

# Supporting Information

## Azobenzene Molecular Machine: Light-Induced Wringing Gel Fabricated from Asymmetric Macrogelator

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### EXPERIMENTAL METHOD

#### *Sample Preparations*

The oriented films for 2D WAXD experiments were obtained by mechanical extruding at 150 °C and thermal annealed for 3 h. A typical sample thickness was about 0.4 mm. The samples prepared for POM had a typical thickness of 10 μm, and they were melt-processed between two bare cover glass slides. The samples for FT IR were sandwiched between two KBr pellets. The sample was first heated to the isotropic state and then cooled to room temperature to eliminate previous thermal history. For the UV-Vis, the sample was collected with  $1 \times 10^{-2}$  mM

concentration in chloroform on the rectangular quartz cell. Xerogel samples for the SEM were prepared by freeze-drying and coated on platinum to maintain the original structure of 1AZ3BP.

#### *Equipment and Experiment*

Proton ( $^1\text{H}$ ) and carbon ( $^{13}\text{C}$ ) nuclear magnetic resonance spectra (NMR, JNM-EX400, JEOL) in deuterated chloroform ( $\text{CDCl}_3$ ) were recorded at room temperature to confirm the chemical structure and purity as shown in Figures S1-4, respectively. Molecular weight and distributions of 1AZ3BP was determined by Matrix-assisted Laser Desorption/ionization Time-of-Flight mass spectroscopy (MALDI-ToF, Voyager DE PRO Spectrometer, PerSeptive Biosystems) assisted by 2,5-dihydroxybenzoic acid (DHB, Aldrich) as matrix on a spectrometer.

The thermal ability of 1AZ3BP was analyzed by thermogravimetry (TGA, TA instrument, US/TA5000). Molecular origins at various temperature were also evaluated by FT IR (Jasco FT/IR-300E) equipped with a temperature controller. The 40 scans were collected at a spectral resolution of  $1\text{ cm}^{-1}$ . Differential scanning calorimetry (DSC) are performed TA-Q20 instrument operated at various cooling and heating scan rate over the temperature range of 30 - 200 °C under nitrogen gas. For the DSC experiments, the sample weights were controlled to be about 5.0 mg and the pan weights were kept constant with a precision of  $\pm 0.001\text{ mg}$ . Heating experiments always progressed the cooling experiments to eliminate previous thermal histories, and the cooling and heating rates were always kept identical.

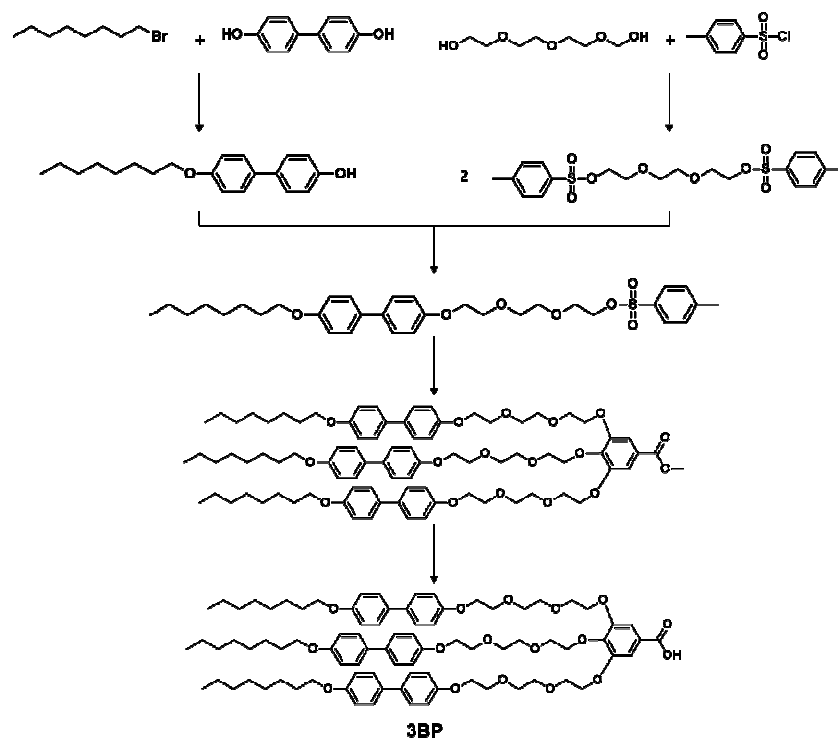
The 1D powder pattern and oriented 2D WAXD patterns were obtained using a Rigaku x-ray imaging system with an 18 kW rotating anode x-ray generator. Silicon crystal powder, used as an internal reference, shows a diffraction ring at a  $2\theta$  value of  $28.466^\circ$ . For 2D WAXD experiments, background scatterings were subtracted from the sample scans. The Cerius<sup>2</sup> (version 4.6) simulation software from Accelrys was also used to calculate the global equilibrium

conformation of the 1AZ3BP in the isolated gas phase utilizing the COMPASS force field. The 1D SAXS measurements are used to study the phase structure. The X-ray beam is produced by a CuK $\alpha$  microsource. The SAXS intensity profiles were plotted against  $q=4\pi\sin \theta/\lambda$ , in which  $\lambda$  is the wavelength of X-ray ( $\lambda=0.154$  nm) and  $2\theta$  is the scattering angle.

Optical textures at different temperatures were taken using a cross-polarized optical microscopy (POM, Nikon ECLIPSE LV100POL) with a METTLER TOLEDO FP90 Central Processor heating stage in order to investigate morphology on the micrometer scale. The surface morphology of the xerogel was studied by utilizing scanning electron microscopy (SEM, JEOL JSM-6400). Absorption spectra were obtained using a UV/Vis spectrometer (Scinco S-3100). The photo-isomerization of 1AZ3BP was examined after exposing UV light (365 nm and 4 mW/cm<sup>2</sup>) to the sample for 10 min.

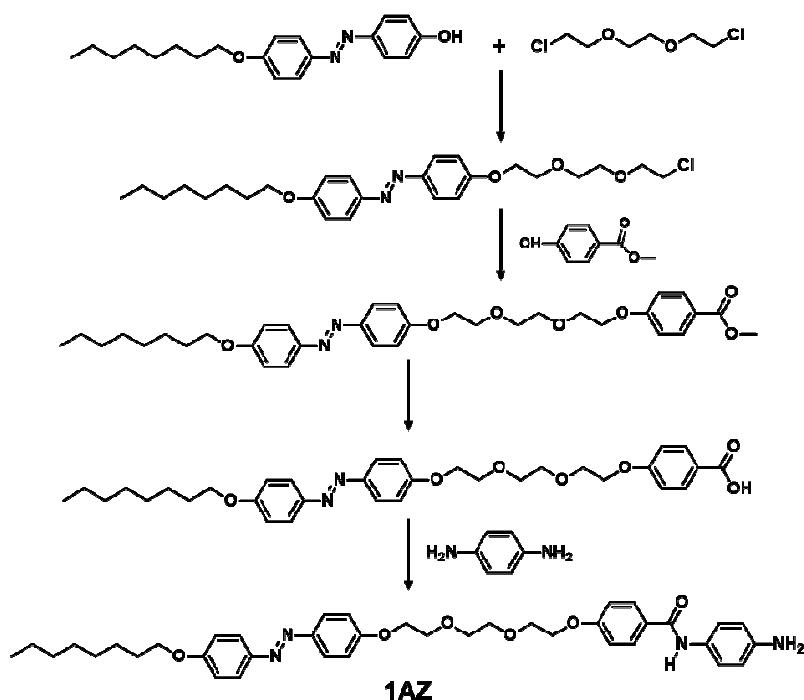
## EXPERIMENTAL SECTION

**Scheme S1.** Synthetic procedures of 3BP dendron.





**Scheme S2.** Synthetic procedures of 1AZ molecular machine.



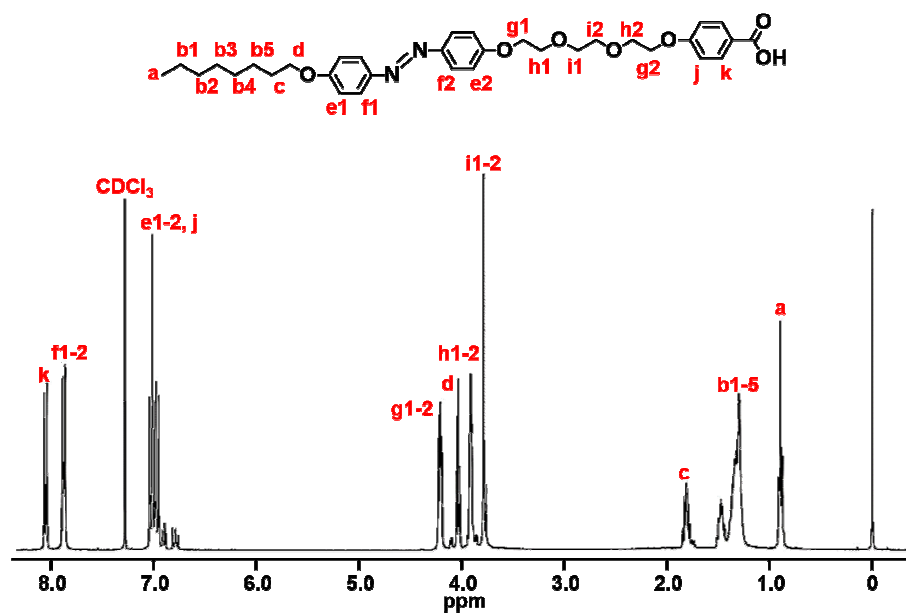
#### *Material Preparations.*

**1AZ.** 1,4-Phenylenediamine (1.868 g, 17.28 mmol), 4-(2-(2-(2-((4'-(octyloxy)-[1,1'-biphenyl]-4-yl)oxy)ethoxy)ethoxy)ethoxy)benzoic acid (1.0 g, 1.73 mmol), and DPTS (4-(dimethylamino)pyridinium-4-toluenesulfonate, 0.254 g, 0.86 mmol) were dissolved in 50 mL MC/THF solution with the ratio MC/THF = 4:1 (v/v) and stirred at 0 °C for 30 min. After DIPC (diisopropylcarbodiimide, 1.090 g, 8.64 mmol) was added into the mixture, the solution was stirred at 0 °C for 24 h. 50 ml of H<sub>2</sub>O was poured into the solution and then extracted with MC (3 × 30 ml). The crude product was subjected to column chromatography (silica, MC/THF = 4:1 (v/v)) to remove disubstituted product. After chromatography, products were re-precipitated from MeOH to obtain the compound as yellow powders (Yield: 74 %, 0.85 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 0.89 (t: 3H), 1.23-1.31 (m: 10H), 1.80 (m: 2H), 3.62 (s: 2H), 3.77 (t: 4H),

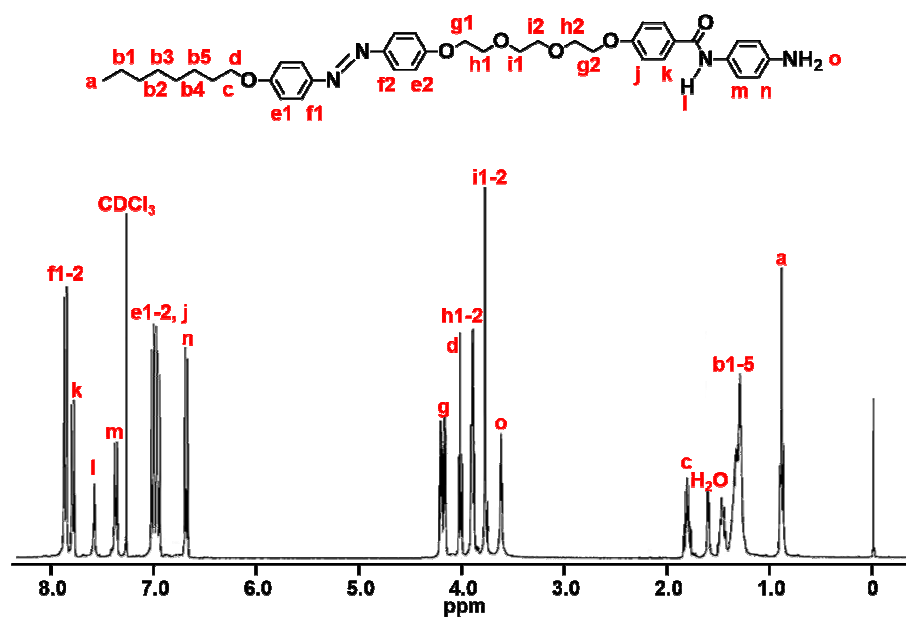
3.89 (m: 4H), 4.02 (t: 2H), 4.20 (m: 4H), 6.68 (d: 2H), 6.99 (m: 6H), 7.36 (d: 2H), 7.57 (s: 1H), 7.84 (q: 4H), 8.01 (d: 2H).

**3BP.** A solution of methyl 3,4,5-tris(2-(2-(2-((4'-(octyloxy)-[1,1'-biphenyl]-4-yl)oxy)ethoxy)ethoxy)ethoxy)benzoate (0.5 g, 0.352 mmol) in THF/MeOH (9 mL/6 mL) was added into an aqueous NaOH (ca. 10 M, 2 ml). The mixture was refluxed for 5 h and then neutralized with hydrochloric acid to gain precipitates. The precipitated solids were filtered and washed with distilled H<sub>2</sub>O. The crude product was purified by re-precipitation in CHCl<sub>3</sub> and EtOH and dried under vacuum to afford 3BP as a white waxy solid (Yield: 90 %, 0.45 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 0.87 (t: 9H), 1.28-1.47 (m: 30H), 1.75-1.82 (m: 6H), 3.70 (m: 12H), 3.88 (m: 12H), 3.95 (t: 6H), 4.10 (m: 6H), 4.17 (t: 4H), 4.23 (t: 2H), 6.90 (m: 12H), 7.29 (s: 2H), 7.44 (m: 12H).

**1AZ3BP.** 1AZ (0.11 g, 0.15 mmol), 3BP (0.1 g, 0.07 mmol), EDC·HCl (N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride, 0.05 g, 0.35 mmol), and HOBt (1-hydroxybenzotriazole, 0.05 g, 0.30 mmol) were dissolved in 15 mL MC/DMF (4:1 (v/v)) and stirred at room temperature for 5 days. After the reaction, solvents were removed and remaining residues were dissolved in CHCl<sub>3</sub> and re-precipitated in MeOH. The crude product was purified by column chromatography with silica gel (MC/THF = 3:1 (v/v) as eluent). The solid product was washed several times with EtOH in ultrasonicator and then filtered. The resulting product was sand-like yellow powder (Yield: 22.5 %, 0.07 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 0.89 (s: 3H), 1.23-1.31 (m: 40H), 1.78 (m: 8H), 3.73 (m: 16H), 3.68 (m: 16H), 3.79-3.92 (m: 16H), 3.92-4.04 (t: 8H), 4.04-4.28 (t: 16H), 6.85-7.04 (m: 18H), 7.18 (s: 2H), 7.38-7.46 (q: 12H), 7.54-7.66 (q: 4H), 7.73 (s: 1H), 7.76-7.82 (d: 2H), 7.82-7.89 (d: 4H), 8.11 (s: 1H).



**Figure S1.**  $^1\text{H}$  NMR spectrum of 4-(2-(2-(2-((4'-(octyloxy)-[1,1'-biphenyl]-4-yl)oxy)ethoxy)ethoxy)ethoxy)benzoic acid.



**Figure S2.**  $^1\text{H}$  NMR spectrum of 1AZ.

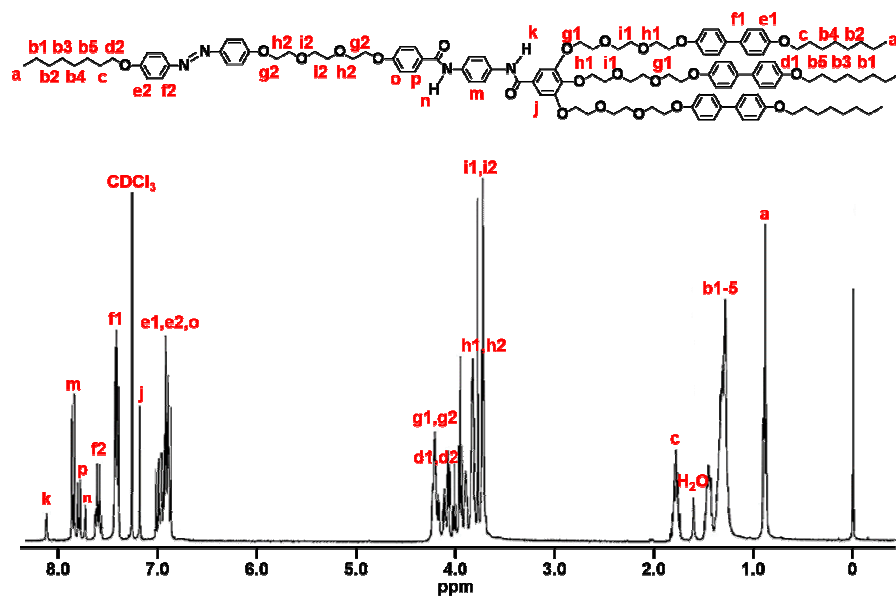


Figure S3.  $^1\text{H}$  NMR spectrum of 1AZ3BP.

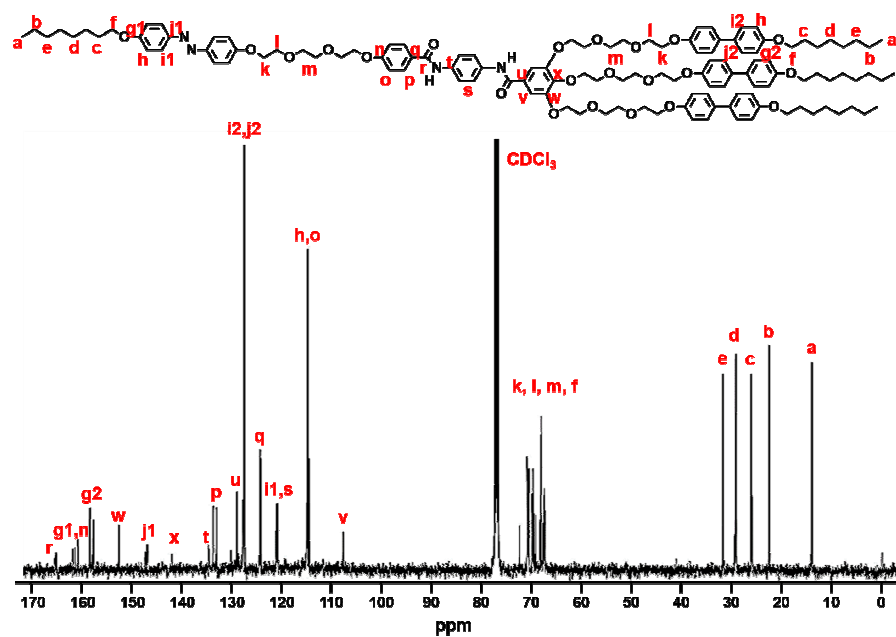


Figure S4.  $^{13}\text{C}$  NMR spectrum of 1AZ3BP.

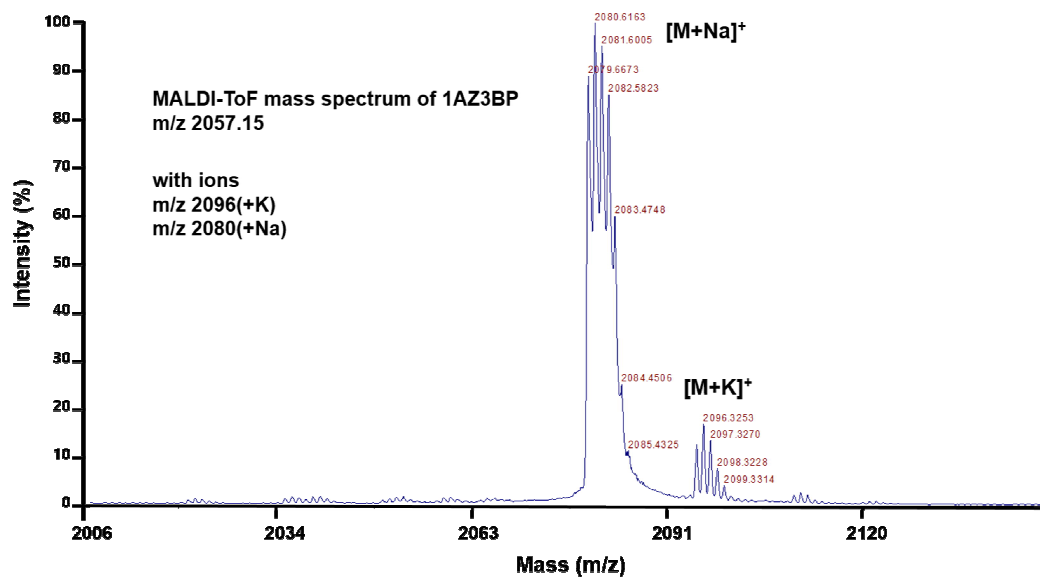


Figure S5. MALDI-ToF spectrum of 1AZ3BP.

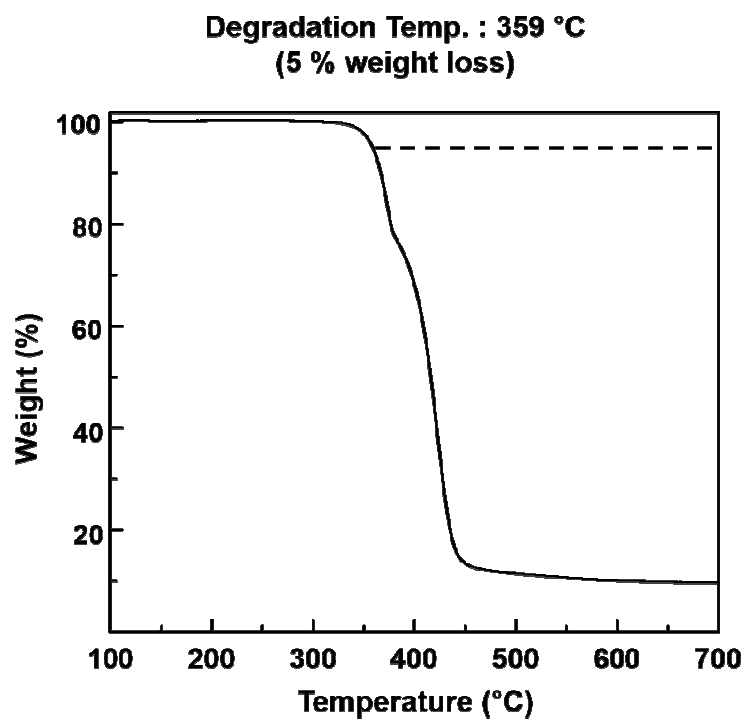
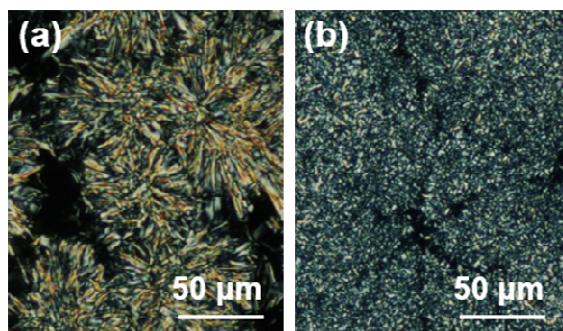
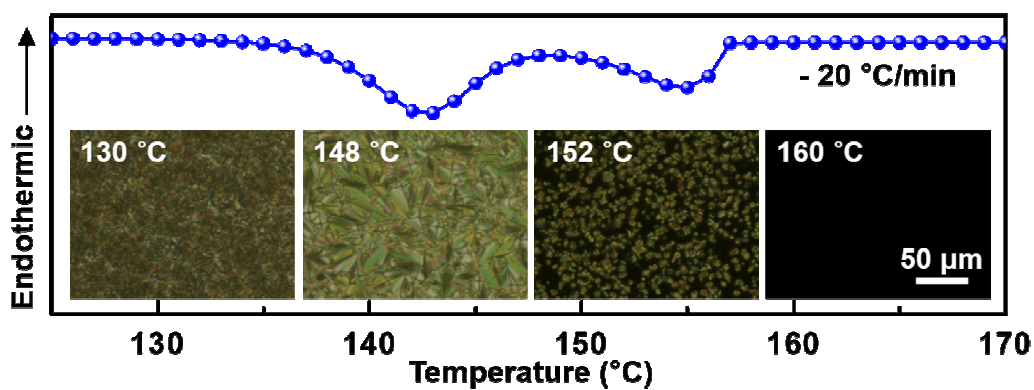


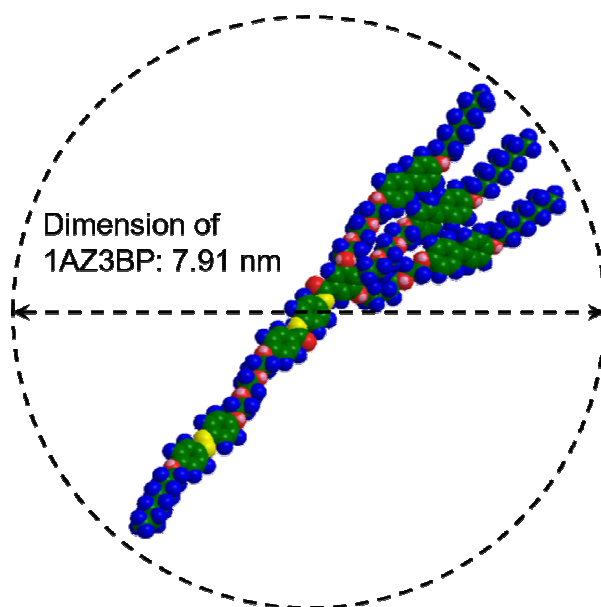
Figure S6. Thermogravimetric curve of 1AZ3BP.



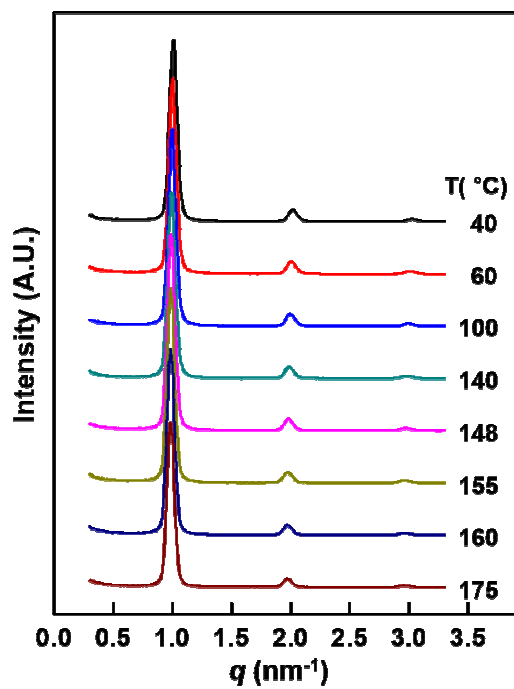
**Figure S7.** POM images taken at room temperature by cooling at (a) - 2.5 °C/min and (b) - 20 °C/min, respectively.



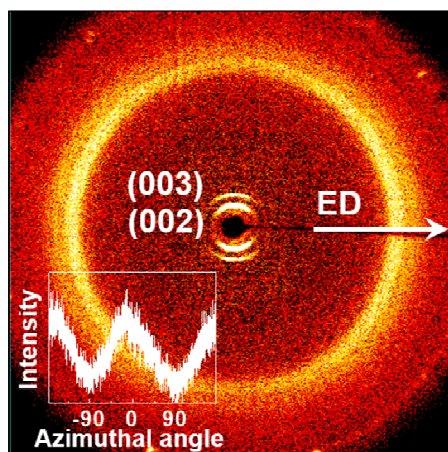
**Figure S8.** Magnified DSC thermogram of 1AZ3BP at -20 °C/min with corresponding POM images taken at different temperatures.



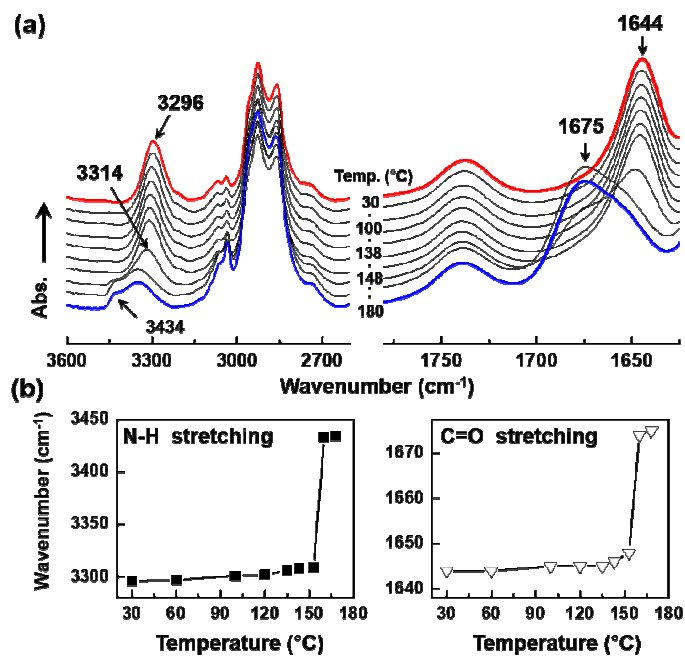
**Figure S9.** Energy minimized molecular geometry of 1AZ3BP.



**Figure S10.** 1D SAXS powder patterns of 1AZ3BP at different temperatures during heating process at 2.5 °C/min.



**Figure S11.** 2D WAXD patterns for a smectic crystal phase at 25 °C.



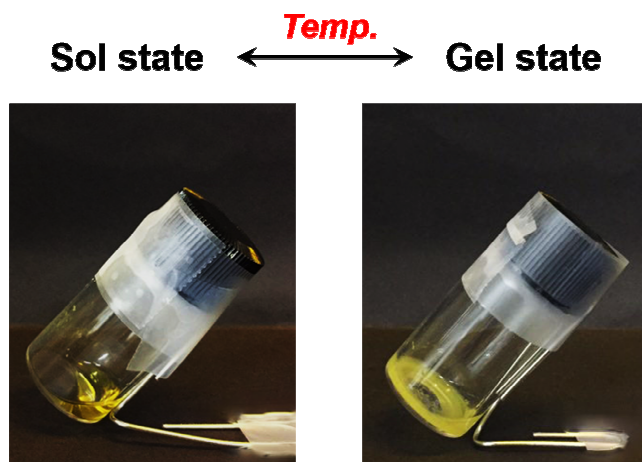
**Figure S12.** (a) FT IR spectra of 1AZ3BP during heating from 30 °C to 180 °C at 2.5 °C/min: wavenumber variations for (b) N-H and (c) C=O stretching vibrations at different temperatures.



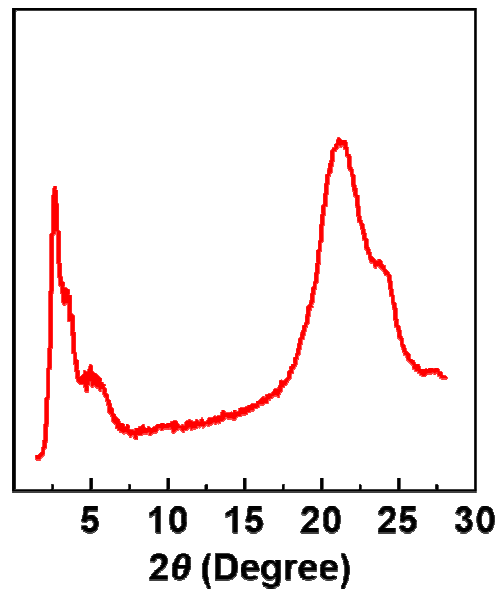
**Table S1.** Gelation properties of 1AZ3BP in organic solvents, 3 wt%.

	Solvent	Polarity Index	1AZ3BP
<b>Non-polar solvent</b>	Hexane	0.1	I
	Cyclohexane	0.2	G
	Toluene	2.4	PG
	Chloroform	4.0	S
<b>Polar solvent</b>	Tetrahydrofuran	4.0	S
	Ethyl acetate	4.4	P
	Acetone	5.1	P
	DMF	6.4	P

**G: Gel / PG: Partial gel / P: Precipitate / S: Solution / I: Insoluble**



**Figure S13.** Sol-Gel transition by heat treatment of organogel consisted of 3 wt% 1AZ3BP.



**Figure S14.** 1D WAXD pattern of xerogel after exposing UV light.