Construction of a photo-responsive supra-amphiphile based on a tetracationic cyclobis(paraquat-*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+.}4Cl⁻ **H**, **M** and **G** were synthesized according to literature procedures.^{S1,S2} Solvents were either employed as purchased or dried according to procedures described in the literature. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance DMX 400 spectrophotomete. 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.



Fig. S1 Partial 2D ¹H-¹H COSY spectrum (400 MHz, D₂O, 298 K) of H \rightarrow trans-M.



Fig. S2 Partial HMBC spectrum (400 MHz, D₂O, 298 K) of *H* ¬*trans-M*.



Fig. S3 Partial 2D ¹H-¹H COSY spectrum (400 MHz, D₂O, 298 K) of *cis*-M.



Fig. S4 Partial HMBC spectrum (400 MHz, D₂O, 298 K) of cis-M.







Fig. S6. Partial NOESY NMR spectrum (500 MHz, D_2O , room temperature) of $H \supset cis$ -M (10.0 mM).





Fig. S7 Mole ratio plot for the complexation between **H** and *trans*-**G**, indicating a 1:1 binding stoichiometry.



Fig. S8. Microcalorimetric titration of *trans-M* (2.00 mM, 10 μ L per injection) with **H** (0.100 mM) in water at 298.15 K.



Fig. S9. Microcalorimetric titration of *cis*-M (2.00 mM, 10 μ L per injection) with H (0.100 mM) in water at 298.15 K.

Table S1. Association constants (K_a), enthalpy changes (ΔH°) and entropy changes (ΔS°) obtained from ITC experiments for the 1:1 complexes of **H** with *trans*-**M** and *cis*-**M**.^a

	K_a (M ⁻¹)	ΔH (J/mol)	ΔS (J/mol/deg)
trans-M	(1.07 ± 0.14)E6	-(1.28 ± 0.17)E4	73.1
cis-M	(2.51 ± 0.25) E5	$-(1.56 \pm 0.23)$ E4	51.3

^a Microcalorimetric titration experiments were conducted in water at 298.15 K.

6. Critical aggregation concentration (CAC) determinations of $H \supset$ trans-G



Fig. S10 The concentration-dependent conductivity of $H \supset trans-G$ (H/trans-G = 1:4, molar ratio). The critical aggregation concentration (CAC) was determined to be 2.62×10^{-6} M (based on the concentration of G).





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

Fig. S12 DLS result of $H \supset cis$ -G. The average diameter of the nanoparticles was determined to be 161 nm.

8. Atomic Force Microscope (AFM) image of nanosheets formed by $H \supset$ trans-G



Fig. S13 Atomic Force Microscope (AFM) image of nanosheets formed by H⊃*trans*-G. The thickness was measured to be 3.0 nm.

9. Calculation of the transformation rate.



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



Fig. S15 ¹H 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*) : $T = I_{\text{trans}}/(I_{\text{cis}} + I_{\text{trans}}) = 1/(0.12 + 1) = 89\%$.



10. The measurement of the best molar ratio between H and G.

Fig. S16 DLS count rates of **H** and **G** at different charge ratios. The concentration of **H** was fixed at 1.25×10^{-5} M.

11. The NMR and MS spectra for **G** and **M** guests.





Fig. S19 Electrospray ionization mass spectrum of M. Assignment of main peaks: m/z 305.4

[M – Na]-



Fig. S20 The ¹H 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:

- S1. B. Odell, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *Angew. Chem. Int. Ed.*, 1988, 27, 1547–1550.
- S2. J. Yang, L. Shao and G. Yu, Chem. Commun., 2016, 52, 3211–3214.