

(1,3-butadiene) or a minimum (glyoxal) at the cis position, the potential functions for the diaza compounds have their maxima at the cis position. The barriers to internal rotation around the N—N bond are predicted to be much higher ( $\Delta E_{MP}^{MP} = 14.5$  and  $14.7$  kcal mol<sup>-1</sup>, respectively) than those around C—C bonds ( $\Delta E_{HF}^{HF} = 6.07^3$  and  $5.7^{17}$  kcal mol<sup>-1</sup> in 1,3-butadiene and its perfluorinated species or  $6.80^{10a}$  and  $5.23^{20}$  kcal mol<sup>-1</sup> in glyoxal or oxalyl fluoride). Further distinct differences between 1,3-butadiene and glyoxal on one hand and 2,3-diaza-1,3-butadiene on the other hand, are the geometry changes occurring during internal rotation. The C—C bond lengths have their minimum values at the trans configuration, their maximum values near the barrier, and intermediate values at the cis position.<sup>3,10c</sup> (The variations of the C—C bond lengths in glyoxal reported in ref 10a differ from those reported in ref 10c.) On the other hand, the N—N bond in CH<sub>2</sub>=N—N=CH<sub>2</sub> shortens in going from trans to gauche by about 0.028 Å and increases to a maximum value at the cis position. In CF<sub>2</sub>=N—N=CF<sub>2</sub> the N—N bond has

its maximum length at the trans configuration and shortens monotonically in going to cis. A strong difference between the =C—C= and =N—N= skeletons is also evident from the variations in the bond angles upon internal rotation; whereas the C—C=C and C—C=O bond angles increase only slightly by 3.2 and 1.6° between trans and cis configuration, the N—N=C angles increase by 10.0 and 15.5° in the parent and fluorinated species. This strong angle distortion can be considered as a consequence of the much smaller value for the "unstrained" N—N=C angle in the trans position (112.3°) relative to the corresponding values for C—C=C (124.0°) or C—C=O (121.1°).

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## Photophysical, Photochemical, and Electrochemical Properties of Mononuclear and Dinuclear Ruthenium(II) Complexes Containing 2,2'-Bipyridine and the 3,5-Bis(pyridin-2-yl)-1,2,4-triazolate Ion

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The absorption spectra, luminescence spectra (from 77 to 298 K), luminescence lifetimes (from 77 to 298 K), luminescence quantum yields, photochemical quantum yields, and redox potentials of the complexes Ru(bpy)<sub>2</sub>(bpt)<sup>+</sup> (**1**) and [Ru(bpy)<sub>2</sub>]<sub>2</sub>(bpt)<sup>3+</sup> (**2**), where bpy = 2,2'-bipyridine and Hbpt = 3,5-bis(pyridin-2-yl)-1,2,4-triazole, are reported. The properties exhibited by **1** and **2** are compared with those of Ru(bpy)<sub>3</sub><sup>2+</sup>. For both **1** and **2**, the lowest energy absorption band and the luminescence band are attributed to Ru → bpy metal-to-ligand charge-transfer (MLCT) singlet and triplet excited states, respectively. Electrochemical oxidation is centered on the metal(s) and electrochemical reduction is centered on the ligands, with bpy being reduced at potentials less negative than those of bpt<sup>-</sup>. Because of the stronger σ-donor ability of bpt<sup>-</sup> compared with bpy, the Ru → bpy CT absorption and emission bands of **1** ( $\lambda_{\max}^{\text{abs}} = 480$  nm and  $\lambda_{\max}^{\text{em}} = 678$  nm in CH<sub>3</sub>CN at room temperature) are red-shifted compared with those of the parent Ru(bpy)<sub>3</sub><sup>2+</sup> complex. Both absorption and emission move to higher energies in going from **1** to **2** (for **2**:  $\lambda_{\max}^{\text{abs}} = 453$  nm and  $\lambda_{\max}^{\text{em}} = 648$  nm). In nitrile rigid matrix at 77 K the emission lifetimes are 2.8 and 3.6 μs for **1** and **2**, respectively. For both complexes increasing temperature causes a strong decrease of the emission lifetime (0.16 μs for **1** and 0.10 μs for **2** at room temperature), but the ln(1/τ) vs 1/T plots between 77 and 298 K are quite different in the two cases, indicating that (i) the luminescent excited state of **1** is much more sensitive than that of **2** to the melting of the solvent matrix and (ii) the luminescent excited state of **2**, but not that of **1**, undergoes a thermally activated ( $\Delta E = 3200$  cm<sup>-1</sup>) radiationless transition to an upper, short-lived excited state (presumably, a triplet metal-centered level <sup>3</sup>MC). In agreement with the expectation based on the temperature dependence of the luminescence lifetime, **2**, but not **1**, undergoes a photodissociation reaction in CH<sub>2</sub>Cl<sub>2</sub> solutions containing Cl<sup>-</sup> ions. Such a photoreaction leads to **1** and Ru(bpy)<sub>2</sub>Cl<sub>2</sub>. All the observed properties show that in **2** the lowest unoccupied molecular orbital does not belong to the bpt<sup>-</sup> bridging ligand but to the terminal bpy ligands. Because of the nonequivalence of the coordinating positions of the bridging ligand, in **2** the MLCT and MC levels related to the two Ru(bpy)<sub>2</sub><sup>2+</sup> units are not isoenergetic. It is found that the lowest excited state of **2** (responsible for the luminescence) is a <sup>3</sup>MLCT level centered on one Ru(bpy)<sub>2</sub><sup>2+</sup> unit, whereas photochemistry takes place from a <sup>3</sup>MC level centered on the other Ru(bpy)<sub>2</sub><sup>2+</sup> unit.

### Introduction

Ruthenium(II)-polypyridine complexes constitute a quite large family of coordination compounds. In the past 15 years this family has been the object of extensive investigation related to the interesting photochemical, photophysical, and electrochemical properties of most of its members.<sup>2-6</sup>

In recent years there has been a growing interest toward supramolecular species (dinuclear and polynuclear complexes, host-guest systems, etc.) with the aim to arrive at the design of photochemical molecular devices (proper assemblies of molecular components capable of performing useful light-induced functions).<sup>7</sup> Ruthenium(II)-polypyridine complexes are excellent building blocks for the construction of such devices, especially for light-induced migration and/or collection of electronic energy or electronic charge. Therefore, it is not surprising that the number of investigations concerning the photochemical and photophysical

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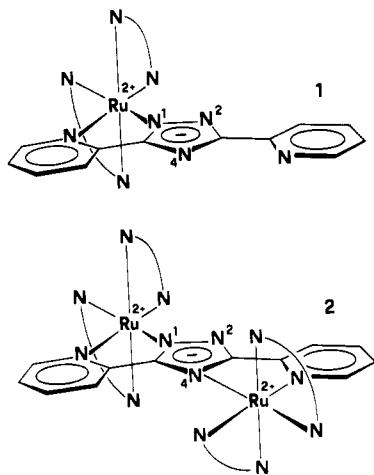


Figure 1. Schematic representation of the complexes studied. Note that 2 is actually a mixture of several isomers.<sup>9</sup>

behavior of dinuclear or polynuclear ruthenium(II)–polypyridine complexes is rapidly growing.<sup>8–25</sup>

- (8) The research activity on polynuclear complexes is extremely vast. A general reference concerning the results obtained before 1983 is *Prog. Inorg. Chem.* **1983**, *30* (dedicated to H. Taube). For some recent photochemical and photophysical studies, see ref 9–24.
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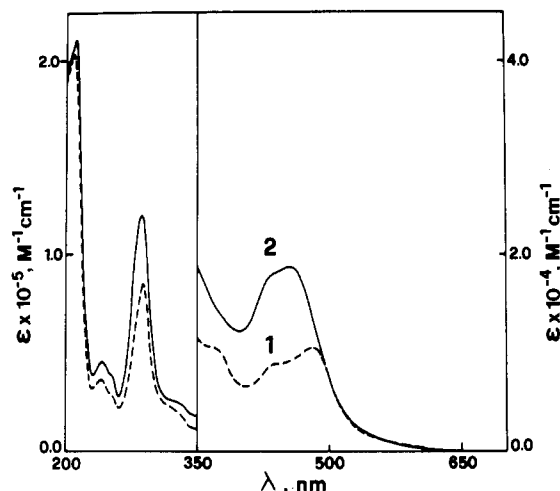


Figure 2. Absorption spectra in acetonitrile solution at room temperature: (1) Ru(bpy)<sub>2</sub>(bpt)<sup>+</sup>; (2) [Ru(bpy)<sub>2</sub>]<sub>2</sub>(bpt)<sup>3+</sup>.

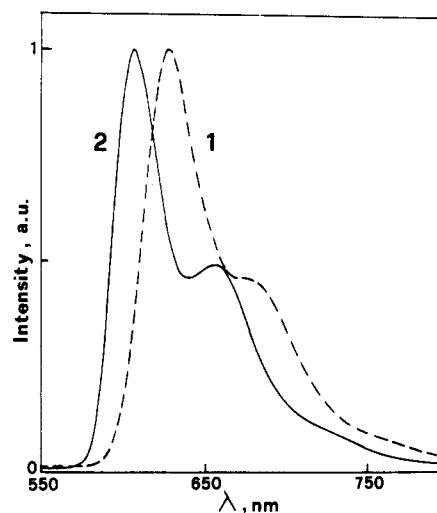


Figure 3. Luminescence spectra in nitrile rigid matrix at 77 K: (1) Ru(bpy)<sub>2</sub>(bpt)<sup>+</sup>; (2) [Ru(bpy)<sub>2</sub>]<sub>2</sub>(bpt)<sup>3+</sup>.

A key component in such systems is the bridging ligand, since the interaction between the bridged units, and thereby the properties of the supramolecular species, is critically dependent on the size, shape, and electronic nature of the bridge.<sup>26</sup> In several instances the bridge is also directly involved in electrochemical reduction and/or light excitation and emission processes. The anion of 3,5-bis(pyridin-2-yl)-1,2,4-triazole<sup>27</sup> is a particularly interesting bridge because, contrary to most of the previously used polypyridine bridges, it carries a negative charge and exhibits a high  $\sigma$ -donor and a low  $\pi$ -acceptor ability. Furthermore, its two bidentate functions are different, because the central triazole ring uses the N<sup>1</sup> (or N<sup>2</sup>) and N<sup>4</sup> nitrogen atoms for coordination.

In a previous paper<sup>9a,b</sup> the synthesis and characterization of the mononuclear Ru(bpy)<sub>2</sub>(bpt)<sup>+</sup> (1) and dinuclear [Ru(bpy)<sub>2</sub>]<sub>2</sub>(bpt)<sup>3+</sup> (2) complexes (Figure 1) have been reported together with the redox potentials and some spectroscopic properties. The X-ray structure of [Ru(bpy)<sub>2</sub>(bpt)]PF<sub>6</sub>·1/2H<sub>2</sub>O has also been published.<sup>9c</sup> In this paper we report the luminescence spectra and lifetimes of 1 and 2 in the temperature range 77–298 K, the luminescence and photoreaction quantum yields, and the complete reduction patterns. The results obtained are discussed and compared with those of Ru(bpy)<sub>3</sub><sup>2+</sup>.

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**Table I.** Absorption Bands and Luminescence Properties

	abs <sup>a</sup> (298 K)		emission <sup>b</sup>							photochem <sup>c</sup> (298 K) $\Phi_d$
			77 K		298 K			$10^3 \Phi_{em}^e$		
	$\lambda_{max}$ , nm	$\epsilon_{max}$ , M <sup>-1</sup> cm <sup>-1</sup>	$\lambda_{max}$ , nm	$\tau$ , $\mu$ s	$\lambda_{max}$ , nm	$\tau$ , <sup>d</sup> $\mu$ s	$\tau$ , <sup>e</sup> $\mu$ s			
Ru(bpy) <sub>3</sub> <sup>2+</sup>	452	13 000	582	4.8	615	0.80	0.17	14.0	$2.2 \times 10^{-3}$	
Ru(bpy) <sub>2</sub> bpt <sup>+</sup>	480	9 900	628	2.8	678	0.16	0.07	3.0	$<5.0 \times 10^{-5}$	
[Ru(bpy) <sub>2</sub> ] <sub>2</sub> bpt <sup>3+</sup>	453	18 500	608	3.6	648	0.10	0.056	2.1	$4.4 \times 10^{-3}$	

<sup>a</sup> Acetonitrile solution. <sup>b</sup> Nitrile solution. <sup>c</sup> CH<sub>2</sub>Cl<sub>2</sub> solutions containing Cl<sup>-</sup> ions (see text). <sup>d</sup> Deaerated solution. <sup>e</sup> Aerated solution.

### Experimental Section

3,5-Bis(pyridin-2-yl)-1,2,4-triazole (Hbpt) was prepared according to literature methods.<sup>27</sup> The mononuclear Ru(bpy)<sub>2</sub>(bpt)(PF<sub>6</sub>) and dinuclear [(Ru(bpy)<sub>2</sub>]<sub>2</sub>(bpt)(PF<sub>6</sub>)<sub>3</sub> complexes were obtained and characterized as previously described.<sup>9</sup> All the employed solvents were of the best grade commercially available.

The absorption spectra were recorded with a Perkin-Elmer  $\lambda_5$  or Kontron Uvikon 860 spectrophotometer. Uncorrected emission spectra were obtained with a Perkin-Elmer MPF-44B spectrofluorometer equipped with a Hamamatsu R928 tube. Corrected emission spectra were obtained with a Perkin-Elmer LS5 spectrofluorometer using a calibrated light source. Emission quantum yields were obtained with the optically diluted method using Ru(bpy)<sub>3</sub><sup>2+</sup> in deaerated CH<sub>3</sub>CN solution as a standard ( $\Phi_{em} = 0.062$ ).<sup>28</sup>

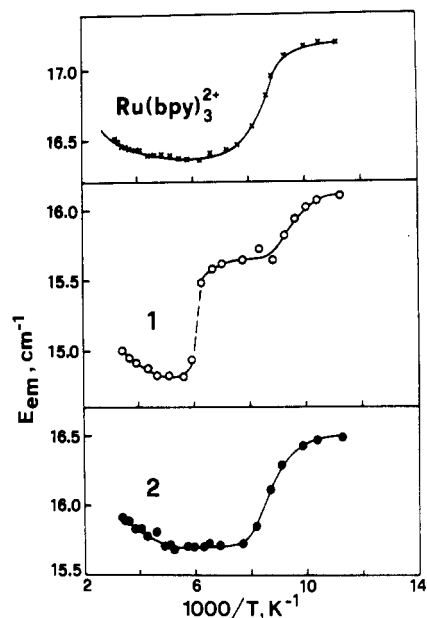
The temperature-dependence experiments were carried out in a mixture (hereafter called "nitrile") of freshly distilled propionitrile–butyronitrile (4:5 v/v). A dilute solution of each complex was sealed under vacuum in a 1-cm quartz cell after repeated freeze–pump–thaw cycles. The cell was placed inside a Thor C600 nitrogen flow cryostat, equipped with a Thor 3030 temperature controller. The absolute error on the temperature is estimated to be  $\pm 2$  K. The emission lifetimes were measured by an Edinburgh 199 single-photon-counting equipment. In order to minimize solvent dynamic effects in the melting region of the solvent,<sup>29</sup> the emission decay was always monitored at the maximum of the emission band by using interference filters. The single-exponential analysis on the luminescence decay was performed with nonlinear programs,<sup>30</sup> and the quality of the fit was assessed by the  $\chi^2$  value close to unity and by a regular distribution of the residuals along the time axis. The experimental error on the lifetime is estimated to be  $\leq 8\%$ . Standard iterative nonlinear programs<sup>30</sup> were also employed to extract the parameters for the temperature dependence of the lifetime.

The photochemical experiments were carried out on **1**, **2**, and Ru(bpy)<sub>3</sub><sup>2+</sup> (as PF<sub>6</sub><sup>-</sup> salts,  $\sim 5.0 \times 10^{-4}$  M) at room temperature in air-equilibrated CH<sub>2</sub>Cl<sub>2</sub> solutions containing an excess (0.005 M) of Cl<sup>-</sup> ions as benzyltriethylammonium chloride. Excitation was performed with a tungsten halogen lamp using a Balzers interference filter to isolate a band centered at 463 nm. The incident light intensity ( $1.3 \times 10^{-7}$  einstein/min) was measured with an Aberchrome actinometer.<sup>31</sup> The irradiated solution was contained in a 3-mL spectrophotometric cell housed in a thermostated holder. The occurrence of photoreaction was followed by monitoring absorption and emission spectral changes. The quantum yield for the photodissociation of **2** was measured from the change in absorbance at 455 or 555 nm.

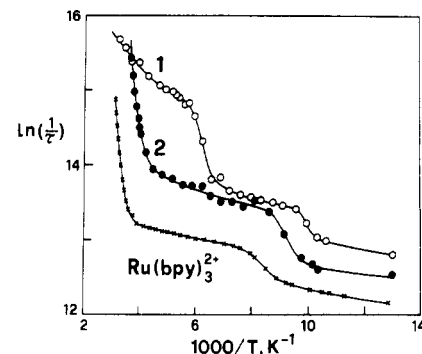
Electrochemical measurements were carried out at room temperature, in acetonitrile with 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. All experiments were performed on an EG&G PAR C Model 303 polarograph with an EG&G 384B polarographic analyzer. A glassy-carbon electrode was used as working electrode, a platinum wire as auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode. The redox potentials were estimated by using differential-pulse polarography (dpp) at a scan rate of 4 mV s<sup>-1</sup> with a pulse height of 20 mV. Cyclic voltammograms (CV) were obtained at a scan rate of 100 mV s<sup>-1</sup>. The separation between cathodic and anodic peaks and the relative intensities of the cathodic and anodic currents were taken as criteria for reversibility.

### Results

The absorption spectra of **1** and **2** in acetonitrile at room temperature are shown in Figure 2. The luminescence spectra in nitrile solution at 77 K are shown in Figure 3. At room



**Figure 4.** Shift of the maximum of the luminescence band with temperature: (1) Ru(bpy)<sub>2</sub>bpt<sup>+</sup>; (2) [Ru(bpy)<sub>2</sub>]<sub>2</sub>bpt<sup>3+</sup>. The behavior of Ru(bpy)<sub>3</sub><sup>2+</sup> is also shown for comparison purposes.



**Figure 5.** Temperature dependence of the luminescence lifetime: (1) Ru(bpy)<sub>2</sub>bpt<sup>+</sup>; (2) [Ru(bpy)<sub>2</sub>]<sub>2</sub>bpt<sup>3+</sup>. The behavior of Ru(bpy)<sub>3</sub><sup>2+</sup> is also shown for comparison purposes.

temperature, the emission bands were broader and their maxima were displayed toward the red region. The wavelengths and extinction coefficients of the lowest energy absorption maxima at 298 K, the wavelengths of the emission maxima at 77 and 298 K, the luminescence lifetimes at 77 and 298 K, and the luminescence quantum yields at 298 K are summarized in Table I. The luminescence spectra and lifetimes were examined in the entire temperature range 77–298 K, and the results obtained are summarized by the plots shown in Figures 4 and 5.

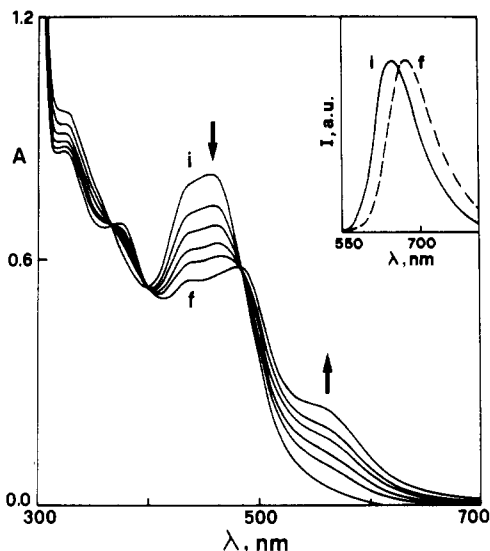
In CH<sub>2</sub>Cl<sub>2</sub> solutions containing 0.005 M Cl<sup>-</sup>, irradiation with 463-nm light (see Experimental Section) did not cause any change in the absorption and emission spectra of **1**. Conversely, irradiation was strongly effective on **2**, as shown in Figure 6 where the changes observed in the absorption and emission spectra are reported. As one can see, irradiation leads to photostable products and clean isosbestic points are maintained throughout the photoreaction. The emission spectra shown in the inset of Figure 6 are normalized, but there is actually an overall decrease in the luminescence

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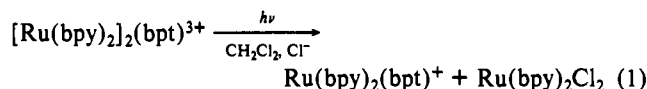
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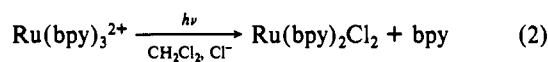


**Figure 6.** Changes in the absorption spectrum and emission spectrum (inset) on irradiation of **2** in CH<sub>2</sub>Cl<sub>2</sub> solution containing Cl<sup>-</sup> ions. *i* and *f* indicate the initial and final spectra.

intensity on irradiation by a factor of about 3. As we will better see in the Discussion, the photochemical reaction involves the fragmentation of **2** with formation of **1** and Ru(bpy)<sub>2</sub>Cl<sub>2</sub>:



The quantum yield of this photoreaction was obtained from the changes in absorption at 456 or 555 nm. For comparison purposes, the quantum yield of the previously known photoreaction<sup>2,4,6</sup>



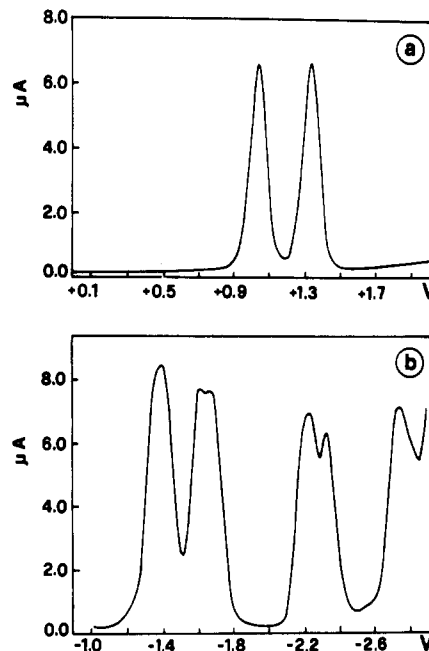
was also measured. The values of the photoreaction quantum yield, Φ<sub>0</sub>, are shown in Table I.

Electrochemical measurements in the potential window from +2.00 to -2.80 V vs SCE showed several waves. The monomer exhibits one oxidation wave at +0.85 V<sup>9a</sup> and reduction waves at -1.47, -1.72, -2.28, -2.45, and -2.52 V.<sup>9b</sup> The dinuclear compound (Figure 7) exhibits two oxidation waves at +1.04 and +1.34 V<sup>9a</sup> and six reduction waves at -1.40, -1.62, -1.67, -2.23, -2.33, and -2.74 V.<sup>9b</sup> The reduction peaks below -2.0 V for both complexes were irreversible. As one can see from Figure 7, for the dinuclear complex the first reduction wave (-1.40 V) is clearly bielectronic. A summary of the observed potential waves is shown in Figure 8, where the values obtained<sup>2</sup> for Ru(bpy)<sub>3</sub><sup>2+</sup> are also reported for comparison purposes. It is also interesting to note that no clear reduction wave can be observed for Hbpt in the 0.0/-2.8 V potential window.

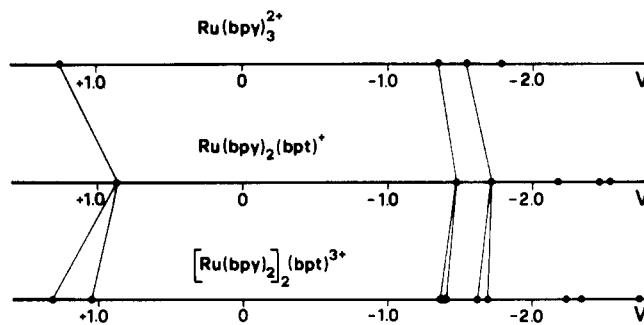
### Discussion

Appropriate assembling of molecular components that exhibit suitable ground- and excited-state properties can lead to the construction of photochemical molecular devices<sup>32</sup> capable of performing valuable functions such as transmembrane photosensitization, luminescence concentration, multielectron photocatalysis, signal processing, etc.

In a photochemical molecular device there must be an appropriate energy ordering of the lowest (longest lived, redox active, and/or luminescent) excited state and of the first oxidation and reduction potentials of the various components. A quite important role is also played by the bridge, since it should (i) ensure a correct spatial arrangement of the entire system, (ii) provide an appropriate degree of electronic communication between the components, and (iii) not compromise the useful properties of the components.



**Figure 7.** Differential-pulse polarograms of the dinuclear compound [Ru(bpy)<sub>2</sub>]<sub>2</sub>(bpt)<sup>3+</sup> in AN solution: (a) oxidation; (b) reduction.



**Figure 8.** Comparison of redox waves for Ru(bpy)<sub>3</sub><sup>2+</sup>, Ru(bpy)<sub>2</sub>(bpt)<sup>+</sup>, and [Ru(bpy)<sub>2</sub>]<sub>2</sub>(bpt)<sup>3+</sup>.

Linkage between ruthenium(II)-polypyridine type components may be obtained either by means of connectors (e.g., a -(CH<sub>2</sub>)-chain) present as substituents in peripheral positions of the aromatic polypyridine ligands<sup>15,16</sup> or by replacement of a nonbridging ligand of each component with a bridging ligand that may be as simple as the CN<sup>-</sup> ion<sup>10,23</sup> or complicated as multichelating aromatic type molecules.<sup>9,11-14,17-22,24</sup> In the case of bridging ligands much caution must be used, since it is well-known that subtle changes in coordination about Ru(II) can lead to the loss of valuable properties (e.g., luminescence) of the original component.<sup>2</sup>

Taking Ru(L)<sub>3</sub><sup>2+</sup> (L = bipyridine type ligand) complexes as precursors of the building blocks of the components, substitution of an L ligand by a bridging aromatic ligand BL may lead to two different classes of compounds,<sup>1,2a</sup> depending on whether the lowest π\* level of BL is lower (class a) or higher (class b) than the lowest π\* level of L. In class a compounds, BL is directly involved in the formation of the lowest metal-to-ligand charge-transfer excited state and of the one-electron reduction product of the system; in other words, BL plays the role of energy and electron trap. In class b compounds, BL has only a minor effect on the excited-state and redox properties of the building blocks and it may allow the occurrence of vectorial energy or electron transfer along a suitably organized (in spectroscopic energy or redox potential) sequence of components.

**Absorption and Emission Spectra.** Hbpt (pK<sub>a</sub> = 8.4<sup>9a</sup>) is a much weaker acid than Hbpy<sup>+</sup> (pK<sub>a</sub> = 4.4<sup>33</sup>), and bpt<sup>-</sup> is expected to be much more difficult to reduce than bpy. On these grounds one can expect that in coordination compounds bpt<sup>-</sup> is a better

**Table II.** Kinetic Parameters for Radiative and Radiationless Decay<sup>a</sup>

	$k^r, {}^b \text{s}^{-1}$	$k_0^{\text{nr}}, {}^c \text{s}^{-1}$	$A_1, {}^d \text{s}^{-1}$	$\Delta E_1, {}^d \text{cm}^{-1}$	$A_2, {}^e \text{s}^{-1}$	$\Delta E_2, {}^e \text{cm}^{-1}$	$B_1, {}^f \text{s}^{-1}$	$T_{B_1}, \text{K}$	$B_2, {}^g \text{s}^{-1}$	$T_{B_2}, \text{K}$
Ru(bpy) <sub>3</sub> <sup>2+</sup>	$8.0 \times 10^4$	$1.3 \times 10^5$	$5.6 \times 10^5$	90	$1.3 \times 10^{14}$	3960	$2.0 \times 10^5$	121		
Ru(bpy) <sub>2</sub> (bpt) <sup>+</sup>	$4.3 \times 10^4$	$3.1 \times 10^5$	$4.0 \times 10^6$	260	$6.5 \times 10^7$	660	$1.9 \times 10^5$	101	$1.5 \times 10^6$	163
[Ru(bpy) <sub>2</sub> ] <sub>2</sub> (bpt) <sup>3+</sup>	$3.6 \times 10^4$	$2.4 \times 10^5$	$2.7 \times 10^6$	260	$8.2 \times 10^{13}$	3200	$3.1 \times 10^5$	109		

<sup>a</sup>Nitrile solutions. Estimated uncertainties on derived quantities are 20% on energy and 10% on ln rate. <sup>b</sup>Radiative rate constant obtained from luminescence quantum yield and lifetime at 298 K (eq 7). <sup>c</sup>Nonradiative rate constant at 77 K (eq 8). <sup>d</sup>Frequency factor and activation energy of the Arrhenius term describing a nonradiative process taking place at low temperature ( $T < 250 \text{ K}$ ). <sup>e</sup>Frequency factor and activation energy of the Arrhenius term describing a nonradiative process taking place at high temperature ( $T > 250 \text{ K}$ ). <sup>f</sup>Increase in the nonradiative rate constant related to solvent melting around  $T = T_{B_1}$ . <sup>g</sup>Increase in the nonradiative rate constant related to solvent melting around  $T = T_{B_2}$ .

$\sigma$  donor and a worse  $\pi$  acceptor than bpy (class b). The absorption and emission spectra of **1** and **2** are in agreement with this expectation. Replacement of a bpy ligand of Ru(bpy)<sub>3</sub><sup>2+</sup> by bpt<sup>-</sup> to give Ru(bpy)<sub>2</sub>(bpt)<sup>+</sup> causes an increase in the electronic charge of the metal, with a consequent red shift of the metal-to-ligand (Ru  $\rightarrow$  bpy) charge-transfer absorption and emission bands (Figures 2 and 3, Table I). Coordination of a second Ru(bpy)<sub>2</sub><sup>2+</sup> unit to the bpt<sup>-</sup> bridging ligand implies the sharing of its negative charge between two Ru(bpy)<sub>2</sub><sup>2+</sup> units, with a decrease of electronic charge on the Ru(II) ions and a consequent blue shift of the Ru  $\rightarrow$  bpy CT levels. A similar behavior has been observed for complexes containing imidazole type bridging ligands.<sup>17</sup> By contrast, in class a compounds the lowest CT band and the emission band move to the red in going from the mononuclear to the dinuclear compound because the  $\pi^*$  orbital involved belongs to the bridge.

It should be noted that in the dinuclear complex the coordination environment of the two Ru(II) ions is not exactly the same because the coordinating atoms N<sup>4</sup> and N<sup>1</sup> (=N<sup>2</sup>) of the triazole ring are not equivalent. As shown by previous work, in the bpt<sup>-</sup> ligand the  $\sigma$ -donor ability on the N<sup>1</sup> (or N<sup>2</sup>) position is greater than that on the N<sup>4</sup> position.<sup>9</sup> On these grounds, in **2** the lowest energy luminescent <sup>3</sup>MLCT state (of Ru  $\rightarrow$  bpy origin) is expected to be centered on the Ru-containing unit attached to the N<sup>1</sup> (or N<sup>2</sup>) position. No evidence, however, has been found for the presence of two distinct chromophoric units because their energy separation is too small and/or there is energy transfer from the higher to the lower energy level.

The temperature dependence of the emission maxima will be discussed in the next section.

**Excited-State Decay.** The temperature dependence of the luminescence properties between 77 and 298 K has revealed important differences between **1** and **2**. The plots of  $E_{\text{em}}$  and  $\ln(1/\tau)$  vs  $1/T$  are shown in Figures 4 and 5. For Ru(bpy)<sub>3</sub><sup>2+</sup> these plots have already been discussed<sup>34</sup> and are reported in the same figures for comparison purposes. To account for the temperature dependence of the luminescence lifetime of Ru(bpy)<sub>3</sub><sup>2+</sup> and several other coordination compounds,<sup>2</sup>  $1/\tau$  can be expressed as a sum of a temperature-independent and several temperature-dependent terms

$$1/\tau = k_0 + \sum_i k_i(T) \quad (3)$$

The temperature-independent term can be expressed by

$$k_0 = k^r + k_0^{\text{nr}} \quad (4)$$

where  $k^r$  is the radiative rate constant (usually taken to be temperature independent above 77 K<sup>35</sup>) and  $k_0^{\text{nr}}$  is a radiationless rate constant related to deactivation to the ground state via a weak-coupling mechanism. The temperature-dependent terms can be associated with radiationless processes related, in a schematic way, either to an activated surface crossing to another excited state, described by the Arrhenius equation

$$k_i^{\text{nr}} = A_i \exp(-\Delta E_i/RT) \quad (5)$$

or to the coming into play of effects (e.g., solvent repolarization) that do not occur at low temperature because of the frozen en-

vironment,<sup>36-38</sup> this second type of thermally activated process can be dealt with by the empirical equation<sup>36</sup>

$$k_i^{\text{nr}} = \frac{B_i}{1 + \exp[C_i(1/T - 1/T_{B_i})]} \quad (6)$$

which describes a stepwise change of lifetime centered at a certain temperature  $T_{B_i}$ . In equation 6,  $C_i$  is a temperature related to the smoothness of the step and  $B_i$  is the increment for  $k_i^{\text{nr}}$  at  $T \gg T_{B_i}$ . This equation is particularly useful to describe the behavior of a system in the glass-fluid region of a solvent matrix.

The radiative rate constant for the various complexes (Table II) can be obtained from the luminescence lifetime and luminescence quantum yield measured at room temperature (Table I):

$$k^r = \phi_{\text{em}}/\tau \quad (7)$$

As one can see,  $k^r$  is almost the same for Ru(bpy)<sub>3</sub><sup>2+</sup>, **1**, and **2**, as expected because the emitting unit is Ru-bpy in all cases. The values of  $k_0^{\text{nr}}$  for the various complexes (Table II) can be obtained from the lifetime at 77 K, assuming that the radiative rate constant is temperature independent (vide supra):

$$k_0^{\text{nr}}{}_{77\text{K}} = 1/\tau_{77\text{K}} - k^r \quad (8)$$

The values so obtained are found to increase with decreasing energy of the luminescent level, as expected on the basis of the energy gap law.<sup>6,39,40</sup>

Figure 5 shows that for both **1** and **2** the  $\ln(1/\tau)$  vs  $1/T$  plots exhibit a stepwise behavior in the temperature range 100–110 K, comparable to that exhibited by Ru(bpy)<sub>3</sub><sup>2+</sup>. In the same temperature range,  $E_{\text{em}}$  moves to the red region (Figure 4). As previously discussed for Ru(bpy)<sub>3</sub><sup>2+</sup>,<sup>41</sup> this behavior may be related to relaxation of metal-ligand bonds and/or small rearrangements of the solvent molecules as the matrix begins to melt.

The increment  $B_1$  for  $k_1^{\text{nr}}$  at  $T \gg T_{B_1}$  is practically the same for Ru(bpy)<sub>3</sub><sup>2+</sup>, **1**, and **2** (Table II), indicating that this step is related to the same physical process in all cases. On increase of temperature after this first step, the behavior of **1** differs considerably from that of **2** and of the parent Ru(bpy)<sub>3</sub><sup>2+</sup> complex. A second step is in fact observed in both the  $\ln(1/\tau)$  vs  $1/T$  and  $E_{\text{em}}$  vs  $1/T$  plots of **1** around 160 K, which is not present for the other two complexes. Such a two-step behavior, however, has a precedent in the case of Ru(bpy)<sub>2</sub>(CN)<sub>2</sub>,<sup>36</sup> where the second step was attributed to reorientation of the solvent molecules. Such a reorientation is required by the strong change in the dipole moment caused by the Ru  $\rightarrow$  bpy CT excitation and can only take place when the solvent has acquired the property of a nonviscous fluid. The mononuclear Ru(bpy)<sub>2</sub>(bpt)<sup>+</sup> complex, in fact, is quite similar to Ru(bpy)<sub>2</sub>(CN)<sub>2</sub>, since (i) both CN<sup>-</sup> and bpt<sup>-</sup> are charged, strong  $\sigma$ -donor ligands, (ii) the CT excitation involves

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a Ru → bpy electron transfer, and (iii) both CN<sup>-</sup> and bpt<sup>-</sup>, when not used as bridging ligands, can be involved in strong specific interactions (e.g., hydrogen bonds) with the solvent.

On increase of temperature above the solvent melting region ( $T > 170$  K), the emission maxima show, as usual,<sup>36</sup> a small hypsochromic shift (Figure 4), indicating a decrease in solvent polarization caused by thermal motions.

In the case of Ru(bpy)<sub>3</sub><sup>2+</sup>, the linear behavior with very small slope of the  $\ln(1/\tau)$  vs  $1/T$  plot at low temperature (before and after the step corresponding to the melting region) is accounted for by activation to a nearby MLCT level that exhibits a slightly faster decay.<sup>34</sup> The same explanation can account for the behavior of **1** and **2** in the same temperature region since, as one can see from Table II, the  $A_1$  and  $\Delta E_1$  values obtained for the three complexes are of the same order of magnitude.

At higher temperature ( $T > 250$  K) the  $\ln(1/\tau)$  vs  $1/T$  plot of Ru(bpy)<sub>3</sub><sup>2+</sup> exhibits a steep, linear behavior, which is accounted for<sup>34</sup> by an Arrhenius term with high frequency factor,  $A_2$ , and large  $\Delta E_2$  (Table II). This term is associated with an activated surface crossing to an upper lying <sup>3</sup>MC (metal-centered) excited state, which can then undergo fast deactivation to ground state and/or ligand dissociation.<sup>2,40,42-45</sup> Because of the strong  $\sigma$ -donor power of bpt<sup>-</sup>, the metal-centered levels are expected to lie at higher energy than for Ru(bpy)<sub>3</sub><sup>2+</sup>. Coupled with the lower energy of the luminescent <sup>3</sup>MLCT level (Table I), this leads to the conclusion that the <sup>3</sup>MC-<sup>3</sup>MLCT energy gap for Ru(bpy)<sub>2</sub>(bpt)<sup>+</sup> is considerably higher than that of Ru(bpy)<sub>3</sub><sup>2+</sup>. Thus, the slightly activated radiationless decay process with  $A_2 = 6.5 \times 10^7$  s<sup>-1</sup> and  $\Delta E_2 = 660$  cm<sup>-1</sup>, which corresponds to the high-temperature region ( $T > 180$  K) of the  $\ln(1/\tau)$  vs  $1/T$  plot of **1**, cannot concern population of the lowest <sup>3</sup>MC level. Most likely it is related to the presence of another <sup>3</sup>MLCT level, as discussed by Kober and Meyer,<sup>46</sup> whose presence is usually masked by the surface crossing to <sup>3</sup>MC levels. Other activation steps are not present in this complex. This leads to the prediction that **1** should be photochemically inert toward ligand substitution. In the dinuclear complex **2**, however, the ligand field strength of bpt<sup>-</sup> is certainly much lower than in the mononuclear complex **1**. Therefore, for the dinuclear complex the Arrhenius term with  $A_2 = 8.0 \times 10^{13}$  s<sup>-1</sup> and  $\Delta E_2 = 3200$  cm<sup>-1</sup> may correspond again to a thermally activated radiationless transition from the emitting <sup>3</sup>MLCT level to the lowest <sup>3</sup>MC level, with the prediction of an observable photoreactivity, as it happens for Ru(bpy)<sub>3</sub><sup>2+</sup>. It should also be recalled that in the dinuclear complex the two moieties are not equivalent because of the different N atoms of the triazole ring used in the Ru(II) coordination (see below).

**Photochemical Behavior.** It is well-known that Ru(bpy)<sub>3</sub><sup>2+</sup> is photosensitive in CH<sub>2</sub>Cl<sub>2</sub> solutions containing Cl<sup>-</sup>, yielding Ru(bpy)<sub>2</sub>Cl<sub>2</sub> and free bpy (eq 2). The reaction is thought to take place from a <sup>3</sup>MC excited state reached by thermal activation from the luminescent <sup>3</sup>MLCT level.<sup>2,4,6</sup> As discussed above, such an activated process corresponds to the Arrhenius term, with high frequency factor ( $A_2 = 1.3 \times 10^{14}$  s<sup>-1</sup>) and high activation energy ( $\Delta E_2 = 3960$  cm<sup>-1</sup>), needed to explain the temperature dependence of the luminescent lifetime of Ru(bpy)<sub>3</sub><sup>2+</sup> in the high-temperature region ( $T > 250$  K). We have also seen above that such an activated step is not present in **1**, because of the larger energy gap between <sup>3</sup>MC and <sup>3</sup>MLCT. The lack of photosensitivity of **1** is therefore in full agreement with the photophysical results. For **2**, an activated step with  $A_2 = 8.2 \times 10^{13}$  s<sup>-1</sup> and  $\Delta E_2 = 3200$  cm<sup>-1</sup> was found, with the consequent prediction of a photochemical reactivity, as is indeed observed.

In principle, ligand photodissociation of **2** could lead to the replacement of a bpy ligand or the rupture of the coordination at the bridging ligand. The second possibility could lead either

to Ru(bpy)<sub>2</sub>Cl<sub>2</sub> and **1**, as shown in eq 1, or to Ru(bpy)<sub>2</sub>Cl<sub>2</sub> and the unstable and unknown isomer of **1** where the triazole ring should be coordinated with the nitrogen N<sup>4</sup>.<sup>9</sup> For the simpler 3-(pyridin-2-yl)-1,2,4-triazole ligand, the two isomers in which the Ru(bpy)<sub>2</sub><sup>2+</sup> unit is coordinated to triazole by N<sup>1</sup> or N<sup>4</sup> are known to exhibit clearly distinct absorption and emission spectra.<sup>47</sup> This is also expected to be the case for **1** and its unknown isomer. The absorption and emission spectra of fully irradiated solutions agree quantitatively with an equimolecular mixture of **1** and Ru(bpy)<sub>2</sub>Cl<sub>2</sub>, showing that the photoreaction is indeed described by eq 1. This result in turn indicates that photoreaction takes place through population of a <sup>3</sup>MC level centered on the Ru-containing unit attached to the N<sup>4</sup> position. Note also that, since Ru(bpy)<sub>2</sub>Cl<sub>2</sub> is not luminescent in fluid solution at room temperature, bpy replacement by Cl<sup>-</sup> on **2** would likely lead to a nonluminescent complex.

Because of the nonequivalence of the coordinating positions of the bridging ligand, an interesting situation arises concerning the luminescent and the photoreactive Ru-containing units. As discussed above, the lowest <sup>3</sup>MLCT level of **2** should involve the Ru-containing unit attached to the N<sup>1</sup> (or N<sup>2</sup>) position of the bridge. Such unit should also experience a ligand field stronger than the other unit because it involves a stronger  $\sigma$ -donor nitrogen of the triazole ring. It follows that the luminescent level of **2**, i.e. the lowest <sup>3</sup>MLCT level, does not involve the Ru-containing unit, where the lowest <sup>3</sup>MC excited state, responsible for the photodissociation reaction (eq 1), is localized.

**Electrochemical Behavior.** Some aspects of the electrochemical behavior of the two complexes have been discussed elsewhere.<sup>9a,b</sup> We would only like to emphasize the following points, with reference to Figure 8: (i) the (metal-centered) oxidation potential becomes less positive going from Ru(bpy)<sub>3</sub><sup>2+</sup> to Ru(bpy)<sub>2</sub>bpt<sup>+</sup>, as expected because bpt<sup>-</sup> is a better  $\sigma$  donor and a worse  $\pi$  acceptor than bpy; (ii) on coordination of a second Ru(bpy)<sub>2</sub><sup>2+</sup> unit to Ru(bpy)<sub>2</sub>bpt<sup>+</sup>, the first oxidation wave moves to more positive potentials, because the negative charge of bpt<sup>-</sup> has now to be shared between two Ru(bpy)<sub>2</sub><sup>2+</sup> units; (iii) as previously noticed,<sup>9a</sup> the two well-separated oxidation waves of the dinuclear complex may be due to the nonequivalence of the bridge concerning coordination of two Ru(bpy)<sub>2</sub><sup>2+</sup> units and to electronic interactions between the two metal centers; (iv) the first and second reduction potentials of Ru(bpy)<sub>2</sub>bpt<sup>+</sup> correlate well with the first and second reduction potentials of Ru(bpy)<sub>3</sub><sup>2+</sup> and can thus be assigned to reduction of the coordinated bpy ligands, as also supported by resonance Raman measurements;<sup>9b</sup> (v) the shift toward negative potentials in going from Ru(bpy)<sub>3</sub><sup>2+</sup> to Ru(bpy)<sub>2</sub>bpt<sup>+</sup> is again explained by the differences in the coordination properties of bpy and bpt<sup>-</sup> (see above); (vi) on coordination of another Ru(bpy)<sub>2</sub><sup>2+</sup> unit to Ru(bpy)<sub>2</sub>bpt<sup>+</sup>, the reduction waves concerning bpy split into two components and move to less negative potentials because the negative charge of bpt<sup>-</sup> can now be shared by two Ru(bpy)<sub>2</sub><sup>2+</sup> units; (vii) the wave splitting on reduction is much smaller than that observed on oxidation in going from **1** to **2** because the two centers involved in the reduction are more separated than the two centers involved in the oxidation.

A more complete discussion of the reduction behavior of the two complexes cannot be done because the reduction waves below -2.0 V are irreversible under the experimental conditions used. It would certainly be worthwhile to extend the present investigation to low-temperature (-54 °C) conditions, where a higher number of reversible waves are usually observed even for mononuclear ruthenium-polyypyridine complexes.<sup>48</sup>

## Conclusions

The mononuclear Ru(bpy)<sub>2</sub>(bpt)<sup>+</sup> and dinuclear [(Ru(bpy)<sub>2</sub>)<sub>2</sub>bpt]<sup>3+</sup> complexes show a quite interesting photophysical, photochemical, and electrochemical behavior. The bridging bpt<sup>-</sup> ligand is not involved in the  $\pi^*$  LUMO orbital, which is responsible

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for the lowest energy MLCT singlet and triplet excited levels and for the less negative reduction potentials. The luminescence and reduction properties are substantially those of the  $\text{Ru}(\text{bpy})_2^{2+}$  unit, perturbed to a different degree in the monomer and dimer.

A detailed study of the temperature dependence of the luminescence (spectra and lifetimes) has allowed us to obtain a complete picture of the role played by the radiative and nonradiative transitions and to show that (i) the luminescent level of the monomer is much more sensitive to the environment than that of the dimer and (ii) the deactivation via the reactive  $^3\text{MC}$  level can occur for the luminescent level of the dimer but not for that of the monomer. The latter conclusion is in full agreement with the photochemical results in  $\text{CH}_2\text{Cl}_2/\text{Cl}^-$ , which show that the monomer is photoinert whereas the dimer is strongly photosen-

sitive. Because of the nonequivalence of the coordinating positions of the bridging ligand, the luminescent excited state (namely, the lowest  $^3\text{MLCT}$  level) and the reactive excited state (namely, the lowest  $^3\text{MC}$  level) are localized on different Ru-containing units in the dinuclear complex 2.

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## Oligomeric Dicyanobis(polypyridine)ruthenium(II) Complexes. Synthesis and Spectroscopic and Photophysical Properties

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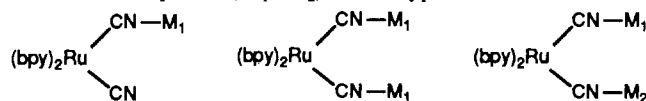
The polychromophoric systems  $\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{II}}(\text{bpy})_2\text{-CN}^+$  (2,2),  $\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{II}}(\text{phen})_2\text{-CN}^+$  (2,2'), and  $\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{II}}(\text{bpy})_2\text{-NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN}^{2+}$  (2,2,2) have been synthesized. Their redox, spectroscopic, and photophysical properties have been studied and compared with those of the  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  and  $\text{Ru}(\text{phen})_2(\text{CN})_2$  complexes. In the series  $\text{Ru}(\text{bpy})_2(\text{CN})_2$ , (2,2), (2,2,2),  $\text{Ru}(\text{phen})_2(\text{CN})_2$ , and (2,2') the ease of oxidation of the ruthenium atoms increases in the order  $\text{NC-Ru-CN}$ ,  $\text{CN-Ru-CN}$ ,  $\text{CN-Ru-CN}$ . All the complexes were found to be emitting, with monoexponential decays of the emission intensity at 298 K as well as at 77 K. The energy of the emissions undergoes a bathochromic shift in going from mononuclear to polynuclear species, indicating that the lowest  $d-\pi^*$  triplet excited state is on the N-bonded  $\text{Ru}(\text{bpy})_2^{2+}$  or  $\text{Ru}(\text{phen})_2^{2+}$  chromophoric unit and that intramolecular energy transfer between the C-bonded and N-bonded chromophores is very efficient. The singly oxidized forms of the polynuclear complexes  $\text{NC-Ru}^{\text{III}}(\text{bpy})_2\text{-CN-Ru}^{\text{II}}(\text{bpy})_2\text{-CN}^{2+}$  (2,3),  $\text{NC-Ru}^{\text{III}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{phen})_2\text{-CN}^{2+}$  (2,3'), and  $\text{NC-Ru}^{\text{III}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{bpy})_2\text{-NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN}^{3+}$  (2,3,2) were electrochemically or chemically generated in  $\text{D}_2\text{O}$  solutions. The intense metal-to-metal ( $\text{Ru}^{\text{II}} \rightarrow \text{Ru}^{\text{III}}$ ) IT transitions observed for the mixed-valence species in the near-infrared region indicate a high degree of electron delocalization relative to that of typical class II mixed-valence compounds. The lack of emission for (2,3), (2,3'), and (2,3,2) is assigned to highly efficient intramolecular electron-transfer quenching processes.

### Introduction

There has been recently considerable interest in the synthesis and characterization of polynuclear transition-metal complexes in which a photosensitizer moiety is covalently bound to other moieties that can function as electron donors or acceptors<sup>2-11</sup> or as energy acceptors.<sup>12-17</sup> The interest in this area is related to

the possibility to use coordination compounds as building blocks in the design of photochemical molecular devices.<sup>18</sup>

In this context, a number of adducts between the *cis*- $\text{Ru}(\text{bpy})_2(\text{CN})_2$  chromophore and solvated metal ions or transition-metal complexes ( $\text{M}_1$ ,  $\text{M}_2$ ) of the type



have been synthesized and described in the last few years.<sup>9,10,14,19-26</sup> Depending on the properties (excited-state energies, redox po-

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