

Photoinduced Charge Separation Promoted by Ring Opening of a Piperazine Radical Cation

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Metal complex dyads, M–D, comprise a transition metal chromophore (M) covalently linked to an organic electron donor (D).^{1–3} Photochemical excitation of these assemblies produces a charge-separated state, M^{•–}–D^{•+}, which has a lifetime that is controlled by the dynamics of the highly exothermic (inverted region) charge recombination reaction.^{2,3} In previous studies it has been shown that the lifetime of the charge-separated state in M–D assemblies increases with the driving force for charge recombination^{2b,3c} or the separation distance between M and D.^{3b} Herein we report a new approach to increasing the lifetime of a charge-separated state in a metal complex dyad which relies on the reversible ring opening of the radical cation of a piperazine electron donor. Thus, metal complex dyad **c-1** contains the (bpy)Re^I(CO)₃–(Re) chromophore⁷ covalently linked to a 2,3-diaryl-1,4-dimethylpiperazine electron donor. Intramolecular electron transfer from piperazine to photoexcited Re produces a charge-separated state in which Re is reduced and the piperazine is a cation radical. Carbon–carbon bond fragmentation in the piperazine cation radical produces a new charge-separated state in which the donor exists as an open-chain distonic cation radical. The net result is the production of a charge-separated state having a lifetime which is 5–10-fold longer than that observed in structurally related metal complex dyads.

The isomeric complexes **c-1** and **t-1** were synthesized and fully characterized.⁸ The near-UV absorption of both compounds is dominated by the dπ(Re) → π* (bpy) metal-to-ligand charge transfer (MLCT) transition of the Re chromophore.⁹ Irradiation of a solution of **c-1** in air-saturated or Ar-degassed CH₃CN at 366 nm affords **t-1** as the sole chemical product with high quantum efficiency (Φ_{c-1→t-1} = 0.46 ± 0.05 in Ar-degassed solution).¹⁰

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(1) Examples of metal complex dyads comprising a metal complex and an electron acceptor also exist.^{4–6}
(2) (a) Chen, P.; Westmoreland, T. D.; Danielson, E.; Schanze, K. S.; Anthon, D.; Neveaux, P. E., Jr.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1116. (b) Chen, P.; Duesing, R.; Graff, D. K.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 5850. (c) Mecklenburg, S. L.; Peek, B. M.; Schoonover, J. R.; McCafferty, D. G.; Wall, C. G.; Erickson, B. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 5479.

(3) (a) Schanze, K. S.; Cabana, L. A. *J. Phys. Chem.* **1990**, *94*, 2740. (b) Perkins, T. A.; Hauser, B. T.; Eyley, J. R.; Schanze, K. S. *J. Phys. Chem.* **1990**, *94*, 8745. (c) MacQueen, D. B.; Schanze, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 7470.

(4) (a) Cooley, L. F.; Headford, C. E. L.; Elliott, C. M.; Kelley, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 6673. (b) Ryu, C. K.; Wang, R.; Schmehl, R. H.; Ferrere, S.; Ludwikow, M.; Merkert, J. W.; Headford, C. E. L.; Elliott, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 430.

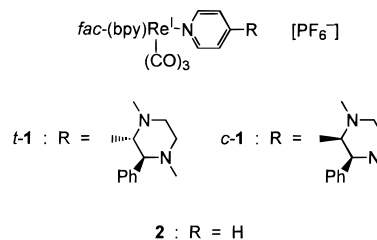
(5) (a) Yonemoto, E. H.; Riley, R. L.; Kim, J. I.; Atherton, S. J.; Schmehl, R. H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1992**, *114*, 8081. (b) Yonemoto, E. H.; Saupé, G. B.; Schmehl, R. H.; Hubig, S. M.; Riley, R. L.; Iverson, B. L.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 4786.

(6) Schanze, K. S.; Sauer, K. *J. Am. Chem. Soc.* **1988**, *110*, 1180.

(7) bpy = 2,2'-bipyridine.

(8) A description of the synthesis, purification, and characterization of **c-1** and **t-1** is available as supporting information.

(9) Worl, L. A.; Duesing, R.; Chen, P. Della Ciana, L.; Meyer, T. J. *J. Chem. Soc., Dalton Trans.* **1991**, 849.



A mechanism for **c-1** → **t-1** photoisomerization is provided in Scheme 1. Near-UV excitation produces MLCT excited state **c-1**^{*}, which subsequently relaxes either by radiative and nonradiative decay to **c-1** (step 1) or by forward electron transfer (step 2) to afford charge-separated state **c-3** in which the piperazine donor is oxidized and the bpy acceptor ligand is reduced (i.e., bpy^{•–}). The occurrence of step 2 in **c-1**^{*} is indicated by the fact that the MLCT emission lifetime of **c-1** (τ_{em} = 55 ns) is suppressed compared to that of model complex **2** (τ_{em} = 235 ns). The emission lifetimes of **c-1** and **2** allow estimation of *k*₂ (1.4 × 10⁷ s⁻¹) and the efficiency for formation of charge-separated state **c-3** (φ₂ = 0.76).¹¹ Piperazine isomerization is believed to occur via fragmentation of the 2,3-C–C bond (step 3) to form a new charge-separated state in which the piperazine exists as a distonic cation radical with two possible structures (**4a** or **4b**). Carbon–carbon bond fragmentation in radical cations is well precedented in acyclic systems.^{12,13} Indeed, recent studies indicate that for acyclic 1,2-diaryl-1,2-diaminoethanes C–C bond fragmentation is exoergic and occurs with *k* > 10⁸ s⁻¹.^{13e} Since C–C bond fragmentation in **4** is probably exoergic,¹⁴ the reverse process (e.g., **4** → **3**) cannot occur, and therefore isomerization occurs via charge recombination (step 4) followed by coupling of 1,6-diradical **5** (step 6).¹⁶

A significant question is why **t-1** → **c-1** photoisomerization does not occur. Quite remarkably, the MLCT emission lifetime of **t-1** (τ_{em} = 233 ns) is *not* suppressed substantially from that of model **2**, which indicates that forward electron transfer is too slow to compete with normal decay of the MLCT excited state, **t-1**^{*}. The lack of electron transfer quenching in **t-1**^{*} precludes formation of charge-separated state **t-3** (not shown in Scheme 1), thereby closing off the pathway to **t-1** → **c-1** isomerization via fragmentation of the piperazine cation radical.

(10) Φ_{c-1→t-1} is an overall quantum efficiency determined by analysis of solutions subjected to steady state irradiation for a sufficient time to allow ≤10% conversion of **c-1** to **t-1**.

(11) The rate constant (*k*₂) and quantum yield (φ₂) are calculated by *k*₂ = [1/τ_{c-1} – 1/τ₂] and φ = [1 – (τ_{c-1}/τ₂)], where τ_{c-1} and τ₂ are MLCT emission lifetimes of **c-1** and **2**, respectively.

(12) For leading references on C–C bond fragmentation in radical cations, see: Maslak, P.; Chapman, W. H., Jr.; Vallombroso, T. M.; Watson, B. M. *J. Am. Chem. Soc.* **1995**, *117*, 12380 and references therein.

(13) (a) Kellett, M. A.; Whitten, D. G. *J. Am. Chem. Soc.* **1989**, *111*, 2314. (b) Leon, J. W.; Whitten, D. G. *J. Am. Chem. Soc.* **1993**, *115*, 8038. (c) Wang, Y.; Schanze, K. S. *J. Phys. Chem.* **1995**, *99*, 6876. (d) Wang, Y.; Lucia, L. A.; Schanze, K. S. *J. Phys. Chem.* **1995**, *99*, 1961. (e) Lucia, L. A.; Wang, Y.; Nafisi, K.; Netzels, T. L.; Schanze, K. S. *J. Phys. Chem.* **1995**, *99*, 11801.

(14) The free energy for step 3 (Δ*G*₃) is estimated by^{15a} Δ*G*₃ = Δ*G*_{CC} – F[E_o(pip/pip^{•+}) – E_{red}(R–CH=N⁺R₂/R–CH–NR₂)], where Δ*G*_{CC} is the free energy for homolysis of the 2,3-C–C bond (≈ +32 kcal/mol),^{15b} E_o(pip/pip^{•+}) is the oxidation potential for the piperazine (≈ +0.95 V for **c-1**), E_{red}(R–CH=N⁺R₂/R–CH–NR₂) is the reduction potential of a dialkyliminium ion (≈ –0.92 V),^{15c} and F is Faraday's constant. These values lead to the estimate that Δ*G*₃ ≈ –11 kcal/mol.}}

(15) (a) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287. (b) McMillin, D. F.; Golden, E. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493. (c) Andriux, C. P.; Saveant, J. M. *J. Electroanal. Chem.* **1970**, *26*, 223.

(16) The overall quantum yield for **c-1** to **t-1** isomerization is given by Φ_{c-1→t-1} = φ₂φ₃φ₆, where φ_{*i*} is the efficiency of the *i*th step in Scheme 1 (this assumes that step 3 is irreversible). It is of interest to use the experimental data to determine φ₃ and φ₆; however, since only Φ_{c-1→t-1} and φ₂ are known, it is only possible to conclude that φ₃ and φ₆ are both within the range 0.59–1.0.

Scheme 1

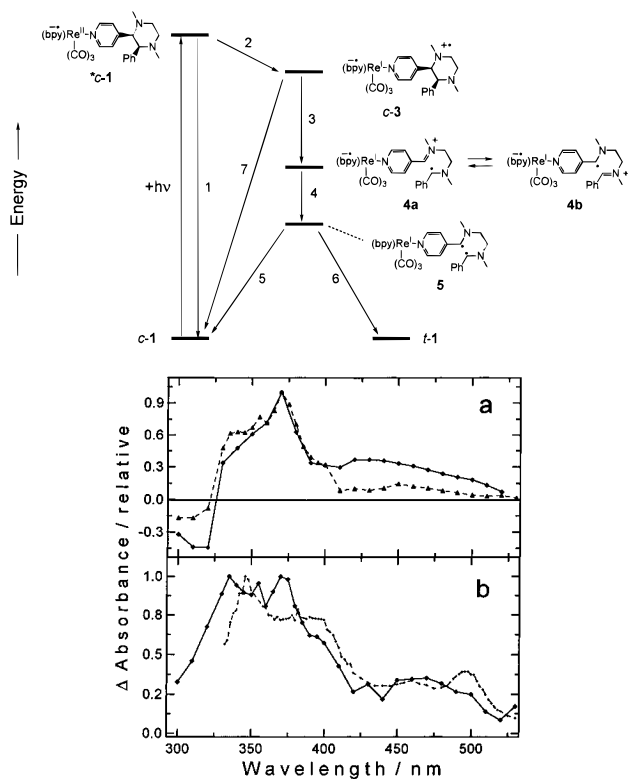


Figure 1. Transient absorption difference spectra of the principal spectral components extracted by factor analysis of multiwavelength transient absorption kinetic data obtained in argon-degassed CH_3CN . (a) Solid line, the only component for $t\text{-1}$ ($\tau = 247$ ns); dashed line, first component observed for $c\text{-1}$ ($\tau_{\text{decay}} = 47$ ns). (b) solid line, second component observed for $c\text{-1}$ ($\tau_{\text{rise}} = 47$ ns, $\tau_{\text{decay}} = 150$ ns); dashed line, spectrum of $[(\text{bpy}^{\bullet-})\text{Re}^{\text{I}}(\text{CO})_3(\text{pyridine})]^0$ formed by photoinduced electron transfer quenching with $\text{PhCH}_2\text{BPh}_3^-$.

Forward electron transfer is slower in $t\text{-1}$ than in $c\text{-1}$ because the *trans*-piperazine is more difficult to oxidize than the *cis*-piperazine by approximately 300 mV.¹⁷

Nanosecond transient absorption studies carried out on $c\text{-1}$ and $t\text{-1}$ provide evidence for the existence of the unique charge-separated state **4**. First, excitation of $t\text{-1}$ in degassed CH_3CN solution with a 10 ns, 355 nm pulse produces a single transient having a strong absorption band at 370 nm which is assigned to MLCT excited state $t\text{-1}^*$ (Figure 1a, solid line).^{13e} Factor analysis¹⁹ of the transient absorption data indicates that $t\text{-1}^*$ decays with a lifetime of $\tau = 247$ ns, in accord with the emission lifetime. By contrast, excitation of $c\text{-1}$ under the same conditions affords a transient absorption spectrum that evolves with time, and factor analysis indicates that the data comprises two

(17) $c\text{-1}$ and $t\text{-1}$ exhibit an irreversible anodic wave due to piperazine oxidation at $E_p(\text{pip}/\text{pip}^+) \approx +0.95$ and $+1.25$ V, respectively (potentials vs SCE). The driving force for photoinduced piperazine to Re electron transfer (step 2) is estimated by $\Delta G_2 \approx E_p(\text{pip}/\text{pip}^+) - E_{1/2}(*\text{Re}^+/ \text{Re}^0)$, where $E_{1/2}(*\text{Re}^+/ \text{Re}^0)$ is the reduction potential of the Re complex in the MLCT state ($+1.22$ V).¹⁸ Using this equation and the values of $E_p(\text{pip}/\text{pip}^+)$ listed above leads to $\Delta G_2(c\text{-1}) \approx -0.27$ eV and $\Delta G_2(t\text{-1}) \approx +0.03$ eV. Although E_p values may poorly reflect the thermodynamic potentials of the piperazines, the calculated ΔG_2 values are consistent with the observed rate data (e.g., $c\text{-1}^*$ is quenched, and $t\text{-1}^*$ is not quenched).

(18) Schanze, K. S.; MacQueen, D. B.; Perkins, T. A.; Cabana, L. A. *Coord. Chem. Rev.* **1993**, *122*, 63.

(19) Stultz, L. K.; Binstead, R. A.; Reynolds, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 2520.

transients. The first is MLCT state $c\text{-1}^*$; its spectrum (Figure 1a, dotted line) is very similar to that of $t\text{-1}$, and its decay lifetime (47 ns) is consistent with the MLCT emission lifetime of $c\text{-1}$. The second transient (Figure 1b, solid line), which is attributed to charge-separated species **4**, has rise and decay lifetimes of 47 and 150 ns, respectively. Assignment of the second transient to **4** is based on (1) the similarity of its transient absorption spectrum to that of the reduced Re chromophore (i.e., $(\text{bpy}^{\bullet-})\text{Re}^{\text{I}}(\text{CO})_3^-$) produced by photoinduced electron transfer (Figure 1b, dotted line) and (2) the absence of an absorption band at 600 nm which would be expected if the 1,4-dimethylpiperazine cation radical is present.²⁰

The dynamics of charge recombination in structurally related $(\text{bpy})\text{Re}^{\text{I}}(\text{CO})_3^-$ (donor) complexes have been studied extensively.^{2,3} Although the rates generally decrease weakly with increasing driving force or separation distance, in these dyads charge recombination in polar solvents typically occurs with $k \geq 5 \times 10^7$ s⁻¹. Indeed, charge recombination rates $< 10^7$ s⁻¹ have only been achieved in metal complex systems by using elaborate donor/acceptor "triad" assemblies.^{2c} In view of this, it is remarkable that charge recombination in the charge-separated state **4** is considerably slower (i.e., $k = 6.7 \times 10^6$ s⁻¹) than in the related metal complex dyads. The comparatively long lifetime of the charge-separated state arises because relaxation of **4** to $c\text{-1}$ (or $t\text{-1}$) involves diradical **5** as an intermediate. Thus, the rate-determining step for decay of **4** is step 4, which is a weakly exothermic Marcus normal region electron transfer reaction ($\Delta G_4 \approx -0.2$ eV)²¹ because the product (**5**) is a high-energy diradical intermediate. The observed decay rate of **4** is in accord with a Marcus normal region electron transfer between an electron donor and acceptor (i.e., $\text{bpy}^{\bullet-}$ and $\text{R}-\text{CH}=\text{N}^+\text{R}_2$, respectively) that are weakly coupled.²⁻⁵

This study outlines a conceptually general means of augmenting the lifetime of a charge-separated state by coupling photoinduced electron transfer with a rapid, but reversible, chemical process. A similar concept has recently been successfully applied to increase the lifetime of the charge-separated state in a porphyrin-quinone dyad by coupling electron transfer with a rapid proton transfer step.²² Work in progress in our laboratory seeks to extend this concept to new reactive donors in an effort to further prolong the lifetime of charge-separated intermediates produced by photoinduced electron transfer.

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Supporting Information Available: Full details concerning the synthesis and characterization of $c\text{-1}$ and $t\text{-1}$ (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(20) Gebicki, J.; Marcinek, A.; Stradowski, C. *J. Phys. Org. Chem.* **1990**, *3*, 606.

(21) Step 4 occurs by intramolecular electron transfer from $\text{bpy}^{\bullet-}$ to an iminium ion, $\text{R}-\text{CH}=\text{N}^+\text{R}_2$. The driving force for this reaction, $\Delta G_4 = -0.24$ eV, is calculated by: $\Delta G_4 = E_{1/2}(\text{bpy}/\text{bpy}^{\bullet-}) - E_{1/2}(\text{R}-\text{CH}=\text{N}^+\text{R}_2/\text{R}-\text{CH}-\text{NR}_2)$, where the $E_{1/2}$ values refer, respectively, to the half-wave reduction potentials for the coordinated bpy (-1.16 V) and for a dialkyliminium ion (-0.92 V).^{15c}

(22) Huang, S.-C.; Macpherson, A. N.; Lin, S.; Liddell, P. A.; Seely, G. R.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1995**, *117*, 1657.