

Electronic Supplementary Information (ESI)

# **Topological transformation across different dimensions of supramolecular polymer via photo-isomerization**

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## 1. Materials and Measurements

### *Materials*

1,6,7,12-Tetrachloroperylene tetracarboxylic acid dianhydride (95%, J&K), 1-phenylethylamine (97%, Innochem) and 4-tert-butylphenol (99%, Innochem) were used as received. All other chemical reagents were commercially available and used as received.

### *Measurements*

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra in solution were obtained from Bruker Avance 400 instruments. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, and m = multiplet.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a Bruker Autoflex II instrument with 2,5-dihydroxybenzoic acid (DHB) employed as the matrix substance.

Fourier transform infrared spectra (FTIR) were recorded on a Nicolet iS50 infrared spectrometer.

Atomic force microscopy (AFM) images were obtained under ambient conditions on a Bruker Dimension FastScan instrument.

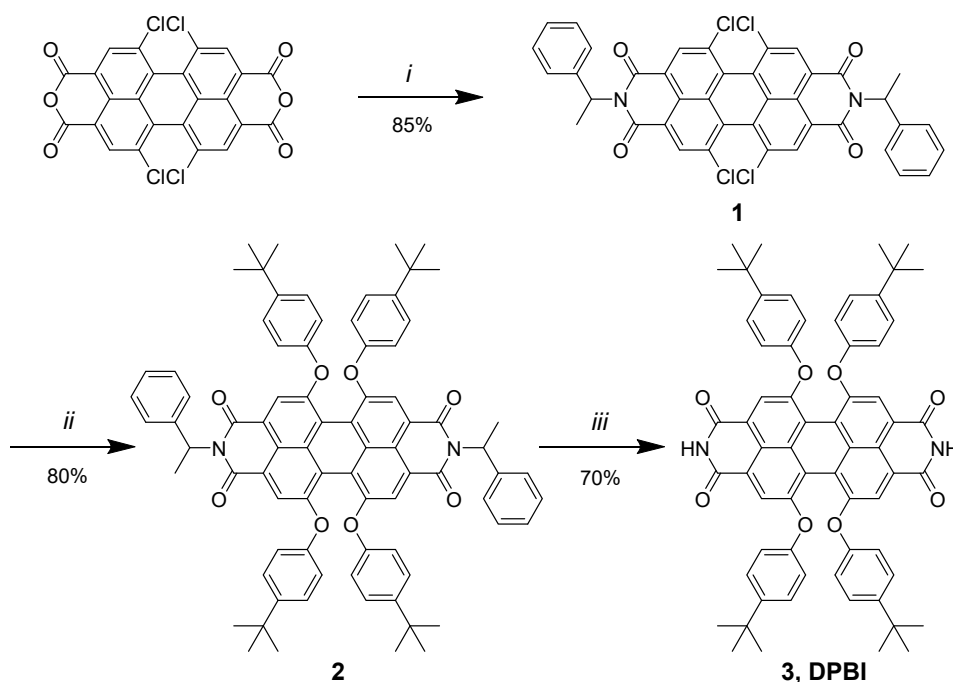
Dynamic light scattering (DLS) measurements were carried out on a Brookhaven BI-9000AT system using a 200 mW polarized laser source ( $\lambda = 630$  nm).

X-ray scattering experiments were performed with an Anton Paar SAXSpoint 2.0 small-angle X-ray scattering instrument. The scattering vector  $q$  is defined as  $4\pi\sin\theta/\lambda$ , where the wavelength  $\lambda$  is 0.1542 nm of Cu- $K_\alpha$  radiation and  $2\theta$  is the scattering angle.

Ultraviolet visible (UV-vis) absorption spectra were recorded on a Shimadzu UV-2550 spectrometer.

## 2. Synthesis of Supramolecular Polymers

The synthesis of TCS was reported in our previous publication.<sup>1</sup> DPBI was synthesized according to the procedures described in the literature.<sup>2</sup>



**Scheme S1.** Synthesis route of DPBI. Reagents and conditions: (i) 1-phenylethylamine, propionic acid, 180 °C, 48 h; (ii) 4-tert-butylphenol, potassium carbonate, 1-methyl-2-pyrrolidone, 130 °C, 12 h; (iii) boron tribromide, 0 °C.

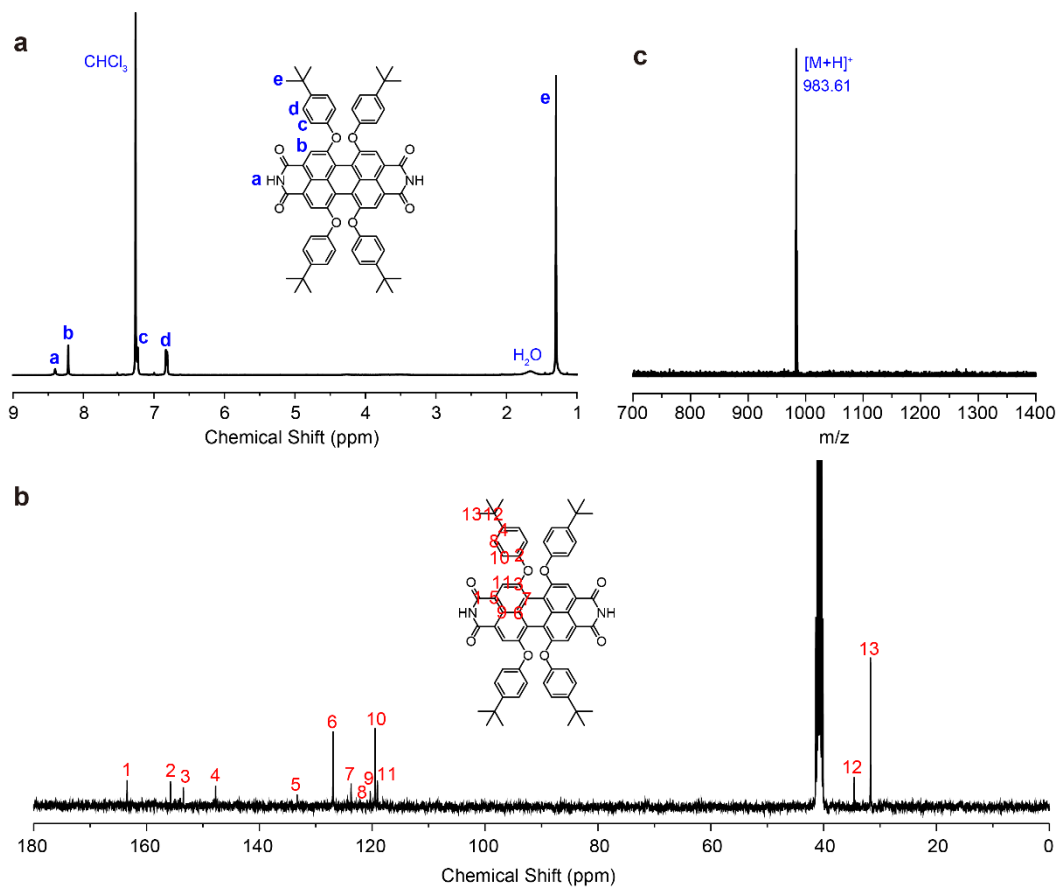
**5,6,12,13-tetrachloro-2,9-bis(1-phenylethyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (1).** A mixed solution of 1,6,7,12-tetrachloroperylene tetracarboxylic acid dianhydride (2.1 g, 3.8 mmol), 1-phenylethylamine (1.8 g, 15.2 mmol) in 40 mL propionic acid was stirred at 180 °C for 48 h. After cooling to room temperature, a large amount of water was added, and then the formed precipitate was collected by filtration and washed by potassium bicarbonate aqueous solution and water. Finally, the obtained crude product was purified by silica-gel column chromatography with mixed solvent of petroleum ether and dichloromethane (3:2) as the eluent to obtain the desired product (7.4 g) in orange-red solid. Yield 85%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ (ppm) = 8.66 (s, 4H), 7.54 (s, 4H), 7.36 (s, 4H), 6.56 (m, 2H), 2.04 (d, 6H).

**5,6,12,13-tetrakis(4-(tert-butyl)phenoxy)-2,9-bis(1-phenylethyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (2).** A mixed solution of **1** (2.4 g, 3.2 mmol), 4-tert-butylphenol (2.9 g, 19.4 mmol) and potassium carbonate (3.1 g, 22.6 mmol) in 50 mL 1-methyl-2-pyrrolidone was stirred at 130 °C under nitrogen atmosphere for 12 h. After cooling to room temperature, hydrochloric acid aqueous solution was added until the pH become 1, and then the precipitate was collected by filtration and washed by water and methanol. Finally, the obtained crude product was purified by silica-gel column chromatography with dichloromethane as the eluent to obtain the desired product (3.1 g) in dark-red solid. Yield 80%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ (ppm) = 8.21 (s, 4H), 7.44 (d, 5H), 7.32 (d, 4H), 7.25-7.21 (m, 11H), 6.82 (d, 9H), 6.48 (m, 2H), 1.94 (d, 6H), 1.30 (s, 36H).

**5,6,12,13-tetrakis(4-(tert-butyl)phenoxy)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (3, DPBI).** To a solution of **2** (3.1 g, 2.6 mmol) in 30 mL dichloromethane, boron tribromide (3.9 g, 15.8 mmol) was gradually added at 0 °C under nitrogen atmosphere. After reaction for 4 h at room temperature, a mixed solvent of water and methanol (4:1) was added to quench the reaction. After extraction with chloroform, the crude product was purified by silica-gel column chromatography with chloroform as the eluent to obtain the desired product (1.8 g) in dark-blue solid. Yield 70%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ (ppm) = 8.40 (s, 2H), 8.22 (s, 4H), 7.24 (d, 8H), 6.82 (d, 8H), 1.30 (s, 36H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 120 °C): δ (ppm) = 163.44, 155.76, 153.47, 147.74, 133.31, 126.96, 123.75, 120.35, 119.52, 119.09, 34.59, 31.68. MALDI-TOF-MS (m/z): [M + H]<sup>+</sup> calcd 983.43, found 983.61.

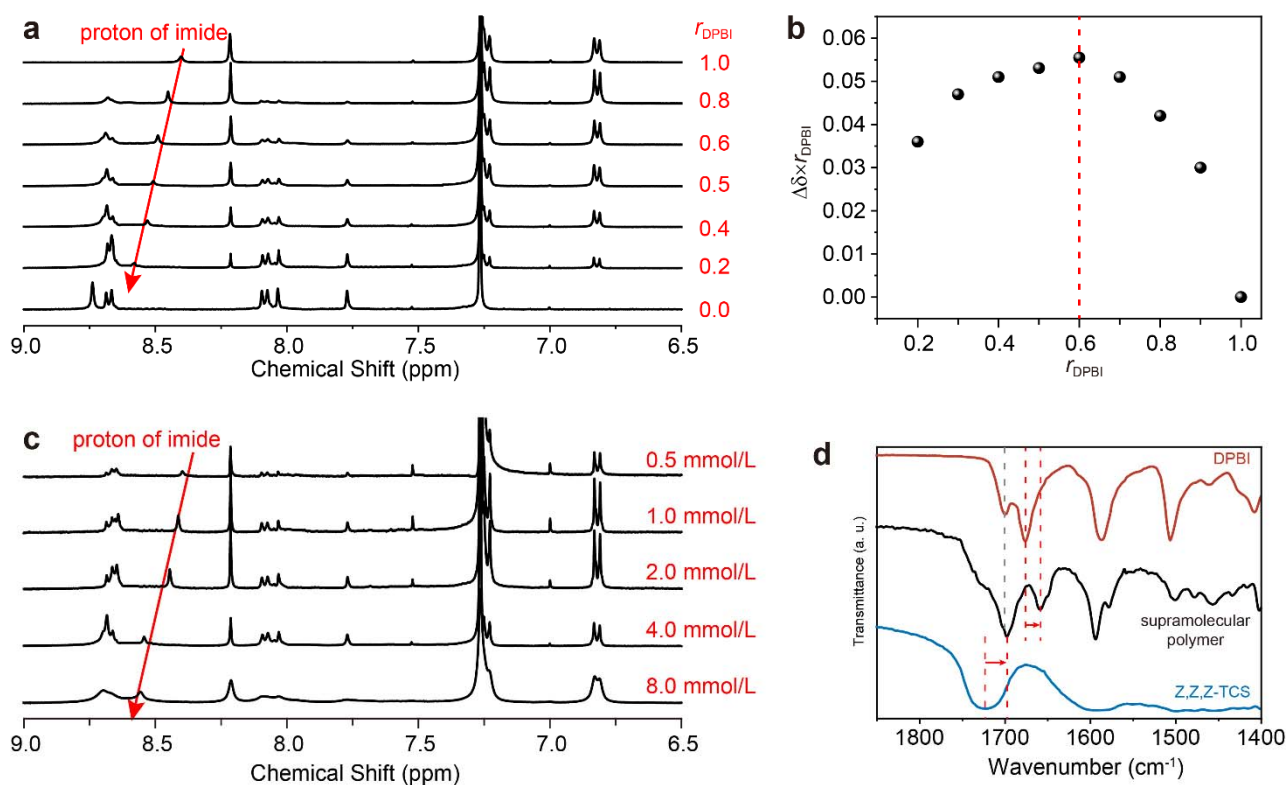
**2D supramolecular polymer.** Two components of *Z,Z,Z*-TCS and DPBI compounds with a molar ratio of 2:3 were dissolved in chloroform. The resulting solution was allowed to reflux for several hours before solvent evaporation under reduced pressure. The obtained 2D supramolecular polymer was finally dried in vacuum overnight.

**1D supramolecular polymer.** The 1D supramolecular polymer was obtained from the 2D supramolecular polymer by photo-induced trans-cis isomerization under 365 nm light irradiation in a chloroform solution (4 mmol/L) until reaching the photostationary state monitored by UV-vis spectroscopy over two hours. The obtained 1D supramolecular polymer was finally dried in vacuum overnight.

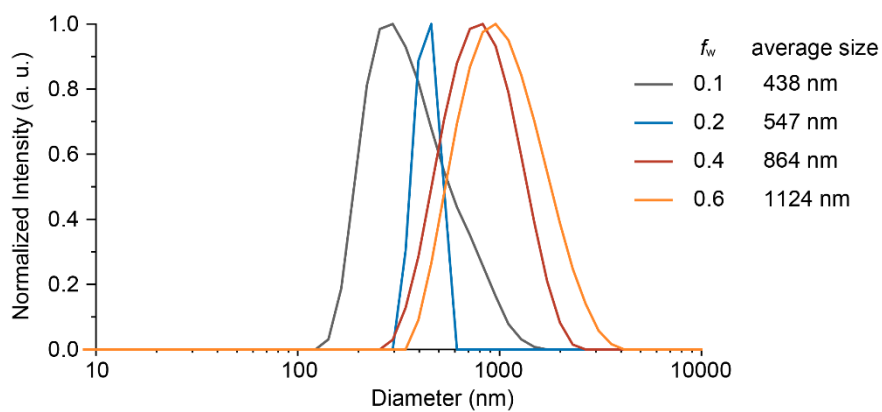


**Figure S1.** Molecular characterization of DPBI. (a)  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  at 25 °C, (b)  $^{13}\text{C}$  NMR spectrum in  $\text{DMSO-}d_6$  at 120 °C, and (c) MALDI-TOF-MS spectrum of DPBI.

### 3. Characterization of Supramolecular Polymers



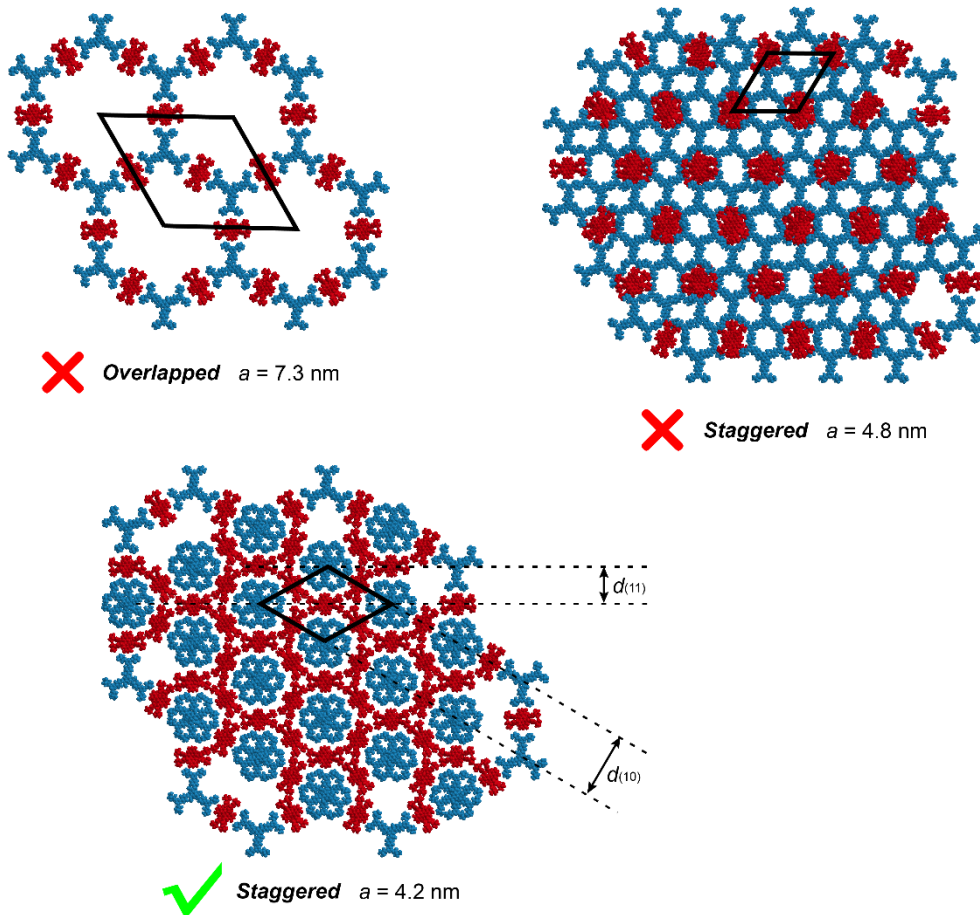
**Figure S2.** (a)  $^1\text{H}$  NMR spectra and (b) the corresponding Job plot of Z,Z,Z-TCS and DPBI in  $\text{CDCl}_3$  with variant ratios (4 mmol/L).  $r_{\text{DPBI}}$  represents the molar ratio of DPBI. The value of  $\Delta\delta \times r_{\text{DPBI}}$  reached a maximum when  $r_{\text{DPBI}}$  was 0.6, confirming the stoichiometry of 2:3. (c) Concentration-dependent  $^1\text{H}$  NMR spectra of the 2:3 supramolecular polymer. (d) Comparison of FT-IR spectra for identifying the formation of hydrogen-bonded supramolecular polymer. The C=O stretching vibration of amide group in Z,Z,Z-TCS is at  $1722\text{ cm}^{-1}$ , while the C=O stretching vibration of imide group in DPBI is at  $1676\text{ cm}^{-1}$ , both of which were shifted towards a lower wavenumber of  $1698$  and  $1658\text{ cm}^{-1}$ , respectively, after supramolecular polymerization via intermolecular triple hydrogen-bonding interactions.



**Figure S3.** DLS diameter distribution of the 2D supramolecular polymer in tetrahydrofuran/water solutions with varying water fractions ( $f_w$ ).

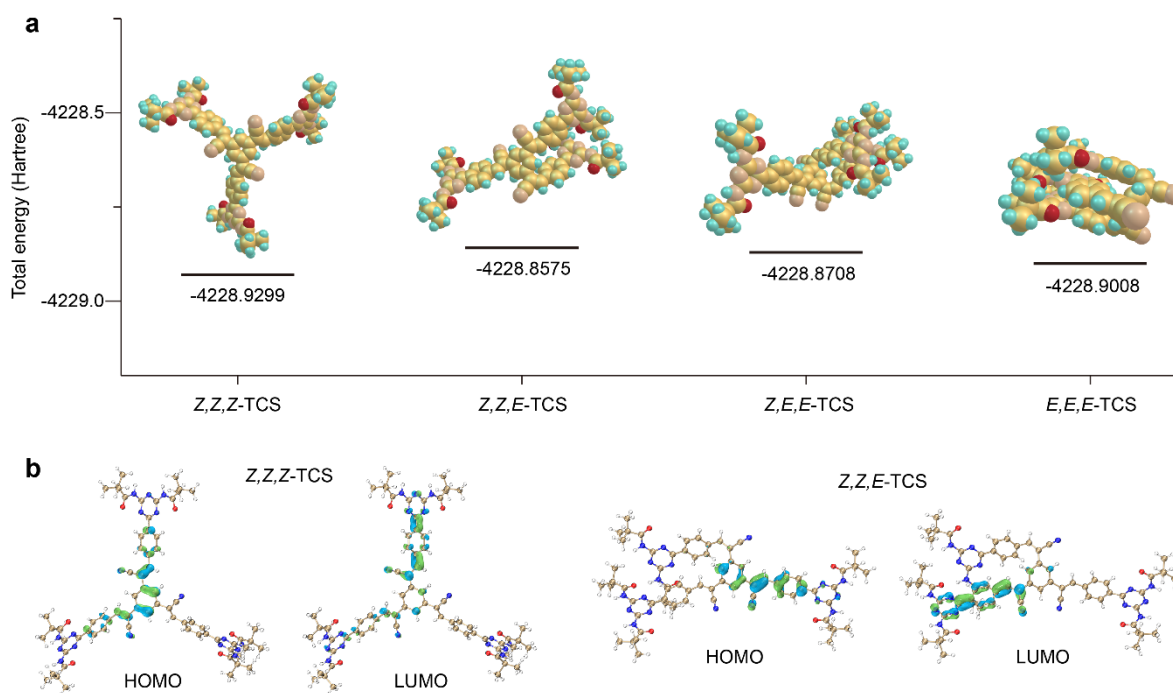
**Table S1.** X-ray scattering data for the 2D supramolecular polymer.

polymer	symmetry	$hkl$	$d_{obs}$ (nm)	$d_{cacl}$ (nm)	lattice parameter (nm)
2D polymer	hexagonal	110	2.10	2.10	$a = 4.20$ nm
		200	1.81	1.82	
		210	1.37	1.37	
		310	1.00	1.01	
		330	0.70	0.70	
$d_{interlayer} = 0.47$					



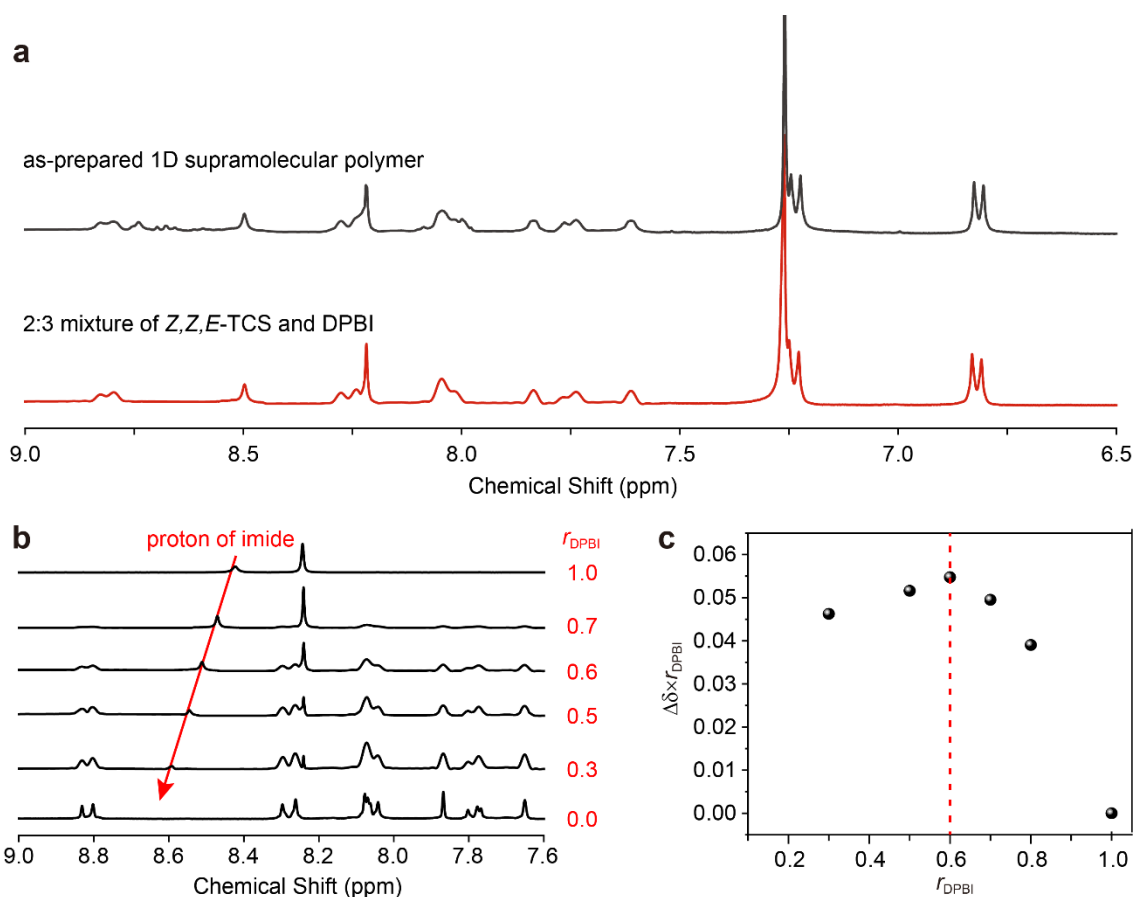
**Figure S4.** Representations of space averaged multiple layer supramolecular polymer with hexagonal correlation, with the TCS and DPBI monomers presented in blue and red color, respectively. The black parallelogram is the crystallographic unit cell.



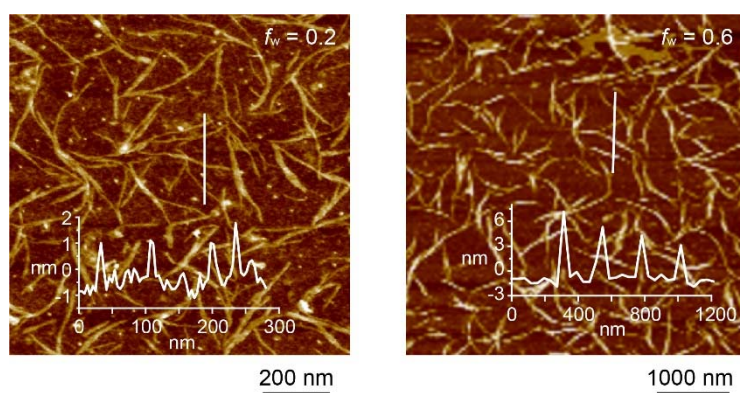


**Figure S5.** (a) DFT optimized structures and the corresponding energy diagram of the TCS compound in different isomerization states. (b) HOMO and LUMO distributions of *Z,Z,Z*-TCS and *Z,Z,E*-TCS.

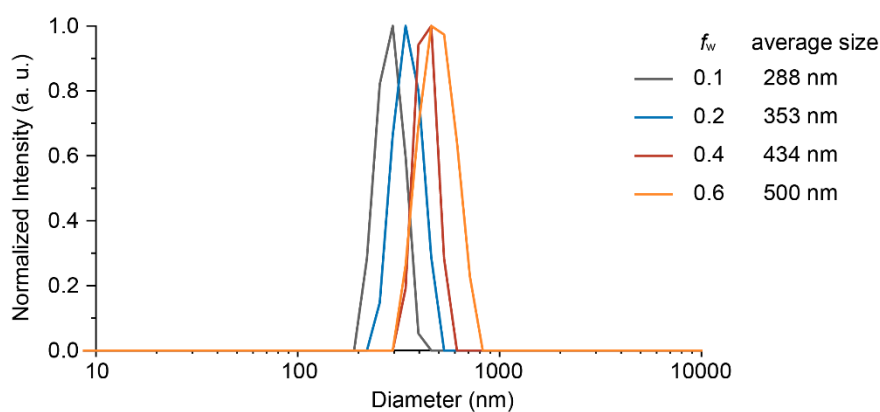
To gain a mechanistic insight into the photo-isomerization process, we employed density functional theory (DFT) calculations to investigate the chemical structure change of the TCS. Four possible isomers of TCS, with the three cyanostyrene arms adopting different trans-cis isomerism, were optimized at the B3LYP/6-311G(d) level.<sup>3</sup> The total energies of these isomers were found to be comparable (Figure S5a), implying the possibility of generating multiple isomers. However, experimental findings only supported the formation of *Z,Z,E*-TCS during photo-isomerization. To explain this phenomenon, we scrutinized the electronic excitation process (Figure S5b). Notably, the HOMO and LUMO of *Z,Z,E*-TCS are located on the remaining two *Z*-cyanostyrene arms, manifesting a charge transfer process between them. This charge transfer hindered further isomerization of the *Z*-cyanostyrene arms. Conversely, both HOMO and LUMO of *Z,Z,Z*-TCS reside on the same *Z*-cyanostyrene arm, thereby facilitating the occurrence of isomerization. Therefore, the theoretical calculations accord with the experiment results, corroborating the photo-isomerization process from *Z,Z,Z*-TCS to *Z,Z,E*-TCS.



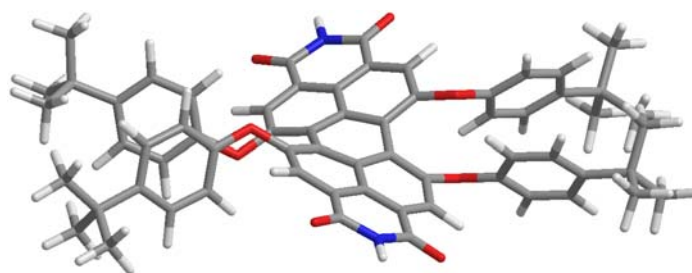
**Figure S6.** (a) <sup>1</sup>H NMR spectra comparison of the as-prepared 1D supramolecular polymer and the 2:3 mixture of Z,Z,E-TCS and DPBI in CDCl<sub>3</sub>. (b) <sup>1</sup>H NMR spectra and (c) the corresponding Job plot of Z,Z,E-TCS and DPBI in CDCl<sub>3</sub> with variant ratios (4 mmol/L).  $r_{\text{DPBI}}$  represents the molar ratio of DPBI. The value of  $\Delta\delta \times r_{\text{DPBI}}$  reached a maximum when  $r_{\text{DPBI}}$  was 0.6, confirming the stoichiometry of 2:3.



**Figure S7.** AFM images with height profiles of the formed 1D supramolecular polymer from tetrahydrofuran/water solutions with varying water fractions ( $f_w$ ).



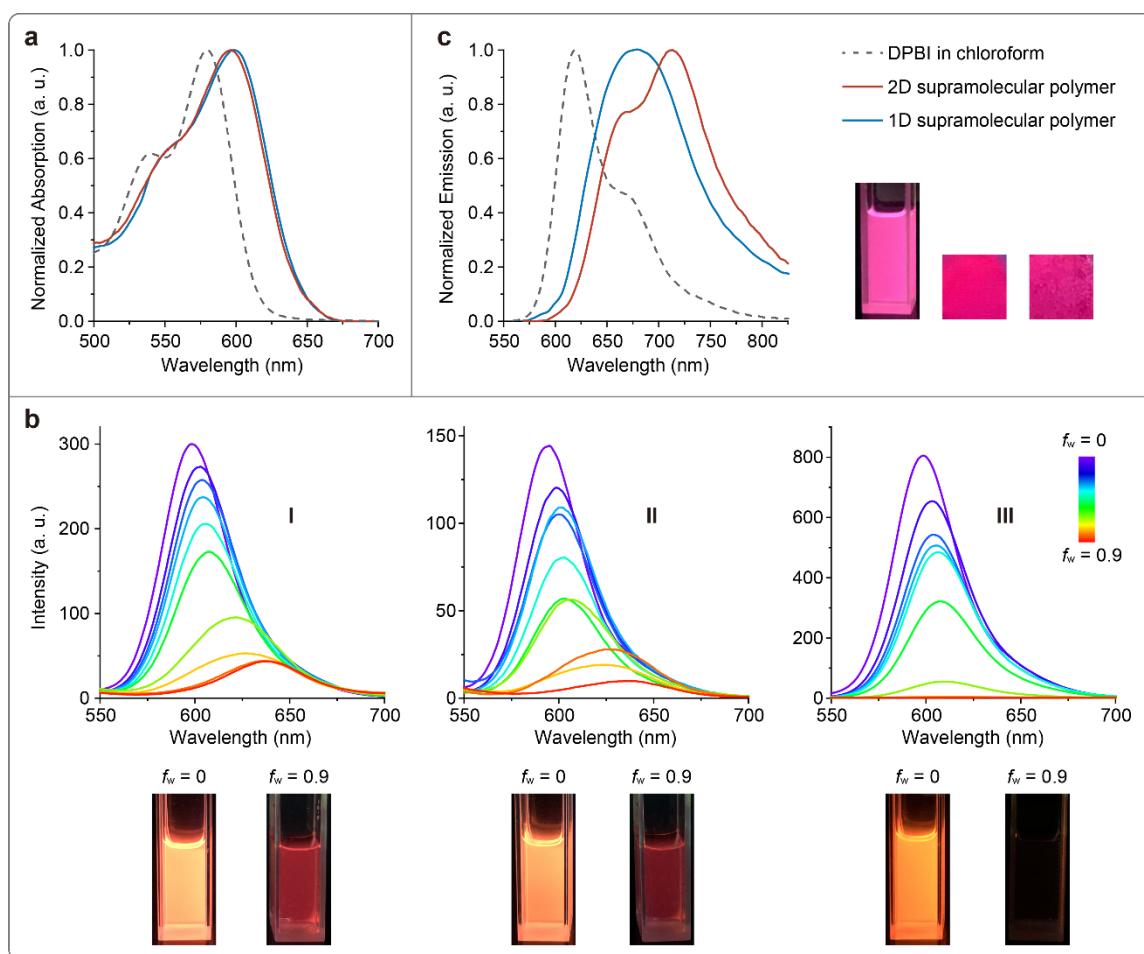
**Figure S8.** DLS diameter distribution of the 1D supramolecular polymer in tetrahydrofuran/water solutions with varying water fractions ( $f_w$ ).



**Figure S9.** Optimized molecular structure of DPBI.

**Table S2.** X-ray scattering data for the 1D supramolecular polymer.

polymer	symmetry	$hkl$	$d_{obs}$ (nm)	$d_{cacl}$ (nm)	lattice parameter (nm)
1D polymer	lamellar	002	2.35	2.35	$l = 4.70$ nm
		003	1.57	1.57	
		004	1.17	1.18	
		005	0.94	0.94	
		006	0.78	0.78	
		008	0.60	0.59	



**Figure S10.** (a) Normalized UV-vis absorption and (c) fluorescence emission spectra of the resulting 2D and 1D supramolecular polymer in the solid state and DPBI in chloroform solution. (b) Fluorescence emission spectra of (I) 2D and (II) 1D supramolecular polymers and (III) DPBI in tetrahydrofuran/water systems with varied water fractions ( $f_w$ ). Insets display corresponding fluorescence images taken under UV light illumination.

## 4. References

- (1) B. Mu, Z. Zhang, X. Quan, X. Hao and W. Tian. *ACS Appl. Mater. Interfaces*, 2021, **13**, 57786-57795.
- (2) F. Würthner, C. Thalacker and A. Sautter, *Adv. Mater.*, 1999, **11**, 754-758.
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