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Modifying the Luminescent Properties of a Cu(I) Diphosphine Complex Using Ligand-Centered Reactions in Single Crystals

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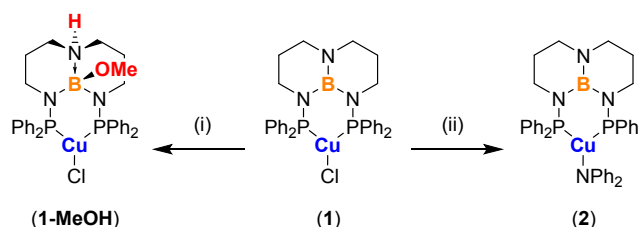
Here we report how reactions at a chemically reactive diphosphine shifts the long-lived luminescent colour of a crystalline three-coordinate Cu(I) complex from green to blue. The results demonstrate how vapochromism and single-crystal-to-single-crystal transformations can be achieved using ligand-centered reactions.

Luminescent Cu(I) complexes are highly sought after as potential alternatives to those containing iridium, platinum, and ruthenium due to the higher abundance and lower cost of copper. Cu(I) complexes typically exhibit photoluminescence via thermally-activated delayed fluorescence (TADF), which occurs when the energy gap between the S_1 and T_1 excited states (ΔE_{ST}) is thermally accessible, and/or by phosphorescence induced by appreciable spin-orbit coupling.¹ This gives rise to widely tuneable emission lifetimes needed for use in diverse applications such as OLEDs,² chemical sensing,³ photosensitizers,⁴ and photocatalysis.⁵

A challenge that has limited the use of luminescent Cu(I) complexes is their propensity to adopt tetrahedral coordination geometries that undergo large excited-state geometric distortions that increase non-radiative decay processes and decrease quantum efficiencies.^{1a, 3a, 4c, 6} It has been shown, however, that non-radiative decay processes can be suppressed by using ligands with sterically-bulky substituents to form two- or three-coordinate Cu(I) complexes.^{6b, 7} Another challenge is developing stable and efficient blue emitters, which has proven difficult with noble metal complexes because of energetically low-lying metal-centered (3MC) $d-d$ states that provide an alternate pathway of non-radiative decay.⁸ In contrast, d^{10} complexes have no 3MC states, and several efficient Cu(I) blue emitters have been reported.^{7e, 9}

We recently described a new class of triaminoborane-bridged diphosphine ligands derived from 1,8,10,9-triazaboradecalin (TBD)

called TBDPhos.¹⁰ When bound to Ni(II) and Pd(II), phenyl-substituted TBDPhos (Ph TBDPhos) can undergo cooperative ligand-centered reactions with water and alcohols to form *trans* N-H and B-OH or B-OR bonds on the TBD backbone (Scheme 1).^{10a} Given that numerous examples of luminescent Cu(I) diphosphine complexes are known,^{1a, 2d, 4c, 11} and some form highly emissive three-coordinate complexes,^{6b, 7d, 7e} we postulated that ligand-centered reactions in Cu(I) TBDPhos complexes could be used to modify their photophysical properties. Here we report the first such examples using single crystals of (Ph TBDPhos)CuCl (**1**).



Scheme 1. Structure of (Ph TBDPhos)CuCl (**1**) and synthesis of **1-MeOH** and **2**. (i) Excess MeOH at RT. (ii) Addition of 1 eq. of HNPPh₂ and KN(SiMe₃)₂ in toluene at -78 °C.

Complex **1** was prepared by treating CuCl with Ph TBDPhos in CH_2Cl_2 (Scheme 1). The reaction was monitored by NMR spectroscopy, and new signals supporting the formation of **1** were observed at δ 24.8 ppm and δ 40.9 ppm in the ^{11}B and ^{31}P NMR spectra, respectively. Light greenish-yellow crystals were grown from CH_2Cl_2 solution by vapor diffusion with Et_2O . As expected, the crystals were highly luminescent, appearing green when exposed to UV light. X-ray diffraction data collected on the crystals revealed the structure to be three-coordinate monomeric **1** (Figure 1). The geometry around Cu and B are best described as trigonal planar with the sum of the bond angles being 359.81(4)° and 360.0(3)°, respectively, though the three angles around Cu are less congruent due to the Ph TBDPhos bite angle (P-Cu-P) of 101.52(2)°. The Cu-P bond distances of 2.1952(6) and 2.1953(6) Å are 0.04 – 0.06 Å shorter compared to other CuCl complexes with aryl-substituted diphosphines.^{6b, 12}

To give insight into how different ancillary ligands affect the photophysical properties of Cu(I) Ph TBDPhos complexes, we replaced

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the chloride in **1** with diphenylamide, another ligand known to yield luminescent Cu(I) complexes with diphosphines.^{7e} The synthesis of (P^hTBDPhos)Cu(NPh₂) (**2**) was performed by treating a mixture of **1** and HNPh₂ in toluene with KN(SiMe₃)₂ at -78 °C, which formed an intense yellow solution (Scheme 1). A sharp singlet was observed at δ 41.9 ppm in the ³¹P NMR spectrum (C₆D₆), as was a broad singlet at δ 25.0 ppm in the ¹¹B NMR spectrum. XRD studies on single crystals obtained by diffusion of pentane into toluene confirmed the three-coordinate complex and revealed similar P^hTBDPhos bond distances and angles as **1** (Figure S2; SI). Crystals of **2** exhibit similarly green luminescence like **1** despite the change in ancillary ligand.

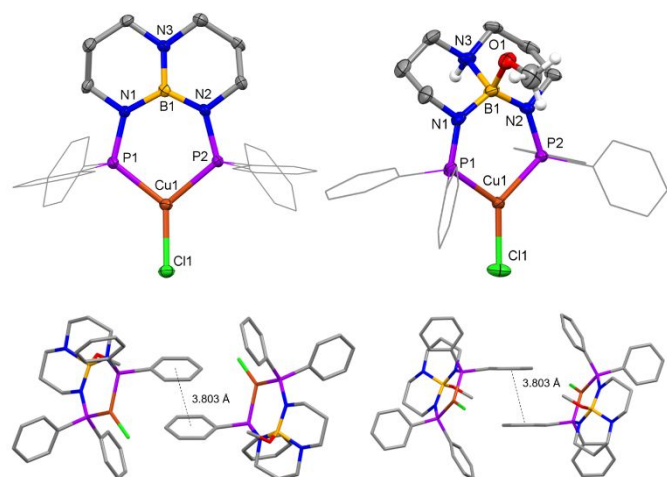


Figure 1. Top – Molecular structures of **1** (left) and **1-MeOH** (right) with thermal ellipsoids at the 50% probability level. Phenyl groups are depicted in wire frames, and hydrogen atoms except for NH and OCH₃ were omitted from the figures. Bottom – Intermolecular π - π stacking in the observed in the extended XRD structure of **1-MeOH**.

Although **1** is highly luminescent in the solid-state, its luminescence is dramatically attenuated in solution, which is attributed in part to dynamic changes in its composition and structure when dissolved. NMR analysis of isolated crystals of **1** in CD₂Cl₂ revealed small, broad resonances in the baseline that became more resolved upon cooling (Figures S6 – S7; SI). The ³¹P NMR spectrum collected at -80 °C for example revealed three resonances, suggesting that monomeric **1** dimerizes to some extent in solution and/or undergoes ligand exchange to form [Cu(P^hTBDPhos)₂][CuCl₂], as has been reported for other CuCl diphosphine complexes.¹³ Further evidence of these other species was afforded by the solution UV-vis data for **1** (Figure S1; SI). The UV-vis spectrum in toluene revealed an intense absorption band at 301 nm and a broad, tailing shoulder at 333 nm (a similar spectrum was obtained in CH₂Cl₂). The intense absorption at 301 nm corresponds to metal-to-ligand charge transfer (MLCT), as reported in other Cu(I) diphosphine complexes and confirmed by our (TD)DFT calculations (*vide infra*). The tailing shoulder at 333 nm, however, was not observed in TDDFT calculations on monomeric **1**, whereas the single absorption observed in the UV-vis spectrum of monomeric **2** in toluene at 287 nm (*i.e.* no shoulder) is in good agreement with TDDFT (Table S3; SI).

Fortunately, the attenuated solution luminescence did not prevent our investigation of ligand-centered reactivity on the photophysical properties of **1**. We discovered that crystals of **1** are not appreciably soluble in MeOH, but soaking them for a few hours

to overnight depending on their size (which varied from a few tenths of a mm to a few mm at the longest edge) changes their photoluminescence from green to blue. To ensure complete conversion, the crystals were soaked for two days and then analyzed by single-crystal XRD. The crystals had the same monoclinic space group as **1** with similar cell parameters, although the cell setting changed from P2₁/n to P2₁/c and the unit cell volume increased from 2850.3(5) to 3017.4(5) Å³ (Table S1; SI). Modeling the crystal data revealed these changes to be due to *trans* addition of MeOH to the TBD backbone to yield (P^hTBDPhos-MeOH)CuCl (**1-MeOH**; Figure 1). The Cu-P and Cu-Cl distances in **1** and **1-MeOH** are effectively identical (Table S2; SI), but the P-Cu-P angle increased from 101.52(2)° in **1** to 105.13(4)° in **1-MeOH**. As expected, the biggest change occurred at the diphosphine. The N-B bond distances of 1.427(3), 1.464(3), and 1.468 Å in **1** increase to 1.628(5), 1.529(5), and 1.544(5) Å in **1-MeOH**. The new B-OMe bond distance of 1.467(5) Å is slightly longer (0.02 – 0.03 Å) than those reported previously in P^hTBDPhos complexes with NiCl₂ and PdCl₂.^{10a}

One of the most remarkable features of the ligand-centered reactivity with **1** is that it also occurs when crystals are exposed to MeOH vapor. Crystal changes that occur in response to vapor are called solvent-induced single-crystal-to-single-crystal (SCSC) transformations.¹⁴ Not surprisingly, the SCSC transformation was slower than that observed when soaking the crystals in MeOH, as followed over the course of several days by the photoluminescent colour change from green to blue. Vapochromism with luminescent Cu(I) complexes is known,^{2d, 3e, 3f, 15} and it is typically initiated by solvent induced rearrangement of ligands and metal coordination geometry,¹⁶ solvent intercalation in the crystal lattice,¹⁷ or solvent binding at the metal.¹⁸ Complex **1** is unique because it relies on a ligand-centered reaction to induce the SCSC and the vapochromic response with MeOH. The vapochromic reaction with **1** did not appear to be reversible; the blue luminescence persisted when placing **1-MeOH** under dynamic vacuum at ca. 10⁻² torr overnight. Moreover, the crystals appeared to decompose when heated above 60 °C under vacuum, as indicated by their quenched luminescence.

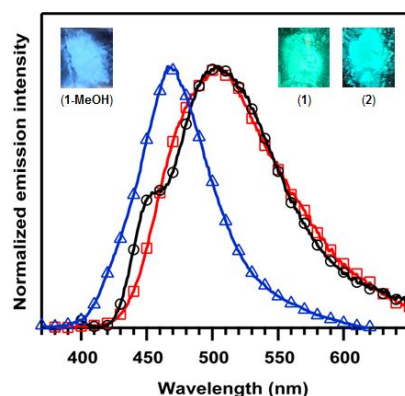


Figure 2. Emission spectra for **1** (red; \square), **2** (black; \circ) and **1-MeOH** (blue; Δ) in the solid-state. Photoluminescence colours for **1**, **2**, and **1-MeOH** are provided at the upper right or left corners of the figure. Data were collected every 1 nm, and the symbols are present to help distinguish the overlaid plots.

In contrast to **1**, attempts to test the ligand-centered reactivity of **2** were unsuccessful. Exposing **2** to MeOH, for example, quenched its photoluminescence. Given that Cu-NPh₂ bonds in **2** are highly

susceptible to protonolysis, as described previously for similar Cu(I) amido complexes,^{7e} and because emission of **2** is quenched in the solid state when exposed to MeOH, we did not pursue further investigations into its reactivity.

Table 1. Solid-state emission data for **1**, **2**, and **1-MeOH** at room temperature.

Complex	λ_{em}/nm	Φ_{PL}	$\tau/\mu s$	$k_r/10^2 s^{-1}$	$k_{nr}/10^2 s^{-1}$
1	502	0.67(1)	670	11	5
2	454(sh), 505	0.33(1)	550	6.4	12
1-MeOH	466	0.092(6)	770	1.3	12

Room-temperature excitation of solid samples of **1** at 360 nm yielded an emission peak at 502 nm consistent with its green luminescence (Figure 2), and triplicate measurements revealed the quantum yield (Φ_{PL}) to be 67(1)%. The emission spectrum for **2** is similar to **1** with $\lambda_{max} = 505$ nm and a slight shoulder at 454 nm, but the quantum yield decreased to $\Phi_{PL} = 33(1)\%$. The MeOH-bound complex **1-MeOH** showed the most significant change, as expected based on the change in photoluminescence colour; excitation at 310 nm yielded a blue-shifted λ_{max} of 466 nm and $\Phi_{PL} = 9.2(6)\%$.

Photoemission decay plots for **1**, **2**, and **1-MeOH** showed bi-exponential curves with weighted-average lifetimes of 670, 550, and 770 μs , respectively. The average radiative decay rates (k_r) decreased across the series in the order **1** > **2** > **1-MeOH** from 1.1×10^3 to $1.3 \times 10^2 s^{-1}$, whereas the non-radiative decay rates (k_{nr}) increased from $5.0 \times 10^2 s^{-1}$ in **1** to $1.2 \times 10^3 s^{-1}$ in **2** and **1-MeOH** (Table 1). Such long lifetimes suggest that phosphorescence is the dominant photoemission processes,^{7e} and the lifetimes are remarkable when combined with their relatively high quantum yields. Among the best examples known include a two-coordinate Cu(I) complex described by Thompson and coworkers that exhibited 82% quantum yield and a 550 μs lifetime when doped in a polystyrene film.^{7e} The Feng group also recently reported that $[N(C_3H_7)_4][CuBr_2]$ has an 83% quantum yield with a 249 μs lifetime.¹⁹ In complexes more representative of ours, Eisenberg and coworkers reported Cu(I) diphosphine complexes with lifetimes ranging from few μs to 3 ms in both solutions and solid-state, but the quantum yields were either low in solution (< 3%) or not reported in the solid-state.²⁰ Su and coworkers also reported long-lived Cu(I) complexes up to 260 μs , but the quantum yields were again below 5%.²¹

DFT and TDDFT calculations were used to investigate the photophysical differences in **1**, **1-MeOH**, and **2**. The calculations were performed in the gas phase and using SMD solvation models with toluene and CH_2Cl_2 for comparison. Consistent with our solution UV-vis data,²² analysis of the TDDFT calculations and associated Kohn-Sham orbitals confirm that UV absorptions in **1** are best assigned as MLCT transitions between the HOMO (Cu-Cl π^* and Cu-P σ^*) and unoccupied phenyl-derived π orbitals localized on the ^{Ph}TBDPhos ligand. Despite addition of MeOH to the TBD backbone, the calculated absorption transitions for **1-MeOH** are effectively the same as **1**. In contrast, the UV absorption assignments for **2** differ in that they are better described as mixtures of XLCT and MLCT transitions involving ligand π orbitals localized on the NPh₂ ligand.

Evaluating the emissive properties of the Cu(I) complexes required determining the structures of their T₁ excited states. The optimized structures revealed that **1** undergoes a distortion from

trigonal planar in the ground state to T-shaped in the T₁ state, similar to that reported for other emissive three-coordinate complexes (Figure 3).^{6b, 23} The *cis* and *trans* P-Cu-Cl angles were 113.2° and 150.7° and the P-Cu-P angle was 96.1° ($\Sigma = 360.0^\circ$). A similar, albeit less dramatic bending distortion was calculated for the T₁ structure of **2**, but also with rotation of the NPh₂ phenyl groups around the Cu-N bond. In contrast to **1** and **2**, **1-MeOH** undergoes a different Jahn-Teller distortion in the excited state. Instead of trigonal planar to T-shaped, the T₁ coordination geometry in **1-MeOH** is trigonal pyramidal with more congruent P-Cu-Cl angles of 123.4° and 119.4° and a P-Cu-P angle of 86.7° ($\Sigma = 329.5^\circ$). Given that structural excited-state distortions are known to influence the availability of non-radiative decay modes, it is likely that the different excited-state Jahn-Teller distortions for **1-MeOH** compared to **1** contributes to its decreased quantum yield.

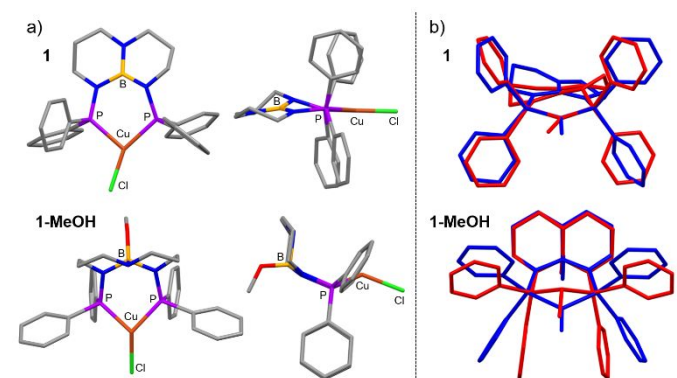


Figure 3. a) Top and side views of optimized gas-phase DFT structures for the triplet state (T₁) of **1** (top) and **1-MeOH** (bottom). b) Stack plot of calculated structures for **1** and **1-MeOH**: gas-phase singlet ground state (S₀; red) and triplet excited state (T₁; blue).

Calculations performed on discrete complexes of **1** and **1-MeOH** did not offer a clear reason for the colorimetric shift between the two, which suggests that the shift is tied to differences in their extended solid-state structures. The Kohn-Sham orbitals involved in the transitions do not have appreciable boron or nitrogen character in the optimized ground- and excited-state structures, which appears to rule out that the colour change is associated with chemical engagement of boron and nitrogen orbitals on the ligand (Figures S3 – S4; SI). Analysis of the calculated T₁→S₀ emission energies was also inconclusive because they varied in magnitude and sign depending on the conditions selected (gas-phase vs. solvation model vs. solvent selection; Table S4). As has been described for luminescent complexes containing aryl-substituted ligands,^{17, 24} we suspect that the change in luminescence colour can be attributed to solid-state differences in intermolecular π - π stacking between adjacent aryl groups in response to the SCSC transformation. Evidence in support of this hypothesis is afforded by analysis of the XRD data. The crystal structure of **1** shows no intermolecular π - π stacking, whereas the extended structure of **1-MeOH** has adjacent complexes with overlapping, parallel-offset phenyl groups with Ph...Ph centroid distances of 3.803 Å (Figure 1).

We briefly investigated the scope of the solid-state ligand-centered reactivity of **1** with other Bronsted acids. As with MeOH, the green photoluminescence of crystalline **1** slowly turns blue when exposed to vapor from water and aqueous HCl solutions (Figure 4). It

appears that $\text{Ph}^{\text{TBDPhos}}$ in crystals of **1** undergoes solid-state ligand-centered reactions in the same way as it does with MeOH under these conditions, and this observation is consistent with solution reactivity reported previously with $(\text{Ph}^{\text{TBDPhos}})\text{NiCl}_2$ and $(\text{Ph}^{\text{TBDPhos}})\text{PdCl}_2$.^{10a, 10b}

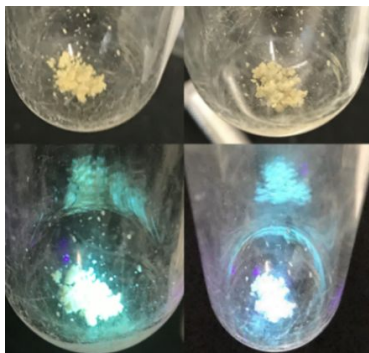


Figure 4. Single crystals of **1** before (left) and after (right) exposure to vapor from an aqueous HCl solution for 12 h under normal light (top) and commercial violet laser pointer (bottom).

In summary, we have described how three-coordinate Cu(I) complexes with a reactive diphosphine ligand called $\text{Ph}^{\text{TBDPhos}}$ exhibit green photoemission, relatively high quantum yields, and long luminescent lifetimes. Exposing crystals of **1** to MeOH solution or vapor turns the photoemission blue by way of ligand-centered reactions at the TBD backbone that cause a single-crystal-to-single-crystal transformation. Similar ligand-centered reactivity appears to be operative when **1** is exposed to vapor from water and aqueous HCl solutions. Collectively, these results demonstrate how ligand-centered reactions can be used to modify the luminescent properties of crystalline Cu(I) complexes, which may be useful for the development of new materials for optical sensing and luminescent devices.

Conflicts of interest

There are no conflicts to declare.

Notes and references

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