Supporting Information

Self-Assembled Hierarchical Superstructures from the Benzene-1,3,5-Tricarboxamide Supramolecules for the Fabrication of Remote-Controllable Actuating and Rewritable Films

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EXPERIMENTAL METHOD

Materials and Sample Preparations

The oriented samples for 2D WAXD experiments were obtained by mechanical extruding in the liquid crystalline phase and thermally treated at different temperatures. 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 prepared 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 prepared with 1.25×10^{-3} mg/ml concentration in chloroform. Xerogel samples for the SEM was prepared by freeze-drying and coated on platinum.

Equipment and Experiment

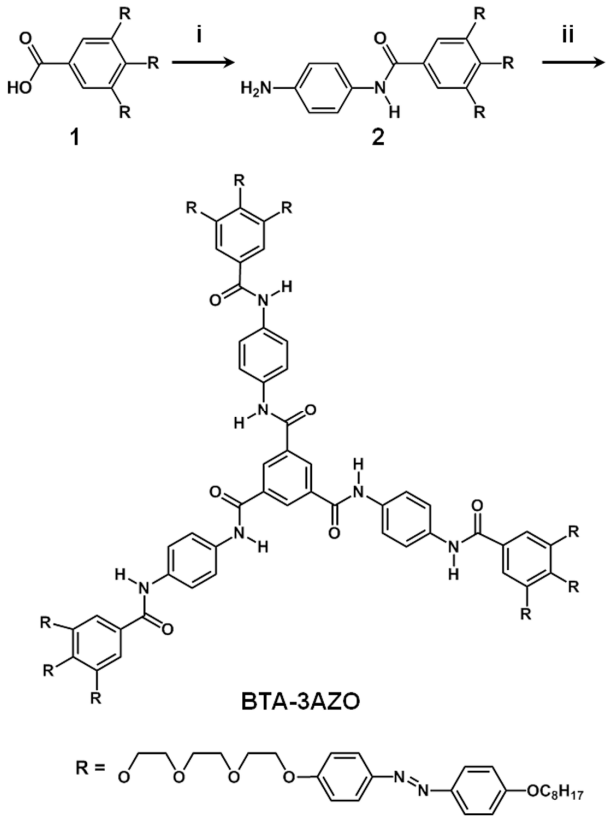
Chemical structure and purity of BTA-3AZO were confirmed by proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR, JNM-EX400, JEOL) in deuterated chloroform ($CDCl_3$) and dimethyl sulfoxide (DMSO-d_6). Chemical shifts were quoted in part per million (ppm) with a reference of tetramethylsilane (TMS) and each NMR spectra were shown in Figures S1-3, respectively. Molecular weight of BTA-3AZO was confirmed by Matrix-assisted Laser Desorption/ionization Time-of-Flight mass spectroscopy (MALDI-ToF MS, Voyager DE PRO Spectrometer, PerSeptive Biosystems). 2,5-dihyroxybenzoic acid (DHB, Aldrich) was used as the matrix on a spectrometer. Elemental analysis was performed by an EA1110 (CE instrument). The analysis of results was determined by the ratio of elements within the sample, and working out a chemical formula that fits with those results. Molecular orientations in the uniaxially oriented films were also evaluated by FT IR (Jasco FT/IR-300E) equipped with a temperature controller. The resolution of FT IR was 1 cm^{-1}, and 40 scans were averaged for spectrum.

Thermal transition behavior was studied using differential scanning calorimetry (DSC, PYRIS Diamond DSC, Perkin-Elmer), For the DSC experiments, the sample weights were controlled to be about 6.0 mg and the pan weights were kept constant with a precision of ± 0.001 mg. The temperature and heat flow scales were calibrated using standard materials at different cooling and heating rates. Transition temperatures were determined using the onset temperatures. Heating experiments always preceded the cooling experiments to eliminate previous thermal histories, and the cooling and heating rates were always kept identical. Optical textures of the ordered phases at different temperatures were observed with POM (Nikon ECLIPSE LV100POL) coupled with a METTLER TOLEDO FP90 Central Processor heating stage in order to investigate morphology on the micrometer scale.

The 1D WAXD experiments were conducted in the reflection mode of a Rigaku 12 kW rotating anode X-ray (CuKα radiation) generator coupled with a diffractometer. The diffraction peak positions and widths were calibrated with silicon crystals in the high 2θ-angle region (>15°) and silver behenate in the low 2θ-angle region. To monitor the structural evolutions with temperature changes, a hot stage calibrated to be within ± 1 °C error was coupled to the diffractometer. Samples were scanned across a 2θ-angle range of 1.5° to 35° at a scanning rate of 2 °C/min.

The 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 2θ value of 28.466°. A hot stage was also used to obtain diffraction peaks from the ordered structures at different temperatures. A 30 min exposure time was required for a high-quality pattern. In 2D WAXD experiments, background scatterings were subtracted from the sample scans. The Cerius[2] (version 4.6) simulation software from Accelrys

was also used to calculate the global equilibrium conformation of the BTA-3AZO in the isolated gas phase utilizing the COMPASS force field. The 1D and 2D SAXS measurements are used to study the phase structure. The X-ray beam is produced by a CuKα microsource. The SAXS intensity profiles were plotted against $q=4\pi\sin\theta/\lambda$, in which λ is the wavelength of X-ray (λ =0.154 nm) and 2θ is the scattering angle.



Scheme S1. Synthetic route of BTA-3AZO. Reagents and conditions: (i) 1,4-penylenediamine, *N,N′*-diisopropylcarbodiimide (DIPC), 4-(dimethylamino) pyridinium toluene-*p*-sulfonate (DPTS) and MC/THF at r.t. for 24 h; (ii) benezene-1,3,5- tricarbonyl chloride, pyridine and THF at r.t. for 24 h.

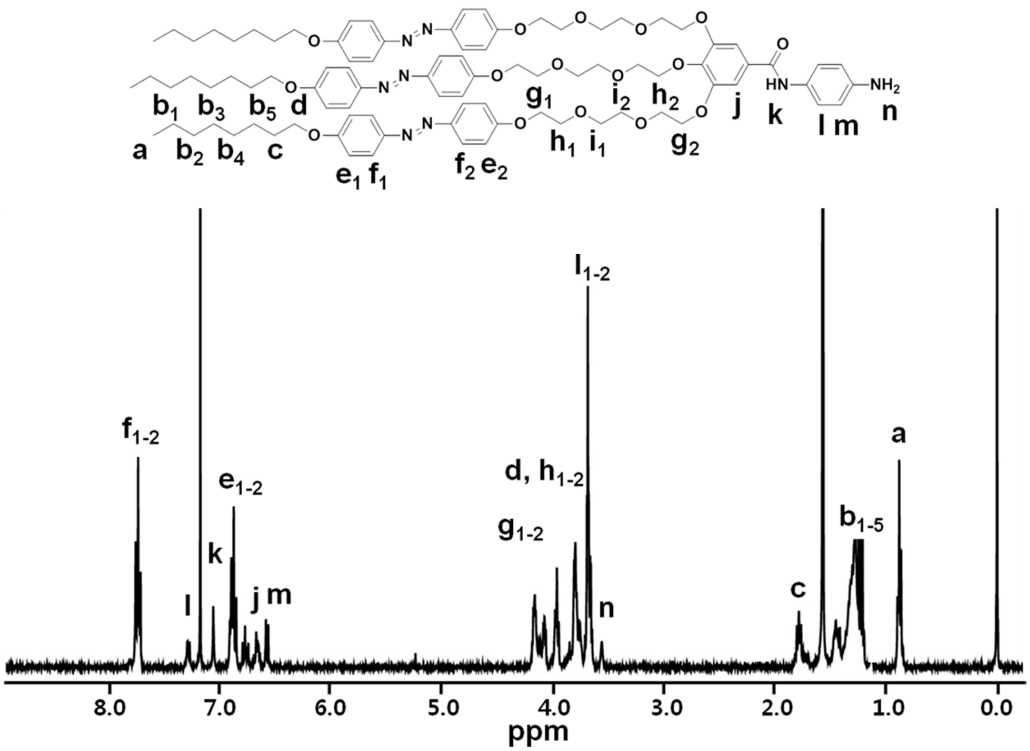


Figure S1. ^{1}H NMR spectrum of compound 2.

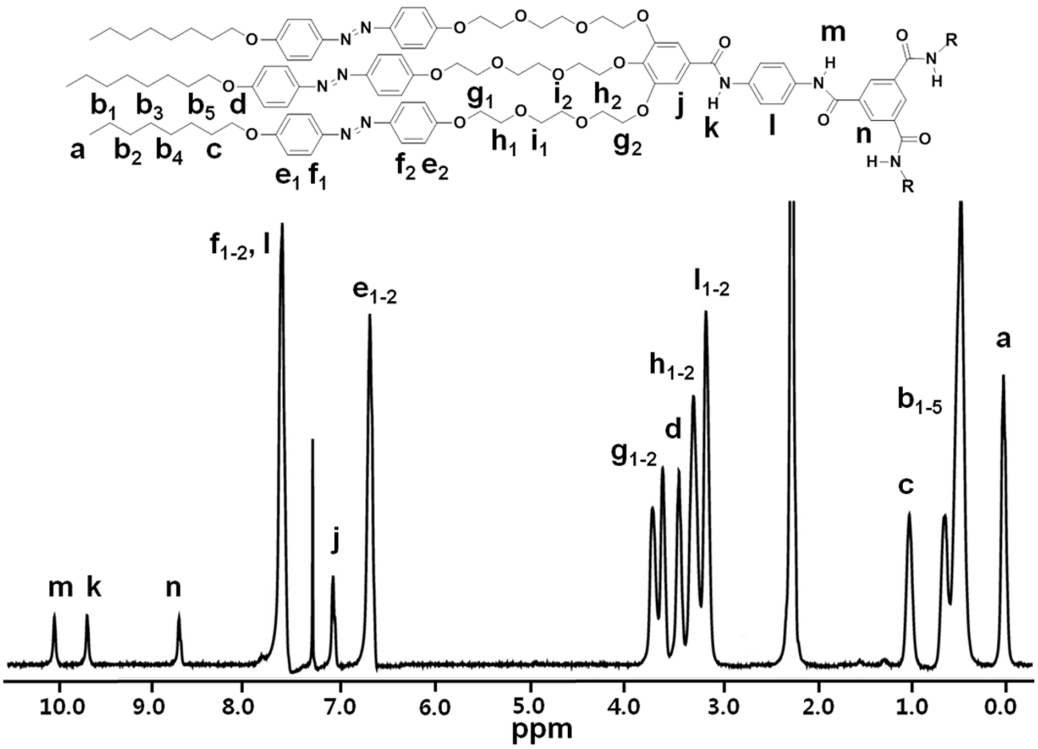


Figure S2. ^{1}H NMR spectrum of BTA-3AZO.

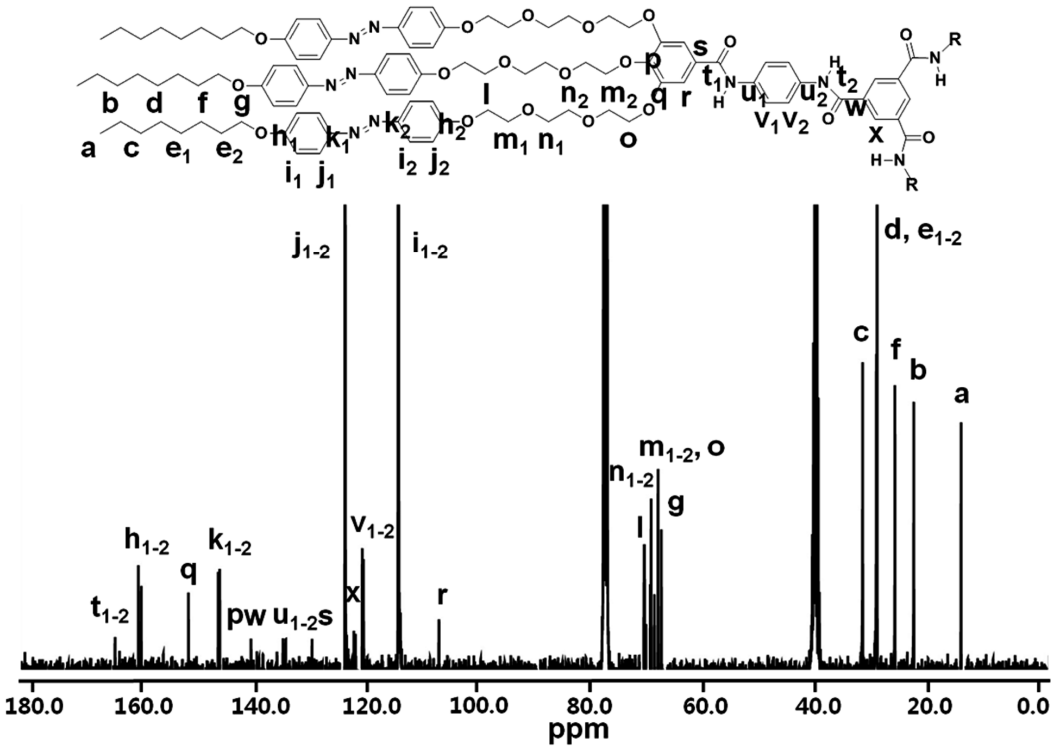


Figure S3. ^{13}C NMR spectrum of BTA-3AZO.

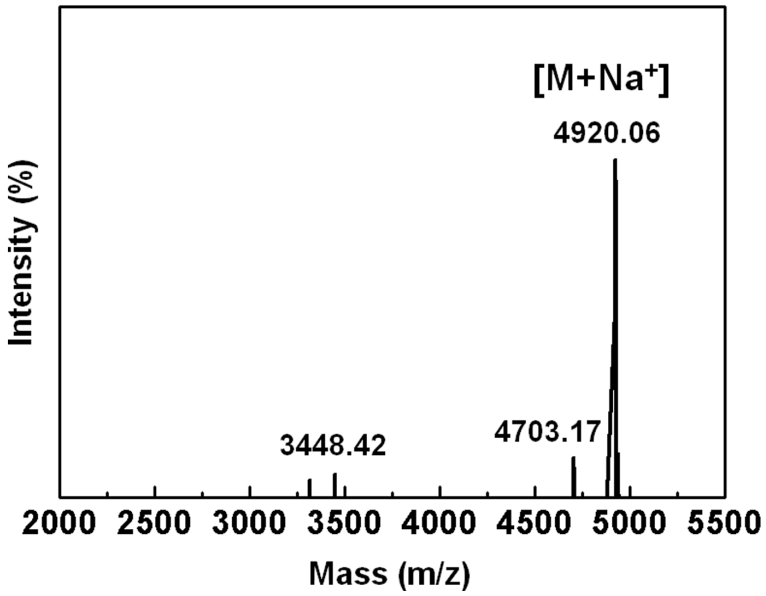


Figure S4. MALDI-ToF spectrum of BTA-3AZO.

Table S1. C, N, H contents of BTA-3AZO by elemental analysis.

	Calculated content (wt%)	Experimental content (wt%)
C	69.09	68.82 69.26 68.99
N	6.86	6.762 6.756 6.756
H	7.40	7.242 7.233 7.022

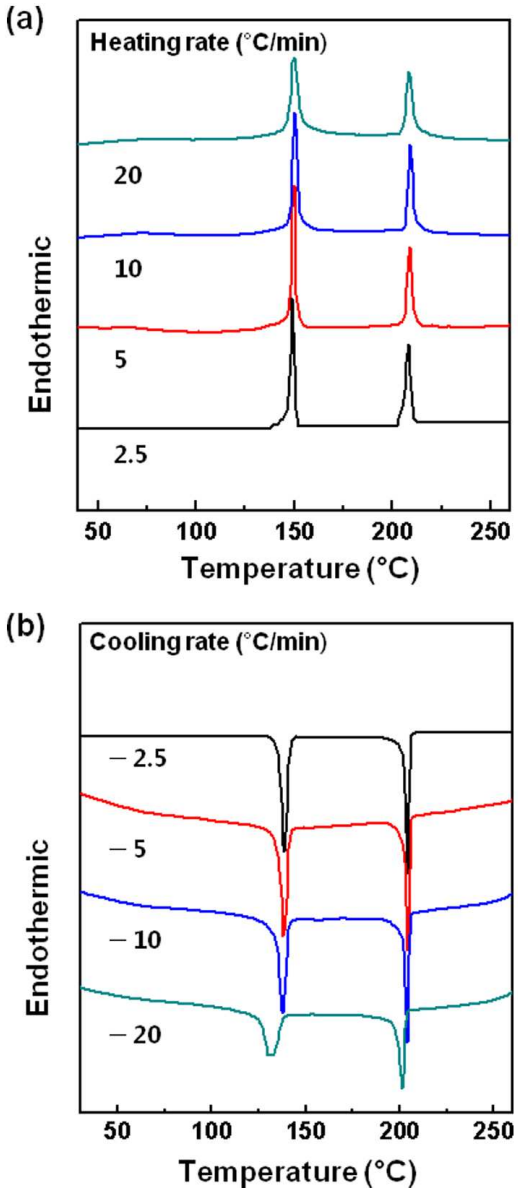


Figure S5. Sets of DSC (a) heating and (b) subsequent cooling thermal scans for BTA-3AZO at the scanning rates ranging from 2.5 to 20 °C/min.

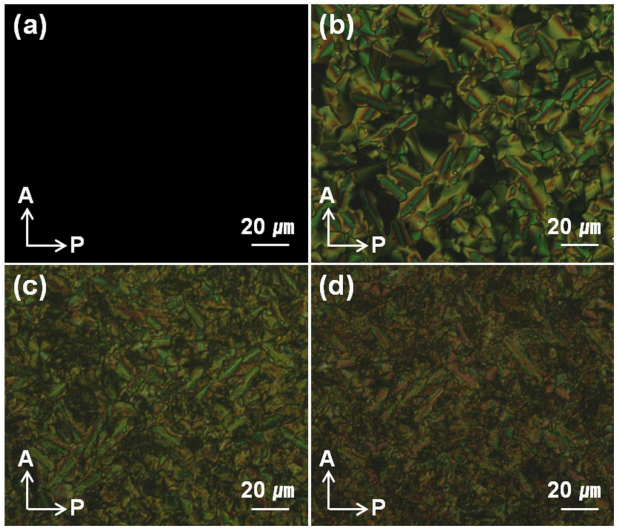


Figure S6. POM morphological observations of BTA-3AZO during cooling (2.5 °C/min) at (a) 206 °C, (b) 160 °C, (c) 100 °C and (d) 30 °C, respectively.

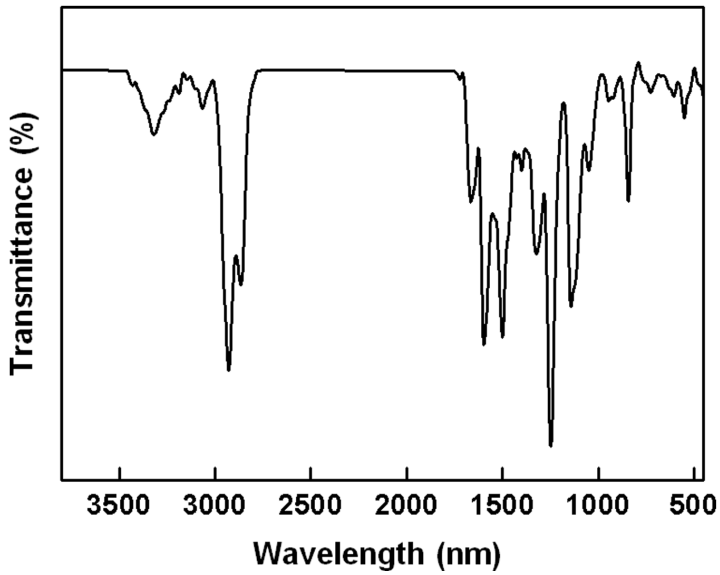


Figure S7. FT IR spectrum of BTA-3AZO at room temperature after cooling from the isotropic phase at 10 °C/min.

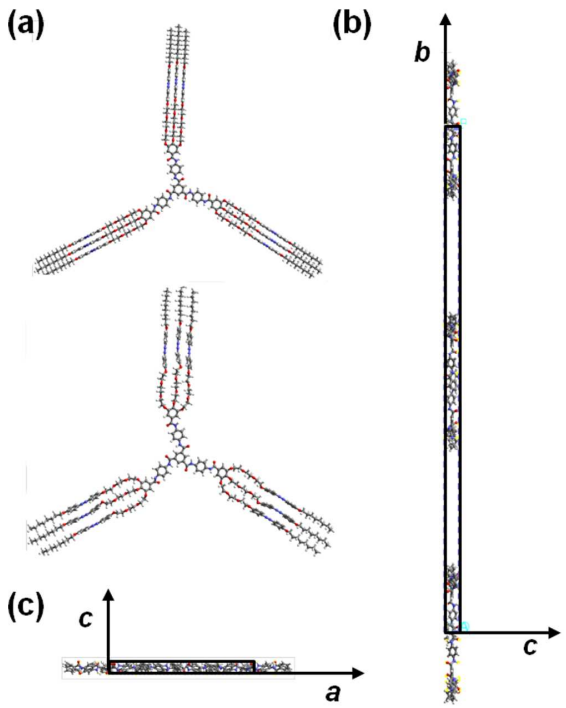


Figure S8. (a) Molecular models before (top) and after (down) energy minimization. Computer simulated molecular packing in the K_{Cr} phase: projections of (b) *bc*-plane and (c) *ac*-plane.

Table S2. Experimental and calculated crystallographic parameters of the 2D *sub* lattice of K_{Cr} phase.

	2θ (deg)		*d*-spacing (nm)	
(*hkl*)	Expt[a]	Calc[b]	Expt[a]	Calc[b]
(110)	20.0	20.0	0.44	0.44
(020)	20.8	20.8	0.43	0.43

[a] Experimental values observed in both WAXD. [b] The calculated data listed are based on the orthorhombic unit cell with $a' = 0.55$ nm, $b' = 0.85$ nm and $\gamma = 90^{o}$.

Table S3. Experimental and calculated crystallographic parameters of the K_{Cr} phase of BTA-3AZO.

	2θ (deg)		*d*-spacing (nm)	
(*hkl*)	Expt[a]	Calc[b]	Expt[a]	Calc[b]
(020)	1.22	1.2	7.28	7.27
(110)	2.2	2.2	4.01	4.01
(040)	2.4	2.4	3.65	3.64
(130)	2.8	2.8	3.15	3.16
(060)	3.65	3.6	2.42	2.43
(150)	3.7	3.7	2.41	2.39
(001)	20.8	20.8	0.43	0.43

[a] Experimental values observed in both WAXD. [b] The calculated data listed are based on the orthorhombic unit cell with $a = 4.17$ nm, $b = 14.56$ nm, $c = 0.43$ nm, $\alpha = \beta = \gamma = 90^{o}$.

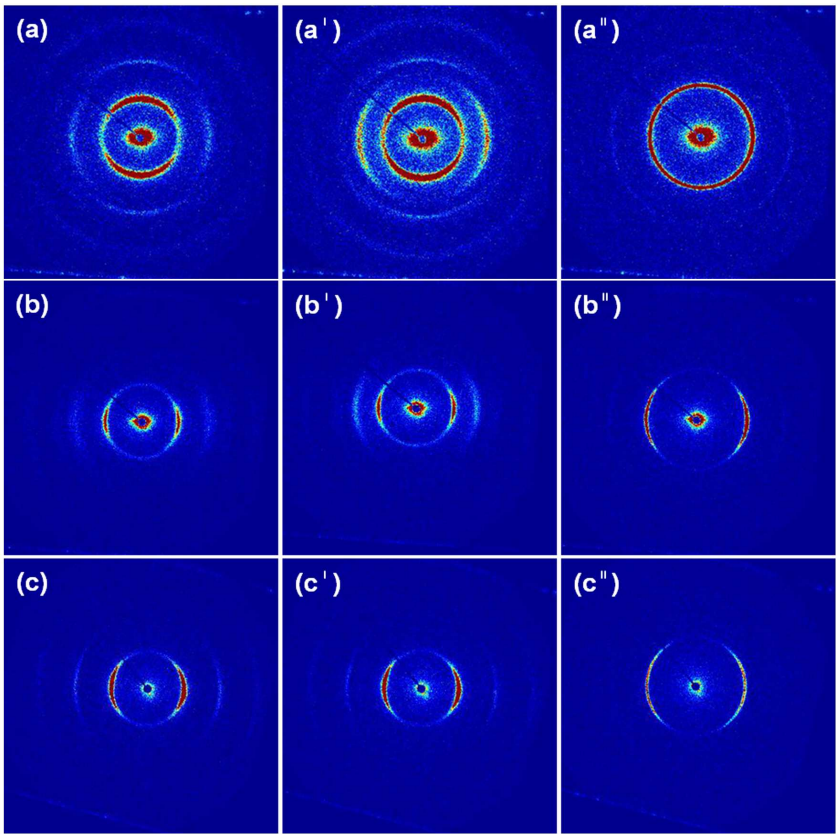


Figure S9. 2D SAXS patterns of BTA-3AZO at r.t. with X-ray beam parallel to (a) the *z*-axis, (b) *y*-axis and (c) *x*-axis of mechanically oriented sample, respectively. Here, the (') and (") symbols represent the status at 100 °C and 160 °C, respectively.

Table S4. Gelation properties of BTA-3AZO in organic solvents, 1 wt%

	Solvent	Polarity Index	BTA-3AZO
Non-polar Solvent	Cyclohexane	0.2	PG
	Toluene	2.4	S
	Methylene choloride	3.1	S
	Chloroform	4.0	S
Polar solvent	Ethyl acetate	4.4	P
	Acetone	5.1	P
	DMF	6.4	P
	DMSO	7.2	P

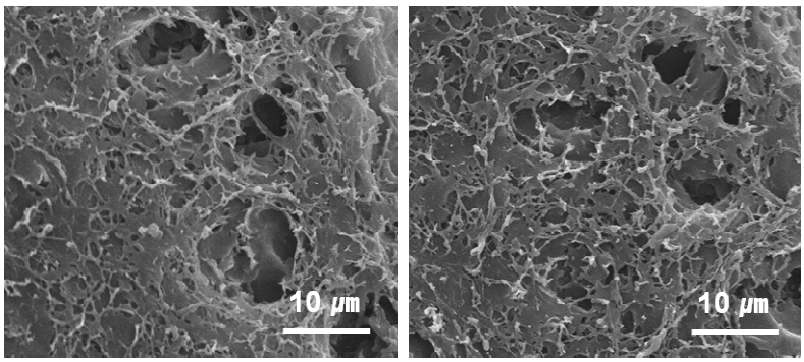


Figure S10. SEM images of the xerogel obtained from cyclohexane with MeOH of BTA-3AZO.