

# Decanuclear Homo- and Heterometallic Polypyridine Complexes: Syntheses, Absorption Spectra, Luminescence, Electrochemical Oxidation, and Intercomponent Energy Transfer

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Received September 23, 1991

**Abstract:** Decanuclear homo- and heterometallic complexes of the general formula  $M_c[(BL)M_i(BL)M_p(L)_2]_3^{20+}$  have been prepared as  $PF_6^-$  salts. The central ( $M_c$ ), intermediate ( $M_i$ ), and peripheral ( $M_p$ ) metal ions are  $Ru^{2+}$  or  $Os^{2+}$ , BL is the bridging ligand 2,3-bis(2-pyridyl)pyrazine (2,3-dpp), and L is either 2,2'-bipyridine (bpy) or 2,2'-biquinoline (biq). The decanuclear complexes have been synthesized by the reaction of appropriate building blocks, namely  $M_c(BL)_3^{2+}$  cores, which contain three free chelating sites, with  $M_i[(BL)M_p(L)_2]Cl_2^{4+}$  species, which contain easily replaceable  $Cl^-$  ligands. The six compounds prepared contain the following metals (M) and ligands (L) (BL is 2,3-dpp in all cases): **1**,  $M_c = M_i = M_p = Ru^{2+}$ , L = bpy; **2**,  $M_c = M_i = M_p = Ru^{2+}$ , L = biq; **3**,  $M_c = Os^{2+}$ ,  $M_i = M_p = Ru^{2+}$ , L = bpy; **4**,  $M_c = Os^{2+}$ ,  $M_i = M_p = Ru^{2+}$ , L = biq; **5**,  $M_c = M_p = Os^{2+}$ ,  $M_i = Ru^{2+}$ , L = bpy; **6**,  $M_c = M_i = Ru^{2+}$ ,  $M_p = Os^{2+}$ , L = bpy. **1-6** display extremely intense L- and BL-centered absorption bands in the UV region ( $\epsilon$  up to  $\sim 6 \times 10^5 M^{-1} cm^{-1}$ ) and intense  $M \rightarrow L$  and  $M \rightarrow BL$  charge transfer (CT) bands in the visible region ( $\lambda_{max}$  around 550 nm,  $\epsilon$  about  $1.3 \times 10^5 M^{-1} cm^{-1}$ ). Cyclic voltammetry and differential pulse voltammetry measurements show that in **1** and **2** the first oxidation wave ( $E_{1/2} = +1.43$  and  $+1.62$  V, respectively) represents a six-electron process, as expected for independent reversible one-electron transfer, at the same potential, of the six peripheral  $Ru^{2+}$  ions, while oxidation of the central and of the three intermediates  $Ru^{2+}$  ions cannot be observed in the potential window examined ( $< +1.8$  V vs SCE). For **3** and **4**, two reversible waves are observed at  $+1.17$  and  $+1.50$  V (for **3**) and at  $+1.24$  and  $+1.59$  V (for **4**) with 1:6 intensity ratio, as expected for oxidation of the central  $Os^{2+}$  ion followed by oxidation of the six peripheral  $Ru^{2+}$  ions. For **5**, a reverse intensity pattern is observed (waves at  $+1.05$  and  $+1.39$  V, with 6:1 intensity ratio), as expected for oxidation of the six peripheral  $Os^{2+}$  ions followed by oxidation of the central  $Os^{2+}$  ion. For **6**, a six-electron process with  $E_{1/2} = +1.00$  V is observed, assigned to the oxidation of the six peripheral  $Os^{2+}$  ions. Compounds **1-4** exhibit luminescence in deaerated acetonitrile solution ( $\lambda_{max} = 809, 789, 808,$  and  $789$  nm;  $\tau = 55, 130, 65,$  and  $125$  ns, respectively), while no luminescence can be observed (below the instrumental limit of our equipment, 880 nm) for **5** and **6**. Corrected excitation spectra, luminescence lifetimes, and comparison with the known properties of analogous complexes of lower nuclearity show that (i) in **1** and **2** 100% efficient energy transfer occurs from the central and intermediate components to the peripheral components, where the lowest energy luminescent  $^3CT$  level is localized; (ii) in **3** and **4**, the broad luminescence band can be resolved into a weak emission resulting from the central Os-based component, which contains the lowest energy  $^3CT$  level, and a stronger emission originating from the peripheral Ru-based components; (iii) in **5** and **6**, the potentially luminescent  $M_c-$  and  $M_i-$  based components are quenched by the nonluminescent (at  $\lambda < 880$  nm) peripheral Os-based components. Supramolecular species like **1-6** are interesting because they contain many chromophoric and redox centers and, at least in four cases, display luminescence from relatively long-lived excited states.

## Introduction

Much attention is currently devoted to supramolecular species obtained by assembling molecular components.<sup>2</sup> When the components exhibit suitable properties and are assembled according to appropriate patterns, the resulting supramolecular systems may perform useful functions in several fields, such as information recording and conversion of light into chemical energy.

Transition metal complexes may be used as building blocks to synthesize polynuclear compounds which behave as supramolecular species. In most of the available polynuclear metal complexes, however, the number of metal atoms is either very small (di- and trinuclear compounds)<sup>2c</sup> or large and/or not well defined (polymeric species<sup>3</sup>).<sup>4</sup> New synthetic strategies are needed to obtain oligonuclear compounds where suitable components occupy specific and well defined sites in supramolecular arrays.

In the last few years we and others have developed a procedure to synthesize oligonuclear metal complexes of desired nuclearity and chemical structure. Such a procedure is based on the use of complexes in the place of both the metal (M) and the ligands (L) in the synthetic reaction



In eq 1 the place of M can be taken by mono- or polynuclear complexes which possess easily replaceable ligands, and the place

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(2) The literature on this topic is too vast to be exhaustively quoted. For recent reviews, see: (a) *Molecular Electronic Devices*; Carter, F. L., Siatkowski, R. E., Wohltjen, H., Eds.; North-Holland: Amsterdam, 1988. (b) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. (c) Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. *Top. Curr. Chem.* **1990**, *158*, 73. (d) *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, J., Dürr, H., Eds.; VCH: Weinheim, Germany, 1991. (e) Sauvage, J.-P. *Acc. Chem. Res.* **1990**, *23*, 319. (f) Vögtle, F. *Supramolecular Chemistry*; Wiley: Chichester, U.K., 1991. (g) Lindsey, J. S. *New J. Chem.* **1991**, *15*, 153. (h) Diederich, F. *Cyclophanes*; Royal Society of Chemistry: Cambridge, U.K., 1991. (i) Symposium on Molecular Architecture: Design, Synthesis, and Function of Supramolecular Structures; *J. Chem. Educ.* **1990**, *67*, 812-841. (j) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, U.K., 1991.

(3) See, e.g.: Strouse, G. F.; Worl, L. A.; Younathan, J. N.; Meyer, T. *J. Am. Chem. Soc.* **1989**, *111*, 9101.

(4) For a recent example of a species containing a large and well-defined number of metal-complex units, see: Beer, P. D.; Tite, E. L.; Ibbotson, A. *J. Chem. Soc., Dalton Trans.* **1991**, 1691.

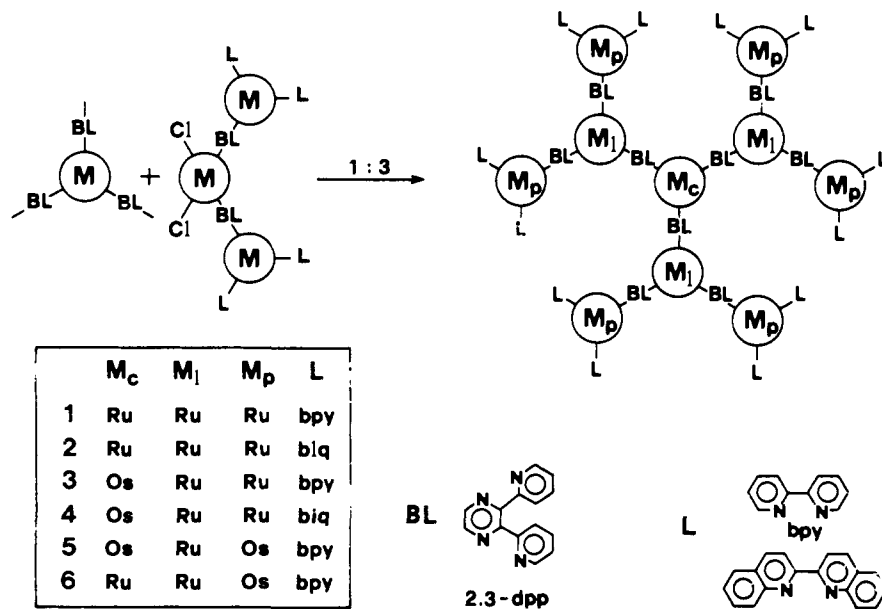


Figure 1. Schematic representation of the abbreviations used and of the synthesis of the decanuclear compounds.

Table I. Yields, Analytical Data, Selected IR Absorption Maxima and Conductivity Values of the Decanuclear Complexes

no.	yield <sup>a</sup>	elemental anal., <sup>b</sup> %			IR data <sup>c</sup>	$\Delta^d$
		C	H	N		
1 <sup>e</sup>	80	36.19 (36.60)	2.70 (2.57)	10.83 (10.41)	1605 (m), 1560 (w, br), 1470 (s), 1450 (s), 1420 (s), 1399 (s)	791
2 <sup>f</sup>	72	45.03 (44.99)	2.89 (2.63)	9.02 (9.20)	1592 (s), 1572 (w, sh), 1555 (w, sh), 1509 (s), 1460 (w, br), 1431 (w), 1412 (m), 1391 (m)	829
3 <sup>g</sup>	75	36.81 (36.36)	2.52 (2.50)	10.31 (10.34)	1605 (m), 1560 (w, br), 1468 (s), 1448 (s), 1420 (s), 1398 (s)	795
4 <sup>e</sup>	73	43.39 (43.97)	2.69 (2.73)	8.66 (8.97)	1592 (s), 1575 (w, sh), 1565 (w, sh); 1510 (s), 1465 (w, br), 1431 (w), 1415 (m), 1391 (m)	838
5 <sup>e</sup>	78	33.39 (33.97)	2.33 (2.39)	9.84 (9.66)	1609 (m), 1560 (w, br), 1469 (s), 1450 (m), 1425 (s), 1389 (s)	781
6 <sup>e</sup>	87	34.05 (34.47)	2.33 (2.37)	9.47 (9.80)	1605 (m), 1560 (w, br), 1466 (s), 1449 (m), 1420 (s), 1389 (s)	859

<sup>b</sup> Found (Calcd). <sup>c</sup>  $\text{cm}^{-1}$ , KBr pellets. <sup>d</sup>  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Approximately  $1 \times 10^{-3} \text{M}$  solutions in nitromethane, 20 °C. <sup>e</sup> Formulated with 10 mol of  $\text{H}_2\text{O}$ . <sup>f</sup> Formulated with 2 mol of  $\text{H}_2\text{O}$ . <sup>g</sup> Formulated with 8 mol of  $\text{H}_2\text{O}$ .

of L can be taken by mono- or polynuclear complexes which contain free chelating sites ("complexes as metals" and "complexes as ligands" strategy).

Ru(II)<sup>5</sup> and Os(II)<sup>6</sup> polypyridine complexes are ideal components to synthesize luminescent and redox-active oligonuclear species where energy and electron transfer can be driven by light. In the last few years we have concentrated our efforts on Ru(II) and Os(II) systems that contain the 2,3- and 2,5-bis(2-pyridyl)pyrazine (2,3- and 2,5-dpp) bridging ligands, and the 2,2'-bipyridine (bpy) and 2,2'-biquinoline (biq) terminal ligands. A great number of binuclear compounds of this family have been prepared in the past few years,<sup>2c,7</sup> and several trinuclear<sup>8</sup> and tetranuclear<sup>7d,9</sup>

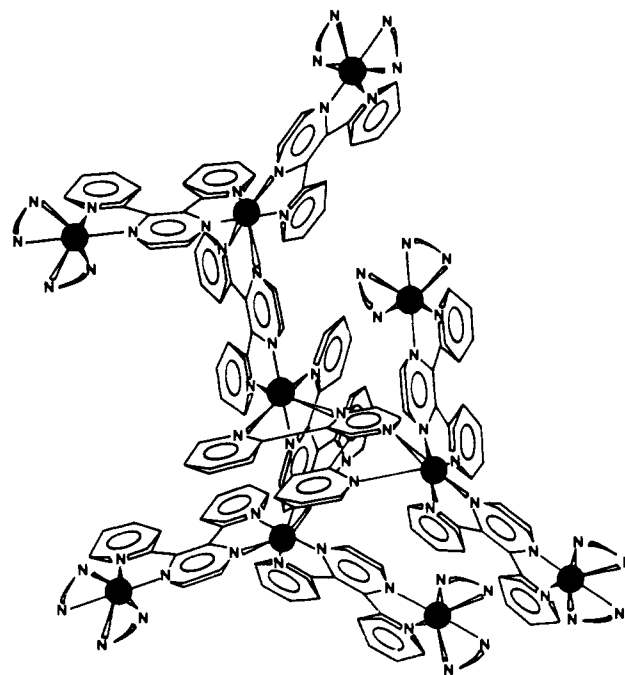


Figure 2. Schematic view of the structure of the decanuclear compounds. N-N stands for bpy or biq.

compounds, both homo- and heterometallic, have also been obtained. More recently, we have succeeded in preparing homo- and heterometallic hexanuclear compounds<sup>10</sup> and homometallic

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Table II. Spectroscopic, Photophysical and Electrochemical Data of the Building Blocks<sup>a</sup>

		absorption $\lambda_{\max}^b$ , nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )	luminescence				electrochemistry $E_{1/2}^{\text{ox}}$
			298 K		77 K <sup>c</sup>		
			$\lambda_{\max}$ , nm	$\tau$ , ns	$\lambda_{\max}$ , nm	$\tau$ , $\mu$ s	
7	Ru[(BL)Ru(bpy) <sub>2</sub> ] <sub>2</sub> Cl <sub>2</sub> <sup>4+</sup>	618 (24 300)	no luminescence for $\lambda < 880$ nm				+0.72, +1.45 <sup>d</sup>
8	Ru[(BL)Ru(biq) <sub>2</sub> ] <sub>2</sub> Cl <sub>2</sub> <sup>4+</sup>	624 (24 000)	no luminescence for $\lambda < 880$ nm				+0.88, +1.63 <sup>d</sup>
9	Ru[(BL)Os(bpy) <sub>2</sub> ] <sub>2</sub> Cl <sub>2</sub> <sup>4+</sup>	600 (25 200)	no luminescence for $\lambda < 880$ nm				+0.75, +1.15 <sup>d</sup>
10	Ru(BL) <sub>3</sub> <sup>2+</sup>	455 (13 000)	623	183 <sup>e</sup>	600	5.05	+1.68
11	Os(BL) <sub>3</sub> <sup>2+</sup>	475 (18 000)	766	82	723	0.85	+0.79

<sup>a</sup> Deaerated acetonitrile solution, unless otherwise noted; BL stands for 2,3-dpp. <sup>b</sup> Lowest energy maximum. <sup>c</sup> Methanol/ethanol 4:1 v/v rigid matrix. <sup>d</sup> Dielectronic wave. <sup>e</sup> Aerated solution.

heptanuclear species.<sup>11</sup> In this paper we report the synthesis of the decanuclear compounds 1–6, and we describe their absorption spectra, electrochemical oxidation, emission spectra, luminescence lifetimes and quantum yields, and intercomponent energy transfer.<sup>12</sup> The structural formulas of the compounds studied are shown in Figure 1. A schematic representation of the decanuclear compounds is shown in Figure 2.

### Experimental Section

**Materials and Methods.** The preparation of the precursor complexes M(2,3-dpp)<sub>3</sub><sup>2+</sup><sup>7c,9a</sup> and Ru[( $\mu$ -2,3-dpp)M(L)<sub>2</sub>]<sub>2</sub>Cl<sub>2</sub><sup>4+</sup><sup>9b,10</sup> as well as details and procedures<sup>14</sup> for characterization, absorption spectra, luminescence spectra and lifetimes, and electrochemical measurements has been previously reported. All reactions were performed under argon; those involving biq derivatives were also protected from light. Yields, elemental analyses, IR data, and conductivity values of the novel decanuclear compounds are collected in Table I.

[Ru( $\mu$ -2,3-dpp)Ru( $\mu$ -2,3-dpp)Ru(bpy)<sub>2</sub>]<sub>2</sub>(PF<sub>6</sub>)<sub>20</sub> (1). To a solution of [Ru( $\mu$ -2,3-dpp)Ru(bpy)<sub>2</sub>]<sub>2</sub>Cl<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub> (0.116 g, 0.057 mmol) in 2:1 (v/v) methanol/water (4 mL) was added solid AgNO<sub>3</sub> (0.019 g, 0.112 mmol). After 2 h of stirring at room temperature [Ru(2,3-dpp)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (0.0206 g, 0.019 mmol) and ethylene glycol (4 mL) were added, and the mixture was refluxed for 48 h. After removal of AgCl by repeated centrifugation, an excess of solid NH<sub>4</sub>PF<sub>6</sub> was added to the mother liquor and the cyclamen solid thus obtained filtered out. The product was purified by size exclusion (chromatography) on Sephadex G-25 (acetonitrile eluant). From the eluate the product was recovered as a cyclamen powder by addition of ethanol and partial evaporation in vacuo. Yield after purification: 0.118 g (80%).

[Ru( $\mu$ -2,3-dpp)Ru( $\mu$ -2,3-dpp)Ru(biq)<sub>2</sub>]<sub>2</sub>(PF<sub>6</sub>)<sub>20</sub> (2). The synthetic procedure was analogous to that for 1: employed quantities, [Ru( $\mu$ -2,3-dpp)Ru(biq)<sub>2</sub>]<sub>2</sub>Cl<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub> (0.0460 g, 0.019 mmol) suspended in 1:1 (v/v) methanol/water (3 mL); AgNO<sub>3</sub> (0.0064 g, 0.038 mmol); [Ru(2,3-dpp)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (0.0068 g, 0.0063 mmol); and ethylene glycol, 3 mL. At the end of the reaction, together with an excess of NH<sub>4</sub>PF<sub>6</sub>, methanol (2 mL) and diethyl ether (8 mL) were added in order to facilitate the precipitation of the crude product that was obtained as a violet powder and purified as 1: yield after purification, 0.041 g (72%).

[Os( $\mu$ -2,3-dpp)Ru( $\mu$ -2,3-dpp)Ru(bpy)<sub>2</sub>]<sub>2</sub>(PF<sub>6</sub>)<sub>20</sub> (3). The synthetic procedure was analogous to that used for 1: employed quantities, [Ru( $\mu$ -2,3-dpp)Ru(bpy)<sub>2</sub>]<sub>2</sub>Cl<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub> (0.0495 g, 0.0242 mmol) suspended in 1:1 (v/v) methanol/water (3 mL); AgNO<sub>3</sub> (0.0082 g, 0.048 mmol); [Os(2,3-dpp)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (0.0095 g, 0.008 mmol); and ethylene glycol, 3 mL; violet powder; yield after purification, 0.048 g (75%).

[Os( $\mu$ -2,3-dpp)Ru( $\mu$ -2,3-dpp)Ru(biq)<sub>2</sub>]<sub>2</sub>(PF<sub>6</sub>)<sub>20</sub> (4). The synthetic procedure was analogous to that used for 2: employed quantities, [Ru( $\mu$ -2,3-dpp)Ru(biq)<sub>2</sub>]<sub>2</sub>Cl<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub> (0.053 g, 0.022 mmol); 95% ethanol (3 mL); AgNO<sub>3</sub> (0.0073 g, 0.044 mmol); [Os(2,3-dpp)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (0.0085 g, 0.007 mmol); and ethylene glycol, 3 mL; violet powder; yield after purification, 0.048 g (73%).

[Os( $\mu$ -2,3-dpp)Ru( $\mu$ -2,3-dpp)Os(bpy)<sub>2</sub>]<sub>2</sub>(PF<sub>6</sub>)<sub>20</sub> (5). The synthetic procedure was analogous to that used for 1: employed quantities, [Ru( $\mu$ -2,3-dpp)Os(bpy)<sub>2</sub>]<sub>2</sub>Cl<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub> (0.080 g, 0.036 mmol) suspended in

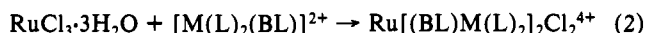
95% ethanol (6 mL); AgNO<sub>3</sub> (0.012 g, 0.072 mmol) dissolved in water (2 mL); [Os(2,3-dpp)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (0.0142 g, 0.012 mmol); and ethylene glycol, 3 mL; violet powder; yield after purification, 0.080 g (78%).

[Ru( $\mu$ -2,3-dpp)Ru( $\mu$ -2,3-dpp)Os(bpy)<sub>2</sub>]<sub>2</sub>(PF<sub>6</sub>)<sub>20</sub> (6). The synthetic procedure was analogous to that used for 2: employed quantities, [Ru( $\mu$ -2,3-dpp)Os(bpy)<sub>2</sub>]<sub>2</sub>Cl<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub> (0.0836 g, 0.037 mmol) suspended in 95% ethanol (3 mL); AgNO<sub>3</sub> (0.0128 g, 0.075 mmol) dissolved in water (1.5 mL); [Ru(2,3-dpp)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (0.0137 g, 0.012 mmol); and ethylene glycol, 3 mL; violet powder; yield after purification, 0.091 g (87%).

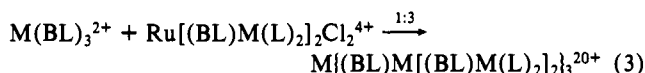
Luminescence spectra at room temperature were obtained with a Perkin-Elmer 650-40 spectrofluorimeter and those at 77 K with a Perkin-Elmer LS-50 spectrofluorimeter. The red limit of this equipment is 880 nm. Emission lifetimes were measured with an Edinburgh single-photon counting equipment. Electrochemical measurements were carried out at room temperature with a PAR 273 multipurpose equipment interfaced to a PC. The working electrode was a Pt microelectrode. 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<sup>-4</sup> M. Tetraethylammonium tetrafluoroborate was used as supporting electrolyte. The scan rate was 20 mV s<sup>-1</sup> and the pulse height was 50 mV. For reversible processes, half-wave potentials (vs SCE) were calculated as an average of the cathodic and anodic peaks. The criteria for reversibility were the separation between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. Ferrocene (5 × 10<sup>-4</sup> M) was always present as a standard. Experimental errors in the reported data are as follows: absorption maxima, 2 nm; emission maxima, 5 nm; emission lifetimes, 10%; emission quantum yields, 20%; redox potentials, 20 mV. As far as the molar absorption coefficients are concerned, the uncertainty in their absolute values is ~10% because of the highly diluted solutions used (10<sup>-5</sup>–10<sup>-4</sup> M).

### Results

The trinuclear compounds {Ru[(BL)M(L)<sub>2</sub>]<sub>2</sub>Cl<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub> (7, M = Ru, L = bpy; 8, M = Ru, L = biq; 9, M = Os, L = bpy) have been synthesized as shown in eq 2, by using two M(L)<sub>2</sub>(BL)<sup>2+</sup> complexes<sup>6b,14</sup> as entering ligands on RuCl<sub>3</sub>·3H<sub>2</sub>O:



The decanuclear compounds 1–6 have been obtained (Figure 1, eq 3) from the reaction of the mononuclear M(BL)<sub>3</sub><sup>2+</sup> "complex ligand" cores<sup>7c,9a</sup> (10, M = Ru; 11, M = Os) with the appropriate "complex metal" species 7–9:<sup>9b,10</sup>



To promote the Cl<sup>-</sup> equation reaction, which is usually a somewhat difficult thermal process, the trinuclear complexes have been treated at room temperature with 2 equiv of Ag<sup>+</sup>. For the following step a reaction temperature of 120–130 °C was adopted, so that the reaction could be complete within 2 days. The preparation and characterization data, including elemental analysis, IR spectra, conductivity values, and FAB mass spectra, for the building blocks 7–11 are reported elsewhere.<sup>9a,10</sup>

For the decanuclear complexes, satisfactory elemental analyses and consistent conductivity values were obtained (Table I). IR spectra were in agreement with the presence of  $\mu$ -dpp ligands, as already discussed for other oligonuclear species.<sup>14</sup>

The absorption, luminescence, and electrochemical data for the precursor complexes 7–11 are collected in Table II. The wavelengths and molar absorption coefficients of the lowest energy

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(12) For a preliminary communication, see ref 13.

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Table III. Spectroscopic, Photophysical and Electrochemical Data of the Decanuclear Compounds<sup>a</sup>

		absorption $\lambda_{\max}$ , nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )	luminescence					electrochemistry $E_{1/2}^{\text{ox}}$ [V] <sup>c</sup>
			298 K			77 K <sup>b</sup>		
			$\lambda_{\max}$ , nm	$\tau$ , ns	$\Phi$	$\lambda_{\max}$ , nm	$\tau$ , $\mu$ s	
1	Ru{(BL)Ru[(BL)Ru(bpy) <sub>2</sub> ] <sub>2</sub> ] <sub>3</sub> } <sup>20+</sup>	541 (125 000)	809	55	$1.0 \times 10^{-3}$	725	1.28	+1.43[5.7]
2	Ru{(BL)Ru[(BL)Ru(biq) <sub>2</sub> ] <sub>2</sub> ] <sub>3</sub> } <sup>20+</sup>	555 (109 500)	789	130	$0.6 \times 10^{-3}$	722	1.65	+1.62[5.4]
3	Os{(BL)Ru[(BL)Ru(bpy) <sub>2</sub> ] <sub>2</sub> ] <sub>3</sub> } <sup>20+</sup>	550 (117 000)	808, (860) <sup>d</sup>	65	<i>e</i>	720	1.33	+1.17[1.0], +1.50[5.5]
4	Os{(BL)Ru[(BL)Ru(biq) <sub>2</sub> ] <sub>2</sub> ] <sub>3</sub> } <sup>20+</sup>	556 (117 500)	789, (860) <sup>f</sup>	125	<i>g</i>	722	1.71	+1.24[0.9], +1.59[5.5]
5	Os{(BL)Ru[(BL)Os(bpy) <sub>2</sub> ] <sub>2</sub> ] <sub>3</sub> } <sup>20+</sup>	563 (140 500)			no luminescence for $\lambda < 880$ nm			+1.05[6.0], +1.39[0.9]
6	Ru{(BL)Ru[(BL)Os(bpy) <sub>2</sub> ] <sub>2</sub> ] <sub>3</sub> } <sup>20+</sup>	560 (132 500) 721 (35 000)			no luminescence for $\lambda < 880$ nm			+1.00[5.9]

<sup>a</sup> Deaerated acetonitrile solution, unless otherwise noted; BL stands for 2,3-dpp. <sup>b</sup> Methanol/ethanol 4:1 v/v rigid matrix. <sup>c</sup> The numbers between brackets indicate the relative areas of the differential pulse voltammetric waves normalized to the area of the first oxidation wave of 3; estimated uncertainty, 10%. <sup>d</sup> Emission maximum obtained after subtraction of the luminescence spectrum of 1 from that of 3. <sup>e</sup>  $\Phi$  around  $5 \times 10^{-4}$ , but its actual value depends on the excitation wavelength, see text. <sup>f</sup> Emission maximum obtained after subtraction of the luminescence spectrum of 2 from that of 4. <sup>g</sup>  $\Phi$  around  $3 \times 10^{-4}$ , but its actual value depends on the excitation wavelength, see text.

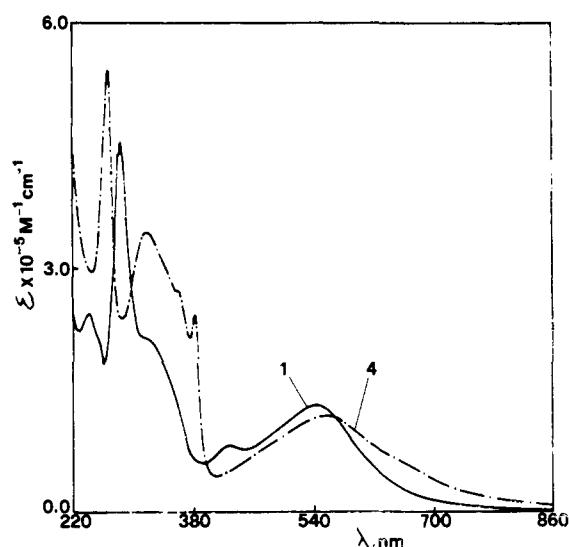


Figure 3. Absorption spectra of compounds 1 and 4.

absorption maxima, the luminescence data, and some electrochemical potentials of complexes 1–6 are collected in Table III. The absorption spectra of complexes 1 and 4 in acetonitrile solutions at 298 K are displayed in Figure 3. For compounds 1 and 3, only one emission band was observed, and corrected excitation spectra have shown that the intensity of the luminescence band is independent of the excitation wavelength. Compounds 3 and 4 exhibited a single emission band at 77 K, whereas at room temperature the luminescence band was very broad and apparently constituted by two components (see, e.g., Figure 4). For 3 and 4, different excitation spectra were obtained depending on the wavelength at which emission was recorded. Recording on the blue side of the emission band increases the relative intensity of the Ru-centered CT absorption bands, whereas recording in the red-side increases the relative intensity of the Os-centered CT absorption. By subtracting a normalized spectrum of 1 and 2 from the emission band of 3 and 4, respectively, a lower energy band was obtained whose maximum is also shown in Table III. No luminescence (below 880 nm) was observed for 5 and 6 both at room temperature and in rigid matrix at 77 K.

The electrochemical behavior was studied in acetonitrile solution by cyclic voltammetry and differential pulse voltammetry. The differential pulse voltammograms for the oxidation of compounds 1, 3, and 5, recorded in the presence of ferrocene as an internal standard, are shown in Figure 5. The half-width of the differential pulse voltammetry peaks is  $(95 \pm 5)$  mV for the ferrocene wave and  $(110 \pm 10)$  mV for the waves of the complexes. In the case of 3, a reversible oxidation wave at +1.17 V is followed by a much higher, reversible wave at +1.50 V. The ratio of the areas of the two waves is approximately 1:6. Two waves with about 1:6 area ratio are also observed for 4 at +1.24 and +1.59 V. In the case of 5 two waves with 1:6 area ratio were again observed, but the

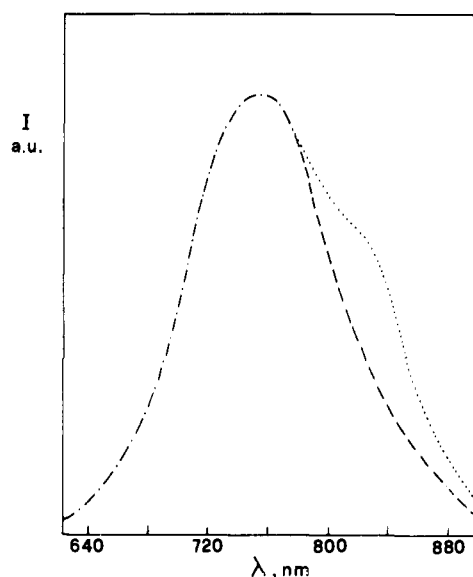


Figure 4. Uncorrected luminescence spectra of 4 (dotted line) and 2 (dashed line).

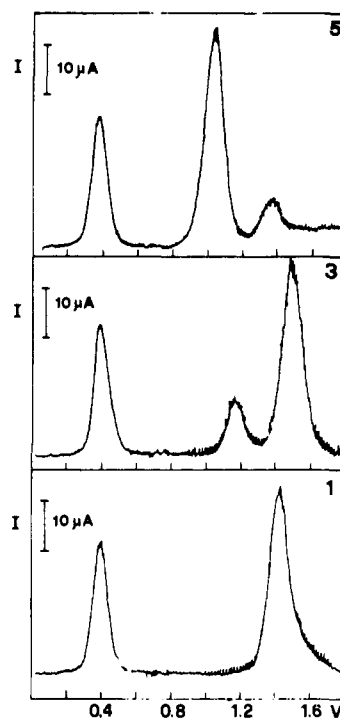


Figure 5. Differential pulse voltammograms of compounds 1, 3, and 5. The peak at 0.40 V is ferrocene used as a reference.

one with the larger area occurs at a less positive potential (+1.05 V) than the other one (+1.39 V). For **1**, **2**, and **6** only one wave can be observed, at +1.43, +1.62, and +1.00 V, respectively. The areas of all the oxidation waves have been normalized to that of the first oxidation wave of **3** by comparison with the area of the oxidation band of ferrocene, which was present in the same concentration in all the experiments (for more details, see Discussion). The values so obtained are shown in Table III.

### Discussion

**Syntheses.** The synthetic work reported in this paper shows that the "complexes as metals" and "complexes as ligands" strategy can profitably be used to obtain polynuclear species where the desired components are located in selected sites of the supramolecular array. This synthetic strategy represents an example of "structure-directed" synthesis<sup>15</sup> which allows complicated compounds to be prepared with high yield and satisfactory purity through relatively simple procedures. The key point of the complexes as metals and complexes as ligands strategy is obviously the availability of suitably designed building blocks. In our case such building blocks are the  $M(\text{BL})_3^{2+}$  "ligand" cores ( $M = \text{Ru}$  or  $\text{Os}$ ) and the  $\text{Ru}[(\text{BL})\text{M}(\text{L})_2]\text{Cl}_2^{4+}$  "complex metals". These precursor compounds are well characterized and can be obtained as pure materials.<sup>7c,7d,9a,9b,10</sup> The successive step (Figure 1, eq 3), which leads to the decanuclear species, is straightforward and takes place with high yield (70–90%). Possible side reactions would lead to hepta- and tetranuclear compounds with one and, respectively, two free chelating sites. No evidence for the formation of such compounds, which should have easily been detected by IR, TLC, and elemental analysis, was obtained. Furthermore, the (hypothetical) side products would display absorption, emission, and/or electrochemical properties clearly distinct from those of the decanuclear compounds. All the precursor complexes and the decanuclear compounds are stable in the reaction medium, and no evidence for ligand exchange was obtained.

The polymetallic species described in this work exhibit a three-dimensional branching structure of the type of those shown by the otherwise completely different compounds based on polyamidoamines or other organic components.<sup>16–19</sup> With the current procedure, equivalent supramolecular sites (e.g., the six peripheral ones in the decanuclear complexes, Figure 1) can only be occupied by the same type of metal ion. With the development of a protection-deprotection procedure of one of the chelating sites of the bridging ligands, which is in progress in our laboratories,<sup>10b</sup> it will be possible to synthesize less symmetric structures.

In principle, each decanuclear compound of the type described in this work can exist as different geometrical isomers, depending on the arrangement of the ligands around the metal ions. Preliminary <sup>99</sup>Ru and <sup>1</sup>H NMR data indicate that the  $\text{Ru}(\text{BL})_3^{2+}$  precursor is a single species and has a *mer* structure.<sup>20</sup> Each complex can also be a mixture of several diastereomeric species, owing to the chiral nature of each metal center. For these reasons, structural investigations on these systems are difficult.<sup>14</sup> Differences arising from the possible presence of isomeric species are not expected to be sizable in the electrochemical and spectroscopic results described in this paper.<sup>21</sup>

In the decanuclear compounds **1–6**, neglecting differences arising from the possible presence of geometrical or optical isomers, there are distinct topological sites (Figure 1): three for the metal ions (central (one), intermediate (three), and peripheral (six))

and two for the bridging ligands (inner (three) and outer (six)). The 12 L ligands occupy equivalent positions.

**Electrochemistry.** Because of the presence of as many as 21 polypyridine ligands, each one of which is capable of undergoing reduction processes,<sup>5</sup> the electrochemical reduction of the decanuclear compounds shows a very complex pattern. A first broad wave, which corresponds to the first one-electron reduction of the nine interacting bridging ligands, occurs at about –0.50 V and is followed by several other overlapping waves. In an attempt to arrive at an interpretation of the reduction processes, we plan to perform an investigation in DMF at low temperature (220 K).

A detailed study has been performed on the electrochemical oxidation (Table III, Figure 5). Previous investigations carried out on mono-, di-, tri-, tetra-, hexa-, and heptametallic compounds of this family<sup>6b,7–14</sup> have shown that (i) oxidation is metal centered; (ii)  $\text{Os}^{2+}$  is oxidized at potentials considerably less positive than  $\text{Ru}^{2+}$ ; (iii) the electron donor power decreases in the ligand series  $\text{bpy} > \text{biq} \geq \text{BL}$ ; and (iv) the interaction between equivalent metals is noticeable for metals coordinated to the same bridging ligand, whereas it is negligible for metals that are sufficiently far apart. The electrochemical behavior of the decanuclear compounds is fully consistent with such four statements.

Let us begin our discussion with compound **3** which contains one  $\text{Os}^{2+}$  and nine  $\text{Ru}^{2+}$  ions. On the basis of point (ii), the  $\text{Os}^{2+}$  ion is expected to be oxidized at less positive potentials than the nine  $\text{Ru}^{2+}$  ions, and, because of the different electron donor properties of the ligands (point (iii)), the six peripheral  $\text{Ru}^{2+}$  ions are expected to be oxidized at less positive potentials than the three intermediate  $\text{Ru}^{2+}$  ions. The differential pulse voltammogram of **3** (Figure 5) shows an oxidation wave at +1.17 V which is in the expected range for  $\text{Os}^{2+}$  oxidation<sup>6,9a</sup> and can therefore be assigned to one-electron oxidation of the central  $\text{Os}^{2+}$  metal ion and another wave at +1.50 V which has the same bandwidth but a six times higher intensity. Bard, Anson, and co-workers<sup>23</sup> have shown that molecules containing a number of identical noninteracting centers exhibit current-potential responses having the same shape as that obtained with the corresponding molecule containing a single center. Only the magnitude of the current is enhanced by the presence of additional electroactive centers. Accordingly, the wave at +1.50 V can be assigned to the independent one-electron oxidation of the six peripheral noninteracting  $\text{Ru}^{2+}$  ions. Oxidation of the three intermediate  $\text{Ru}^{2+}$  ions is further shifted toward more positive potentials (point (iii)) and cannot be observed in the potential window examined.

On the basis of similar arguments the two waves observed for **4** (Table III) can be assigned to oxidation of the central  $\text{Os}^{2+}$  ion followed by oxidation of the six peripheral  $\text{Ru}^{2+}$  ions. As expected on the basis of the above discussion (point (iii)), the oxidation potential of the peripheral  $\text{Ru}^{2+}$  ions is more positive in **4** than in **3**.

For **5**, one expects that oxidation involves first the six peripheral  $\text{Os}^{2+}$  ions and then the central one (point (iii) above). This is fully consistent with the differential pulse voltammetry results (Figure 5). The more positive oxidation potential of the central  $\text{Os}^{2+}$  ion in **5** compared to those of the same metal ion in **3** and **4** is obviously due to the presence of six already oxidized osmium ions when the central ion of **5** undergoes oxidation.

For **1**, **2**, and **6** only one oxidation wave is observed, so that internal comparison cannot be made. On the other hand, evaluation of the numbers of electrons involved in these waves by *direct* comparison with the area of the ferrocene oxidation wave would require a correction for the very different diffusion coefficients of ferrocene and of the decanuclear species. Such a procedure can be avoided since ferrocene is present at equal concentration in each experiment, so that it is possible to normalize the areas of the waves of complexes **1**, **2**, and **6** to those of complexes **3**, **4**, and **5** by using the wave of ferrocene as a comparison. The

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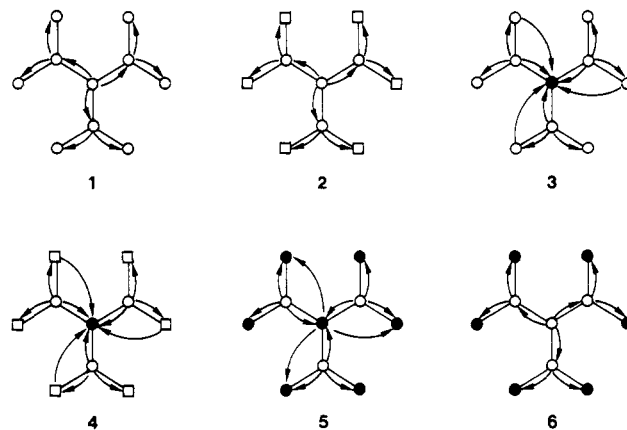
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values so obtained (Table III) show that the oxidation waves of **1**, **2**, and **6** correspond to the one-electron oxidation of six non-interacting units and can thus be assigned to the oxidation of the peripheral metal ions. It can also be noticed that the first oxidation potentials of the six compounds substantially follow the trend expected on the basis of points (ii) and (iii) discussed above.

**Absorption Spectra.** The absorption spectra of compounds **1–6** in acetonitrile solution (Figure 3) show extremely intense (up to  $\sim 600\,000\text{ M}^{-1}\text{ cm}^{-1}$ ) bands in the UV region and broad, intense (up to  $140\,000\text{ M}^{-1}\text{ cm}^{-1}$ ) bands in the visible region. The bands with maxima at 262 and 380 nm can be assigned to  $\pi \rightarrow \pi^*$  transitions of the biq ligands, the band at 282 nm to  $\pi \rightarrow \pi^*$  transitions on the bpy ligands, and the broad absorption in the 300–350-nm region to  $\pi \rightarrow \pi^*$  transitions in the biq and 2,3-dpp ligands. The broad bands observed in the visible region receive contribution by several types of metal-to-ligand charge-transfer (MLCT) transitions. The energies of these transitions depend on the nature of the donor metal ion, the acceptor ligand, and the ancillary ligands. Even in the case of the homometallic complexes **1** and **2**, five different types of "proximate"<sup>24</sup> MLCT transitions are expected because of the presence of three nonequivalent metal positions ( $M_c$ ,  $M_i$ , and  $M_p$ ) and two nonequivalent sites for the bridging ligands (Figure 1).

From the spectra of parent complexes<sup>6b,7-14</sup> and from the above discussed electrochemical data, the following trends can be predicted for the energy ordering of the metal-to-ligand charge-transfer transitions: (i) for the same acceptor ligand and the same ancillary ligands,  $\text{Os}^{2+} \rightarrow \text{acceptor ligand} < \text{Ru}^{2+} \rightarrow \text{acceptor ligand}$ ; (ii) for the same metal and ancillary ligands,  $M \rightarrow \text{BL} < M \rightarrow \text{biq} < M \rightarrow \text{bpy}$ ; (iii) for the same metal and the same acceptor ligands,  $(\text{bpy})_2M \rightarrow \text{acceptor ligand} < (\text{biq})_2M \rightarrow \text{acceptor ligand} < (\text{BL})_2M \rightarrow \text{acceptor ligand}$ . From a comparison of the absorption spectra of **1** and **4** (Figure 3) it is easy to assign the absorption band at about 430 nm to  $M \rightarrow \text{bpy}$  CT transitions. The broad band with maximum at  $\sim 550$  nm receives contributions from  $M \rightarrow \text{biq}$  and  $M \rightarrow \text{BL}$  CT transitions (see also Table III). It should be noticed that in the Os-containing compounds (particularly, in **5** and **6**) the absorption bands extend to the red because the probability of the singlet  $\rightarrow$  triplet transitions is relatively high owing to the enhanced spin-orbit coupling.<sup>6</sup>

**Luminescence Properties and Intercomponent Energy Transfer.** In the Ru(II) and Os(II) polypyridine complexes luminescence originates from the lowest MLCT excited state which is formally spin forbidden.<sup>5,6</sup> Deactivation of the upper excited states to the lowest one is a very fast (picosecond time scale)<sup>26</sup> and highly efficient (100%)<sup>27</sup> process. In the "localized molecular orbital" approach,<sup>5</sup> the excited electron and the corresponding hole are considered to be centered on the ligand and on the metal, respectively. In polynuclear Ru(II) and Os(II) polypyridine complexes<sup>2c,j,28</sup> both the coulombic and exchange energy transfer mechanisms may play a role, but the exchange mechanism (involving the lowest excited state of the donor) seems to be more effective, especially for short separation distances.<sup>2c,j</sup> Exchange energy transfer between two different ( $M_1 \rightarrow L_1$  and  $M_2 \rightarrow L_2$ ) CT excited states of a polynuclear complex can be viewed as a



**Figure 6.** Schematic representation of the energy-transfer processes in the decanuclear compounds. The arrows indicate the exoergic energy transfer steps. Empty and full circles indicate  $\text{Ru}^{2+}$  and  $\text{Os}^{2+}$ , respectively. In the peripheral positions, circles and squares indicate  $M(\text{bpy})_2$  and  $M(\text{biq})_2$  components, respectively.

two-electron transfer process,  $M_2 \rightarrow M_1$  and  $L_1 \rightarrow L_2$ .

On the basis of the electrochemical behavior and the absorption spectra of compounds **1–6** and of the properties of parent compounds, it can be expected that the energy of the (lowest) MLCT excited state of the various components which are present in the decanuclear compounds increases in the series  $(\text{bpy})_2\text{Os}_p \rightarrow \text{BL} < (\text{BL})_2\text{Os}_c \rightarrow \text{BL} < (\text{bpy})_2\text{Ru}_p \rightarrow \text{BL} < (\text{biq})_2\text{Ru}_p \rightarrow \text{BL} < (\text{BL})_2\text{Ru}_i \rightarrow \text{BL} < (\text{BL})_2\text{Ru}_c \rightarrow \text{BL}$ . The emission energies of the  $(\text{bpy})_2\text{Ru}_p \rightarrow \text{BL}$ ,  $(\text{biq})_2\text{Ru}_p \rightarrow \text{BL}$ , and  $(\text{BL})_2\text{Os}_c \rightarrow \text{BL}$  excited states should be very similar to the emission energies of the parent tetranuclear compounds  $\text{Ru}[(\text{BL})\text{Ru}(\text{bpy})_2]_3^{8+}$  (811 nm),<sup>14</sup>  $\text{Ru}[(\text{BL})\text{Ru}(\text{biq})_2]_3^{8+}$  (795 nm),<sup>14</sup> and  $\text{Os}[(\text{BL})\text{Ru}(\text{bpy})_2]_3^{8+}$  (860 nm).<sup>9a</sup> The emission of the  $(\text{bpy})_2\text{Os}_p \rightarrow \text{BL}$  excited state can be predicted to occur above 900 nm on the basis of the emission of  $\text{Os}[(\text{BL})\text{Ru}(\text{bpy})_2]_3^{8+}$  (870 nm)<sup>9a</sup> and the difference between the first oxidation potentials of **5** and **3** (0.12 V, Table III). The emission energy of the  $(\text{BL})_2\text{Ru}_c \rightarrow \text{BL}$  excited state can be estimated to occur at about 690 nm from comparison of the spectroscopic and electrochemical data of the  $M(\text{BL})_3^{2+}$  and  $M[(\text{BL})\text{Ru}(\text{bpy})_2]_3^{8+}$  complexes ( $M = \text{Ru}$  or  $\text{Os}$ ).<sup>29</sup> Finally, the emission energy of the  $(\text{BL})_2\text{Ru}_i \rightarrow \text{BL}$  excited state is expected to be slightly lower than that of the  $(\text{BL})_2\text{Ru}_c \rightarrow \text{BL}$  level; these components, in fact, have the same chemical constitution and only differ because the building blocks bound to the BL ligands are slightly different in the two cases.

The luminescent properties of compounds **1–6** (Table III) can be discussed on the basis of the above expectations and of the occurrence of intercomponent energy-transfer processes. The directions along which such processes are exoergic are schematically indicated by arrows in Figure 6. **1** displays a luminescence band at 809 nm that can be straightforwardly assigned to the peripheral  $(\text{bpy})_2\text{Ru} \rightarrow \text{BL}$  excited states. The lack of luminescence at shorter wavelengths and the constancy of the luminescence efficiency on changing the excitation wavelength indicate that the chromophoric groups based on the central and intermediate  $\text{Ru}^{2+}$  ion undergo an efficient deactivation to the  $\text{Ru}_p$ -based levels, as expected because energy transfer is exoergic in the direction from center to periphery (**1**, Figure 6). **2** exhibits exactly the same behavior as **1**. For compounds **3** and **4**, a broad luminescence band is observed at room temperature, with a shoulder on its low energy tail (see, e.g., Figure 4). The maxima of the luminescence bands almost coincide with those of the bands exhibited by **1** and **2**, respectively. The predominant emission can thus be assigned to the peripheral units, i.e., to the  $(\text{bpy})_2\text{Ru}_p \rightarrow$

(24) Charge-transfer transitions between remote centers can also be expected, but they give rise to much weaker absorption bands.<sup>25</sup>

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(29) The difference between the emission energies of  $\text{Os}(\text{BL})_3^{2+}$  and  $\text{Os}[(\text{BL})\text{Ru}(\text{bpy})_2]_3^{8+}$  is  $1600\text{ cm}^{-1}$ . Taking the emission energy of  $\text{Ru}(\text{BL})_3^{2+}$  ( $16050\text{ cm}^{-1}$ ) and assuming that the difference in the emission energies between the  $M(\text{BL})_3$  units of the mono- and tetranuclear compounds is the same for  $M = \text{Ru}$  or  $\text{Os}$ , one gets a value of  $\sim 14\,400\text{ cm}^{-1}$  ( $\sim 690\text{ nm}$ ) for the  $\text{Ru}_c(\text{BL})_3$  unit.

BL and  $(\text{biq})_2\text{Ru}_p \rightarrow \text{BL CT}$  excited states, respectively. Subtraction (after normalization) of the luminescence band of **1** from that of **3** and of **2** from that of **4** yields a band with maximum at  $\sim 860$  nm, as expected for a  $\text{Os}_c$ -based luminescence (vide supra). We conclude that at room temperature, **3** and **4** emit from both the central and the peripheral units. Such a behavior is consistent with the fact that in **3** and **4** the lowest excited state of the intermediate  $\text{Ru}_p$ -based units lies at higher energy ( $\sim 2000$   $\text{cm}^{-1}$ ) than the lowest excited state of the peripheral units. Thus for **3** and **4**, the two-step energy transfer process from the peripheral units to the central one (where the lowest energy excited state of the supramolecular array is located) must be very slow since its first step is endoergic by  $\sim 2000$   $\text{cm}^{-1}$ . Direct (through space) energy transfer from the peripheral to the central units is exoergic but should be slow because of the large separation distance. A quantitative evaluation of the energy transfer efficiency from the peripheral to the central unit is difficult to make from luminescence quantum yield data because of the strong overlap between the absorption bands of the various units. From a comparison of the luminescence lifetime data for **1** and **3** and **2** and **4**, respectively, it is clear, however, that the quenching of the peripheral excited states by the central one in **3** and **4** is negligible.

For **5** and **6** the lowest excited states are localized on the peripheral  $(\text{bpy})_2\text{Os} \rightarrow \text{BL}$  units which are expected to emit around 900–950 nm. As mentioned above, such an emission is outside the sensitivity range of our equipment.<sup>30</sup> The lack of luminescence for **6** is therefore an expected result in view of the central-to-periphery gradient for energy transfer, as shown in Figure 6. For **5**, deactivation of the central  $\text{Os}$ -based unit by the peripheral ones should not occur because the first step of this process is endoergic (Figure 6). The lack of observable luminescence from such a central unit may simply be due to the fact that most of the light, at any excitation wavelength, is absorbed by the much more numerous peripheral and intermediate units.

### Conclusions

By using the "complexes as ligands" and "complexes as metals" strategy we have synthesized six decanuclear, homo- and heterometallic, complexes of general formula  $\text{M}_c\{(\text{BL})\text{M}_i\}[(\text{BL})\text{M}_p-$

$(\text{L})_2]_2\}_3^{20+}$  (Figures 1 and 2). The synthetic procedure, based on the reaction of  $\text{M}_c(\text{BL})_3^{2+}$  cores with trinuclear  $\text{M}_i\{(\text{BL})\text{M}_p-(\text{L})_2\}_2\text{Cl}_2^{4+}$  species, is relatively simple and versatile. By changing the metals and/or the ligands of the building blocks, it is possible to prepare complexes where different metals and/or ligands occupy predetermined positions in the supramolecular array.

The decanuclear complexes exhibit extraordinarily large molar absorption coefficients in the UV and visible spectral region. Furthermore, the excitation energy can be channeled in the desired direction (e.g., from the center to the periphery or vice versa) by a suitable choice of the components. Strong absorption in the visible range and the possibility to predetermine the direction of energy migration are important properties for the design of "photochemical molecular devices"<sup>31</sup> (e.g., for spectral sensitization of semiconductor electrodes<sup>32,33</sup>). The luminescent properties of the decanuclear complexes are useful to investigate the energy migration processes and are also interesting for fundamental reasons.

The examined complexes contain not only several chromophoric units but also a great number of redox-active centers. Each one of the 21 ligands (Figure 1) may be reduced, and each one of the 10 metal ions can be oxidized. While the reduction processes have not been examined in detail, the oxidation behavior has evidenced a selectivity based on the nature of the metal ion and on its location in the supramolecular array. Therefore, the electrochemical data offer a fingerprint of the chemical and topological structure of the compounds. Because of the presence of interacting and noninteracting redox centers, these complexes are good candidates to play a role of multielectron-transfer catalysts. These and other interesting aspects of the chemistry of the decanuclear compounds (e.g., intervalence-transfer transitions in partly oxidized species; interaction between excited states of the same compound after simultaneous multiphoton absorption; and bimolecular-type interactions) are presently under investigation in our laboratories.

**Acknowledgment.** We thank Dr. F. Stillitani, Mr. V. Cacciari, Mr. L. Minghetti, and Mr. G. Gubellini for technical assistance. Financial support from the Ministero della Pubblica Istruzione and Progetto Finalizzato CNR Chimica Fine II is gratefully acknowledged.

(31) Reference 2j, chapter 12.

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(30) Preliminary experiments performed with an infrared sensitive equipment have shown that **5** and **6** exhibit a luminescence band at about 900 nm at 80 K (work in progress with H. G. Güdel and G. Frei).