

Electronic Supplementary Information

Binary Stacks of $[\text{CuC}_6\text{F}_5]_4$ with Arenes**

*Ami Doshi, Krishnan Venkatasubbaiah, Arnold L. Rheingold and Frieder Jäkle**

Materials and General Methods. Naphthalene was purchased from Acros Organics and used without further purification. $[\text{CuC}_6\text{F}_5]_4^{[1]}$ and 2,2'-bithiophene were prepared according to literature procedures. Deuterated chloroform (CDCl_3 >99.7%) was obtained from Cambridge Isotope Laboratories (CIL). All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen in an inert-atmosphere glove box (MBraun Glovebox Technology or Innovative Technologies). 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 degassed via several freeze pump thaw cycles. Elemental analyses were performed by Quantitative Technologies Inc. Whitehouse, NJ.

Synthesis of 2 and 4: Compound **1**•(tol)₂ (82.5 mg, 0.0745 mmol) was mixed with naphthalene (19.1 mg, 0.149 mmol) in CH_2Cl_2 (5 mL) at room temperature. The mixture was stirred for 10 min and then layered with hexanes (2 mL). The solution was kept for crystallization at $-35\text{ }^\circ\text{C}$ for 3 days to give **2** as colorless needle-like crystals. Yield: 78 mg (0.0662 mmol), 89%. T_m : 150-155 $^\circ\text{C}$, the material starts to change color to black at T_{dec} : 170-175 $^\circ\text{C}$; for $\text{C}_{44}\text{H}_{16}\text{Cu}_4\text{F}_{20}$ calcd C 44.83, H 1.37; found C 44.67, H 1.25. A similar reaction in a 1:1 stoichiometric ratio gave a mixture of compounds **2** and **4**, from which a crystal was hand-picked for X-ray diffraction analysis of **4**.

Synthesis of 3: Compound **3** was prepared in analogy to **2** from **1** (51.0 mg, 0.0553 mmol) and 2,2'-bithiophene (18.4 mg, 0.111 mmol), and isolated in the form of colorless needle-like crystals. Yield: 60 mg (0.0478 mmol), 86%. T_m : 165-170 $^\circ\text{C}$, the material starts to change color to black at ca. T_{dec} : 128-135 $^\circ\text{C}$; for $\text{C}_{40}\text{H}_{12}\text{Cu}_4\text{F}_{20}\text{S}_4$ calcd C 38.28, H 0.96; found C 38.23, H 0.89.

Synthesis of 5: Compound **1**•(tol)₂ (75.2 mg, 0.0680 mmol) was mixed with 2,2'-bithiophene (11.3 mg, 0.0680 mmol) in CH_2Cl_2 (5 mL). The solution was kept at $-35\text{ }^\circ\text{C}$ for 2 days to give **5** as colorless plates. Yield: 65 mg (0.0597 mmol), 88%. T_m : 175-180 $^\circ\text{C}$, the material starts to change color to black at ca. T_{dec} : 150-155 $^\circ\text{C}$; for $\text{C}_{32}\text{H}_6\text{Cu}_4\text{F}_{20}\text{S}_2$ calcd C 35.30, H 0.56; found C 35.36, H 0.41.

X-ray crystal structure analyses:

X-ray diffraction intensities were collected on a Bruker SMART APEX CCD diffractometer at $T = 203(2)$ (**3**) and $100(2)$ K (**2**, **4**, **5**) using $\text{MoK}\alpha$ (0.71073 \AA) (**3**) and $\text{CuK}\alpha$ (1.54178 \AA) (**2**, **4**, **5**) radiations. SADABS^[2] or numerical absorption corrections were applied, the structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least squares procedures on F^2 . All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms, with the exception of the thiophene hydrogen that is attached to the copper-bound carbon in **3**; the latter was located from the difference map and refined isotropically. All software and source scattering factors are contained in the SHELXTL program package.^[3]

For **2**: $\text{C}_{44}\text{H}_{16}\text{Cu}_4\text{F}_{20}$, $M_r = 1178.73$, monoclinic, space group $P2_1/c$, $a = 11.7660(5)$, $b = 6.4260(3)$, $c = 26.2579(10) \text{ \AA}$, $\beta = 102.9340(10)$, $V = 1934.94(14) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 2.023 \text{ g cm}^{-3}$, $\lambda(\text{CuK}\alpha) = 1.54178 \text{ \AA}$, $T = 100(2)$ K, crystal dimensions $0.24 \times 0.18 \times 0.12 \text{ mm}^3$, $\mu(\text{CuK}\alpha) = 3.701 \text{ mm}^{-1}$, θ range from 3.85 to 68.08 , 12142 measured reflections, 3440 independent reflections ($R_{\text{int}} = 0.0377$), $RI [I > 2(I)] = 0.0356$, $wR2 [I > 2(I)] = 0.0889$, GOF = 1.236, No. of parameters = 308, final difference map within 0.696 and -0.905 e\AA^{-3} .

For **3**: $\text{C}_{40}\text{H}_{12}\text{Cu}_4\text{F}_{20}\text{S}_4$, $M_r = 1254.90$, monoclinic, space group $P2_1/c$, $a = 11.8629(15)$, $b = 6.3870(8)$, $c = 26.727(3) \text{ \AA}$, $\beta = 97.690(2)^\circ$, $V = 2006.8(4) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 2.077 \text{ g cm}^{-3}$, $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, $T = 203(2)$ K, crystal dimensions $0.37 \times 0.10 \times 0.07 \text{ mm}^3$, $\mu(\text{MoK}\alpha) = 2.426 \text{ mm}^{-1}$, θ range from 1.54 to 28.26 , 13608 measured reflections, 4762 independent reflections ($R_{\text{int}} = 0.0228$), $RI [I > 2(I)] = 0.0305$, $wR2 [I > 2(I)] = 0.0849$, GOF = 1.076, No. of parameters = 312, final difference map within 0.589 and -0.452 e\AA^{-3} . For **3**, S(2) and C(18) are disordered (thiophene ring flip) with ca. $76/24$ occupancy ratio; the disorder was treated by occupancy refinement: S(2), occ. = 0.87; C(18), occ. = 1.24. A fully configured disorder model with complete alternative ring orientations could not be supported by the excellent, but nonetheless inadequate, resolution in the diffraction data. A full model would have required constrained bond distances and angles, and thus could not provide any additional information about this structure not now provided by the more realistic occupancy based refinement methods

used. The hydrogen atom H13A was located from the difference map since C13, by virtue of its coordination to Cu, creates an uncertain environment for the associated H atom and there is no clear idealization of C13 and therefore the location of H13a cannot be idealized.

For **4**: $C_{34}H_8Cu_4F_{20}$, $M_r = 1050.56$, triclinic, space group $P-1$, $a = 9.2770(11)$, $b = 9.2816(10)$, $c = 10.6576(11)$ Å, $\alpha = 69.563(3)^\circ$, $\beta = 72.278(2)^\circ$, $\gamma = 74.354(3)^\circ$, $V = 805.27(15)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 2.166$ g cm⁻³, $\lambda(\text{CuK}\alpha) = 1.54178$ Å, $T = 100(2)$ K, crystal dimensions 0.39 x 0.35 x 0.29 mm³, $\mu(\text{CuK}\alpha) = 4.334$ mm⁻¹, θ range from 4.55 to 64.87, 5335 measured reflections, 2452 independent reflections ($R_{\text{int}} = 0.0200$), $RI [I > 2(I)] = 0.0276$, $wR2 [I > 2(I)] = 0.0724$, GOF = 1.175, No. of parameters = 263, final difference map within 0.315 and -0.282 eÅ⁻³.

For **5**: $C_{32}H_6Cu_4F_{20}S_2$, $M_r = 1088.65$, triclinic, space group $P-1$, $a = 11.0271(7)$, $b = 11.5270(7)$, $c = 14.6181(10)$ Å, $\alpha = 86.590(3)^\circ$, $\beta = 82.263(3)^\circ$, $\gamma = 61.462(2)^\circ$, $V = 1617.46(18)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 2.235$ g cm⁻³, $\lambda(\text{CuK}\alpha) = 1.54178$ Å, $T = 100(2)$ K, crystal dimensions 0.34 x 0.30 x 0.13 mm³, $\mu(\text{CuK}\alpha) = 5.522$ mm⁻¹, θ range from 4.37 to 67.78, 13129 measured reflections, 5277 independent reflections ($R_{\text{int}} = 0.0186$), $RI [I > 2(I)] = 0.0283$, $wR2 [I > 2(I)] = 0.0717$, GOF = 1.207, No. of parameters = 523, final difference map within 0.395 and -0.366 eÅ⁻³.

CCDC 664119-664122 contain the supplementary crystallographic data. 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).

- [1] A. Cairncross, W. A. Sheppard, E. Wonchoba, W. J. Guildford, C. B. House, R. M. Coates, *Org. Synth.* **1980**, *59*, 122.
- [2] G. M. Sheldrick, SADABS, Version 2. Multi-Scan Absorption Correction Program, University of Göttingen, Germany, 2001.
- [3] G. M. Sheldrick, *SHELXTL*, Version 6.14, Bruker AXS Inc., Madison, WI, 2004.