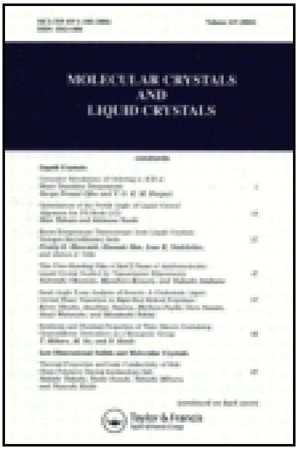

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Photoinduced Processes in Dinuclear Complexes Containing Rigid Bridging Ligands

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PHOTOINDUCED PROCESSES IN DINUCLEAR COMPLEXES CONTAINING RIGID BRIDGING LIGANDS

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Abstract We report the synthesis and the properties of some dinuclear ruthenium and/or osmium complexes bridged by rigid ligands. We focus on the nature of the bridging ligand and on its effect on the electrochemical, structural, and photophysical behavior of the complexes. Intercomponent energy and electron transfer processes are discussed.

Keywords: dinuclear complexes, supramolecular, bridging ligand, electron transfer, energy transfer, ruthenium, osmium

INTRODUCTION

The design and bottom-up construction of nanostructures and nanomachines capable of performing specific functions is one of the most important challenges now facing chemistry.[1-4] Advancement in this field requires the availability of molecular components and supramolecular species having well defined *structures and properties*. Recently considerable progress has been made concerning the study of photoinduced energy and electron transfer processes in supramolecular species made of organic components separated by rigid bridges.[5,6] The situation is much less advanced, however, as far as photoinduced energy and electron transfer processes between components made of metal complexes are concerned. The 2,2'-bipyridine (bpy) ligand has been extensively used to obtain metal complexes that exhibit outstanding photochemical, photophysical, and electrochemical properties.[7] Most of the bis(bipyridine) bridging ligands used so far to build up oligonuclear complexes consist of two bpy units linked by a flexible spacer (usually, an oligomethylenic chain, $(\text{-CH}_2\text{-})_n$).[8,9] In the resulting compounds the structure (i.e., the metal-metal separation distance) is undefined because of the lack of rigidity of the bridge. We have now designed and synthesized *long, rigid, rod-like bis(bipyridine) bridging ligands* and we have prepared their mono and dimetallic Ru and/or Os complexes.[10] In the dimetallic complexes the metal-metal distance is 1.7 nm. Absorption, luminescence, and electrochemical data show that in the dimetallic complexes the metal-metal interaction is weak but sufficient to allow efficient intercomponent energy and electron transfer processes.

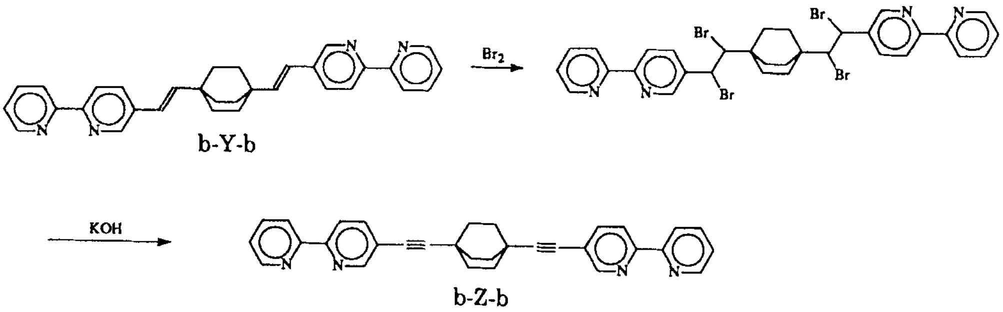
EQUIPMENT AND METHODS

The synthesis and characterization of the ligands and complexes has been described in more details in the original papers.[10]
Luminescence experiments were performed in acetonitrile at room temperature. Luminescence quantum yields were measured using $[\text{Ru(bpy)}_3]^{2+}$ in deaerated CH_3CN, $\Phi = 0.062$ and $[\text{Os(bpy)}_3]^{2+}$ in deaerated CH_3CN, $\Phi = 0.005$ as standards.[11] The absorption spectra, emission spectra, luminescence decays, and electrochemical potentials were obtained as previously described.[12] The procedure used to obtain values for the quenching of the luminescence of the Ru-based components and the sensitization of the luminescence of the Os-based component in the mixed-metal compounds has been previously described.[13]

RESULTS AND DISCUSSION

The two bridging ligands have the same length and are strictly related.

The ligand b-Z-b has been prepared from the E-E diene b-Y-b upon bromination and subsequent dehydrobromination (sheme 1). X-ray structure of b-Z-b[10] has shown that the ligand is linear and the edge-to-edge distance is 1 nm. The distance between the two metals is 1.7 nm for both the b-Y-b and b-Z-b dinuclear compounds.



Scheme 1

The electrochemical and photophysical properties of the complexes containing b-Y-b or b-Z-b (Figure 1) are very similar (Table I) .

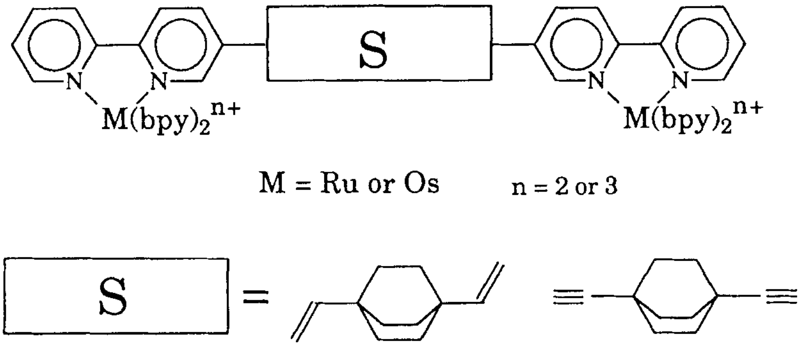


FIGURE 1 Schematic representation of the systems studied

The electrochemical and photophysical data of the monomers and the corresponding homometallic dimers are the same, suggesting that the interactions between the two metal centers are very weak.

Table I. Luminescence and electrochemical data[a]

	luminescence						electrochemistry[b]	
	Ru			Os			Ru	Os
	λ_{max} nm	τ ns	Φx10^2	λ_{max} nm	τ ns	Φx10^2	$E_{1/2}$, V (r.c.i.)	
$[b_2Rub\text{-}Y\text{-}b]^{2+}$	625	205	1.4	--	--	--	+1.25 (1)	
$[b_2Osb\text{-}Y\text{-}b]^{2+}$	--	--	--	736	40	0.23		+0.81 (1)
$[b_2Rub\text{-}Y\text{-}bRub_2]^{4+}$	628	209	1.4	--	--	--	+1.25 (2)	
$[b_2Osb\text{-}Y\text{-}bOsb_2]^{4+}$	--	--	--	740	40	0.23		+0.81 (2)
$[b_2Rub\text{-}Y\text{-}bOsb_2]^{4+}$	625	18	0.14	740	39[c]	0.23	+1.25 (1)	+0.81 (1)
$[b_2Rub\text{-}Z\text{-}b]^{2+}$	635	226	1.5	--	--	--	+1.25 (1)	
$[b_2Osb\text{-}Z\text{-}b]^{2+}$	--	--	--	787	28	0.18		+0.84 (1)
$[b_2Rub\text{-}Z\text{-}bRub_2]^{4+}$	635	231	1.5	--	--	--	+1.28 (2)	
$[b_2Osb\text{-}Z\text{-}bOsb_2]^{4+}$	--	--	--	787	29	0.18		+0.84 (2)
$[b_2Rub\text{-}Z\text{-}bOsb_2]^{4+}$	638	22	0.13	787	29[d]	0.18	+1.27 (1)	+0.84 (1)
$[Ru(bpy)_3]^{2+}$	615	170	1.5	--	--	--	+1.26 (1)	
$[Os(bpy)_3]^{2+}$		--	--	743	49	0.32		+0.83(1)

[a] Acetonitrile solution, room temperature. [b] $E_{1/2}$ values vs SCE and, within parentheses, relative current intensities. All the oxidation peaks are reversible. [c] Part of the luminescence signals shows a risetime of 22 ns. [d] Part of the luminescence signals shows a risetime of 21 ns.

Species containing two different luminescent centers (Ru(II) and Os(II)) are particularly suitable for energy transfer studies.

The $[(b_2Rub\text{-}Y\text{-}bOsb_2]^{4+}$, $[(b_2Rub\text{-}Y\text{-}b]^{2+}$, and $[(b_2Osb\text{-}Y\text{-}b]^{2+}$ "parent" compounds exhibit an isosbestic point at 464 nm in the absorption spectra. The complexes containing b-Z-b as bridging ligand, the isosbestic point is slightly shifted (466 nm). Emission spectra of solutions of the mixed-metal complexes and and of a 1:1 mixture of the parent mononuclear Ru and Os complexes show that the quenching of the Ru-based luminescence is (90%) is accompanied by the quantitative sensitization of the Os-based luminescence (see e.g. Figure 2). Such results are confirmed by the decrease in the excited state lifetime of the ruthenium unit and the corresponding rise-time observed monitoring on the osmium emission (Table I). The rate constants for the energy

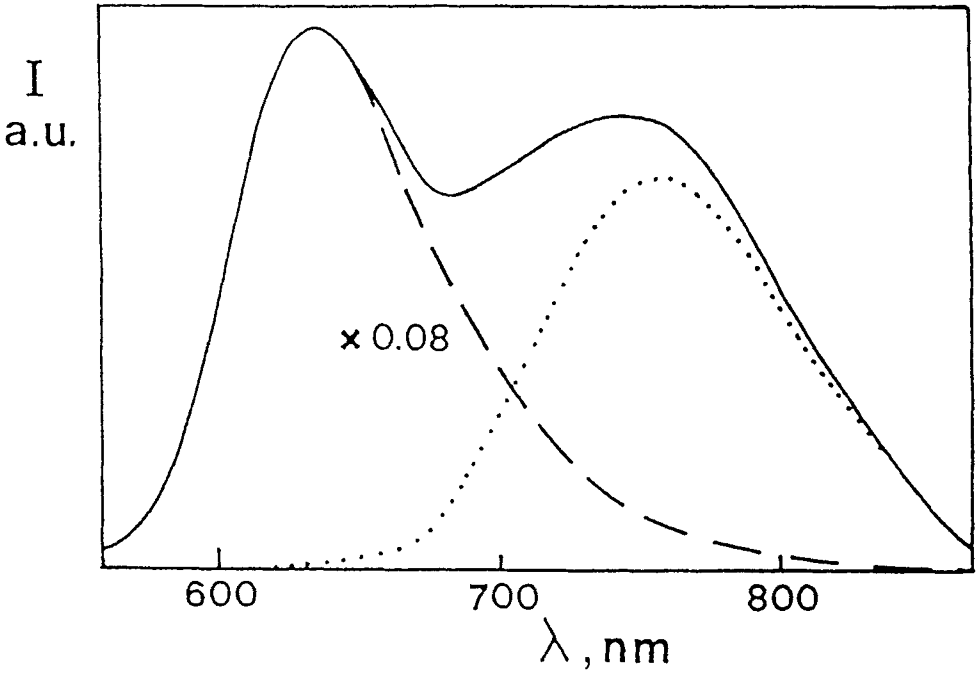


FIGURE 2 Luminescence spectra of isoabsorptive acetonitrile solutions (298 K) of: $[(b_2Rub\text{-}Z\text{-}bOsb_2]^{4+}$ *(—),* $[(b_2Osb\text{-}Z\text{-}bOsb_2]^{4+}$ *(···), and* $[(b_2Rub\text{-}Z\text{-}bRub_2]^{4+}$*(---). The last spectrum has been normalized to the maximum of the spectrum. Excitation wavelength 464 nm.*

transfer in $[(b_2Rub\text{-}Y\text{-}bOsb_2]^{4+}$ and in $[(b_2Rub\text{-}Z\text{-}bOsb_2]^{4+}$ are $k_{en}= 5.0x10^7$ s^{-1} and $k_{en}= 4.1x10^7$ s^{-1} respectively. Energy transfer may occur via a Förster-type mechanism.[14] However an exchange mechanism[15] cannot be ruled out because the experimental value is somewhat larger than that calculated for a dipole-dipole interaction.

Partial oxidation of species containing two identical metal centers (e.g. two Ru(II) units) leads to mixed-valence (Ru(II)/Ru(III)) species where photoinduced electron transfer processes can be investigated. Luminescence tecniques can be used to monitor the degree of interaction between the two components, since the oxidized species does not luminesce and quenching of the excited state of the M(II) unit can occur if the two units communicate. Oxidation with Ce(IV) of one metal center in the $[(b_2Mb\text{-}Y\text{-}bMb_2]^{4+}$ has shown that a fast electron transfer occurs with rate constant $1.1x10^9$, $8.7x10^9$, and $5.0x10^9$ s^{-1} for $[(b_2Ru^{III}b\text{-}Y\text{-}bRu^{II}b_2]^{5+}$, $[(b_2Ru^{II}b\text{-}Y\text{-}bOs^{III}b_2]^{5+}$, and $[(b_2Os^{III}b\text{-}Y\text{-}bOs^{II}b_2]^{5+}$,

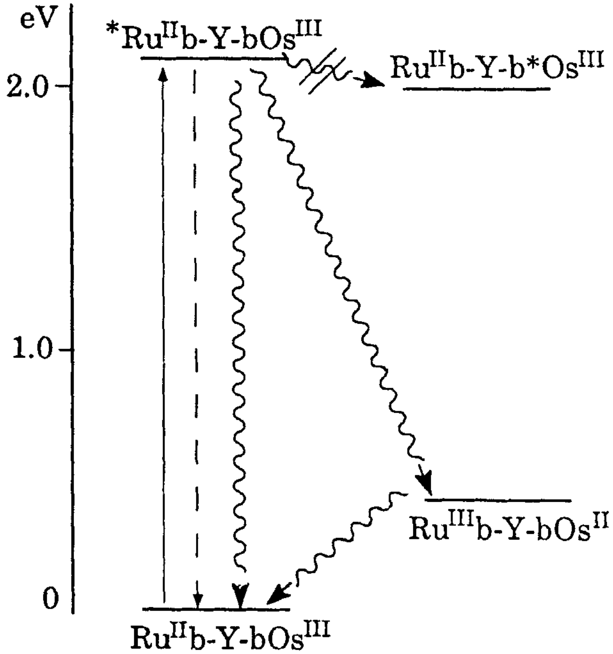


FIGURE 3 Energy level diagram showing the photoinduced electron transfer deactivation processes in $[(b_2Ru^{II}b\text{-}Y\text{-}bOs^{III}b_2]^{5+}$ Full line excitation; dotted line, luminescence; wavy lines: radiationless decay.

respectively. In the case of $[(b_2Ru^{II}b\text{-}Y\text{-}bOs^{III}b_2]^{5+}$ (Figure 3) the electron transfer quenching process leads to the intervalence transfer isomer $[(b_2Ru^{III}b\text{-}Y\text{-}bOs^{II}b_2]^{5+}$ which then relaxes to the thermodynamically stable species by a nonadiabatic, activated electron transfer process ($k_b = 1.0\text{x}10^6\ s^{-1}$).

CONCLUSIONS

We have synthesized rigid bis(bipyridine) bridging ligands which have then been used to construct rod-like dinuclear metal complexes of nanometric dimension. In spite of the long metal-metal separation distance (1.7 nm), in the dinuclear heterometallic $[(b_2Rub\text{-}Y\text{-}bOsb_2]^{4+}$ and $[(b_2Rub\text{-}Z\text{-}bOsb_2]^{4+}$ compounds light excitation of the Ru-based unit is followed by a fast energy transfer process ($k_{en} = 5\text{x}10^7\ s^{-1}$ and $k_{en} = 4.1\text{x}10^7\ s^{-1}$ respectively) which causes the sensitized luminescence of the Os-based unit. In the mixed valence Ru(II)/Ru(III), Os(II)/Os(III), and Ru(II)/Os(III) of the b-Y-b ligand a fast photoinduced electron transfer takes place.

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