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Partial Fluorination Overcomes Herringbone Crystal Packing in Small Polycyclic Aromatics[†]

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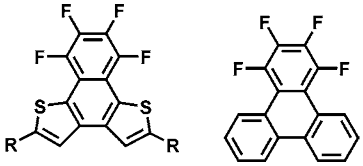
ABSTRACT



We report the synthesis and characterization of partially fluorinated condensed tetracyclic aromatic compounds. Typical edge-to-face/herringbone packing of nonfluorinated analogues is replaced here by columnar stacks with disk planes orthogonal to the columnar axes. Enhanced π-overlap results with overlaid electron-poor and -rich regions.

Polycyclic aromatic hydrocarbons tend toward edge-to-face (herringbone) solid-state packing motifs.[1] Face-to-face stacking is favored with increasing ratio of π-surface to circumference or with peripheral substituents. On the other hand, the “soft” interaction between arenes (Ar) and highly fluorinated arenes (ArF) leads to alternating face-to-face stacks. This principle appears nearly universally applicable based on the broad range of molecular frameworks with which it has been demonstrated.[2] Materials with covalently bound Ar and ArF units crystallize likewise with ArF portions stacked face-to-face with Ar portions. In addition to this supramolecular aspect, (partially) fluorinated π-systems show practical promise as active components in organic electronics, with facile electron injection and transport.[3]

The question addressed here is whether Ar−ArF interactions operate in partially fluorinated, *fused* π-systems, or will the effect be “smeared out” across the π-surface? Based on molecular electrostatic potential[4] (MEP, Figure 1), one would predict face-to-face stacking in a head-to-tail fashion. As test cases, we chose naphthodithiophenes **2** and triphenylene **3** for which we present here synthesis, preliminary characterization, and single-crystal analysis.

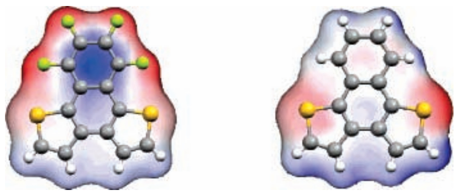


Figure 1. MEP maps of **2a** (left) and **2c** (right).[4]

Naphthodithiophenes **2** were prepared in two steps from readily available starting materials via modified published[5]

[†] Dedicated to Prof. Dr. Klaus Müllen.

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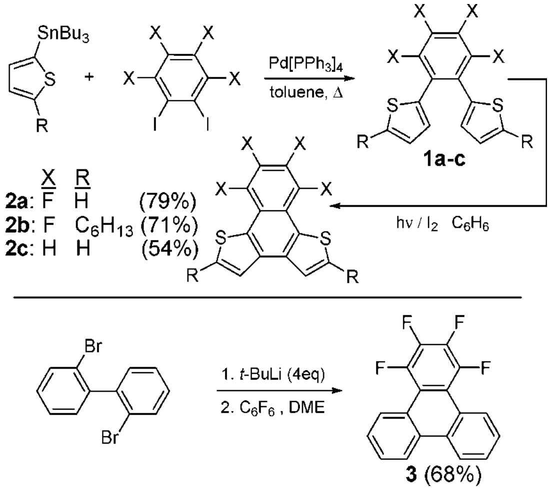
10.1021/ol050019c CCC: $30.25

Scheme 1. Synthesis of Fused Tetracyclics



procedures (Scheme 1). At 110 °C, the Stille coupling gave poor conversions even after 3 days. When conducted at 150 °C in a sealed vessel, good yields were realized within 12 h. Proper conditions[6] for the cyclizations such as those that follow depend on the substitution pattern: Mallory-type photocyclization[7] was effective for **2**, while chemical oxidation with $FeCl_3$ resulted in extensive side reactions including polymerization.

The synthesis of **3** via benzyne intermediates has been reported with minimal characterization.[8] We prepared a tetrafluoro-*o*-terphenyl analogously to compounds **1**, but it resisted fusion by either of the methods described above. Target **3** could be prepared, however, in one pot via double-nucleophilic attack of 2,2′-dilithiobiphenyl on hexafluorobenzene. Little product is observed by GC−MS after 12 h in ether, but starting material is consumed rapidly after addition of DME.[9]

Crystalline packing of compounds **2a**,**c** and **3** is shown in Figure 2. A typical herringbone-like motif is observed for **2c**, similar to that of nonfluorinated triphenylene.[10] However, both **2a** and **3** form face-to-face columnar stacks with disk planes orthogonal to the stacking axis. This arrangement could prove crucial to performance as organic semiconductors.[11] Compound **3** is significantly distorted from planarity, as are perhalogenated triphenylenes;[12] however, this does not alter the packing motif.

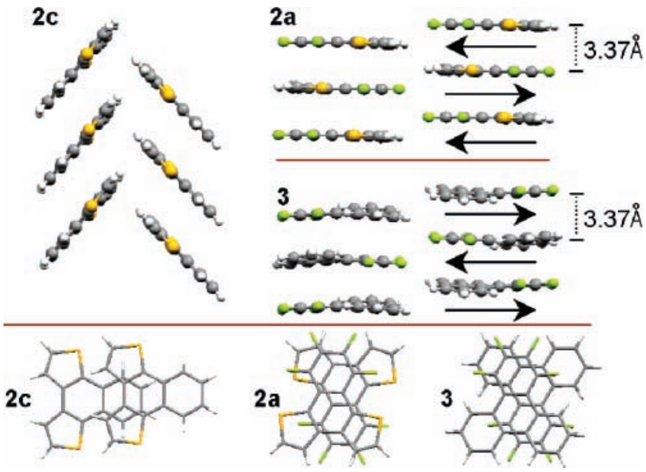


Figure 2. Crystal packing for **2a**,**c** and **3**. Views parallel (top) and perpendicular (bottom) to molecular planes. Arrows indicate lateral orientation of fluorinated “heads”.

While C_6H_6:C_6F_6 cocrystals consist of alternating stacks with essentially eclipsed rings, other Ar:ArF cocrystals display variable lateral offsets between successive disks, correlating to MEP’s or quadrupole moments.[13] Despite differing electronic structures, **2a** and **3** stack with nearly identical offsets (Figure 2, bottom) with the fluorinated rings bisected by C−C bonds of successive molecules. Their π-overlap is much increased compared to **2c**.

Compound **2b** is our first attempt at a thermotropic liquid crystal exploiting this design. At room temperature, the alkyl chains of **2b** interdigitate the stacks, limiting π-overlap between every second and third disk to just one peripheral bond. Within dimer pairs, face-to-face stacking is similar to **2a**, but with lateral offsets approaching that of ABAB/hexagonal crystalline graphite (see Supp Info).

Future studies will involve (opto)electronic characterization of these materials and various substituted derivatives as well as analogues with more fused rings.

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Supporting Information Available: Experimental details and spectroscopic and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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