Photophysics of Dinuclear Ru(II) and Os(II) Complexes Based on the Tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴-3‴-*j*]phenazine (tpphz) Bridging Ligand

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The photophysical properties of mono- and dinuclear complexes based on the bridging ligand tpphz (tpphz = tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴-3‴-*j*]phenazine) were investigated. The complexes are of general formula $[M(bpy)_2(tpphz)]^{2+}$ [M = Ru(II), Os(II)] and $[(bpy)_2M_1(tpphz)M_2(bpy)_2]^{n+}$ [$M_1 = M_2$ = Ru(II), $n = 4$; $M_1 = M_2$ = Os(II), $n = 4$; M_1 = Ru(II), M_2 = Os(II), $n = 4$; M_1 = Ru(II), M_2 = Os(III), $n = 5$]. The tpphz bridging ligand, being aromatic, rigid, and planar, has interesting structural features for the design of covalently linked donor−acceptor systems. In this work particular attention was devoted to the electronic properties of this bridge and their effect on the photophysical behavior. All of the results are consistent with direct involvement of the tpphz bridge in the photophysically active, lowest MLCT excited states. Relevant findings are as follows: (i) in mononuclear complexes, MLCT excited-state energies are highly sensitive to interactions at the free bpy-like end of the tpphz ligand, such as metalation and protonation; (ii) in the dinuclear complexes, the electronic ground state behaves as a valence-localized, supramolecular system, while a substantial amount of intercomponent electronic coupling is indicated by MLCT excited-state behavior; (iii) in the heterodinuclear complex, fast ($k > 10^9$ s^{-1}) energy and/or electron transfer processes take place across the tpphz bridge.

Introduction

Covalently linked donor−acceptor systems[1] are supramolecular systems of great photochemical interest. Simple two-component systems (dyads) are suited for the study of photoinduced electron and energy transfer processes under well-defined geometric conditions.[1−43] For more complex systems (triads, tetrads, etc.), interesting functions based on electron and energy transfer can be envisioned.[44−49] Among these, light-driven vectorial transport of electronic charge (photoinduced charge separation),[6,50−53] and light energy harvesting and channeling (antenna effect)[54−62] are particularly relevant. On this basis, sensible approaches toward more complex supramolecular systems for artificial photosynthesis can be devised.[6,50−53]

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In inorganic dyads, the donor and acceptor components are transition metal complexes and the covalent linkage is provided by a bridging ligand. These systems are particularly attractive from the viewpoint of synthetic tailoring, as the energetics (excited-state energies, ground- and excited-state redox potentials) can be easily controlled by the appropriate choice of metals and ligands. A great number of dyads based on metal polypyridine units have been synthesized and studied in recent years.[15−43] Among these, Ru(II)−Os(II) dyads have been particularly useful in the investigation of Ru(II) → Os(II) energy transfer involving the lowest metal-to-ligand charge transfer (MLCT) states of the two units.[63] One-electron oxidation of such species, on the other hand, yields the Ru(II)−Os(III) species, suitable for the study of intramolecular electron, rather than energy, transfer. Typical dyads are of the type $[(bpy)_2Ru{-}BL{-}Os(bpy)_2]^{4+}$, where bpy = 2,2′-bipyridine and BL represents bridging ligands of various lengths and chemical nature. These studies indicate that the bridging ligand plays a very important role in the energy transfer kinetics.

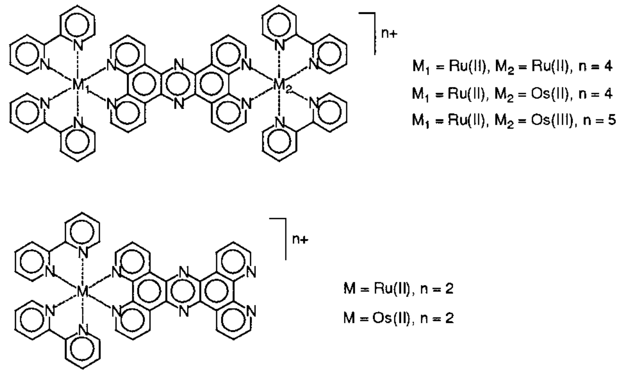

Figure 1.

Mononuclear and dinuclear complexes based on the new bridging ligand tpphz (tpphz = tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴-3‴-*j*]phenazine) have recently been developed in one of our laboratories.[64] They are of general formula $[M(bpy)_2(tpphz)]^{2+}$ [M = Ru(II), Os(II)] and $[(bpy)_2M_1(tpphz)M_2(bpy)_2]^{4+}$ [M_1, M_2 = Ru(II), Os(II)] (Figure 1). These complexes are interesting for a number of reasons. Many polypyridyl-based bridging ligands have been developed in recent years. Interesting ones are rodlike ligands often termed as “rigid”,[63] in the sense that their bond structure prevents flexibility and guarantees controlled metal−metal distance. Such ligands generally involve some single bonds, however, and are thus not rigid in a torsional sense. The tpphz ligand is the first example of a rodlike polypyridine bridging ligand that, because of its polyaromatic structure and lack of single bonds, is both longitudinally and torsionally rigid. This guarantees not only fixed metal−metal distance but also fully controlled geometry of the attached metal-containing moieties and is of great potential interest toward the design of binuclear complexes,[65] rigid polymers,[66] and dendrimeric structures.[67,68] Another point of interest for complexes of tpphz comes from the fact that its planar structure is similar

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to (though more extended than) that of the dppz (dipyrido[3,2-*a*:2′,3′-*c*]phenazine) ligand, and its metal complexes are expected[64] to possess properties similar to those of DNA intercalators[69] and could thus be useful as luminescent probes or cleaving reagents. Given these interesting features, detailed studies on the photophysical behavior of mono- and binuclear complexes of the tpphz ligand are worthwhile. Some preliminary photophysical results were reported in a previous paper.[64] In this paper, we report on a detailed study of the photophysical behavior on mono- and binuclear complexes of Ru and Os (Figure 1). Particular attention will be devoted to (i) the electronic properties of tpphz as a connector, (ii) the occurrence of intercomponent energy transfer in Ru(II)−Os(II) species, (iii) the occurrence of intercomponent electron transfer in Ru(II)−Os(III) species, and (iv) solvent and medium effects.

Experimental Section

Materials. The synthesis and the characterization of the mononuclear complexes $[(bpy)_2Ru(tpphz)]^{2+}$ and $[(bpy)_2Os(tpphz)]^{2+}$, of the homodinuclear complexes $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$ and $[(bpy)_2Os(tpphz)Os(bpy)_2]^{4+}$, and of the heterodinuclear complex $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$ were already reported.[64]

In all of the experiments, spectrograde solvents were used without further purification.

Methods and Instrumentation. UV−vis spectra were taken on a Kontron Uvicon model 860 spectrophotometer.

Near IR spectra were recorded with a Perkin-Elmer model 323 spectrophotometer.

Steady-state luminescence studies were performed using a Perkin-Elmer MPF 44E spectrofluorimeter. For 77 K emission spectra and lifetimes, an Oxford DN704 cryostat equipped with an Oxford DTC-2 temperature controller was used. Emission lifetimes were measured using a PRA system 3000 time-correlated single photon counting apparatus equipped with a Norland model 5000 MCA card and a hydrogen discharge pulsing lamp (50 kHz, halfwidth 2 ns). The decays were analyzed by means of Edinburgh FLA900 software. Alternatively, an Applied Photophysics laser flash photolysis apparatus was used, with a Continuum model Surelite II Nd:YAG laser (halfwidth 4−6 ns), frequency doubled (532 nm, 330 mJ) or tripled (355 nm, 160 mJ). The photomultiplier (Hamamatsu R928) signals were processed by means of a LeCroy 9360 (600 MHz, 5 Gs/s) digital oscilloscope.

Time-resolved excited-state absorption spectra and time-resolved emission spectra were collected using an optical multichannel analyzer PARC OMA III equipped with a spectrograph and a gated image intensified diode-array detector (PARC, model 1455); the detector has a minimum gate window of 5 ns with an adjustable delay from 0 to 256 ns (PARC, model 1302 fast pulser).

Luminescence quantum yields were measured in optically diluted solutions, using $[Ru(bpy)_3]^{2+}$ in oxygen-free CH_3CN ($\Phi = 0.06$) as reference emitter. Estimated experimental error in the reported data are as follows: absorption and emission maxima ± 2 nm, emission lifetimes and emission quantum yields ± 10%.

When required, deaeration of the solutions was carried out by multiple freeze−pump−thaw cycles.

The mixed-valence Ru(II)−Os(III) species was obtained by oxidation of the $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$ dinuclear complex in CH_3CN/water (10/1 v/v) with stoichiometric amounts of ammonium Ce(IV) nitrate in HNO_3 (6%) solution. Under these conditions, selective oxidation of the osmium center is obtained.[22]

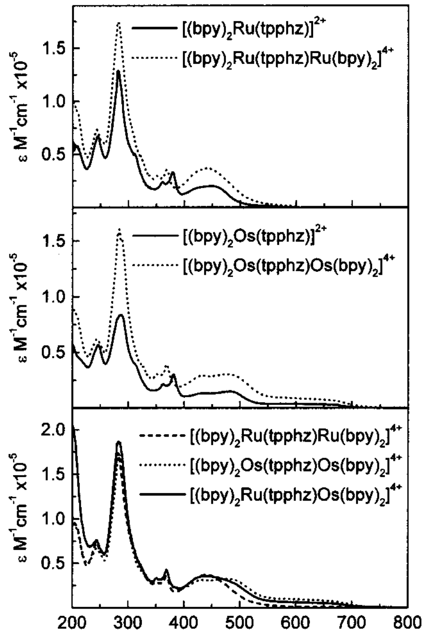

Figure 2. Absorption spectra of the mononuclear and binuclear compounds in CH_3CN.

Results

Absorption Spectra. The absorption spectra of the investigated complexes in CH_3CN solution are shown in Figure 2. Figure 2a shows the absorption spectra of both $[(bpy)_2Ru(tpphz)]^{2+}$ and $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$. In Figure 2b the spectra of both $[(bpy)_2Os(tpphz)]^{2+}$ and $[(bpy)_2Os(tpphz)Os(bpy)_2]^{4+}$ are reported. Figure 2c shows the spectrum of the heterodinuclear complex $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$ together with those of the two homodinuclear complexes. For all of the complexes only minor effects on the absorption spectra are observed when the solvent is changed (CH_3CN, DMSO, EtOH, CH_2Cl_2, and H_2O). In particular, a small red shift (5−10 nm) of all of the absorption bands is observed for DMSO relative to the other solvents.

The effect of the addition of $HClO_4$ on CH_3CN solutions of the complexes was extensively investigated. In Figure 3a,b are reported the variations in the absorption spectra of $[(bpy)_2Ru(tpphz)]^{2+}$ and $[(bpy)_2Os(tpphz)]^{2+}$ (3.2×10^{-5} M solution), obtained by adding different amounts of $HClO_4$ up to an acid/complex concentration ratio of 1.8/1. The addition of $HClO_4$ gives rise to very similar modifications of the absorption spectrum for both complexes: (i) in the near UV region a blue shift of the LC transitions assigned to the tpphz ligand is observed (these variations occur with the maintenance of three isosbestic points at 356, 368, and 377 nm for the Ru complex and at 358, 365, and 377 nm for the Os complex); (ii) in the visible region a blue shift of the system of MLCT transitions together with the formation of a new absorption band at longer wavelength is observable (an isosbestic point is maintained at 482 nm for Ru and 510 nm for Os complexes). The addition of larger amounts of $HClO_4$ to the solution of mononuclear complexes does not induce further modification of the absorption spectra up to an acid/complex concentration ratio of 100/1. By contrast to the behavior observed with mononuclear complexes, addition of $HClO_4$ to CH_3CN solutions of dinuclear complexes (1.5×10^{-5} M) does not affect the absorption spectra at least up to an acid/complex concentration ratio of 100/1.

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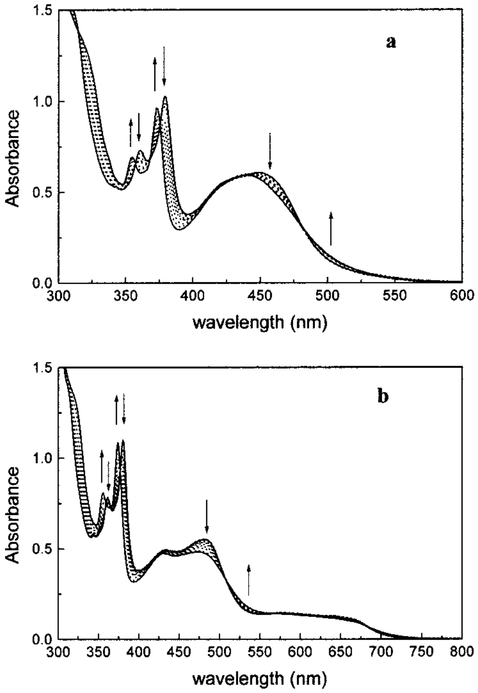

Figure 3. Spectral changes observed upon addition of $HClO_4$: (a) $[(bpy)_2Ru(tpphz)]^{2+}$; (b) $[(bpy)_2Os(tpphz)]^{2+}$. Solutions of complex 3.2 × 10^{-5} M in CH_3CN; $HClO_4$/complex concentration ratios ranging from 0/1 to 1.8/1.

Table 1. Photophysical Properties of the Investigated Complexes[a]

	room temp[b]			77 K[c]	
complexes	λ_{max}, nm	τ, ns	Φ_{em}, $\times 10^2$	λ_{max}, nm	τ, ns
$[(bpy)_3Ru]^{2+}$	620	1100	6.0	580	5100
$[(bpy)_2Ru(tpphz)]^{2+}$	628	1090	4.5	580	4000
$[(bpy)_2Os(tpphz)]^{2+}$	765	20	0.12	705	750
$[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$	740	90	0.084	585	2800
$[(bpy)_2Os(tpphz)Os(bpy)_2]^{4+}$	790[d]	1.5[d]		716	570
$[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$	790[d]	1.5[d]		707	650

[a] Emission maxima are corrected for the PMT response. [b] CH_3CN, deaerated solutions, unless otherwise noted. [c] EtOH/MeOH (4/1) rigid matrix. [d] CH_2Cl_2.

Emission Measurements. The photophysical properties of the investigated complexes are collected in Table 1.

At room temperature the photophysical properties (emission maximum, quantum yield, and lifetime) of the $[(bpy)_2Ru(tpphz)]^{2+}$ mononuclear complex in CH_3CN solution are close to those of other ruthenium–bpy complexes (see Table 1), while the emission maximum of the dinuclear $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$ complex is substantially red-shifted and has a shorter lifetime with respect to the mononuclear compound $[(bpy)_2Ru(tpphz)]^{2+}$ ($\lambda_{max} = 740$ nm vs $\lambda_{max} = 628$ nm, $\tau = 90$ns vs $\tau = 1090$ ns, Figure 4a and Table 1). Regarding the corresponding Os complexes, only the mononuclear compound has a detectable emission at room temperature in CH_3CN solution ($\lambda_{max} = 765$ nm, $\tau = 20$ ns, Figure 4b). No steady-state emissions are observable for the homodinuclear $[(bpy)_2Os(tpphz)Os(bpy)_2]^{4+}$ and for the heterodinuclear $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$ complexes at room temperature in CH_3CN solutions.

All of the investigated complexes are emitting at 77 K in 4/1 EtOH/MeOH glasses. The emission spectra are reported in Figure 5. The 77 K emission spectra of the mononuclear and binuclear Ru complexes are shown in Figure 5a. The shapes, energies, and lifetimes of both emissions are very similar to those of $[Ru(bpy)_3]^{2+}$ (Table 1). In Figure 5b are reported the 77 K emission spectra of the $[(bpy)_2Os(tpphz)]^{2+}$, $[(bpy)_2Os(tpphz)Os(bpy)_2]^{4+}$, and heterodinuclear $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$ complexes. The emissions of the mononuclear Os complex and of the homo- and heterodinuclear complexes in rigid matrix at 77 K are very similar in shape, energy, and lifetime (Table 1).

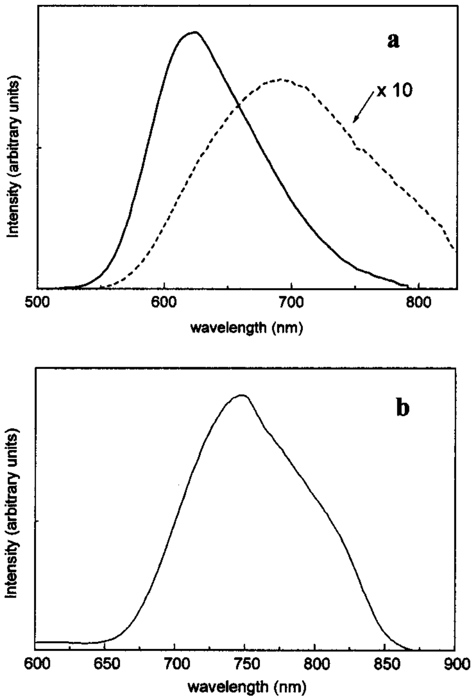

Figure 4. Room-temperature emission spectra in CH_3CN solution of (a) $[(bpy)_2Ru(tpphz)]^{2+}$ (—) and $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$ (- - -) and (b) $[(bpy)_2Os(tpphz)]^{2+}$.

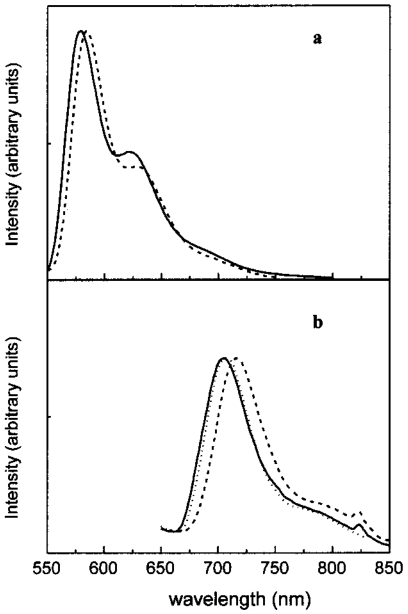

Figure 5. 77 K emission spectra in 4/1 EtOH/MeOH of (a) $[(bpy)_2Ru(tpphz)]^{2+}$ (—), and $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$ (- - -) and (b) $[(bpy)_2Os(tpphz)]^{2+}$ (—), $[(bpy)_2Os(tpphz)Os(bpy)_2]^{4+}$ (- - -), and $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$ (•••). Excitation wavelength = 460 nm.

The effects of different solvents (CH_3CN, DMSO, EtOH, CH_2Cl_2, and H_2O) on the emission spectra of the complexes were examined. The results are summarized in Table 2. The solvent has a remarkable effect on both emission energies and lifetimes. In particular it is to be noted that (i) in H_2O the

Table 2. Influence of Solvent on the Photophysical Properties of the Investigated Complexes[a]

	λ_{max}, nm (τ, ns)				
complexes	H_2O	DMSO	CH_3CN	EtOH	CH_2Cl_2
$[(bpy)_2Ru(tpphz)]^{2+}$	683 (~5)	654 (450)	628 (1090)	625 (690)	605 (480)
$[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$		780 (27)	740 (90)	725 (20)	680 (325)
$[(bpy)_2Os(tpphz)]^{2+}$			765 (16)	760	730 (80)
$[(bpy)_2Os(tpphz)Os(bpy)_2]^{4+}$					790 (1.5)
$[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$					790 (1.5)

[a] Emission maxima are corrected for the PMT response.

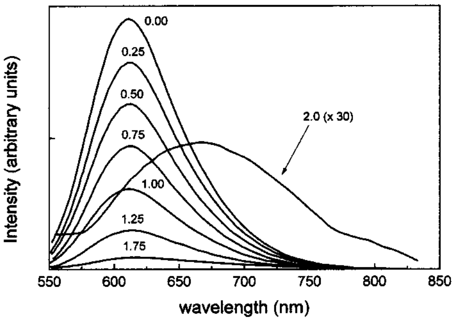

Figure 6. Effect of the addition of $HClO_4$ on the emission of $[(bpy)_2Ru(tpphz)]^{2+}$. Complex 3.2×10^{-5} M in CH_3CN. The numbers over the curves indicate the $HClO_4$/complex concentration ratios.

emission of all of the complexes is almost completely quenched; (ii) the emission of the homodinuclear $[(bpy)_2Os(tpphz)Os(bpy)_2]^{4+}$ and the heterodinuclear $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$ complexes is observable, at room temperature, only in CH_2Cl_2 solutions.

The effect of the addition of $HClO_4$ on the emission of $[(bpy)_2Ru(tpphz)]^{2+}$ in aerated CH_3CN solution is reported in Figure 6. The acid clearly quenches the $[(bpy)_2Ru(tpphz)]^{2+}$ emission. The intensity quenching is not accompanied by a parallel quenching of the emission lifetime, which remains appreciably constant. The quenching of the original emission is practically complete at an H^+/complex concentration ratio larger than 1.8/1. However, a weak residual emission is still present, red-shifted ($\lambda_{max} = 670$ nm) and short-lived ($\tau = 25$ ns) with respect to the original one. This new emission is stable at least up to an H^+/complex concentration ratio of 100/1. The initial slope of a plot of the relative emission intensity (I/I_0) vs the H^+/complex concentration ratio is -0.7 ± 0.1.

With the $[(bpy)_2Os(tpphz)]^{2+}$ complex the variations observed upon addition of $HClO_4$ were very similar to those of the corresponding Ru complex. The only difference was that no residual emission was detectable after the complete quenching of the original one.

Addition of $HClO_4$ to a CH_3CN solution of $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$ has no effect on the emission of the complex at least up to an acid/complex concentration ratio of 100/1.

Excited-State Absorption Spectra. Laser flash photolysis experiments were performed in CH_3CN solutions, at room temperature, of $[(bpy)_2Ru(tpphz)]^{2+}$, $[(bpy)_2Ru(tpphz)(bpy)_2]^{4+}$, and $HClO_4/[(bpy)_2Ru(tpphz)]^{2+}$ (concentration ratio 2.5/1). Transient absorption spectra are reported in Figure 7. All of the transient spectra exhibit bleaching of the ground state at ca. 450 nm. Those of $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$ and $HClO_4/[(bpy)_2Ru(tpphz)]^{2+}$ exhibit an additional transient absorption at ca. 575 nm. All of the transients decay with the same kinetics and lifetimes as observed for the corresponding emissions.

Because of the very short lifetimes of the Os-containing complexes, no reliable transient absorption spectra were recorded for these complexes.

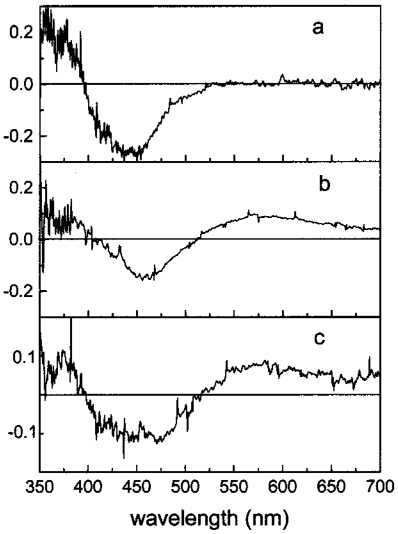

Figure 7. Transient absorption spectra of $[(bpy)_2Ru(tpphz)]^{2+}$ (a), $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$ (b), and $HClO_4/[(bpy)_2Ru(tpphz)]^{2+}$ (concentration ratio 2.5/1) (c). CH_3CN solutions. Spectra recorded 5 ns after laser pulse. Excitation wavelength = 355 nm.

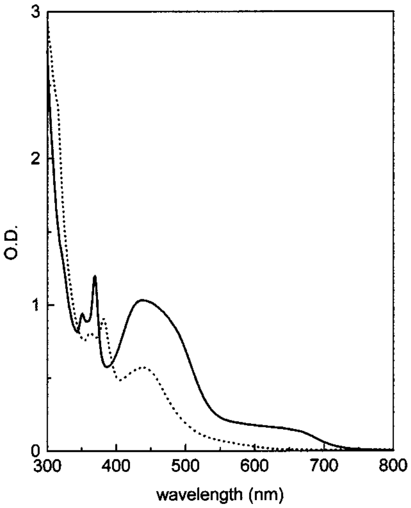

Figure 8. Absorption spectra of a 1.3×10^{-5} M solution of $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$ in 50% CH_3CN/water before (—) and after (···) the addition of a stoichiometric amount of Ce(IV).

Mixed Valence Compound. The generation of a mixed-valence compound was possible only for the heterodinuclear complex $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$. Addition of Ce(IV) solution (see Experimental Section) to a 1.3×10^{-5} M CH_3CN/water solution of $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$ causes strong variations in the absorption spectrum of the complex (Figure 8), consistent with the oxidation of the osmium center. No intervalence transfer transitions of appreciable intensity ($\epsilon \leq 500$ M^{-1} cm^{-1}) were observable in the visible and near IR region. No detectable emission from the mixed-valence species

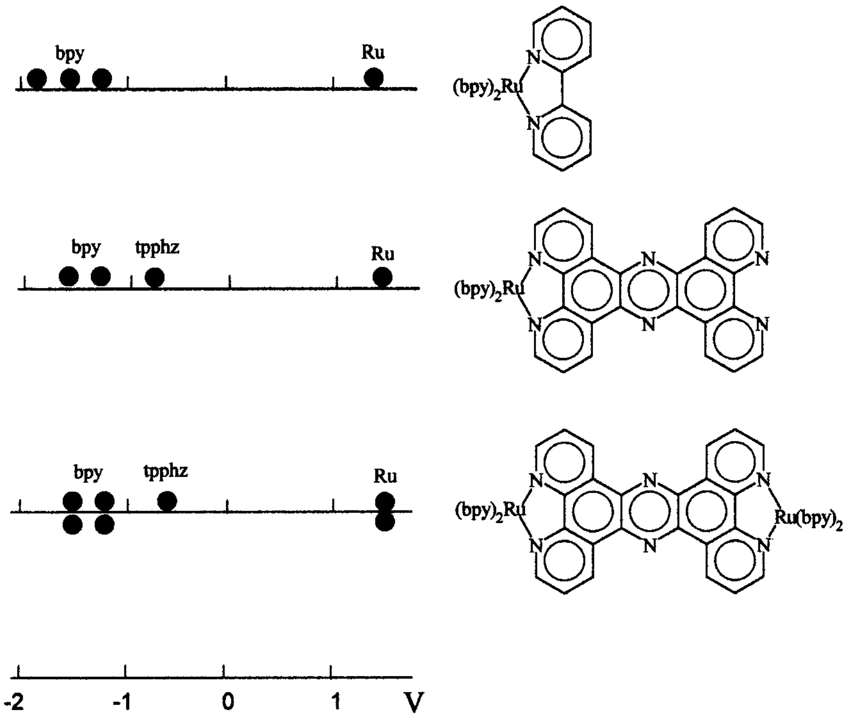

Figure 9. Schematic comparison of the redox potentials for the mononuclear and binuclear ruthenium complexes.

could be observed ($\Phi_{em} \leq 1 \times 10^{-5}$) in the 500−850 nm spectral region.

Discussion

Mononuclear Complexes. The absorption spectra were discussed in some detail in a previous paper.[64] They consist of three distinct spectral regions: (i) the visible region, where intense absorption is attributed to metal-to-ligand charge transfer (MLCT) transitions from the d orbitals of the metal to the π^* orbitals of the bpy and tpphz ligands; (ii) the UV region, below 340 nm, dominated by the $\pi \rightarrow \pi^*$ ligand-centered (LC) transitions of the bpy and tpphz ligands; (iii) two sharp bands between 340 and 380 nm, corresponding to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ LC tpphz transitions. All of these bands correspond to spin-allowed (singlet−singlet) transitions, except for the osmium complex (Figure 2b), where the tail at $\lambda > 550$ nm corresponds to formally spin forbidden (singlet−triplet) MLCT transitions. The MLCT bands of the osmium complexes are red-shifted with respect to those of the corresponding ruthenium complexes, reflecting the different ease of oxidation[64] of the two metal centers. An important question concerns the type of ligand (bpy vs tpphz) involved in the lowest MLCT excited state.

In principle, information on this problem could be obtained from the electrochemical data, reported in a previous paper[64] and summarized, for the Ru-containing species, in Figure 9. On the basis of the large positive shift (0.47 V) of the first reduction potential of $[(bpy)_2Ru(tpphz)]^{2+}$ relative to $[Ru(bpy)_3]^{2+}$, it seems likely that the lowest MLCT state in $[(bpy)_2Ru(tpphz)]^{2+}$ is of the Ru → tpphz type. It should be noticed, however, that MLCT excited-state energies are related to orbital energy (and redox potential) differences via various electronic interaction terms, including electrostatic attraction between the promoted electron on the ligand and the positive hole on the metal.[70] Given the different electron−hole distances involved,[71] these Coulombic terms could provide partial compensation for the redox asymmetry between the ligands of $[(bpy)_2Ru(tpphz)]^{2+}$. Thus, the electrochemical results provide a hint in favor of the tpphz localization, but cannot be considered as conclusive.

Absorption spectra are not very informative in this respect, due to the large bandwidth and strongly overlapping situation of the various MLCT transitions. Some information can nevertheless be obtained from the clean changes undergone by such spectra upon addition of perchloric acid in CH_3CN (Figure 3). The changes in the visible region clearly demonstrate the composite nature of the MLCT band system and provide a basis for its resolution into bpy-based and tpphz-based transitions. Using $[(bpy)_2Ru(tpphz)]^{2+}$ as an example, the intense absorption in the 410−440 nm region, which hardly undergoes any change upon acid addition, must correspond to MLCT transitions involving the (nonprotonatable) bpy ligands. The observed bleaching in the 440−482 nm region and increased absorption in the 482−550 nm region very likely reflect the red shift (from 465 to 500 nm, as inferred from difference spectra) of a MLCT transition involving the protonatable tpphz ligand. The concentration dependence of the spectral variations (see Results) suggests a single protonation process taking place in the $HClO_4$ concentration range investigated. Among the two types of available sites, pyrazine-like and bpy-like nitrogens, the latter are expected to be stronger Brönsted bases. The fact that the spectral changes are very similar to those obtained upon metalation (see below) confirms the involvement of the free bpy-like end of the tpphz ligand in the protonation process.[72]

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(71) Extended Huckel MO calculations[64] indicate that, in the free tpphz ligand, the LUMO is largely localized on the pyrazine-like central portion of the ligand. Another π^* orbital, mainly localized on the bpy-like portions of the ligand, lies higher in energy by 0.638 eV. In the complex, some mixing between these orbitals cannot be excluded. Moreover, the interaction with the oxidized metal in the MLCT excited state could bring the energies of these two orbitals substantially closer than in the free ligand.

In heteroleptic complexes of this type, MLCT emission is expected to come uniquely from the lowest excited state, and thus to be free from the overlap problems that complicate MLCT absorption spectra. In practice, the interpretation of the emission results is complicated by solvent dependence. In solvents of medium polarity, such as, e.g., CH_3CN, the emissions of $[(bpy)_2Ru(tpphz)]^{2+}$ and $[(bpy)_2Os(tpphz)]^{2+}$ are similar in energy, lifetime, and quantum yield (Table 1) to those of the corresponding tris bpy complexes.[73−75] This indicates that in these solvents the emitting state is either a M → bpy MLCT state, or a M → tpphz state lying at very similar energy. In high-polarity solvents such as DMSO and H_2O, however, the emission of $[(bpy)_2Ru(tpphz)]^{2+}$ undergoes a strong red shift (Table 2), indicating substantial stabilization of the polar MLCT state. This shift is much larger for $[(bpy)_2Ru(tpphz)]^{2+}$ than for $[Ru(bpy)_3]^{2+}$,[76] consistent with a more pronounced charge separation in the MLCT state of the tpphz complex and supporting the assignment of the lowest excited state as a M → tpphz state. A substantial red shift, parallel to what observed in absorption, is also observed in emission upon protonation of the $[(bpy)_2Ru(tpphz)]^{2+}$ complex (Figure 6). The shift is accompanied by a strong reduction in intensity, as expected on the basis of general trends in lifetime with emission energy (see below). Overall, the emission measurements provide strong indication that the lowest, emitting excited state of the mononuclear complexes involves the tpphz ligand.

The lifetimes of the mononuclear complexes are, as usual, longer for the ruthenium than for the osmium complex (Table 1). Within each complex, they change as a function of solvent in a relatively complex way (Table 2). This is not unexpected, as the solvent may simultaneously change many parameters relevant to excited-state deactivation (ground-state to MLCT energy gap, activation energy for deactivation mediated by metal-centered states, degree of MLCT excited-state distortion, coupling to specific solvent vibrations).[77,78] Albeit with some exceptions, a general trend of decreasing lifetimes with decreasing emission energy is discernible. The energy-gap law for radiationless transitions[74,75] is certainly one of the factors contributing to this trend.

At 77 K, the emission shows the usual blue shift relative to room temperature (Table 1), consistent with the charge transfer nature of the transition and the blocking of solvent repolarization in the rigid glass.

Homodinuclear Complexes. A comparison between the absorption spectra of the mono- and homo dinuclear complexes (Figure 2a,b) shows that the various MLCT and LC bands retain their identity and scale up in intensity with the number of metal centers and ligands. This rules out extensive delocalization in the dinuclear complexes, which can thus be described as true, weakly interacting, supramolecular systems.

The electrochemical results (Figure 9) indicate that the lowest tpphz π^* orbital undergoes substantial stabilization (ca. 0.15 eV in all cases) upon conversion of mononuclear to dinuclear species. This shift can be viewed as a result of the electron-withdrawing effect of the second metal and/or of increased π-delocalization in the system and is in line with previous experience with other conjugated bridging polypyridine ligands.[20,43,79] As the oxidation potential of the metal remains appreciably constant (Figure 9), this is expected to result in a red shift of the Ru → tpphz MLCT transitions in going from mono- to dinuclear complexes. Given the above-discussed problems of bandwidth and overlapping, this shift is not apparent from the absorption spectra in the MLCT region (Figure 2a,b). The effect is clearly seen, on the other hand, in room-temperature emission (Table 1, Figure 4), where the spectrum of $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$ is red-shifted as expected (by about 0.18 eV) relative to that of $[(bpy)_2Ru(tpphz)]^{2+}$. The difference between mono- and dinuclear emissions is almost absent in rigid matrixes at 77 K where, however, all of the spectra are strongly blue shifted, due to the absence of solvent relaxation.

The shorter lifetime, at room temperature and in the same solvent, of the dinuclear relative to mononuclear complexes (Table 1) can be easily explained on the basis of the red shift, given the energy-gap dependence of radiationless deactivation.[74,75] For the $[(bpy)_2Os(tpphz)Os(bpy)_2]^{4+}$, given the already short lifetime of the mononuclear species and the expected red shift, the lifetime is probably so short as to prevent the observation of any emission in CH_3CN. In the comparison between $[(bpy)_2Ru(tpphz)]^{2+}$ and $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$, the observed decrease in quantum yield (ca. 1/100) is an order of magnitude greater than the factor (ca. 1/10) expected on the basis of the lifetime shortening, implying a substantial decrease in radiative rate constant for MLCT emission upon addition of the second metal.[80] This could be ascribed to the electron-withdrawing effect of the second metal center, leading to an increase of charge separation distance and a consequent decrease in electronic coupling in the MLCT state. In this context, it should be noticed that a strong solvatochromism is observed for the emission of the dinuclear complexes (Table 2). It is of the same type as, but of larger magnitude than, that observed for the mononuclear complexes, again suggesting an increase in charge separation distance upon addition of the second metal moiety. In this regard, it is interesting to notice the difference in the transient absorption spectra, i.e., in the spectra of the lowest MLCT states, of the dinuclear and mononuclear Ru complexes (Figure 7). The binuclear complex has a more pronounced absorption in the red spectral region, indicative of a more delocalized ligand radical anion. A very similar transient absorption is obtained for the mononuclear complex under acidic conditions (Figure 7), again stressing the very similar effects of metalation and protonation on MLCT properties of $[(bpy)_2Ru(tpphz)]^{2+}$.

As for the mononuclear complexes, also for the dinuclear systems the lifetime generally decreases with decreasing emission energy, in qualitative correlation with the energy-gap law. It should be pointed out that only in CH_2Cl_2, the lifetime of $[(bpy)_2Os(tpphz)Os(bpy)_2]^{4+}$ is long enough to allow the observation of room-temperature emission (Table 2).

No consequence of the addition of $HClO_4$ is observed with the dinuclear complexes, in agreement with the above conclusion that the protonation of the mononuclear species involved the bpy-like rather than the pyrazine-like nitrogens.

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(72) Further proof of this conclusion comes from the lack of any effect, in this acid concentration range, for the $[Ru(bpy)_2(dppz)]^{2+}$ (dppz = dipyridophenazine) complex, where pyrazine-like nitrogens, but not bpy-like ones, are available (C. Chiorboli, unpublished results).

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(80) This effect is analogous to the observation of a small oscillator strength for the red-shifted Ru → tpphz MLCT transition in the protonated form of the $[Ru(bpy)_2(tpphz)]^{2+}$ complex (Figure 3).

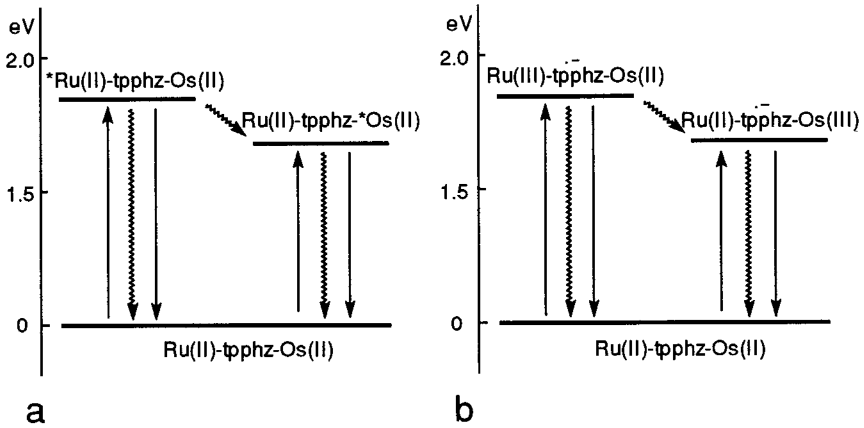

Figure 10. Two alternative representations of the interconversion between the lowest excited states of the $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$ complex: (a) as a conventional intramolecular energy transfer; (b) considering the electronic distribution of the MLCT states, as an osmium-to-ruthenium electron transfer.

Heterodinuclear Complex. In $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$, the absorption spectrum is an exact average of those of the two homodinuclear analogues (Figure 2c), supporting the view of the heterodinuclear complex as a supramolecular system. In such a system, distinct Ru-based and Os-based MLCT states can be considered, with energies that can be deduced from the emission of the corresponding homodinuclear complexes (Table 1). The Ru-based MLCT state is higher than the Os-based one, both in room-temperature CH_2Cl_2 (by ca. 0.38 eV) and in low-temperature alcohol glasses (by 0.25 eV) (Tables 1 and 2). Therefore, as in many other Ru(II)−Os(II) dinuclear systems investigated,[63] conversion from the Ru-based MLCT state to the Os-based MLCT state is thermodynamically possible (Figure 10a). The experimental results, i.e., complete quenching of the Ru → tpphz MLCT emission and sensitization of the Os → tpphz MLCT emission, clearly demonstrate the occurrence of this process. From the experimental results, the efficiency is ≥ 0.99 and the rate constant is $\geq 10^9$ s^{-1}. These figures are in line with the behavior of other Ru(II)−Os(II) complexes with unsaturated bridging ligands that favor Dexter-type energy transfer processes.[63]

A word of caution should be said about the description of this process as *energy* transfer. In the Dexter mechanism, energy transfer can be viewed as a simultaneous electron transfer from the LUMO of the donor to that of the acceptor and from the HOMO of the acceptor to that of the donor. In a dinuclear complex of the type discussed here, both units have a well-defined metal-localized HOMO. The LUMO, on the other hand, seems to be localized on the bridging tpphz ligand, which is common to both units. Thus, the definition of the process as energy transfer could not be completely accurate. In fact, to the extent to which the excited electron remains in a common tpphz-localized LUMO (Figure 10b), the process could be also (perhaps better) viewed as a metal-to-metal, Os → Ru *electron* transfer (or Ru → Os "hole" transfer).

Electron transfer is certainly involved in the photophysical behavior of the oxidized complex $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{5+}$. This complex, as clearly indicated by the disappearance of the Os-based MLCT transitions in the absorption spectrum (Figure 8), is a Ru(II)−Os(III) mixed-valence species.[81] In this complex the Ru-based MLCT emission is completely quenched relative to, e.g., $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$, and this is most probably due to the intramolecular electron transfer process shown in Figure 11. An experimental lower limit for the rate constant of this process can be estimated as ca. 10^9 s^{-1}. The process is probably very fast, consistent with the notion that it is highly exergonic and it involves electron transfer between close sites, i.e., from the tpphz bridging ligand to the Os(III) center (Figure 11). The same type of electron transfer process is involved in the radiationless deactivation of the lowest MLCT state of $[(bpy)_2Os(tpphz)Os(bpy)_2]^{4+}$, which is actually known (Table 1) to be very short-lived. The product of the quenching process is the Ru(III)−Os(II) intervalence transfer state, expected to decay to the ground state by an Os → Ru back electron transfer process of relatively small driving force. As commonly found for Ru(II)−Os(III) complexes involving unsaturated bridging ligands,[63] this process is too fast ($k \geq 2 \times 10^8$ s^{-1}) to be monitored by nanosecond laser spectroscopy. Overall, the results on the $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{5+}$ complex indicate that the tpphz bridge is highly efficient in promoting intercomponent excited-state electron transfer processes as well.

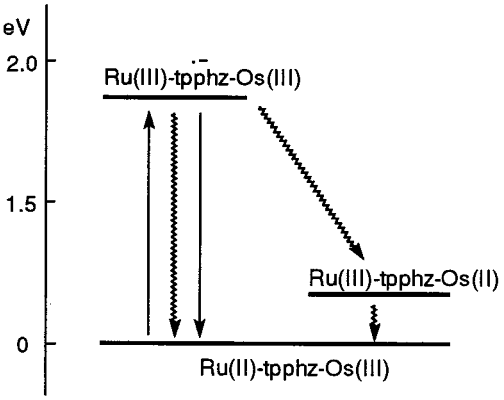

Figure 11. Schematic representation of the quenching pathway for the mixed-valence $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{5+}$ complex.

Conclusion

Being a planar, fully aromatic bridging ligand, tpphz has interesting structural features for the design of covalently linked donor−acceptor systems.[64−68] In this work, its electronic properties have been particularly investigated. In mononuclear $[M(bpy)_2(tpphz)]^{2+}$ complexes, the medium dependence of the emission supports the assignment of the lowest energy MLCT excited state as a M → tpphz state. The energies, lifetimes, and

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[81] Attempts to detect the presence of intervalence transitions (expected λ_{max}, 600−700 nm) were unsuccessful. In practice, the absorption spectrum of $[(bpy)_2Ru(tpphz)Os(bpy)_2]^{5+}$ and that of $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$ (intensity divided by a factor of 2) were not significantly different. In these experiments, we estimate $\epsilon \leq 500$ M^{-1} cm^{-1}.

emission quantum yields of these MLCT excited states are highly sensitive to donor−acceptor interactions at the free bpy-like end of the tpphz ligand. This can be relevant to the use of these complexes as luminescent probes. In the $[(bpy)_2M_1(tpphz)M_2(bpy)_2]^{4+,5+}$ dinuclear complexes, the electrochemical, spectroscopic, and photophysical results show that the electronic ground states can be adequately considered as valence-localized, supramolecular systems. Looking at the properties of the MLCT excited states, on the other hand, tpphz proves to behave as a "connector" providing relatively strong intercomponent electronic coupling. In particular, in heterodinuclear Ru(II)−Os(II) and Ru(II)−Os(III) complexes, the tpphz ligand is found to mediate efficiently the occurrence of fast intercomponent energy and/or electron transfer processes. This difference in behavior between ground and excited states is a consequence of the direct involvement of the tpphz bridge in the lowest MLCT excited state.

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