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Assembling Metal Complexes and Bridging Ligands for Photoactive Supramolecular Systems

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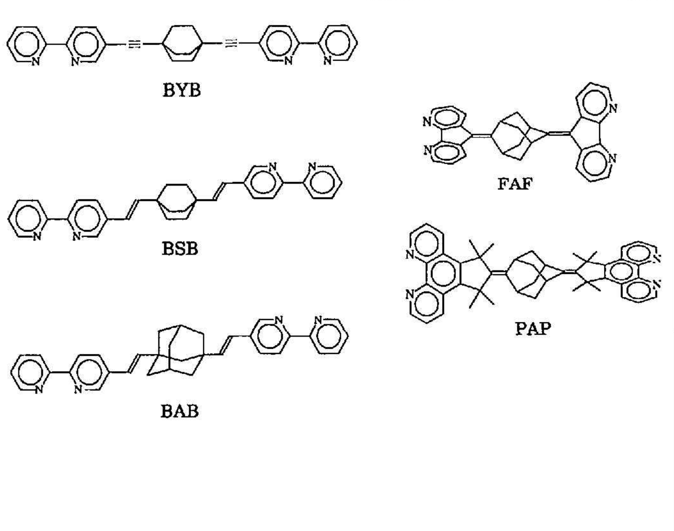
Abstract. Metal complexes and bridging ligands can provide useful building blocks for the design and construction of nanostructures and molecular devices capable of performing specific photoinduced functions. The choice of molecular components with appropriate structural and photophysical properties will be discussed and some multicomponent systems reviewed.

Introduction

Photoinduced processes over long distance in artificial multicomponent architectures, has been the object of several investigations in the last few years [1–4]. Such development is motivated by the new synthetic methodologies for preparing large polynuclear complexes [5–9], and by the interesting functions that a structurally organized system can perform elaborating the energy and information input of photons [10–13].

Progress in this field requires the availability of molecular components (building blocks) having well-defined structures and properties. As far as light- and/or redox-active units are concerned much attention is presently focussed on $M(N–N)_3^{n+}$ complexes, where M is a metal ion of the second or third transition rows (in particular, Ru^{II} and Os^{II}) and N–N is a bidentate bpy-type or phen-type ligand (bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline) [14–19].



$(bpy)_2Ru(BL)Ru(bpy)_2^{4+}$	$Ru^{II}.BL.Ru^{II}$
$(bpy)_2Os(BL)Os(bpy)_2^{4+}$	$Os^{II}.BL.Os^{II}$
$(bpy)_2Ru(BL)Os(bpy)_2^{4+}$	$Ru^{II}.BL.Os^{II}$
$(bpy)_2Os(BL)Os(bpy)_2^{5+}$	$Os^{II}.BL.Os^{III}$
$(bpy)_2Ru(BL)Os(bpy)_2^{5+}$	$Ru^{II}.BL.Os^{III}$

Fig. 1. *Schematic structures of the bridging ligands and their abbreviations* (top). General formulas of the dinuclear complexes investigated and abbreviations used (bottom).

In order to assembly these metal-containing building blocks it is necessary to have a connector between the metal units. Such structural component, the bridging ligand, should contain sites able to coordinate the metal center, and suitable spacers in order to control distance and orientation of the chromophores. In most of the structures that have been investigated, the bridging ligands are not particularly rigid [7c][14][15]. Therefore, there is a need for systematic studies in which the overall geometry can be controlled, the bridges are completely rigid, and their lengths can be varied over a range of values. In the attempt to realize this need we have devoted some effort in the design, synthesis, and photochemical and photophysical studies of dinuclear compounds containing rigid, linear bridging ligands [16][17].

Properties of the Components

The design of polynuclear complexes capable of performing photoinduced energy migration or charge separation requires the assembly, in an appropriate spacial sequence, of building blocks that exhibit different excited-state energies or redox potentials. From this point of view, the two families of Ru^{II}- and Os^{II}-polypyridine complexes exhibit quite interesting photochemical, photophysical, and redox properties [18][19]. For both families of complexes, oxidation processes are metal-centered, reduction processes are ligand-centered, and the lowest (luminescent and long-lived) excited state is a triplet metal-to-ligand charge-transfer (^3MLCT) level. Furthermore, such complexes nicely complement each other because the Os^{II} complexes can be oxidized at less positive potentials than the Ru^{II} analogues, which also implies that the luminescent ^3MLCT level of an Os^{II} complex lies lower in energy than that of an analogous Ru^{II} complex.

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Key component in polynuclear complexes are the bridging ligands, since the interaction between the bridged units and, thereby, the properties of the polynuclear complex, are critically dependent on the size, shape, and electronic nature of the bridge. In the last few years we have prepared, and investigated series of dinuclear compounds containing the bridging ligands (BL) reported in *Fig. 1* [16][17]. The choice of bridging ligands based on bpy derivatives, is very appropriate from an electronic viewpoint. In terms of structure, however, such a choice is not ideal because even using a rigid and linear spacer like the bicyclo[2.2.2]octane [16], (*Fig 1*, BYB and BSB) substitution of a single position on a bpy ligand leads to different possible conformers due to free rotation around the single bond, and as a consequence, a strict control of geometry and metal-metal distance cannot be completely achieved. To overcome these problems we have recently designed and realized two bridging ligands (*Fig. 1*, FAF and PAP) [17] that fulfill all the requirements needed for the construction of a photoactive geometrically controlled multicomponent system. Using the ligands FAF and PAP the two metal units, $[Ru(bpy)_2]^{2+}$ and/or $[Os(bpy)_2]^{2+}$, lie on the same axis of the bridging ligands in a linear arrangement, and the distance between the two chromophores can be controlled and if necessary increased by adding another adamantane unit.

All the dinuclear complexes of general formula M.BL.M, where M = $[Ru(bpy)_2]^{2+}$ and/or $[Os(bpy)_2]^{n+}$ and BL = BYB, BSB, BAB, FAF, PAP (see *Fig. 1*), show the following photophysical and electrochemical properties. They exhibit ligand-centered (LC) bands in the UV region accompanied by the characteristic [18][19] metal-to-ligand charge-transfer (MLCT) bands in the visible region. For illustration purposes, the absorption spectra of the Ru^{II}.BAB.Ru^{II}, Os^{II}.BAB.Os^{II}, and Ru^{II}.BAB.Os^{II} species are shown in *Fig. 2*.

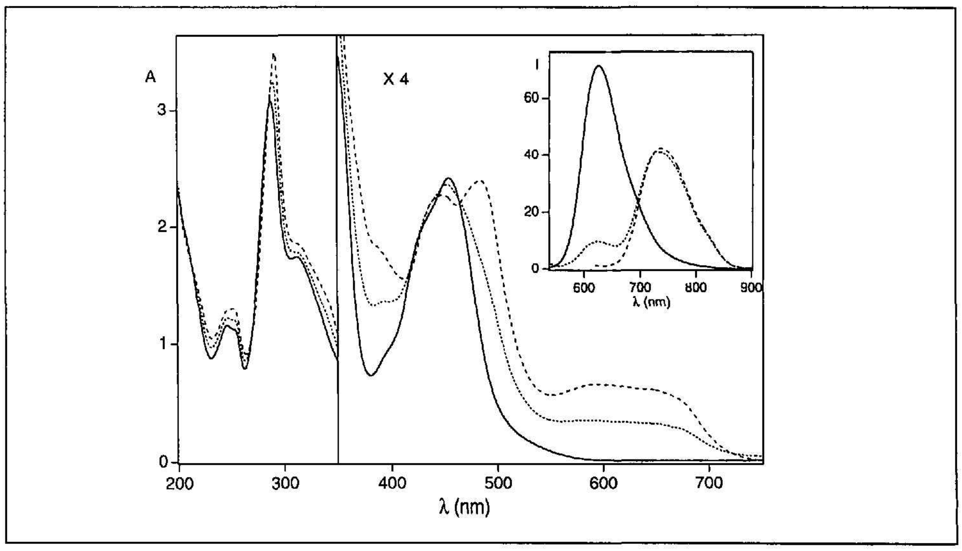

Fig. 2. *Absorption and* (inset) *emission spectra in acetonitrile solution at room temperature of Ru^{II}BAB.Ru^{II}* (——), *Ru^{II}BAB.Os^{II}* (······), *and Os^{II}BAB.Os^{II}* (----). The emission spectra were obtained by exciting isoabsorptive solutions in the isosbestic point at 465 nm.

Regardless of the excitation wavelength, all the Ru^{II} and/or Os^{II} metal complexes exhibit the characteristic [18][19] MLCT luminescence both in rigid matrix at 77 K and in fluid solution at room temperature (*Fig. 2* inset). All the luminescence data are collected in *Table 1*.

An important point to notice is that the electronic interaction between the metal-containing components is very weak. Such indication comes from the following observations: *a*) the almost identical oxidation potentials of the Os-based moieties in Os^{II}.BL.Os^{II} and Ru^{II}.BL.Os^{II}, and of the Ru-based moieties in Ru^{II}.BL.Ru^{II} and Ru^{II}.BL.Os^{II} (see *Table 1*); *b*) the identical absorption spectra exhibited by the mixed-metal Ru^{II}.BL.Os^{II} complex and the 1:1 mixture of its homometallic 'parent' complexes Ru^{II}.BL.Ru^{II} and Os^{II}.BL.Os^{II}. The absence of intense ($\varepsilon > 50$ M^{-1} cm^{-1}) intervalence transfer bands in the mixed-valence compounds further confirms the lack of strong intercomponent interaction. It should be recalled, however, that even an interaction of a few cm^{-1} (which cannot be noticed in spectroscopic and electrochemical experiments) is sufficient to cause fast

Table 1. *Luminescence and Electrochemical Data of Some Dinuclear Compounds* [16][17]

	298 K[a]				77 K[b]				Redox potentials [V][c], (rel. current intensity)		
	Ru		Os		Ru		Os		Ru	Os	
	λ_{max} [nm]	τ [ns]	λ_{max} [nm]	τ [ns]	λ_{max} [nm]	τ [µs]	λ_{max} [nm]	τ [µs]	Oxidation		Reduction
Ru.BAB.Ru	625	210	–	–	598	4.8	–	–	+1.27(2)		–1.29(2)
Os.BAB.Os	–	–	738	39	–	–	725	1.0		+0.80(2)	–1.25(2)
Ru.BAB.Os	626	1.7	736	38	595	0.050	720	1.1	+1.26(1)	+0.80(1)	–1.27(2)
Ru.FAF.Ru	605	0.300	–	–	577	5.5	–	–	+1.26(2)		–1.28(2)
Os.FAF.Os	–	–	720	41	–	–	710	1.1		+0.80(2)	–1.25(2)
Ru.FAF.Os	605	0.290	720	41	577	0.0039	703	1.1	+1.26(1)	+0.80(1)	–1.28(2)
Ru.PAP.Ru	610	150	–	–	583	5.5	–	–	+1.24(2)		–1.38(2)
Os.PAP.Os	–	–	717	41	–	–	709	1.0		+0.80(2)	–1.31(2)
Ru.PAP.Os	610	17	712	40	581	0.041	705	1.2	+1.24(1)	+0.80(1)	–1.35(2)

[a] Air-equilibrated acetonitrile soln.

[b] Butyronitrile soln.

[c] Acetonitrile soln., r.t.; potential values *vs.* SCE.

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intercomponent energy- and electron-transfer processes [10].

Intercomponent Energy Transfer in $Ru^{II}.BL.Os^{II}$

Excitation of an acetonitrile solution (10^{-5} M) of $Ru^{II}.BL.Os^{II}$ leads to the characteristic MLCT luminescence of the Ru and Os units. However, comparison with an isoabsorptive solution of $Ru^{II}.BL.Ru^{II}$ shows that the luminescence intensity of the Ru-based component is quenched by the Os-based component. Depending on the compound investigated, the intensity of the Ru-based luminescence in the mixed metal complex can decrease from 9 to 50% compared with the reference compound.

In principle, the quenching can be due to electron- or energy-transfer processes. From the excited-state energy of the Ru-based unit and the redox potentials shown in *Table 1*, it can be estimated that the reductive quenching process (*Eqn. 3*) would be slightly endoergonic and that the oxidative quenching process (*Eqn. 4*) would be endoergonic.

Table 2. *Rate Constants for Photoinduced Processes in Acetonitrile Solution at 298 K*

k [s^{-1}] ΔG° [eV] d_{MM} [Å]

	k [s^{-1}]	ΔG° [eV]	d_{MM} [Å]
Energy Transfer:			
$^*Ru.BSB.Os \rightarrow Ru.BSB.^*Os$	5.0×10^7	−0.35	17
$^*Ru.BAB.Os \rightarrow Ru.BAB.^*Os$	5.8×10^8	−0.36	14–15
$^*Ru.FAF.Os \rightarrow Ru.FAF.^*Os^{a)}$	2.6×10^8	−0.40	16
$^*Ru.PAP.Os \rightarrow Ru.PAP.^*Os$	4.0×10^7	−0.38	21
Electron Transfer:			
$^*Os^{II}.BSB.Os^{III} \rightarrow Os^{III}.BSB.Os^{II}$	5.0×10^9	−1.71	17
$^*Os^{II}.BAB.Os^{III} \rightarrow Os^{III}.BAB.Os^{II}$	3.5×10^9	−1.71	14–15
$^*Os^{II}.FAF.Os^{III} \rightarrow Os^{III}.FAF.Os^{II}$	3.9×10^8	−1.75	16
$^*Os^{II}.PAP.Os^{III} \rightarrow Os^{III}.PAP.Os^{II}$	2.7×10^7	−1.74	21
$^*Ru^{II}.BSB.Os^{III} \rightarrow Ru^{III}.BSB.Os^{II}$	8.7×10^9	−1.62	17
$^*Ru^{II}.BAB.Os^{III} \rightarrow Ru^{II}.BAB.Os^{III}$	2.8×10^9	−1.61	14–15
$^*Ru^{II}.FAF.Os^{III} \rightarrow Ru^{III}.FAF.Os^{II}$	8.3×10^8	−1.69	16
$^*Ru^{II}.PAP.Os^{III} \rightarrow Ru^{III}.FAF.Os^{II}$	7.5×10^6	−1.68	16
$Ru^{III}.BSB.Os^{II} \rightarrow Ru^{II}.BSB.Os^{III}$	1.0×10^6	−0.44	17
$Ru^{III}.BAB.Os^{II} \rightarrow Ru^{II}.BAB.Os^{III}$	4.0×10^7	−0.46	14–15
$Ru^{III}.FAF.Os^{II} \rightarrow Ru^{II}.FAF.Os^{III}$	2.9×10^7	−0.46	16
$Ru^{III}.PAP.Os^{II} \rightarrow Ru^{II}.PAP.Os^{III}$	8.3×10^3	−0.44	21

$$^*Ru^{II}.BL.Os^{II} \xrightarrow{\text{electron transfer (red.)}} Ru^{I}.BL.Os^{III} \qquad (3)$$

$$^*Ru^{II}.BL.Os^{II} \xrightarrow{\text{electron transfer (red.)}} Ru^{III}.BL.Os^{I} \qquad (4)$$

Therefore, quenching by electron transfer, which implies a large reorganizational energy in polar solvents, is unlikely. By contrast, quenching *via* energy transfer (*Eqn. 5*)

$$^*Ru^{II}.BL.Os^{II} \xrightarrow{\text{energy transfer}} Ru^{II}.BL.^*Os^{II} \qquad (5)$$

is exoergonic. Evidence for energy transfer was obtained from a comparison between the corrected luminescence intensities of $Ru^{II}.BL.Os^{II}$ and $Os^{II}.BL.Os^{II}$, which showed that the quenching of the luminescence of the Ru-based unit is accompanied quantitatively by the sensitization of the luminescence of the Os-based unit (*Fig. 2* inset). Furthermore, as one can see from *Table 1*, the quenching of the luminescence intensity of the Ru-based component is accompanied by a parallel quenching of the excited-state lifetime and by the rise of the Os-based excited state. The rate constant for energy transfer can be calculated from the equations:

$$k_{en} = 1/\tau - 1/\tau^0 \qquad (1)$$

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

where τ and I are the Ru-based luminescence lifetime and intensity of the Ru-BL-Os dinuclear compound, and τ^0 and I^0 are the luminescence lifetime and intensity of a suitable model compound.

The rate constants for the energy-transfer process for the $Ru^{II}.BL.Os^{II}$ complexes are reported in *Table 2*.

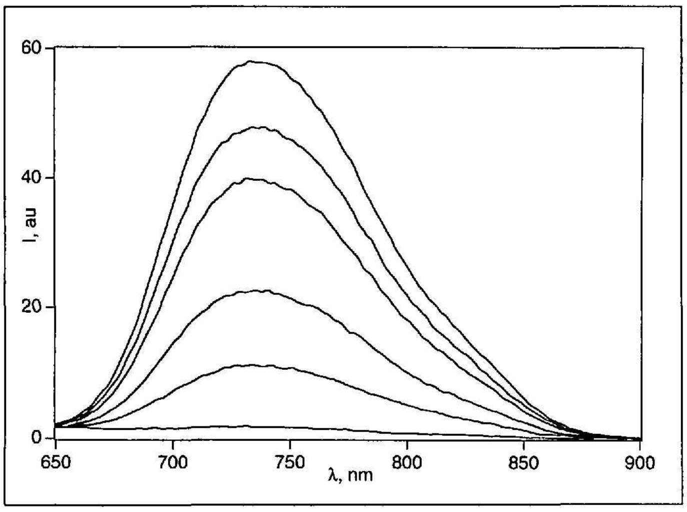

Fig. 3. *Changes in the emission spectra for an acetonitrile solution* (2×10^{-5} M) *of* $Os^{II}BAB.Os^{II}$ *upon addition of* Ce^{IV}

Intercomponent Electron Transfer in Mixed Valence Compounds

Oxidation of the osmium moiety can be achieved upon addition of an acidic solution of Ce^{IV} or HNO_3 and can be spectrophotometrically followed because the formation of the Os^{III} species [20] causes strong changes in the absorption spectra. In the case of Ru^{II}.BL.Os^{II}, selective oxidation of the Os-based unit can be achieved, because the two metal ions have substantially different oxidation potentials (*Table 1*) and do not interact appreciably.

In the case of Os^{II}.BL.Os^{II} and Ru^{II}.BL.Ru^{II}, the behavior upon oxidation is more complicated because the two metal units in each supramolecular species are oxidized at the same potential (*Table 1*). Therefore, addition of the oxidant leads to a statistical distribution of the M^{II}.BL.M^{II}, M^{II}.BL.M^{III}, and M^{III}.BL.M^{III} species, and for the Ru^{II}.BL.Ru^{II} oxidation, very drastic condition must be applied in order to oxidize the Ru moiety, and stabilize the Ru^{III} eventually obtained.

A quenching of the luminescence of the not-oxidized metal unit is always observed (*Fig. 3*), and a parallel decrease in the lifetimes is recorded (*Table 1*).

For the homonuclear Os^{II}BLOs^{III} complexes, the electron-transfer process is always very exoergonic, and the ground state is recovered by formation of the symmetric complex Os^{III}BLOs^{II} through a nonradiative process. In the case of the mixed metal, compounds, Ru^{II}BLOs^{III} (*Fig. 4*), upon excitation of the ruthenium unit, electron transfer occurs, leading to an intermediate state Ru^{III}BLOs^{II} that can be observed by transient flash photolysis [17][18]. Such intermediate state, comparable to a charge-separated state for more formal systems containing donor and acceptor chromophores, can have a quite long lifetime. The rate constants for the electron-transfer processes at room temperature, reported in *Table 2*, span on 10^9 s^{-1} to 10^6 s^{-1} interval. It is interesting to notice that the back electron transfer in these type of systems (*Table 2*) is always slower than the forward process, because of the lower exergonicity of the process (see *Table 2*), and the large distance over which the electron is transferred. In the dinuclear compounds the distance between metal centers spans 14–21 Å.

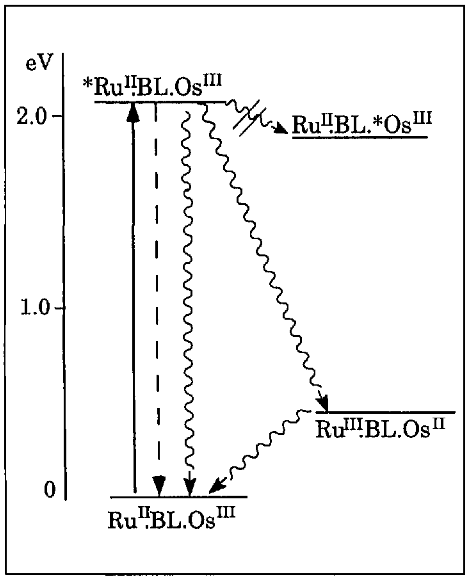

Fig. 4. *Energy-level diagram showing the photoinduced electron-transfer processes in Ru^{II}.BL.Os^{III}*

Conclusions

All the investigated compounds in the last few years [16][17] have shown that even for short distances, the interaction between the metal units is quite small. The rate constants, for energy- and electron transfer-processes in several of these systems, have been measured, and some effort has been devoted to understand which factors play a role in determining the rates of photoinduced processes. Some criteria have been suggested in order to covalently link building blocks for the construction of rigid and linear structures capable of performing useful light-induced functions.

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