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Coordination Chemistry Reviews
190–192 (1999) 671–682

COORDINATION CHEMISTRY REVIEWS

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Photoinduced processes in multicomponent arrays containing transition metal complexes

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Received 29 September 1998; accepted 13 March 1999

Contents

Abstract

The authors' recent activity in the study of photoinduced energy and electron transfer in linear arrays containing porphyrins assembled around a Ru(II) ion, is reviewed. The effect of substituents and distance and the role of the heavy metal ion is discussed. The photophysical and electrochemical properties of Ir(III) terpyridine complexes indicate that Ir(III) ion is a

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PII: S0010-8545(99)00105-8

good candidate to successfully replace Ru(II) in the construction of multiporphyrinic linear arrays to achieve efficient photoinduced electron transfer. Preliminary results on multi-porphyrinic systems based on Ir(III) bis-terpyridine are presented.

Keywords: Energy transfer; Electron transfer; Porphyrins; 2,2′:6′,2″-Terpyridine complexes; Ruthenium; Iridium

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1. Introduction

The ability of a transition metal ion to organize ligands around its coordination sphere has been successfully used to assemble multicomponent systems with the twofold result of including the metal complex in the structure and directing the orientation of components [1]. Functionalization of the ligands by suitable photo-active/electroactive units can lead to the construction of molecular assemblies with a selected geometry, able to perform useful photoinduced acts [2]. The use of Ru(II), Os(II), Rh(III) with terdentate terpyridine substituted at the 4′ position afforded one-dimensional systems, particulary suited to achieve photoinduced vectorial energy and electron transfer [3]. The use of 1,4-phenylene spacers allows modulation of the distance and electronic coupling between the components [4].

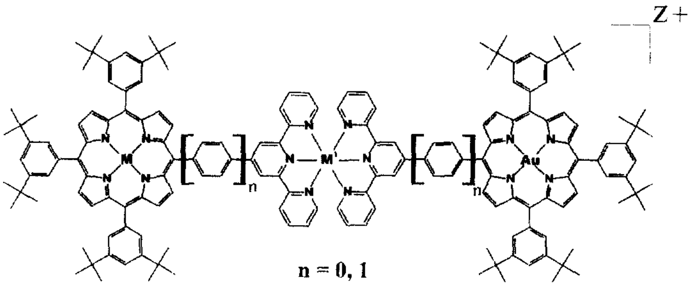
A previous report on molecular triads consisting of a Zn (or free-base)-etio porphyrin and a gold(III)-tetra-aryl porphyrin assembled via a Ru(II)-terpyridine unit, has successfully demonstrated the occurrence of efficient photoinduced electron transfer from the Zn (or free-base)-ethio porphyrin to the Au(III) porphyrin mediated by the interposed ruthenium complex over a distance of 3 nm [5]. Following the excitation of the zinc etio-porphyrin in the excited singlet state a primary electron transfer to the nearby Ru(II) occurs; the reduced complex, consisting of a Ru(II) and the radical anion of the ligand, is able to reduce the nearby gold porphyrin unit leading to a fully charge-separated state whose lifetime is 30 ns. In spite of the good performances of this assembly (60% yield), the need for substitution of the etio-porphyrin with a more robust tetra-aryl porphyrin urged for the development of new assemblies.

Introduction of an aryl-porphyrin, less liable to oxidation than the etio- derivative was, in fact, expected to alter the overall thermodynamic balance with dramatic changes in the properties. A further aspect we wanted to investigate is related to the replacement of the ruthenium(II)bis(terpyridine) complex. This chromophore is characterized [6] by: (i) a short excited state life time (< 1 ns) which makes useful processes scarcely competitive toward the intrinsic deactivation to the ground state and (ii) energy level of the lowest excited state (^{3}MLCT) very close to those of the other components, therefore it can play a role as quencher of the other excited chromophores by energy transfer, a parasitic process toward the desired electron transfer.

This report summarizes our groups' recent activity in this field, aimed at the development of multi-component structures based on the assembling of active components by a templating metal center and at the optimization of the factors influencing the vectorial electron transduction. Scheme 1 depicts the type of systems discussed.

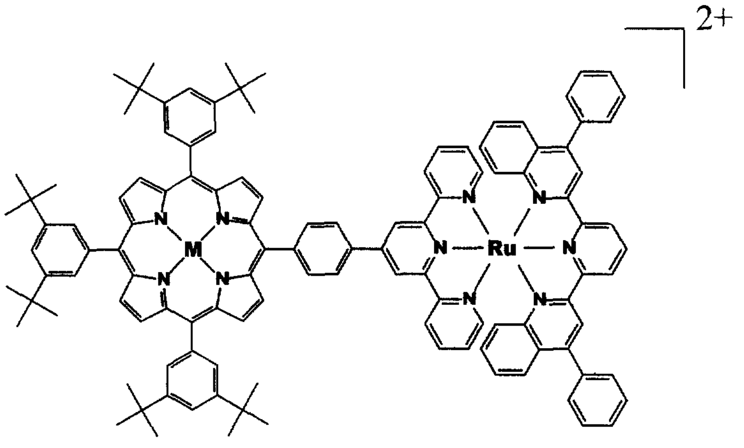
2. Experimental

Butyronitrile (BuCN) of the purest commercially available grade, and acetonitrile (MeCN), methanol (MeOH), ethanol (EtOH) of spectroscopic grade were used for photophysical determinations. Cyclic voltammetry experiments were performed using an EG&G 273 A potentiostat, a Pt working electrode, a Pt counter-electrode, a saturated calomel electrode (SCE), 0.1 M Bu_4NPF_6 as supporting electrolyte and nitriles or dimethylformamide (DMF) as solvents. Absorption spectra were recorded with a Perkin Elmer Lambda 9 spectrophotometer and luminescence spectra with a Spex Fluorolog II equipped with Hamamatsu R928 or R3896 phototubes. A phosphorimeter accessory 1934D (Spex) was used to detect delayed spectra. Emission lifetimes were determined by: (i) an IBH single-photon counting apparatus (nanosecond range); (ii) a system based on a Nd:YAG laser and a Streak Camera (20 ps resolution); (iii) a system based on a nanosecond Nd:YAG laser and a photomultiplier (microsecond range). Transient absorption spectra and lifetimes were determined by: (i) a laser- flash-photolysis apparatus based on a Nd:YAG laser (from 20 ns to millisecond range); (ii) a pump and probe system based on a 35 ps Nd:YAG laser and an OMA (30 ps to 3.3 ns range). Experiments performed at 77 K used a home-made quartz dewar filled with liquid nitrogen to hold the sealed cuvettes or the capillary tubes. For experiments at temperatures above 100



M = Zn, 2H **M' = Ru(II),** Z = 3
M' = Ir(III), Z = 4

Scheme 1.



1^{2+} **: M = 2H**

2^{2+} **: M = Zn**

Fig. 1. Schematic formulae of arrays $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$.

K, the sample cell was placed in a Thor cryostat. Details on experimental conditions have been reported previously [7].

3. Results and discussion

3.1. Systems based on Ru(II)

Our first approach was directed at substituting the chemically fragile etio-porphyrin with a more robust tetraryl free-base or zinc derivative [7]. Since the latter derivatives are less electron rich, a Ru(II)-terpyridine derivative more prone to reduction was used in order to maintain the driving force for charge separation. The use of a strong π-acceptor ligand such as 2,6-bis (4-phenyl-2-quinolyl) pyridine (bpqpy), Fig. 1, with a reduction potential lower than that of the 4′-(p-tolyl)-2,2′:6′,2″-terpyridine (ttpy), i.e. -0.83 V versus SCE versus -1.24 V versus SCE, respectively, provided favourable conditions for the charge separation. For this Ru-based unit, the low energy content of the ^{3}MLCT excited state (1.83 eV) was expected to result in a long-lived excited state of the complex [6]. The upper lying metal-centered excited states, responsible for the fast deactivation, were in fact expected to be less accessible for energetic reasons, producing an increase in the mlifetime and therefore favouring the direct involvement of the ^{3}MLCT state, in the intercomponent photoprocesses.

Spectroscopic and electrochemical data in BuCN allow the construction of an energy level diagram as reported in Fig. 2(a,b) [7b] for the free-base derivative $\mathbf{1}^{2+}$ and Zn-porphyrin derivative $\mathbf{2}^{2+}$, respectively. In these schemes the excited states energy levels are derived from the maxima of the experimental emission band at 77 K and the energy of the charge- separated states are calculated from the electrochemical data in the same solvent [8]. At 77 K the energy levels are the same as those reported for room temperature in Fig. 2 except for the charge- separated state which is destabilized by the lack of reorientation of the solvent in the frozen matrix and is lifted to higher, unaccessible energies [3d,9]. For the sake of simplicity the data at 77 K will be discussed first [7a].

At 77 K, quenching of the porphyrin fluorescence occurs with rate constants of 9×10^9 s^{-1} and $> 5 \times 10^{10}$ s^{-1} (beyond our resolution) in the case of the free-base $\mathbf{1}^{2-}$ and Zn-derivative $\mathbf{2}^{2-}$, respectively. The quenching is assigned to energy transfer to the ^{3}MLCT level localized on the Ru(ttpy-bpqpy) complex, which is in turn quenched with a rate similar for the two derivatives, ca. 2×10^8 s^{-1}, by the triplet localized on the porphyrin. The so-formed porphyrin triplets in the dyads decay to the ground state with a rate constant very close to that of the models, showing that the heavy Ru(II) ion is exerting a modest perturbation on the intersystem

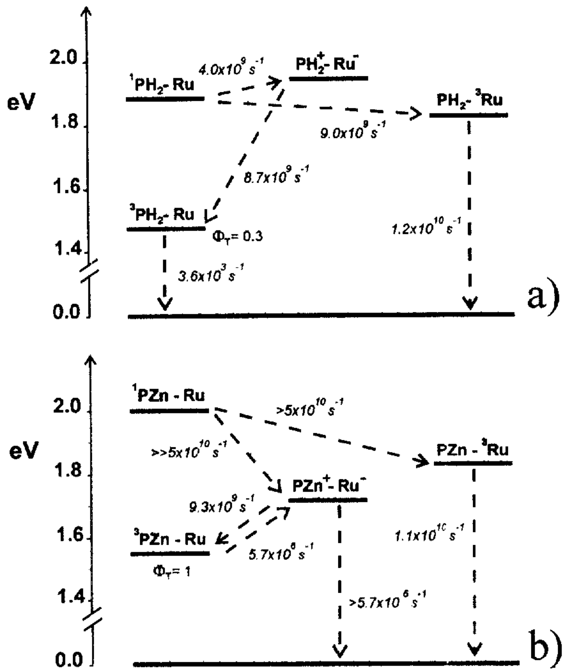
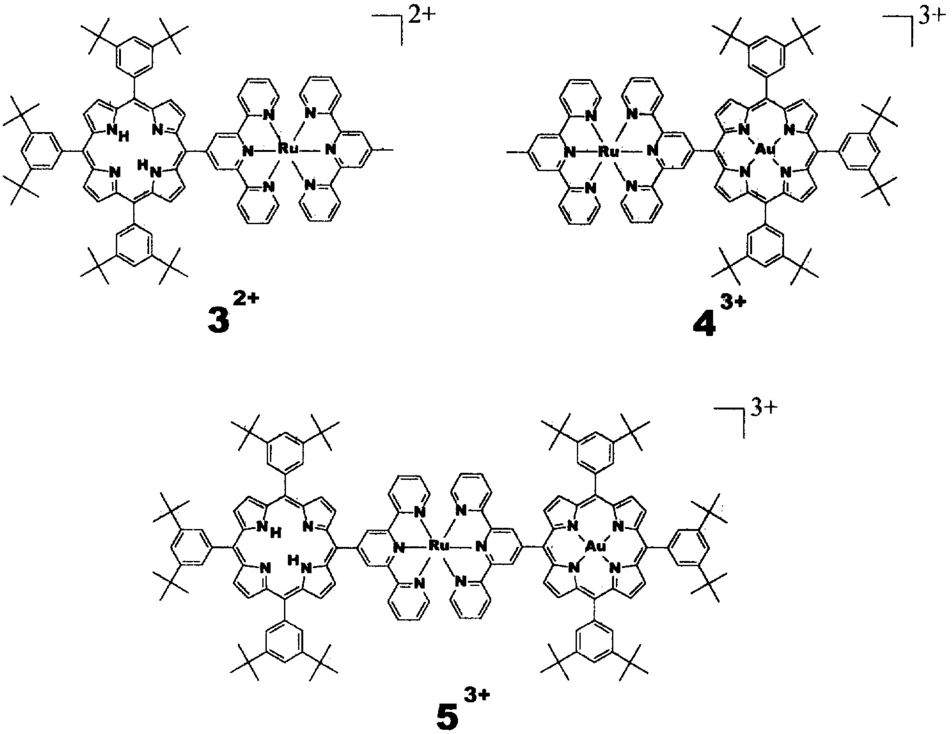


Fig. 2. Energy level diagram of $\mathbf{1}^{2+}$ (a) and $\mathbf{2}^{2+}$ (b) at room temperature. The dyads have been schematized by their constituting unit. Reaction rates of the deactivation processes are indicated. The yield of the porphyrin triplet (ϕ_T) are calculated by taking into account the quanta absorbed by the porphyrin unit at the excitation wavelength (at 532 nm 33% for $\mathbf{1}^{2+}$ and 20% for $\mathbf{2}^{2-}$).



3^{2+}

4^{3+}

5^{3+}

Fig. 3. Schematic formulae of dyads 3^{2+}, 4^{3+}, and triad 5^{3+}.

crossing step of the nearby porphyrin. By discussing the room temperature results illustrated in Fig. 2 we should bear in mind that energy transfer processes monitored at 77 K are also possible at room temperature with a rate at least comparable to the one detected in glass [10].

At room temperature electron transfer steps are identified, mainly for the case of the dyad containing the Zn-porphyrin, which features a charge-separated state with lower energy than the free-base derivative. Interestingly, an activated process from the long-lived Zn porphyrin triplet to the upper lying charge separated state takes place. However, no long-lived charge-separated states were formed and the occurrence of energy transfer processes was found to be effective. We want to point out that the primary parasitic energy transfer step occurs from a porphyrin excited singlet to an MLCT excited state localized on the metal complex which is formally a triplet. The role of the heavy metal ion in perturbing the spin multiplicity of the system is one of the peculiarity of this type of arrays containing heavy metal ions. The unexpectedly short lifetime of the complex at room temperature (80 ps) is probably caused by a perturbation of the ligand field brought about by the steric crowding of the bpqpy ligand, with a consequent deactivation through a thermally accessible metal-centered excited state [6]. In spite of the fact that electron transfer was fast and effective, competitive energy transfer to the Ru(II) complex could occur and in this case the metal complex performed as an energy drain, because of its intrinsically short excited state lifetime.

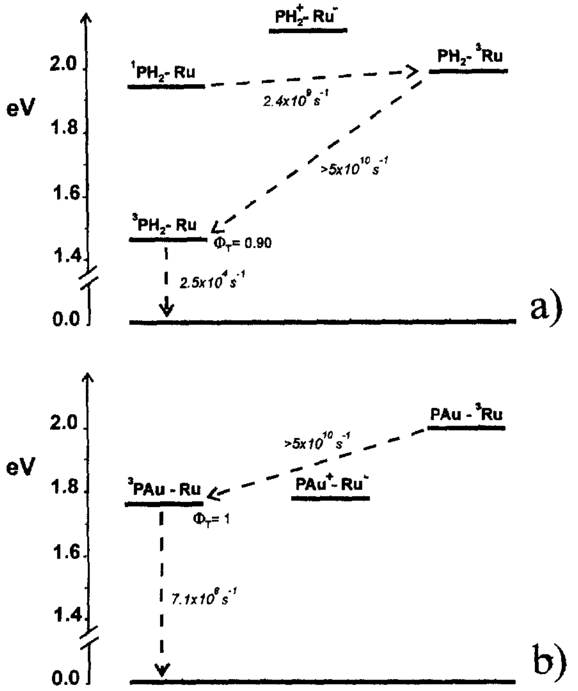


Fig. 4. Energy level diagram for dyads 3^{2+} (a) and 4^{3+} (b) at room temperature. Reaction rates of the deactivation processes are indicated. The yield of the triplet (ϕ_T) are calculated on the basis of the quanta absorbed by the *whole* array. At 532 nm the photons absorbed by the porphyrin unit are 45% for 3^{2+} and 70% for 4^{3+}.

A subsequent approach was aimed at reducing the distance between the electron donor and acceptor components, and the triad reported in Fig. 3 was studied [11]. This should increase the coupling of the components possibly by promoting a stronger interaction between the terminal porphyrins, so as to produce the thermodynamically allowed direct electron transfer from the free-base to the gold porphyrin. In spite of the strong coupling of the components, the electrochemical and spectroscopic data showed that the components, basically, retain their individual properties allowing the assumption of nonadiabatic conditions. A detailed study of photoinduced processes in the model molecular dyads 3^{2+} and 4^{3+} allowed the complex processes occurring in the triad to be unravelled.

A simplified energetic scheme in BuCN where the energy levels are derived as previously stated, is reported in Fig. 4(a,b) for dyads 3^{2+} and 4^{3+} and in Fig. 5 for on the ruthenium unit. The latter, with a rate faster than our resolution, transfers energy to the porphyrin localized triplet, where all the energy delivered to the system is conveyed. In 4^{3+}, excitation of the Au–porphyrin results in the immediate (for our resolution) formation of the lowest triplet, to which also the energy absorbed by the excited state localized on the ruthenium complex is transferred. In triad 5^{3+}, upon excitation of the free base porphyrin, a series of energy transfer processes similar to those detected in the dyads occurs, leading to the triplet of the two porphyrins with a relative efficiency of four in favour of the gold porphyrin triplet. It has to be noticed that the triplet localized on the gold porphyrin is also formed by direct absorption of photons (50% at 532 nm). The triplet states so-formed decay with little perturbation with respect to the model; in particular the charge-separated state corresponding to a reduced gold porphyrin and an oxidized free-base porphyrin unit was not populated, in spite of its thermal accessibility from the triplet localized on the gold porphyrin. This behaviour is ascribable to the short lifetime, 1.4 ns at room temperature, of the gold (III) porphyrin triplet. In none of the arrays we find any spectroscopic or kinetic evidence for the formation of a charge separated state. Experiments on triad 5^{3+} in a rigid alcoholic glass at 100 K [12], showed the occurrence of a triplet–triplet energy transfer from the gold to the free-base porphyrin (center to center distance 2.1 nm) with a rate constant of 2.5×10^7 s^{-1}. Since the geometry of the structure seems to prevent a direct electronic contact of the donor and the acceptor units, the triplet energy transfer which occurs by an electron exchange mechanism (Dexter mechanism) [13] must involve the intermediacy of the ruthenium complex spacer, whose HOMO and LUMO orbitals are to be involved in a 'superexchange' mechanism [14]. Once again in the above system we found that energy transfer processes are extremely competitive toward electron transfer processes with similar (or even more favourable) driving forces. This probably reflects the lower reorganizational energy required by an energy transfer process (no net charge transferred) [15]. The role of the heavy metal ion of the complex in promoting fast energy transfer steps which are formally spin-forbidden is essential.

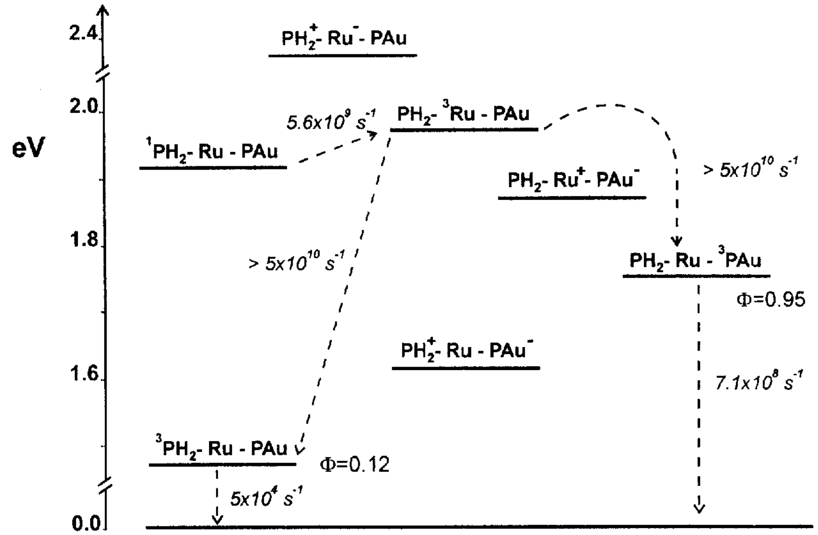
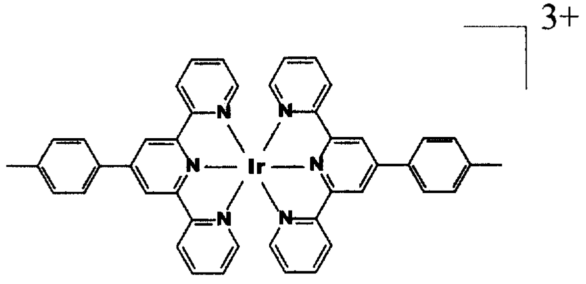


Fig. 5. Energy level diagram for the triad 5^{3+} at room temperature. The reaction rates of the deactivation processes are indicated. The yield of the triplet (ϕ_T) are calculated as in Fig. 4. The partition of absorbed photons at 532 nm is 20% on the free base porphyrin, 30% on the ruthenium complex and 50% on the gold porphyrin.



6^{3+}

Fig. 6. Schematic formula of $\mathbf{6}^{3+}$.

3.2. Systems based on Ir(III)

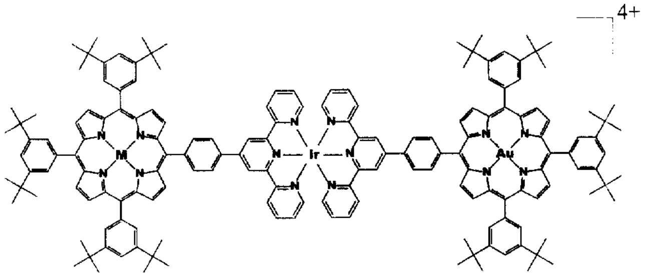
A consequent development of this project is the search for a different metal complex (M^n) which should: (i) preserve the favourable geometry of the terpy ligand which warrants a linear and rigid arrangement of the components and inhibit scrambling of the terpy units; (ii) possess excited states at energy > 2.3 eV in order to prevent energy dissipation by undesired energy transfer and (iii) possess electrochemical properties so as to be easily reduced by the Zn-(or free base) porphyrin excited state which is the primary electron donor ($E_{1/2}$ $M^{n/n-1} >$ ca. -0.9 V vs. SCE), and (iv) in its reduced form act as electron donor toward the gold porphyrin ($E_{1/2}$ $M^{n/n-1} < -0.47$ V vs. SCE). With this objective in mind, the photophysical and electrochemical properties of a newly prepared series of Ir (III) terpyridine-type complexes have been determined [16]. One of the investigated complexes is reported in Fig. 6 and some of its photophysical and electrochemical properties are collected in Table 1.

As one can see, the properties of $\mathbf{6}^{3+}$ are well suited to replace Ru(II)–terpyridine derivatives successfully in the construction of linear arrays of the type examined above and of other non-porphyrinic arrays. In particular the lifetime (2.4 μs in air equilibrated solutions) and the energy of the excited state (2.5 eV) are particulary attractive

Table 1
Photophysical and electrochemical properties of $\mathbf{6}^{3+}$ [a]

λ_{max} emission, RT	506 nm
τ, RT (air equilibrated)	2.4 μs
τ, RT (deaerated)	9.5 μs
Φ_{em} (air equilibrated)	0.029
λ_{max} emission, 77 K	494 nm
Excited state energy	2.5 eV
τ, 77 K	39 μs
$E_{1/2}$ $\mathbf{6}^{3+}/\mathbf{6}^{2+}$ vs. SCE	-0.81 V

[a] Photophysical data at room temperature in MeCN, at 77 K in BuCN; electrochemical data in DMF.



7^{4+} : M = 2H
8^{4+} : M = Zn

Fig. 7. Schematic formulae of Ir(III) based triads 7^{4+} and 8^{4+}.

for the reasons outlined above. The reduction potential ($E_{1/2}$ vs. SCE = −0.81 V for $6^{3+}/6^{2+}$) indicates the feasibility of the reduction of the complex by the excited state of the Zn(or free-base) porphyrin and the possibility for the complex, once reduced, to transfer an electron to the gold porphyrin. In addition, the lowest excited state of

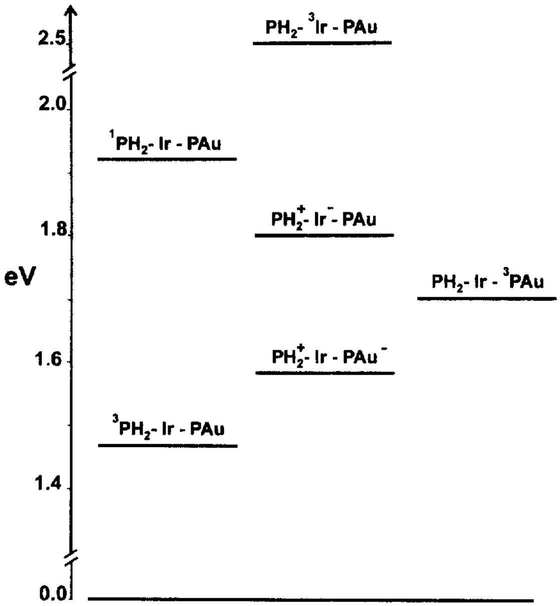


Fig. 8. Tentative energy level scheme for triad 7^{4+}. The levels are based on the spectroscopic energies and the redox potentials of the molecular models.

this complex, a ligand-centered triplet, has also very intense green emission, out of the spectral range of emission of porphyrins, and a rather strong triplet–triplet absorption around 650 nm. Furthermore the rate of quenching by oxygen is of the order of 10^8 M^{-1} s^{-1}, quite low for pyridyl-type complexes; which should conveniently allow to work in air-equilibrated solutions.

The building up of molecular assemblies using Ir(III) as templating ion for terpyridine ligands appended to suitable electro and photoactive units is possible. Triads containing Zn (or free-base) porphyrin on one end and gold(III) porphyrin on the other (Fig. 7), have an energy level scheme of the type illustrated in Fig. 8, for the case of free-base porphyrin 7^{4+}.

We expect $\mathbf{8}^{4+}$, the zinc derivative, will display an even more favourable energetics with respect to 7^{4+} for giving long-range electron transfer. The driving force for the primary charge separated state Zn^+ - Ir^- - Au should in fact increase, because of the higher energy content of the excited state localized on the Zn porphyrin with respect to the free-base (2 vs. 1.9 eV, respectively) and the lower oxidation potentials of the Zn derivative with respect to the free-base porphyrin ($E_{1/2} = 0.86$ vs. ca. 1 V vs. SCE in BuCN, respectively).

Preliminary measurements on the triad 7^{4+} indicate a very efficient quenching at room temperature of the porphyrin free-base luminescence. In contrast, no quenching is detected in rigid glass at 77 K. These facts indicate that, at least the primary electron transfer from the free-base porphyrin to the iridium center is extremely efficient. Work is currently in progress to elucidate the detailed nature of the processes occurring within these supramolecular arrays.

4. Conclusions

This report outlines the results achieved in the optimization of the performances of multi-porphyrin linear arrays assembled around a metal centre, designed to achieve photoinduced charge separation. Replacement of the etio-porphyrin with the more robust aryl porphyrin has produced important changes in the outcome of the system which is essentially deactivating by parasitic energy transfer processes. The key role of the central Ru(II) complex in promoting such deactivation has been recognized so that a more convenient metal center, Ir(III), has been employed. Ir(III) terpyridine-type complexes have proven to possess the desired characteristics, namely high energy and long lifetime of the lowest-lying excited state, convenient redox properties and convenient strong diagnostic signals both in emission and absorption. Preliminary measurements on a multy-porphyrin linear array assembled around a terpiridyl Ir(III) complex are indicative of efficient electron transfer processes. Further investigations on this system are in progress.

Acknowledgements

We thank Valérie Heitz, Jean-Olivier Dalbavie and Vincenzo Balzani for their collaboration in the early part of this research. The financial support of CNR

(Italy), CNRS (France),the French Ministry of Education, Research and Technology and the Royal Society (UK) is acknowledged.

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