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Photodriven Electron and Energy Transfer from Copper Phenanthroline Excited States

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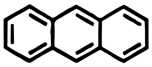
Electron and energy transfer from copper 1,10-phenanthroline excited states is observed at room temperature in organic solvents. The copper phenanthroline excited states are metal-to-ligand charge-transfer in nature and have lifetimes of ∼70−250 ns in dichloromethane solution if methyl or phenyl substituents are placed in the 2- and 9-positions of the phenanthroline ligand. The unsubstituted cuprous compound $\mathrm{Cu(phen)_2(PF_6)}$ is nonemissive under these conditions, and the excited state lifetime is <20 ns. The rate and efficiency of energy transfer to anthracene or electron transfer to viologens is reported. The cage escape efficiency of $[\mathrm{Cu(dpp)_2}^{2+}, \mathrm{MV}^{+\bullet}]$, where dpp is 2,9-diphenyl-1,10-phenanthroline, is close to unity within experimental error. Back electron transfer to ground state products occurs at the diffusion limit, $2 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$.

Research into molecular solar energy conversion with inorganic excited states has focused mainly on porphyrin and $d\pi^6$ transition metal chromophores.[1] There has been growing interest in the excited state and redox properties of cuprous phenanthroline derivatives.[2] These compounds possess broad absorption bands in the visible region with high extinction coefficients potentially useful for solar harvesting. Much of the interest in the excited state properties of these compounds was motivated by the pioneering work of McMillin and coworkers, who first established that visible excitation of $\mathrm{Cu(dmp)_2}^+$ (dmp is 2,9-dimethyl-1,10-phenanthroline) produces room-temperature photoluminescence in dichloromethane solution.[3] This and related copper phenanthroline compounds with alkyl or aryl substituents in the 2,9-positions of phenanthroline also have long-lived excited states and display excellent photostability.[4−7] The excited states are potent reductants that have been employed in potentially practical processes, such as the production of hydrogen gas from water[8] and an electrical current by sensitization of wide band gap semiconductors.[9]

In a recent communication,[10] we reported the first spectroscopic observation of photodriven energy transfer from excited copper phenanthroline compounds. The acceptors were the triplet states of anthracene, and the energy transfer dynamics were quantitated by the appearance of the triplet-to-triplet anthracene absorption, eq I. This process is important as it results in a state with well-defined spin multiplicity, a 3-order-of-magnitude increase in excited state lifetime, and little loss in potential energy. In related processes, anthracene has been employed as an energy transfer shuttle from ruthenium tris(bipyridine) ($\mathrm{Ru(bpy)_3}^{2+}$) to methyl viologen (MV^{2+}) electron acceptors.[11] Here we explore related excited state electron and energy transfer processes with a family of cuprous phenanthroline compounds.

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



(An)

Experimental Section

Reagents. Copper(I) oxide (97%), 1,10-phenanthroline (abbreviated phen) (99+%), neocuproine (2,9-dimethyl-1,10-phenanthroline, dmp) (99+%), bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, bcp) (98+%), and anthracene (zone refined, 99%) were purchased from Aldrich Chemical Co. Methyl viologen dichloride hydrate (MV^{2+}) (97%) and benzyl viologen dichloride (BV^{2+}) (98%) (Aldrich Chemical Co.) were metathesized to the $\mathrm{PF_6}$ salts by reaction with $\mathrm{NH_4PF_6}$ in aqueous solution. Electrochemical grade (>99%) tetrabutylammonium

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hexafluorophosphate (TBAH) and tetrabutylammonium benzoate were used as received from Fluka Chemical Co. Anhydrous diethyl ether (Fisher) was used as received. Dichloromethane and acetonitrile (Fisher) were distilled under argon over calcium hydride (Aldrich).

Preparations. $Cu(CH_3CN)_4(PF_6)$ was prepared and satisfactorily characterized by a published procedure.[12] $Ru(bpy)_3(PF_6)_2$ was available from previous studies.[18]

dpp. The ligand 2,9-diphenyl-1,10-phenanthroline (abbreviated dpp) was prepared and characterized by a published procedure.[13]

General Preparation of Copper Phenanthroline Derivatives. A general procedure for the synthesis of cuprous compounds of the type $Cu(NN)_2(PF_6)$ is as follows. Two equivalents (1−2 mmol) of a phenanthroline derivative was dissolved in 10 mL of acetonitrile, and the resultant solution was deaerated with argon. This solution was added, with stirring, to solid $Cu(CH_3CN)_4(PF_6)$ under an argon atmosphere. An orange-red color was immediately observed, and the reaction mixture was stirred for an additional 10 min. The product was then precipitated by adding ∼50 mL of argon-saturated diethyl ether. The solid was filtered onto a glass frit and redissolved in a minimum of CH_2Cl_2. Slow, layered addition of diethyl ether produced air-stable crystals of the product in 88−94% yield. The solids were stored in air until use.

$Cu(phen)_2(PF_6)$. Yield: 88%. ^1H NMR ($(CD_3)_2CO$), δ: 8.08 (m, 4H, H_2, H_9), 8.34 (s, 4H, H_5, H_6), 8.89 (d, 4H, H_3, H_8), 9.13 (d,4H, H_4, H_7). FAB-MS: *m/e* 423 (M^+), 243 ($M^+ - L$). Anal. Calcd for $C_{24}H_{16}N_4CuPF_6$: C, 50.67; H, 2.83; N, 9.85. Found: C, 50.72; H, 2.69; N, 9.85.

$Cu(dmp)_2(PF_6)$. Yield: 90%. ^1H NMR ($CDCl_3$), δ: 2.44 (s, 12H, CH_3), 7.78 (d, 4H, H_3, H_8), 8.02 (s, 4H, H_5, H_6), 8.49 (d, 4H, H_4, H_7). FAB-MS: *m/e* 497 (M^+), 271 ($M^+ - L$). Anal. Calcd for $C_{28}H_{24}N_4CuPF_6$: C, 53.81; H, 3.87; N, 8.96. Found: C, 53.46; H, 3.66; N, 8.88.

$Cu(dpp)_2(PF_6)$. Yield: 88%. ^1H NMR ($CDCl_3$), δ: 6.53 (t, 8H, phenyl), 6.80 (t, 4H, phenyl), 7.39 (d, 8H, phenyl), 7.88 (d, 4H, H_3, H_8), 8.02 (s, 4H, H_5, H_6), 8.51 (d, 4H, H_4, H_7). FAB-MS: *m/e* 727 (M^+), 395 ($M^+ - L$). Anal. Calcd for $C_{48}H_{32}N_4CuPF_6$: C, 66.02; H, 3.69; N, 6.42. Found: C, 64.68; H, 3.84; N, 6.29.

$Cu(bcp)_2(PF_6)$. Yield: 94%. ^1H NMR ($CDCl_3$), δ: 2.60 (s, 12H, CH_3), 7.60 (m, 20H, phenyl), 7.76 (d, 4H, H_3, H_8), 8.05 (s, 4H, H_5, H_6). FAB-MS: *m/e* 783 (M^+), 423 ($M^+ - L$). Anal. Calcd for $C_{52}H_{40}N_4CuPF_6$: C, 67.21; H, 4.34; N, 6.03. Found: C, 67.46; H, 4.17; N, 6.01.

$Cu(dmp)_2AnCO_2$. A suspension of AnCOOH (1 g) in a solution of $NaHCO_3$ in H_2O (2.5 g/50 mL) was heated to 60 °C and stirred for 1.5 h, 20 mL of H_2O was added, and the solution was evaporated to dryness. The solid was partially dissolved in 250 mL of ethanol, the mixture was filtered, and the filtrate was evaporated to dryness. The product, formulated as $NaAnCO_2$, was recrystallized from ethanol. In a separate beaker, $Cu(dmp)_2(PF_6)$ (100 mmol) was dissolved in a minimal amount of acetone with 5 equiv of tetrabutylammonium chloride and stirring. An additional 10 mL of acetone was added, and the solution was placed in a freezer for 30 min. An orange solid was vacuum-filtered onto a medium-porosity glass frit. The complex, formulated as $Cu(dmp)_2Cl$, was recrystallized from a minimal amount of warm water. The $Cu(dmp)_2Cl$ was then dissolved in a minimal amount of water with slight heating. Separately, 5.0 equiv of $NaAnCO_2$ was dissolved in a minimal amount of water. The two solutions were mixed with stirring, and an orange precipitate immediately formed. The resultant mixture was stirred for 2 h, and the product $Cu(dmp)_2AnCO_2$ was vacuum-filtered onto a medium-porosity glass frit. The yield, based on copper, was 80%. ^1H NMR, δ: from dmp, 2.39 (s, 12H, CH_3), 7.97 (d, 4H, H_3, H_8), 8.23 (s, 4H, H_5, H_6), 8.77 (d, 4H, H_4, H_7); from anion, 7.44 (m, 4H, H_2, H_3, H_6, H_7), 7.89 (m, 4H, H_1, H_4, H_5, H_8), 8.10 (s, 1H, H_9).

$Cu(dmp)_2(C_6H_5CO_2)$. $Cu(dmp)_2Cl$ was dissolved in a minimal amount of water with a small amount of heat. Separately, 1.5 equiv of tetrabutylammonium benzoate was dissolved in a minimal amount of water. The two solutions were then mixed with stirring, and a small amount of precipitate formed. The resultant mixture was stirred for 2 h, and an orange solid was vacuum-filtered onto a medium-porosity glass frit. The yield was 63%. ^1H NMR, δ: from dmp, 2.40 (s, 12H, CH_3), 7.97 (d, 4H, H_3, H_8), 8.23 (s, 4H, H_5, H_6), 8.77 (d, 4H, H_4, H_7); from anion, 7.20 (m, 2H), 7.81 (m, 3H).

Experimental Procedures. Absorbance Measurements. Steady state absorption measurements were performed on either an HP 8451A diode array or a Cary 14 spectrometer. The reference was neat dichloromethane. The apparatus used to measure excited state absorbance spectra was previously described.[14] The second harmonic from a Continuum Surelite Nd:YAG laser provided excitation ($\lambda_{ex} = 532$ nm; 5 mJ/pulse; fwhm 5−7 ns). Alternatively, the third harmonic was used to pump an in-house constructed high-pressure Raman shifter filled with H_2 gas (400 psi) and the first Stokes line isolated ($\lambda_{ex} = 416$ nm; 4 mJ/pulse). A pulsed 150 W Xe lamp (Applied Photophysics) probe beam was focused onto the entrance slit of an Applied Photophysics *f*/3.4 monochromator coupled to an R446 photomultiplier tube in a shielded housing. The instrument response function (IRF) was 20 ns.

Photoluminescence Measurements. Corrected photoluminescence (PL) and excitation spectra were recorded on a SPEX Fluorolog, Model 1681/1680, which had been calibrated with an NBS standard lamp. Excitation spectra were recorded by reference to a Rhodamine B quantum counter. PL quantum yields were made with $Ru(bpy)_3(PF_6)_2$ as a quantum counter in the optically dilute technique.[15] The PL quantum yield for $Ru(bpy)_3(PF_6)_2$ in argon-purged water is $\Phi_r = 0.042$.[16] The refractive indices are 1.3387 for water and 1.424 for dichloromethane.[17]

Time-resolved PL measurements were obtained on an apparatus that was previously described.[18] The IRF was 14 ns. The samples were excited with 460 nm light.

Quenching Experiments. For quenching experiments with anthracene, 100 mL stock solutions of the copper phenanthroline compounds (OD = 0.05−0.15) in dichloromethane were prepared. In these solutions were dissolved appropriate amounts of anthracene in 5 or 10 mL volumetric flasks. After transfer to long-neck quartz cuvettes, these solutions were then deaerated with CH_2Cl_2-saturated argon for 20 min. The PL spectra, time-resolved PL decays, and the excited state absorption spectra were recorded. Electron transfer studies were performed in the same general manner except stock solutions of $Cu(dpp)_2(PF_6)$ in 0.1 M TBAH/CH_3CN were used. UV/vis absorbance measurements were performed before and after quenching experiments to ensure that no photochemistry had occurred.

Electrochemical Measurements. Cyclic voltammetry was performed in a one-compartment cell with a Pt button working electrode, a Pt gauze counter electrode, and a $Ag/AgNO_3$ reference electrode. The reference electrode (BAS) consisted of a silver wire in a 0.1 M TBAH, 0.01 M $AgNO_3$ acetonitrile solution. A BAS CV 27 potentiostat was employed in conjunction with an HP 7035B X-Y chart recorder. Typical solutions consisted of ∼10 mM concentrations of the copper compounds in 0.1 M TBAH in CH_2Cl_2 or CH_3CN.

^1H NMR spectra were obtained on a Bruker AMX-300 MHz instrument with a TMS reference. FAB mass spectra were measured at the Johns Hopkins University mass spectrometry facility. Elemental analyses (C, H, N) were obtained from Atlantic Microlab, Inc., Norcross, GA, or Desert Analytics, Tuscon, AZ.

Results

The cuprous phenanthroline hexafluorophosphate salts were prepared in high yields by a simple synthetic scheme. Despite the fact that these compounds have been known for some time,[3a,4b] the known lability of cuprous compounds led us to characterize our products by proton NMR, FAB-MS, and

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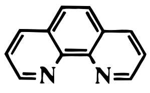
Table 1. Photophysical and Redox Properties of Cuprous Phenanthroline Derivatives[a]

compound	λ_{abs}, nm (ϵ)[b]	λ_{PL}, nm[c]	$10^4\Phi_{PL}$[d]	τ, ns[e]	ΔG_{es},[f] eV	$E_{1/2}^{ox}$,[g] V	$E^*_{1/2}{}^{ox}$,[h] V
$Cu(phen)_2(PF_6)$	458 (6880)			< 20		0.19	
$Cu(dmp)_2(PF_6)$	454 (7950)	740	2.3	85	2.04	0.64	−1.4
$Cu(dpp)_2(PF_6)$	448 (3440)	715	9.7	250	1.99	0.58	−1.4
$Cu(bcp)_2(PF_6)$	478 (13 200)	765	1.5	70	1.98	0.58	−1.4

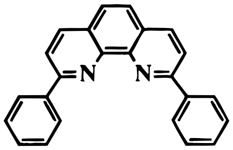
[a] Photophysical data were measured in neat dichloromethane. [b] The molar extinction coefficient at the absorption maximum is given in parentheses M^{-1} cm^{-1}. This data are in excellent agreement with previously reported spectra.[2b] [c] Corrected photoluminescence maximum, ±4 nm. [d] Lower limits for the PL quantum yields. See Results for more details. [e] Excited state lifetime in argon-saturated dichloromethane, ±5%. [f] Estimated free energy in the excited state, ±50 mV. [g] Measured in 0.1 M $TBAH/CH_2Cl_2$, ±0.01 V *vs* $Ag/AgNO_3$, which was found to be +0.35 *vs* SCE using ferrocene as an internal standard. [h] Excited state oxidation potential calculated using eq II in the text.

elemental analysis to ensure their purity and identity. The compounds were characterized electrochemically and optically as described below.

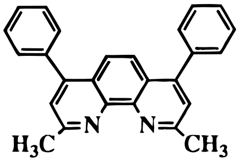


phen

dmp



dpp



bcp

Figure 1 displays cyclic voltammograms of $Cu(phen)_2(PF_6)$, $Cu(dmp)_2(PF_6)$, $Cu(dpp)_2(PF_6)$, and $Cu(bcp)_2(PF)_6$ in dichloromethane electrolyte solution versus the $Ag/AgNO_3$ reference. The observed wave is assigned to the $Cu^{II/I}$ couple. A ferrocene standard demonstrates that the process involves one electron. The redox chemistry shows equivalent anodic and cathodic peak currents, $i_{pa}/i_{pc} \sim 1$, and a peak-to-peak separation of $\Delta E_{pp} \sim$ 100 mV. ΔE_{pp} observed for the copper compounds is less than or equal to that observed with the ferrocene$^{+/0}$ couple in this electrolyte. Plots of the square root of the peak current versus scan rate are linear as expected for a diffusional process.[19] Attempts to reduce the compounds led to irreversible processes at a platinum working electrode. Electrochemical results are summarized in Table 1.

Excitation into the broad visible absorbance bands produces room-temperature photoluminescence (PL) for all the compounds except $Cu(phen)_2(PF_6)$. A lower limit for the PL quantum yield was calculated, since the PL tails into the near-infrared beyond the sensitivity of the photomultiplier tube. Excitation spectra confirm that the PL is from the copper compounds. A tangent drawn to the high-energy side of the corrected PL spectra was used to crudely estimate the free energy in the excited state, ΔG_{es}.[20a] Ignoring work terms, ΔG_{es} can be used to estimate the excited state oxidation potential, $E^*_{1/2}{}^{ox}$ by eq II.[20] Within experimental error, the excited state

$$E^*_{1/2}{}^{ox} = E_{1/2}{}^{ox} - \Delta G_{es} \qquad \text{(II)}$$

oxidation potentials are the same for the three emissive copper compounds, −1.4 V vs $Ag/AgNO_3$. Time-resolved PL decays are first order, independent of the observation wavelength from 650 to 750 nm and the laser irradiance from 40 to 60 μJ/pulse. The lifetimes were typically within 5% from 0.01 to 0.1 mM concentrations. The photophysical data are summarized in Table 1.

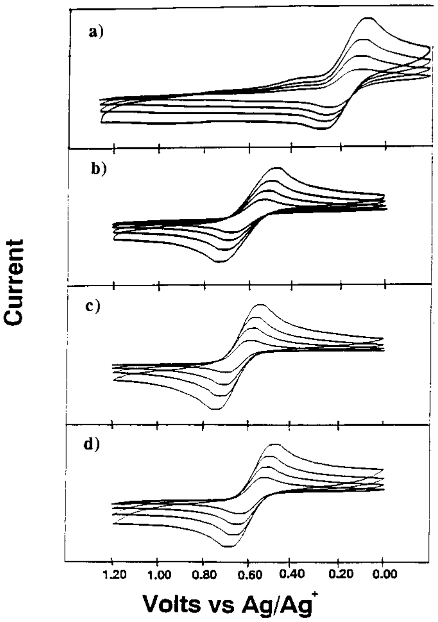


Figure 1. Cyclic voltammograms for the four copper diimine compounds in 0.1 M TBAH dichloromethane solution: (a) $Cu(phen)_2(PF_6)$; (b) $Cu(bcp)_2(PF_6)$; (c) $Cu(dmp)_2(PF_6)$; (d) $Cu(dpp)_2(PF_6)$. The data were collected at 200, 100, 50, and 20 mV/s. Other details can be found in the Experimental Section and under Results.

Excited state absorption difference spectra were obtained for all compounds except $Cu(phen)_2(PF_6)$, which displayed no transient absorbance signals after 20 ns. The excited state absorption difference spectra, obtained 20, 100, and 200 (or 500) ns after a 532 nm laser pulse, show isosbestic points in dichloromethane, Figure 2. Positive absorption features observed at ~340 and ~580 nm are assigned to the reduced ligand.[21] A bleach of the visible charge transfer bands is also observed. The absorption features decay by a first-order process with kinetics which are the same as those obtained from time-resolved PL measurements. The kinetics are also in good agreement with previously reported lifetimes under similar conditions.[2b]

The addition of anthracene to a dichloromethane solution of an emissive copper compound leads to quenching of the PL intensity and lifetime. The concentration-dependent quenching is well fit to the Stern−Volmer model, eq III.[22] Here PLI_0 is

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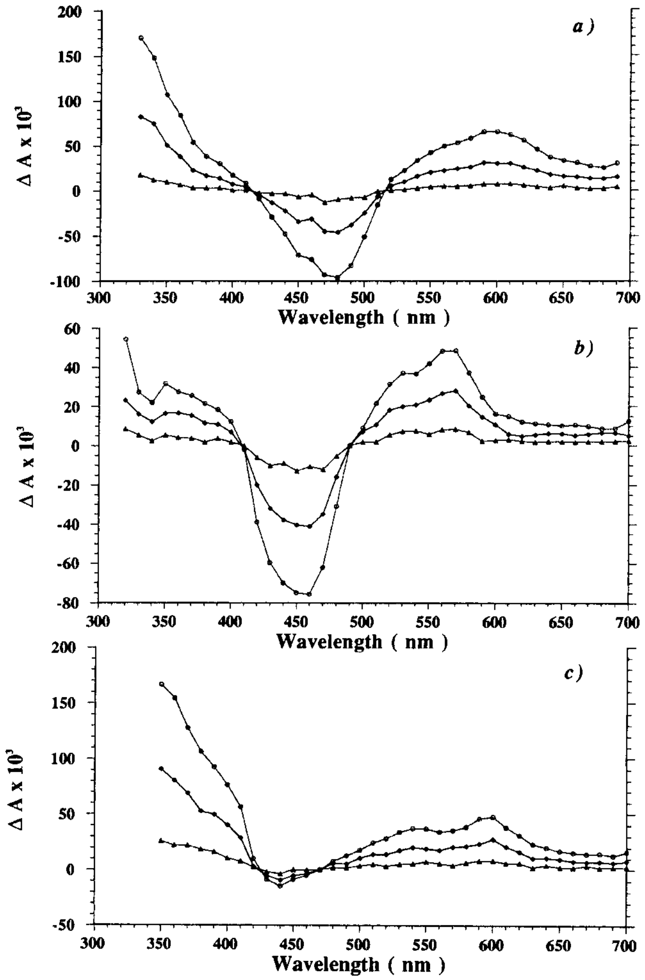

Figure 2. Excited state absorption difference spectra obtained in neat dichloromethane after excitation with 532 nm light: (a) for $Cu(bcp)_2(PF_6)$, recorded at 20, 100, and 200 ns; (b) for $Cu(dmp)_2(PF_6)$, recorded 20, 100, and 200 ns; (c) for $Cu(dpp)_2(PF_6)$, recorded 20, 100, and 500 ns.

$$\frac{\mathrm{PLI}_0}{\mathrm{PLI}} = \frac{\tau_0}{\tau} = 1 + K_{\mathrm{SV}}[\mathrm{An}] \qquad \text{(III)}$$

the integrated PL intensity in the absence of anthracene, τ_0 is the excited state lifetime in the absence of anthracene, PLI and τ are the corresponding quantities in the presence of anthracene, and K_{SV} is the Stern–Volmer quenching constant. Plots of PLI_0/PLI and τ_0/τ are linear and coincident for $Cu(dpp)_2^{+*}$ and $Cu(dmp)_2^{+*}$ quenching. Typical maximum PLI_0/PLI and τ_0/τ values were between 2 and 3. Anthracene concentrations from 1×10^{-5} to 7×10^{-2} M were utilized. $Cu(bcp)_2^{+*}$ was also quenched by anthracene; however, the short lifetime, inefficient energy transfer, and the low solubility of anthracene in dichloromethane frustrated our attempts to obtain a reliable K_{SV} value. From these attempts, K_{SV} is clearly <5 M^{-1}. However, a much more accurate value for the rate of energy transfer from $Cu(bcp)_2^{+*}$ to anthracene was obtained by excited state absorption spectroscopy, Table 2.

Table 2. Copper Phenanthroline Energy Transfer to Anthracene

compound	Φ_{ent}[a]	K_{SV},[b] M^{-1}	k_Q,[b] M^{-1} s^{-1}	k_{ent},[c] M^{-1} s^{-1}
$Cu(dmp)_2(PF_6)$	0.25	17	$(1.9 \pm 0.3) \times 10^8$	$(2.2 \pm 0.2) \times 10^8$
$Cu(dpp)_2(PF_6)$	0.15	7	$(2.6 \pm 0.3) \times 10^7$	$(2.5 \pm 0.2) \times 10^7$
$Cu(bcp)_2(PF_6)$	0.10	*d*	*d*	$(1.8 \pm 0.2) \times 10^7$

[a] Quantum yield for energy transfer, relative to $Ru(bpy)_2^{2+*}$ as a donor. [b] Obtained from Stern–Volmer analysis in argon-saturated CH_2Cl_2. [c] Measured by the appearance of the triplet-to-triplet An absorbance following selective excitation of the copper compounds in argon saturated CH_2Cl_2. The error represents one standard deviation from at least three separate trials. [d] The quenching was inefficient and the Stern–Volmer model could not be quantitatively tested. If the quenching data do fit the model, $K_{sv} < 5$ M^{-1}.

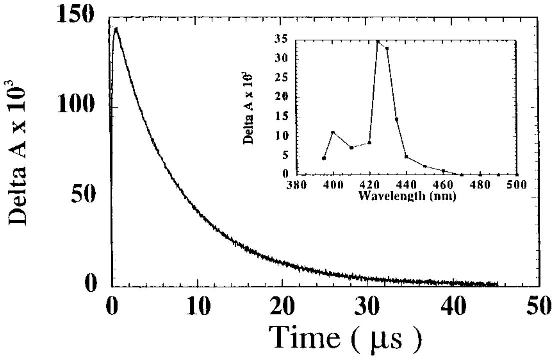

Figure 3. Time-resolved absorption kinetics recorded at 410 nm after selective excitation of $Cu(dmp)_2(PF_6)$ in dichloromethane solution with 0.1 M anthracene. The inset shows the excited state absorption difference spectra, assigned to the triplet-to-triplet absorption of ^{3}An, recorded 2 μs after excitation with a 532 nm laser pulse.

The appearance of the triplet-to-triplet absorption of triplet anthracene, ^{3}An, centered at 430 nm following selective laser excitation of the copper phenanthroline compounds directly demonstrates energy transfer, Figure 3. All the copper phenanthroline compounds except $Cu(phen)_2(PF_6)$ transfer energy to anthracene. No ^{3}An absorption is observed in the absence of the copper compounds under these conditions. The ^{3}An assignment is made on the basis of previous literature reports[23] and the appearance of a similar absorbance feature following direct 355 nm excitation of anthracene.

The relative efficiency of energy transfer 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, $A_{532} = 0.070 \pm 0.005$. The relative yield of triplet anthracene was then measured 2 μs after 532 nm laser excitation for each solution. 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. The yields are summarized in Table 2. The most efficient donor is $Cu(dmp)_2^{+*}$, which produces one-fourth of the amount of ^{3}An that $Ru(bpy)_3^{2+*}$ does under these conditions. 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.[11]

The triplet-to-triplet absorbance growth reflects the kinetics of energy transfer from the copper excited states. In our previous studies, the formation of ^{3}An was monitored at 430 nm, where the kinetics were complicated somewhat by contributions from unquenched copper excited states. Inefficient energy transfer and poor solubility of anthracene precluded complete quenching, and this contribution was subtracted. Here, we monitored ^{3}An at the isosbestic points shown in Figure 2 and could cleanly observe the energy transfer process. We note that the kinetics measured at the isosbestic wavelength are in excellent agreement with those reported previously[10] and plots of the observed rate versus anthracene concentration are linear.

$Cu(dmp)_2(AnCO_2)$, where $AnCO_2^-$ is the 9-anthracenecarboxylate anion, and $Cu(dmp)_2(C_6H_5CO_2)$, which serves as a

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

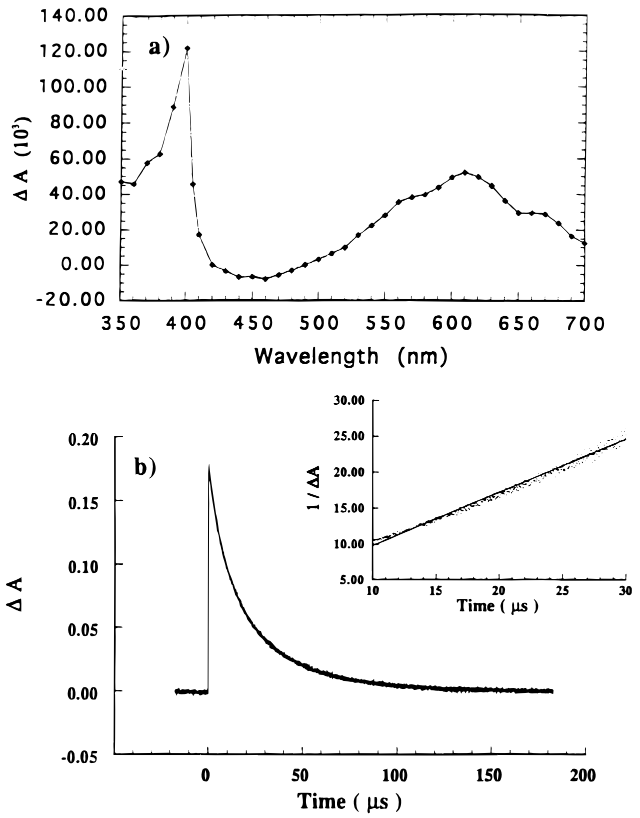

Figure 4. (a) Excited state absorption difference spectrum of a Cu(dpp)$_2$(PF$_6$) acetonitrile solution with 0.1 M TBAH and 10 mM MV^{2+} recorded 5 μs after a 532 nm laser pulse. (b) Time-resolved absorbance measured at 396 nm. The inset shows the fit of these same data to a second-order equal-concentration kinetic model.

model, were prepared by metathesis reactions. Integration of the proton NMR confirms that the cation and anion are present in a 1:1 molar ratio. The lifetimes and PL intensities are highly concentration dependent. At low concentrations, the lifetimes reach a limiting upper value which decreases rapidly with increased concentration into our instrument response function, 14 ns. At low concentrations, the lifetimes of the AnCO$_2^-$ and C$_6$H$_5$CO$_2^-$ salts are comparable to the lifetime of the PF$_6^-$ salt, $\tau = 80 \pm 10$ ns. Using the low-concentration lifetime as τ_0, plots of τ_0/τ are linear and give Stern−Volmer constants of 4000 M^{-1} for Cu(dmp)$_2$(C$_6$H$_5$CO$_2$) and 4400 M^{-1} for Cu(dmp)$_2$(AnCO$_2$). The excited state absorption spectrum is essentially identical to that of Cu(dmp)$_2$(PF$_6$), with kinetics which agree well with PL data. No absorption feature due to ^{3}AnCO$_2^-$ was observed under any conditions.

Electron transfer from copper diimine excited states to methyl viologen (MV^{2+}), benzyl viologen (BV^{2+}), and monoquat (MQ$^+$) were explored in CH$_3$CN/0.1 M TBAH electrolyte. Acetonitrile was chosen due to the poor solubility of the viologen salts in dichloromethane. The only compound which is emissive in CH$_3$CN/0.1 M TBAH electrolyte is Cu(dpp)$_2$(PF$_6$), which has a lifetime of 110 ns and a corrected PL maximum at 750 nm. In all cases, electron transfer quenching was observed by the appearance of the reduced viologen after selective excitation of Cu(dpp)$_2^+$.

Table 3. Electron Transfer of Cu(dpp)$_2^+$ Viologens in 0.1 M TBAH/CH$_3$CN

acceptor[a]	$-\Delta G_f$,[b] V	$10^{-9}k_f$,[b] M^{-1} s^{-1}	Φ_{CE}[c]	$-\Delta G_b$,[d]	$10^{-10}k_b$,[d] M^{-1} s^{-1}
MQ$^+$	0.20	4.3 ± 0.5		2.0	
MV^{2+}	0.55	6.6 ± 0.5	0.95 ± 0.05	1.4	2.0 ± 0.1
BV^{2+}	0.63	6.7 ± 0.5	0.57 ± 0.05	1.3	2.1 ± 0.1

[a] Electron acceptors where MQ$^+$ is monoquat, MV^{2+} is methyl viologen, BV^{2+} is benzyl viologen. [b] Driving force and electron for electron transfer from Cu(dpp)$_2^{+*}$ to the viologens calculated as described in the Results. [c] Cage escape yields calculated with eq IV. The error represents one standard deviation from three separate measurements. [d] Driving force and rates for back electron transfer from the reduced viologen acceptor to Cu(dpp)$_2^{2+}$.

Electron transfer to MV^{2+} after selective excitation of Cu(dpp)$_2^+$ was explored in most detail, Figure 4.[24] Plots of the observed electron transfer rates monitored at 396 nm versus the viologen concentrations are linear. The driving forces for the electron transfer processes were calculated on the basis of the estimated −1.4 V excited state oxidation potential of Cu(dpp)$_2^{+*}$ and the reduction potential of the acceptors measured in the same electrolyte by cyclic voltammetry. The reduction potentials were measured to be −0.85 V for MV$^{2+/+\bullet}$, −0.77 V for BV$^{2+/+\bullet}$, and −1.38 V for MQ$^{+/0}$ under these conditions. The back electron transfer processes follow second-order equal concentration kinetics (inset, Figure 4b). The kinetic data are summarized in Table 3. Cage escape efficiencies with [Cu(dpp)$_2^{2+}$, MV$^{+\bullet}$] were determined in samples where the fraction of PL quenched was typically >95%. Actinometry was performed before and after each experiment by measuring the MLCT-state transient absorbance of an aqueous Ru(bpy)$_3^{2+}$ solution, assuming a quantum yield of unity for formation of the MLCT excited state and $\Delta\epsilon_{360} = 2.2 \times 10^4$ M^{-1} cm^{-1}. The changes in extinction coefficient ($\Delta\epsilon$) for MV$^{+\bullet}$ at $\lambda = 396$ and 606 nm were taken to be 41 800 and 13 900 M^{-1} cm^{-1}, respectively.[24] Cage escape yields (Φ_{CE}) were then calculated from the absorbances of the sample and actinometer solution at 416 or 532 nm, eq IV, in conjunction with percent PL

$$\Phi_{CE} = \frac{(\Delta A_\lambda/\Delta\epsilon_\lambda)_{A^-}}{(\Delta A_{360}/\Delta\epsilon_{360})_{\text{actinometer}}} \frac{(1 - 10^{-A_{532\text{ or }416}})_{\text{actinometer}}}{(1 - 10^{-A_{532\text{ or }416}})_{\text{Cu(dpp)}_2^+}} \times \frac{1}{\text{fraction of PL quenched}} \quad \text{(IV)}$$

quenched determined from extrapolation of Stern−Volmer plots. For five different samples, Φ_{CE} was 0.95 ± 0.05. In contrast, Φ_{CE} for [Ru(bpy)$_3^{3+}$, MV$^{+\bullet}$] was measured to be 0.25 ± 0.05 under the same conditions, in agreement with literature values.[25] A series of experiments were conducted to verify the higher cage escape efficiency for the copper compound. TBAH (0.1 M) solutions with 10 mM MV^{2+} and either Ru(bpy)$_3^{2+}$ or Cu(dpp)$_2^+$ were prepared so that the absorbance at 532 (or 416) nm was the same, typically 0.05 (or 0.3). The relative amount of MV$^{+\bullet}$ formed after the laser pulse was then monitored by excited state absorption spectroscopy. The yield was typically 3 times greater for Cu(dpp)$_2^{2+}$. The cage escape yield for [Cu(dpp)$_2^{2+}$, BV$^{+\bullet}$] was measured analogously with the known extinction coefficient of BV$^{+\bullet}$.[26]

Discussion

Cuprous phenanthroline compounds are photostable and display broad charge transfer bands in the visible region, potentially useful for solar harvesting. In some cases, these excited states sensitize the reduction of viologens and/or energy transfer to anthracene. Below, we discuss the excited state and

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(24) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

(25) Hoffman, M. Z. *J. Phys. Chem.* **1988**, *92*, 3458 and references therein.

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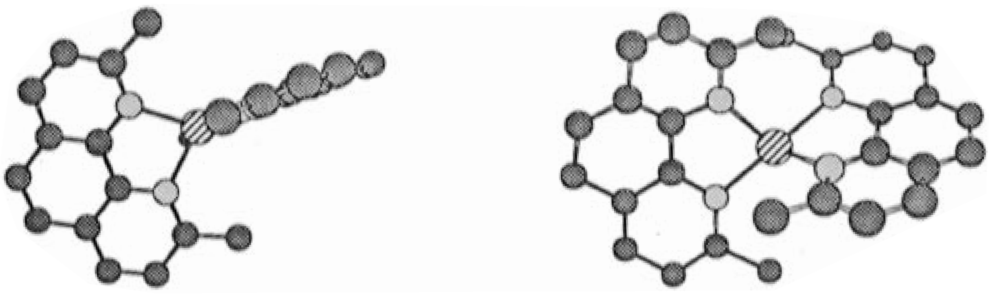
Chart 1



$Cu(dmp)_2^+$ $Cu(dmp)_2^{2+}$

redox properties of the compounds, followed by the interesting energy and electron transfer processes.

Excited State and Redox Properties. All four copper compounds are reversibly oxidized in dichloromethane electrolyte. A strikingly more negative oxidation potential for $Cu(phen)_2^+$ compared to the other copper compounds is observed. Williams and James first reported that the oxidation potential of $Cu(phen)_2^+$ is 420 mV more negative than that of $Cu(dmp)_2^+$ in water.[27] The results here show a similar effect in a noncoordinating solvent. The observation cannot be rationalized by electronic considerations but can be based on steric interactions. The known crystal structures of $Cu(dmp)_2^+$ and $Cu(dmp)_2^{2+}$ show that the cupric state places the methyl groups in the 2- and 9-positions of the ligand into an unfavorable geometry, Chart 1.[28] Therefore, the presence of substituents in these positions favors the tetrahedral cuprous state. The slightly more positive oxidation potential for $Cu(bcp)_2^+$ can be rationalized on the basis of addition of the phenyl substituents.[29] We note that, despite the large inner-sphere reorganization energy which accompanies this redox chemistry, the voltammetry observed is nearly ideal.

The broad visible absorption bands were previously attributed to metal-to-ligand charge transfer (MLCT) excited states.[2] Excited state absorption spectroscopy of $Cu(dmp)_2^+$, $Cu(dpp)_2^+$, and $Cu(bcp)_2^+$ supports this assignment. In the one-electron transfer localized extreme, the excited state can be viewed as a Cu^{II} metal center coordinated to a reduced ligand. Difference spectra show isosbestic points consistent with the formation of a reduced ligand and Cu^{II} metal.[21] Further, the dramatic red shift in the PL spectra can be taken as evidence for emission from a geometrically relaxed Cu(II) excited state. The lack of a resolvable excited state absorption spectrum for $Cu(phen)_2^+$ is indicative of rapid nonradiative decay, $k_{nr} > 5 \times 10^7\ s^{-1}$, which is expected on the basis of the energy gap law.[30]

Energy Transfer. Dynamic triplet−triplet energy transfer from the long-lived copper MLCT excited states to anthracene is observed. The energy transfer rates measured by Stern−Volmer analysis of the PL quenching and the appearance of the triplet-to-triplet ^{3}An absorption are in excellent agreement. The order-of-magnitude-faster energy transfer from $Cu(dmp)_2^{+*}$ can be rationalized on the basis of ∼50 mV larger driving force, Table 1. The lack of energy transfer from $Cu(phen)_2^{+*}$ is likely kinetic in origin, since these excited states do not live long enough to undergo diffusional quenching.

While the demonstration of energy transfer is clear, the efficiency is low in all cases. Relative to that of $Ru(bpy)_3^{2+*}$, which is known to transfer energy to anthracene derivatives with a quantum yield near unity under a variety of conditions,[11] the yield from the copper excited states is at best 0.25. $Cu(dmp)_2(AnCO_2)$ was prepared with the hope that ion-pairing and, possibly, exciplex formation would mediate energy transfer and thereby increase the efficiency.[31,32] While our results reveal some indirect evidence of excited state complex (exciplex) formation, there is no spectroscopic evidence of energy transfer. Instead, the concentration-dependent quenching can be satisfactorily rationalized on the basis of an ion-pair exciplex model proposed by McMillin in which counterion coordination to the Cu center promotes nonradiative decay. A fundamental prediction of this model is that the extent of quenching should mirror the nucleophilicity of the anion. A comparison of published data to these indicates that the nucleophilicity of anions decreases in the order $PF_6^- > AnCO_2^- \geq C_6H_5CO_2^- > NO_3^-$. The ion-pair exciplex quenching process deactivates the excited state rather than providing a conduit for energy transfer.

Electron Transfer. Electron transfer from $Cu(dpp)_2^{+*}$ to three viologens, k_f, is clearly observed in the reduced viologen absorption spectra. The increased rate for MV^{2+} and BV^{2+} when compared to MQ^+ is consistent with electron transfer in the normal region, Table 3. The yield of $MV^{+\bullet}$ observed after the laser pulse is 3−4 times higher than that observed when $Ru(bpy)_3^{2+*}$ is the donor. The increased yield can be traced to a cage escape yield near unity within the $[Cu(dpp)_2^{2+}, MV^{+\bullet}]$ charge-separated pair. Previous studies have shown that spin changes are a key factor in determining cage escape efficiencies, and they do explain the results here. Triplet ion pairs yield higher cage escape efficiencies than do singlet ion pairs.[11d,33] For the $[Ru(bpy)_3^{3+}, MV^{+\bullet}]$ pair, spin−orbit coupling increases the singlet character and the cage escape yield drops in comparison to the case of an organic triplet donor, such as ^{3}An.[11d] For the copper donors, spin−orbit coupling likely plays a lesser role and the excited state is closer to a pure triplet state, which results in a triplet ion pair and a high cage escape yield. An alternative explanation is that a structural barrier exists for recombination within the $[Cu(dpp)_2^{2+}, MV^{+\bullet}]$ solvent cage since different geometries are expected for the forward and reverse electron transfer processes. In either case, high cage escape yields may be a general phenomena for chromophoric copper diimine donors. In this regard, we note that the cage escape yield for $[Cu(dpp)_2^{2+}, BV^{+\bullet}]$ is also very high. Recombination of the charge-separated pairs to ground state products, k_b, occurs within experimental error of the diffusion limit. The diffusion

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(28) The compounds were generated with Chem-Draw 3D from the reported crystal structure coordinates. For clarity, the nitrate adduct in the cupric compound was eliminated from Chart 1. (a) Dessy, G.; Fares, V. *Cryst. Struct. Commun.* **1979**, *8*, 507. (b) Van Meersche, M.; Germain, G.; Declercq, J. P.; Wilputte-Steinert, L. *Cryst. Struct. Commun.* **1981**, *10*, 47.

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limit in acetonitrile at 25 °C based on the Smoluchowski–Stokes–Einstein equation is 1.9×10^{10} M^{-1} s^{-1}.[34]

The conclusion of a cage escape yield near unity stands somewhat in conflict with the results of Edel et al.[8] These workers found a greater than 60-fold increase in $MV^{+\bullet}$ production when anthracenecarboxylate was added to a $Cu(dpp)_2{}^+$/ethanol solution which contained triethanolamine, TEOA, as a sacrificial electron donor. This observation was later interpreted as due to a cage escape yield of less than 0.02 for $[Cu(dpp)_2{}^{2+}, MV^{+\bullet}]$.[11d] An alternative explanation, in accord with the results presented here, is that the increased yield of $MV^{+\bullet}$ is due to more efficient oxidation of TEOA by $AnCO_2{}^\bullet$ than by $Cu(dpp)_2{}^{2+}$. We note also that TEOA oxidation products are known to undergo subsequent dark reactions, which can artificially increase the quantum yield of $MV^{+\bullet}$ to 2.[35] In either case, the increased yield of $MV^{+\bullet}$ upon addition of anthracenecarboxylate anion is not due to a low cage escape yield for the $[Cu(dpp)_2{}^{2+}, MV^{+\bullet}]$ pair.

Conclusions

Dynamic electron and energy transfers have been clearly demonstrated for cuprous phenanthroline derivatives. $Cu(phen)_2(PF_6)$ has an excited state lifetime which is too short to undergo diffusional quenching processes, $\tau < 20$ ns. The rate and efficiency of energy transfer to anthracene or electron transfer to viologens are comparable with those for $Ru(bpy)_3{}^{2+}$. The ability to sensitize these processes to visible light with simple inexpensive copper diimines is in itself noteworthy. An apparent advantage of copper phenanthroline excited states over those of $Ru(bpy)_3{}^{2+*}$ is the high cage escape yields observed after oxidative quenching by viologens.

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Supporting Information Available: Visible absorption and photoluminescence spectra (2 pages). Ordering information is given on any current masthead page.

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