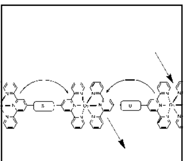
Photoactive molecular wires based on metal complexes



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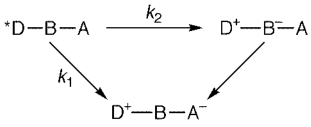
Received 28th June 1999

Molecular wires incorporating polypyridine metal complexes are amenable to studies of directional energy and electron transfer. The complexes are chromophores mainly based on Ru(II), Os(II), Rh(III), and Re(I) centres, which usually exhibit luminescence and can play as donor (D) or acceptor (A) units. A bridging ligand (B) provides both the structural and electronic connectivity between D and A and the DAB wires are flexible or rigid, depending on the spacers included within the bridge. Developments regarding multicentre systems and stereochemically interesting systems are taken into account.

1 Introduction

When can a molecular arrangement be termed a wire? The answer has certainly to do with *structural* (geometric) features, which may be easily identified from the molecular shape. However, some well-defined electronic properties are required if *functional* expectations are taken into account.[1] Thus, the large interest in studies of energy or electron transport schemes has resulted in the preparation of molecular wires (or rods, if these molecules are sufficiently rigid) containing photoactive components, usually placed at the *termini* of the wire.[1–5] These active units, as a consequence of specific interactions with light or after undergoing electrochemical processes, can be the initial and final sites for the temporary storage of energy. Other components, the linkers or bridges, are bound to play a structural role and to provide the electronic connection between the active centres.

A family of structurally well defined organic conjugated compounds may serve as a reference example of molecular wiring.[1] These compounds incorporate tetracene as an electron donor (D), *p*-phenylenevinylene oligomers of variable length as bridges (B), and pyromellitimide as the electron acceptor (A). For this paradigmatic case it was found that the electron transfer rate constant, which is of the order of 10^{10}–10^{11} s^{-1} over a distance separation up to 40 Å, does not follow a monotonic dependence on the distance between D and A. The authors carefully identify the favourable factors that allow this remarkable performance. These include a good energy matching between the donor and bridge components (at larger and larger distances, the energy difference between excited levels localized on D and B is < 0.1 eV) and relevant steric details at the DB connection. The mechanistic suggestions derived from this study have to do with the interplay of two mechanisms: electron tunnelling and electron hopping,[1] see Scheme 1. These come into play depending on the energy levels of the HOMOs and LUMOs involved, in turn affected by the length of B (HOMO and LUMO are the highest occupied and the lowest unoccupied MO, respectively).



Scheme 1

At short DA distance, $k_1 >> k_2$ and the bridge only plays a structural role or, at best, provides an electronic mediation

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according to a superexchange mechanism. With the more efficient electron hopping, states can be identified whereby a temporary stepping of the electron on the bridge takes place, $k_2 >> k_1$. We will see below that similar reference schemes may be useful for both energy and electron transfer within wires based on metal complexes.

In this work, we will survey some recent literature in a field that includes molecular threads incorporating metal complexes of polypyridine ligands.[2–5] The optical properties (absorption and luminescence) of these units have been extensively studied and many efforts are devoted to design and synthesise multinuclear complexes in view of their uses for energy storage and transfer schemes,[2–5] for sensing the chemical environment,[6] and, on general grounds, for information transduction purposes. In these DBA arrays the photoactive units, the metal complexes, can play as energy or electron donors (D) and energy or electron acceptors (A), respectively, and the bridge is usually an organic, in many cases modular component. The complexes can frequently undergo well-defined oxidation and reduction processes, and in the presence of identical metal units (homometallic cases) the conducting properties of the bridge can be evaluated *via* intervalence studies, which we will not discuss.

We will examine some interesting species from a number of viewpoints which include (i) the role of the energetic and geometric factors for energy and electron transfer processes, (ii) the role of the electronic properties of B and of delocalization of the metal-to-ligand charge transfer (MLCT) excited states, (iii) mechanisms of energy transfer and long-distance transfer, (iv) differences brought about by the use of the tris-bidentate coordination as opposed to bis-tridentate coordination, (v) developments in the field of molecular devices, and (vi) approaches towards the preparation of chiral species.

We notice that, at the moment, in wires based on metal complexes and with respect to electron transfer, the energy transfer process has been more systematically investigated.[2–6] This outcome is probably due to practical reasons: for polypyridine complexes it has proved feasible to assemble luminescent D and A components. In this way, for a high number of cases, both luminescence quenching at D and luminescence sensitisation at A (occurring *via* energy transfer) have been measured by using luminescence spectroscopy.

2 Energy transfer

From a conceptual viewpoint, DBA dyads represent simple systems and some examples are discussed first where the octahedral coordination is provided by bidentate ligands, mostly derived from the basic 2,2′-bipyridine (bpy). In Fig. 1 are shown cases where B is flexible, as in complexes **1**[7] and **2**,[8] or rigid, as in complex **3**.[3]

For **1** and **2**, the alkane chain does not provide a good electronic interaction between D and A, and the DA interaction is of the dipole–dipole type.[9] This mechanism is describable in terms of a treatment due to Förster.[9] The exoergonic Ru→Os energy transfer is moderately fast, k_{en} is 1.7×10^8 and 4.5×10^8 s^{-1} for **1** and **2**, respectively, Table 1. It is useful to compare cases **1** and **2** with case **3**. In complex **3** the energetic and spatial (intermetal separation, d_{MM}) parameters are quite similar to those of **1** and **2**, however the Ru→Os energy step is faster by two orders of magnitude, Table 1. This behaviour is due to the fact that the alkyne bridge provides an efficient electronic interaction between the D and A centres; accordingly, a through-bond Dexter-type mechanism[10] is found to be involved.

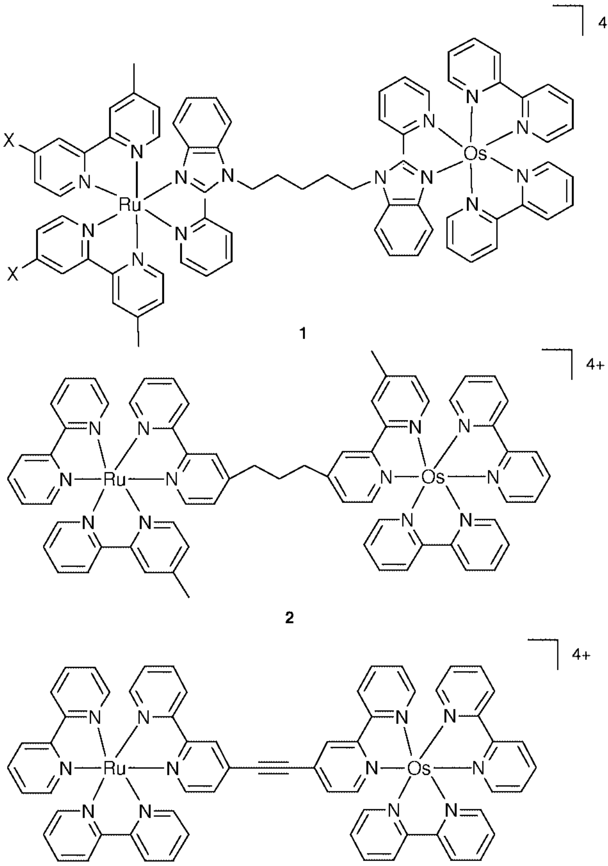

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Fig. 1 Schematic formulae for **1**–**3**.

Table 1 Energy transfer parameters

	Metal centers	10^{-8} k_{en}/s^{-1}	d_{MM}/Å	ΔG/eV	Mechanism[a]	Ref.
1	Ru^{II}/Os^{II}	1.7	13.0	−0.24	F	7
2	Ru^{II}/Os^{II}	4.5	12.8	−0.32	F	8
3	Ru^{II}/Os^{II}	250.0	13.8	−0.34	D	3
4	Ru^{II}/Os^{II}	5.8	< 18.1	−0.36		5
6	Ru^{II}/Os^{I}	> 10.0	12.8			11
7	Ru^{II}/Os^{II}	2.6	16.0	−0.40		5
8	Ru^{II}/Os^{II}	0.4	21.0	−0.38		5
9	Ru^{II}/Os^{II}	0.13	19.2	−0.35	F/D	12
10	Ru^{II}/Os^{II}	0.1	13.7	−0.35	F/D	12
11	Ru^{II}/Os^{II}	7	18.3	−0.33		4
15	Ru^{II}/Os^{II}	6.7	24.0	−0.37	D	14
16	Ru^{II}/Os^{II}	0.1	32.5	−0.37	D	14
17	Ru^{II}/Os^{II}	0.013	42.0	−0.37	D	14
21	Ru^{II}/Os^{II}	500.0	16.2	−0.11	D	12
22	Ru^{II}/Os^{II}	> 100.0	20.0	−0.25	D	17
23	Ru^{II}/Os^{II}	0.044	24.0	−0.25		16
24	Ru^{II}/Os^{II}	< 0.2	20.0	−0.18	D	15

[a] Mechanism of energy transfer, Förster (F), Dexter (D).

The series of complexes of Fig. 2 further illustrate the spatial and electronic role of the bridge with respect to Ru→Os energy transfer. In **4** and **5**,[5] B does not allow complete control of the DA spatial separation, mainly because of rotations about single bonds. By contrast, in **6**,[11] **7** and **8**,[5] B ensures a high degree of control of the geometry of the complexes. For **6**, B may be viewed as a good electronic conductor as $k_{en} > 1 \times 10^9$ s^{-1} . For **7** and **8**, which contain the same type of both unsaturated (conducting) and saturated (isolating) units, the energy transfer rate constant, $k_{en} = 2.6 \times 10^8$ and 4.0×10^7 s^{-1}, respectively, is clearly related to the intermetal separation, $d_{MM} = 16$ and 21 Å, respectively.

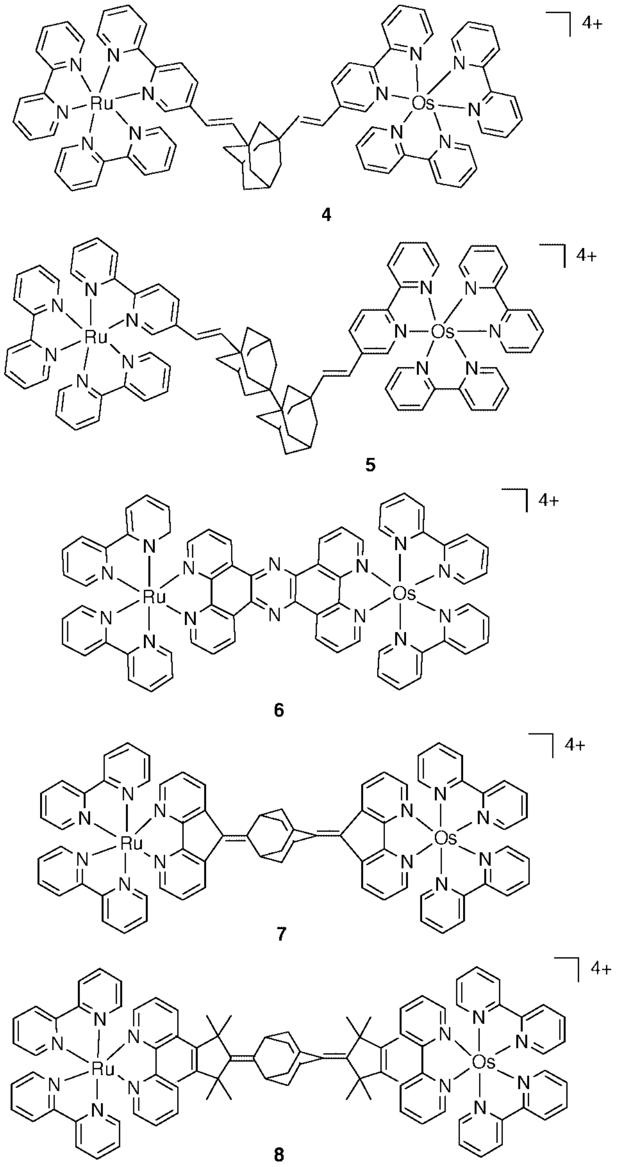


Fig. 2 Schematic formulae for **4**–**8**.

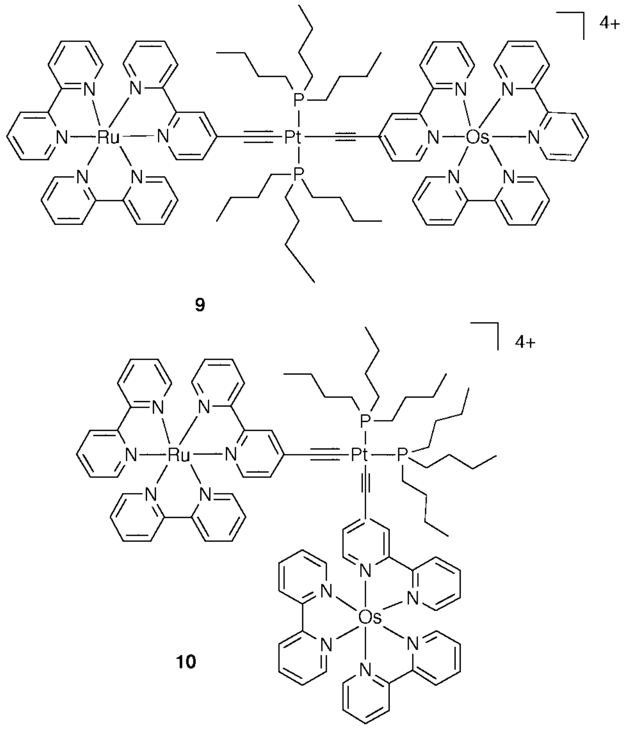


Fig. 3 Schematic formulae for **9** and **10**.

The shape of the wire can be controlled to a high degree. Complexes **9** and **10** contain the same D and A centres which are linked in both complexes by a connecting Pt$^{\text{II}}$ bis(trialkynephosphine) interposed unit, Fig. 3.[12]

In **9** the arrangement is linear while it is L-shaped for **10**; this brings about a substantial difference in the d_{MM} separation, 19.2 *vs* 13.7 Å, respectively, Table 1. The fact that the rate constants in **9** and **10** are very close to each other is ascribed to balanced contributions by both the dipole–dipole and through-bond mechanisms of energy transfer, given that the Pt$^{\text{II}}$ centre somewhat decouples the terminal units.[12]

There are DBA cases where an active role for B has been addressed. Fig. 4 compares the behaviour of three related systems in which the bridge contains a phenyl, **11**, a naphthyl, **12**, and an anthryl, **13**, group.[4]

A systematic variation of the energy levels of the HOMOs and LUMOs and, as a consequence, of the involved excited states of B is thus designed. Actually, while for **11** B plays the usual mediating role, for **12** a two step energy transfer has been found, with the excitation stepping at the naphthyl component, Fig. 4. For the case of **13**, the anthryl group acts as an excitation trap, preventing the Ru→Os transfer of energy. A different case of energy trapping can be identified by looking at the homometallic complex **14**,[13] where the anthraquinone unit collects the excitation energy from either of the two identical metal centres, Fig. 4.

A long distance transfer of excitation occurs in the series of complexes shown in Fig. 5.[14] Here the modular approach based on the inclusion within B of a variable number of spacer units allows the construction of dyads **15**, **16** and **17**, where the photoactive units are separated by 3, 5 and 7 phenylene groups, respectively.

The three dyads represent excellent models of rigid systems particularly suited for the study of Ru→Os energy over the remarkable distance of up to 42 Å. For these cases, it has been possible to draw the firm conclusion that the dipole–dipole mechanism cannot be responsible for the energy transfer step. On the other hand, by plotting ln(k_{en}) against the intermetal separation, Fig. 6, a linear dependence is observed, in accord with expectations based on the Dexter approach, eqn. (1).

$$k_{\text{en}} \propto \exp(-\beta d_{\text{MM}}) \qquad (1)$$

From these results an attenuation factor β = 0.32 Å^{-1} has been evaluated,[14] while previous work dealing with the effect of polyphenylene spacers[15] suggested β = 0.66 Å^{-1}; the data points concerned are also displayed in Fig. 6. It is noteworthy that nearly identical results are obtained at 77 K and at room temperature,[14,15] showing that energy transfer, unlike electron transfer, is not affected by temperature or state of the (fluid or frozen) solvent. This probably happens because the reorganization energy, λ, for the energy transfer step is very close to the exhothermicity, $-\Delta G$, of the process.[16]

A close inspection of the schematic structures for some of the complexes where the photoactive centres are based on the tris-bpy coordination points to a few problems.[2,5,17] For instance, the geometry, *i.e.* d_{MM}, of systems like **4** and **5** may be ill-

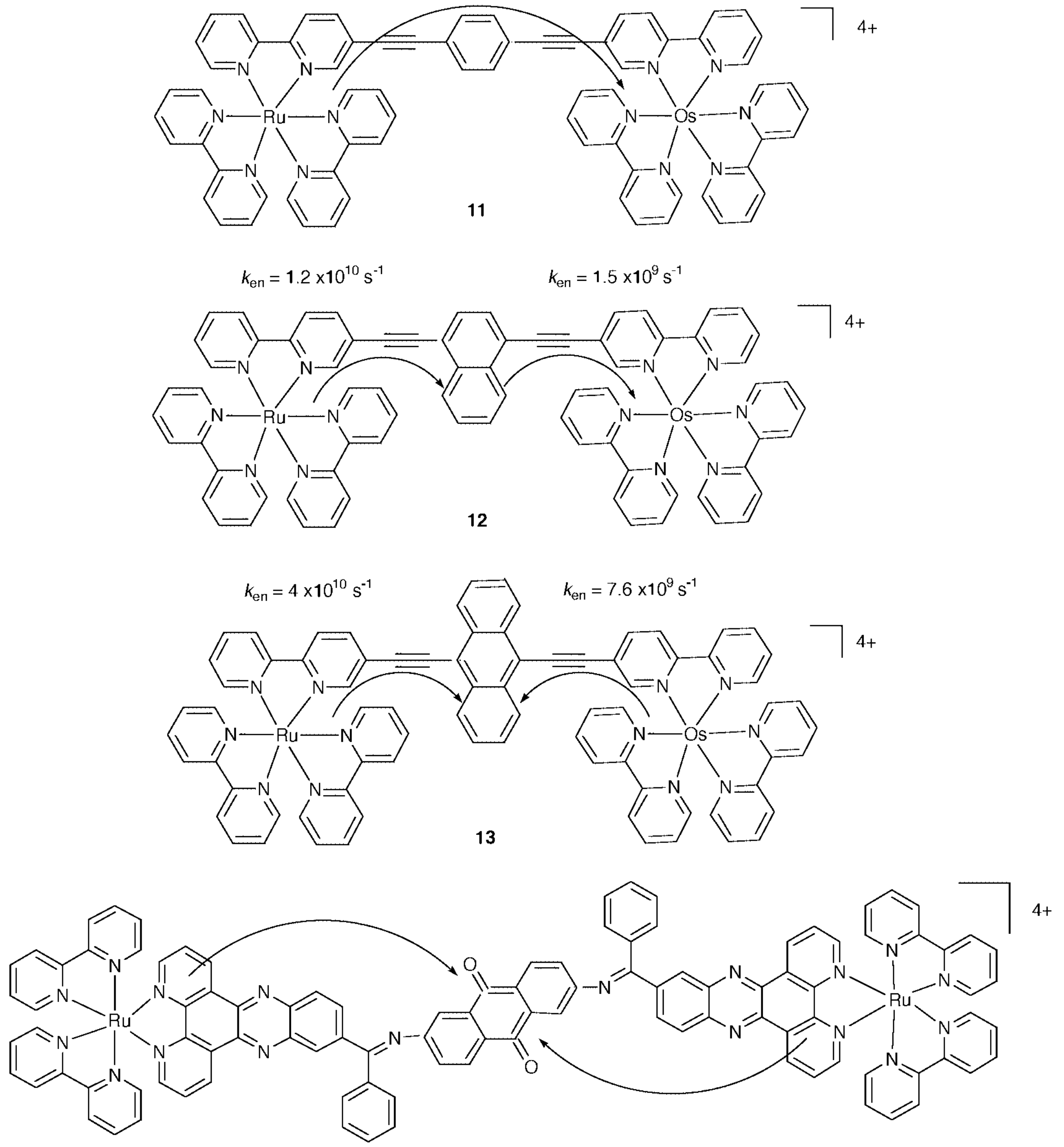


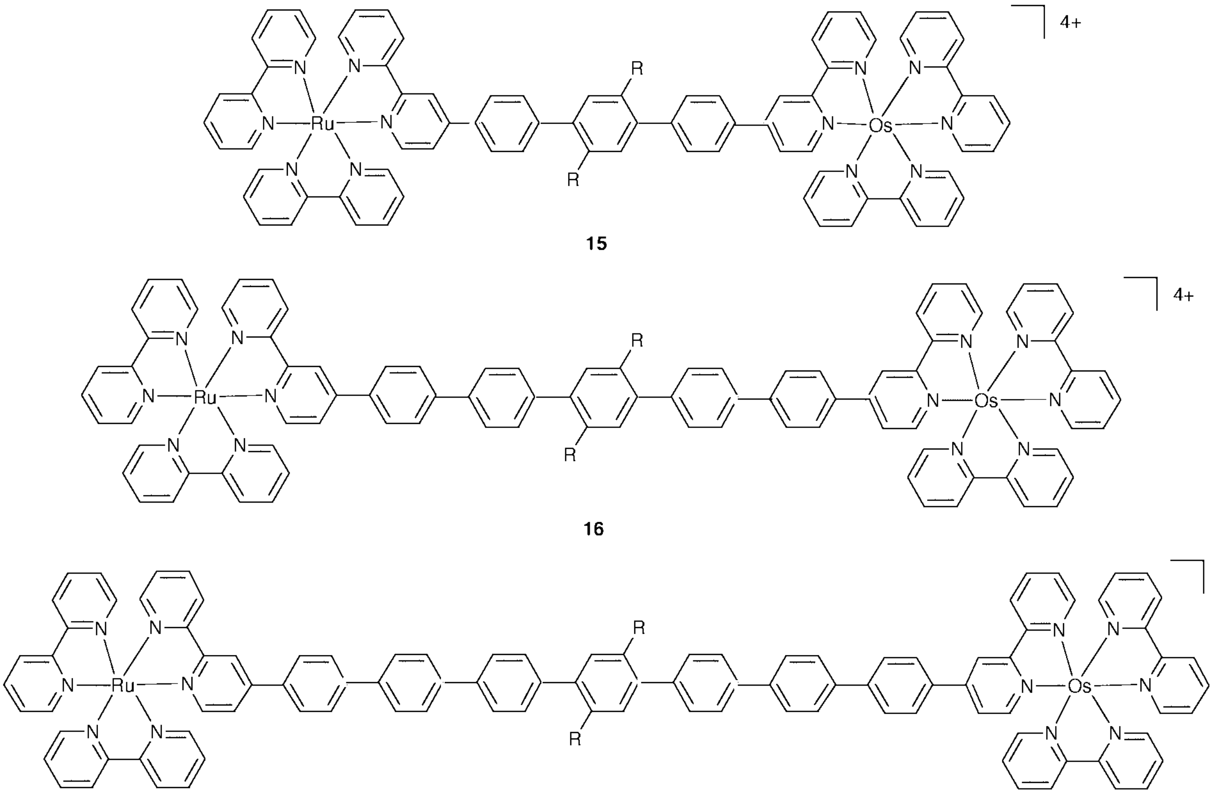
Fig. 4 Schematic formulae for **11**–**14**.

defined because of rotations about single bonds. A relevant feature related to the tris-bidentate coordination is the possible coexistence of different stereoisomers, which may cause specific difficulties in the study of the photoinduced processes.[17] With regard to these aspects, a better choice for the ligand coordination is represented by the bis-tridentate coordination as ensured by use of the 2,2′:6′,2″-terpyridine ligand (tpy), Fig. 7.

Here, the $M(tpy)_2{}^{2+}$ unit represents an appealing building block *via* the possible use of the 4′ position of tpy for developing wires. Unfortunately, the basic $Ru(tpy)_2{}^{2+}$ centre, **18**, which might be employed as an energy donor in DBA systems, exhibits poor luminescence properties, ϕ = < 10^{-5} and τ = 0.25 ns.[17] This indicates that in excited **18** the intrinsic deactivation rate is rather fast and that its use as an energy donor is restricted to cases where the competing energy transfer step is even faster ($k_{en} > 4 \times 10^9$ s^{-1}). Recent studies have revealed reasons for such poor luminescence behaviour, and ways for improving the luminescence performances of Ru-tpy-type units. For instance, this has been documented for complexes **19**[3] and **20**[18] where the luminescence properties are much improved with respect to **18**, basically due to extended conjugation over B.

In Fig. 8, cases are illustrated where the convenient geometric properties of the tpy coordination are combined with the use of polyphenylene spacers, which ensure a high control of the intermetal distance (rigidity).

For **21**[3] and **22**[17] the Ru→Os energy transfer is very fast, $k_{en} > 10^{10}$ s^{-1}, which is explained by the role of B in delocalizing the MLCT excitation. By contrast, for **23**[16] and **24**[15] the energy transfer rate constant is much lower, Table 1. For **23**, studied at T < 200 K, this is ascribed to the insertion of the saturated bicyclooctane unit within B. For **24**, this is due to the fact that B is a dianion, which results in the MLCT states being localized on the terminal ligands, as opposed to the cases of **21** and **22** (where B is involved in the delocalization of the MLCT state). In Fig. 8, an illustration is provided of some mechanistic aspects of the energy transfer step, described in terms of two



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16

17

R = n-hexyl

Fig. 5 Schematic formulae for **15**–**17**.

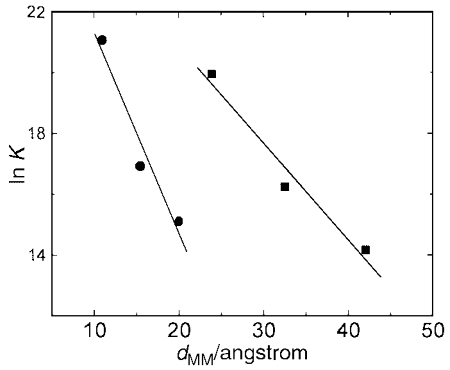
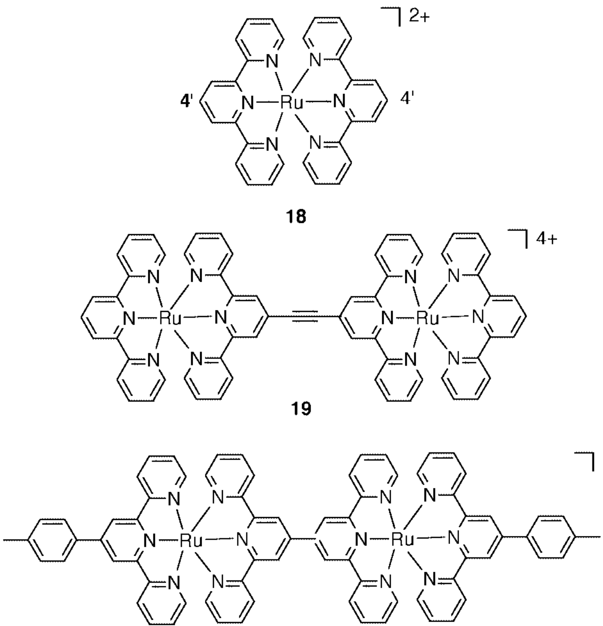


Fig. 6 Distance dependence of k_{en} for Ru–B–Os complexes where B contains an n-phenylene chain; circles, $n = 0, 1, 2$, ref. 15; squares, $n = 3, 5, 7$, ref. 14. Data points obtained at 77 K.

simultaneous electron transfers, M→M and L→L; for the geometrically identical cases of **22** and **24** the different distance associated with the latter step may explain the different rate constants observed,[19] Table 1.



18

19

20

Fig. 7 Schematic formulae for **18**–**20**.

3 Mechanism of energy transfer

What is the relative importance of the Förster and Dexter mechanisms for the transmission of the excitation along a Ru–B–Os wire? According to a spectroscopic approach based on the luminescence properties of the donor and the absorption properties of the acceptor, and taking care of the d_{MM} separation of the D and A components,[9] it is possible to evaluate k_{en}^{F}, the rate constant for the Förster mechanism, see Appendix. In turn, also the contribution of the Dexter mechanism, k_{en}^{D}, can be estimated.

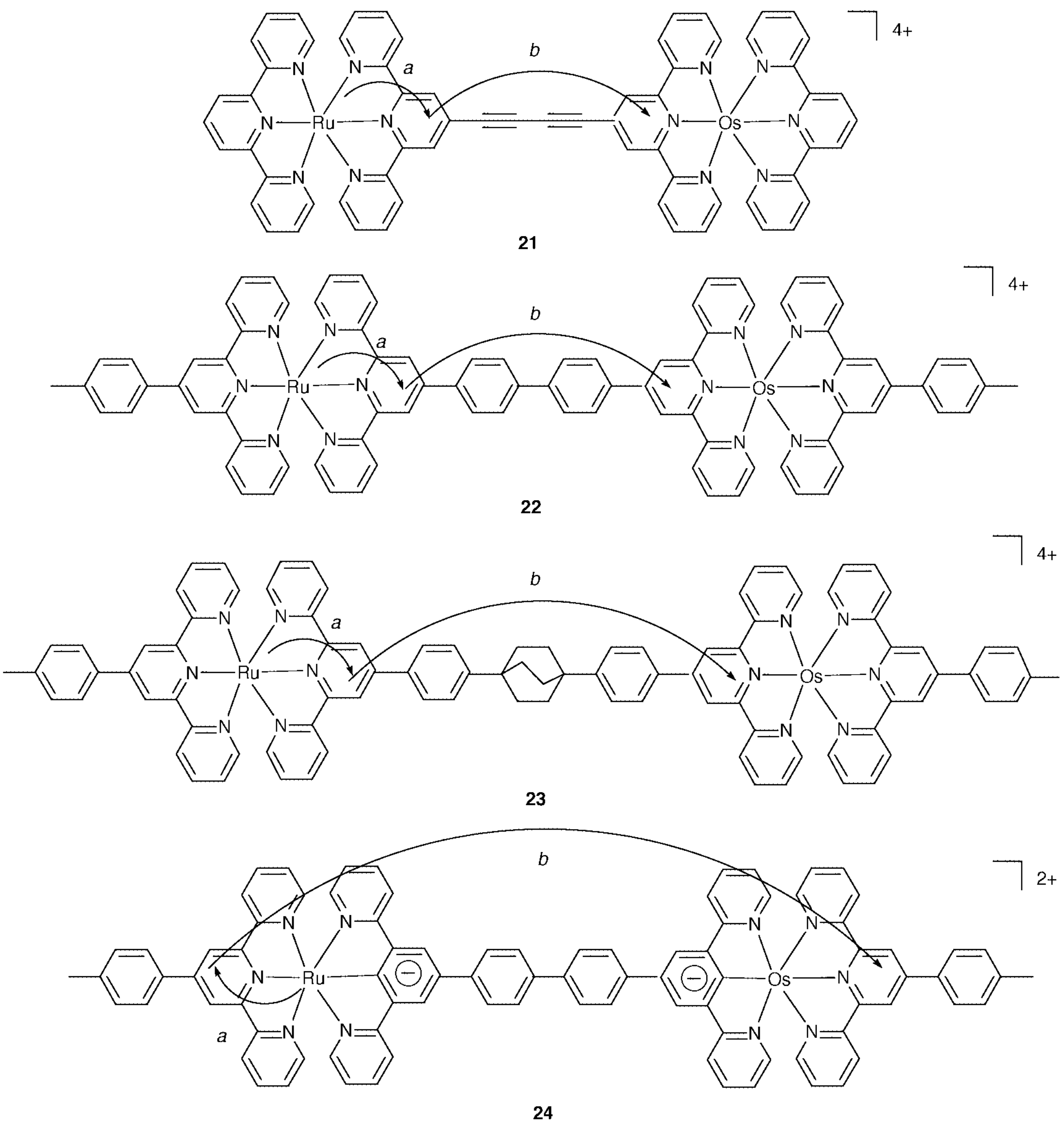


Fig. 8 Description of energy transfer in terms of dual electron exchange (M-to-M and L-to-L transfers). (a) MLCT transition, (b) L-to-L electron transfer; the concomitant M-to-M electron transfer is not shown.

Results of *model* calculations for the couple $Ru(bpy)_3^{2+}$ (D) and $Os(bpy)_3^{2+}$ (A), as connected by polyphenylene bridges for which $\beta = 0.32$ Å^{-1},[14] are shown in Fig. 9, top panel. Results for the analogous case of the $Ru(ttp)_2^{2+}$ (D) and $Os(ttp)_2^{2+}$ (A) chromophores (ttp = 4′-tolyl-tpy) are also illustrated, bottom panel. Further details are reported in the Appendix.

Relevant points are that (i) k_{en}^{D} is always larger than k_{en}^{F}, and that (ii) the competition with the intrinsic deactivation at the donor unit causes a dramatic drop of the energy transfer efficiency at d_{MM} of *ca.* 40 and *ca.* 25 Å, for the $M(bpy)_3^{2+}$ and $M(ttp)_2^{2+}$ couples, respectively. This suggests that for efficient energy transfer to occur over larger distances, bridges exhibiting a significantly weaker distance dependence ($\beta << 0.32$ Å^{-1}) are required.[3]

4 Electron transfer

In DBA dyads based on metal complexes, photoinduced electron transfer has also been investigated. Frequently, the Ru^{II}–B–Os^{II} dyads employed for studies of energy transfer, see above, have been shown to be amenable to investigations of electron transfer after selective oxidation of the Os^{II} centre. This can be performed both with chemical and electrochemical means and relatively stable Ru^{II}–B–Os^{III} species are made available. A few results obtained with complexes **1**,[7] **4** and **5**,[5] are collected in Table 2. This series is relatively homogeneous in terms of energetic parameters, while the intermetal separation d_{MM} is varied. Thus, comparison of the rate constants, k_{el}, for the $^{*}Ru^{II}$–B–Os^{III} → Ru^{III}–B–Os^{II} step (the forward electron transfer) shows that the results are in line with expectations based on the Marcus treatment of the relation among thermodynamic, electronic and kinetic parameters.[1,2]

An interplay of geometric and energetic factors can also come into play, as illustrated by the sufficiently homogeneous series of complexes **25**,[20] **26** and **27**,[21] Fig. 10.

Here the electron transfer step is $^{*}Ru^{II}$–B–Rh^{III} → Ru^{III}–B–Rh^{II}, with unfavourable thermodynamics because the process is slightly endoergonic, $\Delta G = 0.1$ eV, Table 2. In fact, electron

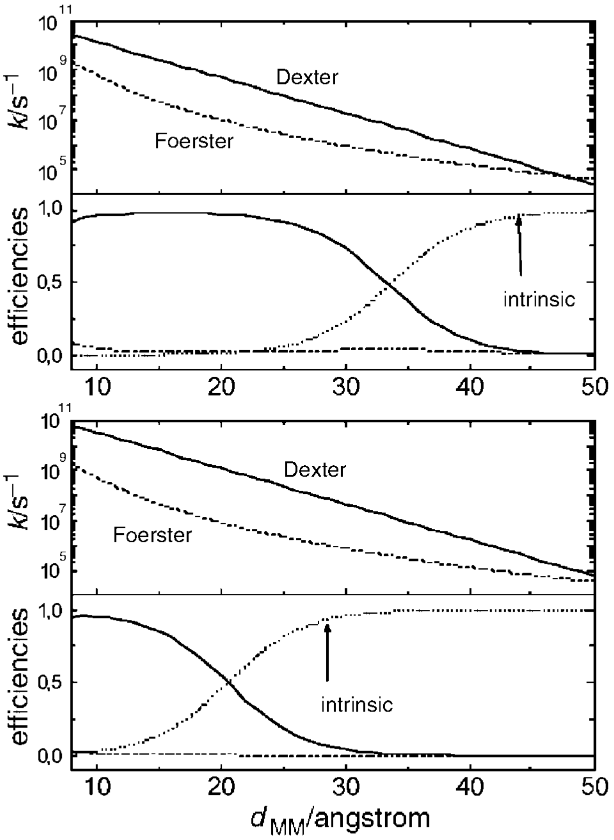


Fig. 9 Calculated distance dependence of the energy transfer rate constants and efficiencies for Ru–B–Os complexes where B contains an *n*-phenylene chain: Dexter (full line), Förster (dashed line) and intrinsic (dotted line) contributions. Top: case of $Ru(bpy)_3^{2+}/Os(bpy)_3^{2+}$. Bottom: case of $Ru(ttp)_2^{2+}/Os(ttp)_2^{2+}$.

Table 2 Electron transfer parameters

	Metal centers	10^{-9} k_{el}/s^{-1}	d_{MM}/Å	ΔG/eV	Ref.
1	Ru^{II}/Os^{III}	5.5	13.0	−1.68	7
4	Ru^{II}/Os^{III}	2.8	< 18.1	−1.61	5
5	Ru^{II}/Os^{III}	0.9	< 22.3	−1.71	5
7	Ru^{II}/Os^{III}	0.8	16.0	−1.69	5
25	Ru^{II}/Rh^{III}	1.7	13.5	0.1	20
26	Ru^{II}/Rh^{III}	⩾3.0	15.5	0.1	21
27	Ru^{II}/Rh^{III}	< 0.5	20.0	0.1	21

transfer takes place in **25** and **26** but not in **27**, where d_{MM} is the largest in the series.

An interesting case is also illustrated in Fig. 10 and regards the Ru^{II}–B–Os^{III} species **28** and **29**.[22] In these complexes B contains two different diimides. In the former case, the bridge plays the usual structural role and the $Ru^{II} \rightarrow Os^{III}$ step is of low efficiency. For **29**, a more complicated behaviour is documented because B becomes an active component and the complex behaves like a triad, D–A–A′. Thus, a two-step electron transfer gives rise to the final charge separated state with a production yield of 75%; remarkably, the charge recombination process is relatively slow, $k_{CR} = 9.1 \times 10^6$ s^{-1}.

5 High nuclearity wires

For the series of Ru-tpy-type complexes in Fig. 11 the increase of the nuclearity has been pursued in view of particular purposes.

Complexes **30**[23] and **31**[24] are aimed at the extension of the electronic conjugation over the rod either by using fused bridges (**30**) or strongly interacting spacers (**31**). For the latter case, the resulting rod is luminescent, which represents an improvement with respect to the basic non-luminescent mononuclear chromophore **18**. Complexes **32**[3] illustrate ways for the building up of nm length rods by using metal-based non-photoactive connectors. In complex **33**[25] a free bipyridine site is available for the interaction with various cations. The luminescence properties undergo changes in the presence of the guest and this may be taken as an illustration of an useful approach towards molecular-based devices for chemical sensing.[6]

6 Molecular devices

Metal-based rods prove to be amenable to use within signalling schemes.[6] Recent examples include those shown in Fig. 12. In complex **34**[26] no luminescence can be detected because the intermediate azo group acts as a trap for the excitation based on the two terminal chromophores.

Reduction of the azo group allows the occurrence of Ru→Os energy transfer, so that **34** plays as a redox-responsive molecular switch. In complex **35**,[27] the energy transfer rate constant is decreased by the presence of the anion, which also represents a signalling event based on the occurrence of energy transfer.

The field of molecular-based devices is expanding broadly. Energy-processing and storing are key events that can be triggered by light. Metal-based wires are finding wider use in molecular-based schemes, as further illustrated by the few examples in Fig. 13. Complex **36** is a wire composed by 5 chromophores based on Re^{I} and Ru^{II} centres.[28]

Each component of the wire can absorb light, and an energy excitation cascade, occurring within a fast timescale, leads to localisation of the excitation at one extreme of the wire. The final collection point can be anchored to a wide-bandgap semiconductor, and the wire works as a multi-photon harvesting system.

A two-photon collection scheme can be envisaged by the use of the trimetallic complex **37**,[29] Fig. 13. Through sequential second order steps involving a donor (D, dimethylaniline), the two ligands coordinated to the Rh^{III} metal centre store two electrons, which might be available for subsequent two-electron reduction processes.

7 Chiral complexes

There has been a recent surge of interest in chiral complexes. As noted above, multinuclear species based on the basic bis-tpy octahedral coordination are devoid of stereoisomerism at the metal centre. Conversely, the tris-bpy (or the stereochemically equivalent tris-phen) coordination may result in a rich chemistry associated with chiral properties.[30,31] This has generated lines of activity for the setting up of synthetic and separation procedures, in order to gain control over stereoisomers. Successful procedures are frequently based on the assembly of precursors with pre-determined chiralities and on chromatographic techniques, as for the examples in Figs. 14 and 15.

Thus, the homometallic dinuclear complexes **38**[32] and **39**,[33] were prepared *via* the assembly of enantiomerically pure

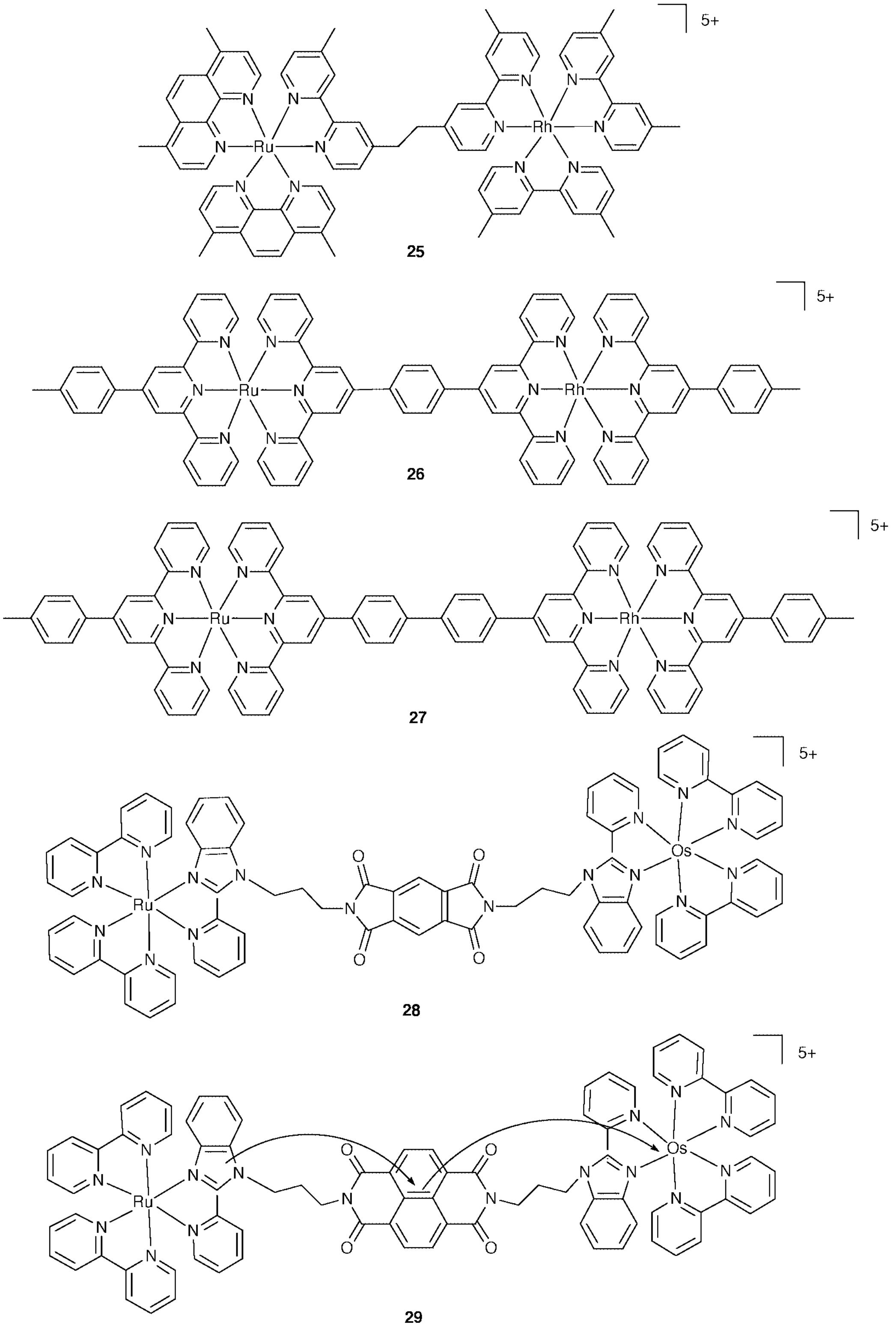
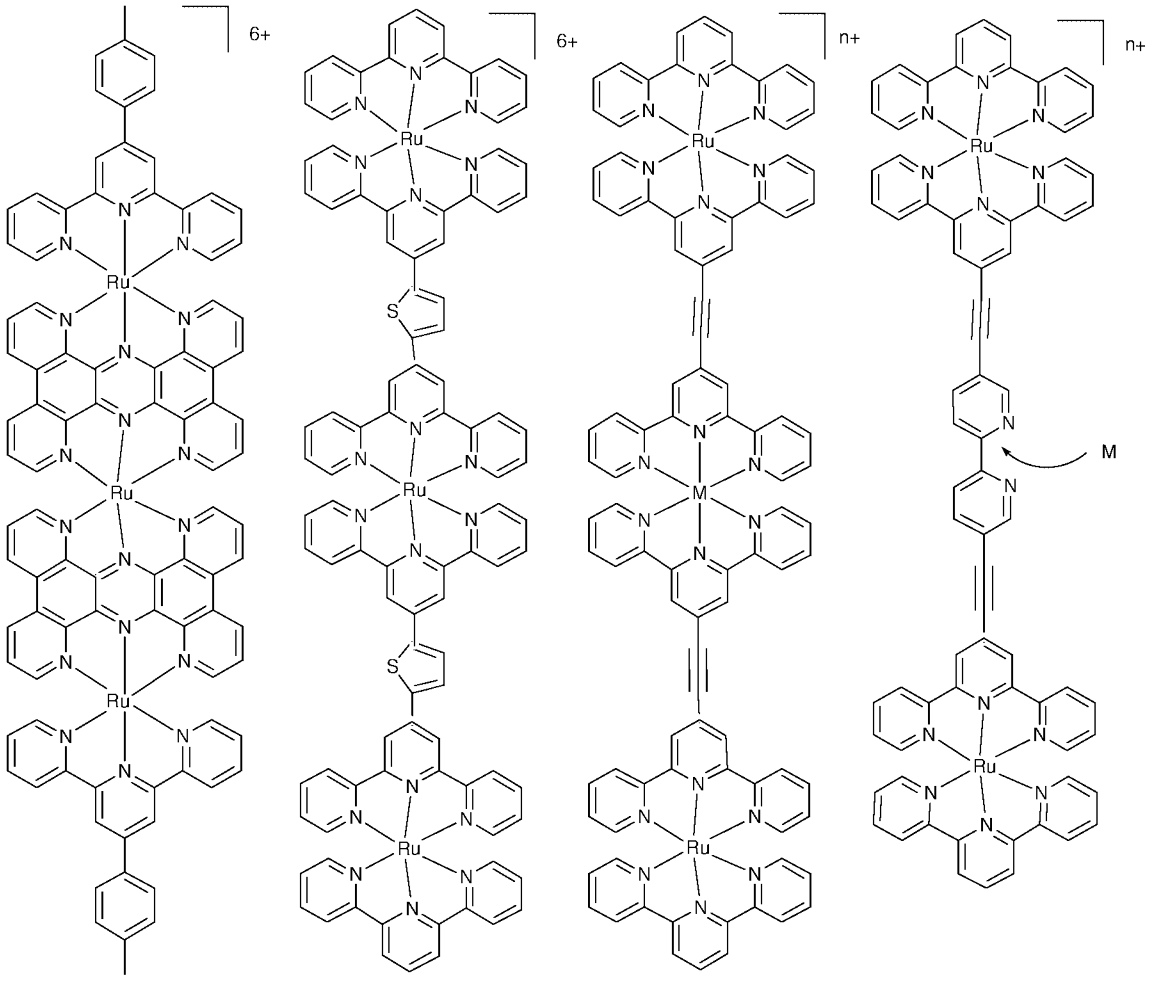


Fig. 10 Schematic formulae for **25**–**29**.

components. In the former case, the bridge confers a high degree of rigidity to the dinuclear species, while in the latter rotations around single bonds might result in some uncertainty for the d_{MM} separation.

An interesting rod-like arrangement is likewise maintained in complex **40**,[34] a species which was also prepared by using enantiomerically pure building-blocks. Preparation of **40**, and related species, was probably the first example of controlled synthesis of stereochemically defined multinuclear complexes based on Ru^{II} centres. The mixed-metal Ru^{II}–Pd^{II} trinuclear **41**,[35] is another example of a remarkable nm rod based on enantiomerically pure Ru-centres.



30 **31** **32** **33**

M = Zn^{2+}, Fe^{2+}, Co^{3+}

M = Zn^{2+}, Ba^{2+}, H^{+},...

Fig. 11 Schematic formulae for **30–33**.

The approach based on the use of enantiomerically pure building blocks has been extended to include the use of metal centres where the predetermined stereochemistry is dictated by *chiragen* ligands, which can confer the desired metal helicity in a controlled way.[36] A relevant example is provided by the case of the trinuclear species **44**, Fig. 15.[37] In this complex, two types of chiragen ligands are employed. One ligand is the so-called chiragen[0], which allows the preparation of the basic building block **42**. The assembling of **44** is then performed based on the use of superchiragen[0] bridging ligand **43**.

The study of the excited state properties of chiral transition metal complexes appears very promising,[30,31] at the moment however the extension to cases of mixed metal enantiomerically pure complexes does not seem easy. Of course, these complexes would be suitable for energy or electron transfer studies of the type treated above, which would seem to be an appropriate subject for further development.

Appendix. Energy transfer rate constants

The energy transfer rate constant for the dipole–dipole (Förster) mechanism, $k_{en}{}^{F}$, can be estimated by using spectroscopic quantities and according to eqns. (A1) and (A2),[9,15]

$$k_{en}^{F} = \frac{8.8\times10^{-25}K^{2}\Phi}{n^{4}\tau d_{MM}{}^{6}}J_{F} \qquad \text{(A1)}$$

$$J_{F} = \frac{\int F(\bar{\upsilon})\varepsilon(\bar{\upsilon})/\bar{\upsilon}^{4}d\bar{\upsilon}}{\int F(\bar{\upsilon})d\bar{\upsilon}} \qquad \text{(A2)}$$

where K^2 is a geometric factor, Φ and τ are the luminescence quantum yield and lifetime of the donor, respectively, n is the refractive index of the solvent and J_F is the Förster overlap integral between the luminescence spectrum of the donor, $F(\bar{\upsilon})$ and the absorption spectrum of the acceptor, $\varepsilon(\bar{\upsilon})$, on an energy scale (cm^{-1}).

34 **35**

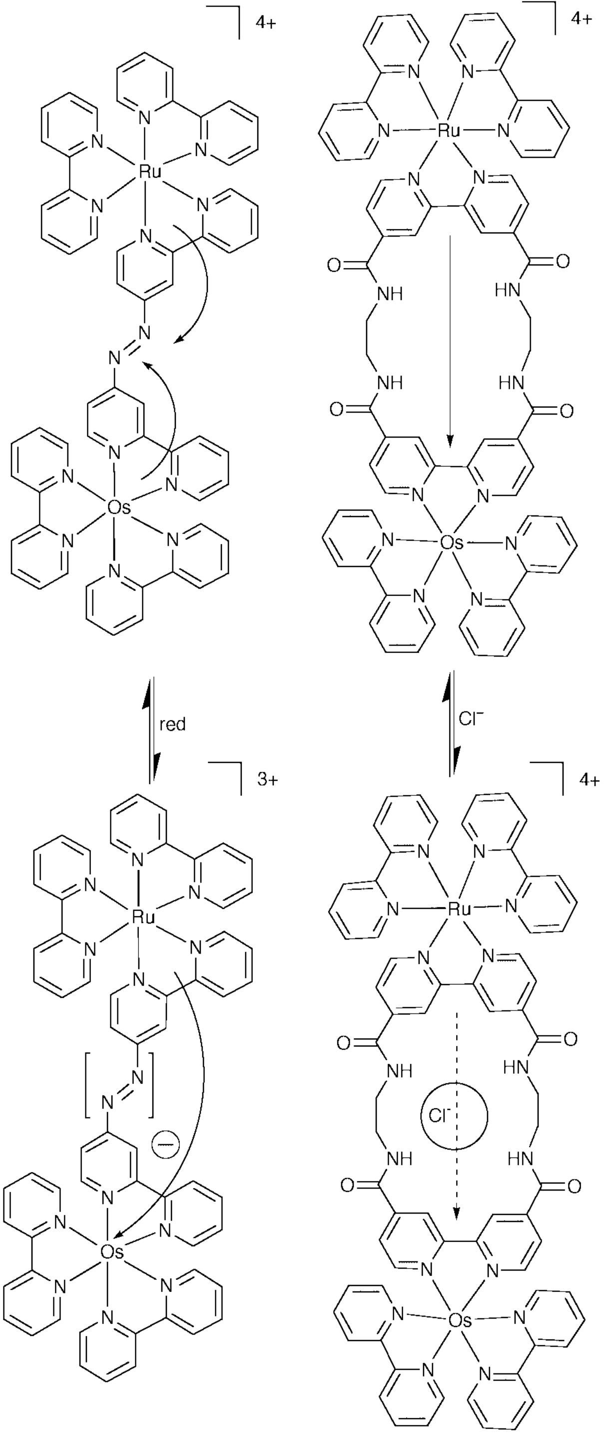
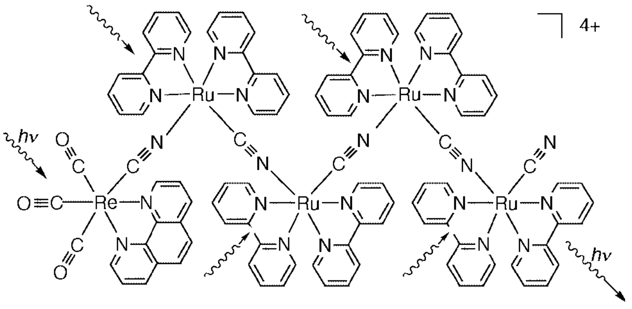
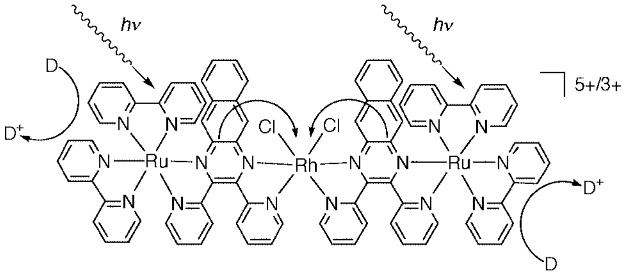


Fig. 12 Schematic formulae for **34** and **35**.



36



37

Fig. 13 Schematic formulae for **36** and **37**.

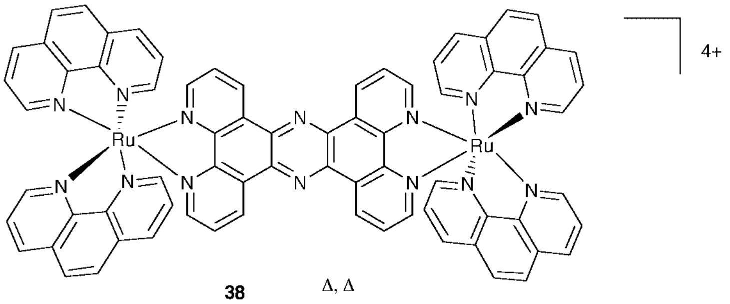
In order to estimate the exchange rate constant (Dexter),[10] $k_{\mathrm{en}}{}^{\mathrm{D}}$, eqns. (A3) and (A4) can be employed in the presence of a weak interaction, H, between the donor and acceptor units, J_{D} is the Dexter integral.

$$k_{\mathrm{en}}{}^{\mathrm{D}} = \frac{4\pi^2 H^2}{h} J_{\mathrm{D}} \qquad \text{(A3)}$$

$$J_{\mathrm{D}} = \frac{\int F(\bar{\upsilon})\varepsilon(\bar{\upsilon})\mathrm{d}\bar{\upsilon}}{\int F(\bar{\upsilon})\mathrm{d}\bar{\upsilon}\int \varepsilon(\bar{\upsilon})\mathrm{d}\bar{\upsilon}} \qquad \text{(A4)}$$

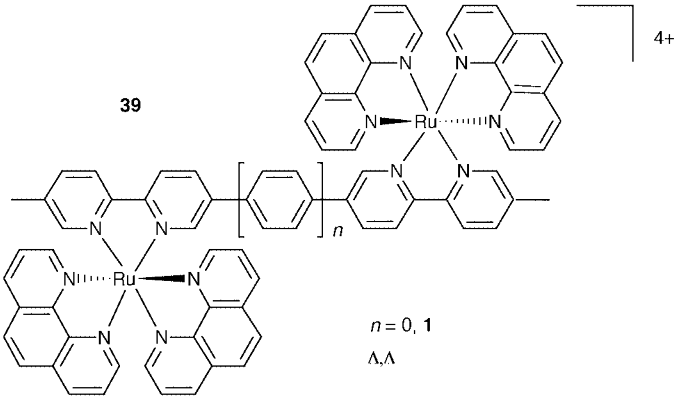
In practice one proceeds through a few calculation steps: (a) J_{F}, J_{D}, $k_{\mathrm{en}}{}^{\mathrm{F}}$ and its distance dependence can be evaluated from the photophysical and spectroscopic data; (b) based on $k_{\mathrm{en}}{}^{\mathrm{exp}} = k_{\mathrm{en}}{}^{\mathrm{F}} + k_{\mathrm{en}}{}^{\mathrm{D}}$, one obtains $k_{\mathrm{en}}{}^{\mathrm{D}}$ (and H), if any, at a certain d_{MM} separation; (c) for the distance dependence, $k_{\mathrm{en}}{}^{\mathrm{D}} = k_{\mathrm{o}}{}^{\mathrm{D}} \exp(-\beta d_{\mathrm{MM}})$, β may be available from experiments; in that case the rate constant at van der Waals distance, $k_{\mathrm{o}}{}^{\mathrm{D}}$, can also be assessed.

For both cases in Fig. 9, the solvent was aerated acetonitrile and β was taken to be 0.32 Å^{-1}.[14] Other used parameters are as follows. For the couple $\mathrm{Ru(bpy)_3}^{2+}$/$\mathrm{Os(bpy)_3}^{2+}$ (bpy = 2,2′-bipyridine): K^2 = 2/3, Φ = 1.6 $\times 10^{-2}$ and τ = 170 ns; calculations gave J_{F} = 3.8 $\times 10^{-14}$ cm^3 M^{-1} , J_{D} = 1.4 $\times 10^{-4}$ cm and H = 13.7 cm^{-1} at d_{MM} = 8 Å (estimated VDW distance). For the couple $\mathrm{Ru(ttp)_2}^{2+}$/$\mathrm{Os(ttp)_2}^{2+}$ (ttp = 4′-tolyl-2,2′:6’,2″-terpyridine): K^2 = 2/3, Φ = 3.5 $\times 10^{-5}$ and τ = 0.95 ns; calculations gave J_{F} = 8.3 $\times 10^{-14}$ cm^3 M^{-1}, J_{D} = 2.9 $\times$ 10^{-3} cm and H = 14 cm^{-1} at d_{MM} = 8 Å. Computations were performed with the help of Matlab 5.2 (MatWorks).



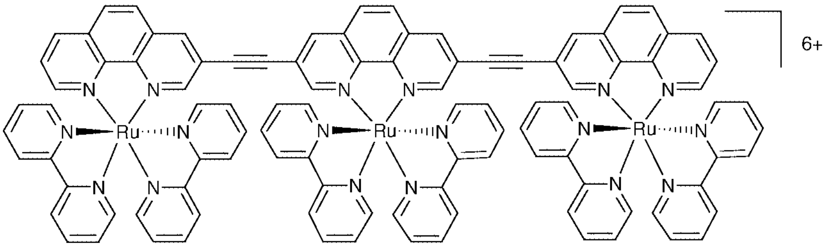
38 Δ, Δ

39

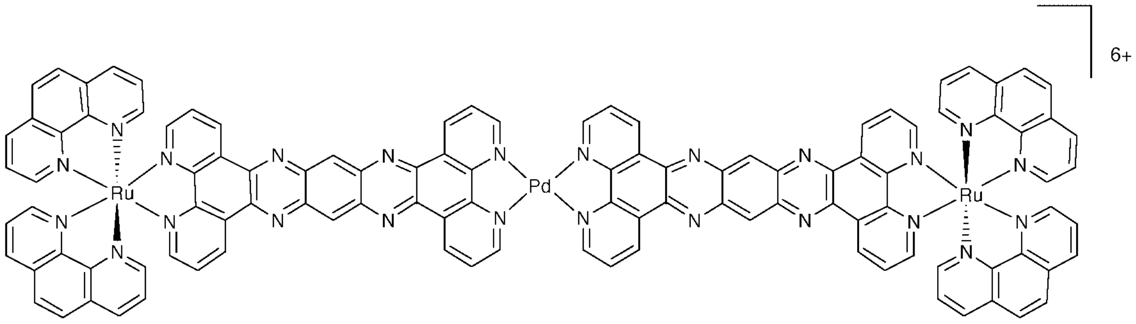


$n = 0$, **1**

Λ,Λ



40 Λ,Λ,Λ



41 Δ,Δ

Fig. 14 Schematic formulae for **38**–**41**.

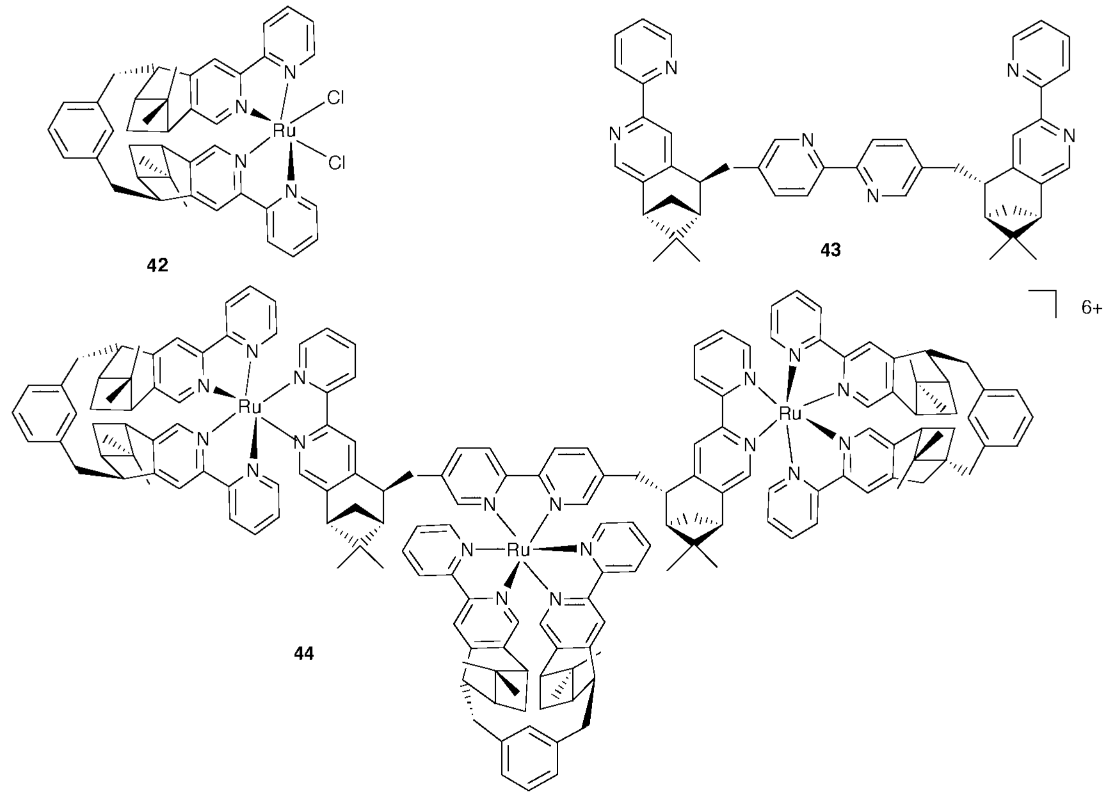


Fig. 15 Schematic formulae for **42**–**44**.

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