Multilayered Nanofibers from Stacks of Single-Molecular Thick Nanosheets of Hexakis(alkoxy)triphenylenes

*Gayane Koshkakaryan, Peng Jiang, Virginia Altoe, Dennis Cao, Liana M. Klivansky, Yue Zhang, Sungwook Chung, Allard Katan, Florent Martin, Miquel Salmeron, James J. DeYoreo, Biwu Ma, Shaul Aloni, Yi Liu**

The Molecular Foundry, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, California, USA 94720.

Email: yliu@lbl.gov

Supporting Information

METHODS AND MATERIALS

Materials. Reagents were purchased from Aldrich or synthesized according to literature methods.[s1]

Sample Preparation. The nanofiber samples were prepared by dropcasting solutions of **HAT** derivatives onto various substrates, such as glass slides, silicon wafers, mica, or copper TEM grids. In the case of concentrated solutions where fibril aggregates phase separated from the solution, the suspension was transferred to the corresponding substrate and allowed to dry in air before imaging.

Characterization. Proton and carbon nuclear magnetic resonance spectra (^{1}H-NMR and ^{13}C-NMR) spectra were recorded on a Bruker Avance500 II, using the deuterated solvent as lock and the residual solvent as internal standard. All chemical shifts were quoted using the δ scale, and all coupling constants (*J*) are expressed in Hertz (Hz). Powder XRD data was collected on a Bruker-AXS D8 Discover with GADDS powder X-ray diffractometer with Cu K_α radiation. Transmission electron microscopy (TEM) images and nanobeam electron diffraction were recorded on JEOL 2100F using Gatan 915 double-tilt cryo sample holder at LN_2 temperature. SEM images were recorded on a Zeiss Gemini Ultra-55 Analytic Scanning Electron Microscope. Tapping mode AFM images were taken using a Molecular Imaging PicoPlus AFM under ambient condition. Optical and polarized optical images were taken using a Leica DM4500P microscope. UV-vis absorption and fluorescence spectra were recorded on Cary 500 UV-vis-NIR spectrophotometer and Nanolog spectrofluorometer, respectively.

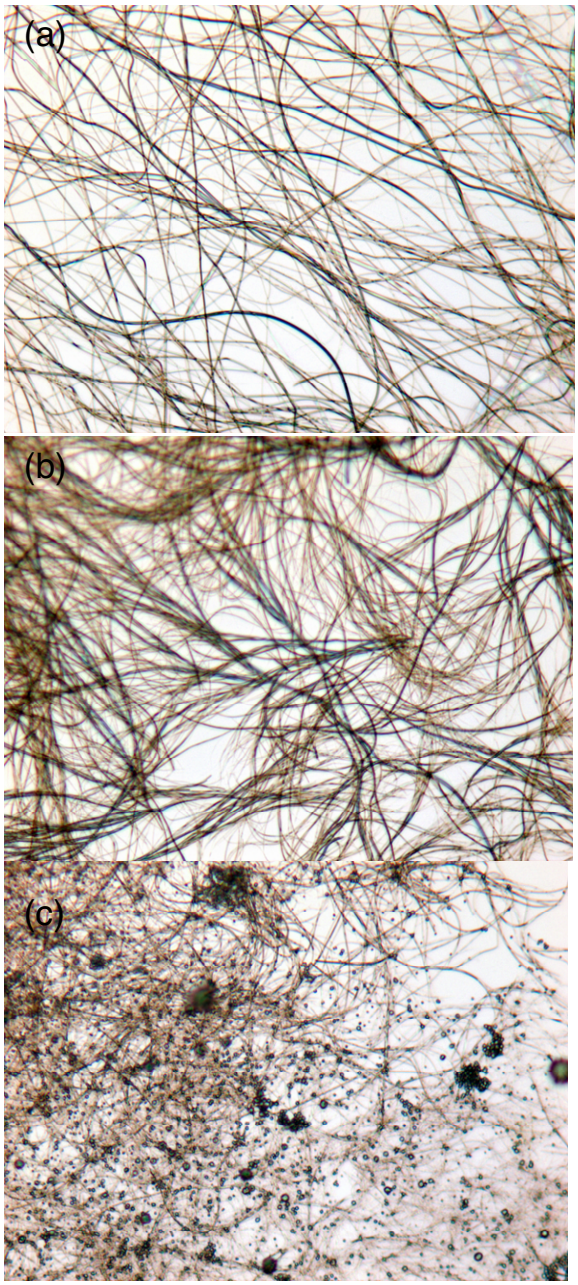

Figure S1. Optical images (× 500) of (a) **HAT5**, (b) **HAT7** and (c) **HAT12** nanofibers formed by dropcasting the individual MeCN solutions onto glass substrates. The concentration is 0.5 mg / mL for **HAT5** and **HAT7**. In the case of **HAT12**, the solution was prepared after dissolving 1 mg sample in 20 mL MeCN. In (c), ill-defined aggregates were observed together with nanofibers.

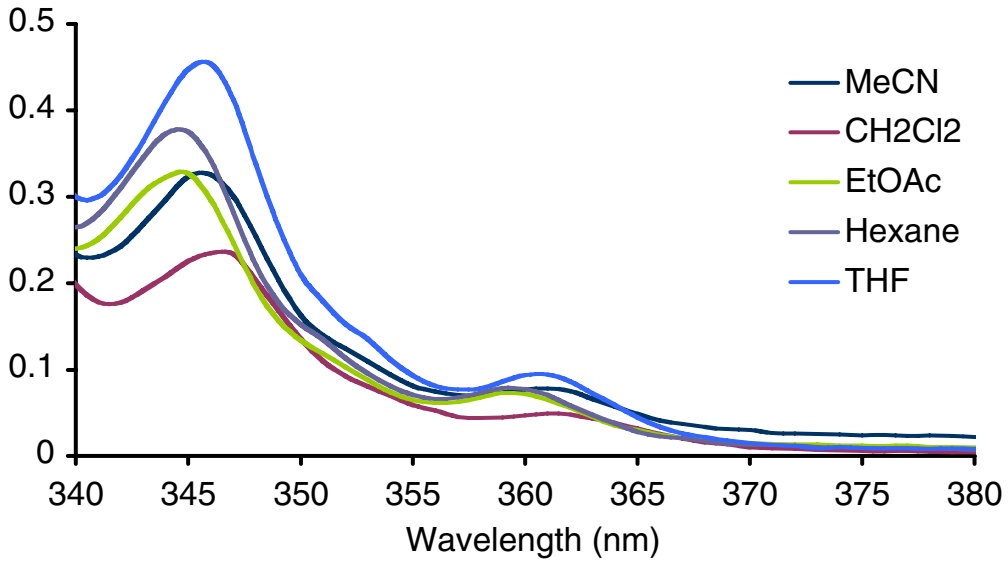

Figure S2. UV-vis spectra of **HAT6** in different solvents (c = 1.0 x 10^{-4} M)

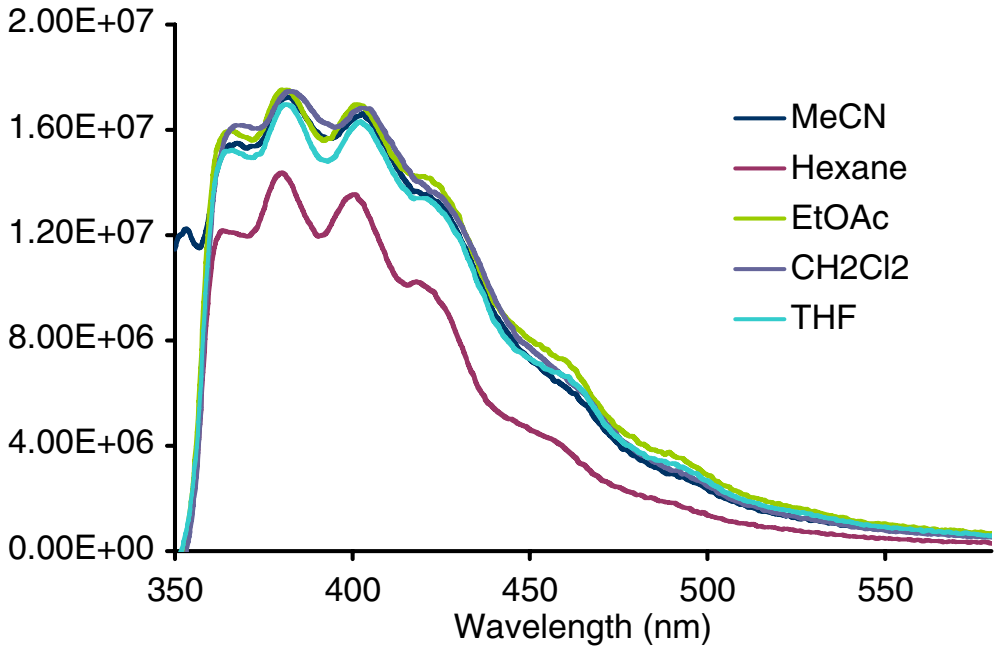

Figure S3. Fluorescent spectra of **HAT6** in different solvents (c = 9.0 x 10^{-5} M)

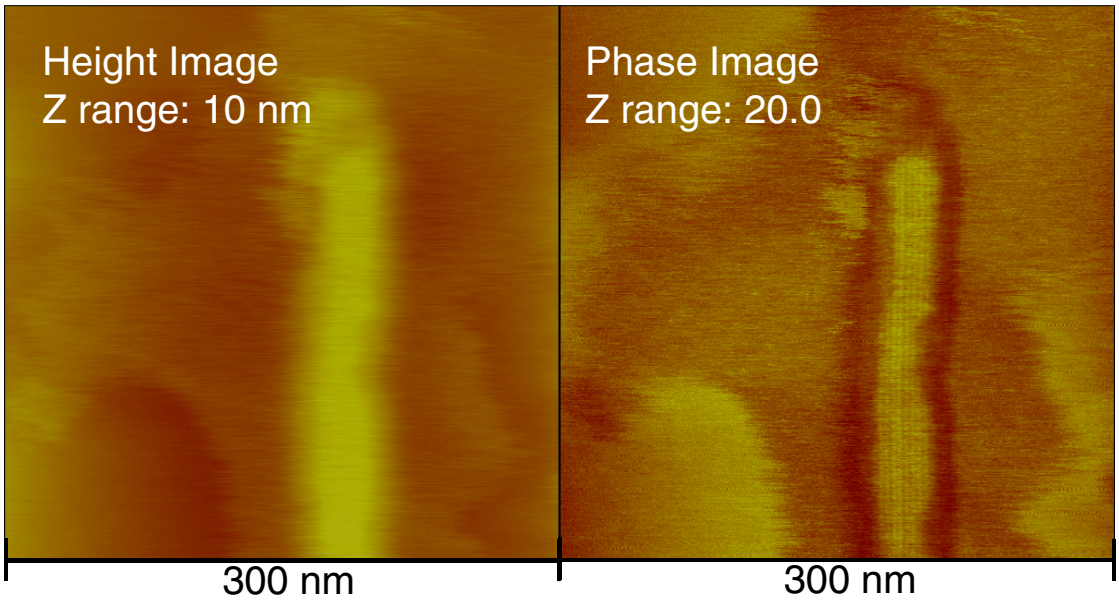

Figure S4. The height (left) and phase (right) images of **HAT6** nanofibers. The stripes that are only observed on the nanofiber in the phase image indicate the ordering of triphenylene domains along the nanowires. The line spacing is around 1—2 nm, consistent with the spacing observed from XRD experiments. The height of the nanofiber in the right image is 2.1 nm.

Concentration-Dependent Nanofiber Formation Followed by UV-vis Spectroscopy.

Concentration dependent aggregation was followed by UV-vis spectroscopy at different time intervals (See Figure S5). Significant intensity reduction at absorption maxima around 360 nm and 345 nm was observed (Figure S5a) within eight minutes if started with a 8.0 mM solution, concomitant with the formation of large amount of fibril aggregates. The change of absorption intensity was much smaller and slower when started with a lower concentration (2.0 mM, Figure S5b). Small amount of aggregates together with intensity loss were observed after 18 hours. If the initial concentration was further lowered to 1.0 mM, the intensity change in 18 hours was negligible, with no fibril

aggregate formation (Figure S5c). If sufficient standing time (a few days) was allowed, fibril aggregates did precipitate from solution, consistent with a concentration-dependent nucleation/crystalization process.

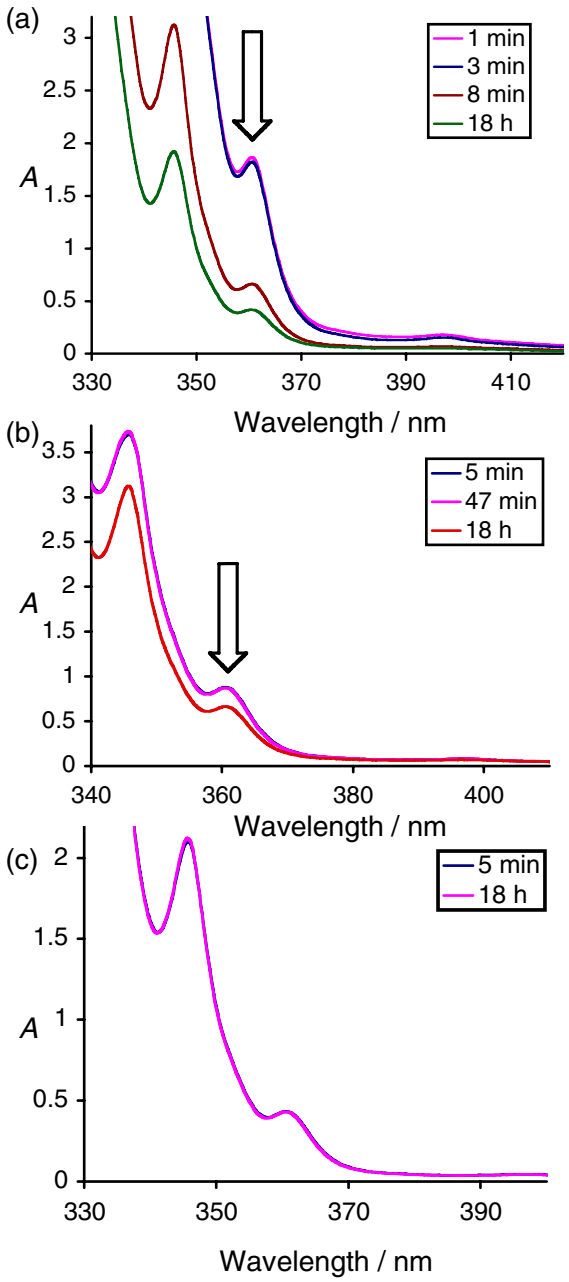

Figure S5. UV-vis spectra of **HAT6** solutions with initial concentrations of (a) 8.0 mM, (b) 2.0 mM, and (c) 1.0 mM at different time intervals. Solvent: MeCN.

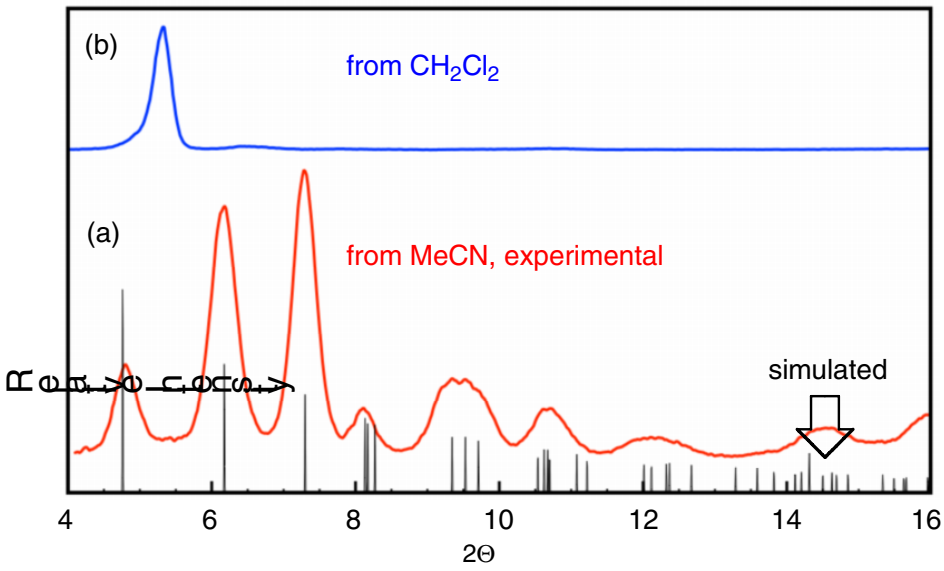

Figure S6. Powder XRD patterns of two **HAT6** samples. (a) nanofibers from MeCN (in red), and (b) dropcasted film from CH_2Cl_2 (blue). The stick diagram shows the simulated XRD peak locations of the proposed triclinic structure of the **HAT6** fibers.

Table S1. Experimental and theoretical X-ray diffraction data of **HAT6** nanofibers.

Lattice Parameters	*d*-spacing observed (nm)	*d*-spacing calculated (nm)	Miller indices
	18.50	18.54	0 0 1
	14.31	14.30	0 1 0
Triclinic	12.12	12.10	0 1 -1
a = 1.14 nm	10.86	10.81	1 0 0
b = 1.46 nm	9.46	9.45	1 –1 0
c = 1.95 nm	9.28	9.27	0 0 2
α = 95°	9.11	9.10	-1 1 1
β = 107°	8.33	8.32	1 0 1
γ = 98°	8.24	8.26	1 1 -1
	7.30	7.30	-1 1 2
	6.10	6.10	1 –1 2
	5.55	5.55	-2 1 1

Reference:

S1. Cammidge, A. N.; Beddall, A. R.; Gopee, H. Unexpected Mesophase Behaviour in Novel Triphenylene Multi-Alkenes. *Tetrahedron Lett.* **2007**, *48*, 6700-6703.