calculations, but parameters were not refined. Methyl and methylene hydrogen atoms were placed in calculated positions. Hydrogen atoms were assigned isotropic displacement values based approximately on the value for the attached atom. The largest peak maximum and minimum on a final difference electron density map were 0.21 and -0.25 e Å^{-3}. Scattering factors for hydrogen atoms for both **5** and **6** were obtained from Stewart et al.[19] and those for other atoms were taken from ref. [19]. Programs used in this work include locally modified versions of the following programs: CARESS (Broach, Coppens, Becker, and Blessing), peak-profile analysis, Lorentzian and polarization corrections; ORFLS (Busing, Martin, and Levy), structure-factor calculation and full-matrix least-squares refinement; SHELXL (Sheldrick), crystal structure refinement; SHELX86 (Sheldrick), crystal structure solution; ORTEP (Johnson). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101178. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A Photoluminescent Copper(I) Complex with an Exceptionally High Cu^{II}/Cu^{I} Redox Potential: [Cu(bfp)$_2$]$^+$ (bfp = 2,9-bis-(trifluoromethyl)-1,10-phenanthroline)**

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The continued exploration of copper(I) bis(1,10-phenanthroline) complexes primarily results from their interesting photophysical properties.[1] In these systems it has been established that emission originates from low-lying metal-to-ligand charge transfer (MLCT) excited states.[2] Since these states are best described as copper in the +2 oxidation state, it is believed that these pseudotetrahedral copper(I) complexes reorganize towards square-planar geometry in the excited state.[3] Substituents at the 2 and 9 positions reduce the degree of excited-state distortion,[3, 4] leading to room-temperature emission for most copper(I) complexes of 2,9-disubstituted-1,10-phenanthrolines.[5] Photochemical studies of [Cu(N–N)$_2$]$^+$ complexes (N–N = 1,10-phenanthroline ligand) with 2,9-dialkyl and 2,9-diaryl substituents have demonstrated that the steric bulk of the substituents has a profound effect on the ground-state electrochemistry and the emission properties of the complexes in solution.[3, 4, 5b,g, 6] Bulkier substituents increase the Cu^{II}/Cu^{I} redox potential by stabilization of the copper(I) species, and increase both the lifetimes and energies of the MLCT excited states.

Metal complexes of electron-deficient ligands are often studied as catalysts due to their high chemical stability and, in certain cases, enhanced reactivity.[7] Since copper(I) complexes have been widely studied in photocatalytic processes,[1b,c, 8] the effects of electron-withdrawing groups on the photochemistry of these complexes are of interest. Here we report the first investigation of the copper(I) complex cation [Cu(bfp)$_2$]$^+$ (bfp = 2,9-bis(trifluoromethyl)-1,10-phenanthroline). In comparison to previously studied luminescent [Cu(N–N)$_2$]$^+$ complexes, the trifluoromethyl groups dramatically perturb the electronic structure of the complex, and consequently enhance the ability of the copper(I) complex to act as a photooxidant.

The air-stable complex [Cu(bfp)$_2$](PF$_6$) was characterized by ^{1}H NMR spectroscopy, mass spectrometry, and X-ray crystallography.[9] An ORTEP view of the cation is shown in Figure 1. The structure of [Cu(bfp)$_2$]$^+$ resembles the known structures of the [Cu(dmp)$_2$]$^+$ complex (dmp = 2,9-dimethyl-1,10-phenanthroline).[10] However, there are notable differences. In the solid state, the [Cu(dmp)$_2$]$^+$ cation tends to show variable degrees of distortion from D_{2d} symmetry, which has

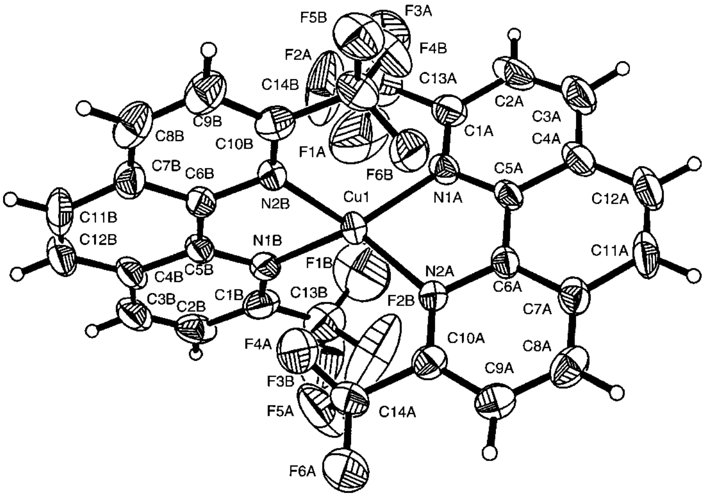

Figure 1. ORTEP diagram of the complex cation [Cu(bfp)$_2$]$^+$. Selected bond distances [Å] and angles [°]: Cu1–N1A 2.037(6), Cu1–N2A 2.052(6), Cu1–N1B 2.025(6), Cu1–N2B 2.063(7); N1A-Cu1-N2A 83.3(3), N1B-Cu1-N1A 134.6(3), N1A-Cu1-N2B 118.4(3), N1B-Cu1-N2A 124.2(3), N2A-Cu1-N2B 117.0(3), N1B-Cu1-N2B 83.2(3).

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been attributed to crystal packing forces.[11] The primary distortion usually seen is a flattening of the two ligands relative to one another (towards a square-planar geometry), with a dihedral angle of 72–83° between the ligand planes. However, in the structure of $[Cu(bfp)_2]^+$ the interligand dihedral angle is 87°, closer to 90°, to minimize the interactions between the CF_3 groups on opposing ligands. In addition, the structure of the complex $[Cu(bfp)_2]^+$ is significantly distorted from D_{2d} symmetry with a coordination geometry best described as distorted trigonal pyramidal (Figure 1).[12] Unlike what is typically seen with complexes of $[Cu(dmp)_2]^+$, there are no intermolecular ligand stacking interactions in $[Cu(bfp)_2](PF_6)$.

The absorption and corrected emission spectra of $[Cu(bfp)_2](PF_6)$ in dichloromethane at room temperature are shown in Figure 2. The absorption bands centered at 462 nm ($\varepsilon_{462} = 10900\,\text{M}^{-1}\text{cm}^{-1}$) are assigned to MLCT transitions, analogous to those of $[Cu(dmp)_2]^+$.[2f] The excitation spectrum measured at 650 nm (not shown) parallels the absorption spectrum in the range of 400–500 nm. From the room-temperature emission spectrum, the free energy of the excited state is estimated to be 2.1 eV[13] (Figure 2).

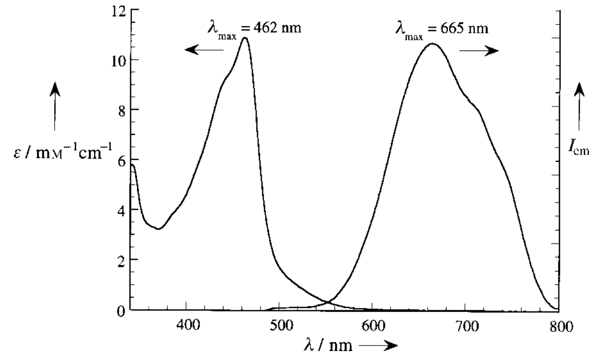

Figure 2. Absorption spectrum and corrected emission spectrum ($\lambda_{ex} = 450$ nm) of $[Cu(bfp)_2](PF_6)$ in CH_2Cl_2 at room temperature.

Excited-state lifetimes and quantum yields were determined at room temperature in deoxygenated dichloromethane. Data for the two well-studied complexes $[Cu(dmp)_2]^+$ and $[Cu(dpp)_2]^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline) provide useful comparisons.[5a,b] The lifetime of the excited state of $[Cu(bfp)_2](PF_6)$ was 165 ns, which is approximately twice that of $[Cu(dmp)_2](PF_6)$ ($\tau = 83$ ns), yet shorter than that of $[Cu(dpp)_2](PF_6)$ ($\tau = 243$ ns).[14] Significantly, the quantum yield for $[Cu(bfp)_2]^+$ is approximately four times that for $[Cu(dpp)_2]^+$, and approximately fourteen times that for $[Cu(dmp)_2]^+$.[15] The quantum yield for $[Cu(bfp)_2]^+$ in dichloromethane is clearly one of the highest ever measured for a $[Cu(N-N)_2]^+$ system, although the uncertainties associated with the determination of quantum yield preclude absolute ranking.[5g] Among the three complexes, the trend observed for the quantum yields (dmp < dpp < bfp) is also the trend observed for the energies of the associated excited states.[13] Examination of the nonradiative ($k_{nr} = (1-\phi)/\tau$) and radiative ($k_r = \phi/\tau$) decay rate constants reveals that the trend in quantum yields is primarily due to changes in the radiative decay rates. These results indicate that k_r values in these systems increase as excited-state energies increase, which is consistent with theory.[16]

Cyclic voltammetry[17] of $[Cu(bfp)_2](PF_6)$ displays two reversible waves (both single-electron processes) that are assigned to a ligand-based redox couple[18] ($E_{1/2} = -1220$ mV vs. saturated calomel electrode (SCE); $\Delta E_p = 70$ mV; $i_{pa}/i_{pc} = 0.92$) and the Cu^{II}/Cu^{I} couple[2h, 5g, 18] ($E_{1/2} = +1550$ mV vs. SCE; $\Delta E_p = 62$ mV; $i_{pa}/i_{pc} = 0.93$). To the best of our knowledge, this is the highest potential ever measured for a reversible Cu^{II}/Cu^{I} couple in a mononuclear copper complex (Figure 3).[19] The highly efficient electron-withdrawing nature of the CF_3 groups combined with their steric bulk result in a remarkable stabilization of the copper(I) oxidation state for $[Cu(bfp)_2]^+$; the redox existence range (RER) of the copper(I) species is 2.77 V. The largest RER value previously reported for a $[Cu(N-N)_2]^+$ system is 2.69 V.[5g]

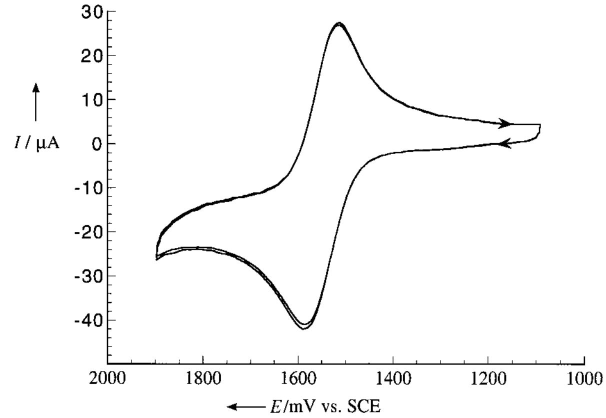

Figure 3. Cyclic voltammogram (two cycles) of $[Cu(bfp)_2](PF_6)$ in CH_2Cl_2. Conditions: 5 mM $[Cu(bfp)_2](PF_6)$, 0.1 M $(Bu_4N)(PF_6)$, glassy carbon working electrode, scan rate 0.3 V s^{-1}, internal reference $E_{1/2}$(ferrocene/ferrocenium) = +450 mV.

Estimates of the energetics of $[Cu(bfp)_2]^+$ in the excited state, $*[Cu(bfp)_2]^+$, reveal the potential use of the complex in photocatalytic and electron-transfer quenching processes. The excited-state potentials are $E(Cu^{I}*/Cu^{0}) = +920$ mV and $E(Cu^{II}/Cu^{I}*) = -590$ mV (vs. SCE).[20] These data signify that $*[Cu(bfp)_2]^+$ is a very potent photooxidant, and also an effective photoreductant. For $*[Cu(bfp)_2]^+$ to act as a photooxidant however, a significant barrier to reductive quenching may limit the electron-transfer kinetics. This barrier results from the high inner-sphere reorganization energy associated with the repopulation of a dσ^* orbital.[6, 21] On the other hand, oxidative quenching of $*[Cu(bfp)_2]^+$, which involves removal of an electron from a ligand orbital with primarily π^* character, is expected to occur with much faster kinetics.[2h, 21, 22] In addition, oxidative quenching with viologens can be anticipated to occur with very high cage-escape yields.[2h] Thus, a photocatalytic cycle that generates the highly oxidizing $[Cu(bfp)_2]^{2+}$ complex in the ground state can be envisioned. Investigations of $[Cu(bfp)_2]^+$ in photocatalytic processes are in progress.

Experimental Section

[$Cu(dmp)_2$](PF_6) and [$Cu(dpp)_2$](PF_6) were prepared according to reference [2h].

[$Cu(bfp)_2$](PF_6): Ligand bfp[24] (2 equiv) is added to [$Cu(CH_3CN)_4$](PF_6)[23] (1 equiv) in deoxygenated CH_2Cl_2, and the solution is taken to dryness. Recrystallization (CH_2Cl_2/Et_2O) affords bright orange crystals in 76% yield. ^1H NMR ($CDCl_3$): $\delta = 8.35$ (d, $H_{4,7}$), 8.42 (s, $H_{5,6}$), 9.00 (d, $H_{3,8}$); FAB-MS: m/z (%): 695 (100) [M^+].

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[15] Quantum yields (±20%) were determined from the corrected emission spectra in deoxygenated CH_2Cl_2 with [$Ru(bpy)_3$](PF_6)$_2$ (bpy = 2,2′-bipyridine) as the standard ($\phi = 0.042$ in H_2O): J. V. Caspar, T. J. Meyer, *J. Am. Chem. Soc.* **1983**, *105*, 5583–5590. For [$Cu(bfp)_2$](PF_6) $\phi = 3.3 \times 10^{-3}$ and for [$Cu(dpp)_2$](PF_6) $\phi = 8.7 \times 10^{-4}$. The quantum yield for [$Cu(dmp)_2$](PF_6) has been reported as $\phi = 2.3 \times 10^{-4}$.[2h]

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