

Photoinduced two-step energy transfer in a Re/Ru dinuclear complex as mediated by an interposed 'reservoir' unit†

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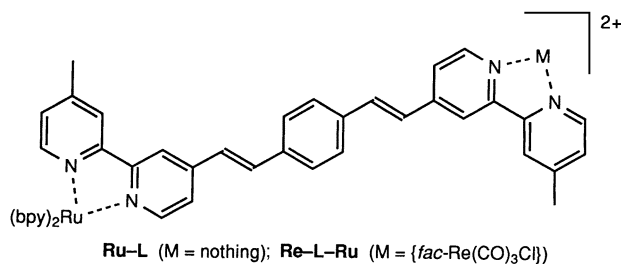
Received (in Cambridge, UK) 10th October 2000, Accepted 12th December 2000

First published as an Advance Article on the web 23rd January 2001

In a dinuclear complex containing both [ReCl(CO)₃(bpy)] and [Ru(bpy)₃]²⁺ chromophores, the bis(bipyridylethenyl)-benzene bridge acts as an intermediate reservoir of energy for two-step Re→Ru photoinduced energy transfer.

Photoinduced energy transfer between transition metal polypyridine centres is studied because of the widespread interest in processes concerned with light energy collection and conversion.^{1,2} The properties of the bridging ligand (L) interposed between the energy donor (D) and acceptor (A) components have accordingly been the object of extensive investigations, because the bridging ligand controls both the important *geometric* properties of the complex (inter-centre distance) and the *electronic* properties (electronic metal-metal coupling). Thus, careful control of the bridging ligand is of great importance in studies of photoinduced energy transfer in D-L-A complexes. However, not many examples are available of cases where L behaves as a photoactive component within the triad D-L-A.³ This is in contrast to the conceptually similar process of photoinduced electron transfer, a process that can gain in effectiveness if the electron transfer occurs in several discrete steps *via* the bridging ligand.⁴

Here we present spectroscopic results for the dinuclear complex [ReCl(CO)₃-L-Ru(bpy)₂]²⁺ (**Re-L-Ru**), where L is the bis-bipyridyl bridging ligand 1,4-bis[2-(4'-methyl-2,2'-bipyridyl-4-yl)ethenyl]benzene (dstyb), first described by



Schmehl and coworkers⁵⁻⁷ (ESI †). Data for the reference mononuclear complex [Ru(bpy)₂(dstyb)]²⁺ (**Ru-L**) are also discussed. We show that within **Re-L-Ru**, L behaves as a reservoir of excitation energy collected at the Re-based chromophore and passes some amount of it to the Ru-based emitter, according to a two-step energy transfer scheme [eqn. (1)].

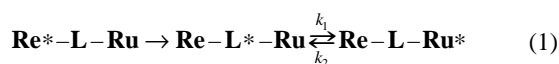


Fig. 1 shows the absorption spectra of **Re-L-Ru** and of the reference mononuclear complex **Ru-L**; the luminescence

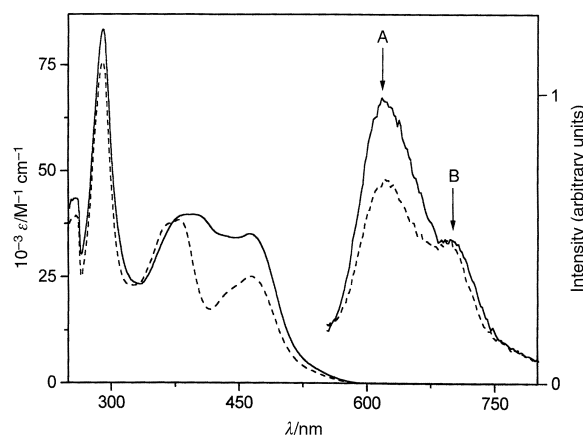


Fig. 1 Room temperature absorption and luminescence spectra of dinuclear **Re-L-Ru** (—) and reference mononuclear **Ru-L** (---) complexes; excitation was at 372 nm, solvent was DMF-CH₂Cl₂. The two luminescence bands are termed A (³Ru→L CT character) and B (³IL[dstyb] character).

spectra recorded at room temperature are also shown, as obtained after excitation at 372 nm (an isoabsorbing point for two cases). Luminescence data obtained both at room temperature and at 77 K are collected in Table 1 (ESI †). Comparison of the absorption profiles and intensities for **Re-L-Ru** and **Ru-L** with cases from literature⁵⁻⁷ allows the following assignments. (i) The bands peaking at 290 nm are of intra-bpy ¹IL(bpy) nature; (ii) the bands with maxima in the 360–390 nm region are of intra-dstyb character, ¹IL(dstyb); (iii) the bands with maxima at 464 nm are of ¹Ru→L MLCT nature; (iv) for **Re-L-Ru**, the flat region of absorbance in the 380–450 nm region includes the expected ¹Re→L CT transition.⁶

The luminescence spectra of both **Re-L-Ru** and **Ru-L** at room temperature (Fig. 1) show two distinct emission features. The band maximum at 621 nm (Table 1, Fig. 1, band A) is ascribed to emission from the ³Ru→L CT excited state; the

Table 1 Luminescence data^a

	298 K			77 K		
	$\lambda_{\text{max}}/\text{nm}$	τ/ns	ϕ^{Ru}	$10^{-4}k_{\text{r}}^b$	$\lambda_{\text{max}}/\text{nm}$	$\tau/\mu\text{s}$
Ru-L ^c	621 (A)	183 ^d	3.3×10^{-4e}	0.18	591 (A)	5.3
	695 (B)	210			693 (B)	11
Re-L-Ru ^c	621 (A)	188	4.5×10^{-4e}	0.24	591 (A)	5.3
	695 (B)	216 ^d			705 (B)	10
[Ru(bpy) ₃] ²⁺	608	210	1.5×10^{-2}	7.1	582	5.0

^a In air-equilibrated DMF-CH₂Cl₂ (9:1, v/v) solvent, unless otherwise noted. ^b $k_{\text{r}} = \phi^{\text{Ru}}/\tau$, $\lambda_{\text{exc}} = 372 \text{ nm}$. ^c A is the ³MLCT maximum, B is the ³IL band maximum. ^d Major (>95%) contribution of a dual-exponential decay; the other τ value was $3 \div 4 \text{ ns}$. ^e From separation of the overlapping bands constituting the luminescence spectrum.

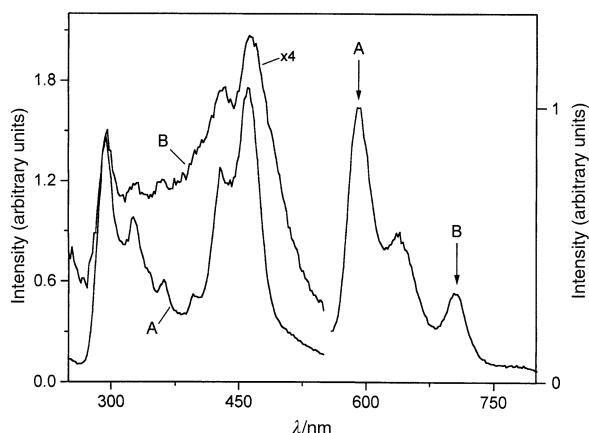
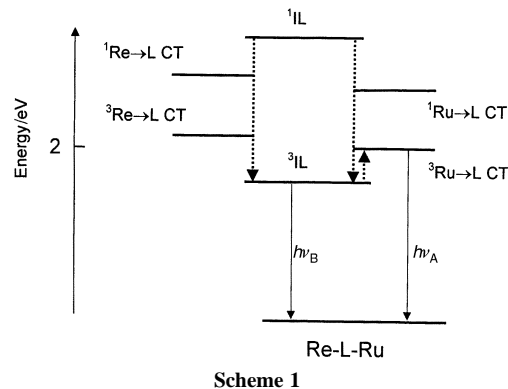


Fig. 2 77 K luminescence spectrum for **Re-L-Ru** under excitation at 372 nm, and excitation spectra taken at 591 nm (A band, $^3\text{Ru}\rightarrow\text{L}$ CT character) and 705 nm (B band, $^3\text{IL}[\text{dstyb}]$ character); solvent was $\text{DMF-CH}_2\text{Cl}_2$.

band maximum peaking at 695 nm (Table 1, Fig. 1, band B), in contrast has previously been established by Schmehl and coworkers as arising from the $^3\text{IL}(\text{dstyb})$ excited state.⁵⁻⁷ In addition, the same authors found that the $^3\text{Ru}\rightarrow\text{L}$ and $^3\text{IL}(\text{dstyb})$ levels in the homometallic dinuclear complex (**Ru-L-Ru**, according to our notation above, but where the ancillary ligand was 4,4'-Me₂bpy) are thermally coupled. We are seeing the same effect here for both **Re-L-Ru** and **Ru-L**: viz there are two thermally coupled luminescent excited states, of $^3\text{Ru}\rightarrow\text{L}$ CT and $^3\text{IL}(\text{dstyb})$ character, separated by an energy gap of ca. 1750 cm⁻¹. The similar emission lifetime values observed for both A and B bands (for instance, at r.t. for **Ru-L**, $\tau = 183$ and 210 ns, respectively; see Table 1), are consistent with this coupling. Significantly, we note that for **Re-L-Ru** no Re-based emission is detected. Any such emission would be expected to be on the blue side of the Ru-based emission maximum. The lack of Re-based emission for **Re-L-Ru** is ascribed to fast deactivation of the Re-based $^3\text{MLCT}$ energy levels, populated after light absorption, in favour of lower lying levels centred on the bridging ligand and/or the Ru fragment (see below).

Fig. 2 shows the 77 K luminescence spectrum for **Re-L-Ru** (excitation at 372 nm) and the excitation spectra obtained for observation at the emission maxima, 591 nm (band A, $^3\text{Ru}\rightarrow\text{L}$ CT nature, $\tau = 5 \mu\text{s}$) and 705 nm [band B, $^3\text{IL}(\text{dstyb})$ nature, $\tau = 10 \mu\text{s}$]. At this temperature, the two states are less coupled than at r.t. and comparison of the excitation spectra of **Re-L-Ru** with the absorption spectra for **Re-L-Ru** and **Ru-L** (Fig. 1) allows identification of the relaxation paths for the excitation energy occurring within the dinuclear complex. For **Re-L-Ru** the $^3\text{IL}(\text{dstyb})$ emission (band B), in addition to intraligand transitions, receives contributions from both $^1\text{Ru}\rightarrow\text{L}$ CT (sharp feature at ca. 460 nm in the excitation and absorption spectra) and $^1\text{Re}\rightarrow\text{L}$ CT transitions (flat region between 380 and 450 nm of the excitation and absorption spectra). Conversely, the $^3\text{Ru}\rightarrow\text{L}$ CT emission (band A) is apparently lacking any direct contribution from $^1\text{Re}\rightarrow\text{L}$ CT transitions; there is a much weaker intensity in the region characteristic of $^1\text{Re}\rightarrow\text{L}$ CT transitions in the excitation spectrum at 77 K and the weak residual intensity in this region of excitation spectrum A may be ascribed to the $^1\text{IL}(\text{dstyb})$ transition. We note that at room temperature the excitation spectra taken for the A and B bands of **Re-L-Ru** are more closely overlapping, as a consequence of the thermal redistribution between the luminescent states.

These results indicate that emission from the $^3\text{IL}(\text{dstyb})$ state is directly sensitised by Re-based absorption, whereas the $^3\text{Ru}\rightarrow\text{L}$ CT emission is not directly sensitised by Re-based absorption. Thus, some portion of excitation light absorbed by the Re-based chromophore of **Re-L-Ru** is (i) first transferred to the bridging ligand (giving the ^3IL state), and (ii) subsequently redistributed between the luminescent $^3\text{IL}(\text{dstyb})$ and $^3\text{Ru}\rightarrow\text{L}$ CT levels, a process which is governed by temperature (Scheme 1). According to this description, in **Re-L-Ru** the overall excitation energy collection process includes an indirect, two-



Scheme 1

step **Re** \rightarrow **Ru** energy transfer which is mediated by the spatially interposed **dstyb** unit such that the $^3\text{IL}(\text{dstyb})$ level acts as a 'reservoir' for excitation energy. This reservoir effect has been recognised and documented in a number of recent studies.⁸⁻¹¹

In order to model the r.t. thermal redistribution between the $^3\text{IL}(\text{dstyb})$ and $^3\text{Ru}\rightarrow\text{L}$ CT levels [eqn. (1)] of **Re-L-Ru** and **Ru-L**, we have employed $\tau = 8 \mu\text{s}$ and 210 ns (Table 1) as intrinsic lifetime values for the separate $^3\text{IL}(\text{dstyb})$ and ^3CT (Ru-based) luminophores and an energy gap of $\Delta E = 1750 \text{ cm}^{-1}$ between them. We calculate¹² that the thermally equilibrated state contains 86% of the $^3\text{Ru}\rightarrow\text{L}$ MLCT level and its decay takes place following a dual exponential law, with $\tau_1 = 240 \text{ ns}$ and $\tau_2 = 1.4 \text{ ns}$, provided $k_1/k_2 = 6$ and $k_2 = 1 \times 10^8 \text{ s}^{-1}$ [where k_1 and k_2 are defined in eqn. (1)]. These estimates suggest that the interconversion between the $^3\text{IL}(\text{dstyb})$ and $^3\text{Ru}\rightarrow\text{L}$ MLCT levels may be affected by different electronic and nuclear factors for the forward (k_1) and backward (k_2) paths, possibly due to the presence of rotamers of **dstyb**.¹³ The fact that the apparent radiative rate constant for the Ru-based luminescence, $k_r \approx 0.2 \times 10^4 \text{ s}^{-1}$ (Table 1), is much lower than that for $[\text{Ru}(\text{bpy})_3]^{2+}$, $7.1 \times 10^4 \text{ s}^{-1}$ (Table 1) has been ascribed to a low efficiency of intersystem processes.⁵ However it may well be that the intermixing of $^3\text{Ru}\rightarrow\text{L}$ MLCT and $^3\text{IL}(\text{dstyb})$ states is in part responsible for this outcome, given that for the latter case k_r is expected $10\text{--}10^2 \text{ s}^{-1}$.⁷

We thank the European Community for a post-doctoral fellowship (S. E., contract no. 980226) within the project ERB FMRX-CT98-0226 and for a COST award (COST-D11-0004/98); and the EPSRC (UK) for a Ph.D. studentship (to A. M. B.).

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