Polynuclear Polypyridine Complexes Incorporating Ru(II), Os(II), and Pt(II): Decanuclear Dendrimeric Antennas

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The "complexes as metal/complexes as ligand" strategy has been used to prepare new polynuclear heterometallic complexes containing two, 3, 4, and ten metal units. The metal ions employed are Ru^{2+}, Os^{2+}, and Pt^{2+}; the bridging ligands are 2,3- and 2,5-dpp (dpp = bis(2-pyridyl)pyrazine), and the terminal ligands are Cl^- and bpy (bpy = 2,2′-bipyridine). $[Os(bpy)_2(\mu\text{-}2,3\text{-dpp})Ru\{(\mu\text{-}2,3\text{-dpp})PtCl_2\}_2](PF_6)_4$ ($OsRuPt_2$) and $[Os\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})PtCl_2]_2\}_3](PF_6)_8$ ($OsRu_3Pt_6$), which have a dendritic structure, are the first examples of polynuclear complexes based on the dpp bridging ligand simultaneously containing three different metals. All of the new compounds feature absorption spectra with intense ligand-centered transitions in the UV region and metal-to-ligand charge transfer (MLCT) bands in the visible region. The complexes are luminescent both at room temperature in acetonitrile solution and at 77 K in butyronitrile rigid matrix. $OsRuPt_2$ and $OsRu_3Pt_6$ luminesce in the near-infrared spectral region at 975 and 875 nm, respectively, at room temperature. This indicates that the emitting state is a (formally triplet) MLCT involving Os^{2+} and the bridging ligand μ-2,3-dpp and that all the absorbed energy is efficiently channeled to the single Os-based unit. $OsRu_3Pt_6$ appears to be the first decanuclear species displaying such efficient antenna effect.

Introduction

Molecular level devices can be defined as assemblies of a discrete number of molecular components designed to achieve a specific function.[1−4] These devices can also be considered as supramolecular species and are typically built by synthetic chemists using the bottom-up approach starting with simple molecular components. A variety of intermolecular forces have been employed for the assembly of the single components, including hydrogen bonds, donor−acceptor interactions, or even covalent bonds.[4−6]

Particular strategies are necessary when covalent bonds are used to link molecular building blocks containing transition metals. Using the complexes as metal/complexes as ligand[7] strategy, coupled with an appropriate protection/deprotection scheme,[8] it is possible to construct large monodispersed polynuclear metal complexes via metal−ligand coordination bonds. In the past few years, we have synthesized a variety of dendritic polynuclear transition metal complexes based on the 2,3- and 2,5-dpp bridging ligands (dpp = bis(2-pyridyl)pyrazine), exhibiting interesting photophysical and electrochemical properties.[9,10] Until now, many metal units have been used in the assembly of dpp-based polynuclear complexes, namely, Re(I), Fe(II), Ru(II), Os(II), Rh(III), Ir(III), Pd(II), Pt(II), Pt(IV), and Cu(I),[11,12] but so far, no more than two different metals have been introduced in a single compound.

One of the advantages of the complexes as metal/complexes as ligand synthetic strategy is that one can introduce the desired building block at each stage of the synthesis. We have taken advantage of this flexibility to prepare a series of new polynuclear complexes incorporating the $PtCl_2$ unit. The metal units and ligands used to build up our compounds are shown in Figure 1, together with their graphic symbols and abbreviations. Figure 2 shows the schematic representations of the compounds dealt with in this paper. The abbreviations indicate the type and number of metal atoms contained in the compound; in the two compounds containing the 2,5-dpp bridging ligand, the label b

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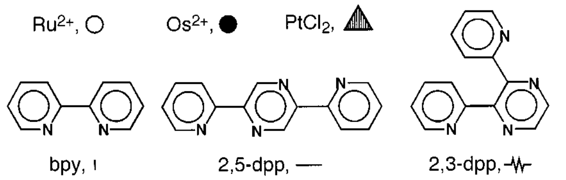

Figure 1. Metal units, ligands, and abbreviations used.

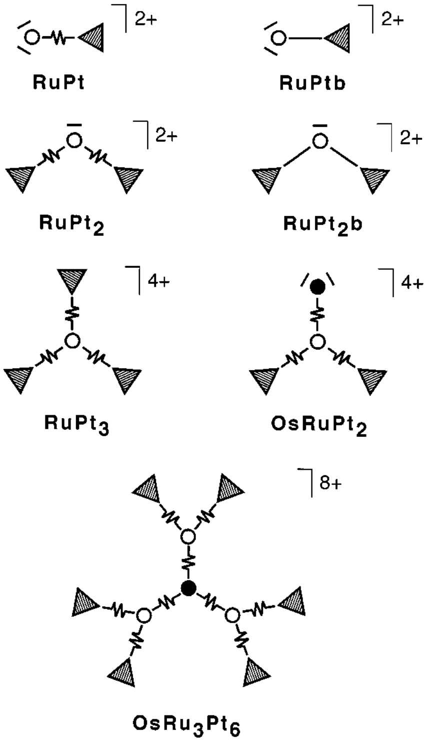

Figure 2. Schematic representations of the compounds investigated. The graphic symbols used to represent metal units and ligands are explained in Figure 1. All the compounds were obtained as PF_6^- salts. The label indicates the type and number of metal atoms contained in the compound; the final b letter denotes the presence of the 2,5-dpp bridging ligand.

has been added at the end of the abbreviation. The compound RuPt was previously reported by other authors.[13,14]

It is worth noting that $OsRuPt_2$ and $OsRu_3Pt_6$ are the first examples of polynuclear complexes based on the dpp bridging ligand simultaneously containing three different metals. The interest in these dendrimeric species is related to the presence of many chemically different units since each unit introduces into the supramolecular structure its own pieces of information (in the form of specific properties such as excited states, redox levels, etc.), thus making available more complex functions. Indeed, in the complexes $OsRuPt_2$ and $OsRu_3Pt_6$, a clear antenna effect is observed; the latter is (to our knowledge) the first decanuclear species where all the energy absorbed is efficiently transferred to a single unit.

Experimental Section

Methods. Mass spectra were obtained using a VG Autospec double-focusing mass spectrometer operating in the FAB^+ mode in a 2-nitrophenyl octyl ether (NPOE) matrix. IR spectra (KBr pellets) were recorded with a Perkin-Elmer 1330 IR spectrophotometer. NMR spectra were obtained with a Varian CFT-20 NMR spectrometer operating at 80 MHz for ^1H using tetramethylsilane (TMS) as an internal reference. Metal analyses were performed either by X-ray fluorescence using an automatic spectrometer Philips PW 1480 or by ICP−MS using a Varian-Liberty 200 ICP−AES spectrometer after microwave-assisted decomposition in sealed Teflon vessels. The stability of the novel complexes in solution was tested by keeping them in the dark for at least 2 days; all samples showed a constant absorption spectrum.

Absorption spectra were recorded with a Perkin-Elmer λ16 or a Perkin-Elmer λ40 spectrophotometer. Luminescence experiments were performed in dilute (ca. 10^{-5} M) acetonitrile solutions at room temperature and in butyronitrile rigid matrix at 77 K, using a Perkin-Elmer LS-50 spectrofluorimeter equipped with a red-sensitive Hamamatsu R928 photomultiplier in the range up to 850 nm. For the observation of luminescence in the range of 800−1200 nm, a modified Edinburgh Instruments FS900 spectrofluorimeter was used. Excitation was performed with the 514-nm line of a Spectra-Physics 265 Ar^+ laser. Detection was accomplished using a cooled (77 K) North Coast EO-817L Ge detector in combination with a Stanford Research SR lock-in amplifier. Tabulated luminescence maxima are corrected for detector response. Luminescence lifetimes were measured with an Edinburgh 199 single-photon counting apparatus (D_2 lamp, 310 nm, time resolution of 0.5 ns). Luminescence quantum yields were measured with a Perkin-Elmer LS-50 spectrofluorimeter, following the optical dilute method,[15] with $[Ru(bpy)_3]^{2+}$ in air-equilibrated aqueous solution as the quantum yield standard ($\Phi = 0.028$).[16] Estimated errors are as follows: molar absorption coefficients, 10%; λ_{max}, ±2 nm; excited-state lifetimes, 10%.

Materials. $[Ru(bpy)_2(2,5\text{-dpp})](PF_6)_2$,[17] $[Ru(bpy)(2,3\text{-dpp})_2](PF_6)_2$,[17] $[Ru(bpy)(2,5\text{-dpp})_2](PF_6)_2$,[17] $[Ru(2,3\text{-dpp})_3](PF_6)_2$,[18] $[Os\{(\mu\text{-}2,3\text{-dpp})Ru(2,3\text{-dpp})_2\}_3](PF_6)_8$,[19] $PtCl_2(DMSO)_2$,[20] $[RuCl_2(2,3\text{-Medpp})_2](PF_6)_2$,[8] and $[Os(bpy)_2(2,3\text{-dpp})](PF_6)_2$ [21] were prepared according to literature methods. All solvents were dried and distilled by standard methods before use.[22] The new complexes were prepared under a nitrogen atmosphere using Schlenk techniques. Filtration and purification of the products were usually performed in the air.

Syntheses of the Precursors to $OsRuPt_2$. $[Os(bpy)_2(\mu\text{-}2,3\text{-dpp})Ru(2,3\text{-Medpp})_2](PF_6)_6$ (2,3-Medpp$^+$ = 2-[2-(1-Methylpyridiniumyl)]-3-(2-pyridyl)pyrazine). Solid $AgNO_3$ (0.033 g, 0.194 mmol) was added to a suspension of $[RuCl_2(2,3\text{-Medpp})_2](PF_6)_2$ (0.093 g, 0.097 mmol) in H_2O/EtOH 1:2 (v/v, 12 mL). After being stirred for 1 h at room temperature, $[Os(bpy)_2(2,3\text{-dpp})](PF_6)_2$ (0.100 g, 0.097 mmol) was added, and the reaction mixture was refluxed for 72 h. After being cooled at room temperature, the AgCl formed was removed by repeated centrifugations. An excess of solid NH_4PF_6 was added, and the mixture obtained was rotary evaporated till precipitation of a deep violet solid. Recrystallization from CH_3CN/EtOH provided the product, which was washed several times with EtOH and then with Et_2O and vacuum-dried (0.158 g, 74%). Anal. Calcd for $C_{64}H_{52}N_{16}OsRuP_6F_{36}$: C, 34.84; H, 2.37; N, 10.15. Found: C, 34.87; H, 2.41; N, 10.15. ^1H NMR (80 MHz, CD_3CN, 298 K): δ 7−9.2 (m, 46H, aromatic H); 4−4.6 (m, 6H $-CH_3$).

$[Os(bpy)_2(\mu\text{-}2,3\text{-dpp})Ru(2,3\text{-dpp})_2](PF_6)_4$. The previously obtained $[Os(bpy)_2(\mu\text{-}2,3\text{-dpp})Ru(2,3\text{-Medpp})_2](PF_6)_6$ (0,120 g, 0.054 mmol) and a large excess of 1,4-diazabicyclo[2.2.2]octane (DABCO, 0,140 g, 1.25 mmol) were refluxed in dry acetonitrile (12 mL) for 20 h. After being cooled at room temperature, the solution was partially evaporated to ca. 3 mL, and a saturated ethanolic solution of NH_4PF_6 (5 mL) was added. The solid obtained was separated by filtration, dissolved in a small amount of CH_3CN, and purified by chromatography on an

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Table 1. Elemental Analysis and FAB$^+$ Data for the New Complexes

compound	elemental analysis %: found (calcd) C	H	N	Ru	Os	Pt	FAB$^+$, *m/e* [nature of the cluster] (% rel int)
$[Ru(bpy)_2(\mu\text{-}2,5{-}dpp)PtCl_2](PF_6)_2{\cdot}2H_2O$	32.61	2.24	9.04				1059 $[M - PF_6]^+$ (14)
(RuPtb)	(32.94)	(2.43)	(9.03)				914 $[M - 2PF_6]^+$ (11)
$[Ru(bpy)\{(\mu{-}2,3\text{-}dpp)PtCl_2\}_2](PF_6)_2$	29.03	1.71	9.03	7.71^a	0	28.48^a	1403 $[M - PF_6]^+$ (7)
($RuPt_2$)	(29.49)	(1.82)	(9.05)	(6.53)	(0)	(25.21)	1257 $[M - 2PF_6]^+$ (14)
$[Ru(bpy)\{(\mu{-}2,5\text{-}dpp)PtCl_2\}_2](PF_6)_2{\cdot}6H_2O$	27.12	2.37	8.54	5.56^a	0	25.63^a	1403 $[M - PF_6]^+$ (11)
($RuPt_2b$)	(27.56)	(2.41)	(8.45)	(6.10)	(0)	(23.55)	1257 $[M - 2PF_6]^+$ (25)
$[Ru\{(\mu{-}2,3\text{-}dpp)PtCl_2\}_3](PF_6)_2{\cdot}H_2O$	26.53	1.71	8.79			29.6^b	
($RuPt_3$)	(26.41)	(1.69)	(8.80)			(30.64)	
$[Os(bpy)_2(\mu\text{-}2,3{-}dpp)Ru\{(\mu\text{-}2,3{-}dpp)PtCl_2\}_2](PF_6)_4$	30.43	1.89	9.16	4.01^a	7.61^a	13.70^a	
($OsRuPt_2$)	(30.79)	(1.91)	(9.26)	(4.18)	(7.87)	(16.13)	
$[Os\{(\mu{-}2,3\text{-}dpp)Ru[(\mu{-}2,3\text{-}dpp)PtCl_2]_2\}_3](PF_6)_8{\cdot}5MeOH$	29.00	2.35	9.11			19.5^b	
($OsRu_3Pt_6$)	(28.51)	(2.17)	(9.13)			(21.85)	

[a] ICPMS analyses. [b] X-ray fluorescence analyses.

alumina column (eluent CH_2Cl_2/MeOH 9:1). The first fraction (light brown) and the third fraction (blue) were discarded; the second fraction (deep violet) was collected and concentrated (3 mL), and a saturated ethanolic solution of NH_4PF_6 (ca. 5 mL) was added. The solid obtained was separated by filtration, washed several times with ethanol, and dried in a vacuum (70%). The NMR analysis showed that the signals due to the methyl protons of the precursor (4−4.6 ppm) had disappeared. Anal. Calcd for $C_{62}H_{46}N_{16}OsRuP_4F_{24}{\cdot}5\ H_2O$: C, 37.68; H, 2.85; N, 11.34. Found: C, 37.62; H, 2.62; N, 11.36.

Synthesis of $PtCl_2$-Containing Complexes. Complexes shown in Figure 2 have been synthesized by refluxing in methanol the appropriate complex ligand with a stoichiometric amount of $PtCl_2(DMSO)_2$. Yields ranged between 65 and 90%.

In a typical synthesis, $[Ru(bpy)_2(2,5\text{-}dpp)](PF_6)_2$ (0,169 g, 0.18 mmol) and $PtCl_2(DMSO)_2$ (0.076 g, 0.18 mmol) were refluxed in methanol (5 mL) for 1 h. The solution turned from purple-red to violet, while a violet solid started to precipitate. The suspension was cooled at room temperature, and the solid was filtered, recrystallized from CH_3CN/MeOH, and vacuum-dried. $[Ru(bpy)_2(\mu\text{-}2,5\text{-}dpp)PtCl_2](PF_6)_2$ (RuPtb) was recovered as a blue-violet powder (0.143 g, 66%).

$OsRu_3Pt_6$ and $RuPt_3$ were less soluble, and their purification was achieved by washing them several times with methanol and CH_2Cl_2. All products gave consistent elemental analyses (Table 1) within the experimental errors of each technique. IR spectra showed the presence of medium-weak bands between 350 and 400 cm^{-1}, because of the Pt−Cl stretching. In complexes containing the 2,3-dpp ligand, the band at 990 cm^{-1}, diagnostic for the unbridged ligand, was absent; in complexes containing the 2,5-dpp ligand, a band at 1200 cm^{-1} was detected, which is characteristic of the bridged ligand. Positive FAB−MS spectra for di- and trinuclear complexes are consistent with the formulation proposed (Table 1). Ion clusters of charge +1 are observed, deriving from the loss of one or two PF_6^- units; the latter species comes from a reduction process induced by FAB$^+$, as already observed for similar Ru(II) systems.[23]

Results

Absorption Spectra. The absorption spectra of selected compounds are shown in Figure 3, and lowest energy absorption maxima (together with ϵ values) are given in Table 2. The absorption spectra of the compounds look like those of typical Ru(II) and Os(II) polynuclear polypyridine complexes: the UV region is dominated by intense ^{1}LC (ligand-centered) transitions, whereas metal-to-ligand charge transfer (^{1}MLCT) bands are present in the visible region. In Os(II)-containing compounds, the absorption to the ^{3}MLCT state is also evident at lower energies.

Luminescence Properties. Luminescence spectra of selected compounds at room temperature are shown in Figure 4. Luminescence maxima, quantum yields (Φ_{em}), and lifetimes (τ) values are collected in Table 2. All the complexes examined are luminescent both in rigid matrix at 77 K and in fluid solution at room temperature, with typical emission properties of Ru− and Os−polypyridine complexes.[24,25] Excitation spectra were performed on all complexes featuring luminescence at $\lambda < 850$ nm using the Perkin-Elmer LS-50 spectrofluorimeter, obtaining a good match with the respective absorption spectra. For the complexes $OsRuPt_2$ and $OsRu_3Pt_6$, which emit in the infrared spectral region, excitation spectra could not be recorded due to the fixed excitation wavelength available.

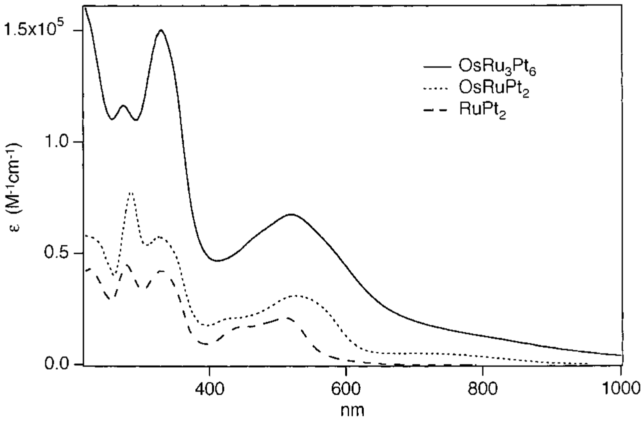

Figure 3. Absorption spectra of $RuPt_2$, $OsRuPt_2$, and $OsRu_3Pt_6$ at room temperature in acetonitrile solution.

Discussion

Synthesis. As shown in early works done in our laboratories,[26] protection/deprotection methods coupled with the so-called complexes as metals/complexes as ligands synthetic strategy are very effective for the construction of dendritic coordination species by convergent or divergent synthetic pathways.[19] In the present case, the use of $PtCl_2(DMSO)_2$ as a complex metal in reaction with a multifunctional complex ligand allows the preparation of trimetallic species having nuclearities up to 10.

It is noteworthy that $PtCl_2$ terminal units present on these species confer to them the unusual nature of multifunctional complex metal, and in fact, preliminary experiments have shown

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Table 2. Spectroscopic and Photophysical Data[a]

	absorption	luminescence				
	298 K	298 K[b]			77 K	
compound	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	λ_{max}, nm	τ, ns	Φ_{em}	λ_{max}, nm	τ, μs
RuPt[c]	507 (16 300), 282 (55 700)	815	29/88[d]	1.4×10^{-3}	718	2.20
RuPtb	561 (13 800), 358 (35 200)	855	580	$<1 \times 10^{-3}$	795	0.71
RuPt$_2$	510 (21 000), 332 (42 300)	750	220	6.4×10^{-3}	685	3.30
RuPt$_2$b	553 (28 500), 350 (82 400)	810	115	5.2×10^{-3}	748	2.00
RuPt$_3$	487 (33 200), 337 (61 800)	690			657	
OsRuPt$_2$	524 (31 400), 328 (57 700)	975			875	
OsRu$_3$Pt$_6$	520 (67 100), 331 (150 000)	875			860	

[a] In acetonitrile solution at room temperature and in butyronitrile rigid matrix at 77 K. [b] Deaerated solution. [c] This work, in agreement with refs 13 and 14. [d] Biexponential decay.

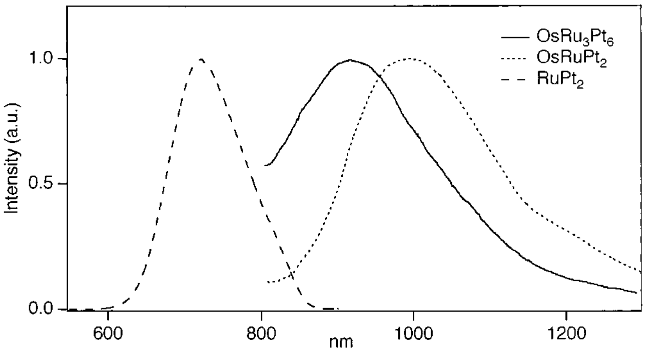

Figure 4. Emission spectra of RuPt$_2$, OsRuPt$_2$, and OsRu$_3$Pt$_6$ at room temperature in acetonitrile solution. The spectra are uncorrected for detector response.

that metathesis reaction of chloride ions with chelating ligands, such as ethylenediamine, are possible. Such reactivity can in principle be used to increase the molecular complexity of the structure. Further studies on this direction have been undertaken.

General Properties. It should be recalled that Pt(II) species feature square-planar coordination, so that in the dpp−PtCl$_2$ unit, the two Cl$^-$ ions must be in cis positions, and no geometrical or optical isomers are possible. On the contrary, Ru(II) and Os(II) possess an octahedral coordination geometry, so that, because of the inequivalence of the dpp nitrogens, two bridging ligands can be arranged either in cis or trans configuration, and three bridging ligands can produce either *fac* or *mer* isomers. Moreover, each octahedral metal is a stereogenic center, so that the preparation of polymetallic complexes necessarily leads to mixtures of several diastereoisomeric species. For this reason, structural investigations on these systems are difficult. The representations of Figure 2 are only to be considered schemes of the topological connectivity inside the compound. On the other hand, differences in the electrochemical and spectroscopic properties arising from the presence of isomeric species are not expected to be large[27] and were indeed not observed in stereochemically pure tetranuclear species based on Ru−polypyridine units.[28]

The species of high nuclearity possess a three-dimensional branching structure and may thus be considered to belong to the class of dendrimers.[29] The molecular model of the compound OsRu$_3$Pt$_6$ displayed in Figure 5 gives an idea of the shape of one of the many possible isomers. The approximate diameter of the molecule is 3 nm. We would like to stress that these species possess two particular properties that are not usual in most known dendrimers: (i) Each metal-containing unit can exhibit valuable intrinsic properties such as absorption of visible (solar) light, luminescence, and oxidation and reduction levels at accessible potentials.[24,25,30,31] (ii) By a suitable choice of the building blocks, they can incorporate many pieces of information; therefore, they can be used to perform valuable functions such as light harvesting, directional energy transfer, and exchange of a controlled number of electrons at a certain potential.[9,10,32]

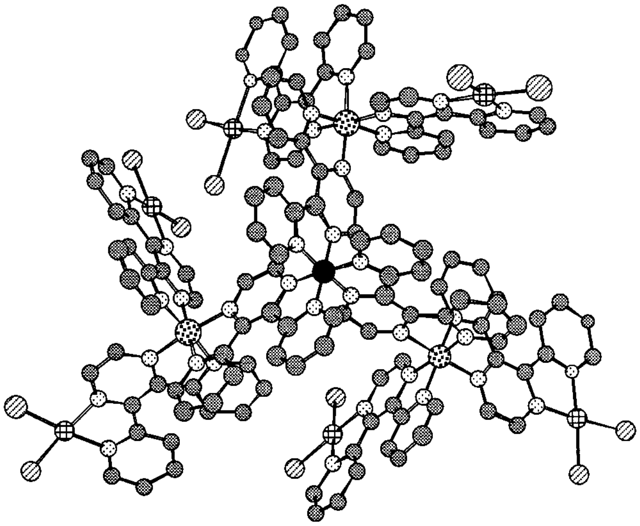

Figure 5. Molecular model of one of the possible isomers of OsRu$_3$Pt$_6$. H atoms are hidden for clarity.

Previous investigations carried out on mono- and polynuclear compounds of the Ru(II)− and Os(II)−polypyridine family[8,17,21,33−36] have shown the following: (i) Oxidation is metal centered. (ii) Os(II) is oxidized at potentials considerably less positive than Ru(II). (iii) The electron donor power decreases in the ligand series bpy > 2,3-dpp > 2,5-dpp ≥ μ-2,3-dpp > μ-2,5-dpp. (iv) The interaction between equivalent metal centers is noticeable for metals coordinated to the same bridging ligand, whereas it is negligible for metals that are more far apart. (v)

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The interaction between equivalent ligands is noticeable for ligands coordinated to the same metal, whereas it is negligible for ligands that are more far apart.

It is now well-established that for Ru(II), Os(II), and Pt(II) complexes of aromatic N-heterocycles the ground state, the low-energy excited states, and the redox forms can be described in a sufficiently approximate way by localized molecular orbital configurations.[13,37−41] With such an assumption, the various electronic transitions are classified as metal-centered (MC), LC, and charge transfer (CT: either MLCT or ligand-to-metal, LMCT), and the oxidation and reduction processes can be considered as metal- and ligand-centered, respectively. Most often, these complexes exhibit very intense LC bands in the UV region and intense MLCT bands in the visible region. In Ru(II) and Os(II) complexes, regardless of the excitation wavelength, the originally populated excited states undergo fast radiationless decay[42−44] to the lowest triplet ^{3}MLCT, which is luminescent both in rigid matrix at 77 K and in fluid solution at room temperature. As far as the solution behavior of Pt(diimine)Cl$_2$ complexes is concerned, most often their lowest excited state is of ^{3}MC nature, and luminescence can be observed only in rigid matrix at 77 K.[45,46]

In the polynuclear species, each metal-based unit will bring its own excited-state and redox properties. From the above considerations, it follows that the expected energy order of the lowest excited states for the metal-based units relevant for our discussion (see later) is $[(bpy)_2Os(\mu\text{-}2,3\text{-dpp})]^{2+} < [Os(\mu\text{-}2,3\text{-dpp})_3]^{2+} < [(bpy)_2Ru(\mu\text{-}2,5\text{-dpp})]^{2+} < [(bpy)_2Ru(\mu\text{-}2,3\text{-dpp})]^{2+} < [(bpy)Ru(\mu\text{-}2,5\text{-dpp})_2]^{2+} < [(bpy)Ru(\mu\text{-}2,3\text{-dpp})_2]^{2+} < [Ru(\mu\text{-}2,3\text{-dpp})_3]^{2+}$. It is not possible to assign a priori a position in the above series for the (μ-2,3-dpp)PtCl$_2$ unit. The photophysical behavior of the present complexes (vide infra) indicates, however, that the energy of the lowest excited state of the (μ-2,3-dpp)PtCl$_2$ unit must be higher than that of the $[Ru(\mu\text{-}2,3\text{-dpp})_3]^{2+}$ unit.

Absorption Spectra. UV−Vis absorption data are collected in Table 2; spectra of selected compounds are shown in Figure 3. The absorption spectra of all these compounds is essentially similar to that of other Ru(II)- and Os(II)-based polypyridine complexes and can be accordingly interpreted. The high-intensity absorption bands in the UV region can be ascribed to ^{1}LC transitions. In particular, the peak at 280 nm can be attributed to the bpy terminal ligand, the band around 330 nm is attributed to the 2,3-dpp bridging ligand, whereas the 2,5-dpp gives rise to absorption in the range 350−360 nm. Moderately intense ^{1}MLCT bands are observed in the 400−600 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}MLCT transition.

One can note the non-chromophoric nature of the PtCl$_2$ fragments in the sense that there is no absorption band that clearly involves this unit. However, the absorption spectrum shows indication of the connection of PtCl$_2$ to the free end of the dpp ligands: both the ^{1}MLCT band in the visible region and the LC band around 330 nm are different before and after coordination of PtCl$_2$.

As far as the ϵ values are concerned, to a first approximation, each metal-based unit carries its own absorption properties in the polynuclear species so that the light-harvesting capability increases with increasing nuclearity.

The position of the lowest energy MLCT transition Ru→dpp changes when different units are connected to the bridging ligand. Thus, for example, in the three complexes $(bpy)_2Ru(2,3\text{-dpp})^{2+}$,[17] RuPt, and $(bpy)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2{}^{4+}$,[17] the lowest energy ^{1}MLCT transitions Ru→2,3-dpp are observed at 465, 507, and 527 nm, respectively. This is due to progressive lowering of the π^* orbital of the bridging ligand when the free chelating site connects to a formally uncharged unit (PtCl$_2$) or a formally 2+ charged unit ($Ru(bpy)_2{}^{2+}$). The same effect can be seen when comparing the new PtCl$_2$-containing compounds with their respective precursors.

In analogous complexes containing different bridging ligands (RuPt and RuPtb, RuPt$_2$ and RuPt$_2$b), the lowest energy ^{1}MLCT transition Ru→2,3-dpp is present at higher energy with respect to the corresponding Ru→2,5-dpp transition, as expected on the basis of the energy ordering discussed above and as normally verified in similar polynuclear complexes.[7,10]

On passing from RuPt$_2$ to RuPt$_3$, the lowest energy prominent absorption band moves to the blue, indicating that Ru oxidation is more difficult in the latter compound. This is in agreement with the substitution of a bpy ligand (a stronger electron donor) in RuPt$_2$ with a (μ-2,3-dpp)PtCl$_2$ group to obtain RuPt$_3$.

In the complexes OsRuPt$_2$ and OsRu$_3$Pt$_6$, the lowest energy prominent ^{1}MLCT transition moves to the red, as compared with the previously considered 2,3-dpp compounds. This is due to the fact that Os(II) is easier to oxidize than Ru(II) so that this transition is formally a Os→μ-2,3-dpp charge transfer.

In summary, all the absorption data indicate that the lowest energy, most prominent absorption band is of Ru→dpp MLCT nature in all cases, except for OsRuPt$_2$ and OsRu$_3$Pt$_6$, where it is of Os→dpp MLCT nature.

Luminescence Properties. All the complexes luminesce both at room temperature in fluid solution and in rigid matrix at 77 K. Figure 4 shows representative examples of emission bands at room temperature; all the relevant data are collected in Table 2.

In all complexes containing only Ru(II) and Pt(II), emission is clearly due to ^{3}MLCT states of Ru→μ-dpp, as evidenced by (i) position and shape of the emission band, (ii) blue shift of the emission band after lowering the temperature, and (iii) lifetime values that are in the expected range. The effect produced on the emission band (^{3}MLCT, Ru-based) by coordination of PtCl$_2$ to the bridging ligand appears different to that observed (vide supra) in the lowest energy absorption band (^{1}MLCT, Ru-based). For example, at 77 K, starting from $(bpy)_2Ru(2,3\text{-dpp})^{2+}$ ($\lambda_{em} = 618$ nm), one observes $\lambda_{em} = 718$ nm for RuPt and $\lambda_{em} = 719$ for $(bpy)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2{}^{4+}$, indicating that in the triplet excited state, the position of the π^* orbital is the same when a PtCl$_2$ or a $Ru(bpy)_2{}^{2+}$ unit is coordinated to the precursor ligand complex. At room temperature, the emission energy of the complexes with bridging ligands connected to PtCl$_2$ units is even lower than that observed

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replacing $PtCl_2$ with $Ru(bpy)_2^{2+}$. At the moment, we have no rationale for this experimental result.

In the two Os(II)-containing compounds, $OsRuPt_2$ and $OsRu_3Pt_6$, only one luminescence band is observed at much lower energy (λ > 850 nm) with respect to the previous complexes based only on Ru(II) and Pt(II), indicating that the emitting state is ^{3}MLCT Os→μ-2,3-dpp. The position of the emission bands is in agreement with the expected energy ordering (vide supra) of the lowest excited states of the different emitting units ($(bpy)_2Os(\mu\text{-}2,3\text{-dpp})^{2+}$ and $Os(\mu\text{-}2,3\text{-dpp})_3^{2+}$). The absence of luminescence emission due to Ru(II)-based excited states (which lie at higher energy) indicates that efficient energy transfer occurs from the other component units to the Os-based unit.

Antenna Effect. Natural photosynthetic systems show that for solar energy conversion purposes, supramolecular arrays are needed that absorb as much visible light as possible and are able to channel the resulting excitation energy toward a specific site of the array, thus obtaining an antenna effect.

Tetranuclear antennas based on Ru(II) and Os(II) polypyridine units have already been constructed,[35,36] but efficient harvesting of solar energy needs more complex structures. Simply increasing the nuclearity using only two types of metals (Ru(II) and Os(II)) and ligands such as bpy and dpp results, however, in structures where unidirectional energy transfer to the center cannot be obtained.[9,19,34] An example of a misbehaving decanuclear antenna is the $OsRu_9$ dendrimer[34] shown in Figure 6a. As indicated in the energy level diagram, the lowest energy excited state localized on the peripheral $(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2^{2+}$ units lies at lower energy with respect to the lowest energy excited state of the intermediate units $Ru(\mu\text{-}2,3\text{-dpp})_3^{2+}$. As a result, there is no efficient energy transfer from the peripheral units to the center one, and experimentally, two emission bands are observed ($h\nu$ and $h\nu'$).

Substitution of the peripheral $Ru(bpy)_2^{2+}$ fragments with $PtCl_2$ gives rise to the decanuclear trimetallic complex $OsRu_3Pt_6$ (Figure 6b), where only one emission band is observed due to the central $Os(\mu\text{-}2,3\text{-dpp})_3^{2+}$ unit. This trimetallic compound is, to our knowledge, the first decanuclear species that can work as an antenna device, where all the energy absorbed is efficiently transferred to a single unit. In particular, the energy-level diagram of $OsRu_3Pt_6$ can be discussed as follows.

To a first (but rather good) approximation, one can consider that the central and intermediate units in $OsRu_9$ and $OsRu_3Pt_6$ are the same, so that the energy levels are also the same. Indeed, the emission bands from the central units of $OsRu_9$ and $OsRu_3Pt_6$ are observed at room temperature at 11 600[34] and 11 400 cm^{-1}, respectively. The energy level of the intermediate unit in $OsRu_3Pt_6$ can thus confidently be taken equal to that of $OsRu_9$, 14 400 cm^{-1},[34] taking into account that connection of a $PtCl_2$ unit to a free chelating position of dpp has the same effect as a $Ru(bpy)_2^{2+}$ unit on the position of the lowest excited state (as seen above in the luminescence section).

It is more difficult to estimate the position of the lowest energy excited state of the peripheral $PtCl_2$-based unit of $OsRu_3Pt_6$, as we do not observe emission from this unit in any of the compounds prepared, and also, in the absorption spectra, there is no band involving this nonchromophoric unit. Nevertheless, in the mononuclear complex $Pt(2,3\text{-dpp})Cl_2$, a ^{3}MC excited state is observed at 15 800 cm^{-1},[47] so that a ^{3}MC state around this energy should also be present in $OsRu_3Pt_6$. The position of the Pt→μ-2,3-dpp ^{3}MLCT state is unknown, but considering that such a state is expected to be luminescent but is not experimentally observed in our case, we deduce that its position must be higher than that of the intermediate unit (14 400 cm^{-1}). Indeed, experimental results on similar compounds have shown that exoergonic energy transfer between contiguous units is so fast that the luminescence of the units whose ^{3}MLCT excited state lies at higher energy can no longer be observed.

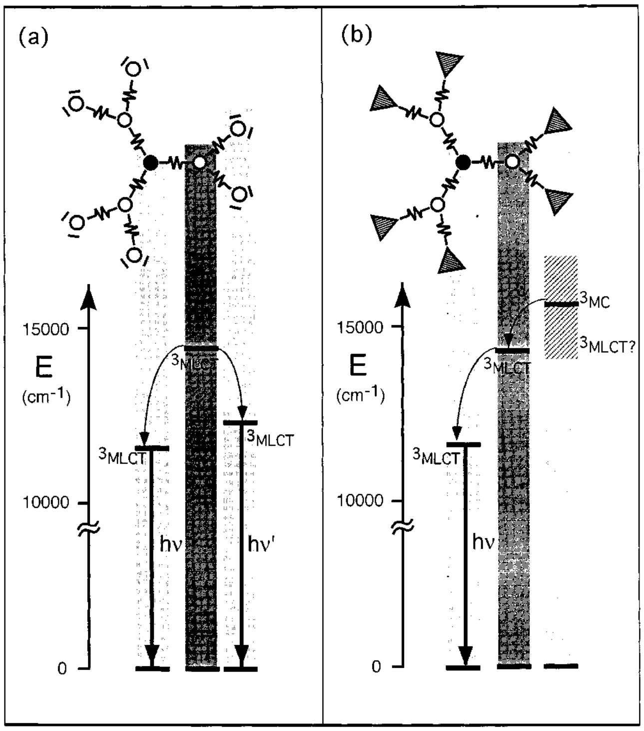

Figure 6. (a) Schematic representation of the compound $Os\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2\}_3^{20+}$, $OsRu_9$, and its energy-level diagram.[34] The lowest energy levels of the various units are not in a cascade arrangement, and the absorbed energy is emitted from the central and peripheral units. (b) In the compound $OsRu_3Pt_6$, the energy levels are in a cascade arrangement, and all the energy is channeled to the central unit. The position of the ^{3}MLCT level of the peripheral unit is not known.

In summary, following the synthetic strategy described above, we have succeeded in synthesizing the compound $OsRu_3Pt_6$, where the lowest energy excited states of the various units are in a cascade arrangement from the periphery to the center of the structure, thus obtaining a periphery-to-center energy gradient that resulted in an efficient antenna effect. It is worth underlining that introduction of the third metal (Pt) was essential to reach this goal.

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