

Binary stacks of [CuC₆F₅]₄ with arenes†

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Received (in Berkeley, CA, USA) 28th April 2008, Accepted 6th June 2008

First published as an Advance Article on the web 25th July 2008

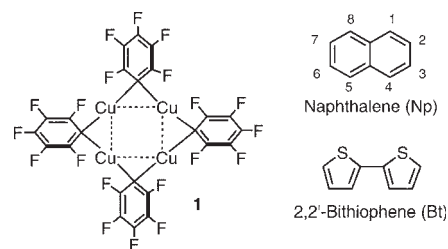
DOI: 10.1039/b807128d

Formation of the first binary stacks of an intact organocopper aggregate with the arenes naphthalene and 2,2'-bithiophene is reported; crystallographic data suggest that the supramolecular assembly process is supported by Cu– π , Cu–S, and perfluoro-arene–arene π -interactions.

Polynuclear coinage–metal complexes are known to form fascinating supramolecular structures with unusual luminescence behaviour.¹ Many of their exciting properties originate from a pronounced tendency for formation of stacks through metalphilic interactions. Another interesting motif is that of binary structures, where polynuclear complexes interact with arenes. For instance, stacking of trinuclear silver(i) pyrazolates [$\{[3,5-(CF_3)_2pz]Ag\}_3$] (pz = pyrazolate) with electron rich arenes (benzene, mesitylene and toluene) has been demonstrated.² The trimeric organomercury species [$\{(o-C_6F_4)Hg\}_3$] also forms one-dimensional stacks with arenes, which in turn show strong phosphorescence due to the heavy atom effect of Hg.³ Fluorination of the ligand is a key feature that supports complex formation with these metal complexes. The reverse situation is encountered with electron-rich trinuclear gold complexes such as [$\{(RN=COMe)Au\}_3$], which bind to electron-poor arenes.⁴ In yet another twist, this Au₃ trimer forms alternating stacks with [$\{(o-C_6F_4)Hg\}_3$].⁵

Polynuclear copper species and their assembly are comparatively less explored. A particularly interesting building block is [C₆F₅Cu]₄ (**1**), because the electron-deficient perfluorophenyl rings support the binding of even weakly basic substrates and allow for formation of unusual supramolecular structures.⁶ Compound **1** itself exists in the solid state as a tetrameric aggregate, which is maintained in weakly or non-coordinating solvents, but breaks up in the presence of strong donor solvents.^{7,8} For instance, upon addition of an equimolar amount of pyridine the monomeric units [C₆F₅Cu(Py)] are formed, which in the solid state assemble into highly luminescent one-dimensional Cu(i) chains with unusually short Cu···Cu separations of 2.8924(3) Å.⁹ In contrast, toluene binds to the *intact* tetramer in a 2 : 1 ratio to form the π -complex **1**·(tol)₂⁸ in a rare example of complexation of aromatic species to Cu(i)^{10,11} that is unique in organocopper

chemistry.¹² We demonstrate here for the first time how multiple interactions of this type lead to luminescent supramolecular structures that feature an intact organocopper aggregate (**1**) as the building block.



Treatment of **1** or **1**·(tol)₂ in CH₂Cl₂ with two equiv. of naphthalene (Np) and 2,2'-bithiophene (Bt), respectively, and subsequent low-temperature crystallization by careful layering with hexanes gave colorless crystals of the bis-adducts **1**·(arene)₂ (**2**, arene = Np; **3**, arene = Bt) in high yields. The 1:1 complex $\{1\text{-arene}\}_n$ (**5**, arene = Bt) was similarly obtained in 88% yield from a 1 : 1 mixture of **1**·(tol)₂ and Bt. However, the respective complex with Np (**4**) could only be obtained in a mixture with the bis-adduct **2**. All compounds form colorless crystals, but the different adducts are easily distinguished since **2** and **3** form needles, while **4** and **5** give plate-like crystals. Complexation was further confirmed by NMR, elemental analysis and X-ray diffraction studies. The ¹H and ¹⁹F NMR spectra of the adducts in CDCl₃ show similar chemical shifts as the corresponding precursors, which not only confirms that both building blocks are incorporated into the products, but also suggests that dissociation takes place in solution.

Single-crystal X-ray structure analyses (see ESI†) were performed for all complexes and the plots are displayed in Fig. 1 and 2. They reveal sandwich-like structures of the intact tetramer **1** and the corresponding arene in **2** and **3**, and the

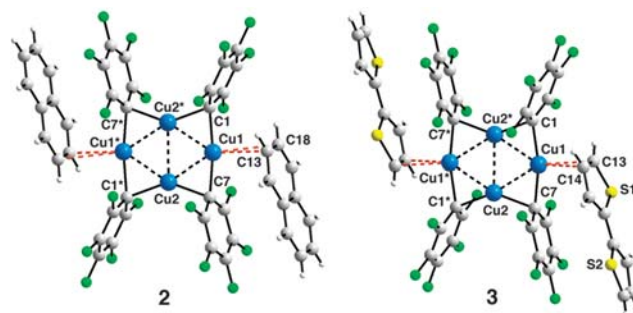


Fig. 1 Plots of the structures of **2** and **3**. Symmetry operations used to generate equivalent atoms for **2**: $-x + 2, -y + 1, -z + 1$. For **3**: $-x + 1, -y + 1, -z$.

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† Electronic supplementary information (ESI) available: Experimental procedures and data. CCDC 664119–664122. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b807128d

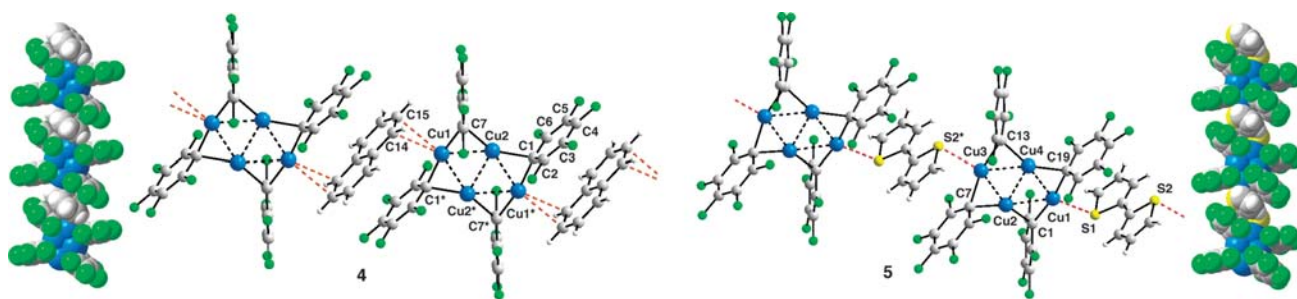


Fig. 2 Plots of the polymeric structures of **4** and **5** and plots illustrating their extended structures. Symmetry operations used to generate equivalent atoms for **4**: $-x + 2, -y + 1, -z + 2$; $-x + 1, -y + 2, -z + 2$; $x - 1, y + 1, z$. For **5**: $x - 1, y + 1, z$.

formation of highly unusual one-dimensional binary stacks in **4** and **5**. For all structures, the four copper atoms of the $[\text{C}_6\text{F}_5\text{Cu}]_4$ building block form a rhombus-like geometry with one short (2.58–2.68 Å) and one long diagonal $\text{Cu}\cdots\text{Cu}$ distance (4.14–4.22 Å) (Table 1). This structural motif is similar to that found for other arylcopper donor complexes^{13,14} and contrasts the square planar arrangement typically observed for the respective base-free complexes, including that of **1**. The Cu tetramer in **2**, **3** and **4** sits on a crystallographic inversion centre, meaning that the Cu atoms at opposite corners are equivalent and the Cu_4 core is planar. While the structure of **5** does not feature this inversion symmetry, the Cu_4 unit shows only a slight deviation from planarity with an interplanar angle $\text{Cu1-Cu2Cu4//Cu2Cu3Cu4}$ of 6.31° , in stark contrast to the angle of 37.53° observed for **1**-(tol)₂.⁸ It is also interesting to note that the C–Cu–C angles for the arene-complexed Cu atoms are considerably wider than in **1**-(tol)₂ and the Cu atoms in complexes **2–5** actually point toward the arene.

Secondary $\text{Cu}\cdots\pi$ interactions are observed for the sandwich-like structures, **2** and **3**. The two copper atoms that are furthest apart from one another engage in interactions with the arene molecules. The difference in the $\text{Cu}\cdots\text{C}$ distances of 2.643(4) and 2.910(4) Å for **2** is reminiscent of the typical unsymmetric η^2 -binding of arenes to Cu(I). They are considerably longer than those observed for **1**-(tol)₂⁸ or other Np complexes of Cu(I) (2.129–2.414 Å).¹¹ However, they are well within the sum of the van der Waals radii for Cu ($r_{\text{vdw}} = 1.40$ Å) and C ($r_{\text{vdw}} = 1.70$ Å). It should be emphasized that the thiophene moiety in **3**

is not bound through S, but rather also engages in π -interactions with slightly shorter $\text{Cu}\cdots\text{C}$ distances in comparison to those observed for **2**.^{11,15} The thiophene rings are slightly tilted with an interplanar angle of $\text{Th//Th} = 8.32^\circ$.

When studying the respective 1 : 1 complexes **4** and **5** we discovered that they form highly unusual extended binary stacks in the solid state, where the intact tetramer **1** alternates with the arene (Fig. 2). One of the aromatic rings of the Np and Bt moiety, respectively, interacts with the Cu_6F_5 group of one copper tetramer and the second ring shows short contacts to that of another tetramer. A comparison of the $\text{Cu}\cdots\pi$ interactions for **2** and **4** shows that the former interacts through the 2,3-positions, while the latter forms short contacts to the 1,2-positions of naphthalene. Even more surprisingly, short Cu–S contacts lead to the extended structure of **5**, in stark contrast to the $\text{Cu}\cdots\pi$ motif of **3**. The sulfur atoms coordinate to copper with Cu–S distances of 2.5389(8) and 2.5356(7) Å, respectively, which are within the sum of the van der Waals radii for Cu ($r_{\text{vdw}} = 1.40$ Å) and S ($r_{\text{vdw}} = 1.80$ Å). The contacts are slightly longer than those reported in the literature for thioether adducts of organocopper tetramers (2.316–2.407 Å),¹⁴ which is to be expected based on the lower basicity of the thiophene S atom. The structure of **5** is highly unusual as there are very few known examples of thiophene coordinating to Cu(I) and the $\text{Cu}\cdots\text{S}$ distances for **5** are the shortest reported to date.¹⁶

As can be seen from the extended structures shown in Fig. 2, arene binding is further supported by perfluoroarene–arene π -interactions¹⁷ with the shortest arene (centroid) $\cdots\text{C}$ contacts being 3.358, 3.270, 3.360 and 3.332 Å to the Cu-bound *ipso*-carbon of the C_6F_5 groups for **2**, **3**, **4** and **5**, respectively. These distances are in a range typically associated with strong π -interactions. Ring slippage is evident from slightly longer centroid–centroid distances between the perfluorophenyl group and the respective arenes (3.599–3.802 Å).

Finally, we discovered that irradiation of solid samples of the Bt complexes, **3** and **5**, with a hand-held UV lamp leads to strong yellow luminescence at RT ($\lambda_{\text{em}} = 540$ nm, see Fig. 3). Due to the presence of triplet states that lie below the singlet excited S_1 state, 2,2'-bithiophene itself shows only very weak blue fluorescence at 390 nm; moreover, relaxation from the triplet states is radiationless and no phosphorescence can be detected.¹⁸ The parent tetramer **1** also gives no observable luminescence at RT, and emits red light at 77 K. While the exact origin of the yellow RT emission of **3** and **5** is difficult to

Table 1 Comparison of selected geometric parameters (Å, °)^a

	1 -(Np) ₂ (2)	1 -(Bt) ₂ (3)	{ 1 -(Np) _n } (4)	{ 1 -(Bt) _n } (5)
$\text{Cu}_{\text{nb}}\cdots\text{Cu}_{\text{nb}}^c$	2.6343(11)	2.5866(6)	2.6779(8)	2.6556(5)
$\text{Cu}_{\text{b}}\cdots\text{Cu}_{\text{b}}^c$	4.1796(11)	4.2220(6)	4.1401(8)	4.1468(6)
$\text{C}_{\text{Pr}}\text{--Cu}_{\text{nb}}\text{--C}_{\text{Pr}}$	140.8(2)	139.56(8)	142.66(11)	142.09(11)
$\text{C}_{\text{Pr}}\text{--Cu}_{\text{b}}\text{--C}_{\text{Pr}}$	167.7(2)	166.96(9)	169.48(11)	143.55(10)
				169.36(10)
				159.61(11)
$\text{Cu}\cdots\text{C}(\pi)$	2.643(4)	2.507(2)	2.665(3)	2.5389(8) ^b
	2.910(4)	2.706(2)	2.815(3)	2.5356(7) ^b

^a $\text{Cu}_{\text{b}}/\text{Cu}_{\text{nb}}$: Cu that is bound/not bound to the arene; C_{Pr} : *ipso*-C of the C_6F_5 moiety. ^b $\text{Cu}\cdots\text{S}$ distance. ^c Symmetry operations used to generate equivalent Cu atoms for **2** $-x + 2, -y + 1, -z + 1$; for **3** $-x + 1, -y + 1, -z$; for **4** $-x + 1, -y + 2, -z + 2$.

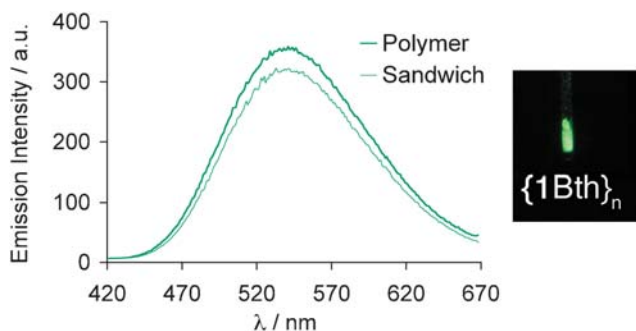


Fig. 3 Luminescence spectra of **3** and **5** at RT ($\lambda_{\text{exc}} = 365$ nm) and photograph of a solid sample of **5** irradiated with a UV lamp (365 nm) at RT.

assign and the subject of current detailed photophysical studies, the observation of RT luminescence is clearly related to the cocrystallization of bithiophene with **1**.^{19,20}

In conclusion, we report the first example of supramolecular assembly of organocopper aggregates through Cu $\cdots\pi$ and Cu \cdots S interactions. The stacked structures with [C₆F₅Cu]₄ are highly unusual and have been observed for the first time in the case of organocopper aggregates. The discovery of RT luminescence will be the subject of in-depth photophysical and theoretical studies.

We gratefully acknowledge support by the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (NSF CRIF-0443538). F. J. thanks the Alfred P. Sloan Foundation for a research fellowship and the NSF for a CAREER award (CHE-0346828).

Notes and references

- (a) Y.-A. Lee and R. Eisenberg, *J. Am. Chem. Soc.*, 2003, **125**, 7778; (b) G. Yang and R. G. Raptis, *Inorg. Chem.*, 2003, **42**, 261; (c) R. L. White-Morris, M. M. Olmstead, S. Attar and A. L. Balch, *Inorg. Chem.*, 2005, **44**, 5021; (d) A. Kishimura, T. Yamashita and T. Aida, *J. Am. Chem. Soc.*, 2005, **127**, 179; (e) H. V. R. Dias, H. V. K. Diyabalanage, M. G. Eldabaja, O. Elbjeirami, M. A. Rawashdeh-Omary and M. A. Omary, *J. Am. Chem. Soc.*, 2005, **127**, 7489.
- H. V. R. Dias, C. S. P. Gamage, J. Keltner, H. V. K. Diyabalanage, I. Omari, Y. Eyobo, N. R. Dias, N. Roehr, L. McKinney and T. Poth, *Inorg. Chem.*, 2007, **46**, 2979.
- (a) M. R. Haneline, M. Tsunoda and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2002, **124**, 3737; (b) C. N. Burrell, M. I. Bodine, O. Elbjeirami, J. H. Reibenspies, M. A. Omary and F. P. Gabbaï, *Inorg. Chem.*, 2007, **46**, 1388.
- A. A. Mohamed, M. A. Rawashdeh-Omary, M. A. Omary and J. P. Fackler, Jr, *Dalton Trans.*, 2005, 2597.
- A. Burini, J. P. Fackler, Jr, R. Galassi, A. Macchioni, M. A. Omary, M. A. Rawashdeh-Omary, B. R. Pietroni, S. Sabatini and C. Zuccaccia, *J. Am. Chem. Soc.*, 2002, **124**, 4570.
- F. Jäkle, *Dalton Trans.*, 2007, 2851.
- A. Cairncross, H. Omura and W. A. Sheppard, *J. Am. Chem. Soc.*, 1971, **93**, 248.
- A. Sundararaman, R. A. Lalancette, L. N. Zakharov, A. L. Rheingold and F. Jäkle, *Organometallics*, 2003, **22**, 3526.
- A. Sundararaman, L. N. Zakharov, A. L. Rheingold and F. Jäkle, *Chem. Commun.*, 2005, 1708.
- (a) R. G. Solomon and J. K. Kochi, *J. Chem. Soc., Chem. Commun.*, 1972, 559; (b) M. Pasquali, C. Floriani and A. Gaetani-Manfredotti, *Inorg. Chem.*, 1980, **19**, 1191; (c) R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, 1966, **88**, 1877; (d) M. B. Dines and P. Bird, *J. Chem. Soc., Chem. Commun.*, 1973, 12; (e) H. Schmidbaur, W. Bublak, B. Huber, G. Reber and G. Müller, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1089; (f) A. M. Dattelbaum and J. D. Martin, *Inorg. Chem.*, 1999, **38**, 6200; (g) D. S. Laitar, C. J. N. Mathison, W. M. Davis and J. P. Sadighi, *Inorg. Chem.*, 2003, **42**, 7354; (h) Y. M. Badiei and T. H. Warren, *J. Organomet. Chem.*, 2005, **690**, 5989; (i) S.-B. Zhao, R.-Y. Wang and S. Wang, *Inorg. Chem.*, 2006, **45**, 5830; (j) E. D. Blue, T. B. Gunnoe, J. L. Petersen and P. D. Boyle, *J. Organomet. Chem.*, 2006, **691**, 5988; (k) Y. Sevryugina and M. A. Petrukhina, *Eur. J. Inorg. Chem.*, 2007, 219; (l) Y. Sevryugina, O. Hietsoi and M. A. Petrukhina, *Chem. Commun.*, 2007, 3853.
- R. R. Conry, W. S. Striejewske and A. A. Tipton, *Inorg. Chem.*, 1999, **38**, 2833.
- Cu $\cdots\pi$ interactions have been observed in organometallic chelates: M. Niemeyer, *Organometallics*, 1998, **17**, 4649.
- E. Wehman, G. van Koten, M. Knotter, H. Spelten, D. Heijdenrijk, A. N. S. Mak and C. H. Stam, *J. Organomet. Chem.*, 1987, **325**, 293.
- (a) S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1983, 1156; (b) D. M. Knotter, W. J. J. Smeets, A. L. Spek and G. van Koten, *J. Am. Chem. Soc.*, 1990, **112**, 5895; (c) M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1990, **112**, 8008; (d) B. Lenders, D. M. Grove, W. J. J. Smeets, P. van der Sluis, A. L. Spek and G. van Koten, *Organometallics*, 1991, **10**, 786.
- (a) Indole was found to bind to Cu(I) through C rather than N: Y. Shimazaki, H. Yokoyama and O. Yamauchi, *Angew. Chem., Int. Ed.*, 1999, **38**, 2401; (b) A benzophospholide ligand that is π -bound to Cu(I) has been reported: D. Gudat, M. Nieger, K. Schmitz and L. Szarvas, *Chem. Commun.*, 2002, 1820.
- L. R. Hanton, C. Richardson, W. T. Robinson and J. M. Turnbull, *Chem. Commun.*, 2000, 2465, and references therein.
- (a) C. R. Patrick and G. S. Prosser, *Nature*, 1960, **187**, 1021; (b) J. C. Collings, K. P. Roscoe, R. L. Thomas, A. S. Batsanov, L. M. Stimson, J. A. K. Howard and T. B. Marder, *New J. Chem.*, 2001, **25**, 1410; (c) A. S. Batsanov, J. C. Collings, J. A. K. Howard, T. B. Marder and D. M. Perepichka, *Acta Crystallogr., Sect. C*, 2001, **57**, 1306; (d) C. E. Smith, P. S. Smith, R. L. Thomas, E. G. Robins, J. C. Collings, C. Dai, A. J. Scott, S. Borwick, A. S. Batsanov, S. W. Watt, S. J. Clark, C. Viney, J. A. K. Howard, W. Clegg and T. B. Marder, *J. Mater. Chem.*, 2004, **14**, 413; (e) S. W. Watt, C. Dai, A. J. Scott, J. M. Burke, R. L. Thomas, J. C. Collings, C. Viney, W. Clegg and T. B. Marder, *Angew. Chem., Int. Ed.*, 2004, **43**, 3061; (f) K. Reichenbacher, H. I. Süß and J. Hulliger, *Chem. Soc. Rev.*, 2005, **34**, 22; (g) J.-P. Zhang, Y.-B. Wang, X.-C. Huang, Y.-Y. Lin and X.-M. Chen, *Chem. Eur. J.*, 2005, **11**, 552; (h) S. Bacchi, M. Benaglia, F. Cozzi, F. Demartin, G. Filippini and A. Gavezzotti, *Chem. Eur. J.*, 2006, **12**, 3538; (i) A. Hori, A. Shinohe, M. Yamasaki, E. Nishibori, S. Aoyagi and M. Sakata, *Angew. Chem., Int. Ed.*, 2007, **46**, 7617.
- (a) S. Y. Yang, Y. H. Kan, G. C. Yang, Z. M. Su and L. Zhao, *Chem. Phys. Lett.*, 2006, **429**, 180; (b) B. Gombojav, N. Namsrai, T. Yoshinari, S. Nagasaka, H. Itoh and K. Koyama, *J. Solid State Chem.*, 2004, **177**, 2827; (c) R. S. Becker, J. Seixas de Melo, A. L. Macüanita and F. Elisei, *J. Phys. Chem.*, 1996, **100**, 18683.
- The naphthalene derivative **2** is like the parent base-free organocopper tetramer **1** only very weakly luminescent at RT. However, at 77 K yellow luminescence can be also observed for **2**.
- For reviews on the photophysical properties of Cu(I) compounds, see: (a) P. C. Ford, E. Cariati and J. Bourassa, *Chem. Rev.*, 1999, **99**, 3625; (b) V. W.-W. Yam and K. K.-W. Lo, *Chem. Soc. Rev.*, 1999, **28**, 323.