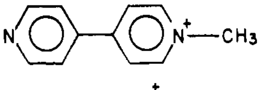
Directed Charge Transfer. Reductive Quenching in a Chromophore-Quencher Complex

Sir:

A number of chromophore-quencher complexes have been reported in which optical excitation is followed by intramolecular, oxidative quenching to lead to charge separation at the molecular level. The chemical systems involved have included quinones attached to porphyrins,[1] as well as related systems based on metal-to-ligand charge-transfer (MLCT) excited states,[2,3] e.g. $[Ru^{II}(bpy)_2(MeQ)_2]^{4+}$ or $[(bpy)Re^{I}(CO)_3(MeQ)]^{2+}$ (bpy = 2,2′-bipyridine).



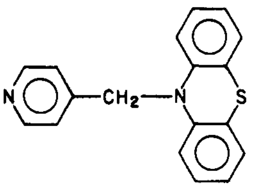
MeQ^+

In the systems containing attached oxidative quenchers, transient measurements have shown that the initial excitation is followed by intramolecular electron-transfer quenching, eq 1, and, in the

$$\begin{tikzcd}
{[(bpy^{-}\cdot)Re^{II}(CO)_3(MeQ)]^{2+}} \arrow[r, shift left, "k_q"] \arrow[d, shift right, "h\nu"'] & {[(bpy)Re^{II}(CO)_3(MeQ^{-}\cdot)]^{2+}} \arrow[l, shift left, "k_{-q}"] \arrow[dl, "1/\tau_2^*"] \\
{[(bpy)Re^{I}(CO)_3(MeQ)]^{2+}} \arrow[u, shift right, "1/\tau_1^*"'] &
\end{tikzcd} \qquad (1)$$

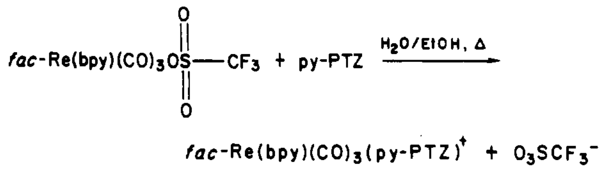
net sense, optically induced, directed charge transfer along selected molecular axes. MLCT excited states like $[(bpy)_2Ru^{III}(bpy^{-}\cdot)]^{2+*}$ are known to undergo reductive[4] as well as oxidative quenching by bimolecular processes, $Re(bpy)_3^{2+*} + D \rightarrow Ru(bpy)_3^{+} + D^{+}$. Clearly the possibility exists for preparing chromophore-quencher complexes in which the sense of the quenching is reversed in that initial excitation to a MLCT excited state is followed by intramolecular reductive quenching.[5]

In order to explore this possibility, we have prepared the complex $[(bpy)Re^{I}(CO)_3(py\text{-}PTZ)]^{+}$. The structure of the electron-transfer donor ligand is as follows:



py-PTZ

The ligand was prepared by the reaction between an excess of the lithio salt of the phenothiazine anion and a suspension of $[H(NC_5H_4)CH_2Cl]Cl$ in dry THF solution. After purification of the ligand by column chromatography and recrystallization, the chromophore-quencher complex was prepared by using an established procedure summarized by the reaction in eq 2. The



$$fac\text{-}Re(bpy)(CO)_3OS(O)_2\text{—}CF_3 + py\text{-}PTZ \xrightarrow{H_2O/EtOH,\ \Delta} fac\text{-}Re(bpy)(CO)_3(py\text{-}PTZ)^{+} + O_3SCF_3^{-} \qquad (2)$$

complex was conveniently purified by recrystallization and gave satisfactory elemental analysis results and an NMR spectrum consistent with the proposed formulation.

The rhenium-based chromophore-quencher complex has optical and electrochemical properties closely related to model systems such as $[(bpy)Re(CO)_3(py\text{-}Et)]^{+}$ (py-Et = 4-ethylpyridine).[6,7] In acetonitrile the lowest MLCT transition for $[(bpy)Re(CO)_3(py\text{-}PTZ)]^{+}$ occurs as a broad shoulder centered at approximately $\lambda = 348$ nm ($\epsilon = 4584$ m^{-1} cm^{-1}). The complex is oxidized at $E_{1/2} = +0.83$ V (vs. SCE), which is very near the potential for oxidation of the free ligand, $E_{1/2} = +0.76$ V. An additional, irreversible wave, which could be due to the Re(II/I) couple, is found at $E_p = +1.6$ V. From the bpy-based reduction of $[(bpy)Re(CO)_3(py\text{-}PTZ)]^{+}$ at -1.13 V and the room-temperature emission energy of $[(bpy)Re(CO)_3(py\text{-}Et)]^{+}$ (580 nm = 2.14 V) the estimated excited-state reduction potential for the couple $[(bpy^{-}\cdot)Re^{II}(CO)_3(py\text{-}PTZ)]^{+*}/[(bpy^{-}\cdot)Re^{I}(CO)_3(py\text{-}PTZ)]$ is $E_{1/2} = +1.01$ V. From this potential and the potential for the coordinated $-PTZ^{+/0}$ couple, intramolecular reductive quenching is thermodynamically favored by ~0.2-0.3 V.

At 80 K in 4:1 ethanol-methanol the photophysical properties of the MLCT excited state of the chromophore-quencher complex ($\lambda_{max}^{em} = 510$ nm, $\tau = 4100$ ns) are essentially the same as those of the 4-ethylpyridine model complex ($\lambda_{max}^{em} = 505$ nm, $\tau = 5000$ ns). However, at room temperature the properties of the two complexes are extraordinarily different. For the model complex a relatively strong emission occurs at $\lambda_{max}^{em} = 580$ nm, with τ 213 ns. The matrix-induced shift in the emission energy and the decrease in lifetime for the model complex are consistent with observations made earlier on related complexes. The chromophore-quencher complex however shows no observable emission at room temperature. A related observation has been made for complexes containing the MeQ^{+} quenching ligand where intramolecular quenching appears to be induced at the glass to fluid transition where there is sufficient rotational mobility for the two aromatic rings to begin to flatten.[3]

The most revealing results have come from transient absorption experiments. In Figure 1 the first spectrum is of the model complex at room temperature, which shows the characteristic difference spectrum expected for the MLCT-based excited state, $[(bpy^{-}\cdot)Re^{II}(CO)_3(pyEt)]^{+*}$. The room-temperature transient difference spectrum obtained for the chromophore-quencher complex is also shown. The most striking feature in the latter spectrum is the appearance of a strong absorption feature at $\lambda_{max} \simeq 500$ nm. There is also evidence for the $(bpy^{-}\cdot)$-based chromophore in the 320-390 nm region. It is quite evident that at room temperature the chromophore-quencher and model complexes have profoundly different thermally equilibrated excited states. Our results are consistent with initial excitation into the MLCT chromophore followed by intramolecular quenching to give the charge-separated state, $[(bpy^{-}\cdot)Re^{I}(CO)_3(py\text{-}PtZ^{+}\cdot)]^{+*}$, as shown in eq 3. At room temperature, the quenching step (k_q)

$$\begin{tikzcd}
{[(bpy^{-}\cdot)Re^{II}(CO)_3(py\text{-}PTZ)]^{+*}} \arrow[r, shift left, "k_q"] \arrow[d, shift left, "1/\tau_1^*"] & {[(bpy^{-}\cdot)Re^{I}(CO)_3(py\text{-}PTZ^{+}\cdot)]^{+*}} \arrow[l, shift left, "k_{-q}"] \arrow[dl, "1/\tau_2^*"] \\
{[(bpy)Re^{I}(CO)_3(py\text{-}PTZ)]^{+}} \arrow[u, shift left, "h\nu"] &
\end{tikzcd} \qquad (3)$$

occurs within the laser pulse (~10 ns) and is too rapid for us to

---

(1) (a) Ho, T.; McIntosh, A. R.; Bolton, J. R. *Nature (London)* **1980**, *286*, 254. (b) Nishitani, S.; Kurata, N.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1981**, *22*, 2099. (c) Bergkamp, M. A.; Dalton, J.; Netzel, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 253.

(2) Sullivan, B. P.; Abruna, H. D.; Finklea, H. O.; Salmon, D. J.; Nagle, J. K.; Meyer, T. J.; Sprintschnik, H. *Chem. Phys. Lett.* **1978**, *58*, 389.

(3) Westmoreland, T. D.; LeBozec, H.; Murray, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5952.

(4) (a) Balzani, V.; Bolleta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1. (b) Sutin, N.; Creutz, C. *Pure. Appl. Chem.* **1980**, *52*, 2717. (c) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94. (d) Kalyanasundaran, K. *Coord. Chem. Rev.* **1982**, *46*, 159.

(5) Root, M. J.; Deutsch, E.; Sullivan, J. C.; Meisel, D. *Chem. Phys. Lett.* **1983**, *101*, 353.

(6) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998.

(7) (a) Luong, J. C. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1981. (b) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952.

0020-1669/85/1324-2596$01.50/0

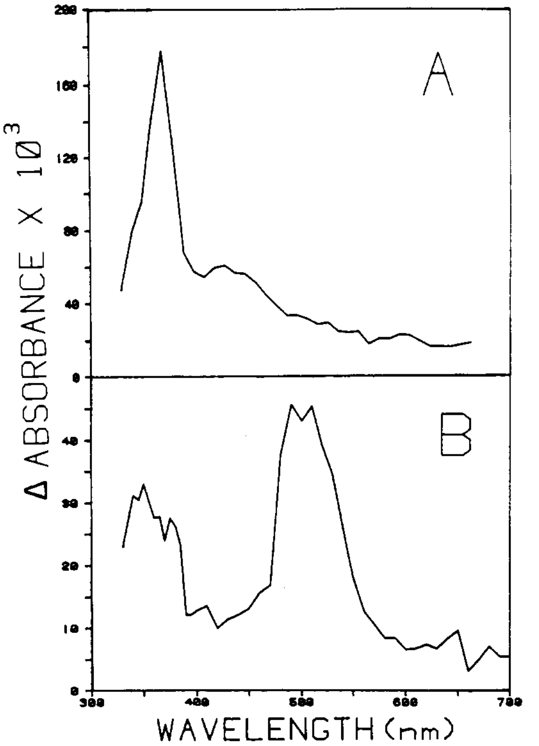


Figure 1. Transient absorbance spectra in acetonitrile solution for the model and chromophore-quencher complexes: (*a*) $[(bpy)Re(CO)_3(py\text{-}Et)](PF_6)$; (B) $[(bpy)Re(CO)_3(py\text{-}PTZ)][PF_6]$. Spectra are plotted as $\Delta A = \log (I_0/I_t)$ vs. wavelength, where t is the delay time following the laser pulse. Both spectra were obtained in solutions containing sufficient complex that the ground-state absorbance was 0.5 at the exciting wavelength, 355 nm. The laser pulse energy was 10 mJ/pulse, and the delay times were 50 ns for spectrum A and 25 ns for spectrum B. The decreased delay time for spectrum B lessens the quality of the signal but was necessary given the short-lived nature of the charge-separated state for $[(bpy)Re(CO)_3(py\text{-}PTZ)]^+$.

observe by transient absorption measurements. The subsequent decay of the charge separated state ($1/\tau_2°$) is rapid and occurs with τ = 25 ns ($k = 4 \times 10^8$ s^{-1}) at room temperature.

The observation of the appearance and subsequent decay of the charge-separated state for the chromophore-quencher complex gives useful insight into related processes and allows some interesting analogies to be made: (1) The intramolecular quenching step produces a chemically linked organic "exciplex", which decays by electron transfer through the intervening Re(I) "bridge" or, perhaps, by direct, through-space overlap. (2) The excitation-quenching sequence results in intramolecular sensitization of a low-lying interligand charge-transer (ILCT) state. An absorption band arising from the direct transition, $[(bpy)Re(CO)_3(py\text{-}PTZ)]^+ \xrightarrow{h\nu} [(bpy^{-}\cdot)Re(CO)_3(py\text{-}PTZ^+)]^+$, is not observed, presumably because of negligible electronic coupling between PTZ and bpy. (3) Decay of the charge-separated state is highly favored thermodynamically ($\Delta G°' = -1.9$ eV). Nonetheless, its decay is relatively slow ($k = 4 \times 10^8$ s^{-1}), consistent with an electron-transfer reaction in the "inverted region" where the energy-gap law is expected to dictate the energy dependence of k. (4) When combined with the earlier work on attached oxidative quenchers, the results described here introduce the possibility of devising charge-separation devices at the molecular level where both acceptor and donor quenchers are attached to a common chromophore:

$$\text{D–ML–A} \xrightarrow{h\nu} \text{D–M}^+\text{L}^-\text{–A} \rightarrow {}^+\text{D–ML–A}^-$$

Acknowledgments are made to the National Science Foundation under Grant No. CHE-8008922 and the Army Research Office—Durham under Grant No. DAAG-29-82-K-0111 for support of this research.

Registry No. py-PTZ, 97170-93-9; *fac*-Re(bpy)$(CO)_3$(py-PTZ)$^+O_3SCF_3^-$, 97170-96-2; *fac*-Re(bpy)$(CO)_3OSO_2CF_3$, 97170-94-0; $[(bpy)Re(CO)_3(py\text{-}Et)]^+$, 84028-68-2; $[H(NC_5H_4)CH_2Cl]Cl$, 1822-51-1; lithium phenothiazinate, 4442-10-8.

Department of Chemistry
The University of North Carolina
Chapel Hill, North Carolina 27514

T. David Westmoreland
Kirk S. Schanze
Paul E. Neveux, Jr.
Earl Danielson
B. Patrick Sullivan
Pingyun Chen
Thomas J. Meyer*

Received August 28, 1984