Construction of pillar[6]arene-based CO$_2$ and UV dual-responsive supra-amphiphile and application in controlled self-assembly

Jie Yang,* Li Shao and Guocan Yu*

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China;
Email: jieyang@zju.edu.cn; guocanyu@zju.edu.cn

Electronic Supplementary Information (11 pages)

1. Materials and methods
2. Synthesis of compounds DEAP$_6$ and trans-AZO
3. Photo-isomerization of trans-TY-I
4. 2D NOESY spectrum of CP$_6$→trans-TY
5. Isothermal titration calorimetry (ITC) experiment
6. Critical aggregation concentration (CAC) determination of trans-AZO and CP$_6$→trans-AZO
7. References
1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compound \textit{trans-TY-1} 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 \textbf{DEAP6} and \textbf{trans-AZO}

\textbf{Scheme S1.} Synthetic route to \textbf{DEAP6} and \textbf{trans-AZO}.

Synthesis of \textbf{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 \textit{vacuo} to give \textbf{DEAP6} as a dense oil (3.14 g, 98%). The $^1$H NMR spectrum of \textbf{DEAP6} is shown in Fig. S1. $^1$H NMR (400 MHz, CDCl$_3$-d, 293 K) $\delta$ (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 \textbf{DEAP6} is shown in Fig. S2. $^{13}$C NMR (100 MHz, CDCl$_3$-d, 293 K) $\delta$ (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$_2$CO$_3$ (41.4 g, 300 mmol) were added to a solution of trans-Tropaeolin Y (18.0 g, 60.0 mmol) in CH$_3$CN (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$_3$CN. 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 1H NMR spectrum of trans-AZO is shown in Fig. S4. 1H 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 13C NMR spectrum of trans-AZO is shown in Fig. S5. 13C 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$_4$N$_2$S, 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-\textbf{TY-1}

\textbf{Fig. S7} $^1$H NMR spectra (400 MHz, D$_2$O, room temperature): (a) \textit{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 \( \rightarrow \) 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\(_2\)O, 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\(_2\)O, room temperature).
5. *Isothermal titration calorimetry (ITC) experiment*

![Graph showing microcalorimetric titration of trans-TY with CP6 in water at 298.15 K.](image)

**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 ($\Delta H^\circ < 0$; $T\Delta S^\circ < 0$; $|\Delta H^\circ| > |T\Delta S^\circ|$), indicating that this complexation was primarily driven by the enthalpy changes.
6. Critical aggregation concentration (CAC) determinations of trans-AZO and CP6$\rightarrow$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$\rightarrow$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$\rightarrow$trans-AZO.

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

Fig. S12 The concentration-dependent conductivity of CP6$\rightarrow$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 $4.36 \times 10^{-5}$ M.
7. Reference:

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