

## ARTICLES

## Photoinduced Processes in Dyads Made of a Porphyrin Unit and a Ruthenium Complex

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A Ru(II) complex (**Ru**) containing as ligands a tridentate 4'-p-tolyl-2,2':6',2''-terpyridine (ttpy) and a tridentate 2,6-bis(4'-phenyl-2'-quinolyl)pyridine (bpqpy) has been covalently linked to a porphyrin module (**PH<sub>2</sub>**) to obtain a **PH<sub>2</sub>-Ru** dyad. The corresponding **PZn-Ru** dyad has then been obtained by metalation of the free base porphyrin with Zn(II) acetate. The photoinduced processes which occur on excitation of the **PH<sub>2</sub>-Ru** and **PZn-Ru** dyads, as well as of the **PH<sub>2</sub>** and **PZn** porphyrin units and the [Ru(tppy)(bpqpy)]<sup>2+</sup> model compound **Ru**, have been investigated in butyronitrile rigid matrix at 77 K and fluid solution at 295 K. In both dyads at low temperature, the lowest singlet excited state of the porphyrin moiety (**S<sub>1</sub>**) is quenched by energy transfer to give the triplet metal-to-ligand charge-transfer excited state of the Ru complex (<sup>3</sup>MLCT) which, in its turn, is quenched by energy transfer to yield the triplet excited state of the porphyrin moiety (**T<sub>1</sub>**). At room temperature, a charge-transfer (CT) excited state corresponding to the transfer of an electron from the porphyrin moiety to the Ru-based moiety comes into play. For the **PZn-Ru** dyad, where the CT state lies below the **S<sub>1</sub>** excited state of the porphyrin moiety, the deactivation of **S<sub>1</sub>** ( $k \geq 5 \times 10^{10} \text{ s}^{-1}$ ) occurs mainly by electron transfer to give the CT level that then deactivates to the **T<sub>1</sub>** excited state of the porphyrin moiety (100% efficiency;  $k = 9.3 \times 10^9 \text{ s}^{-1}$ ). Since the **T<sub>1</sub>** level is intrinsically long lived ( $\tau \sim 210 \mu\text{s}$ ), its deactivation occurs essentially via an activated process through the upper lying CT level ( $k = 5.7 \times 10^6 \text{ s}^{-1}$ ). The <sup>3</sup>MLCT excited state of the Ru-based moiety directly formed by light absorption appears to decay unperturbed with its intrinsic lifetime ( $k = 1.1 \times 10^{10} \text{ s}^{-1}$ ). In the case of the **PH<sub>2</sub>-Ru** dyad, the CT level lies slightly above **S<sub>1</sub>**. As a consequence, only a fraction (ca. 30%) of the **S<sub>1</sub>** excited states are quenched by electron transfer, the remaining part being quenched by energy transfer to give the <sup>3</sup>MLCT excited state of the Ru-based moiety. Deactivation of the CT state leads to the formation of **T<sub>1</sub>** ( $k = 8.7 \times 10^9 \text{ s}^{-1}$ ), whereas the <sup>3</sup>MLCT excited state undergoes unperturbed deactivation ( $k = 1.2 \times 10^{10} \text{ s}^{-1}$ ) directly to the ground state. For the latter dyad, the **T<sub>1</sub>** excited state is very long lived (280  $\mu\text{s}$ ) since deactivation via the upper lying CT level is precluded for energetic reasons.

## Introduction

Photoinduced energy- and electron-transfer processes in artificial multicomponent systems are currently the object of extensive studies.<sup>1</sup> The interest for these processes is related to the following goals: (i) a better understanding of natural photosynthesis;<sup>2</sup> (ii) the development of artificial photochemical systems capable of converting solar energy into electricity or fuels;<sup>3</sup> (iii) the design of supramolecular luminescence-based systems capable of sensing the environment;<sup>3d,4</sup> and (iv) the construction of nanometer-scale wires,<sup>5</sup> switches,<sup>6</sup> logic gates,<sup>7</sup> and other components for the development of molecular electronic devices.<sup>8</sup>

In investigations on photoinduced processes in multicomponent systems, porphyrins have been extensively used as electron donors.<sup>9</sup> In some cases, porphyrin modules have also been connected to transition metal complexes.<sup>10</sup> In an attempt to improve the performance of such systems, we have designed a new Ru(II) complex, Ru(tppy)(bpqpy)<sup>2+</sup> (where ttpy is 4'-p-tolyl-2,2':6',2''-terpyridine, and bpqpy is 2,6-bis(4'-phenyl-2'-quinolyl)pyridine), which has a low-energy excited state and is easy to reduce. Then we have covalently linked this complex (**Ru**) to tetraaryl porphyrins (a free base, **PH<sub>2</sub>**, and a zinc(II) species, **PZn**) which are less electron-rich but more robust than *etio*-porphyrins. The photoinduced processes which occur on excitation of the **PH<sub>2</sub>-Ru** and **PZn-Ru** dyads, as well as of the **Ru**, **PH<sub>2</sub>**, and **PZn** reference compounds, have been investigated in butyronitrile fluid solution at room temperature and in rigid matrix at 77 K. The results of a preliminary investigation on the **PZn-Ru** and **PH<sub>2</sub>-Ru** dyads at 77 K have been reported.<sup>11</sup>

The schematic formulas of the investigated compounds are shown in Figure 1.

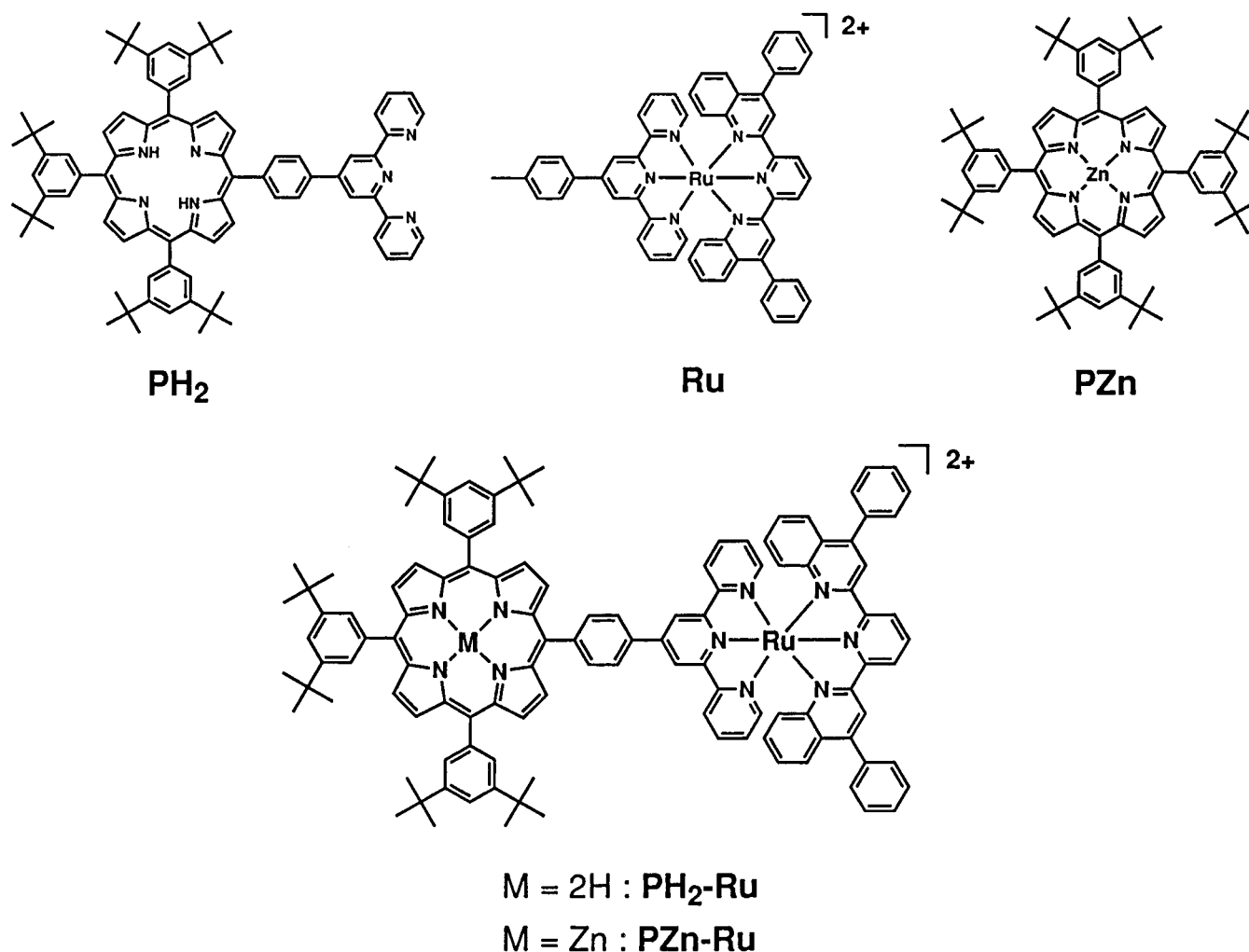
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**Figure 1.** Schematic formulas of the investigated compounds.

### Experimental Section

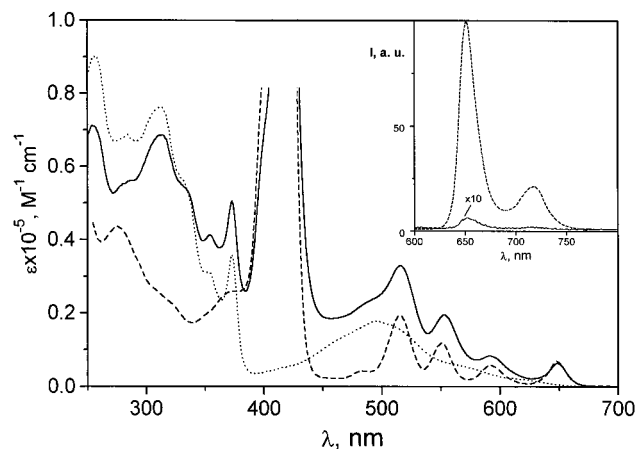
The synthesis of the compounds shown in Figure 1 has been previously reported.<sup>11</sup>

**Electrochemical Measurements.** The experiments were carried out in butyronitrile (BuCN) or dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) solution with 0.1 M <sup>n</sup>Bu<sub>4</sub>NBF<sub>4</sub> and 0.1 M Et<sub>4</sub>NPF<sub>6</sub>, respectively, as supporting electrolyte. The equipment used was previously described.<sup>12</sup> The reference electrode was a saturated calomel electrode (SCE). The potential values were determined by cyclic voltammetry at a scan rate of 100 mV/s.

**Spectroscopic and Photophysical Measurements.** The solvent used was butyronitrile (Fluka). Absorption spectra were recorded at room temperature with a Perkin-Elmer Lambda 5 spectrophotometer. Uncorrected emission spectra were obtained with a Spex Fluorolog II spectrofluorometer, equipped with a Hamamatsu R-928 photomultiplier tube. Fluorescence quantum yields were measured with the method described by Demas and Crosby<sup>13</sup> using tetraphenylporphyrin, H<sub>2</sub>TTP, as standard ( $\Phi = 0.11$ <sup>14</sup>). The delayed luminescence spectra of porphyrin triplets were recorded by a Perkin-Elmer LS50 spectrofluorometer equipped with a red enhanced photomultiplier (Hamamatsu R-3896); the same apparatus was used to measure the phosphorescence lifetimes in the millisecond time scale ( $\lambda_{\text{exc}} = 560$  nm). An IBH single-photon counting apparatus ( $\lambda_{\text{exc}} = 337$  nm, 1 ns time resolution) and a system based on a Nd:YAG laser and a Hamamatsu C1587 streak camera ( $\lambda_{\text{exc}} = 532$  nm, 20 ps time resolution)<sup>15a</sup> were used to detect fluorescence lifetimes.

Nanosecond flash photolysis studies were made with the second harmonic of a Nd:YAG laser whose energy was attenuated by a diverging lens. The absorbance of the solutions was adjusted to 0.3–0.4 at 532 nm. Details on the experimental setup are reported elsewhere.<sup>15b</sup> Yields of formation of the porphyrin triplets ( $\Phi_T$ ) in the dyads were determined taking into account (i) the corresponding values of the model compounds **PH<sub>2</sub>** and **PZn**,<sup>10a</sup> and (ii) the fraction of light absorbed at 532 nm by the porphyrin fragment, assuming that the molar absorption coefficients are unaffected in passing from models to dyads.

Transient absorption spectra in the picosecond time domain were measured by a pump and probe system. The second harmonic of a Nd:YAG laser (Continuum PY62-10) with a 35 ps pulse (fwhm), a frequency of 10 Hz, and an energy of 1–2 mJ per pulse was used to excite the samples whose absorbances at 532 nm were about 0.1 for model porphyrins and 0.3–0.4 for the dyads and **Ru**. The residual 1064 nm beam was focused on a 10 cm cell containing a mixture of D<sub>2</sub>O/D<sub>3</sub>PO<sub>4</sub> to produce a white light continuum which was used as analyzing light. A computer-controlled optical delay stage (Ealing Electro-optics) on the path of the excitation beam, provided a variable delay (0–3.3 ns) between the excitation and analysis. The analyzing light was split in two parts probing, respectively, irradiated and unirradiated portions of the sample, and crossed the cuvette in a nearly-parallel geometry to the excitation. The transmitted probes were fed via optical fibers into a spectrograph (Spectrapro 275, ARC) and were detected by a double-diode array (Princeton



**Figure 2.** Absorption spectra in butyronitrile at 295 K of the **PH<sub>2</sub>-Ru** dyad (—) and of the reference compounds **PH<sub>2</sub>** (---) and **Ru** (···). The inset shows the emission spectrum of **PH<sub>2</sub>** (---) and **PH<sub>2</sub>-Ru** (—) under the same experimental conditions ( $\lambda_{\text{exc}} = 418$  nm, Soret band).

Instruments). The controller units for delay line (SMC-500), the Optical Simultaneous Multichannel Analyzer (SI-180), and the software for acquisition of time-resolved spectra were supplied by Spectroscopy Instrument. Typically 200–400 laser shots were averaged for any single spectrum. Kinetic analyses were made by selecting, at the specific wavelength, the absorbance values of successive time resolved spectra (from 20 to 40) and by applying standard iterative procedures. The instrumental response profile (60 ps) and the calibration of the delay line was obtained by measuring the buildup of the absorption of a solution of (3,3'-diethyloxadicorbyocyanine iodide) in methanol at 450 nm.<sup>16</sup> Zero time was assumed to be at the complete evolution of the absorbance of the standard.

For experiments at room temperature the samples were placed in fluorometric 1 cm path cuvettes and, when necessary, purged from oxygen by bubbling argon. For low-temperature experiments the samples were put in a special homemade 1 cm path quartz cuvette, deaerated with four freeze–pump–thaw cycles, and sealed under vacuum. For 77 K experiments the cells were immersed in a quartz Dewar filled with liquid nitrogen whereas they were placed in the modified holder of a liquid nitrogen chryostat (Thor) for experiments in the range 105–295 K.

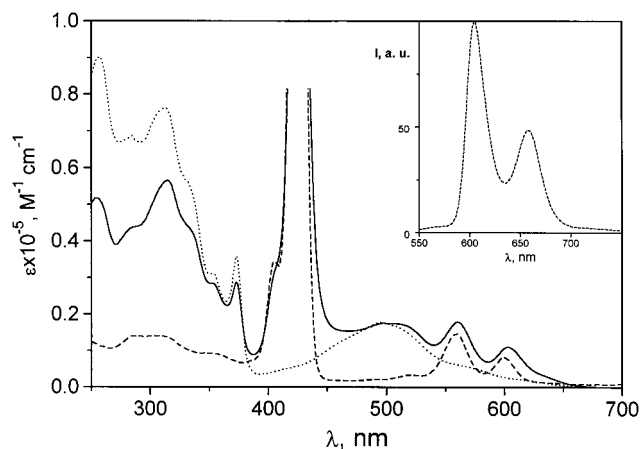
The spectroscopic energy of the electronic levels of the various compounds is derived from the maxima of the luminescence bands at 77 K.

Experimental uncertainties are estimated to be  $\pm 8\%$  for lifetime determination,  $\pm 20\%$  for quantum yields, and  $\pm 3$  nm for emission and absorption peaks.

## Results and Discussion

The ground-state absorption spectra in BuCN at 295 K of the **PH<sub>2</sub>-Ru** and **PZn-Ru** dyads and the **Ru**, **PH<sub>2</sub>**, and **PZn** reference compounds are shown in Figures 2 and 3. The emission spectra of **PH<sub>2</sub>**, **PH<sub>2</sub>-Ru**, and **PZn** in BuCN at 295 K are displayed in the insets of the same figures. The redox potentials of the dyads are shown in Table 1, and the luminescence and transient absorption data of dyads and model compounds at room temperature and at 77 or 105 K are gathered in Tables 2 and 3. Several transient absorption spectra are also shown, as discussed below.

**Properties of the Reference Compounds.** *Ru(tppy)-(bppy)<sup>2+</sup>(Ru)*. The absorption spectrum of **Ru** in BuCN at 295 K (Figure 2) shows the ligand-centered (LC) and metal-to-ligand charge-transfer (MLCT) bands typical of Ru(II) polypyridine complexes. It can be noted that the charge-transfer



**Figure 3.** Absorption spectra in butyronitrile at 295 K of the **PZn-Ru** dyad (—) and of the reference compounds **PZn** (---) and **Ru** (···). The inset shows the emission spectrum of **PZn** ( $\lambda_{\text{exc}} = 425$  nm, Soret band). Under the same experimental conditions **PZn-Ru** does not display any luminescence (see text).

**TABLE 1: Redox Potentials (vs SCE) Measured by Cyclic Voltammetry for the Reference Compounds Ru, PH<sub>2</sub>, and PZn and the Dyads PH<sub>2</sub>-Ru and PZn-Ru in BuCN and CH<sub>2</sub>Cl<sub>2</sub><sup>a</sup>**

	$E_{1/2}(\text{ox}), \text{V}$			$E_{1/2}(\text{red}), \text{V}$			
	Ru <sub>ox1</sub>	P <sub>ox1</sub>	P <sub>ox2</sub>	Ru <sub>red1</sub>	P <sub>red1</sub>	Ru <sub>red2</sub>	Ru <sub>red3</sub>
BuCN							
<b>Ru</b>	+1.45			−0.83		−1.21	−1.52
<b>PH<sub>2</sub></b>		+1.10			−1.12		
<b>PZn</b>		+1.21	+0.86		−1.33		
<b>PH<sub>2</sub>-Ru</b>	+1.50	+1.33	+1.13	−0.81	−1.07	−1.20	−1.50
<b>PZn-Ru</b>	+1.48	+1.21	+0.88	−0.83	−1.20	−1.29	−1.50
CH <sub>2</sub> Cl <sub>2</sub>							
<b>Ru</b>	+1.43			−0.95		−1.37	−1.67
<b>PH<sub>2</sub></b>		+0.98			−1.16		
<b>PZn</b>		+1.07	+0.75		−1.43		
<b>PH<sub>2</sub>-Ru</b>	+1.45	+1.27	+0.92	−0.95	−1.21	−1.39	−1.58
<b>PZn-Ru</b>	+1.45	+1.05	+0.75	−0.95	−1.37	−1.37	−1.63

<sup>a</sup> Ru and P indicate, respectively, Ru(II)- and porphyrin-centered redox processes. Experimental error:  $\pm 10$  mV.

**TABLE 2: Luminescence and Transient Absorption Data in BuCN at 295 K**

	Ru-MLCT <sup>a</sup>	P-singlet <sup>b</sup>			P-triplet <sup>a</sup>		
		$\lambda_{\text{max}}, \text{nm}$	$\tau, \text{ns}$	$\Phi_{\text{fluor}}$	$\lambda_{\text{max}}, \text{nm}$	$\tau, \mu\text{s}$	$\Phi_{\text{T}}$
<b>Ru</b>	90						
<b>PH<sub>2</sub></b>		653	11.3	0.15	450	200	0.6 <sup>c</sup>
<b>PZn</b>		609	2.0	0.08	480	210	0.72 <sup>c</sup>
<b>PH<sub>2</sub>-Ru</b>	80	654	0.076	0.0015	450	280	0.3 <sup>d</sup>
<b>PZn-Ru</b>	88	620	$\leq 0.020$	<i>e</i>	480	0.175	1.1 <sup>d</sup>

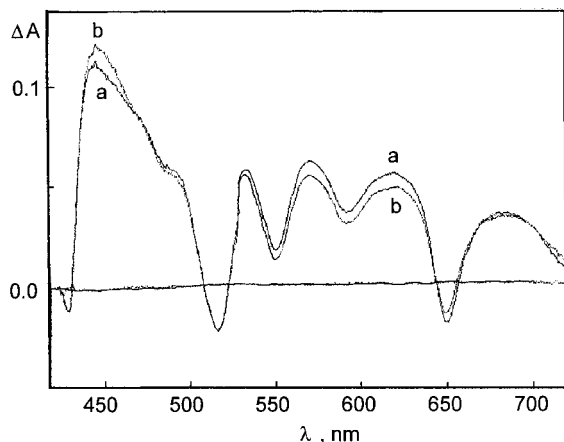
<sup>a</sup> From transient absorbance. <sup>b</sup> Emission experiments, single-photon or streak camera. <sup>c</sup> From ref 10a. <sup>d</sup> On the basis of the photons absorbed at 532 nm by the porphyrine moiety only: 33% in **Ru-PH<sub>2</sub>** and 20% in **Ru-PZn**, (from absorption spectra). <sup>e</sup> Too weak to be measured.

absorption in the visible region is considerably broad, as expected because of the presence of two different ( $\text{Ru} \rightarrow \text{tpy}$  and, at lower energy,  $\text{Ru} \rightarrow \text{bppy}$ ) charge-transfer transitions. The strong and long-lived phosphorescence band observed at 77 K (Table 3) can be assigned to the lowest energy <sup>3</sup>MLCT excited state, which involves the (easier to reduce) bppy ligand. As it happens for most Ru(II) complexes of terpyridine-type ligands, at room temperature **Ru** does not show any emission detectable by either steady-state or time-resolved techniques,<sup>17</sup> presumably because of a fast deactivation via an upper lying metal-centered excited state.<sup>5a,18</sup> The transient differential

**TABLE 3: Luminescence and Transient T-T Absorption in BuCN Rigid Matrix**

	Ru-MLCT <sup>a</sup>		P-Singlet <sup>a</sup>		P-Triplet	
	$\lambda_{\text{max}}$ , nm	$\tau$ , $\mu$ s	$\lambda_{\text{max}}$ , nm	$\tau$ , ns	$\lambda_{\text{max}}$ , nm	$\tau$ , ms
<b>Ru</b>	677	10.8				
<b>PH<sub>2</sub></b>			648	11.9	840 <sup>a</sup> 445 <sup>b</sup>	6.0 <sup>a</sup> 4.7 <sup>b</sup>
<b>PZn</b>			617	2.3	804 <sup>a</sup> 480 <sup>b</sup>	18.9 <sup>a</sup> 15.0 <sup>b</sup>
<b>PH<sub>2</sub>-Ru</b>	677	0.0046	649	0.110	840 <sup>a</sup> 450 <sup>b</sup>	5.6 <sup>a</sup> 3.8 <sup>b</sup>
<b>PZn-Ru</b>	677	0.0057	620	$\leq 0.020$	807 <sup>a</sup> 485 <sup>b</sup>	12.0 <sup>a</sup> 11.0 <sup>b</sup>

<sup>a</sup> Luminescence, 77 K in quartz Dewar. <sup>b</sup> Transient T-T absorbance in chrysoat at 105 K.

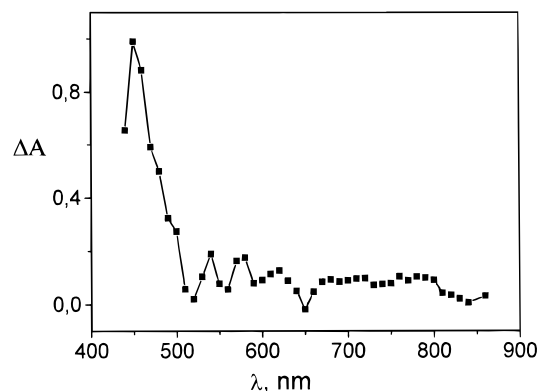


**Figure 4.** Transient differential absorption spectra of the **PH<sub>2</sub>** reference compound in BuCN at 295 K. The spectrum (a) registered immediately after excitation with a 35 ps laser pulse corresponds to the  $S_1$  excited state; for spectrum (b), registered 3.3 ns after the laser pulse, see text.

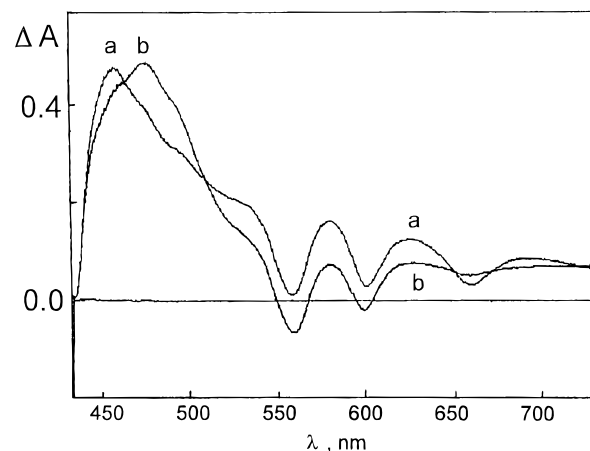
absorption spectrum of the **Ru** complex in BuCN solution at 295 K, assigned to the  $^3\text{MLCT}$  level, shows the typical bleaching band which corresponds to the ground-state MLCT absorption ( $\lambda_{\text{max}} = 495$  nm) and two positive bands with maxima at 430 and 650 nm. The decay is monoexponential and corresponds to a lifetime of 90 ps.

The **Ru** complex undergoes reversible one-electron oxidation and reduction. The metal center is rather difficult to oxidize ( $E_{1/2} = +1.45$  V), while the first reduction, which involves the bpqpy ligand, occurs at a potential that is not too negative ( $E_{1/2} = -0.83$  V).

**Free Base Porphyrin (PH<sub>2</sub>).** The absorption spectrum of the **PH<sub>2</sub>** reference compound in BuCN at 295 K (Figure 2) shows the well-known<sup>19</sup> very intense Soret band with a maximum at 418 nm and the weaker Q bands in the 500–650 nm region. Under these conditions, the fluorescence spectrum (Figure 2, inset) shows a structured band with maxima at 653 and 718 nm. In the rigid matrix at 77 K, a phosphorescence band with  $\lambda_{\text{max}} = 840$  nm, decaying in the millisecond range, can be observed (Table 3). The fluorescence lifetime is little affected by temperature, being 11.9 ns at 77 K and 11.3 ns at 295 K. The room temperature transient differential absorption spectrum detected with a pump and probe picosecond system at the end of the pulse is assigned to  $S_1$  and shows a well-pronounced maximum at 445 nm and other less important features determined by the bleaching of the Q bands (Figure 4a). Its decay is incomplete during the time window of the experiment (0–3.3 ns) but it is evident that the conversion to  $T_1$  causes a slight red shift and an increase of the 445 nm band and a lower absorbance in the region of the Q bands. The absorption of



**Figure 5.** Transient differential absorption spectrum of the **PH<sub>2</sub>** reference compound in BuCN at 295 K detected 300 ns after excitation with a 20 ns laser pulse. The spectrum corresponds to the  $T_1$  excited state.



**Figure 6.** Transient differential absorption spectra of the **PZn** reference compound in BuCN at 295 K. The spectrum (a), registered immediately after excitation with a 35 ps laser pulse, corresponds to the  $S_1$  excited state. The spectrum (b) registered 3.3 ns after the laser pulse, shows the changes occurring in the  $S_1 \rightarrow T_1$  conversion.

the fully evolved  $T_1$  species can be detected by nanosecond flash photolysis in deaerated solutions (Figure 5). The maximum is at 450 nm, the decay is exponential with a lifetime of 200  $\mu$ s under excitation with low energy. The absorption spectrum of  $T_1$  at 105 K in the rigid matrix is identical with that at room temperature and the lifetime is comparable to the one measured for the phosphorescence at 77 K (Table 3).

The potentials for oxidation and reduction processes found for **PH<sub>2</sub>** are shown in Table 1.

Our results for the **PH<sub>2</sub>** model are in agreement with those reported for the similar free base without the terpy substituent 5,10,15,20-tetrakis(3,5-ditertbutylphenyl)porphyrin in *N,N*-dimethylformamide.<sup>10a</sup>

**Zn Porphyrin (PZn).** The absorption spectrum of the **PZn** reference compound in BuCN at 295 K, Figure 3, shows the Soret band with a maximum at 425 nm. The fluorescence spectrum exhibits maxima at 609 and 657 nm (Figure 3, inset). A long-lived phosphorescence band with  $\lambda_{\text{max}} = 804$  nm can be observed in the rigid matrix at 77 K (Table 3). The fluorescence lifetime is 2.0 and 2.3 ns at 298 and 77 K, respectively. The transient differential absorption spectrum of the singlet (Figure 6a) shows a maximum at 460 nm and less pronounced bands in the 550–750 nm region whose features are determined by the bleaching of the Q bands. Partial formation of the  $T_1$  excited state can be observed in the same picosecond absorption experiment (time range 0–3.3 ns), Figure 6b. The  $T_1$  spectrum shows a maximum at 480 nm, where the

absorbance is higher than that of  $S_1$ , and an extended absorption, lower than that of  $S_1$ , in the 520–720 nm region. The triplet absorption persists over the time range of the nanosecond flash spectroscopy apparatus and, in deaerated solution and low excitation energy, has a monoexponential lifetime of 210  $\mu$ s. The triplet spectrum at 105 K in rigid glass is similar to the room temperature spectrum of  $T_1$ , and its lifetime is comparable with the phosphorescence lifetime measured at 77 K.

The potentials for oxidation and reduction processes found for **PZn** are shown in Table 1.

Our results for this model compound are in agreement with previous reports on the same porphyrin in *N,N*-dimethylformamide.<sup>10a</sup>

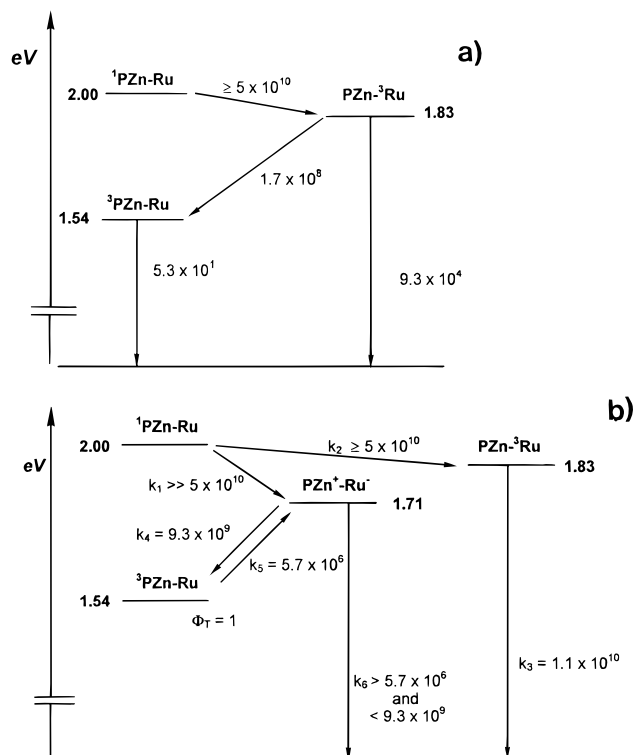
**Properties of  $PH_2$ -Ru and PZn-Ru Dyads.** The absorption spectra of the dyads (Figures 2 and 3) are not coincident with the sum of the spectra of the corresponding reference compounds, especially in the UV region. This suggests a not-negligible electronic interaction between the porphyrin and the Ru-based moiety. The data collected in Tables 2 and 3 show that the lifetimes of the porphyrin-based and of the Ru-based excited states are strongly reduced in going from the reference compounds to the dyads, showing that fast intercomponent quenching processes take place. In principle, quenching can occur by energy or electron transfer. In the following discussion we will try to elucidate the nature of the quenching processes and to evaluate their rate constants. As we will see later, the behavior of the **PH<sub>2</sub>-Ru** dyad is more complex than that of the **PZn-Ru** dyad. Furthermore, in both cases the behavior in fluid solution at 295 K is much more complex than the behavior in rigid matrix at 77 K. Therefore we will first discuss the **PZn-Ru** dyad, and for each dyad we will first discuss the behavior in rigid matrix.

**PZn-Ru dyad. (a) Rigid Matrix at 77 K.** According to the redox potentials (Table 1) and the energy of the  $S_1$  excited state, in rigid matrix at 77 K neither reductive nor oxidative electron-transfer quenching are thermodynamically allowed.<sup>20</sup> On the other hand, the  $^3MLCT$  excited state of the Ru-based moiety lies slightly below the  $S_1$  excited state of the porphyrin moiety, as one can see from the position of the corresponding emission bands (Table 3). Therefore, energy transfer is the most likely quenching mechanism, as will be proved below. The rate constant of the quenching process of an excited state can be obtained from the equation:

$$k_q = 1/\tau - 1/\tau^\circ \quad (1)$$

where  $\tau$  and  $\tau^\circ$  are the lifetime of the excited state in the presence and absence of quenching. Although no porphyrin fluorescence is detected by steady-state techniques, streak camera experiments recorded a well-resolved spectrum with the same spectral shape of **PZn** and a time profile coincident with the excitation. Therefore the lifetime of this transient has to be  $\leq 20$  ps, which is the time resolution of the instrumentation after deconvolution. From the fluorescence lifetimes of the dyad and of the reference compound (Table 3), the energy-transfer quenching constant for the  $S_1 \rightarrow ^3MLCT$  process in **PZn-Ru** has to be  $\geq 5 \times 10^{10} \text{ s}^{-1}$ . Since this rate is much faster than the intrinsic deactivation rate of the  $S_1$  level ( $4.3 \times 10^8 \text{ s}^{-1}$ ), the energy-transfer process is almost 100% efficient.

It should be noted that the  $S_1 \rightarrow ^3MLCT$  energy-transfer process does not cause sensitization of the phosphorescence of the Ru-based moiety. In fact, the data shown in Table 3 indicate that the Ru-based phosphorescence is *quenched* in the dyad. This result can be explained by considering that the lowest triplet level,  $T_1$ , of the porphyrin moiety lies below the  $^3MLCT$  excited state of the Ru-based moiety (Table 3, Figure 7), so that the



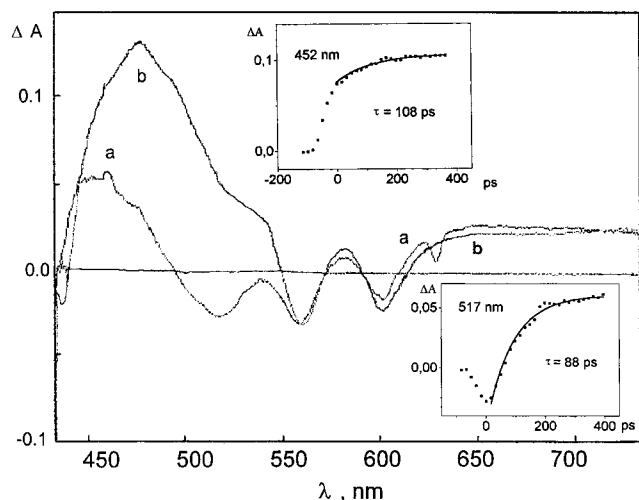
**Figure 7.** Energy level diagrams for the **PZn-Ru** dyad (a) in rigid BuCN matrix at 77 K, and (b) in fluid BuCN solution at 295 K.

latter excited state, in its turn, can be quenched via energy transfer. This is indeed the case, since the phosphorescence of the porphyrin-based moiety can be observed even upon excitation of the Ru-based moiety. More specifically, the 77 K excitation spectrum read on the porphyrin phosphorescence matches its absorption spectrum (i.e. it also displays the typical Ru-centered absorption bands at 373 and 495 nm). Therefore, the efficiency of population of the  $T_1$  excited state of the porphyrin moiety is the same regardless of whether excitation occurs on the porphyrin or Ru-based moiety. From the lifetime of the  $^3MLCT$  excited state of the **Ru** reference compound and of the Ru-based moiety of the dyads, one can calculate (eq 1) a value of  $1.7 \times 10^8 \text{ s}^{-1}$  for the rate constant of the  $^3MLCT \rightarrow T_1$  process. Since this rate is much faster than the intrinsic deactivation rate of the  $^3MLCT$  level ( $9.3 \times 10^4 \text{ s}^{-1}$ ), the energy-transfer process is practically 100% efficient.

In conclusion, the photoinduced processes occurring in the **PZn-Ru** dyad at 77 K can be schematically indicated as shown in Figure 7a. Because the two  $S_1 \rightarrow ^3MLCT$  and  $^3MLCT \rightarrow T_1$  energy-transfer processes are very fast, all the absorbed photons lead to formation of the lowest excited state of the supramolecular structure,  $T_1$ , regardless of the excitation wavelength. It has to be noticed that the presence of the heavy metal in this dyad induces spin-orbit coupling and, as a consequence, allows formally spin-forbidden processes to occur with high rate.

**(b) Fluid Solution at 295 K.** The energy level diagram for the **PZn-Ru** dyad in fluid solution at 295 K differs from that in rigid matrix at 77 K (Figure 7) for the presence of the charge-transfer (CT) excited state corresponding to the transfer of an electron from the porphyrin to the Ru-based moiety. Such a CT excited state, indicated as **PZn<sup>+</sup>-Ru<sup>-</sup>**, has an energy of 1.71 eV judging from the electrochemical data (Table 1), i.e. it can be placed between the  $^3MLCT$  level of the Ru-based moiety and the  $T_1$  level of the porphyrin moiety.

In fluid solution at 295 K the spectrofluorometer did not detect any porphyrin fluorescence. Similar to the 77 K data, a



**Figure 8.** Transient differential absorption spectra detected after laser excitation of **PZn-Ru** in BuCN at 295 K. Spectrum (a) is registered at the end of the excitation pulse, and spectrum (b) at 300 ps after the end of the pulse. The insets show the decay at selected wavelengths.

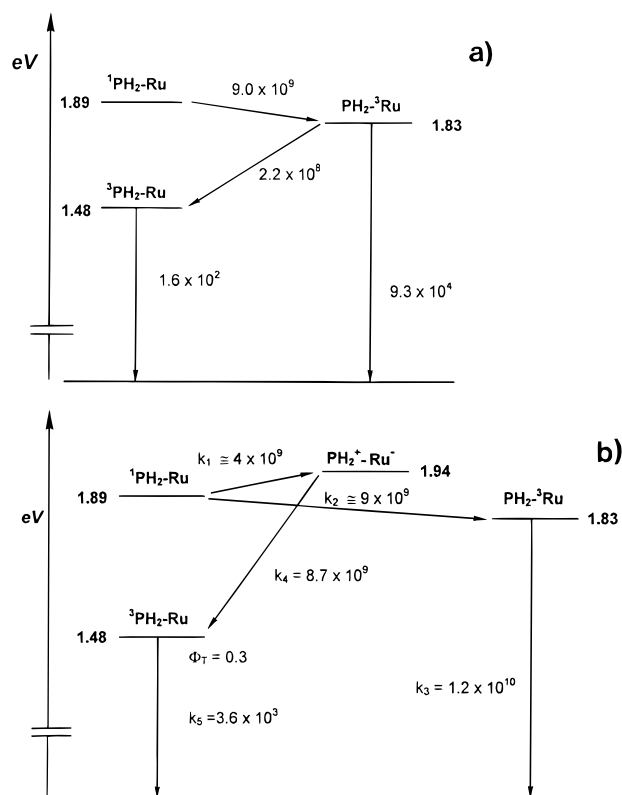
time-resolved emission spectrum was detected, with a spectral profile very similar to the model **PZn** but with the duration coincident with the laser profile. Therefore, the lifetime of this transient is  $\leq 20$  ps.

The transient absorption spectrum (Figure 8) shows a quite complex time evolution. At the end of the pulse the spectrum (8a) shows some absorption at the porphyrin singlet maximum (460 nm), while the bleaching of the Ru-based moiety is weak since it is compensated by the positive signal of both the porphyrin triplet and singlet up to 550 nm. The porphyrin triplet formation was measured at 452 nm, the isosbestic point of ground and excited **Ru**, and a lifetime of 108 ps was determined. The lifetime measured on the bleaching band of the Ru-based excited state is 88 ps, as for the model compound. It should be noted, however, that the latter kinetic could be contaminated by the triplet porphyrin formation since the spectra of the two species overlap. In such a case, the real decay of the Ru-based excited state would be faster, indicating the presence of another decay channel deactivating  $^3\text{MLCT}$  with respect to the model compound. In a few hundred picoseconds the triplet excited state of the porphyrin moiety is fully formed (Figure 8b) and persists on a longer time scale, accessible to nanosecond flash photolysis, where the absorption band assigned to the porphyrin triplet shows a biexponential decay with lifetimes 175 ns and 25  $\mu\text{s}$  (10% of the total decay) in deaerated solutions. The slowest component (presumably an impurity) has a very similar spectral feature as the triplet porphyrin, and its relative weight is constant with temperature. The temperature dependence of the fast component, analyzed according to the equation  $k = k_0 + A \exp(-\Delta E/RT)$ , yields an activation energy ( $\Delta E$ ) of approximately 0.35 eV. The yield of porphyrin triplet in the dyad upon excitation on the porphyrin moiety appears to be 1.5 times larger than that of the model **PZn**. Since the intersystem-crossing yield of **PZn** is 0.72,<sup>10a</sup> the yield of conversion from singlet to triplet porphyrin in the **PZn-Ru** dyad is approximately 1. In conclusion, the results can be summarized as follows: (i) the  $S_1$  excited state of the porphyrin moiety decays with rate constant  $\geq 5 \times 10^{10} \text{ s}^{-1}$ ; (ii) the  $^3\text{MLCT}$  level of the Ru-based moiety decays with rate constant  $1.1 \times 10^{10} \text{ s}^{-1}$ , although a faster decay cannot be excluded; (iii) the  $T_1$  excited state of the porphyrin moiety is formed with unity quantum yield and with rate constant  $9.3 \times 10^9 \text{ s}^{-1}$ ; and (iv) the  $T_1$  excited state of the porphyrin moiety decays with rate constant  $5.7 \times 10^6 \text{ s}^{-1}$  and an activation energy of 0.35 eV.

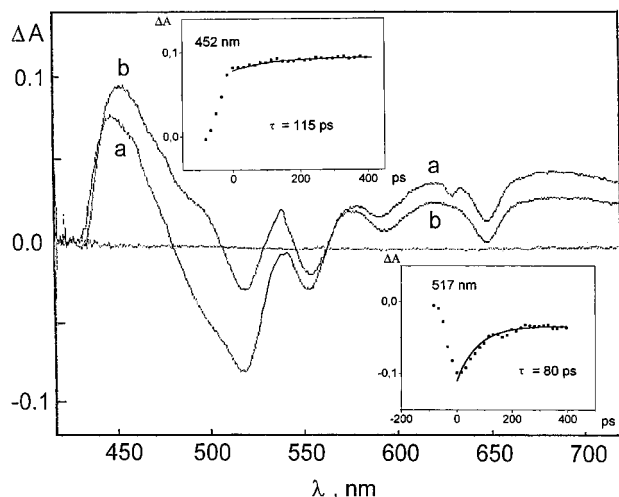
Our interpretation of these results is as follows (Figure 7b). The  $S_1$  excited state of the porphyrin moiety decays mostly (but not completely) via electron transfer to give the CT excited state. Since the electron-transfer process (rate constant  $k_1$ ) must compete with the energy-transfer process (rate constant  $k_2$ ) which at 77 K has a value  $\geq 5 \times 10^{10} \text{ s}^{-1}$  and is assumed to be very little affected by temperature, it follows that  $k_1 \gg 5 \times 10^{10} \text{ s}^{-1}$ . The  $^3\text{MLCT}$  level of the Ru-based moiety formed via energy transfer decays to the ground state with rate constant  $k_3 = 1.1 \times 10^{10} \text{ s}^{-1}$ , as it happens for the reference compound. Given the uncertainty associated with the determination of this rate constant (see above), we cannot exclude that from this state a parallel, minor channel to the CT state can originate. The energy-transfer process from the  $^3\text{MLCT}$  to the porphyrin triplet (rate  $1.7 \times 10^8 \text{ s}^{-1}$  at 77 K) is ineffective in competing with the intrinsic decay of this state. The species that have reached the CT level via the electron-transfer process decay to the lower lying porphyrin triplet  $T_1$  with rate constant  $k_4 = 9.3 \times 10^9 \text{ s}^{-1}$  (which is the formation of  $T_1$ ). Because of its very long intrinsic lifetime (210  $\mu\text{s}$  in the **PZn** reference compound), in the dyad the  $T_1$  level essentially decays by an activated process back to the upper lying CT level ( $k_5 = 5.7 \times 10^6 \text{ s}^{-1}$ ). The rate constant for decay of the CT level to the ground state ( $k_6$ ) must be smaller than  $k_4$  but larger than  $k_5$ . The free energy change of charge separation can be calculated by the expression  $\Delta G = -RT \ln(k_5/k_4)$ , a  $\Delta G$  value of 0.19 eV is obtained in BuCN, in excellent agreement with the energy difference between the two levels (0.17 eV).<sup>21</sup> The value of 0.35 eV obtained from the temperature dependence of the decay of  $T_1$  could well correspond to the activation energy of the process. The CT state is expected to decay faster<sup>22</sup> than its formation rate, therefore there is no accumulation of the CT state and no chance to detect  $k_6$ .

**$\text{PH}_2\text{-Ru}$  Dyad. (a) Rigid Matrix at 77 K.** The behavior of the  **$\text{PH}_2\text{-Ru}$**  dyad is very similar to that of the **PZn-Ru** dyad. According to the redox potentials, Table 1, and the energy of the  $S_1$  excited state of the porphyrin moiety, in rigid matrix at 77 K the CT excited state (1.94 eV at room temperature) is expected to lie at much higher energy than  $S_1$  (Figure 9a).<sup>20</sup> The fluorescence of the porphyrin moiety decays with rate constant  $9.0 \times 10^9 \text{ s}^{-1}$ . Since this rate is much faster than the intrinsic deactivation rate of the  $S_1$  level ( $8.4 \times 10^7 \text{ s}^{-1}$ ), energy transfer to the  $^3\text{MLCT}$  excited state of the Ru-based moiety is almost 100% efficient. As in the case of the other dyad, the  $S_1 \rightarrow ^3\text{MLCT}$  process does not cause sensitization of the phosphorescence of the Ru-based moiety. The  $^3\text{MLCT}$  excited state, in fact, is in its turn quenched by the lower lying  $T_1$  level of the porphyrin-based moiety. From the lifetime of the  $^3\text{MLCT}$  excited state of the **Ru** reference compound and of the Ru-based moiety of the dyad, the rate constant of the  $^3\text{MLCT} \rightarrow T_1$  process results to be  $2.2 \times 10^8 \text{ s}^{-1}$ . The yield of triplet porphyrin is the same regardless of the excitation wavelength. Again, all the absorbed photons lead to formation of  $T_1$ , the lowest excited state of the supramolecular structure, regardless of which moiety is excited.

**(b) Fluid Solution at 295 K.** As in the case of the previously examined dyad, also for  **$\text{PH}_2\text{-Ru}$**  the energy level diagram in fluid solution at 295 K differs from that in rigid matrix at 77 K (Figure 9a,b) because of the presence of a CT excited state corresponding to the transfer of an electron from the porphyrin to the Ru-based moiety. On the basis of the electrochemical data (Table 1), such a CT excited state, indicated by  **$\text{PH}_2^+ - \text{Ru}^-$** , can be placed around 1.94 eV, i.e. slightly above the  $S_1$  excited state of the porphyrin moiety (1.89 eV). The situation is therefore substantially different from that exhibited by **PZn-Ru**, Figure 7b.



**Figure 9.** Energy level diagram for the **PH<sub>2</sub>-Ru** dyad (a) in rigid BuCN matrix at 77 K and (b) in fluid BuCN solution at 295 K.



**Figure 10.** Transient differential absorption spectra registered after excitation of **PH<sub>2</sub>-Ru** in BuCN at 295 K (a) immediately after and (b) 300 ps after the end of the pulse. The insets show the decay at selected wavelengths.

The fluorescence of the porphyrin moiety is quenched compared to that of the reference compound, but the form of the spectrum is the same. The presence of a residual emission is also confirmed by time-resolved spectra which reveal a fluorescence signal with lifetime 80 ps.

The transient absorption spectrum recorded at the end of the laser pulse (Figure 10a) shows features that can be assigned to the <sup>3</sup>MLCT Ru-based moiety (the bleaching at 517 nm) and to the S<sub>1</sub> excited state of the porphyrin moiety (maximum at 445 nm). The absorbance in the 550–720 nm region is difficult to assign to a specific species. The time evolution of the spectrum shows (a) a slight increase of the 445 nm band with a shift to 450 nm, assigned to formation of T<sub>1</sub>, and (b) the recovery of the bleaching due to the <sup>3</sup>MLCT excited state. Kinetic analysis

performed at 517 (disappearance of <sup>3</sup>MLCT) and 452 nm (growing of T<sub>1</sub>) yielded lifetimes of 80 and 115 ps, respectively. The wavelength of 452 nm was chosen since, being the isosbestic point of the ground and excited **Ru** absorption, the T<sub>1</sub> formation can be cleanly measured. The formation of the triplet is complete in a few hundred picoseconds (Figure 10b) and its evolution can be followed by nanosecond flash photolysis. The spectrum obtained is identical with that of the **PH<sub>2</sub>** reference compound, and the lifetime is even higher (280 μs). The yield of T<sub>1</sub> in the **PH<sub>2</sub>-Ru** dyad, taking into account the relative absorbance of the porphyrin moiety, is about half that of the **PH<sub>2</sub>** reference compound (0.61), i.e. 0.3.

The results obtained indicate that (i) the S<sub>1</sub> excited state is quenched with rate constant  $1.3 \times 10^{10} \text{ s}^{-1}$ , (ii) the T<sub>1</sub> excited state is formed with 30% efficiency and with rate constant  $8.7 \times 10^9 \text{ s}^{-1}$ , (iii) the <sup>3</sup>MLCT level of the Ru-based moiety decays with rate constant  $1.2 \times 10^{10} \text{ s}^{-1}$ , and (iv) the T<sub>1</sub> excited state decays with rate constant  $3.6 \times 10^3 \text{ s}^{-1}$ .

It should be noted that the T<sub>1</sub> level cannot be formed via the S<sub>1</sub> → <sup>3</sup>MLCT → T<sub>1</sub> energy-transfer route (Figure 9b) since the rate of the <sup>3</sup>MLCT → T<sub>1</sub> energy transfer, as measured at 77 K ( $2.2 \times 10^8 \text{ s}^{-1}$ ), cannot compete with the intrinsic decay of the <sup>3</sup>MLCT level to the ground state ( $k_3 = 1.2 \times 10^{10} \text{ s}^{-1}$ ). Since at 77 K the S<sub>1</sub> → <sup>3</sup>MLCT energy transfer occurs with rate constant  $k_2 = 9.0 \times 10^9 \text{ s}^{-1}$  and the S<sub>1</sub> excited state at 295 K is quenched with a higher rate constant  $k_{\text{TOT}} = 1.3 \times 10^{10} \text{ s}^{-1}$ , about 30% of the S<sub>1</sub> excited state can decay by electron transfer to give the **PH<sub>2</sub><sup>+</sup>-Ru<sup>-</sup>** CT state ( $k_1 \sim 4 \times 10^9 \text{ s}^{-1}$ ), in the reasonable hypothesis that the energy-transfer rate is temperature independent. Subsequent back electron transfer ( $k_4 = 8.7 \times 10^9 \text{ s}^{-1}$ ) can then yield the T<sub>1</sub> level. Contrary to what happens in the case of **PZn-Ru**, the T<sub>1</sub> level of the **PH<sub>2</sub>-Ru** dyad cannot undergo an activated decay because the CT level is much higher in energy (Figure 9b). Therefore, T<sub>1</sub> can only decay directly to the ground state (process 5), as does the T<sub>1</sub> excited state of the **PH<sub>2</sub>** reference compound.

## Conclusions

The **PH<sub>2</sub>-Ru** and **PZn-Ru** dyads exhibit interesting photochemical properties. For both dyads in butyronitrile rigid matrix at 77 K, the lowest singlet excited state of the porphyrin moiety (S<sub>1</sub>) is quenched by energy transfer to give the triplet metal-to-ligand charge-transfer excited state of the Ru complex (<sup>3</sup>MLCT) which, in its turn, is quenched by energy transfer to yield the triplet excited state of the porphyrin moiety (T<sub>1</sub>). Since the two energy-transfer processes are very fast, all the absorbed photons lead to the formation of the lowest excited state of the supramolecular structure, T<sub>1</sub>, regardless of the excitation wavelength. At room temperature, a CT excited state corresponding to the transfer of an electron from the porphyrin to the Ru-based moiety comes into play. Because of the different excited state and redox properties of **PH<sub>2</sub>-Ru** and **PZn-Ru**, the CT level lies below the S<sub>1</sub> level in **PZn-Ru**, and slightly above S<sub>1</sub> in **PH<sub>2</sub>-Ru**. In the case of **PZn-Ru**, deactivation of S<sub>1</sub> occurs essentially by electron transfer ( $k \geq 5 \times 10^{10} \text{ s}^{-1}$ ) to give the CT level that then deactivates to the T<sub>1</sub> excited state of the porphyrin moiety (100% efficiency;  $k = 9.3 \times 10^9 \text{ s}^{-1}$ ). In the case of **PH<sub>2</sub>-Ru**, only a fraction (ca. 30%) of the S<sub>1</sub> excited states are quenched by electron transfer to give the CT level that then deactivates to the T<sub>1</sub> excited state. The remaining part of the S<sub>1</sub> excited states is quenched by energy transfer to give the <sup>3</sup>MLCT level of the Ru-based moiety which undergoes very fast deactivation ( $k = 1.2 \times 10^{10} \text{ s}^{-1}$ ) directly to the ground state. Once populated, the T<sub>1</sub> excited state of the **PZn-Ru** dyad deactivates via an activated process through the upper lying

CT level ( $k = 5.7 \times 10^6 \text{ s}^{-1}$ ). This route, however, is precluded in the case of **PH<sub>2</sub>-Ru** because the CT level lies too high in energy. As a consequence the T<sub>1</sub> excited state of **PH<sub>2</sub>-Ru** is very long-lived (ca. 280  $\mu\text{s}$ ). The direct detection of the CT state is precluded both by kinetic reasons (poor accumulation of CT state) and by its spectroscopic features in comparison to other intermediates. In fact the absorption characteristics of **Ru<sup>+</sup>**, the reduced complex, are very similar to those of the <sup>3</sup>MLCT excited state, both having an electron in the peripheral ligand, and the oxidized porphyrins **PH<sub>2</sub><sup>+</sup>** and **PZn<sup>+</sup>** have absorption bands not so well-characterized with respect to singlet and triplet excited states of the same porphyrin.

These results show that the design of dyads based on porphyrins as donors and Ru complexes as acceptors to obtain fast, long-lived, and high-yield charge separation is quite difficult. Small differences in excited-state energies and redox potentials or changes in the solvent properties can cause inversion in the relative position of localized and CT levels, with the consequent choice of different deactivation routes. Moreover the perturbation introduced by the heavy metal favors processes of energy transfer which can effectively compete with electron transfer. The **PZn-Ru** system in fluid solution at room temperature is particularly interesting since the CT level, obtained by a very fast and 100% efficient process, is in equilibrium with the lower lying, but longer-lived, T<sub>1</sub> porphyrin level.

To improve the efficiency of the electron-transfer reaction and to slow recombination, we envisage some modifications in the design of such systems. First we are thinking of using acceptors with higher excited-state energy levels to inhibit, at least in part, energy-transfer processes which compete with the desired electron-transfer reaction for the present system. Second, other parameters such as the number of components, the nature of connectors between them, and the exergonicity of each individual electron-transfer step are very important features and will contribute to the lifetime of the photoinduced charge-separated state.

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- (22) The lifetime of charge-separated states in structurally and energetically similar systems<sup>10ij</sup> is of the order of nanoseconds.