Supporting Information

Stimuli-Responsive Supramolecular Chirality Switching and Nanoassembly Constructed by n-Shaped Amphiphilic Molecules in Aqueous Solution

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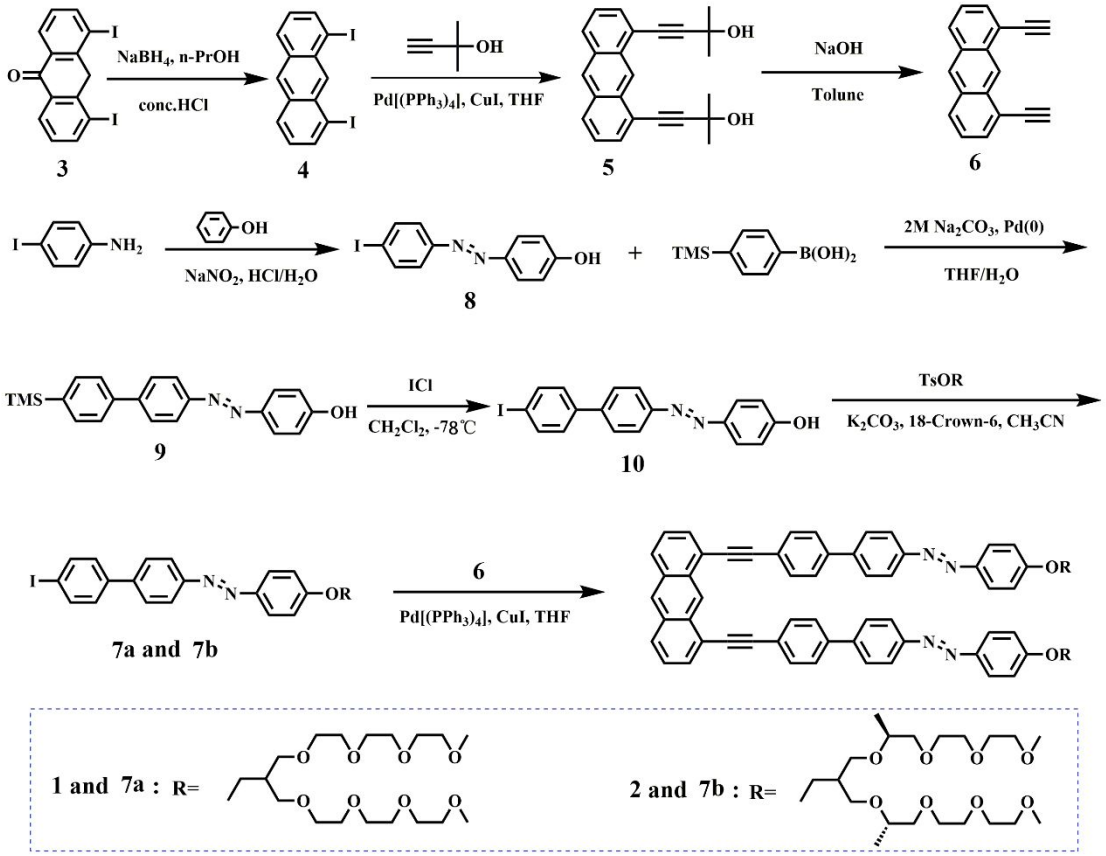
Synthesis



Scheme S1 Synthetic route of molecules 1-2.

Compounds **3-8** and oligoether (chiral) chains was prepared according to the similar procedures reported previously.[1-4]

Synthesis of compound 9

Compound **8** (1.92 g, 5.9 mmol) and 4-(Trimethylsilyl) Phenylboronic Acid (1.49 g, 7.7 mmol) and Pd (0) (0.6 g, 0.52 mmol) were dissolved into a 250 ml single-neck flask with

50 ml of a mixed solution (2 M Na_2CO_3 and THF). The mixture was degassed and refluxed for 24 h under Ar. Last, the solution was concentrated and washed by water. The mixture was extracted with CH_2Cl_2 and dried over anhydrous magnesium sulphate and filtered. After the solvent was removed in a rotary evaporator, the crude product was purified by silica gelchromatography using ethyl acetate/methanol (10:1 v/v) as eluent to yield a yellow solid (0.92 g, 45.0%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 7.95 (q, *J*=9.0 Hz, 4H), 7.75 (d, 2H), 7.62-7.65 (m, 4H), 6.98 (s, 2H), 0.32 (s, 9H).

Synthesis of compound 10

Compound **9** (1.34 g, 3.9 mmol) was dissolved in 20 ml of ultra-dry dichloromethane solution in a 50 ml two-necked flask. The mixture was degassed and refluxed under Ar. The reaction flask was moved to a low temperature reactor and injected 1M iodine chloride solution (5.8 ml) with a syringe for 1.5 hours (ethanol solution -78℃), next, the reaction mixture was stirred 3-5 hours at room temperature. To the mixture were added sodium metabisulfite solution for quenching. The organic layer was separated and the aqueous layer was extracted with dichloromethane, The organic layers were combined and dried with $MgSO_4$. The solvent was removed on a rotorvap and the residue was purified by column chromatography (silica gel) using EA / CH_3OH=10 / 1(V/V)) as eluent to yield (0.93 g, 60.0%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 7.95 (q, *J*=9.0 Hz, 4H), 7.81 (d, 2H), 7.70 (d, 2H), 7.41 (d, 2H), 6.97 (d, 2H), 5.16 (s, 1H).

Synthesis of compound 7

Compounds **7a** and **7b** were synthesized using the same procedure.[5] A representative example is described for **7a**. Compound **10** (0.37g, 0.92 mmol) was dissolved in 100 ml of acetonitrile solvent, then added dendrimer chain[4] (0.61g, 1.1 mmol) and K_2CO_3 (0.51 g, 3.7 mmol). The mixture was degassed and refluxed for 24 h. Last, the solution was concentrated and washed by water. The mixture was extracted with ethyl acetate, dried over anhydrous magnesium sulfate and filtered. The crude product was purified by column

chromatography (silica gel) to yield (0.38 g, 53%). ^{1}H-NMR (300MHz, $CDCl_3$, δ, ppm): 7.95 (q, *J*=6.0 Hz, 4H), 7.80 (d, 2H), 7.69 (d, 2H), 7.40 (d, 2H), 4.15 (d, 2H), 3.50-3.68 (m, 28H), 3.37 (s, 6H), 2.41-2.49(m, 1H).

compound 7b ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 7.94 (q, *J*=9.0 Hz, 4H), 7.80 (d, 2H), 7.69 (d, 2H), 7.41 (d, 2H), 7.04 (d, 2H), 4.13 (d, 2H), 3.52-3.69 (m, 26H), 3.37 (s, 6H), 2.33-2.40 (m, 1H), 1.14 (q, *J*=3.0 Hz, 6H).

Methods

TEM experiments. A drop of each sample solution was placed on a carbon-coated copper grid and the solution was allowed to evaporate under ambient conditions. These samples were stained by uranyl acetate aqueous solution (0.2-0.4 wt%) on the surface of the sample-loaded grid. The dried specimen was observed by TEM at 120 or 200 KV.

AFM experiments. A drop of each sample solution was placed on mica surface and was prepared by evaporation of sample solutions. The dried specimen was observed by AFM.

UV-irradiation experiments. After all the compounds involved in photoreaction are prepared into conventional solutions, the substrate (mica and copper mesh) is prepared in advance, and the sample is dropped on the substrate. UV-irradiation of the solution for the isomerization experiments was carried out at different time in a dark space and in a dark room with the help with 365 nm UV lamps. It will be kept in a small box wrapped in tin foil until the test.

Molecular Simulations. Molecules were performed by Desmond program, molecular dynamic simulations by Maestro (SCHRÖDINGER 2015-4) with the following parameters; Simulation time (ns): total 1.2, elapsed: 0.0, Recording interval (ps) energy: 1.2, trajectory: 4.8, Ensemble class: NVT, Solvent: H_2O, Temperature (K): 300K or 320K or 340K, Pressure (bar): 1.01325, Surface tension (bar Å): 4000.0.

Techniques.

Proton nuclear magnetic resonance (^{1}H NMR, 300 MHz) spectra were recorded in $CDCl_3$ or DMSO on a Bruker AM-300 instrument. MALDI-TOF-MS analysis was performed on a PerSeptive Biosystems Voyager-DESTR instrument using 2-cyano-3-(4-hydroxyphenyl) acrylic acid (CHCA) as the matrix. The UV-vis and FL spectra were obtained with JASCO UV-V650 UV-vis and FP-8200 FL spectrometers, respectively. CD spectra were obtained with an Applied Photophysics Chirascan Spectrometer. Transmission electron microscope (TEM) experiments were performed with a JEOL 2010Plus microscope. Atomic force microscope (AFM) images were produced by an Agilent 5500 Atomic Force Microscope.

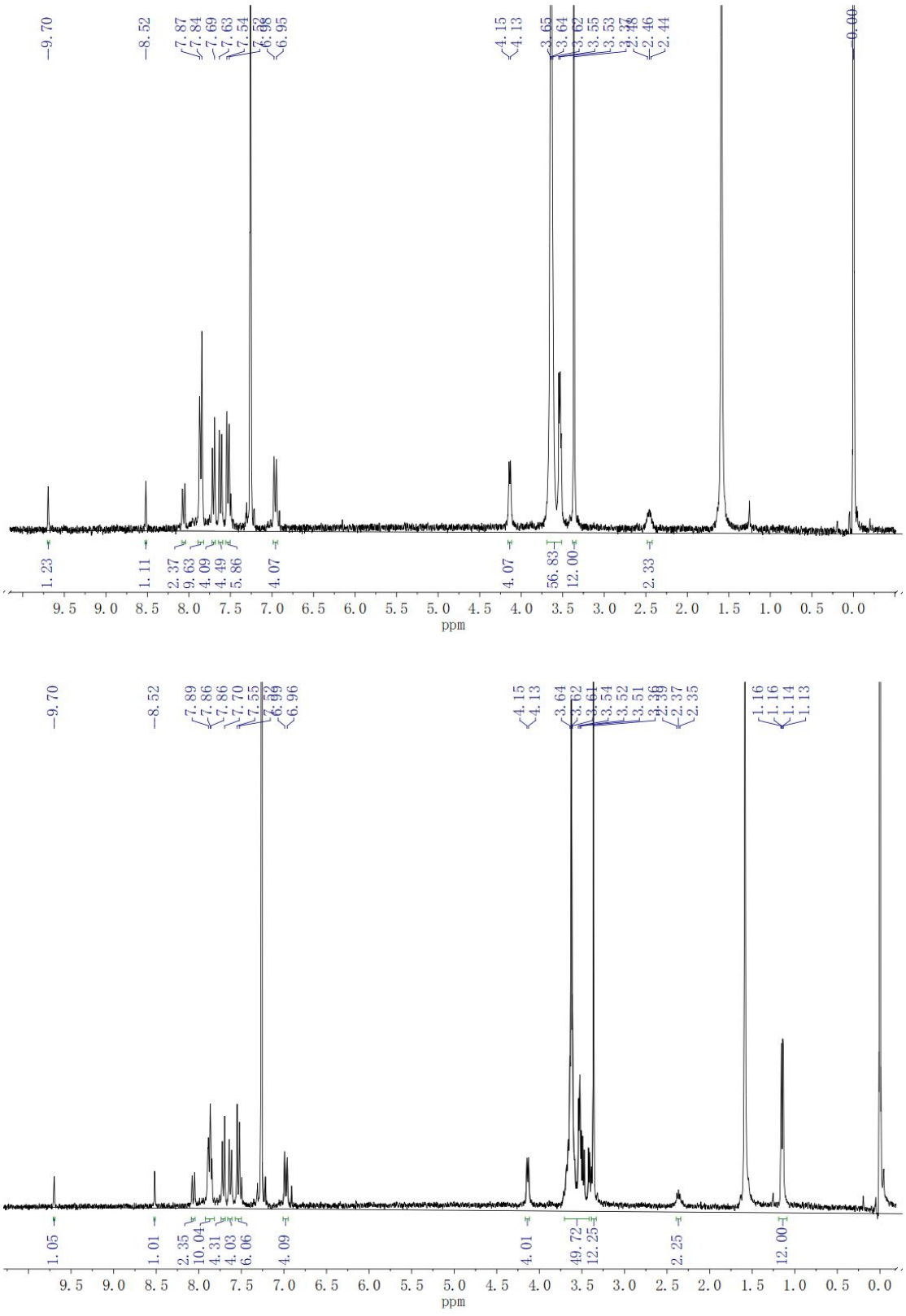


Figure S1. ^{1}H-NMR spectra of molecules **1-2** in $CDCl_3$.

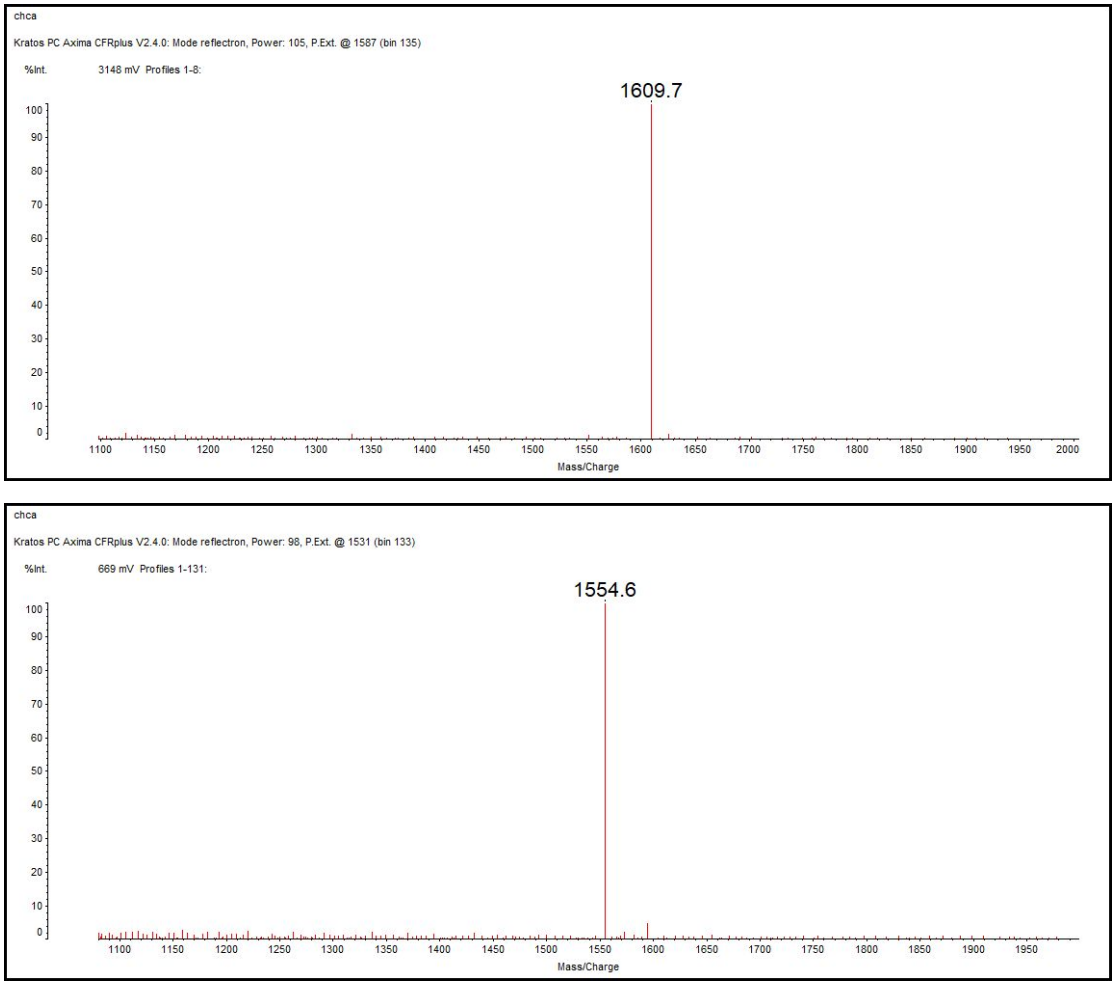


Figure S2. MALDI-TOF-Mass spectra of molecules **1-2** (matrix: CHCA).

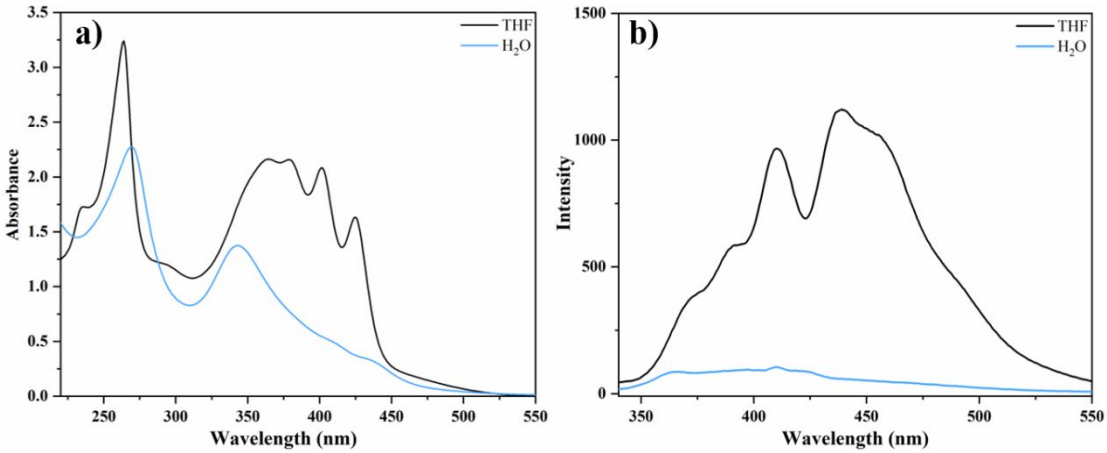


Figure S3. Absorption and emission spectra of **1** (a) and (b) in THF and aqueous solutions (0.005 wt %).

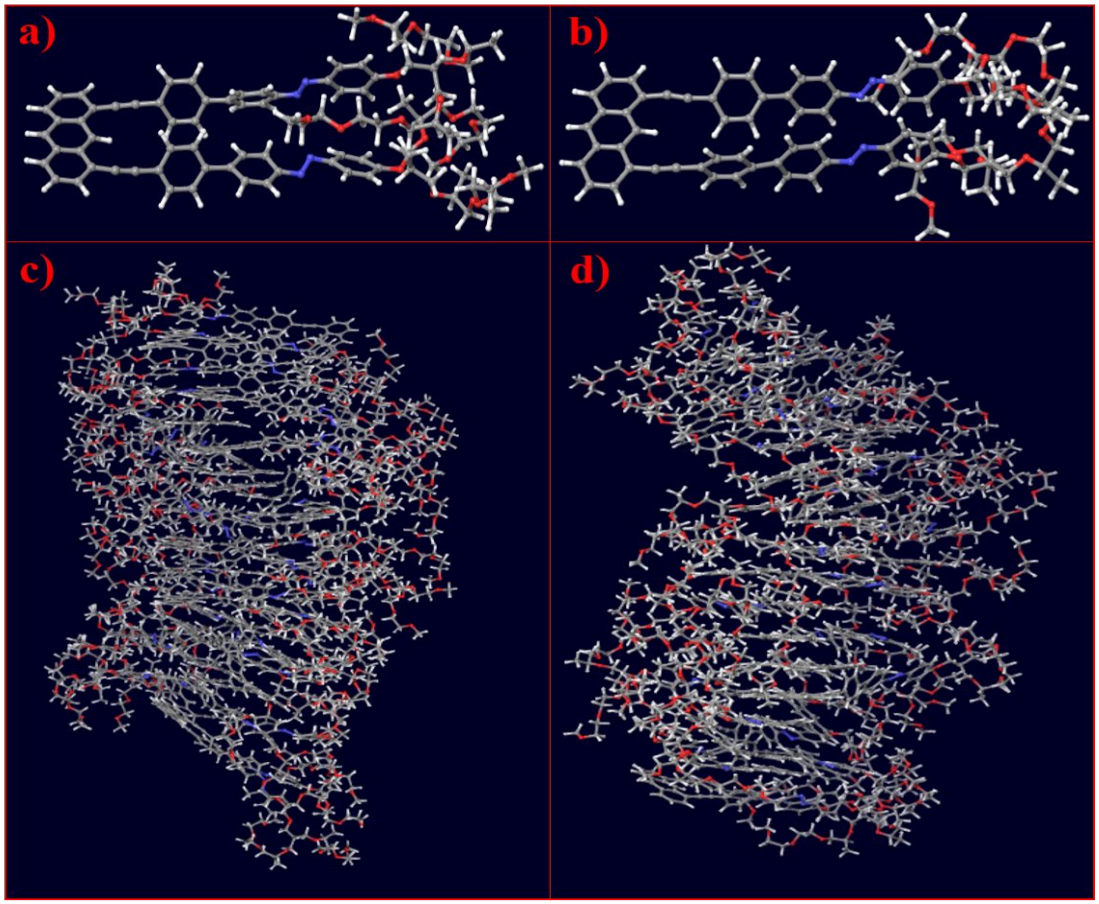


Figure S4. Desmond program, molecular dynamic simulations result of **2** in water environment at 300 K and 320 k by Maestro (SCHRÖDINGER 2015-

4); a) and b) Single molecule conformation of **2** at 300 K and 320 k; c) and d) Aggregates of **2** at 300 K and 320 k in aqueous solution.

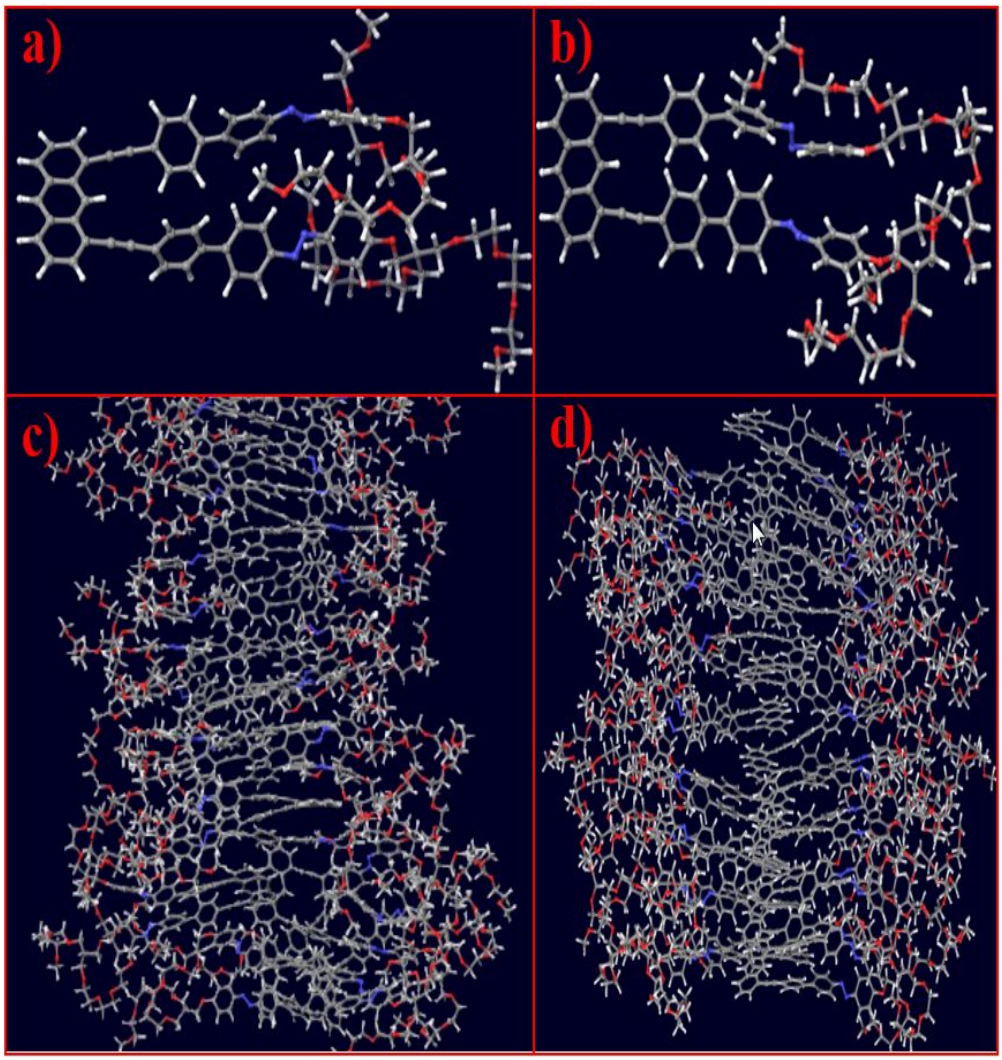


Figure S5. Desmond program, molecular dynamic simulation results of **1** in water environment at 300 K and 340 k by Maestro (SCHRÖDINGER 2015-4); a) and b) Single molecule conformations of **1** at 300 K and 340 k; c) and d) Aggregates of **1** at 300 K and 340 k in aqueous solution.

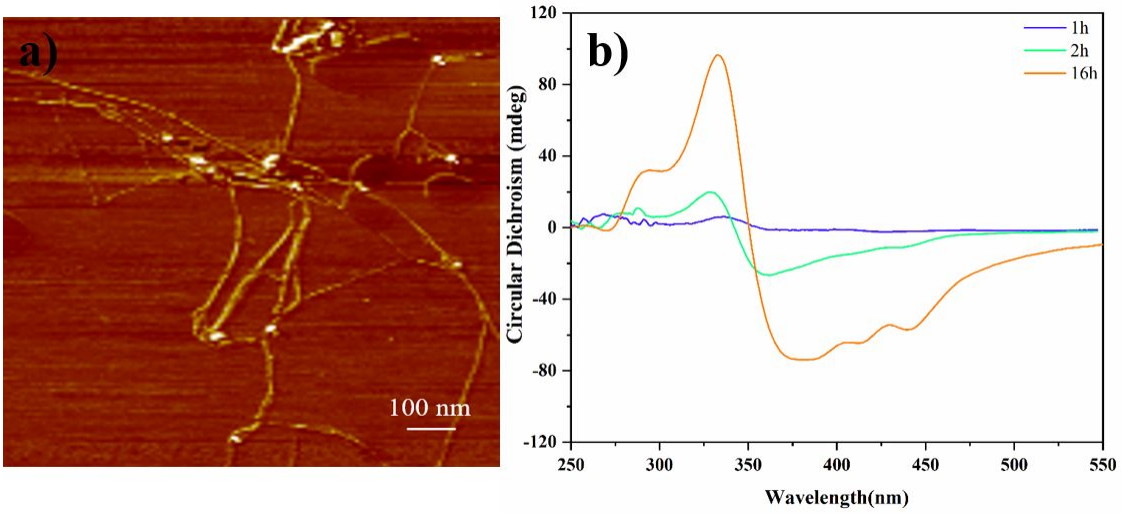


Figure S6. a) AFM image of **2** (obtained from 0.00125 wt % in aqueous solution); b) Time-dependent CD spectra of **2**.

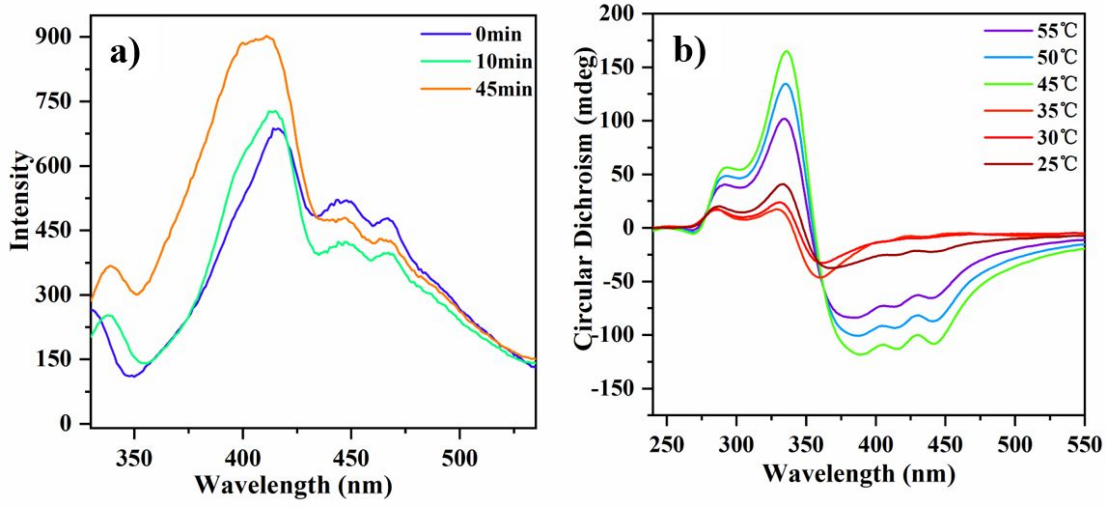


Figure S7. a) FL images f **2** at 25 °C under UV light at different times; b) Temperature-dependent CD spectra of **2** under cooling state.

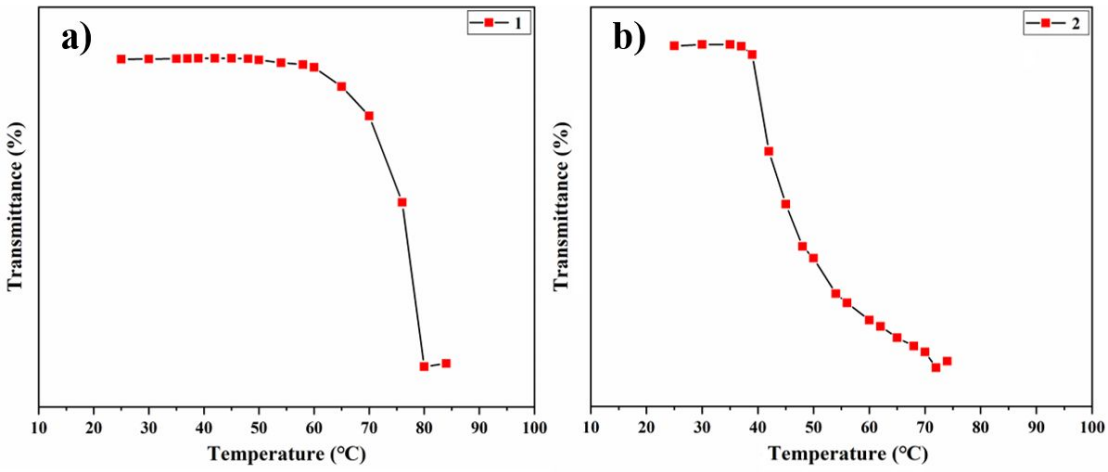


Figure S8. Transition temperatures of solution **1**(a) and **2** (b).

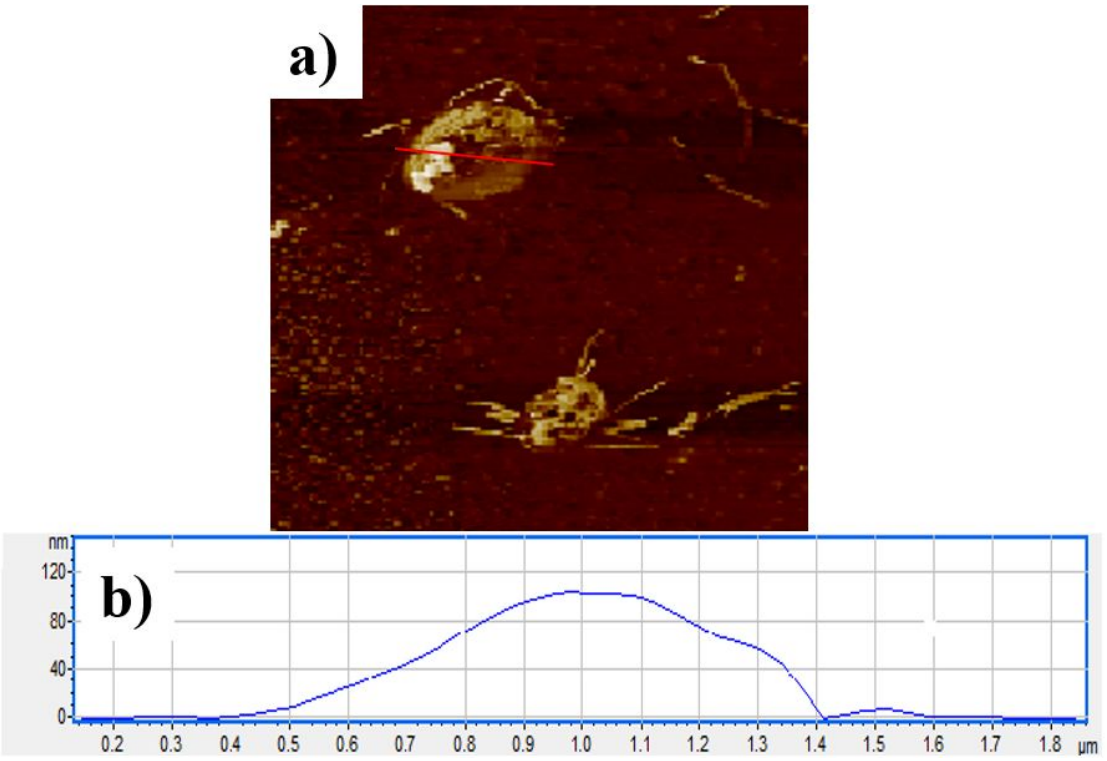


Figure S9. a) AFM phase image of **2** at 45 °C (Freeze-dried by freeze dryer) and b) the corresponding height profile analysis.

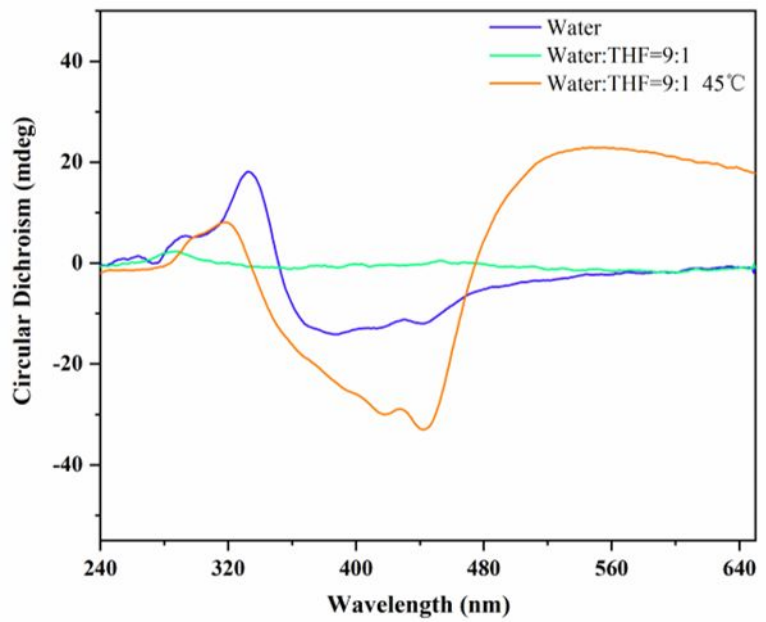


Figure S10. CD spectra of **2** in the mixed solvent (H_2O/THF) at 25 °C and 45 °C (0.005 wt % in solution).

References for supporting information

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