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Enforced Face-to-Face Stacking of Organic Semiconductor Building Blocks within Hydrogen-Bonded Molecular Cocrystals

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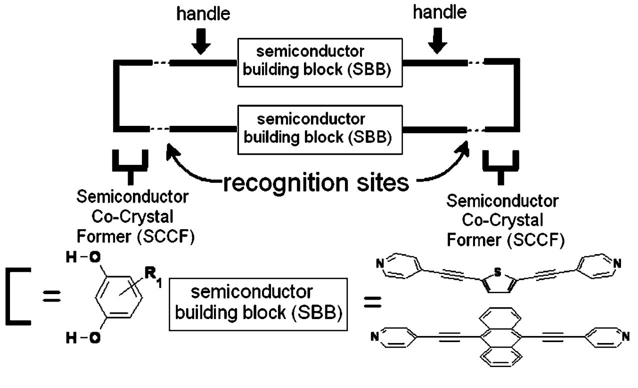
Enforced face-to-face stacking of aromatics in the solid state is an important topic in the field of semiconductor materials.[1] In this context, oligothiophenes, anthracenes, and related acenes (e.g., pentacene) have emerged as leading candidates for the construction of organic semiconductor crystalline solids. Many reports have underscored the importance of maximizing π-orbital overlap to achieve efficient charge transport properties of such solids.[1]

Efforts to promote face-to-face stacking of semiconductor molecules in the solid state have focused on the use of functional groups expected to direct the assembly process to the prerequisite packing.[2] The intermolecular forces used to promote such arrangements have, thus far, been relatively weak, being based on van der Waals and/or dipole−dipole interactions. The most successful implementation of this strategy has, arguably, involved pentacene, where steric effects of bulky substituents prevented $C-H\cdots\pi$ forces.[3] A much greater π-orbital overlap was achieved, as compared to pure pentacene. Admittedly, however, the amount of π-orbital overlap cannot be correlated to the size and position of the functional groups, owing to a difficulty to control slipping along the pentacene short axis.[3] Indeed, these observations attest to the sensitivity of crystal packing to changes to molecular structure and create a challenge to devise methods that employ stronger intermolecular forces to direct face-to-face stacking so as to be able to reliably optimize the performances of such organic semiconductor solids.

With this in mind, we wish to describe here an approach to control the organization of the aromatic rings of semiconductor molecules in the solid state that enforces face-to-face π-stacking using the strength and directionality of hydrogen bonds. In particular, our design involves cocrystallizing[4] a bifunctional molecule, hereafter referred to as a semiconductor cocrystal former (SCCF), with a semiconductor building block (SBB) functionalized with an appropriate recognition site, or "handle" (Scheme 1).[5] The SCCF thus employs hydrogen bonds[6] to segregate the structure of the SBB from vexatious effects of crystal packing so as to reliably enforce π-orbital overlap. Our initial experiments to test this strategy involve SBBs with a minimal number of thiophene and acene rings since such semiconductor units generally exhibit less π-orbital overlap in the solid-state owing to a high number of $C-H\cdots\pi$ forces.[7,8]

Scheme 1. General Scheme of Noncovalent Enforcement of Face-to-Face Stacking of Semiconductor Building Blocks



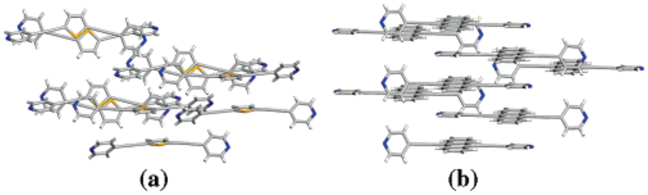


Figure 1. X-ray crystal structures of (a) **1** and (b) **2**.

The SCCF used in this study is based on 1,3-dihydroxybenzene, or resorcinol. We envisioned that a resorcinol could enforce face-to-face π-stacking of two SBBs based on thiophene and anthracene, namely 2,5-bis(4-pyridylethynyl)thiophene (**1**) and 9,10-bis(4-pyridylethynyl)anthracene (**2**). The parent SBBs (i.e., thiophene, anthracene) prefer herringbone packing, as demonstrated by both experimental and computational studies.[8] To provide recognition sites for the hydrogen bonds, the SBBs were functionalized with 4-pyridylacetylene handles.[9,10] The formulations of **1** and **2** were confirmed by ^{1}H NMR spectroscopy and single-crystal X-ray diffraction.[11]

As a control experiment, we examined the crystal structures of the functionalized SBBs **1** and **2** (i.e., in the absence of a SCCF).[11] Whereas the structure of **2** has been recently reported,[11] single crystals of **1** suitable for X-ray diffraction analysis were obtained by slow evaporation of CH_3CN. In the case of **1**, the solid[11] consists of dimeric assemblies sustained by $C-H_{\text{pyridine}}\cdots\pi_{\text{pyridine}}$ forces such that the thiophene rings lie approximately antiparallel and offset (Figure 1). The dimers interact in an offset and parallel manner via $C-H_{\text{thiophene}}\cdots N$ forces to form one-dimensional chains along the N−N axis. Dimers of adjacent chains lie approximately perpendicular, being held together by $C-H_{\text{pyridine}}\cdots N$ forces. The pyridyl groups of **1** lie twisted out of the plane of the thiophene ring by 38.7(3)° and 46.7(2)°. In the case of **2**, the pyridyl and anthracene groups participate in alternating face-to-face π-stacked arrays. Adjacent arrays are held together via $C-H_{\text{pyridine}}\cdots\pi_{\text{pyridine}}$, $C-H_{\text{pyridine}}\cdots\pi_{\text{anthracene}}$, and $\pi_{\text{pyridine}}-\pi_{\text{anthracene}}$ forces. In contrast to **1**, a single pyridyl group is twisted out of the plane of the central anthracene ring, being twisted by 64.5(1)°. As a consequence of these forces, extended face-to-face stacking of the SBBs is not observed in **1** and **2**, the closest centroid-to-centroid distances being 4.05 and 7.11 Å, respectively.

Having examined the crystal structures of each pure SBB, we cocrystallized **1** and **2** with a resorcinol. Specifically, cocrystals of composition 2(5-methylresorcinol)·2(**1**) (**3**) and 2(5-iodoresorcinol)·2(**2**) (**4**) were obtained by slow evaporation from CH_3CN and $CHCl_3$/MeOH 5:1 (v:v) solutions, respectively. The formulations of **3** and **4** were confirmed by ^{1}H NMR spectroscopy and single-crystal X-ray diffraction.

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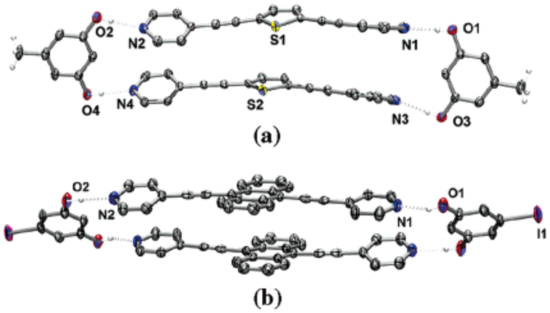

Figure 2. Hydrogen-bonded molecular assemblies of (a) **3** and (b) **4**.

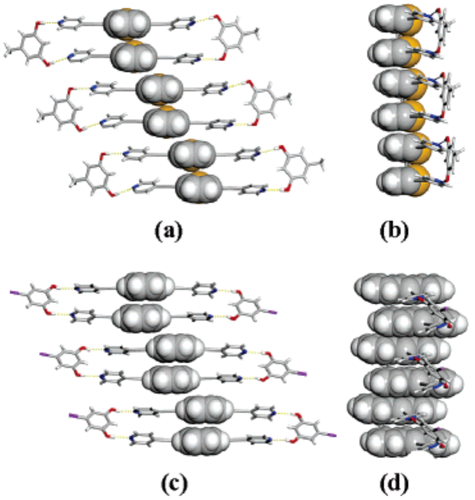

Figure 3. Views of face-to-face stacking of **3**: (a) perpendicular and (b) along the N−N axis and **4**: (c) perpendicular and (d) along the N−N axis.

As anticipated, the components of each solid have assembled to form four-component molecular assemblies held together by four O−H⋯N hydrogen bonds (Figure 2). Two complete assemblies and one-half of an assembly define the asymmetric units of **3** [O⋯N distances (Å): O1⋯N1 2.742(5), O2⋯N2 2.819(5), O3⋯N4 2.812(5), O4⋯N4 2.733(5), O5⋯N5 2.815(6), O6⋯N6 2.721(5), O7⋯N7 2.742(6), O8⋯N8 2.823(5)] and **4** [O⋯N distances (Å): O1⋯N1 2.735(5), O2⋯N2 2.782(5)], respectively. The latter sits around a center of inversion. Importantly, the functionalized SBBs of **3** (centroid⋯centroid distances: 3.75 and 3.80 Å) and **4** (centroid⋯centroid distance: 3.78 Å), in contrast to those of **1** and **2**, both participate in face-to-face π-stacking. For **3**, the bent thiophene units are oriented parallel.[12] To achieve the face-to-face arrangement, the stacked aromatic groups of each functionalized SBB lie approximately coplanar, varying in the angle of the twist with respect to the central ring.[13] In **3**, the coplanar orientation and twisting of the stacked pyridine and thiophene rings give rise to chiral assemblies that adopt helical conformations, which account for the two assemblies being in the asymmetric unit.

The coplanar conformations adopted by each functionalized SBB in **3** and **4** have led to extended face-to-face stacking of the SBBs and hydrogen-bonded assemblies in each solid. Specifically, the assemblies of **3** (SBB⋯SBB distances: 3.56 and 3.64 Å) and **4** (SBB⋯SBB distance: 3.44 Å) self-organize in slipped face-to-face arrangements (Figure 3). The face-to-face geometries can be ascribed to the larger van der Waals surfaces of the molecular assemblies, or supermolecules,[14] which enable each assembly to form an extended π-stacked structure.

In this report, we have described a new approach to enforce face-to-face stacking of the aromatic rings of semiconductor molecules in the solid state. Specifically, we have employed cocrystals involving SCCFs to stack SBBs in face-to-face arrangements. We are currently investigating the ability of this approach to serve as a synthon[14] to control face-to-face stacking of additional SBBs (e.g., larger) as well as hybrids. The electronic properties of these, and related, hydrogen-bonded solids will also be reported.

Acknowledgment. We are grateful to the University of Iowa Mathematical and Physical Sciences Funding program for support of this work.

Supporting Information Available: Synthesis of **1** and **2** and ^{1}H NMR and single-crystal data for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA057939A