

CuCN Pillars Induce Face-to-Face  $\pi$ -Overlap of Anthracene-Based Thioether Molecules within a Hybrid Coordination NetworkYan-Qiong Sun,<sup>†</sup> Chun-Kwan Tsang,<sup>†</sup> Zhengtao Xu,<sup>\*,†</sup> Guo Huang,<sup>†</sup> Jun He,<sup>†</sup> Xiao-Ping Zhou,<sup>†</sup> Matthias Zeller,<sup>‡</sup> and Allen D. Hunter<sup>‡</sup>*Department of Biology and Chemistry, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong, P. R. China, and Department of Chemistry, Youngstown State University, One University Plaza, Youngstown, Ohio 44555*

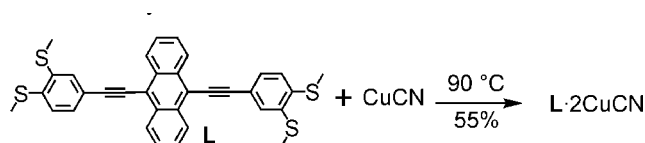
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**ABSTRACT:** The large aromatic ligand 9,10-bis[3,4-bis(methylthio)phenyl]ethynyl]anthracene (**L**) interacts with CuCN to form a 2D, fluorescent hybrid network, **L**·2CuCN. Although the edge-to-face stacking between the organic  $\pi$ -electron systems prevails in the molecular crystal structure of **L**, the face-to-face stacking becomes more distinct in **L**·2CuCN. A preliminary survey on similar hybrid networks in the Cambridge Structural Database (CSD) suggests that 1D inorganic moieties may help maintain and induce cofacial stacking of the associated aromatic ligands.

**Introduction.** Crystal packing closely impacts electronic properties of potential organic semiconductors such as the intensely studied oligothiophenes, anthracenes and pentacenes. It is generally recognized that effective face-to-face stacking of the aromatic cores tends to maximize the  $\pi$ -orbital overlap that is crucial for the charge transport processes in these molecular electronic materials.<sup>1</sup> A number of approaches have been explored to promote face-to-face stacking of aromatic molecules in the solid state.<sup>2–4</sup> For example, Anthony and co-workers demonstrated the effectiveness of bulky substituents in preventing C–H $\cdots\pi$  interactions and enhancing the cofacial  $\pi$ -stacking of pentacene units.<sup>3</sup> In comparison to the above molecular functionalization, MacGillivray's group recently introduced directional intermolecular hydrogen bonding as an effective medium for organizing semiconductive building units into the face-to-face stacking mode.<sup>4</sup> This latter approach is of particular interest, because of its intent to import the rational design principles that have proven effective for the assembly of supramolecular structures and solid state networks.<sup>5</sup>

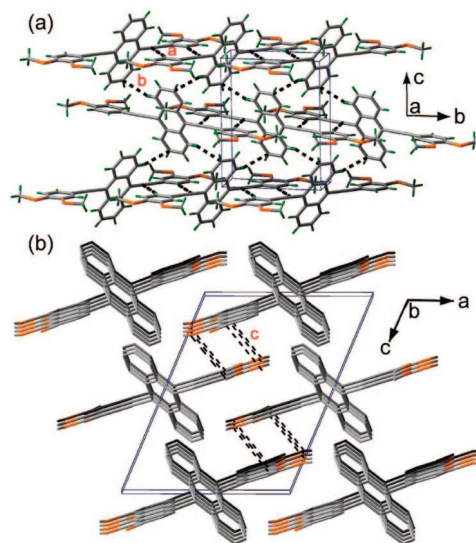
As a preliminary step to explore alternative methods for enforcing cofacial stacking of aromatic molecules, we here present the crystal structure of a coordination network based on 9,10-bis[3,4-bis(methylthio)phenyl]ethynyl]anthracene (**L**) and CuCN, which features chains of the CuCN component interconnected by the thioether ligand (network composition: **L**·2CuCN). We demonstrate that, while the edge-to-face stacking between the organic  $\pi$ -electron systems is predominant in the molecular crystal structure of **L**, molecules of **L** in the network of **L**·2CuCN are organized into the face-to-face stacking mode with significant aromatic  $\pi$ - $\pi$  interaction. To probe the generality of this observation, we will also discuss the molecular packing motifs in a series of hybrid coordination networks retrieved from the Cambridge Structural Database (CSD).

The synthesis and crystallization of compound **L** are included in the Supporting Information. Complex **L**·2CuCN was prepared by treating **L** with CuCN in acetonitrile/benzene at 90 °C for 72 h (see Scheme 1).<sup>6</sup> Compound **L** crystallizes in the space group  $P2_1/n$ , with the **L** molecule adopting a centrosymmetric conformation in which the phenyl rings are twisted 65.2° with respect to the anthracene plane.<sup>7</sup> The molecules of **L** are aligned into columns along the crystallographic  $b$  axis, in which the anthracene and acetylene units of the molecules are arranged in a parallel fashion (Figure 1a). The neighboring molecules are significantly offset (i.e., slipped by 59.2°), and the nonplanar shape of **L** results in no significant face-to-face  $\pi$ - $\pi$  interactions around the ethynylan-

Scheme 1. Synthesis of **L**·2CuCN

thracene unit. Instead, the anthracene unit forms extensive edge-on C–H $\cdots\pi$  contacts with the phenyl and anthracene groups from neighboring molecules (see Figure 1a). These C–H $\cdots\pi$  interactions organize the molecules into layers in the (101) plane (Figure 1a), and the only face-to-face interactions exist between the bis(methylthio)phenyl groups across the layers (e.g., C $\cdots$ S, 3.616 Å, see Figure 1b).

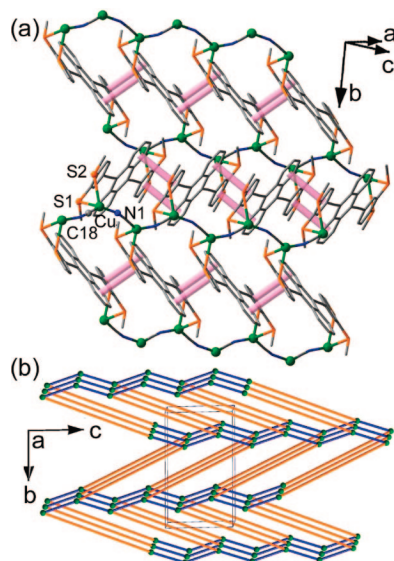
By comparison, the molecules of **L** in the complex **L**·2CuCN take on a more planar conformation, and significant face-to-face  $\pi$ - $\pi$  interactions are induced around the anthracene units. As shown



**Figure 1.** (a) Layer of **L** molecules and two types of edge-on C–H $\cdots\pi$  contacts (C $\cdots$ H distances:  $a$ , 2.899 Å and  $b$ , 2.805 Å); (b) side view of the layers of **L** and the C $\cdots$ S contacts of the face-to-face interaction between the bis(methylthio)phenyl groups across the layers. The intermolecular contacts are shown as black dotted lines. Color code: S, orange; C, grey; H, green.

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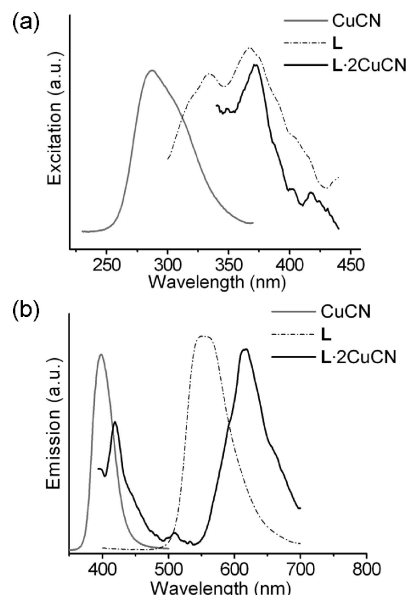


**Figure 2.** (a) 2D coordination network of  $L \cdot 2CuCN$ , showing that all  $L$  molecules on the same side of the  $CuCN$  chain are involved in offset face-to-face  $\pi$ - $\pi$  interactions between the phenyl rings and the anthracene rings. Interactions are shown as pink sticks. Color code: Cu, green; S, orange; C, grey; N, blue. (b) The topology of the structure of  $L \cdot 2CuCN$ , and the packing of honeycomb sheets. The  $L$  ligands and cyano linkers are shown as orange and blue rods, respectively.

in Figure 2, the  $CuCN$  component forms parallel zigzag chains with an  $N-Cu-C$  angle of  $141.66(9)^\circ$  ( $Cu-N$  distances:  $1.885(2)$  and  $1.916(2)$  Å). The  $Cu(I)$  ion is further chelated by two sulfur atoms from the  $L$  molecule to form a distorted tetrahedral coordination sphere ( $Cu-S$  distances:  $2.5737(8)$  and  $2.6553(8)$  Å). The coordination between the  $L$  ligands and the inorganic  $CuCN$  chains results in a distorted 2D honeycomb net along the  $bc$  plane (Figure 2b), with the  $Cu(I)$  atoms serving as 3-connected nodes and the  $L$  ligands and cyano groups as linear bridges. The  $L$  ligands, with an almost planar conformation (the phenyl rings are twisted only  $8.45^\circ$  with respect to the anthracene plane), are organized into columns that are parallel and alternate with the  $CuCN$  chains within the honeycomb sheet. The neighboring  $L$  molecules are packed in an offset manner to generate face-to-face  $\pi$ - $\pi$  interactions between the phenyl ring and the anthracene unit with an interplanar separation of ca.  $3.35$  Å.

As part of our ongoing effort to promote electronic interaction across organic molecules and inorganic components within hybrid networks,<sup>8</sup> we here present the photoexcitation and luminescence spectra on the solid samples of molecule  $L$  and network  $L \cdot 2CuCN$  (Figure 3). Molecule  $L$  and  $CuCN$  in their separate solid state forms feature emission peaks at  $549$  and  $400$  nm, respectively. The complex  $L \cdot 2CuCN$ , by comparison, gives an emission maximum at  $614$  nm, which is red-shifted by  $75$  nm from the emission peak of the pure ligand. This significant red shift observed for  $L \cdot 2CuCN$ , as well as its different peak profile (e.g., slower slope and shouldering features), could be ascribed to the different packing motif of the molecules as well as the electronic interaction across the  $L$  molecules and the  $CuCN$  chains. Complex  $L \cdot 2CuCN$  also features an emission peak at  $420$  nm, with a  $20$  nm red shift compared with the corresponding emission from pure  $CuCN$ . This emission is generally ascribed to the  $Cu$ -centered transitions of the type  $3d \rightarrow (4s, 4d)$ .<sup>9</sup>

Comparison of the structures of  $L$  and  $L \cdot 2CuCN$  has made us wonder if the inorganic component might help enforce cofacial stacking of the organic ligands in other coordination hybrids. Of particular interest are 1D inorganic moieties that serve as rigid pillars for anchoring organic molecules with coordination bonds. Because of the translational symmetry along the pillar, the individual molecular planes within such an organic-inorganic 1D structure



**Figure 3.** (a) Solid-state excitation spectra for  $CuCN$  ( $\lambda_{em} = 400$  nm),  $L$  ( $\lambda_{em} = 549$  nm) and  $L \cdot 2CuCN$  ( $\lambda_{em} = 614$  nm) at room temperature; (b) solid-state emission spectra for  $CuCN$  ( $\lambda_{ex} = 284$  nm),  $L$  ( $\lambda_{ex} = 360$  nm) and  $L \cdot 2CuCN$  ( $\lambda_{ex} = 372$  nm) at room temperature.

might be forced into a parallel array; in other words, the edge-to-face mode might not be as compatible with the periodicity of the inorganic pillar. We suspected that the parallel array thus imposed might help induce the cofacial stacking and suppress the edge-to-face stacking, especially along the pillar direction.

To test this idea, we looked to the hybrids of large aromatic molecules and polymeric metal halides (systems of  $CuCN$  chains and large aromatic molecules are relatively rare). From the hits of a CSD search, we selected structures (20 in total) with large (i.e., with three or more fused rings), planar aromatic molecules bonded to 1D metal halide components, and compared the packing motifs with those of the corresponding molecular crystal structures (see the Supporting Information for the query and the cif files exported). The molecules in these hits are generally pyridyl-based fused aromatics (e.g., acridine, phenanthrolines and phenazine).

The 20 hybrids all feature parallel stacks of the molecules (and consequently, cofacial stacking, see also Table S1 and Figures S2–S12 in the Supporting Information) along the inorganic pillar. Notably,  $C-H \cdots \pi$  interactions are observed in only five of the hybrids (these contain 1,7- and 3,7-phenanthrolines, and acridine), and such interactions only exist across the stacks. By contrast,  $C-H \cdots \pi$  interaction occurs in most molecular crystals—the only one that lacks  $C-H \cdots \pi$  interaction is 2,7-diazapyrene (see Table S1 and Figures S2–S12 in the Supporting Information). The contrast is especially strong in the situation of 1,10-phenanthroline: although the molecular crystal features extensive  $C-H \cdots \pi$  interaction and no cofacial stacking, the 10 hybrids uniformly feature cofacial stacking (with interplanar distances down to  $3.24$  Å) and no  $C-H \cdots \pi$  interaction.

The maintenance and inducement of the cofacial stacking are therefore quite apparent in the above hybrid nets. It remains to be seen how the electronic transport properties of the hybrid might differ from the molecular systems, be it because of the new stacking propensities of the molecules or the interaction with the inorganic moieties throughout the hybrid net.

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**Supporting Information Available:** X-ray crystallographic data for **L** and **L**·2CuCN in CIF format; CSD search results in CIF format (CSDmolecules.cif and CSDhybrid.cif); description of experimental procedures, additional figures of crystal structures, X-ray powder diffraction patterns of **L** and **L**·2CuCN, and solution fluorescence spectra for **L** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (6) Complex **L**·2CuCN was synthesized as follows: **L** (5.6 mg, 10.0  $\mu\text{mol}$ ) and CuCN (2.6 mg, 30.0  $\mu\text{mol}$ ) were loaded into a heavy-wall glass tube, and acetonitrile (0.2 ml, anhydrous) and benzene (0.8 ml, anhydrous) were then added. The tube was then sealed and heated at 90 °C in an oil bath for 72 h followed by naturally cooling down to rt, during which red blocklike single crystals suitable for single-crystal X-ray diffraction were formed (4.1 mg, 55% yield based on **L**). Anal. Calcd for  $\text{C}_{36}\text{H}_{26}\text{S}_4\text{Cu}_2\text{N}_2$ : C, 58.28; H, 3.53; N, 3.78. Found: C, 58.49; H, 3.73; N, 3.67.
- (7) Crystal data for **L**:  $\text{C}_{34}\text{H}_{26}\text{S}_4$ ,  $M_r = 562.83$ , monoclinic, space group  $P2_1/n$ ,  $a = 10.942(1)$  Å,  $b = 9.586(1)$  Å,  $c = 13.986(2)$  Å,  $\beta = 112.61(2)^\circ$ ,  $V = 1354.2(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho = 1.380$  g cm<sup>-3</sup>, GOF = 1.047,  $R_1 = 0.0428$ ,  $wR_2 = 0.1162$  [ $I > 2\sigma(I)$ ]. For **L**·2CuCN:  $\text{C}_{36}\text{H}_{26}\text{Cu}_2\text{N}_2\text{S}_4$ ,  $M_r = 741.91$ , monoclinic, space group  $P2_1/c$ ,  $a = 11.381(2)$  Å,  $b = 15.574(2)$  Å,  $c = 9.312(1)$  Å,  $\beta = 104.36(2)^\circ$ ,  $V = 1599.0(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho = 1.541$  g cm<sup>-3</sup>, GOF = 1.058,  $R_1 = 0.0399$ ,  $wR_2 = 0.0954$  [ $I > 2\sigma(I)$ ].
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