Vectorial transfer of electronic energy in rod-like ruthenium–osmium dinuclear complexes

Francesco Barigelletti,[a] **Lucia Flamigni,**[a] **Jean-Paul Collin**[b] **and Jean-Pierre Sauvage**[b]

[a] *Istituto FRAE-CNR, Via P. Gobetti 101, 40129 Bologna, Italy*
[b] *Laboratoire de Chimie Organo-Minerale, Université Louis Pasteur, Faculté de Chimie, 1 rue Blaise Pascal, F-67008, Strasbourg, France*

Dinuclear complexes containing ruthenium and osmium-based bis-terpyridyl chromophoric termini are prepared and their luminescence properties investigated. The two chromophoric units are connected by 1,4-phenylenes only, or phenylene and bicyclooctane spacers. In this way complete control of the geometry of the dinuclear complexes is achieved and these rigid species resemble molecular rods or girders featuring intermetal distances in the range 11–24 Å. The Ru $\rightarrow$ Os transfer of electronic excitation is energetically allowed and we have studied the effect on this process both of the intermetal separation and the electronic properties of the spacers. The main conclusions are that the phenylene spacers are very efficient in transmitting the intermetal electronic communication but an important role is also played by the spatial localization of the metal-to-ligand charge-transfer excited states involved in the excitation-transfer process.

Introduction

The study of vectorial photoinduced processes is of great importance in large-size molecular assemblies that combine light-sensitive components and molecular functionalities for carrying out useful functions (artificial photochemical molecular devices, PMD[1]). Basically, these molecular assemblies can be obtained either by action of weak intermolecular forces[2] or by covalently linking molecular subunits.[3] The latter approach may lead to the building up of very large species where the spatial organization of the active components is provided by suitable bridging ligands, BLs. Thus, in the presence of properly arranged energy gradients for inter-component energy- or electron-transfer steps, light absorption may drive the intercomponent processes sought for. For instance, bearing in mind the mimicry of natural systems, investigated systems include high-nuclearity light-harvesting assemblies[4] and di-, tri- or multi-partite systems for performing charge separation.[5] In all cases, the BL is expected not only to provide the spatial organization of the active components but also to be responsible for a certain amount of electronic interaction between them. Clearly, it is of importance to achieve control of the electronic factor in order to tune the various kinetic steps and ensure an efficient energy cascade.

Systems convenient for study are those in which the BLs contain a variable number of identical molecular subunits. This allows the construction of series of compounds in which (*i*) the distance between the active components is gradually varied and, as a consequence, (*ii*) the electronic interaction between them is modulated. We survey here results for relatively simple but geometrically well defined dinuclear species (Figs. 1 and 2).† These contain ruthenium- and osmium-based centres (the photochemically active units[6]), connected by bischelating BLs. In the cases illustrated here, the bridges contain (*i*) terpyridyl-[7,8] or bipyridylbenzene-like[9] chelating sites; the external ligand being 4′-*p*-tolylterpyridine in each case, and (*ii*) a spacer S that includes phenylene and bicyclooctane units. The employed BLs allow a high degree of geometric control of the dinuclear

species because the metal centres are kept at fixed distances and are linearly aligned with BL.

We will only be concerned with intramolecular (intercomponent) processes because in dilute solutions (concentration *ca.* 10^{-5} mol dm^{-3}) intermolecular processes do not take place within the considered timescales. Recent reports deal with the behaviour of BLs which include spacers like cyanide,[10] ethenyl,[11] ethenylbenzene,[12] ethenylbicyclooctane,[13] ethynylbenzene,[14] ethynylbicyclooctane[15] and polyenes.[16] These BLs are capable of providing a high degree of rigidity to the dinuclear species. We will not concern ourselves with a close comparison between our and other results;[17–19] instead we will only briefly comment on problems arising with dinuclear complexes where the ruthenium- and osmium-based photo-active units employ a tris-bipyridine instead of the bis-terpyridine-type coordination discussed here.

Synthetic strategies

The strategy employed for the synthesis of Ru–BL–Os dinuclear complexes starts with the synthesis of the symmetrical BLs (terpyridyl- or dipyridylbenzene-type ligand). Two successive steps with the suitable precursor (Ru or Os) afford the heterodinuclear complexes. In fact, the key step is the preparation of the mononuclear ruthenium complex bearing a free coordination site. The yield for this reaction can be optimized by using an excess of bridging ligand *vs.* the labile solvated ruthenium precursor, [Ru(ttp)(Me$_2$CO)$_3$]$^{2+}$. All the compounds reported here were isolated as PF$_6$$^-$ salts and characterized by ^{1}H NMR and FABMS.

The terpyridyl-type BLs were prepared by homocoupling of the appropriate terpyridine units either following the method reported by Constable and Ward,[20] or by the method of Kröhnke[21] in the case of the series with the tpy–ph$_n$–tpy BLs. Suzuki's cross-coupling procedure[22] was used for the bis-terpyridine BL incorporating the bicyclo[2.2.2]octane spacer, tpy–ph–bco–ph–tpy.

The bis-cyclometallating dipyridylbenzene BLs were also prepared by reductive coupling or Suzuki's cross-coupling reaction utilizing 1-bromo-3,5-dipyridylbenzene as the building block.[23] This latter compound was prepared by a palladium-catalysed C–C coupling procedure based on aromatic stannanes.[24]
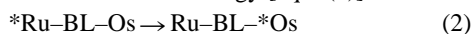
The experimental approach

In our systems, the lowest-lying excited energy levels centred on the ruthenium- and osmium-based active components are triplet states of metal-to-ligand charge-transfer (MLCT) nature.[6] These excited levels can be populated by absorption of visible light. In order to observe the Ru $\rightarrow$ Os electronic energy transfer we have performed both steady-state and time-resolved measurements.[7–9] Unfortunately, selective excitation of the donor is not possible and in the former case we have excited the Ru–BL–Os dinuclear species corresponding to an isosbestic point for the absorption of the ruthenium- and osmium-based

reference complexes. In this way 50% of the excited dinuclear species will have excitation centred on the ruthenium-based chromophore and 50% will have excitation centred on osmium-based chromophores [eqn. (1)].

$$2\ Ru–BL–Os + h\nu \rightarrow {}^*Ru–BL–Os + Ru–BL–{}^*Os \qquad (1)$$

The ruthenium- and osmium-based luminescence spectra fall in different wavelength regions and with steady-state luminescence spectroscopy it has been possible to monitor the quenching of the ruthenium-based luminescence and sensitization of the osmium-based luminescence, owing to the $Ru \rightarrow Os$ transfer of the excitation energy [eqn. (2)].

$$^*Ru–BL–Os \rightarrow Ru–BL–{}^*Os \qquad (2)$$

The same information has been obtained by employing time-resolved spectroscopic methods. In this case we have monitored the lifetime of the excited ruthenium-based unit (the energy donor), τ, in the dinuclear complex, with respect to the lifetime of the excited reference compound, τ_o, and derived the energy transfer rate, k [eqn. (3)].

$$k = \frac{1}{\tau} - \frac{1}{\tau_0} \qquad (3)$$

In some cases it has also been possible to observe time-resolved sensitization of the osmium-based component, followed by its decay.[8]

Transfer of electronic excitation energy

From the spectroscopic properties of the ruthenium- and osmium-based components,[6–9] it is possible to see that the $Ru \rightarrow Os$ transfer of electronic excitation energy [eqn. (2)] is exoergonic. This transfer takes place according to the exchange (Dexter)[25] mechanism, whereas the Coulombic (Förster)[26] mechanism has been found to be negligible.[7,9]

The exchange mechanism may be conveniently visualized as a simultaneous double electron exchange between the donor and the acceptor partners.[27] On this basis, it is possible to follow a classical approach that parallels that for non-adiabatic electron transfer.[28] Thus, in the weak interaction limit between involved centres, the Dexter energy transfer can be cast in terms of thermodynamic quantities [eqn. (4)].

$$k = \nu \exp(-\Delta G^\ddagger/RT) \qquad (4a)$$

$$\nu = \frac{2H^2}{h} \left(\frac{\pi^3}{\lambda RT} \right)^{1/2} \qquad (4b)$$

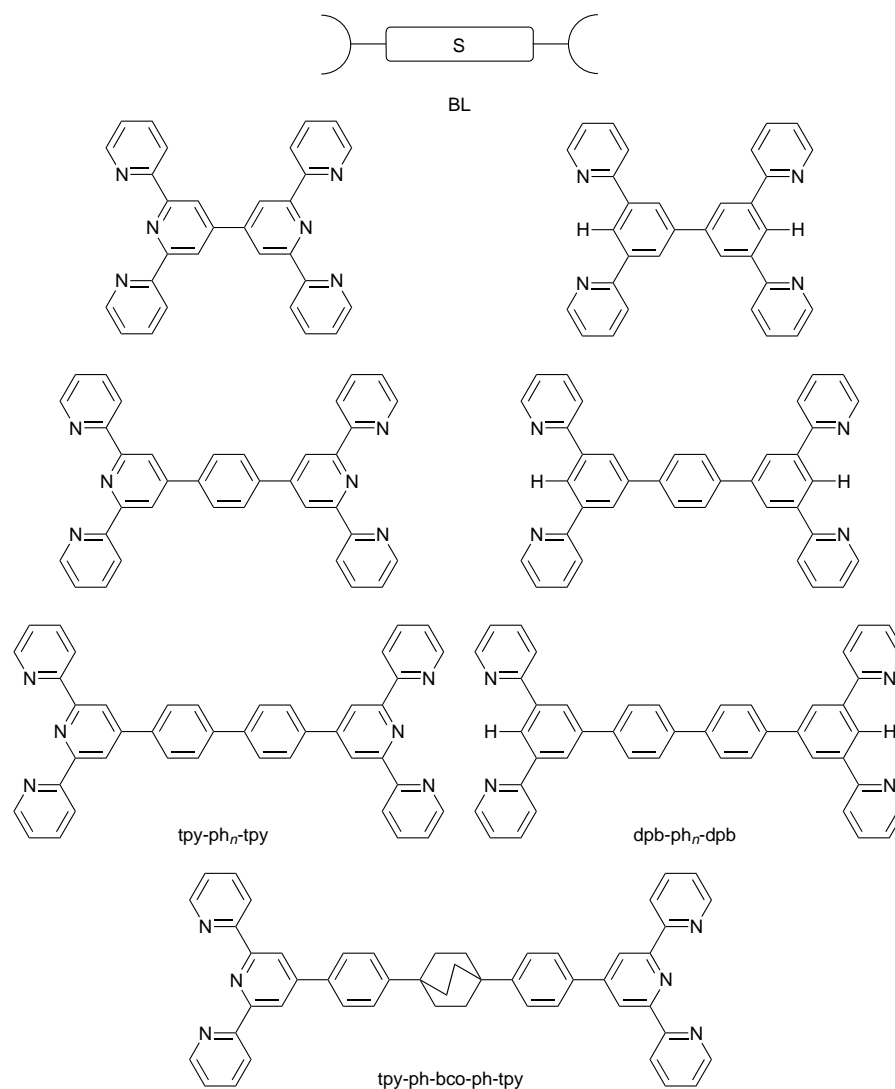$$\Delta G^\ddagger = \frac{\lambda}{4} \left(1 + \frac{\Delta G^0}{\lambda} \right)^2 \qquad (4c)$$

Fig. 1 The employed bridging ligands, BLs: tpy–ph$_n$–tpy is a series of bis-tpy BLs containing phenylene spacers, n = 0–2; dpb–ph$_n$–dpb is a series of bis-dipyridylbenzene BLs containing phenylene spacers, n = 0–2 (in the Ru–BL–Os complexes, these latter BLs are dianions); and tpy–ph–bco–ph–tpy is a BL where a bicyclooctane unit has been interposed between two phenylene groups

In these equations ν is a frequency factor, λ is the reorganization energy, H is the intercomponent electronic interaction energy and $\Delta G^{\ddagger}$ and ΔG^0 are the activation energy and the free energy change, respectively, for the transfer of excitation energy. The free energy change is evaluated from the maxima of the emission bands of the donor and acceptor reference compounds, as measured at 77 K.[6–9] For the osmium-based complexes, the reorganization energy, λ^{Os}, may be estimated from the Stokes shift of absorption and emission spectra, $2\lambda^{Os} = SS$.[29] For structurally similar ruthenium- and osmium-based complexes, it is usually assumed that $\lambda^{Ru} = \lambda^{Os}$.[9,13] Table 1 collects estimates for ΔG^0 and λ values concerned with some structurally similar ruthenium- and osmium-based couples of reference complexes.

From Table 1, it can be seen that electronic excitation transfer between the selected donor and acceptor couples occurs under nearly activationless conditions since $\Delta G^0 \approx -\lambda$ [eqn. (4a–c)]. Thus the double electron exchange is expected to be governed by electronic factors. Under these conditions, the distance dependence of the interaction energy, H, can be described by eqn. (5).

$$H = H_0 \exp(-\beta d_{MM}) \qquad (5)$$

where d_{MM} indicates the distance between the metal centres, β is an attenuation factor and H_0 is the interaction energy at intercomponent orbital contact.

Energy transfer in the series of complexes containing the tpy–ph$_n$–tpy BLs

Pertinent photophysical data for the $[(ttp)Ru(tpy–ph_n–tpy)Os(tpy)]^{4+}$ series of complexes are collected in Table 2. For these complexes, the d_{MM} intermetal distance changes from 11 to 20 Å, depending on n. The excited $Ru(ttp)_2^{2+}$ chromophore exhibits a room-temperature lifetime $\tau = 0.95$ ns in acetonitrile. Thus, because of the competition with intrinsic deactivation of the ruthenium-based component, only $Ru \rightarrow Os$ processsess occurring with rates $k > 10^9$ s^{-1} are expected to take place. Actually, the transfer of energy was found to occur with $k > 10^{10}$ s^{-1} even for $n = 2$ and one concludes that the polyphenylene bridge behaves as an extremely good energy transducer over the remarkable intermetal separation of 20 Å.[7] Interposition of a bicyclooctane (bco) unit in $[(ttp)Ru(tpy–ph–bco–ph–tpy)Os(tpy)]^{4+}$ leads to an intermetal separation of 24 Å, and results in a dramatic decrease of the energy transfer rate, $k = 4.4 \times 10^6$ s^{-1} as measured at 77 K,[8] Table 2. To some extent, this effect is due to the increased intermetal distance, however a major role must be ascribed to the electronically insulating properties of the bco saturated group. This group breaks the $\pi\pi^*$ frame of molecular orbitals centred on the phenylene units and only provides less efficient $\sigma\sigma^*$ orbitals for the transmission of the intermetal interaction.

Energy transfer in the series of complexes containing the dpb–ph$_n$–dpb biscyclometallating BLs

The dinuclear complexes that contain these dianionic BLs exhibit the same geometrical properties as the previous series, with distances between the metal centres ranging from 11 to 20 Å, depending on the size of the phenylene spacer.[9] For the cyclometallated series, the rate of $Ru \rightarrow Os$ energy transfer proved to be much lower than for the structurally identical series seen in the previous section. Thus, at room temperature no energy transfer was observed, despite the fact that the excited $[Ru(ttp)(dpb)]^+$ chromophore exhibits a lifetime $\tau_o = 4.5$ ns in
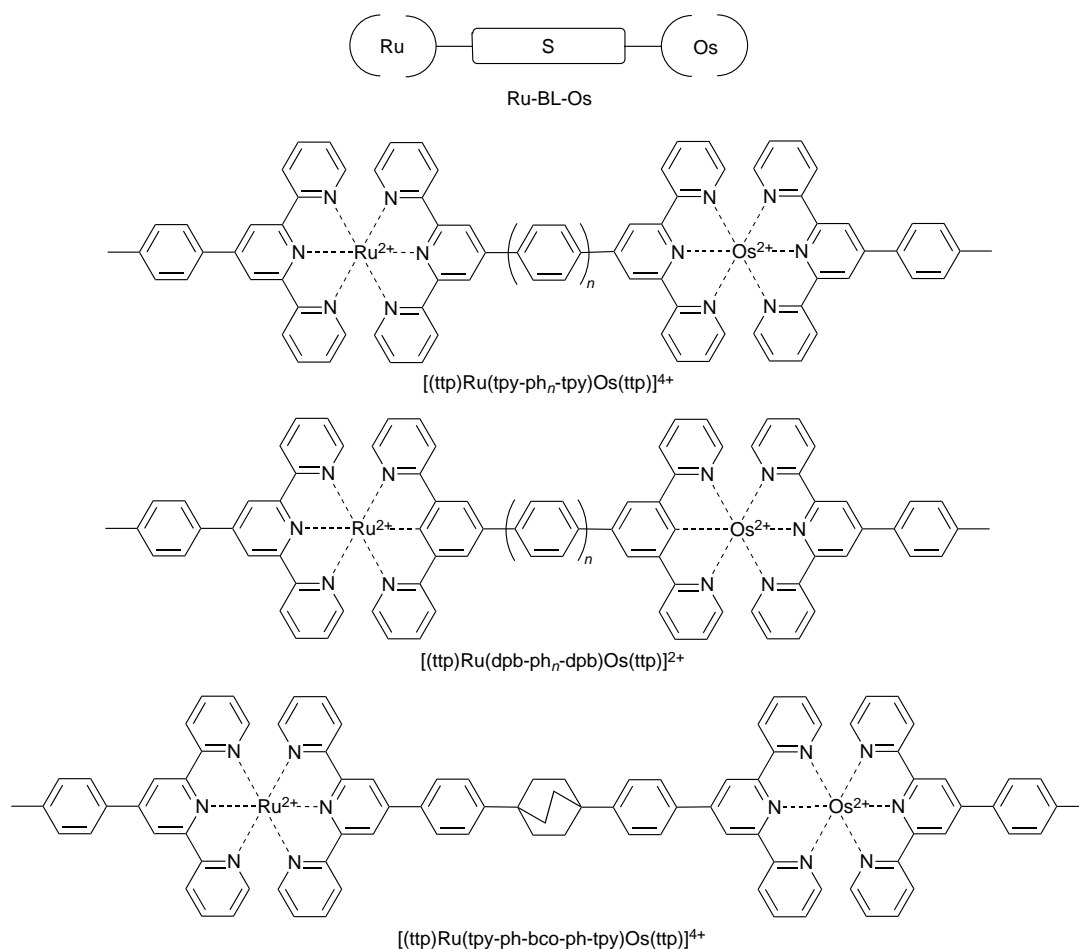

Fig. 2 The Ru–BL–Os dinuclear complexes

acetonitrile, *i.e.* significantly longer than that of its [Ru(ttp)₂]²⁺ homologue (τ_o = 0.95 ns). As a consequence, it was necessary to monitor the process at 77 K, where the intrinsic deactivation of the excited [Ru(ttp)(dpb)]⁺ species is sufficiently slow, τ_o = 496 ns, Table 2. The Ru → Os energy- transfer rates for the [(ttp)Ru(dpb–ph$_n$–dpb)Os(ttp)]²⁺ series were obtained both according to the steady-state approach outlined above (in this case we used 550 or 514 nm light excitation so as to excite 40 and 60% of the ruthenium- and osmium-based chromophores, respectively), and by time-resolved experiments [eqn. (3)]. As one can see from Table 2, the energy-transfer rate is affected to a large degree by the presence of the phenylene spacers and it was possible to draw a sizeable attenuation factor β = 0.33 Å⁻¹ [eqn. (5)] for the phenylene units.[9]

Table 1 Parameters for Ru → Os electronic energy transfer[a]

Reference donor	Reference acceptor	$\Delta G^{0\,b}$/eV	λ^c/eV	Ref.
[(ttp)Ru(ttp)]²⁺	[(ttp)Os(ttp)]²⁺	−0.25	0.15	7
[(ttp)Ru(dpb)]⁺	[(ttp)Os(dpb)]⁺	−0.18	0.15	9
[(bpy)₂Ru(bpy)]²⁺	[(bpy)₂Os(bpy)]²⁺	−0.38	0.40	13

[a] See eqn. (4a–c), solvent is acetonitrile, butyronitrile or dmf–CH₂Cl₂ (9:1). [b] Estimated from luminescence band maxima of the reference donor and acceptor complexes at 77 K. [c] Estimated from Stokes shifts for the acceptor complex.

Table 2 Photophysical results and Ru → Os energy-transfer rates[a]

		293 K			77 K			
	d_{MM}/Å	τ_0^b/ns	τ^b/ns	k^c/s⁻¹	τ_o^b/ns	τ^b/ns	k^c/s⁻¹	Ref.
[(ttp)Ru(ttp)]²⁺		0.95			9100			7
[(ttp)Ru(tpy–tpy)Os(ttp)]⁴⁺	11		<0.03	>10¹⁰		<0.03	>10¹⁰	7
[(ttp)Ru(tpy–ph–tpy)Os(ttp)]⁴⁺	15.5		<0.03	>10¹⁰		<0.03	>10¹⁰	7
[(ttp)Ru(tpy–ph–ph–tpy)Os(ttp)]⁴⁺	20		<0.03	>10¹⁰		<0.03	>10¹⁰	7
[(ttp)Ru(tpy–ph–bco–ph–tpy)Os(ttp)]⁴⁺	24		0.95	—[d]		220	4.4 × 10⁶	8
[(ttp)Ru(dpb)]⁺		4.5			496			9
[(ttp)Ru(dpb–dpb)Os(ttp)]²⁺	11		0.35	2.6 × 10⁹		0.72	1.4 × 10⁹	9
[(ttp)Ru(dpb–ph–dpb)Os(ttp)]²⁺	15.5		3.5	6.3 × 10⁷		42	2.2 × 10⁷	9
[(ttp)Ru(dpb–ph–ph–dpb)Os(ttp)]²⁺	20		4.9	<2.2 × 10⁷		178	3.6 × 10⁶	9

[a] Solvent is acetonitrile, butyronitrile or dmf–CH₂Cl₂ (9:1). [b] Lifetimes of the ruthenium-based chromophore. [c] $k = (1/\tau) - (1/\tau_o)$. [d] No energy transfer takes place at room temperature.
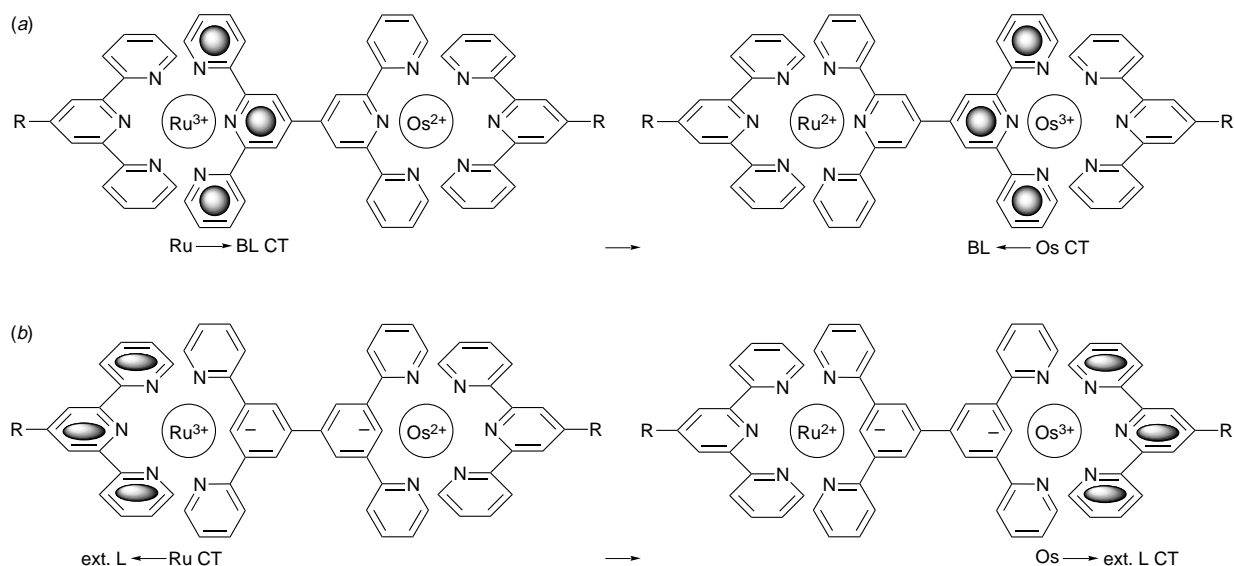
Electronic properties of the chromophores in the [(ttp)Ru(tpy–ph$_n$–tpy)Os(ttp)]⁴⁺ and [(ttp)Ru(dpb–ph$_n$–dpb)Os(ttp)]²⁺ series

For the two series of complexes, which are geometrically identical (see Fig. 2), there is a difference of orders of magnitude in the Ru → Os energy-transfer rate, Table 2. As the energy-transfer step is nearly activationless in both cases, a minor rôle is played by nuclear (reorganization) factors [eqn. (4a–c)] whereas a possible explanation relies on a different role of the electronic factor.

A pictorial description of the energy-transfer process for the two smallest members of the two series is provided in Fig. 3. Here we emphasize the spatial properties of the ruthenium- and osmium-centred MLCT states involved in the excitation transfer. In particular (*a*) for the case of the tpy–tpy BL the MLCT excited states are described with the promoted electron residing on the tpy fragment of BL, and (*b*) for the dpb–dpb²⁻ BL the promoted electron is placed on the external ttp ligand. Actually, in the former case the tpy–tpy bridging ligand is a better electron acceptor with respect to the ttp terminal ligand because of electronic delocalization[7] and in the latter case the ttp terminal ligand is a better electron acceptor than the dianionic dpb–dpb²⁻ BL.[9]

Fig. 3 describes the Ru → Os simultaneous double electron exchange in terms of a metal–metal hole transfer (HT) and a ligand–ligand electron transfer (ET).[30] Clearly, HT occurs over identical distances in the two series (for the same *n*, $d_{HT} = d_{MM}$

Fig. 3 Spatial properties of the MLCT excited states involved in the Ru → Os excitation-transfer step for [(ttp)Ru(tpy–tpy)Os(ttp)]⁴⁺ (*a*) and [(ttp)Ru(dpb–dpb)Os(ttp)]²⁺ (*b*); R = 4′-*p*-tolyl. The shaded areas indicate localization regions for the promoted electron of the MLCT excited state: M → BL (*a*) and M → external L (*b*).

and is thought to involve the available highest- occupied molecular orbitals (HOMOs) of the bridge.[31] In contrast, ET involves the chelating sites of BL for case (*a*), $d_{ET} < d_{MM}$, and the external ligands for case (*b*), $d_{ET} > d_{MM}$. Thus ET occurs in remarkably different conditions in the two series, both in terms of intercentre spatial separation and of electronic coupling. The latter point may be appreciated by noting that around each metal centre the external ligand system is arranged perpendicularly with respect to the chelating site belonging to the bridge (Fig. 3). Given that ET occurs by involving the available lowest π* unoccupied molecular orbitals (LUMOs, which are ligand-centred), the electron travelling from one external ligand to the opposite external ligand will cross at least two regions where the π orbital systems are perpendicularly arranged. In this case therefore, one expects a low electronic coupling for the ligand–ligand ET. In conclusion, it seems possible that the difference in energy-transfer rates between the two series is mainly ascribable to a different rôle of the electronic factor for the two cases.

Future developments

One limitation in the development of larger species for the study of long-range vectorial energy transfer is related to the lifetime of the excited donor, the ruthenium-based chromophore. This happens because the energy-transfer process, which becomes slower and slower with increasing size of the bridge, is in direct competition with intrinsic deactivation of the excited donor. Actually, long-lived ruthenium-based chromophores with the tris-bpy coordination ($\tau \approx$ hundreds of ns)[6] are employed in building dinuclear and higher nuclearity complexes.[30,32] Unfortunately, this latter type of coordination results in some geometric disadvantages with respect to that based on the bis-tpy coordination. For the purpose of illustration, Fig. 4 depicts some geometrical properties of such a complex, [(bpy)₂Ru(bpy–S–bpy)Os(bpy)₂]⁴⁺, where S includes double bonds and a bicyclooctane unit.[13] Because of the properties of the tris-bpy coordination, the bpy–S–bpy BL is not linearly aligned with the metal centres (and with the peripheral ligands). In addition, because of rotations around single bonds, the intermetal separation is 17 Å as an average, with an uncertainty estimated at ±1 Å.
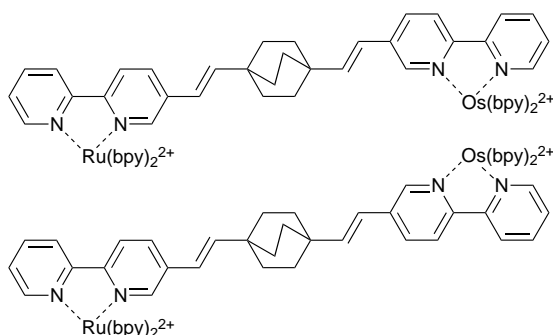
For the building up of new dinuclear complexes there may be different strategies. One useful approach is to combine the electronic properties of the tris-bpy arrangement and the geometrical properties of a perfectly aligned, more symmetric bridge. An example of such type of approach is illustrated in Fig. 5. In this species, the Ru(bpy)₂(phen)²⁺ chromophore exhibits a long-lived excitation, τ = 145 ns, and the phen–adamantane–phen BL ensures the sought-for alignment of the various components, with a fixed intermetal separation of 21 Å.[33]

Another useful approach may be based on the improvement of the spectroscopic properties of Ru–tpy type fragments by appending suitable groups at the 4′ position of the external tpy ligand. Actually, by using both electron-withdrawing and attracting appended groups[34] or groups that affect electronic delocalization over the tpy fragment[14] it has been possible to obtain long-lived Ru–tpy type units. Also, the use of protonable appended sites to the Ru–tpy chromophore may be of interest.[35] Literature examples of these possible approaches are illustrated in Fig. 6.

Conclusions

In order to develop molecular assemblies it is of obvious importance to gain control of the energetic and geometric factors. Our studies show that, for assemblies incorporating ruthenium– and osmium–terpyridine type and related cyclo-metallated analogues, the additional possibility exists of a fine

Fig. 6 Perturbation of the basic Ru(tpy)₂²⁺ chromophore (*a*),[7] may result in long-lived excited states centred on the ruthenium-based unit: (*b*) ref. 34 and (*c*) ref. 35. The diagrams show various Ru–tpy chromophores linked to a spacer for incorporation in dinuclear complexes.

Fig. 4 Two possible nuclear configurations resulting from the use of the tris-bpy coordination in a [(bpy)₂Ru(bpy–S–bpy)Os(bpy)₂]⁴⁺ dinuclear complex: there is no linear alignment along the M–BL–M axis and the intermetal distance is subject to some uncertainty
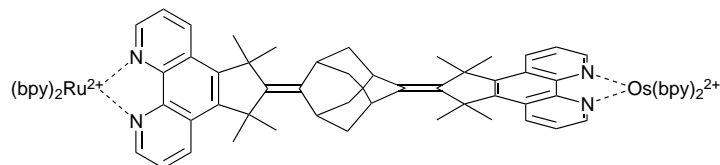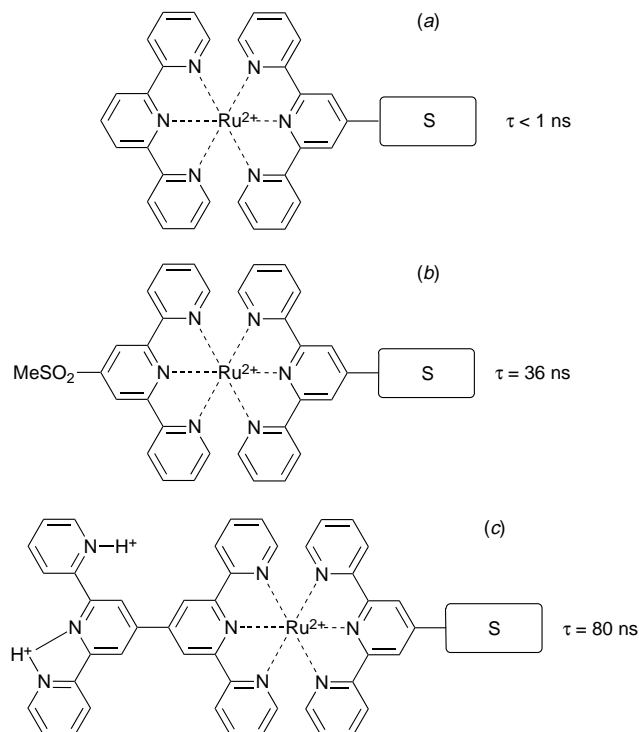
Fig. 5 A linear alignment of the metals and the BL results from the use of the phen–adamantane–phen BL;[33] the metal centres are at a fixed separation of 21 Å

modulation of photoinduced intermetal processes which is based on control of the spatial distribution of the metal-to-ligand charge-transfer excited states involved in the processes. We have performed our studies by employing cyclometallating analogues of the terpyridine ligand but a similar approach is likely to work with other types of ligand fragments. In principle, our results indicate ways for substantial manipulation of rates of energy transduction along molecular rods.

Acknowledgements

Francesco Barigelletti was born in 1944. He obtained his 'Laurea' in Chemistry in 1970 at the Faculty of Science, University of Bologna. After a postdoctoral fellowship spent in the Photochemical and Radiation Chemistry Laboratory (later, FRAE Institute) that was established a few years before and leave for a draft in the Army, he joined the National Research Council of Italy in 1973. His current interests include the photochemistry and photophysics of molecular and supramolecular systems for light-energy conversion and storage.

Lucia Flamigni obtained her 'Laurea' in Chemistry in 1973 at the University of Bologna. She had postdoctoral experience at the Chemistry Department of the University of Manchester and at the Center for Fast Kinetic Research, University of Texas at Austin. She has been researcher at the FRAE Institute since 1982. Her current interests include photoreactivity of dyes in organized media and photoinduced energy and electron transfer in molecular assemblies containing ruthenium and osmium centres.

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

Jean-Pierre Sauvage was born in 1944 in Paris. After studying at Strasbourg University, he did his PhD with J.-M. Lehn on cryptates and spent some time as a post-doc with M. L. H. Green at Oxford, UK. He is now a research director (CNRS) at the Faculty of Chemistry. His main scientific interests range from chemical topology (catenanes and knots) to models of the photosynthetic reaction centres and one-dimensional multicomponent transition complexes.

Footnote

† Abbreviations used: tpy = 2,2′:6′,2″-terpyridine, Hdpb = di-2-pyridyl-1,3-benzene, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, ph = phenylene unit, bco = bicyclo[2.2.2]octane unit, BL = bridging ligand, ttp = 4′-p-tolyl-2,2′:6′,2″-terpyridine, S = spacer, i.e. unit(s) included in a BL, ext. L = external or peripheral or terminal ligand, Ru–BL–Os = dinuclear complex.

References

1 V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Horwood, Chichester, UK, 1991, ch. 12.

2 J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995.

3 A representative, but not exhaustive, collection of contributing lines of work can be found in *Supramolecular Chemistry*, ed. V. Balzani and L. De Cola, Kluwer, Dordrecht, 1992.

4 F. Denti, S. Campagna and V. Balzani, in *Mesomolecules. From molecules to materials*, ed. G. D. Mendenhall, A. Greenberg and J. F. Liebaman, Chapman and Hall, New York, 1995, ch. 3.

5 Comprehensive reviews in this field can be found in special issues of *Tetrahedron,* 1989, **45**; and *Top. Curr. Chem.*, 1990, **156**; 1990, **158**; 1991, **159**; no attempt has been made here to cover more recent literature.

6 T. J. Meyer, *Pure Appl. Chem.*, 1986, **58**, 1193; A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85; J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Chem. Rev.,* 1994, **94**, 993.

7 F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage, A. Sour, E. D. Constable and A. M. W. Cargill Thompson, *J. Am. Chem. Soc.*, 1994, **116**, 7692.

8 F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage and A. Sour, *New J. Chem.*, 1995, **19**, 793.

9 F. Barigelletti, L. Flamigni, M. Guardigli, A. Juris, M. Beley, S. Chodorowski-Kimmes, J.-P. Collin and J.-P. Sauvage, *Inorg. Chem.*, 1996, **35**, 136; M. Beley, S. Chodorowski-Kimmes, J.-P. Collin, J.-P. Sauvage, L. Flamigni and F. Barigelletti, *Inorg. Chem.*, 1994, **33**, 2543.

10 F. Scandola, R. Argazzi, C. A. Bignozzi and M. T. Indelli, *Photochem. Photobiol. A: Chem.*, 1994, **82**, 191.

11 S. Boyde, G. F. Strouse, W. E. Jones Jr. and T. J. Meyer, *J. Am. Chem. Soc.*, 1990, **112**, 7395.

12 J. R. Show, R. T. Webb and R. H. Schmehl, *J. Am. Chem. Soc.*, 1990, **112**, 11 117.

13 L. De Cola, V. Balzani, F. Barigelletti, L. Flamigni, P. Belser, A. von Zelewsky, M. Franck and F. Vögtle, *Inorg. Chem.*, 1993, **32**, 5228.

14 A. C. Benniston, V. Groosshenny, A. Harriman and R. Ziessel, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1884.

15 F. Vögtle, M. Franck, M. Nieger, P. Belser, A. von Zelewsky, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1643.

16 A. C. Benniston, V. Goulle, A. Hariman, J.-M. Lehn and B. Marczinke, *J. Phys. Chem.*, 1994, **98**, 7798.

17 For the development of large-size molecular wires based on ethynyl-containing bridges, see V. Groosshenny, A. Harriman and R. Ziessel, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1100; 2705; V. Groosshenny, A. Harriman, M. Hissler and R. Ziessel, *Platinum Met. Rev.*, 1996, **40**, 26.

18 A rich metallosupramolecular chemistry arises from the use of various oligopyridines, see E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, 1992, 3467; E. C. Constable, *Prog. Inorg. Chem.*, 1994, **42**, 67; E. C. Constable and A. M. W. Cargill Thompson, *New J. Chem.*, 1996, **20**, 65.

19 Linear polynuclear complexes can also contain cyano-bridged *trans*-tetrakis-pyridine metal units, B. J. Coe, T. J. Meyer and P. S. White, *Inorg. Chem.*, 1995, **34**, 3600.

20 E. C. Constable and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1990, 1405.

21 F. Krönke, *Synthesis*, 1975, 1.

22 N. Miyama, T. Yanagi and A Suzuki, *Synth. Commun.*, 1981, **11**, 513.

23 M. Beley, S. Chodorowsky, J.-P. Collin and J.-P. Sauvage, *Tetrahedron Lett.*, 1993, **34**, 2933.

24 J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 508.

25 D. L. Dexter, *J. Chem. Phys.*, 1993, **21**, 836.

26 Th. H. Förster, *Discuss. Faraday Soc.*, 1959, **27**, 7.

27 P. Closs and J. R. Miller, *Science,* 1989, **244**, 35.

28 V. Balzani, F. Bolletta and F. Scandola, *J. Am. Chem. Soc.*, 1980, **102**, 2552; F. Scandola and V. Balzani, *J. Chem. Educ.*, 1983, **60**, 814.

29 N. Sutin, *Acc. Chem. Res.,* 1982, **15**, 275.

30 F. Scandola, M. T. Indelli, C. Chiorboli and C. A. Bignozzi, *Top. Curr. Chem.*, 1990, **158**, 73.

31 From intervalence studies of homometallic dinuclear complexes it has been found that there is a strong intermetal electronic communication when the coordination environment includes cyclometallating positions, see M. Beley, J.-P. Collin and J.-P. Sauvage, *Inorg. Chem.*, 1993, 32, 4539; E. C. Constable, A. M. W. Cargill Thompson and S. Greulich, *J. Chem. Soc., Chem. Commun.*, 1993, 1444.

32 V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759.

33 V. Balzani, F. Barigelletti, P. Belser, S. Bernhard, L. De Cola and L. Flamigni, *J. Phys. Chem.*, 1996, **100**, 16 786.

34 M. Maestri, N. Armaroli, V. Balzani, E. C. Constable and A. M. W. Cargill Thompson, *Inorg. Chem.*, 1995, **34**, 2759.

35 F. Barigelletti, L. Flamigni, M. Guardigli, J.-P. Sauvage, J.-P. Collin and A. Sour, *Chem. Commun.*, 1996, 1329.

6/03623F