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Coordination Chemistry Reviews
171 (1998) 309–322

Electron and energy transfer from Cu^I MLCT excited states

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Received 7 July 1997; accepted 19 November 1997

Contents

Abstract

Electron and energy transfer processes from Cu^I MLCT excited states are reviewed. New results demonstrate clearly that these excited states undergo oxidative electron transfer quenching and energy transfer processes. The yields and dynamics of these processes have been spectroscopically quantified. Interfacial electron transfer from Cu^I MLCT excited states to wide band gap semiconductors has been observed. When utilized in photoelectrochemical cells, this interfacial electron transfer process provides a means for the conversion of light directly into electrical power. © 1998 Elsevier Science S.A.

Keywords: Copper excited states; Photochemistry

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PII S0010-8545(98)00036-8

1. Introduction

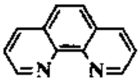
The quest for new materials and compounds that efficiently harvest solar energy continues to be an important goal [1]. Recently, there has been growing interest in the excited state and redox properties of cuprous phenanthroline and bipyridine derivatives [2–5]. These compounds possess broad absorption 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 $Cu(dmp)_2^+$ (dmp is 2,9-dimethyl-1,10-phenanthroline) produces room temperature photoluminescence in dichloromethane solution [6]. $Cu(dmp)_2^+$, related copper phenanthroline compounds with alkyl or aryl substituents in the 2,9-positions of phenanthroline, and $Cu(LL)(PR_3)_2^+$ compounds (where LL is a chromophoric ligand and PR_3 are phosphine ligands) have long-lived excited states and display excellent photostability [2–5]. The excited states are potent reductants that have been employed in light energy conversion assemblies, such as the production of (1) hydrogen gas from water [7] and (2) an electrical current by sensitization of wide band gap semiconductors [8–10].

Here, we review electron and energy transfer processes from Cu^I metal-to-ligand charge transfer (MLCT) excited states. Excellent reviews of these and related excited states have recently been presented in the literature [2–5]. Therefore, as background, we briefly summarize the features of these novel MLCT states most relevant to photoinduced energy and electron transfer. The review will instead focus on energy and electron transfer processes that can be driven with visible light.

2. Background

Soon after the first observation of room temperature photoluminescence (PL) upon excitation of $Cu(dmp)_2^+$ in dichloromethane solution, it was found that other bis-phenanthroline compounds with aryl or alkyl substituents in the 2- and 9-positions also display room temperature PL. In addition, Cu^I bisphosphine compounds with one chromophoric ligand were also shown to photoluminesce at room temperature in fluid solution and the solid state [2–5]. Shown below are phenanthroline ligands that have recently been coordinated to Cu^I and characterized in our labs. The absorption and PL spectra of the bis-chelate compounds in dichloromethane are shown in Figs. 1 and 2. Photophysical and electrochemical properties are summarized in Table 1. All the compounds except $Cu(phen)_2^+$ display room temperature PL.

The bis-chelate compounds display quasi-reversible $Cu^{II/I}$ redox chemistry in CH_2Cl_2 electrolyte [11]. It is approximately 400 mV easier to oxidize $Cu(phen)_2^+$ than it is to oxidize the analogous compounds that contain alkyl or aryl groups in the 2- and 9- positions of phenanthroline. The increased oxidation potential observed for the substituted phenanthrolines cannot be rationalized through inductive substituent effects on the phenanthroline ligands. Rather, it is a result of steric interactions



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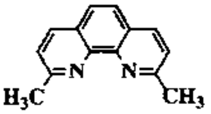

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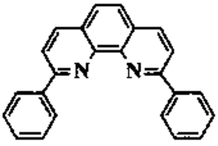

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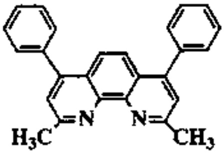
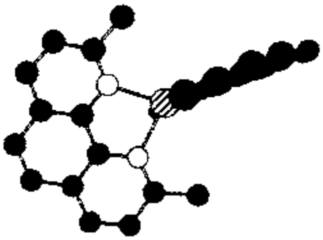


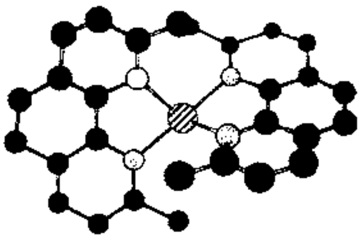
bcp

between the two chelating ligands, as discussed below. The more facile oxidation of Cu(phen)$_2^+$ results in a small energy gap and likely explains the short excited state lifetime, $\tau < 10$ ns, and lack of room temperature PL observed for this compound.

Shown below are models based on reported crystal structures of Cu(dmp)$_2^+$ and Cu(dmp)$_2^{2+}$ [12–14]. The Cu^{I} state has a d^{10} electronic configuration with a nearly tetrahedral geometry. The Cu^{II} state, on the other hand, has a d^{9} electronic configuration and prefers a more planar geometry for the phenanthroline ligands with a fifth, Jahn–Teller distorted ligand. The fifth ligand in this case is a coordinated nitrate anion, not shown for clarity. Substituents in the 2- and 9- positions interact unfavorably with subsituents on the opposite ligand in the Cu^{II} state. This process disfavors oxidation of the Cu^{I} compound as originally proposed by James and Williams over 35 years ago [15].



Cu(dmp)$_2^+$



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

The excited states of copper phenanthroline compounds, Cu(LL)$_2^+$, have been described as metal-to-ligand charge transfer (MLCT), Eq. (1) [16]. Therefore, the excited state can be

$$\mathrm{Cu^{I}(LL)_2^+} \xrightarrow{h\nu} [\mathrm{Cu^{II}(LL)(LL^{-\cdot})}]^{+*} \quad (1)$$

thought of as a formally Cu^{II} metal center coordinated to a reduced ligand. Excited state absorption spectroscopy of Cu(dmp)$_2^+$, Cu(dpp)$_2^+$, Cu(bcp)$_2^+$ and related

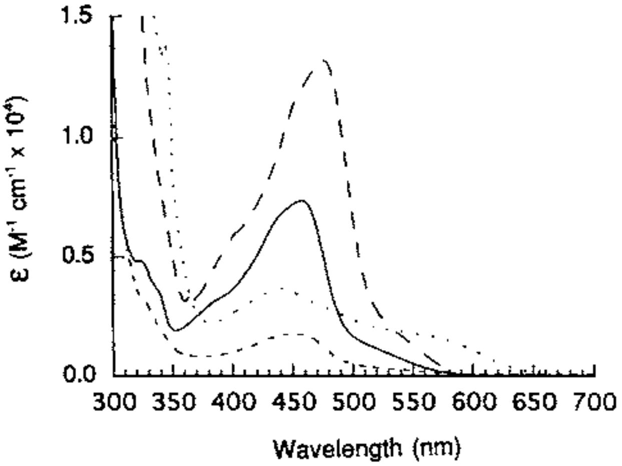


Fig. 1. Room temperature visible absorption spectra in dichloromethane of: Cu(phen)$_2$(PF$_6$) (- - -); Cu(bcp)$_2$(PF$_6$) (— — —); Cu(dmp)$_2$(PF$_6$) (-———); Cu(dpp)$_2$(PF$_6$) (– – -).

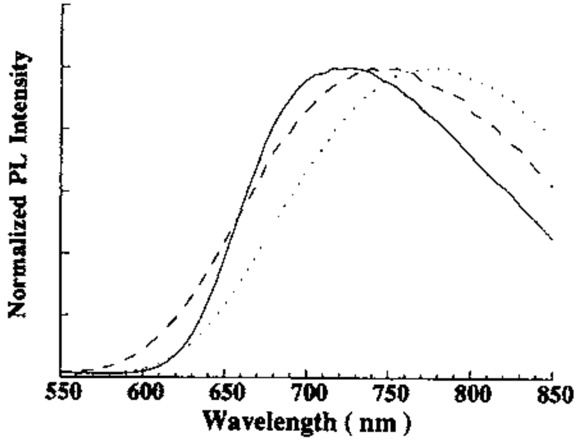


Fig. 2. Room temperature, corrected photoluminescence spectra in dichloromethane of: Cu(bcp)$_2$(PF$_6$) (- - -); Cu(dmp)$_2$(PF$_6$) (- - –); Cu(dpp)$_2$(PF$_6$) (———-). The samples were excited with 460 ± 2 nm light.

catenates supports this assignment [11,17]. In addition, Raman studies indicate that the excited electron is localized on one ligand [18,19]. Therefore, the excited state structure should closely resemble the Cu^{II} state as shown above. The dramatic red shift in the PL onset (Table 1) can be taken as evidence for PL from a geometrically relaxed Cu^{II}-like excited state.

In addition to the significant geometric change following light excitation, availability to the copper center is increased for ligand coordination to the more electron deficient Cu^{II}. Indirect evidence for coordination to a fifth site has been documented in "exciplex" quenching studies by McMillin and coworkers [20,21]. In the presence

Table 1
Photophysical and redox properties of cuprous phenanthroline derivatives[a]

Compound	λ_{abs} (nm) (ϵ)[b]	λ_{PL} (nm)[c]	Φ^{d}_{PL} $\times 10^4$	τ (ns)[e]	ΔG^{f}_{es} (eV)	$E^{g}_{1/2}$	E^{*h}_{yz}
Cu(phen)$_2$(PF$_6$)	458 (6880)	–		< 10	–	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 was measured in neat dichloromethane. From Ref. [11].

[b] Molar extinction coefficient at the absorption maximum is given in parenthesis, ϵ (M^{-1} cm^{-1}).

[c] The corrected photoluminescence maximum, ±4 nm.

[d] Lower limits for the PL quantum yields.

[e] The excited state lifetime in argon saturated dichloromethane, ±5%.

[f] The estimated free energy in the excited state, ±50 mV.

[g] Measured in 0.1M TBAH CH_2Cl_2, ±0.01 V vs Ag/AgNO$_3$ which was found to be +0.35 V vs SCE using ferrocene as an internal standard.

[h] The excited state $Cw^{II/I*}$ potential.

of Lewis bases, nucleophilic anions, or strongly coordinating solvents, the excited state lifetime of Cu(dmp)$_2^-$ is shortened dramatically. For example, the lifetime of Cu(dmp)$_2^{+*}$ is 85 ns in CH_2Cl_2 but is only 2 ns in acetonitrile [21]. Furthermore, addition of acetonitrile to a dichloromethane–Cu(dmp)$_2^+$ solution leads to excited state quenching. Detailed quenching studies as a function of temperature and donor strength establish that a reversible complex is formed between the excited state and Lewis bases prior to quenching, and the adduct is interpreted to be a five-coordinate exciplex [20,21]. Therefore, in some cases, exciplex quenching may represent a relaxation pathway competitive with energy and electron transfer.

A final point of relevance to light induced electron and energy transfer from copper MLCT excited states is the associated excited state energetics. A potential complication for Cu^{I} diimine compounds is that both singlet and triplet states have been identified [22]. In principle, excited state energy and electron transfer could occur from either of these states. This could complicate kinetic analysis as two different states with different spin multiplicities are expected to yield different rate constants for energy and electron transfer. However, since the energy gap between the two states is estimated to be reasonably high, ΔE 1500 to 2000 cm^{-1}, the equilibrium population of the singlet state should be quite small. In fact, as will be discussed further below, excited state kinetics measured thus far are well described by a single excited state.

The excited state redox potentials are typically estimated from the ground state potentials and the free energy stored in the excited states [23]. The excited state $C_w^{II/I*}$ potentials given in Table 1 were estimated in this manner [11]. Oxidation of Cu^{I} to Cu^{II} is easily accomplished and the MLCT excited states are, therefore, potent reductants, $E^{*}_{yz} = -1.4$ V vs Ag/Ag$^+$. Reduction of the copper compounds is more difficult and the Cu MLCT excited states are likely only mild oxidants. In fact, there exist no clear examples of reductive quenching of Cu MLCT excited states.

3. Electron and energy transfer

3.1. Early studies

The first examples of photoinduced electron transfer from Cu^{I} excited states were reported by McMillin and coworkers, who found that visible excitation of $Cu(dmp)_2^+$ in the presence of Co^{III} compounds led to redox chemistry [24]. Analysis of the reaction products demonstrates that a 1:1 stoichiometry of Cu^{II} and Co^{II} species were formed in an argon saturated

$$Cu^{I}(dmp)_2^{+*} + Co^{III} \rightarrow Cu^{II} + Co^{II} + \text{products} \tag{2}$$

buffered ethanol/water mixture, Eq. (2). The quantum yields were in general low, $\phi < 10^{-2}$, and markedly dependent on the nature of the Co^{III} complex. It remains unclear whether the redox process is static or dynamic in nature. Note, however, that the excited state lifetime of $Cu(dmp)_2^+$ is expected to be very short in this solvent mixture. These studies were later extended to Cr^{III} acceptors and molecular oxygen [25]. Indirect evidence for O_2 reduction was obtained by spin trapping EPR studies. No evidence of energy transfer quenching by the Cr^{III} compounds was obtained under these conditions.

3.2. Photoluminescence quenching studies

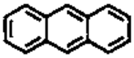
Early studies demonstrated that the steady-state PL intensity from $Cu(dmp)(PPh_3)_2^{+*}$ was quenched by the addition of organic and inorganic acceptors [26]. The kinetics of quenching $Cu(dpp)_2^{+*}$ by a series of $Cr(acac)_3$ and nitroaromatics were later explored in CH_2Cl_2 [27]. The quenchers are known electron acceptors that span an ~1.6 eV range of reduction potentials. Steady-state PL quenching measurements were frustrated by inner-filter effects from the Cr^{III} quenchers. Dynamic quenching rate constants, k_q, were therefore measured by lifetime quenching and standard Stern–Volmer analysis. Significantly, the kinetic analysis allowed an estimate of the $Cu(dpp)_2^{2+}/Cu(dpp)_2^{+*}$ self-exchange rate, $k = 8 \times 10^9 M^{-1} s^{-1}$. For the nitroaromatic compounds, k_q values are near the diffusion limit when the free energy for electron transfer is significantly exergonic and decrease monotonically with decreased driving force. In contrast, the Cr^{III} quenchers exhibited a more complex dependence of k_q with driving force. As the driving force for electron transfer became unfavorable, k_q began to level off. This behavior could not be modeled by electron transfer theory and suggested a competitive energy transfer quenching pathway. In agreement with this hypothesis, CrL_3 compounds possess nearly isoenergetic low-lying doublet ligand field states [28] that could accept energy from the excited $Cu(dpp)_2^+$.

More recent quenching studies with $Cu(dpp)_2^+$ and these same quenchers in CH_2Cl_2, $CHCl_3$ and THF as a function of hydrostatic pressure (0.1–250 MPa) further support the notion of competitive energy and electron transfer mechanisms [29,30]. For Cr^{III} quenchers where electron transfer is not favorable, little effect of pressure on the quenching rate constants was observed. This is expected for an energy transfer process where solvation plays a lesser role. In contrast, for electron transfer quenching significant variations in k_q with pressure were realized. The change in rate constant with pressure was expressed by the volume of activation, $\Delta V_q^{\pm}$. Under conditions where k_q was near the diffusion limit, negative $\Delta V_q^{\pm}$ values approaching $-20\ \mathrm{cm^3\ mol^{-1}}$ were observed. At slower quenching rates, positive $\Delta V_q^{\pm}$ values (up to $+8\ \mathrm{cm^3\ mol^{-1}}$) reflect pressure induced increases in solution viscosity.

3.3. Energy transfer quenching

The first direct spectroscopic observation of energy transfer from $\mathrm{Cu^I}$ MLCT excited states was recently reported [31]. Specifically, photodriven energy transfer from $\mathrm{Cu(dpp)_2(PF_6)}$, $\mathrm{Cu(bcp)_2(PF_6)}$ and $\mathrm{Cu(dmp)_2(PF_6)}$ to anthracene was quantified in dichloromethane solution, Eq. (3). These reactions are important in photocatalysis as anthracene can function as an efficient energy relay between light absorbing donors and electron acceptors [32–34].

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



(An)

By selectively exciting the copper compounds with 532 or 416 nm light in the presence of anthracene, the triplet-to-triplet absorption of triplet anthracene, ^{3}An, was observed by nanosecond absorption spectroscopy. In the absence of a Cu(I) phenanthroline compound, the ^{3}An absorption was not observed, and in the absence of anthracene, only the excited state absorption spectrum of the copper compound was observed. The ^{3}An spectral assignment was 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. Steady-state absorption measurements before and after photophysical experiments revealed no measurable decomposition of the copper compounds. Taken together, these observations clearly demonstrate energy transfer.

Probing at the isosbestic point between the $\mathrm{Cu(LL)_2^+}$ ground and excited states allows the formation of ^{3}An to be cleanly observed. The energy transfer dynamics are summarized in Table 2. The order of magnitude faster energy transfer rate from $\mathrm{Cu(dmp)_2^{+*}}$ can be rationalized based on ~50 mV larger driving force, Table 1. The lack of energy transfer from $\mathrm{Cu(phen)_2^{+*}}$ is likely kinetic in origin since these excited states do not live long enough to undergo diffusional quenching.

The efficiency of energy transfer from $\mathrm{Cu(LL)_2^{+*}}$ to anthracene was compared to that obtained with $\mathrm{Ru(bpy)_3^{+*}}$ as the donor. In the best case, the relative yield of triplet anthracene was 1/4 that of $\mathrm{Ru(bpy)_3^{2+*}}$. Energy transfer from $\mathrm{Ru(bpy)_3^{2+*}}$

Table 2
Copper phenanthroline energy transfer to anthracene

Compound	Φ^{a}_{ent}	K_{SV} $(M^{-1})^{b}$	k_q $(M^{-1}\,s^{-1})^{b}$	k_{ent} $(M^{-1}\,s^{-1})^{c}$
$Cu(dmp)_2(PF_6)$	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 tested.

to anthracene has been shown to occur with a quantum yield close to unity under a variety of conditions [32–34]. In an attempt to increase the energy transfer efficiency for copper, the compound $Cu(dmp)_2(AnCO_2)$, where $AnCO_2^-$ is the 9-anthracene carboxylate anion, was prepared. The hope was that ion pairing, and perhaps exciplex formation, would enhance the energy transfer yield. Instead, no evidence for energy transfer was observed. The concentration dependent quenching was satisfactorily rationalized based on an ion-pair exciplex model proposed by McMillin in which counter ion coordination to the Cu center promotes nonradiative decay [20,21,35]. A fundamental prediction of this model is that the extent of quenching should mirror the nucleophilicity of the anion. A comparison of published data indicates that the nucleophilicity of anions increases in the order: $PF_6^- < AnCO_2^- \leq C_6H_5CO_2^- < NO_3^-$. The ion-pair exciplex quenching process in $Cu(dmp)_2(AnCO_2)$ vibrationally deactivates the excited state rather than providing a conduit for energy transfer.

Nevertheless, energy transfer from Cu(I) phenanthroline derivatives was clearly demonstrated for the first time. For the copper excited states described here, energy transfer to anthracene results in: (1) a state with well defined spin multiplicity, (2) a three 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.

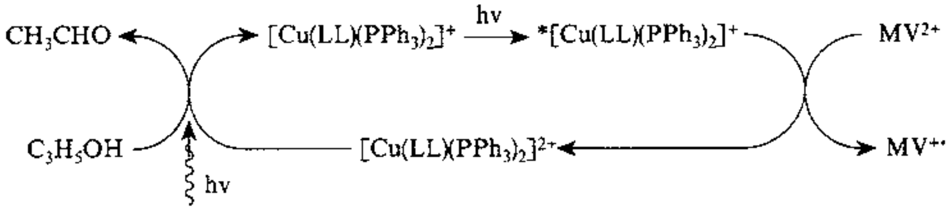
3.4. Electron transfer quenching

3.4.1. $Cu(LL)(PR_3)_2^{+*}$ donors

In 1986, Sakaki and coworkers reported the photocatalytic reduction of methyl viologen by copper diimine bistriphenylphosphine sensitizers in an alcohol water-mixed solvent [36–39]. Irradiation of a solution containing $[Cu(dmp)(PPh_3)_2]^+$ and MV^{2+} induces electron transfer from the Cu(I) MLCT excited state to MV^{2+} and yields the methyl viologen radical, $MV^{+\cdot}$. An amazing feature of this system is that the concentration of viologen radical accumulates with continued light excitation.

This is unusual, as rapid recombination from the reduced viologen to $[Cu^{II}(dmp)(PPh_3)_2]^{2+}$ is thermodynamically expected.

A proposed mechanism for these observations is shown below. After oxidative quenching of the MLCT excited state, alcohol reduces the Cu^{II} center back to Cu^{I}, completing the catalytic cycle. Analysis of the reaction mixture indicates that acetaldehyde is formed from ethanol oxidation in the photoreaction. It is suggested that the ethanol oxidation is promoted by light and occurs from the $[Cu^{II}(dmp)(PPh_3)_2]^{2+}$ excited state. In support of this mechanism, oxidation of ethanol after 390 nm excitation of $Cu(dmp)_2^{2+}$ has been reported [40]. Unfortunately, this assembly produced low turnover values for MV^{2+} reduction. The quantum yields (ϕ) in 60:40 ethanol–water solution for $MV^{+\cdot}$ production were reported for the following $Cu(LL)(PPh_3)_2^+$ compounds: where LL are dmp (2.9×10^{-3}); 4,4′,6,6′-tetramethyl-2,2′-bipyridine (7.8×10^{-4}); 4,4′-dimethyl-2,2′-bipyridine (3×10^{-5}); 1,10-phenanthroline (1×10^{-5}); 2,2′-bipyridine (~ 0); and 4,7-diphenyl-1,10-phenanthroline (~ 0).



Significant solvent effects have been documented in copper compounds of this type [2–5]. In the previously mentioned experiments with $Cu(dmp)(PPh_3)_2^+$, the quantum yield of methyl viologen radical formation was dependent on the alcohol concentration. Sakaki proposed that as the solvent polarity decreases, ion-pair formation would be favorable in both the copper and MV^{2+} salts. In regards to the formation of an encounter complex, a MV^{2+} cation approaching a positive $[Cu(dmp)(PPh_3)_2]^+$ would seem difficult from a coulombic perspective, but in pure ethanol, there would be little ion-pair dissociation, and thus less coulombic repulsion between reactants would occur. The formation of an encounter complex is therefore more favorable in alcohol, which leads to a higher quantum yield in the less polar solution. To test this hypothesis, electron transfer from the $[Cu(dmp)\{PPh_2(m\text{-}C_6H_4OSO_3)\}_2]^-$ anion or the $[Cu(dmp)(PPh_3)]^+$ cation to the electron acceptors, neutral propylviologen disulfonate (PVS°) or the dicationic methyl viologen was studied. The redox potentials of the donors and acceptors are similar so the kinetics for electron transfer depend on other factors such as the electrostatic interactions between the photosensitizer and viologen. The results are shown in Table 3.

In the case of $[Cu(dmp)(PPh_3)_2]^+$, the quantum yield is higher for the neutral PVS° acceptor than with the MV^{2+} cation. For the negatively charged donor, the reverse is observed. The largest quantum yield of reduced viologen occurs between the negatively charged copper complex, $[Cu(dmp)\{PPh_2(m\text{-}C_6H_4OSO_3)\}_2]^-$, and the

Table 3
Spectral data and quantum yields for MV^{2+} reduction[a]

Compound	λ_{max} (nm)	ϵ ($M^{-1} cm^{-1}$)	$\phi_{em} \times 10^3$	τ (µs)	$\phi_{et} \times 10^3$
$[Cu(dmp)(PPh_3)_2]^+$	365	3090	1.4	0.70	2.9 ± 0.1 6.3[b]
$[Cu(dmp)(PCyPh_2)_2]^+$	366	2730	5.1	[c]	4.5 ± 0.1
$[Cu(dmp)\{P(p\text{-}C_6H_4)Me)_3\}_2]^+$	373	2070	7.3	–[c]	34.9 ± 0.3
$[Cu(dmp)\{PPh_2(m\text{-}C_6H_4SO_3)\}_2]^-$	363	2800		0.65	26.7 14.4[b]

[a] From Refs. [36–39].

[b] The electron acceptor was PVS^-.

[c] Lifetimes reported to be 3.6 and 5.2 relative to $[Cu(dmp)(PPh_3)_2]^+$ for $[Cu(dmp)(PCyPh_2)_2]^+$ and $[Cu(dmp)\{P(p\text{-}C_6H_4)Me)_3\}_2]^+$, respectively, based on relative emission maxima intensities.

positively charged methyl viologen acceptor, consistent with the idea that the quantum yield is dependent on the electrostatic interactions between the electron donor and acceptors.

In an effort to improve the efficiency of methyl viologen production, tris-(p-methoxyphenyl)phosphine, $P(p\text{-}C_6H_4OMe)_3$ and cyclohexyl-diphenylphosphine, $PCyPh_2$, were substituted for triphenylphosphine in the $[Cu(LL)(PR_3)_2]^+$ complexes in order to study steric and electronic effects of the phosphines. The results of this substitution compared to other phosphine compounds are shown in Table 3. $[Cu(dmp)\{P(p-C_6H_4OMe)_3\}]_2^+$ has the longest-lived excited state leading to the greatest $\phi(MV^{+\cdot})$. $[Cu(dmp)(PCyPh_2)_2]^+$ also has a longer-lived excited state and a slightly larger $\phi(MV^{+\cdot})$ than the PPh_3 analog. The larger quantum yields can be rationalized by the increased basicity of these two phosphine ligands and sterics of the latter. It has been documented that excited state adduct formation to a solvent molecule is an important factor in promoting nonradiative decay in copper diimine compounds [20,21]. Bulky ligands, such as in $Cu(dpp)_2^+$, have been shown to shield solvent molecules from the copper center and increase the excited state lifetime [2–5]. $PCyPh_2$ has a larger cone angle than PPh_3 and would be expected to suppress solvent coordination in a similar manner. Adduct formation with solvent is also influenced by the donating ability of a phosphine. Stronger electron donation from a phosphine to the copper center should induce less of an effect from solvent donors. In these experiments, the better donor phosphines, $P(p\text{-}C_6H_4OMe)_3$ and $PCyPh_2$, displayed higher quantum yields than the PPh_3 adducts in their respective copper complexes.

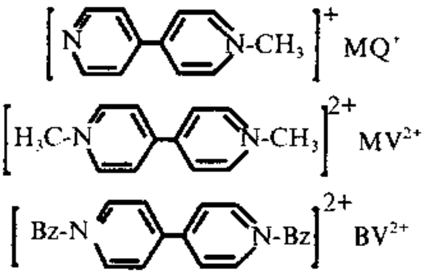
From these studies, it can be concluded that solvent effects, charge of the donor and acceptor compounds, sterics of the coordination sphere, and donor ability of the monodentate phosphines all induce substantial effects which determine the efficiency of charge separation in copper diimine compounds. It is important to note that these features allow the electron transfer processes in these systems to be systematically tuned to create desired effects.

3.4.2. $Cu(dpp)_2^{+*}$ *donors*

A separate study described electron transfer from $Cu(dpp)_2^{+*}$ to viologen acceptors, shown below, in acetonitrile electrolyte [11]. Electron transfer from $Cu(dpp)_2^+$ excited states to methyl viologen, benzyl viologen (BV^{2+}) and monoquat (MQ^+), was reported in CH_3CN/0.1M tetrabutylammonium hexafluorophosphate, (TBAH), electrolyte. Acetonitrile was chosen due to the poor solubility of the viologen salts in dichloromethane. $Cu(dpp)_2(PF_6)$ has a lifetime of 110 ns and a corrected PL maximum at 750 nm in this electrolyte. In all cases, electron transfer quenching was observed by the appearance of the reduced viologen after selective excitation of $Cu(dpp)_2^+$.

$$Cu(dpp)_2^{+*} + MV^{2+} \xrightarrow{k_f} Cu^{II}(dpp)_2^{2+} + MV^{+\cdot} \quad (4)$$

$$Cu^{II}(dpp)_2^{2+} + MV^{+\cdot} \xrightarrow{k_b} Cu^{I}(dpp)_2^{+} + MV^{2+} \quad (5)$$



The measured kinetics and estimated driving forces are summarized in Table 4. The increased forward electron transfer rate, k_f, from the MLCT excited states to MV^{2+} and BV^{2+} when compared to MQ^+ is consistent with electron transfer in the normal region, Table 4. Recombination of the charge separated pairs to ground

Table 4
Electron transfer of $Cu(dpp)_2^+$–viologens in 0.1M TBAH CH_3CN

Acceptor[a]	$-\Delta G_f^b$	$k_f \times 10^{-9}$ $(M^{-1} s^{-1})^b$	Φ_{CE}^c	$-\Delta G_b^d$	$k_b \times 10^{-10}$ $(M^{-1} s^{-1})^d$
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 (eV) and electron transfer rate constants for electron transfer process from $Cu(dpp)_2^{+*}$ to the viologens.

[c] Cage escape yields, where error represents one standard deviation from three separate measurements.

[d] Driving force (eV) and back electron transfer rate constants for electron transfer from the reduced viologen acceptor to $Cu(dpp)_2^{2+}$.

state products, k_b, occurs with second order equal concentration kinetics within experimental error of the diffusion limit.

Interestingly, the yield of MV$^{+\cdot}$ observed after the pulse light excitation 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$^{+\cdot}$] charge separated pair. A spin argument was used to rationalize this unexpected observation as triplet ion-pairs are known to yield higher cage escape efficiencies than do singlet ion-pairs [41,42]. For the [Ru(bpy)$_3^{3+}$, MV$^{+\cdot}$] pair, spin orbit coupling increases the singlet character and the cage escape yield drops in comparison to an organic triplet donor, such as ^{3}An [41]. 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$^{+\cdot}$] 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 phenomenon for chromophoric copper diimine donors.

The conclusion of a cage escape yield near unity stands somewhat in conflict with the results of Edel et al. [7]. These workers found a greater than 60-fold increase in MV$^{+\cdot}$ production when anthracene carboxylate was added to a Cu(dpp)$_2^+$ ethanol solution that contained triethanolamine, TEOA, as a sacrificial electron donor. An explanation, in accord with the results presented here, is that the increased yield of MV$^{+\cdot}$ is due to more efficient oxidation of TEOA by AnCO$_2^{\cdot}$ than by Cu(dpp)$_2^{2+}$. It should also be noted that TEOA oxidation products are known to undergo subsequent dark reactions that can artificially increase the quantum yield to ϕ(MV$^{+\cdot}$)=2 [43]. In either case, the increased yield of MV$^{+\cdot}$ upon addition of anthracene carboxylate anion is not necessarily due to a low cage escape yield for the [Cu(dpp)$_2^{2+}$, MV$^{+\cdot}$] pair.

3.5. *Interfacial electron transfer*

A potentially important application of Cu$^{\text{I}}$ MLCT compounds is as sensitizers for regenerative solar cells. Photovoltaic devices based on large band gap semiconductors such as tin oxide, zinc oxide and titanium dioxide, do not appreciably absorb visible light and the solar conversion efficiency is therefore low. Recently, it has been shown that the efficiency of these materials can be increased dramatically by sensitizing them to visible light with ruthenium polypyridyl compounds [44]. In principle, Cu$^{\text{I}}$ MLCT compounds could serve as less expensive sensitizers for this same purpose.

Early sensitization studies of tin oxide and zinc oxide materials demonstrated that the MLCT excited states of Cu$^{\text{I}}$ phenathroline compounds did inject electrons into the semiconductor [8,9]. The most direct evidence for interfacial electron transfer comes from a comparison of the absorption and photoaction spectra. The photoaction spectrum is generally a plot of photocurrent efficiency versus excitation wavelength. The coincidence of the photoaction and absorption spectra demonstrates that light excitation forms the MLCT excited states that subsequently inject an electron into the semiconductor. Unfortunately, information on the rate and efficiency of this interfacial process is still lacking. Nevertheless, monochromatic photocurrent efficiencies of a few percent have been reported [8–10].

Recently, Sauvage and coworkers utilized colloidal films of zinc oxide and titanium dioxide as substrates [10]. The high surface areas of the materials allow a higher concentration of Cu^I sensitizers to be utilized. The sensitizer used in this study was a derivative of $Cu(dpp)_2^+$ where NaO_2C groups were placed in the *para* positions of the phenyl substituents. The carboxylate groups interact with the semiconductor surface and enhance the surface coverage.

The photoelectrochemical properties of Cu^I sensitized TiO_2 and ZnO materials were explored in aqueous hydroquinone electrolyte. Again, the photoaction spectrum strongly resembles the sensitizer absorption spectrum demonstrating sensitization. Monochromatic quantum efficiencies as high as 10% were observed on TiO_2 and the efficiency was found to depend on the degree of sensitizer surface coverage. Significantly, in a regenerative solar cell containing iodide and proplyene carbonate, an open circuit photovoltage of 600 mV and a short circuit photocurrent of 0.6 mA cm^{-2} were observed. Unfortunately, the photocurrent efficiency decreased with prolonged illumination.

4. Conclusions

In conclusion, oxidative electron and energy transfer quenching of Cu^I MLCT excited states has clearly been observed. Recent data provides quantitative information on the dynamics and efficiencies of these processes. Cu^I MLCT excited states have also been utilized to sensitize wide band gap semiconductors to visible light. The excellent stability of these compounds in the ground, oxidized and excited states coupled with efficient solar harvesting suggest a bright future for further study.

Acknowledgements

We would like to thank the National Renewable Energy Laboratory (NREL XAD-3-12113-04) and the National Science Foundation (CHE-9322559, CHE-9402935) for support of this research.

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