Notes

Photoinduced Charge Separation through a Negatively Charged Bridge

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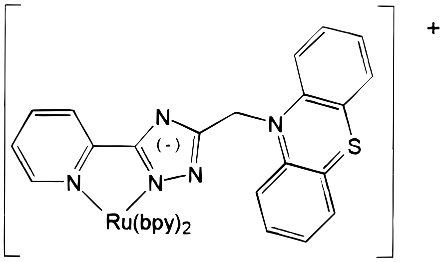
Introduction

Photoinduced charge separation processes in natural and artificial systems are currently the object of extensive investigations.[1] In these systems a photoinduced sequence of electron-transfer steps generates a charge-separated state in which part of the light absorbed by a photosensitizer is stored, for as long as possible, as redox energy.

Systems investigated include dyad and triad assemblies based on ruthenium polypyridyl complexes in which the ruthenium center plays the role of photosensitizer and the acceptor or donor moieties are covalently attached to polypyridyl moieties. Previous studies on such systems have highlighted the importance of several factors, such as the distance and the stereochemical relationships between the components of the complex, the rigidity and electronic properties of the bridging group, and the role played by the solvent.[2] In all systems reported the electron donor or acceptor is bound to a nonpolypyridyl ligand. Since the lowest energy excited level in such assemblies is normally a polypyridyl-based triplet metal-to-ligand charge-transfer state, ^{3}MLCT, coupling between the acceptor/donor moieties and the photosensitizers is expected to be strong. In a new approach, we have recently started an investigation on dyad chromophore−quencher systems where a donor group is linked to a bridging ligand which is *not involved* in the luminescent ^{3}MLCT state and is *negatively charged*. These investigations were prompted by the notion that by decreasing the coupling between the donor and the excited state, the rate of the intramolecular charge recombination, which eventually leads to the decay of the charge separated state, might decrease. Moreover, while it has been shown that negative bridges facilitate metal−metal communication,[3] to the best of our knowledge, their effect on the formation of photoinduced charge separation has not been addressed.

5-(Pyridine-2-yl)-1,2,4-triazole ligands (pt) are suitable building blocks for this purpose. It has been demonstrated [4] that when pt ligands are coordinated to Ru(II), the triazole moiety is easily deprotonated leading to a negatively charged triazolate. Furthermore, it has been well established that in complexes bearing two bpy moieties and a pt ligand, the emitting ligand is *always* bpy based.[5]

In this study we report a new system in which a pt moiety is linked to phenothiazine (PTZ) (see below) a group which has been extensively used as a donor in dyads or triads.[2a−e] Thus, a comparison between analogous dyads in which similar chromophores and donors are linked by *neutral* and *negative* bridges is now possible. Toward this goal 3-(CH$_2$-*N*-phenothiazine)-5-(pyridine-2-yl)-1,2,4-triazole ligand **1** (pt-PTZ) and the corresponding Ru(bpy)$_2$ complex **2** (where the triazole has been deprotonated to a negatively charged triazolate) have been prepared. The photophysical results obtained for this complex have been compared with those found for the model compound **3**[4] containing 3-methyl-5-(pyridine-2-yl)-1,2,4-triazolate (pt-Me) and with those reported for an analogous dyad (compound **5**) in which a Ru(dmb)$_2$ chromophore (dmb = 4,4′-dimethyl-2,2′-bipyridine) and the PTZ are connected by the *neutral* dmb moiety.[6a] These results represent the first attempt of a comparative study of the properties of *negative* and *non-negative* bridging ligand on a charge-separated system.



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Experimental Section

3-(CH$_2$-*N*-phenothiazine)-5-(pyridine-2-yl)-1,2,4 triazole (1). Phenothiazine (4.6 g, 23 mmol) and NaH (0.55 g, 23 mmol) were dissolved in 20 mL of dry DMF at 0 °C, and the orange mixture was stirred for

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[1] The literature on this topic is too vast to be exhaustively quoted. For recent books or review articles, see: (a) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759. (b) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, 1991; Chapter 5. (c) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435. (d) Norris, J. R. Deishenofer, J. (Eds.) *The Photosynthetic Reaction Center*; Academic: New York, 1993. (e) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198. (f) Hagfelt, A.; Graetzel, M. *Chem. Rev.* **1995**, *95*, 49. (g) Harriman, A.; Sauvage, J.-P. *Chem. Soc. Rev.* **1996**, 41. (h) Bignozzi, C. A.; Schoonover, J. R.; Scandola, F. *Prog. Inorg. Chem.* **1997**, *44*, 1.

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[3] (a) Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; Louis, R.; Launay, J.-P.; Sauvage, J.-P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1775. (b) Haga, M.; Bond, M. A. *Inorg. Chem.* **1991**, *30*, 475. (c) Hage, R.; Haasnoot, J. G.; Nieuwenhuis, H. A.; Reedijk, J.; de Ridder, D.; Vos, J. G. *J. Am. Chem. Soc.* **1990**, *112*, 9245.

[4] Hage, R.; Prins. R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *J. Chem. Soc., Dalton. Trans.* **1986**, 1389.

[5] Barigelletti, F.; De Cola, L.; Balzani, V.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Inorg, Chem.* **1989**, *28*, 4344.

[6] (a) Treadway, J. A.; Chem, P.; Rutherford, T. J.; Keene, F. R.; Meyer, T. J.; *J. Phys. Chem.* **1997**, *101*, 6824. (6b) These authors used Ru(dmb)$_3$ as model compound in ref 6a.

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Table 1. Photochemical and Electrochemical Data at 20 ± 3 °C

			$E_{1/2}$ (vs SSCE) (in V)		
complex	τ (ns)	ϕ	PTZ^+/PTZ^0	Ru^{3+}/Ru^{2+}	ligand-based reduction
2[a]	150	3×10^{-3}	+0.72	+0.84	−1.43
3[a]	100	2×10^{-3}	−	+0.82	−1.45
5[a,c]	680	0.044	+0.80	+1.22	−1.37
2[b]	220	0.018	+0.78	+0.95	−1.38
3[b]	120	8×10^{-3}	−	+0.92	−1.40

[a] Acetonitrile. [b] Dichloromethane. [c] Reference 9.

15 min. Bromoethyl acetate (2.1 mL, 23 mmol) in 10 mL of dry DMF was added dropwise, and the resulting reaction mixture stirred overnight at room temperature in subdued light. The DMF was removed under reduced pressure, and the residue was redissolved in $CHCl_2$ and washed once with a 10% HCl solution and twice with water. The organic layer was removed under reduced pressure, and the residue was recrystallized from methanol to give 4.5 g (67%) of the ethyl acetate N-derivative of PTZ. The ester so obtained was reacted with a 30-fold molar excess of hydrazide hydrate in 25 mL of DMF at 70 °C for 20 h, after which 3.8 g (90%) of the PTZ *N*-acetylhydrazide were recovered by filtration. A 0.650 g (6.2 mmol) amount of 2-cyanopyridine was dissolved in 6 mL of methanol containing a catalytic amount of sodium methoxide (prepared by previously adding 70 mg of sodium), and the solution was refluxed for 3 h after which 1.7 g (6.2 mmol) of the previously synthesized PTZ *N*-acetylhydrazide was added in parts. The resulting mixture was refluxed overnight, and the white precipitate that was obtained was collected by filtration and refluxed in 10 mL of diethyleneglycol for 30 min. The crude product was purified by vacuum column chromatography on silica gel, using a 50:50 ethyl acetate/dichloromethane mixture as eluent. The second band that eluted was collected, and after removal of the solvent 0.8 g of the desired target was obtained as a white powder (36%).

$[Ru(bpy)_2(pt\text{-}PTZ)]PF_6$ (2). This complex was synthesized following standard procedures[4] and purified by chromatography on neutral alumina (acetonitrile as eleuent). Yield: 50%. All new compounds gave satisfactory NMR data and elemental analyses.

The syntheses of pt-Me and its $Ru(bpy)_2$ complex **3** have been reported elsewhere.[4]

Single photon counting[7] and electrochemical techniques[8] have been reported before. Flash photolysis measurements were carried out in acetonitrile with a 4-fold excess of MV^{2+} using 0.1 mmol concentrations of **2** and **3**. Employing the third harmonic (355 nm) of a Spectron Q-switched Nd:YAG laser with a 250 W xenon-arc lamp as a monitoring source for the latter measurements, transients were monitored on an applied photophysics (f/3.4) monochromator and photomultiplier coupled to an oscilloscope. Samples were deaerated by using argon. Standard iterative techniques were employed to fit transients using Microsoft Excel.

Results and Discussion

Photophysical and electrochemical studies on **2** and **3** were performed in acetonitrile and dichloromethane. The results obtained are summarized in Table 1.

The absorption spectra of dyad **2** and of its reference compound **3** are identical in the visible region, indicating that in the ground state only very weak interaction occurs between the chromophore and the PTZ quencher. Surprisingly, going from the model complex **3** to complex **2** an *increase* of the emission lifetime and quantum yield is observed in both solvents studied. This is unusual behavior for such systems since a *decrease* in lifetime and quantum yield is anticipated if a donor group is linked to the complex. Electrochemical and luminescence data (see Table 1) indicate that reductive quenching is thermodynamically uphill by ~0.1 eV.[9] Similarly unfavorable thermodynamics have been observed by Meyer et al.[6a] for complex **5**. In this case, however, partial reductive quenching was observed.[6b] It seems likely that since for **2** the emission lifetime is significantly shorter than that observed for **5**, reductive quenching of the excited state is not competitive with direct deactivation to the ground state. Yet this observation alone does not account for the longer emission lifetime and the higher quantum yield observed when moving from the model complex **3** to the dyad **2**. The explanation for this behavior is by no means simple, and any hypothesis advanced at the moment would be purely speculative.

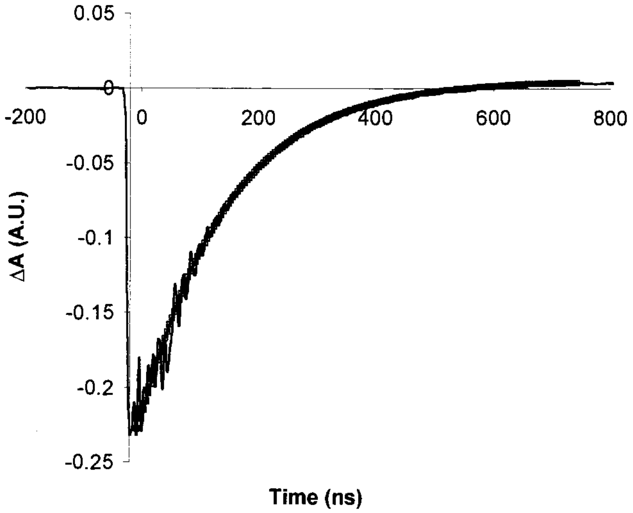

Figure 1. Recovery of the Ru(II) center in **2** after photoexcitation in the presence of MV^{2+}. (—) Data; (□) model.

The redox potentials suggest that in both solvents studied PTZ is capable of reducing Ru^{III} in the ground state with a driving force of about −0.12 eV. This observation suggests that while quenching of the excited state is unfavorable thermodynamically, in an experiment where the ^{3}MLCT state is quenched by an electron acceptor, the phenothiazine donor should be able to act as an electron donor to the Ru^{III} center. Indeed, when monitoring **2** at 530 nm in the presence of methyl viologen (MV^{2+}) as sacrificial acceptor,[10] time-resolved spectroscopy has shown the formation of a long-lived transient which grows-in with a lifetime of 170 ns and decays following second-order kinetics ($k = 5 \times 10^9$ dm^3 mol^{-1} s^{-1}). For the model compound **3** such a signal is not observed Therefore, the behavior observed for **2** is likely to be due to the formation of a $PTZ^{•+}$ radical cation. This assignment is in agreement with literature values which indicate that the PTZ radical does indeed absorb in this spectral region.[2e] Monitoring at 450 nm allows for the investigation of the Ru(II) center through the analysis of the recovery of the ^{1}MLCT band. This recovery is double exponential in nature with lifetimes of 170 (80%) and 110 ns (20%) (See Figure 1). The latter value is consistent with the

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(9) The ΔG for the excited-state electron transfer from PTZ to Ru(III)* was calculated using the (approximated) equation $\Delta G = E_{ox} - E_{red}^*$, where E_{ox} is the reducing potential of the PTZ moiety (see Table 1) and E_{red}^* is the reducing potential for the excited state (Ru(III)*). E_{red}^* was calculated from the free energy content of the excited state (E_{o-o}) and the first anodic potential (E_{red}) found for the ground state (see Table 1): $E_{red}^* = E_{red} - E_{o-o}$. E_{o-o} was assumed to be equal to the energy relative to the emission maximum (λ_{max}) of complex **2** in butyronitrile at 77 K ($\lambda_{max} = 620$, i.e., 2.00 eV).

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emission lifetime observed in the presence of MV^{2+}, (90 ns) and can be attributed to the presence of unquenched complex. The former is associated with the grown-in lifetime of the 530 nm transient ($k_{et} = 5.9 \times 10^6$ s^{-1}). Under the same conditions, recovery of this absorption band for **3** is not complete even after 100 μs. For both **2** and **3** long-lived transients are observed at 405 and 650 nm, which are attributable to the MV^+ radical.[10] For compound **2**, the decay of this transients follows, at both wavelengths, the same second-order kinetics observed for the decay of the PTZ^+ radical, suggesting that bimolecular recombination is the major pathway for loss of these two radicals. For compound **3**, the decay remains incomplete after 100 μs.

Finally, in experiments carried out with free ligand **1** and MV^{2+} no photoproducts, transient or otherwise, were observed, ruling out a direct photochemical reaction between MV^{2+} and PTZ.

These results strongly suggest that the transient observed for **2** at 530 nm is due to the formation of a $PTZ^{\bullet+}$ radical cation following electron transfer to Ru^{III} and indicate the ability of the PTZ moiety in this dyad to reduce Ru^{III} by electron transfer through the anionic bridge.

In conclusion, these results clearly shows that anionic bridges can effectively mediated electron-transfer processes in covalently linked chromophore–quencher complexes. However, to better understand the role played by the negative charged bridging ligand, it is essential to make the reductive excited-state quenching from PTZ to ^{3}MLCT *exoergonic*. We are now planning the synthesis of new complexes in an attempt to *modulate* the thermodynamics of the reductive quenching from PTZ to ^{3}MLCT.

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Supporting Information Available: Figures S1–3 containing (S1) the proton NMR spectrum of free ligand **1**, (S2) the proton NMR spectrum of **2**, and (S3) the transient absorption spectrum of **2** in the presence of MV^{2+}, 200 ns after excitation (3 pages). Ordering information is given on any current masthead page.

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