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Tuning Charge Recombination Rate Constants through Inner-Sphere Coordination in a Copper(I) Donor−Acceptor Compound

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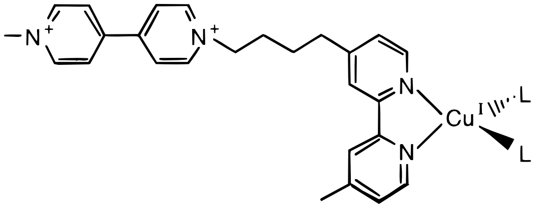
The coordination compounds [Cu(bpy-MV^{2+})(PPh$_3$)$_2$](PF$_6$)$_3$, where bpy-MV^{2+} is the 1-(4-(4′-methyl-2,2′-bipyridin-4-yl)butyl)-1′-methyl-4,4′-bipyridinediium(2+) cation, and [Cu(dmb)(PPh$_3$)$_2$](PF$_6$), where dmb is 4,4′-dimethyl-2,2′-bipyridine, have been prepared and characterized. Visible light (417 nm) excitation of [Cu(bpy-MV^{2+})(PPh$_3$)$_2$]$^{3+}$ at room temperature leads to rapid intramolecular electron transfer, $k_{cs} > 1 \times 10^8$ s^{-1}, to form a charge-separated state with an electron localized on the pendant viologen group and a copper(II) metal center, abbreviated [Cu^{II}-bpy-MV$^{\bullet+}$]. This state recombines to ground-state products with first-order rate constants that can be tuned with solvent over a $\sim 10^7 - 10^5$ s^{-1} range. The activation parameters were determined from temperature-dependent electron-transfer data with Arrhenius analysis. A model is proposed wherein a solvent molecule is coordinated to Cu(II) in the charge-separated state, [(S)Cu^{II}-bpy-MV$^{\bullet+}$]. Visible light excitation of [Cu(dmb)(PPh$_3$)$_2$](PF$_6$) in argon-saturated dichloromethane produces long-lived photoluminescent excited states, $\tau = 80$ ns, that are dynamically quenched by the addition of Lewis basic solvents. The measured quenching constants each correlate well with the lifetime of the charge-separated state measured after excitation of [Cu(bpy-MV^{2+})(PPh$_3$)$_2$]$^{3+}$ in the corresponding solvent.

Introduction

Electron-transfer processes that are accompanied by large conformational changes represent an important class of redox events in biology and chemistry.[1,2] In principle, a conformational change can be the rate-limiting step, and in such cases, “gated” or “directional” electron transfer is predicted to occur.[3−5] The extent to which nature utilizes structural changes to modulate electron-transfer dynamics represents an important area of ongoing research.[6,7] Rate constants for electron transfer or structural reorganization have been experimentally obtained on millisecond and longer time scales by NMR, EPR, electrochemical, and stopped-flow techniques, but these measurements are often frustrated by diffusional encounters of the electron donor and acceptor that can be rate limiting. Nevertheless, examples of fully gated electron transfer have been realized in model systems.[8]

We recently communicated a strategy for quantifying these important processes that circumvents the diffusion limitations of bimolecular redox chemistry and opens up new time windows for characterization.[9] The key ideas were to (1) exploit the known geometric changes that are novel to Cu(II/I) redox chemistry and (2) photoinitiate the process such that transient spectroscopic techniques could be employed to gain insight into mechanistic details of structural reorganization and electron transfer. This strategy was successful. Visible light excitation of the Cu(I) donor−acceptor compound where L is triphenylphosphine, in fluid solution at room temperature led to rapid intramolecular charge separation, $k_{cs} > 1 \times 10^8$ s^{-1}, to form a charge-separated state with an electron localized on the pendant methyl viologen and an oxidized copper metal center. Back electron transfer to generate ground-state products, MV$^{\bullet+}$ → Cu(II), was first order with rate constants that could be tuned with solvent over a $k_{cr} \sim 10^7 - 10^5$ s^{-1} range. To account for this remarkable solvent dependence, a model was proposed wherein the coordination number at Cu(II) increased to 5 in the charge-separated state.[9] In support of this model, it was noted that Cu(II) compounds are subject to Jahn−Teller distortions and thus Cu(II) generally adopts higher coordination numbers than does Cu(I).[10]



Here we report a more detailed study of the photodriven electron transfer in this first-generation copper(I) dyad including temperature-dependent electron-transfer data acquired in four

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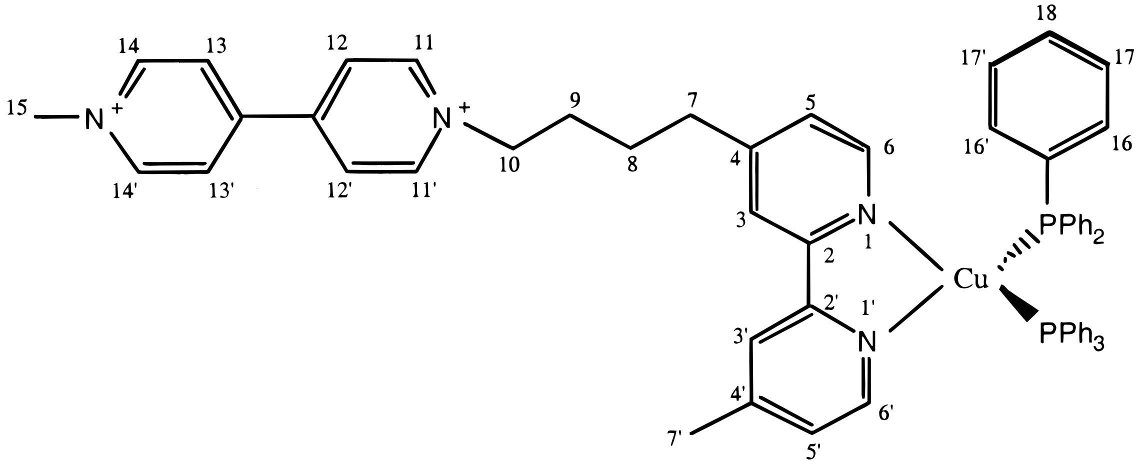
Chart 1. Atom Numbering for $[Cu(bpy\text{-}MV)(PPh_3)]^{3+}$



different solvents. These data are contrasted with excited-state properties of $[Cu(dmb)(PPh_3)_2]^+$ in the presence and absence of Lewis basic solvents that quench the excited state. The excited-state-quenching constants are found to be correlated with the charge-separated-state lifetimes observed after excitation of the dyad. The results support the hypothesis that inner-sphere reorganization at copper underlies the remarkable solvent tuning of electron-transfer dynamics.

Experimental Section

Materials. Spectroscopic grade solvents were purchased from Burdick & Jackson and used as received. $[Cu(CH_3CN)_4](PF_6)$ and bpy-MV^{2+} were prepared by published methods.[11,12]

Synthesis. The cuprous phosphine compounds were prepared by stirring 1 equiv each of $[Cu(CH_3CN)_4](PF_6)$ and [1-(4-(4′-methyl-2,2′-bipyridin-4-yl)butyl)-1′-methyl-4,4′-bipyridinediium]$(PF_6)_2$ (abbreviated bpy-MV^{2+}) or 4,4′-dimethyl-2,2′-bipyridine (abbreviated dmb; Aldrich) with 2.5 equiv of triphenylphosphine (Aldrich; recrystallized from ethanol) under an argon atmosphere in acetonitrile for 10 min. The solution was evaporated to dryness under vacuum at room temperature, the residue was dissolved in acetone, and the yellow product was precipitated by layering diethyl ether over the acetone solution. Typical yields were 80−90% for $[Cu(dmb)(PPh_3)](PF_6)$ and 65−75% for $[Cu(bpy\text{-}MV^{2+})(PPh_3)](PF_6)_3$.

[Cu(4,4′-dimethyl-2,2′-bipyridine)(PPh$_3$)$_2$](PF$_6$): ^1H NMR (CD_3CN) δ CH_3− 2.5 (singlet), PPh_3 7.0 (doublet), 7.2 (triplet), 7.35 (triplet), dmb 7.12 (doublet), 8.11 (doublet), 8.30 (singlet). Anal. Calc (found): C, 62.85 (62.83); H, 4.61 (4.68); N, 3.05 (3.00).

[Cu(4-(4-(1′-methyl-4,4′-bipyridinediium-1-yl)butyl)-4′-methyl-2,2′-bipyridine)(PPh$_3$)$_2$](PF$_6$)$_3$•H$_2$O: ^1H NMR (CD_3CN) (atom numbering: Chart 1) δ $-CH_2-$ 1.9 (2H, H_9, quintet), $-CH_2-$ 2.1 (2H, H_8, quintet), $-CH_3$ 2.5 (3H, $H_{7'}$, singlet), $-CH_2-$ 2.8 (2H, H_7, triplet), N^+CH_3 4.4 (3H, H_{15}, singlet), N^+CH_2- 4.7 (2H, H_{10}, triplet), 7.14 (12H, H_{16}, doublet), 7.27 (14H, H_{17}, H_5, multiplet), 7.40 (6H, H_{18}, triplet), 8.28 (2H, H_3, singlet), 8.38−8.44 (5H, $H_{3'}$, H_{12}, H_{13}, m), 8.60−8.67 (2H, H_6, dd), 8.85−8.95 (4H, H_{11}, H_{14}, dd). Anal. Calc (found): C, 51.80 (50.96); H, 4.21 (4.24); N, 3.90 (4.05).

Spectroscopy. (a) UV−Vis. All UV−visible ground-state absorption spectra were acquired at ambient temperature using a Hewlett-Packard 8453 diode array spectrometer.

(b) NMR. ^1H NMR spectra were obtained on a Bruker 300AMX FT-NMR spectrometer.

(c) Transient Absorption. Transient absorption measurements were carried out on an apparatus previously described.[13] Briefly, excitation was carried out using 355 nm pulses, ca. 8 ns and 1−30 mJ cm^{-2}, from a Continuum Surelite II Nd:YAG laser or 417 nm pulses obtained by focusing the 355 nm line in an H_2-pressurized Raman shifter. The 5 mm diameter beam was expanded to ensure homogeneous illumination of the cuvette. The sample was protected from the probe light using a fast shutter and appropriate UV- and heat-absorbing glass and solution filter combinations. In general, kinetic traces represent the average of 10−50 laser shots.

(d) Photoluminescence. Corrected photoluminescence (PL) spectra were obtained with a Spex Fluorolog instrument that had been calibrated with a standard NBS tungsten−halogen lamp. PL lifetimes were obtained with pulsed 336 nm light excitation from a nitrogen laser and with a detection apparatus that was previously described.[13]

Electrochemistry. Cyclic voltammetry experiments were performed in a 0.1 M tetrabutylammonium hexafluorophosphate (TBAH)/acetonitrile electrolyte. A BAS Model CV27 potentiostat was used in a standard three-electrode arrangement consisting of a 1 cm^2 Pt working electrode, a Pt gauze counter electrode, and an SCE reference electrode. Approximately millimolar concentrations of the compounds were dissolved in the electrolyte and the solutions were subsequently purged with argon.

Results

The ground-state absorption spectra of $[Cu(bpy\text{-}MV^{2+})(PPh_3)_2](PF_6)_3$ and $[Cu(dmb)(PPh_3)_2](PF_6)$ display a broad charge-transfer band centered at ∼360 nm in all the solvents examined. The absorption band tails into the visible region, giving the solutions a yellow color. Photoluminescence, PL, is observed for $[Cu(dmb)(PPh_3)_2](PF_6)$ in dichloromethane solution with a maximum centered around 680 nm. The PL is red-shifted significantly from the absorption band and extends beyond the sensitivity of our fluorimeter, as shown in the Supporting Information. No detectable PL is observed for $[Cu(bpy\text{-}MV^{2+})(PPh_3)_2](PF_6)_3$ under the same conditions.

Time-resolved PL data for $[Cu(dmb)(PPh_3)_2](PF_6)$ in argon-saturated dichloromethane display nonexponential kinetics. The PL decays comprise a fast component that can not be time-resolved, $\tau < 10$ ns, and a slower exponential component with an 80 ns lifetime. The fast component is present when a 10-fold increase in triphenylphosphine is added to the dichloromethane solution. Pulsed laser excitation of $[Cu(dmb)(PPh_3)_2](PF_6)$ in argon-saturated dichloromethane at room temperature results in the transient absorption spectra shown in Figure 1.

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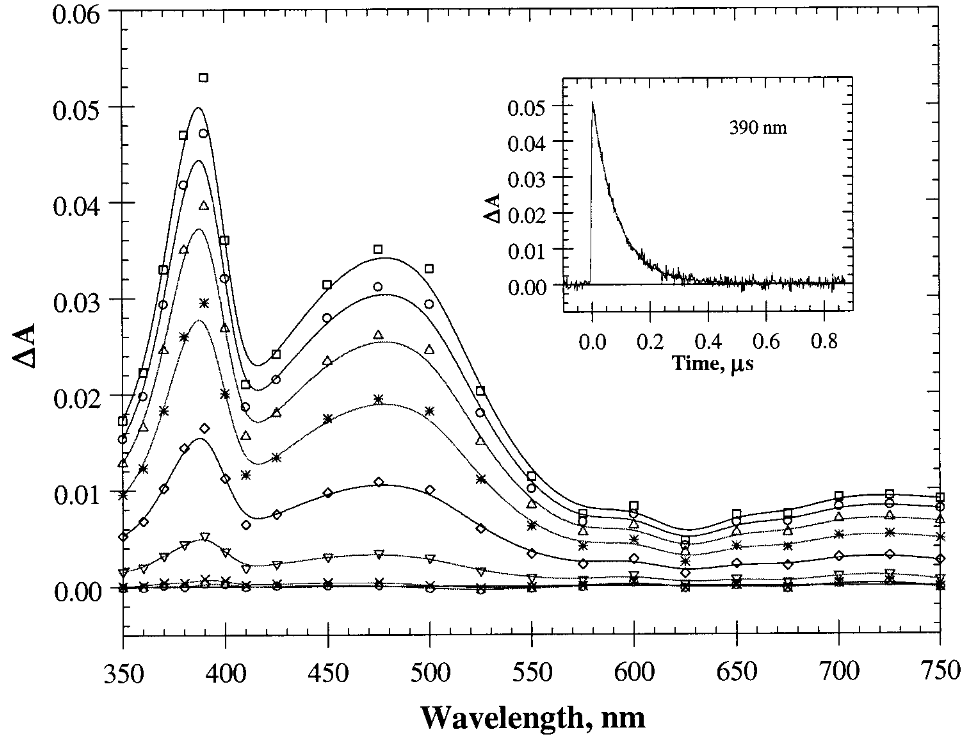

Figure 1. Absorption difference spectra after pulsed 417 nm light excitation (~3 mJ/cm^2, 8 ns fwhm) of [Cu(dmb)(PPh$_3$)$_2$]$^+$ in argon-saturated dichloromethane at room temperature. The spectra are shown at the following delay times: 0 ns (squares); 10 ns (circles); 25 ns (up triangles); 50 ns (stars); 100 ns (diamonds); 200 ns (down triangles); 400 ns (crosses); and at infinite time (circles). The inset displays single-wavelength absorption transients monitored at 390 nm with a superimposed first-order fit to the data.

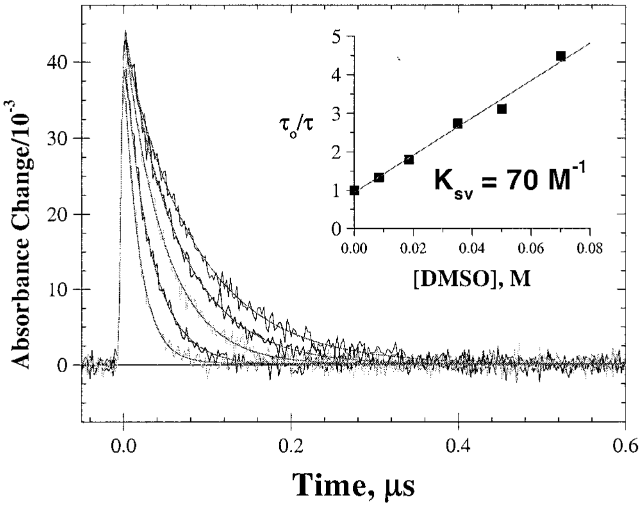

Figure 2. Single-wavelength absorption transients monitored at 390 nm after pulsed 417 nm excitation (~5 mJ/cm^2, 8 ns fwhm) of [Cu(dmb)(PPh$_3$)$_2$]$^+$ in dichloromethane at room temperature as a function of added DMSO. From top to bottom the transients were recorded in the following DMSO concentrations: 0, 8, 20, 35, 50 mM. The inset displays a Stern−Volmer plot of these data from which a Stern−Volmer constant was abstracted, K_{SV} = 70 M^{-1}.

The kinetics are first order, independent of the monitoring wavelength within experimental error, and the transients return to pre-excitation levels cleanly. The measured lifetime is 80 ± 5 ns. No evidence is found for a second component. Ground-state absorption measurements before and after pulsed laser excitation reveal negligible photochemistry.

The [Cu(dmb)(PPh$_3$)$_2$]$^{+}$* excited state is dynamically quenched by the addition of Lewis bases to the dichloromethane solution. Shown in Figure 2 are typical time-resolved absorption traces recorded at 380 nm as a function of dimethyl sulfoxide, DMSO, concentration. The decrease in lifetime is well described by the Stern−Volmer model, eq 1. The inset of Figure 2 displays

$$\tau_o/\tau = 1 + K_{SV}[Q] = 1 + (k_q[Q]\tau_o) \qquad (1)$$

Stern−Volmer analysis of the data shown, from which a Stern−Volmer constant, K_{SV}, and an apparent quenching rate constant, $k_q = 8.3 \times 10^8$ M^{-1} s^{-1}, were abstracted. The K_{SV} and k_q values for a number of Lewis bases found to dynamically quench the excited state are given in the Supporting Information. No evidence for static quenching was found over the concentration range 0.0−0.2 M. [Cu(dmb)(PPh$_3$)$_2$](PF$_6$) is nonemissive in neat CH$_3$CN and DMSO with excited-state lifetimes that could not be time-resolved with our instrumentation, $\tau < 10$ ns.

Pulsed laser excitation (λ = 355 or 416 nm) of the donor−acceptor complex, [Cu(bpy-MV^{2+})(PPh$_3$)$_2$]$^{3+}$, leads to the immediate appearance of the absorption difference spectra shown in Figure 3. Charge recombination follows first-order kinetics in argon-saturated DMSO, 1,2-dichloroethane (DCE), DMF, and CH$_3$CN solvents (Table 1) and in argon-saturated CH$_2$Cl$_2$. The inset in Figure 3 displays typical time-resolved absorption data monitored at 400 nm following excitation with 416 nm light. Superimposed on these data is the fit to a first-order kinetic model. The recombination kinetics are independent of the monitoring wavelength (λ = 330−650 nm), the sample concentration (0.1−20 mM), and the excitation irradiance (355 or 417 nm, 3−30 mJ/cm^2). Ground-state absorption measurements before and after laser excitation reveal negligible sample decomposition in DMSO and acetonitrile. In dichloromethane, a decrease in the absorption band centered near 350 nm was occasionally observed after prolonged laser irradiation. The extent of the photochemistry could be minimized by employing 417 nm excitation light and was sufficiently small that it did not represent an obstacle to these experimental studies.

The temperature dependence of charge recombination was

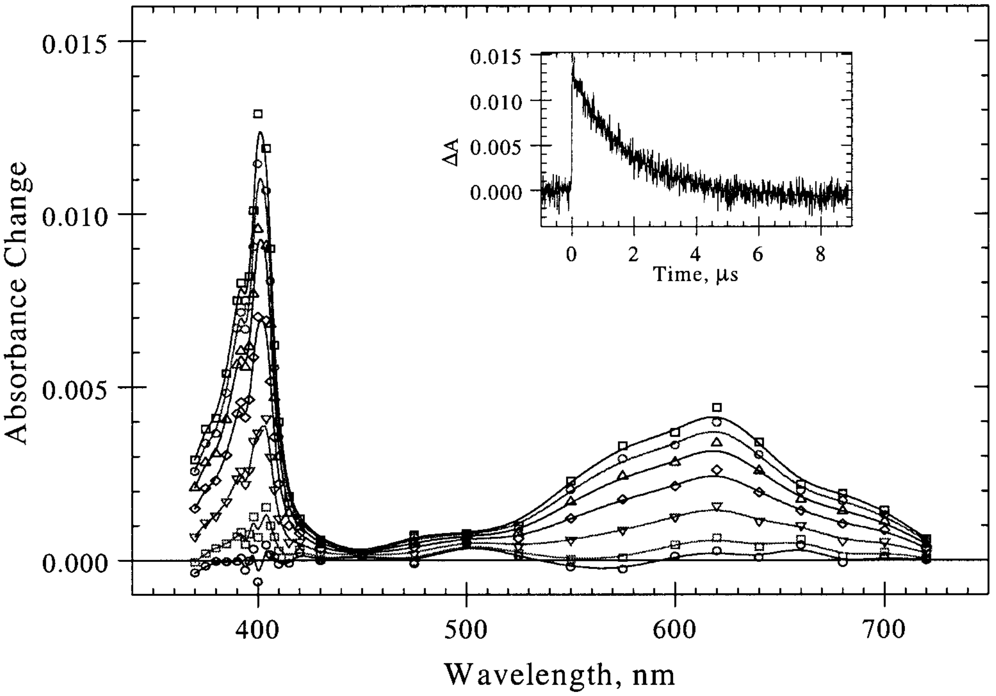

Figure 3. Absorption difference spectra observed after laser excitation (417 nm; 8 ns fwhm, 4 mJ/pulse) of $[Cu(bpy\text{-}MV^{2+})(PPh_3)_2](PF_6)_3$ in argon-saturated dichloromethane at the following delay times: 0 ns (squares); 10 ns (circles); 25 ns (up triangles); 50 ns (diamonds); 100 ns (down triangles); 200 ns (squares); and at infinite time (circles). The inset displays a single-wavelength transient monitored at 400 nm with a superimposed fit to a first-order kinetic model.

Table 1. Kinetic Data and Activation Parameters[a]

solvent	$\Delta G^{\ddagger}$ (kJ/mol)	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta S^{\ddagger}$ (J/(K mol))	k_{cr} (s^{-1})[b]	k_q (M^{-1} s^{-1})[c]
CH_2ClCH_2Cl	31 ± 4	2 ± 0.5	−90 ± 10	4.9 × 10^7	–
CH_3CN	32 ± 4	4 ± 1	−90 ± 10	3.1 × 10^7	1.5 × 10^8
DMF	40 ± 3	18 ± 2	−70 ± 6	9.7 × 10^5	6.2 × 10^8
DMSO	39 ± 3	25 ± 3	−60 ± 6	5.6 × 10^5	8.3 × 10^8

[a] Thermodynamic activation parameters for charge recombination measured from Arrhenius analysis of the temperature-dependent first-order rate constants for charge recombination. [b] k_{cr} is the first-order electron-transfer rate constant for charge recombination measured at 25 °C. The estimated error is ±10%. [c] Rate constants for the excited-state quenching of $[Cu(dmb)(PPh_3)_2]^{+}*$ by CH_3CN, DMF, and DMSO in CH_2Cl_2, from Table S1 (Supporting Information) measured at 25 °C.

monitored at 400 nm after 417 nm excitation of $[Cu(bpy\text{-}MV^{2+})(PPh_3)_2]^{3+}$ in DMSO, DMF, CH_3CN, and DCE. DCE was chosen for its more favorable temperature window when compared to CH_2Cl_2. At all temperatures, the rate of charge separation could not be time-resolved. Arrhenius plots of the observed first-order rate constants for charge recombination are given in the Supporting Information, and the abstracted thermodynamic data are given in Table 1. The rate constants were independent of the temperature change direction and were found to be reversible.

The electrochemical properties were measured by cyclic voltammetry in 0.1 M TBAH/acetonitrile solutions. $[Cu(bpy\text{-}MV^{2+})(PPh_3)_2](PF_6)_3$ and $[Cu(dmb)(PPh_3)_2](PF_6)$ both displayed an irreversible oxidation wave at ~0.7 V vs SCE with scan rates from 20 to 200 mV/s. Irreversible Cu(II/I) redox chemistry was also observed for $[Cu(dmb)(PPh_3)_2]^+$ in dichloromethane and dimethyl sulfoxide electrolytes. For $[Cu(bpy\text{-}MV^{2+})(PPh_3)_2](PF_6)_3$, a reversible viologen reduction at −0.39 vs SCE was observed in acetonitrile electrolyte.

Discussion

Excited-State Behavior. Room-temperature photoluminescence is observed after light excitation of $[Cu(dmb)(PPh_3)_2]^{+}*$ in dichloromethane solution.[14] The transient absorption spectra of $[Cu(dmb)(PPh_3)_2]^{+}*$ are consistent with a metal-to-ligand charge-transfer excited state, MLCT, eq 2.[15] The positive

$$[Cu(dmb)(PPh_3)_2]^+ \xrightarrow{h\nu} [Cu^{II}(dmb^-)(PPh_3)_2{}^{+}* \equiv Cu(dmb)(PPh_3)_2]^{+}* \quad (2)$$

absorption features at 390 and 550 nm are expected for the reduced dmb ligand.[16] The high-energy absorption obscures the expected bleach of the ground-state MLCT band. The positive feature at ~475 nm is tentatively assigned to a $PR_3 \rightarrow Cu(II)$ ligand-to-metal charge-transfer (LMCT) band.[17] A similar band is observed at lower energy, ~500 nm, in the charge-separated state, $[Cu^{II}(bpy\text{-}MV^{\bullet+})(PPh_3)_2]^{3+}$. The shift to lower energy is expected for an LMCT transition and a fully oxidized Cu(II)

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center. Charge-transfer transitions have also been previously observed in the excited-state absorption spectra of Os(II) coordination compounds with phosphine ligands.[17]

$[Cu(dmb)(PPh_3)_2]^{+*}$ excited-state relaxation measured by transient absorption is first order with a lifetime of 80 ns at room temperature, while the time-resolved photoluminescence displays this component and a fast component (or component(s)) that could not be time-resolved. The discrepancy between the transient photoluminescence and absorption data indicates either is an emissive impurity present in low concentrations or that the change in extinction coefficient between the ground state and the fast component(s) excited state(s) is too small to be detected by absorption. We note that the fast component is present in rigorously purified $[Cu(dmb)(PPh_3)_2]^{+*}$ and in other substituted bpy complexes but is not observed for $[Cu(dmp)(PPh_3)_2]^{+*}$, where dmp is 2,9-dimethyl-1,10-phenanthroline.[18] The origin of the short-lived luminescent component is the subject of ongoing studies.[19]

Solvent Tuning. The $[Cu(dmb)(PPh_3)_2]^{+*}$ MLCT excited state is dynamically quenched by the addition of Lewis bases to the dichloromethane solution. The quenching follows the Stern−Volmer model, and the quenching rate constants vary from $\sim 8 \times 10^7$ M^{-1} s^{-1} for tetrahydrofuran to 8.3×10^8 M^{-1} s^{-1} for DMSO. McMillin and co-workers have observed similar behavior for $[Cu(dmp)_2]^{+*}$ and other emissive Cu(I) diimines and have explored the phenomena in considerable detail.[20] Their results and interpretation are consistent with quenching via a 5-coordinate Lewis base excited state adduct, or “exciplex”. An exciplex, by definition, is unstable with respect to ground-state products, and formation promotes nonradiative decay. In support of this mechanism being operative for $[Cu(dmb)(PPh_3)_2]^{+*}$ quenching, trends in measured quenching constants, where comparisons are possible, are in agreement with this previous work.[20] Furthermore, at the irradiances utilized here, only a shortened excited state is observed with no spectroscopic evidence for 5-coordinate Cu(I) compounds, ground-state adducts, or other chemical products.

The quenching rate constants abstracted from Stern−Volmer analysis are below what one would expect for a diffusion-limited process in dichloromethane, $k_{diff} = 1.6 \times 10^{10}$ M^{-1} s^{-1} on the basis of the Smoluchowski−Stokes−Einstein equations.[21] To account for the relatively low quenching constants measured, a simplified mechanism depicted by eqs 3 and 4 is proposed where

$$[Cu^{II}(dmb^-)(PPh_3)_2]^{+*} + S \underset{k_d}{\overset{k_a}{\rightleftharpoons}} [(S)Cu^{II}(dmb^-)(PPh_3)_2]^{+*} \quad (3)$$

$$[(S)Cu^{II}(dmb^-)(PPh_3)_2]^{+*} \xrightarrow{k_4} [Cu^I(dmb)(PPh_3)_2]^+ + S \quad (4)$$

S is a solvent molecule that acts as a Lewis base quencher. An important consequence of invoking a composite mechanism is that the measured quenching constants, k_q, may not be elementary rate constants.[20]

The adduct shown as the product of eq 3 is not a simple encounter complex but must be thought of as an excited-state complex, or “exciplex”. The exciplex has never been directly observed, but the indirect evidence for its presence is compelling.[20] Since both the transient absorption and PL spectra are essentially independent of solvent and since the spectral properties of the 5-coordinate solvent adducts are expected to differ significantly from those of the 4-coordinate complex,[22] it seems reasonable to conclude that the transient species observed is the uncomplexed MLCT excited state $[Cu(dmb)(PPh_3)_2]^{+*}$.

We consider two possible kinetic limits based on eqs 3 and 4 that are consistent with the observed results. The first is that eq 3 represents a rapid preequilibrium, $k_a + k_d \gg k_4$. In this case, the measured quenching rate constant is approximately equal to the product of the equilibrium constant and the exciplex quenching rate; i.e., $k_q \sim k_4K_3$. Alternatively, if solvent addition to the excited state is slow such that $k_a + k_d \ll k_4$, then equilibrium is not achieved and $k_q \sim k_a$.

Table 1 shows that the Lewis base induced excited-state-quenching rate constant, k_q, of $[Cu(dmb)(PPh_3)_2]^{+*}$ is inversely related to the first-order rate constant, k_{cr}, and activation enthalpy, $\Delta H^\ddagger$, for charge recombination observed after pulsed light excitation of $[Cu(bpy\text{-}MV^{2+})(PPh_3)_2]^{3+}$. The proposed mechanism for charge recombination and solvent coordination is shown in eqs 5 and 6. In contrast to the excited-state chemistry of $[Cu(dmb)(PPh_3)_2]^+$, “full” electron transfer to the viologen moiety yields a spectroscopically distinguishable intermediate attributed to the solvent adduct, $[(S)Cu^{II}(bpy\text{-}MV^{\bullet +})(PPh_3)_2]^{3+}$; that is, $K_5 \gg 1$ and the reaction is rate-limited by eq 6. This is consistent with eqs 3 and 5, both being rapid equilibria with $K_3 \ll 1$ and $K_5 \gg 1$ due to the stronger Lewis acidity of the Cu^{II} center in the charge-separated state compared to the more electron delocalized d → π* excited state. The charge recombination reaction is therefore rate-limited by k_{cr} and $k_{obs} \sim k_{cr}$. The solvent donor strength correlations with excited-state-quenching rate constants, charge recombination rates, and enthalpies of activation support the notion that inner-sphere coordination controls the charge recombination rate: the stronger the Cu^{II}−S bond strength, the longer-lived the charge-separated state.

$$[Cu^{II}(bpy\text{-}MV^{\bullet +})(PPh_3)_2]^{3+} + S \underset{k_d'}{\overset{k_a'}{\rightleftharpoons}} [(S)Cu^{II}(bpy\text{-}MV^{\bullet +})(PPh_3)_2]^{3+} \quad (5)$$

$$[(S)Cu^{II}(bpy\text{-}MV^{\bullet +})(PPh_3)_2]^{3+} \xrightarrow{k_{cr}} [Cu^I(bpy\text{-}MV^{2+})(PPh_3)_2]^{3+} + S \quad (6)$$

Conclusion

Two Cu(I) coordination compounds, $[Cu(bpy\text{-}MV^{2+})(PPh_3)_2](PF_6)_3$ and $[Cu(dmb)(PPh_3)_2](PF_6)$, have been prepared and characterized. An interesting solvent correlation was discovered that relates the excited-state-quenching efficiency of the latter compound to the electron-transfer dynamics of the former. This correlation is consistent with the hypothesis that inner-sphere coordination underlies the remarkable solvent tuning of the electron-transfer dynamics. The data supporting this hypothesis are compelling yet indirect. Future studies will be directed toward utilizing time-resolved vibrational spectroscopies of

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related copper donor−acceptor compounds to directly probe the coordination number of copper.

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Supporting Information Available: Ground-state absorption and emission spectra, Arrhenius plots, and a table of Stern−Volmer quenching constants. This material is available free of charge via the Internet at http://pubs.acs.org.

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