

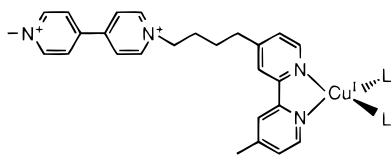
Long-Lived Charge-Separated States Following Light Excitation of Cu(I) Donor–Acceptor Compounds

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Photoinduced charge separation is of fundamental interest in photosynthesis and is of practical importance for light energy conversion.¹ A considerable research effort has been set forth to gain molecular control of charge separation processes.¹ A key goal is to achieve long-lived charge separation by inhibiting energy-wasting charge recombination reactions to ground state products. The preparation of “donor–acceptor” compounds, in which a chromophoric donor and an electron acceptor are covalently bound within a single molecule, affords intramolecular control of charge separation and recombination processes.^{2–14} Photophysical studies of donor–acceptor compounds have provided a detailed understanding of the driving force, distance, and spin dependence of these processes.^{1–14} For inorganic systems, there exist examples of intramolecular electron transfer producing charge-separated states after optical excitation of Ru(II)^{4–9} and Re(I)^{10,11} metal-to-ligand charge transfer (MLCT) and porphyrin $\pi \rightarrow \pi^*$ chromophores.^{12–14} Here, we report the first example of a charge-separated state created after visible excitation of Cu(I) bipyridyl donor–acceptor compounds. Furthermore, the charge-separated state is remarkably long-lived and the lifetime can be tuned by varying the solvent.



Preparation and characterization of the donor–acceptor compounds, $[\text{Cu}(\text{bpy-MV}^{2+})(\text{PPh}_3)_2](\text{PF}_6)_3$ and $[\text{Cu}(\text{bpy-MV}^{2+})_2](\text{PF}_6)_5$, where bpy-MV^{2+} is $[1-(4-(4'-\text{methyl-2,2'-bipyridin-4-yl)butyl)-1'-methyl-4,4'-bipyridinium)]^{2+}$, and the analogous model compounds, $\text{Cu}(\text{dmb})(\text{PPh}_3)_2(\text{PF}_6)$ and $\text{Cu}(\text{dmb})_2(\text{PF}_6)_3$, where dmb is 4,4'-dimethyl-2,2'-bipyridine, are given in the

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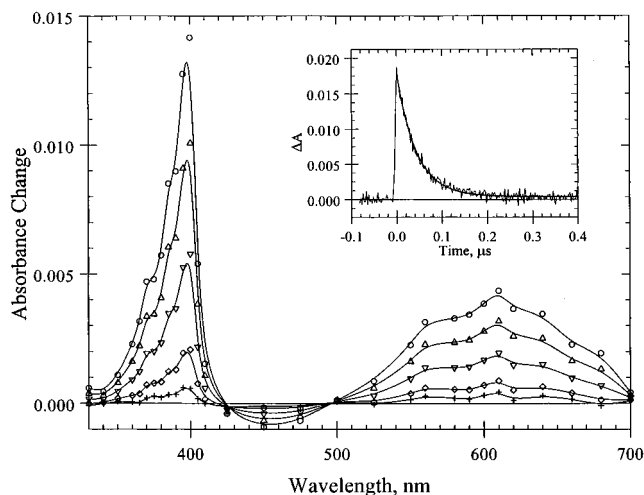


Figure 1. Excited state absorption difference spectra observed after laser excitation (416 nm; 8–10 ns fwhm, 4 mJ/pulse) of $[\text{Cu}(\text{bpy-MV}^{2+})_2](\text{PF}_6)_5$ in acetonitrile at the following delay times: (circles) 10 ns; (triangles) 25 ns; (upside down triangles) 50 ns; (diamonds) 100 ns; and (+) 200 ns. Also shown as an inset are single-wavelength kinetics monitored at 400 nm that correspond to charge recombination. The solid line is a fit to a first-order model.

Supporting Information. We note that closely related copper phenanthroline compounds have been reported in the literature^{15,16} and have been utilized for intermolecular electron transfer studies.^{16–18} The electrochemical and spectroscopic properties of the copper compounds were measured as previously described¹⁸ and are tabulated in the Supporting Information. Briefly, in acetonitrile, the $\text{Cu}^{\text{I}}(\text{LL})(\text{PPh}_3)_2^{n+}$ compounds are yellow with a broad charge transfer band centered at ~ 360 nm, while the $\text{Cu}^{\text{I}}(\text{LL})_2^{n+}$ compounds are orange, $\lambda_{\text{max}} \sim 440$ nm. For $\text{Cu}(\text{bpy-MV}^{2+})(\text{PPh}_3)_2(\text{PF}_6)_3$, an irreversible copper(I) oxidation peak, $E_{\text{pa}} \sim 0.7$ V, and two reversible viologen reductions at -0.39 and -0.84 V vs SCE are observed. $\text{Cu}(\text{bpy-MV}^{2+})_2(\text{PF}_6)_5$ displays a quasi-reversible Cu^{I} oxidation at 0.05 V and viologen reductions at -0.40 and -0.88 V.

Pulsed laser excitation ($\lambda = 355$ or 416 nm) of the donor–acceptor compounds leads to the prompt appearance of an absorption difference spectra consistent with the presence of a charge separated state with an electron localized on the pendant viologen group and a Cu(II) metal center, abbreviated $[\text{Cu}^{\text{II}}(\text{bpy-MV}^{+\cdot})]$. Shown in Figure 1 is a representative absorption difference spectrum observed after excitation of $\text{Cu}(\text{bpy-MV}^{2+})_2^{5+}$ in acetonitrile. Two isosbestic points, a bleach of the MLCT band, and positive absorption features due to the viologen radical cation¹⁹ are clearly identified. A similar spectrum is observed for $\text{Cu}(\text{bpy-MV}^{2+})(\text{PPh}_3)_2^{3+}$ in acetonitrile; however, the bleach of the charge transfer band is masked by the absorbance of the reduced viologen.

The rate of charge separation is faster than our instrument resolution, $k_{\text{cs}} > 10^8 \text{ s}^{-1}$. It is therefore unclear whether the electron is promoted directly from copper to the viologen or first to the bipyridine ligand and subsequently to the pendant viologen group. The edge-to-edge distance from the bipyridine

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Table 1. Charge Recombination Kinetics^a

compound ^b	k_{cr} (s ⁻¹)		
	CH ₂ Cl ₂	CH ₃ CN	DMSO
Cu(bpy-MV ²⁺) ₂ (PF ₆) ₅	<i>c</i>	2.4×10^7	1.2×10^6
Cu(bpy-MV ²⁺)(PPh ₃) ₂ (PF ₆)	4.9×10^7	3.1×10^7	5.6×10^5

^a First-order charge recombination rate constants measured at room temperature in the indicated solvent, $\pm 10\%$. ^b Donor–acceptor compounds given where bpy-MV²⁺ is [1-(4-(4'-methyl-2,2'-bipyridin-4-yl)butyl)-1'-methyl-4,4'-bipyridinediium]²⁺. ^c Poor solubility in this solvent precluded spectroscopic measurements.

to the extended viologen has been estimated to be 5 Å. While only a lower limit of the charge separation rate can be provided, it is of interest to note that charge separation occurs in solvents that are known to quench Cu(I) MLCT excited states by exciplex formation, i.e., the formation of a complex between the excited copper compound and the solvent.²⁰ In coordinating solvents such as CH₃CN and DMSO, the model compounds and related Cu(I) diimine compounds are nonemissive with short excited state lifetimes, $\tau < 10$ ns. Nevertheless, the donor–acceptor compounds reported here separate charge in these solvents.²¹

Charge recombination follows first-order kinetics in argon-saturated DMSO, CH₂Cl₂, and CH₃CN solvents (Table 1). The inset of Figure 1 displays the time-resolved absorption monitored at 400 nm for Cu(bpy-MV²⁺)₂⁵⁺ in acetonitrile following excitation with 416-nm light. Superimposed on this data is the fit to a first-order kinetic model. The recombination kinetics are independent of the monitoring wavelength ($\lambda = 330$ –650 nm). Ground state absorption measurements before and after laser excitation reveal negligible sample decomposition under these experimental conditions.²² From the spectroscopic and the electrochemical data, it can be concluded that light excitation of Cu(bpy-MV²⁺)₂⁵⁺ produces a [(bpy-MV²⁺)Cu^{II}(bpy-MV⁺)]⁵⁺ charge-separated state that stores 0.45 eV of potential energy for 45 ns in CH₃CN. Light excitation of Cu(bpy-MV²⁺)(PPh₃)₂³⁺ under the same conditions stores about 1.1 eV for 33 ns. The energy stored in the charge-separated state is estimated, ignoring work terms, as the difference between the copper oxidation and the viologen reduction potentials. Due to the irreversible Cu(bpy-MV²⁺)(PPh₃)₂³⁺ oxidation, the 1.1-eV value is best thought of as an upper limit.

Strong experimental evidence exists from crystallographic,^{23,24} electrochemical,^{18,25} and spectroscopic^{16,20} studies that significant inner-sphere reorganizational changes accompany copper(II/I) redox processes. Cu^I(LL)₂⁺ compounds, where (LL) is a

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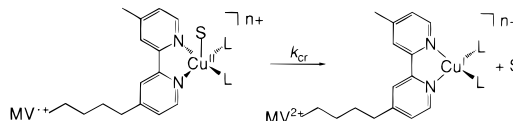
(21) Preliminary charge separation quantum yields measured by relative actinometry with Ru(bpy)₃²⁺ and the known extinction coefficient of MV⁺ (ref 19) indicate that the yield is dependent on solvent. For Cu(bpy-MV²⁺)(PPh₃)₂³⁺ in acetonitrile, the quantum yield for charge separation is less than unity, indicating that excited state relaxation can compete with charge separation in some cases.

(22) Incomplete recovery of the transient absorbance was observed over a 500-ns time scale in CH₂Cl₂ with 355-nm excitation. Photochemistry has previously been observed after pulsed UV excitation of Cu(dmp)₂⁺ (dmp is 2,9-dimethyl-1,10-phenanthroline) in CH₂Cl₂: Berger, R. M.; McMillin, D. R.; Dallinger, R. F. *Inorg. Chem.* **1987**, *26*, 3802.

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Scheme 1

bipyridine or phenanthroline derivative, have d¹⁰ electronic configurations and generally adopt pseudo-tetrahedral geometries.²³ In the oxidized state, Cu(II) has a d⁹ electronic configuration and the chelating ligands adopt a more planar geometry, often with a fifth, Jahn–Teller distorted, axial ligand derived from solvent or counterion, resulting in a distorted square pyramidal or trigonal bipyramidal geometry.²⁴ In addition, variable-temperature photoluminescence studies reveal that copper MLCT excited states in CH₂Cl₂ are quenched by DMSO and CH₃CN through a postulated five-coordinate exciplex.^{20d} Provided that these structural changes are operative in the donor–acceptor compounds reported here, charge recombination is expected to involve a change from distorted square pyramidal (or trigonal bipyramidal) to a pseudo-tetrahedral geometry and a coordination number change, from 5 to 4, (Scheme 1). Consequently, the Cu(II)–S bond energy is incorporated into the total reorganization energy that accompanies back electron transfer. This could account for the remarkably long-lived charge-separated states realized in DMSO, since DMSO is a better ligand for Cu(II) than CH₂Cl₂ or CH₃CN.²⁶

The charge-separated states reported here are notably long-lived with respect to analogous ruthenium–pyridinium donor–acceptor compounds. For example, Mallouk and co-workers measured hundred-picosecond lifetimes after light excitation of Ru(bpy-MV²⁺)(bpy)₂⁴⁺ in acetonitrile.⁵ Kelly and Rodgers also observed picosecond recombination in related compounds with a pendant viologen group bound to bipyridine through an ester linkage.⁸ Likewise Elliot, Kelly, and co-workers reported <30-ps lifetimes for Ru(II) polypyridyl compounds with covalently bound diquat acceptors.⁶ In sharp contrast, the lifetime of [Cu^{II}(bpy-MV⁺)(PPh₃)₂]³⁺ is 33 ns in acetonitrile and 1.8 μs in DMSO. An explanation for the increased lifetime of the copper charge-separated states when compared to ruthenium is unknown but may lie in the driving force, spin restrictions, and reorganization energies associated with charge recombination. Studies designed to test these possibilities are underway.

In conclusion, long-lived charge-separated states induced by visible light excitation of copper(I) donor–acceptor compounds have been realized for the first time. In favorable cases, a 416-nm photon is converted into ~1 eV of potential energy that is stored for 1.8 μs. Significantly, the rate of charge separation is >100 times faster than charge recombination. It is particularly encouraging that these first-generation charge-separated states are so notably long-lived. This suggests that other copper donor–acceptor compounds can be fine tuned for applications in photocatalysis and artificial photosynthetic assemblies.¹ More fundamentally, the geometric and coordination number changes that are novel to Cu(II/I) redox chemistry will allow intramolecular electron transfer processes with large inner-sphere reorganization energy changes to be systematically explored.

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Supporting Information Available: Preparation and characterization details (3 pages). See any current masthead page for ordering and Internet access instructions.

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