# Electronic Supplementary Information (ESI)

## Photoreversible Switching between Assembly and Disassembly of Supramolecular Polymer Involving an Azobenzene-Bridged Pillar[5]arene Dimer

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## Experimental section

**Materials.** All solvents and reagents were used as supplied except the following. Anhydrous *N*,*N*-dimethylformamide (DMF) was purchased from Kanto Reagents, Chemicals & Biologicals.

**Measurements.** The $^1$H NMR spectra were recorded at 500 MHz and $^{13}$C NMR spectra were recorded at 125 MHz with a JEOL-ECA500 spectrometer. High-resolution mass spectra (HRMS) were obtained on a high resolution sector type double focusing mass spectrometer (ionization mode: FAB) and a time-of-flight (TOF) analyzer (ionization mode: ESI).

**H3.** Under a nitrogen atmosphere, **H2**$^{S1}$ (800 mg, 1.10 mmol) was dissolved in DMF (80 mL). Sodium hydride (53.0 mg, 2.20 mmol) was added and the reaction mixture was stirred. Then, propargyl bromide (0.47 mL, 5.40 mmol) was added and the reaction mixture was heated at 80 $^{o}$C for 24 h. After removal of the solvent, the resulting solid was dissolved in chloroform and water. The organic layer was dried over anhydrous $Na_2SO_4$. After filtration, the filtrate was evaporated to give a solid. Column chromatography (silica gel; ethyl acetate : hexane = 1 : 4) afforded a solid (**H3**, 690 mg, 0.890 mmol, Yield: 81%). $^1$H NMR ($CDCl_3$, 500 MHz, ppm): δ 6.70-6.79 (m, 10H, phenyl), 4.39 (d, 2H, methylene adjacent to alkyne), 3.60-3.78 (m, 37H, methylene bridge and methylene), 1.79 (t, 1H, alkyne). $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): δ 151.2, 150.8, 148.9, 128.9, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 115.5, 114.4, 114.3, 114.1, 114.0, 113.9, 78.8, 74.6, 56.2, 55.9, 55.8, 55.7, 30.4, 29.7, 29.6, 29.0. HRFABMS: *m*/*z* Calcd for $C_{47}H_{50}O_{10}$ $[M]^+$: 774.3404, found 774.3341.

**4,4'-Bis(azidomethyl)azobenzene.** 4,4'-Bis(bromomethyl)azobenzene$^{S2}$ (735 mg, 2.00 mmol) was dissolved in dry *N*,*N*-dimethylformamide (80 mL), and sodium azide (650 mg, 16.0 mmol) was added. The reaction mixture was heated at 80 $^{o}$C for 24 h, cooled to room temperature and added to ethyl acetate. The solution was washed with water, and dried ($Na_2SO_4$). After evaporation of the solvent, the residue was purified by column chromatography (silica gel; hexane : ethyl acetate = 9 : 1) to give a solid (560 mg, 1.92 mmol, Yield: 96%). $^1$H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.95 (d, 4H, azobenzene), 7.48 (d, 4H, azobenzene), 4.45 (s, 4H, methylene). $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): δ 152.4, 138.4, 128.9, 123.4, 54.4. HRFABMS: *m*/*z* Calcd for $C_{14}H_{13}N_8$ $[M+H]^+$: 293.1263, found 293.1269.

***trans*-H4.** To a solution of **H3** (387 mg, 0.500 mmol) and 4,4'-bis(azidomethyl)azobenzene (29.0 mg, 0.100 mmol) in chloroform (10 mL), TBTA[S3] (53.0 mg, 0.100 mmol) was added. To the mixture, $Cu(CH_3CN)_4PF_6$ (37.0 mg, 0.100 mmol) was added, and the mixture was stirred at 25 °C for 24 h. The resulting solution was concentrated under *vacuo*. Column chromatography (silica gel; ethyl acetate : dichloromethane = 1 : 5) afforded a solid (*trans*-**H4**, 497 mg, 0.270 mmol, Yield: 54%). $^1$H NMR ($CD_2Cl_2$, 500 MHz, ppm): δ 7.86 (d, 4H, azobenzene), 7.62 (s, 2H, triazole), 7.37 (d, 4H, azobenzene), 6.64-6.88 (m, 20H, phenyl protons from pillar[5]arene), 5.55 (s, 4H, methylene), 5.00 (s, 4H, methylene), 3.39-3.65 (m, 74H, methyl and methylene bridge of pillar[5]arene). $^{13}$C NMR ($CD_2Cl_2$, 125 MHz, ppm): δ 152.5, 151.0, 150.5. 150.4, 150.3, 149.0, 145.6, 138.2, 128.9, 128.7, 128.3, 128.2, 128.0, 123.6, 122.7, 114.8, 113.4, 113.3, 113.2, 62.7, 55.7, 55.6, 55.5, 55.4, 55.3, 29.2, 29.1. HRESIMS: *m/z* Calcd for $C_{108}H_{112}N_8NaO_{20}$ $[M+Na]^+$: 1863.7891, found 1863.7893.

### Complex Formation

Formation of the host-guest complexes, equimolar mixtures of **G1** and *trans*-**H4** were dissolved in $CD_2Cl_2$. To inhibit the photoisomerization, the samples were placed in dark place.

### Photoisomerization

A xenon light source (MAX-303, Asahi Spectra) equipped with interference filters centered at 365 nm (XBPA365, Asahi Spectra) and at 436 nm (XBPA436, Asahi Spectra) was used for photoisomerization. To reach equilibrium, irradiation time with UV and visible light was 10h.

### DOSY NMR Study[S4]

DOSY NMR investigations revealed a diffusion coefficient of $D = 6.22 \times 10^{-9}$ m$^2$s$^{-1}$ for *trans*-**H4**, while for **G1** a $D$ value of $3.70 \times 10^{-9}$ m$^2$s$^{-1}$ was obtained in dilute concentration (2 mM). The large difference in $D$ values of *trans*-**H4** and **G1** indicates considerably different hydrodynamic radii. The average value observed for a 2 mM solution of *trans*-**H4** and **G1** ($D_{av}$) was $4.96 \times 10^{-9}$ m$^2$s$^{-1}$. The average size of the self-assembled species of a mixture of can therefore be estimated using following equations:

$$DP = (D / D_{av})^3$$

where $D$ is the diffusion coefficient of the host and guest mixture determined from

DOSY NMR measurements. The average degree of polymerization (DP) derived from such comparison is just a rough approximation because the polymers are assumed to be hydrodynamically spherical.

# $^1$H NMR spectrum of H3

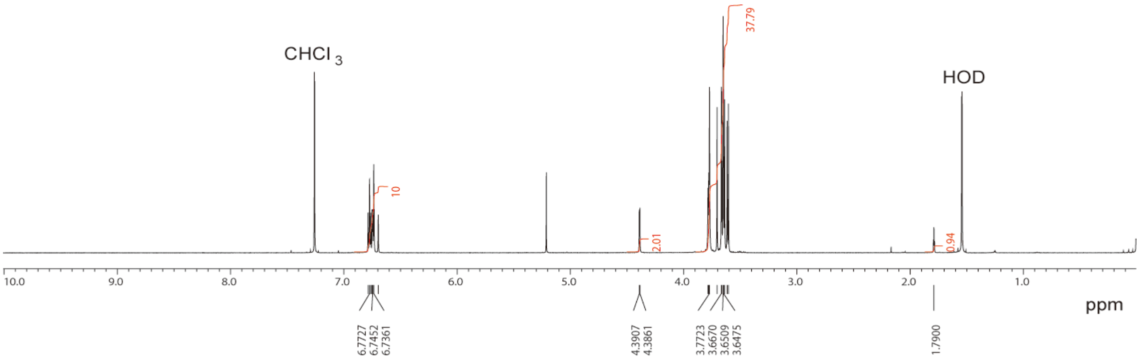

**Fig. S1** $^1$H NMR spectrum of **H3** in $CDCl_3$ at 25 °C.

## $^{13}$C NMR spectrum of H3

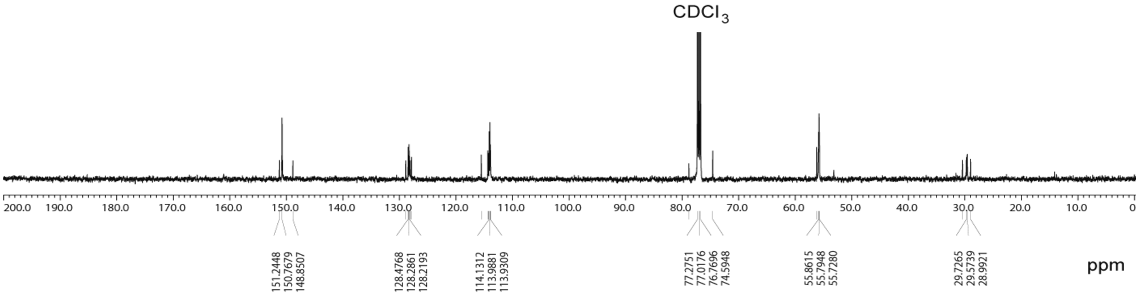

**Fig. S2** $^{13}$C NMR spectrum of **H3** in CDCl$_3$ at 25 $^{o}$C.

## $^1$H NMR spectrum of 4,4'-bis(azidomethyl)azobenzene

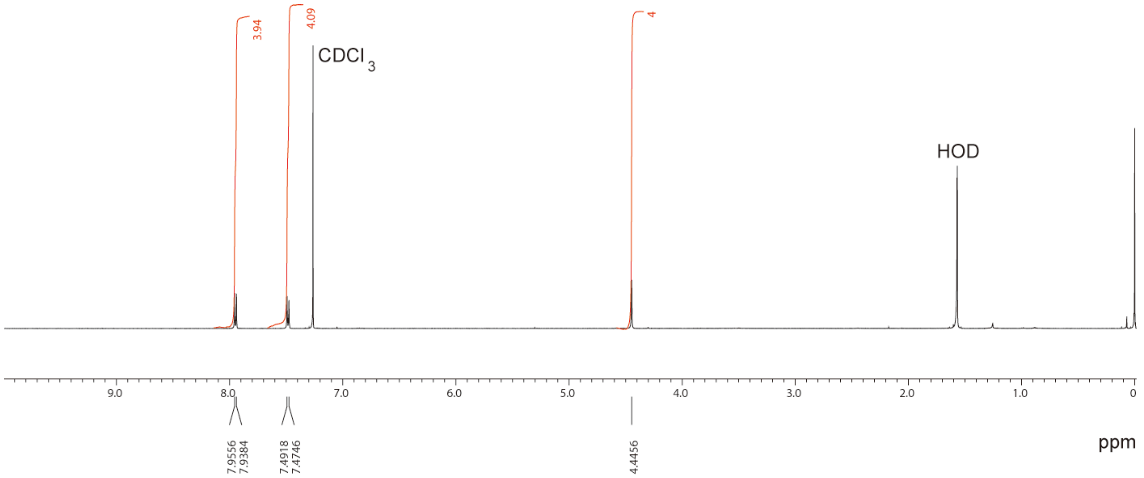

**Fig. S3** $^1$H NMR spectrum of 4,4'-bis(azidomethyl)azobenzene in $CDCl_3$ at 25 °C.

# $^{13}$C NMR spectrum of 4,4'-bis(azidomethyl)azobenzene

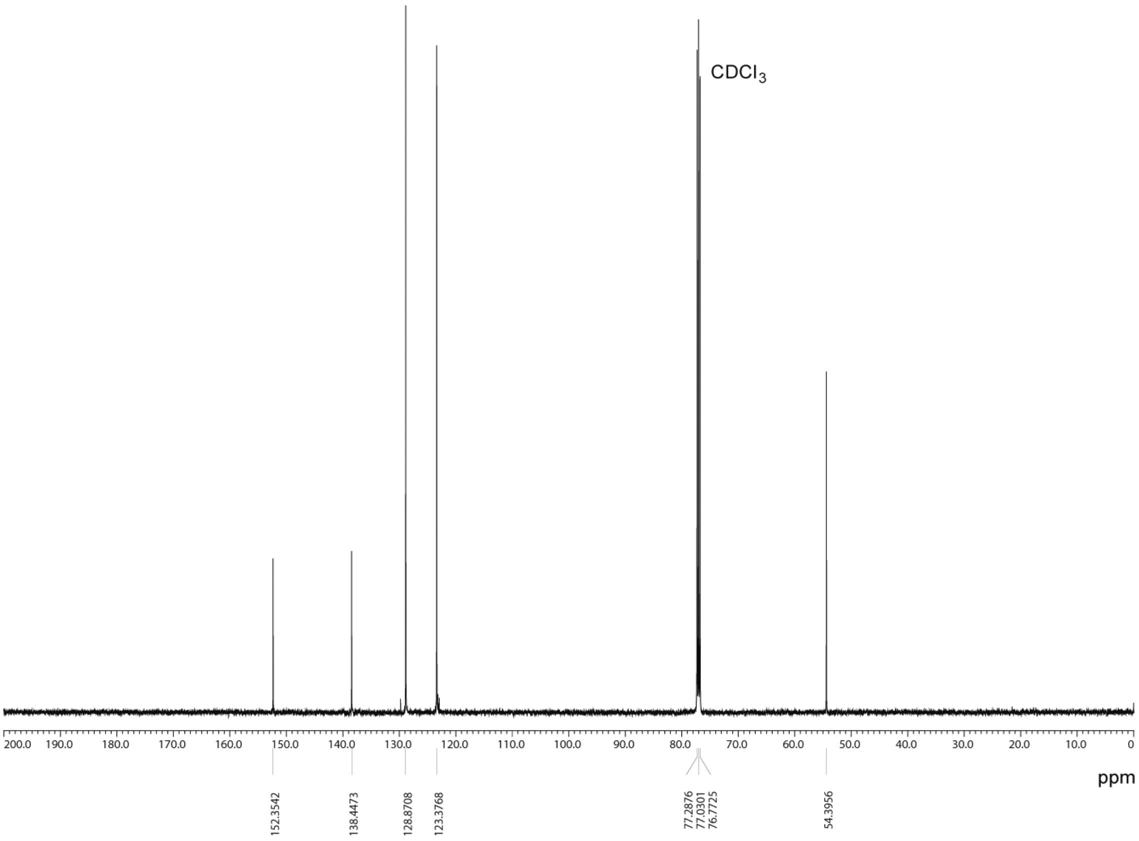

**Fig. S4** $^{13}$C NMR spectrum of 4,4'-bis(azidomethyl)azobenzene in CDCl$_3$ at 25 $^{o}$C.

## $^1$H NMR spectrum of *trans*-H4

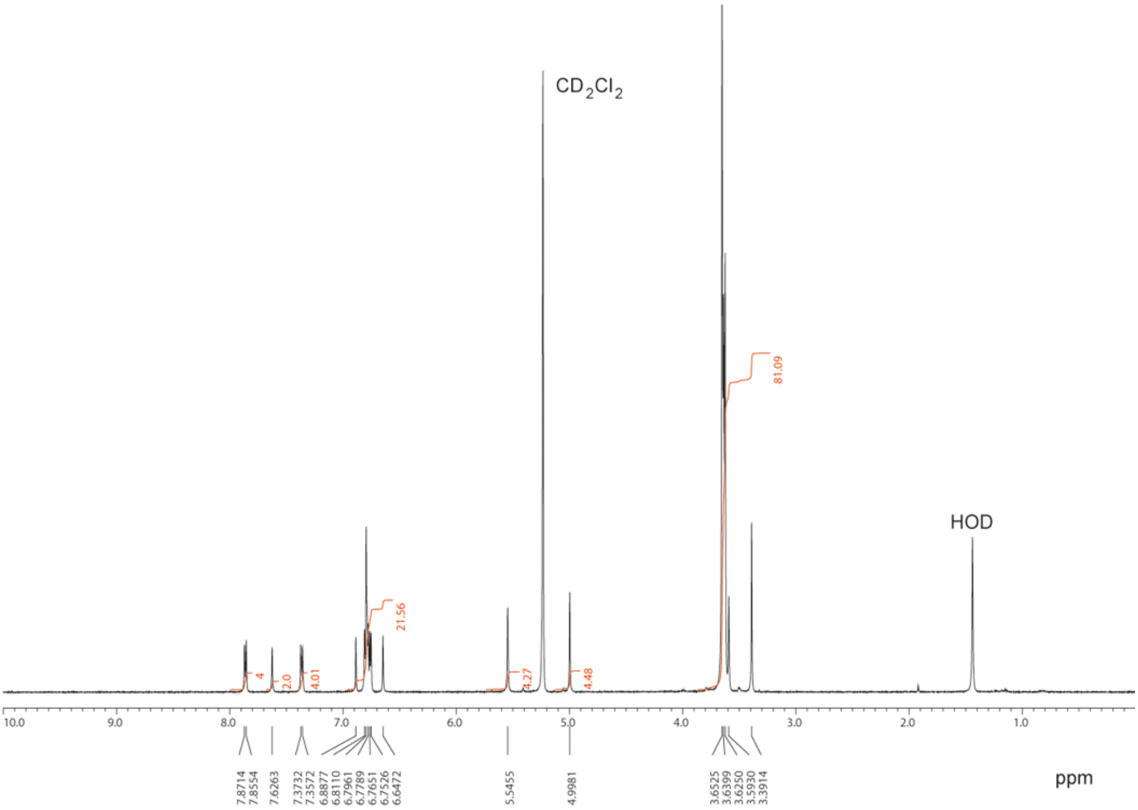

**Fig. S5** $^1$H NMR spectrum of *trans*-**H4** in $CD_2Cl_2$ at 25 $^{o}$C.

## $^{13}$C NMR spectrum of *trans*-H4

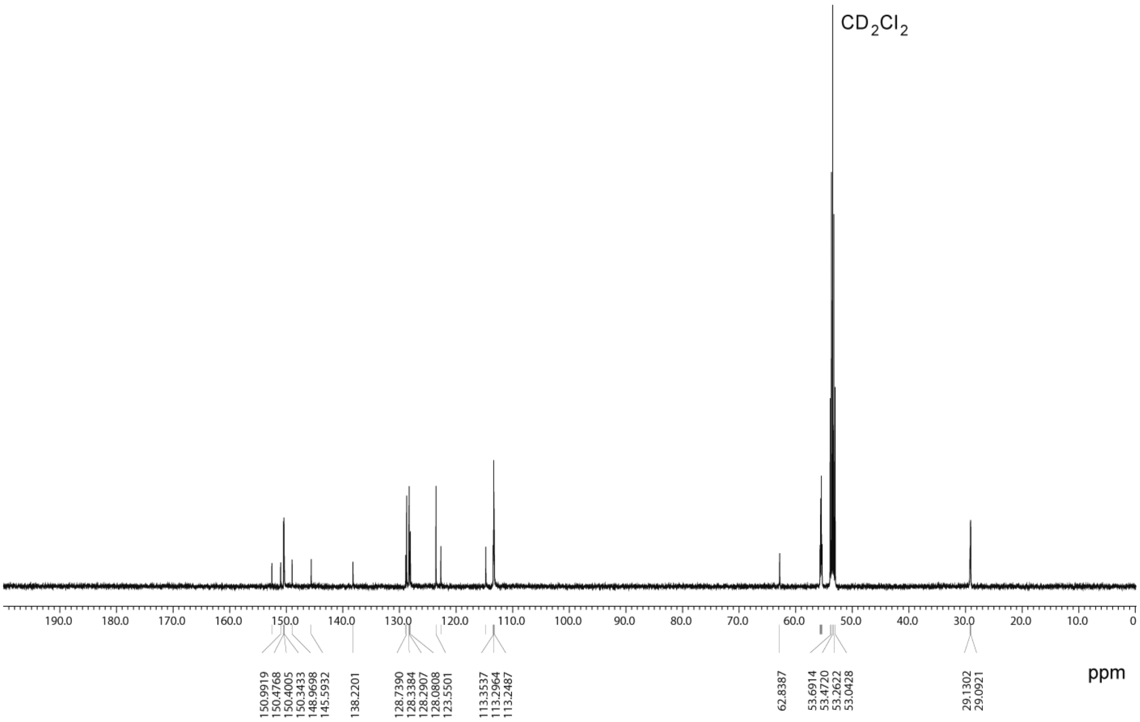

**Fig. S6** $^{13}$C NMR spectrum of *trans*-**H4** in CD$_2$Cl$_2$ at 25 $^{o}$C.

## Photoisomerization of *trans*-H4 to *cis*-H4

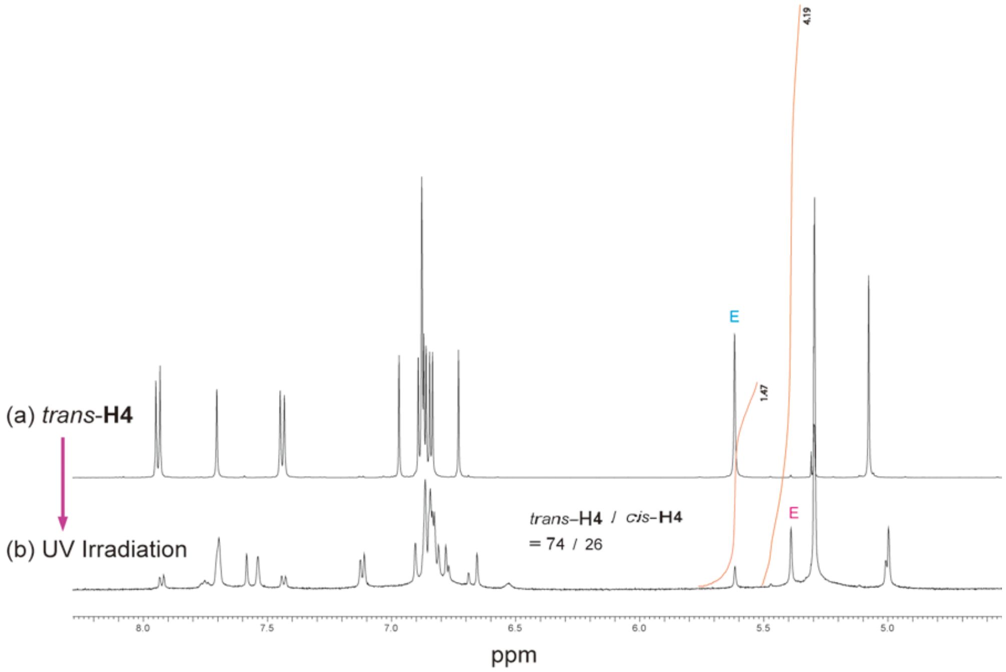

**Fig. S7** Partial $^1$H NMR spectra (500 MHz, 298 K, $CD_2Cl_2$, 100 mM) of *trans*-**H4** (a) without and (b) with UV light irradiation. Resonances are labeled in Fig. 1.

## References

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(S3) M. von Delius, E. M. Geetsema and D. A. Leigh, *Nat. Chem.*, 2010, **2**, 96.
(S4) R. Schmidt, M. Stolte, M. Grüner and F. Würthner, *Macromolecules*, 2011, **44**, 3766.