

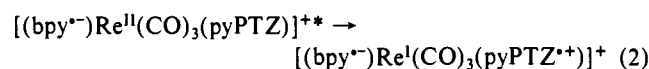
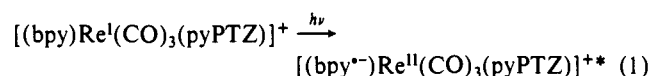
Long-Range, Light-Induced Redox Separation across a Ligand Bridge

Rich Duesing, Gilles Tapolsky, and Thomas J. Meyer*

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

Received December 26, 1989

Molecular systems have been designed that undergo intramolecular photochemical electron transfer to give spatially separated oxidative and reductive equivalents.¹ In that sense, they begin to mimic the redox splitting characteristics of the reaction center in photosynthesis.² A chemically versatile approach to the design of such systems exists based on polypyridyl complexes of Re^I, Ru^{II}, or Os^{II}. In these complexes, metal to ligand charge transfer (MLCT) excitation leads to well-defined excited states that undergo facile electron transfer. Examples are known wherein MLCT excitation is followed by intramolecular electron transfer to give a redox-separated state, e.g., eqs 1 and 2 (bpy is 2,2'-bipyridine).³ In other cases, MLCT excitation has been shown



to lead to photochemical electron transfer with the oxidative and reductive equivalents spatially separated on different ligands,⁴ or on a metal ion across a ligand bridge.⁵

One of our interests in this area is in establishing and cataloging the approaches at the molecular level that can lead to light-induced redox splitting. We describe here the results of a study on the complex $[(\text{PTZ-bpy})(\text{CO})_3\text{Re}^{\text{I}}(4,4'\text{-bpy})\text{Re}^{\text{I}}(\text{CO})_3(\text{bpy})]^{2+}$ (bpz is 2,2'-bipyrazine; 4,4'-bpy is 4,4'-bipyridine; PTZ-bpy is 4-phenothiazinyl-4'-methyl-2,2'-bipyridine). With this complex, we

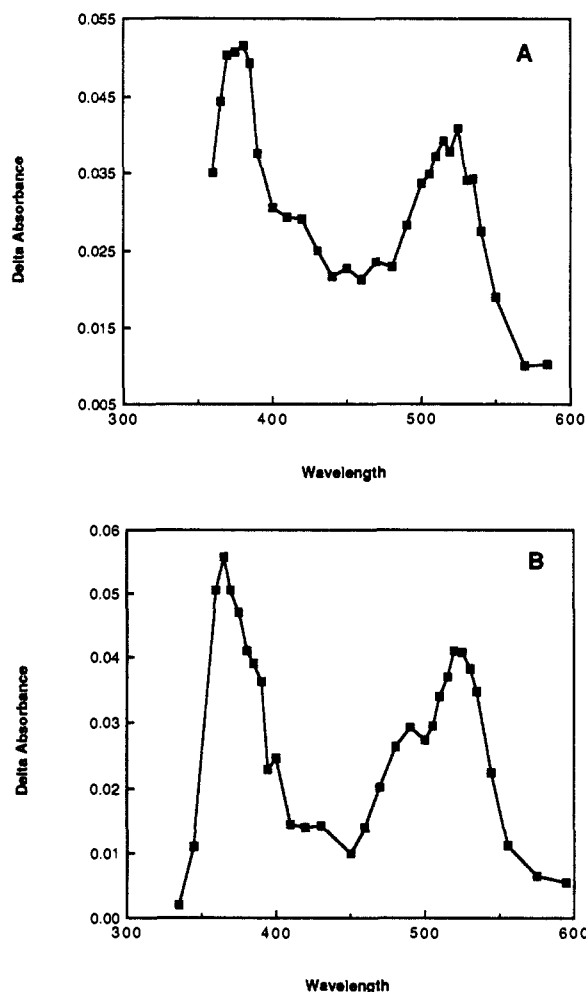


Figure 1. Transient absorbance difference spectra obtained 10 ns after laser excitation in freeze-pump-thaw deoxygenated 1,2-dichloroethane solutions at 294 ± 1 K for (A) $[(\text{PTZ-bpy})(\text{CO})_3\text{Re}^{\text{I}}(4,4'\text{-bpy})\text{Re}^{\text{I}}(\text{CO})_3(\text{bpz})]^{2+}$ and (B) $[(\text{bpz})\text{Re}^{\text{I}}(\text{CO})_3(\text{py-PTZ})]^+$. The ground-state absorbance was ~ 0.7 at the excitation wavelength, 355 nm. The laser pulse energy was 6 mJ/pulse.

have been able to utilize MLCT excitation, the electron-transfer characteristics of the PTZ and bpz groups, and the 4,4'-bpy bridging ligand to achieve long-range, ligand-based, light-induced redox splitting across a ligand bridge.

The redox properties of the electron transfer donor PTZ^{3,4,7} and acceptor bpz⁶ sites have been well characterized in previous studies. Synthetic procedures for related complexes of Re^I are available,⁸

(1) (a) Gust, D.; Moore, T. A. *Science* **1989**, *244*, 35 and references therein. (b) Connolly, J. S. In *Photochemical Conversion and Storage of Solar Energy 1982*; Rabani, J., Ed.; Weizmann Science Press of Israel: Jerusalem, 1982; Part A, p 174. (c) Fajer, J.; Fujita, I.; Davis, M. S.; Forman, A.; Hanson, L. K.; Smith, K. M. *Adv. Chem. Ser.* **1982**, *201*, 489. (d) Bolton, J. R.; Hall, D. O. *Annu. Rev. Energy* **1979**, *4*, 353. (e) Loach, P. A.; Runquist, J. A.; Kong, J. L. Y.; Dannhauser, T. J.; Spears, K. G. *Adv. Chem. Ser.* **1982**, *201*, 515. (f) Whitten, D. G. *J. Chem. Educ.* **1983**, *60*, 867. (g) Connolly, J. S., Ed. *Photochemical Conversion and Storage of Solar Energy*; Academic Press: New York, 1981. (h) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163. (i) Barber, J. *Photosynthesis in Relation to Model Systems*; Elsevier: New York, 1979. (j) Clayton, R. K. *Photosynthesis: Physical Mechanisms and Chemical Patterns*; Cambridge University Press: London, 1980. (k) Grätzel, M., Ed. *Energy Resources Through Photochemistry and Catalysis*; Academic Press: New York, 1983. (l) Balzani, V., Ed. *Supramolecular Photochemistry*; D. Reidel Publishing Company: Dordrecht, Holland, 1987. (m) Connolly, J. S.; Bolton, J. R. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: New York, 1988.

(2) (a) Jortner, J. *J. Am. Chem. Soc.* **1980**, *102*, 6676. (b) Sauer, K. *Annu. Rev. Phys. Chem.* **1979**, *30*, 155. (c) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385; (d) *Nature* **1985**, *318*, 618. (e) Creed, D.; Caldwell, R. A. *Photochem. Photobiol.* **1985**, *41*, 715. (f) Sarai, A. *Biochim. Biophys. Acta* **1980**, *589*, 71. (g) Gust, D.; Moore, T. A. *J. Photochem.* **1985**, *29*, 173. (h) Tabushi, I.; Koga, N.; Yanagita, M. *Tetrahedron Lett.* **1979**, 257. (i) Kong, J.; Spears, K. G.; Loach, P. *Photochem. Photobiol.* **1982**, *35*, 545 and references therein. (j) Netzel, T. L.; Kroger, P.; Chang, C. K.; Fujita, I.; Fajer, J. *Chem. Phys. Lett.* **1979**, *67*, 223. (k) Michel-Beyerle, M. E.; Plato, M.; Deisenhofer, J.; Michel, H.; Bixon, M.; Jortner, J. *Biochim. Biophys. Acta* **1988**, *932*, 52. (l) Windsor, M. W. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2237 and references therein. (m) Deisenhofer, J.; Michel, H.; Huber, R. *Trends Biochem. Sci.* **1985**, *10*, 243.

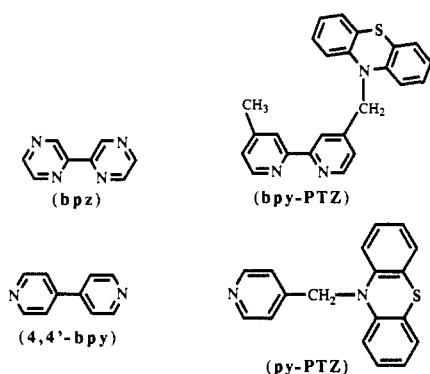
(3) (a) Westmoreland, T. D.; Schanze, K. S.; Neveux, P. E., Jr.; Danielson, E.; Sullivan, B. P.; Chen, P.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2596. (b) Chen, P.; Westmoreland, T.; Danielson, E.; Schanze, K. S.; Anthon, D.; Neveux, P. E., Jr.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1116. (c) Chen, P.; Duesing, R.; Tapolsky, G.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 8305. (4) Danielson, E.; Elliott, C. M.; Merkert, J. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2519.

(5) (a) Schanze, K. S.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2121. (b) Schanze, K. S.; Neyhart, G. A.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 2182.

(6) (a) Haga, M.-A.; Dodsworth, E. S.; Eryavec, G.; Seymour, P.; Lever, A. B. P. *Inorg. Chem.* **1985**, *24*, 1901. (b) Dodsworth, E. S.; Lever, A. B. P.; Eryavec, G.; Crutchley, R. J. *Inorg. Chem.* **1985**, *24*, 1906. (c) Crutchley, R. J.; Kress, N.; Lever, A. B. P. *J. Am. Chem. Soc.* **1983**, *105*, 1170. (d) Crutchley, R. J.; Lever, A. B. P. *J. Am. Chem. Soc.* **1980**, *102*, 7128. (e) Crutchley, R. J.; Lever, A. B. P. *Inorg. Chem.* **1982**, *21*, 2276. (f) Crutchley, R. J.; Lever, A. B. P.; Poggi, A. *Inorg. Chem.* **1983**, *22*, 2647. (g) Gonzalez-Velasco, J.; Rubinstein, I.; Crutchley, R. J.; Lever, A. B. P.; Bard, A. J. *Inorg. Chem.* **1983**, *22*, 822. (h) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617. (i) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613. (j) Shinozaki, K.; Kaizu, Y.; Hirai, H.; Kobayashi, H. *Inorg. Chem.* **1989**, *28*, 3675. (k) Shinozaki, K.; Ohno, O.; Kaizu, Y.; Kobayashi, H.; Sumitani, M.; Yoshihara, K. *Inorg. Chem.* **1989**, *28*, 3680.

(7) (a) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley Interscience: New York, 1969. (b) Foster, R. *Organic Charge Transfer Complexes*; Academic Press: New York, 1973. (c) Root, M. J.; Deutsch, E.; Sullivan, J. C.; Meisel, D. *Chem. Phys. Lett.* **1983**, *101*, 353. (d) Kroener, R.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1988**, *27*, 558. (e) Alkatis, S. A.; Beck, G.; Grätzel, M. *J. Am. Chem. Soc.* **1975**, *97*, 5723. (f) Maestri, M.; Grätzel, M. *Ber. Bun. Gell.* **1977**, *81*, 504. (g) Hanson, P.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 264.

and the photophysical properties of these complexes have been studied in detail.^{3,9}



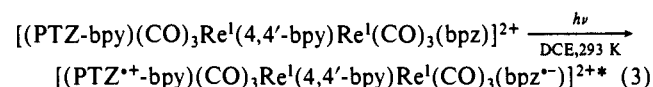
In the preparation of the ligand-bridged complex, the coupling reaction between [(PTZ-bpy)Re^I(CO)₃(4,4'-bpy)](PF₆) and [(bpy)Re^I(CO)₃(CF₃SO₃)] was utilized in THF as the solvent.¹⁰ On the basis of cyclic voltammetric measurements in 0.1 M [N-(*n*-C₄H₉)₄](PF₆) in CH₃CN, (1) a reversible PTZ⁺⁰ wave appears at $E_{1/2} = +0.80$ V vs the saturated sodium calomel electrode (SSCE), (2) irreversible Re^{III/I} waves appear at $E_{pa} = 1.75$ V and 1.95 V for the Re(bpy) and Re(bpz) sites, and (3) a reversible bpz⁻⁰ wave appears at $E_{1/2} = -0.65$ V followed by overlapping waves at ca. -1.2 V, for reduction at both the bpy and 4,4'-bpy ligands. The absorption spectrum of the complex is dominated by ligand-centered $\pi \rightarrow \pi^*$ transitions at high energy (<330 nm) and at >330 nm by transitions that are $d\pi(\text{Re}) \rightarrow \pi^*(\text{bpz}, \text{PTZ-bpy}, 4,4'\text{-bpy})$ in character. On the basis of spectral comparisons with related complexes, the $d\pi(\text{Re}) \rightarrow \pi^*(\text{bpy})$ and $d\pi(\text{Re}) \rightarrow \pi^*(\text{bpz})$ transitions occur at 355 and 415 nm, respectively.¹¹

There is no intrinsic emission from the complex. A transient absorbance difference spectrum obtained 10 ns after 355-nm laser excitation in 1,2-dichloroethane (DCE) is shown in Figure 1A.¹² Absorption features that are characteristic of PTZ⁺⁺, at $\lambda_{\text{max}} = 515$ nm, and of bpz⁻, at $\lambda_{\text{max}} = 380$ nm, appear in the spectrum.^{3,4,9c} These features were present at our earliest observation times (≤ 5 ns). They decay exponentially with $k = (3.03 \pm 0.30) \times 10^7$ s⁻¹ in CH₃CN or $k = (1.82 \pm 0.15) \times 10^7$ s⁻¹ in DCE, independently of the excitation (355 or 420 nm) or monitoring wavelengths (340–600 nm). Excitation of [(bpy)Re^I(CO)₃(4,4'-bpy)]⁺ at 355 nm under the same conditions gave rise to

the characteristic $\pi \rightarrow \pi^*(\text{bpz}^-)$ transition at 380 nm for [(bpy)Re^{II}(CO)₃(4,4'-bpy)]⁺⁺. This MLCT excited state decays with $k = (3.03 \pm 0.30) \times 10^7$ s⁻¹ in CH₃CN or $k = (1.10 \pm 0.06) \times 10^7$ s⁻¹ in DCE. Following excitation of [(PTZ-bpy)Re^I(CO)₃(4-Etpy)]⁺ at 355 nm, absorption features appear for the redox-separated state, [(PTZ⁺⁺-bpy⁻)Re^I(CO)₃(4-Etpy)]⁺, at $\lambda_{\text{max}} = 515$ nm [$\pi \rightarrow \pi^*(\text{PTZ}^{++})$] and 370–400 nm [$\pi \rightarrow \pi^*(\text{bpy}^-)$]. This state decays with $k = (1.14 \pm 0.06) \times 10^7$ s⁻¹ in CH₃CN or $k = (4.65 \pm 0.25) \times 10^6$ s⁻¹ in DCE. By comparison with rate constants for processes such as that depicted in eq 2,^{3c} its relatively long lifetime is a consequence of the large free energy change associated with the reaction. For all of the complexes investigated, the decay processes followed single-exponential kinetics.

The most revealing comparison is with the chromophore-quencher complex [(bpy)Re^I(CO)₃(py-PTZ)]⁺, Figure 1B.^{3c} Following 355-nm excitation of this complex, the same absorption features appear at 370 and 515 nm as in the ligand-bridged complex. However, they decay with $k > 10^8$ s⁻¹ in CH₃CN or $k = (9.1 \pm 1.5) \times 10^7$ s⁻¹ in DCE. Under identical conditions of absorption and excitation, laser photolysis of [(bpy)Re^I(CO)₃(py-PTZ)]⁺ or [(PTZ-bpy)(CO)₃Re^I(4,4'-bpy)Re^I(CO)₃(bpy)]²⁺ gave comparable ΔA values ($\pm 15\%$) at 375 and 515 nm.

From these comparisons, laser excitation of the ligand-bridged complex leads to photochemical redox splitting over a distance of ~ 11 Å across the 4,4'-bpy bridging ligand, eq 3. From redox potential measurements, the redox-separated state that is the product of the photolysis, [(PTZ⁺⁺-bpy)Re^I(CO)₃(4,4'-bpy)Re^I(CO)₃(bpy)]²⁺⁺, lies at ~ 1.4 eV above the ground state and returns to the ground state with $k = (1.82 \pm 0.15) \times 10^7$ s⁻¹. This state lies ~ 0.4 eV lower than the next lowest excited state in the complex.



We are currently investigating the pathways by which the redox-separated state is formed. Because of spectral convolution, excitation at 355 nm occurs via the transitions $d\pi(\text{Re}) \rightarrow \pi^*(\text{bpy})$, $d\pi(\text{Re}) \rightarrow \pi^*(\text{bpz})$, $d\pi[\text{Re}(\text{bpy})] \rightarrow \pi^*(4,4'\text{-bpy})$, and $d\pi[\text{Re}(\text{bpy})] \rightarrow \pi^*(4,4'\text{-bpy})$. At 420 nm, absorbance is dominated by the transition $d\pi(\text{Re}) \rightarrow \pi^*(\text{bpz})$ (>75%). It is a remarkable fact that the redox-separated state is formed rapidly (≤ 5 ns) and with efficiencies of formation that are comparable following excitation into any of the four transitions. From time resolved absorbance measurements on [(PTZ-bpy)Re^I(CO)₃(4-Etpy)]⁺ and [(bpy)(CO)₃Re^I(4,4'-bpy)]⁺, the (PTZ⁺⁺-bpy⁻) and Re^{II}(bpz⁻)-based states probably play a role in leading to the final redox-separated state but they do not build up as discrete intermediates. The lifetimes of [(PTZ⁺⁺-bpy⁻)Re^I(CO)₃(4-Etpy)]⁺⁺ and of [(bpy)(CO)₃Re^{II}(4,4'-bpy)]⁺⁺ are longer than the lifetime of the final redox-separated state in DCE. No spectral evidence for a 4,4'-bpy-based state has been obtained; this state is known to have a low energy absorption feature at $\lambda_{\text{max}} = 600$ nm.¹²

Our results demonstrate that it is possible to achieve rapid, excitation wavelength independent, light-induced redox splitting over a distance of 11 Å across a ligand bridge. The redox characteristics of the system are poised so that broad-band excitations of a variety of transitions all lead to the redox-separated state with comparable efficiencies. The lifetime of this state in the ligand-bridged complex is enhanced by a factor of 5 compared to [(bpy)Re^I(CO)₃(py-PTZ)]⁺. Lifetimes in both cases may, in part, be dictated by through-space, back electron transfer. Molecular models show that, given the folding abilities of the bpy-PTZ ligand and the facial geometry at the metal complex sites, it is possible for the photoproduced oxidant/reductant pair to reach a separation distance of ~ 4 Å in the py-PTZ monomer and ~ 6 Å in the ligand-bridged dimer.

Acknowledgment is made to P. Chen for the synthesis of [(PTZ-bpy)Re^I(CO)₃(4-Etpy)]⁺, to the National Science Foundation for support of this research through Grant CHE-8806664, and to the Rhone-Poulenc group for support for G. Tapolsky.

- (8) (a) Wrighton, M. S.; Morse, D. L. *J. Organomet. Chem.* **1975**, *97*, 405. (b) Morse, D. L.; Wrighton, M. *J. Am. Chem. Soc.* **1974**, *96*, 998. (c) Luong, J. C.; Nadjio, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790. (d) Sullivan, B. P.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1244. (e) Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2104. (f) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1414. (g) Kalyanasundaram, K. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2401. (h) Juris, A.; Campagna, S.; Ibiad, I.; Lehn, J.-M.; Ziessel, R. *Inorg. Chem.* **1988**, *27*, 4007. (9) (a) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952. (b) Chen, P.; Danielson, E.; Meyer, T. J. *J. Phys. Chem.* **1988**, *92*, 3708. (c) Chen, P.; Curry, M.; Meyer, T. J. *Inorg. Chem.* **1989**, *28*, 2271. (d) Tapolsky, G.; Duesing, R.; Meyer, T. J. *J. Phys. Chem.* **1989**, *93*, 3885. (e) Westmoreland, T. D.; LeBozec, H.; Murray, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5952. (f) Tapolsky, G.; Duesing, R.; Meyer, T. J. *J. Phys. Chem.*, submitted.

(10) The salt [(PTZ-bpy)(CO)₃Re^I(4,4'-bpy)Re^I(CO)₃(bpy)](CF₃SO₃)₂ was prepared by adding a slight excess of [(bpy)Re^I(CO)₃(CF₃SO₃)] to [(PTZ-bpy)Re^I(CO)₃(4,4'-bpy)](CF₃SO₃) in THF and heating the solution at reflux for 4 h. The product was precipitated by adding ethyl ether. After addition to a saturated aqueous solution of [NH₄](PF₆), to exchange the counterion, the complex was further purified by chromatography on silica gel (75–230 mesh) by using a CH₃CN/CH₂Cl₂ solvent mixture as eluent. Satisfactory elemental analyses were obtained for all of the complexes in this study. ¹H NMR (CD₃CN, 200 MHz) spectra were consistent with the proposed formula. Complete experimental procedures will be described in a subsequent paper.

(11) Spectral assignments were based on difference spectra and comparisons with related complexes of Re^I. (a) Tapolsky, G.; Duesing, R.; Meyer, T. J. *Inorg. Chem.*, in press. (b) Chen, P.; Duesing, R.; Meyer, T. J., manuscript in preparation.

(12) The apparatus has been described in: Tapolsky, G.; Duesing, R.; Meyer, T. J. *J. Phys. Chem.* **1989**, *93*, 3885.