

Supporting Information for

Photo/Chemo Dual-controlled Reversible Morphological Conversion and Chiral Modulation of Supramolecular Nanohelix with Nanosquare and Nanofiber

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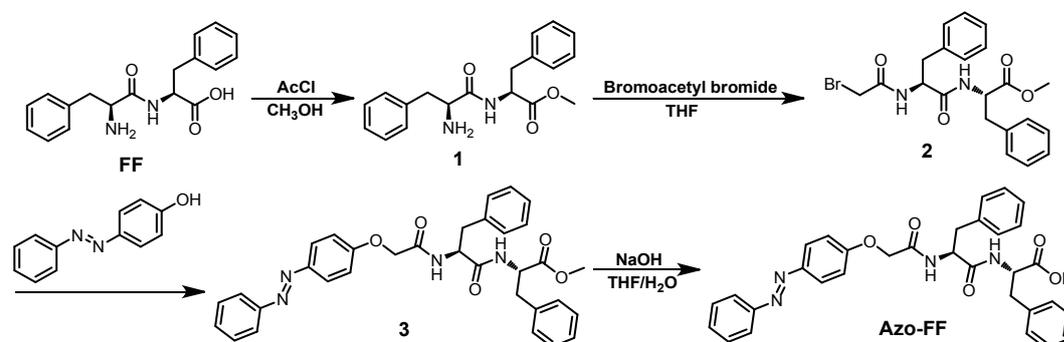
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Instrumentation and methods

All solvents and reagents were commercially available and used without further purification, unless otherwise noted. All experiments were performed in deionized water at 25 °C. NMR spectra were recorded on Bruker 400 MHz instrument in D₂O, and chemical shifts were recorded in parts per million (ppm). High resolution mass spectra were performed on Q-TOF LC-MS with an ESI mode. Absorption spectra were recorded on Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller. CD spectra were collected on a spectropolarimeter in a light path 10 mm quartz cell. The temperature was controlled by a TCU accessory with temperature probe which was plunged into the cuvette to measure the sample temperature.

Scheme S1 Synthesis route of Azo-FF



Synthesis of azobenzene–diphenylalanine (Azo–FF)

A solution of diphenylalanine (FF) peptide (1561.8 mg, 5.00 mmol) in MeOH (50 mL) was treated with AcCl (1.6 mL, 22.5 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 12 h and concentrated *in vacuo*. The residue was used directly to the next step.

The product of the previous step **1** (1631.9 mg, 5 mmol) was dissolved in dry tetrahydrofuran (30 mL) with diisopropylethylamine (1.074 mL, 6.5 mmol) and cooled

to -10°C . under nitrogen. Bromoacetyl bromide (0.53 mL, 6 mmol), dissolved in 10 mL tetrahydrofuran, was added dropwise to the cold solution, keeping $T \cong -5^{\circ}\text{C}$. The reaction was stirred in the cold for 1.5 hr, and 25 mL methanol added. The solids were filtered and rinsed and the combined filtrate was concentrated, which was purified by flash chromatography (petroleum ether/ethyl acetate). The product **2** was obtained as a white solid (yield, 80%).

To a stirred mixture of sodium iodide 450mg (3 mmol) and **2** (3.32 mmol, 1.48 g) in dry acetone (10 ml) was added potassium carbonate (414mg, 3.36 mmol) after 18 min, hydroxyl-azobenzene (594.66mg, 3 mmol) and acetone (30 ml). The reaction mixture was heated under reflux (N_2 atmosphere) with stirring for 5 h and, after cooling, filtered and washed thoroughly with fresh acetone. Evaporation of the solvent and then the product **3** was purified by petroleum ether/ethyl acetate and obtained as an orange solid (yield, 73%).

3 (564.63mg, 1mmol) was dissolved into the mixture of THF (4.5 mL) and water (1.5 mL), and then hydrolyzed by addition of NaOH (80mg, 2 mmol). The resulting mixture was stirred at room temperature for 1.5 h, neutralized with NH_4Cl (267.45 mg, 5 mmol), and then concentrated in vacuo. The residue was purified by flash chromatography ($\text{CHCl}_3/\text{CH}_3\text{OH}$) to give Azo-FF (418.5 mg, 76%) as an orange solid.

^1H NMR (400 MHz, $\text{D}_2\text{O}/\text{DMSO-d}_6$ (v/v=9:1)) δ 7.76 – 7.72 (m, 3H), 7.53 – 7.49 (m, 3H), 7.16 – 7.06 (m, 10H), 6.87 – 6.85 (m, 3H), 4.57 – 4.53 (m, 2H), 4.49 – 4.51 (m, 1H), 4.34 – 4.31 (m, 1H), 3.08 – 3.00 (m, 2H), 2.82 – 2.74 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.02, 170.27, 168.18, 159.02, 152.58, 147.90, 135.78, 135.45,

130.79, 129.32, 129.26, 129.11, 128.82, 128.59, 127.29, 127.22, 124.94, 122.71, 114.93, 67.14, 53.73, 53.21, 37.57, 37.26. MALDI-MS for $C_{60}H_{50}N_{10}C_{14}Ru$: calcd. $[M + Na^+]^+$: 573.2114, found: 573.2110.

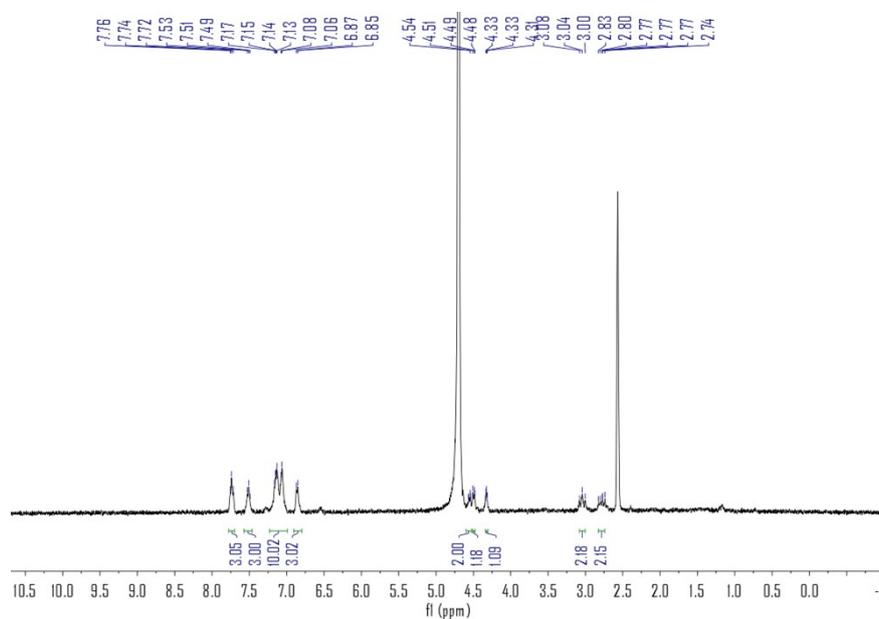


Figure S1. 1H NMR spectrum (400 MHz, $D_2O/DMSO-d_6$ (v/v=9:1), 298 K) of Azo-FF.

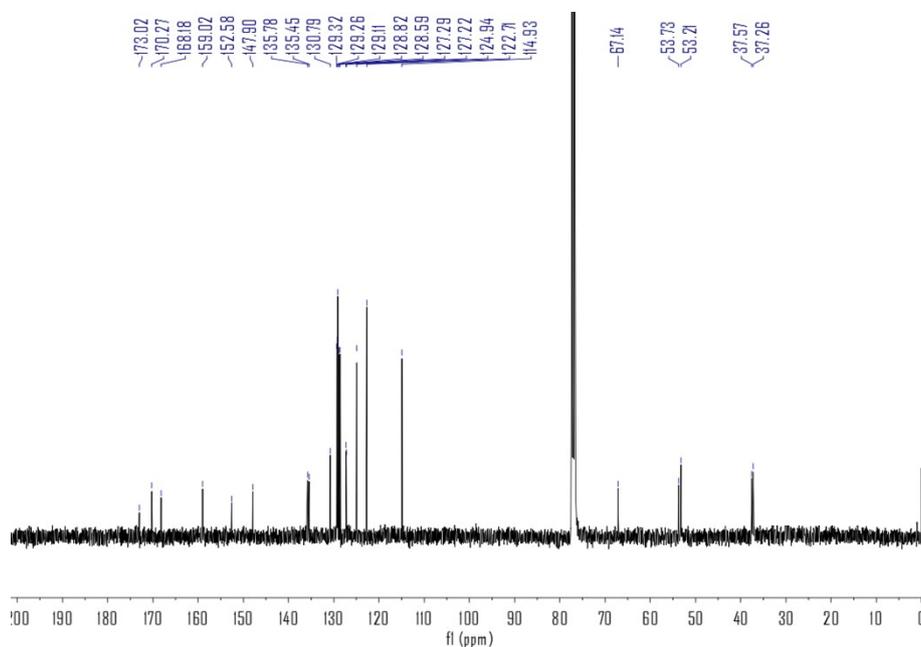


Figure S2. ^{13}C NMR spectrum (400 MHz, $CDCl_3$, 298 K) of Azo-FF.

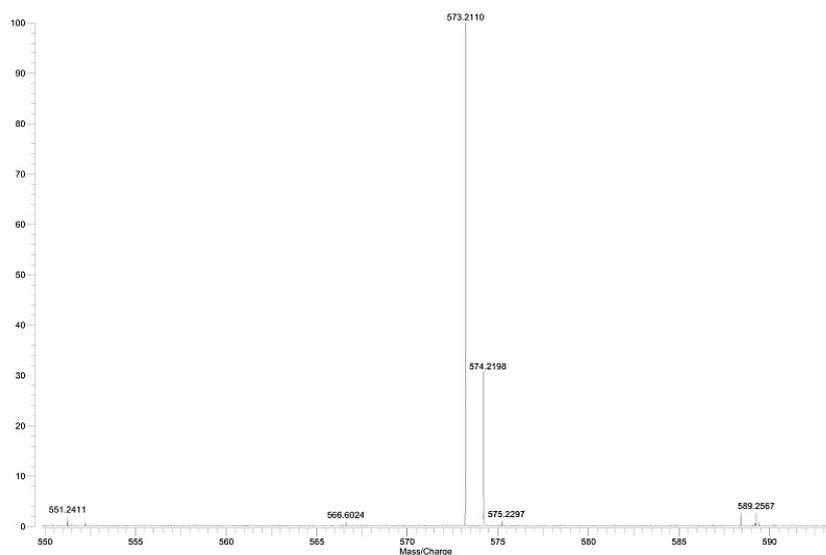


Figure S3. MALDI-MS spectrum of guest Azo-FF ($C_{32}H_{30}N_4O_5$): calcd. $[M + Na^+]^+$: 573.2114, found: 573.2110.

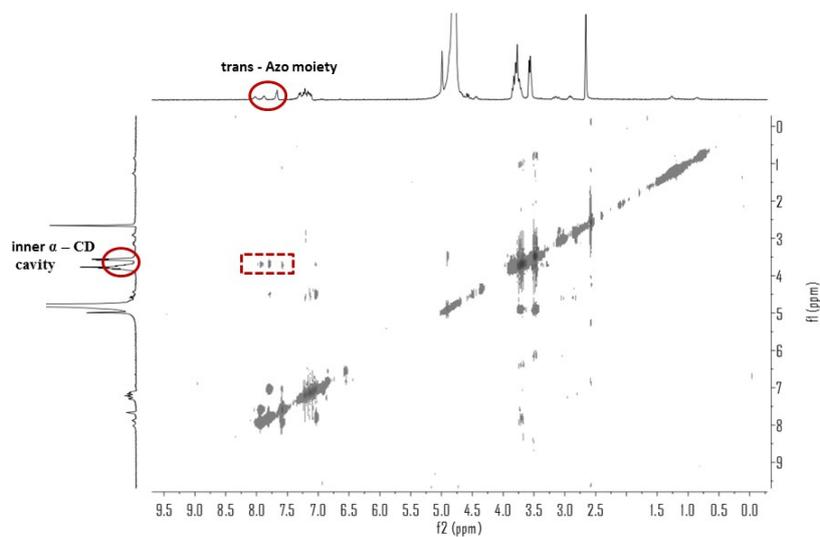


Figure S4 Two-dimensional NOESY spectra of trans-Azo-FF (0.5 mM) in the presence of α -CD (0.5 mM) in D_2O / DMSO ($v/v=9/1$) at 25 °C.

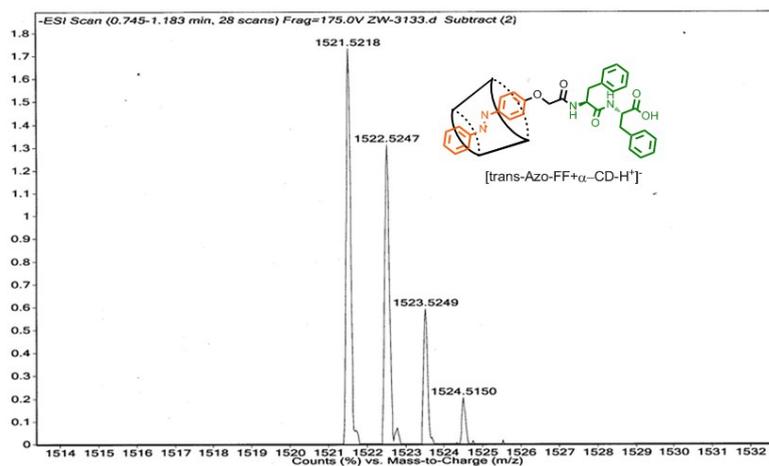


Figure S5 ESI-MS spectrum of guest *trans*-Azo-FF- α -CD ($C_{68}H_{89}N_4O_{35}$): calcd. $[M - H^+]$: 1521.5305, found: 1521.5218.

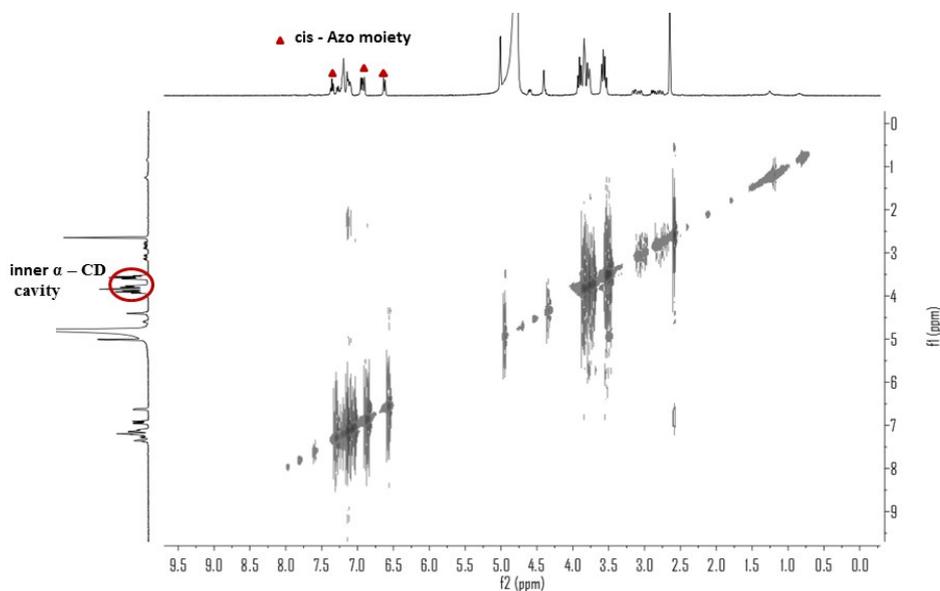


Figure S6 Two-dimensional NOESY spectra of *trans*-Azo-FF (0.5 mM) in the presence of α -CD (0.5 mM) after UV irradiation in D_2O/d -DMSO (V/V=9/1) at 25 °C.

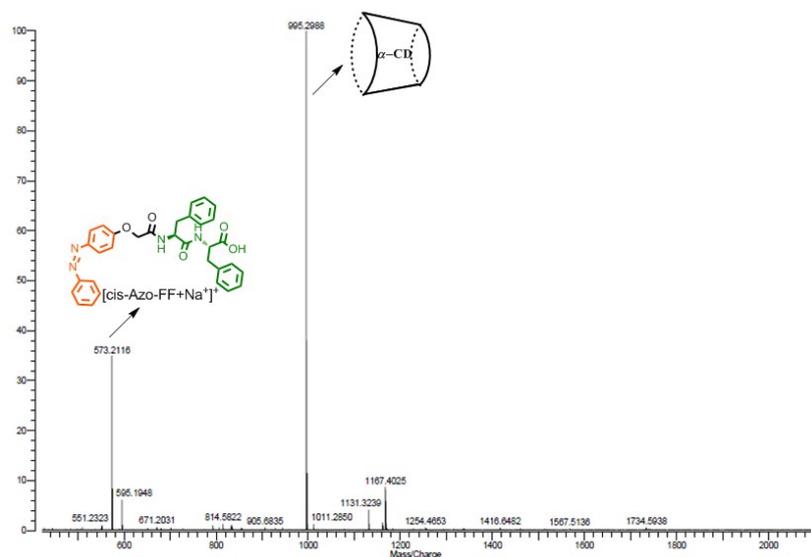


Figure S7 MALDI-MS spectrum of trans-Azo-FF in the presence of α -CD after UV irradiation.

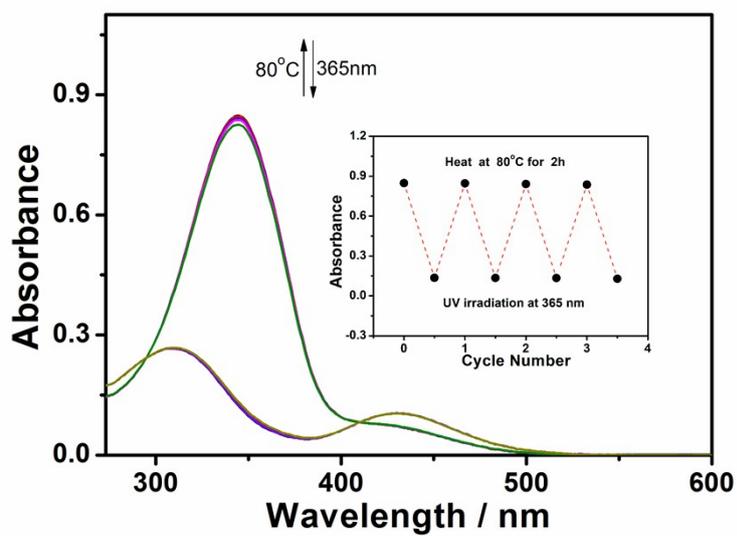


Figure S8 Cyclic responses of the absorbance values at 344 nm for aqueous solution of trans-Azo-FF/ α -CD (1:1) (0.03 mM) under heating and UV irradiation.

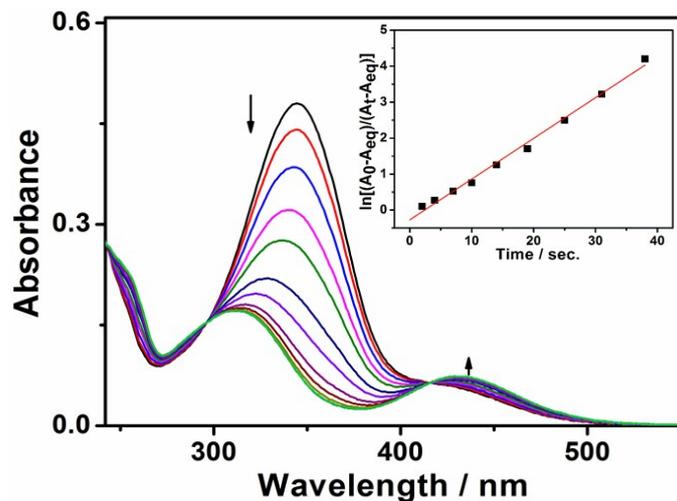


Figure S9 UV/vis spectroscopic of Azo-FF (0.03 mM) to determine the photoisomerization rate constant (k_t) in water. Inset: determination of k_t value of Azo-FF upon exposure to UV light at 365 nm.

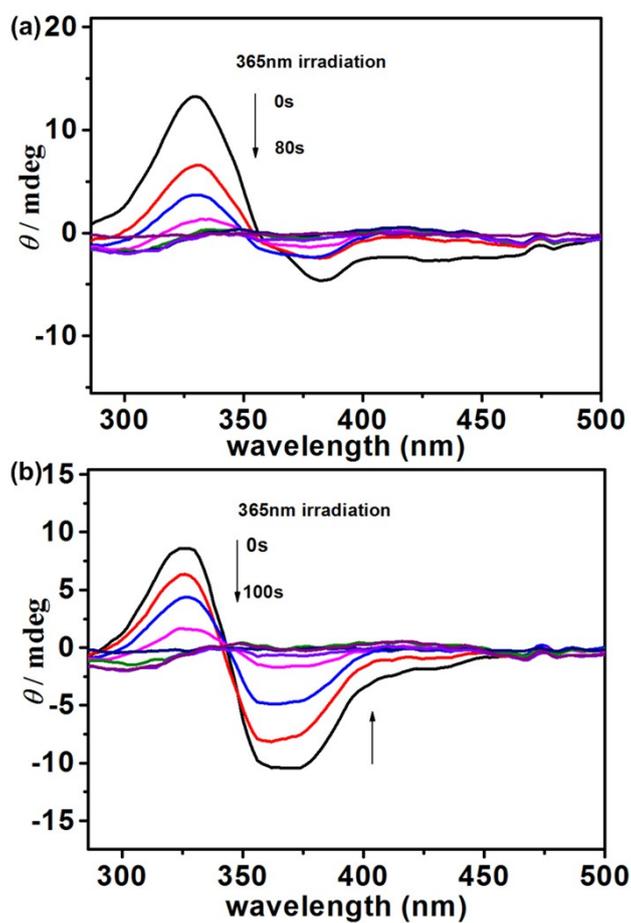


Figure S10. Circular dichroism spectra of (a) trans-Azo-FF/ α -cyclodextrin and (b) trans-Azo-FF in water under UV light irradiation. ($[\text{trans-Azo-FF}] = [\alpha\text{-cyclodextrin}] = 1 \text{ mM}$). The duration of UV light irradiation was set at 0 s, 20 s, 30 s, 40 s, 50 s, 60 s, 70 s, 80 s, 100s (b) at 365 nm.

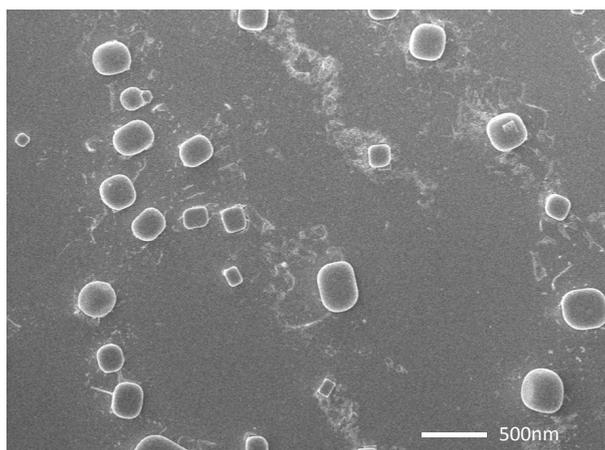


Figure S11 SEM image of trans-Azo-FF irradiated by UV light (365 nm) for 3 min.

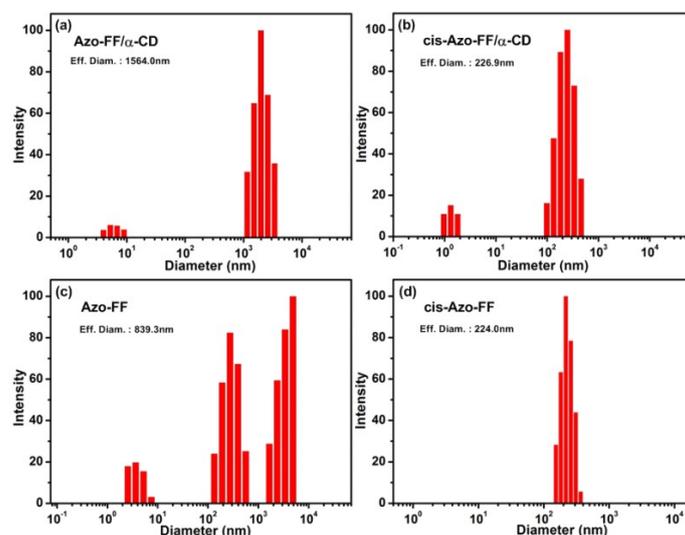


Figure S12 DLS of (a) trans-Azo-FF/ α -CD; (b) irradiate (a) with UV light (365 nm) for 3 min; (c) trans-Azo-FF; (d) irradiate (c) with UV light (365 nm) for 3 min; $[\text{Azo-FF}] = [\alpha\text{-CD}] = 0.1 \text{ mM}$.

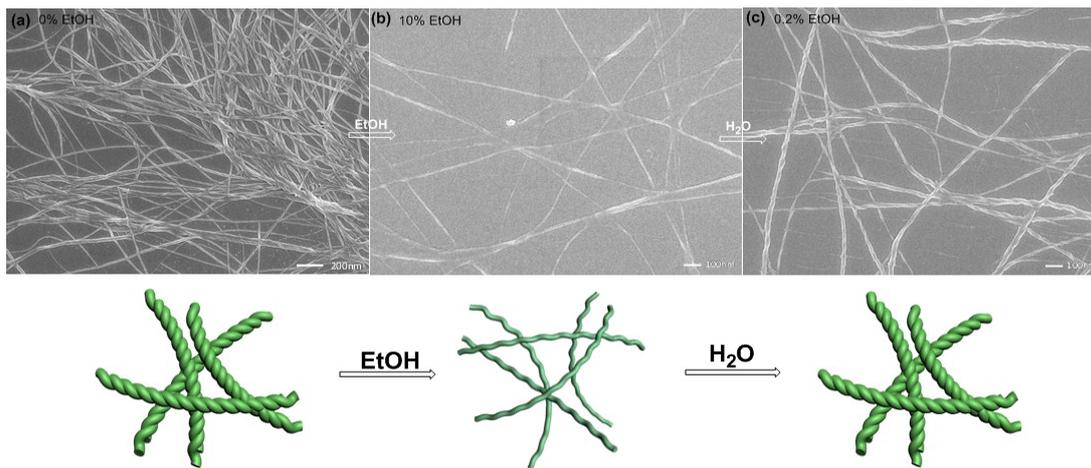


Figure S13. SEM images of polarity-controlled nanohelix-nanofiber conversion (a) 0% EtOH; (b) 10% EtOH; (c) 0.2% EtOH.