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A pillar[6]arene-based UV-responsive supra-amphiphile: synthesis, self-assembly, and application in dispersion of multiwalled carbon nanotubes in water[†]

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A UV-responsive supra-amphiphile based on a water-soluble pillar[6]arene was constructed. Its self-assembly and application in dispersion of multi-walled carbon nanotubes in water were studied.

Supra-amphiphiles, a class of captivating supramolecules, carry both hydrophilic and hydrophobic parts and can self-assemble in an aqueous phase or an oil phase to form well-defined nanostructures depending on the repelling and coordinating forces generated from the interactions of the amphiphiles and surrounding medium.¹ In order to get controllable supramolecular architectures from self-assembly of supra-amphiphiles for applications in controlled release, gene delivery, and electro-optic materials, the introduction of stimuli-responsive functional groups into these building blocks is indispensable. Multitudinous external stimuli such as temperature, pH, redox, and enzyme have been utilized in the construction of supra-amphiphiles.² Among them, photo-stimulus is especially attractive on account of its easy operation, non-invasiveness, low cost, sensitivity, and excellent penetration depth.³

Host-guest chemistry has attracted considerable attention over the past decades because of the topological importance and application of host-guest structures in the fabrication of artificial molecular machines, supramolecular polymers, supramolecular gels and other functional supramolecular systems.⁴ As a new kind of macrocyclic hosts, pillar[*n*]arenes have been investigated by more and more chemists due to their symmetrical pillar architecture, facile and high-yield syntheses, and accessible derivatizations.⁵ The host-guest chemistry of pillararenes has been employed in the fabrication of supra-amphiphiles.⁶ However, its application in the preparation of photo-responsive supra-amphiphiles has been rarely investigated.^{6d} Herein, a UV-responsive supra-amphiphile based on host-guest interactions between a water-soluble pillar-[6]arene (**WP6**) containing carboxylate anionic groups on both rims and a UV-responsive guest (G) bearing the 2-nitrobenzyl ester moiety (Scheme S1, ESI⁺) was constructed (Fig. 1). Furthermore, its UV-responsive self-assembly in water and application in dispersion of multi-walled carbon nanotubes (MWNTs) in water were studied.

Firstly, UV irradiation was conducted to investigate the photocleavage properties of the 2-nitrobenzyl ester moiety of



Fig. 1 Chemical structures of compounds used here and schematic representation of UV-responsive self-assembly in water studied here.

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Fig. 2 UV-vis spectra of G (1.00 \times 10 $^{-5}$ M) before and after irradiation with UV light (365 nm) for 30 min.

the guest molecule. It is well known that the cleavage of 2-nitrobenzyl ester leads to the formation of 2-nitrobenzaldehyde which weakly absorbs at 360 nm and can be detected using absorption spectroscopy.^{7a} So the aqueous solution of **G** was subjected to irradiation with UV light (365 nm) for about 30 min, as shown in UV-vis spectra; UV absorbance at ~360 nm increased clearly, accompanied by the decrease of the absorbances at 320 nm and 345 nm (Fig. 2), demonstrating the photo-stimulated cleavage of the 2-nitrobenzyl ester moiety and the generation of a 2-nitrobenzaldehyde derivative (Fig. 1).^{7b}

The solubility of **G** in water is very poor. In order to study the interactions between **G** and **WP6**, we designed a model compound **DMPy** (Scheme S2, ESI[†]) and studied its complexation with **WP6**. The host–guest complexation between **WP6** and **DMPy** was first studied by ¹H NMR spectroscopy. As shown in Fig. S17 (ESI[†]), when an equimolar amount of **WP6** was added into a solution of **DMPy** (1.00 mM), the signals related to the protons on **DMPy** significantly shifted upfield. Additionally, extensive broadening effects occurred when **DMPy** interacted with **WP6** due to complexation dynamics.^{6*a*} The reason is that these protons were located within the cavity of **WP6** and shielded by the electron-rich cyclic structure by forming a threaded structure between **DMPy** and **WP6**.^{5*p*}

For estimation of the binding constant, fluorescence titrations of **WP6** with **DMPy** were conducted. As shown in Fig. S13 (ESI[†]), the quenching of fluorescence was observed upon gradual addition of **DMPy**. A mole ratio plot based on the fluorescence titration experiments demonstrated that the complex between **WP6** and **DMPy** has a 1:1 stoichiometry (Fig. S14, ESI[†]) and the association constant (K_a) was calculated to be (1.24 ± 0.07) × 10^5 M⁻¹ in water by using a non-linear curve-fitting method (Fig. S15, ESI[†]). Further evidence for the formation of the inclusion complex **WP6** \supset **DMPy** was obtained from UV-vis absorption spectroscopy. When **DMPy** and **WP6** were mixed in water in a 1:1 molar ratio, the spectrum exhibited a broad absorption above 400 nm, which corresponds to the characteristic absorption of the charge-transfer complex (Fig. S16, ESI[†]).

After the establishment of the recognition motif between **WP6** and **G** in water, we utilized it to construct a supra-amphiphile and investigated its UV-responsive self-assembly in water. By using the



Fig. 3 TEM images: (a) G_i (b) $WPG \supset G_i$ (c) intermediate state of $WPG \supset G_i$; (d) $WPG \supset G$ treated with UV light irradiation. Fluorescence microscopic images: (e) bright field, G_i (f) G_i (g) $WPG \supset G_i$ (h) $WPG \supset G$ treated with UV light irradiation. TEM images: (i) MWNTs; (j) MWNTs treated with $WPG \supset G_i$ (k) enlarged image of $WPG \supset G$ -MWNTs; (l) $WPG \supset G$ -MWNTs treated with UV light irradiation.

concentration-dependent conductivity, the critical aggregation concentration (CAC) of **G** was determined to be 1.1×10^{-7} M (Fig. S18, ESI†). As revealed using TEM, the typical amphiphilic **G** itself self-assembled in water to form two-dimensional nanosheets (Fig. 3a), which was confirmed by fluorescence microscopy (Fig. 3e and f).

In the presence of WP6, the critical aggregation concentration of **WP6**⊃**G** increased to 1.0×10^{-6} M (Fig. S19, ESI⁺). The enhancement of the CAC value was attributed to the stable host-guest complexation between WP6 and G. As shown in TEM images, the nanosheets of G disappeared and nanorods were observed instead upon addition of WP6, which was also proved by fluorescence microscopy images (Fig. 3b and g). The average diameter of the nanorods was about 500 nm. Interestingly, from the enlarged image of the nanorods, we found that the nanorods were full of cores, so we supposed that the nanorods were composed of nanospheres. Fortunately, we observed the intermediate state, which indicated the transition from nanospheres to nanorods (Fig. 3c). Therefore, a mechanism was proposed to explain the transformation from nanosheets to nanospheres and then to nanorods upon addition of WP6. Because of strong π - π stacking interactions between pyrene aromatic rings in water, 2D nanosheets were obtained for G alone. Upon complexation with WP6, the anionic hosts were introduced into the hydrophilic membrane of nanosheets and caused the increase of the membrane curvature due to the existence of steric hindrance and electrostatic repulsion generated by WP6,8 resulting in the disappearance of nanosheets and the formation of nanospheres. With the extended self-assembly, the cores of the nanospheres expanded and became exposed to water transiently. Consequently, the cores adhered to other nanospheres and formed nanorods driven by the high interactions between the exposed pyrene blocks to minimize the portion of the hydrophobic segment.9

Upon irradiation with UV light for about 30 min, the selfassembly of the building blocks experienced dramatic changes as indicated by the transition from nanorods to nanosheets

ChemComm

(Fig. 3d and h). Moreover, we also investigated the aggregation behavior of pyrene-1-butyric acid alone in water. As shown in the TEM images, the pyrene-1-butyric acid also self-assembled to form nanosheet structures through π - π stacking interactions (Fig. S20, ESI†). Therefore, we drew the conclusion that the change of the self-assembly of the building blocks was attributed to the generation of pyrene-1-butyric acid by photo-cleavage of **WP6** \supset **G** complexes.

Because strong π - π interactions can exist between MWNTs and pyrenyl rings in water,^{6b} we utilized this supra-amphiphile to disperse MWNTs in aqueous solution. Direct evidence for the **WP6** \supset **G**-MWNTs interactions was obtained using TEM. From TEM images of initiative MWNTs, large aggregates of nanotubes were observed (Fig. 3i). Upon addition of a solution of **WP6** \supset **G**, the hydrophobic pyrenyl ring part of **WP6** \supset **G** clung to the surface of the MWNTs through π - π interactions, while the hydrophilic **WP6** stuck out into the water. Therefore, well dispersed MWNTs could be distinguished (Fig. 3g and k). Furthermore, we could control the dispersion behavior of MWNTs by UV light irradiation. When the **WP6** \supset **G**-MWNTs complexes were subjected to UV irradiation for about 30 min, the aggregation of MWNTs was observed again (Fig. 31) for the sake of the photocleavage of the hydrophilic segment from the hybrids.

In conclusion, we have successfully constructed a UV-responsive supra-amphiphile based on the host–guest complexation between **WP6** and **G**. In contrast to the nanosheets formed by the amphiphilic molecule **G** alone, **WP6** \supset **G** self-assembled into nanorods. Upon irradiation with UV light, the transformation from nanorods to nanosheets was obtained. Furthermore, we applied this supramolecular system in the UV-responsive dispersion of MWNTs in water. This new kind of UV-responsive supra-amphiphile has numerous potential applications in many fields, including nanocontainers, nanoelectronics, sensors, drug-delivery and controlled release.

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