$	AN	SSCE	SSCE	1760	1180		Differential pulse polarography, E_{ox1} = irr.	440
1	1	1	1	61			$Ru(bpy)_2(bpym)(bpy)_2Ru^{4+}$	AN	SCE	SCE	1620	1440		E_{ox} from peak max $(\Delta i/\Delta E)$ plot	360
1	1	1	1	61			$Ru(bpy)_2(bpym)(bpy)_2Ru^{4+}$	AN	SSCE	SSCE	1690	1530	−410	-	454
1	1	1	1	61			$Ru(bpy)_2(bpym)(bpy)_2Ru^{4+}$	AN	$Ru(bpy)_3^{2+}$	NHE	1740	1550		-	361
1	1	1	1	61	Cl	Cl	$Ru(bpy)_2(Cl)(bpym)(Cl)(bpy)_2Ru^{2+}$	AN	SSCE	SSCE	990	870		-	490
1	1	1	1	62			$Ru(bpy)_2(4,4'\text{-dm-bpym})(bpy)_2Ru^{4+}$	AN	SCE	SCE	1600	1430		E_{ox} from peak max $(\Delta i/\Delta E)$ plot	360

1	1	1	1	Cl	Cl		$Ru(bpy)_2(Cl)_2(bpy)_2Ru^{2+}$	CH_2Cl_2	SSCE	SSCE	1460	910		–	457
1	1	1	1	138	Cl	Cl	$Ru(bpy)_2(Cl)(pyr)(Cl)(bpy)_2Ru^{2+}$	AN	SSCE	SSCE	1020	890		Differential pulse polarography	440
1	1	1	1	138	Cl	Cl	$Ru(bpy)_2(Cl)(pyr)(Cl)(bpy)_2Os^{2+}$	AN	SSCE	SSCE	1010	510		Differential pulse polarography	440
1	1	1	1	138	Cl	Cl	$Ru(bpy)_2(Cl)(pyr)(Cl)(bpy)_2Ru^{2+}$	AN	SSCE	SSCE	1010	890		–	466
1	1	1	1	139	Cl		$Ru(bpy)_2(Cl)(pyzc)(bpy)_2Ru^{2+}$	AN	SSCE	SSCE	1140	930		Differential pulse polarography	440
1	1	1	1	139	Cl		$Ru(bpy)_2(Cl)(pyzc)(bpy)_2Os^{2+}$	AN	SSCE	SSCE	1060	620		Differential pulse polarography	440
1	1	1	1	144	144		$Ru(bpy)_2(pz)_2(bpy)_2Ru^{2+}$	AN	SSCE	SSCE	1210	830		–	367
1	1	1	1	177			$Ru(bpy)_2(BiBzim)(bpy)_2Ru^{2+}$	AN	SCE	SCE	1040	740		–	485
1	1	1	1	267			$Ru(bpy)_2(dpp)(bpy)_2Ru^{4+}$	AN	Ag/AgCl	NHE	1756	1566		$E_{ox} = (E/p,a + E/p,c)2$	103
1	1	1	1	268			$Ru(bpy)_2(BL1)(bpy)_2Ru^{4+}$	AN	SSCE	SSCE	1620	1470	−370	–	454
1	1	1	1	269			$Ru(bpy)_2(BL2)(bpy)_2Ru^{4+}$	AN	SSCE	SSCE		1450	−160	–	454
1	1	1	1	270			$Ru(bpy)_2(BL3)(bpy)_2Ru^{4+}$	AN	SSCE	SSCE		1420	−670	–	372

TABLE 3 (continued)

(b) Polynuclear complexes

Ligands							Complex	Solvent	Reference	Standard	E_{ox1}	E_{ox2}	E_{red}	Notes	Ref.
1	1	1	1	275			$Ru(bpy)_2(difln)(bpy)_2Ru^{4+}$	AN	$Ag/AgNO_3$	NHE	1415	1415	−240	-	511
1	1	1	1	277			$Ru(bpy)_2(2diphen)(bpy)_2Ru^{4+}$	Acetone	Ag/AgCl	Ag/AgCl	1470		−1090	-	451
1	1	1	1	278			$Ru(bpy)_2(4diphen)(bpy)_2Ru^{4+}$	Acetone	Ag/AgCl	Ag/AgCl	1440		−1100	-	451
1	1	1	1	279			$Ru(bpy)_2(2amdiphen)(bpy)_2Ru^{4+}$	Acetone	Ag/AgCl	Ag/AgCl	1460		−1000	-	451
1	1	1	1	280			$Ru(bpy)_2(3amdiphen)(bpy)_2Ru^{4+}$	Acetone	Ag/AgCl	Ag/AgCl	1520		−960	-	451
1	1	57	57	$(NH_3)_{10}$			$(Ru(bpy)_2(Ru(4,4'\text{-bpy})(NH_3)_5)_2^{6+}$	AN	SSCE	SSCE	1370	430		-	459
1	1	57	Cl	NH_3	NH_3	$(NH_3)_3$	$Ru(bpy)_2(Cl)(4,4'\text{-bpy})(NH_3)_5Ru^{3+}$	AN	SSCE	SSCE	830	430		-	510
1	1	61	257	257			$Ru(bpy)_2(bpym)(biq)_2Ru^{4+}$	AN	$Ag/AgNO_3$	NHE	1765	1620	−275	-	511
1	1	68	68	177			$Ru(bpy)_2(BiBzim)(phen)_2Ru^{2+}$	AN	SCE	SCE	1020	730		-	485
1	1	111	138	Cl	NH_3	$(NH_3)_3$	$Ru(bpy)_2(Cl)(pyr)(py)(NH_3)_4Ru^{3+}$	AN	SCE	SCE	1012	735		-	508
1	1	114	138	Cl	NH_3	$(NH_3)_3$	$Ru(bpy)_2(Cl)(pyr)(3\text{-Cl-py})(NH_3)_4Ru^{3+}$	AN	SCE	SCE	1005	770		-	508
1	1	138	Cl	NH_3	NH_3	$(NH_3)_3$	$Ru(bpy)_2(Cl)(pyr)(NH_3)_5Ru^{3+}$	AN	SCE	SCE	965	545		-	508

1	1	138	Cl	NH_3	NH_3	$(NH_3)_3$	$Ru(bpy)_2$ (Cl)(pyr) $(NH_3)_5Ru^{3+}$	AN	SCE	SCE	1030	610		-	510
1	1	138	138	$(NH_3)_{10}$			$(Ru(bpy)_2$ (Ru(pyr) $(NH_3)_5)_2^{6+}$	AN	SSCE	SSCE	1790	700		-	459
1	1	159	Cl	NH_3	NH_3	$(NH_3)_3$	$Ru(bpy)_2$ (Cl)(BPA) $(NH_3)_5Ru^{3+}$	AN	SSCE	SSCE	790	370		-	510
1	1	159	159	$(NH_3)_{10}$			$(Ru(bpy)_2$ (Ru(BPA) $(NH_3)_5)_2^{6+}$	AN	SSCE	SSCE	1270	360		-	459
1	1	160	Cl	NH_3	NH_3	$(NH_3)_3$	$Ru(bpy)_2$ (Cl)(BPE) $(NH_3)_5Ru^{3+}$	AN	SCE	SCE	810	410		-	510
1	1	160	160	$(NH_3)_{10}$			$(Ru(bpy)_2$ (Ru(BPE) $(NH_3)_5)_2^{6+}$	AN	SSCE	SSCE	1320	400		-	459
1	1	CN	CN	$(NH_3)_5$			$Ru(NH_3)_5$ $CN(bpy)_2$ $RuCN^{2+}$	DMF	SCE	SCE	1140	−170		-	518
1	1	CN	CN	$(NH_3)_5$			$Ru(NH_3)_5$ $CN(bpy)_2$ $RuCN^{2+}$	H_2O	SCE	SCE	−100			-	518
1	1	CN	CN	$(NH_3)_{10}$			$Ru(bpy)_2$ $(CN)_2(Ru$ $(NH_3)_5)_2^{4+}$	DMF	SCE	SCE	−90	−174	−1520	-	518
1	1	CN	CN	$(NH_3)_{10}$			$Ru(bpy)_2$ $(CN)_2(Ru$ $(NH_3)_5)_2^{5+}$	DMF	SCE	SCE	1240	−90	−174	-	518
1	1	CN	CN	$(NH_3)_{10}$			$Ru(bpy)_2$ $(CN)_2(Ru$ $(NH_3)_5)_2^{4+}$	H_2O	SCE	SCE	−55	−125		-	518
1	1	CN	CN	$(NH_3)_{10}$			$Ru(bpy)_2$ $(CN)_2(Ru$ $(NH_3)_5)_2^{5+}$	H_2O	SCE	SCE	1170	−55		-	518
61	$(NH_3)_8$						$Ru(NH_3)_4$ (bpym) $(NH_3)_4Ru^{4+}$	H_2O		NHE	1020	830		-	460

F. APPENDIX

(i) Abbreviations for ligands

Numbered ligands

N		
4	4-a-bpy	4-amino-2,2′-bipyridine
119	4-acetyl-py	4-acetyl-pyridine
113	2-AEP	2-(2-aminoethyl)pyridine
116	3-AEP	3-(2-aminoethyl)pyridine
154	All-trz	4-allyl-1,2,4-triazole
279	2amdiphen	3-oxopentamethylenebis(1,10-phenanthroline-2-carboxamide)
280	3amdiphen	3,6-dioxooctamethylenebis(1,10-phenanthroline-2-carboxamide)
82	5-a-phen	5-amino-1,10-phenanthroline
181	Azpy	2-(phenylazo)pyridine
22	4,4′-BAA-bpy	4,4′-bis(acetoamido)-2,2′-bipyridine
52	5,5′-BAA-bpy	5,5′-bisacetoamido-2,2′-bipyridine
89	4,7-bbr-phen	4,7-bis-(*p*-bromophenyl)-1,10-phenanthroline
105	BDCMP	4,7-bis(dicyanomethylydene)-1,4,7,10-tetrahydro-1,10-phenanthroline
106	BDCMPH2	4,7-bis(dicyanomethylydene)-1,4,7,10-tetrahydro-1,10-phenanthroline
177	BiBzim	2,2′-dibenzimidazolate dianion
178	BiBzimH	2,2′-dibenzimidazolate anion
179	$BiBzimH_2$	2,2′-dibenzimidazole
174	Biim	2,2′-biimidazolate dianion
175	BiimH	2,2′-biimidazolate anion
176	$biimH_2$	2,2′-biimidazole
257	biq	2,2′-biquinoline
268	BL1	2,3-di-2-pyridylquinoxaline
269	BL2	2,3,7,8-tetra-2-pyridylpyrazino[2,3-*g*]quinoxaline
270	BL3	2,2′,3,3′-tetra-2-pyridyl-6,6′-biquinoxaline
271	BL4	1,2-bis[4-(4′-methyl-2,2′-bipyridyl)]ethane
272	BL5	1,5-bis[4-(4′-methyl-2,2′-bipyridyl)]pentane
273	BL6	1,4-bis[4-(α-ethyl)-4′-methyl-2,2′-bipyridyl]benzene
274	BL7	1,12-bis[4-(4′-methyl-2,2′-bipyridyl)]dodecane
90	4,7-bmo-phen	4,7-bis(*p*-methoxyphenyl)-1,10-phenanthroline
8	4-bo-bpy	4-benzyl-oxy-2,2′-bipyridine
159	BPA	1,2-bis-(4-pyridyl)-ethane

95	4,7-bpbr-phen	4-*p*-biphenylyl-7-*p*-bromophenyl-1,10-phenanthroline
160	BPE	*trans*-1,2-bis-(4-pyridyl)-ethylene
91	4,7-bph$_2$-phen	4,7-bis-(biphenylyl)-1,10-phenanthroline
76	4-bph-phen	4-*p*-biphenylyl-1,10-phenanthroline
96	4,7-bpmo-phen	4-*p*-biphenylyl-7-*p*-methoxyphenyl-1,10-phenanthroline
97	4,7-bpph-phen	4-*p*-biphenylyl-7-phenyl-1,10-phenanthroline
64	bprid	3,3′-bipyridazine
1	bpy	2,2′-bipyridine
57	4,4′-bpy	4,4′-bipyridine
49	bpyCOOH	polymeric bpy ligand (see figure)
61	bpym	2,2′-bipyrimidine
59	bpz	2,2′-bipyrazine
60	bpzH	protonated bpz
3	4-Br-bpy	4-bromo-2,2′-bipyridine
98	4,7-brmo-phen	4-*p*-bromophenyl-7-*p*-methoxyphenyl-1,10-phenanthroline
80	5-Br-phen	5-bromo-1,10-phenanthroline
77	4-BrPh-phen	4-*p*-bromophenyl-1,10-phenanthroline
187	bt	2,2′-bi-2-thiazoline
186	Btz	4,4′-bithiazole
35	C12B	*N*,*N*′-di(dodecyl)-2,2′-bipyridine-4,4′-dicarboxyamide
36	C16B	*N*,*N*′-di(hexadecyl)-2,2′-bipyridine-4,4′-dicarboxyamide
87	4,7-Cl$_2$-phen	4,7-dichloro-1,10-phenanthroline
2	4-Cl-bpy	4-chloro-2,2′-bipyridine
72	4-Cl-phen	4-chloro-1,10-phenanthroline
79	5-Cl-phen	5-chloro-1,10-phenanthroline
114	3-Cl-py	3-chloro-pyridine
127	4′-Cl-stylb	4′-Cl-*trans*-4-stilbazole
45	4,4′-cm-bpy	4-carboxy-4′-methyl-2,2′-bipyridine
129	4′-CN-stylb	4′-cyano-*trans*-4-stilbazole
19	4,4′-da-bpy	4,4′-diamino-2,2′-bipyridine
25	4,4′-DBO-bpy	4,4′-dibenzyloxy-2,2′-bipyridine
17	4,4′-dBr-bpy	4,4′-dibromo-2,2′-bipyridine
27	4,4′-dbz-bpy	4,4′-dibenzyl-2,2′-bipyridine
44	4,4′-DCA-bpy	*N*,*N*′-di(ethyl)-2,2′-bipyridine-4,4′-dicarboxamide
40	4,4′-DCB-bpy	4,4′-dicarboxybenzyl-2,2′-bipyridine
29	4,4′-dc-bpy	4,4′-dicarboxy-2,2′-bipyridine

39	4,4′-DCC-bpy	4,4′-dicarboxycyclohexyl-2,2′-bipyridine
37	4,4′-DCE-bpy	4,4′-dicarboxyethyl-2,2′-bipyridine
51	5,5′-DCE-bpy	5,5′-dicarboxyethyl-2,2′-bipyridine
14	3,3′-DCI-bpy	3,3′-dicarboxyisopropyl-2,2′-bipyridine
38	4,4′-DCI-bpy	4,4′-dicarboxyisopropyl-2,2′-bipyridine
53	5,5′-DCI-bpy	5,5′-dicarboxyisopropyl-2,2′-bipyridine
16	4,4′-dCl-dpy	4,4′-dichloro-2,2′-bipyridine
34	4,4′-DCM-bpy	4,4′-dicarboxymethyl-2,2′-bipyridine
41	4,4′-DCNE-bpy	4,4′-dicarboxynaphth-2-yl-2,2′-bipyridine
42	4,4′-DCNY-bpy	4,4′-dicarboxynaphthan-1-yl-2,2′-bipyridine
21	4,4′-DEA-bpy	4,4′-bis(diethylamino)-2,2′-bipyridine
23	4,4′-DEO-bpy	4,4′-diethoxy-2,2′-bipyridine
43	4,4′-DHC-bpy	4,4′-dicarboxydihydrocholesteryl-2,2′-bipyridine
250	DHCH	See figure
94	4,7-dhy-phen	4,7-dihydroxy-1,10-phenanthroline
107	DIAF	4,5-diazafluorene
108	DIAFO	4,5-diazafluoren-9-one
275	difln	see figure
168	diim	glyoxal-diimine
256	dinapy	5,6-dihydro-dipyrido[3,2-*b* : 2′,3′-*j*][1,10]phenanthroline
277	2diphen	2,2′-(3-oxopentamethylenedioxy)bis(1,10-phenanthroline)
278	4diphen	2,2′-(3,6,9-trioxoundecamethylenedioxy)bis(1,10-phenanthroline)
5	4-dma-bpy	4-dimethylamino-2,2′-bipyridine
258	dm-biq	4,4′-dimethyl-2,2′-biquinoline
13	3,3′-dm-bpy	3,3′-dimethyl-2,2′-bipyridine
15	4,4′-dm-bpy	4,4′-dimethyl-2,2′-bipyridine
50	5,5′-dm-bpy	5,5′-dimethyl-2,2′-bipyridine
54	6,6′-dm-bpy	6,6′-dimethyl-2,2′-bipyridine
62	4,4′-dm-bpym	4,4′-dimethyl-2,2′-bipyrimidine
63	6,6′-dm-bpym	6,6′-dimethyl-4,4′-bipyrimidine
251	DMCH	5,6-dihydro-4,7-dimethyldibenzo[3,2-*b* : 2′,3′-*j*][1,10]phenanthroline
143	2,7-dm-napy	2,7-dimethyl-1,8-naphthyridine
85	2,9-dm-phen	2,9-dimethyl-1,10-phenanthroline
86	4,7-dm-phen	4,7-dimethyl-1,10-phenanthroline
99	5,6-dm-phen	5,6-dimethyl-1,10-phenanthroline
104	2,7-dm-TAP	2,7-dimethyl-1,4,5,8-tetraazaphenanthrene
18	4,4′-dn-bpy	4,4′-dinitro-2,2′-bipyridine
31	4,4′-dnd-bpy	4,4′-dinonadecyl-2,2′-bipyridine

261	DP	dipyrido[3,2-*a* : 2′,3′-*c*]phenazine
162	DPA	di-2-pyridylamine anion
163	DPAH	di-2-pyridylamine
252	DPCH	See figure
158	DPE	di-(2-pyridyl)-ethane
26	4,4′-dph-bpy	4,4′-diphenyl-2,2′-bipyridine
157	DPM	di-(2-pyridyl)-methane
24	4,4′-DPO-bpy	4,4′-diphenoxy-2,2′-bipyridine
267	dpp	2,3-bis(2-pyridyl)-pyrazine
285	dpt	6,6′-diphenyl-2,2′,2″-terpyridine
284	dqp	2,6-di-(2′-quinolyl)pyridine
20	4,4′-ds-bpy	4,4′-disulphonate-2,2′-bipyridine
92	4,7-dsph-phen	disulfonated 4,7-diphenyl-1,10-phenanthroline
32	4,4′-dst-bpy	4,4′-distearyl-2,2′-bipyridine
28	4,4′-dsty-bpy	4,4′-distyryl-2,2′-bipyridine
30	4,4′-DTB-bpy	4,4′-di-tert-butyl-2,2′-bipyridine
93	4,7-dtol-phen	4,7-ditolyl-1,10-phenanthroline
229	e1	hydroxyimatoacetophenone
231	e2	hydroxyimatopropiophenone
233	e3	α-benzil-oximato
235	e4	biacetyl-oximato
237	e5	hydroxyimatopropyl-methyl-ketone
239	e6	α-hydroxyimato-α-phenylacetone
241	e7	hydroxyimatomalonamide
242	e8	alloxane-5-oximato
208	EtTrOCl	1-ethyl-3-*p*-chlorphenyltriazene-1-oxidato
209	EtTROCOOEt	1-ethyl-3-*p*-carboxyethylphenyltriazene-1-oxidato
207	EtTROH	1-ethyl-3-phenyltriazene-1-oxidato
206	EtTROMe	1-ethyl-3-*p*-tolyltriazene-1-oxidato
210	EtTRONO2	1-ethyl-3-*p*-nitrophenyltriazene-1-oxidato
260	H2por	See figure
56	H4-bpy	3,4,5,6-tetrahydro-2,2′-bipyridine
276	HCpz3	tris-(pyrazolyl)-methane
230	He1	hydroxyiminoacetophenone
232	He2	hydroxyiminopropiophenone
234	He3	α-benzil-oxime
236	He4	biacetyl-oxime
238	He5	hydroxyiminopropyl-methyl-ketone
240	He6	α-hydroxyimino-α-phenylacetone
219	HHyamCl	*p*-chlorphenylhydroxamato
218	HHyamH	phenylhydroxamato
217	HHyamMe	*p*-tolylhydroxamato

220	HHyamNO2	*p*-nitrophenylhydroxamato
216	HHyamOMe	*p*-methoxyphenylhydroxamato
190	HL1	α-(phenylazo)acetaldoximato-*N*, *N*″
192	HL2	α-(phenylazo)benzaldoximato-*N*, *N*″
194	HL3	α-(*p*-tolylazo)benzaldoximato-*N*, *N*″
196	HL4	α-(phenylazo)-*p*-tolualdoximato-*N*, *N*″
201	hmd	1,4-di(2,6-dimethyl-phenyl)-1,4-diazabutadiene
67	h-phen	5,6-dihydro-1,10-phenanthroline
245	hpiq	3,4-dihydro-1(2-pyridyl)-isoquinoline
155	Htrz	1,2,4-triazole cation (+ H)
202	htt	1,4-di(*p*-tolyl)-1,4-diazabutadiene
227	HyamH	phenylhydroximato
228	HyamNO2	*p*-nitrophenylhydroximato
226	HyamOMe	*p*-methoxyphenylhydroximato
259	i-biq	3,3′-biisoquinoline
146	imid	imidazole
167	impy	pyridyl-2-imine
120	i-nic	isonicotinic acid
121	i-nicam	isonicotinic acidamide
164	ipa	isopropylideneamido anion
115	3-I-py	3-iodo-pyridine
189	L1	α-(phenylazo)acetaldoxime-*N*, *N*″
191	L2	α-(phenylazo)benzaldoxime-*N*, *N*″
193	L3	α-(*p*-tolylazo)benzaldoxime-*N*, *N*″
195	L4	α-(phenylazo)-*p*-tolualdoxime-*N*, *N*″
263	L-LH	1,3,5,7-tetrakis(2-(4-*sec*-butylpyridyl)imino)benzodi-pyrrole-anion
58	m-4,4′-bpy	*N*-methyl-4,4′-bipyridine
10	6-m-bpy	6-methyl-2,2′-bipyridine
131	m-cinn	*N*-(3-pyridyl)cinnamamide
199	mdm	1,4-di(3,5-dimethyl-phenyl)-2,3-dimethyl-1,4-diazabutadiene
182	MeAzpy	2-(3-tolyl-azo)pyridine
265	Me-bpy-2DQ + 2	See figure
266	Me-bpy-3DQ + 2	See figure
264	Me-bpy-me-bpy	1,2-bis[4-(4′-methyl-2,2′-bipyridyl)]ethane
224	MeHyamCl	*N*-methyl-*p*-chlorphenylhydroxamato
223	MeHyamH	*N*-methyl-phenylhydroxamato
222	MeHyamMe	*N*-methyl-*p*-tolylhydroxamato
225	MeHyamNO2	*N*-methyl-*p*-nitrophenylhydroxamato
221	MeHyamOMe	*N*-methyl-*p*-methoxyphenylhydroxamato
243	4′-MeL	1,3-bis(2-(4-methylpyridyl)imino)isoindolinato

70	2-meo-phen	2-methoxy-1,10-phenanthroline
248	MMCH	See figure
200	mmd	1,4-di(2,6-dimethyl-phenyl)-2,3-dimethyl-1,4-di - azabu- tadiene
142	2-m-napy	2-methyl-1,8-naphthyridine
6	4-mo-bpy	4-methoxy-2,2′-bipyridine
78	4-MoPh-phen	4-*p*-methoxyphenyl-1,10-phenanthroline
249	MPCH	See figure
69	2-m-phen	2-methyl-1,10-phenanthroline
73	4-m-phen	4-methyl-1,10-phenanthroline
83	5-m-phen	5-methyl-1,10-phenanthroline
197	mpp	1,4-diphenyl-2,3-dimethyl-1,4-diazabutadiene
152	m-trz	4-methyl-1,2,4-triazole
198	mtt	1,4-di(*p*-tolyl)-2,3-dimethyl-1,4-diazabutadiene
183	NA	2-((4-nitrophenyl)azo)pyridine
140	napy	1,8-naphthyridine
7	4-n-bpy	4-nitro-2,2′-bipyridine
134	N-Me-py	*N*-(4-pyridyl)-*β*-(3-*N*- methylpyridyl)acrylamide(PF_6)
147	NMI	*N*-methyl-imidazole
102	NOphen	2,2′,2″-tris((1,10-phenanthrolin-2- yloxy)ethyl)amine
81	5-n-phen	5-nitro-1,10-phenanthroline
203	NPP	2-(3-nitrophenyl)-pyridine
204	OBzim	2-(*o*-hydroxyphenyl)-benzimidazolate anion
205	OBzimH	2-(*o*-hydroxyphenyl)-benzimidazole
255	OMCH	4,7-dimethyldibenzo[3,2-*b* : 2′,3′- *j*][1,10]phenanthroline
128	4′-OMe-stylb	4′-methoxy-*trans*-4-stilbazole
165	opdi	*o*-phenylenediimine
172	PBzim	2-(2-pyridyl)benzimidazolate anion
173	PBzimH	2-(2-pyridyl)benzimidazole
161	PC2	bis-(4-pyridyl)-acetylene
132	p-CH2-cinn	*N*-(4-pyridylmethyl)cinnamamide
130	p-cinn	*N*-(4-pyridyl)cinnamamide
71	Pc-phen	*N*-n-propyl-1,10-phenanthroline-2-carboxamide
262	9-PDP	9-phenyldipyrido[3,2-*a* : 2′,3′-*c*]phenazine cation
133	p-fum	*N*-(4-pyridyl)fumaramide ethylester
166	phedi	*o*-phenanthroline-5,6-diimine
68	phen	1,10-phenanthroline
110	phen-dione	1,10-phenanthroline-5,6-dione

88	4,7-Ph_2-phen	4,7-diphenyl-1,10-phenanthroline
74	4-Ph-phen	4-phenyl-1,10-phenanthroline
84	5-Ph-phen	5-phenyl-1,10-phenanthroline
213	PhTROCl	1-phenyl-3-*p*-chlorphenyltriazene-1-oxidato
214	PhTrOCOOEt	1-phenyl-3-*p*-carboxyethylphenyltriazene-1-oxidato
212	PhTROH	1-phenyl-3-phenyltriazene-1-oxidato
211	PhTROMe	1-phenyl-3-*p*-tolyltriazene-1-oxidato
215	PhTRONO2	1-phenyl-3-*p*-nitrophenyltriazene-1-oxidato
153	Ph-trz	4-phenyl-1,2,4-triazole
118	pic	4-methyl-pyridine
170	Pim	2-(2-pyridyl)imidazolate anion
171	PimH	2-(2-pyridyl)imidazole
244	piq	1-(2-pyridyl)-isoquinoline
112	PMA	2-aminomethylpyridine
185	pmth	2-(2-pyridyl)-4-methyl-thiazole
33	4,4′-poeg-bpy	See figure
141	ppyz	pyrido[2,3-*b*]pyrazine
246	pq	2-(2-pyridyl)-quinoline
48	P(St-Vbpy)	copolymer styrene/4-methyl-4′-vinyl-2,2′-bipyridine
188	PTPI	2-*p*-tolyl-pyridinecarboxaldimine
156	PTZ	phenothiazine
149	PVI	polyvinylimidazole
124	PVP	poly(4-vinylpyridine)
111	py	pyridine
137	pyd	pyridazine
180	pydipy	1-(2-pyridyl)-3,5-dimethyl-pyrazole
135	pym	pyrimidine
136	pymH	protonated pyrimidine
169	pymi	*N*-methyl-(2-pyridyl)-imine
247	pynapy	2-(2-pyridyl)-1,8-naphthyridine
65	4-py-prim	4-methyl-2(2′-pyridyl)-pyrimidine
66	6-py-prim	6-methyl-4-(2′-pyridyl)-pyrimidine
138	pyr	pyrazine
117	3-pyr-py	3-(pyrrol-1-ylmethyl)-pyridine
139	pyzc	pyrazine carboxylate
144	pz	pyrazole anion
145	pzH	pyrazole
11	6-sty-bpy	6-*p*-styryl-2,2′-bipyridine
126	c-stylb	*c*-stilbazole
125	t-stylb	*t*-stilbazole

103	TAP	1,4,5,8-tetraazaphenanthrene
109	taphen	dipyrido[3,2-*c* : 2′,3′-*e*]pyridazine
122	t-bupy	4-*tert*-butyl-pyridine
9	4-tep-bpy	4-(triethylphosphonio)-2,2′-bipyridine
184	thpy	2-(2′-thiazolyl)-pyridine
55	tm-bpy	4,4′,5,5′-tetramethyl-2,2′-bipyridine
253	TMCH	See figure
100	tml-phen	3,4,7,8-tetramethyl-1,10-phenanthroline
101	tm2-phen	3,5,6,8-tetramethyl-1,10-phenanthroline
12	6-tol-bpy	6-*p*-tolyl-2,2′-bipyridine
75	4-tol-phen	4-tolyl-1,10-phenanthroline
254	TPCH	See figure
286	TPTZ	2,4,6-tripyridyl-*s*-triazine
282	tro	4′-phenyl-2,2′,2″-tripyridine
281	trpy	2,2′,2″-tripyridine
151	trz	1,2,4-triazole
150	trza	1,2,4-triazole anion
283	tsite	4,4′,4″-triphenyl-2,2′,2″-tripyridine
47	VB	polymeric v-bpy ligand
46	v-bpy	4-vinyl-4′-methyl-2,2′-bipyridine
148	viz	*N*-vinylimidazole
123	4-vpy	4-vinylpyridine

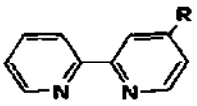
Unnumbered ligands

2SA	1,2-bis(methylthio)ethane
2SB	1,2-bis(ethylthio)ethane
2SC	1,2-bis(phenylthio)ethane
2SD	3,4-bis(methylthio)toluene
aca	acetylacetonato anion
ADP	1,2-bis(diphenylphosphino)acetylene
AN	acetonitrile
BA	butylamine
BBB	tributylphosphine
Bic	benzyl isocyanide
Br	bromide anion
Cl	chloride anion
CLO	perchlorate anion
CN	cyanide ion
CO	carbonyl
DAC	*trans*-1,2-diamminocyclohexane
DAM	1,2-diamino-2-methyl-propane

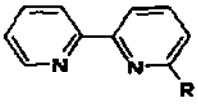
dia	*o*-phenylenebis(dimethylarsine)
dmp	1,2-bis(diphenylphosphino)ethane
ECN	acrylonitrile
EDP	*cis*-1,2-bis(diphenylphosphino)ethylene
en	1,2-ethylenediamine
For	formiate anion
gly	glycinate anion
H	hydride anion
H2	di-hydrogen
H2O	water
Hed	H_2-ethylenediaminetetraacetate
I	iodide anion
IPA	isopropylamine
ipp	isonitrosopropiophenonato anion
MDP	1,1-bis(diphenylphosphino)methane
MeP	tritolylphosphine
MMP	dimethyl-phenyl-phosphine
Mpc	4-methoxyphenylcyanide
MPP	methyl-diphenyl-phosphine
N3	azide anion
NO	nitrosonium cation
NO2	nitrite anion
nor	norbornadiene
OH	hydroxide anion
ON1	methylnitrite
ON2	ethylnitrite
ON3	n-butylnitrite
ON4	i-propylnitrite
OX	oxalate anion
Pas	triphenylarsine
PCN	benzonitrile
PDA	1,1-bis(diphenylarsino)methane
PDP	1,3-bis(diphenylphosphino)propane
PEA	3-amino-1-propene
PMA	benzylamine
PPP	triphenylphosphine
PRC	butyronitrile
PSB	triphenylstibine
PTS	*p*-toluol-sulfonate anion
SCN	thiocyanate anion
SEE	diethylsulfide
SF	pentafluorothiophenolato anion

SMM	dimethylsulfide
SMP	methyl-phenylsulfide
SNA	2-(methylthio)1-aminoethane
SNB	2-(benzylthio)-1-aminoethane
SNC	2-(phenylthio)-1-aminoethane
SND	8-(methylthio)-quinoline
SNE	8-mercaptoquinoline anion
SNO	2-(methylsulfinyl)-1-aminoethane
SP	thiophenolato anion
SSB	pyrrolidinecarbodithionato anion
SSE	diethyldithiocarbamato anion
SSM	dimethyldithiocarbamato anion
SSO	ethylxanthato anion
TFA	trifluoroacetate anion
TN	propylenediamine
tu	thiourea

Structural formulae of the ligands

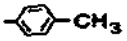


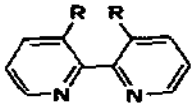
1 R = H
2 R = Cl
3 R = Br
4 R = NH_2
5 R = $N(CH_3)_2$
6 R = OCH_3
7 R = NO_2
8 R = $OCH_2C_6H_5$
9 R = $P(C_2H_5)_3^+$



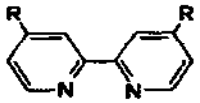
10 R = CH_3

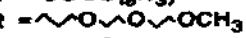
11 R = 

12 R = 

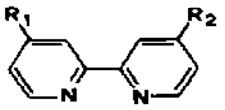


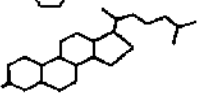
13 R = CH_3
14 R = $COO-CH(CH_3)_2$

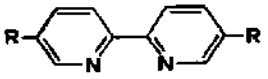


15 R = CH_3
16 R = Cl
17 R = Br
18 R = NO_2
19 R = NH_2
20 R = SO_3H
21 R = $N(C_2H_5)_2$
22 R = $NHCOCH_3$
23 R = OC_2H_5
24 R = OC_6H_5
25 R = $OCH_2C_6H_5$
26 R = C_6H_5
27 R = $CH_2C_6H_5$
28 R = $CH=CHC_6H_5$
29 R = COOH
30 R = $C(CH_3)_3$
31 R = $C_{19}H_{39}$
32 R = $COOC_{18}H_{37}$
33 R = 
34 R = $COOCH_3$
35 R = $CONHC_{12}H_{25}$

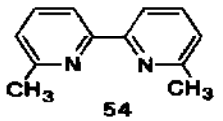
36 R = $CONHC_{18}H_{33}$
37 R = $COOC_2H_5$
38 R = $COO-CH(CH_3)_2$
39 R = COO-



40 $R_1 = R_2 = COOCH_2C_6H_5$
41 $R_1 = R_2 =$ COO- 
42 $R_1 = R_2 =$ COO- 
43 $R_1 = R_2 =$ COO- 
44 $R_1 = R_2 = CON(C_2H_5)_2$
45 $R_1 = COOH$, $R_2 = CH_3$
46 $R_1 = CH=CH_2$, $R_2 = CH_3$
47 $R_1 = -[CH-CH_2]_n-$, $R_2 = CH_3$
48 as 47, copolymer with styrene
49 $R_1 = COOH$
$R_2 = CONH-C_6H_4-(CH-CH_2)_n-$
copolymer with N-vinyl pyrrolidone



50 R = CH_3
51 R = $COOC_2H_5$
52 R = $NHCOCH_3$
53 R = $COO-CH(CH_3)_2$



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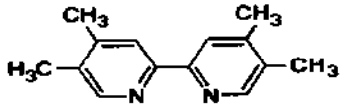

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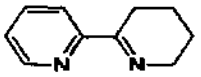

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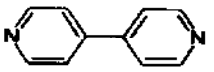

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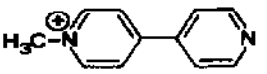

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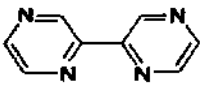

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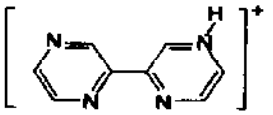

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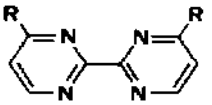
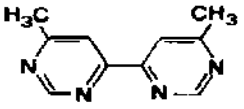


61 R = H
62 R = CH_3



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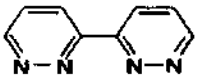

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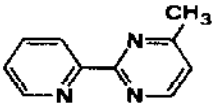

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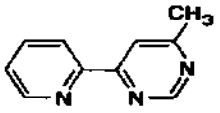

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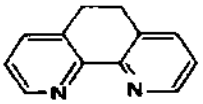

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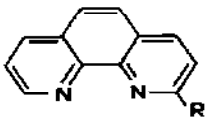
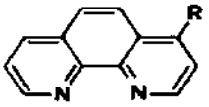
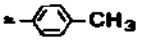
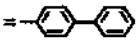
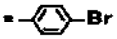
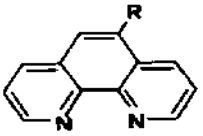


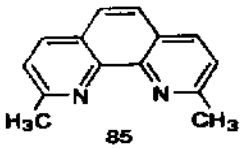
68 R = H
69 R = CH_3
70 R = OCH_3
71 R = $CONHC_3H_7$



72 R = Cl
73 R = CH_3
74 R = C_6H_5
75 R = 
76 R = 
77 R = 
78 R = 



79 R = Cl
80 R = Br
81 R = NO_2
82 R = NH_2
83 R = CH_3
84 R = C_6H_5



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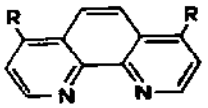
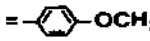
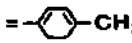
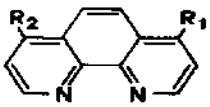
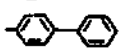
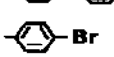
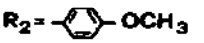
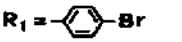
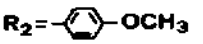
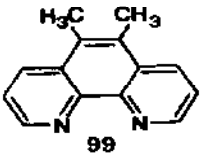


86 R = CH_3
87 R = Cl
88 R = C_6H_5
89 R = 
90 R = 
91 R = 
92 R = 
93 R = 



94 R_1 = R_2 = OH
95 R_1 = 
R_2 = 
96 R_1 = 
R_2 = 
97 R_1 = 
R_2 = C_6H_5
98 R_1 = 
R_2 = 



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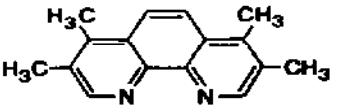

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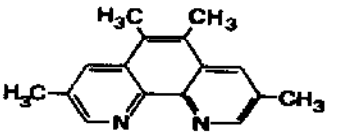

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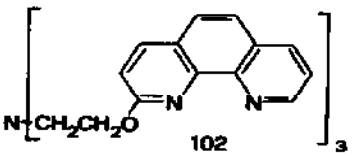

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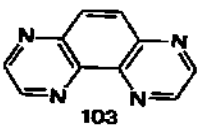

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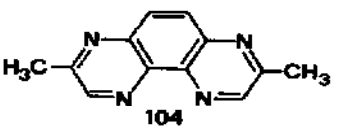

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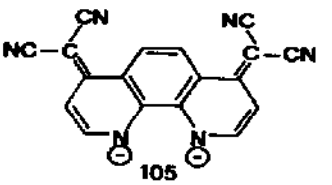

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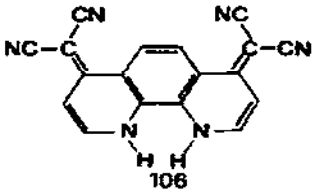
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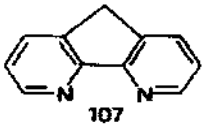
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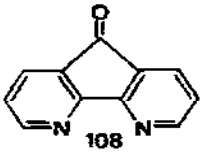
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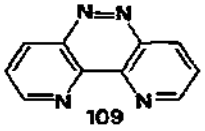
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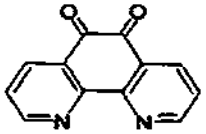
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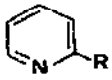
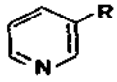
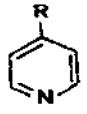
111

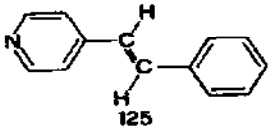

112 R = CH_2NH_2
113 R = $CH_2CH_2NH_2$


114 R = Cl
115 R = I
116 R = $CH_2CH_2NH_2$

117 R = CH_2– 


118 R = CH_3
119 R = $COCH_3$

120 R = COOH
121 R = $CONH_2$
122 R = $C(CH_3)_3$
123 R = $CH=CH_2$
124 R =
polymeric form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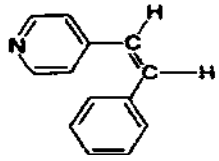
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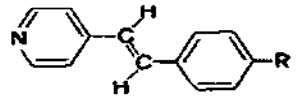
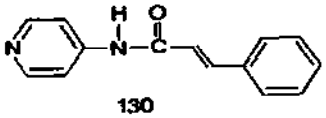

127 R = Cl
128 R = OCH_3
129 R = CN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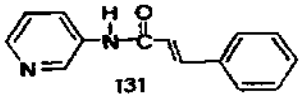
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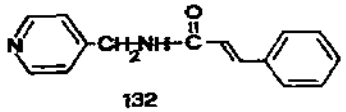
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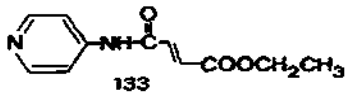
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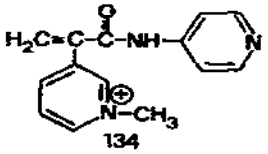

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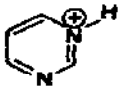

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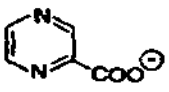

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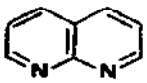

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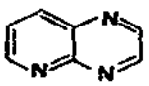

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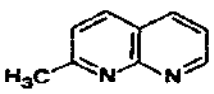

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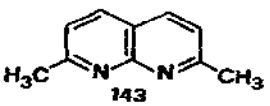

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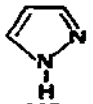

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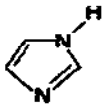

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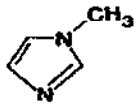

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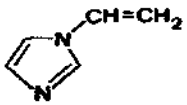

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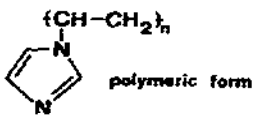

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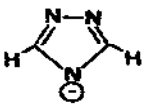

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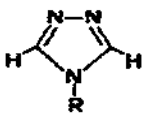
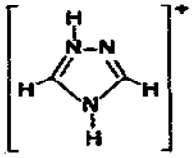


151 R = H
152 R = CH_3
153 R = C_6H_5
154 R = CH_2–CH=CH_2



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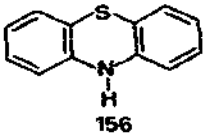

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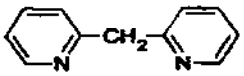

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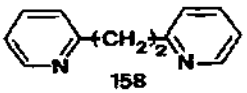

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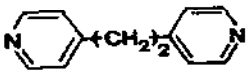

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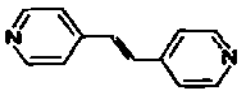

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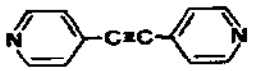
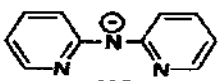
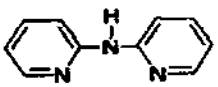


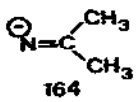
161



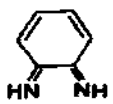
162



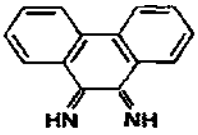
163



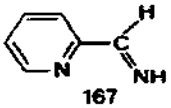
164



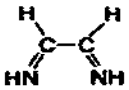
165



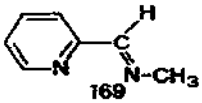
166



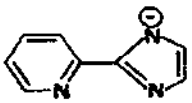
167



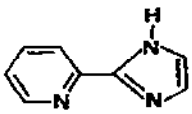
168



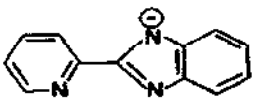
169



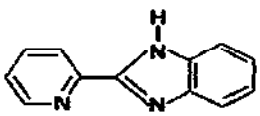
170



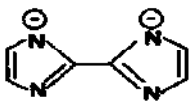
171



172



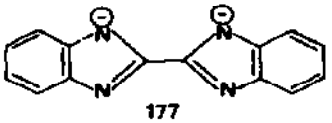
173



174

175 monoprotonated form of 174

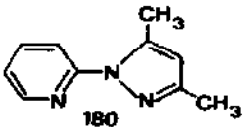
176 biprotonated form of 174



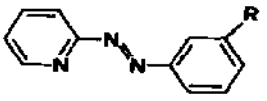
177

178 monoprotonated form of 177

179 biprotonated form of 177

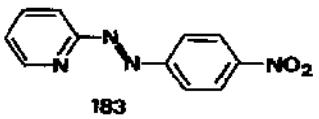


180

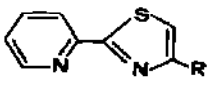


181 R = H

182 R = CH_3

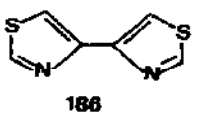


183

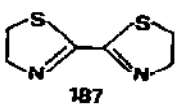


184 R = H

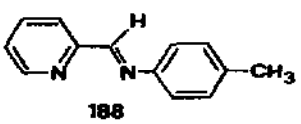
185 R = CH_3



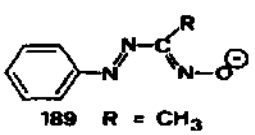
186



187



188

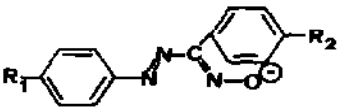


189 R = CH_3

190 protonated form of 189

191 R = C_6H_5

192 protonated form of 191

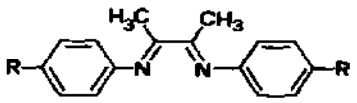


193 R_1 = CH_3 R_2 = H

194 protonated form of 193

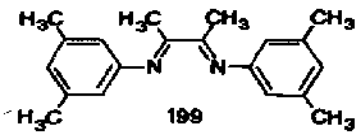
195 R_1 = H R_2 = CH_3

196 protonated form of 195

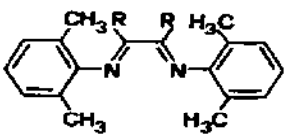


197 R = H

198 R = CH_3

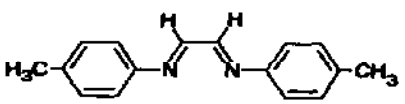


199

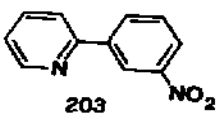


200 R = CH_3

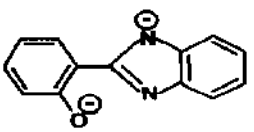
201 R = H



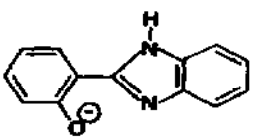
202



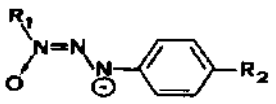
203



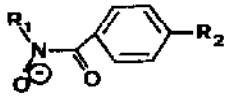
204



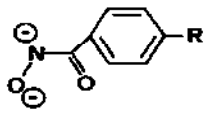
205



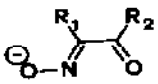
206 $R_1 = CH_2CH_3, R_2 = CH_3$
207 $R_1 = CH_2CH_3, R_2 = H$
208 $R_1 = CH_2CH_3, R_2 = Cl$
209 $R_1 = CH_2CH_3, R_2 = COOCH_2CH_3$
210 $R_1 = CH_2CH_3, R_2 = NO_2$
211 $R_1 = C_6H_5, R_2 = CH_3$
212 $R_1 = C_6H_5, R_2 = H$
213 $R_1 = C_6H_5, R_2 = Cl$
214 $R_1 = C_6H_5, R_2 = COOCH_2CH_3$
215 $R_1 = C_6H_5, R_2 = NO_2$



216 $R_1 = H, R_2 = OCH_3$
217 $R_1 = H, R_2 = CH_3$
218 $R_1 = R_2 = H$
219 $R_1 = H, R_2 = Cl$
220 $R_1 = H, R_2 = NO_2$
221 $R_1 = CH_3, R_2 = OCH_3$
222 $R_1 = CH_3, R_2 = CH_3$
223 $R_1 = CH_3, R_2 = H$
224 $R_1 = CH_3, R_2 = Cl$
225 $R_1 = CH_3, R_2 = NO_2$



226 R $= OCH_3$
227 R $= H$
228 R $= NO_2$



229 $R_1 = H$ $R_2 =$

230 protonated form of 229

231 $R_1 = CH_3$ $R_2 =$ 

232 protonated form of 231

233 $R_1 = R_2 =$ 

234 protonated form of 233

235 $R_1 = R_2 = CH_3$

236 protonated form of 235

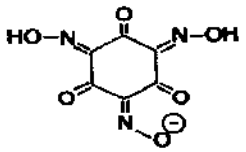
237 $R_1 = CH_2CH_3$ $R_2 = CH_3$

238 protonated form of 237

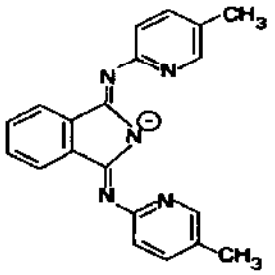
239 $R_1 =$  $R_2 = CH_3$

240 protonated form of 239

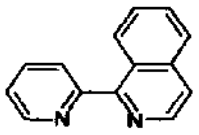
241 $R_1 =$  $R_2 = NH_2$



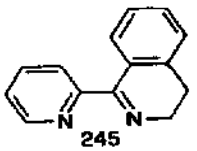
242



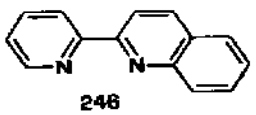
243



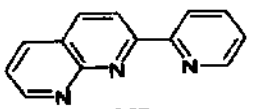
244



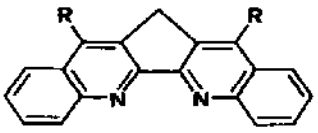
245



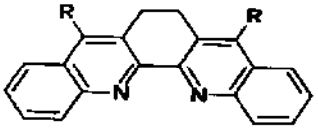
246



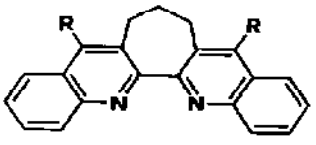
247



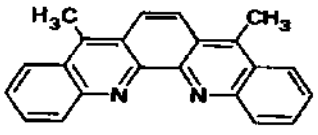
248 R = CH_3
249 R = 



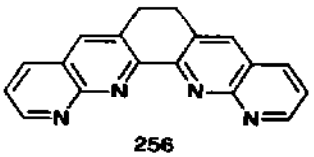
250 R = H
251 R = CH_3
252 R = 



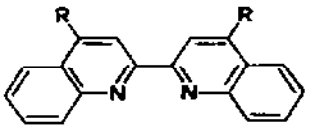
253 R = CH_3
254 R = 



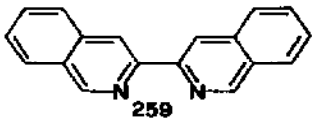
255



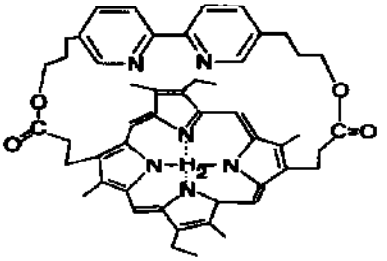
256



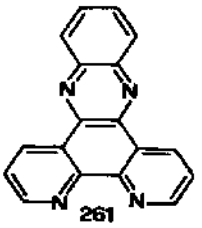
257 R = H
258 R = CH_3



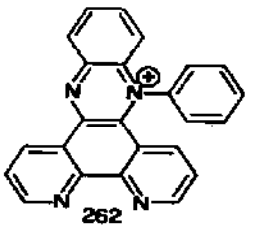
259



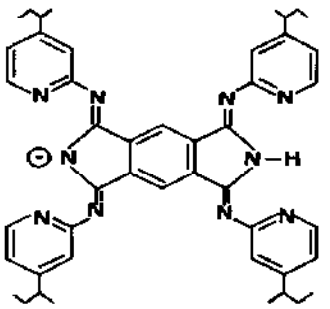
260



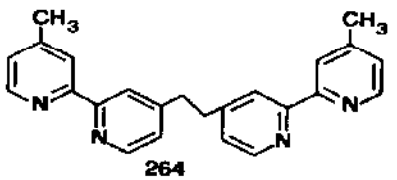
261



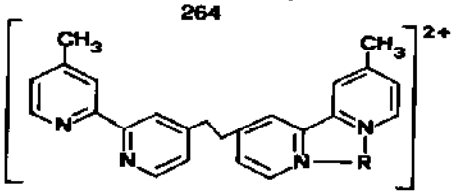
262



263

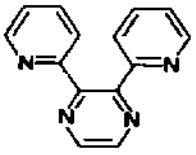


264

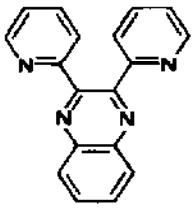


265 R = CH_2CH_2

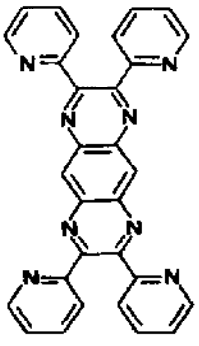
266 R = $CH_2CH_2CH_2$



267



268



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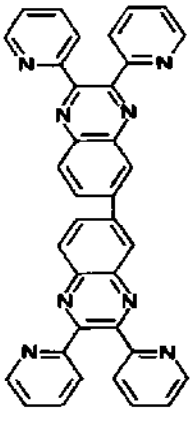

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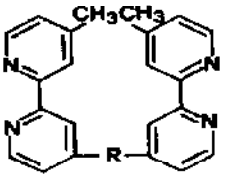
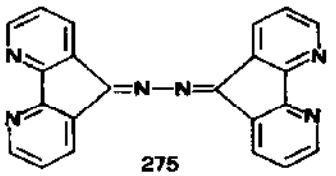


271 R = $(CH_2)_2$

272 R = $(CH_2)_5$

273 R = $(CH_2)_2$-C$_6$H$_4$-$(CH_2)_2$

274 R = $(CH_2)_{12}$



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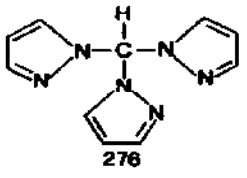
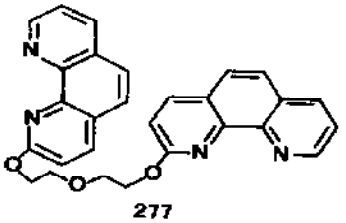
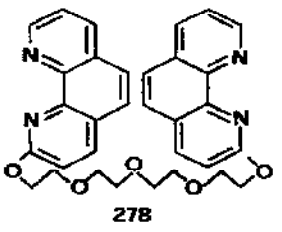


276



277



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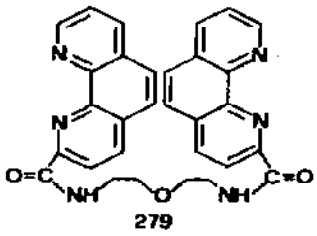

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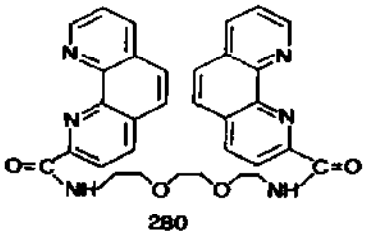

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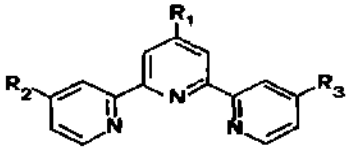
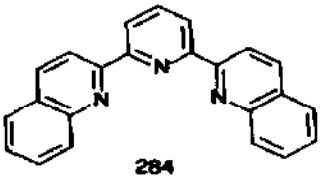


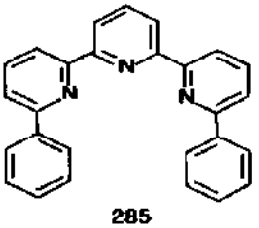
281 R_1= R_2= R_3= H

282 R_1= , R_2= R_3= H

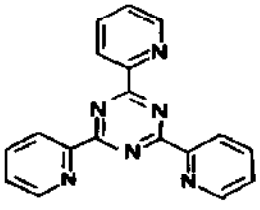
283 R_1= R_2= R_3= 



284



285



286

Other abbreviations

1,2-dme	1,2-dimethoxyethane
Ac. anh.	acetic anhydride
AgRE	Ag reference electrode
AN	acetonitrile
BN	benzonitrile
BzOH	benzil alcohol
DMF	dimethylformamide
DMSO	dimethylsulfoxide
E/p,a	anodic peak potential
E/p,c	cathodic peak potential
eglyc	ethyleneglycol
EPA	ether/iso-pentane/ethanol (5 : 5 : 2)
EtCN	ethyl cyanide
EtOH	ethanol
$Fc^+/0$	ferrocenium/ferrocene
i, irr	irreversible
iBN	isobutyronitrile
MeOH	methanol

mer	meridional
MF	*N*-methylformamide
NaLS	sodium laurilsulfate
NHE	normal hydrogen electrode
nitrile	propionitrile/butyronitrile (4 : 5)
PC	propylene carbonate
PMM	polymethylmethacrylate
SCE	saturated calomel electrode
SSCE	sodium saturated calomel electrode
surf	surface
THF	tetrahydrofuran

REFERENCES

1 H.H. Jaffe′ and M. Orchin, Theory and Applications of Ultraviolet Spectroscopy, Wiley, New York, 1962.
2 V. Balzani and V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, London, 1970.
3 J.B. Birks, Photophysics of Aromatic Molecules, Wiley-Interscience, London, 1970.
4 N.J. Turro, Modern Molecular Photochemistry, Benjamin, Menlo Park, California, 1978.
5 A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd edn., Elsevier, Amsterdam, 1984.
6 G.B. Porter, V. Balzani, and L. Moggi, Adv. Photochem., 9 (1974) 147.
7 V. Balzani, L. Moggi, M.F. Manfrin, F. Bolletta, and G.S. Laurence, Coord. Chem. Rev., 15 (1975) 321.
8 V. Balzani, F. Bolletta, M.T. Gandolfi, and M. Maestri, Top. Curr. Chem., 75 (1978) 1.
9 G.J. Kavarnos and N.J. Turro, Chem. Rev., 86 (1986) 401.
10 F. Scandola and V. Balzani, J. Chem. Educ., 60 (1983) 814.
11 N. Sutin and C. Creutz, J. Chem. Educ., 60 (1983) 809.
12 N. Sutin and C. Creutz, Adv. Chem. Ser., 168 (1978) 1.
13 N. Sutin and C. Creutz, Pure Appl. Chem., 52 (1980) 2717.
14 K. Kalyanasundaram, Coord. Chem. Rev., 46 (1982) 159.
15 E.A. Seddon and K.R. Seddon, The Chemistry of Ruthenium, Elsevier, Amsterdam, 1984, Chap. 15.
16 M.Z. Hoffman, L. Moggi, F. Bolletta, and G.L. Hugh, J. Phys. Chem. Ref. Data, to be published.
17 N. Sutin, Acc. Chem. Res., 15 (1982) 275.
18 V. Balzani and F. Scandola in M. Graetzel (Ed.), Energy Resources through Photochemistry and Catalysis, Academic Press, New York, 1983, p. 1.
19 N. Sutin, Prog. Inorg. Chem., 30 (1983) 441.
20 R.A. Marcus and N. Sutin, Biochim. Biophys. Acta, 811 (1985) 265.
21 V. Balzani, F. Bolletta, and F. Scandola, J. Am. Chem. Soc., 102 (1980) 2152.
22 V. Balzani and F. Scandola, Inorg. Chem., 25 (1986) 4457.
23 R.A. Marcus, Annu. Rev. Phys. Chem., 15 (1964) 155.
24 R.A. Marcus, J. Phys. Chem., 72 (1968) 891.
25 R.D. Levine and N. Agmon, Chem. Phys. Lett., 52 (1977) 197.
26 R. Ballardini, G. Varani, M.T. Indelli, F. Scandola, and V. Balzani, J. Am. Chem. Soc., 100 (1978) 7219.

27 V. Balzani and F. Scandola in J.S. Connolly (Ed.), Photochemical Conversion and Storage of Solar Energy, Academic Press, New York, 1981, p. 97.
28 D. Rehm and A. Weller, Ber. Bunsenges. Phys. Chem., 73 (1969) 834; Isr. J. Chem., 8 (1970) 259.
29 C. Creutz and N. Sutin, J. Am. Chem. Soc., 99 (1977) 241.
30 R.A. Marcus and P. Siders, J. Phys. Chem., 86 (1982) 622.
31 T.J. Meyer, Prog. Inorg. Chem., 30 (1983) 389.
32 M.D. Newton and N. Sutin, Annu. Rev. Phys. Chem., 35 (1984) 437.
33 M.T. Indelli, R. Ballardini, F. Scandola, J. Phys. Chem., 88 (1984) 2547.
34 V. Balzani, F. Scandola, G. Orlandi, N. Sabbatini, and M.T. Indelli, J. Am. Chem. Soc., 103 (1981) 3370.
35 D. Sandrini, M.T. Gandolfi, M. Maestri, F. Bolletta, and V. Balzani, Inorg. Chem., 23 (1984) 3017.
36 D. Sandrini, M. Maestri, P. Belser, A. von Zelewsky, and V. Balzani, J. Phys. Chem., 89 (1985) 3675.
37 U. Furholz and A. Haim, Inorg. Chem., 24 (1985) 3091.
38 V. Balzani, F. Bolletta, M. Ciano, and M. Maestri, J. Chem. Educ., 60 (1983) 447.
39 V. Balzani and F. Bolletta, Comments Inorg. Chem., 2 (1983) 211.
40 V. Balzani, A. Juris, F. Barigelletti, P. Belser, and A. von Zelewsky, Riken Q., 78 (1984) 78.
41 V. Balzani, A. Juris, and F. Scandola in E. Pelizzetti and N. Serpone (Eds.), Homogeneous and Heterogeneous Photocatalysis, Reidel, Dordrecht, 1986, p. 1.
42 J.S. Connolly (Ed.), Photochemical Conversion and Storage of Solar Energy, Academic Press, New York, 1981.
43 G. Porter in J.D. Coyle, R.R. Hill, and D.R. Roberts, (Eds.), Light, Chemical Change and Life, Open University Press, Walton Hall, Milton Keynes, 1982, p. 362.
44 A. Harriman and M.A. West, Photogeneration of Hydrogen, Academic Press, London, 1982.
45 M. Graetzel (Ed.), Energy Resources through Photochemistry and Catalysis, Academic Press, New York, 1983.
46 A.J. Bard and D. Laser, J. Electrochem. Soc., 122 (1975) 632.
47 G.H. Brilmyer and A.J. Bard, J. Electrochem. Soc., 127 (1980) 104.
48 G.A. Crosby, Acc. Chem. Res., 8 (1975) 231.
49 G.A. Crosby, Adv. Chem. Ser., 150 (1976) 149.
50 E.M. Kober and T.J. Meyer, Inorg. Chem., 21 (1982) 3967.
51 K. Mandal, T.D.L. Pearson, W.P. Krug, and J.N. Demas, J. Am. Chem. Soc., 105 (1983) 701.
52 D.P. Rillema, D.S. Jones, and H.A. Levy, J. Chem. Soc. Chem. Commun., (1979) 849.
53 L.E. Orgel, J. Chem. Soc., (1961) 3683.
54 R.J. Watts, J. Chem. Educ., 60 (1983) 834.
55 J.N. Demas, J. Chem. Educ., 60 (1983) 803.
56 A.W. Adamson, J. Chem. Educ., 60 (1983) 797.
57 P.D. Fleischauer and P. Fleischauer, Chem. Rev., 70 (1970) 199.
58 G.A. Crosby, R.J. Watts, and D.H.W. Carstens, Science, 170 (1970) 1195.
59 N.E. Tokel-Takvoryan, R.E. Hemingway, and A.J. Bard, J. Am. Chem. Soc., 95 (1973) 6582.
60 T. Saji and S. Aoyagui, J. Electroanal. Chem. Interfacial Electrochem., 58 (1975) 401.
61 A.A. Vlcek, Coord. Chem. Rev., 43 (1982) 39.
62 Y. Ohsawa, M.K. DeArmond, K.W. Hanck, and D.E. Morris, J. Am. Chem. Soc., 105 (1983) 6522.

63 Y. Ohsawa, M.H. Whangho, K.W. Hanck, and M.K. DeArmond, Inorg. Chem., 23 (1984) 3426.
64 J.L. Kahl, K.W. Hanck, and M.K. DeArmond, J. Phys. Chem., 83 (1978) 540; B. Divisia-Blohorn, Inorg. Chim. Acta, 117 (1986) 97.
65 M.K. DeArmond and C.M. Carlin, Coord. Chem. Rev., 36 (1981) 325.
66 M.K. DeArmond, K.W. Hanck, and D.W. Wertz, Coord. Chem. Rev., 64 (1985) 65.
67 A.G. Motten, K.W. Hanck, and M.K. DeArmond, Chem. Phys. Lett., 79 (1981) 541.
68 D. Morris, K.W. Hanck, and M.K. DeArmond, J. Electroanal. Chem., 149 (1983) 115.
69 D.E. Morris, K.W. Hanck, and M.K. DeArmond, J. Am. Chem. Soc., 105 (1983) 3032.
70 C.M. Elliott, J. Chem. Soc. Chem. Commun., (1980) 261.
71 G.A. Heath, L.J. Yellowlees, and P.S. Braterman, J. Chem. Soc. Chem. Commun., (1981) 287.
72 G.A. Heath, L.J. Yellowlees, and P.S. Braterman, Chem. Phys. Lett., 92 (1982) 646.
73 Y. Ohsawa, M.K. DeArmond, K.W. Hanck, and C.G. Moreland, J. Am. Chem. Soc., 107 (1985) 5383.
74 S.M. Angel, M.K. DeArmond, R.J. Donohoe, K.W. Hanck, and D.H. Wertz, J. Am. Chem. Soc., 106 (1984) 3688.
75 H.C. Stynes and J.A. Ibers, Inorg. Chem., 10 (1971) 2304.
76 E.C. Constable and K.R. Seddon, J. Chem. Soc. Chem. Commun., (1982) 34.
77 F.P. Dwyer and E.C. Gyarfas, Proc. R. Soc. N.S. Wales, 83 (1949) 170.
78 W.W. Brandt, F.P. Dwyer, and E.C. Gyarfas, Chem. Rev., 54 (1954) 954.
79 W.W. Brandt and G.S. Smith, Anal. Chem., 21 (1949) 1313.
80 F.H. Burstall, J. Chem. Soc., (1936) 173.
81 T. Kakutani, Y. Morihiro, M. Senda, R. Takahashi, and K. Matsumoto, Bull. Chem. Soc. Jpn., 51 (1978) 2847.
82 G.A. Barbieri, Atti Accad. Naz. Lincei, Cl. Sci. Fis. Mat. Nat. Rend. [8], 4 (1948) 561.
83 F.E. Lytle and D.M. Hercules, Photochem. Photobiol., 13 (1971) 123.
84 C. Creutz and N. Sutin, Proc. Natl. Acad. Sci. U.S.A., 72 (1975) 2858.
85 K. Kalyanasundaram, O. Micic, E. Pramauro, and M. Graetzel, Helv. Chim. Acta, 62 (1979) 2432.
86 J.M. Lehn, J.P. Sauvage, and R. Ziessel, Nouv. J. Chim., 4 (1980) 355.
87 V.Y. Shafirovich, N.K. Khannanov, and V.V. Strelets, Nouv. J. Chim., 4 (1980) 81; Kinet. Katal., 22 (1981) 248.
88 A. Juris and L. Moggi, Int. J. Solar Energy, 1 (1983) 273.
89 A. Harriman, G. Porter, and P. Walters, J. Chem. Soc., Faraday Trans 2, 77 (1984) 2373.
90 P.K. Ghosh, B.S. Brunschwig, M. Chou, C. Creutz, and N. Sutin, J. Am. Chem. Soc., 106 (1984) 4772; D. Kotker, V. Joshi, and P. Ghosh, Inorg. Chem., 25 (1986) 4344.
91 Q.G. Mulazzani, S. Emmi, P.G. Fuochi, M.Z. Hoffman, and M. Venturi, J. Am. Chem. Soc., 100 (1978) 981.
92 C.P. Anderson, D.J. Salomon, T.J. Meyer, and R.C. Young, J. Am. Chem. Soc., 99 (1977) 1980.
93 P. Bugnon and R.E. Hester, Chem. Phys. Lett., 102 (1983) 537.
94 J.H. Baxendale and M. Fiti, J. Chem. Soc., Dalton Trans., (1972) 1995.
95 T.J. Kemp, Prog. React. Kinet., 10 (1980) 301.
96 F.E. Lytle and D.M. Hercules, J. Am. Chem. Soc., 91 (1969) 253.
97 D.M. Klassen and G.A. Crosby, J. Chem. Phys., 48 (1968) 1853.
98 E.M. Kober, B.P. Sullivan, and T.J. Meyer, Inorg. Chem., 23 (1984) 2098.
99 R. Bensasson, C. Salet, and V. Balzani, J. Am. Chem. Soc., 98 (1976) 3722; C.R. Acad. Sci. Paris, 289B (1979) 41.

100 U. Lachish, P.P. Infelta, and M. Graetzel, Chem. Phys. Lett., 62 (1979) 317.
101 C. Creutz, M. Chou, T.L. Netzel, M. Okumura, and N. Sutin, J. Am. Chem. Soc., 102 (1980) 1309.
102 P.C. Bradley, N. Kress, B.A. Hornberger, R.F. Dallinger, and W.H. Woodruff, J. Am. Chem. Soc., 103 (1981) 7441.
103 C.H. Brauenstein, A.D. Baker, T.C. Strekas, and H.D. Gafney, Inorg. Chem., 23 (1984) 857.
104 J.N. Demas and G.A. Crosby, J. Am. Chem. Soc., 93 (1971) 2841.
105 J.N. Demas and D.G. Taylor, Inorg. Chem., 18 (1979) 3177.
106 F. Bolletta, A. Juris, M. Maestri, and D. Sandrini, Inorg. Chim. Acta, 44 (1980) L175.
107 R.W. Harrigan and G.A. Crosby, J. Phys. Chem., 59 (1973) 3468.
108 G.D. Hager and G.A. Crosby, J. Am. Chem. Soc., 97 (1975) 7031.
109 G.D. Hager, R.J. Watts, and G.A. Crosby, J. Am. Chem. Soc., 97 (1975) 7037.
110 K.W. Hipps and G.A. Crosby, J. Am. Chem. Soc., 97 (1975) 7042.
111 G.A. Crosby and W.H. Elfring Jr., J. Phys. Chem., 80 (1976) 2206.
112 S. Sprouse, K.A. King, P.J. Spellane, and R.J. Watts, J. Am. Chem. Soc., 106 (1984) 6647.
113 K.A. King, P.J. Spellane, and R.J. Watts, J. Am. Chem. Soc., 107 (1985) 1431.
114 M. Maestri, D. Sandrini, V. Balzani, L. Chassot, P. Jolliet, and A. von Zelewsky, Chem. Phys. Lett., 122 (1985) 375.
115 J.E. Hillis and M.K. DeArmond, J. Lumin., 4 (1971) 273.
116 M.K. DeArmond and J.E. Hillis, J. Phys. Chem., 54 (1971) 2247.
117 L. Chassot, A. von Zelewsky, D. Sandrini, M. Maestri, and V. Balzani, J. Am. Chem. Soc., 108 (1986) 6084.
118 M. Maestri, D. Sandrini, V. Balzani, U. Mader, and A. von Zelewsky, Inorg. Chem., 26 (1987) 1323.
119 J. Van Houten and R.J. Watts, J. Am. Chem. Soc., 98 (1976) 4853.
120 S.R. Allsop, A. Cox, S.H. Jenkins, T.J. Kemp, and S.M. Turnstall, Chem. Phys. Lett., 43 (1976) 135.
121 J. Van Houten and R.J. Watts, Inorg. Chem., 17 (1978) 3381.
122 S.R. Allsop, A. Cox, T.J. Kemp, and W.J. Reed, J. Chem. Soc., Faraday Trans. 1, 74 (1978) 1273.
123 W.H. Elfring Jr. and G.A. Crosby, J. Am. Chem. Soc., 103 (1981) 2683.
124 B. Durham, J.V. Caspar, J.K. Nagle, and T.J. Meyer, J. Am. Chem. Soc., 104 (1982) 4803.
125 J.V. Caspar, B.P. Sullivan, E.M. Kober, and T.J. Meyer, Chem. Phys. Lett., 91 (1982) 91.
126 J.M. Calvert, J.V. Caspar, R.A. Binstead, T.D. Westmoreland, and T.J. Meyer, J. Am. Chem. Soc., 104 (1982) 6620.
127 S.F. Agnew, M.L. Stone, and G.A. Crosby, Chem. Phys. Lett., 85 (1982) 57.
128 F. Barigelletti, A. Juris, V. Balzani, P. Belser, and A. von Zelewsky, Inorg. Chem., 22 (1983) 3335.
129 J.V. Caspar and T.J. Meyer, J. Am. Chem. Soc., 105 (1983) 5583.
130 W.R. Cherry and L.J. Henderson Jr., Inorg. Chem., 23 (1984) 983.
131 A. Juris, F. Barigelletti, V. Balzani, P. Belser, and A. von Zelewsky, Inorg. Chem., 24 (1985) 202.
132 F. Barigelletti, P. Belser, A. von Zelewsky, A. Juris, and V. Balzani, J. Phys. Chem., 89 (1985) 3680.
133 W.M. Wacholtz, R.A. Auerbach, R.H. Schmehl, M. Ollino, and W.R. Cherry, Inorg. Chem., 24 (1985) 1758.

134 S. Anderson, E.C. Constable, K.R. Seddon, J.E. Turp, J.E. Baggott, and M.J. Pilling, J. Chem. Soc., Dalton Trans., (1985) 2247.
135 W.F. Wacholtz, R.A. Auerbach, and R.H. Schmehl, Inorg. Chem., 25 (1986) 227.
136 F. Barigelletti, A. Juris, V. Balzani, P. Belser, and A. von Zelewsky, J. Phys. Chem., 90 (1986) 5190.
137 F. Barigelletti, A. Juris, V. Balzani, P. Belser, and A. von Zelewsky, J. Phys. Chem., 21 (1987) 1095.
138 J. Van Houten and R.J. Watts, J. Am. Chem. Soc., 97 (1975) 3843.
139 R. Englman and J. Jortner, Mol. Phys., 18 (1970) 145.
140 W.M. Gelbart, K.F. Freed, and S.A. Rice, J. Chem. Phys., 52 (1970) 2460.
141 D.J. Robbins and A.J. Thomson, Mol. Phys., 25 (1973) 1103.
142 T.J. Meyer, Pure Appl. Chem., 58 (1986) 1193.
143 M. Gleria, F. Minto, G. Beggiato, and P. Bortolus, J. Chem. Soc., Chem. Commun., (1978) 285.
144 G.B. Porter and R.H. Sparks, J. Photochem., 13 (1980) 123.
145 M.L. Fetterolf and H.W. Offen, J. Phys. Chem., 89 (1985) 3320.
146 M.L. Fetterolf and H.W. Offen, J. Phys. Chem., 90 (1986) 1828.
147 J.C. Rodriguez-Ubis, B. Alpha, D. Plancherel, and J.M. Lehn, Helv. Chim. Acta, 67 (1984) 2264.
148 V. Balzani, N. Sabbatini, and F. Scandola, Chem. Rev., 86 (1986) 319.
149 C.T. Lin, W. Boettcher, M. Chou, C. Creutz, and N. Sutin, J. Am. Chem. Soc., 98 (1976) 6536.
150 J.R. Kirchoff, D.R. McMillin, P.A. Marnot, and J.P. Sauvage, J. Am. Chem. Soc., 107 (1985) 1138.
151 G.S. Laurence and V. Balzani, Inorg. Chem., 13 (1974) 2976.
152 H.D. Gafney and A.W. Adamson, J. Am. Chem. Soc., 94 (1972) 8238.
153 J.N. Demas and A.W. Adamson, J. Am. Chem. Soc., 95 (1973) 5159.
154 C.R. Bock, T.J. Meyer, and D.G. Whitten, J. Am. Chem. Soc., 96 (1974) 4710.
155 G. Navon and N. Sutin, Inorg. Chem., 13 (1974) 2159.
156 P. Natarajan and J.F. Endicott, J. Phys. Chem., 77 (1973) 971.
157 P. Natarajan and J.F. Endicott, J. Phys. Chem., 77 (1973) 1823.
158 N. Sabbatini, M.A. Scandola, and V. Carassiti, J. Phys. Chem., 77 (1973) 1307.
159 N. Sabbatini, M.A. Scandola, and V. Balzani, J. Phys. Chem., 78 (1974) 541.
160 A. Juris, M.T. Gandolfi, M.F. Manfrin, and V. Balzani, J. Am. Chem. Soc., 98 (1976) 1047.
161 R. Ballardini, G. Varani, F. Scandola, and V. Balzani, J. Am. Chem. Soc., 98 (1976) 7432.
162 A. Juris, M.F. Manfrin, M. Maestri, and N. Serpone, Inorg. Chem., 17 (1978) 2258.
163 I. Fujita and H. Kobayashi, J. Chem. Phys., 52 (1970) 4904.
164 I. Fujita and H. Kobayashi, J. Chem. Phys., 59 (1972) 2902.
165 I. Fujita and H. Kobayashi, Ber. Bunsenges. Phys. Chem., 76 (1972) 115.
166 N. Sabbatini and V. Balzani, J. Am. Chem. Soc., 94 (1972) 7857.
167 F. Bolletta, M. Maestri, L. Moggi, and V. Balzani, J. Chem. Soc., Chem. Commun., (1975) 901.
168 C. Creutz and N. Sutin, J. Am. Chem. Soc., 98 (1976) 6384.
169 C. Creutz, Inorg. Chem., 17 (1978) 1046.
170 B. Brunschwig and N. Sutin, J. Am. Chem. Soc., 100 (1978) 7568.
171 M.A. Hoselton, C.-T. Lin, H.A. Schwarz, and N. Sutin, J. Am. Chem. Soc., 100 (1978) 2383.

172 C.-Y. Mok, A.W. Zanella, C. Creutz, and N. Sutin, Inorg. Chem., 23 (1984) 2891.
173 H.D. Gafney and A.W. Adamson, J. Chem. Educ., 52 (1975) 480.
174 F. Bolletta and S. Bonafede, Pure Appl. Chem., 58 (1986) 1229.
175 D.K. Liu, B.S. Brunschwig, C. Creutz, and N. Sutin, J. Am. Chem. Soc., 108 (1986) 1749.
176 F. Bolletta, M. Ciano, V. Balzani, and N. Serpone, Inorg. Chim. Acta, 62 (1982) 207.
177 H.S. White and A.J. Bard, J. Am. Chem. Soc., 104 (1982) 6891.
178 J.E. Martin, E.J. Hart, A.W. Adamson, H. Gafney, and J. Halpern, J. Am. Chem. Soc., 94 (1972) 9238.
179 C.D. Jonah, M.S. Matheson, and D. Meisel, J. Am. Chem. Soc., 100 (1978) 1449.
180 L.M. Hercules and F.E. Lytle, J. Am. Chem. Soc., 88 (1966) 4795.
181 I. Rubinstein and A.J. Bard, J. Am. Chem. Soc., 103 (1981) 512.
182 V. Balzani and F. Bolletta, J. Photochem., 17 (1981) 179.
183 J.D. Luttmer and A.J. Bard, J. Electrochem. Soc., 125 (1978) 1423.
184 L.R. Faulkner and A.J. Bard, in A.J. Bard (Ed.) Electroanalytical Chemistry, Vol. 10, Dekker, New York, 1977, Chap. 1.
185 D. Ege, W.G. Becker, and A.J. Bard, Anal. Chem., 56 (1984) 2413.
186 R.A. Marcus, Discuss. Faraday Soc., 29 (1960) 21.
187 R.A. Marcus, Int. J. Chem. Kinet., 13 (1981) 865.
188 W.L. Wallace and A.J. Bard, J. Phys. Chem., 83 (1979) 1350.
189 K. Itoh and K. Honda, Chem. Lett., (1979) 99.
190 S. Bonafede, M. Ciano, F. Bolletta, V. Balzani, L. Chassot, and A. von Zelewsky, J. Phys. Chem., 90 (1986) 3836.
191 D.G. Whitten, Acc. Chem. Res., 13 (1980) 83.
192 R.C. Young, T.J. Meyer, and D.G. Whitten, J. Am. Chem. Soc., 97 (1973) 4781.
193 T.J. Meyer, Isr. J. Chem., 15 (1977) 200.
194 M. Graetzel, in J.S. Connolly (Ed.), Photochemical Conversion and Storage of Solar Energy, Academic Press, New York, 1981, p. 131.
195 J.-M. Lehn, in J.S. Connolly (Ed.), Photochemical Conversion and Storage of Solar Energy, Academic Press, New York, 1981, p. 161.
196 K.I. Zamaraev and V.N. Parmon, in M. Graetzel (Ed.), Energy Resources through Photochemistry and Catalysis, Academic Press, New York, 1983, p. 23.
197 J. Kiwi, in M. Graetzel (Ed.), Energy Resources through Photochemistry and Catalysis, Academic Press, New York, 1983, p. 297.
198 T. Watanabe, A. Fujishima, and K. Honda, in M. Graetzel (Ed.), Energy Resources through Photochemistry and Catalysis, Academic Press, New York, 1983, p. 359.
199 C.-T. Lin and N. Sutin, J. Phys. Chem., 80 (1976) 97.
200 N.N. Lichtin, in J.R. Bolton (Ed.), Solar Power and Fuels, Academic Press, New York, 1977, Chapter 5.
201 D.P. Rillema, W.J. Dressick, and T.J. Meyer, J. Chem. Soc., Chem. Commun. (1980) 274.
202 F. Bolletta and V. Balzani, J. Am. Chem. Soc., 104 (1982) 4250.
203 F. Bolletta, Q.G. Mulazzani, M. Venturi, N. Serpone, and V. Balzani, Gazz. Chim. Ital., 115 (1985) 137.
204 M.J. Cook and A.J. Thomson, Chem. Br., (1984) 914.
205 M.J. Cook, A.P. Lewis, G.S.G. McAuliffe, V. Skarda, A.J. Thomson, J.L. Glasper, and D.J. Robbins, J. Chem. Soc., Perkin Trans. 2, (1984) 1293.
206 P.C. Alford, M.J. Cook, A.P. Lewis, G.S.G. McAuliffe, V. Skarda, A.J. Thomson, J.L. Glasper, and D.J. Robbins, J. Chem. Soc., Perkin Trans. 2, (1985) 705.
207 G. Gremand, Ph.D. Thesis, Fribourg (Switzerland), in preparation.
208 M.K. DeArmond, Acc. Chem. Res., 7 (1974) 309.

209 D.P. Segers and M.K. DeArmond, J. Phys. Chem., 86 (1982) 3768.
210 J.V. Caspar and T.J. Meyer, Inorg. Chem., 22 (1983) 2444.
211 J.V. Caspar, T.D. Westmoreland, G.H. Allen, P.G. Bradley, T.J. Meyer, and W.H. Woodruff, J. Am. Chem. Soc., 106 (1984) 3492.
212 K.A. King, M.F. Finlayson, P.J. Spellane, and R.J. Watts, Riken Q., 78 (1984) 97.
213 E.M. Kober, J.V. Caspar, R.S. Lumpkin, and T.J. Meyer, J. Phys. Chem., 90 (1986) 3722.
214 Y. Ohsawa, S. Sprouse, K.A. King, M.K. DeArmond, K.W. Hanck, and R.J. Watts, J. Phys. Chem., 91 (1987) 1047.
215 P. Belser, A. von Zelewsky, A. Juris, F. Barigelletti, A. Tucci, and V. Balzani, Chem. Phys. Lett., 89 (1982) 101.
216 L.J. Henderson Jr., F.R. Fronczek, and W.R. Cherry, J. Am. Chem. Soc., 106 (1984) 5876.
217 P. Belser, A. von Zelewsky, A. Juris, F. Barigelletti, and V. Balzani, Gazz. Chim. Ital., 113 (1983) 731.
218 S.H. Peterson and J.N. Demas, J. Am. Chem. Soc., 98 (1976) 7880.
219 S.H. Peterson and J.N. Demas, J. Am. Chem. Soc., 101 (1979) 6571.
220 A. Juris, F. Barigelletti, V. Balzani, P. Belser and A. von Zelewsky, J. Chem. Soc., Faraday Trans. 2, in press.
221 P. Belser, A. von Zelewsky, A. Juris, F. Barigelletti, and V. Balzani, Gazz. Chim. Ital., 115 (1985) 723.
222 C.A. Bignozzi, C. Chiorboli, M.T. Indelli, M.A. Rampi Scandola, G. Varani, and F. Scandola, J. Am. Chem. Soc., 108 (1986) 7872.
223 K. Nakamaru, Bull. Chem. Soc. Jpn., 55 (1982) 1639.
224 V. Skarda, M.J. Cook, A.P. Lewis, G.S.G. McAuliffe, A.J. Thomson, and D.J. Robbins, J. Chem. Soc., Perkin Trans. 2, (1984) 1309.
225 G.H. Allen, R.P. White, D.P. Rillema, and T.J. Meyer, J. Am. Chem. Soc., 106 (1984) 2613.
226 T. Matsumura-Inoue, H. Tomono, M. Kasai, and T. Tominaga-Morimoto, J. Electroanal. Chem., 95 (1979) 109.
227 D.P. Rillema and K.B. Mack, Inorg. Chem., 21 (1982) 3849.
228 A.R. Chakravarty and A. Chakravorty, J. Chem. Soc., Dalton Trans., (1982) 1765.
229 D.P. Rillema, G. Allen, T.J. Meyer, and D. Conrad, Inorg. Chem., 22 (1983) 1617; J.C. Curtis, B.P. Sullivan, and T.J. Meyer, Inorg. Chem., 22 (1983) 224.
230 S. Goswami, R. Mukherjee, and A. Chakravorty, Inorg. Chem., 22 (1983) 2825.
231 R. Mukherjee and A. Chakravorty, J. Chem. Soc., Dalton Trans., (1983) 2197.
232 Y. Kawanishi, N. Kitamura, Y. Kim, and S. Tazuke, Riken Q., 78 (1984) 212.
233 Y. Ohsawa, K.W. Hanck, and M.K. DeArmond, J. Electroanal. Chem., 175 (1984) 229.
234 P. Ghosh and A. Chakravorty, Inorg. Chem., 23 (1984) 2242.
235 D.E. Morris, Y. Ohsawa, D.P. Segers, M.K. DeArmond, and K.W. Hanck, Inorg. Chem., 23 (1984) 3010.
236 A.B.P. Lever, S.R. Pickens, P.C. Minor, S. Licoccia, B.S. Ramaswamy, and K. Magnell, J. Am. Chem. Soc., 103 (1981) 6800; E.S. Dodsworth and A.B.P. Lever, Chem. Phys. Lett., 119 (1985) 61.
237 E.S. Dodsworth and A.B.P. Lever, Chem. Phys. Lett., 124 (1986) 152.
238 A. Juris, P. Belser, F. Barigelletti, A. von Zelewsky, and V. Balzani, Inorg. Chem., 25 (1986) 256.
239 P. Belser and A. von Zelewsky, Helv. Chim. Acta, 63 (1980) 1675.
240 F. Barigelletti, A. Juris, V. Balzani, P. Belser, and A. von Zelewsky, Inorg. Chem., in press.

241 N. Kitamura, Y. Kawanishi, and S. Tazuke, Chem. Phys. Lett., 97 (1983) 103.
242 E.S. Dodsworth and A.B.P. Lever, Chem. Phys. Lett., 112 (1984) 567.
243 J.-C. Chambron, J.-P. Sauvage, E. Amouyal, and P. Koffi, Nouv. J. Chim., 9 (1985) 527.
244 Th. Foerster in O. Sinanoglu (Ed.), Modern Quantum Chemistry, Part III, Academic Press, New York, 1965.
245 P. Day and N. Sanders, J. Chem. Soc. A, (1967) 1530.
246 J. Hanazaki and S. Nagakura, Inorg. Chem., 8 (1969) 648.
247 N. Mataga and T. Kubota, Molecular Interaction and Electronic Spectra, Dekker, New York, 1970, p. 102.
248 R. Hoffmann, Acc. Chem. Res., 4 (1971) 1.
249 W. Halper and M.K. DeArmond, J. Lumin., 5 (1972) 225.
250 I. Fujita and H. Kobayashi, Inorg. Chem., 12 (1973) 2758.
251 R.A. Krause and C.J. Ballhausen, Acta Chem. Scand. Part A, 31 (1977) 535.
252 M. Kral, Theor. Chim. Acta (Berl.), 43 (1977) 273.
253 R.F. Dallinger and W.H. Woodruff, J. Am. Chem. Soc., 101 (1979) 4391.
254 R.F. Dallinger and W.H. Woodruff, J. Am. Chem. Soc., 101 (1979) 4391.
255 F. Felix, J. Ferguson, H.U. Guedel, and A. Ludi, Chem. Phys. Lett., 62 (1979) 153.
256 J. Ferguson, W.-H. Mau, and H.F. Sasse, Chem. Phys. Lett., 68 (1979) 21.
257 S. Anderson, K.R. Seddon, R.D. Wright, and A.T. Cocks, Chem. Phys. Lett., 71 (1980) 220.
258 M.K. DeArmond, C.M. Carlin, and W.L. Huang, Inorg. Chem., 19 (1980) 62.
259 F. Felix, J. Ferguson, H.U. Guedel, and A. Ludi, J. Am. Chem. Soc., 102 (1980) 4096.
260 K.W. Hipps, Inorg. Chem., 19 (1980) 1390.
261 M. Kral, Theor. Chim. Acta (Berl.), 55 (1980) 333.
262 P. Belser, C. Daul, and A. von Zelewsky, Chem. Phys. Lett., 79 (1981) 596.
263 A. Ceulemans and L.G. Vanquickenborne, J. Am. Chem. Soc., 103 (1981) 2238.
264 C.A. Daul and J. Weber, Chem. Phys. Lett., 77 (1981) 593.
265 M. Forster and R.E. Hester, Chem. Phys. Lett., 81 (1981) 42.
266 R.W. Balk, D.I. Stufkens, R.J. Crutchley, and A.B.P. Lever, Inorg. Chim. Acta, 64 (1982) L49.
267 A. Basu, H.D. Gafney, and T.C. Strekas, Inorg. Chem., 21 (1982) 2231.
268 A.T. Cocks, R.D. Wright, and K.R. Seddon, Chem. Phys. Lett., 85 (1982) 369.
269 C.M. Carlin and M.K. DeArmond, Chem. Phys. Lett., 89 (1982) 297.
270 C.M. Elliott and E.J. Hersenhart, J. Am. Chem. Soc., 104 (1982) 7519.
271 J. Ferguson and F. Herren, Chem. Phys. Lett., 89 (1982) 371.
272 J. Ferguson and E.R. Krausz, Chem. Phys. Lett., 93 (1982) 21.
273 J. Ferguson, F. Herren, and G.M. Mc Laughlin, Chem. Phys. Lett., 89 (1982) 376.
274 D.M. Klassen, Chem. Phys. Lett., 93 (1982) 383.
275 J.E. Baggott, G.K. Gregory, M.J. Pilling, S. Anderson, K.R. Seddon, and J.E. Turp, J. Chem. Soc., Faraday Trans. 2, 79 (1983) 195.
276 P.S. Braterman, A. Harriman, G.A. Heath, and L.J. Yellowlees, J. Chem. Soc., Dalton Trans., (1983) 1801.
277 E.M. Kober and T.J. Meyer, Inorg. Chem., 22 (1983) 1614.
278 R.J. Crutchley, M. Kress, and A.B.P. Lever, J. Am. Chem. Soc., 105 (1983) 1170.
279 S, Mc Clanahan, T. Hayes and J. Kincaid, J. Am. Chem. Soc., 105 (1983) 4486.
280 W.K. Smothers, M.S. Wrighton, J. Am. Chem. Soc., 105 (1983) 1067.
281 W.H. Woodruff, Adv. Chem. Ser., 211 (1983) 473.
282 H. Yersin, E. Gallhuber, A. Vogler, and H. Kunkely, J. Am. Chem. Soc., 105 (1983) 4155.

283 P.S. Braterman, Chem. Phys. Lett., 104 (1984) 405.
284 E.M. Kober and T.J. Meyer, Inorg. Chem., 23 (1984) 3877.
285 B.J. Pankuch, D.E. De Lacky, and G.A. Crosby, J. Phys. Chem., 84 (1984) 2061.
286 H. Yersin and E. Gallhuber, J. Am. Chem. Soc., 106 (1984) 6582.
287 H. Yersin and E. Gallhuber, Inorg. Chem., 23 (1984) 3745.
288 T.C. Strekas and S.K. Mandal, J. Raman Spectrosc., 15 (1984) 109.
289 P.S. Braterman, G.A. Heath, and L.J. Yellowlees, J. Chem. Soc., Dalton Trans., (1985) 1081.
290 C.M. Carlin and M.K. DeArmond, J. Am. Chem. Soc., 107 (1985) 53.
291 Y.C. Chung, N. Leventis, P.J. Wagner, and G.E. Leroi, J. Am. Chem. Soc., 107 (1985) 1416.
292 Y.C. Chung, N. Leventis, P.J. Wagner, and G.E. Leroi, Inorg. Chem., 24 (1985) 1966.
293 J. Ferguson, E.R. Krausz, and M. Maeder, J. Phys. Chem., 89 (1985) 1852.
294 J. Ferguson, F. Herren, E.R. Krausz, M. Maeder, and J. Vrbancich, Coord. Chem. Rev., 64 (1985) 21.
295 E. Gallhuber, G. Hensler, and H. Yersin, Chem. Phys. Lett., 120 (1985) 445.
296 J.S. Gold, S.J. Milder, J.W. Lewis, and D.S. Kliger, J. Am. Chem. Soc., 107 (1985) 8285.
297 E. Krausz, Chem. Phys. Lett., 116 (1985) 501.
298 E.M. Kober and T.J. Meyer, Inorg. Chem., 24 (1985) 106.
299 S.F. Mc Clanahan, R.F. Dallinger, F.J. Holler, and J.R. Kincaid, J. Am. Chem. Soc., 107 (1985) 4853.
300 A.J. Thomson, V. Skarda, M.J. Cook, and D.J. Robbins, J. Chem. Soc., Dalton Trans., (1985) 1781.
301 H. Yersin, E. Gallhuber, G. Hensler, J. Phys., 46 (1985) 453.
302 P.S. Braterman, Inorg. Chem., 25 (1986) 1732.
303 J. Ferguson and E.R. Krausz, Chem. Phys. Lett., 127 (1986) 551.
304 G. Hensler, E. Gallhuber, and H. Yersin, Inorg. Chim. Acta, 113 (1986) 91.
305 N. Kitamura, H.-B. Kirn, Y. Kawanashi, R. Obata, and S. Tazuke, J. Phys. Chem., 90 (1986) 1488.
306 S.J. Milder, J.S. Gold, and D.S. Kliger, J. Phys. Chem., 90 (1986) 548.
307 P.A. Mabrouk and M.S. Wrighton, Inorg. Chem., 25 (1986) 526.
308 C.D. Tait, D.M. McQueen, R.J. Donohue, M.K. DeArmond, K.W. Hanck, and D.W. Waltz, J. Phys. Chem., 90 (1986) 1766.
309 R.L. Blakley, M.L. Myrick, and M.K. DeArmond, J. Am. Chem. Soc., 108 (1986) 7843.
310 E. Danielson, R.S. Lumpkin and T.J. Meyer, J. Phys. Chem., 91 (1987) 1305.
311 J. Ferguson and E.R. Krausz, Inorg. Chem., 25 (1986) 3333.
312 J.N. Gex, M.K. DeArmond, and K.W. Hanck, J. Phys. Chem., 91 (1987) 251.
313 R.S. Lumpkin and T.J. Meyer, J. Chem. Phys., in press.
314 M.L. Myrick, R.L. Blackey, and M.K. DeArmond, J. Am. Chem. Soc., 109 (1987) 2841.
315 P. Belser, A. von Zelewsky, A. Juris, F. Barigelletti, and V. Balzani, Chem. Phys. Lett., 104 (1984) 100.
316 J. Ferguson and F. Herren, Chem. Phys., 76 (1983) 45.
317 H. Kobayashi and Y. Kaizu, Coord. Chem. Rev., 64 (1985) 540.
318 D.V. Pinnick and B. Durham, Inorg. Chem., 23 (1984) 1440.
319 J.G. Vos, J.G. Haasnoot, and G. Vos, Inorg. Chim. Acta, 71 (1983) 155.
320 J.N. Demas and G.A. Crosby, J. Mol. Spectrosc., 26 (1968) 72.
321 R.C. Young, T.J. Meyer, and D.G. Whitten, J. Am. Chem. Soc., 98 (1976) 286.
322 B.L. Hauenstein Jr., W.J. Dressick., S.L. Buell, J.N. Demas, and B.A. DeGraff, J. Am. Chem. Soc., 105 (1983) 4251.

323 J.N. Demas, J.W. Addington, S.H. Peterson, and E.W. Harris, J. Phys. Chem., 81 (1977) 1039.
324 C. Bartocci, C.A. Bignozzi, F. Scandola, R. Rumin, and P. Courtot, Inorg. Chim. Acta, 76 (1983) L119.
325 C.A. Bignozzi and F. Scandola, Inorg. Chem., 23 (1984) 1540.
326 G.L. Gaines Jr., J. Phys. Chem., 83 (1979) 3088.
327 J.N. Demas, E.W. Harris, and R.P. McBride, J. Am. Chem. Soc., 99 (1977) 3547.
328 R.J. Watts, R.W. Harrigan, and G.A. Crosby, Chem. Phys. Lett., 8 (1971) 49.
329 A. Juris, V. Balzani, P. Belser, and A. von Zelewsky, Helv. Chim. Acta, 64 (1981) 2175.
330 Y. Kaizu, H. Ohta, K. Kobayashi, H. Kobayashi, K. Takuma, and T. Matsuo, J. Photochem., 30 (1985) 93.
331 G.A. Crosby, W.G. Perkins, and D.M. Klassen, J. Chem. Phys., 43 (1965) 1498.
332 A. Harriman, J. Chem. Soc. Chem. Commun., (1977) 777.
333 S.-M.Y. Huang and H.D. Gafney, J. Phys. Chem., 81 (1977) 2602.
334 O. Johansen, A. Launikonis, A.W.H. Mau, and W.H.F. Sasse, Aust. J. Chem., 33 (1980) 1643.
335 T. Guarr, M. McGuire, S. Strauch, and G. McLendon, J. Am. Chem. Soc., 105 (1983) 616.
336 H. Veening and W.W. Brandt, Anal. Chem., 32 (1960) 1426.
337 J.N. Demas and J.W. Addington, J. Am. Chem. Soc., 98 (1976) 5800.
338 K. Nakamaru, Bull. Chem. Soc. Jpn., 55 (1982) 2697.
339 L.J. Henderson Jr. and W.R. Cherry, J. Photochem., 28 (1985) 143.
340 B.S. Brunschwig and N. Sutin, Inorg. Chem., 18 (1979) 1731.
341 M. Maestri and M. Graetzel, Ber. Bunsenges. Phys. Chem., 81 (1977) 504.
342 R.J. Watts and G.A. Crosby, J. Am. Chem. Soc., 94 (1972) 2606.
343 R.J. Watts, J.S. Harrington, and J. Van Houten, Adv. Chem. Ser., 168 (1978) 57.
344 A. Juris, F. Barigelletti, V. Balzani, P. Belser, and A. von Zelewsky, Isr. J. Chem., 22 (1982) 87.
345 J.M. Kelly, C. Long, C.M. O'Connell, J.G. Vos, and A.H.A. Tinnemans, Inorg. Chem., 22 (1983) 2818.
346 S.J. Valenty, D.E. Behnken, and G.L. Gaines Jr., Inorg. Chem., 18 (1979) 2160.
347 P.J. Giordano, C.R. Bock, M.S. Wrighton, L.V. Interrante, and R.F.X. Williams, J. Am. Chem. Soc., 99 (1977) 3187.
348 P.A. Lay and W.H.F. Sasse, Inorg. Chem., 23 (1984) 4123.
349 T. Shimidzu, T. Iyoda, and K. Izaki, J. Phys. Chem., 89 (1985) 642.
350 R. Memming and F. Schroeppel, Chem. Phys. Lett., 62 (1979) 207.
351 G.L. Gaines Jr., Inorg. Chem., 19 (1980) 1710.
352 W.E. Ford and M. Calvin, Chem. Phys. Lett., 76 (1980) 105.
353 K. Monserrat, M. Graetzel, and P. Tundo, J. Am. Chem. Soc., 102 (1980) 5527.
354 P.J. DeLaive, J.T. Lee, H.W. Sprintschnik, T.J. Meyer, and D.G. Whitten, J. Am. Chem. Soc., 99 (1977) 7094.
355 M. Kaneko, A. Yamada, E. Tsuchida, and Y. Kurimura, J. Polym. Sci., Polym. Lett. Ed., 20 (1982) 593.
356 Y. Kurimura, N. Shinozaki, F. Ito, Y. Uratani, K. Shigehara, E. Tsuchida, M. Kaneko, and A. Yamada, Bull. Chem. Soc. Jpn., 55 (1982) 380.
357 B.P. Sullivan, H. Abruna, H.O. Finklea, D.J. Salmon, J.K. Nagle, T.J. Meyer, and H. Sprintschnik, Chem. Phys. Lett., 58 (1978) 389.
358 J.C. Curtis, J.S. Bernstein, and T.J. Meyer, Inorg. Chem., 24 (1985) 385.
359 J.C. Curtis, J.S. Bernstein, R.H. Schmehl, and T.J. Thomas, Chem. Phys. Lett., 81 (1981) 48.

360 E.V. Dose and L.J. Wilson, Inorg. Chem., 17 (1978) 2660.
361 M. Hunziker and A. Ludi, J. Am. Chem. Soc., 99 (1977) 7370.
362 L.D. Margerum, R.W. Murray, and T.J. Meyer, J. Phys. Chem., 90 (1986) 728.
363 P.J. Giordano, C.R. Bock, and M.S. Wrighton, J. Am. Chem. Soc., 100 (1978) 6960.
364 J.M. Calvert and T.J. Meyer, Inorg. Chem., 21 (1982) 3978.
365 R.A. Krause, Inorg. Chim. Acta, 22 (1977) 209.
366 L.J. Henderson, M. Ollino, V.K. Gupta, G.R. Newkome, and W.R. Cherry, J. Photochem., 31 (1985) 199.
367 B.P. Sullivan, D.J. Salmon, T.J. Meyer, and J. Peedin, Inorg. Chem., 18 (1979) 3369.
368 M.-A. Haga, Inorg. Chim. Acta, 75 (1983) 29.
369 P.J. Steel, F. Lahousse, D. Lerner, and C. Marzin, Inorg. Chem., 22 (1983) 1488.
370 L.J. Fitzpatrick, H.A. Goodwin, A. Launikonis, A.W.H. Mau, and W.H.F. Sasse, Aust. J. Chem., 36 (1983) 2169.
371 P. Reveco, R.H. Schmehl, W.R. Cherry, F.R. Fronczek, and J. Selbin, Inorg. Chem., 24 (1985) 4078.
372 D.P. Rillema, R.W. Callahan, and K.B. Mack, Inorg. Chem., 21 (1982) 2589.
373 R.H. Schmehl, R.A. Auerbach, W.F. Wacholtz, C.M. Elliott, R.A. Freitag, and J.W. Merkert, Inorg. Chem., 25 (1986) 2440.
374 J.M. Calvert and T.J. Meyer, Inorg. Chem., 20 (1981) 27.
375 R.A. Krause and K. Krause, Inorg. Chem., 21 (1982) 1714.
376 S. Wolfgang, T.C. Strekas, H.D. Gafney, R.A. Krause, and K. Krause, Inorg. Chem., 23 (1984) 2650.
377 M.J. Root, E. Deutsch, J.C. Sullivan, and D. Meisel, Chem. Phys. Lett., 101 (1983) 353.
378 A. Basu, M.A. Weiner, T.C. Strekas, and H.D. Gafney, Inorg. Chem., 21 (1982) 1085.
379 R.H. Fabian, D.M. Klassen, and R.W. Sonntag, Inorg. Chem., 19 (1980) 1977.
380 P.J. DeLaive, T.K. Foreman, C. Giannotti, and D.G. Whitten, J. Am. Chem. Soc., 102 (1980) 5627.
381 B.L. Hauenstein Jr., K. Mandal, J.N. Demas, and B.A. DeGraff, Inorg. Chem., 23 (1984) 1101.
382 W.J. Dressick, B.L. Hauenstein Jr., J.N. Demas, and B.A. DeGraff, Inorg. Chem., 23 (1984) 1107.
383 R.J. Watts and G.A. Crosby, J. Am. Chem. Soc., 93 (1971) 3184.
384 D. Markovitsi, R. Knoesel, and J. Simon, Nouv. J. Chim., 6 (1982) 531.
385 R.J. Crutchley and A.B.P. Lever, Inorg. Chem., 21 (1982) 2276.
386 J. Gonzales-Velasco, I. Rubinstein, R.J. Crutchley, A.B.P. Lever, and A.J. Bard, Inorg. Chem., 22 (1983) 822.
387 M. Haga, E.S. Dodsworth, G. Eryavec, P. Seymour, and A.B.P. Lever, Inorg. Chem., 24 (1985) 1901.
388 K. Kalyanasundaram, J. Phys. Chem., 90 (1986) 2285.
389 R.J. Crutchley and A.B.P. Lever, J. Am. Chem. Soc., 102 (1980) 7128.
390 H. Duerr, G. Doerr, K. Zengerle, E. Mayer, J.M. Curchod, and A.M. Braun, Nouv. J. Chim., 9 (1985) 717.
391 C.M. White and W.E. Ohnesorge, J. Inorg. Nucl. Chem., 34 (1972) 1453.
392 W.J. Dressick, B.L. Hauenstein Jr., T.B. Gilbert, J.N. Demas, and B.A. DeGraff, J. Phys. Chem., 88 (1984) 3337.
393 J.E. Baggott and M.J. Pilling, J. Phys. Chem., 84 (1980) 3012.
394 J.I. Cline III, W.J. Dressick, J.N. Demas, and B.A. DeGraff, J. Phys. Chem., 89 (1985) 94.
395 M.N. Ackermann and L.V. Interrante, Inorg. Chem., 23 (1984) 3904.

396 J.E. Baggott, J. Phys. Chem., 87 (1983) 5223.
397 A. Kirsch-De Mesmaeker, R. Nasielski-Hinkens, D. Maetens, D. Pauwels, and J. Nasielski, Inorg. Chem., 23 (1984) 377.
398 A. Kirsch-De Mesmaeker, D. Maetens, R. Nasielski-Hinkens, J. Electroanal. Chem. Interfacial Electrochem., 182 (1985) 123.
399 R.A. Krause and K. Krause, Inorg. Chem., 23 (1984) 2195.
400 W.P. Krug and J.N. Demas, J. Am. Chem. Soc., 101 (1979) 4394.
401 D.M. Klassen, Inorg. Chem., 15 (1976) 3166.
402 E. Binamira-Soriaga, S.D. Sprouse, R.J. Watts, and W.C. Kaska, Inorg. Chim. Acta, 84 (1984) 135.
403 K.J. Brewer, W.R. Murphy Jr., S.R. Spurlin, and J.D. Petersen, Inorg. Chem., 25 (1986) 882.
404 R.C. Young, J.K. Nagle, T.J. Meyer, and D.G. Whitten, J. Am. Chem. Soc., 100 (1978) 4773.
405 D.M. Klassen, C.W. Hudson, and E.L. Shaddix, Inorg. Chem., 14 (1975) 2733.
406 M.L. Stone and G.A. Crosby, Chem. Phys. Lett., 79 (1981) 169.
407 G.A. Crosby, J. Chim. Phys., 64 (1967) 160.
408 A. Vogler and J. Kisslinger, Inorg. Chim. Acta, 115 (1986) 193.
409 D.V. Pinnick and B. Durham, Inorg. Chem., 23 (1984) 3841.
410 J.M. Kelly, C.M. O'Connell, and J.G. Vos, J. Chem. Soc., Dalton Trans., (1986) 253.
411 J.M. Clear, J.M. Kelly, C.M. O'Connell, J.G. Vos, C.J. Cardin, S.R. Costa, and A.J. Edwards, J. Chem. Soc., Chem. Commun., (1980) 750.
412 D. Choudhuri and D.J. Cole-Hamilton, J. Chem. Soc., Dalton Trans, (1982) 1885.
413 R.W. Callahan and T.J. Meyer, Inorg. Chem., 16 (1977) 574.
414 J.M. Kelly and J.G. Vos, J. Chem. Soc., Dalton Trans., (1986) 1045.
415 B. Durham, S.R. Wilson, D.J. Hodgson, and T.J. Meyer, J. Am. Chem. Soc., 102 (1980) 600.
416 G.M. Brown, R.W. Callahan, and T.J. Meyer, Inorg. Chem., 14 (1975) 1915.
417 T.K. Foreman, J.B.S. Bonilha, and D.G. Whitten, J. Phys. Chem., 86 (1982) 3436.
418 W.M. Wallace and P.E. Hoggard, Inorg. Chem., 19 (1980) 2141.
419 G. Giro, P.G. Di Marco, and G. Casalbore, Inorg. Chim. Acta, 50 (1981) 201.
420 J.G. Xu and G.B. Porter, Can. J. Chem., 60 (1982) 2856.
421 L.J. Henderson and W.R. Cherry, Chem. Phys. Lett., 114 (1985) 553.
422 J.M. Clear, J.M. Kelly, D.C. Pepper, and J.G. Vos, Inorg. Chim. Acta, 33 (1979) L139.
423 B. Durham, J.L. Walsh, C.L. Carter, and T.J. Meyer, Inorg. Chem., 19 (1980) 860.
424 P.P. Zarnegar and D.G. Whitten, J. Am. Chem. Soc., 93 (1971) 3776.
425 P.P. Zarnegar, C.R. Bock, and D.G. Whitten, J. Am. Chem. Soc., 95 (1973) 4367.
426 P.E. Hoggard and G.B. Porter, J. Am. Chem. Soc., 100 (1978) 1457.
427 J.P. Collin and J.P. Sauvage, Inorg. Chem., 25 (1986) 135.
428 R.R. Ruminski and J.D. Petersen, Inorg. Chem., 21 (1982) 3706.
429 P. Bonneson, J.L. Walsh, W.T. Pennington, A.W. Cordes, and B. Durham, Inorg. Chem., 22 (1983) 1761.
430 K.K. Cloninger and R.W. Callahan, Inorg. Chem., 20 (1981) 1611.
431 M.A. Weiner and A. Basu, Inorg. Chem., 19 (1980) 2797.
432 S. Goswami, R. Mukherjee, and A. Chakravorty, Inorg. Chem., 22 (1983) 2825.
433 J.G. Gaudiello, P.R. Sharp, and A.J. Bard, J. Am. Chem. Soc., 104 (1982) 6373.
434 A.R. Chakravarty and A. Chakravorty, J. Chem. Soc., Dalton Trans., (1982) 1756.
435 S. Goswami, A.R. Chakravarty, and A. Chakravorty, Inorg. Chem., 22 (1983) 602.
436 R.J. Crutchley, A.B.P. Lever, and A. Poggi, Inorg. Chem., 22 (1983) 2647.

437 N.E. Tokel and A.J. Bard, J. Am. Chem. Soc., 94 (1972) 2862.
438 J.G. Gaudiello, P.G. Bradley, K.A. Norton, W.H. Woodruff, and A.J. Bard, Inorg. Chem., 23 (1984) 3.
439 R. Mukherjee and A. Chakravorty, J. Chem. Soc., Dalton Trans., (1983) 2197.
440 K.A. Goldsby and T.J. Meyer, Inorg. Chem., 23 (1984) 3002.
441 D.W. Pipes and T.J. Meyer, Inorg. Chem., 23 (1984) 2466.
442 P. Ghosh and A. Chakravorty, Inorg. Chem., 23 (1984) 2242.
443 H. Duerr, G. Doerr, K. Zengerle, J.-M. Curchod, and M.A. Braun, Helv. Chim. Acta, 66 (1983) 2652.
444 C.M. Elliott, R.A. Freitag, and D.D. Blaney, J. Am. Chem. Soc., 107 (1985) 4647.
445 G.A. Lawrance, Polyhedron, 4 (1985) 817.
446 G. Bidan, A. Deronzier, and J.-C. Moutet, Nouv. J. Chim., 8 (1984) 501.
447 T. Guarr, M.E. McGuire, and G. McLendon, J. Am. Chem. Soc., 107 (1985) 5104.
448 J.M. Calvert, R.H. Schmehl, B.P. Sullivan, J.S. Facci, T.J. Meyer, and R.W. Murray, Inorg. Chem., 22 (1983) 2151.
449 J.V. Caspar, B.P. Sullivan, and T.J. Meyer, Organometallics, 2 (1983) 551.
450 J.L. Walsh and B. Durham, Inorg. Chem., 21 (1982) 329.
451 A.H.A. Tinnemans, K. Timmer, M. Reinten, J.G. Kraaijkamp, A.H. Alberts, J.G.M. van der Linden, J.E.J. Schmitz, and A.A. Saaman, Inorg. Chem., 20 (1981) 3698.
452 S. Goswami, A.R. Chakravarty, and A. Chakravorty, Inorg. Chem., 20 (1981) 2246.
453 O. Haas, M. Kriens, and J.G. Vos, J. Am. Chem. Soc., 103 (1981) 1318.
454 D.P. Rillema and K.B. Mack, Inorg. Chem., 21 (1982) 3849.
455 P. Denisevich, H.D. Abruna, C.R. Leidner, T.J. Meyer, and R.W. Murray, Inorg. Chem., 21 (1982) 2153.
456 B.P. Sullivan, D.J. Salmon, and T.J. Meyer, Inorg. Chem., 17 (1978) 3334.
457 E.C. Johnson, B.P. Sullivan, D.J. Salmon, S.A. Adeyemi, and T.J. Meyer, Inorg. Chem., 17 (1978) 2211.
458 R.J. Staniewicz, R.F. Sympson, and D.G. Hendricker, Inorg. Chem., 16 (1977) 2166.
459 M.J. Powers, R.W. Callahan, D.J. Salmon, and T.J. Meyer, Inorg. Chem., 15 (1976) 894.
460 R.R. Ruminski and J.D. Petersen, Inorg. Chem., 21 (1982) 3706.
461 J.L. Walsh, R. Morris Bullock, and T.J. Meyer, Inorg. Chem., 19 (1980) 865.
462 J.A. Connor, T.J. Meyer, and B.P. Sullivan, Inorg. Chem., 18 (1979) 1388.
463 B.A. Moyer and T.J. Meyer, Inorg. Chem., 20 (1981) 436.
464 F.R. Keene, D.J. Salmon, J.L. Walsh, H.D. Abruna, and T.J. Meyer, Inorg. Chem., 19 (1980) 1896.
465 J. Watanabe, T. Saji, and S. Aoyagui, Bull. Chem. Soc. Jpn., 55 (1982) 327.
466 R.W. Callahan, F.R. Keene, T.J. Meyer, and D.J. Salmon, J. Am. Chem. Soc., 99 (1977) 1064.
467 H.Y. Al-Saigh and T.J. Kemp, J. Chem. Res. (S), (1984) 212.
468 A.R. Chakravarty, Indian J. Chem., 21A (1982) 1128.
469 K.M. Iwamura, Nippon Kagaku Kaishi, 10 (1983) 1456.
470 S.L. Tan, M.K. DeArmond, and K.W. Hanck, J. Electroanal. Chem., 181 (1984) 187.
471 S. Roffia and M. Ciano, J. Electroanal. Chem., 77 (1977) 349.
472 S. Geraty and J.G. Vos, J. Electroanal. Chem., 176 (1984) 389.
473 Y. Ohsawa, K.W. Hanck, and M.K. DeArmond, J. Electroanal. Chem., 175 (1984) 229.
474 Y. Matsuda, Y. Takasu, M. Morita, K. Tanaka, M. Okada, and T. Matsumura, Denki Kagaku Oyobi Kogyo Butsuri Kagaku, 53 (1985) 632.
475 O. Haas and J.G. Vos, J. Electroanal. Chem., 113 (1980) 139.
476 G.M. Brown, R.W. Callahan, and T.J. Meyer, Inorg. Chem., 14 (1975) 1915.

477 T. Matsumura-Inoue, J. Electroanal. Chem., 95 (1979) 109.
478 J.M. Calvert, D.L. Peebles, and R.J. Nowak, Inorg. Chem., 24 (1985) 3111.
479 B.P. Sullivan, D. Conrad, and T.J. Meyer, Inorg. Chem., 24 (1985) 3640.
480 C.A. Goss and H.D. Abruna, Inorg. Chem., 24 (1985) 4263.
481 A.A. Diamantis and J.V. Dubrawski, Inorg. Chem., 22 (1983) 1934.
482 C.R. Bock, J.A. Connor, A.R. Gutierrez, T.J. Meyer, D.G. Whitten, B.P. Sullivan, and J.K. Nagle, J. Am. Chem. Soc., 101 (1979) 4816.
483 B.P. Sullivan, J.V. Caspar, S.R. Johnson, and T.J. Meyer, Organometallics, 3 (1984) 1241.
484 P. Bonneson, J.L. Walsh, W.T. Pennington, A.W. Cordes, and B. Durham, Inorg. Chem., 22 (1983) 1761.
485 M.-A. Haga, Inorg. Chim. Acta, 45 (1980) L183.
486 M.J. Root, B.P. Sullivan, T.J. Meyer, and E. Deutsch, Inorg. Chem., 24 (1985) 2731.
487 D.G. Whitten, Angew. Chem., 91 (1979) 472.
488 R.W. Callahan and T.J. Meyer, Inorg. Chem., 16 (1977) 574.
489 B. Durham, J.L. Walsh, C.L. Carter, and T.J. Meyer, Inorg. Chem., 19 (1980) 860.
490 M.J. Powers and T.J. Meyer, Inorg. Chem., 17 (1978) 2955.
491 A.D. Hamilton, H.-D. Rubin, and A.B. Bocarsly, J. Am. Chem. Soc., 106 (1984) 7255.
492 F.R. Keene, D.J. Salmon, and T.J. Meyer, J. Am. Chem. Soc., 98 (1976) 1884.
493 P.A. Adcock and F.R. Keene, J. Am. Chem. Soc., 103 (1981) 6494.
494 M.J. Ridd and F.R. Keene, J. Am. Chem. Soc., 103 (1981) 5733.
495 G.M. Brown, T.R. Weaver, F.R. Keene, and T.J. Meyer, Inorg. Chem., 15 (1976) 190.
496 D.F. Mahoney and J.K. Beattie, Inorg. Chem., 12 (1973) 2561.
497 B.P. Sullivan, J.A. Baumann, T.J. Meyer, D.J. Salmon, H. Lehmann, and A. Ludi, J. Am. Chem. Soc., 99 (1977) 7368.
498 D.N. Marks, W.O. Siegl, and R.R. Gagne, Inorg. Chem., 21 (1982) 3140.
499 A.R. Chakravarty and A. Chakravorty, Inorg. Chem., 20 (1981) 3138.
500 R.A. Krause and K. Krause, Inorg. Chem., 19 (1980) 2600.
501 J.C. Curtis, B.P. Sullivan, and T.J. Meyer, J. Am. Chem. Soc., 104 (1983) 224.
502 H.D. Abruna and A.J. Bard, J. Am. Chem. Soc., 104 (1982) 2641.
503 P.A. Adcock, F.R. Keene, R.S. Smythe, and M.R. Snow, Inorg. Chem., 23 (1984) 2336.
504 J. Desilvestro, D. Duonghong, M. Kleijn, and M. Graetzel, Chimia, 39 (1985) 102.
505 H. Tom Dieck, W. Kollvitz, and I. Kleinwaechter, Inorg. Chem., 23 (1984) 2685.
506 C.M. Elliott and R.A. Freitag, J. Chem. Soc., Chem. Commun., (1981) 156.
507 P. Bernhard, H. Lehmann, and A. Ludi, J. Chem. Soc., Chem. Commun., (1981) 1216.
508 R. de la Rosa, P.J. Chang, F. Salaymeh, and J.C. Curtis, Inorg. Chem., 24 (1985) 4231.
509 Y. Ohsawa, T. Saji, and S. Aoyagui, J. Electroanal. Chem., 106 (1980) 327.
510 R.W. Callahan, G.M. Brown, and T.J. Meyer, Inorg. Chem., 14 (1975) 1443.
511 D. Beer, Master Thesis, University Fribourg (1980).
512 P. Belser, Proceedings of the Swiss Chem. Soc. Meeting, Bern (1986).
513 K. Haarmann, Master Thesis, University Fribourg (1986).
514 P. Belser, unpublished results.
515 S.-M.Y. Huang and H.D. Gafney, J. Phys. Chem., 81 (1977) 2602.
516 K. Monserrat, T.K. Foreman, M. Graetzel, and D.G. Whitten, J. Am. Chem. Soc., 103 (1981) 6667.
517 R.J. Staniewicz and D.G. Hendricker, J. Am. Chem. Soc., 99 (1977) 6581.
518 S. Roffia, C. Paradisi, and C.A. Bignozzi, J. Electroanal. Chem., 200 (1986) 105.