

Abstract No. nuck390

Self-Assembled Nanostructures for Energy Transport and Conversion

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Beamline(s): X3B1

Introduction: Recently, I and four students—Mark Bushey, Qian Miao, Wei Zhang, and Austin Hwang—initiated a program of research to design and synthesize two new classes of molecules **1** and **2** [(a) and (b) below]. In collaboration with Prof. Peter Stephens at the National Synchrotron Light Source (X3B1) we have determined the superstructures they adopt upon self-assembly. The results are summarized below. The novel design principle is to force the recognition groups—amides in **1** and sulfinamides in **2**—out of the plane of the aromatic ring so that a synergy between the π -stacking and hydrogen bonding would cause the molecules to stack in columns.

The energy-minimized molecular model of dimers **1** is shown above. The dimer has its π -surfaces “in-registration” stacked within 3.8 Å of each other. Also shown in the model carbonyl dipoles of each subunit point in the same direction. As the molecules stack, this dipole can be amplified. For **2**, our models indicate that the stereochemical information within the sulfinamide functionality should encode stacking in a stereodefined manner. We have three goals in studying these new classes of molecules: (1) to determine if there is measurable *polar order in isolated nanostructures*, (2) to measure *electrical conduction in single columns*, and (3) to synthesize monodisperse oligomers of **1** that self-fold and aggregate so as to form *tertiary structures in solution*.

Results: Our initial study on these materials (M. L. Bushey, A. Hwang, P. W. Stephens, and C. Nuckolls *J. Am. Chem. Soc.* **2001**, 123, 8157–8158; “Editor’s Choice” in *Science* **2001**, 293, 1224; “Science Concentrate” in *Chemical and Engineering News* **2001**, 79, 36) outlined a six-step synthesis that made a variety of molecules like **1** accessible. Primarily relying on synchrotron X-ray diffraction with Peter Stephens at the Brookhaven NSLS and polarized light microscopy we showed that **1a** and **1b** assemble into columnar superstructures.

With up to 5th-order lattice spacings, the molecules form near perfect columns that stack with a high degree of regularity. Microscopy shows that **1a** forms soft or plastic crystals [(b) above] whose columns are parallel to the surface. An important finding of our initial study was how influential the sidechains are in controlling the liquid crystallinity and self-assembly characteristics of these molecules.

In contrast to **1a**, **1b** forms a liquid crystalline phase whose lattice is slightly distorted from hexagonal to rectangular by the bulky glycine ester sidechains. Importantly, the columns orient roughly perpendicular to the surface, opposite from the orientation exhibited by **1a**.

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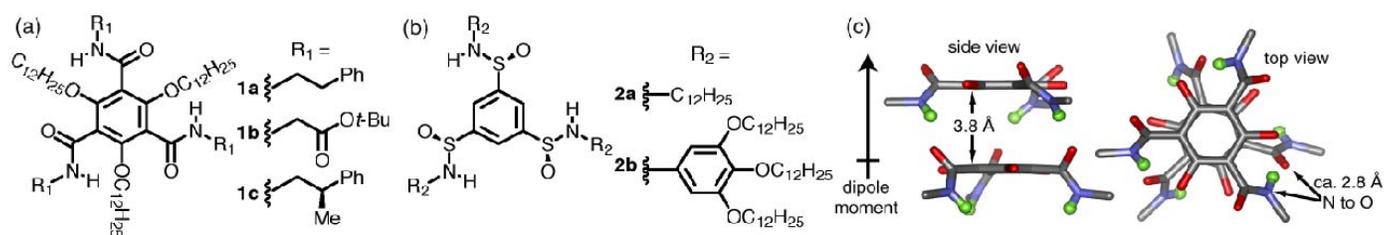


Figure 1. (a) crowded arenes. (b) tris-sulfinamides. (c) molecular model of a dimer of **1**.

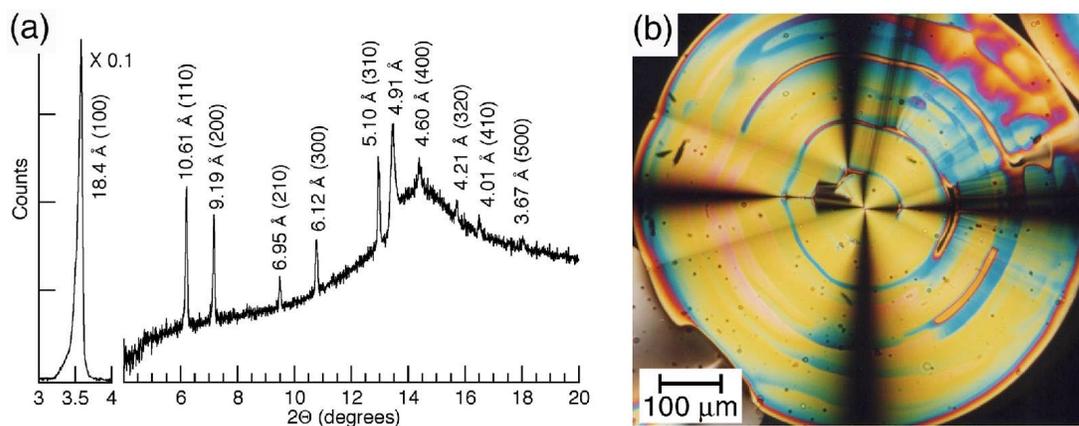


Figure 2. (a) synchrotron X-ray diffraction from **1a**. (b) polarized light micrograph as material is cooled from an isotropic liquid.

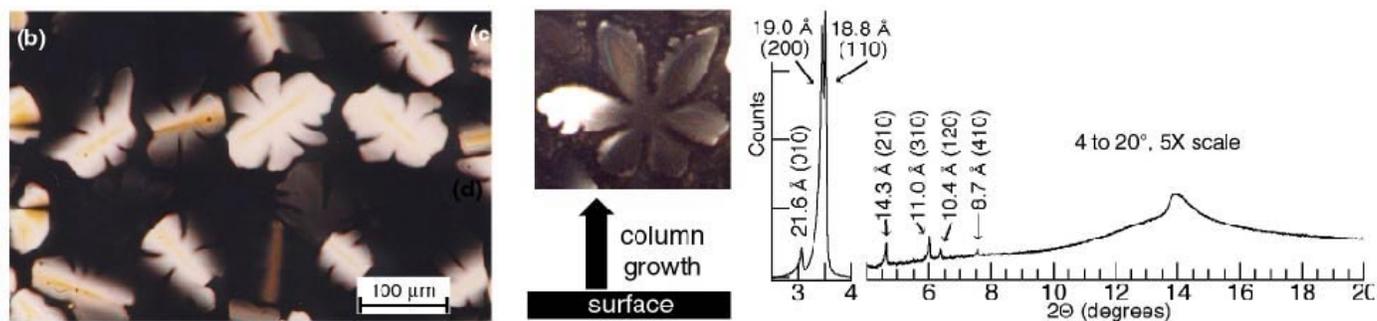


Figure 3. Polarized light micrograph and synchrotron x-ray diffraction from **1b**.