

## Electronic Supplementary Information

### A photochromic supramolecular polymer based on *bis-p*-sulfonatocalix[4]arene recognition in aqueous solution

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#### 1. Materials, general procedures and syntheses

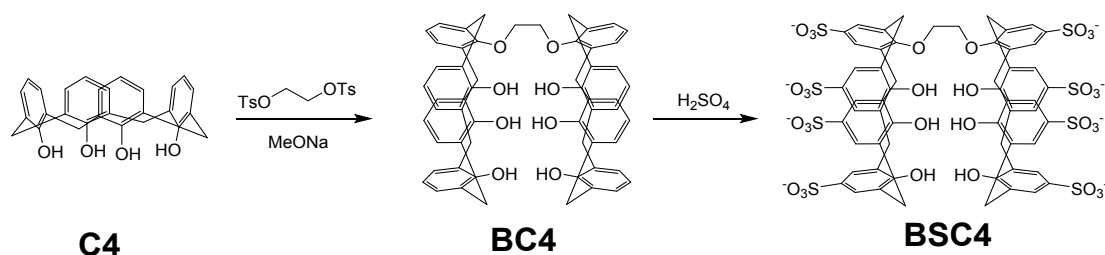
**1.1 Materials.** Unless stated otherwise, all reagents were purchased from Sigma-Aldrich or TCI Chemicals and used without further purification. Solvents were purified according to standard laboratory methods. The molecular structures were confirmed using <sup>1</sup>H NMR and high-resolution ESI mass spectroscopy.

**1.2. General.** <sup>1</sup>H NMR spectra were measured on a Brüker AV-400 spectrometer. ROESY and DOESY were measured on a Brüker AV-500 spectrometer. The electronic spray ionization (ESI) high resolution mass spectra were tested on a HP 5958 mass spectrometer. DLS were measured on MALV RN, ZETA SIZER, Model ZEN3600, 25°C. AFM images were recorded on a MicroNano D5-A machine. The samples (1.5 × 10<sup>-5</sup> M) were dropped on a mica plate on a spin coating machine at a rotating speed of 50 r/min and further dried in vacuum. TEM images were record on a JEOL JEM-1400 apparatus. The samples (1.5 × 10<sup>-5</sup> M) were dropped on a perforated copper grid (400 mesh) covered with a carbon film and then negative-stained by phosphotungstic acid. The samples in aqueous solution were irradiated under UV/Vis light on a SPOT LIGHT SOURCE machine (model: L9588-01A, HAMAMATSU PHOTONICS K.K.) with different filters. The samples in solid state were irradiated under a portable UV lamp (6W).

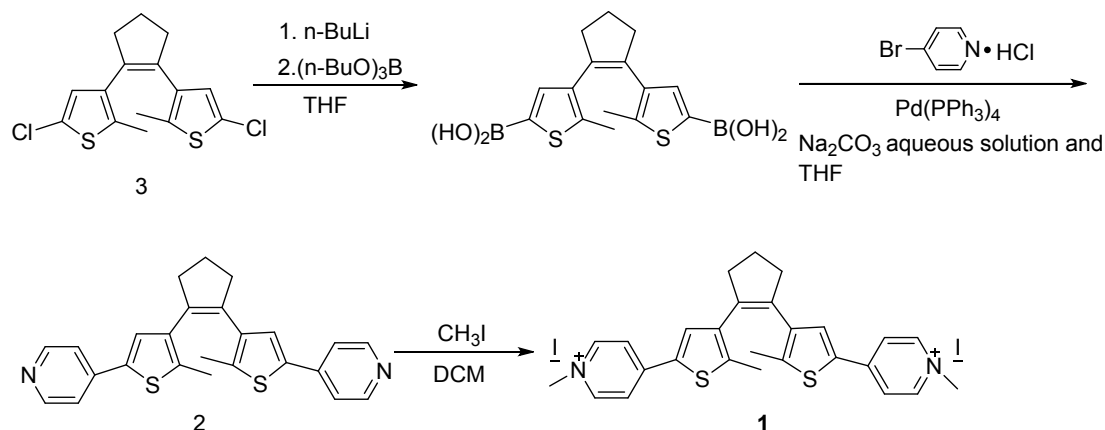
#### 1.3. Synthesis.

##### 1.3.1 Synthesis of *bis-p*-sulfonatocalix[4]arene (BSC4)

BSC4 was synthesized according to previous research.<sup>1</sup>



### 1.3.2 Synthesis of 1, 2-bis [2-methyl-5-(4-methylpyridyl)-3-thienyl] cyclopentene (**1**)<sup>2</sup>



1, 2-bis (2-methyl-5-chloro-3-thienyl) cyclopentene (**3**) was synthesized by the classical method according to the previous reference.<sup>3</sup> 1, 2-bis(2-methyl-5-chloro-3-thienyl) cyclopentene (0.66 g, 2 mmol) was dissolved in redistilled THF (10 mL) in Schlenk flask under anhydrous and Ar conditions at  $-78\text{ }^{\circ}\text{C}$ , and n-BuLi (2.4M in hexane, 1.92 mL, 4.6 mmol ) was added dropwise. The solution gradually turned deep red, with vigorous stirring continued at  $-78\text{ }^{\circ}\text{C}$  for 30min.  $\text{B}(\text{OC}_3\text{H}_7)_3$  (1.20 mL, 5.06 mmol) was injected rapidly, then the reaction mixture was gradually restored to room temperature and stirring for at least 3 h.

Bromopyridine hydrochloride (1 g, 5.06 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (230 mg, 0.2 mmol) were added to THF (20 mL), then mixed with aqueous solution of  $\text{Na}_2\text{CO}_3$  (6 g) 10mL under Ar condition and the reaction mixture was heated to  $55\text{ }^{\circ}\text{C}$  with vigorous stirring for 1 h. Then the reaction solution obtained in the processing was injected using a syringe and the reaction mixture was refluxed for 6 h. After cooling down to room temperature, the mixture was poured into water (50 mL). The organic phase was extracted using EtOAc and washed with brine, dried over  $\text{Na}_2\text{SO}_4$ . The crude residue was chromatographed over silica gel using a mixture of EtOAc/petroleum ether (1:2) to give **2** (0.40 g, 0.97 mmol, 48% yield).

1, 2-bis [2-methyl-5-(4-pyridyl)-3-thienyl] cyclopentene (**2**) (0.27 g, 0.65 mmol) was dissolved in DCM (8 mL) and  $\text{CH}_3\text{I}$  (1 mL) was injected. The mixture was stirred at room temperature for 3 h. Then acquired yellow solid and the reaction mixture was filtered, washed with DCM and dried in vacuum to give yellow solid **1** (0.35 g, 77% yield).

## 2. Rotating Frame Overhauser Effect Spectroscopy (ROESY) and Diffusion Ordered Spectroscopy (DOSY)

### 2.1 Rotating Frame Overhauser Effect Spectroscopy (ROESY)

The correlations between methyl groups of **1** and protons on phenols of BSC4 (red square A) and the correlations between pyridine groups of **1** and protons on phenols of BSC4 (red square B) were found on ROESY spectra. However, there was no signal between protons of **1** and protons on methylenes of BSC4 (blue squares). The results demonstrated that the 2-bis[2-methyl-5-(4-methylpyridyl)-3-thienyl] cyclopentene molecules were selectively bound with the calixrene cavities, which have sulfo groups as anchor points.

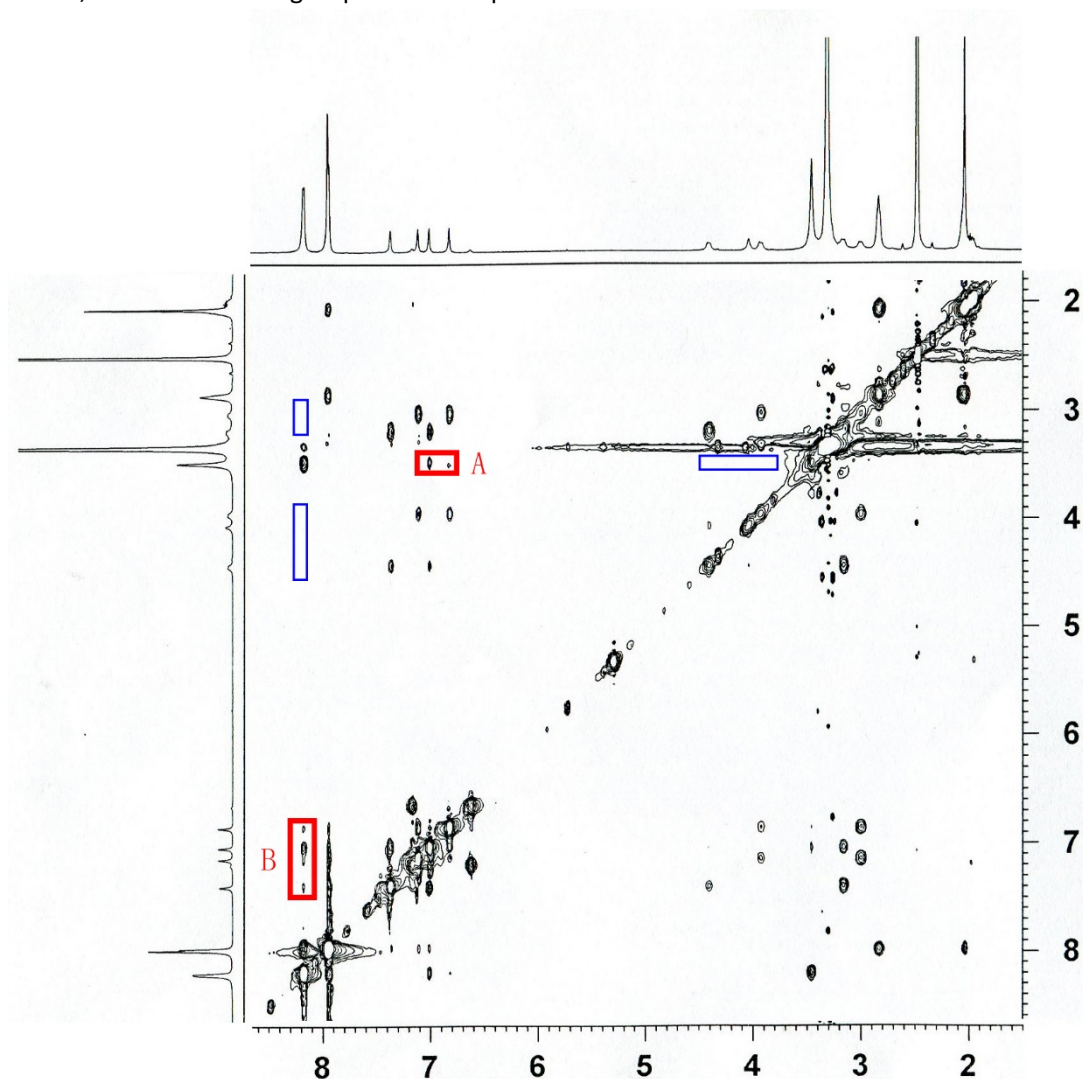


Fig. S1 ROESY of supramolecular polymer PSP.

## 2.2 Diffusion Ordered Spectroscopy (DOSY)

Diffusion Ordered Spectroscopy (DOSY) was carried out to determine the diffusion coefficient of **1** ( $3.6 \times 10^{-3}$  mol/L) as  $1.725 \times 10^{-10}$  m<sup>2</sup>/s and that in PSP ( $9 \times 10^{-4}$  mol/L) as  $7.212 \times 10^{-11}$  m<sup>2</sup>/s in DMSO-d<sub>6</sub>. Due to the limited concentration of PSP, the corresponding diffusion coefficient of BSC4 at certain concentration ( $9 \times 10^{-4}$  mol/L) could not be obtained. However, the slower diffusion rate of **1** in PSP demonstrated the formation of supramolecular polymers.

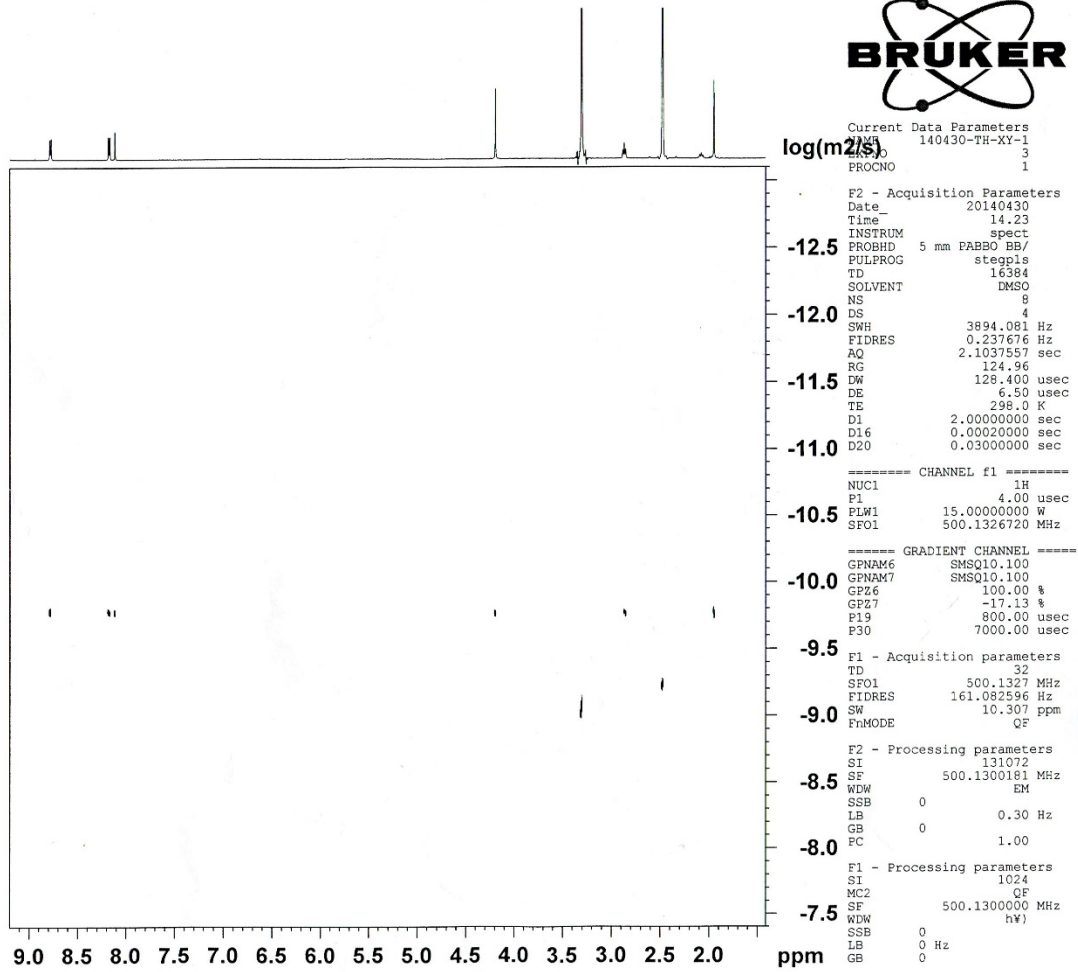


Fig. S2 Diffusion Ordered Spectroscopy (DOSY) of monomer **1**. Diffusion coefficient =  $1.725 \times 10^{-10}$  m<sup>2</sup>/s.

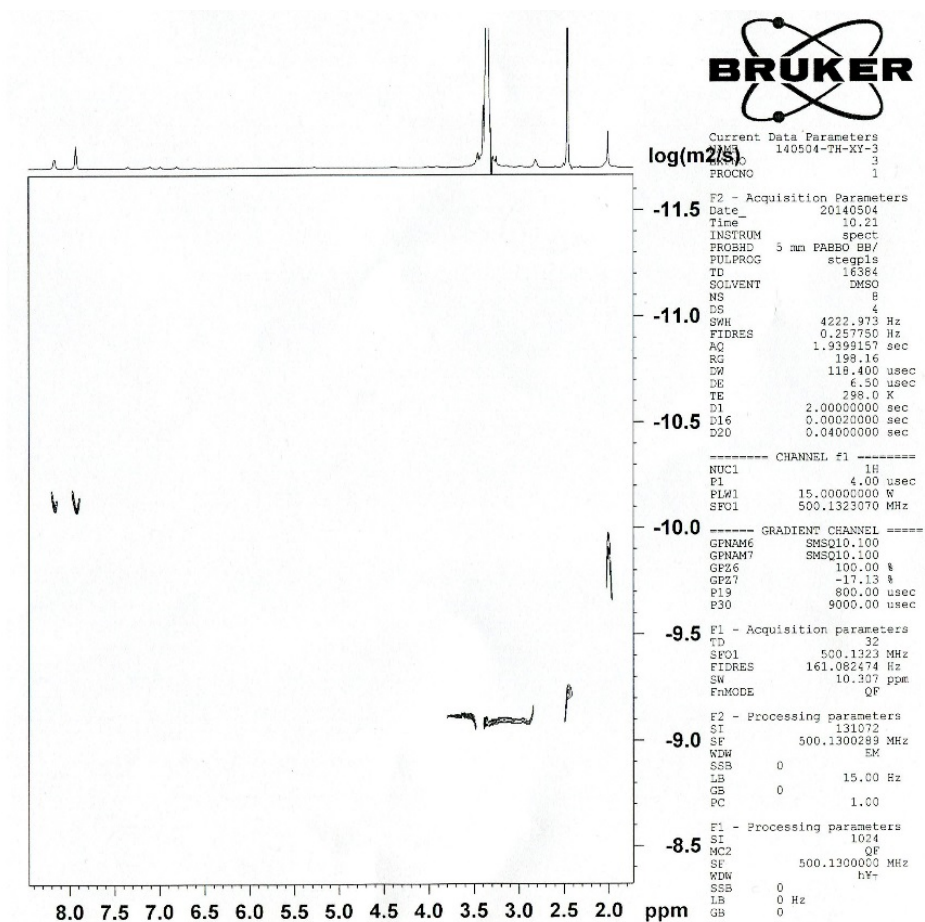


Fig. S3 Diffusion Ordered Spectroscopy (DOSY) of supramolecular polymer **PSP**. Diffusion coefficient =  $7.212 \times 10^{-11} \text{ m}^2/\text{s}$ .

### 3. Job's plots, reversibility test and photos of solid state

#### 3.1 Job's plots

The job's plot experiments were carried out as follows. The host/guest ratio was varied from 0:1 to 1:0 with ([host] + [guest]) at a fixed concentration of  $1.5 \times 10^{-5} \text{ M}$ . The intensity of UV absorbance at major absorption peak was recorded each time the molar ratio was changed. The change of the absorption reached at a maximum at a ratio of 0.8 for **[1]** / **[1] + [BSC4]**, confirming the 4:1 stoichiometry between **1** and **BSC4**. The process is same for **1c** and **BSC4** to give a stoichiometry of 4:1. (Fig. S1)

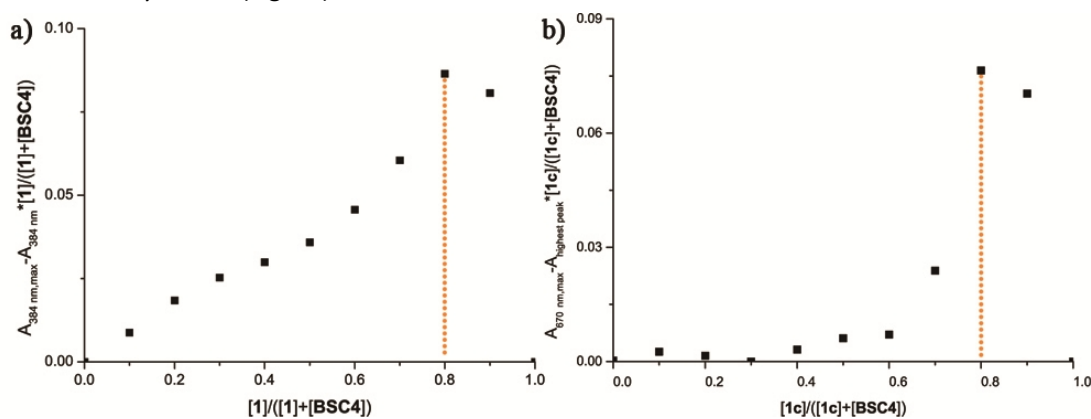


Fig. S4 Job's plots of (a) **1** with **BSC4** and (b) **1c** with **BSC4**.

### 3.2 Evaluation of photochromic yield of free **1** and **1** in PSP

The ring-closing yield of dithienylethene derivative was evaluated by NMR. Both  $^1\text{H}$  NMR of free **1** and **1** in PSP were carried out before and after UV irradiation to steady state in DMSO- $d_6$  (concentration of  $3.6 \times 10^{-3}$  mol/L for free **1** and  $9 \times 10^{-4}$  mol/L for PSP). From the result, it was clear that the free **1** performed a mainly complete close-ring process while it was about 48.4% for **1** in PSP.

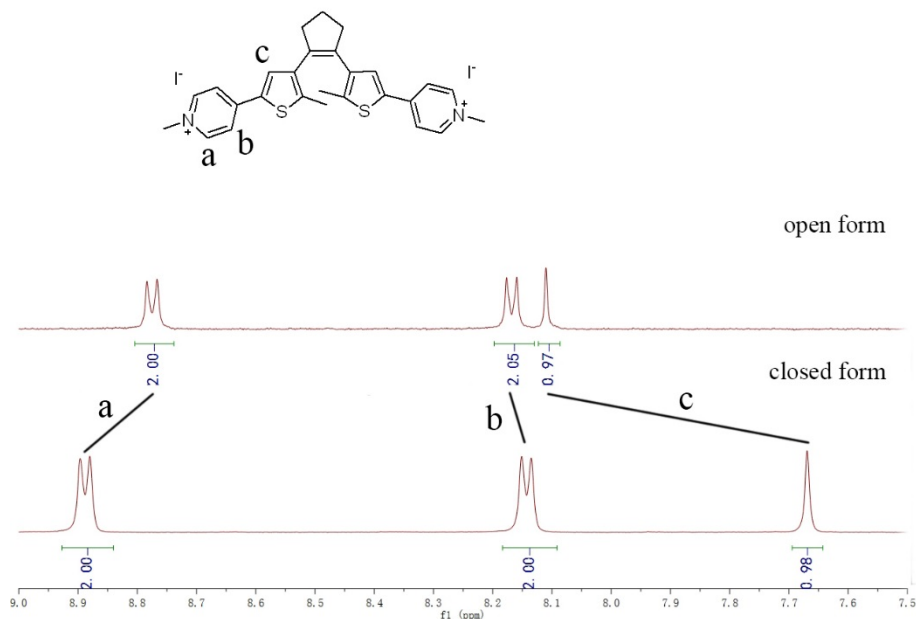


Fig. S5 Partial  $^1\text{H}$  NMR of free **1** before (top) and after (bottom) UV irradiation

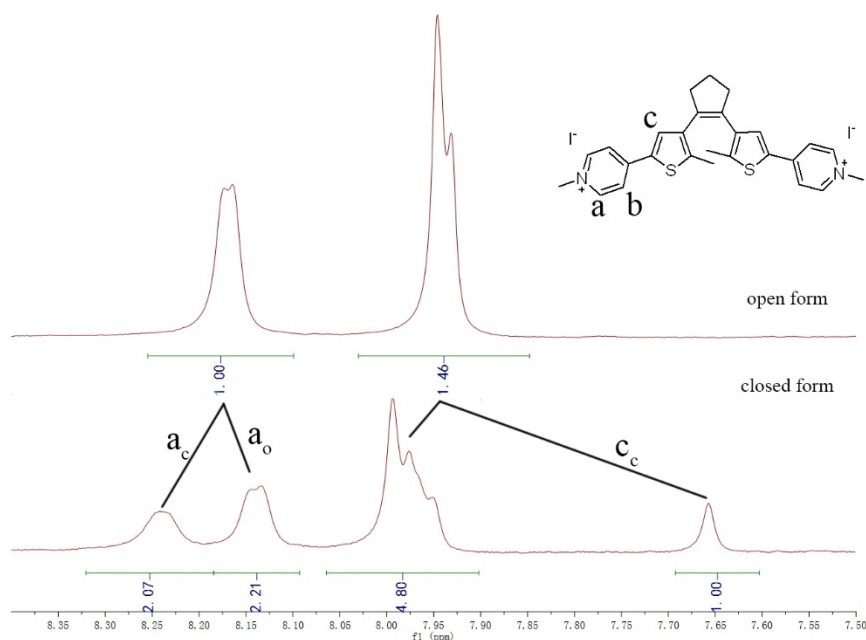


Fig. S6 Partial  $^1\text{H}$  NMR of **1** in PSP before (top) and after (bottom) UV irradiation

### 3.3 Reversibility test of photochromic property of **1** and PSP

The sample in a quartz cell (1×1 cm) were irradiated under a handheld UV lamp (power: 6W) at a

wavelength of 254nm for 13 min (from **1** to **1c**) and 30 min (form **PSP** with **1c**). After recording corresponding absorbance, the sample was irradiated under visible light on a SPOT LIGHT SOURCE machine (model: L9588-01A, HAMAMATSU PHOTONICS K.K.; intensity set as 40%) with an optical filter of >510nm to recover. The reversibility test was repeated for 3 cycles and corresponding absorption changes were recorded (Fig. S7).

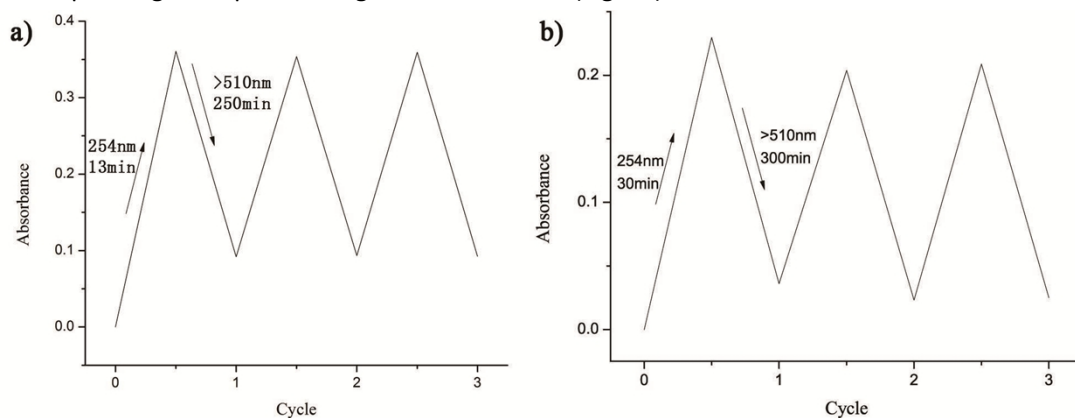


Fig. S7 The representation of the reversibility and repeatability of a) **1** and b) photochromic supramolecular polymer (**PSP**).

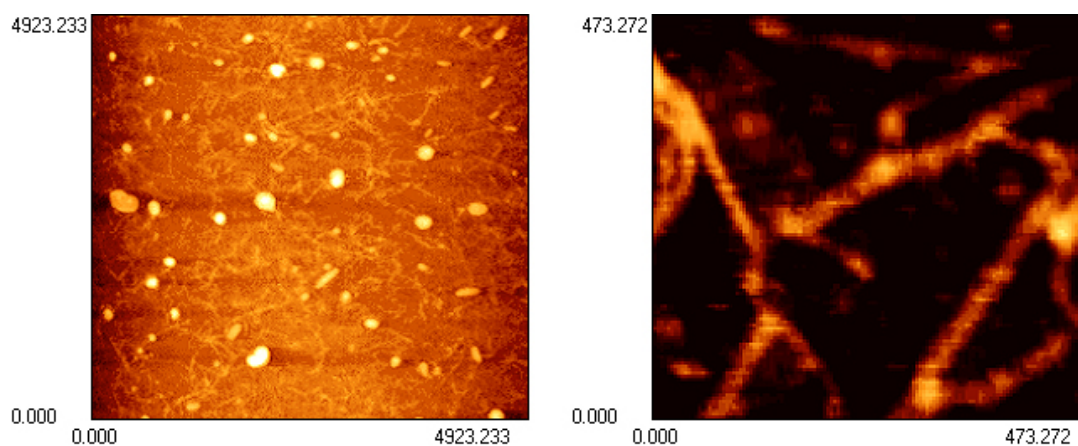


Fig. S8 More AFM images of the linear polymers **PSP**.

#### 4. References.

- S1. D.-S. Guo, S. Chen, H. Qian, H.-Q. Zhang and Y. Liu, *Chem. Commun.*, 2010, **46**, 2620.
- S2. B. Qin, R. Yao, X. Zhao and H. Tian, *Org. Biomol. Chem.*, 2003, **1**, 2187.
- S3. L. N. Lucas, J. van Esch, R. M. Kellogg and B. L. Feringa, *Chem. Commun.*, 1998, 2313.

#### 5. Additional spectra.



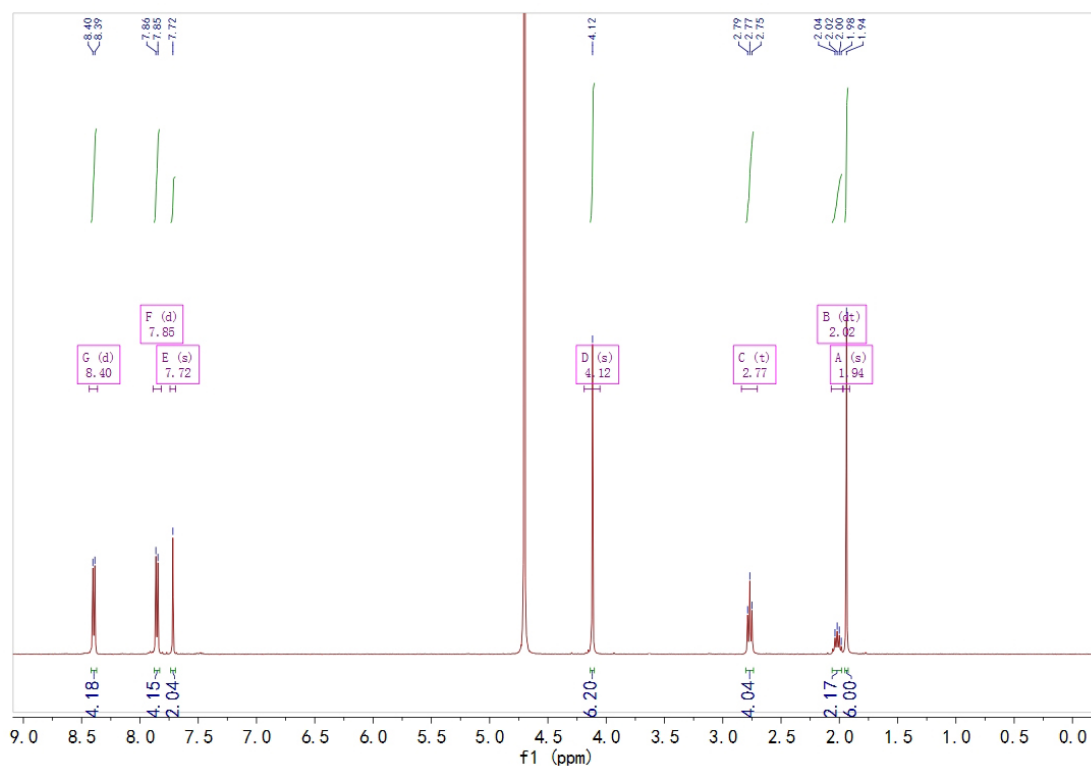


Fig. S9  $^1\text{H}$  NMR spectrum of compound **1**.

$^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  8.40 (d,  $J = 7.0$  Hz, 4H), 7.85 (d,  $J = 7.1$  Hz, 4H), 7.72 (s, 2H), 4.12 (s, 6H), 2.77 (t,  $J = 7.5$  Hz, 4H), 2.02 (dt,  $J = 14.1, 7.1$  Hz, 2H), 1.94 (s, 6H).

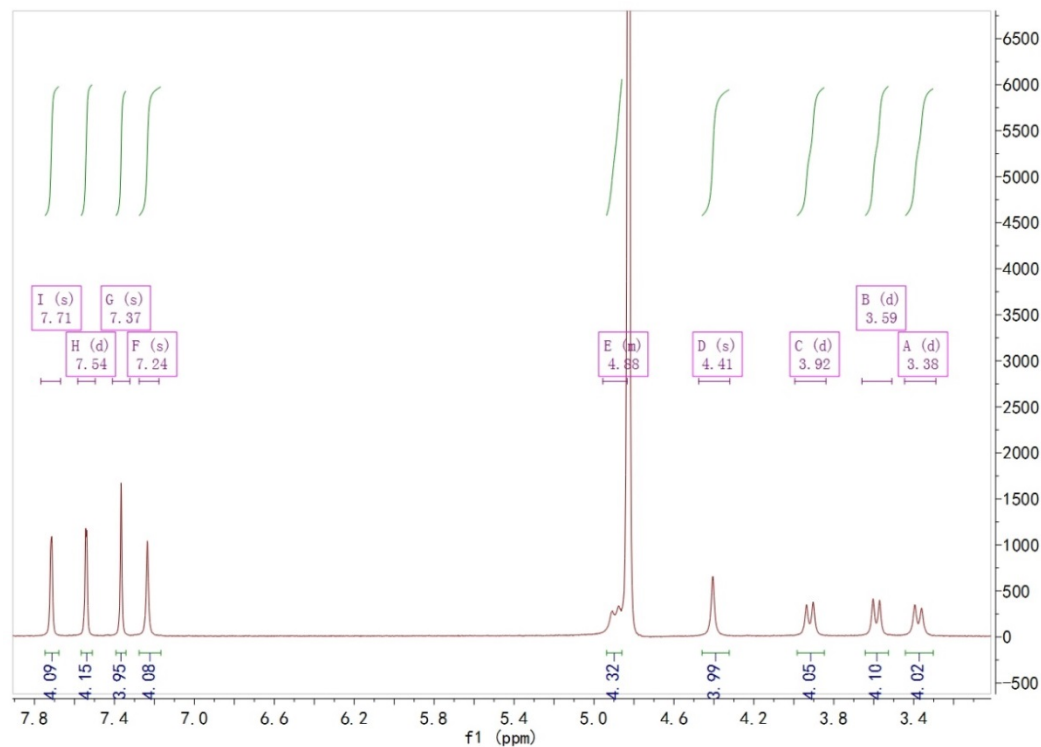


Fig. S10  $^1\text{H}$  NMR spectroscopy of compound **BSC4**.

$^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  7.71 (s, 4H), 7.54 (d,  $J = 1.9$  Hz, 4H), 7.37 (s, 4H), 7.24 (s, 4H), 4.96 – 4.83 (m, 4H), 4.41 (s, 4H), 3.92 (d,  $J = 13.4$  Hz, 4H), 3.59 (d,  $J = 12.8$  Hz, 4H), 3.38 (d,  $J = 13.4$  Hz,



4H).

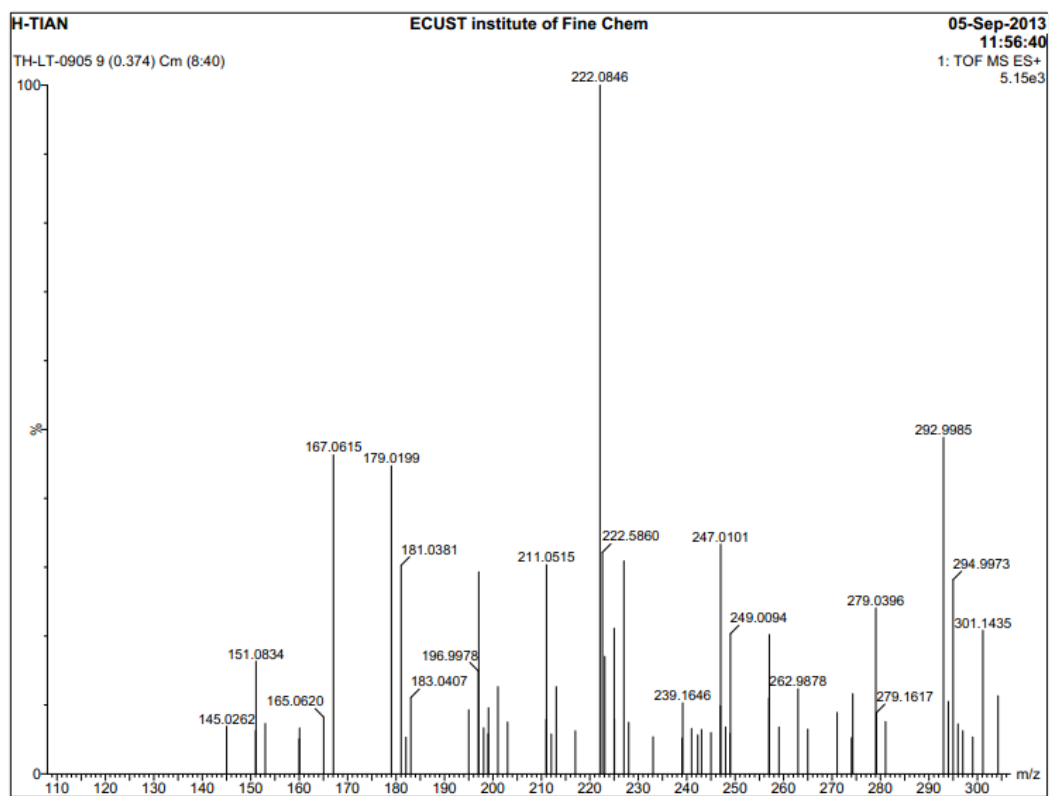


Fig. S11 TOF-MS of compound 1.  $([M-2H]^{2+})/2=222.0842$ , found 222.0846.