Intramolecular energy transfer through phenyl bridges in rod-like dinuclear Ru(II)/Os(II) terpyridine-type complexes

F. Barigelletti,[a] L. Flamigni,[a] V.Balzani,[a] J.-P. Collin,[b] J.-P. Sauvage,[b] A. Sour,[b] E.C. Constable [c] and A.M.W. Cargill Thompson [c]

[a] *Istituto FRAE-CNR and Dipartimento di Chimica "G. Ciamician" dell' Universita', 40126 Bologna, Italy.*

[b] *Laboratoire de Chimie Organo-Minerale, Institut de Chimie, Universite' L. Pasteur, 67000 Strasbourg, France.*

[c] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom*

ABSTRACT

The spectroscopic properties (ground state absorption and luminescence) of a series of three dinuclear heterometallic compounds are described. The complexes contain $Ru(tpy)_2{}^{2+}$- and $Os(tpy)_2{}^{2+}$-type components [tpy = 2,2':6',2"-terpyridine] which are either directly linked or connected by n phenyl spacers [n = 0, 1, and 2] through the 4' position of the coordinating ligand. The metal-to-metal distance, which is controlled by the intervening rigid bridges, varies in the range 12 to 20 Å. The dinuclear complexes are luminescent and the energy transfer process from the Ru-based to the Os-based centers is investigated by luminescence spectroscopy. For the three dinuclear complexes it is found that $k_{en} \geq 10^{10}$ s^{-1}. A Dexter (electron exchange) mechanism of energy transfer is most likely responsible for the observed behaviour.

A. INTRODUCTION

In the field of transition metal complexes [1,2], most of the supramolecular species employed so far for studies of photoinduced electron and energy transfer are based on $M(N\text{-}N)_3{}^{2+}$ fragments (M = metal, N-N = bipyridine-type ligands) [3-11]. In several cases such components are bridged by flexible spacers which do not allow a unique and well defined geometrical structure. We have synthesized a series of dinuclear heterometallic compounds, $(ttpy)Ru(tpy\text{-}tpy)Os(ttpy)^{4+}$ **[Ru•Os]**, $(ttpy)Ru(tpy\text{-}ph\text{-}tpy)Os(ttpy)^{4+}$ **[Ru•(ph)•Os]**, and $(ttpy)Ru(tpy\text{-}ph_2\text{-}tpy)Os(ttpy)^{4+}$ **[Ru•(ph)₂•Os]** by employing the back-to-back bis-terpy bridging ligand with one (see Figure 1) and two intervening phenyl units, respectively [ttpy = 4'-(p-tolyl)-

0010-8545/94/$26.00
SSDI 0010-8545 (94) 02025–E

2,2':6',2"-terpyridine]. In this way rigid rod-like structures are obtained for which the metal-to-metal distance is fixed at 12, 16, and 20 Å, respectively [12].

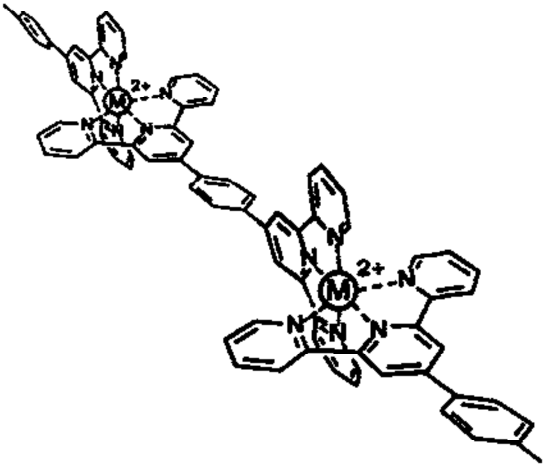

Figure 1. Schematic structure of **Ru•(ph)•Os**.

We describe the spectroscopic and electrochemical properties of the dinuclear compounds with reference to the parent mononuclear complexes, $Ru(ttpy)_2^{2+}$ and $Os(ttpy)_2^{2+}$ [13]. Photoinduced energy transfer was monitored by using stationary and time resolved luminescence spectroscopy. The role of the phenyl-containing bridges is discussed and it is shown that the Dexter (electron exchange) energy transfer mechanism [14] is most likely responsible for the highly efficient energy transfer from the Ru-based to the Os-based component.

B. EXPERIMENTAL

The ligands tpy, tpy-tpy, tpy-ph-tpy and tpy-ph_2-tpy and the complexes $Ru(ttpy)_2^{2+}$ and $Os(ttpy)_2^{2+}$ have been synthesized following literature methods. The complexes **Ru•Os**, **Ru•(ph)•Os**, and **Ru•(ph)$_2$•Os** have been obtained by reaction of $Os(ttpy)Cl_3$ with the corresponding complex $(ttpy)Ru\{(tpy\text{-}ph_n\text{-}tpy)\}^{2+}$, [n = 0, 1, and 2] in refluxing Bu^nOH for 7 hours and have been characterized by 1H NMR and FAB mass spectroscopy.

The instruments and procedure used to obtain cyclic voltammograms and ground state absorption spectra have been described in previous papers [13].

Luminescence spectra of deaerated solutions ($\leq 1.0 \times 10^{-5}$ M) were obtained with a Spex Fluorolog II spectrofluorimeter. Luminescence quantum yields were computed by using corrected spectra, as obtained by employing software provided by the firm, and relative to $Os(ttpy)_2^{2+}$, $\phi = 2.1 \times 10^{-2}$ [13b]. At the employed concentration values, no intermolecular energy transfer occurred.

Time resolved luminescence experiments were performed either with an IBH single photon equipment or with a picosecond fluorescence spectrometer based on a Nd:YAG (PY62-10 Continuum) laser and a Hamamatsu C1587 streak camera.

C. RESULTS AND DISCUSSION

Absorption, luminescence, and electrochemical data for the investigated dinuclear species and for the reference complexes are collected in Table 1. Wavelength maxima and extinction coefficients of the absorption bands refer to the MLCT energy region. The spectroscopic results clearly indicate that (i) there is a sizable intercomponent electronic interaction (the absorption spectra of the dinuclear species are not superimposable with the sum spectrum of the reference compounds, as would be expected for a weak electronic intercomponent interaction [15]), and (ii) the Os-based luminescence maxima for the dinuclear species occur at longer wavelength than for the reference complex $Os(ttpy)_2^{2+}$.Consideration of the spectroscopic results suggests that this intercomponent interaction increases in the series **Ru.(ph)$_2$.Os** < **Ru.(ph).Os** < **Ru.Os**.

TABLE 1

Spectroscopic and electrochemical data[a]

	Absorption[b]	Luminescence[c]			Electrochemistry[d]		
	λ_{max} (ε) nm (M^{-1} cm^{-1})	λ_{max} nm	τ ns	ϕ x10^2	E_{ox} V		E_{red} V
$Os(ttpy)_2^{2+}$	490 (26000) 667 (6600)	734[e]	230[e]	2.1[e]	+0.97		-1.23
$Ru(ttpy)_2^{2+}$	490 (28000)	640[f]	0.95[f]	0.003[f]		+1.25	-1.24
Ru.Os	522 (62100) 678 (10500)	800[g]	110[g]	0.13[g]	+0.94	+1.31	-0.97
Ru.(ph).Os	500 (65600) 671 (8500)	746[g]	190[g]	1.5[g]	+0.94	+1.29	-1.16
Ru.(ph)$_2$.Os	496 (66100) 670 (7700)	738[g]	200[g]	1.3[g]	+0.94	+1.28	-1.18

[a]Room temperature. Data for the reference mononuclear complexes are taken in part from ref. [13]. [b]ACN solutions, MLCT energy region. [c]Deaerated butyronitrile solutions. [d]ACN solutions, V vs SCE. [e]Excitation at 650 nm. [f]Excitation at 500 nm. [g]Excitation at 650 nm, ref. [12]. Excitation at 500 nm only results in an Os-based luminescence, see text.

The ligand-centered reduction potentials, Table 1, are consistent with a remarkable interaction between the two components of the dinuclear species. Actually, for the reference compounds the ligand-centered reduction, which involves the lowest unoccupied molecular orbital (LUMO) of ttpy, occurs at -1.23 and -1.24 V, while it occurs at -1.18, -1.16, and -0.97 V for **Ru.(ph)$_2$.Os**, **Ru.(ph).Os**, and

Ru.Os, respectively. Extended Hückel MO calculations show that the LUMO level for the ligand tpy-tpy (i) spreads over the two tpy submoieties, and that (ii) is lower in energy than the LUMO for the ligands ttpy and tpy-ph-tpy.These findings suggest that for the dinuclear species, ligand-centered reduction involves the bridging ligand and not the ttpy teminal ligands. On the basis of the known correlation between first ligand-centered reduction and absorption and luminescence data [2], one concludes that the Ru-based and Os-based lowest lying MLCT excited states for the dinuclear compounds involve the bridging ligand.

In Table 1, the luminescence intensities for $Os(ttpy)_2^{2+}$ and the dinuclear complexes have been obtained by exciting isoabsorptive solutions at 650 nm. (where direct excitation of the Os-based chromophore takes place). These luminescence results indicate that the intrinsic electronic properties of the Os-based component are different for the three dinuclear species, consistent with a different degree of intercomponent interaction for the three cases.

D. INTRAMOLECULAR ENERGY TRANSFER

Isoabsorptive solutions of the reference complexes and of the dinuclear compounds have been irradiated with light of 500 nm. For the dinuclear complexes a ~1:1 production of Ru-based and Os-based MLCT excited states is expected to take place [12]. However, their luminescence spectra exhibit (i) disappearance of the Ru-based luminescence and (ii) Os-based luminescence properties (intensity and wavelength maxima) which are identical, within experimental errors, to those obtained by exciting isoabsorptive solutions at 650 nm, where only the Os-based component absorbs light. This shows that complete quenching of the Ru-based excited state and sensitization of the Os-based luminescent excited state takes place in **Ru•Os**, **Ru•(ph)•Os**, and **Ru•(ph)$_2$•Os**.

In order to obtain the energy transfer rate one can use equations 1 or 2, where τ^0 and I^0 are the luminescence lifetime and intensity , respectively, of the model complex, $Ru(ttpy)_2^{2+}$, and τ and I are the Ru-based luminescence lifetime and intensity, respectively, of the dinuclear species.

$$k_{en} = 1/\tau - 1/\tau^0 \tag{1}$$

$$k_{en} = 1/\tau^0 (I^0/I - 1) \tag{2}$$

For the investigated dinuclear complexes the intramolecular energy transfer rate is $k_{en} \geq 10^{10}$ s^{-1}, as (i) $\tau \leq 20$ ps, from direct observation of the extremely weak time-resolved luminescence at 640 nm, and (ii) $I^0/I \geq 20$, from stationary luminescence measurements at the same wavelength.

According to Förster [16,17] and Dexter [14], two mechanisms of energy transfer should be taken into account. In the former case, energy transfer is explained in terms of a dipole-dipole interaction between the donor and the acceptor partners. The other type of mechanism is based on a contact interaction between the partners. According to the Förster approach, which makes use of easily accessible spectral parameters, it is possible to calculate the critical transfer radius, R_0, equation (3) and k_{en}^F, equation (4). At a donor-acceptor distance equal to R_0 the energy transfer rate and the intrinsic deactivation rate of the donor are the same (50% transfer efficiency for energy transfer).

$$R_o^6 = 5.87 \times 10^{-25}\, \phi^o / n^4 \int F(\nu)\, \varepsilon(\nu) \nu^{-4} d\nu \qquad (3)$$

$$k_{en}^F = 1/\tau^o\, (R_o/r)^6 \qquad (4)$$

In the above equations, n, ϕ^o, and r are the refractive index of the solvent, the luminescence quantum yield of the donor (the reference complex $Ru(ttpy)_2^{2+}$, Table 1) and the metal-to-metal distance, respectively. In equation (3) the spectral overlap between the luminescence spectrum of the donor and the absorption spectrum of the acceptor (the reference complex $Os(ttpy)_2^{2+}$, Table 1) is calculated to be 9.8×10^{-14} M^{-1} cm^3, and R_o is 9.1 Å.

Table 2 reports energy transfer parameters, as obtained according to the Förster treatment outlined above. As one can see, for the investigated dinuclear complexes the estimated rate for energy transfer seems by far too low to explain the experimentally observed value, $k_{en} \geq 10^{10}$ s^{-1}.

TABLE 2
Energy transfer parameters according to the Förster mechanism

	r^a Å	k_{en}^F s^{-1}	$efficiency^F$ %
Ru.Os	12	2.0×10^8	16
Ru.(ph).Os	16	3.6×10^7	3
Ru.(ph)$_2$.Os	20	9.3×10^6	1

[a]Metal-to-metal distance, Ro = 9.1 Å, see text.

On the basis of the above discussion, the reported results are consistent with a contact (Dexter) mechanism [18], which, in simple terms, has been described as a double exchange of electrons. It is to be noticed that for the presented series of dinuclear complexes, the **Ru** → **Os** intramolecular energy transfer appears to be largely a metal-to-metal hole transfer, as the lowest-lying Ru-based and Os-based MLCT excited state is localized on the bridging ligand in both cases.

Work is in progress to extend the series of complexes by using bridging ligands which incorporate -(phenyl)$_n$- fragments with n > 2.

E. ACKNOWLEDGMENT. We thank L. Minghetti and G. Gubellini for technical assisistance. This work was supported by CNRS and Ministere de la Recherche (France) and Programma Finalizzato Chimica Fine, CNR (Italy). A NATO Research Grant (No 920446, Supramolecular Chemistry) is also aknowledged.

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