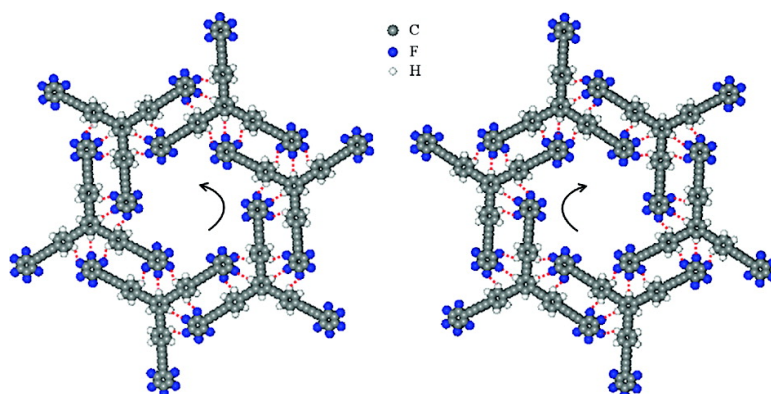


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Two Dimensional Chiral Networks Emerging from the Aryl–F···H Hydrogen-Bond-Driven Self-Assembly of Partially Fluorinated Rigid Molecular Structures

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Self-assembly of organic molecules at the solid/liquid interface has attracted particular attention to provide patterned surfaces, spatially defined arrangements of molecules, laterally controlled supramolecular architectures, and as case study of two-dimensional crystal engineering.¹ While the surface deposition is entropically driven, the molecular arrangement on the surface is controlled by intermolecular interactions like hydrogen bonding and/or van der Waals interactions as well as molecule/substrate interactions. Of particular interest are self-assembled systems yielding in porous networks, providing a well-defined two-dimensional (2D) pattern as template for functional guests, such as quantum dots.² So far, 2D porous networks have been assembled by directional intermolecular forces like hydrogen bonding,³ metal–ligand interactions,⁴ and van der Waals interactions of interdigitating alkyl chains.⁵

Perfluorobenzene subunits have been used as rather electron-poor aromatic building blocks to tailor inter- and intramolecular properties. Stacking with electron-rich aromatic systems as a supramolecular motif has been investigated in detail⁶ and has been applied successfully in supermolecules,⁷ crystal engineering,⁸ topochemistry,⁹ material design,¹⁰ and even in biomolecules.¹¹ At the single molecule level, perfluorobenzene subunits unbalanced the electron distribution on a molecular rod, providing rectification properties.¹²

At the solid/liquid interface, alkylated molecular rods comprising a perfluorobenzene subunit yielded parallel stripes as a perfectly ordered large area surface pattern.¹³ Of particular interest is the unbalanced electron distribution in these rods providing a dipole moment which might support or even drive the molecule's arrangement at the solid/liquid interface.

Here we present new rigid-rod-type structures forming well-defined 2D porous networks comprising chiral cavities. Both structures, the branched star-shaped compound **1** and the angulate rod **2** (Figures 1a and 2a), have a central core consisting of acetylene interlinked aromatic subunits, and their branches are terminally functionalized with pentafluorobenzenes connected via diacetylenes.

As displayed in Scheme 1, in a three-step synthesis, both structures **1** and **2** were assembled. Starting from commercially available 1,3,5-triiodobenzene (**3**) or 1,3-diiodobenzene (**6**), the iodines are substituted by monoprotected *para*-diethynylbenzene in a Sonogashira coupling reaction. After deprotection, the free acetylenes are capped with bromoethynylpentafluorobenzene in a palladium-catalyzed version of the Cadiot–Chodkiewicz reaction to provide both target structures **1** and **2** as brown solids in yields of 52 and 55%, respectively. Detailed synthetic protocols are provided in the Supporting Information (SI-1).

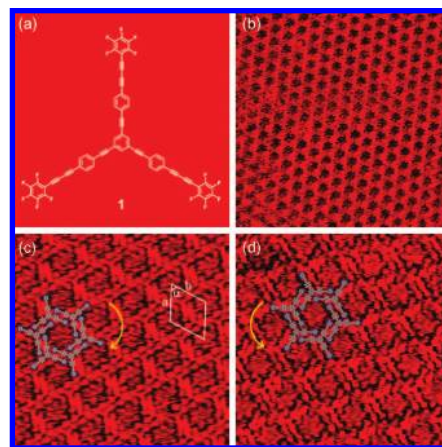


Figure 1. (a) Chemical structure of **1**. (b) Large-scale STM image of **1** (50.0 nm × 50.0 nm, $V_{\text{bias}} = 0.5$ V, $I_{\text{set}} = 0.60$ nA). (c and d) High-resolution STM image of **1** (18.0 nm × 18.0 nm, $V_{\text{bias}} = -0.5$ V, $I_{\text{set}} = 1.43$ nA). (d) A domain displaying a mirrored arrangement compared with (c). In both cases, six molecules of **1** are overlaid to illustrate both the proposed packing model and the resulting chiral cavities.

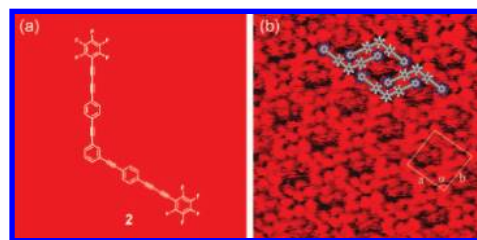


Figure 2. (a) Chemical structure of **2**. (b) High-resolution STM image of **2** (12.0 nm × 12.0 nm, $V_{\text{bias}} = 0.5$ V, $I_{\text{set}} = 0.5$ nA). Four molecules of **2** are overlaid to illustrate the proposed packing model.

The structures **1–7** have been fully characterized by ¹H and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis. However, the combination of very limited solubility of the compounds with low signal intensity due to extensive F coupling did not allow observing the ¹³C signals of the fluorinated carbons.

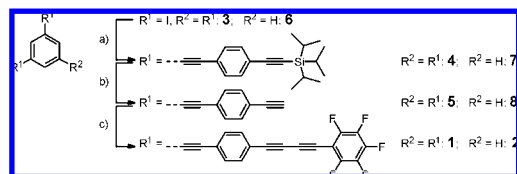
The self-assembly properties of **1** and **2** have been studied at the solid/liquid interface by depositing a droplet of a nearly saturated solution of **1** or **2** in phenyloctane on a highly oriented pyrolytic graphite (HOPG) surface. Subsequent investigation of the surface by STM displayed the formation of a homogeneous and ordered large area honeycomb structure in the case of **1** (Figure 1b). The bright areas correspond to the π -conjugated molecular backbones due to high electronic densities, while the dark areas are voids in the network. The high-resolution STM image (Figure 1c) even allows identifying

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Scheme 1. Synthesis of the Molecular Star **1** and the Molecular Angle **2**^a



^a Conditions: (a) $\text{HC}_2(\text{C}_6\text{H}_4)\text{C}_2\text{Si}(\text{C}_3\text{H}_7)_3$, $\text{Pd}(\text{PPh}_3)_4$, $\text{N}(\text{Et})_3$, CuI , 40 °C, 20 h, **4**: 77%, **7**: 94%; (b) TBAF, wet THF, rt, **5**: 71%, **8**: 80%; (c) $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$, (*i*-Pr)₂EtN, CuI , toluene, rt, 3 h, **1**: 52%, **2**: 55%.

the branches of individual star-shaped **1**. The parameters of a unit cell have been determined to be $a = b = 3.3 \pm 0.2$ nm, $\alpha = 60 \pm 2^\circ$. The length of the individual bright stripe corresponds with 2.14 nm to the length of the molecular branches (2.16 nm by MM2 calculation). Two adjacent branches belonging to two different molecules are antiparallel to each other, maximizing their overlap. The terminal pentafluorobenzene units point to the *meta*-di(phenylethynyl)benzene center of the neighboring molecule allowing the formation of three aryl–H \cdots F hydrogen bonds (SI, Figure S1). Thus, in the resulting porous 2D network, two neighboring molecules are stabilized by both antiparallel arrangement of the branches comprising a dipole moment and the formation of six aryl–H \cdots F hydrogen bonds, which have already been reported for monolayers consisting of self-assembled fluorinated phthalocyanines.¹⁴ The crucial role of this intermolecular stabilizing interaction was further emphasized by control experiments with the structurally related star-shaped molecule lacking the F atoms (see **11** in Supporting Information SI-1), which failed to form self-assembled monolayers under similar conditions.

Closer inspection of the structure reveals the branches of six interacting molecules defining a void with a diameter of about 2.0 nm. The six branches surrounding the void are arranged either clockwise or anticlockwise, defining a chiral cavity in different domains (Figure 1c,d). Two images containing the domain boundary are shown in SI-2 (Figure S2a,b). Driven by the close-packed arrangement of the molecules within a domain, all voids have the same chirality, yielding in a chiral separation arising from the self-assembly of **1**, as observed for other systems.¹⁵ Alteration of current and bias allowed the inspection of the underlying substrate lattice, revealing an angle of 4.0 ± 2 or $-4.0 \pm 2^\circ$ between the unit cell vector **a** and the main symmetry axis of the HOPG (SI, Figure S2c,d). While the intermolecular interactions result in a 2D porous structure, the molecule–graphite interaction is assumed to dictate its orientation.

To further investigate the potential of these rigid rod branches to stabilize molecules on surfaces, the angulate rod **2** lacking one branch compared with **1** has been investigated. In similarity to **1**, compound **2** in phenyloctane also forms stable and homogeneous monolayers on graphite. The high-resolution image (Figure 2b) displays the paired arrangement of two intercalating molecules **2**. The antiparallel arrangement of their branches results in opposite directions of their dipole moments but also maximizes the number of intermolecular aryl–H \cdots F hydrogen bonds to six. These dimers are arranged in infinite one-dimensional stripes stabilized by four hydrogen bonds between each set of two dimers and opening a quadrangle void with dimension of 1.3 nm \times 0.6 nm. The entire surface is covered by parallel stripes which are staggered with respect to each other to enable the formation of interstripe aryl–H \cdots F hydrogen bonds. The parameters of a unit cell were determined to be $a = 2.3 \pm 0.2$ nm, $b = 2.4 \pm 0.2$ nm, $\alpha = 92 \pm 2^\circ$. In analogy to **1**, also **2** forms entire domains comprising exclusively voids of the same 2D chirality. An angle of 5.5 ± 2 or

$-5.5 \pm 2^\circ$ between the unit cell vector **a** and the main symmetry axis of HOPG was observed as shown in SI (Figure S3).

In conclusion, the self-assembly of two molecular structures **1** and **2** comprising diacetylene and acetylene interlinked benzene and pentafluorobenzene branches at the solid/liquid interface resulting in two-dimensional chiral porous networks is described. The spontaneous formation of these stable large area surface architectures is assumingly driven by the compensation of the dipole moments of the branches and the formation of aryl–H \cdots F hydrogen bonds. The absence of alkyl chains, which are known to direct the self-assembly of rigid molecular cores,⁵ is noteworthy. Currently, we are further functionalizing these synthons to profit from their large area periodicity.

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Supporting Information Available: Synthetic protocols and analytical data of all mentioned molecules, the additional STM images and the molecular packing model are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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