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A dual-responsive supra-amphiphile based on a water-soluble pillar[7]arene and a naphthalene diimide-containing guest†

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A dual-responsive supra-amphiphile was firstly constructed based on a water-soluble pillar[7]arene and a naphthalene diimide-containing guest with a long alkyl chain and a trimethylammonium group. The morphologies of the self-assembly formed from this supra-amphiphile could be adjusted by changing solution pH or adding α-cyclodextrin.

The emergence of any new macrocycles can promote the development of supramolecular chemistry.[1] Different kinds of macrocycles, such as crown ethers,[2] cyclodextrins,[3] calixarenes[4] and cucurbiturils,[5] have played an indispensable part in host–guest chemistry over the past few decades. Pillar[*n*]arenes,[6] which are made up of hydroquinone units linked by methylene bridges at their opposite positions, have a perfectly symmetric structure, providing a promising platform for the construction of diverse supramolecular systems.[7] The corresponding studies of pillar[5]arenes[8] and pillar[6]arenes[9] have been elaborately investigated. Due to the differences in cavity sizes, pillar[*n*]arenes possessing different repeating units exhibit size-selective host–guest complexations.[10] For example, pillar[5]arenes can complex with relatively small molecules, like alkyl chains, dialkylammonium salts and benzene rings, while pillar[6]arenes can complex with relatively larger guests, such as 1,4-diazabicyclo[2.2.2]octane, adamantanylammonium, and azobenzene-containing cations.[6d,9b] The search for guests for pillar[*n*]arenes ($n > 6$) with larger cavity sizes is of particular interest and importance not only in fundamental research but also in practical applications of pillar[*n*]arenes-based supramolecular systems, because only a limited amount of endeavour has been devoted so far.

Supra-amphiphiles refer to amphiphiles based on non-covalent interactions or dynamic covalent bonds which can self-assemble into well-defined nanostructured soft materials.[11] The reversible and dynamic nature of non-covalent interactions endows supra-amphiphiles with interesting stimuli-responsive properties, which can be applied in various fields, ranging from drug delivery systems, memory storage, supramolecular polymers to functional nanodevices.[12] Stimuli-responsive supra-amphiphiles based on pillar[5]arenes and pillar[6]arenes have been widely explored. However, most of them are responsive to single stimulus. Herein, we firstly reported a dual-responsive supra-amphiphile based on a water-soluble pillar[7]arene (**WP7**) and a NDI-containing guest (**G**). Size-selective complexation was achieved between **WP7** and **G**, because the size of NDI was suitable for the cavity of pillar[7]arenes rather than pillar[5]arenes and pillar[6]arenes (Scheme S3, ESI†). Moreover, this supra-amphiphile **WP7**$\supset$**G** exhibited dual-responsiveness. The morphologies of the self-assembly formed from this supra-amphiphile could be adjusted by changing solution pH or adding α-cyclodextrin (Scheme 1).

In order to study the host–guest interactions between **WP7** 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 **WP7** and **M** was first studied by ^{1}H NMR spectroscopy. As shown in Fig. 1b, after the addition of 1 equimolar **WP7**, chemical shift changes of signals related to some protons on **M** appeared. The signals related to protons H_d, H_h and H_e of **M** shifted upfield ($\Delta\delta = -1.13$, -0.66 and -0.33 ppm, respectively) and exhibited a broadening effect. On the other hand, the resonance peaks related to H_f and H_g disappeared after complexation.[13] The reason was that these protons were located in the cavity of **WP7** and shielded by the electron-rich cyclic structure upon forming a threaded structure between **M** and **WP7**.[6c] Moreover, the peaks corresponding to the protons on **WP7** also exhibited slight chemical shift changes owing to the interactions between **WP7** and **M** (Fig. 1b). The peak related to H_1 shifted downfield slightly, and the peaks of H_2 and H_3 shifted upfield ($\Delta\delta = -0.16$ and -0.14 ppm, respectively).

In order to further study the chemical shift changes of the protons corresponding to the model compound, excess **M** (3 equiv.) was added. A broadening effect could also be observed, and the signals related to the protons of **M** appeared clearly (Fig. S21, ESI†). Due to the host–guest interactions between **WP7** and **M**, chemical shift changes were observed

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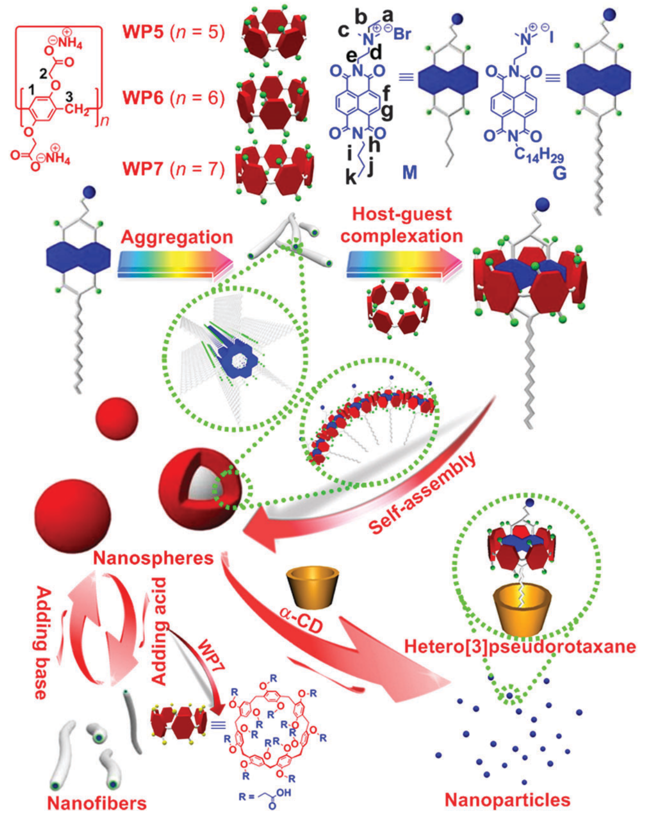

Scheme 1 Structures of chemicals (**WP5**, **WP6**, **WP7**, **G** and **M**) used here and cartoon representation of the dual-responsive self-assembly between **WP7** and **G**.

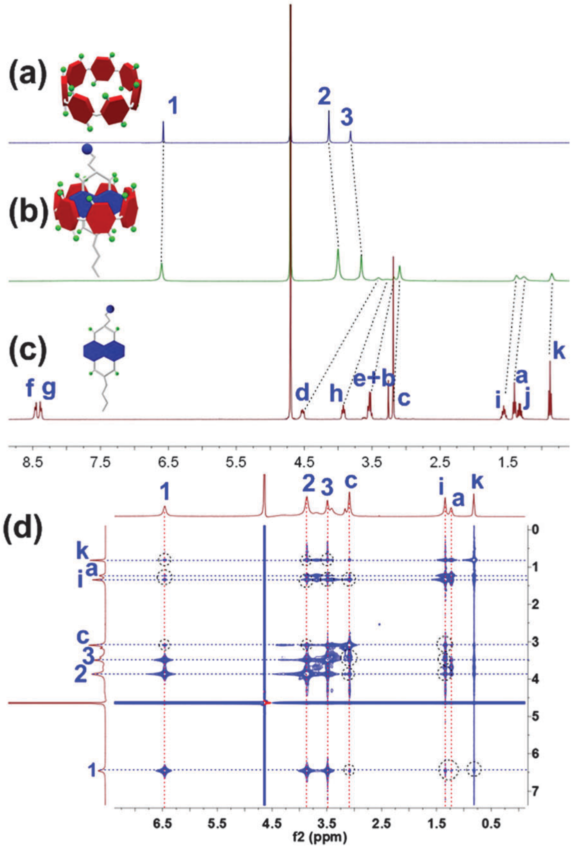

Fig. 1 Partial ^{1}H NMR spectra (400 MHz, D_2O, room temperature): (a) **WP7** (2.00 mM); (b) **WP7** (2.00 mM) and **M** (2.00 mM); (c) **M** (2.00 mM). (d) Partial NOESY NMR spectrum (600 MHz, D_2O, room temperature) of **WP7** (10.0 mM) and **M** (10.0 mM).

for the peaks corresponding to the protons on **M**. For example, the signals of the protons H_f and H_g on the NDI group shifted upfield effectively, which resulted from the formation of a threaded structure between **WP7** and **M**.[6c] A 2D NOESY NMR experiment was conducted to study the relative positions of the components in the host–guest inclusion complex (Fig. 1d). NOE correlation signals were observed between protons $H_{1,2,3}$ on **WP7** and $H_{a,c,i,k}$ on **M**, which indicated that the NDI group threaded deeply into the cavity of **WP7**, resulting in the formation of a [2]pseudorotaxane.

The cavity sizes of **WP7**, analogous water-soluble pillar[6]arene **WP6** and pillar[5]arene **WP5** were calculated to be about 8.7, 6.7 and 4.7 Å, respectively (Scheme 1 and Scheme S3, ESI†).[10a] The width of the NDI part of **G** was calculated to be about 8.6 Å (Scheme S4, ESI†). Due to the size-selective effect, the NDI part could completely thread into the cavity of **WP7** and partly thread into the cavity of **WP6**, but it was too big to thread into the cavity of **WP5**. ^{1}H NMR spectra provided convincing evidence for the size-selective effect. The ^{1}H NMR spectrum of **WP6** and **M** showed that the resonance peaks related to protons $H_{a,b,d,e}$ of **M** shifted upfield and exhibited a broadening effect (Fig. S15, ESI†), while the peaks related to H_f and H_g changed slightly, which indicated that the cationic part of **M** threaded into the cavity of **WP6** and part of the NDI was located in the cavity of **WP6**.[8c] For the ^{1}H NMR spectrum of **WP5** and **M**, only the peaks related to $H_{a,b,c}$ of **M** showed chemical shift changes (Fig. S16, ESI†), demonstrating that the cavity size of **WP5** was suitable for the cationic part rather than the NDI group.[8c]

Isothermal titration calorimetry (ITC) is a useful tool to explore the inclusion complexation, which not only provides the association constant (K_a) but also yields their thermodynamic parameters (enthalpy ΔH° and entropy changes ΔS°).[14] To estimate the association constant (K_a) for the complexation between **WP7** and **M**, ITC experiments were conducted. From Table 1, the association constant (K_a) between **WP7** and **M** was calculated to be $(2.87 \pm 0.265) \times 10^5\ M^{-1}$ (Fig. S23, ESI†), which is higher than those of **WP5**$\supset$**M** $[(2.49 \pm 0.354) \times 10^4\ M^{-1}]$ and **WP6**$\supset$**M** $[(4.98 \pm 0.993) \times 10^4\ M^{-1}]$ (Fig. S24 and S25, ESI†).

The difference in the association constants among these systems was caused by size-selective complexations. It was speculated that the strong complexation stability of **WP7**$\supset$**M** was driven by the cooperativity of multiple electrostatic interactions, hydrophobic interactions and charge transfer interactions between the electron-rich host **WP7** and the electron-deficit guest **M**. When **WP7** and **M** (molar ratio = 1 : 1) were mixed in water, the resulting solution had a red color, indicating the formation of a typical charge-transfer complex (Fig. 2b).[6c] As shown in UV-vis spectra (Fig. 2c), the spectrum exhibited a broad absorption peak above 400 nm upon addition of 1 equiv. of **WP7** into the aqueous solution of **M**, corresponding to the characteristic absorption of

Table 1 Association constants (K_a), enthalpy changes (ΔH°) and entropy changes (ΔS°) obtained from ITC experiments for the 1 : 1 complexes of **M** with the hosts (**WP7**, **WP6**, **WP5** and α-CD)[a]

	K_a (M^{-1})	ΔH° (cal mol^{-1})	ΔS° (cal mol^{-1} deg^{-1})
WP7	$(2.87 \pm 0.265) \times 10^5$	$-(1.180 \pm 0.162) \times 10^4$	−14.6
WP6	$(4.98 \pm 0.993) \times 10^4$	$-(1.212 \pm 0.750) \times 10^4$	−19.2
WP5	$(2.49 \pm 0.354) \times 10^4$	$-(3.835 \pm 0.311) \times 10^3$	7.26
α-CD	$(1.07 \pm 0.149) \times 10^4$	$-(1.319 \pm 0.072) \times 10^3$	14

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

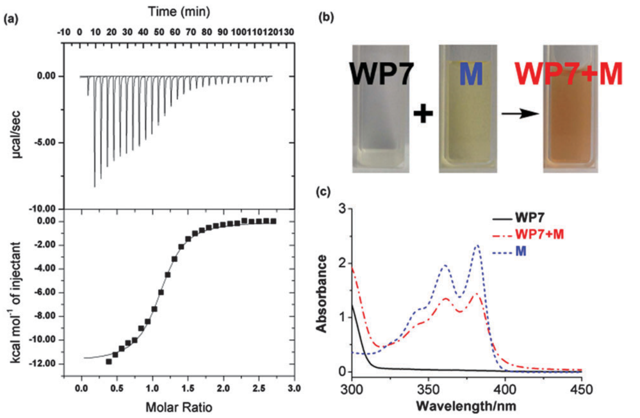

Fig. 2 (a) Microcalorimetric titration of **WP7** (2.00 mM, 10 μL per injection) with **M** (0.100 mM) in water at 298.15 K. Top: raw ITC data for 29 sequential injections (10 μL per injection) of a **WP7** solution (2.00 mM) into an **M** solution (0.100 mM); bottom: net reaction heat obtained from the integration of the calorimetric traces. (b) The solution color changes upon the complexation of **WP7** with 1 equiv. of **M**. (c) UV-vis spectra of **M**, **WP7** and **M** in the presence of 1 equiv. of **WP7** (1.00×10^{-4} M) in water.

the charge-transfer interactions.[6c] On the other hand, the maximum absorption of **M** red-shifted from 360.46 nm and 381.61 nm to 361.37 nm and 381.90 nm, respectively, upon addition of 1 equiv. of **WP7** (Fig. 2c), confirming the electrostatic interactions between **WP7** and **M**.[6c]

With the novel molecular recognition motif between **WP7** and **M** in hand, we further applied it in the fabrication of a supra-amphiphile by utilizing amphiphilic **G** as a guest. By using the concentration-dependent conductivity, the critical aggregation concentration (CAC) of **G** was determined to be 3.54×10^{-7} M (Fig. S17, ESI†). However, the CAC value of **G** increased to 4.49×10^{-5} M in the presence of **WP7** (Fig. S18, ESI†) by a factor of *ca.* 127, which was ascribed to the host–guest complexation.[7c] The morphologies of the self-assemblies formed by **G** and **WP7⊃G** were investigated by employing transmission electron microscopy (TEM). Nanofibers were obtained in an aqueous solution of **G** driven by π–π stacking interactions between the NDI cores. The length of the nanofibers was about several micrometers and the average diameter of the nanofibers was 6 nm (Fig. 3a and b), which was close to the length of two **G** molecules with antiparallel packing and overlapped NDI rings. After the addition of **WP7**, the nanofibers transformed into solid nanospheres with an average diameter of 70 nm resulting from the host–guest complexation (Fig. 3c and d). As revealed by dynamic light scattering (DLS), the average diameter of the **WP7⊃G** nanospheres was ∼87 nm (Fig. S19, ESI†), in good agreement with the TEM image in Fig. 3d.

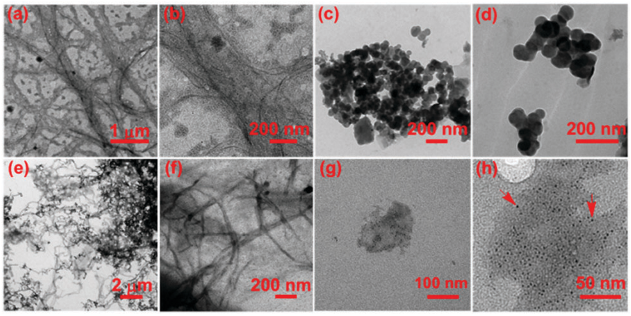

Fig. 3 TEM images: (a) nanofibers self-assembled from **G**; (b) enlarged image of (a); (c) nanospheres self-assembled from **WP7⊃G**; (d) enlarged image of (c); (e) **WP7⊃G** treated with HCl; (f) enlarged image of (e); (g) **WP7⊃G** in the presence of 1 equiv. of α-cyclodextrin; and (h) enlarged image of (g).

More interestingly, supra-amphiphile **WP7⊃G** exhibited dual-responsiveness. Adjusting the solution pH to 6.0 by adding hydrochloric acid, the nanospheres transformed into nanofibers again (Fig. 3e and f), because the carboxylate groups on **WP7** were protonated and the host was precipitated from the aqueous solution.[6e] For **G**, it dethreaded from the cavity of **WP7** and self-assembled into nanofibers again. On the other hand, the alkyl chain part of **G** is also an ideal guest for α-CD because it can thread into the cavity of α-CD to form a stable inclusion complex through hydrophobic interactions.[15] Driven by the hydrophobic interaction, the alkyl chain of **G** threaded into the cavity of α-CD with the K_a value of $(1.07 \pm 0.149) \times 10^4$ M^{-1} (Table 1). The nanospheres transformed into nanoparticles about 2 nm in diameter upon addition of α-CD into a solution of **WP7⊃G** (Fig. 3g and h), which indicated that the nanospheres formed by **WP7⊃G** disassembled by the addition of α-CD. The reason was that the amphiphilicity of the supra-amphiphile **WP7⊃G** was destroyed due to the formation of a water-soluble hetero[3]-pseudorotaxane-type complex **WP7⊃G⊂α-CD** (Scheme 1). Fluorescence titration experiments provided insight into the formation of this ternary host–guest complex. The fluorescence intensity increased gradually upon addition of α-CD into the solution of **WP7⊃G** (Fig. S28, ESI†), because the π–π stacking interactions between the NDI cores were inhibited effectively by the formation of **WP7⊃G⊂α-CD**.[16]

In conclusion, size-selective complexations between a NDI-containing guest (**M**) and water-soluble pillar[*n*]arenes (*n* = 5, 6, 7) were investigated. In comparison with **WP5** and **WP6**, the internal cavity of **WP7** was suitable for the NDI group, resulting in the formation of a stable host–guest inclusion complex. Based on this molecular recognition motif, a dual-responsive supra-amphiphile was firstly constructed by using **WP7** as the host and a NDI-containing amphiphile (**G**) as the guest. The morphologies of the self-assemblies formed from the supra-amphiphile **WP7⊃G** could be regulated by changing the solution pH or adding α-CD. The nanofibers formed by **G** and the solid nanospheres self-assembled from **WP7**$\supset$**G** could be reversibly adjusted by changing the solution pH due to the pH-controlled association and disassociation between **WP7** and **G**, which resulted from the deprotonation and protonation of **WP7**. Furthermore, the nanospheres transformed into nanoparticles upon addition of α-CD due to the hydrophobic interactions between α-CD and the alkyl chain, resulting in the formation of a water-soluble hetero[3]pseudorotaxane. This dual-responsive supra-amphiphile can be used to fabricate nanostructures which have potential applications in biological/pharmaceutical fields, such as drug delivery and controlled release.

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