

## Triplet–Triplet Energy Transfer between Porphyrins Linked via a Ruthenium(II) Bisterpyridine Complex

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The photophysical properties of a multicomponent array consisting of a free-base aryl-porphyrin and a gold(III) aryl-porphyrin, assembled via a central bis(terpyridine) ruthenium(II) complex,  $\text{PH}_2\text{-Ru-PAu}$ , have been studied in low-temperature glassy media by steady state and time-resolved methods. Comparison of the photophysical properties of this triad with those of the reference molecular models and of the related dyads ( $\text{Ru-PH}_2$ ,  $\text{Ru-PAu}$ ) allows the photoinduced processes occurring in  $\text{PH}_2\text{-Ru-PAu}$  to be elucidated. The photoinduced processes in glassy media in the dyads  $\text{Ru-PH}_2$  and  $\text{Ru-PAu}$  are basically similar to those occurring at room temperature where the absorbed energy is transferred with 100% efficiency to the pertinent porphyrin lowest triplet state. For  $\text{Ru-}^3\text{PAu}$  the decay to the ground state is similar to the model  $^3\text{PAu}$  and displays double-exponential behavior, while in the case of  $\text{Ru-}^3\text{PH}_2$  some perturbing effect of the ruthenium center in accelerating the inter-system crossing to the ground state by the heavy atom effect can be noticed. In the triad  $\text{PH}_2\text{-Ru-PAu}$  the primary photoinduced steps are similar to those occurring at room temperature and, by energy-transfer steps, populate both triplets of peripheral porphyrins. In contrast with room-temperature events, a further energy-transfer step from  $\text{PH}_2\text{-Ru-}^3\text{PAu}$  to the spatially opposed  $^3\text{PH}_2\text{-Ru-PAu}$  (center to center distance = 2.1 nm) occurs in glassy media with a rate constant of  $2.5 \times 10^7 \text{ s}^{-1}$ , as probed by transient absorption spectroscopy. This process, which occurs by an exchange mechanism, is mediated by the interposed Ru(II) bisterpyridine complex, which acts as an electron relay.

### Introduction

Porphyrins and ruthenium(II) polypyridine complexes are currently employed as components of arrays both for the mimicry of processes taking place in nature and for the development of devices at the molecular level.<sup>1</sup>

We have recently demonstrated the importance of energy transfer processes in the deactivation of the excited states of multicomponent arrays containing porphyrins and polypyridine-type Ru(II) complexes.<sup>2</sup> The transition metal plays a major role in perturbing the spin multiplicity of the excited states, thus promoting fast energy transfer between states forbidden by spin-

multiplicity conservation rules. This is a peculiarity of multicomponent arrays containing the heavy metal ions, and, in general, it favors energy-transfer processes with respect to the desired electron transfer. Energy transfer involving triplets generally occurs by an exchange mechanism<sup>3</sup> where a direct, or spacer-mediated, orbital overlap is needed to promote a double-electron exchange between the partners. This type of process can be treated with a formalism<sup>4,5</sup> similar to that employed for electron transfer,<sup>6,7</sup> and it is not surprising that it is favored with respect to electron transfer itself in the presence of a less favorable driving force. In fact, a lower reorganizational energy is required by an exchange energy-transfer process (no net charge transferred) with respect to the reorganizational energy required by an electron transfer (charge actually moved

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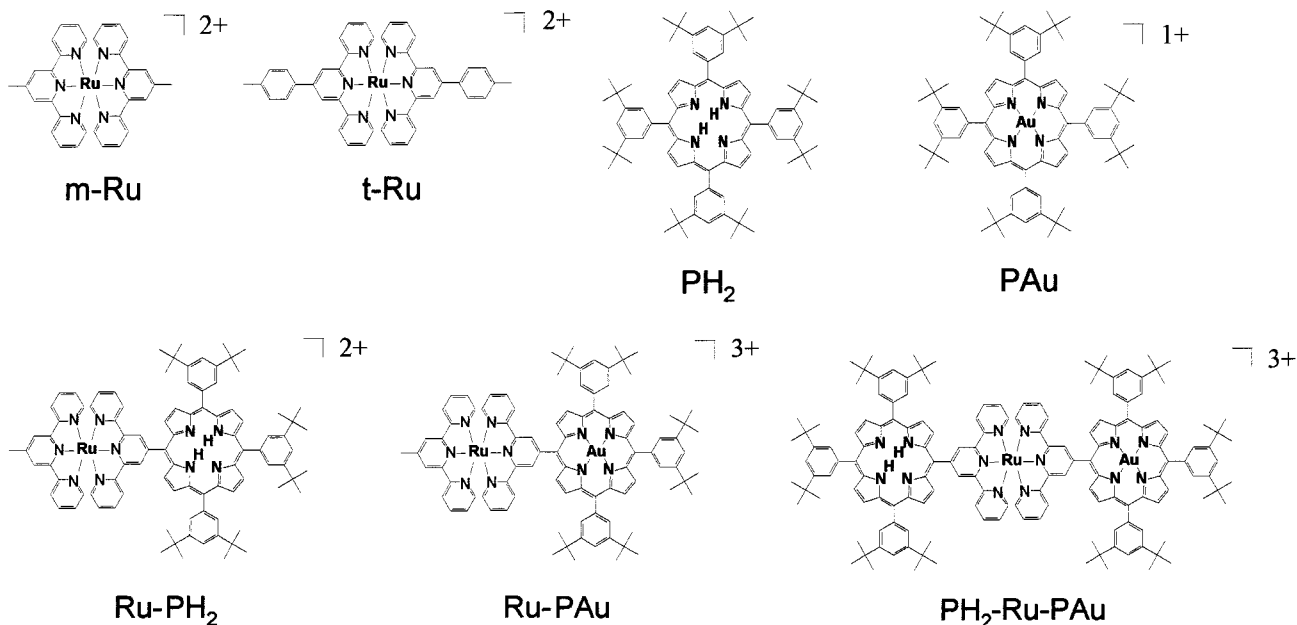
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**Figure 1.** Schematic formulas of models and arrays.

from one part of the molecule to the other). Thus, these multicomponent arrays may fail to act as efficient devices for charge separation, but they are expected to display a wide variety of energy-transfer reactions which make them very good models for the study of these processes.

We recently reported on the synthesis and the photoinduced processes of the triad  $\text{PH}_2\text{-Ru-PAu}$  and related models (Figure 1) in butyronitrile at room temperature.<sup>2c</sup> We found that excitation of the free porphyrin moiety yields the free-base porphyrin-localized excited state ( $^1\text{PH}_2\text{-Ru-PAu}$ ) which rapidly transfers energy to the  $^3\text{MLCT}$  excited-state localized on the ruthenium complex ( $\text{PH}_2\text{-}^3\text{Ru-PAu}$ ). This state does not accumulate since it is quenched mainly by the gold(III) porphyrin-localized triplet ( $\text{PH}_2\text{-Ru-}^3\text{PAu}$ ) and to a minor extent by the free-base porphyrin-localized triplet ( $^3\text{PH}_2\text{-Ru-PAu}$ ). Both porphyrin triplet excited states decay to ground state without further reactions. The thermodynamically allowed long-range energy transfer from the triplet localized on the gold(III) porphyrin (energy = 1.75 eV) to the free-base porphyrin-localized triplet state (energy = 1.47 eV) did not occur, probably because of the short lifetime of the donor (1.4 ns) together with a poor ability of the central ruthenium complex to promote an efficient coupling between the donor and acceptor. Likewise, no spectroscopic or kinetic evidence of the involvement of charge-separated states emerged from our results.

The present low-temperature work has been undertaken in order to assess unambiguously the occurrence of triplet energy transfer between the peripheral porphyrins under conditions where the lifetime of the donor is of the order of tens of microseconds. Actually the gold(III) porphyrin triplet in a low-temperature matrix displays a biexponential decay, probably because of the presence of different conformations, with both lifetimes being in the range of  $10^{-5}$ – $10^{-4}$  s,<sup>8</sup> and this may allow energy migration to occur between the two peripheral porphyrins, kept at a distance of 2.1 nm (center to center) by the interconnecting bis(terpyridyl) ruthenium complex. As described below, this is the case, and our three-component assembly displays a vectorial energy transfer at room temperature<sup>2c</sup> and

a round-trip energy migration at low temperature. Thus, the phosphorescence of the free-base porphyrin (840 nm) could be enhanced and that of the gold(III) porphyrin (700 nm) could be quenched by tuning the temperature. Our results indicate that it is possible to achieve a certain degree of control of energy flow in this type of system, and this might find a variety of applications in the field of photonic molecular devices.<sup>9</sup> In addition, a further insight on the exchange energy-transfer mechanism and on the electronic properties of the ruthenium complex spacer (acting as an electron relay) can be obtained from the present study.

### Experimental Section

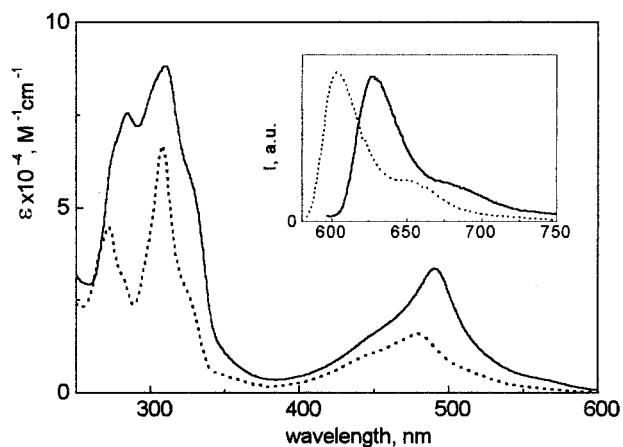
Solvents used were ethanol (Analyticals, RS Absolute for Spectroscopy, C. Erba), methanol (Analyticals, RS for Spectrofluorimetry, C. Erba), and butyronitrile (Fluka) without further purification. An ethanol/methanol (4:1 by volume) mixture was used to perform flash photolysis experiments in glass, to improve the quality of the matrix; in all other cases the solvent used was butyronitrile. For steady state and time-resolved luminescence experiments at 77 K, solutions were placed in a Pyrex capillary tube (diameter 5 mm) immersed in liquid nitrogen contained in a homemade quartz Dewar. Transient absorbance measurements were made at 100 K, on deaerated alcoholic samples contained in homemade 1 cm path quartz cells, placed in the modified holder of a liquid nitrogen cryostat (Thor C600).

Absorption spectra were recorded at room temperature with a Perkin-Elmer Lambda 5 spectrophotometer. Uncorrected emission spectra were obtained with a Spex Fluorolog II spectrofluorimeter, equipped with a Hamamatsu R-928 photomultiplier tube. The delayed luminescence spectra of gold(III) porphyrin triplets were recorded by the same spectrofluorimeter by employing a 1934D phosphorimeter accessory (Spex). Phosphorescence spectra were registered at delays of 40  $\mu\text{s}$  after the excitation, for 100  $\mu\text{s}$ . A system based on a Nd:YAG laser and a Hamamatsu C1587 streak camera ( $\lambda_{\text{exc}} = 532$  nm, 20 ps time resolution) and an IBH single-photon counting apparatus ( $\lambda_{\text{exc}} = 337$  nm, 1 ns time resolution) were used to detect fluorescence lifetimes in the region from picoseconds to a few microseconds. Experimental details on the picosecond system are reported elsewhere.<sup>10</sup> For longer luminescence

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**Figure 2.** Room-temperature absorption spectra in butyronitrile of m-Ru (···) and t-Ru (—). In the inset the emission spectra at 77 K are shown.

lifetimes the second harmonic of a Nd:YAG laser ( $\lambda = 532$  nm, 20 ns pulse, 1–2 mJ) was used to excite the sample. The emitted light was collected at right angles to the excitation beam by a system of lenses, passed through a monochromator, and was detected by an R 936 Hamamatsu photomultiplier tube. Acquisition and processing of the signal were performed by a digital oscilloscope interfaced to a PC.

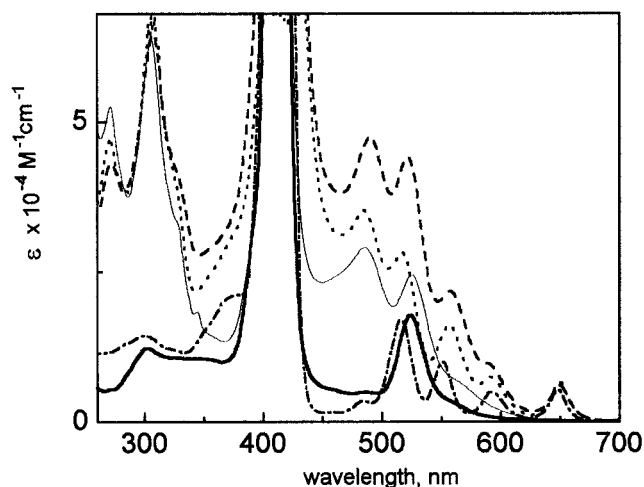
Nanosecond flash photolysis studies were made with the second harmonic of a Nd:YAG laser ( $\lambda = 532$  nm, 20 ns pulse, 1–2 mJ). A pulsed xenon arc lamp was used as the probe in a right angle geometry relative to the excitation. The light transmitted by the sample passed through a monochromator and was detected by a Hamamatsu R936 photomultiplier with only five dynodes connected, to improve the time resolution to 20 ns. The minimum detectable absorbance change ( $\Delta A$ ) is 0.002. Further details on the experimental setup have been reported previously.<sup>11</sup>

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

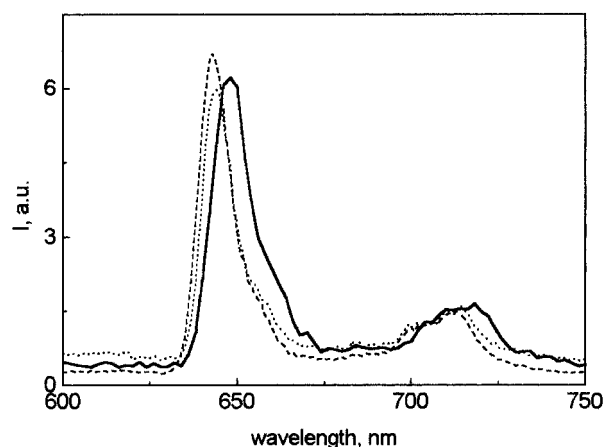
Experimental uncertainties are estimated to be 10% for lifetime determinations and 3 nm for emission and absorption peaks.

## Results and Discussion

**The Models.** Both m-Ru and t-Ru (see Figure 1) have been studied as models for the metal complex in supramolecular arrays. As already pointed out in the study at room temperature,<sup>2c</sup> a convenient model for the ruthenium-based unit in the triad is t-Ru, while in the dyads the properties of the ruthenium moiety can be regarded as an average of those of the methylated and tolylated metal complexes. The room-temperature absorption spectra of the two terpyridine derivatives and the normalized emission spectra at 77 K are reported in Figure 2. The methyl derivative has a lower absorption coefficient throughout the UV–vis region, and the position of the metal-to-ligand charge-transfer (MLCT) band is blue-shifted with respect to the tolyl derivative, in agreement with a higher energy of the <sup>1</sup>MLCT state. A similar effect has been explained in terms of electron delocalization and perturbation by substitution at the 4' position of the terpyridyl unit.<sup>12</sup> Accordingly the <sup>3</sup>MLCT emitting state of m-Ru lies at higher energy ( $\lambda_{\text{max}} = 604$  nm) than that of t-Ru ( $\lambda_{\text{max}} = 628$  nm). The emission lifetimes, which differ by a factor of 20 at room temperature (40 ps for m-Ru and 700 ps for t-Ru), are 9.1 and 9.7  $\mu\text{s}$  for t-Ru and m-Ru, respectively, at 77 K, which can be considered the same within experimental error. This is in agreement with the <sup>3</sup>MLCT emitting excited



**Figure 3.** Room-temperature absorption spectra in butyronitrile of PH<sub>2</sub> (---), PAu (—), Ru–PH<sub>2</sub> (···), Ru–PAu (— · —), PH<sub>2</sub>–Ru–PAu (---).



**Figure 4.** Fluorescence spectra at 77 K in butyronitrile glass of PH<sub>2</sub> (—), Ru–PH<sub>2</sub> (---), PH<sub>2</sub>–Ru–PAu (···). Excitation at 520 nm. The signal has been scaled to be comparable in the three cases.

state being quenched via an activated step to metal-centered orbitals, from which nonradiative processes occur; this behavior has been found to be typical both of tris-bipyridyl ruthenium(II)<sup>13</sup> and bis-terpyridyl ruthenium(II)<sup>1g,14</sup> complexes.

The room-temperature absorption spectra of both porphyrin models PH<sub>2</sub> and PAu are reported in Figure 3. At 77 K the free-base porphyrin model, PH<sub>2</sub>, displays an intense fluorescence (Figure 4) which decays with a lifetime of 11 ns. The phosphorescence of this porphyrin, weak and located around 840 nm, requires an infrared sensitive photomultiplier for the detection.<sup>2a</sup> The triplet excited state can be conveniently monitored by its transient absorption spectrum in good quality glasses. To this aim an ethanol/methanol glass was used as matrix to perform the measurement at 100 K. The free-base porphyrin triplet, detected by a nanosecond flash photolysis apparatus, displays a spectrum very similar to the one at room temperature, with a band peaking at 450 nm and a long tail extending to the infrared, characterized by the bleaching signals of the ground-state Q-bands. The lifetime of <sup>3</sup>PH<sub>2</sub> in alcoholic glasses at 100 K, determined by the decay of its absorption, is 3 ms.

The PAu model does not fluoresce; the <sup>3</sup>PAu formed immediately after excitation displays a modest phosphorescence

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**Table 1.** Photophysical Parameters in Rigid Matrices

	state	luminescence <sup>a</sup>			transient
		$\lambda_{\max}$ (nm)	$\tau$ ( $\mu$ s)	energy (eV)	absorbance <sup>b</sup> $\tau$ ( $\mu$ s)
t-Ru	<sup>3</sup> MLCT	628	9.1	1.97	
m-Ru	<sup>3</sup> MLCT	604	9.7	2.05	
PH <sub>2</sub>	<sup>1</sup> PH <sub>2</sub>	647	0.011	1.92	3000
	<sup>3</sup> PH <sub>2</sub>				
PAu	<sup>3</sup> PAu	710	10; 100	1.75	8; 90
Ru-PH <sub>2</sub>	<sup>1</sup> PH <sub>2</sub>	643	0.0015	1.93	800
	<sup>3</sup> PH <sub>2</sub>				
Ru-PAu	<sup>3</sup> PAu	700	10; 100	1.77	9; 87
PH <sub>2</sub> -Ru-PAu	<sup>1</sup> PH <sub>2</sub>	645	0.0015	1.92	760
	<sup>3</sup> PH <sub>2</sub>				
	<sup>3</sup> PAu				

<sup>a</sup> 77 K butyronitrile glass. <sup>b</sup> 100 K alcoholic matrices. <sup>c</sup> Extremely weak signal,  $\lambda_{\max}$  ca. 710 nm. <sup>d</sup> No luminescence detected by time-resolved methods.

with a maximum at 710 nm; the decay of this phosphorescence is biexponential, in agreement with previous reports which ascribe such behavior to different conformations in rigid matrix.<sup>8,15</sup> The lifetimes in butyronitrile glass at 77 K are 10 and 100  $\mu$ s. The <sup>3</sup>PAu can also be characterized by its typical absorption spectrum displaying maxima at 445 and 610 nm. The decay of <sup>3</sup>PAu, determined by the flash photolysis of alcoholic solutions at 100 K, is biphasic with lifetimes of 9 and 90  $\mu$ s, in good agreement with the luminescence data.

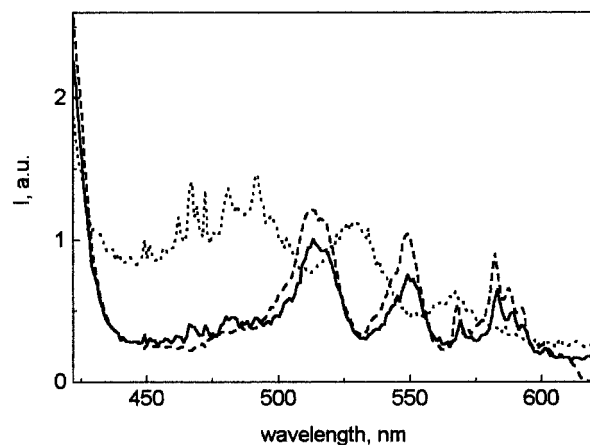
The data for the model compounds are summarized in Table 1.

**The Arrays.** The room-temperature absorption spectra of the dyads Ru-PH<sub>2</sub> and Ru-PAu and of the triad PH<sub>2</sub>-Ru-PAu are reported in Figure 3 with those of the model porphyrins PH<sub>2</sub> and PAu. The spectrum of each array is in fair agreement with the sum of the spectra of the components (note: for the dyads an average of the spectra of m-Ru and t-Ru has to be taken for the ruthenium complex moiety) in the region of the porphyrin Q-bands and the ruthenium complex MLCT band. A poorer agreement between the experimental and sum spectra is found in the region of the porphyrin Soret band (not shown) and in the complex LC bands, indicative of some intercomponent interaction in these transitions.

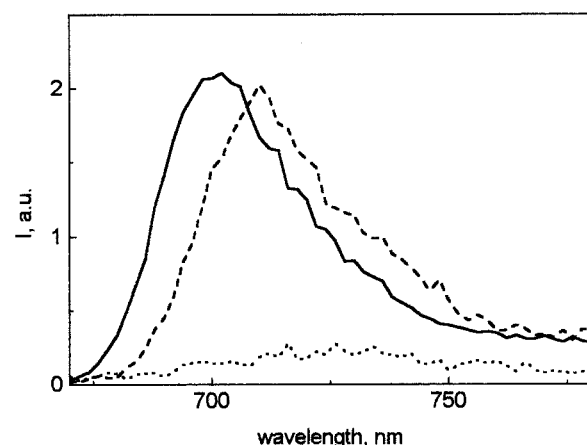
The luminescence spectra of Ru-PH<sub>2</sub> and PH<sub>2</sub>-Ru-PAu in butyronitrile glass at 77 K upon excitation at 520 nm, where all the components absorb, are reported in Figure 4, together with the spectrum of the model PH<sub>2</sub>. Excitation spectra of Ru-PH<sub>2</sub> and PH<sub>2</sub>-Ru-PAu, read on the PH<sub>2</sub> fluorescence maximum ( $\lambda = 640$  nm), are shown in Figure 5. These are identical to PH<sub>2</sub> absorbance and do not show any contribution from the MLCT ruthenium complex band which is present in the absorption spectra of both Ru-PH<sub>2</sub> and PH<sub>2</sub>-Ru-PAu.

The phosphorescence spectra of PAu, Ru-PAu, and PH<sub>2</sub>-Ru-PAu in butyronitrile at 77 K are shown in Figure 6. Although the signals are not quantitatively comparable, the absence of emission in the triad is indicative of a strong quenching. The excitation spectrum of the Ru-PAu dyad, read on the phosphorescence maximum ( $\lambda = 700$  nm) is reported in Figure 5 and shows, in addition to the porphyrin bands, contribution also from the MLCT band of the ruthenium complex.

The lifetimes of the luminescent excited singlet state localized on the free-base porphyrin in the dyad Ru-PH<sub>2</sub> and in the triad



**Figure 5.** Excitation spectra in butyronitrile glass at 77 K of Ru-PAu (···)  $\lambda_{\text{em}} = 700$  nm, Ru-PH<sub>2</sub> (—)  $\lambda_{\text{em}} = 640$  nm, PH<sub>2</sub>-Ru-PAu (- - -),  $\lambda_{\text{em}} = 640$  nm.



**Figure 6.** Phosphorescence spectra in butyronitrile glass at 77 K of PAu (—), Ru-PAu (- - -), PH<sub>2</sub>-Ru-PAu (···). Excitation wavelength 530 nm; the luminescence was detected in the time interval from 40 to 140  $\mu$ s after the excitation.

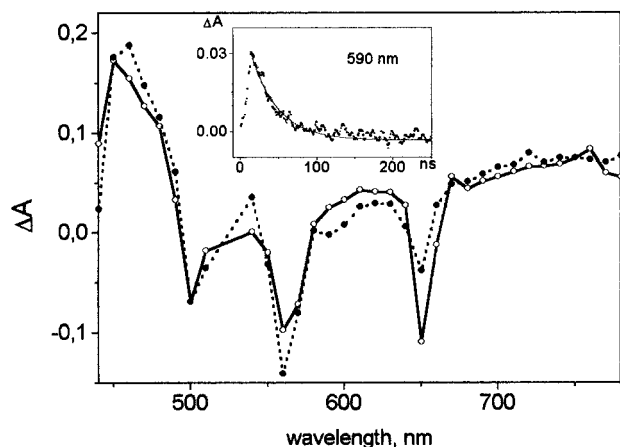
PH<sub>2</sub>-Ru-PAu, as measured in a butyronitrile glass at 77 K, are 1.5 ns in both cases, i.e., quenched with respect to the model ( $\tau = 11$  ns). The luminescence decay of the triplet localized on the gold(III) porphyrin is biexponential in the case of Ru-PAu, with lifetimes of 10 and 100  $\mu$ s, the same as the model PAu. On the contrary, no signal could be detected in the case of the triad PH<sub>2</sub>-Ru-PAu.

The emission from the <sup>3</sup>MLCT excited state of the ruthenium complex in the arrays could not be detected in any case, either by steady state or time-resolved methods (resolution 20 ps), indicating the fast quenching of this excited state.

A nanosecond flash photolysis apparatus was used to detect absorbing intermediates, in particular the porphyrin triplet states. In these experiments the butyronitrile matrix was replaced by an alcoholic matrix, which was found to yield transparent glasses, and the working temperature was 100 K. The spectrum obtained upon excitation of a Ru-PH<sub>2</sub> glassy solution, quite similar to the one detected in the PH<sub>2</sub> model, is assigned to the triplet localized on the free-base porphyrin, Ru-<sup>3</sup>PH<sub>2</sub>. This triplet decays with a lifetime of 0.8 ms, shorter than the model <sup>3</sup>PH<sub>2</sub> (3 ms) probably because of the heavy atom effect exerted by the ruthenium ion. The transient absorbance spectrum of the other dyad, Ru-PAu, can be ascribed to the triplet localized on the gold(III) porphyrin, Ru-<sup>3</sup>PAu. Actually the measured lifetimes are 9 and 87  $\mu$ s, in excellent agreement with the lifetimes derived from the phosphorescence and coincident,

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**Figure 7.** Absorbance changes following laser excitation (532 nm, 2 mJ) of  $\text{PH}_2\text{-Ru-PAu}$  in an alcoholic matrix at 100 K. The spectra are registered 20 ns after the laser ( $\circ$ ), and 150 ns after the laser pulse ( $\bullet$ ). In the inset the experimental absorbance decay at 590 nm and the fitting according to a lifetime of 40 ns are shown.

within experimental error, with the decay of the triplet excited state in the model,  ${}^3\text{PAu}$ .

The same flash photolysis experiment performed on the triad,  $\text{PH}_2\text{-Ru-PAu}$ , produces the optical changes reported in Figure 7. The immediate spectrum, displaying maxima around 450 and 600 nm, evolves to a spectrum with a maximum around 450–460 nm and a lower absorbance around 600 nm. This change is consistent with a  ${}^3\text{PAu} \rightarrow {}^3\text{PH}_2$  transformation, and we assign it to energy transfer from the gold(III) porphyrin-localized triplet to the free-base localized triplet,  $\text{PH}_2\text{-Ru-}{}^3\text{PAu} \rightarrow {}^3\text{PH}_2\text{-Ru-PAu}$ , occurring with a lifetime of 40 ns (inset of Figure 7). The final spectrum decays on a slower time scale, with a lifetime of 760  $\mu\text{s}$ , similar to the decay of the free-base porphyrin triplet in the dyad  $\text{Ru-}{}^3\text{PH}_2$ .

The data for the arrays are summarized together with those of the models in Table 1.

**Photoinduced Processes.** The photophysical results obtained are summarized in the energy level diagrams of Figure 8, where the deactivation processes of the excited states and the pertinent rate constants in a glassy matrix at 77–100 K are reported. The energy levels of the excited states are derived from the emission maxima at 77 K (from Table 1) or, in the absence of emission, the energy of the excited state in the array is assumed to be identical to the one of the model. The energy of  ${}^3\text{PH}_2$  in butyronitrile has been measured previously from its phosphorescence spectrum at 77 K.<sup>2a</sup> The charge-separated states, which lie at energies comparable to those of excited states at room temperature,<sup>2c</sup> are destabilized in glassy media by the lack of solvent repolarization. Their energy levels are expected to increase by at least 0.5 eV<sup>15,16</sup> and, as a consequence, they are not taken into account here. The rate constants for the intramolecular processes are calculated from the expression

$$k = 1/\tau - 1/\tau_0 \quad (1)$$

where  $\tau$  and  $\tau_0$  refer to the lifetime of the particular excited state in the array and in the model, respectively.

In the dyad  $\text{Ru-PH}_2$  the lowest-lying porphyrin-localized singlet is quenched with respect to the model and the residual luminescence displays an excitation spectrum which does not show any involvement of the ruthenium complex. The lumines-

cence of the ruthenium complex is, in turn, completely quenched at a rate higher than the resolution of our equipment ( $k > 5 \times 10^{10} \text{ s}^{-1}$ ). The only detectable product within a few nanoseconds after excitation is the porphyrin triplet. We interpret these data as a quenching of the singlet porphyrin excited state by the MLCT triplet localized on the ruthenium complex, followed by a very rapid energy transfer to the triplet localized on the free-base porphyrin,  $\text{Ru-}{}^3\text{PH}_2$ . The former reaction, which is spin forbidden and is made possible only by the mixed nature of the spin multiplicity of the  ${}^3\text{MLCT}$  state of the acceptor, is slightly endoergonic and, in fact, proceeds with a slower rate than at room temperature. The latter reaction, which is thermodynamically favored and spin allowed, proceeds with a rate faster than our resolution, similar to the behavior at room temperature.<sup>2c,17</sup>

Excitation of the ruthenium complex in the  $\text{Ru-PAu}$  dyad leads to the  ${}^3\text{MLCT}$  level localized on the ruthenium complex,  ${}^3\text{Ru-PAu}$ , which immediately (within our resolution, 20 ps) transfers energy to the gold(III) triplet porphyrin,  $\text{Ru-}{}^3\text{PAu}$ . The latter decays to the ground state unperturbed with respect to the model, displaying the same biexponential behavior as that found for the model  $\text{PAu}$ .

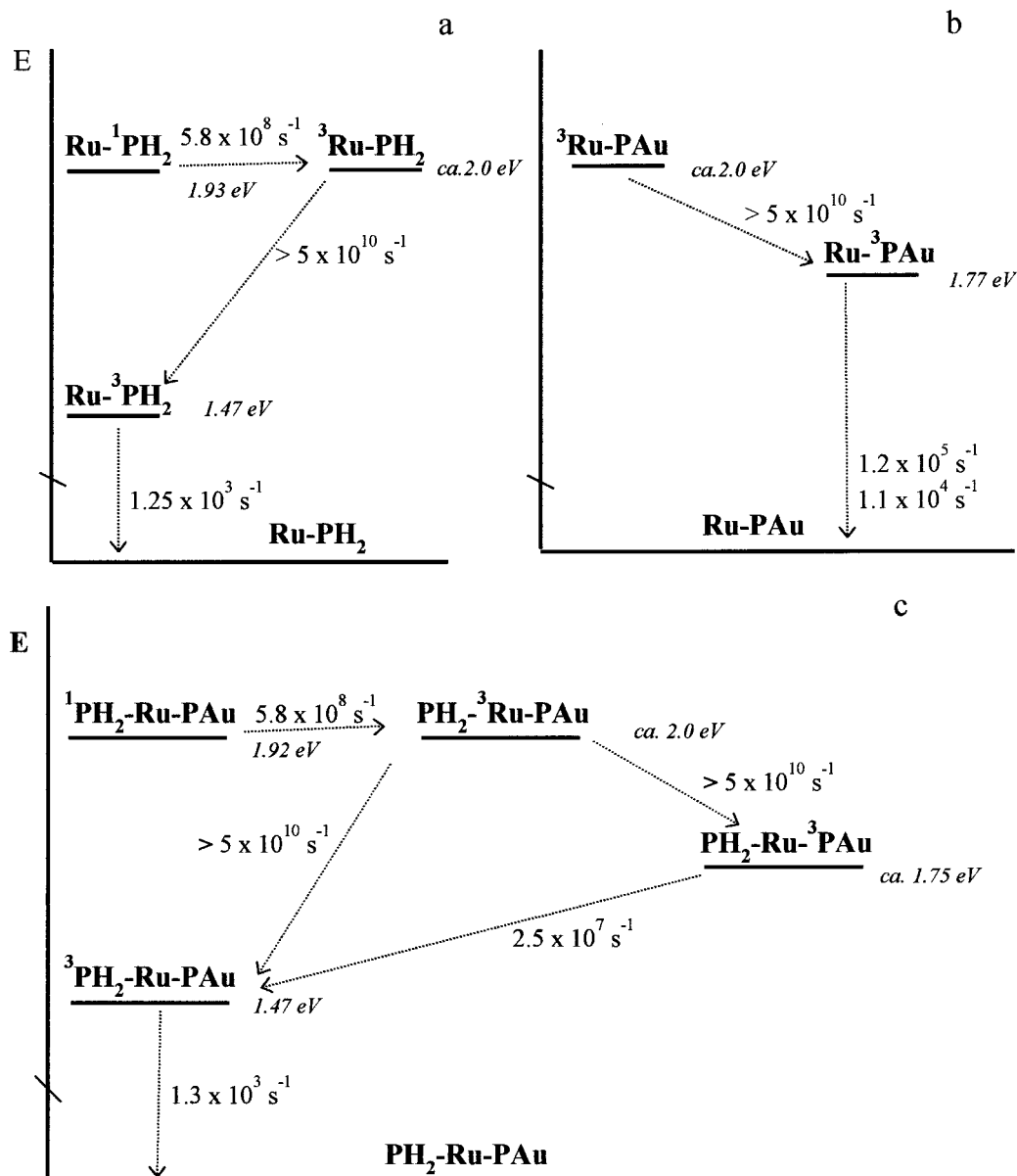
In the triad  $\text{PH}_2\text{-Ru-PAu}$ , the fluorescence of the free-base localized singlet,  ${}^1\text{PH}_2\text{-Ru-PAu}$ , is quenched with the same rate as that detected in the dyad  $\text{PH}_2\text{-Ru}$ , therefore we assign the quenching step to the same process, namely, the slightly endoergonic energy transfer from the free-base porphyrin-localized singlet to the  ${}^3\text{MLCT}$  state localized on the ruthenium complex,  ${}^1\text{PH}_2\text{-Ru-PAu} \rightarrow \text{PH}_2\text{-}{}^3\text{Ru-PAu}$ . We have learned from the behavior of the dyads that both triplets localized on the porphyrins,  ${}^3\text{PH}_2\text{-Ru-PAu}$  and  $\text{PH}_2\text{-Ru-}{}^3\text{PAu}$ , can efficiently quench the triplet localized on the metal complex,  $\text{PH}_2\text{-}{}^3\text{Ru-PAu}$ . At room temperature the quenching by gold(III) localized porphyrin is 4 times more efficient than the quenching by the free-base porphyrin;<sup>2c</sup> we were unable to verify this in the glass but expect a similar partition, given the modest effect of temperature on thermodynamically allowed energy-transfer processes.<sup>18</sup> Nonetheless, a few nanoseconds after the excitation a mixture of  ${}^3\text{PH}_2\text{-Ru-PAu}$  and  $\text{PH}_2\text{-Ru-}{}^3\text{PAu}$  (presumably more rich in the latter than at room temperature) is present. The exoergonic step of triplet energy transfer from  $\text{PH}_2\text{-Ru-}{}^3\text{PAu}$  to  ${}^3\text{PH}_2\text{-Ru-PAu}$ , which could not occur at room temperature because of the short lifetime of the donor, takes place in glass, as probed by transient absorbance determination, with a rate of  $2.5 \times 10^7 \text{ s}^{-1}$ .

**Triplet Energy Transfer.** In the present system we observe different triplet energy transfer steps: (i) very fast processes ( $k > 5 \times 10^{10} \text{ s}^{-1}$ ) occurring from the  ${}^3\text{MLCT}$  localized on the central ruthenium complex,  $\text{PH}_2\text{-}{}^3\text{Ru-PAu}$ , to the peripheral porphyrins directly connected to the donor and (ii) a slower energy transfer ( $k = 2.5 \times 10^7 \text{ s}^{-1}$ ), occurring between the two extreme porphyrins, separated by a center-to-center distance of 2.1 nm, with the bis(terpyridyl)ruthenium complex interposed. The mechanism of triplet energy transfer is of exchange type:<sup>3</sup> it involves the concerted migration of an electron and a hole from the donor to the acceptor and, in the weak interaction limit,

(17) At room-temperature we were able to demonstrate the occurrence of an energy transfer from  ${}^1\text{PH}_2\text{-Ru}$  to  ${}^3\text{Ru-PH}_2$  and from here to  $\text{Ru-}{}^3\text{PH}_2$ , rather than an induced heavy atom effect on the intersystem crossing rate of the transition  ${}^1\text{PH}_2\text{-Ru} \rightarrow {}^3\text{PH}_2\text{-Ru}$ , by making use of the experimentally determined triplet yields upon excitation of the different moieties of the dyad. This cannot be done in glass because of experimental difficulties but we do not see any sensible reason for expecting a different behavior.

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**Figure 8.** Schematic energy level diagrams and photoinduced processes for Ru-PH<sub>2</sub> (a), Ru-PAu (b), and PH<sub>2</sub>-Ru-PAu (c).

can be treated in terms of thermodynamic quantities by eqs 2–4, according to a classical approach similar to the one used for nonadiabatic electron transfer.<sup>4–6</sup>

$$k = \nu \exp(-\Delta G^\ddagger/RT) \quad (2)$$

$$\nu = 2H^2/h(\pi^3/\lambda RT)^{1/2} \quad (3)$$

$$\Delta G^\ddagger = \lambda/4(1 + \Delta G^\circ/\lambda)^2 \quad (4)$$

In eqs 2–4,  $\lambda$  is the reorganizational energy,  $H$  is the intercomponent electronic interaction, and  $\Delta G^\circ$  is the free energy change of the process. The free energy change is conveniently assumed to correspond to the difference between the spectroscopic energies of the states. For an energy-transfer process, the reorganizational energy  $\lambda$  is mainly due to internal contributions related to the rearrangement of angles and distances in passing from ground to excited states and can be calculated from spectroscopic data.<sup>4</sup>

We now examine in some detail the two different classes of triplet energy transfer outlined above.

(i) In both cases where a fast rate is observed, one electron has to move from the terpy ligand to the close tetrapyrrole ring, and concertedly a hole has to move from the central ruthenium ion to the tetrapyrrole ring. The  $\lambda$  parameter, given the close similarities of the acceptor states involved and the fact that the donor is the same, is expected to be similar in the two cases and is assumed to be ca. 0.2 eV.<sup>19</sup> At room temperature, the ratio of the energy-transfer rates from the central ruthenium unit to the two porphyrins was measured and is in favor of the gold(III) porphyrin triplet by a factor of 4.<sup>2c</sup> The fact that the less exergonic process to the gold(III) porphyrin triplet ( $\Delta G^\circ = -0.22$ ) prevails over the more exergonic energy transfer to the free-base porphyrin triplet ( $\Delta G^\circ = -0.5$ ) could be explained by the latter being in the Marcus inverted region ( $\lambda > -\Delta G^\circ$ ).

(19) The  $\lambda$  of both donor and acceptor in a triplet energy transfer reaction correspond to  $1/2$  of the Stokes shifts between absorption ( $S_0 \rightarrow T_1$ ) and emission ( $T_1 \rightarrow S_0$ ); the overall  $\lambda$  of the reaction can be taken as an average of donor and acceptor individual  $\lambda$ 's. In most systems it is difficult to locate the  $S_0 \rightarrow T_1$  transition. A value of  $\lambda$  ca. 0.2 is assumed which is in line with the few cases where this location is possible.<sup>18,25</sup>

Moreover the preferred localization of the electron in the  $^3\text{MLCT}$  state on the ligand linked to the gold(III) porphyrin, which is positively charged, with a consequent higher intercomponent electronic interaction term,  $H$ , could contribute to an increase in the rate to the gold(III) porphyrin. Both of these energy-transfer steps occur according to a typical exchange mechanism, where the direct orbital overlap of donor and acceptor plays the key role. This is generally referred to as the through-space mechanism of electron exchange.

(ii) The energy-transfer step which results in the sensitization of the  $^3\text{PH}_2\text{—Ru—PAu}$  state by the  $\text{PH}_2\text{—Ru—}^3\text{PAu}$  state, given the rigid geometry of the structure which seems to prevent a direct overlap of donor and acceptor orbitals, must occur by the intermediacy of the ruthenium complex spacer. Since at the low-temperature investigated, we can exclude the involvement of  $\text{PH}_2\text{—}^3\text{Ru—PAu}$  as intermediate in an activated energy transfer,<sup>20,21</sup> the occurrence of energy transfer requires that the electron exchange involves the ruthenium complex orbitals. The intermediacy of the bridging ligand in both energy (by exchange mechanism) and electron transfer has been the object of systematic studies where the effects of distances, number of interposed bonds and, in some cases, also stereochemistry, and localization of excited states have been addressed.<sup>5,7,22–24</sup> In particular, the work by Closs and co-workers has related the rate of triplet–triplet energy transfer (less ambiguous than singlet–singlet energy transfer where a dipole–dipole mechanism could be important) to the electron and hole transfer along a series of aliphatic bonds.<sup>5</sup> These authors successfully demonstrated that the probability of triplet–triplet transfer for a given bridge is proportional to the product of the probabilities of electron- and hole-transfer for the same bridge. The energy transfer is postulated to occur by an electron-transfer involving the LUMO orbitals of the spacer, placed at higher energy than the LUMO of the donor and acceptor, and a concerted hole transfer involving the HOMO of the spacer, lower in energy than the HOMO of donor and acceptor. Coupling of the HOMO and LUMO of the bridge between themselves and with those of the donor and acceptor is needed to promote such a step. The degree of mixing, and therefore the ability of the bridge in promoting this “superexchange” mechanism, is inversely proportional to the energy spacing between orbitals to be coupled.

In our case the LUMO of the bridge is ligand centered, therefore localized on the periphery of the complex and spatially close to the LUMO of both donor and acceptor sites localized on the tetrapyrrole rings. On the contrary the HOMO is metal centered, more secluded with respect to the HOMO of the donor and acceptor, and localized on the tetrapyrrole rings. The degree of mixing is also determined by parameters other than proximity, i.e., energy and symmetry, but this pictorial view suggests more

difficult hole transfer than electron transfer. From equations 2–4 an estimate of the intercomponent electronic interaction  $H$  could be attempted. Assuming the reorganizational energy  $\lambda$  similar to the free energy change of the process ( $\Delta G^\circ = -0.28$  eV), an activationless condition could be hypothesized. In this case the experimental rate ( $k = 2.5 \times 10^7$  s<sup>-1</sup>) can be considered to be nearly coincident with  $\nu$ , and  $H \cong 0.2$  cm<sup>-1</sup> is derived. This is indeed a very low value and was derived with a very approximate approach, nevertheless it is well assessed that coupling matrix elements as small as a few cm<sup>-1</sup> are sufficient to promote extremely fast (picoseconds) electron or hole transfer when other parameters are maximized.<sup>25</sup>

An attempt to compare the transmission properties of the Ru(II) complex with other bridges is inconclusive since no other determination of energy transfer between the same donor and acceptor couple has been performed. In a similar case, related to triplet energy transfer from a gold(III) porphyrin to zinc porphyrin separated by a rigid 2,9-diphenyl-1,10-phenanthroline, a rate of  $4.5 \times 10^6$  s<sup>-1</sup> was found.<sup>15</sup> Since the driving force of the reaction was lower ( $\Delta G^\circ = -0.18$ ) than the present case ( $\Delta G^\circ = -0.28$ ) and the geometry of the array did not exclude the occurrence of a direct overlap between the orbitals of donor and acceptor (through space), rather than a through-bond mechanism, a comparison of our spacer with the aryl bridge is not straightforward. Nevertheless in qualitative terms the ability of the Ru(II)terpyridine complex in mediating the energy transfer, i.e., the electron and hole migration, does not appear to differ dramatically from that of the aryl bridge. In conclusion, the ruthenium terpyridine complex can be regarded as a moderately coupling bridge in mediating electron and hole transfer from the donor to the acceptor. Different conclusions can be made from the reported interposition of a Pt(II) phosphine complex in an ethynyl chain, which acts as a switch of energy transfer from Ru(II)tris(bipyridyl) to Os(II)tris(bipyridyl).<sup>26,27</sup>

## Conclusions

In the present work the photoinduced processes occurring in molecular arrays containing porphyrins and a terpyridine ruthenium complex have been determined in glassy solvents at low temperature. Deactivation of the excited states occurs by a series of energy transfer steps, whose nature has been discussed. The occurrence at low temperature of triplet energy transfer between the peripheral porphyrins separated by a center to center distance of 2.1 nm (prevented at room temperature by the short lifetime of the donor) indicates the intermediacy of the interposed ruthenium complex in promoting with some efficiency a through bond energy transfer process.

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