

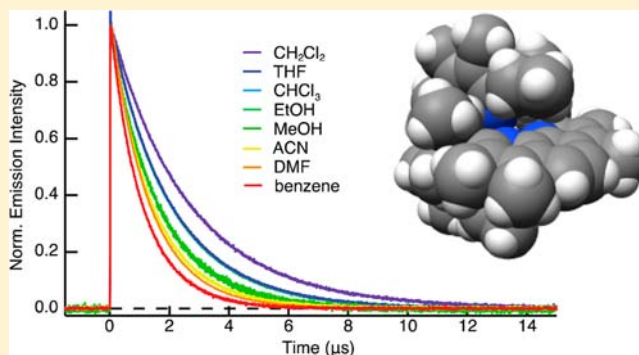
Design of a Long-Lifetime, Earth-Abundant, Aqueous Compatible Cu(I) Photosensitizer Using Cooperative Steric Effects

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Supporting Information

ABSTRACT: A new homoleptic Cu(I) photosensitizer, $[\text{Cu}(\text{dsbtmp})_2]^+$ (dsbtmp = 2,9-di(*sec*-butyl)-3,4,7,8-tetramethyl-1,10-phenanthroline), designed to exhibit cooperative steric hindrance, unexpectedly produced strong photoluminescence ($\Phi = 1.9\text{--}6.3\%$) and long excited state lifetimes ($\tau = 1.2\text{--}2.8 \mu\text{s}$) in a broad range of coordinating and non-coordinating solvents. The combination of the 2,9-*sec*-butyl substituents with the neighboring 3,8-methyl groups led to a Cu(I) complex with small degrees of ground and excited state distortion ultimately producing a molecule with robust metal-to-ligand charge transfer photophysics largely insulated from solvent interactions, reversible redox chemistry serving as a strong excited state reductant, along with impressive thermodynamic and photochemical stability in solution.



INTRODUCTION

The photophysical properties of copper(I) *bis*-1,10-phenanthroline complexes have been extensively studied for more than 30 years.^{1–36} In the ground state the copper center is d^{10} , and prefers a pseudotetrahedral (D_{2d}) geometry. However, in the metal-to-ligand charge transfer (MLCT) excited state, the copper center is formally d^9 and therefore undergoes a significant Jahn–Teller distortion, leading to a low energy, short-lived excited state and rendering the copper center susceptible to exciplex formation in donor solvents or with coordinating counterions.^{6,10,25,37,38} As a consequence, with one notable exception,²³ most copper(I) diimine complexes are substantially quenched in coordinating Lewis basic solvents, thereby limiting the potential application of these complexes as photosensitizers, particularly in aqueous-based solar fuels photochemistry.^{39–41}

A successful photosensitizer must meet several requirements, depending on the desired application. Most importantly, the complex must absorb light, and for solar-based applications, that light should be in the visible or near-infrared region of the spectrum. Another basic requirement for compositions relying on diffusional electron or energy transfer (rather than covalently linked donor–acceptor systems) is a long ($\sim\mu\text{s}$) excited state lifetime. In photosensitization through an energy transfer mechanism, the long-lived excited state should be highly energetic for favorable energy transfer to occur. In photosensitization through an electron transfer mechanism, the excited state must be a strong oxidizing or reducing agent. Also, the oxidation or reduction should be reversible so that the sensitizer can be regenerated to its ground state.

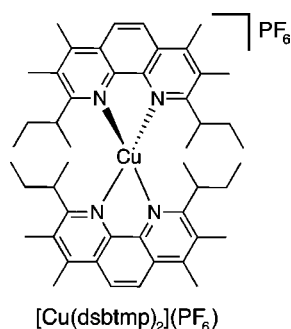
Substitution in the 2 and 9- positions of the phenanthroline ligands has proven effective in sterically restricting excited state distortion thereby lengthening the excited state lifetime.^{4,16,34,42–44} Pioneering work from the McMillin group has also shown that methyl groups in the 3- and 8- positions of the phenanthroline serve to cooperatively enhance the steric effect imparted by the 2,9 substituents. For example, $[\text{Cu}(\text{dbtmp})_2]^+$ (dbtmp = 2,9-di(*n*-butyl)-3,4,7,8-tetramethyl-1,10-phenanthroline) has an excited state lifetime of 920 ns compared to 150 ns for the nonmethylated version.¹⁹ We postulated that replacing the straight *n*-butyl chain with a branched *sec*-butyl chain, that is, 2,9-di(*sec*-butyl)-3,4,7,8-tetramethyl-1,10-phenanthroline (dsbtmp), will further restrict the excited state distortion, but will not be bulky enough to render the homoleptic copper(I) complex thermodynamically unstable, as is observed with the 2,9-di(*tert*-butyl) substituted copper(I) complex.^{34,45} Fortuitously, the photophysical properties of $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ far exceeded expectations, yielding a high energy excited state with impressive lifetimes ($\tau = 1.2\text{--}2.8 \mu\text{s}$) and photoluminescence quantum yields ($\Phi = 1.9\text{--}6.3\%$), even in coordinating solvents and aqueous solutions, concomitant with potent excited state oxidation potentials ($-1.5 \text{ V vs Fc}^{+/0}$).

RESULTS AND DISCUSSION

Synthesis. The dsbtmp ligand was prepared by adapting the method of Sauvage and co-workers,⁴⁶ departing from the

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commercially available 3,4,7,8-tetramethyl-phenanthroline. This versatile procedure uses either alkyl or aryl lithium reagents to selectively add substituents to the 2 and 9-positions of a phenanthroline or substituted phenanthroline ligand. The final dsbtmp ligand is easily purified by column chromatography and is isolated as a mixture of diastereomers, as seen by NMR spectroscopy (Supporting Information, Figure S1). No attempts were made to separate the diastereomers.

$[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ was prepared using the standard literature method as executed with related molecules.⁴⁷ A solution of dsbtmp was added to tetrakis(acetonitrile)copper(I) hexafluorophosphate solid under inert atmosphere. $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ was precipitated by addition of ether and purified by recrystallization. As with the previously reported $[\text{Cu}(\text{dsbp})_2]^+$ (dsbp = 2,9-di(*sec*-butyl)-1,10-phenanthroline), $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ was isolated as a mixture of diastereomers (Supporting Information, Figure S3).⁴² No attempt was made to separate these diastereomers, as they had no measurable influence on the resultant photophysical properties.

Ground State Spectroscopy. The absorption spectrum of $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ in CH_2Cl_2 is presented in Figure 1. The

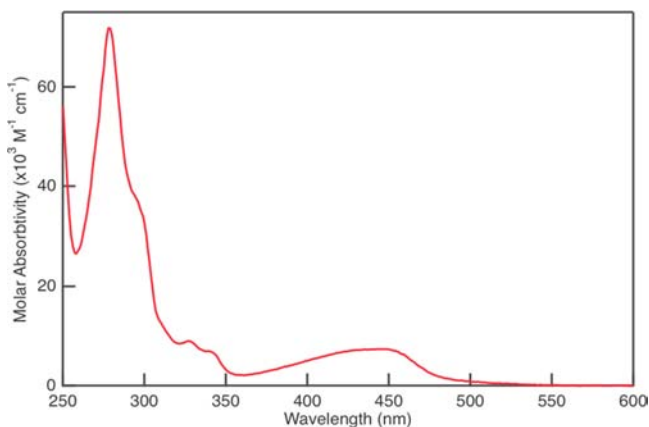


Figure 1. Absorption spectrum of $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ in dichloromethane solution.

intense absorption feature around 280 nm is assigned to the $\pi-\pi^*$ transitions of the phenanthroline ligand. The metal-to-ligand charge transfer (MLCT) absorption dominates the visible region of the spectrum, with a maximum of 445 nm. The shape of the MLCT absorption band is a good indicator of the ground state geometry of copper(I) bis-phenanthroline complexes.¹¹ In a perfect pseudotetrahedral geometry (D_{2d} symmetry) the higher energy component of the MLCT transition is symmetry allowed while the lower energy component is symmetry forbidden. When the geometry distorts from pseudotetrahedral and the symmetry is lowered to D_2 , the

lower energy component of the MLCT transition becomes symmetry allowed. The absence of a pronounced red shoulder on the MLCT absorption band in $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ strongly suggests that the complex has adopted the pseudotetrahedral D_{2d} symmetry in the ground state. Figure 2

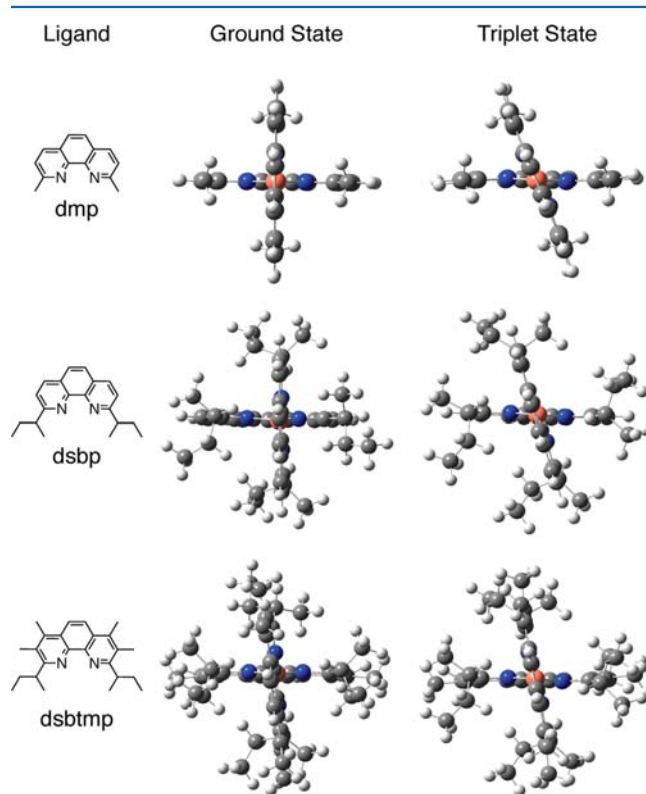


Figure 2. Optimized ground state and lowest energy triplet state structures of $[\text{Cu}(\text{dmp})_2](\text{PF}_6)$, $[\text{Cu}(\text{dsbp})_2](\text{PF}_6)$, and $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ optimized at the UB3LPY/6-31g(d) level of theory in a dichloromethane solvent continuum.

depicts the optimized structure of the ground (singlet) state and lowest energy triplet state of $[\text{Cu}(\text{dsbtmp})_2]^+$ in a CH_2Cl_2 continuum, illustrating both a near-perfect tetrahedral ligand arrangement around the Cu(I) center in the ground state and the degree of steric restriction imposed by the *sec*-butyl and methyl substituents. The calculated structures also illustrate the minimal degree of distortion in the lowest energy triplet state, as compared to $[\text{Cu}(\text{dsbp})_2]^+$ and $[\text{Cu}(\text{dmp})_2]^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline).

Room Temperature Photoluminescence. The photoluminescence from $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ in deaerated CH_2Cl_2 has an impressive 2.8 μs lifetime and 6.3% quantum yield, a vast improvement over the $[\text{Cu}(\text{dsbp})_2](\text{PF}_6)$ and $[\text{Cu}(\text{dmp})_2](\text{PF}_6)$ model chromophores (Table 1).¹⁷ Moreover, unlike the similarly long-lived 2,9-di(*tert*-butyl)-1,10-phenanthroline complex,^{34,45} this new chromophore is thermodynamically stable in solution and under light excitation making it a viable option for photosensitization applications (Supporting Information, Figures S5–S6). Similarly, $[\text{Cu}(\text{dsbtmp})_2]^+$ exhibits moderate emission energies and retains microsecond lifetimes in coordinating donor solvents such as acetonitrile, ethanol, and mixtures of acetonitrile and water (Figure 3), significantly longer than that exhibited by the benchmark MLCT sensitizer $[\text{Ru}(\text{bpy})_3]^{2+}$ in all solvents investigated.^{48,49} Table 1 collects the photophysical properties of $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ in

Table 1. Photophysical Properties of Alkyl Substituted Copper *bis*-Phenanthroline Complexes^a

	λ_{Em} (nm)	Φ_{Em} (%)	τ_{Em} (μs)	k_{r} ($\times 10^4 \text{ s}^{-1}$)	k_{nr} ($\times 10^5 \text{ s}^{-1}$)
[Cu(dsbtmp) ₂](PF ₆)					
CH ₂ Cl ₂	631	6.3 ± 0.4 ^b	2.80	2.28	3.39
ACN	649	2.9 ± 0.3 ^b	1.46	1.99	6.65
1:1 ACN:H ₂ O	654	1.9 ± 0.4 ^b	1.20	1.58	8.18
[Cu(dsbp) ₂](PF ₆)					
CH ₂ Cl ₂ ^c	690	0.45	0.40	1.13	24.9
ACN	700	0.15 ± 0.05 ^d	0.13	1.15	76.8
1:1 ACN:H ₂ O	700	0.11 ± 0.05 ^d	0.12	0.93	84.7
[Cu(dmp) ₂](PF ₆)					
CH ₂ Cl ₂ ^c	730	0.04	0.09	0.44	111
ACN ^e					
1:1 ACN:H ₂ O ^e					

^aMeasured in deaerated solutions. ^bAbsolute quantum yield measurement. ^cValues from ref 17. ^dMeasured relative to aerated [Ru(bpy)₃](PF₆)₂ in ACN ($\Phi = 0.018$). ^eNo detectable emission signal.

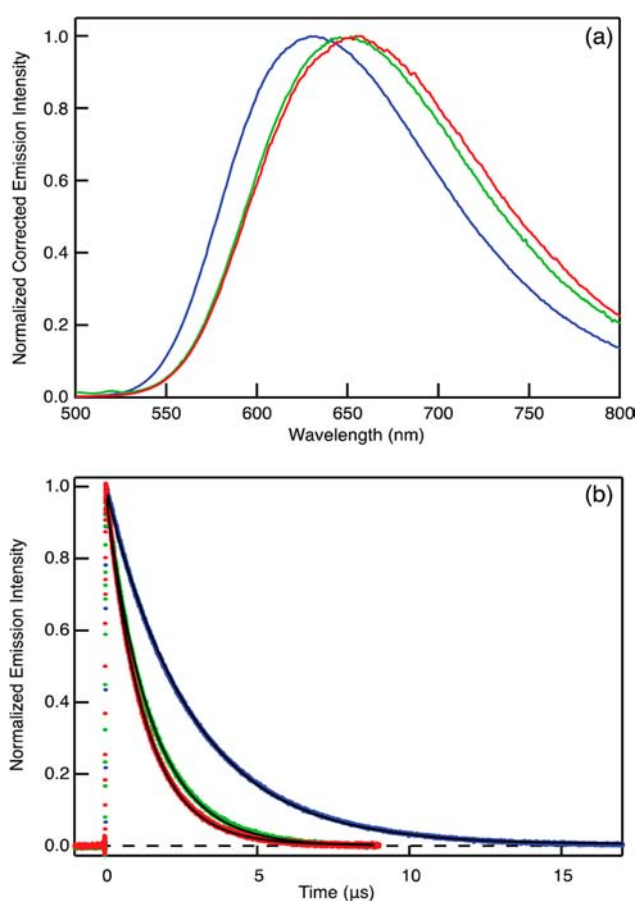


Figure 3. (a) Normalized emission spectra of [Cu(dsbtmp)₂](PF₆) in CH₂Cl₂ (blue), CH₃CN (green), and 1:1 CH₃CN:H₂O (red). (b) Normalized time-resolved emission intensity decays of [Cu(dsbtmp)₂](PF₆) in CH₂Cl₂ (blue), CH₃CN (green), and 1:1 CH₃CN:H₂O (red). Black lines are the result of single exponential fits, yielding lifetimes of 2.80 μs for CH₂Cl₂, 1.46 μs for CH₃CN, and 1.20 μs for 1:1 CH₃CN:H₂O.

CH₂Cl₂, CH₃CN, and a 1:1 mixture of CH₃CN and water, directly compared to the model complexes, [Cu(dsbp)₂](PF₆) and [Cu(dmp)₂](PF₆). From the calculated values of k_{r} and k_{nr} it can be inferred that the enhancement in molecular photophysics is a direct result of the factor of ~ 100 decrease in k_{nr} in the title chromophore versus [Cu(dmp)₂](PF₆). The

decrease in k_{nr} across the series has some contribution from the increase in energy gap from 730 nm in [Cu(dmp)₂](PF₆) to 631 nm in [Cu(dsbtmp)₂](PF₆), but the energy gap law alone is not enough to account for the 2 orders of magnitude change in k_{nr} . In the case of osmium(II) phenanthroline complexes, where the excited state nonradiative decay can be completely described by the energy gap law, a similar change in energy gap leads to a much smaller decrease in k_{nr} .^{50,51} The additional decrease in nonradiative decay presumably results from minimizing the excited state distortion, as can be inferred from the observed Stokes shift between the absorption and emission spectrum, and a significant lack of exciplex formation in the coordinating solvents upon MLCT excitation seemingly enforced by cooperative steric effect from the 3,8-methyl substituents.

Variable Temperature Emission. Unlike most transition metal photosensitizers, in copper(I) diimine complexes the lowest energy singlet and triplet MLCT states are close in energy.^{5,12,29,52,53} At room temperature, the two states are in equilibrium, and the observed photoluminescence is a superposition of phosphorescence from the ³MLCT state and E-type delayed fluorescence from the ¹MLCT state.^{26,34,53–56} The emission lifetime of [Cu(dsbtmp)₂](PF₆) in EtOH solution was measured at temperatures between 65 and -105 °C, Figure 4; EtOH was selected for its ability to provide a large fluidic temperature range and its high boiling point. As the temperature decreases, the thermal population of the ¹MLCT state also decreases leading to a longer emission lifetime. The change in the observed emission decay rate (k_{obs}) vs temperature can be fit with eq 1 to extract the energy gap between the ¹MLCT and ³MLCT states (ΔE) as well as the individual decay rates of the singlet and triplet states (k_{s} and k_{t}).⁵⁵ This analysis suggests that the singlet–triplet energy gap is on the order of 1100 cm^{-1} , which is similar to what has been observed in other copper(I) charge transfer complexes.^{5,26,29,53,55}

$$k_{\text{obs}} = \frac{3k_{\text{t}} + k_{\text{s}} \exp\left(\frac{-\Delta E}{k_{\text{b}}T}\right)}{3 + \exp\left(\frac{-\Delta E}{k_{\text{b}}T}\right)} \quad (1)$$

Transient Absorption. The transient absorption difference spectrum of [Cu(dsbtmp)₂](PF₆) in deaerated CH₂Cl₂ solution is shown in Figure 5. The difference spectrum features

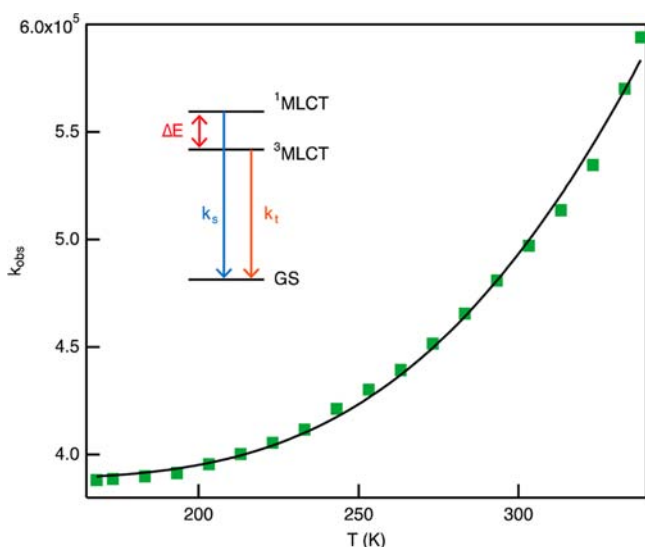


Figure 4. Temperature dependence of the excited state lifetime of $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ in deaerated EtOH solution after 453 nm excitation. The black line is the result of fitting with eq 1, where $k_t = 3.89 \pm 0.1 \times 10^5 \text{ s}^{-1}$, $k_s = 7.73 \pm 1.5 \times 10^7 \text{ s}^{-1}$, and $\Delta E = 1150 \pm 50 \text{ cm}^{-1}$.

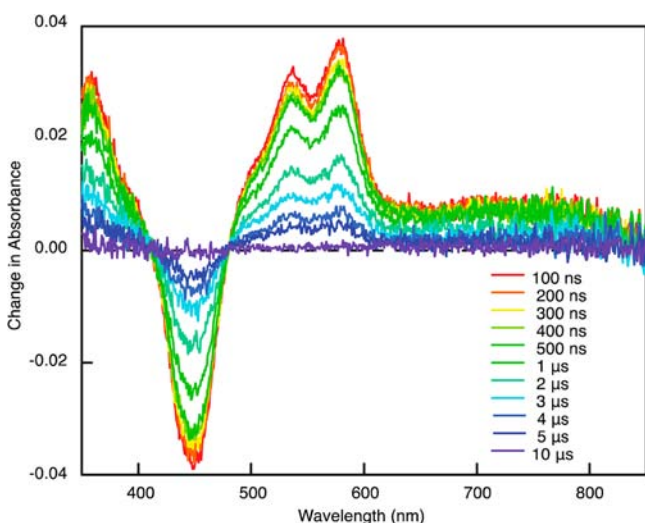


Figure 5. Transient absorption difference spectrum of $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ in deaerated CH_2Cl_2 solution after 460 nm excitation (1.8 mJ/pulse, 1 Hz). Delay times are provided in the legend.

a bleach of the ground state MLCT absorption feature around 450 nm, but the spectrum is dominated by the broadly absorbing phenanthroline radical anion which has strong positive features near 350 and 550 nm and a weaker absorption transient in the red. This spectral signature is very similar to those seen in $[\text{Cu}(\text{dmp})_2]^+$ and other related homoleptic Cu(I) complexes with MLCT excited states.^{25,37,47,57} Single wavelength transients measured throughout the difference spectrum were adequately fit to single exponential kinetics and quantitatively matched that acquired in the photoluminescence intensity decays, implying that the photoluminescence and the absorption transients are reporting on the identical MLCT excited state.

Electrochemistry. The cyclic and differential pulse voltammetry of $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ was investigated in acetonitrile (CH_3CN) solution containing 0.1 M TBAPF₆

(Table 2 and Supporting Information, Figures S9 and S10). The molecule exhibits a single reversible wave corresponding to

Table 2. Electrochemical Properties of $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ and $[\text{Cu}(\text{dsbp})_2](\text{PF}_6)$

	E_{ox} (V)	E_{red} (V)	E_{ox}^* (V) ^b
$[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)^a$	0.428	-2.38	-1.48
		-2.59	
$[\text{Cu}(\text{dsbp})_2](\text{PF}_6)^c$	0.5	-2.19	-1.27

^aPotentials measured in CH_3CN with 0.1 M TBAPF₆ as the supporting electrolyte vs Ag/AgNO₃ and are reported relative to $\text{Fc}^{+/0}$ redox couple added as an internal standard. ^b $E_{\text{ox}}^* = E_{\text{ox}} - E_{00}$ where E_{00} was approximated as λ_{Em} in CH_3CN (Table 1). ^cValues from reference 17 are reported relative to the $\text{Fc}^{+/0}$ redox couple.

the one-electron oxidation of the copper center at +0.428 V vs $\text{Fc}^{+/0}$. The electron donating methyl groups render the copper center more easily oxidized by approximately 70 mV compared to the related $[\text{Cu}(\text{dsbp})_2]^+$,¹⁷ Table 2. The complex also displays two sequential reversible reduction waves, located at -2.38 and -2.59 V vs $\text{Fc}^{+/0}$, corresponding to the reduction of the first and second dsbtmp ligands ($\text{dsbtmp}^{0/-}$) of this homoleptic complex. The methyl groups have a more significant perturbation on the ligand reduction, shifting the reduction potential more negative by almost 200 mV compared to $[\text{Cu}(\text{dsbp})_2]^+$.¹⁷ The electron rich phenanthroline ligands also serve to shift the irreversible copper reduction ($\text{Cu}^{+/0}$) wave to potentials more negative than the observed ligand reductions. Therefore, unlike most copper(I) bis-phenanthroline complexes, the title complex can be both reversibly oxidized and reduced which means it can potentially act as either an electron donor or electron acceptor in photodriven electron transfer reactions. Excited state oxidation potentials (E_{ox}^*), where the excited state becomes oxidized after electron transfer, and excited state reduction potentials (E_{red}^*), where the excited state is reduced subsequent to electron transfer, are both functions of the ground state redox properties of the sensitizer and the excited state energy: $E_{\text{ox}}^* = E_{\text{ox}} - E_{00}$ and $E_{\text{red}}^* = E_{\text{red}} + E_{00}$.^{58,59} The combination of the high excited state energy and the ground state redox properties of $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ lead to quite negative excited state oxidation potentials (-1.5 V), rendering this sensitizer quite susceptible to oxidative quenching following light excitation.

CONCLUSIONS

A new Cu(I) MLCT sensitizer featuring cooperative steric hindrance has been synthesized and characterized, exhibiting unprecedented photophysical behavior for this class of molecules in a thermodynamically and photochemically stable platform. The 2.8 μs lifetime observed in CH_2Cl_2 makes this new Cu(I) complex amenable as a sensitizer for photochemical upconversion,⁴⁰ as already demonstrated in related Ru(II) chromophores.^{60–62} Similarly, the 1.2 μs lifetime measured in 1:1 CH_3CN :water along with its strong excited state oxidation potential suggests that $[\text{Cu}(\text{dsbtmp})_2]^+$ may serve as a earth-abundant surrogate for $[\text{Ru}(\text{bpy})_3]^{2+}$ in visible-light sensitized solar fuels photocatalysis.^{63–67} Finally, the bright photoluminescence exhibited by this Cu(I) complex in all solvents investigated makes it suitable as an emitter for a variety of luminescence-based technologies.

EXPERIMENTAL SECTION

General Procedures. All reagents were purchased from Sigma-Aldrich or Alfa Aesar and used without further purification. Spectroscopic samples were prepared using spectrophotometric grade CH_2Cl_2 , CH_3CN , EtOH, or a 1:1 mixture of spectrophotometric grade CH_3CN and deionized water and were deoxygenated either by sparging with argon or a minimum of three freeze pump thaw cycles. $[\text{Cu}(\text{dsbp})_2](\text{PF}_6)^{42}$ and $[\text{Cu}(\text{dmp})_2](\text{PF}_6)^{47}$ were prepared as previously reported in the literature. ^1H and ^{13}C NMR spectra were collected on a Bruker Avance 300 spectrometer (300 MHz), and the resulting spectra were processed with the MNova 8.1 software package. Elemental analysis was obtained through the analytical facilities of Bowling Green State University Department of Chemistry. High resolution electrospray mass spectrometry was measured by the Michigan State University Mass Spectrometry Core, East Lansing, MI.

2,9-Di-*sec*-butyl-3,4,7,8-tetramethyl-1,10-phenanthroline (dsbtmp). The ligand was synthesized from *sec*-butyllithium and 3,4,7,8-tetramethyl-1,10-phenanthroline (tmp), following the method of Sauvage and co-workers.⁴⁶ One gram of tmp was dissolved/suspended in 15 mL of anhydrous toluene, and 15 mL of *sec*-butyllithium (1.4 M in cyclohexane) was added dropwise to the solution under inert atmosphere, keeping the temperature below 30 °C. The reaction mixture was stirred at room temperature overnight, then quenched with 20 mL of water and added under inert atmosphere. The mixture was extracted three times with 50 mL of dichloromethane. The combined organic layers were stirred with a large excess of manganese dioxide (~45 g) for 2 h, then dried with magnesium sulfate. After filtering and removing the solvent the final product was purified by column chromatography (silica, 10% MeOH in CH_2Cl_2) yielding a white solid, 0.81 g (54.9%) of dsbtmp as a mixture of diastereomers. ^1H NMR (CDCl_3 , 300 MHz): δ 7.91 (s, 2H), 3.30 (q, $J = 6.7$ Hz, 2H), 2.66 (s, 6H), 2.49 (s, 6H), 2.26–1.74 (m, 4H), 1.49 (dd, $J = 6.7, 2.8$ Hz, 6H), 1.00 (q, $J = 7.4$ Hz, 6H). ^{13}C NMR (CDCl_3 , 300 MHz) δ (164.23, 164.05), 144.02, 140.62, (128.31, 128.26), 125.64, 121.34, 40.19, (29.72, 29.54), (19.78, 19.56), (15.38, 15.35, 15.15), (12.83, 12.72).

Bis(2,9-di-*sec*-butyl-3,4,7,8-tetramethyl-1,10-phenanthroline)copper(I) hexafluorophosphate ($[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$). The copper complex was synthesized using a previously reported literature method.⁴⁷ Tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.260 g) was weighed into a 100 mL Schlenk flask and put under inert atmosphere. A solution of dsbtmp (0.502 g) in 10 mL of dichloromethane was degassed with argon and transferred by cannula to the flask containing the copper solid. Immediately the pale yellow solution became dark orange. The solution was stirred for 15 min, and the product was precipitated by the addition of 90 mL of degassed ether to the reaction flask. The orange solid was collected by vacuum filtration and rinsed well with ether. Additional solid was collected from the filtrate and combined with the first precipitate. Solid was purified by recrystallization, layering hexanes and dichloromethane and dried under vacuum overnight, yielding an orange powder, 0.506 g (78.8%) of $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$ as a mixture of diastereomers. Anal. Calcd (Found) for $\text{C}_{48}\text{H}_{64}\text{CuF}_6\text{N}_4\text{P} \cdot 0.35 \text{H}_2\text{O}$: C, 63.22 (63.31); H, 7.15 (7.25); N, 6.14 (6.14). ^1H NMR (CD_2Cl_2 , 300 MHz) δ 8.20 (s, 2H), 3.74–3.10 (m, 2H), 2.76 (t, $J = 5.7$ Hz, 6H), 2.52 (t, $J = 11.5$ Hz, 6H), 1.76–1.22 (m, 4H), 1.16–0.73 (m, 6H), 0.27 to –0.27 (m, 6H). ^{13}C NMR (CD_2Cl_2 , 300 MHz) δ 163.99, 146.04, (142.05, 141.95), (132.13, 132.08), (127.29, 127.23), 122.66, (49.96, 49.59), (28.07, 28.01, 27.91, 27.83, 27.77), (17.14, 17.09, 17.04), (15.77, 15.71, 15.66), (12.67, 12.42, 12.31, 12.28, 12.21, 12.05, 11.99). MS [HR-ESI (CH_2Cl_2) m/z] 759.4434 $[\text{M}-\text{PF}_6]^+$, calcd ($\text{C}_{48}\text{H}_{64}\text{N}_4^{63}\text{Cu}$) 759.4427.

Calculations. Calculations were performed using the Gaussian 09 software package⁶⁸ through the Ohio Supercomputer Center. Geometry optimizations were done on both the ground (singlet) and the lowest energy triplet states of $[\text{Cu}(\text{dsbtmp})_2]^+$ as well as $[\text{Cu}(\text{dsbp})_2]^+$ and $[\text{Cu}(\text{dmp})_2]^+$ using the UB3LYP/6-31g(d) level of theory. No symmetry restrictions were placed on the geometry optimization. The polarizable continuum model (PCM) was used to simulate the effect of the dichloromethane solvent environment.⁶⁹ Frequency calculations were performed on the optimized geometries

to ensure the calculated geometries corresponded to global minima and no imaginary frequencies were found. The optimized structures were visualized using GaussView 5.

Electrochemistry. Electrochemical measurements were performed in an inert atmosphere glovebox (MBraun) using 0.1 M TBAPF₆ in acetonitrile, dried and degassed with the MBraun SPS solvent purification system, as the supporting electrolyte. Cyclic voltammograms and differential pulse voltammograms were measured using a standard three-electrode arrangement with a platinum disk working electrode, a platinum wire counter electrode, and an Ag/AgNO₃ reference electrode. The ferrocenium/ferrocene redox couple ($\text{Fc}^{+/0}$) was used as an internal reference for all measurements, and potentials are reported relative to $\text{Fc}^{+/0}$. The spectra were recorded with a Bioanalytical Systems (BASi) Epsilon potentiostat.

Room Temperature Spectroscopic Measurements. Absorption spectra were acquired using a Cary 50 spectrophotometer. Steady state emission spectra were collected with a FL/FS920 fluorometer (Edinburgh Instruments) equipped with a 450 W Xe arc lamp and a Peltier cooled, red sensitive PMT (R2658P Hamamatsu). All emission spectra were corrected for detector response. Quantum yields for the complexes were either measured with a Hamamatsu absolute quantum yield spectrometer (C11347) or relative to aerated $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in acetonitrile ($\Phi = 0.018$).⁷⁰ For each measurement, optically dilute ($\text{OD} = 0.1\text{--}0.2$) solutions were excited into the lowest energy absorption feature (460–475 nm).

Time resolved emission and transient absorption data were collected with an LP920 laser flash photolysis system (Edinburgh Instruments). The excitation source was the Vibrant LD 355 II Nd:YAG/OPO system (OPOTEK). Data acquisition was controlled by the LP900 software program (Edinburgh Instruments). Samples were prepared with an optical density of 0.1–0.2 at the excitation wavelength for emission measurements and 0.3–0.5 at the excitation wavelength for transient absorption measurements. Kinetic traces were collected with a PMT (R928 Hamamatsu), and transient absorption spectra were collected with an iStar ICCD camera (Andor Technology). Kinetic traces were fit with single exponential functions using Igor Pro.

Variable Temperature Emission Measurements. Variable temperature photoluminescence decays were collected using a CoolSpeK UV cryostat (Unisoku Scientific Instruments). Sample was measured in a deaerated ethanol solution in a 1 cm² quartz optical cell with an optical density of ~0.15 at the excitation wavelength. The temperature was varied from 65 to –105 °C, and the sample was allowed to equilibrate for ~15 min at each temperature point before measurement. The sample was excited with a pulsed N₂ pumped dye laser (Lasertechnik Berlin), using the Coumarin 47 dye ($\lambda_{\text{max}} = 453$ nm). The emission decay traces at 650 nm were collected with a PMT (Hamamatsu R928) and recorded with a 200 MHz oscilloscope (Tektronix). Kinetic traces were fit with single exponential functions using Igor Pro.

ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra for dsbtmp and $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$, solution stability measurements, variable solvent and variable temperature emission data, and electrochemical data for $[\text{Cu}(\text{dsbtmp})_2](\text{PF}_6)$. 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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