

Synthesis and characterization of phosphorescent three-coordinate Cu(I)-NHC complexes.

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Supporting information.

General

The reactions were performed under nitrogen atmosphere in oven dried glassware. Chloro[1,3-bis(2,6-di-*i*-propylphenyl)imidazol-2-ylidene]copper(I), 1,10-phenanthroline, 2-(2-Pyridyl)benzimidazole were purchased from Sigma-Aldrich[®]. Solvents were obtained from commercial sources and used without further purification except for tetrahydrofuran, which was distilled over sodium/benzophenone. NMR spectra were measured on a Varian 400MR (400MHz) spectrometer. Elemental analysis was carried out by the microanalysis laboratory at University of Illinois, Urbana-Campaign. The UV-visible spectra were recorded in dichloromethane at room temperature on a Hewlett-Packard 4853 diode array spectrometer. Steady state emission measurements were performed on a Photon Technology International QuantaMaster model C-60 fluorimeter. All reported spectra are corrected. Phosphorescence lifetime measurements were performed on the same fluorimeter equipped with a microsecond Xe flash lamp or on IBH Fluorocube instrument equipped with a 405 nm LED excitation source using time-correlated single photon counting method. Quantum yields at room temperature were measured using a Hamamatsu C9920 system equipped with a xenon lamp, calibrated integrating sphere and model C10027 photonic multichannel analyzer. For photophysical characterization solutions were degassed sparging with N₂ gas for 15 minutes. Cyclic voltammetry was performed in anhydrous CH₂Cl₂ using an EG&G potentiostat/galvanostat model 283 under N₂ atmosphere. 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) was used as the supporting electrolyte. A glassy carbon rod was used as the working electrode, a platinum wire was used as the counter electrode, and a silver wire was used as a pseudo reference electrode. The redox potentials are calculated relative to an internal reference ferrocenium/ferrocene (Fc⁺/Fc). DFT calculations were performed using the Titan software package (Wavefunction, Inc.) at a B3LYP/LACVP* level of theory. All calculations were single point calculations using geometric parameters obtained from XRD analysis. The triplet calculations were restricted.

X-ray Crystallography Procedures

X-ray quality crystals were grown as indicated in the experimental procedures for each complex, and the crystals were mounted on a glass fiber with Paratone-N oil. X-ray diffraction data were collected on a Bruker SMART APEX diffractometer using graphite-monochromated Mo K α radiation, and structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package.

Synthesis of [(IPr)Cu(phen)]OTf (1).

Chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) (121.9 mg, 0.25 mmol) and silver triflate (64.2 mg, 0.25 mmol) were mixed under nitrogen in a 25 mL flask and 10 mL of dry THF were added. The reaction mixture was stirred at RT for 30 min. A solution of 1,10-phenanthroline (45.05 mg, 0.25 mmol) in dry THF (5 mL) was added. The reaction mixture turned yellow and was stirred at RT for 3 h. The resulting mixture was filtered through Celite[®] and solvent was removed by rotary evaporation. Recrystallization from CH₂Cl₂ by vapor diffusion of Et₂O gave 120mg (61.4%) of bright yellow crystals. ¹H-NMR (CDCl₃, 400 MHz): δ 1.07 (d, J=7.2 Hz, 12H), 1.30 (d, J=7.2 Hz, 12H), 2.69 (sept, J=6.8 Hz, 4H), 6.74 (dd, J=4.8 Hz, J=1.6 Hz, 2H), 7.40 (s, 2H), 7.51 (d, 8Hz, 4H), 7.60 (dd, J=8.4 Hz, J=4.8 Hz, 2H), 7.78 (t, J=8 Hz, 2H), 7.95 (s, 2H), 8.51 (dd, J=8 Hz, J=1.6 Hz, 2H). ¹³C-NMR (CDCl₃, 400MHz): δ 23.63, 25.08, 28.87, 123.56, 124.74, 125.23, 127.09, 128.99, 130.70, 135.93, 138.99, 143.51, 146.37, 149.65, 183.09. Anal. calcd. for C₄₀H₄₄CuF₃N₄O₃S: C, 61.48; H, 5.68; N, 7.17; Found: C, 61.06; H, 5.61; N, 7.14.

Synthesis of (IPr)Cu(pybim) (2).

2-(2-Pyridyl)benzimidazole (78.1 mg, 0.4 mmol) was dissolved in 10 mL of dry THF under N₂ and this solution was transferred via cannula to suspension of sodium hydride (17.6 mg, 0.44 mmol, 60% in mineral oil) in dry THF. The reaction mixture was stirred at RT for 1 h and then chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) (195.1 mg, 0.4 mmol) was added. The reaction mixture was stirred at RT for 3 h. The resulting mixture was filtered through Celite[®] and solvent was removed by rotary evaporation. Recrystallization by vapor diffusion of diethyl ether into a CH₂Cl₂ solution of product gave 154 mg (60%) of dark yellow crystals. ¹H-NMR (CDCl₃, 400MHz): δ 1.14 (d, J=6.8 Hz, 12H), 1.25 (d, J=6.8 Hz, 12H), 2.77 (sept, J=6.8 Hz, 4H), 5.62 (d, J=8 Hz, 1H), 6.06 (dd, J=4.8 Hz, J=1.2 Hz, 1H), 6.73 (m, 2H), 6.94 (m, 1H), 7.17 (s, 2H), 7.43 (d, J=7.6 Hz, 4H), 7.56 (m, 1H), 7.61 (d, J=8 Hz, 1H), 7.67 (t, J=7.6 Hz, 2H), 8.22 (d, J=7.6 Hz, 1H). ¹³C-NMR (CDCl₃, 400MHz): δ 23.55, 24.72, 28.83, 116.52, 117.80, 119.37, 119.56, 120.07, 121.73, 123.05, 124.49, 130.05, 136.38, 136.98, 144.62, 146.37, 147.38, 148.09, 152.54, 159.81, 184.82. Anal. calcd. for C₃₉H₄₄CuN₅: C, 72.47; H, 6.86; N, 10.48; Found: C, 72.55; H, 6.94; N, 10.84.

Figure S1. Cyclic voltammogram of [(IPr)Cu(phen)]OTf (**1**).

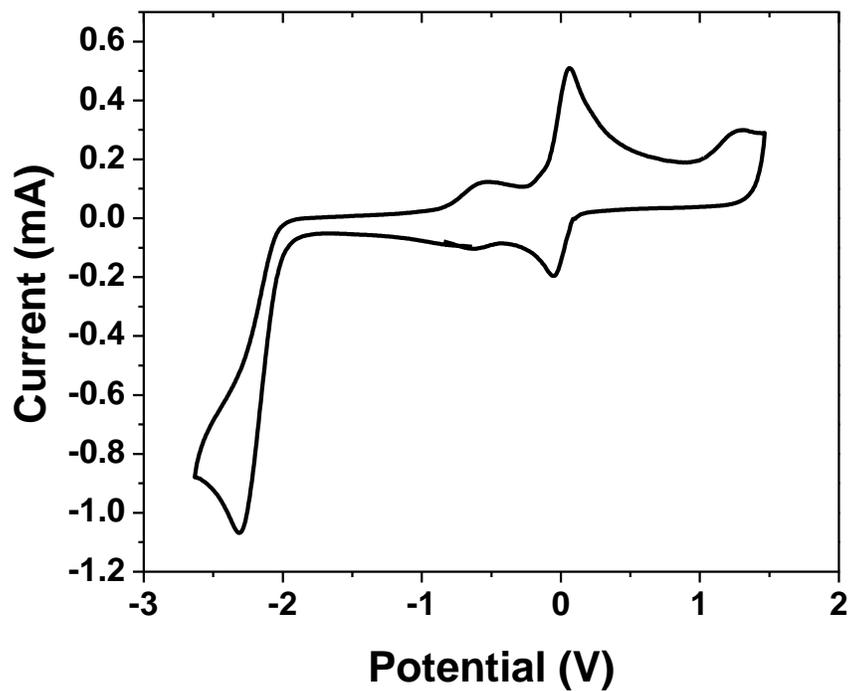


Figure S2. Cyclic voltammogram of (IPr)Cu(pybim) (**2**).

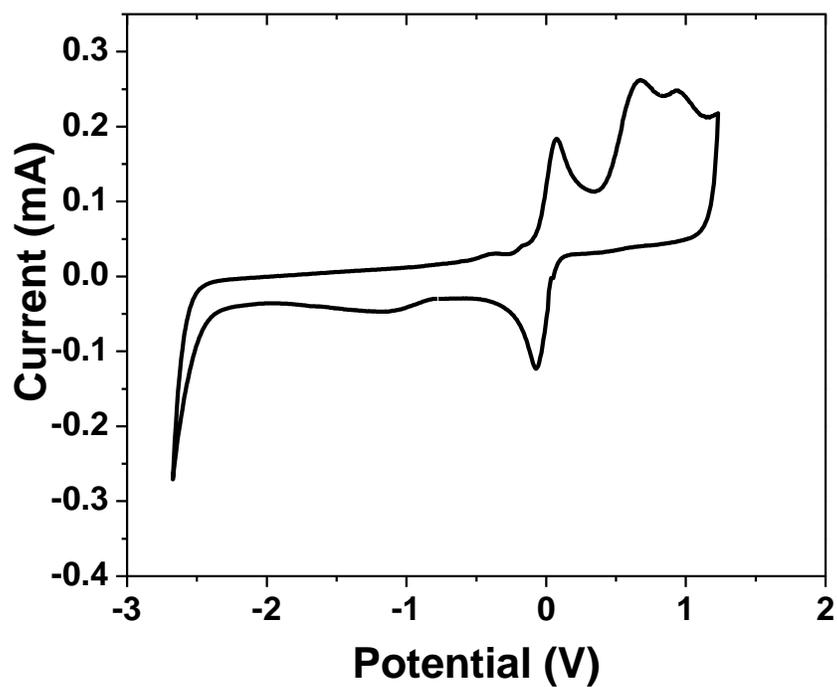


Figure S3. Absorption spectrum of [(IPr)Cu(phen)]OTf (**1**) in CH₂Cl₂ solution.

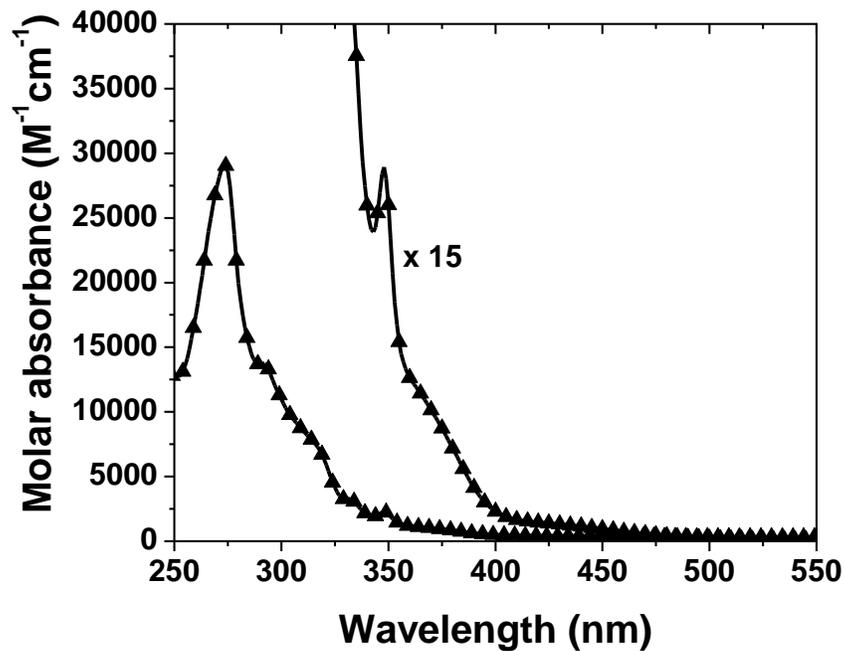


Figure S4. Absorption spectrum of (IPr)Cu(pybim) (**2**) and 2-(2-pyridyl)benzimidazole (Hpybim) in CH₂Cl₂ solution.

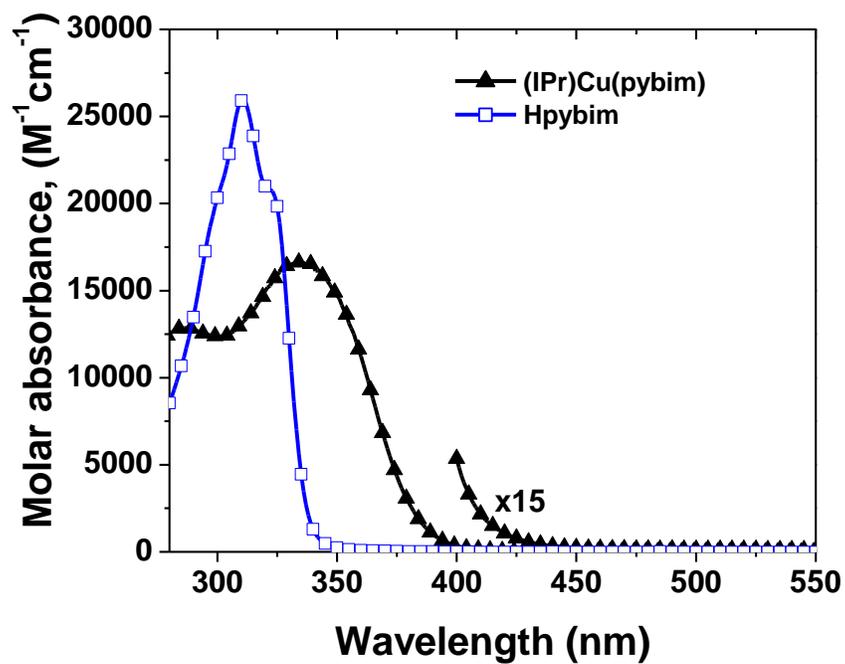


Figure S5. Corrected excitation (open symbol) and emission (closed symbol) spectra of (IPr)Cu(phen) (**1**) in 2Me-THF at 77K.

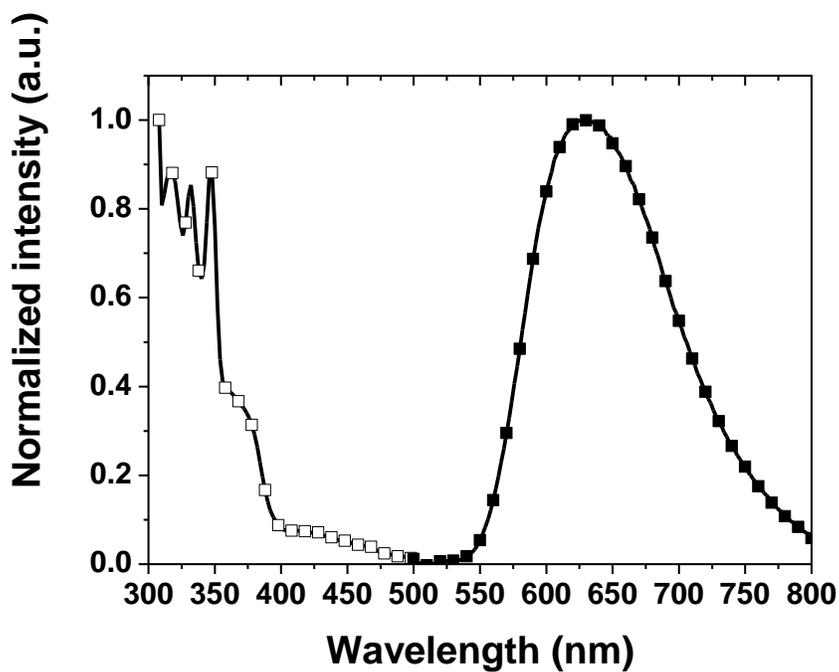


Figure S6. Corrected excitation and emission spectra of (IPr)Cu(pybim) (**2**) in PMMA film (2wt.%)

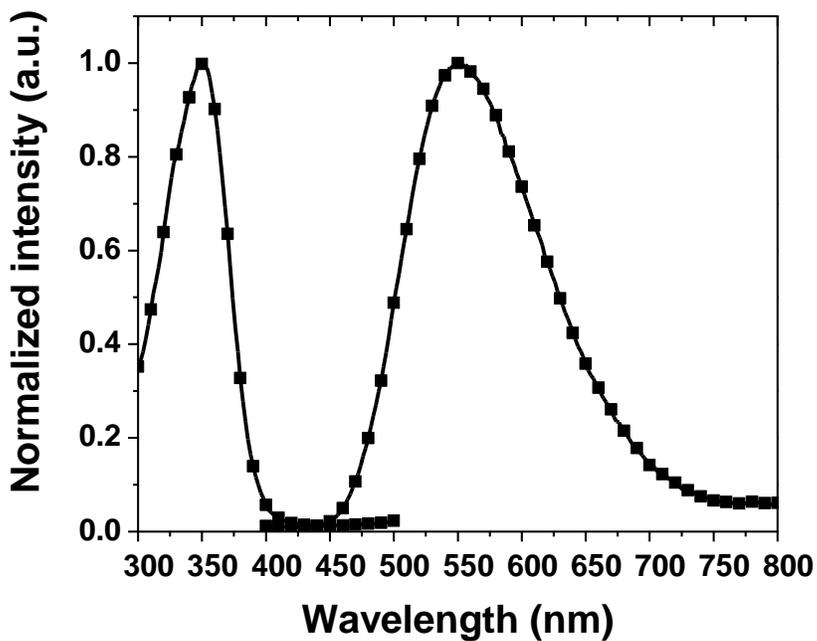


Figure S7. Corrected excitation and emission spectra of crystals of (IPr)Cu(pybim) (2) at RT.

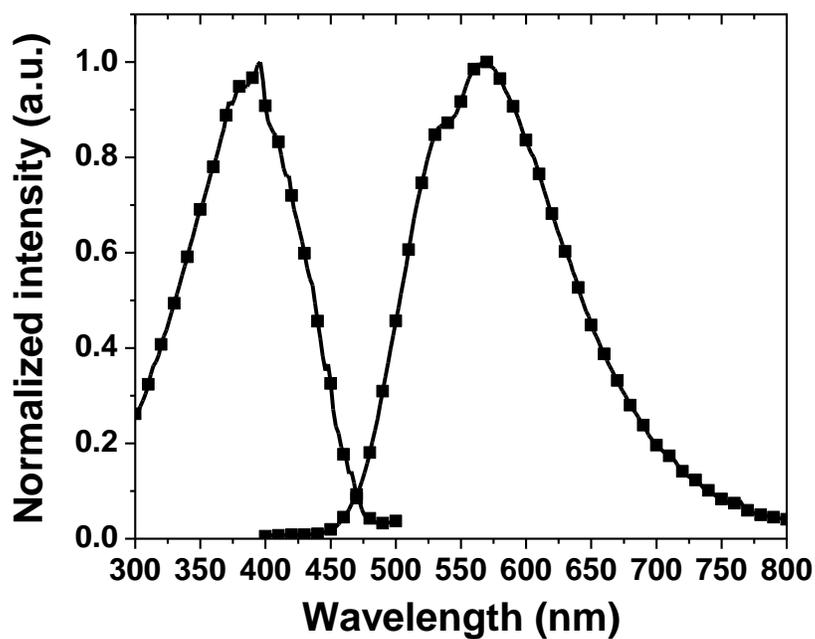


Figure S8. Emission spectra of [(IPr)Cu(phen)]OTf (1) in CH₂Cl₂ at room temperature and in 2-MeTHF at 77K.

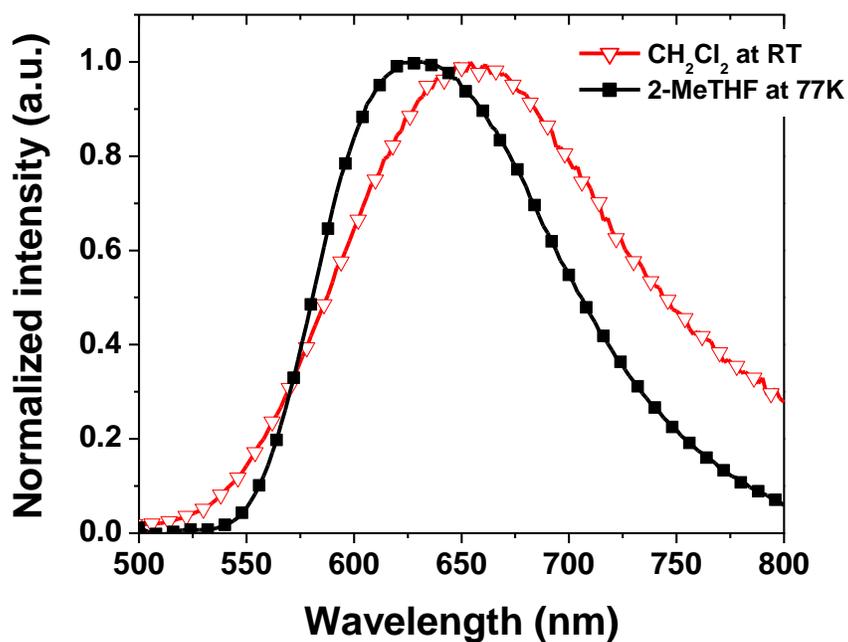


Figure S9. Emission spectra of (IPr)Cu(pybim) (**2**) in CH₂Cl₂ at room temperature and in 2-MeTHF at 77K.

