*Electronic Supplementary Information*

# Toroid-rod supramolecular polymorphism derived from conformational isomerism of a π-conjugated system

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**This PDF file includes:**

## Supplementary methods

### General

All reagents and solvents procured commercially were of reagent grade and were utilized as received. Spectral grade solvents, employed for measurements, were also used as received. $^{1}H$ and $^{13}C$ NMR spectra were obtained using JEOL JNM-ECA500 or Bruker-AVANCE Ⅲ-400M spectrometers. Chemical shifts are reported in ppm ($\delta$), referencing tetramethylsilane (TMS) at 0.00 ppm for $^{1}H$ and $CDCl_3$ at 77.16 ppm for $^{13}C$. Resonance multiplicities for proton signals are reported as s (singlet), d (doublet), dd (double-doublet), m (multiplet), and brs (broad singlet). APCI- and ESI-MS spectra were acquired on an Exactive (Thermo Scientific) instrument. UV/vis absorption spectra were recorded using a JASCO V760 spectrophotometer equipped with a Peltier device, utilizing a screw-capped quartz cuvette (10 mm or 1.0 mm path length). FT-IR spectra were recorded on a JASCO FT/IR-4600 spectrometer. Dynamic light scattering (DLS) measurements were conducted on a Zetasizer Nano (Malvern Instruments) with noninvasive backscattering (NIBS) technology, using a 4.0 mW He-Ne laser (633 nm) at a 173° scattering angle, and measurements were maintained at 293 K in a screw-capped quartz cuvette. AFM imaging was done under ambient conditions using a Multimode 8 Nanoscope V microscope (Bruker Instruments) in peak force tapping (Scanasyst) mode. Silicon cantilevers (SCANASYST-AIR) featuring a spring constant of 0.4 N/m and a frequency of 70 kHz were employed. For sample preparation, solutions (10 μL) were spin-coated at 3000 rpm for 1 min onto freshly cleaved HOPG.

### Preparation of pure Rod of 1

Pure **Rod** of **1** was prepared by cooling a 90:10 methylcyclohexane/chloroform (MCH/$CHCl_3$) solution of **1** ($c_t$ = 100 μM) from 90 to 20 °C at a rate of 1 °C/min. **Rod** was precipitated in the solution after cooling. Only the precipitate was isolated by centrifugation at 8000 rpm and subsequent decantation of the solution. The isolated precipitate was used to measure the FT-IR spectrum of **Rod** shown in Figure S4.

### DFT calculation

Geometry optimizations were performed to calculate dipole moment of compound **1**, using the density functional theory (DFT) with the CAM-B3LYP as functional and 6-31+G(d,p) basis set.

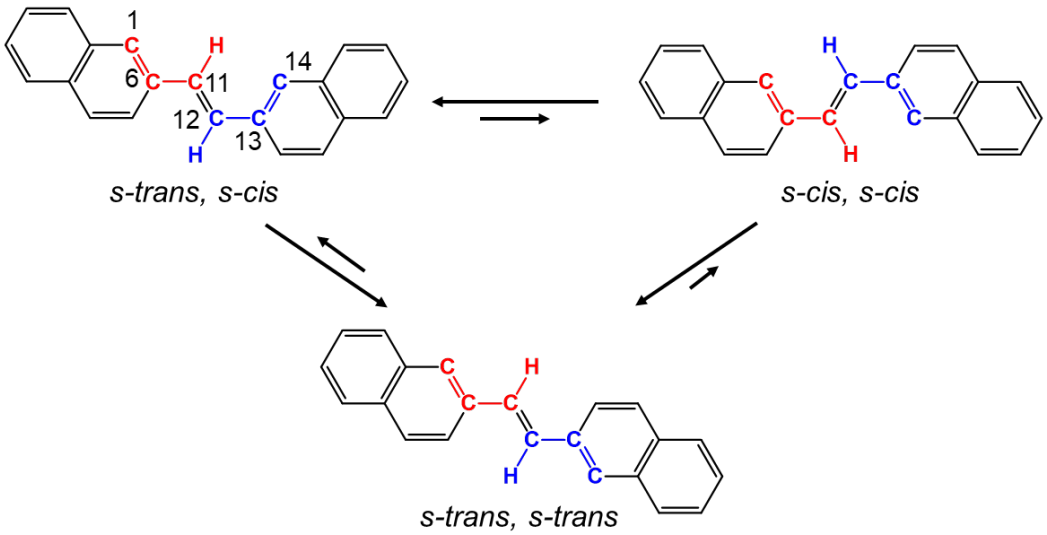
### Molecular mechanics calculation

Conformers of **1** and their rosettes were geometry optimized based on OPLS-2005 force fields installed in MacroModel ver. 12.1 (Schrödinger).

### Molecular Dynamics (MD) simulation

OPLS-AA force field parameters with 1.14*CM1A atomic charges were assigned to four stable conformers (s-*cis*, s-*cis* (*CC*), s-*cis*, s-*trans* (*CT*), s-*trans*, s-*cis* (*TC*) and s-*trans*, s-*trans* (*TT*)) of **1**, and solvent MCH via OPLS/CM1A Parameter Generator for Organic Ligands (LigParGen server).[S1–S3] In order to highlight isomeric features, the rotational motion of the two naphthalene around the central ethylene unit during MD steps was fixed by two additional dihedral potential (± 500 kcal/mol) for C-C-C-H, where the

first and second C atoms are those of naphthalene moieties, and the third C and the forth H are those of the ethylene moiety as follows.



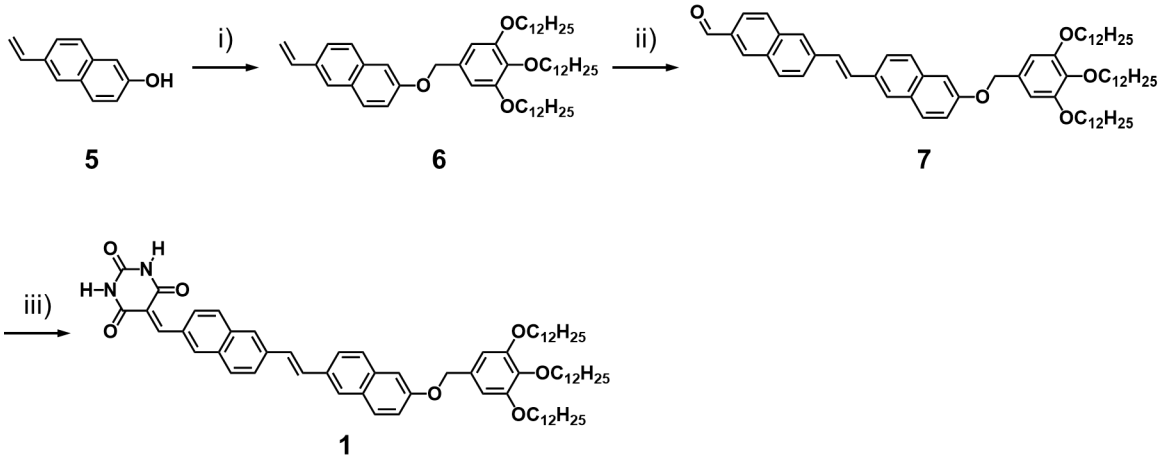

Four homomeric rosettes consisting of each conformer were created by cyclic arrangement of the six monomers with 6.2 Å radius. The 30 rosettes were then vertically stacked with 3.35 Å distance along *z*-direction into periodic unit cell. The cell length of $L_x$, $L_y$, and $L_z$ were 93.56, 98.55, and 100.50 in Å. The top and bottom rosettes in the *z*-direction are continuously stacked under periodic boundary conditions. The space without stacked rosettes in the unit cell were filled with 2,700 molecules of MCH. The density of the initial structure was approximately 0.8 g/cm$^3$.

The initial structure was carefully equilibrated to avoid dispersion of the rosettes. First, the 80,000 MD steps for all atoms except barbituric ring atoms was performed with incremental timestep from very short (0.002 fs) to 2.0 fs under isometric-isothermal ensemble (NVT) at 300 K. Subsequently, the MD for all atoms including barbituric ring atoms were started with 0.2 fs for 250,000 steps under NVT at 300 K. Finally, the system was controlled under isobaric-isothermal ensemble at 1 atm and 300 K for 100,000 steps with 2 fs timestep. All C-H bonds were constrained via the SHAKE algorithm.[S4]

All MD calculations were implemented with the LAMMPS code.[S5,S6]

## Synthesis

Compound **1** was synthesized following the procedure outlined in Scheme S1.




**Scheme S1.** Synthesis of compound **1**. i) 5-(chloromethyl)-1,2,3-tris-(dodecyloxy)benzene[S7], $K_2CO_3$, DMF, 80 °C; ii) 6-bromo-2-naphthaldehyde, P(*o*-tolyl)$_3$, $Et_3N$, $Pd(OAc)_2$, $CH_3CN$, 80 °C, reflux; iii) barbituric acid, EtOH, 70 °C, reflux.

**Synthesis of compound 6**: A 100 mL three-neck round bottom flask connected with refluxing condenser was charged with compound **5**[S8] (292 mg, 1.72 mmol), $K_2CO_3$ (1024 mg, 7.41 mmol) and 5-(chloromethyl)-1,2,3-tris-(dodecyloxy)benzene (1021 mg, 1.50 mmol). The flask was evacuated and refilled three times with $N_2$. Dry DMF (17 mL) was added to the flask, and the mixture was stirred at 80 ˚C for 3 h. The reaction mixture was poured into water and extracted with *n*-hexane/AcOEt = 3:1 mixture, washed with $H_2O$ and then brine. The organic layer separated was dried over $Na_2SO_4$ and then evaporated to dryness under a reduced pressure. The resulting solid was purified by column chromatography over silica gel (eluent: *n*-hexane/AcOEt = 95:5) to give compound **6** as pale yellow solid (1.108 g, 91% yield). $^1$H NMR (400 MHz, $CDCl_3$, 293 K): $\delta$ = 7.74 (d, $J$ = 8.9 Hz, 1H), 7.71 (s, 1H), 7.70 (d, $J$ = 8.4 Hz, 1H), 7.62 (dd, $J_1$ = 1.7 Hz, $J_2$ = 8.7 Hz, 1H), 7.22 (dd, $J_1$ = 2.5 Hz, $J_2$ = 8.7 Hz, 1H), 7.21 (d, $J$ = 2.4 Hz, 1H), 6.86 (dd, $J_1$ = 10.9 Hz, $J_2$ = 17.6 Hz, 1H), 6.68 (s, 2H), 5.84 (dd, $J_1$= 0.7 Hz, $J_2$ = 17.6 Hz, 1H), 5.30 (dd, $J_1$ = 0.7 Hz, $J_2$ = 10.8 Hz, 1H), 5.07 (s, 2H), 4.02–3.95 (m, 6H), 1.84–1.76 (m, 6H), 1.49–1.44 (m, 6H), 1.27 (m, 48H), 0.89–0.86 (m, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$, 293 K): $\delta$ = 156.96, 153.35, 137.99, 136.92, 134.26, 133.10, 131.68, 129.61, 129.07, 127.09, 126.21, 123.77, 119.32, 113.21, 107.20, 106.24, 73,46, 70.51, 69.13, 31.99, 31.97, 30.38, 29.81, 29.79, 29.75, 29.70, 29.54, 29.47, 29.45, 29.42, 26.18, 26.14, 22.74, 14.17; HRMS (APCI): *m/z* calcd for $C_{55}H_{89}O_4$ 813.6755 $[M+H]^+$, found 813.6757.

**Synthesis of compound 7**: A 50 mL three-neck round bottom flask connected with refluxing condenser was charged with compound **6** (509 mg, 0.626 mmol), 6-bromo-2-naphthaldehyde (87 mg, 0.370 mmol), P(*o*-tolyl)$_3$ (24 mg, 0.079 mmol) and $Pd(OAc)_2$ (18 mg, 0.080 mmol). The flask was evacuated and refilled three times with $N_2$. $Et_3N$ (1.7 mL) and $CH_3CN$ (11 mL) was added to the flask, and the mixture was stirred at 80 ˚C for 1 day. The reaction mixture was poured into water and extracted with $CH_2Cl_2$, washed with $H_2O$ and then brine. The organic layer separated was dried over $Na_2SO_4$ and then evaporated to dryness under a reduced pressure. The resulting solid was purified by column chromatography over silica gel (eluent: *n*-hexane/acetone = 9:1) to give compound **7** as yellow solids (151 mg, 42% yield). $^1$H NMR (500 MHz, TCE-$d_2$, 291 K): $\delta$ = 10.09 (s, 1H), 8.30 (s, 1H), 7.99 (d, $J$ = 8.7 Hz, 1H), 7.93–7.86 (m, 5H), 7.79–7.75 (m, 3H), 7.43 (d, $J$ = 16.3 Hz, 1H), 7.34 (d, $J$ = 16.1 Hz, 1H), 7.25 (dd, $J_1$ = 2.5 Hz, $J_2$ = 9.0

Hz, 1H), 7.21 (d, $J$ = 2.3 Hz, 1H), 6.63 (s, 2H), 5.05 (s, 2H), 3.96–3.90 (m, 6H), 1.78–1.68 (m, 6H), 1.44 (m, 6H), 1.23 (m, 48H), 0.86–0.83 (m, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$, 293 K): $\delta$ = 192.13, 157.26, 153.37, 138.38, 138.04, 136.99, 134.48, 134.16, 133.88, 132.41, 132.09, 131.59, 131.12, 129.93, 129.71, 129.19, 129.04, 127.43, 127.36, 127.12, 126.24, 124.79, 124.04, 123.47, 119.59, 107.35, 106.26, 73.47, 70.56, 69.16, 49.42, 31.96, 30.37, 29.80, 29.78, 29.74, 29.69, 29.60, 29.45, 29.43, 29.41, 26.17, 26.13, 22.72, 14.16; HRMS (APCI): *m/z* calcd for $C_{66}H_{93}O_5$ 965.7018 $[M-H]^-$, found 965.7017.

**Synthesis of compound 1**: A 30 mL three-neck round bottom flask connected with Dimroth condenser was charged with compound **7** (111 mg, 0.115 mmol) and barbituric acid (74 mg, 0.578 mmol). Ethanol (7 mL) was added, and then refluxed at 70 ˚C for 17 h. After the reaction mixture was cooled to room temperature, the resulting precipitate was filtered, and washed several times with hot ethanol. The residual solid was further purified by reprecipitation using a $CHCl_3$-MeOH mixture to give pure compound **1** as red solids (70 mg, 57% yield). $^1$H NMR (500 MHz, TCE-$d_2$, 335 K): $\delta$ = 8.72 (s, 1H), 8.69 (s, 1H), 8.25 (dd, $J_1$ = 0.8 Hz, $J_2$ = 8.6 Hz, 1H), 7.96 (d, $J$ = 8.7 Hz, 1H), 7.92 (s, 1H), 7.88–7.83 (m, 4H), 7.78 (d, $J$ = 9.0 Hz, 1H), 7.75 (s + brs, 3H), 7.46 (d, $J$ = 16.1 Hz, 1H), 7.35 (d, $J$ = 16.2 Hz, 1H), 7.26 (dd, $J_1$ = 2.3 Hz, $J_2$ = 8.9 Hz, 1H), 7.23 (d, $J$ = 2.2 Hz, 1H), 6.66 (s, 2H), 5.08 (s, 2H), 3.99–3.94 (m, 6H), 1.80–1.72 (m, 6H), 1.48–1.44 (m, 6H), 1.34–1.27 (m, 48H), 0.89–0.86 (m, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$, 333 K): $\delta$ = 157.42, 153.45, 139.06, 138.72, 137.96, 134.59, 132.50, 132.03, 131.69, 131.48, 130.44, 130.26, 129.65, 129.28, 127.97, 127.83, 127.45, 127.35, 127.02, 125.74, 124.64, 124.13, 119.45, 107.84, 106.81, 73.44, 70.58, 69.50, 31.85, 30.38, 29.67, 29.62, 29.61, 29.58, 29.53, 29.39, 29.28, 29.26, 26.13, 26.10, 22.57, 13.89; HRMS (ESI): *m/z* calcd for $C_{70}H_{97}O_7N_2$ 1077.7290 $[M+H]^+$, found 1077.7288.

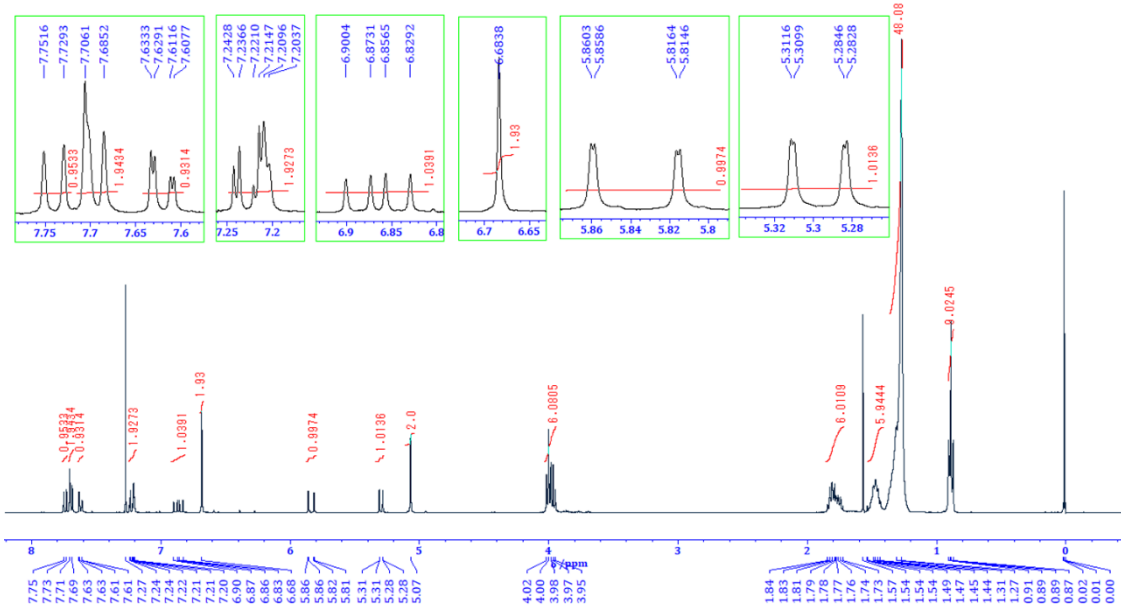


**Chart S1.** $^1$H NMR spectrum of compound **6** in $CDCl_3$ at 293 K.

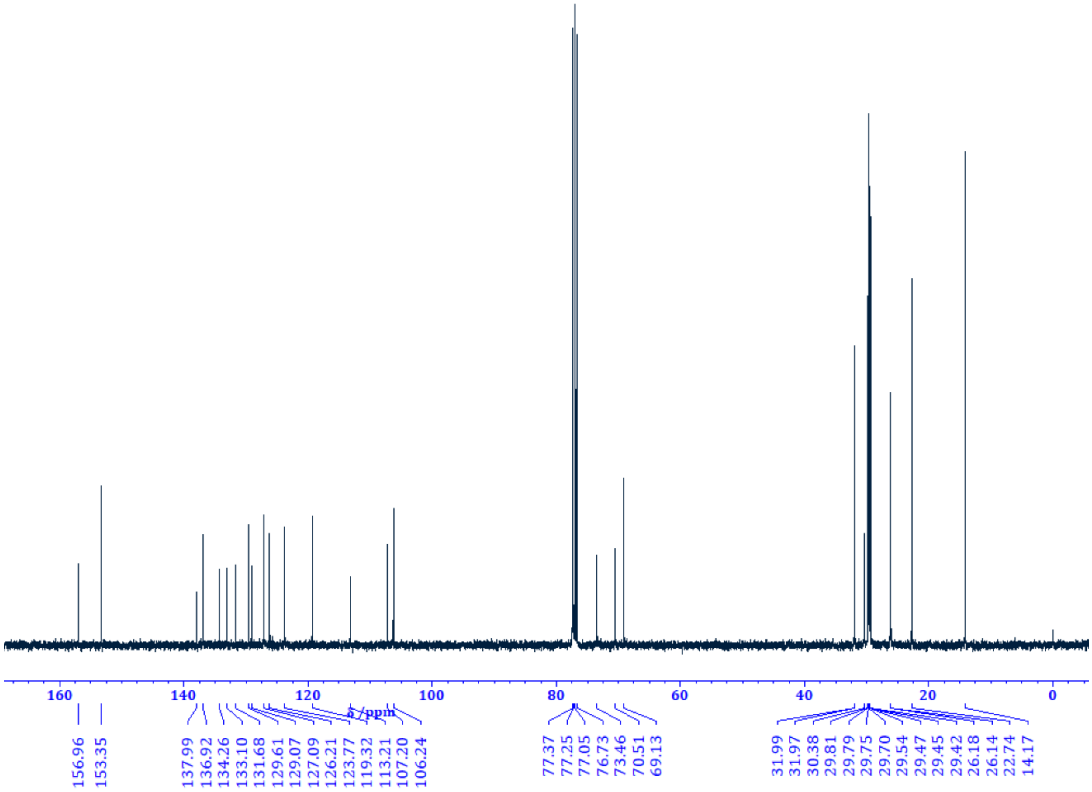


**Chart S2.** $^{13}C$ NMR spectrum of compound **6** in $CDCl_3$ at 293 K.

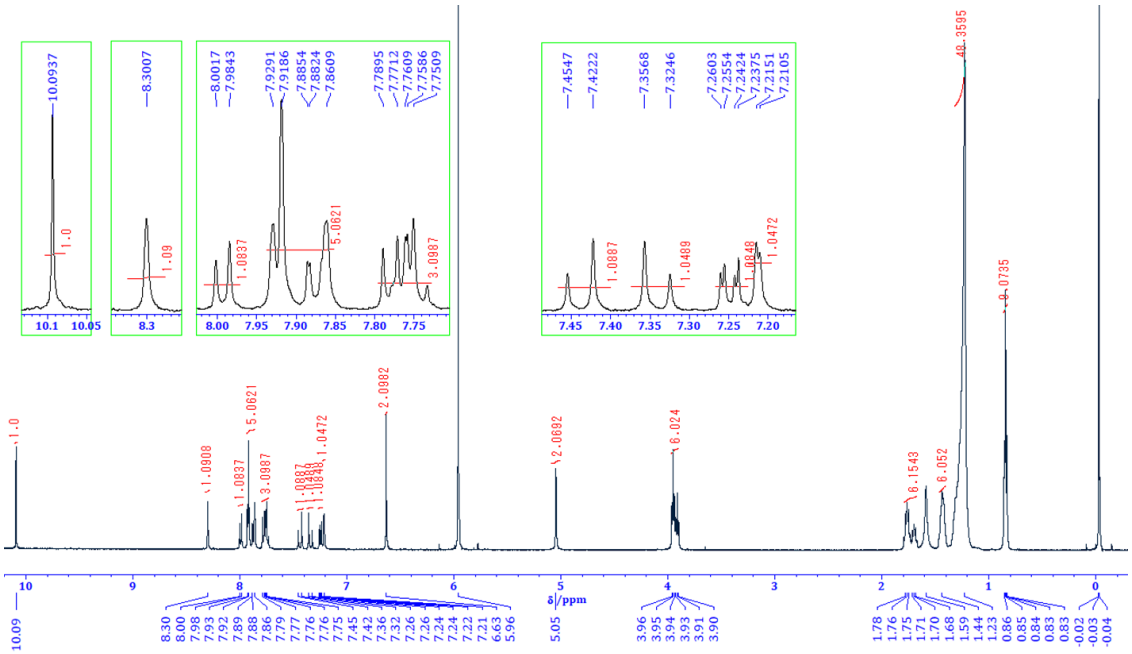


**Chart S3.** $^{1}H$ NMR spectrum of compound **7** in TCE-$d_2$ at 291 K.

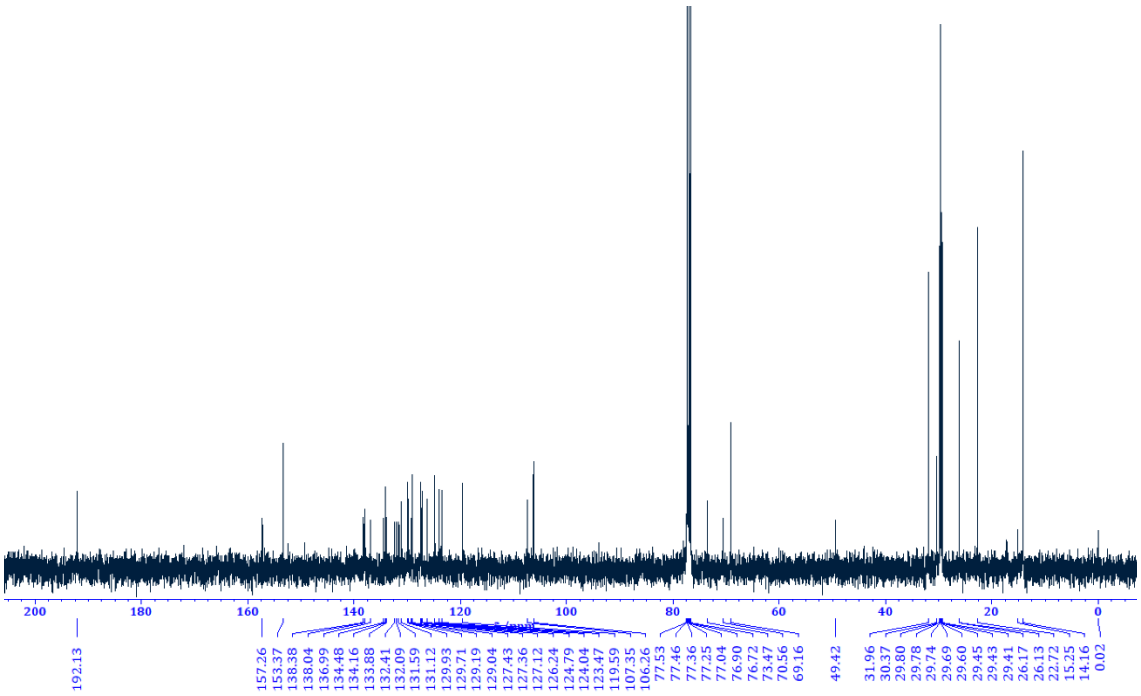


**Chart S4.** $^{13}C$ NMR spectrum of compound **7** in $CDCl_3$ at 293 K.

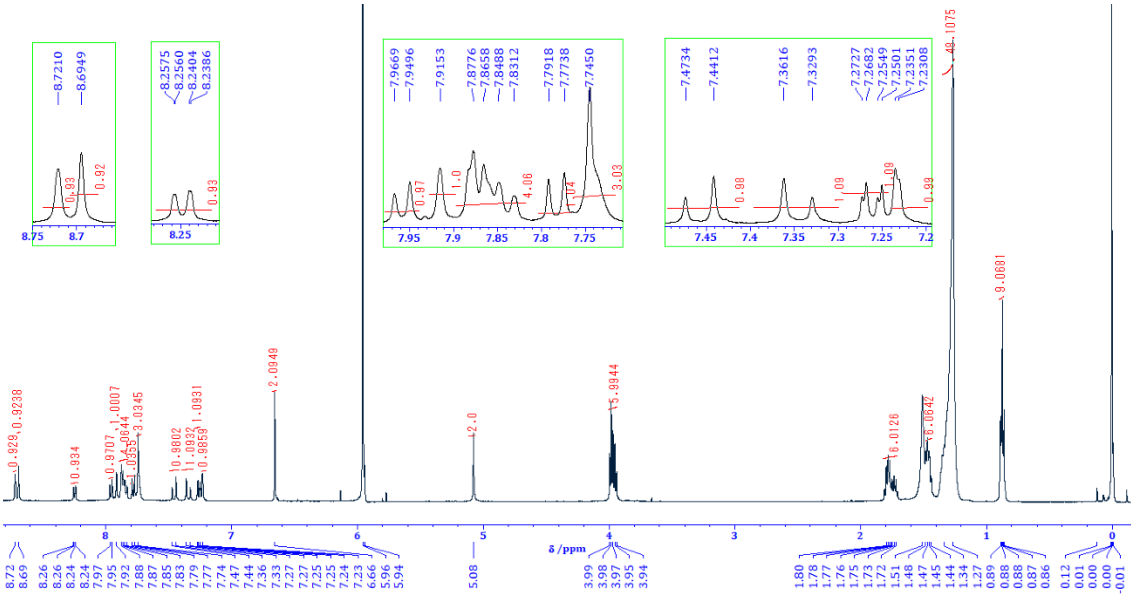


**Chart S5.** $^{1}H$ NMR spectrum of compound **1** in TCE-$d_2$ at 335 K.

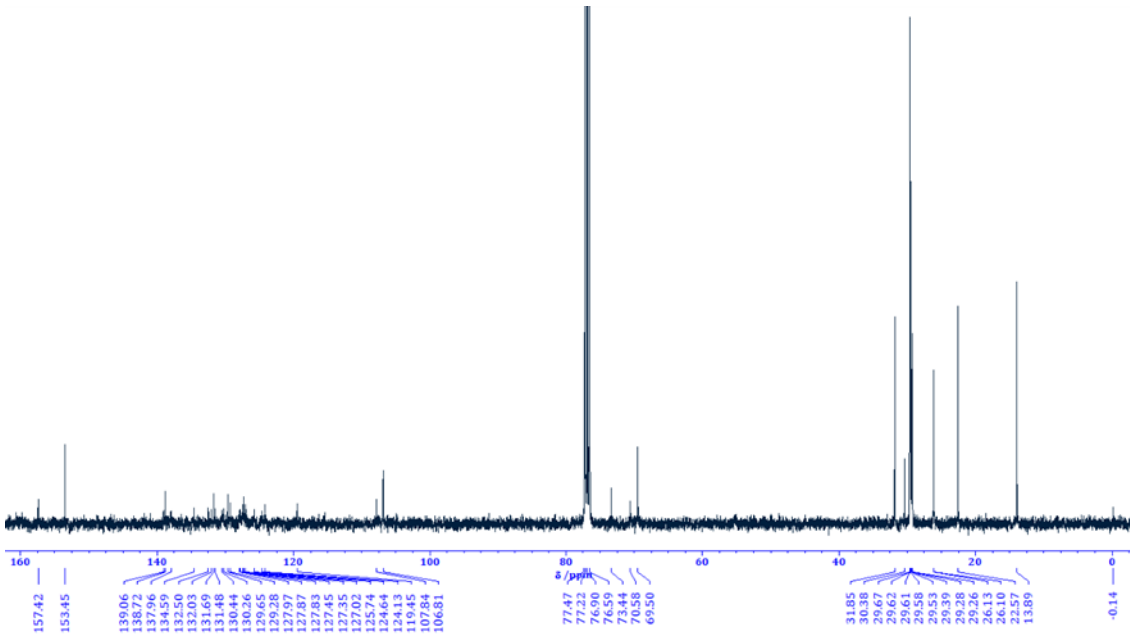



**Chart S6.** $^{13}C$ NMR spectrum of compound **1** in $CDCl_3$ at 333 K.

**Supplementary Figures**

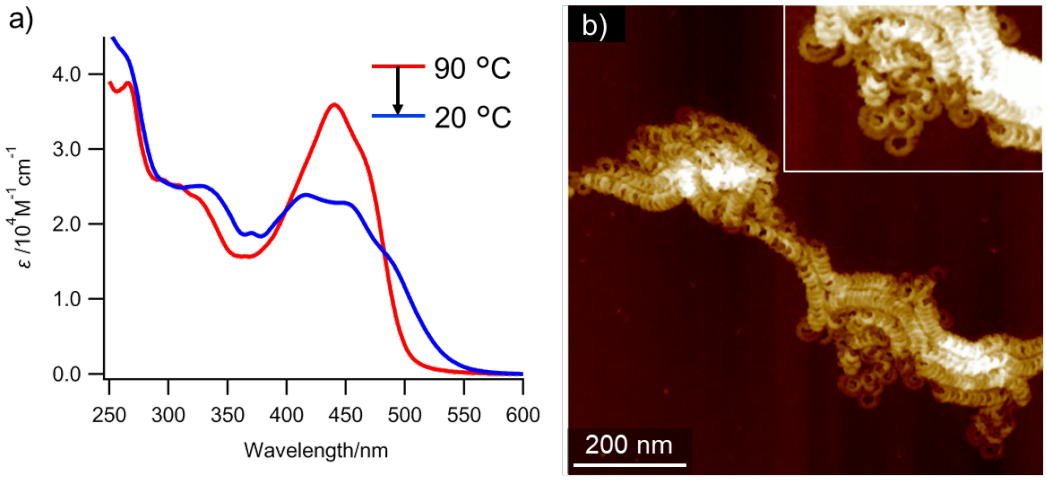



**Fig. S1.** a) Absorption spectra of **1** ($c_t$ = 20 μM in MCH) upon cooling. Cooling rate = 1 °C/min. b) AFM image of a helical supramolecular polymer formed after cooling.

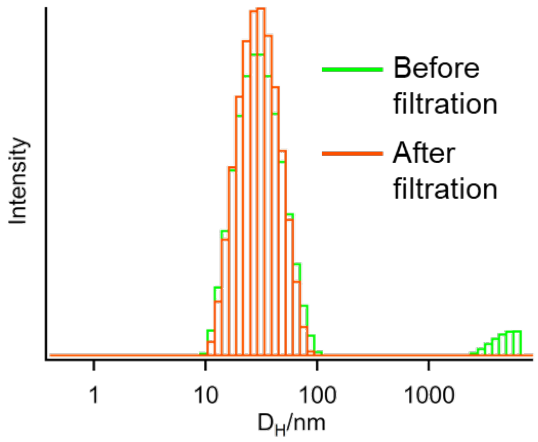



**Fig. S2.** DLS profiles of equilibrated solutions of **1** before filtration (green bars) and after filtration (orange bars). The solutions of **1** was prepared upon injecting a $CHCl_3$ solution of **1** ($c_t$ = 1 mM) into MCH and subsequent aging for 1 day. The final $c_t$ is 100 μM and solvent composition is MCH/$CHCl_3$ = 90:10.

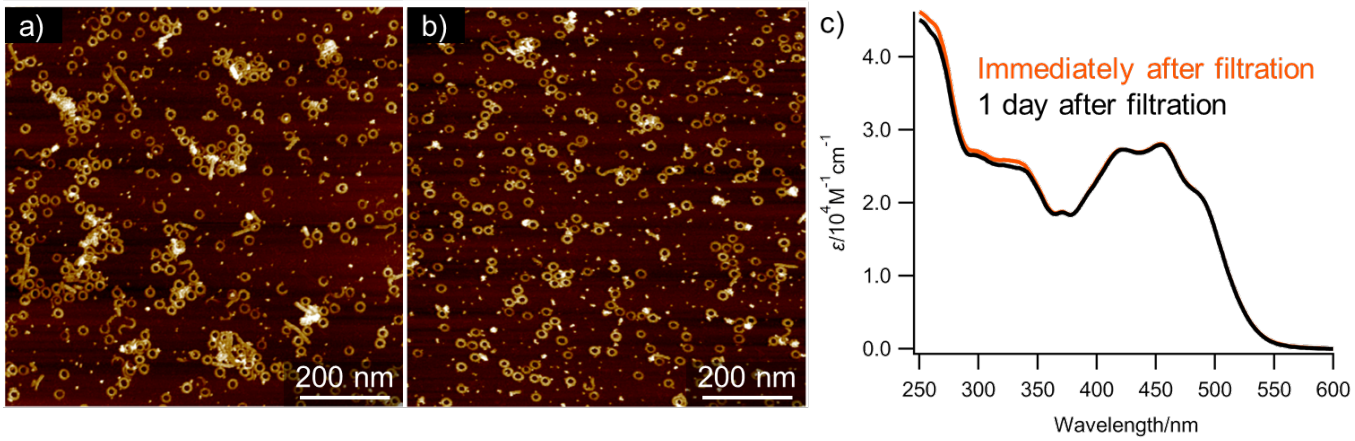



**Fig. S3.** (a,b) AFM image of the assemblies contained in the solution a) immediately after filtration to obtain isolated **Ring**, and b) aged for a day after filtration. c) Absorption spectra of the solution immediately after filtration and that aged for a day after filtration.

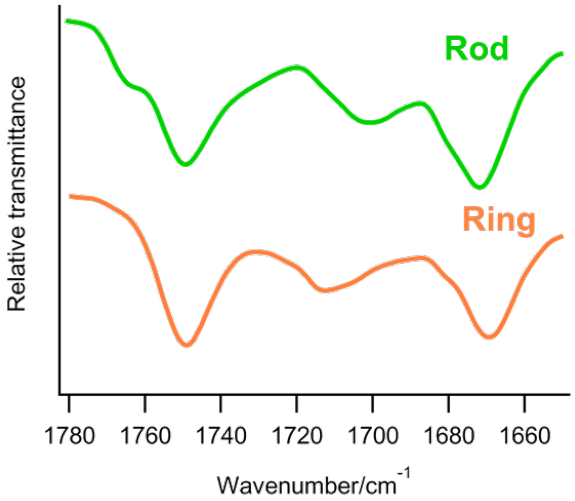



**Fig. S4.** FT-IR spectra of films of **Rod** (green line) and **Ring** (orange line) of **1**. The spectra show the C=O stretching vibrations of the barbituric acid unit. The pure sample of **Rod** was prepared according to the procedure described in the supplementary method section (see page S2).

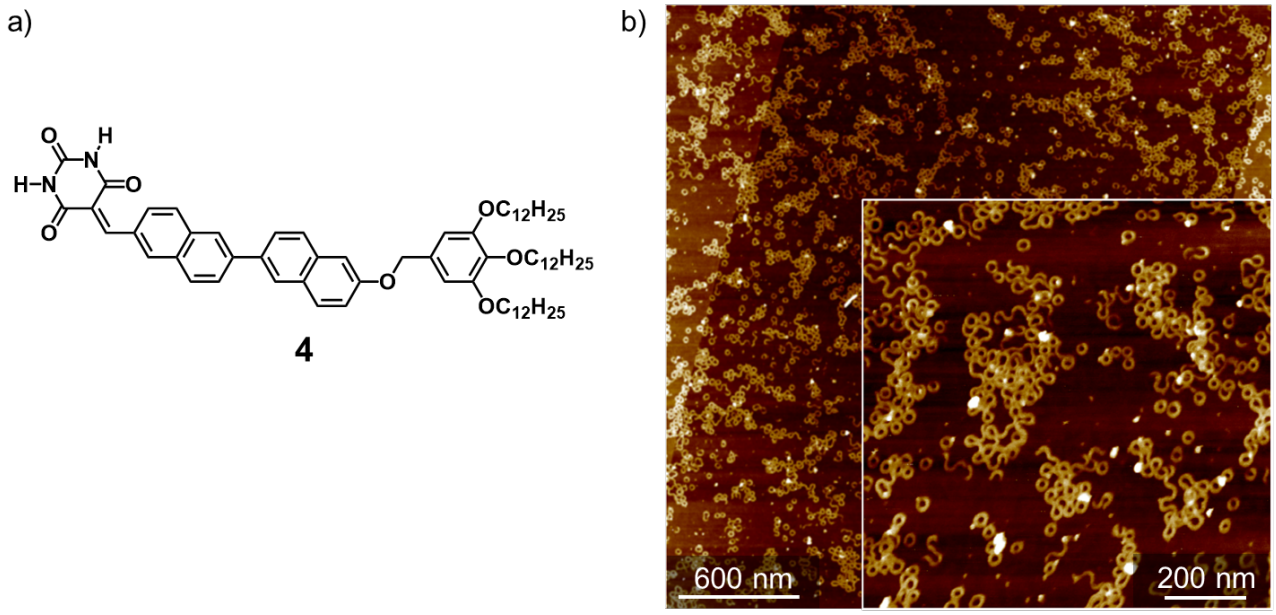



**Fig. S5.** a) Molecular structure of **4**[S9]. b) AFM image of toroidal and randomly coiled fibers of **4** formed by injecting a $CHCl_3$ solution ($c_t$ = 1 mM) into MCH. The final concentration is 100 μM and the final solvent composition is MCH/$CHCl_3$ = 90:10.

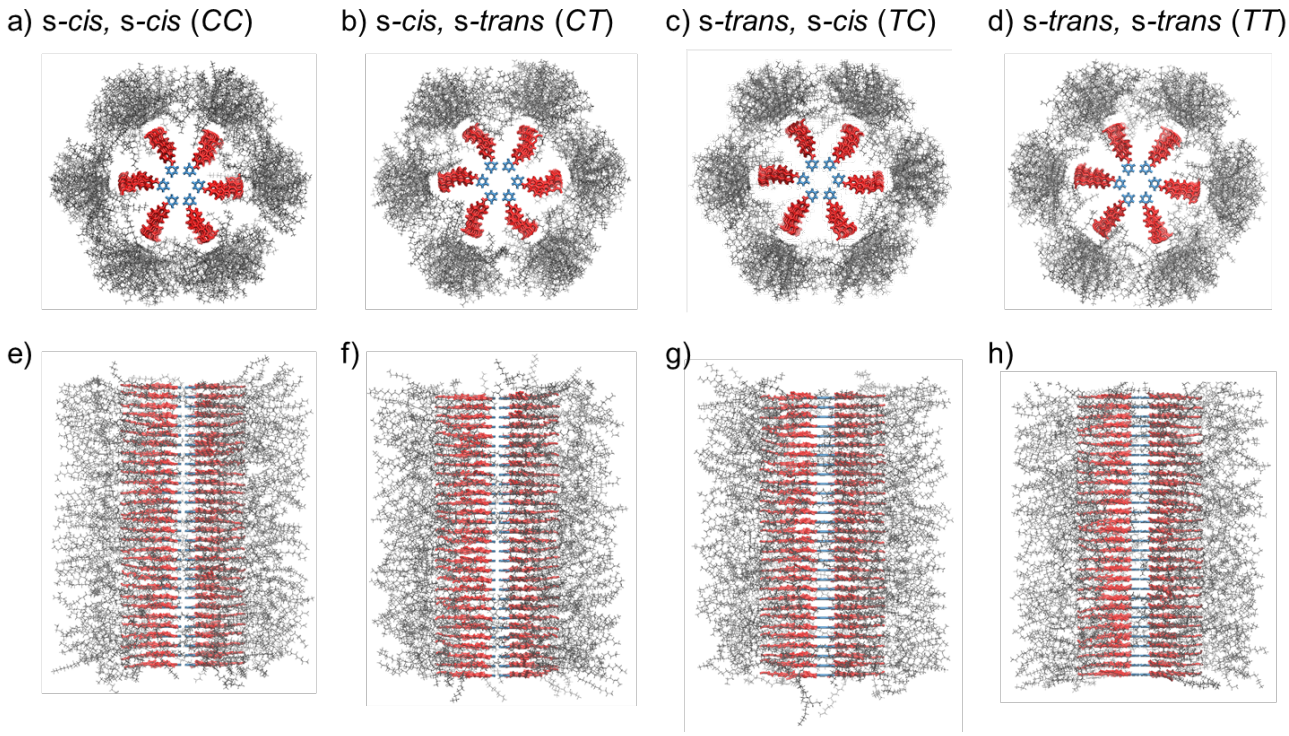



**Fig. S6.** a–d) Top and e–h) side views of prestacked fibers for MD calculations, consisting of 30 homomeric rosettes of four conformational isomers stacked on top of each other.

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## Supplementary Table

**Table S1.** Potential energy of four conformational isomers of **1** and their homomeric rosettes estimated by OPLS-2005 force-field molecular mechanics calculation.

| | s-*cis*, s-*cis* (*CC*) (kJ/mol) | s-*cis*, s-*trans* (*CT*) (kJ/mol) | s-*trans*, s-*cis* (*TC*) (kJ/mol) | s-*trans*, s-*trans* (*TT*) (kJ/mol) |
|---|---|---|---|---|
| Monomer | -26.754 | -26.784 | -26.794 | -26.712 |
| Rosette | -397.01 | -397.20 | -397.14 | -396.76 |

## Supplementary References


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