Electronic Supplementary Material (ESI) for ChemComm.

Construction of pillar[6]arene-based CO_2 and UV dual-responsive supra-amphiphile and application in controlled self-assembly

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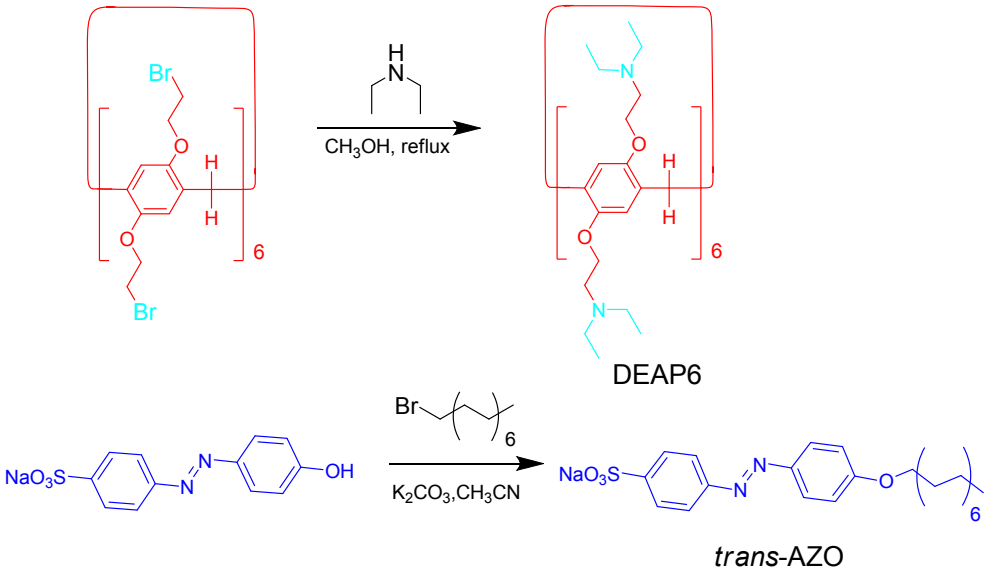
Electronic Supplementary Information (11 pages)

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compound *trans*-**TY-1**[S1] was synthesized according to published procedure. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance Ⅲ-400 spectrometry. The 2D NOESY NMR spectrum was collected on a Bruker Avance DMX-500 spectrometer with internal standard TMS. Mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. HRMS were obtained on a WATERS GCT Premier mass spectrometer. UV-vis spectra were taken on a Shimadzu UV-2550 UV-vis spectrophotometer. The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. Transmission electron microscopy (TEM) investigations were carried out on a HT-7700 instrument. The critical aggregation concentration (CAC) values were determined on a DDS-307 instrument. The ITC experiment was performed on a VP-ITC micro-calorimeter (Microcal, USA).

*2. Synthesis of compounds **DEAP6** and trans-**AZO***

Scheme S1. Synthetic route to ***DEAP6*** *and trans-**AZO***.



Synthesis of **DEAP6:** Diethylamine (4.11 mL, 40 mmol) was added to a solution of bromoethylpillar[6]arene (3.36 g, 2.0 mmol) in methanol (200 mL) under vigorous stirring. The mixture was refluxed for 24 hours. The solvent was evaporated, and the residue was poured into a NaOH solution (1.00 M, 200 mL) and stirred. The solution was extracted with ethyl acetate (3 × 100 mL), and the organic phase was obtained. The yellow oil was isolated after evaporation of the solution as the crude product, which was distilled in *vacuo* to give **DEAP6** as dense oil (3.14g, 98%). The ^{1}H NMR spectrum of **DEAP6** is shown in Fig. S1. ^{1}H NMR (400 MHz, $CDCl_3$-*d*, 293 K) δ (ppm): 6.75 (s, 12H), 3.87 (t, J = 8 Hz, 24H), 3.77 (s, 12H), 2.78 (t, J = 8 Hz, 24H), 2.55 (m, 48H), 0.99 (t, J = 8 Hz, 72H). The ^{13}C NMR spectrum of **DEAP6** is shown in Fig. S2. ^{13}C NMR (100 MHz, $CDCl_3$-*d*, 293 K) δ (ppm): 150.31, 127.95, 115.04, 67.21, 52.08, 47.71, 29.70, 12.02. LRESIMS is shown in Fig. S3: *m*/*z* 1924.0 $[M + H]^+$. HRESIMS: *m*/*z* calcd for $[M + H]^+$ $C_{114}H_{193}O_{12}N_{12}$, 1923.4894; found 1923.4870; error −1.0 ppm.

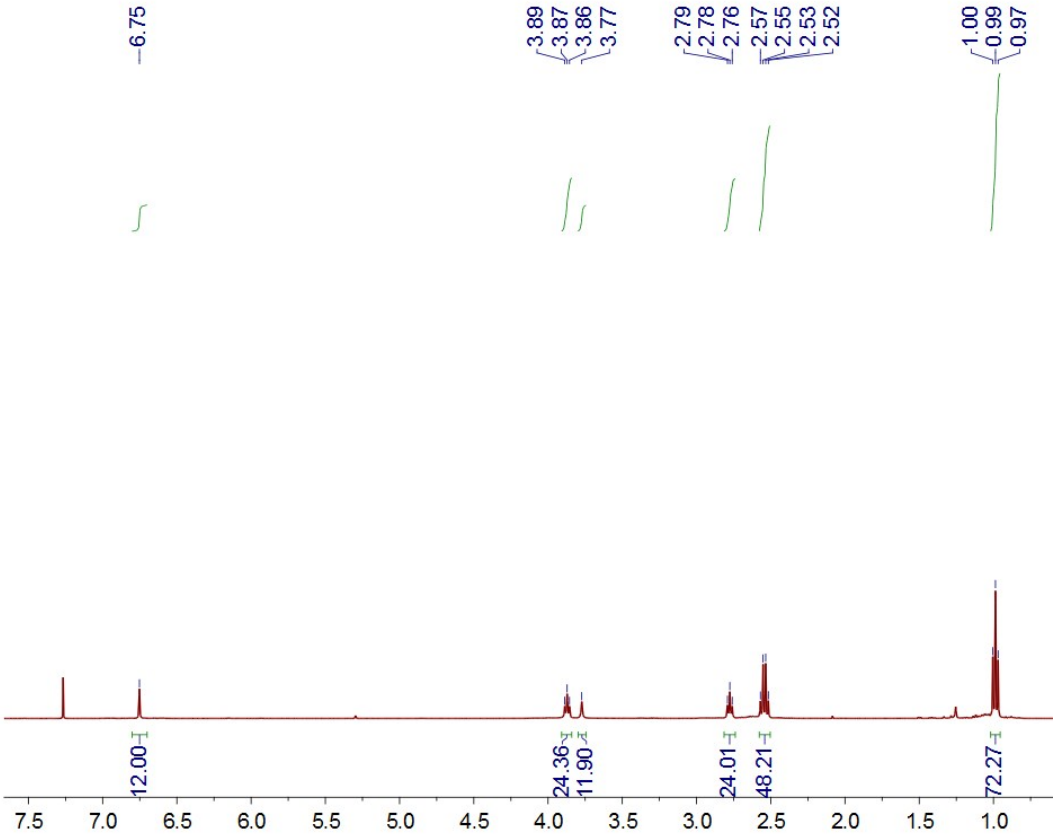


Fig. S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$-*d*, 293 K) of **DEAP6**.

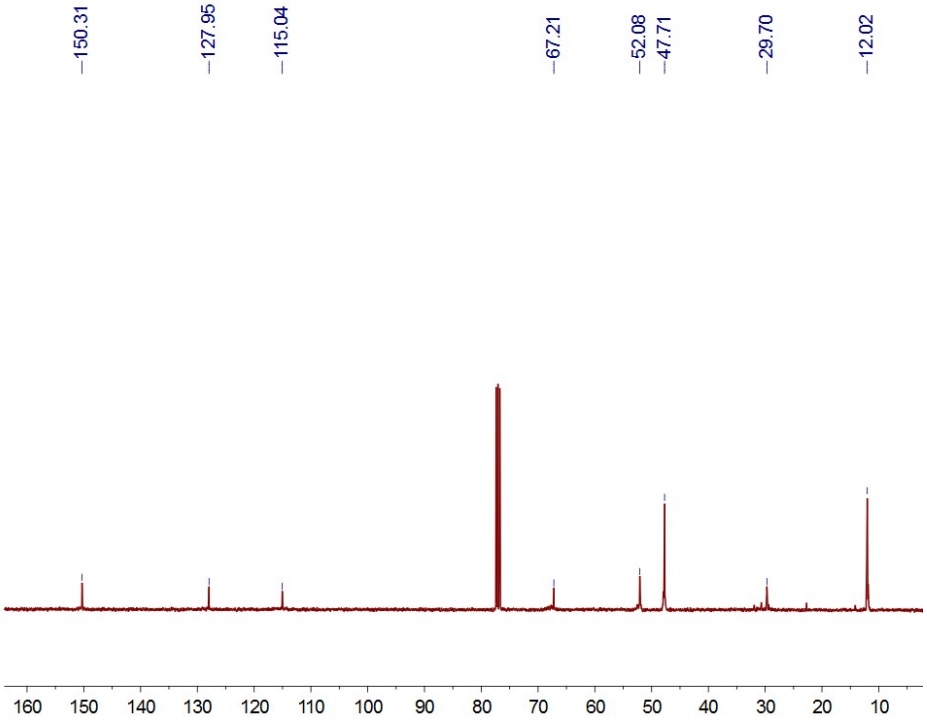


Fig. S2 ^{13}C NMR spectrum (100 MHz, $CDCl_3$-*d*, 293 K) of **DEAP6**.

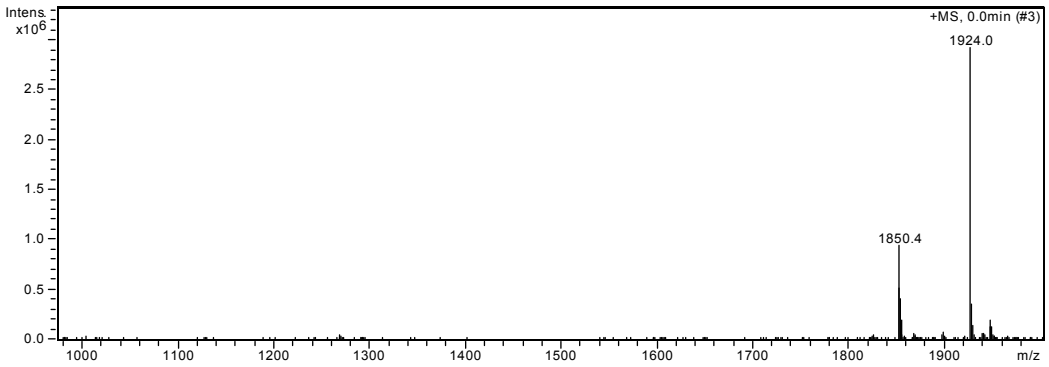


Fig. S3 Electrospray ionization mass spectrum of **DEAP6**. Assignment of the main peak: *m*/*z* 1924.0 $[M + H]^+$ (100%).

Synthesis of *trans*-**AZO:** 1-Bromotetradecane (27.7 g, 100 mmol) and K_2CO_3 (41.4 g, 300 mmol) were added to a solution of *trans*-Tropaeolin Y (18.0 g, 60.0 mmol) in CH_3CN (100 mL). The mixture was heated in a three-necked flask under nitrogen atmosphere at reflux for 24 h. The cooled reaction mixture was filtered and washed with CH_3CN. The filtrate was evaporated under vacuum, and the residue was further washed with water to afford *trans*-**AZO** as a yellowish solid (11.2 g, 38%), m.p. 210.5–211.6 °C. The ^{1}H NMR spectrum of *trans*-**AZO** is shown in Fig. S4. ^{1}H NMR (400 MHz, DMSO-d_6, 293 K) δ (ppm): 7.91 (d, J = 8 Hz, 2H), 7.78 (m, 4H), 7.12 (d, J = 8 Hz, 2H), 4.08 (t, J = 8 Hz, 2H), 1.75 (t, J = 8 Hz, 2H), 1.43 (s, 2H), 1.24 (s, 18H), 0.85 (t, J = 8 Hz, 3H). The ^{13}C NMR spectrum of *trans*-**AZO** is shown in Fig. S5. ^{13}C NMR (125 MHz, TFA-*d*, 293 K) δ (ppm): 174.48, 143.48, 141.29, 138.88, 127.66, 120.05, 117.94, 113.45, 71.00, 30.75, 28.45, 28.43, 28.41, 28.36, 28.27, 28.18, 28.14, 27.88, 27.37, 24.34, 21.30, 11.59. LRESIMS is shown in Fig. S6: *m*/*z* 473.2 $[M - Na]^-$. HRESIMS: *m*/*z* calcd for $[M - Na]^-$ $C_{26}H_{37}O_4N_2S$, 473.2474; found 473.2490; error 3.0 ppm.

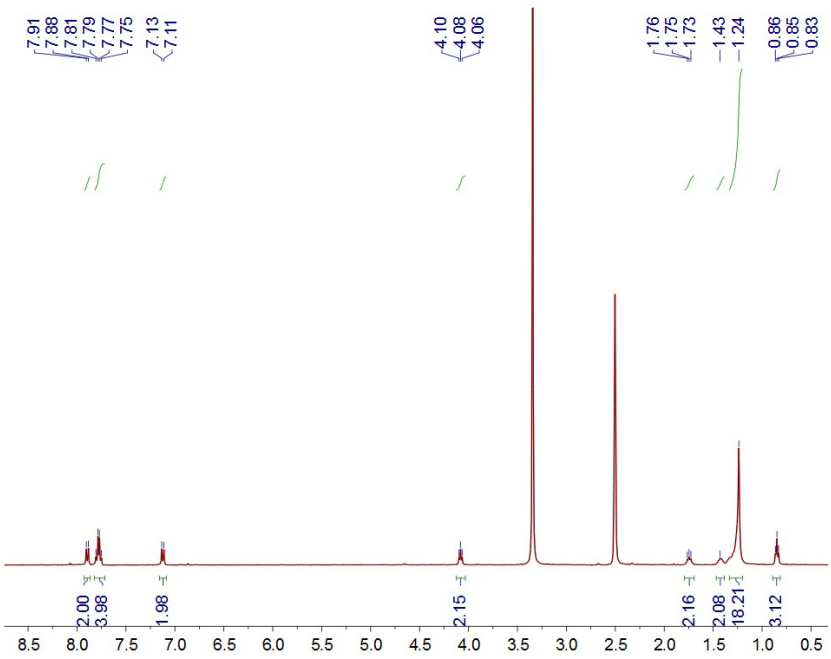


Fig. S4 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 293 K) of *trans*-**AZO**.

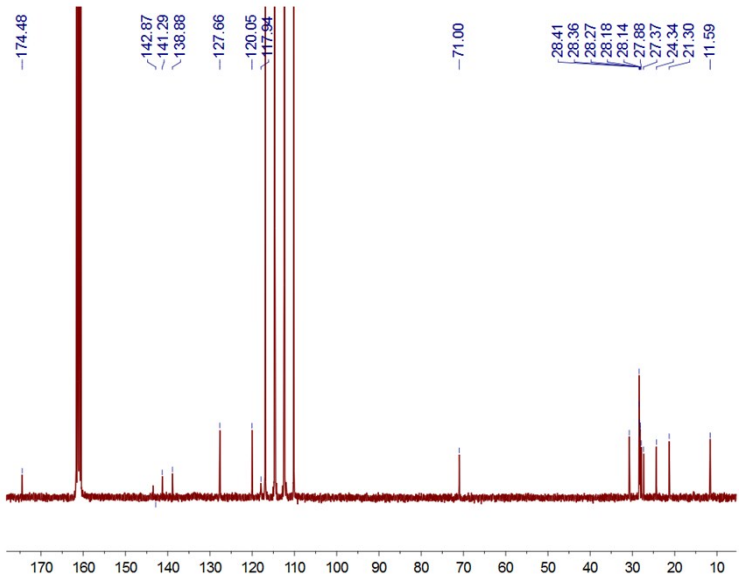


Fig. S5 ^{13}C NMR spectrum (125 MHz, TFA-*d*, 293 K) of *trans*-**AZO**.

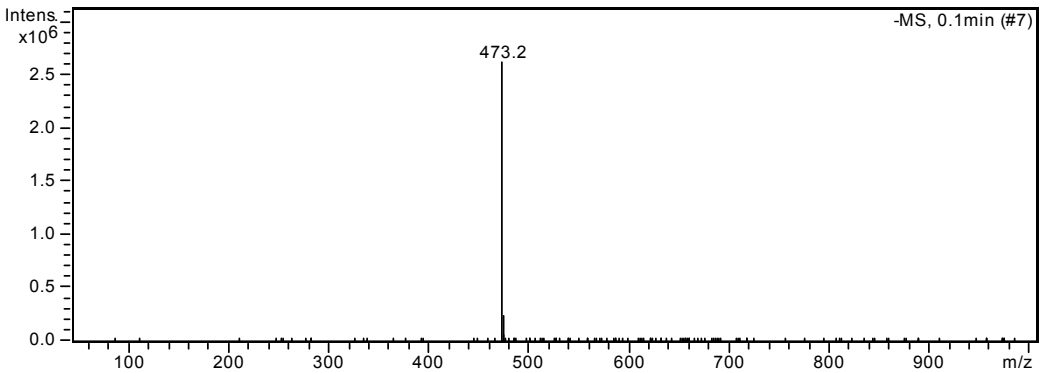


Fig. S6 Electrospray ionization mass spectrum of *trans*-**AZO**. Assignment of the main peak: *m*/*z* 473.2 $[M - Na]^-$ (100%).

*3. Photo-isomerization of trans-**TY-1***

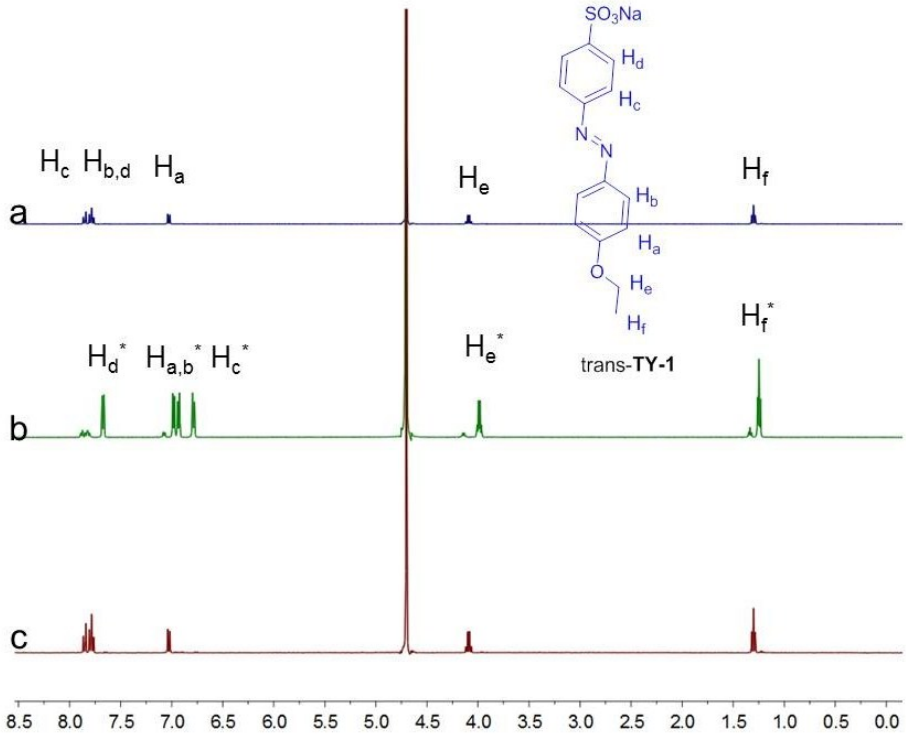


Fig. S7 ^{1}H NMR spectra (400 MHz, D_2O, room temperature): (a) *trans*-**TY-1** (1.00 mM); (b) (a) after UV irradiation at 365 nm for 30 min; (c) (b) after further irradiation at 435 nm for 10 min.

*4. 2D NOESY spectrum of **CP6**⊃trans-**TY***

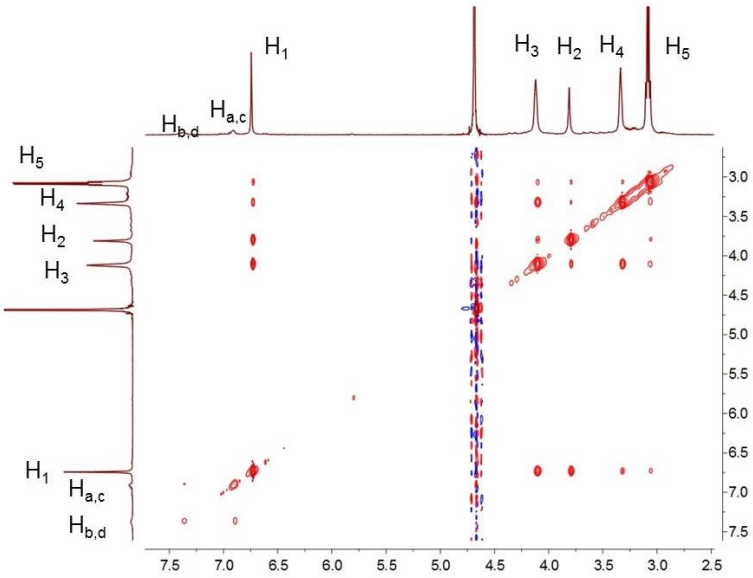


Fig. S8 2D ^{1}H-^{1}H NOESY spectrum of **CP6** (10.0 mM) and *trans*-**TY** (10.0 mM) (500 MHz, D_2O, room temperature).

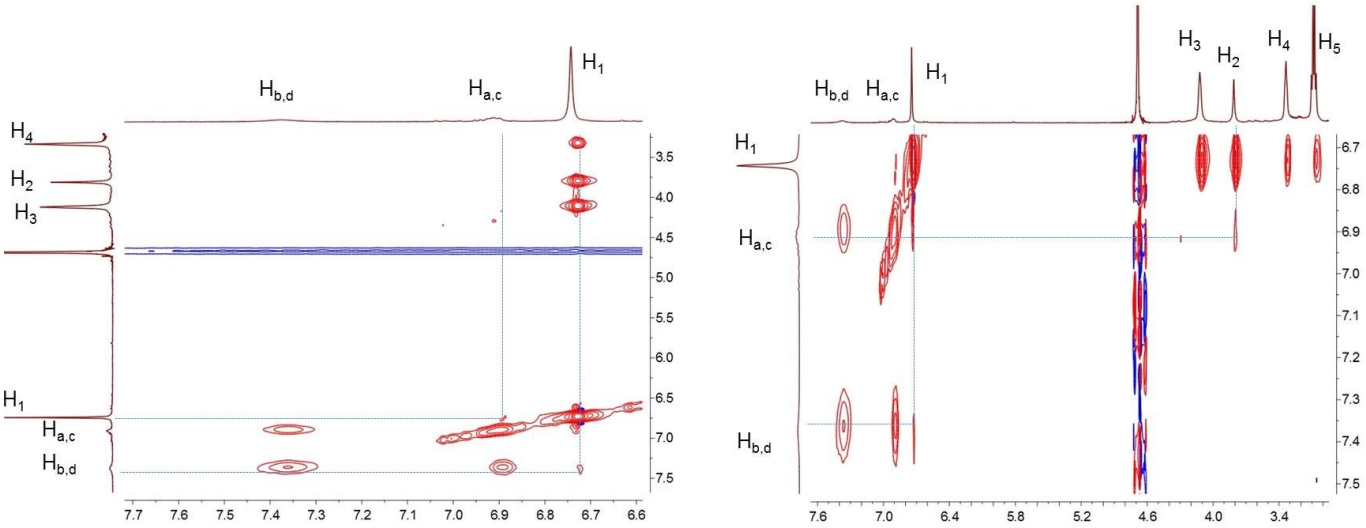


Fig. S9 Partial 2D ^{1}H-^{1}H NOESY spectrum of **CP6** (10.0 mM) and *trans*-**TY** (10.0 mM) (500 MHz, D_2O, room temperature).

5. Isothermal titration calorimetry (ITC) experiment

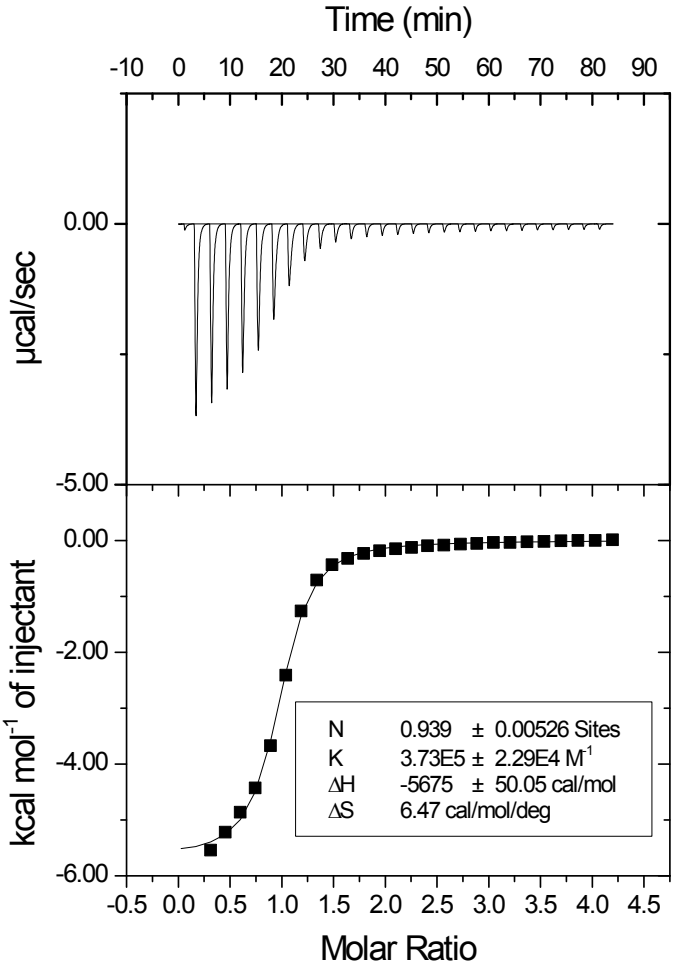


Fig. S10 Microcalorimetric titration of *trans*-**TY** with **CP6** in water at 298.15 K. Top: raw ITC data for 26 sequential injections (10 µL per injection) of a *trans*-**TY** solution (10.0 mM) into a **CP6** solution (0.500 mM); Bottom: net reaction heat obtained from the integration of the calorimetric traces.

Isothermal titration calorimetry (ITC) experiments were performed to provide thermodynamic insight into the inclusion complexation between **CP6** and *trans*-**TY**. As shown in Fig. S10, the K_a value of **CP6**⊃*trans*-**TY** was determined to be $(3.73 \pm 0.23) \times 10^5$ M^{-1} in 1:1 complexation. Furthermore, the enthalpy and entropy changes were obtained ($\Delta H° < 0$; $T\Delta S° < 0$; $|\Delta H°| > |T\Delta S°|$), indicating that this complexation was primarily driven by the enthalpy changes.

*6. Critical aggregation concentration (CAC) determinations of trans-**AZO** and* **CP6**⊃*trans-**AZO***

Some parameters such as the conductivity, fluorescence intensity and surface tension of the solution change sharply around the critical aggregation concentration. The dependence of the solution conductivity on the solution concentration is used to determine the critical aggregation concentration. Typically, the slope of the change in conductivity versus the concentration below CAC is steeper than the slope above the CAC. Therefore, the junction of the conductivity-concentration plot represents the CAC value. To measure the CAC values of *trans*-**AZO** and **CP6**⊃*trans*-**AZO**, the conductivities of the solutions at different concentrations were determined. By plotting the conductivity versus the concentration, we estimated the CAC values of *trans*-**AZO** and **CP6**⊃*trans*-**AZO**.

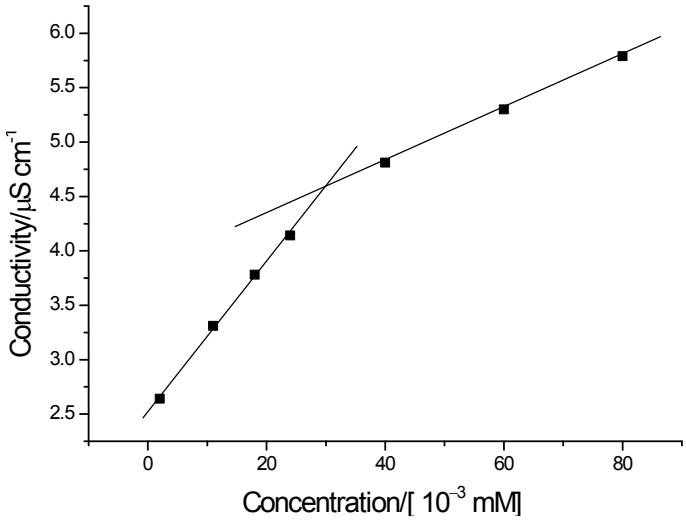


Fig. S11 The concentration-dependent conductivity of *trans*-**AZO**. The critical aggregation concentration (CAC) was determined to be 3.00×10^{-5} M.

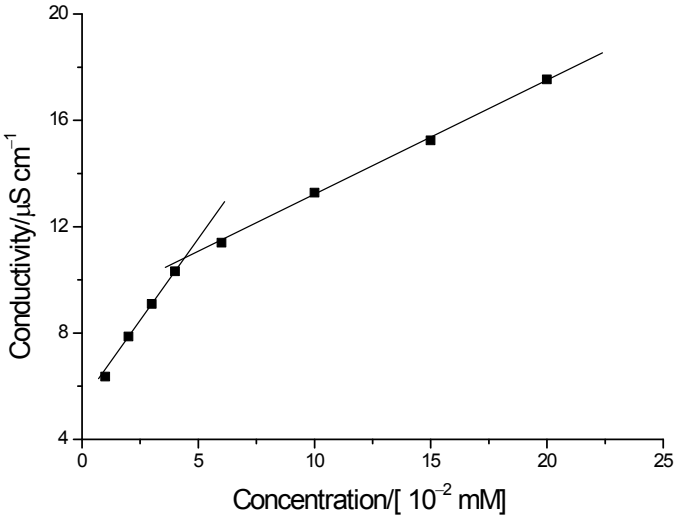


Fig. S12 The concentration-dependent conductivity of **CP6**⊃*trans*-**AZO**. The aqueous solutions used here are equivmolar solutions of **CP6** and *trans*-**AZO** in water. The critical aggregation concentration (CAC) was determined to be 4.36×10^{-5} M.

7. Reference:

S1. H. Ma, J. Fei, Q. Li and J. Li, *Small*, 2015, **11**, 1787-1791.