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Ultrafine nanofibers fabricated from an arylene ethynylene macrocyclic molecule using surface assisted self-assembly

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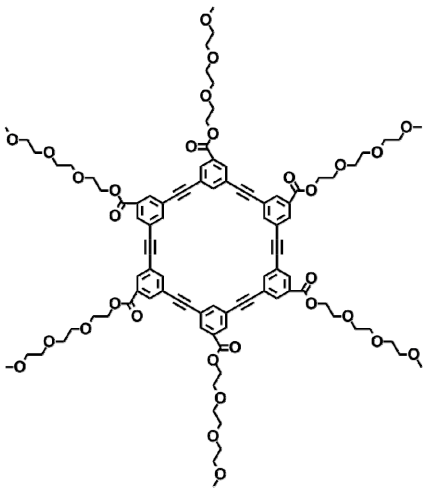
I. Materials and methods



The AEM molecule, ***1***.

Synthesis and characterization of ***1*** were followed the method previously developed in the Moore lab.[1] The starting materials and all solvents (HPLC or spectroscopic grade) were purchased from Fisher and Aldrich, and used as received. UV-vis absorption and fluorescence spectra were measured on a PerkinElmer Lambda 25 spectrophotometer and LS 55 fluorometer, respectively. Pyrex glass cover slips (from Corning Inc.) were used as the support substrate for AFM measurement of the self-assembled nanostructures. Prior to use, the cover slip was cleaned with

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piranha reagent (30:70 H_2O_2 (35%):H_2SO_4), followed by rinsing with water and methanol.[2] *Caution: Piranha solution is an extremely strong oxidizing reagent.*

II. Sample preparation

1. Spin casting

Nanofibril film was obtained by spin-casting hot solution of ***1*** in toluene. Briefly, 1 mM solution of ***1*** was prepared in toluene at room temperature. Just before spin-casting, the solution was heated to 80 ^oC in an oil bath for 5 minutes. This hot solution was then immediately spin-casted on a piranha cleaned glass cover slip at 1500 rpm for 30 seconds. Spin-coated samples were allowed to dry (evaporation) in air for approximately 30 minutes before AFM measurement.

2. Drop casting

One droplet of toluene solution of ***1*** (300 μM) was drop-casted with Drumond micro-capillary onto the substrate of glass, mica or graphite. The solution was allowed to dry (evaporation) in air for approximately 30 minutes before AFM measurement. Hot solution of ***1*** was prepared in the same way as described above, followed by immediate drop-casting on freshly cleaved mica or HOPG surfaces. After complete evaporation of solution, all the samples were allowed to equilibrate in air for approximately 30 minutes before AFM measurement.

III. Drop-casting of *1* from different solvents

Molecule ***1*** is soluble in wide range of organic solvents. Solvents with different polarities and physical properties (i.e. surface tension, boiling point, etc.) will affect the self-assembly of ***1*** as discussed in the main text. Herein, we prepared solutions of ***1*** (300μM) in four solvents, chloroform, methanol, p-xylene and toluene. Chloroform and methanol were chosen due to their hydrophilic nature, while p-xylene and toluene were chosen as the hydrophobic counterparts. All

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the solutions were drop-casted on piranha cleaned glass coverslip. The film morphologies thus formed during evaporation of solvent are imaged with tapping mode AFM as shown in Fig. S1.

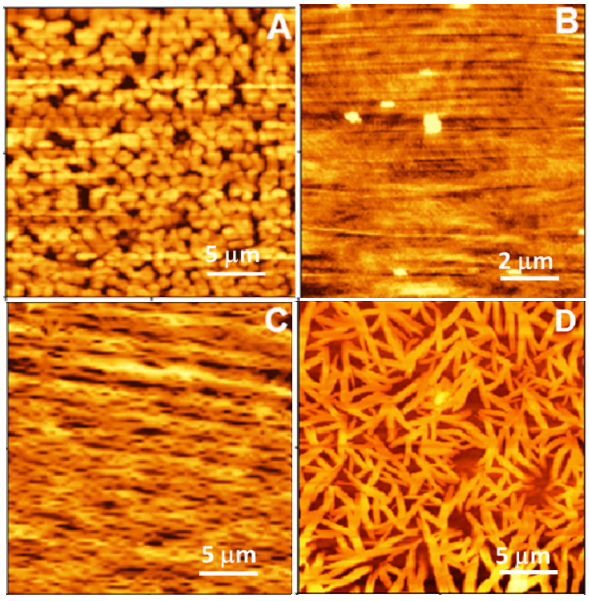

Figure S1. Tapping mode AFM images of the films drop-casting on glass from 300 μM solution of ***1*** dissolved in different solvents at room temperature: (A) chloroform, (B) methanol, (C) p-xylene and (D) toluene.

IV. AFM imaging

AFM measurement was carried out in tapping mode on a TopoMetrix Explorer using antimony doped silicon tip. The largest scanning area is 50×50 μ m, and the highest z-resolution is about 0.2 nm.[2] In addition to the images shown in Fig. 1; Fig. S1 below shows more large-area scanning images of the nanofibrils formed from the same hot spin-casting sample of Fig. 1.

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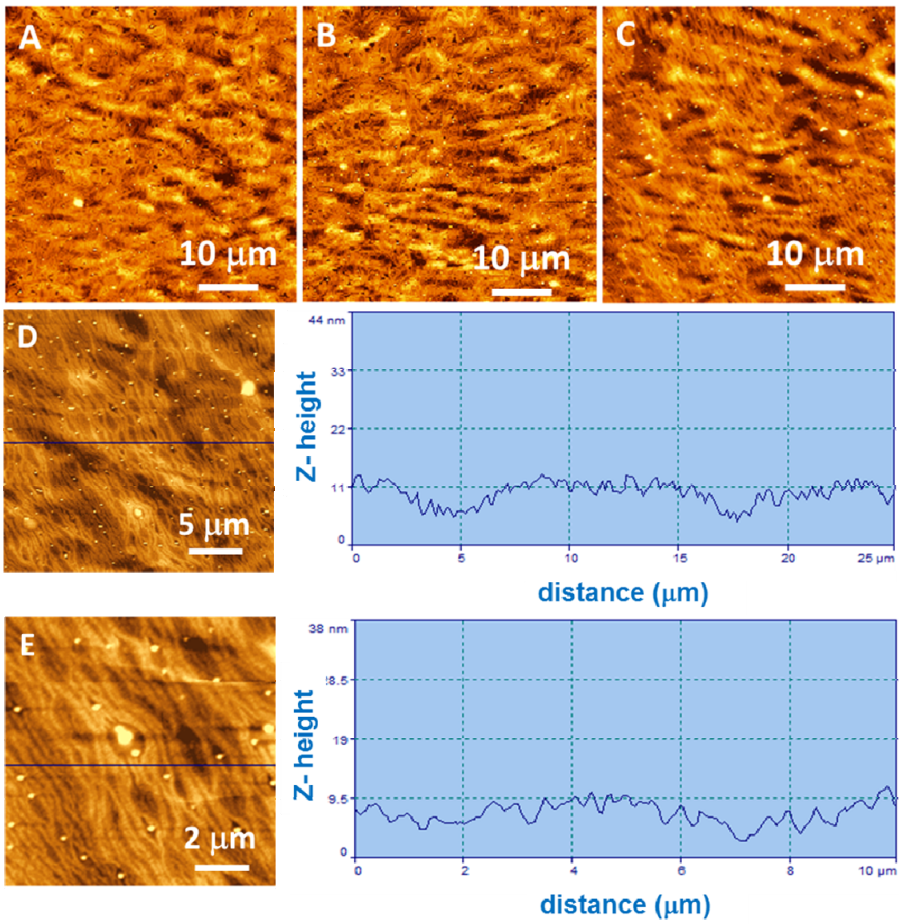

Figure S2. Large-area AFM images (A-C) of the nanofibril film formed on glass substrate by spin-casting 1.0 mM solution of 1 in toluene (heated to 80 ^{o}C) at a speed of 1500 rpm, followed by evaporation (the same sample of Fig. 1). The total z-height for A-C ranges 7-10 nm. (D) and (E) show two zoomed-in areas with the average z-height of 4-5 nm.

V. Polarized optical microscopy imaging of nanofibril film drop-casting from toluene solution of *1*.

The drop-cast film of ***1*** was also examined with polarized optical microscopy (POM) to reveal possible birefringent properties, accounting for the existence of anisotropic organization at the micrometer size scale. Under crossed polarized light, the presence of both dark and bright domains in anisotropic structure represents regions where the optical axis is parallel or

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orthogonal to the polarizer respectively.[4,5] The presence of dark and bright regions through the entire film demonstrates that these materials are anisotropically organized, but the optical axis orientation inside is not homogeneous at millimeter scale.

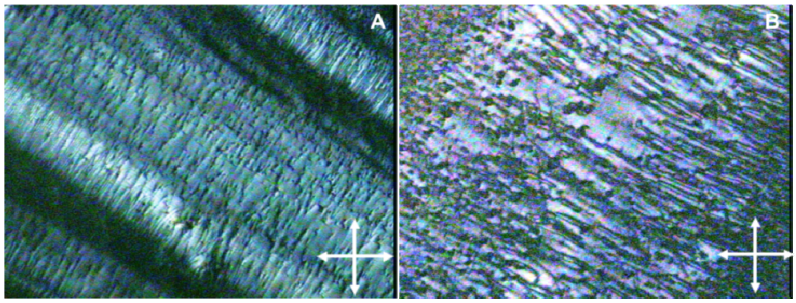

Figure S3. Cross-polarized microscopy images of two different areas (A and B) measured over the film cast from toluene solution of ***1*** (300 μM).

VI. Wide angle X-ray scattering studies on film deposited from toluene

Wide angle X-ray scattering (WAXS) shown in Fig. S4 was performed at 18-ID-BioCAT beamline at Argonne National Lab. The WAXS pattern was collected in the q-range of 0.1 to 3.0 $Å^{-1}$ and $q= 4\pi/\lambda * \sin\theta$; where λ is X-ray wavelength and θ is the X-ray scattering angle. Essentially this *q* range allows us to look at the characteristic peaks from not only the molecule but also from the intermolecular π–π stacking interaction due to the self-assembly. In general the *q* value for the π–π stacking is close to 1.8 which corresponds to 0.34 nm in *d* spacing, in agreement with prior observations of such systems.[6,7]

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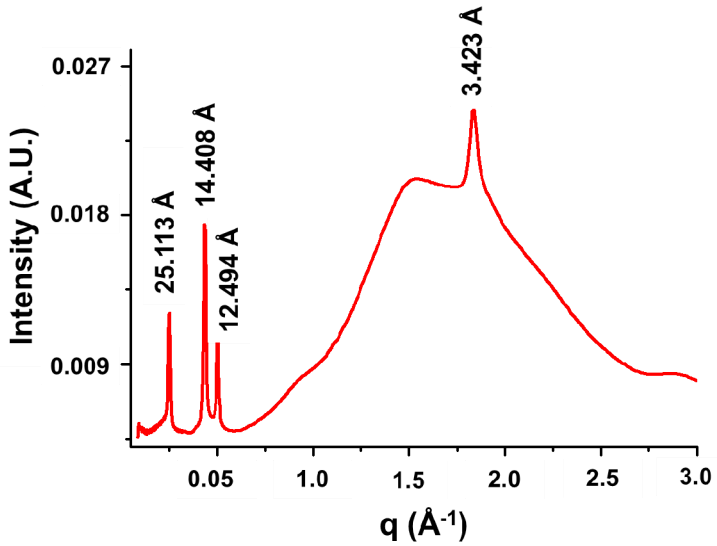

Figure S4. WAXS spectrum obtained for the nanofibers of ***1***.

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