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Photoinduced Multistep Charge Separation in a Heteroleptic Cu(I) Bis(phenanthroline)-Based Donor−Chromophore−Acceptor Triad

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S Supporting Information

ABSTRACT: A molecular triad assembly consisting of an electron donor, a bis(phenanthroline)copper(I) chromophore, and an electron acceptor has been prepared. Under visible-light excitation, this assembly undergoes efficient (ca. 50%) photoinduced, multistep formation of a diradical cation charge-separated state that has a lifetime of >100 ns and stores >1.0 eV of energy. This system constitutes an earth-abundant functional analogue of related Ru(bpy)$_3$ triad systems.

It is not particularly unusual to observe very efficient single-step redox quenching with many types of chromophores as long as they have reasonably long-lived (nanosecond) photoexcited states. Unfortunately, with such single-step processes, the back electron transfer (BET) is usually fast, often faster than the original quenching process. Consequently, little or no charge-separated product is observed, despite efficient redox quenching. For molecular assemblies that provide for multistep charge separation, it is sometimes possible to observe long-lived charge separation.[1,2] For example, in molecular assemblies that incorporate an appropriate chromophore (C) covalently linked to an electron acceptor (A) and an electron donor (D), a so-called D−C−A triad, it is possible to obtain long-lived photoinduced charge separation. The efficiency of charge-separated state (CSS) formation depends on the relative rates of the desirable second electron transfer step and geminate recombination of the initial electron transfer product. Thus, the quantum efficiency of CSS formation, Φ_{CSS}, can be highly variable from system to system even within a collection of structurally similar assemblies.[3−7]

The complex [Ru(bpy)$_3$]$^{2+}$ is the archetypical example of a metal-based chromophore that has been exploited to effect long-lived photoinduced multistep charge separation.[3,4] In molecular assemblies that incorporate a phenothiazine-type electron donor and a viologen- or diquat-type electron acceptor, Φ_{CSS} is approximately unity across a large number of structurally diverse [Ru(bpy)$_3$]$^{2+}$-based D−C−A assemblies having different driving forces for oxidative quenching.[8−13] We have established that the unusually large quantum yield for CSS formation in these Ru(bpy)$_3$$^{2+}$-based D−C−A triads arises as a result of a ground-state association between the donor moiety and the chromophore.[8] The exact nature of the interaction is uncertain but is most likely π-stacking and not charge-transfer in nature. Furthermore, the CSS lifetimes are fairly long (100−300 ns), and for reasons of spin chemical effects, the average CSS lifetime can be extended to ca. 2 μs in a modest applied magnetic field (ca. 0.5 T).[9,14]

Unfortunately, ruthenium and most other similarly employed second- and third- row transition metals (e.g., Os, Re, Pt, Ir) are not earth-abundant. However, 1,10-phenanthroline (P) complexes of earth-abundant Cu(I), [CuP$_2$]$^+$, share many of the desirable photophysical properties of [Ru(bpy)$_3$]$^{2+}$.[3,15−23] The metal-to-ligand charge transfer (MLCT) absorption has a large oscillator strength (ε > 5000 M^{-1} cm^{-1}), and the resulting MLCT excited state is relatively long-lived and is a strong reductant.[3,15−18,21−24] Also, as in [Ru(bpy)$_3$]$^{2+}$, the thermalized MLCT excited state has considerable triplet-spin character.[21,25−27]

The coordination and redox chemistry of Cu(I), however, differ from that of Ru(II) in several important ways: Cu(I) complexes with phenanthroline are highly labile in solution. They generally form tetrahedral complexes rather than octahedral ones, which tend to undergo Jahn−Teller (J−T) distortion in the MLCT state because of the significant Cu(II) character of the metal center. The J−T distortion reduces the dihedral angle between the ligands, which makes the metal accessible to solvent or counterion adduction, thus creating an exciplex.[25,26,28−30] Such exciplex formation increases the rate of nonradiative relaxation and diminishes the driving force for reductive quenching.[15−19,25,26,28−33] Likewise, strong donor solvents shift the ground-state Cu(I/II) potential to more negative values. However, the extent of J−T distortion and the accessibility of the metal center to additional ligation can be influenced by the steric requirements of substituents located at the 2- and 9-positions of the phenanthroline ligand, such as in the donor ligand (L-D) shown in Figure 1.[20,27,30,32,34] In principle, such bulky substituents can increase the MLCT lifetime and affect the energetics of electron transfer.[20,27,32,34]

Despite their similarities to [Ru(bpy)$_3$]$^{2+}$, there are very few reported examples where [Cu(I)P$_2$]$^+$ complexes have been incorporated as the primary chromophore in *multistep* photoinduced charge-separation assemblies. In other words, while there are numerous examples of both inter- and intramolecular oxidative quenching of [CuP$_2$]$^{+*}$ complexes, there are only a handful of examples where the product of oxidative quenching, [Cu(II)P$_2$]$^{2+}$, undergoes a subsequent intramolecular hole transfer to an electron donor.[19,32,35−46,31,47] This situation likely arises for two reasons: First, the lability of Cu(I) generally means that an equilibrium mixture of copper complexes exists in solution if multiple similar-type ligands are present, thus

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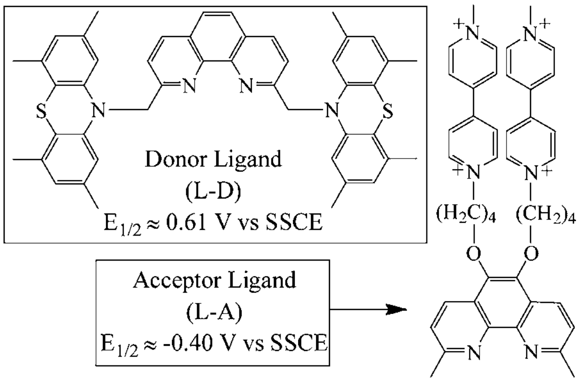


Figure 1. Donor and acceptor ligands based on 1,10-phenanthroline and their redox potentials (as free ligands).

complicating any data interpretation. Second, and probably more importantly, the $[Cu(II)P_2]^{2+}$ product of the initial MLCT oxidative quenching is such a weak oxidant that easily oxidizable donors must be employed.[15,19,32,31] As we demonstrate here, despite the challenges presented by the redox and coordination chemistry of Cu(I), it is possible to assemble a functional $[Cu(I)P_2]^+$-based D−C−A assembly that, like its ruthenium counterparts, undergoes efficient photoinduced multistep formation of a long-lived CSS. In this process, we utilized our extensive experience with $[Ru(bpy)_3]^{2+}$ triad assemblies in designing the $[Cu(I)P_2]^+$-based D−C−A system.

The acceptor- and donor-containing ligands employed here (L-A and L-D, respectively) are shown in Figure 1. L-D in particular incorporates a number of design features derived directly from the past work with ruthenium-based triads: specifically, the use of phenothiazine (PTZ)-type donors located in such a way that they can easily π-stack with one of the phenanthroline ligands, which is a critical feature in efficient CSS formation for the $[Ru(bpy)_3]^{2+}$ triads (see above). Molecular models indicated that in a D_{2d} coordination geometry, attaching the donors to the methyl substituents at the 2- and 9-positions would facilitate the desired facile π-stacking with the second phenanthroline ligand. Also, the four methyl groups on each PTZ moiety were incorporated to shift the redox potential of the parent PTZ to a sufficiently negative value that it can be oxidized by $[Cu(II)P_2]^{2+}$.[48] Finally, it was initially thought that the steric effect of having bulky donors located at the 2- and 9-positions might favor the equilibrium formation of the desired heteroleptic complex (e.g., as opposed to the homoleptic bis-donor complex).[34,49,50] On the basis of ^{1}H NMR studies, this latter hypothesis has some limited merit in more polar solvents; however, in the relatively nonpolar solvent employed in this study, *o*-difluorobenzene (*o*-DFB), a sample containing 1:1:1 stoichiometry of L-D, L-A, and $[Cu(AN)_4]BF_4$ (AN = acetonitrile) resulted in the assembly of all of the Cu(I) into the three complexes $[Cu(L\text{-}A)_2]^{9+}$, $[Cu(L\text{-}D)(L\text{-}A)_2]^{5+}$, and $[Cu(L\text{-}D)_2]^+$ in essentially statistical amounts (i.e., 1:2:1; see the ^{1}H NMR data in the Supporting Information). Pure samples of $[Cu(L\text{-}A)_2]^{9+}$ and $[Cu(L\text{-}D)_2]^+$ were independently prepared and studied. The homoleptic donor complex, $[Cu(L\text{-}D)_2]^+$, is essentially photoinactive because its MLCT excited state is too weak an oxidant to oxidize the donor (Figure 2). On the other hand, $[Cu(L\text{-}A)_2]^{9+}$ undergoes single-step formation of a photoinduced charge-transfer (CT) state in which one of the four viologen acceptor moieties is reduced and the Cu(I) is oxidized. In stark contrast to related $[Ru(bpy)_3]^{2+}$-based C−A diad assemblies, the solvent-dependent recombination rate of its CT state is relatively low [$k_{BET} \approx 2.3 \times 10^7$ s^{-1} in 5% (v/v) MeOH/*o*-DFB] and similar to that observed by Meyer and co-workers for a closely related $[Cu(I)(bpy)_2]$−viologen diad.[24] Unfortunately, the UV−vis spectrum of the oxidized donor and reduced acceptor strongly overlap. Thus, there is no wavelength where only the donor cation absorbs. Consequently, kinetic data for CSS recombination must be deconvoluted from the recombination of the CT state of the diad. Detailed transient absorption (TA) studies of $[Cu(L\text{-}A)_2]^{9+}$ were conducted and will be the subject of another manuscript.

As stated above, the introduction of four methyl substituents onto each *N*-methyl-PTZ unit does shift the one-electron oxidation potential by ca. −160 mV relative to unsubstituted PTZ analogues; nevertheless, in noncoordinating solvents, the cyclic voltammetric waves for the $Cu^{+/2+}$ and $PTZ^{0/+}$ redox couples are not resolvable in solutions of $[Cu(L\text{-}D)_2]^+$. However, spectroelectrochemical measurements on this complex in *o*-DFB made it clear that at least two of the four PTZ moieties are oxidized at a potential more negative than the onset of any metal-based oxidation. Consequently, we conclude that the equilibrium for the second electron transfer in CSS formation (i.e., donor oxidation) is sufficiently favorable as to be essentially complete; thus, the overall CSS formation process is shown in Figure 2 and can be schematically represented as follows:

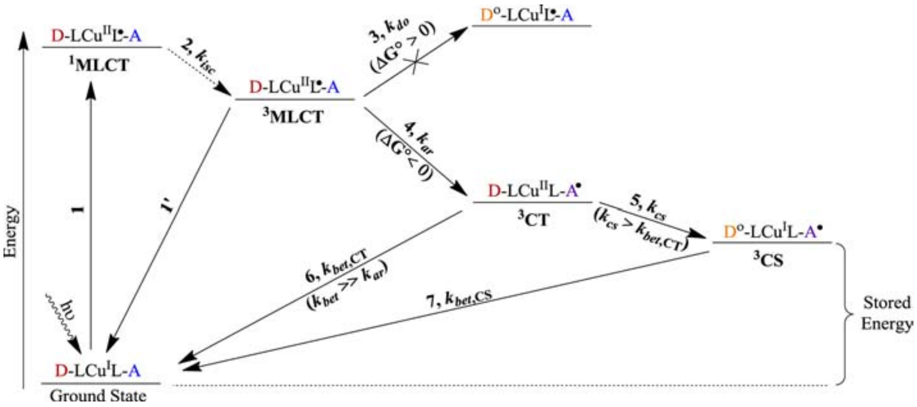


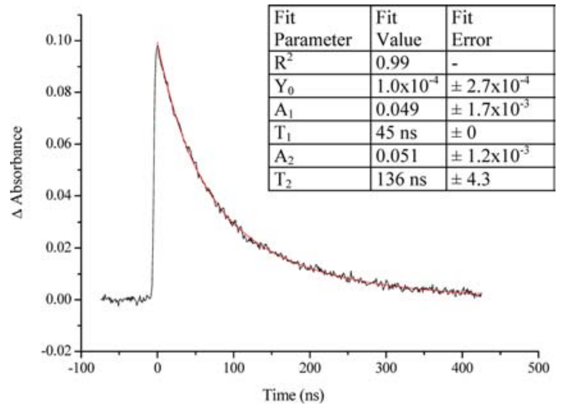
Figure 2. Jablonski diagram (not to scale) indicating the different electron-transfer pathways for $[Cu(L\text{-}D)(L\text{-}A)]^{+5}(TPFB^-)_5$ after photoexcitation. The donor ligand (L-D) is represented as D-L in the figure to emphasize the mode of bonding. The solid dot (●) and open dot (○) superscripts represent the radical electron and hole, respectively.

$$[(MV^{2+}{-}L)Cu(I)(L{-}PTZ)] + h\nu \rightarrow [(MV^{2+}{-}L)Cu(I)(L{-}PTZ)]^{*}$$

$$[(MV^{2+}{-}L)Cu(I)(L{-}PTZ)]^{*} \rightarrow [(MV^{+\bullet}{-}L)Cu(II)(L{-}PTZ)]$$

$$[(MV^{+\bullet}{-}L)Cu(II)(L{-}PTZ)] \rightarrow [(MV^{+\bullet}{-}L)Cu(I)(L{-}PTZ^{+\circ})]$$

Figure 3 shows a typical single-wavelength TA decay at 396 nm after excitation from a ca. 7 ns, 475 nm laser pulse obtained from a solution containing equimolar amounts of L-A, L-D, and Cu(I) in 5% (v/v) MeOH/*o*-DFB; the resulting equilibrium solution had a composition of $[Cu(L\text{-}A)_2]^{9+}$:$[Cu(L\text{-}D)(L\text{-}A)]^{5+}$:$[Cu(L\text{-}D)]^{+}$ = ca. 1:2:1. To enhance the solubility, the complexes were converted to the tetrakis(pentafluorophenyl)borate (TPFB) salts by metathesis with $K^{+}TPFB^{-}$ prior to dissolution in 5% (v/v) MeOH/*o*-DFB. All of the photoproducts appeared entirely within the pulse width of the laser (ca. 7 ns); thus, the rate constants for formation of the CT and CSS states for $[Cu(L\text{-}A)_2]^{9+}$ and $[Cu(L\text{-}D)(L\text{-}A)_2]^{5+}$, respectively, are each $>1.4 \times 10^{8}$ s^{-1}. The solid red line in Figure 3 is the decay calculated from a biexponential fit of the data (in Origin 7.5). Prior to the fit, the lifetime of the fast component was fixed at 45 ns, which was obtained from single-exponential fits of analogous TA data for independently prepared samples of $[Cu(L\text{-}A)_2]^{9+}(TPFB^{-})_9$. Figure 4 shows the spectrum 100−105 ns after 475 nm laser excitation compared with spectra for $MV^{+\bullet}$ and $PTZ^{+\circ}$ obtained spectroelectrochemically in *o*-DFB. Also given in Figure 4 is the simulated spectrum obtained by summing equal-concentration spectra of $MV^{+\bullet}$ and $PTZ^{+\circ}$ and scaling that sum to the average TA absorbance between 518 and 608 nm. Because of the shorter CT lifetime, at 100−105 ns after excitation, >90% of the absorbance at each wavelength should be due to the CSS formed from $[Cu(L\text{-}D)(L\text{-}A)]^{5+}$ (i.e., not the CT state of $[Cu(L\text{-}A)_2]^{9+}$).



Fit Parameter	Fit Value	Fit Error
R^2	0.99	-
Y_0	1.0×10^{-4}	$\pm 2.7 \times 10^{-4}$
A_1	0.049	$\pm 1.7 \times 10^{-3}$
T_1	45 ns	± 0
A_2	0.051	$\pm 1.2 \times 10^{-3}$
T_2	136 ns	± 4.3

Figure 3. TA decay of $[Cu(L\text{-}D^{+\circ})(L\text{-}A^{+\bullet})]^{+5}(TPFB^{-})_5$ at 396 nm in 5% (v/v) MeOH/*o*-DFB. The inset table shows the values of the parameters used to fit the data in Origin 7.5 (red). The decay is biexponential: the fast component (T_1 = 45 ns, determined independently) is the lifetime of the heteroleptic acceptor contaminant, and the slow component (T_2 = 136 ns) is the lifetime of the D−C−A triad. In the inset, A_1 and A_2 are the values of $\Delta A_{t=0}$ for the fast and slow components, respectively, and Y_0 is the value of $\Delta A_{t=\infty}$.

With regard to the data in Figure 3, the biexponential fit is quite good. While the lifetime of the fast component was held constant in the fit, its initial intensity (i.e., at $t = 0$) was allowed to vary. When TA data at various wavelengths (e.g., as in Figure 4) were subjected to the same fit, the same two lifetimes were obtained at each wavelength within experimental error. On the basis of quite preliminary measurements employing $[Ru(bpy)_3]^{2+}$ as an actinometer, the quantum efficiency for CT state formation in $[Cu(L\text{-}A)_2]^{9+}$ is 55 ± 15% in 1.6% (v/v) MeOH/*o*-DFB. Comparing the initial intensity values at $t = 0$ from the fits of the 378−403 nm data (where only $MV^{+\bullet}$ absorbs), correcting for differences in absorbance at the excitation wavelength, and assuming the relative concentrations of $[Cu(L\text{-}A)_2]^{9+}$ and $[Cu(L\text{-}D)(L\text{-}A)_2]^{5+}$ to be the same as those determined by NMR (i.e., 1:2), we estimate Φ_{CSS} for $[Cu(L\text{-}D)(L\text{-}A)_2]^{5+}$ also to be 55 ± 15%.

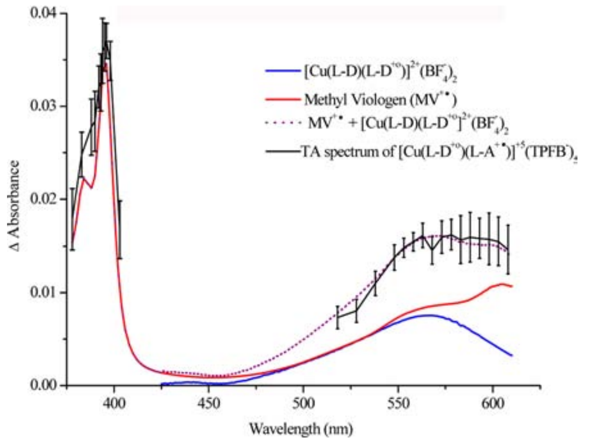


Figure 4. TA spectrum of the $[Cu(L\text{-}D^{+\circ})(L\text{-}A^{+\bullet})]^{+5}(TPFB^{-})_5$ D−C−A triad from 378 to 608 nm (black) after a 100−105 ns delay. For comparison, the predicted TA spectrum is also shown. The spectra of the model reduced acceptor $MV^{+\bullet}$ (red) and the oxidized homoleptic donor complex $[Cu(L\text{-}D)(L\text{-}D^{+\circ})]^{2+}(BF_4^{-})_2$ (blue) were generated spectroelectrochemically, scaled, and summed to produce the predicted TA spectrum for the triad (purple dots). See the text for details.

In conclusion, to our knowledge, these data represent the first demonstration of photoinduced multistep intramolecular CSS formation in a Cu(I)-based D−C−A triad assembly where $[Cu(I)P_2]^{+}$ is the sole chromophore present.[51] In many ways, these results mirror the behavior of related $[Ru(bpy)_3]^{2+}$ triads, but there are some important differences. First, while Φ_{CSS} is relatively large, it is not equal to unity. We speculate that this may have something to do with spin chemistry. The $^{1}MLCT \rightarrow {}^{3}MLCT$ intersystem crossing rate is a factor of ca. 10 lower for $[Cu(I)P_2]^{+}$ than for $[Ru(bpy)_3]^{2+}$, and the singlet−triplet energy difference is smaller.[18,25,52] Because J−T distortion stabilizes the MLCT state with the strongest spin−orbit coupling, which happens to be the lowest-energy ^{3}MLCT state,[25−27] it is possible that the only observable CSS is the one formed with triplet spin multiplicity, at least on the time scale of our current experiments. Preliminary magnetic field studies indicate that there are dramatic magnetic field effects on the CSS recombination kinetics, indicating considerable triplet character in the CSS radical pair.[9,53] A complete understanding will require a picosecond time scale study of the CSS formation kinetics and a detailed magnetic field effect study, each of which is in progress. Finally, it would be highly desirable to study a Cu(I)-based system without the complication of having multiple photoactive species simultaneously present in solution. Very recent preliminary studies indicate that replacing the methyl substituents at the 2- and 9-positions of the L-A ligand with bulkier substituents in combination with our current L-D ligand may shift the complexation equilibrium in such a way that $[Cu(L\text{-}D)(L\text{-}A)_2]^{5+}$ is the almost exclusive equilibrium product.[49,50] This is also under active investigation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Schematic syntheses of L-D and L-A; and ^{1}H NMR and static UV−vis data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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