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 1H NMR and high-resolution ESI mass spectroscopy.

1.2. General. 1H NMR spectra were measured on a Bruker AV-400 spectrometer. ROESY and DOESY were measured on a Bruker 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^-5 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^-5 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.¹
1.3.2 Synthesis of 1, 2-bis [2-methyl-5-(4-methylpyridyl)-3-thienyl] cyclopentene (1)

1, 2-bis (2-methyl-5-chloro-3-thienyl) cyclopentene (3) was synthesized by the classical method according to the previous reference. 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 °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 °C for 30 min. B(OC3H7)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 Pd(PPh3)4 (230 mg, 0.2 mmol) were added to THF (20 mL), then mixed with aqueous solution of Na2CO3 (6 g) 10 mL under Ar condition and the reaction mixture was heated to 55 °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 Na2SO4.

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 CH3I (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 calixarene cavities, which have sulfo groups as anchor points.

2.2 Diffusion Ordered Spectroscopy (DOSY)

Diffusion Ordered Spectroscopy (DOSY) was carried out to determine the diffusion coefficient of 1 (3.6×10^{-3} mol/L) as 1.725×10^{-10} m^{2}/s and that in PSP (9×10^{-4} mol/L) as 7.212×10^{-11} m^{2}/s in DMSO-d_{6}. Due to the limited concentration of PSP, the corresponding diffusion coefficient of BSC4 at certain concentration (9×10^{-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$^2$/s.
Fig. S3 Diffusion Ordered Spectroscopy (DOSY) of supramolecular polymer PSP. Diffusion coefficient = 7.212×10^{-11} m²/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 ×10^{-5} 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 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 $^1$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 3.6×10$^{-3}$ mol/L for free 1 and 9×10$^{-4}$ 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 $^1$H NMR of free 1 before (top) and after (bottom) UV irradiation

Fig. S6 Partial $^1$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 handhold 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).](image)

Fig. S7 More AFM images of the linear polymers PSP.

4. References.


5. Additional spectra.
Fig. S9 $^1$H NMR spectrum of compound 1.

$^1$H NMR (400 MHz, D$_2$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 $^1$H NMR spectroscopy of compound BSC4.

$^1$H NMR (400 MHz, D$_2$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,
Fig. S11 TOF-MS of compound 1. ([M-2I]^2+)/2=222.0842, found 222.0846.