Rigid Rodlike Dinuclear Ru/Os Complexes of a Novel Bridging Ligand. Intercomponent Energy and Electron-Transfer Processes

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The PF_6^- salts of the dinuclear complexes $[(bpy)_2Ru(PAP)Ru(bpy)_2]^{4+}$ ($Ru^{II}PAPRu^{II}$), $[(bpy)_2Os(PAP)Os(bpy)_2]^{4+}$ ($Os^{II}PAPOs^{II}$), and $[(bpy)_2Ru(PAP)Os(bpy)_2]^{4+}$ ($Ru^{II}PAPOs^{II}$) have been prepared, where bpy = 2,2′-bipyridine and PAP is a rodlike bridging ligand made of an adamantane-based spacer collinear with the coordination axis of two 1,10-phenanthroline units. In the prepared complexes, the metal−metal distance is 2.1 nm. In the $Ru^{II}PAPOs^{II}$ compound, photoinduced energy transfer from the Ru^{II}-based to the Os^{II}-based unit takes place with rate constant 5.2×10^7 s^{-1} at room temperature and 2.4×10^7 s^{-1} at 77 K. In the mixed-valence $Ru^{II}PAPOs^{III}$ compound, the luminescent excited state of the Ru^{II}-based unit is quenched via electron transfer by the Os^{III}-based unit with rate constant 7.2×10^6 s^{-1}. The rate constant for the back-electron-transfer reaction is 8.3×10^3 s^{-1}.
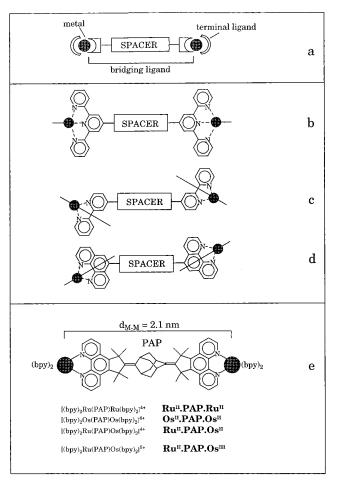
Introduction

Great attention is currently paid to the synthesis of polynuclear transition-metal complexes and the study of their photochemical, photophysical, and electrochemical properties.[2] This interest is stimulated, in particular, by attempts to design and construct multicomponent systems (often called supramolecular species) capable to perform useful light- and/or redox-induced functions.[3]

In polynuclear complexes the metal-based components are linked together by bridging ligands (Figure 1a). The role played by the bridging ligands is extremely important for the following reasons: (i) with their coordinating sites they contribute to determine the spectroscopic and redox properties of the active metal-based units; (ii) their spacers and the connections between spacers and coordinating sites determine the structure of the supramolecular system; (iii) their chemical nature controls the electronic communication between the metal-based units. Therefore the choice of suitable bridging ligands is crucial to obtain polynuclear complexes capable to show luminescence, to exhibit interesting electrochemical properties, and to give rise to photoinduced energy- and electron-transfer processes.

A wide range of bridging ligands have been used in recent years. Many of them contain 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or 2,2′:6′2′′-terpyridine (tpy) as chelating units capable to coordinate Ru(II).[2] From the photophysical viewpoint, bpy and phen are much better ligands than tpy for Ru(II). It is well-known, in fact, that at room temperature in fluid solution $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ exhibit a strong and long-lived luminescence (τ of the order of 10^2-10^3 ns),[4] whereas $[Ru(tpy)_2]^{2+}$ is very weakly luminescent (τ ca. 0.25 ns).[5] From the viewpoint of structure, however, the bridging ligands based on tpy are much more appealing since connection with a spacer can occur along the coordination axis by 4′-substitution yielding linear complexes (Figure 1b), a result that cannot be achieved by simple substitution on bpy and phen (Figure 1c,d).[6]

From the above discussion, it is clear that an ideal component to build linear, rodlike polynuclear complexes of photophysical

Figure 1. Schematic representation of a dinuclear complex (a), of the structures obtained by tpy (b), bpy (c), and phen (d) chelating units, and by the novel PAP bridging ligand (e). The abbrevations used to indicate the metal complexes are also shown.

interest would be a bridging ligand combining the linear structure based on 4′-substituted tpy chelating units with the electronic properties of bpy or phen. We have achieved this

Figure 2. Absorption and (inset) emission spectra in acetonitrile solution at room temperature of Ru^{II}PAPRu^{II} (—), Ru^{II}PAPOs^{II} (- - -), and Os^{II}PAPOs^{II} (···).

goal by preparing the bridging ligand PAP[7] (2,6-adamantanebis-(1,1,3,3-tetramethyl-1,3-dihydro-7,8-diaza)cyclopenta[1]-phenanthrene-2-ylidene) shown in Figure 1e. In this paper we report the luminescence properties of its dinuclear Ru/Ru, Ru/Os, and Os/Os complexes having bpy as terminal ligands (Figure 1e) and the results of an investigation on intercomponent energy- and electron-transfer processes.

Experimental Part

The dinuclear Ru^{II}PAPRu^{II}, Ru^{II}PAPOs^{II}, and Os^{II}PAPOs^{II} complexes were prepared and purified according to previously reported procedures.[8] Characterization was performed by FAB mass spectrometry, and ^{1}H and ^{13}C NMR. The ^{1}H NMR spectrum of the Ru^{II}PAPOs^{II} compound was exactly that expected for the two independent metal-based moieties. Experiments were carried out in acetonitrile (MeCN) solution at 298 K and in butyronitrile rigid matrix at 77 K. The mixed-valence Ru^{II}PAPOs^{III} compound was obtained by oxidation with nitric acid in MeCN−H$_2$O (9:1) solution. The equipment used to measure the absorption spectra, luminescence spectra and lifetimes, transient absorption spectra, and redox potentials has also been previously described.[8]

Results and Discussion

The absorption spectra in MeCN at room temperature are displayed in Figure 2. Oxidation of Ru^{II}PAPRu^{II} and Os^{II}-PAPOs^{II} occurs with bielectronic waves at +1.235 and +0.800 V (vs SCE), respectively, whereas Ru^{II}PAPOs^{II} shows two monoelectronic waves at +1.240 and +0.795 V. These results show that each metal-based unit displays its own absorption spectrum and electrochemical properties, as expected in the case of very weak intercomponent interaction.
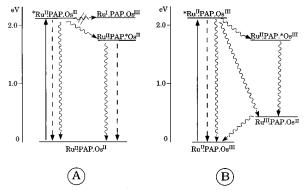
The emission spectra in MeCN at 298 K are displayed in the inset of Figure 2, and the luminescence data are gathered in Table 1. The luminescence properties of Ru^{II}PAPRu^{II} are very similar to those of Ru(bpy)$_2$(phen)$^{2+}$ (λ_{max} = 575 nm, τ = 6.6 μs in MeOH/EtOH at 77 K;[9] λ_{max} = 601 nm, τ = 310 ns in CH$_2$Cl$_2$ at 298 K[10]) and Ru(bpy)$_2$(5,6-Me$_2$phen)$^{2+}$ (λ_{max} = 577 nm, λ = 6.1 μs in MeOH/EtOH at 77 K),[10] showing that the chelating units of PAP, as expected, have the same electronic properties as phen.

The most interesting compound, of course, is the mixed-metal Ru^{II}PAPOs^{II}. As shown in Figure 2 and Table 1, it displays the luminescence bands of both the Ru(II) and Os(II) moieties. The luminescence intensity and lifetime of the Ru(II)-based unit, however, are strongly quenched compared to Ru^{II}PAPRu^{II}, with

TABLE 1: Luminescence Data

| | 298 K[a] | | | | | | 77 K[b] | | | |
| | Ru | | | Os | | | Ru | | Os | |
	λ_{max} (nm)	τ (ns)	I_{rel}[c]	λ_{max} (nm)	τ (ns)	I_{rel}[c]	λ (nm)	τ (μs)	λ (nm)	τ (μs)
Ru^{II}.PAP.Ru^{II}	610	150	100				583	5.5		
Os^{II}.PAP.Os^{II}				717	41	100			709	1.0
Ru^{II}.PAP.Os^{II}	609	17	8	712^f	41^d	95	581	0.041	705	1.2
Ru^{II}.PAP.Os$^{III\,e}$	609	72	48				f	f	f	f

^{a} Air-equilibrated acetonitrile solution. ^{b} Butyronitrile solution. ^{c} Excitation was performed at 464 nm, which is an isosbestic point between the Ru-based and Os-based units. ^{d} Rise time 15 ns. ^{e} MeCN−H$_2$O solution. ^{f} Not investigated.

Figure 3. Energy level diagrams showing the photoinduced energy and electron transfer processes in Ru^{II}PAPOs^{II} (A) and Ru^{II}PAPOs^{III} (B).

a corresponding sensitization of the Os(II)-based luminescence. Under the experimental conditions used (complex concentration 2.0×10^{-5} M), intermolecular energy transfer can be excluded. Therefore the results show that in Ru^{II}PAPOs^{II} an intercomponent (intramolecular) energy-transfer process takes place (Figure 3A), whose rate constant can be obtained from the equation $k = (1/\tau) - (1/\tau°)$, where $\tau°$ and τ are the luminescence lifetimes of the Ru(II)-based component in Ru^{II}PAPRu^{II} and Ru^{II}PAPOs^{II}, respectively. The values obtained are 5.2×10^7 s^{-1} at 298 and 2.4×10^7 s^{-1} at 77 K.

Selective oxidation of the Os-based unit of Ru^{II}PAPOs^{II} by HNO$_3$ converts the emissive Os(II)-based unit into the non-emissive Os(III)-based one. Therefore, the intensity of the luminescence band with λ_{max} = 717 nm decreases linearly and, as expected, disappears after the addition of 1 equiv of oxidant. In the oxidized Ru^{II}PAPOs^{III} species, the lifetime of the Ru-based unit is 72 ns (Table 1). This means that the luminescent Ru(II)-based excited state is quenched by the Os(III)-based component, with rate constant 7.2×10^6 s^{-1}. Laser flash photolysis experiments showed that the quenching process is accompanied by the growth and successive decrease of an absorption band with maximum at 650 nm, characteristic of the Os(II) moiety.[11] This shows that the quenching leads to the formation of the Ru^{III}PAPOs^{II} intervalence-transfer product, either directly or (less likely) via a first energy-transfer step (Figure 3B).[12] The Ru^{III}PAPOs^{II} species then decays to its ground-state isomer Ru^{II}PAPOs^{III} with rate constant 8.3×10^3 s^{-1}.

A detailed and comparative discussion of these data and of those obtained for similar complexes will be given elsewhere.[14] Two very interesting features, however, can already be pointed out: (i) the lifetime of the intermediate electron-transfer product Ru^{II}PAPOs^{III} is very long (130 μs); (ii) for the first time in a dinuclear Ru/Os system,[2] the rate constant of energy transfer

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Letters

from the Ru(II) to the Os(II) unit is faster than the rate of electron transfer from the Ru(II) to the Os(III) unit.

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