Supporting Information

Cuprophilic and π-Stacking Interactions in the Formation of Supramolecular Stacks from Dicoordinate Organocopper Complexes

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Materials and General Methods. Reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (Innovative Technologies). Ether solvents were distilled from Na/benzophenone prior to use. Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies; alumina / copper columns for hydrocarbon solvents), and the chlorinated solvents were subsequently distilled from CaH_2 and degassed via several freeze pump thaw cycles.

399.95 MHz ^{1}H and 376.2 MHz ^{19}F NMR spectra were recorded on a Varian VXR-S and 499.91 MHz ^{1}H, 125.68 MHz ^{13}C NMR, and 470.2 MHz ^{19}F NMR spectra were obtained on a Varian INOVA NMR spectrometer equipped with a 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). All NMR data were recorded at ambient temperature. ^{1}H and ^{13}C NMR spectra were referenced internally to the solvent peaks and ^{19}F NMR spectra were referenced externally to α,α',α''-trifluorotoluene (0.05% in C_6D_6; δ = –63.73).

Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ. Melting points and decomposition temperature were determined in sealed capillary tubes and are not corrected. The solution UV-visible measurement was performed in CH_2Cl_2 (7.23 10^{-5} M) using a Varian Cary 500 scan UV-Vis-NIR spectrophotometer with a 1 cm quartz cuvette. The solid state luminescence data were measured at room temperature on a Varian Cary Eclipse Fluorescence spectrophotometer. The emission spectrum was obtained in phosphorescence mode via excitation at 330 nm (600V; excitation slit: 10 nm; emission slit: 20 nm) and recorded over a range from 350-800 nm with a decay time of 0.002 s, a delay time of 0.100 ms, and a gate time of 1.00 ms. Data intervals were at 1.00 nm with averaging times of 0.100 s. Similar parameters were use for the excitation spectrum, which was recorded at the emission wavelength of 460 nm.

Synthesis of $C_6F_5Cu(py)$ (2). Neat pyridine (80 μL, 1.0 mmol) was added dropwise to a solution of $[C_6F_5Cu]_4$ (277 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) at RT. Upon addition of pyridine an intense yellow color developed which gradually disappeared to yield a colorless solution. Crystallization at –38 °C gave pale yellow crystals of **2**. Yield: 0.25 g (81%). For **2**: T_m: 135-138 °C, T_{dec}: 149-151 °C; ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ = 7.22 (m, 2 H, Py-H2,6), 6.63 (t, *J* = 7.5 Hz, 1 H, Py-H4), 6.16 (m, 2 H, Py-H3,5); ^{19}F NMR (470.2 MHz, C_6D_6, 20 °C): δ = –112.2 (m, 2 F, *ortho*-F), –160.7 (t, *J* (F, F) = 20 Hz, 1 F, *para*-F), –163.6 (m, 2 F, *meta*-F); ^{13}C NMR (125.7 MHz, C_6D_6, 20 °C): δ = 150.9 (dd, *J* (^{19}F, C) = 222 Hz / 28 Hz, Pf-C2,6), 149.5 (Py-C2,6), 139.6 (dm, *J* (^{19}F, C) = n.r., Pf-C4), 138.9 (Py-C4), 137.4 (dm, *J* (^{19}F, C) = 252 Hz, Pf-C3,5), 125.1 (Py-C3,5), 123.9 (t, *J* (^{19}F, C) = 71 Hz, Pf-C1).

Synthesis of $[C_6F_5Cu]_2$(4,4'-bipy) (3). A solution of 4,4'-bipyridine (78 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was carefully layered onto a solution of $[C_6F_5Cu]_4$ (277 mg, 0.25 mmol) in CH_2Cl_2 (5 mL) at RT. Upon diffusion of the two solutions over a period of 24 h pale yellow crystals formed, which were collected on a frit. The crystalline product **3** was washed with toluene

and a small amount of CH_2Cl_2 and dried under high vacuum. Yield: 0.27 g (87%). For **3**: ^{1}H NMR (400 MHz, *ortho*-$C_6Cl_2D_4$, 20 °C): δ 8.44 (br. d, 4 H, bipy-H2,6), 7.49 (br. d, 4 H, bipy-H3,5); ^{19}F NMR (376.2 MHz, *ortho*-$C_6Cl_2D_4$, 20 °C): δ -109.2 (m, 4 F, *ortho*-F), -158.3 (t, J (F, F) = 20 Hz, 2 F, *para*-F), -161.0 (m, 4 F, *meta*-F); for $C_{22}H_8Cu_2F_{10}N_2$ (617.39) calcd C 42.80, H 1.31, N 4.53; found C 42.14, H 1.01, N 4.41%. Preparation of **3** *via* slow diffusion of dichloromethane solutions of **1** and 4,4'-bipyridine gave single crystals with a number of different morphologies. The crystal mixture consisted of colorless plates, rods, flakes with rounded edges, and conglomerate crystals in a rosette pattern. Only the plates and rods yielded data suitable for single crystal structure determination and proved to be polymorphs of the same compound, the dinuclear species $[C_6F_5Cu]_2$(4,4'-bipy) (**3**). The molecular structures that correspond to the plates (**3-α**; T_{dec} = 140-145 °C) and rod-like crystals (**3-β**; T_{dec} = 130-135 °C) are displayed in Fig. 2 and Fig. 3 in the manuscript.

X-ray Crystal Structure Analyses

For **2**: $C_{11}H_5CuF_5N$, M_r = 309.70, orthorombic, space group P_{bcm}, a = 9.8916(10) Å, b = 18.9476(19) Å, c = 5.7846(6) Å, $\alpha = \beta = \gamma = 90°$, V = 1084.2(2) Å^3, Z = 4, ρ_{calcd} = 1.897 g cm^{-3}, λ(MoKα) = 0.71073 Å, T = 100(2) K, crystal dimensions 0.40 x 0.40 x 0.30 mm^3, μ(MoKα) = 2.061 mm^{-1}, θ range from 2.06 to 27.47°, 8592 measured reflections, 1365 independent reflections (R_{int} = 0.0202) which were used for the refinement against F^2, SADABS (T_{min}/T_{max}=0.4927/0.5768), $R1$ [I>2σ(I)] = 0.0274, $wR2$ [I>2σ(I)] = 0.0739, GOF = 1.075, No. of parameters = 109, final difference map within 0.522 and –0.420 eÅ^{-3}.

For **3-α**: $C_{22}H_8Cu_2F_{10}N_2$, M_r = 617.38, orthorombic, space group F_{ddd}, a = 8.071(2) Å, b = 11.127(3) Å, c = 48.264(14) Å, $\alpha = \beta = \gamma = 90°$, V = 4335(2) Å^3, Z = 8, ρ_{calcd} = 1.892 g cm^{-3}, λ(MoKα) = 0.71073 Å, T = 219(2) K, crystal dimensions 0.15 x 0.15 x 0.05 mm^3, μ(MoKα) = 2.062 mm^{-1}, θ range from 1.69 to 28.31°, 5700 measured reflections, 1317 independent reflections (R_{int} = 0.0341) which were used for the refinement against F^2, SADABS (T_{min}/T_{max}=0.7473/0.9039), $R1$ [I>2σ(I)] = 0.0491, $wR2$ [I>2σ(I)] = 0.1255, GOF = 1.401, No. of parameters = 85, final difference map within 0.724 and –0.396 eÅ^{-3}.

For **3-β**: $C_{22}H_8Cu_2F_{10}N_2$, M_r = 617.38, monoclinic, space group $P2_1/n$, a = 9.2876(18) Å, b = 5.0328(10) Å, c = 22.316(4) Å, β = 92.567(4)°, V = 1042.1(4) Å^3, Z = 2, ρ_{calcd} = 1.968 g cm^{-3}, λ(MoKα) = 0.71073 Å, T = 219(2) K, crystal dimensions 0.33 x 0.06 x 0.06 mm^3, μ(MoKα) = 2.144 mm^{-1}, θ range from 1.83 to 28.35°, 7363 measured reflections, 2511 independent reflections (R_{int} = 0.0243) which were used for the refinement against F^2, SADABS (T_{min}/T_{max}=0.5380/0.8821), $R1$ [I>2σ(I)] = 0.0481, $wR2$ [I>2σ(I)] = 0.1020, GOF = 1.228, No. of parameters = 163, final difference map within 0.432 and –0.263 eÅ^{-3}.

For all three structures SADABS (Sheldrick, G.M. SADABS (2.01), Bruker/Siemens Area Detector Absorption Correction Program; Bruker AXS: Madison, WI, 1998) absorption correction was used. Non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contribution. CCDC-250638, CCDC-219364, and CCDC-219363 contain the supplementary crystallographic data for **2**, **3-α**, and **3-β**, respectively. These data can be obtained online free of charge via www.ccdc.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

Fig. S1. Ortep plot for **2** at 50% probability level. Selected interatomic distances (Å) and angles (°) for **2**: Cu(1)-C(1) 1.8913(17), Cu(1)-N(1) 1.9022(15), N(1)-C(7) 1.356(2), N(1)-C(11) 1.346(2), Cu(1)-Cu(1A) 2.8924(3), C(1)-Cu(1)-N(1) 178.54(6), C(7)-N(1)-Cu(1) 121.11(12), C(11)-N(1)-Cu(1) 121.30(11), C(6)-C(1)-Cu(1) 121.80(13), C(2)-C(1)-Cu(1) 124.61(14), C(1)-Cu(1)-Cu(1A) 89.900(5), N(1)-Cu(1)-Cu(1A) 90.097(5), Cu(1)-Cu(1A)-Cu(1B) 179.716(15), (Py) // (Pf) 0.0.

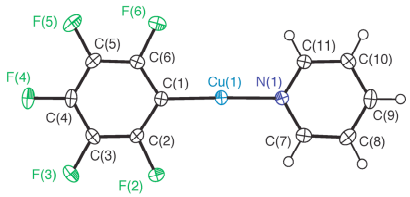

Fig. S2. Ortep plot for **3-β** at 50% probability level. Selected interatomic distances (Å) and angles (°) for **3-β**: Cu(1)-C(1) 1.880(4), Cu(1)-N(1) 1.902(3), N(1)-C(5) 1.347(3), C(7)-C(7A) 1.476(7), C(1)-Cu(1)-N(1) 180.0, C(5)-N(1)-Cu(1) 121.3(2), C(2)-C(1)-Cu(1) 123.3(2), (Py) // (Pf) 3.8, (Py) // (PyA) 44.3.

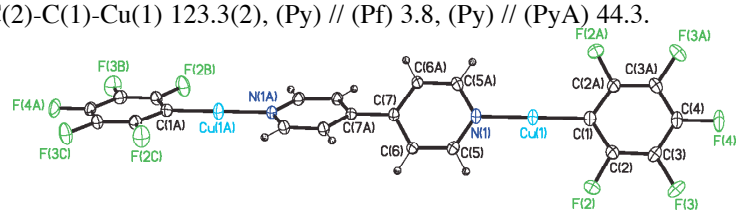

Fig. S3. Ortep plot for **3-α** at 50% probability level. Selected interatomic distances (Å) and angles (°) for **3-α**: Cu(1)-C(1) 1.890(2), Cu(1)-N(1) 1.903(2), N(1)-C(7) 1.324(3), N(1)-C(11) 1.327(3), C(9)-C(9A) 1.485(4), C(1)-Cu(1)-N(1) 178.17(8), C(7)-N(1)-Cu(1) 121.0(2), C(11)-N(1)-Cu(1) 122.4(2), C(2)-C(1)-Cu(1) 124.1(2), (Py) // (Pf) 9.5, (Py) // (PyA) 0.0.

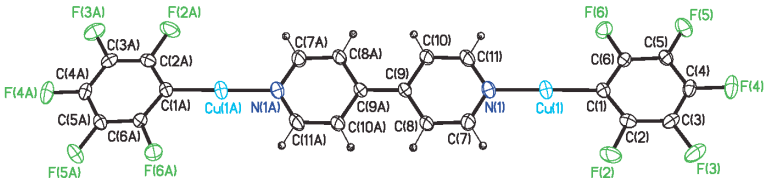

Fig. S4. Packing diagram for **2** viewed along the crystallographic *c*-axis.