Photoinduced Electron Transfer in Ruthenium(II)−Rhodium(III) Terpyridine Dyads

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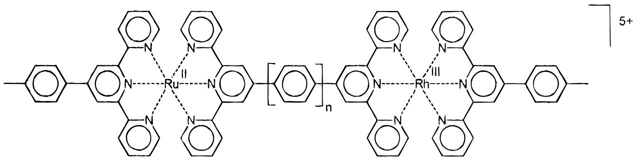
A series of Ru(II)−Rh(III) dyads of general formula (ttpy)Ru−tpy−$(ph)_n$−tpy−Rh(ttpy)$^{5+}$ with $n = 0, 1, 2$ [ttpy = 4′-*p*-tolyl-2,2′:6,2″-terpyridine; tpy−$(ph)_n$−tpy = bridging ligand where two 2,2′:6′,2″-terpyridine units are connected at the 4′-position through a variable number of *p*-phenylene spacers] have been studied, in acetonitrile at room temperature, by picosecond and nanosecond time-resolved emission spectroscopy. When $n = 1$, excitation of the Ru(II)-based molecular component is followed by efficient intramolecular quenching by electron transfer to the Rh(III) center. The rate constant, $k \geq 3 \times 10^9$ s^{-1}, is high despite the relatively small driving force of the process (ca. 0.1 eV). When $n = 2$, with the same driving force as above, no intramolecular electron transfer quenching is observed (upper limit for the rate constant of the electron transfer process: $k < 5 \times 10^8$ s^{-1}). The decrease in electron transfer rate obtained in going from $n = 1$ to $n = 2$ is in line with the behavior of other systems containing poly-*p*-phenylene spacers. The dyad with $n = 0$ is definitely not homogeneous with the other two: the intercomponent electronic coupling is much stronger, the Ru(II)-based excited state is lower in energy, and the electron transfer has a smaller driving force ($\Delta G \approx 0$). The lifetime of the Ru(II)-based emission is 17 ns. The lack of an obvious model compound makes it difficult to draw firm conclusions for this system.

Introduction

Ligand-bridged polynuclear metal complexes are a class of supramolecular systems particularly suited to the study of photoinduced energy and electron transfer processes.[1−4] In the design of dyads (two-component systems), triads (three-component systems), etc. for that purpose, octahedral coordination with terpyridine ligands is particularly attractive, given the unique trans geometry and the absence of chiral complications.[5] In a previous paper, a series of Ru(II)−Rh(III) dyads of general formula **1**, abbreviated hereafter as Ru−Rh ($n = 0$), Ru−(ph)−Rh ($n = 1$), and Ru−$(ph)_2$−Rh ($n = 2$), was described.[6]



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The dyads were designed with the Ru(II)-based unit as the photoexcitable molecular component and the Rh(III)-based unit as the electron acceptor. Energy transfer is energetically forbidden in these systems ($\Delta G \geq 0.4$eV).[6] On the other hand, photoinduced electron transfer (eq 1) is always thermodynamically allowed ($\Delta G \approx -0.1$ eV for $n = 1, 2$; $\Delta G \approx 0.0$ eV for $n = 0$).[6] Its actual efficiency, of course, depends on the competition with excited-state deactivation (eq 2). Given the short (subnanosecond) lifetime of Ru(II) terpyridine complexes at room temperature,[5] the original study was conducted at low temperature (150 K fluid solutions, 77 K rigid glasses) where nano- to microsecond time-resolved methods could be used. The results, however, were somewhat deceptive. For Ru−(ph)−Rh and Ru−$(ph)_2$−Rh, no significant intramolecular quenching was observed by comparing emission intensity and lifetime of the dyads with those of the $Ru(ttpy)_2^{2+}$ (**2**) model. With Ru−Rh ($n = 0$), some indication of photoinduced electron transfer was obtained, although the interpretation of the results was complicated by the lack of an obvious model compound for the Ru-based unit.[6] The final conclusion was that, at least for $n = 1$ and 2, electron transfer at 77−150 K is too slow to

$$^*\mathrm{Ru^{II}}-(\mathrm{ph})_n-\mathrm{Rh^{III}} \xrightarrow{k} \mathrm{Ru^{III}}-(\mathrm{ph})_n-\mathrm{Rh^{II}} \quad (1)$$

$$^*\mathrm{Ru^{II}}-(\mathrm{ph})_n-\mathrm{Rh^{III}} \xrightarrow{1/\tau^0} \mathrm{Ru^{II}}-(\mathrm{ph})_n\text{-}\mathrm{Rh^{III}} \quad (2)$$

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(1) Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. *Top. Curr. Chem.* **1990**, *158*, 73.

(2) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, U.K., 1991; Chapters 5 and 6.

(3) Scandola, F.; Bignozzi, C. A.; Indelli M. T. In *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*; Kalyanasundaram, K., Grätzel, M., Eds.; Kluwer: Dordrecht, The Netherlands, 1993; p 161.

(4) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759.

(5) Chambron, J.-C.; Coudret, C.; Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; Balzani, V.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993.

(6) Indelli, M. T.; Scandola, F.; Collin, J.-P.; Sauvage, J.-P.; Sour, A. *Inorg. Chem.* **1996**, *35*, 303.

(7) Indelli, M. T.; Bignozzi, C. A.; Harriman, A.; Schoonover, J. R.; Scandola, F. *J. Am. Chem. Soc.* **1994**, *116*, 3768.

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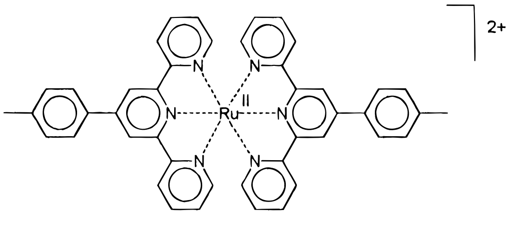

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compete with deactivation of the Ru-based MLCT excited state ($k < 1/\tau^0$, eqs 1 and 2).[6]

Since the electron transfer process (eq 1) in these systems is in the Marcus "normal" region, an obvious way to increase its rate would be to increase the temperature. An increase in temperature, however, is also known to shorten the MLCT excited-state lifetime, as the activated decay pathway involving upper metal-centered states becomes more efficient.[5] Thus, it is difficult to determine *a priori* whether an increase in temperature will increase or decrease the chance to observe photoinduced electron transfer. The answer is given by the present study, where the Ru−(ph)$_n$−Rh dyads are investigated at room temperature using picosecond time-resolved techniques.

Experimental Section

Materials. The complexes were available from previous studies.[6] Acetonitrile (Merck Uvasol) was used without further purification.

Apparatus and Procedures. The instruments and procedures used to obtain absorption and emission spectra were as described in a previous paper.[6] The stationary emission spectra were corrected for instrumental response by calibration with an NBS standard quartz−halogen lamp. Emission quantum yields were obtained using Ru(bpy)$_3^{2+}$ in water ($\Phi = 0.042$) as a reference emitter. Nanosecond emission lifetimes were measured by time-correlated single-photon-counting techniques, using a PRA 3000 nanosecond fluorescence spectrometer.[7] Emission lifetimes shorter than nanoseconds were measured by an apparatus based on a 35 ps pulse Nd:YAG laser (PY62−10 by Continuum) and a streak camera (Hamamatsu C1587 equipped with an M1952 fast single sweep unit). The second harmonic ($\lambda = 532$ nm) with an energy of 3−6 mJ was used to excite the samples ((2−4) × 10^{-4} M solutions, absorbance at the exciting wavelength 2−4). The emitted light passed a spectrograph (HB 250 Jobin-Yvon) and entered the slit of the streak camera. Acquisition and processing of the data were performed with a CCD camera and related software running on a PC. Typical streak camera images were the average of 2000 events collected at 10 Hz, containing 512 time points (4.19 ns total) by 480 wavelength points (165 nm total). Time profiles were selected on a 20 nm interval around the emission maximum and analyzed with standard iterative nonlinear procedures according to single exponentials. The quality of the fit, judged on the basis of χ^2 and the distribution of residuals along the time axis, was always satisfactory. Spectral profiles were obtained by averaging the intensity signals over a number of channels corresponding to the selected time window.

Results

At room temperature in acetonitrile solution, the Ru(ttpy)$_2^{2+}$ model and the Ru−(ph)−Rh and Ru−(ph)$_2$−Rh dyads all give rise to very weak emissions ($\Phi \approx 10^{-6}$−10^{-5}). The emission spectrum of Ru(ttpy)$_2^{2+}$, as measured by picosecond time-resolved spectroscopy (integrated over the 0−1 ns time interval), is shown in Figure 1a. Emission spectra obtained under the same experimental conditions for Ru−(ph)−Rh and Ru−(ph)$_2$−Rh are shown in Figure 1b,c. The emission of Ru−Rh is somewhat stronger ($\Phi = 5 \times 10^{-5}$) than that of the other dyads. Its spectrum, measured by stationary spectrofluorometry, is shown in Figure 2 (curve a).

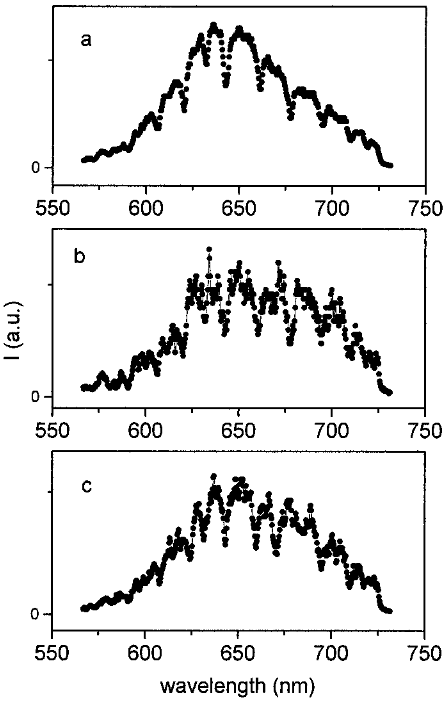

Figure 1. Emission spectra measured after picosecond laser excitation: (a) Ru(ttpy)$_2^{2+}$ model; (b) Ru−(ph)−Rh; (c) Ru−(ph)$_2$−Rh. Intensities are normalized measuring time window 0−1 ns.

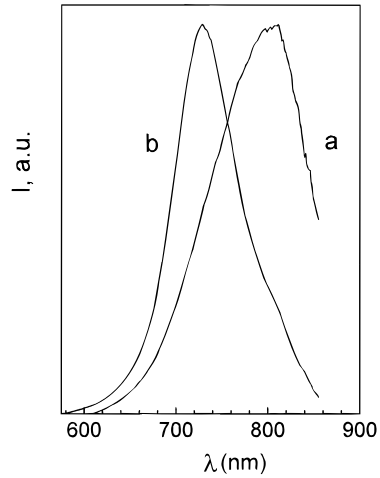

Figure 2. Stationary emission spectra: (a) Ru−Rh; (b) Ru−Ru model. Intensities are normalized .

For Ru(ttpy)$_2^{2+}$, Ru−(ph)−Rh, and Ru−(ph)$_2$−Rh, the decay of the emission was measured using picosecond pulsed laser excitation, taking care to work with rather low pulse intensities and high concentrations of the sample (typically, corresponding to a 10-fold excess of molecules over incident photons), in order to avoid the occurrence of multiphotonic effects (as previously observed at lower temperature[6]). The observed decays are presented in Figure 3. The lifetimes obtained by single-exponential fitting of these decays are as follows: Ru(ttpy)$_2^{2+}$, 860 ps; Ru−(ph)−Rh, 240 ps; Ru−(ph)$_2$−Rh, 1.9 ns. For Ru−Rh, the emission decay takes place on a much longer time scale, allowing the use of nanosecond single-photon counting techniques. The decay was monoexponential with a lifetime of 17 ns.

Discussion

As already noticed,[6,8] the Ru−(ph)$_n$−Rh dyad with $n = 0$ and those with $n = 1$, 2 differ sharply in the extent of

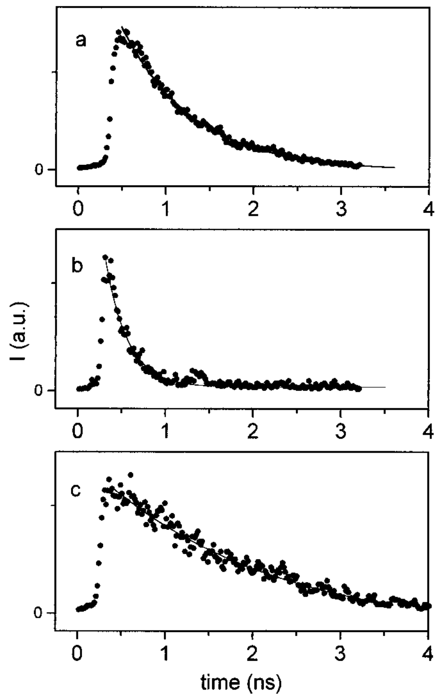

Figure 3. Emission decays measured after picosecond laser excitation: (a) Ru(ttpy)$_2^{2+}$ model; (b) Ru–(ph)–Rh; (c) Ru–(ph)$_2$–Rh. Contiunuous lines represent single-exponential fits yielding lifetimes of (a) 860 ps, (b) 240 ps, and (c) 1.9 ns.

intercomponent coupling. For this reason, the two types of dyads will be discussed separately.

Ru–(ph)–Rh and Ru–(ph)$_2$–Rh. For these dyads, a weak metal–metal coupling is provided by the bridge, and a reasonable model for the intrinsic properties of the Ru-based unit is provided by the Ru(ttpy)$_2^{2+}$ mononuclear complex.[6,8] The coincidence of the emission spectra of Ru(ttpy)$_2^{2+}$, Ru–(ph)–Rh, and Ru–(ph)$_2$–Rh (Figure 1) confirms this assumption and identifies the dyad emissions as originating from the Ru-containing unit.

In principle, the occurrence of photoinduced electron transfer in the dyads should lead to a shortening of the measured lifetime, τ, relative to the intrinsic lifetime of the Ru-containing unit, τ^0 (eq 2). Then, the electron transfer rate constant should be calculated as $k = (1/\tau) - (1/\tau^0)$.[9] The lifetime obtained from the emission decay of the Ru(ttpy)$_2^{2+}$ model, 860 ps (Figure 3a), can be considered as a lower limiting value[10-13] for τ^0 in the Ru–(ph)–Rh and Ru–(ph)$_2$–Rh dyads (eq 2). The decay of the Ru–(ph)–Rh dyad, 240 ps (Figure 3b), is definitely shorter than τ^0, indicating that *the intramolecular electron transfer quenching process (eq 1) is efficient*. A lower limit for the rate constant can be calculated as $k \geq 3.0 \times 10^9$ s^{-1}. For Ru–(ph)$_2$–Rh, on the contrary, the emission decays with a lifetime of 1.9 ns (Figure 3c), longer than that of the Ru(ttpy)$_2^{2+}$ model,[10] implying that intramolecular electron transfer (eq 1) is inefficient. An upper limit for its rate constant is $k \leq 5 \times 10^8$ s^{-1}.

The difference observed between Ru–(ph)–Rh and Ru–(ph)$_2$–Rh can be analyzed in terms of standard electron transfer theory.[14-17] In the weak-interaction (nonadiabatic) limit, the rate constant is given by

$$k = (2\pi/h)H_{AB}^{\;2}(\mathrm{FCWD}) \qquad (3)$$

where H_{AB} is the electronic coupling matrix element and FCWD is the nuclear term (Franck–Condon weighted density of states) which depends on the driving force and on the reorganizational energies of the process. In going from Ru–(ph)–Rh to Ru–(ph)$_2$–Rh, the FCWD term is expected to decrease only slightly, due to the weak dependence of the solvent reorganization on the transfer distance. On the other hand, a strong dependence of the electronic coupling on the bridge length is anticipated. According to standard models, electron transfer rates are expected to fall off exponentially with donor-acceptor distance, r (eq 4).[18-23]

$$H_{AB}^{\;2} = H_{AB}^{\;2}(0)\exp(-\beta r) \qquad (4)$$

Thus, the experimental observation of photoinduced electron transfer for Ru–(ph)–Rh but not for Ru–(ph)$_2$–Rh can be likely explained in terms of bridge effects. In the polyphenylene-bridged porphyrin dyads studied by McLendon,[24] a 6-fold decrease in electron transfer rate was obtained by addition of each phenylene spacer in the bridge. If a similar attenuation factor is applied to our systems, the electron transfer rate for Ru–(ph)$_2$–Rh would become $(3.0 \times 10^9)/6 = 5 \times 10^8$ s^{-1}, clearly too slow to compete with the deactivation of the MLCT excited state.

It is instructive to compare the electron transfer rate constant observed for Ru–(ph)–Rh (3.0×10^9 s^{-1}) with that previously measured (1.7×10^8 s^{-1}) for the dyad **3**.[7] The two dyads are similar in driving force and reorganizational energies (FCWD in eq 3).[6,7] Thus, the main effective difference lies in the bridge (H_{AB} in eq 3). It is seen that, although the metal–metal distance

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(8) While for Ru–(ph)–Rh and Ru–(ph)$_2$–Rh the absorption spectra are practically a superposition of those of the mononuclear models Ru(ttpy)$_2^{2+}$ and Rh(ttpy)$_2^{3+}$ (ttpy = 4′-*p*-tolyl-2,2′:6,2″-terpyridine), Ru–Rh exhibits a marked red shift in the ruthenium-to-ligand charge transfer band.[6] This indicates that the Ru–Rh complex is far from the limit of weak intercomponent interaction and implies that mononuclear Ru(ttpy)$_2^{2+}$ cannot be used as a model for the Ru-based unit in this dyad. The identification of a proper model system for this dyad is problematic (see Discussion).

(9) This derivation assumes that the excited-state electron transfer process (eq 1) is irreversible, i.e., that the back-reaction to re-form the excited-state is too slow to compete with that leading to the ground-state. This is certainly true for the Ru–(ph)–Rh and Ru–(ph)$_2$–Rh dyads, where the former process is substantially uphill in free energy.

(10) It is known that, in Ru(II) terpyridine complexes, the excited-state lifetime is extremely sensitive to variations in the excited-state energy, with large increases in lifetime accompanying red shifts in MLCT spectra.[11-13] A careful inspection of the absorption[6] and emission (Figure 1) spectra indicates small red shifts relative to Ru(ttpy)$_2^{2+}$, increasing from Ru–(ph)$_2$–Rh to Ru–(ph)–Rh, implying that accurate, individual τ^0 values could increase in the same order.

(11) Barigelletti, F.; Flamigni, L.; Guardigli, M.; Sauvage, J.-P.; Collin J.-P.; Sour A. *Chem. Commun.* **1996**, 1329.

(12) Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Thompson, A. M. W. C. *Inorg. Chem.* **1995**, *34*, 2759.

(13) Benniston, A. C.; Grosshenny, V.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1884.

(14) Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860.

(15) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

(16) Miller, J. R.; Beitz, J. V.; Huddlestone, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057.

(17) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(18) This is as expected in the case of through-space electron tunneling,[19] but similar exponential laws hold for through-bond interaction[20] (as a function of the number of intervening chemical bonds) or for superexchange mechanisms[20-22] (as a function of the number of repeating spacer units).

(19) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640.

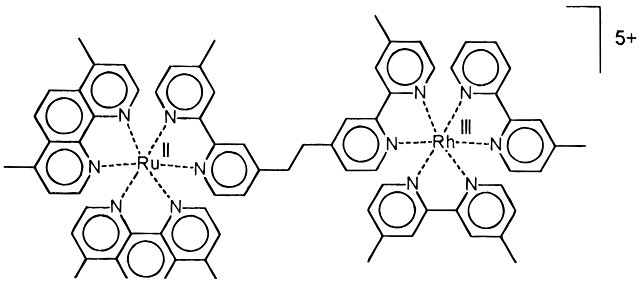
(20) Verhoeven, J. W.; Paddon-Row, M. N.; Warman, J. M. In *Photoprocesses in Transition Metal Complexes, Biosystems and Other Molecules. Experiments and Theory*; Kochanski, E., Ed.; Kluwer: Dordrecht, The Netherlands, 1992.

(21) McConnell, H. *J. Chem. Phys.* **1961**, *35*, 508.

(22) Miller, J. R.; Beitz, J. V. *J. Chem. Phys.* **1981**, *74*, 6746.

(23) Wasielewski, M. R. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, The Netherlands, 1988; Part A, p 161.

(24) Helms, A.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1992**, *114*, 6227.



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is longer in Ru−(ph)−Rh (15.5 Å, relative to 13.5 Å for **3**), the electron transfer is faster. This is a clear indication that not only the length but also the *nature* of the bridge are relevant to this comparison and that polyphenylene bridges are intrinsically more efficient than polymethylene ones in mediating donor−acceptor electronic coupling. In eq 4, specific bridge effects are contained in the exponential attenuation factor β. In this respect, the value $\beta = 0.4$ Å^{-1} obtained for polyphenylene bridges by McLendon[24] should be compared with values in the range $\beta = 0.85-0.95$ Å^{-1} typical of rigid aliphatic bridges.[25,26]

Ru−Rh. It has been previously pointed out[6,8] that, in the $n = 0$ dyad, the direct linkage between the two coordination spheres brings about a much stronger metal−metal electronic coupling than in the other cases. This is manifested by the fact that the MLCT absorption spectrum of Ru−Rh is clearly red-shifted relative to that of the Ru(ttpy)$_2{}^{2+}$ mononuclear complex (and those of the Ru−(ph)−Rh and Ru−(ph)$_2$−Rh dyads).[6] The 77K emission spectrum is also substantially red-shifted (0.1 eV) relative to Ru(ttpy)$_2{}^{2+}$ and the longer dyads.[6] From the energetic standpoint, the main consequence is that, in Ru−Rh, the excited-state electron transfer process (eq 1) is expected to be less exergonic than those in the other dyads, probably with a ΔG value very close to 0.[6]

The main problem in assessing the occurrence of such a process is the lack of a good model for the Ru-based moiety of Ru−Rh. The inadequacy of Ru(ttpy)$_2{}^{2+}$, already suggested by the above-mentioned spectral shifts, is borne out by the lifetimes obtained at room temperature: that of Ru−Rh (17 ns) is much longer than that of Ru(ttpy)$_2{}^{2+}$ (860 ps). In the previous work, it was proposed, on the basis of the similarity in absorption and low-temperature emission spectra, that the analogous binuclear all-ruthenium Ru−Ru complex could be used as a reasonable model for the Ru-based moiety of Ru−Rh.[6] The Ru−Ru complex has an exceptionally long lifetime at room temperature (ca. 600 ns),[27] and if the above assumption is maintained, the measured lifetime of 17 ns would imply the presence of considerable quenching in the Ru−Rh dyad.[28]

As to the nature of such quenching, since $\Delta G \approx 0$, the possibility of reversible excited-state electron transfer should be allowed for in this case. If, taking a limiting view, fast equilibration between reactants and products of eq 1 were assumed to precede any deactivation, the observed lifetime would bear no information on the rate of the electron transfer process but rather would reflect the intrinsic lifetimes of the two states and the equilibrium distribution.[29] An excited-state equilibrium hypothesis of this type could probably help to explain the peculiar aspect of the room-temperature Ru−Rh emission. In Figure 2, this emission is compared with that of the Ru−Ru model complex. It is important to recall that the Ru−Rh and Ru−Ru dyads have practically coincident absorption and low-temperature (77 and 150 K) emission spectra[6] (which was the basis for suggesting Ru−Ru as the model system). It is clear from Figure 2, however, that at room temperature the Ru−Rh emission is strongly shifted to the red and has a much larger bandwidth relative to Ru−Ru. Considering that in a strongly coupled system not only the metal-to-ligand but also a metal-to-metal charge transfer state may be emissive,[30,31] it is tempting to attribute the peculiar aspect of the Ru−Rh emission to the presence of overlapping emissions from these two types of excited states in fast thermal equilibrium.

Conclusions. From a structural point of view, the series of dyads Ru−(ph)$_n$−Rh ($n = 0, 1, 2$) looks ideally suited for a systematic investigation of the effect of the bridge on photoinduced electron transfer. In practice, the experimental window for this type of investigation is rather narrow. On one side, the member with $n = 0$ is of little use due to the strong electronic coupling between the molecular components. Because of this, (i) relevant properties (excited-state energies and lifetimes, electron transfer driving force) are completely out-of-line with respect to the rest of the series and (ii) the interpretation of the experimental results is made difficult by the lack of exact model compounds. Dyads with $n \geq 1$, on the other hand, are free of such problems. With increasing n, however, the limitation comes from the intrinsically short (sub-nanosecond) lifetime of the excited state of the Ru(II) terpyridine chromophore. Thus, photoinduced electron transfer is observed on the picosecond time scale for $n = 1$, but at $n = 2$ the rate is already too slow to compete with excited-state deactivation. It is evident that a long-lived Ru(II) chromophore is needed to study bridge length effects over a wider range, without losing electron transfer efficiency. Studies in this direction are currently under way.[32]

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[25] Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258.

[26] Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440.

[27] Hammarström, L.; Barigelletti, F.; Flamigni, L.; Indelli, M. T.; Armaroli, N.; Calogero, G.; Guardigli, M.; Sour, A.; Collin, J.-P.; Sauvage, J.-P. *J. Phys. Chem.*, submitted for publication.

[28] In principle, information on the occurrence of photoinduced electron transfer could be sought by time-resolved absorption spectroscopy. In practice, however, this possibility is nullified by the fact that the spectra of reactants and products of eq 1 are expected to be very similar (dominated in both cases by the bleaching of the Ru-based MLCT absorption; see, e.g., ref 7).

[29] It can be easily shown that, in this hypothesis, the lifetime is given by

$$\tau = [\exp(-\Delta G/RT) + 1]\frac{\tau_1 \tau_2}{\tau_1 \exp(-\Delta G/RT) + \tau_2}$$

where indexes 1 and 2 refer to the two states in equilibrium.

[30] With respect to that of the MLCT emission, the radiative rate constant of the metal-to-metal charge transfer emission is expected to be somewhat smaller. The decrease corresponding to the smaller electronic coupling is expected to be partially compensated by the larger dipole length of the transition.[31]

[31] Verhoeven, J. W.; Kroon, J.; Paddon-Row, M. N.; Warman, J. M. In *Supramolecular Chemistry*; Balzani, V., De Cola, L., Eds.; Kluwer: Dordrecht, The Netherlands, 1992; p 181.

[32] Indelli, M. T.; Schmehl, R. H.; Scandola, F. Work in progress.