

New luminescent and redox-active mono- and polynuclear ruthenium(II) and osmium(II) polypyridine complexes

Anna Börje,[†] Oliver Köthe,[‡] and Alberto Juris^{*}

Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, I-40126 Bologna, Italy. E-mail: juris@ciam.unibo.it

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A series of mono and polynuclear Ru(II) and Os(II) polypyridine complexes based on the bpy–O–bpy ligand {bpy–O–bpy = bis[4-(2,2'-bipyridinyl)]ether} has been prepared. The redox, absorption and luminescence properties of these species have been measured and compared with those of the [Ru(bpy)₃]²⁺ and [Os(bpy)₃]²⁺ parent compounds. Electrochemical oxidation involves the metal centers, and occurs reversibly in acetonitrile at room temperature at about +1.30 and +0.85 V vs. SCE, respectively, for the Ru- and Os-based units. Reduction is ligand-centered and features a first irreversible wave followed by several reversible processes. Absorption spectra are essentially the sum of the spectra of the component monometallic species. Luminescence emission is observed both in acetonitrile solution (298 K) and in frozen matrix (77 K), originating from ³MLCT states. Homometallic complexes display luminescence properties which are close to that featured by the parent [M(bpy)₃]²⁺ species. In heterometallic species luminescence is observed only from the Os-based unit, indicating that efficient energy transfer takes place from the Ru-based to the Os-based moiety. The results indicate that the electronic communication through the bpy–O–bpy bridging ligand is so small that it doesn't substantially modify the properties of the metal units, which are those of the corresponding isolated [M(bpy)₃]²⁺ units, but large enough to allow efficient energy transfer through the bridge. The bpy–O–bpy bridging ligand appears thus a promising component for the synthesis of multimetallic antenna systems.

Introduction

Much attention is presently devoted to the synthesis and characterization of luminescent and redox-active polynuclear metal complexes.^{1–5} The interest in these species is mainly related to the possibility to construct molecular-level devices,^{6–10} due to the presence of chemically different units imparting to the resulting supramolecular structure specific properties such as the capability to absorb or emit visible light and to reversibly exchange electrons. Particularly appealing are the photochemical molecular devices, which can use light energy for solar energy conversion^{10–13} and information storage purposes.^{9,10,14}

In the past few years we synthesized and studied a series of polynuclear Ru(II) and Os(II) polypyridine complexes containing up to 22 metal centers.^{11,15–18} Proper design of the polynuclear species also gave rise to compounds behaving as light harvesting antenna systems.^{11,19} In all these supramolecular structures the various metal subunits were connected using the 2,3- and 2,5-dpp {dpp = bis(2-pyridyl)pyrazine} bridging ligands (Fig. 1). An unlucky feature of the dpp bridging ligands lies in their very compact and rigid structure. This results in difficulties in preparing large multimetallic systems due to steric congestion problems. Moreover, due to the electronic properties of the dpp bridging ligands, the luminescence intensity and lifetime of these polynuclear species is much lower than those exhibited by the well-known mononuclear [Ru(bpy)₃]²⁺ and [Os(bpy)₃]²⁺ prototype compounds.^{20,21}

In an attempt to overcome these difficulties, we designed²² the new bridging ligand bpy–O–bpy {bpy–O–bpy = bis[4-(2,2'-bipyridinyl)]ether} (Fig. 1), which features a larger, more flexible structure, where the two coordinated metals are further

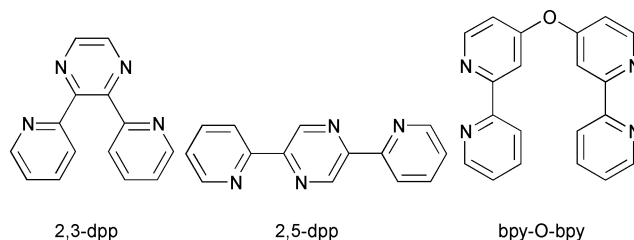


Fig. 1 Structure of the dpp and bpy–O–bpy bridging ligands.

apart and are expected to behave independently. The synthesis of the bpy–O–bpy bridging ligand was achieved by adapting to a monosubstituted bipyridine a reaction scheme first proposed by Constable *et al.* for terpyridine-like ligands.²³ Details on the synthesis of the bpy–O–bpy ligand and preliminary room temperature photophysical characterization of a few complexes were reported in a previous communication.²²

We report here on the synthesis, electrochemical properties, and photophysical characterization of a series of mono and polynuclear Ru(II) and Os(II) polypyridine complexes containing the bpy–O–bpy ligand. It is concluded that ligand bpy–O–bpy (i) allows the construction of polynuclear Ru(II) and Os(II) complexes retaining the luminescence properties of the [Ru(bpy)₃]²⁺ and [Os(bpy)₃]²⁺ model compounds; and (ii) is a good candidate for the construction of light harvesting antenna systems.

Results and discussion

Synthesis

The reaction sequence used to obtain polynuclear species is illustrated in Fig. 2, where the synthesis of [Os{(μ -bpy–O–bpy)Ru(bpy)₂]₃]⁸⁺ is exemplified. Two different strategies are applied in proper sequence to assemble the various units in

[†] Present address: Medicinal Chemistry, Göteborg University, SE-412 96 Göteborg, Sweden.

[‡] Present address: Fraunhofer Institute for Reliability and Mikrointegration, Hansastrasse 27D, D-80686 München, Germany

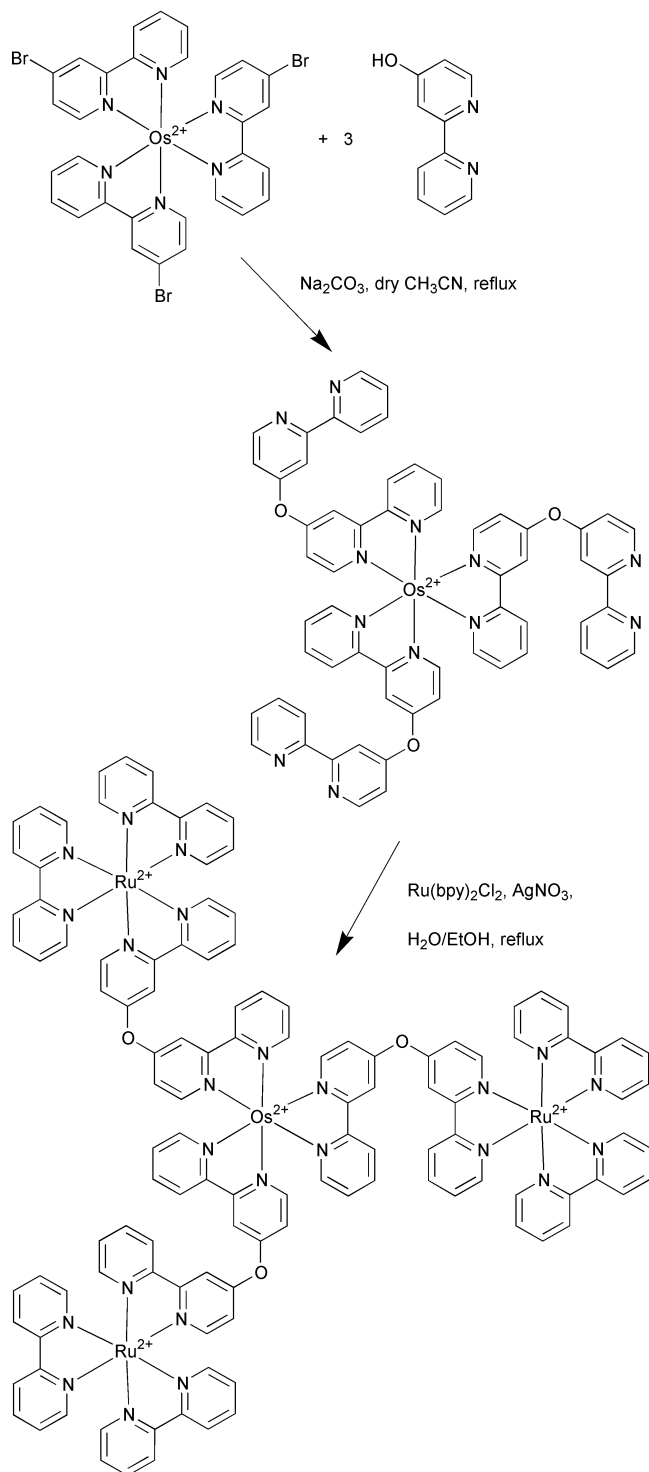


Fig. 2 Scheme illustrating the *in situ* synthesis of the bpy–O–bpy bridging ligand, and subsequent formation of the $[\text{Os}\{\mu\text{-bpy-O-bpy}\}\text{Ru}(\text{bpy})_2\}_3]^{8+}$ species.

the desired position. In the first step, the *in situ* synthesis of the bpy–O–bpy bridging ligand is obtained by exploiting the enhanced reactivity of the coordinated bpy–Br ligand.²³ In the second step, the “complexes-as-metals and complexes-as-ligands” strategy¹⁸ is used to connect the complex metal $\text{Ru}(\text{bpy})_2\text{Cl}_2$ to the trifunctional complex ligand $[\text{Os}(\text{bpy-O-bpy})_3]^{2+}$. Starting from the appropriate $[\text{M}(\text{bpy})_2(\text{bpy-Br})]^{2+}$ or $[\text{M}(\text{bpy-Br})_3]^{2+}$ species it is possible to obtain all the polynuclear complexes listed in Tables 1 and 2.

The preparation of polynuclear complexes necessarily leads to mixtures of several diastereoisomeric species, as each octahedral metal is a stereogenic center. Moreover, in tetranuclear species *fac* or *mer* isomers are possible for the central

unit, due to the inequivalence of the chelating nitrogens of the bridging ligand. However, differences arising from the presence of isomeric species are not expected to be significant as far as electrochemical and photophysical properties are concerned.²⁴

General properties

All the complexes dealt with in this paper are soluble in acetone, acetonitrile, and dichloromethane, and are stable as evidenced by the constancy of the absorption and emission spectra for at least two days. In the methanol–ethanol solvent, on the contrary, the polynuclear compounds undergo fragmentation. For this reason, the 77 K photophysical measurements were taken on freshly prepared solution, which were frozen as quickly as possible.

It is now well established that for Ru(II) and Os(II) complexes of aromatic N-heterocycles the ground state, the redox forms, and the low energy excited states can be described in a sufficiently approximate way by localized molecular orbital configurations.^{25–27} With such an assumption, the oxidation and reduction processes can be considered as metal- and ligand-centered, respectively, and the various electronic transitions are classified as metal-centered (MC), ligand-centered (LC), and charge transfer (CT: either metal-to-ligand, MLCT, or ligand-to-metal, LMCT). Most often, these complexes exhibit very intense LC absorption bands in the UV region and intense MLCT bands in the visible. Regardless of the excitation wavelength, the originally populated excited states undergo fast radiationless decay^{28–30} to the lowest triplet ³MLCT, which is luminescent both in rigid matrix at 77 K and in fluid solution at room temperature. Usually, the emitting level of Os-based complexes is at lower energy than that of the corresponding Ru-based species, mainly due to differences in the potential needed for metal oxidation.

Redox behavior

The results obtained from electrochemical experiments are collected in Table 1, where data concerning the free ligands, $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$ are also listed for comparison purposes.

Investigation of the redox behavior of Ru(II) and Os(II) polypyridine complexes can be very useful because the HOMO and LUMO levels concerned in the redox processes are also involved in the lowest energy excited state. Previous investigations carried out on related mono- and polynuclear compounds^{2,4,20} have shown that: (i) oxidation is metal-centered; (ii) Os(II) is oxidized at potentials considerably less positive than Ru(II); (iii) reduction is ligand-centered. Moreover, in the case of polynuclear complexes, precious information on the interaction between equivalent redox centers can be obtained. Usually, (iv) the interaction between metal centers coordinated to the same bridging ligand is a function of the electronic communication ability of the bridging ligand; (v) the interaction between equivalent ligands is noticeable for ligands coordinated to the same metal, whereas it is negligible for ligands that are further apart.

Oxidation processes

The ligands bpy and bpy–Br are electroinactive up to +2.0 V in oxidation. In the same potential window the homometallic complexes feature a single reversible oxidation process, while two reversible processes are observed in heterometallic compounds, as illustrated in Fig. 3 for the $[(\text{bpy})_2\text{Ru}(\mu\text{-bpy-O-bpy})\text{Os}(\text{bpy})_2]^{4+}$ species. By comparison with the model complexes $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$, the processes occurring around +1.3 V can be readily assigned to the Ru(II) → Ru(III) oxidation, whereas those occurring around +0.8 V are assigned to the Os(II) → Os(III) process.

In the $[\text{M}(\text{bpy})_2(\text{bpy-Br})]^{2+}$ complexes oxidation of the metal occurs at a potential value slightly more positive than in the

Table 1 Electrochemical results in argon-purged acetonitrile solution at room temperature^a

Compound	$E_{\text{ox}}, [n]^b$ (site) ^c	E_{red}
bpy ^d	—	-2.09; -2.69
bpy-Br	—	-1.76 irr; -2.14 irr
[Ru(bpy) ₃](PF ₆) ₂ ^e	+1.29 [1] (Ru)	-1.33; -1.52; -1.78
[Ru(bpy) ₂ (bpy-Br)](PF ₆) ₂	+1.31 [1] (Ru)	-1.17 irr; -1.35; -1.52; -1.77
[(bpy) ₂ Ru(μ-bpy-O-bpy)Ru(bpy) ₂](PF ₆) ₄	+1.29 [1] (Ru)	-0.91 irr; -1.37; -1.62; -1.77
[Ru{(μ-bpy-O-bpy)Ru(bpy) ₂ }] ₃ (PF ₆) ₈	+1.28 [4] (Ru)	-0.84 irr; -1.44; -1.68
[Os(bpy) ₃](PF ₆) ₂ ^f	+0.85 [1] (Os)	-1.26; -1.48; -1.79
[Os(bpy) ₂ (bpy-Br)](PF ₆) ₂	+0.88 [1] (Os)	-0.87 irr; -1.28; -1.45; -1.67; -1.77
[(bpy) ₂ Ru(μ-bpy-O-bpy)Os(bpy) ₂](PF ₆) ₄	+0.85 [1] (Os); +1.30 [1] (Ru)	-0.87 irr; -1.41; -1.67; -1.82
[Os{(μ-bpy-O-bpy)Ru(bpy) ₂ }] ₃ (PF ₆) ₈	+0.85 [1] (Os); +1.31 [3.5] (Ru)	-0.82 irr; -1.35; -1.47; -1.69

^a Potentials in V vs. SCE; the waves are reversible; for irreversible reductions (irr), the potential is evaluated from the DPV peaks. ^b Number of exchanged electrons. ^c Site involved in the redox process. ^d Data in DMF at -54 °C, ref. 31. ^e In agreement with literature data, refs. 20, 21. ^f In agreement with ref. 32.

Table 2 Photophysical properties in acetonitrile solution, unless otherwise noted

Compound	Absorption $\lambda_{\text{max}}/\text{nm}^a$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)	Luminescence				
		298 K ^b			77 K ^d	
		λ/nm^c	τ/ns	Φ_{em}	λ/nm^c	$\tau/\mu\text{s}$
[Ru(bpy) ₃](PF ₆) ₂ ^e	450 (13000)	615	870	0.061	584	4.76
[Ru(bpy) ₂ (bpy-Br)](PF ₆) ₂	452 (13900)	634	920	0.058	593	4.02
[Ru(bpy-Br) ₃](PF ₆) ₂	458 (13900)	618	890	0.058	595	3.84
[Ru(bpy) ₂ (bpy-O-bpy)](PF ₆) ₂	454 (10300)	618	850	0.052	591	4.18
[Ru(bpy-O-bpy) ₃](PF ₆) ₂	458 (13300)	635	480	0.028	599	3.16
[(bpy) ₂ Ru(μ-bpy-O-bpy)Ru(bpy) ₂](PF ₆) ₄	455 (25800)	630	670	0.046	592	4.02
[Ru{(μ-bpy-O-bpy)Ru(bpy) ₂ }] ₃ (PF ₆) ₈	456 (51500)	638	310	0.050	599	3.34
[Os(bpy) ₃](PF ₆) ₂ ^e	579 (1860) 480 (8700)	742	60	0.005	709	0.79
[Os(bpy) ₂ (bpy-Br)](PF ₆) ₂	630 (3400) 483 (13600)	762	22	0.005	714	0.71
[Os(bpy-Br) ₃](PF ₆) ₂	628 (2400) 487 (9500)	746	36	0.002	733	0.65
[Os(bpy) ₂ (bpy-O-bpy)](PF ₆) ₂	615 (3000) 480 (11100)	740	31	9×10^{-4}	717	0.68
[Os(bpy-O-bpy) ₃](PF ₆) ₂	620 (3500) 490 (12800)	763	22	0.008	733	0.32
[(bpy) ₂ Ru(μ-bpy-O-bpy)Os(bpy) ₂](PF ₆) ₄	573 (2700) 455 (20800)	753	23	0.002	713	0.60
[Os{(μ-bpy-O-bpy)Ru(bpy) ₂ }] ₃ (PF ₆) ₈	638 (2800) 455 (45000)	760	19	4×10^{-4}	730	0.43

^a Lowest energy absorption feature(s). ^b Deaerated solutions. ^c Uncorrected for detector response. ^d In MeOH-EtOH 4 : 1 v/v. ^e In agreement with literature data, refs. 20, 21.

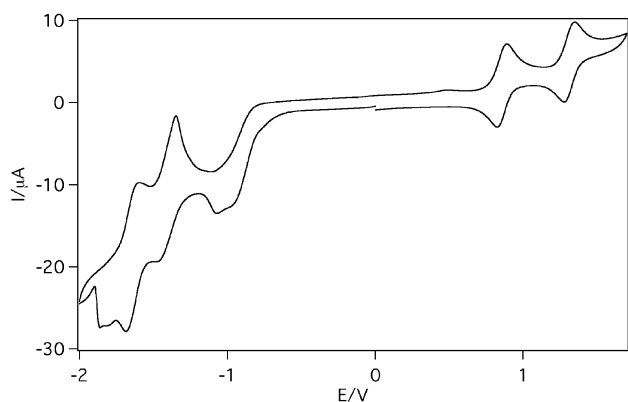


Fig. 3 Cyclic voltammogram of 5×10^{-4} M [(bpy)₂Ru(μ-bpy-O-bpy)Os(bpy)₂]⁴⁺ in argon-purged acetonitrile solution. Scan speed 100 mV s⁻¹, 5×10^{-2} M TEAPF₆ supporting electrolyte, glassy carbon working electrode.

parent [M(bpy)₃]²⁺ species. This difference can be ascribed to the electron-withdrawing properties of the bromo substituent.

Passing to polynuclear species, in both [(bpy)₂Ru(μ-bpy-O-bpy)Os(bpy)₂]⁴⁺ and [Os{(μ-bpy-O-bpy)Ru(bpy)₂}]₃⁸⁺ two processes are observed, which can be readily assigned to the Os metal unit (+0.85 V) and to the Ru metal unit(s) (≈1.3 V). In the presence of equivalent units, as the three peripheral Ru units in the tetranuclear species, multielectronic waves are observed. The number of electrons exchanged in the different processes was evaluated from DPV scans, exploiting the

simultaneous presence of Ru and Os units as internal reference. The values obtained are included in Table 1, and correspond (within experimental errors) with the stoichiometry of these heterometallic complexes. Thus in the tetranuclear species each of the present Ru units undergoes simultaneous and independent one-electron oxidation.

The homometallic species [(bpy)₂Ru(μ-bpy-O-bpy)Ru(bpy)₂]⁴⁺ and [Ru{(μ-bpy-O-bpy)Ru(bpy)₂}]₃⁸⁺ feature a single oxidation process, indicating again simultaneous one-electron oxidation of each of the Ru units present.

It can be concluded that in the presence of the bpy-O-bpy ligand the connected metal units behave as isolated [M(bpy)₃]²⁺ species. In polynuclear complexes the electronic interaction between the connected metal units is negligible from the electrochemical viewpoint, so that each metal unit is oxidized independently. As a consequence, in the presence of several equivalent metal units, polyelectronic processes are observed.

Reduction processes

The reduction processes of the free bpy ligand are known to occur reversibly,³¹ while the bpy-Br ligand features two irreversible processes at potential values less negative than bpy (Table 1). Upon coordination to the Ru(II) and Os(II) metal ions it is expected that these reduction processes are displaced to less negative values.

Because of the presence of several polypyridine ligands, each capable of undergoing several reduction processes, the electrochemical reduction of the complexes is much more complicated

than their oxidation, so that a detailed discussion is difficult. All of the new complexes feature a first irreversible wave followed by a series of reversible processes. In the mononuclear $[M(\text{bpy})_2(\text{bpy}-\text{Br})]^{2+}$ species the irreversible process is attributed to the presence of the $\text{bpy}-\text{Br}$ ligand, while the reversible processes present at more negative potential are assigned to the bpy ligands by comparison with the $[M(\text{bpy})_3]^{2+}$ species. Analogously, in the polynuclear species the first irreversible process, attributed to the $\text{bpy}-\text{O}-\text{bpy}$ bridging ligand, is followed by a series of reversible processes due to bpy units.

Absorption spectra

UV-VIS absorption data are collected in Table 2; spectra of selected compounds are shown in Fig. 4. The absorption spectra

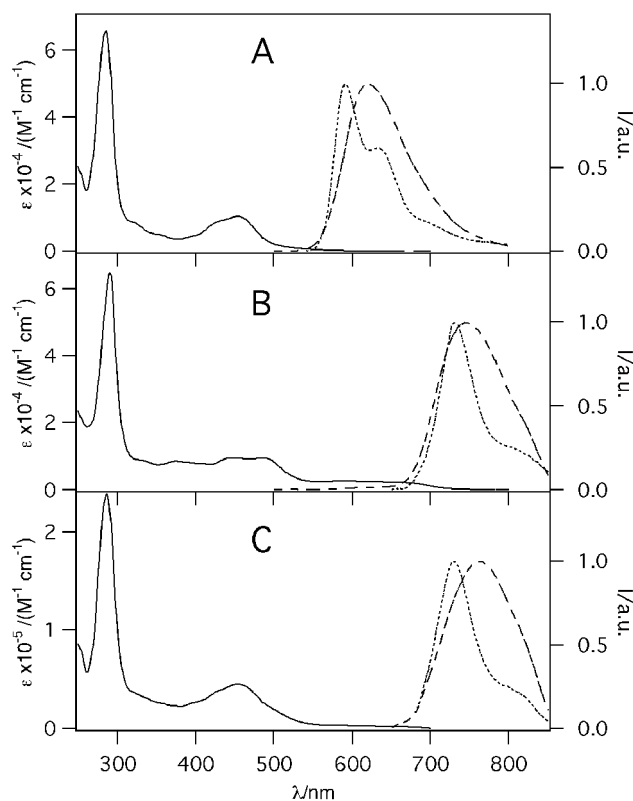


Fig. 4 Absorption spectrum (solid line) and uncorrected luminescence spectra at room temperature (dashed line) and at 77 K (dotted line) for $[\text{Ru}(\text{bpy})_2(\text{bpy}-\text{O}-\text{bpy})]^{2+}$ (A), $[\text{Os}(\text{bpy}-\text{O}-\text{bpy})_3]^{2+}$ (B), and $[\text{Os}\{(\mu-\text{bpy}-\text{O}-\text{bpy})\text{Ru}(\text{bpy})_2\}_3]^{8+}$ (C). Solvents are acetonitrile at room temperature and 4 : 1 v/v methanol-ethanol at 77 K.

of all these compounds are essentially similar to that of other $\text{Ru}(\text{II})$ - and $\text{Os}(\text{II})$ -based polypyridine complexes and can be accordingly interpreted. The high-intensity absorption bands in the UV region can be ascribed to ligand-centered (^1LC) transitions. In particular, the peak at 280 nm can be attributed to the bpy units (present in bpy , $\text{bpy}-\text{Br}$ and $\text{bpy}-\text{O}-\text{bpy}$). Moderately intense metal-to-ligand charge transfer ($^1\text{MLCT}$) bands are observed in the 400–500 nm region. In Os -containing complexes, spin-orbit coupling gives rise to broad and weak absorptions at wavelengths higher than 600 nm, corresponding to the spin-forbidden, formally triplet $^3\text{MLCT}$ transition.

For all the mononuclear complexes, the absorption spectrum is very similar both in shape and in intensity to the parent $[M(\text{bpy})_3]^{2+}$ species, indicating that the changes introduced on the ligand(s) do not modify the chromophore properties.

In the polynuclear species, the measured absorption spectrum is essentially the sum of the absorption spectra of the mononuclear units present, indicating that, in agreement with

the electrochemical results, the electronic communication through the $\text{bpy}-\text{O}-\text{bpy}$ bridging ligand appears negligible, so that the various metal units behave as the corresponding isolated $[M(\text{bpy})_3]^{2+}$ units.

Luminescence properties

All the complexes luminesce both at room temperature in fluid solution and in rigid matrix at 77 K. Fig. 4 shows representative examples of emission bands. Luminescence band maxima, emission quantum yield (Φ_{em}) and lifetime (τ) values are collected in Table 2. Excitation spectra were performed on all complexes, obtaining a good match with the respective absorption spectra.

In all cases, the luminescence emission is clearly due to $^3\text{MLCT}$ states, as evidenced by (i) position and shape of the emission band, (ii) blue shift and appearance of vibrational structure on lowering the temperature, and (iii) lifetime values which are in the expected range for Ru - and Os -polypyridine complexes.^{20,21}

More specifically, all the complexes containing only $\text{Ru}(\text{II})$ show luminescence band maxima, lifetimes, and emission quantum yields which are very close to those featured by the $[\text{Ru}(\text{bpy})_3]^{2+}$ parent complex. It is worth noting that polynuclear homometallic complexes $[(\text{bpy})_2\text{Ru}(\mu-\text{bpy}-\text{O}-\text{bpy})\text{Ru}(\text{bpy})_2]^{4+}$ and $[\text{Ru}\{(\mu-\text{bpy}-\text{O}-\text{bpy})\text{Ru}(\text{bpy})_2\}_3]^{8+}$ also have luminescence properties close to those of $[\text{Ru}(\text{bpy})_3]^{2+}$, that is they are much stronger emitters compared to the analogous species using the dpp bridging ligands³³ instead of $\text{bpy}-\text{O}-\text{bpy}$. Analogously, all the complexes containing only $\text{Os}(\text{II})$ behave much like the $[\text{Os}(\text{bpy})_3]^{2+}$ parent species. This result emphasizes that the changes introduced in the ligands do not alter the intrinsic properties of the metallic units that behave essentially as $[M(\text{bpy})_3]^{2+}$ complexes.

The results concerning the heterometallic species, $[(\text{bpy})_2\text{Ru}(\mu-\text{bpy}-\text{O}-\text{bpy})\text{Os}(\text{bpy})_2]^{4+}$ and $[\text{Os}\{(\mu-\text{bpy}-\text{O}-\text{bpy})\text{Ru}(\text{bpy})_2\}_3]^{8+}$, are particularly interesting, as these polynuclear complexes feature luminescence emission only from the Os -based unit. This clearly indicates that energy transfer takes place from the Ru -based unit(s) to the Os -based moiety. Taking into account that the emission quantum yield of a $[\text{Ru}(\text{bpy})_3]^{2+}$ unit is much greater than that of a $[\text{Os}(\text{bpy})_3]^{2+}$ unit (Table 2), it can be estimated that the intramolecular energy transfer process is taking place with at least 98% efficiency. Thus, the luminescence data indicate that the electronic communication through the $\text{bpy}-\text{O}-\text{bpy}$ bridge is not negligible, as suggested by redox and absorption arguments, but indeed is sufficiently large to allow an efficient energy transfer process between the connected units. It is also worth underlining that the tetranuclear complex $[\text{Os}\{(\mu-\text{bpy}-\text{O}-\text{bpy})\text{Ru}(\text{bpy})_2\}_3]^{8+}$ is working as an antenna system: the energy absorbed by the peripheral $\text{Ru}(\text{II})$ -based moieties is channelled to the central $\text{Os}(\text{II})$ -based unit.

Finally, it can also be noted that although the $\text{bpy}-\text{O}-\text{bpy}$ bridging ligand is flexible, CPK molecular models indicate that the distance between the two connected metals is about 1.0 nm, irrespective of the rotation around the $\text{C}-\text{O}-\text{C}$ bonds of the ether linkage. This fact may be of interest for theoretical analysis of energy- or electron-transfer processes occurring through the $\text{bpy}-\text{O}-\text{bpy}$ bridge.

Conclusions

A series of new $\text{Ru}(\text{II})$ and $\text{Os}(\text{II})$ mono- and polynuclear polypyridine complexes has been synthesized using the bridging ligand $\text{bpy}-\text{O}-\text{bpy}$. The synthetic scheme is very flexible, and homo and heterometallic species can be prepared through simple procedures. The redox and photophysical results indicate that the electronic communication through the $\text{bpy}-\text{O}-\text{bpy}$ bridging ligand is small enough to not modify substantially

the properties of the metal units, which are those of the corresponding isolated $[M(\text{bpy})_3]^{2+}$ units, but large enough to allow efficient energy transfer through the bridge, a necessary condition for the build-up of multimetallic antenna systems.

Experimental

Methods

^1H NMR (400 MHz) measurements were acquired on a Bruker ARX400 spectrometer. MALDI-TOF spectra were run on a Bruker Biflex III using α -cyano-4-hydroxycinnamic acid as matrix.

Absorption spectra were recorded with a Perkin–Elmer $\lambda 16$ or a Perkin–Elmer $\lambda 40$ spectrophotometer. Luminescence experiments were performed in dilute (*ca.* 10^{-5} M) acetonitrile solutions at room temperature and in 4 : 1 v/v methanol–ethanol rigid matrix at 77 K, by using a Perkin–Elmer LS-50 spectrofluorimeter equipped with a red-sensitive Hamamatsu R928 photomultiplier. Luminescence maxima tabulated are uncorrected for detector response. Luminescence lifetimes were measured with an Edinburgh 199 single-photon counting apparatus (D_2 lamp, 310 nm, time resolution 0.5 ns). Luminescence quantum yields were measured with a Perkin–Elmer LS-50 spectrofluorimeter, following the optical dilute method,³⁴ with $[\text{Ru}(\text{bpy})_3]^{2+}$ in air-equilibrated aqueous solution as the quantum yield standard ($\Phi = 0.028$).³⁵

Electrochemical measurements were carried out in argon-purged acetonitrile solution at room temperature with a PAR 273 multipurpose equipment interfaced to a PC computer. The working electrode was a Pt microelectrode or a glassy carbon (8 mm², Amel) electrode. The counter electrode was a Pt wire, and the reference electrode was a SCE separated with a fine glass frit. The concentration of the complexes was 5×10^{-4} M and tetraethylammonium hexafluorophosphate (TEAPF_6) 0.05 M was used as supporting electrolyte. Cyclic voltammograms (CV) were obtained at sweep rates of 20, 50, 100, 200, and 500 mV s⁻¹; differential pulse voltammetry experiments (DPV) were performed with a scan rate of 20 mV s⁻¹, a pulse height of 75 mV, and a duration of 40 ms. For reversible processes the half-wave potential values are reported; the same values are obtained from the DPV peaks and from an average of the cathodic and anodic cyclic voltammetric peaks. For irreversible processes the reported values are those evaluated from the peak potentials in the DPV experiments. The number of exchanged electrons in each redox process was measured from DPV scans.³⁶ To establish the reversibility of a process, we used the criteria of (i) separation close to 60 mV between cathodic and anodic peaks, (ii) close to unity ratio of the intensities of the cathodic and anodic currents, and (iii) constancy of the peak potential on changing sweep rate in the cyclic voltammograms. All the potential values are reported vs. SCE. In the experimental conditions used, the potential of the ferrocene–ferrocenium redox couple was +0.395 V.

Experimental errors in the reported data are as follows: absorption maxima, 2 nm; molar absorption coefficients, 10%; excited state lifetimes, 10%; redox potentials, 10 and 20 mV for reversible and irreversible processes, respectively.

Materials

$[\text{Ru}(\text{bpy})_2(\text{bpy}-\text{Br})](\text{PF}_6)_2$, $[\text{Ru}(\text{bpy}-\text{Br})_3](\text{PF}_6)_2$, $[\text{Ru}(\text{bpy})_2(\text{bpy}-\text{O}-\text{bpy})](\text{PF}_6)_2$, $[\text{Ru}(\text{bpy}-\text{O}-\text{bpy})_3](\text{PF}_6)_2$, $[(\text{bpy})_2\text{Ru}(\mu-\text{bpy}-\text{O}-\text{bpy})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$, $[(\text{bpy})_2\text{Ru}(\mu-\text{bpy}-\text{O}-\text{bpy})\text{Os}(\text{bpy})_2](\text{PF}_6)_4$, and $[\text{Ru}\{\mu-\text{bpy}-\text{O}-\text{bpy}\text{Ru}(\text{bpy})_2\}_3](\text{PF}_6)_8$ and the ligands 4-Br-2,2'-bipyridine (bpy–Br) and 4-hydroxy-2,2'-bipyridine were prepared as previously described.²² All solvents were dried and distilled before use by standard methods.³⁷

Syntheses

$[\text{Os}(\text{bpy})_2(\text{bpy}-\text{Br})](\text{PF}_6)_2$. $\text{Os}(\text{bpy})_2\text{Cl}_2$ (70 mg, 0.12 mmol) and bpy–Br (38 mg, 0.16 mmol) were refluxed in 15 ml EtOH–H₂O 3 : 1 v/v for 48 h. After cooling the solvent was removed under reduced pressure, and the residue was dissolved in water and precipitated adding NH_4PF_6 . This crude product was chromatographed on a neutral alumina column using CH_2Cl_2 –MeOH 95 : 5 as eluant. The greenish fraction was collected, taken to dryness, and finally recrystallized from acetone–water containing a few milligrams NH_4PF_6 . Yield 58%.

$[\text{Os}(\text{bpy})_2(\text{bpy}-\text{O}-\text{bpy})](\text{PF}_6)_2$. $[\text{Os}(\text{bpy})_2(\text{bpy}-\text{Br})](\text{PF}_6)_2$ (32 mg, 0.030 mmol), 4-hydroxy-2,2'-bipyridine (10.0 mg, 0.059 mmol), and dried K_2CO_3 (16.6 mg, 0.17 mmol) were refluxed in anhydrous CH_3CN for 24 h under argon. After cooling the solution was filtered and the solvent was removed under reduced pressure. The crude product was dissolved in acetone, recrystallized twice from water containing a few milligrams of NH_4PF_6 and two drops of conc. NH_3 solution, and finally washed with ether and dried. Yield 68%. ^1H NMR (acetone-*d*₆, 25 °C) δ 7.27 (dd, $J = 6.6, 2.7, 1\text{H}_5$), 7.30 (dd, $J = 6.3, 2.4, 1\text{H}_5$), 7.43–7.57 (m, 5 $\text{H}_5, 1\text{H}_5$), 7.90–8.06 (m, 1 $\text{H}_4, 1\text{H}_6, 5\text{H}_6, 4\text{H}_4$), 8.10 (d, $J = 5.3, 1\text{H}_3$), 8.20 (d, $J = 2.3, 1\text{H}$), 8.51 (d, $J = 8.0, 1\text{H}_3$), 8.61 (d, $J = 2.6, 1\text{H}_3$), 8.66 (d, 1 H_6), 8.73–8.81 (m, 5 $\text{H}_3, 1\text{H}_6$). MALDI-TOF, *m/z*: 1016 $[\text{M}]^+$, 974 $[\text{M} - \text{PF}_6]^+$, 831 $[\text{M} - 2\text{PF}_6]^+$; the isotopic pattern corresponds with the theoretical one.

$[\text{Os}(\text{bpy}-\text{Br})_3](\text{PF}_6)_2$. $(\text{NH}_4)_2\text{OsCl}_6$ (20 mg, 0.045 mmol) and bpy–Br (43 mg, 0.183 mmol) were refluxed in ethylene glycol (5 ml) for 25 h. After cooling, water (10 ml) and an excess of NH_4PF_6 were added to precipitate the crude product. This was column chromatographed on neutral alumina using CH_2Cl_2 –MeOH 9 : 1 as eluent, and then recrystallized twice from acetone–water containing a few milligrams of NH_4PF_6 and two drops of conc. NH_3 . Finally, the product was washed with ether and dried. Yield 33%. MALDI-TOF, *m/z*: 1038 $[\text{M} - \text{PF}_6]^+$, 896 $[\text{M} - 2\text{PF}_6]^+$; the isotopic pattern corresponds with the theoretical one.

$[\text{Os}(\text{bpy}-\text{O}-\text{bpy})_3](\text{PF}_6)_2$. $[\text{Os}(\text{bpy}-\text{Br})_3](\text{PF}_6)_2$ (60.0 mg, 0.050 mmol), 4-hydroxy-2,2'-bipyridine (84 mg, 0.48 mmol), and dried K_2CO_3 (120 mg, 1.22 mmol) were refluxed in anhydrous CH_3CN for 24 h under argon. After cooling the solution was filtered and the solvent was removed under reduced pressure. The crude product was chromatographed on neutral alumina using CH_2Cl_2 –MeOH 9 : 1 as eluent, and then recrystallized twice from acetone–water containing a few milligrams of NH_4PF_6 and two drops of conc. NH_3 . Finally, the product was washed with ether and dried. Yield 49%. ^1H NMR (acetone-*d*₆, 25 °C) δ 7.24–7.35 (m, 6 H_5), 7.42–7.54 (m, 5 $\text{H}_5, 1\text{H}_5$), 7.93–8.24 (m, 6 $\text{H}_4, 3\text{H}_6, 6\text{H}_3$), 8.48–8.54 (m, 3 H_6), 8.61 (d, $J = 2.6, 3\text{H}_3$), 8.66 (d, 3 H_6), 8.72–8.82 (m, 3 $\text{H}_3, 3\text{H}_6$). MALDI-TOF, *m/z*: 1314 $[\text{M} - \text{PF}_6]^+$, 1169 $[\text{M} - 2\text{PF}_6]^+$; the isotopic pattern corresponds with the theoretical one.

$[\text{Os}\{\mu-\text{bpy}-\text{O}-\text{bpy}\text{Ru}(\text{bpy})_2\}_3](\text{PF}_6)_8$. $\text{Ru}(\text{bpy})_2\text{Cl}_2$ (44 mg, 0.091 mmol) and AgNO_3 (33 mg, 0.191 mmol) were stirred under argon at room temperature in 10 ml H₂O–EtOH 1 : 2. $[\text{Os}(\text{bpy}-\text{O}-\text{bpy})_3](\text{PF}_6)_2$ (36 mg, 0.025 mmol) was added and the solution refluxed for 36 h. After cooling, the solution was filtered to remove AgCl , and the solvent was evaporated under reduced pressure. The crude product was recrystallized three times from acetone–water containing a few milligrams of NH_4PF_6 . Yield 24%. ^1H NMR (acetone-*d*₆, 25 °C) δ 7.25–7.37 (m, 6 H_5 , bridging ligand), 7.44–7.48 (m, 18 H_5), 7.80–7.98 (m, 6 H_6 , bridging ligand, 6 H_6), 7.99–8.08 (m, 12 H_6), 8.11–8.24 (m, 18 H_4), 8.52–8.58 (m, 6 H_3), 8.63–8.72 (m, 6 H_3 , bridging ligand), 8.75–8.81 (m, 12 H_3).

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