Inorg. Chem. **1995,** *34,* 3−4

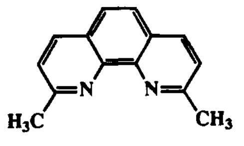
Photodriven Energy Transfer from Cuprous Phenanthroline Derivatives

Felix N. Castellano, Mark Ruthkosky, and Gerald J. Meyer*

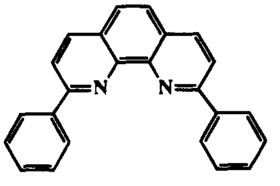
Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218

Received May 27, 1994

An important goal in inorganic photochemistry is the development of new artificial photosynthetic assemblies capable of efficiently harvesting solar energy.[1] In this regard, the excited state properties of cuprous diimine chromophores have received considerable attention.[2] Detailed studies have largely established the geometric and electronic nature of the metal-to-ligand charge-transfer (MLCT) excited states in these compounds.[3−6] The luminescent excited states are quenched by a variety of inorganic and organic compounds, but the underlying mechanism(s) remain speculative. In this communication, we report the first direct spectroscopic observation of energy transfer from cuprous diimine excited states. Specifically, photoexcited Cu(dpp)$_2$(PF$_6$) (dpp is 2,9-diphenyl-1,10-phenanthroline) and Cu(dmp)$_2$(PF$_6$) (dmp is 2,9-dimethyl-1,10-phenanthroline) transfer energy to anthracene in dichloromethane solution, eqs 1 and 2. These reactions are important in photocatalysis as anthracene can function as an efficient energy relay between light absorbing donors and electron acceptors.[7]



(dmp)



(dpp)

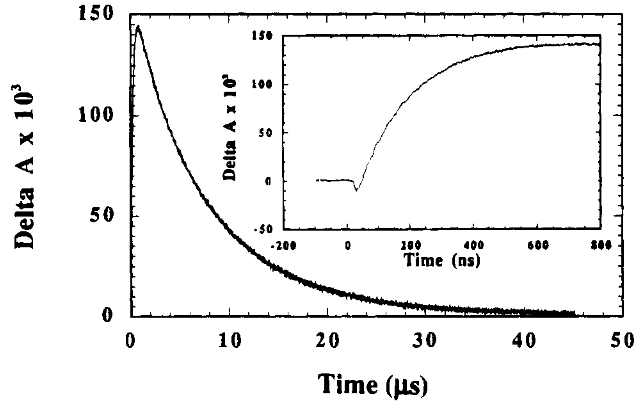


Figure 1. Time-resolved absorbance change monitored at 430 nm showing the growth and decay of ^{3}An after pulsed excitation of an argon-saturated dichloromethane solution containing 3.0 × 10^{-4} M Cu(dpp)$_2$(PF)$_6$ and 1.1 × 10^{-2} M anthracene. The insert displays the appearance of ^{3}An on an expanded time scale. The data are an average of 10 transients. The excitation source was a frequency-doubled Nd:YAG laser (532 nm, 6 mJ/pulse, 5−7 ns (fwhm)).

$$\mathrm{Cu^I(dpp)_2}^{+*} + \mathrm{An} \rightarrow \mathrm{Cu^I(dpp)_2}^{+} + {}^3\mathrm{An}^* \qquad (1)$$

$$\mathrm{Cu^I(dmp)_2}^{+*} + \mathrm{An} \rightarrow \mathrm{Cu^I(dmp)_2}^{+} + {}^3\mathrm{An}^* \qquad (2)$$

Synthesis and characterization of the cuprous phenanthroline derivatives have been previously described.[8,12] These compounds display broad MLCT absorption bands in the visible region. Light excitation into these bands leads to room temperature emission in argon saturated dichloromethane solution.[8] Emission decays are exponential with lifetimes of 250 ± 5 ns for Cu(dpp)$_2$(PF$_6$) and 85 ± 5 ns for Cu(dmp)$_2$(PF$_6$).[9] The addition of anthracene leads to quenching of the emission intensity (I) and quenching of the excited state lifetime (τ). Concentration dependent emission studies are well described by the Stern−Volmer model, $I_0/I = 1 + k_{et}\tau_0[\mathrm{An}]$ and $\tau_0/\tau = 1 + k_{et}\tau_0[\mathrm{An}]$, where k_{et} is the energy transfer rate and [An] is the molar concentration of anthracene. With this model the calculated energy transfer rates are (2.8 ± 0.2) × 10^7 M^{-1} s^{-1} from Cu(dpp)$_2$$^{+*}$ and (2.0 ± 0.2) × 10^8 M^{-1} s^{-1} from Cu(dmp)$_2$$^{+*}$ to anthracene. This model assumes that energy transfer is the sole dynamic quenching mechanism, an assumption justified by the excited state absorption measurements described below.

---

(1) (a) Fox, M. A.; Chanon, M. *Photoinduced Electron Transfer*; Elsevier: Amsterdam, 1988. (b) Gratzel, M. *Heterogeneous Photochemical Electron Transfer*; CRC: Boca Raton, FL, 1989.

(2) For a recent review of copper(I) diamine excited states, see: (a) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes;* Academic Press: London, 1992; Chapter 9. (b) McMillin, D. R.; Kirchhoff, J. R.; Goodwin, K. V. *Coord. Chem. Rev.* **1985**, *64*, 83.

(3) (a) McMillin, D. R.; Buckner, M. T.; Ahn, B. T. *Inorg. Chem.* **1977**, *16*, 943. (b) Ahn, B. T.; McMillin, D. R. *Inorg. Chem.* **1978**, *17*, 2253. (c) Blaskie, M. R.; McMillin, D. R. *Inorg. Chem.* **1980**, *19*, 3519. (d) Ahn, B. T.; McMillin, D. R. *Inorg. Chem.* **1981**, *20*, 1427. (e) Rader, R. A.; McMillin, D. R.; Buckner, M. T.; Matthews, T. G.; Casadonte, D. J.; Lengel, R. K.; Whittaker, S. B.; Darmon, L. M.; Lytle, F. E. *J. Am. Chem. Soc.* **1981**, *103*, 5906. (f) Casadonte, D. J.; McMillin, D. R. *Inorg. Chem.* **1987**, *26*, 3950. (g) Casadonte, D. J.; McMillin, D. R. *J. Am. Chem. Soc.* **1987**, *109*, 331. (h) Berger, R. M.; McMillin, D. R.; Dallinger, R. F. *Inorg. Chem.* **1987**, *26*, 3802. (i) Palmer, C. E. A.; McMillin, D. R.; Kirmaier, C.; Holten, D. *Inorg. Chem.* **1987**, *26*, 3167. (j) Crane, D. R.; DiBenedetto, J.; Palmer, C. E. A.; McMillin, D. R.; Ford, P. C. *Inorg. Chem.* **1988**, *27*, 3698. (k) Everly, R. M.; McMillin, D. R. *Photochem. Photobiol.* **1989**, *50*, 711. (l) Stacy, E. M.; McMillin, D. R. *Inorg. Chem.* **1990**, *29*, 393.

(4) (a) Edel, A.; Marnot, P. A.; Sauvage, J. P. *Nouv. J. Chim.* **1984**, *8*, 495. (b) Gushurst, A. K. I.; Dietrich-Buchecker, C. O.; Sauvage, J. P. *Inorg. Chem.* **1989**, *28*, 4070.

(5) (a) McGarvey, J. J.; Bell, S. E. J.; Bechara, J. N. *Inorg. Chem.* **1986**, *25*, 4327. (b) Bell, S. E. J.; McGarvey, J. J. *Chem. Phys. Lett.* **1986**, *124*, 336. (c) McGarvey, J. J.; Bell, S. E. J.; Gordon, K. C. *Inorg. Chem.* **1988**, *27*, 4003.

(6) (a) Sakaki, S.; Koga, G.; Ohkubo, K. *Inorg. Chem.* **1986**, *25*, 2330. (b) Sakaki, S.; Koga, G.; Hinikuma, S.; Hashimoto, S.; Ohkubo, K. *Inorg. Chem.* **1987**, *26*, 1817.

(7) (a) Johansen, O.; Mau, A.; Sasse, W. H. F. *Chem. Phys. Lett.* **1983**, *94*, 113. (b) Edel, A.; Marnot, P. A.; Sauvage, J. P. *Nouv. J. Chim.* **1984**, *8*, 495. (c) Mau, A.; Johansen, O.; Sasse, W. H. F. *Photochem. Photobiol.* **1985**, *41*, 503. (d) Olmsted, J.; McClanahan, S. F.; Danielson, E.; Younathan, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 3297.

(8) Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P. *Tetrahedron Lett.* **1982**, *23*, 5291.

(9) The excited state lifetimes are known to be concentration dependant; see refs 5b and 3j. The data given here are for concentrations used in quenching studies: [Cu(dpp)$_2$(PF$_6$)] = 1.2 × 10^{-4} M; [Cu(dmp)$_2$(PF$_6$)] = 9.1 × 10^{-5} M.

(10) Livingston, R.; Tanner, D. W. *Trans. Faraday Soc.* **1958**, *54*, 765.

0020-1669/95/1334-0003$09.00/0

By selective excitation the copper compounds with 532 nm light in the presence of anthracene, the triplet–triplet absorption of anthracene, ^{3}An, is observed by nanosecond laser flash photolysis, Figure 1. In the absence of a Cu(I) phenanthroline compound the ^{3}An absorption is not observed, and in the absence of anthracene only the excited state absorption spectrum of the copper compound is observed. The ^{3}An spectral assignment is based on the appearance of a similar absorption feature following direct (355 nm) excitation of anthracene and the coincidence of the excited state absorption spectrum with that previously reported for ^{3}An.[10] Steady-state absorption measurements before and after photophysical experiments indicate no measurable decomposition of the copper compounds. Taken together these observations clearly demonstrate that the mechanism of emission quenching is energy transfer, eqs 1 and 2.

Kinetic analysis of the appearance of ^{3}An yields an estimate of the pseudo-first-order rate constant (k') for energy transfer which can be converted into a second-order rate constant (k) by use of the quencher concentration present in pseudo-first-order excess. For $Cu(dmp)_2^+$, this yields an energy transfer rate of $(4.7 \pm 0.7) \times 10^8$ $M^{-1}s^{-1}$, in good agreement with emission quenching data and the Stern–Volmer model. However, for $Cu(dpp)_2^+$ the transient absorption data yields an energy transfer rate which is about 1 order of magnitude faster than that obtained from the emission quenching data. The inconsistency between absorption and emission data is likely due to the overlap of the Cu(I) MLCT and ^{3}An absorption bands. This is clearly shown in the inset of Figure 1, wherein the small initial negative absorption is due to the MLCT bleach. The longer lifetime and less efficient quenching of $Cu(dpp)_2^{+*}$ make this overlap particularly significant. The observed rate constant, k_{obs}, can be treated as a sum of the pseudo-first-order energy transfer rate, k_{et}', and the reciprocal excited state lifetime assuming that back energy transfer is negligible by rapid product diffusion. Equation 3, with the known anthracene concentration

$$k_{et}' = k_{obs} - 1/\tau_o \qquad (3)$$

yields an energy transfer rate from $Cu(dpp)_2^{+*}$ to anthracene of $(4.5 \pm 0.3) \times 10^7$ $M^{-1}s^{-1}$, in reasonable agreement with Stern–Volmer data. At the high concentrations of anthracene required, the ^{3}An lifetime is limited by self-quenching and typically decays on a μs time scale.

The efficiency of energy transfer from $Cu(dpp)_2^{+*}$ and $Cu(dmp)_2^{+*}$ to anthracene was compared to that obtained with $Ru(bpy)_3^{2+*}$ as the donor. In these experiments, three argon-saturated 0.022 M anthracene dichloromethane solutions were prepared and a donor was added to each solution such that the absorbance at 532 nm was the same, $A_{532} = 0.070 \pm 0.005$ au. The relative yield of triplet anthracene was then measured 2 μs after 532 nm laser excitation (6 mJ/pulse, 5–7 ns fwhm) for each solution. On the basis of these experiments, $Ru(bpy)_3^{2+*}$ produces six times as much ^{3}An as $Cu(dpp)_2^{+*}$ and four times as much as $Cu(dmp)_2^{+*}$. A 2 μs delay was chosen to ensure that the absorbance signal was solely due to ^{3}An; however delays from 100 ns to 10 μs result in the same relative yields. Energy transfer from $Ru(bpy)_3^{2+*}$ to anthracene has been shown to occur with a quantum yield close to unity under a variety of conditions,[7] so the results obtained here imply that these Cu(I) phenanthroline derivatives are also useful sensitizers.

The increased efficiency of energy transfer from $Ru(bpy)_3^{2+*}$ is not surprising considering the high energy of the lowest triplet-excited state, 2.1 eV.[11] The excited state energetics of cuprous phenanthroline compounds are complicated by the existence of singlet and triplet excited states which are thought to be close lying.[12] In principle, both these states are potential energy transfer donors. The symmetric quenching of the corrected emission spectra by anthracene leads us to believe that energy transfer occurs from the luminescent triplet charge-transfer state.[13] This state has been estimated to be ~1.8 eV for $Cu(dpp)_2^{+*}$, and a similar value is expected for $Cu(dmp)_2^{+*}$.[2a,12] The lowest triplet excited state of anthracene is ~1.8 eV,[14] so the driving force for energy transfer is, at best, small. The approximately order of magnitude faster energy transfer rate observed for $Cu(dmp)_2^{+*}$ when compared to $Cu(dpp)_2^{+*}$ is somewhat surprising considering the molecular and optical similarity of the two sensitizers. It has recently been demonstrated that energy transfer rates from related Os(II) polypyridyl compounds display a bell-shaped dependence on thermodynamic driving force.[15] In the copper–anthracene assemblies studied here, energy transfer clearly falls in the normal region where a small difference in driving force could account for the different rates. Alternatively, a slight orientation difference within the encounter complex solvent cage could yield different donor–acceptor distances for the two assemblies. Energy transfer kinetics have recently been shown to be more sensitive to distance than corresponding electron-transfer processes.[16] Therefore, the difference in energy transfer rates between the two copper compounds may be easily explained by energetic or distance considerations.

In conclusion, energy transfer from Cu(I) phenanthroline derivatives has been clearly demonstrated for the first time. Energy transfer processes have been previously implicated in quenching studies with Cr(III) compounds[17] and in photocatalytic production of hydrogen[4a] and may be prevalent in other biological and artificial assemblies. For the copper excited states described here, energy transfer results in (1) a state with well-defined spin multiplicity, (2) a 3 order of magnitude increase in excited state lifetime, and (3) little if any loss in potential energy. Such processes are clearly relevant and important in the design of integrated assemblies capable of efficiently converting sunlight into useful chemical products.

IC940611Q

---

(11) Balzani, V.; Scandola, F. *Supramolecular Photochemistry;* Ellis Harwood: Chichester, U.K., 1990.

(12) Kirchhoff, J. R.; Gamache, R. E.; Blaskie, M. R.; Del Paggio, A. A.; Lengel, R. K.; McMillin, D. R. *Inorg. Chem.* **1983**, *22*, 2380.

(13) A slight *increased* intensity is observed on the high-energy side ($\lambda <$ 600 nm) of the emission spectra after anthracene addition which is not from the copper compounds but is due to the long wavelength tail of singlet anthracene fluorescence.

(14) Birks, J. B. *Photophysics of Aromatic Molecules;* John Wiley & Sons Ltd.: London, 1970; p 258.

(15) Murataza, Z.; Zipp, A. P.; Worl, L. A.; Graff, D.; Jones, W. E.; Bates, W. D.; Meyer, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 5113.

(16) Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotriowak, P. *J. Am. Chem. Soc.* **1989**, *111*, 3751.

(17) (a) Gamache, R. E.; Rader, R. A.; McMillin, D. R. *J. Am. Chem. Soc.* **1985**, *107*, 1141. (b) Crane, D. R.; Ford, P. C. *J. Am. Chem. Soc.* **1991**, *113*, 8510. (c) Crane, D. R.; Ford, P. C. *Inorg. Chem.* **1993**, *32*, 2391.