Construction of One-Dimensional Multicomponent Molecular Arrays: Control of Electronic and Molecular Motions☆

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Transition metals are powerful three-dimensional templates, which can gather various functionalized ligands and orient them in a precise fashion so that complex multicomponent molecular systems can be obtained without constructing covalently-assembled edifices. The compounds thus prepared exhibit precise chemical or physical functions, which are governed by the design of the system. The construction of one-dimensional molecules around ruthenium(II) or osmium(II), using rigid ligands attached to the desired electroactive species, leads to systems that are able to undergo charge separation after photonic excitation. In other related compounds, a ruthenium(II)-based chromophore is, for example, connected to an osmium(II) complex by means of rod-like bridging ligand, thereby ensuring strict control over the Ru···Os distance. By tuning the length and the electronic properties of the bridge, one can control the efficiency of the electronic energy transfer between the two chromophores. In particular, the use of a bis-cyclometallating ligand is very conducive to energy transfer and allows the observation of this process up to a Ru..Os distance of ≈20 Å. By combining the building blocks of these inorganic systems with appropriate porphyrins, long-range (centre-to-centre distance between the donor and the acceptor porphyrins ≈30 Å) and relatively long-lived photoinduced charge separation has been demonstrated. Finally, with copper(I) as the template, compounds of the rotaxane family are obtained, which consist of a coordinating ring threaded by a string-like component. If this acyclic fragment is end-functionalized by two bulky stoppering groups and if it incorporates two different coordination sites (a bi- and a terdentate chelate site), novel dynamic properties are observed. The movement of a given fragment of the molecule is triggered by changing the metal oxidation state. This one-dimensional motion of the ring along the string on which it is threaded is controlled by redox manipulation, resulting in a primitive molecular machine.

Pablo Gaviña (top left) was born in Valencia, Spain, in 1966. He studied chemistry at the Universidad de Valencia, where he received his Ph. D. in 1994 with Professor R. Mestres, on dienediolates of unsaturated carboxylic acids and on the protection and controlled release of aldehydic pheromones. He then spent two years as postdoctoral fellow with Dr. J.-P. Sauvage, working on chemical topology and on electrochemically induced molecular motions. He is currently working with Professor G. Asensio in the Department of Organic Chemistry of the Universidad de Valencia on enantioselective protonation of prochiral enolates.

Valérie Heitz (bottom left) was born in Strasbourg, France, in 1966. After completing a Ph. D. with Dr. J.-P. Sauvage in 1992 on multiporphyrin systems performing photoinduced electron transfer, she did postdoctoral work with Dr A. Harriman at the Center for Fast Kinetic Research at the University of Texas at Austin. She obtained a position as "Maître de Conférences" at the University of Strasbourg in 1993 and carries out research work in the laboratory of J.-P. Sauvage. Her current interest concerns the synthesis of functional models of photosynthetic reaction centres.

Jean-Paul Collin (top right) was born in 1945 in Metz. After his Ph. D. in electrochemistry with Professor J. P. Schwing at the Louis Pasteur University, Strasbourg, he did postdoctoral work with Professor J.-M. Lehn on water photolysis. He is now a CNRS research director. He joined Dr J.-P. Sauvage's group in 1983 and his present research focuses on photoinduced charge separation in multicomponent molecular systems.

Jean-Pierre Sauvage (bottom right) was born in Paris in 1944. He obtained his Ph. D. from the University of Strasbourg, under the supervision of J.-M. Lehn. After postdoctoral research in Oxford (UK), with M.L.H. Green, he went back to Strasbourg, where the started his own research group in 1980. His interests span from models of the photosynthetic reaction centre to molecular topology.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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Contents

1. Introduction

In complex multicomponent molecular systems, the control of physical properties related to electron- and energy-transfer or displacement of molecular fragments relies, to a large extent, on our mastery of the geometrical properties of the ensemble.

For several years, we have been interested in one-dimensional compounds, for which an axis along the largest dimension of the object can be clearly defined[1][2][3]. If rigidity can also be introduced during the design and synthesis steps, distances and, sometimes, angles between the various components located on the axis can be estimated to a good approximation.

Two distinct aspects of our research are discussed in the present review article: (i) electron- or energy-transfer, and (ii) molecular motions, related to "molecular machines", along an axis.

(i) The aims of the first and main topic are manifold. In the short term, it is important to improve our understanding of electron- and energy-transfer processes and to verify the current theories[4][5][6][7] by modifying at will the distances and orientations between the various chromophores and electrophores of the assembly, and by changing their electronic properties as well as those of the spacer groups used in the construction of the systems. An aspect of this approach is to build and study models[8][9][10][11][12] of photosynthetic reaction centres (RC), which function so efficiently in living organisms, and in particular in photosynthetic bacteria[13][14]. In the long term, it would of course be of great interest to build molecular systems or hybrid devices, containing molecules and organic or inorganic solids, capable of converting light energy into electrochemical or chemical energy[15][16][17]. In other words, the creation of artificial systems able to perform real photosynthesis is a special challenge.

(ii) The second line of research is more recent and is concerned with molecular machines and motors[18][19][20], i.e. molecular ensembles for which a large amplitude and reversible motion can be triggered simply by sending a signal to the molecule from outside. This signal is usually electrochemical (reduction or oxidation of an electroactive component) or photochemical. However, many other types of perturbations can be envisaged: magnetic or electric field, temperature or pressure jump, chemical signal (pH change), etc. In our case, the notion of axis and geometrical control is again essential. Scheme 1 illustrates, in a simplified fashion, the two facets of the work discussed herein.

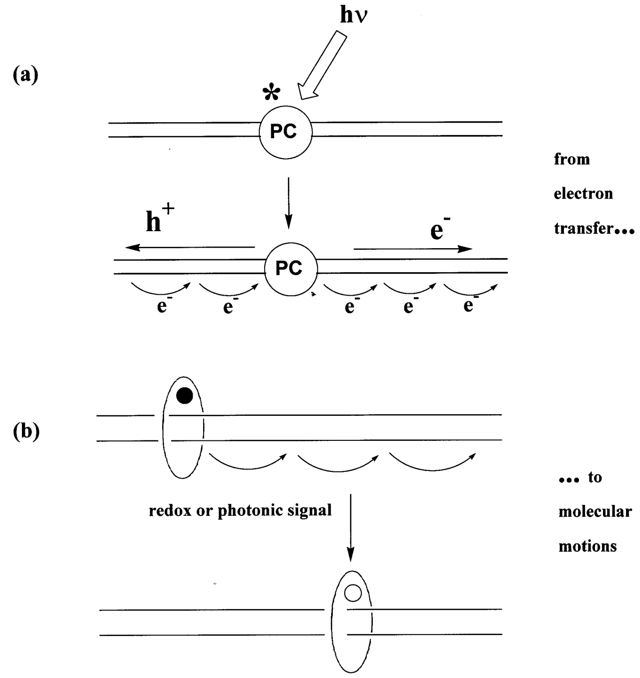
2. Complexes of Ruthenium(II) and Osmium(II) Covalently Linked to Electron Donor and Acceptor Groups

One of the key features of natural photosynthesis is the efficiency of charge separation. In a multistep procedure, light energy absorbed by a photoactive centre is converted into electrochemical energy with formation of a long-lived charge-separated state. This complex process relies on the subtle arrangement of energy levels for the excited or redox states involving the various chromophores, favouring a cascade-like sequence of electron-transfer steps leading to the charge-separated state.

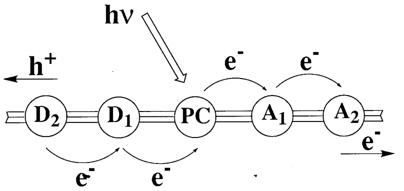
In the field of transition metal complexes, one can design multicomponent systems for which similar charge separation may occur, provided that the electronic properties of the various chromophores are controlled and selected in a precise fashion, and that there is strict control over the geometrical properties of the set of photo- and electroactive species (Scheme 2).

On the basis of their photochemical, photophysical and electrochemical properties, M(II) polypyridine complexes (M = Ru or Os) are, in principle, suitable photosensitizer components for use in multicomponent systems designed to permit efficient photoinduced charge separation[15][21][22][23][24]. However, with ligands such as 2,2′-bipyridine, the building up of multicomponent molecules

Scheme 1. In a one-dimensional multicomponent system, a photoactive centre (PC) is (a) first excited by a photon. The excited state is subsequently able to transfer an electron to an acceptor (on the right of the PC, not represented). This process induces a series of cascade-like electron-transfer steps the overall effect of which is to create a negative charge on the right-side and a positive hole on the left-side of the array. (b) A redox or photonic signal modifies the coordination requirements of a metal centre (black dot) incorporated in a rotaxane, triggering molecular motions. The shift of the ring and the metal is induced by modification of the metal centre coordination sphere

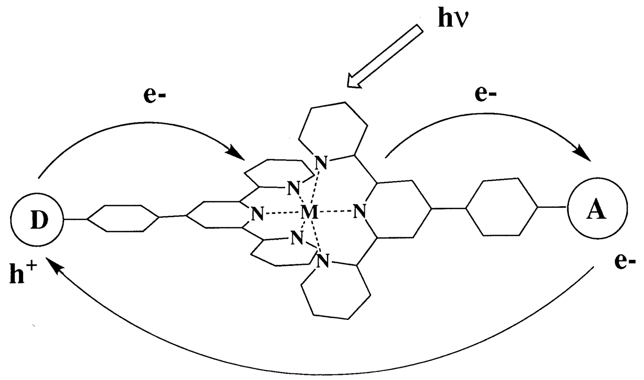


Scheme 2



leads to systems in which the acceptor or donor groups linked to the chromophore are relatively close to one another (*cis*-type configuration)[25]. In contrast, the geometry of terpyridine complexes offers the possibility of designing systems in which the D and A components lie in opposite directions with respect to the chromophore (*trans*-type configuration)[1]. In addition, bis-terpyridine complexes bearing substituents at the 4′-position do not lead to isomeric (enantio- and diastereomeric) mixtures, in contrast to the corresponding substituted bipyridine systems. Furthermore, the interposition of aromatic rings (Figure 1) affords a convenient means of increasing the A−D separation[26].

Figure 1. Schematic representation of the photochemically-induced electron-transfer step in an M(tpy)$_2^{2+}$ complex bearing acceptor (A) and donor (D) groups



2.1. Synthesis of Terpyridine Ligands

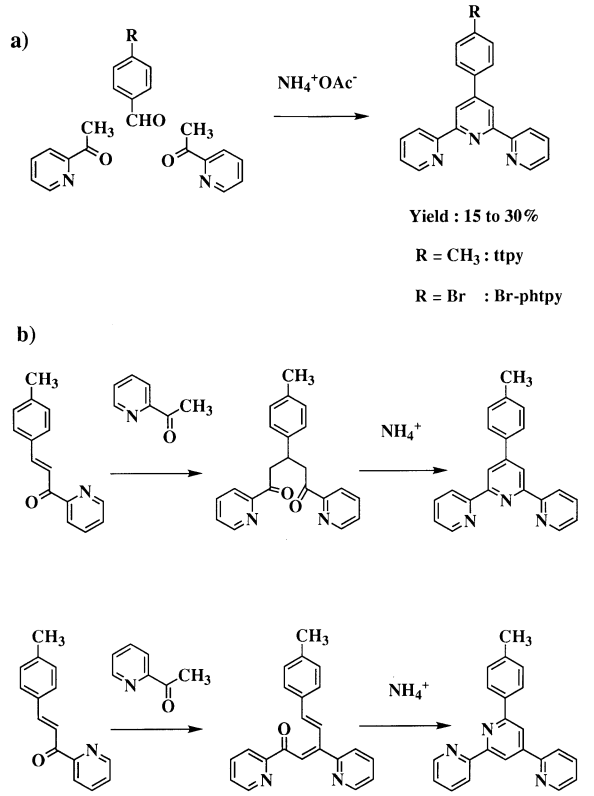
Since the first preparation of the 2,2′:6′,2"-terpyridine ligand 60 years ago by oxidative coupling of pyridine with FeCl$_3$ in an autoclave[27], other strategies involving the coupling of pyridine units (cross-coupling methodology)[28] or the formation of one or two pyridine rings from precursor functions have been developed. Certainly, the most commonly used methodology is the synthesis of the central pyridine ring. The pioneering works of Hantzsch[29], Tschitschibabin[30], Case[31], Kröhnke[32] and others using this principle, have been followed by new developments and improvements. In particular, the works of Constable[33], Potts[34] and Jameson′s group[35] allow the preparation of various substituted terpyridines. In order to obtain large amounts of the 4′-aryl-2,2′:6′,2″-terpyridine, the one-pot Hantzsch synthesis, developed by Case[31] and later by Calzaferri[36], was selected (Figure 2a).

The condensation of the aromatic aldehyde with two equivalents of 2-acetylpyridine gave a 1,5-diketone. Ring closure was achieved using ammonium acetate. In some cases, two terpyridine isomers[37] could be obtained following a 1,2- or 1,4-Michael addition on the unsaturated ketone intermediate (Figure 2b).

The separation of the terdentate ligand, arising from 1,4-addition, from the sterically hindered bidentate ligand was readily achieved by formation of the highly stable Fe(terpyridine)$_2^{2+}$ complex, as described by Constable et al.[33] The iron(II) complex, upon treatment with H$_2$O$_2$ in alkaline solution, yielded the free terpyridine in good yield.

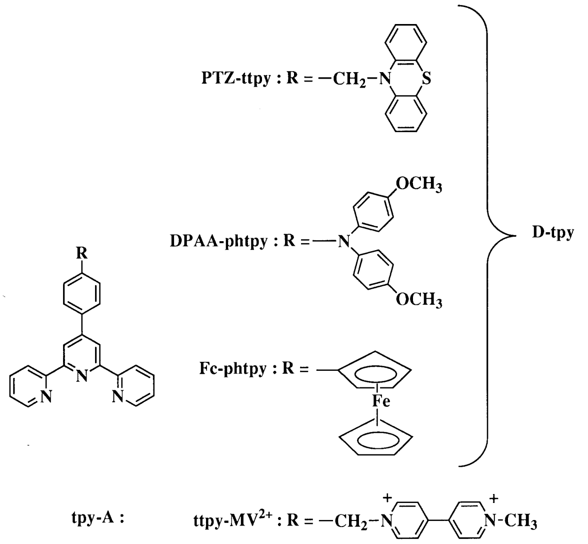
The terpyridine-bearing electroactive compounds could be prepared using one of two general strategies. In the first of these, the ligand is synthesized bearing a suitable functionality and the desired electrophore is then introduced in a second step[37][38]. The other possibility involves introduction of the electroactive function into the aromatic aldehyde prior to the terpyridine formation reaction[37]. Both routes have been explored and used, the method of choice being dictated by the chemical stability of the donor or the acceptor groups, since the second ap-

Figure 2. (a) Synthetic route to various substituted terpyridines. (b) Formation of 2,2′:6′,2″-terpyridine and its isomer (2,2′:4′,6″-) via 1,2- or 1,4-Michael addition



proach implies that the electrophore will have to resist the relatively harsh experimental conditions of the cyclisation reaction. Figure 3 depicts various ligands, containing either D or A units as pendant groups, prepared by these two strategies.

Figure 3. Various tpy derivatives used, with an electrophore rigidly attached to the chelate via a 1,4-phenylene spacer. PTZ = phenothiazine; DPAA = di-*p*-anisylamine; Fc = ferrocene; MV^{2+} = methylviologen



2.2. Synthesis of Diads and Triads Based on Ru(tpy)$_2^{2+}$ -Type Photosensitizers

The various ruthenium(II) complexes prepared and studied are listed in Table 1. The various ligands used are depicted in Figure 3.

Table 1. Preparation of the various ruthenium(II) diad or triad complexes[a] A: sequential method; B: statistical method

Complex	Method[a]	Yield (%)	Reference
(Fc-phtpy)Ru(ttpy)$^{2+}$	A	15	[38]
(Fc-phtpy)Ru(ttpy)$^{2+}$	A	5	[37]
(DPAA-phtpy)Ru(ttpy)$^{2+}$	A	37	[37]
(ttpy)Ru(ttpy-MV^{2+})$^{4+}$	B	8	[26][37]
(PTZ-ttpy)Ru(ttpy-MV^{2+})$^{4+}$	B	5	[26][37]
(DPAA-phtpy)Ru(ttpy-MV^{2+})$^{4+}$	B	8	[26][37]
(Fc-phtpy)Ru(ttpy-MV^{2+})$^{4+}$	B	18	[41]

They have been prepared either in a *sequential manner* (A) or by a *statistical method* (B):

(A): $\mathrm{Ru(ttpy)Cl_3 + tpy{-}D \xrightarrow{(i)} Ru(ttpy)(tpy{-}D)^{2+}}$
(i): reflux in ethanol/water/triethylamine for 1 h

(B): "ruthenium blue" $\mathrm{+ L_1 + L_2 \xrightarrow{(ii)}}$
$\mathrm{Ru(L_1)_2^{2+} + Ru(L_1)(L_2)^{2+} + Ru(L_2)_2^{2+}}$
$\mathrm{(L_1)(L_2)}$: (ttpy)(ttpy−MV^{2+}), (PTZ−ttpy)(ttpy−MV^{2+}), (DPAA−phtpy)(ttpy−MV^{2+})
(ii): reflux in ethanol for 18 h

Method (A) was used for ligands bonded to an electron donor (tpy−D). However, it turned out not to be appropriate for the synthesis of complexes containing the ttpy−MV^{2+} ligand. The triads and the electron acceptor diad Ru(ttpy)(ttpy−MV^{2+})$^{4+}$ were thus prepared according to the statistical procedure (B).

2.3. Synthesis of Diads and Triads Based on Os(tpy)$_2^{2+}$ -Type Photosensitizers

Although the coordination sphere of ruthenium is known to be relatively inert vis-à-vis substitution reactions, it is still very labile as compared to osmium. In fact, substituting ligands within the coordination sphere of osmium is notoriously difficult and requires either extremely harsh conditions or multistep procedures involving different metal oxidation states. Using the ligands shown in Figure 3, various osmium(II) complexes could be prepared[26][38][39][40][41]. Due to the chemical fragility of some of the ligands, the very drastic classical conditions, consisting of heating osmium salts and the ligands at very high temperature (typically, refluxing ethylene glycol) for long periods could not be systematically applied. Consequently, more elaborate, specific methods had to be developed. The two general routes used are indicated in Figure 4.

The series of osmium(II) diad and triad complexes prepared and investigated is listed in Table 2.

Importantly, since photophysical measurements are very sensitive to impurities, special care was taken in order to ensure the isolation of very pure samples of the various ruthenium(II) and osmium(II) complexes. For this purpose,

Figure 4. The two general routes to substituted bis(tpy)osmium(II) complexes

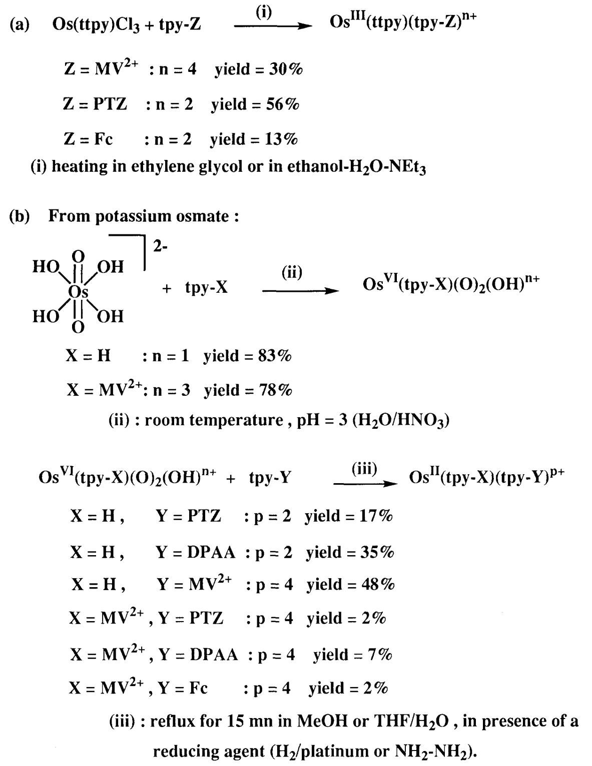


Table 2. The various multicomponent compounds prepared containing a bis-terpyridine osmium(II) central chromophore

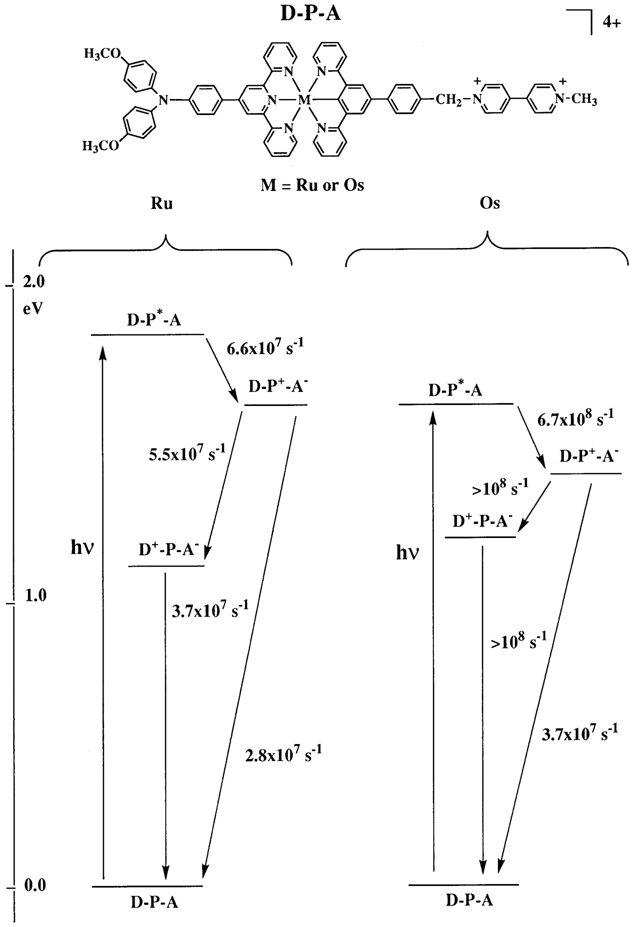
Complex	Method (see Figure 4)	Reference
$(ttpy)Os(ttpy\text{-}MV^{2+})^{4+}$	(a) or (b)	[26][40]
$(PTZ\text{-}ttpy)Os(ttpy)^{2+}$	(a)	[26][40]
$(Fc\text{-}phtpy)Os(ttpy)^{2+}$	(a)	[38]
$(DPAA\text{-}phtpy)Os(ttpy)^{2+}$	(b)	[40]
$(PTZ\text{-}ttpy)Os(ttpy\text{-}MV^{2+})^{4+}$	(b)	[39]
$(DPAA\text{-}phtpy)Os(ttpy\text{-}MV^{2+})^{4+}$	(b)	[39]
$(Fc\text{-}phtpy)Os(ttpy\text{-}MV^{2+})^{4+}$	(b)	[41]

all the compounds prepared were subjected to chromatography on silica gel, with a mixture of solvents (usually CH_3CN and H_2O) containing a salt (KNO_3, for instance) as eluent.

2.4. Photoinduced Processes in Diads and Triads Based on $Ru(tpy)_2^{2+}$ and $Os(tpy)_2^{2+}$-Type Photosensitizers

As is normal for ruthenium(II) and osmium(II) polypyridine complexes, light excitation in the spin-allowed MLCT bands eventually leads to population of the lowest energy ^{3}MLCT level[23][42], which is the state responsible for the observed electron-transfer processes. Since $Ru(tpy)_2^{2+}$ is practically non-emitting at room temperature, the experiments on this species and its derivatives were performed at 155 K[43]. For the compounds based on $Os(ttpy)_2^{2+}$, which is luminescent at room temperature, experiments were performed at both 155 K and 298 K[39]. The solvent used was butyronitrile. Detailed mechanisms of the photoinduced processes in these P–A diads and in the D–P–A triads have been given in a previous review article[1]. Photoinduced processes in the D–P–A triads are depicted in Figure 5. At 155 K, the lifetime of the fully charge-separated state $D^+–P–A^-$ (P = Ru) is estimated to be 27 ns. For the Os-based triads, the deactivation via the fully charge-separated state $D^+–P–A^-$ occurs with $k > 10^8$ s^{-1}. In this case, the transient absorption spectrum of the $D^+–P–A^-$ species is not detected because this species does not accumulate but rapidly reverts to D–P–A.

Figure 5. Photoinduced processes in the $DPAA–P–MV^{2+}$ triads at 155 K, where P is $Ru(ttpy)_2^{2+}$ or $Os(ttpy)_2^{2+}$



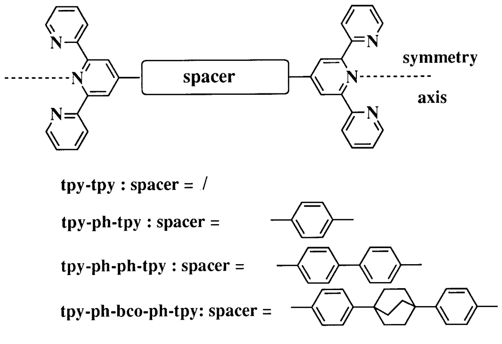
3. Rigid Rod-like Dinuclear Terpyridine-Type Complexes

Symmetrical rigid dinucleating ligands, the syntheses of which are versatile enough to allow modulation of the electronic and geometrical properties, are also promising. The family of compounds discussed in the following section allows us to evaluate the effect of metal-to-metal distance on the rate of energy- or electron-transfer between the donor subunit and the acceptor fragment, and also to assess the influence of the electronic properties of the spacer inserted between the two components.

3.1. Synthesis of Bridging Bis-terpyridine Ligands

By connecting two terpyridine units via a rigid spacer attached to their 4′-positions, bridging ligands displaying axial symmetry can be obtained. The compounds which have been synthesized and used further to make dinuclear complexes are illustrated in Figure 6.

Figure 6. Ligands used in the preparation of the heterodinuclear complexes



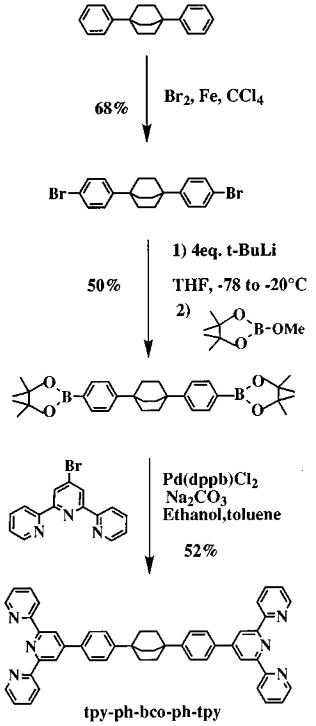
The bis-terpyridine ligand tpy−tpy was synthesized by reductive coupling of 4′-chloro-2,2′:6′,2″-terpyridine, following the methodology recently reported by Constable and Ward[44]. The phenyl-bridged bis-terpyridine ligand tpy−ph−tpy was obtained according to the method developed by Kröhnke et al.[32]. The same reaction has also been used more recently by others[45]. The principle is very general and can allow the preparation of virtually any compound containing several pyridine nuclei attached to aromatic rings. The biphenyl-containing ligand tpy−ph−ph−tpy was obtained by homo-coupling of 4′-*p*-bromophenyl-2,2′:6′,2″-terpyridine in the presence of Ni(0) triphenylphosphane complex and Zn dust in DMF. The yield was 60%, thus allowing preparation of the compound on a gram scale.

It should be noted that the bromo-terpyridine used as starting material is readily available from 2-acetylpyridine and 4-bromobenzaldehyde[36] (Figure 2). This functionalized terpyridine is the ideal precursor to a potentially bridging multi-terpyridine ligand. It should lead to bis-terpyridine systems with various aromatic or saturated spacers, as well as to bridging multi-chelates by connecting several such terpyridine units.

The preparation of the bridging ligand tpy−ph−bco−ph−tpy (bco = 2,2,2-bicyclooctane) was achieved using the multistep procedure shown in Figure 7.

The key intermediate, Br−ph−bco−ph−Br, was prepared following a modification of a procedure previously described by Zimmermann et al.[46]. Treatment of this dibromoarene with 4 equivalents of *t*-butyllithium and 2 equivalents of 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxoborolane[47] afforded a diester derivative, which could be purified by crystallization. The successful cross-coupling of the 4′-bromo-2,2′:6′,2″-terpyridine with the diester using Pd(dppb)Cl_2 [dppb = 1,4-bis(diphenylphosphane)butane] as catalyst was performed following the methodology developed by Suzuki et al.[48] and recently applied to a water-soluble *p*-phenylene-containing polymer[49].

Figure 7. Reaction used in the synthesis of the bridging ligand tpy−ph−bco−ph−tpy



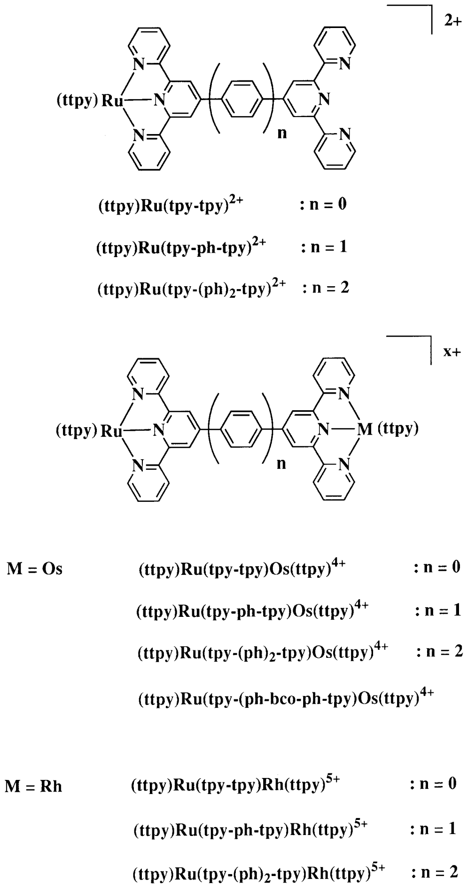
3.2. Synthesis and Photochemical Behaviour of Rigidly Bridged Heterodinuclear Complexes

The rigidly bridged ruthenium(II)-osmium(II)[50][51][52][53] and ruthenium(II)-rhodium(III)[54] complexes are depicted in Figure 8.

The general preparation of the heterodinuclear complexes requires, as a first step, the synthesis of the key complexes (ttpy)Ru[tpy−(ph)$_n$−tpy]$^{2+}$. These intermediate mononuclear compounds were obtained as follows: Ru(ttpy)Cl_3 and $AgBF_4$ were refluxed in acetone in order to remove the chlorine atoms from the metal. The complex obtained was added to a DMF solution of the bridging ligand and the mixture was refluxed for 1 h. After work-up and chromatography on alumina with CH_3CN as eluent, the compounds were isolated as their PF_6^- salts in good yields: (ttpy)Ru(tpy−tpy)$^{2+}$: 85%; (ttpy)Ru(tpy−ph−tpy)$^{2+}$: 77%; (ttpy)Ru(tpy−ph−ph−tpy)$^{2+}$: 76%. All the compounds described were characterized by standard techniques (^{1}H-NMR and FAB-MS). FAB-MS turned out to be particularly useful for these highly positively charged species. In each case, the molecular peak was sufficiently intense to eliminate any ambiguity concerning the structure of the compound.

3.2.1 Ruthenium-Osmium Complexes: The ruthenium complex bearing a free terpyridine site was allowed to react with crude (ttpy)$OsCl_3$ in refluxing *n*BuOH for 7 h. This very insoluble compound was prepared from $OsCl_3.xH_2O$

Figure 8. Mononuclear ruthenium precursors and rigidly bridged ruthenium-osmium and ruthenium-rhodium complexes



and ttpy and used without further purification. In fact, attempts to remove the chloride ions with Ag^+ were of questionable success. Depending upon the starting sample, other ruthenium-osmium complexes could be isolated in low yield[51]. The formation of these by-products seems to reflect the polymeric nature of the poorly-defined starting complex, (ttpy)OsCl$_3$.

Photophysical data (steady-state luminescence spectroscopy and time-resolved spectroscopy methods) indicate a very efficient energy-transfer process from the ruthenium chromophore to the osmium moiety[53][55]. This transfer takes place according to the exchange mechanism of Dexter[4]. Actually, the transfer of energy was found to occur with $k > 10^{10}\ s^{-1}$, even for $d_{MM} = 20$ Å (d_{MM} is the intermetal distance). One concludes that the polyphenylene bridge behaves as an extremely good energy transducer. Insertion of a bicyclooctane (bco) unit leads to an internal separation of 24 Å and results in a dramatic decrease in the rate of energy transfer ($k = 4.4 \times 10^6\ s^{-1}$ as measured at 77 K). This effect is due to the increased internal distance as well as the electronically insulating properties of the saturated bco group. It is nevertheless remarkable that energy transfer still takes place at such a large distance and in spite of the presence of a central insulating group. Studies performed by other groups with systems incorporating ethynyl[56] or other rigid spacers[57][58][59] have led to similar results.

3.2.2. Ruthenium-Rhodium Complexes: The ruthenium complex bearing a free terpyridine site was allowed to react with (ttpy)RhL$_3$ (L = acetone) in refluxing ethanol for 4 h. The latter was obtained similarly to its ruthenium analogue, by replacing the chloride ligands of the complex (ttpy)RhCl$_3$ by solvent molecules using AgBF$_4$ in refluxing acetone. As in the case of ruthenium-osmium complexes, other multinuclear by-products were isolated. Their formation can be explained in terms of reduction of the rhodium(III) centre to rhodium(I) during the complexation reaction, followed by ligand scrambling[54]. Indeed, the coordination sphere of the rhodium(I) metal is labile and the ligand interchange can easily occur.

The photophysics of the binuclear complexes were investigated in 4:1 methanol/ethanol solution at 77 K (rigid glass) and 150 K (fluid solution) and compared with data for the mononuclear Ru(ttpy)$_2^{2+}$and Rh(ttpy)$_2^{3+}$ model compounds[54]. At 77 K, no quenching of the Ru(II)-based excited state was observed, whereas energy transfer from excited state Rh(III) to Ru(II) was observed for all the complexes. At 150 K, energy transfer from excited state Rh(III) to Ru(II) was again observed for all complexes, while quenching of the excited state of Ru(II) by *electron transfer* to Rh(III) was observed, but only in the complex with $n = 0$. The different behaviour between $n = 0$ and $n = 1, 2$ can be rationalized in terms of better suited electronic factors and smaller reorganizational energies for the former species. A number of ruthenium-rhodium diads have also been synthesized and studied in recent years[60][61][62][63]. These display a variety of intercomponent energy- and electron-transfer processes.

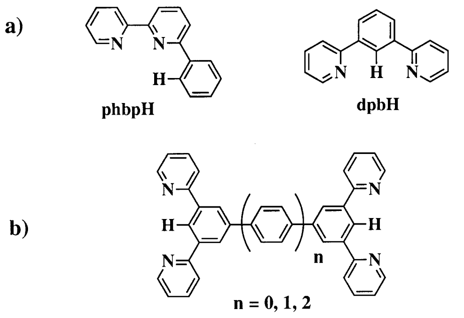
4. Rigid Rod-like Dinuclear Complexes with Biscyclometallating Terpyridine Analogues

Interestingly, the electronic properties of a multidentate ligand containing pyridine nuclei can be dramatically modified by replacing a nitrogen atom by a carbon atom (phenyl group). This procedure permits us to go from a moderate σ- and π-donating neutral species to a negatively charged ligand, provided that the metal can form a σ-bond to the deprotonated CH group of the phenyl ring. The new ligand would then be negatively charged and would, of course, be expected to behave as a strong donor and be able, for instance, to stabilize high oxidation states or to favour high field complexes. Since Ru(ttpy)$_2^{2+}$ is virtually non-luminescent at room temperature ($\tau = 0.96$ ns in CH$_3$CN), different approaches have been explored in order to overcome this difficulty. One possibility is to increase the ligand field (LF) or to diminish (to some extent) the metal-to-ligand charge-transfer (MLCT) energy level so that the MLCT and the LF states become well separated. In this context, cyclometallating ligands such as 6-phenyl-2,2′-bipyridine (phbpH) or 1,3-dipyridylbenzene (dpbH) (Figure 9a) have been combined with one terpyridine in heteroleptic complexes.

4.1. Synthesis of Cyclometallating and Bridging Bis-cyclometallating Ligands

Initially, dpbH was prepared according to a synthetic procedure described previously by Bönnemann for 2,2′-(1,4-phenylene)dipyridine[64][65]. A more convenient method employs the mild aromatic cross-coupling reaction originally described by Stille et al.[66]

Figure 9. (a) Cyclometallating and (b) bridging bis-cyclometallating ligands



The design of multicomponent systems incorporating these new chromophores and electrophores requires the synthesis of rigid, symmetrical bis-cyclometallating ligands. Mild and efficient aromatic cross-coupling reactions catalysed by various transition metal complexes have recently been used in the synthesis of natural products, large organic receptors[67], dendrimers[68] and one-dimensional polymers[69]. Applied to suitable precursors, these methodologies have permitted the preparation of three bis-cyclometallating ligands (Figure 9b), in which aromatic spacers modulate the separation distance between sites[70]. The universal precursor 5-bromo-1,3-dipyridylbenzene (Figure 10) was obtained by reaction of the 2-trimethylstannylpyridine with 1,3,5-tribromobenzene in the presence of $Pd[P(C_6H_5)_3]_2Cl_2$. It was coupled using nickel(0) to afford a 70% yield of $tpbphH_2$ (tpbph denotes tetrapyridylbiphenyl).

The ligands ($tptphH_2$ and $tpqphH_2$; tph and qph denote terphenyl and quaterphenyl, respectively) with one and two phenylene spacers were prepared using Suzuki 's cross-coupling procedure as depicted in Figure 10[48].

4.2. Preparation and Properties of Rigidly Bridged Ruthenium-Osmium Cyclometallated Complexes

By using the bis-cyclometallating ligands depicted in Figure 10, ruthenium-osmium cyclometallated complexes were prepared with the aim of studying photoinduced energy-transfer processes between the two bridged complex subunits[3][71][72]. The synthetic strategy used was the same as that described for the analogous terpyridine-type complexes (3.2.1.). The mononuclear ruthenium precursors bearing a free cyclometallating site and the corresponding heterodinuclear complexes are represented in Figure 11.

Figure 10. Synthetic steps leading to bis-cyclometallating ligands

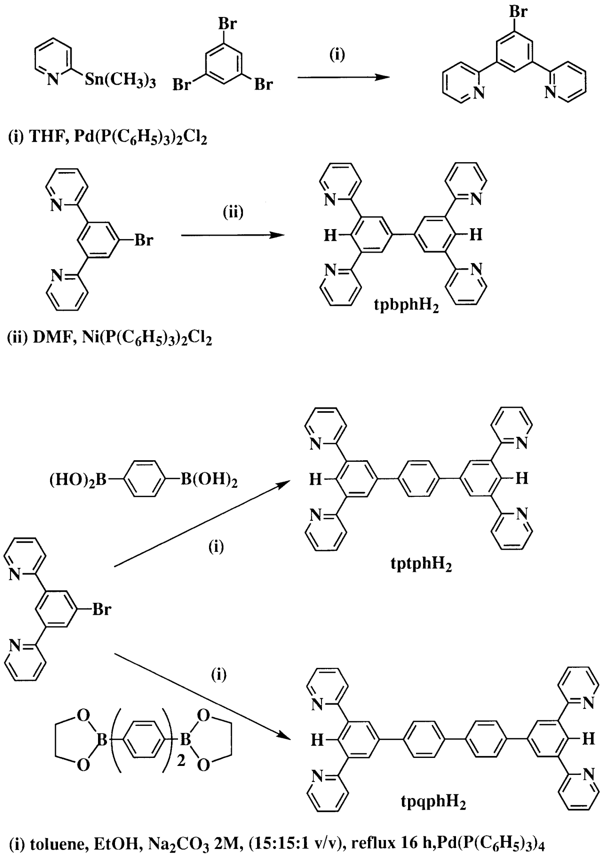
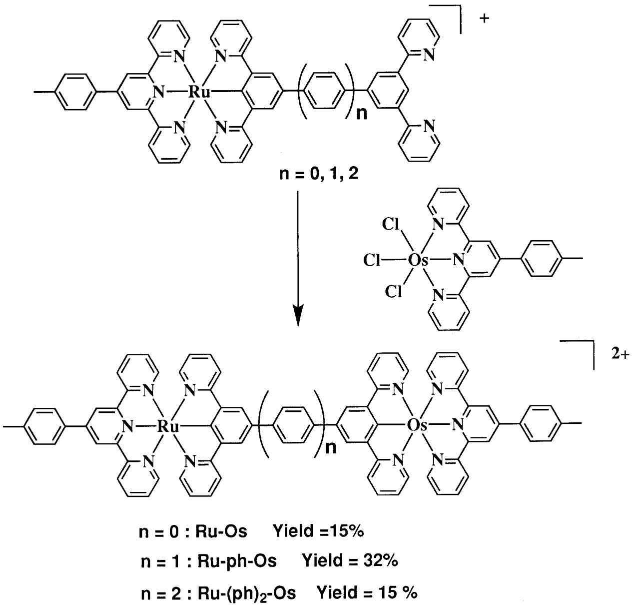


Figure 11. Synthesis of ruthenium-osmium cyclometallated complexes

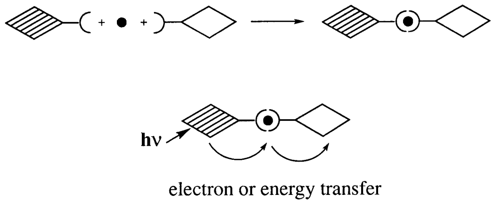


The binuclear complexes containing the dianionic ligands exhibit the same geometrical properties as the previous bis-terpyridine series, with the distance between the metal centres ranging from 11 to 20 Å, depending on the size of the phenylene spacer. For the cyclometallated series, the rate of Ru(II) to Os(II) energy transfer proved to be much slower than for the structurally identical series discussed in the previous section (3.2.1.). Thus, at room temperature, no energy transfer was observed, despite the fact that the excited state of the chromophore [Ru(ttpy)(dpb)$^+$] exhibits a lifetime of 4.5 ns in acetonitrile. At 77 K, the energy-transfer rate is affected to a large degree by the presence of the phenylene spacer. Energy transfer was found to take place according to a Dexter mechanism[4]. Comparison with analogous complexes containing non-cyclometallating bridging ligands, where the MLCT excited states involved in the energy transfer step are localized on the bridge and very fast energy transfer takes place ($k > 5 \times 10^{10}$ s^{-1}), suggests that the energy-transfer step in the cyclometallated complexes is slower because the involved MLCT excited states are directed toward the terminal ligands[3]. This apparently results in a longer transfer pathway. The main conclusions are that the phenylene spacers are very efficient in transmitting the intermetal electronic communication, but that an important role is also played by the spatial localization of the MLCT excited states involved in the excitation-transfer process (peripheral for the cyclometallated series and bridging for the non-cyclometallating family).

5. Multiporphyrin Linear Systems Assembled by Transition Metal Complexes

Multiporphyrin systems are of considerable interest in the fields of molecular electronics and artificial photosynthesis[15] with regard to converting light signals into high energy separated states. An attractive route to such systems is to use transition metals to assemble ligands, each bearing a porphyrin unit. This strategy, which uses coordination rather than covalent chemistry to interconnect the various components, offers several attractive features: (i) its high flexibility should allow easy preparation of multicomponent systems, and (ii) good geometrical control should be possible. The general concept and the synthetic principle are illustrated in Scheme 3.

Scheme 3. Strategy used to assemble asymmetrical bis-porphyrins around a central transition metal cation (black dot). The basic module consists of a porphyrin (lozenge) covalently attached to a chelate (arc of a circle). Provided the transition metal complex is resistant to ligand-exchange processes, stepwise electron- or energy-transfer can be envisaged after selective illumination of a porphyrin ring



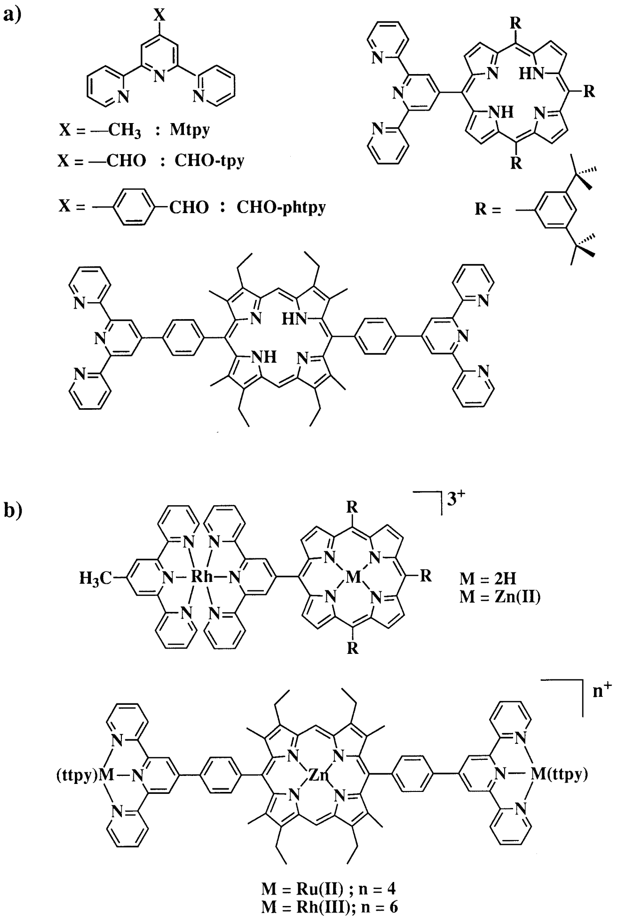
The role of the transition metal is manifold: (i) to gather and orient the system so as to have metallated porphyrins held rigidly at a fixed distance and to have asymmetrical systems able to undergo electron- or energy-transfer; (ii) to modulate the electronic coupling between the donor and acceptor porphyrins, and (iii) to form a complex which could act as a relay in electron transfer or as an antenna in energy transfer.

The ligand to be attached to each porphyrin and the binding mode used to assemble the two modules into the final conjugates are selected so as to facilitate strict stereochemical control, especially with regard to the distance between the porphyrins.

5.1. Synthesis of Porphyrin-Metal Bis-terpyridine Diads

5.1.1. Synthesis of the Ligands: The use of 2,2′:6′,2″-terpyridine as a chelate is indeed very appealing for the strategy outlined in Scheme 3, since substitution at its 4′-position leads to axially symmetric bis-terpyridine complexes. The ligands used in the preparation of the porphyrin-metal bis-terpyridine conjugates are shown in Figure 12a and their syntheses have been described[73].

Figure 12. (a) Structures of the various terpyridine ligands used for the synthesis of the diads. (b) The various terpyridine-porphyrin diads



Although the preparation of 4′-methyl-2,2′:6′,2″-terpyridine (Mtpy) is well-documented[74][75][76], we have developed a new route which gives high yields (87%) and allows the preparation of large amounts (10 g scale) of this compound. This alternative route to Mtpy involves the reaction of 4′-trifluoroacetyl-2,2′:6′,2″-terpyridine[74][77] with tetramethyltin, using the general procedure described by Stille[78]. 4′-Formyl-2,2′:6′,2″-terpyridine (CHO−tpy) was prepared from Mtpy by a modification of a procedure developed by Vismara et al.[79], while a Sommelet reaction applied to 4′-tolyl-2,2′:6′,2″-terpyridine led to the corresponding aldehyde (CHO−phtpy)[73] in 40% yield. The monoterpyridine porphyrin was prepared following Adler's procedure[80] and was isolated in 7% yield. The synthetic strategy for the preparation of bisphenylterpyridine porphyrin is derived from MacDonald's methodology[81], using the improved procedure developed by Lindsey et al.[82] This ligand was obtained pure in 42% yield after two recrystallizations of the crude material.

5.1.2. Synthesis of the Complexes: The complexes synthesized are shown in Figure 12b.

The rhodium(III) and ruthenium(II) complexes were prepared following the same strategy. In the first step, a given substituted terpyridine ligand L was reacted with the metal trichloride according to a literature procedure[37], thereby yielding $MLCl_3$ [M = Ru(III) or Rh(III)]. In the second step, after dechlorination with $AgBF_4$, the solvated complex $ML(acetone)_3^{n+}$ [M = Ru(III) or (RhIII)] was reacted with the appropriate substituted terpyridine in refluxing alcohol (EtOH or *n*BuOH).

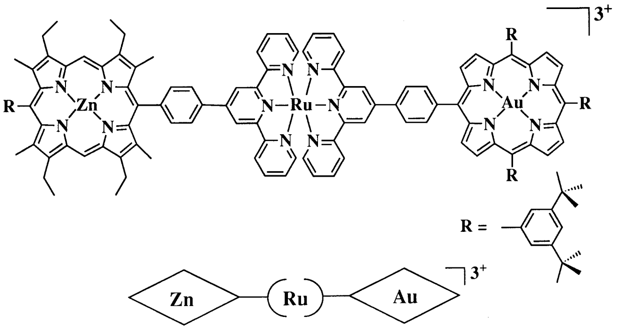
Metallation of the free-base porphyrins in the different compounds by zinc acetate is almost quantitative. The purity of each highly-colored complex was checked by thin-layer chromatography, UV/Vis spectroscopy, high resolution ^{1}H-NMR spectrometry and mass spectroscopy.

5.1.3. Photophysical Properties of the Diads: Photophysical properties have been measured for zinc and free-base porphyrins covalently linked to ruthenium(II) or rhodium(III) bis-terpyridine complexes using ultrafast transient absorption spectroscopy and the full study has been reported[73]. In each compound, the appended metal complex quenches porphyrin fluorescence. The quenching is attributed to intramolecular electron transfer from the excited singlet state of the porphyrin to the metal complex. For directly coupled systems, it appears that both forward and reverse electron-transfer steps are extremely fast, and such materials possess little attraction as building blocks. Insertion of a phenyl ring between the components has a profound effect on the dynamics of electron transfer, especially with regard to charge recombination. In particular, the relatively long lifetime (2 ns) of the charge-separated state of the zinc-porphyrin phenyl-bridged ruthenium(II) bis-terpyridine conjugate (Figure 12b) makes the ruthenium(II) complex attractive as a bridge in multicomponent systems. The ruthenium(II) bis-terpyridine-based system has the additional attraction that light absorbed by the complex is transferred to the triplet excited state of the porphyrin by way of an antenna effect.

5.2. Synthesis of a Bis-porphyrin-Ruthenium(II) Bisphenylterpyridine Triad

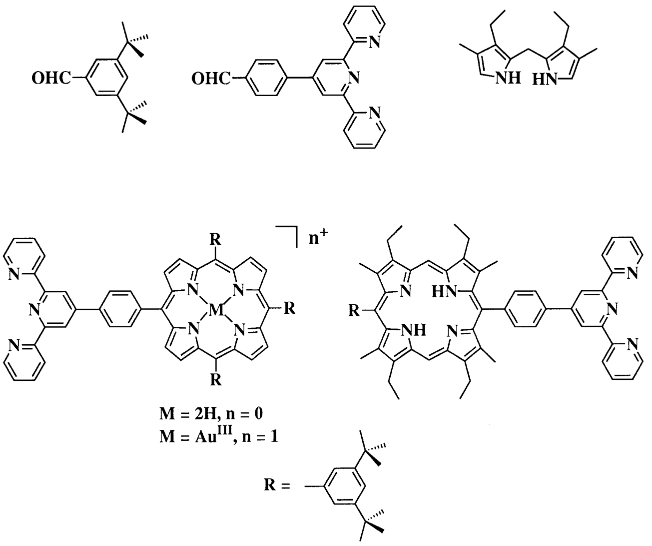
In order to perform long-range charge separation, the triad represented in Figure 13 was prepared[83][84]. It should be noted that it contains two differently substituted porphyrins, a zinc etioporphyrin-like donor and a gold(III) tetraarylporphyrin acceptor. The $-CH_3$ and $-CH_2CH_3$ substituents located at the periphery of the tetrapyrrolic donor increase the electron-donating ability of the singlet excited state (^{1}*PZn) and thus favour electron transfer to the central $Ru(tpy)_2^{2+}$ unit. On the other hand, the tetraarylporphyrin backbone metallated by a gold(III) centre is a better electron acceptor than the analogous gold(III) etioporphyrin.

Figure 13. The triad



5.2.1. Synthesis of the Ligands: The various precursors leading to the triad are depicted in Figure 14.

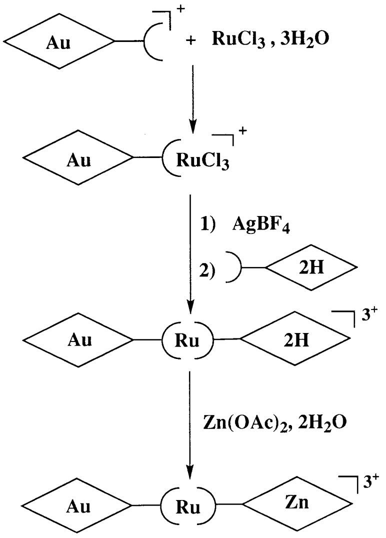
Figure 14. The various reagents and ligands used in the preparation of the triad



Synthesis of the octaalkyl diaryl porphyrin terpyridine was achieved in 20% yield following MacDonald's methodology[81] using Lindsey's conditions[82]: acid-catalysed condensation of dipyrrylmethane with 3,5-di-*tert*-butylbenzaldehyde and terpyridine benzaldehyde in a molar ratio of 6:5:1 in dichloromethane. The tetraaryl-porphyrin terpyridine was prepared using two different sets of conditions: (i) Using Adler's conditions[80], a mixture of 3,5-di-*tert*-butylbenzaldehyde, terpyridine benzaldehyde and pyrrole in a ratio of 18:1:19 was refluxed in propionic acid giving the desired compound in 13% yield after purification by column chromatography. (ii) Using Lindsey's conditions[82], a mixture of 3,5-di-*tert*-butylbenzaldehyde, terpyridine benzaldehyde and pyrrole in a molar ratio of 15:1:16 in dichloromethane containing trifluoroacetic acid was stirred at room temperature for 12 h. The resulting porphyrinogens were oxidized with tetrachloro-1,4-benzoquinone (chloranil) in refluxing dichloromethane. The crude product was purified by column chromatography, giving pure phenylterpyridine porphyrin in 9% yield. Metallation of the free porphyrin site of this compound with gold(III) was achieved in 85% yield using $KAuCl_4$ and NaOAc in refluxing acetic acid.

5.2.2. Synthesis of the Complex: Stepwise formation of the asymmetrical ruthenium(II) complex from the gold(III) porphyrin phenylterpyridine and free-base porphyrin phenylterpyridine components was realized using a procedure similar to the one described in Section 5.1.2., which is shown schematically in Figure 15.

Figure 15. Stepwise formation of the triad

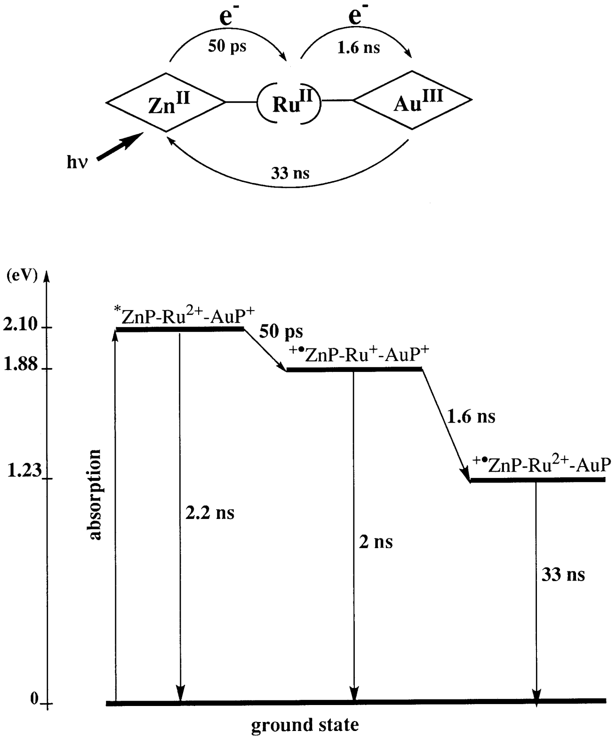


A pure sample of the triad was obtained in 35% yield by successive chromatography on silica gel, eluting with an acetonitrile/water/saturated aq. KNO_3 mixture. Metallation of the free porphyrin site was carried out with $Zn(OAc)_2$ in methanol and afforded the triad as an orange solid in 90% yield.

5.2.3. Electron-Transfer Properties of the Triad: Excitation of the terminal zinc porphyrin in the triad results in electron transfer to the central ruthenium(II) bis-terpyridine complex, which is followed by secondary electron transfer to the appended gold(III) porphyrin (Figure 16). Electron transfer occurs by two consecutive steps over a porphyrin centre-to-centre distance of ca. 30 Å.

Rate constants for the individual steps, as determined from laser photolysis studies[84], are indicated in Figure 16. The primary electron-transfer step leading to reduction of the central Ru(II) complex ($\Delta G^{\circ} = -0.25$ eV) requires 50 ps and is essentially quantitative. The second electron-transfer process follows, resulting in reduction of the distant gold(III) porphyrin. The rate constant for this second step is found to be $6 \times 10^8\ s^{-1}$. This process, for which there is a thermodynamic driving force of ca. 0.6 eV, is in competition with reverse electron transfer to restore the ground state. Subsequent charge transfer between the terminal porphyrinic subunits occurs with a rate constant of $3 \times 10^7\ s^{-1}$ and leads to regeneration of the initial system. It is interesting to compare the lifetime of 33 ns for the ultimate charge-separated state in the triad with the value of 2 ns found for that in the corresponding diad (Section 5.1.3.); this illustrates the advantage of using a multistep electron-transfer pathway.

Figure 16. Energy level diagram showing the electron-transfer sequence for the triad



The salient features of this molecular triad may be summarized as follows: (i) there is rapid interporphyrin electron transfer between linear, fixed-distance subunits, (ii) the ultimate charge-separated state, which has a lifetime of 33 ns, retains almost 60% (1.2 eV) of a photonic input of 2.1 eV and, (iii) the modular synthetic approach is highly versatile, facilitating the preparation of many different $D-A_1-A_2$ triads and higher-order, linear oligomers.

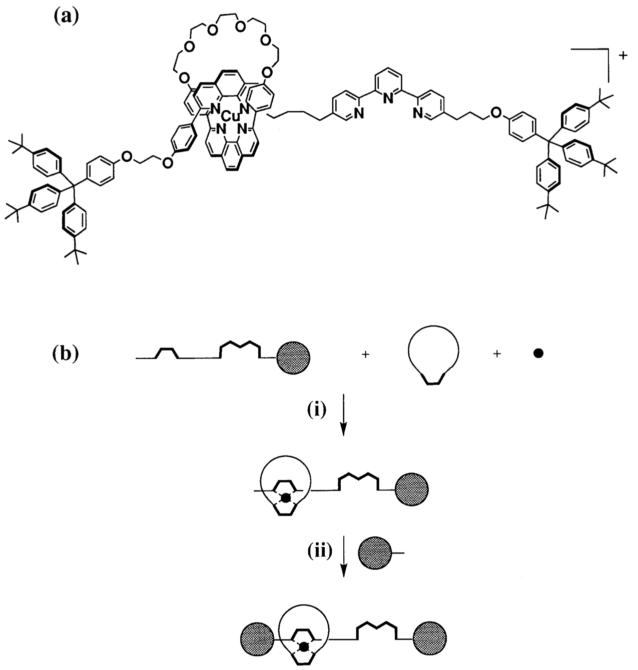
6. A Copper(I) Rotaxane Incorporating Two Different Sites in a Thread: Molecules in Motion

Molecular systems whose motions can be triggered by applying an external signal are currently of special interest, both as mimics of biological systems (redox proteins) and as potential bistable molecular devices[85][86][87][88]. Catenanes and rotaxanes are particularly well-suited in this context since reversible molecular motions using interlocked or threaded rings can be easily performed[18][89][90][91][92]. The use of transition metal-containing systems is also especially favorable since the stereoelectronic requirements of the metal can depend strongly on its oxidation state. This property can be exploited for switching a molecular system from a given geometrical arrangement, corresponding to the most stable coordination for the transition metal(s) involved, to a different geometry, simply by changing the metal oxidation state by chemical or electrochemical means, ultimately leading to the preferred coordination for the new redox state[93][94][95][96].

6.1 Synthesis of the Rotaxane

A [2]-rotaxane is a molecular system consisting of a ring threaded by a string, with two blocking groups attached at either end of the string in order to prevent dethreading[97]. Such compounds were first prepared long ago[98][99], but were largely considered as mere chemical curiosities. Recently, rotaxanes have undergone a notable revival due to the newly developed efficient procedures which make them relatively easy to make[100][101][102], as well as because of their electro- and photochemical properties[103][104][105] and their aptitude for undergoing controlled molecular motions[18][89][92]. Recently, we reported the synthesis of a copper(I)-assembled rotaxane[106] with a coordinating macrocycle containing a 1,10-phenanthroline (phen) moiety forming the ring, and a threaded fragment incorporating both a phen unit and a 2,2′:6′2″-terpyridine (tpy) coordination site (Figure 17a). The key feature of the system is its potentially dual complexing mode towards a metal, involving the phen or tpy moieties.

Figure 17. (a) Representation of the Cu(I)-rotaxane. (b) Construction principle of the Cu(I)-rotaxane

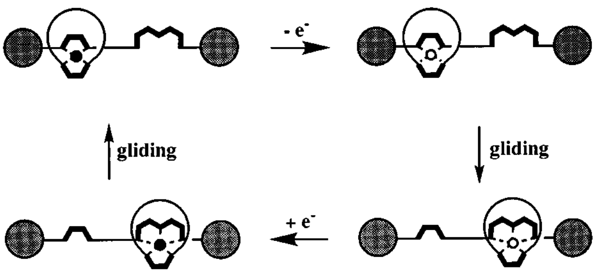


The synthetic strategy is illustrated in Figure 17b. A key step is the metal-directed threading process, often used in the past for making various catenanes and rotaxanes[107]. The bidentate chelate (phen, represented by an inverted U) and the terdentate unit (tpy, represented by a stylized M) are incorporated in an acyclic ligand, already bearing a bulky stopper at one end. The ring contains a phen nucleus. In the threading step (i) of Figure 17, copper(I) (represented by a black circle) forces the string to pass through the ring. Since copper(I) has a pronounced preference for tetracoordination, the threading reaction will selectively lead to the pseudo-rotaxane intermediate. The driving force behind this threading process is the great stability of the pseudotetrahedral bis-chelate complex between copper(I) and the two disubstituted 1,10-phenanthrolines[108]. The blocking reaction is performed by attaching a voluminous group at the other end of the coordinating string.

6.2. Electrochemically-Induced Molecular Motions

The principle of the process is explained in Figure 18. It is based on the difference of preferred coordination number for the two different redox states of the metal: 4 for copper(I) and 5 for copper(II). The electrochemical and chemical steps of the *square scheme* are analysed by a combination of cyclic voltammetry and controlled potential electrolysis experiments. The square scheme of *electron transfer induced* reactions[109] takes place, assuming that the chemical steps (motions of the ring from the phenanthroline to the terpyridine and *vice-versa*) are slow in comparison with the time scale of cyclic voltammetry. The voltammograms obtained demonstrate the perfect reversibility of the system, and also give the orders of magnitude of the rates of the chemical steps.

Figure 18. Square scheme in the copper rotaxane made in Figure 17



The stable 4-coordinate monovalent complex is oxidized to an intermediate tetrahedral divalent species. Due to the preference of copper(II) for a square-base pyramidal-type geometry, the ring moves to the terpyridine site to give the stable 5-coordinate copper(II) complex. Upon reduction, the 5-coordinate monovalent state is formed as a transient. Finally, the latter undergoes the reorganization process (opposite movement of the ring), thereby regenerating the starting complex [the shaded circle represents copper(I) and the white circle represents copper(II)].

Certainly, rotaxanes are very promising compounds with regard to electrochemically and photochemically induced molecular motions, due to the perfect chemical reversibility of the processes. Interestingly, the rates of the movements in the rotaxane are very different from those measured for related catenanes[19][90][91]. The conversion of copper(II) (4-coordinate state) to copper(II) (5-coodinate state) is much faster in rotaxane than in the interlocking ring systems described previously. This difference could reflect a greater ability of the copper(II) (4-coordinate state) in rotaxane to interact with solvent molecules or anions, the copper(II) centre being perhaps loosely bound to a fifth ligand, which would thus stabilize intermediate states on the way to copper(II) (5-coordinate state). Interestingly, the sequence of electrochemical and chemical steps involved in the square scheme of Figure 18 is very different from the classical EC mechanism universally encountered in molecular electrochemistry since, in principle, it does not consume electrons.

7. Conclusion and Prospects

Although there may still be a long way to go from the design and synthesis of multifunctional molecules with predicted electrochemical or photochemical properties to the construction of real molecular devices, utilizable as artificial photosynthetic systems, photovoltaic devices or nanoscale components in electronics, the two last decades have nevertheless witnessed substantial progress as far as complex multicomponent molecules and molecular assemblies are concerned. In particular, the use of transition metals has contributed greatly to progress in the field. In this context, the role of the metal is twofold: (i) to gather ligands bearing various functional groups and thus allow the construction of compounds with a defined arrangement, the electro- and photoactive groups incorporated in the molecule being disposed in space with a good geometrical control, and (ii) to provide interesting functions related to electronic molecular motions and thus become operative parts of the system.

In the field of electron- and energy-transfer, in relation to artificial photosynthesis, terpyridine has been used extensively. The coordination geometry and the symmetry of its complexes has been used to good advantage in the construction of several families of compounds incorporating ruthenium(II) or osmium(II) centres connected to various other electro- or photoactive components. Photoinduced charge separation over a long distance (> 20 Å) has been demonstrated in a few instances. If porphyrins are used as building blocks in conjunction with bis-terpyridine ruthenium(II), long-range (30 Å) and long-lived charge separation takes place. Energy transfer between inorganic chromophores [ruthenium(II) and osmium(II) complexes] has also been shown to occur over more than 20 Å, the success of the process being attributable to the inherent rigidity of the bridging spacer used and, above all, to the electronic properties provided by its bis-cyclometallating nature.

Molecular machines constitute an emerging field and, again, strict control over the geometry of the ensemble used and over the trajectory of the fragment(s) set in motion will be essential. It is of course much too early to know whether molecular machines and nanoscopic motors will one day be used in imaging or as molecular information storage devices, but the search for such systems is important and allows the discovery of interesting properties related to molecular dynamics. The rotaxane discussed in the present review article also has a one-dimensional component since the movement observed is that of a ring gliding on a linear fragment on which it is threaded. Presently, the system is close to bistable, but in the future it should be generalized to less primitive molecular machines, with more complex mobility (2 or several fragments in motion) or several possible geometries.

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☆ Dedicated to the memory of Professor *M. Momenteau*, a creative porphyrin chemist, who recently passed away untimely.

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