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## COMMUNICATION

# Construction of a photo-responsive supra-amphiphile based on a tetracationic cyclobis(paraquat-*p*-phenylene) and an azobenzene-containing guest in water<sup>†</sup>

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A photo-responsive host-guest molecular recognition between a tetracation cyclophane cyclobis(paraquat-*p*-phenylene) host and an azobenzene-containing guest was constructed. <sup>10</sup> Based on this novel recognition, a supra-amphiphile was constructed and the photo-responsive self-assembly behaviors were investigated.

Stimuli-responsive host-guest systems have drawn much attention over the years due to their practical applications in the <sup>15</sup> fabrication of various functional materials, such as drug delivery systems,<sup>1</sup> smart supramolecular polymers,<sup>2</sup> memory storage<sup>3</sup> and other fantastic nanodevices.<sup>4</sup> Different external-stimuli such as pH-changes, temperature-changes, magnetic field, enzymes, redox and light have been adopted in these systems.<sup>5</sup> Among <sup>20</sup> them, light is especially important on account of its easy operation, few by-products, remarkable sensitivity and low cost.<sup>6</sup> Molecules that have unique light responsiveness have been

and relevant functions of different supramolecular systems by <sup>25</sup> scientific community. Azobenzene is a widely used chromophore for the preparation of photo-responsive self-assembly systems since it can undergo *trans-cis* photoisomerization in response to UV and visible light irradiation.

utilized as switching units to control the microscopic structures

Supra-amphiphiles, which can be designed to construct <sup>30</sup> supramolecular materials with interesting stimuli-responsive properties,<sup>7</sup> refer to amphiphiles whose hydrophilic and hydrophobic groups are connected by non-convalent bonds or dynamic covalent bonds,<sup>8</sup> such as hydrogen bonding, electrostatic attractions, host–guest recognitions, charge transfer interactions,

- <sup>35</sup> metal coordinations and so on. Among them, the supraamphiphiles fabricated from host-guest recognitions hold great potential because of the variability and flexibility of starting materials and the availability of synthetic methods. Host-guest recognition motifs based on macrocycle molecules, including
- <sup>40</sup> crown ethers, cyclodextrins, cucurbit[*n*]urils, calix[*n*]arenes and pillar[*n*]arenes, have been elaborately employed for the fabrication of supra-amphiphiles, which can be further applied in controlled release and drug delivery.<sup>9</sup> Thus, it is necessary to

develop novel host-guest recogition motifs to construct photo-<sup>45</sup> responsive supra-amphiphile systems with tunable functions.



Scheme 1 Chemical structures of H, G and M, and cartoon representation of the photo-responsive self-assembly.

Tetracation cyclophane cyclobis(paraquat-*p*-phenylene) <sub>50</sub> (CBPQT<sup>4+</sup>), which incorporates two π-electron-deficient paraquats connected by two *para*-phenylene groups, was first reported by Stoddart and coworkers in the late 1980s.<sup>10</sup> CBPQT<sup>4+</sup> has been extensively utilized to build various interlocked assemblies in supramolecular chemistry. However, CBPQT<sup>4+</sup>ss based supra-amphiphiles have been rarely reported.<sup>11</sup> Herein, we reported a photo-responsive supra-amphiphile based on a CBPQT<sup>4+</sup>·4Cl<sup>-</sup> host (**H**) and an azobenzene-containing guest (**G**). The complexation models between **H** and **G** can be regulated upon irradiation with UV and visible light owing to the *trans-cis* <sup>5</sup> photoisomerization of **G**. Furthermore, the photo-responsive self-assembly behaviors of the supra-amphiphile in aqueous solution were also investigated (Scheme 1).



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Fig. 1 Partial <sup>1</sup>H NMR spectra (500 MHz, D<sub>2</sub>O, room temperature): (a)
In H (2.00 mM); (b) H (2.00 mM) and *trans*-M (2.00 mM); (c) *trans*-M (2.00 mM); (d) *trans*-M (2.00 mM) after irradiation at 365 nm for 10 min; (e) H (2.00 mM) and *trans*-M (2.00 mM) after irradiation at 365 nm for 1 h; (f) Partial NOESY NMR spectrum (500 MHz, D<sub>2</sub>O, room temperature) of H (10.0 mM) and *trans*-M (10.0 mM).

In order to study the host-guest interactions between H and G, a model compound M with a shorter alkyl chain was employed because of the poor water solubility of G. The host-guest complexation between H and M was firstly investigated by <sup>1</sup>H NMR spectroscopy. The signals from H, <sup>20</sup> *trans*-M and *cis*-M were identified clearly through the 2D <sup>1</sup>H- <sup>1</sup>H COSY NMR and HMBC spectra in D<sub>2</sub>O (Fig. S1–S5, ESI<sup>†</sup>). The chemical shift changes of signals related to the protons on H⊃*trans*-M were monitored, in comparison with the <sup>1</sup>H NMR spectra of free H and free *trans*-M (Fig. 1a and <sup>25</sup> 1c). The signals related to protons H<sub>a</sub>, H<sub>b</sub>, H<sub>c</sub> and H<sub>d</sub> of M shifted upfield significantly (Δδ = -1.55, -2.74, -0.95 and -0.38 ppm, respectively), which was ascribed to the electrostatic interactions and charge transfer interactions

between M and H.<sup>12</sup> Moreover, the peaks corresponding to the

<sup>30</sup> protons on **H** also exhibited slight chemical shift changes and broadening effect, owing to the interactions between **H** and **M** (Fig. 1b).<sup>13</sup> It was speculated that the azobenzene part of **M** located in the cavity of **H** upon forming a threaded structure between **H** and **M**.

After irradiation with UV light at 365 nm (8 W medium-35 pressure Hg lamp using a UV filter) for 10 min, trans-M transformed to cis-M with a transformation ratio about 83% (Fig. S14). As shown in Fig. 1e, the signals related to the protons H<sub>a\*</sub> and H<sub>b\*</sub> on *cis*-M exhibited obvious upfield 40 chemical shift changes ( $\Delta \delta = -2.64$  and -2.03 ppm, respectively), while the signals related to protons  $H_{c*}$  and  $H_{d*}$ on *cis*-M shifted downfield slightly ( $\Delta \delta = 0.61$  and 0.07 ppm, respectively). These phenomena indicated that the photo-induced E/Z isomerization of azobenzene group of **M** occurred upon 45 UV irradiation, resulting in the change of the complexation model. The benzene ring bearing a sodium sulfonate group was still inside the cavity of H due to the electrostatic interactions while the rest of *cis*-M was outside the cavity of H because of the high steric hindrance, as illustrated by a 50 cartoon representation in Fig. 1e.

2D NOESY NMR experiment was conducted to study the relative positions of the components in the host-guest inclusion complex. Before UV irradiation (Fig. 1f), NOE correlation signals were observed between protons H<sub>1,2,3</sub> on **H** <sup>55</sup> and H<sub>a,b,c,d</sub> on **M**, which confirmed that the azobenzene group threaded deeply into the cavity of **H**, resulting in the formation of a [2]pseudorotaxane-type structure. After UV irradiation (Fig. S6), NOE correlation signals were also observed between protons H<sub>1,2,3</sub> on **H** and H<sub>a\*,b\*,c\*,d\*</sub> on *cis*-**M**, <sup>60</sup> which verified the hypothesis that part of the azobenzene group still resided in the cavity of **H**, resulting in the formation of a clip-like structure.

Isothermal titration calorimetry (ITC) is a useful tool to investigate the inclusion complexation, which not only 65 provides the association constant  $(K_a)$  but also yields their thermodynamic parameters (enthalpy  $\Delta H^{\circ}$  and entropy changes  $\Delta S^{\circ}$ ).<sup>14</sup> From Table S1, the association constant ( $K_a$ ) of H $\supset$ trans-M was calculated to be (1.07 ± 0.14) × 10<sup>6</sup> M<sup>-1</sup> (Fig. S8, ESI<sup>†</sup>) with a 1:1 stoichiometry complexation, which 70 was in accordance with the mole ratio plot (Fig. S7, ESI<sup>†</sup>). The association constant between H and cis-M was measured to be  $(2.51 \pm 0.25) \times 10^5 \text{ M}^{-1}$  (Fig. S9, ESI<sup>†</sup>), which was much lower than that of H trans-M arising from the inefficient complexation. The decrease of binding ability 75 might attribute to the steric hindrance between **H** and *cis*-M. Notably, the thermodynamic data listed in Table S1 have the same feature ( $\Delta H < 0$ ; T $\Delta S > 0$ ), indicating that these complexations are all driven by enthalpy and entropy changes.

UV-vis absorption spectroscopy was further employed to <sup>80</sup> investigated the photo-responsive properties of **M** and **H** $\supset$ **M**. As shown in Fig. 2a, upon irradiation with UV light at 365 nm for 10 min, the absorption band decreased remarkably at around 350 nm, meanwhile the absorption band around 440 nm increased slightly. The absorption changes at 350 nm and <sup>85</sup> 440 nm were ascribed to  $\pi$ - $\pi$ \* and n- $\pi$ \* transitions of azobenzene, respectively, confirming the photoisomerization of **M** from *trans*- to *cis*-form.<sup>15</sup> Additionally, the



Fig. 2 (a) UV-vis spectra of H ( $5.00 \times 10^{-5}$  M), *trans*-M ( $5.00 \times 10^{-5}$ 5 M) (initial and after irradiation with UV light at 365 nm for 10 min) and an equimolar solution of  $5.00 \times 10^{-5}$  M H $\supset$ trans-M (initial and after irradiation with UV light at 365 nm for 10 min). (b) Changes of the absorbance at 368 nm of an equimolar solution of H \(\to trans-M\)  $(5.00 \times 10^{-6} \text{ M})$  upon alternating irradiation with UV and visible 10 light for 10 min.

With the host-guest recognition motif in hand, the corresponding photo-responsive supra-amphiphile system was constructed by using G as a guest. The critical aggregation concentration (CAC) of **G** was determined to be  $3.00 \times 10^{-5}$  M 15 by using the concentration-dependent conductivity.<sup>16</sup> The selfassembly morphology of G in water was then investigated by transmission electron microscopy (TEM). As shown in Fig. 3a, the amphiphilic G self-assembled in water to form nanoparticles with an average diameter about 60 nm. The best molar ratio <sup>20</sup> between **H** and **G** was measured to be 1:4 (charge ratio = 1:1) by DLS, As shown in Fig. S16, the count rate of the sample increased gradually as the charge ratio changed from 2:1 to 1:1, indicating the effective formation of nanoaggregates. Further addition of anionic G resulted in the decrease of the count rate as 25 the neutral state of the self-assemblies changed into the hydrophilic negatively charged state, thus resulting in disturbing the self-assembly of  $H \supset G$ .<sup>17</sup> At this fraction, the critical aggregation concentration of **G** decreased to be  $2.62 \times 10^{-6}$  M in the presence of H (Fig. S10, ESI<sup>+</sup>), which was attributed to the  $_{\rm 30}$  stable host–guest complexation between H and G.  $^{\rm 7d}$  Moreover, the nanoparticles formed from G disappeared and nanosheets were observed upon addition of H (Fig. 3b and 3c). Notably, after UV irradiation at 365 nm for 10 min, the self-assembly morphology of  $H \supset G$  changed into nanoparticles with an average 35 diameter about 160 nm (Fig. 3d and 3e). Additionally, the nanoparticles transformed to nanosheets again after visible light

- irradiation at 435 nm for 1 h (Fig. 3f), showing reversibility of this photo-responsive self-assembly. Dynamic light scattering (DLS) experiments were conducted to determine the size of the 40 nanoparticles (Fig. S11 and S12, ESI<sup>+</sup>). The average diameters of the self-assembled G and H > trans-G after irradiation at 365 nm
- for 1 h were measured to be 65 and 161 nm, respectively, in good accordance with the TEM images. Based on visible morphology changes of the photo-
- 45 responsive self-assemblies, we wish to propose a reliable mechanism to explain it. Herein, the packi defined by Israelachvili and co-workers,18a sh explain the relationship between the structure of amphiphile molecule and the surface curvature and thus the aggregate 50 morphology.

$$p = V/a_0 l_c \tag{1}$$

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$$(p)$$
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Fig. 3 TEM images: (a) the aggregates of G ( $5.00 \times 10^{-5}$  M), (b) the aggregates of **H** (1.25 ×  $10^{-5}$  M) and *trans*-G (5.00 ×  $10^{-5}$  M), (c) 55 enlarged image of (b), (d) after irradiation with UV light at 365 nm for 10 min of (b), (e) enlarged image of (d), (f) after irradiation with visible light at 435 nm for 1 h of (d).

As depicted in eq. (1), V and  $l_c$  are the volume and the length 60 of the hydrophobic chain and  $a_0$  is the cross-sectional surface area of the headgroup. The connection between p and the aggregate shape is that the amphiphiles with a large p value will aggregate into a structure with small surface curvature.<sup>18b</sup> Specifically, as shown in TEM image, trans-G self-assembled into nanoparticles 65 with high curvature, while the complex H - trans-G selfassembled to form nanosheets with low curvature. The phenomenon indicated that the p value of *trans*-G was smaller than that of H ] trans-G. From the perspective of the chemical structure of amphiphilic molecule, the  $V/l_c$  values of H $\supset$ trans-G 70 and *trans-G* are equal because H trans-G has the same hydrophobic part as that of *trans-G*. However, after the hostguest complexation formed: i) the electron repulsion increased; ii) the steric hindrance increased, both resulting in the increase of  $a_0$ value and the decrease of p value of  $H \supset trans-G$ ,<sup>18d</sup> which is 75 contradictory to the TEM images. To solve this problem, a bilayered packing model of H trans-G with antiparallel packing and overlapped alkyl chain was put forward (Scheme 2b).<sup>18c</sup> This packing model has a V value about twice larger than that of trans-**G** (Scheme 2a), causing the increasing of p value, which favors 80 morphological transformation from nanoparticles with high curvature to nanosheets with low-curvature. In addition, atomic force microscope (AFM) experiment was conducted to support the packing model (Fig. S13). The thickness of the nanosheets was measured to be about 3.0 nm by AFM, in accordance with <sup>85</sup> the length of two **H**⊃*trans*-G complexes with antiparallel packing, where the alkyl chains were overlapped. After UV irradiation, the nanosheets transformed into nanoparticles with larger diameter as revealed by TEM images, indicating that the p value decreased. We speculate that the bilayer structure was 90 destroyed, and the newly formed packing model was similar to that of trans-G (Scheme 2c). Compared with trans-G, the volume of the hydrophobic part (V) increases, accompanied with the decreasing of the length  $(l_c)$ , thereby the p value of **H** $\supset$ *cis*-**G** larger than that of *trans-G*, leading to the formation of larger oparticles with low curvature.



Scheme 2 The packing model: (a) trans-G; (b) H trans-G; (c) H cis-G.

In conclusion, a photo-responsive host-guest system based <sup>5</sup> on a water-soluble tetracation cyclophane cyclobis(paraquat-*p*phenylene) host and a sulfonated azobenzene guest was investigated. Before UV irradiation, *trans*-G threaded into the cavity of **H**. After UV irradiation, *trans*-G transformed to *cis*state, upon forming a clip-like host-guest complex with **H**. <sup>10</sup> Furthermore, a photo-responsive supra-amphiphile was fabricated based on this recognition motif. The self-assembled morphology of **H**⊃G could be transformed from nanosheets to nanoparticles reversibly by UV/vis irradiation. This photo-responsive supraamphiphilie has potential applications in various fields such as <sup>15</sup> controlled release, drug delivery and sensors.

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#### Notes and references

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<sup>†</sup>Electronic Supplementary Information (ESI) available: 2D <sup>1</sup>H–<sup>1</sup>H COSY NMR and HMBC spectra,Mole ratio plot, 2D NOESY spectra, ITC and other materials. See DOI: 10.1039/c0xx00000x.

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