Construction of a photo-responsive supra-amphiphile based on a tetracationic cyclobis(paraquat-\textit{p}-phenylene) and an azobenzene-containing guest in water †

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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compound CBPQT$^{4+}\cdot4\text{Cl}^-$, H, M and G were synthesized according to literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Avance DMX 400 spectrophotometer. The 2D NOESY NMR spectrum was recorded on a Bruker Avance DMX 400 spectrophotometer with TMS as the internal reference. UV-vis spectroscopy was performed on a Shimadzu UV-2550 instrument at room temperature. Dynamic light scattering measurements were performed on a Nano-ZS ZEN3600 instrument.
2. 2D COSY NMR and HMBC spectra of $H\leftrightarrow$trans-M, cis-M and $H\leftrightarrow$cis-M.

**Fig. S1** Partial 2D $^1$H-$^1$H COSY spectrum (400 MHz, D$_2$O, 298 K) of $H\leftrightarrow$trans-M.

**Fig. S2** Partial HMBC spectrum (400 MHz, D$_2$O, 298 K) of $H\leftrightarrow$trans-M.
**Fig. S3** Partial 2D $^1$H-$^1$H COSY spectrum (400 MHz, D$_2$O, 298 K) of cis-M.

**Fig. S4** Partial HMBC spectrum (400 MHz, D$_2$O, 298 K) of cis-M.
Fig. S5 Partial 2D $^1$H-$^1$H COSY spectrum (400 MHz, D$_2$O, 298 K) of H$\rightarrow$cis-M.

3. 2D NOESY NMR spectrum of H$\rightarrow$cis-M

Fig. S6. Partial NOESY NMR spectrum (500 MHz, D$_2$O, room temperature) of H$\rightarrow$cis-M (10.0 mM).
4. Stoichiometry determination for the complexation between H and M

**Fig. S7** Mole ratio plot for the complexation between H and *trans*-G, indicating a 1:1 binding stoichiometry.
5. ITC investigations of host–guest complexation between H and trans-M (or cis-M)

Fig. S8. Microcalorimetric titration of trans-M (2.00 mM, 10 µL per injection) with H (0.100 mM) in water at 298.15 K.
Fig. S9. Microcalorimetric titration of cis-M (2.00 mM, 10 µL per injection) with H (0.100 mM) in water at 298.15 K.
Table S1. Association constants \((K_a)\), enthalpy changes \((\Delta H^o)\) and entropy changes \((\Delta S^o)\) obtained from ITC experiments for the 1:1 complexes of \(H\) with trans-M and cis-M.³

<table>
<thead>
<tr>
<th></th>
<th>(K_a) (M(^{-1}))</th>
<th>(\Delta H) (J/mol)</th>
<th>(\Delta S) (J/mol/deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-M</td>
<td>((1.07 \pm 0.14)E6)</td>
<td>(-(1.28 \pm 0.17)E4)</td>
<td>73.1</td>
</tr>
<tr>
<td>cis-M</td>
<td>((2.51 \pm 0.25)E5)</td>
<td>(-(1.56 \pm 0.23)E4)</td>
<td>51.3</td>
</tr>
</tbody>
</table>

* Microcalorimetric titration experiments were conducted in water at 298.15 K.

6. Critical aggregation concentration (CAC) determinations of \(H\rightleftharpoons\text{trans-G}\)

![Graph](image)

*Fig. S10* The concentration-dependent conductivity of \(H\rightleftharpoons\text{trans-G}\) \((H/\text{trans-G} = 1:4, \text{molar ratio})\). The critical aggregation concentration (CAC) was determined to be \(2.62 \times 10^{-6}\) M (based on the concentration of G).
7. Dynamic light scattering (DLS) results of $G$ and $H \rightarrow \text{cis-} G$

*Fig. S11* DLS result of $\text{trans-} G$ (5.00 $\times$ 10$^{-5}$ M). The average diameter of the nanoparticles was determined to be 65 nm.

*Fig. S12* DLS result of $H \rightarrow \text{cis-} G$. The average diameter of the nanoparticles was determined to be 161 nm.

8. Atomic Force Microscope (AFM) image of nanosheets formed by $H \rightarrow \text{trans-} G$

*Fig. S13* Atomic Force Microscope (AFM) image of nanosheets formed by $H \rightarrow \text{trans-} G$. The thickness was measured to be 3.0 nm.
9. Calculation of the transformation rate.

*Fig. S14* $^1$H NMR of *trans-M* after irradiation at 365 nm for 10 min.

The transformation rate ($T$) was calculated by the integral ($I$): $T = I_{	ext{cis}}/(I_{	ext{cis}} + I_{	ext{trans}}) = 1/(0.21 + 1) = 83\%$.

*Fig. S15* $^1$H NMR of *trans-M* after irradiation at 365 nm for 10 min and further irradiation at 435 nm for 1 h.
The transformation rate \( (T) \) was calculated by the integral \( (I) \): 
\[
T = \frac{I_{\text{trans}}}{I_{\text{cis}} + I_{\text{trans}}} = \frac{1}{0.12 + 1} = 89\%.
\]

10. *The measurement of the best molar ratio between \( H \) and \( G \).*

![Graph showing DLS count rates of \( H \) and \( G \) at different charge ratios. The concentration of \( H \) is fixed at \( 1.25 \times 10^{-5} \) M.](Fig.S16)
11. The NMR and MS spectra for G and M guests.

**Fig. S17** The $^1$H NMR spectrum (500 MHz, D$_2$O, room temperature) of M.

**Fig. S18** The $^{13}$C NMR spectrum (125 MHz, D$_2$O, room temperature) of M.
**Fig. S19** Electrospray ionization mass spectrum of M. Assignment of main peaks: $m/z$ 305.4 [M – Na]^{-}.

**Fig. S20** The $^1$H NMR spectrum (400 MHz, DMSO-$d_6$, room temperature) of G.
**Fig. S21** The $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$, room temperature) of G.

**Fig. S22** Electrospray ionization mass spectrum of G. Assignment of main peaks: $m/z$ 417.5 [M – Na]$^-$. 

12. **References:**
