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Simple Cu(I) Complexes with Unprecedented Excited-State Lifetimes

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This communication describes new mixed-ligand, copper(I) phenanthroline complexes that exhibit unusually efficient, long-lived photoluminescence signals even in a coordinating solvent. The development of practical components for chemical sensors, display devices, and solar-energy conversion schemes has fueled interest in complexes of polypyridine and phenanthroline ligands with transition metals,[1−5] especially heavy metal ions, e.g. ruthenium(II) or rhenium(I).[5,6] Because of the comparative cost advantage, copper-based systems are beginning to receive more attention; however, the emission signals from charge-transfer (CT) excited states of copper(I) complexes are typically weak and short-lived[7−9] because the lowest energy CT state of a d^{10} system involves excitation from a metal−ligand dσ^* orbital.[7] Moreover, in donor solvents the possibility of expanding the coordination number renders the copper systems vulnerable to an unusual, but very effective form of exciplex quenching.[7,8] Mixed-ligand systems involving triphenylphosphine initially looked promising because they exhibit long lifetimes in the solid state and frozen solution.[10,11] However, detailed studies of $[Cu(dmp)(PPh_3)_2]^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline) have shown (1) that exciplex quenching is important in methanol despite the presence of the bulky phosphines[12] and (2) that the speciation is hard to control in the noncoordinating solvent dichloromethane (DCM).[13] An obvious possibility was that incorporation of a chelating phosphine might suppress ligand dissociation, and studies reported herein establish that systems such as $[Cu(dmp)(POP)]^+$ are, in fact, vastly superior luminophores (POP = bis[2-(diphenylphosphino)phenyl]ether).[14] An unanticipated finding is that solvent-induced exciplex quenching is relatively inefficient for the CT excited state of the POP complex, even though the triphenylphosphine moieties in $[Cu(dmp)(PPh_3)_2]^+$ have greater steric requirements.

Reaction of $[Cu(NCCH_3)_4]BF_4$ with POP and a phenanthroline ligand gives good yields of the copper(I) complexes [Cu(NN)(POP)]-BF_4, where NN = 1,10-phenanthroline (phen), dmp, or 2,9-di-*n*-butyl-1,10-phenanthroline (dbp).[15] The ORTEP drawing of the dmp derivative in Figure 1 reveals a distorted tetrahedral coordination environment about Cu(I) with P−Cu−P and N−Cu−N bond angles of 116.44(4)° and 80.88(13)°, respectively. The unbound ether oxygen of the POP ligand lies 3.24 Å, the closest interligand contact, from the C(21) methyl group of the dmp ligand. All three [Cu-$(NN)(POP)]^+$ complexes exhibit similar structures (Figure 1).[16]

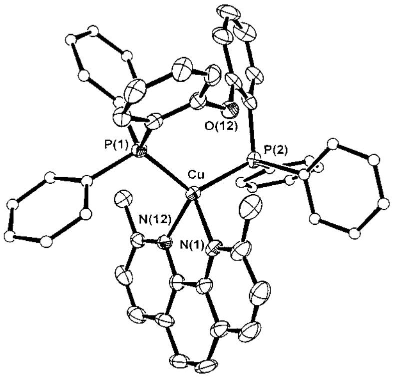

Figure 1. ORTEP representation of the structure of the cation in [Cu-$(dmp)(POP)]BF_4\cdot CH_2Cl_2$. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms of the Ph_2P groups which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: Cu−P(1) 2.2691(11), Cu−P(2) 2.2728(11), Cu−N(1) 2.104(3), Cu−N(12), 2.084(3), Cu···O(12) 3.151; P(1)−Cu−P(2) 116.44-(4), N(1)−Cu−N(12) 80.88(13). Bond distances (Å) and bond angles (deg) in the structure of $[Cu(phen)(POP)]BF_4\cdot 1.5Et_2O\cdot CH_3CN$: Cu−P(1) 2.2314-(8), Cu−P(2) 2.2614(9), Cu−N(1) 2.071(3), Cu−N(10), 2.064(3), Cu···O(12) 3.205; P(1)−Cu−P(2) 110.81(3), N(1)−Cu−N(10) 80.83(11). Bond distances (Å) and bond angles (deg) for $[Cu(dbp)(POP)]BF_4\cdot CH_3CN$: Cu−P(1) 2.2712(7), Cu−P(2) 2.2793(6), Cu−N(1) 2.097(2), Cu−N(12) 2.109-(2), Cu···O(12) 3.257; P(1)−Cu−P(2) 112.91(2), N(1)−Cu−N(10) 80.51(8).

Table 1. Photophysical Data for Mixed Ligand Cu(I) Complexes in DCM at Room Temperature

complex	λ_{max} (Abs) nm	corrected emission λ_{max}, nm	ϕ^a	τ^b, μs
$[Cu(phen)(POP)]^+$	391	700	0.0018	0.19
$[Cu(dmp)(POP)]^+$	383	570	0.15	14.3
$[Cu(dbp)(POP)]^+$	378	560	0.16	16.1
$[Cu(phen)(PPh_3)_2]^{+\,c}$	370	680	0.0007	0.22
$[Cu(dmp)(PPh_3)_2]^{+\,d}$	365	560	0.0014	0.33
$[Cu(dmp)(dppe)]^{+\,e}$	400	630	0.010	1.33

[a] Error ±10%. [b] Error ±5%. [c] Reference 12. [d] Reference 10; recorded in methanol. [e] Cuttell, D. G., unpublished observations.

However, the photophysical properties of $[Cu(NN)(POP)]^+$ systems vary dramatically with the steric requirements of the NN ligand. Whereas the emission from $[Cu(phen)(POP)]^+$ is very similar to that reported for the $[Cu(phen)(PPh_3)_2]^+$ system in room-temperature DCM solution,[12] under the same conditions [Cu(dmp)-$(POP)]^+$ exhibits almost a 100-fold greater emission efficiency and a much longer excited-state lifetime (Table 1). In each case the emission is broad, unstructured, and characteristic of a CT state.[7−9] Energy differences between the absorption and emission maxima reveal that the CT state of $[Cu(phen)(POP)]^+$ suffers by far the largest geometry change of the three $[Cu(NN)(POP)]^+$ species due to the lack of sterically active substituents on the NN moiety. In contrast, the system with the bulkiest phenanthroline ligand, namely $[Cu(dbp)(POP)]^+$, has the highest energy emission and longest excited-state lifetime (16.1 μs in fluid DCM) within the series. The steric influence of the alkyl substituents is also evident in the electrochemistry. Normally, electron-donating groups stabilize the oxidized form of the complex, but cyclic voltammetry reveals that the E_0 of the Cu(II)/Cu(I) couple shifts from +1.23 V vs Ag/AgCl for the phen complex to +1.38 V (+1.39 V) for the dmp (dbp) system. The shift to higher potential occurs for complexes with a bulkier phenanthroline because the ligand framework resists rearrangement to a more flattened structure that is appropriate for the Cu(II) oxidation state.

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At the same time, the structures reveal that the POP ligand meshes with the dmp ligand better than a pair of PPh_3 ligands because the Cu−N and Cu−P distances are about 0.02 Å longer[17] on average in $[Cu(dmp)(PPh_3)_2]^+$ as compared with $[Cu(dmp)(POP)]^+$. Another potentially important consequence of the ether linkage is that the P−Cu−P angle decreases from 122.7° in the $[Cu(dmp)(PPh_3)_2]^+$ complex[17] to 116.4° in $[Cu(dmp)(POP)]^+$. In view of the bulkiness of the PPh_3 ligands, it is striking that a five-coordinate form is more accessible in the case of the $[Cu(NN)(PPh_3)_2]^+$ system. Thus, the lifetime of the CT state of $[Cu(dmp)(PPh_3)_2]^+$ is only 330 ns in methanol due to solvent-induced quenching,[10,12] whereas methanol has little or no effect on the CT state of $[Cu(dmp)(POP)]^+$ ($\tau = 2.4\ \mu s$) or $[Cu(dbp)(POP)]^+$ ($\tau = 5.4\ \mu s$). Note that the presence of a bulky phenanthroline like dmp or dbp is also essential for suppression of exciplex quenching because, like $[Cu(phen)(PPh_3)_2]^+$, $[Cu(phen)(POP)]^+$ exhibits a weak, short-lived emission signal in methanol. Emission from $[Cu(dmp)(POP)]^+$ also persists in acetone ($\tau = 3.8\ \mu s$) and acetonitrile ($\tau = 1.1\ \mu s$) but quenching is essentially complete in the high donor number solvent dimethylformamide. Full details of the solvent dependence will be reported in due course.

The $[Cu(NN)(POP)]^+$ systems with bulky NN ligands are unprecedented in that they exhibit CT states with ca. 15 μs lifetimes in DCM solution and emission efficiencies approaching 20%. Although past work has shown that increasing delocalization within the π system of the phenanthroline ligand can enhance the lifetime,[18] an even more effective strategy is to raise the energy of the excited state so as to take advantage of the energy gap law.[19] To minimize structural relaxation in the CT excited state and retain as much of the excitation energy as possible, most efforts involving $[Cu(NN)_2]^+$ systems have focused on incorporating bulky substituents in the 2,9 positions of the ligand.[7,8] However, σ-antibonding interactions with the lone pair orbitals of the phenanthrolines destabilize the high-energy d orbitals of the D_{2d} ground state and inevitably reduce the energy of the CT excited state.[7] In the case of a mixed-ligand POP complex the CT state shifts to higher energy due to differences in bite angles as well as donor type, and the lifetime becomes much longer.

Establishing the basis of the profound influence the POP ligand has on the ground and excited-state chemistry of the $[Cu(dmp)(POP)]^+$ and $[Cu(dbp)(POP)]^+$ systems will require systematic studies involving ligand variations and theoretical work. As a first step in that direction, a comparison with other data in Table 1 reveals that the excited state of the $[Cu(dmp)(POP)]^+$ system is also significantly longer lived than that of the dppe analogue (dppe = 1,2-bis(diphenylphosphino)ethane). The lifetimes of the photoexcited $[Cu(NN)(POP)]^+$ complexes are the more intriguing because the ether oxygen of the POP ligand is also capable of coordinating to the central metal.[20] One might have expected a hapticity increase to occur in the excited state so as to foster internal exciplex quenching, a process that has been found to be very efficient in other copper(I) systems,[21] but this does not occur. The persistence of microsecond lifetimes for the photoexcited states of $[Cu(dmp)(POP)]^+$ and $[Cu(dbp)(POP)]^+$ in methanol is also remarkable because solvent-induced exciplex quenching is normally a very potent process in copper systems. Perhaps the single most unexpected result is that solvent-induced quenching is so much less efficient for the two POP systems than $[Cu(dmp)(PPh_3)_2]^+$, a structurally similar complex with a bulkier complement of phosphines. Up to now, the unwritten rule has been that "bigger is better" in designing ligand frameworks that suppress solvent-induced quenching.[7−9,17,21] With $[Cu(NN)_2]^+$ systems involving bulky biquinoline ligands, Riesgo et al. have emphasized that interlocking ligand−ligand interactions can also enforce rigidity and suppress solvent-induced quenching,[22] and a similar effect may play a role in the $[Cu(dmp)(POP)]^+$ and $[Cu(dbp)(POP)]^+$ systems. What is clear from our study is that there are easy routes to very simple Cu(I) complexes with highly emissive excited states and obvious potential for luminescence-based applications and devices.

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Supporting Information Available: X-ray crystallographic files (CIF); tables of experimental data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Synthesis of $[Cu(NN)(POP)]BF_4$ complexes. A typical procedure is as follows. A mixture of $[Cu(NCCH_3)_4]BF_4$ (31 mg, 0.10 mmol) and bis-[2-(diphenylphosphino)phenyl]ether[14] (54 mg, 0.10 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 2 h and then treated with a solution of 2,9-dimethyl-1,10-phenanthroline (21 mg, 0.10 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for an additional 1 h and filtered, and the clear yellow filtrate was concentrated to ca. 5 mL. Acetonitrile (about 5 mL) was added and the vapor diffusion of diethyl ether into the resulting solution gave yellow crystals of the complex; yield 57 mg (63%). Anal. Calcd for $C_{50.5}H_{41}BClCuF_4N_2OP_2$ (i.e. $[Cu(dmp)(POP)]BF_4{\cdot}0.5CH_2Cl_2$): C, 64.32; H, 4.43. Found: C, 64.32; H, 4.42.
(16) Crystal data for $[Cu(phen)(POP)]BF_4{\cdot}1.5Et_2O{\cdot}CH_3CN$ (150 K): space group $P\bar{1}$ (No. 2) with $a = 12.9326(3)$ Å, $b = 14.3210(3)$ Å, $c = 15.1443(4)$ Å, $\alpha = 105.8830(13)°$, $\beta = 99.3086(13)°$, $\gamma = 106.9454(12)°$, $V = 2490.1(2)$ Å^3, $Z = 2$, $d_{calcd} = 1.362$ g cm^{-3}, μ(Mo Kα) = 0.561 mm^{-1}, 26584 reflections measured (11164 unique). A cutoff $F_o^2 > 2.0\sigma(F_o^2)$ was used for R-factor calculations to give $R(F_o) = 0.061$, $R_w(F_o^2) = 0.154$, and GOF = 1.030. Crystal data for $[Cu(dmp)(POP)]BF_4{\cdot}CH_2Cl_2$ (150 K): space group $P2_1/c$ (No. 14) with $a = 10.7713(2)$ Å, $b = 14.7971(2)$ Å, $c = 28.8529(5)$ Å, $\beta = 98.1590(7)°$, $V = 4527.6(2)$ Å^3, $Z = 4$, $d_{calcd} = 1.441$ g cm^{-3}, μ(Mo Kα) = 0.727 mm^{-1}, 23669 reflections measured (10274 unique). A cutoff $F_o^2 > 2.0\sigma(F_o^2)$ was used for R-factor calculation to give $R(F_o) = 0.062$, $R_w(F_o^2) = 0.161$, and GOF = 1.050. Crystal data for $[Cu(dbp)(POP)]BF_4{\cdot}CH_3CN$ (150 K): space group $P\bar{1}$ (No. 2) with $a = 11.6779(2)$ Å, $b = 14.0495(2)$ Å, $c = 17.6505(3)$ Å, $\alpha = 77.3452(6)°$, $\beta = 71.4646(7)°$, $\gamma = 66.7766(6)°$, $V = 2508.57(10)$ Å^3, $Z = 2$, $d_{calcd} = 1.353$ g cm^{-3}, μ(Mo Kα) = 0.555 mm^{-1}, 34562 reflections measured (11413 unique). A cutoff $F_o^2 > 2.0\sigma(F_o^2)$ was used for R-factor calculation to give $R(F_o) = 0.049$, $R_w(F_o^2) = 0.125$, and GOF = 1.037.
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