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

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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Water-soluble pillar[7]arene WP7 was 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 or a Bruker Avance DMX 500 spectrophotometer. The 2D NOESY NMR spectrum was recorded on a Bruker Avance DMX 600 spectrophotometer with TMS as the internal reference. Low-resolution electrospray ionization mass spectra (LRESI-MS) were obtained on a Bruker Esquire 3000 Plus spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. High-resolution electrospray ionization mass spectra (HRESI-MS) were obtained on a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. UV-vis spectroscopy was performed on a Shimadzu UV-2550 instrument at room temperature. The fluorescence experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan). Dynamic light scattering measurements were performed on a Nano-ZS ZEN3600 instrument.
2. Syntheses of $G_0$ and $G$

Synthesis of $G_0$: 1,4,5,8-Naphthalenetetracarboxylic dianhydride (4.02 g, 15.0 mmol), $N,N'$-dimethylaminoethylamine (1.32 g, 15.0 mmol), and 1-aminotetradecane (3.20 g, 15.0 mmol) were added into DMF. The mixture was heated in a flask under nitrogen atmosphere at 90 °C for 24 h. The solvent was removed by rotary evaporation and the crude product was isolated by column chromatography (silica gel; petroleum ether:CH$_2$Cl$_2$ = 10:1) to afford a dark red solid $G_0$ (3.05 g, 38%). M.p. 148.3−150.2 °C. The proton NMR spectrum of $G_0$ is shown in Fig. S1. $^1$H NMR (400 MHz, CDCl$_3$, room temperature) $\delta$ (ppm): 8.75 (s, 4H), 4.35 (t, $J = 8$ Hz, 2H), 4.19 (t, $J = 8$ Hz, 3H), 2.68 (t, $J = 4$ Hz, 2H), 2.34 (s, 6H), 1.76−1.72 (m, 4H), 1.38−1.25 (m, 20H), 0.88 (t, $J = 8$ Hz, 3H). The $^{13}$C NMR spectrum of $G_0$ is shown in Fig. S2. $^{13}$C NMR (100 MHz,

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Scheme S1. Synthetic route to G.
CDCl₃, room temperature) δ (ppm): 162.95, 162.75, 131.01, 130.92, 126.76, 126.68, 126.58, 56.94, 45.61, 41.01, 38.65, 31.92, 29.77, 29.69, 29.66, 29.66, 29.64, 29.60, 29.53, 29.36, 29.33, 28.08, 27.09, 22.69, 14.13. LRESIMS is shown in Fig. S3: m/z 534.6 [M + H]⁺ (100%). HRESIMS: m/z calcd for [M + H]⁺ C₃₂H₄₄N₃O₄⁺, 534.3332; found 534.3335; error 0.6 ppm.

Fig. S1 ¹H NMR spectrum (400 MHz, CDCl₃, room temperature) of G₀.
**Fig. S2** $^{13}$C NMR spectrum (100 MHz, CDCl$_3$, room temperature) of $G_0$.

**Fig. S3** Electrospray ionization mass spectrum of $G_0$. Assignment of main peaks: $m/z$ 534.6 [M + H]$^+$. 
Synthesis of G: Excess CH$_3$I (5.00 g, 35.2 mmol) was added into a toluene solution of G$_0$ (6.00 g, 11.2 mmol). The mixture was stirred at 40 °C for 24 h. Then the product was filtered and dried under vacuum to afford a light yellow solid G (5.75 g, 76%). M.p. 216.2−217.5 °C. The proton NMR spectrum of G is shown in Fig. S4. $^1$H NMR (400 MHz, DMSO-$d_6$, room temperature) δ (ppm): 7.26 (t, $J = 8.0$ Hz, 2H), 7.17−7.12 (m, 2H), 3.65 (s, 2H), 3.26 (s, 9H), 2.29 (s, 2H), 1.65 (s, 2H), 1.33 (s, 2H), 1.24−1.22 (m, 24H), 0.84 (t, $J = 8.0$ Hz, 3H). The $^{13}$C NMR spectrum of G is shown in Fig. S5. $^{13}$C NMR (100 MHz, DMSO-$d_6$, room temperature) δ(ppm): 137.29, 128.85, 128.15, 125.27, 52.46, 31.27, 29.16, 29.02, 28.99, 28.95, 28.86, 28.80, 28.76, 28.69, 28.61, 28.58, 26.47, 22.07, 21.01, 13.92. LRESIMS is shown in Fig. S6: m/z 548.4 [M − I]$^+$ (100%). HRESIMS: m/z calcd for [M − I]$^+$ C$_{35}$H$_{46}$N$_3$O$_4^+$, 548.3488; found 548.3478; error −1.8 ppm.

Fig. S4 $^1$H NMR spectrum (400 MHz, DMSO-$d_6$, room temperature) of G.
**Fig. S5** $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$, room temperature) of G.

**Fig. S6** Electrospray ionization mass spectrum of G. Assignment of main peaks: $m/z$ 548.4 [M - I]$^+$. 
3. Syntheses of $M_0$ and $M$

![Scheme S2. Synthetic route to $M$.](image)

Synthesis of $M_0$: 1,4,5,8-Naphthalenetetracarboxylic dianhydride (3.40 g, 12.7 mmol), $N,N'$-dimethylaminoethylamine (1.10 g, 12.7 mmol), and butylamine (0.950 g, 12.7 mmol) were dissolved in DMF. The mixture was heated in a flask under nitrogen atmosphere at 90 °C for 24 h. The solvent was removed by rotary evaporation and the crude product was isolated by column chromatography (silica gel; petroleum ether:CH$_2$Cl$_2$ = 10:1) to get a dark red solid $M_0$ (1.5 g, 30%). M.p. 179.4−180.5 °C. The proton NMR spectrum of $M_0$ is shown in Fig. S7. $^1$H NMR (400 MHz, CDCl$_3$, room temperature) $\delta$ (ppm): 8.76 (s, 4H), 4.35 (t, $J = 8.0$ Hz, 2H), 4.21 (t, $J = 8.0$ Hz, 2H), 2.67 (t, $J = 8.0$ Hz, 4H), 1.73−1.70 (m, 2H), 1.45−1.42 (m, 2H), 0.99 (t, $J = 8.0$ Hz, 3H). The $^{13}$C NMR spectrum of $M_0$ is shown in Fig. S8. $^{13}$C NMR (125 MHz, CDCl$_3$, room temperature) $\delta$ (ppm): 162.91, 162.81, 162.55, 130.98, 130.89, 126.72, 126.64, 126.56, 56.93, 45.77, 40.74, 38.63, 30.14, 20.33, 13.81. LRESIMS is shown in Fig. S9: $m/z$ 394.4 [M + H]$^+$ (100%). HRESIMS: $m/z$ calcd for [M + H]$^+$ C$_{22}$H$_{24}$N$_3$O$_4^+$, 394.1767; found 394.1762; error −1 ppm.
Fig. S7 $^1$H NMR spectrum (400 MHz, CDCl$_3$, room temperature) of M$_0$.

Fig. S8 $^{13}$C NMR spectrum (125 MHz, CDCl$_3$, room temperature) of M$_0$. 
**Fig. S9** Electro spray ionization mass spectrum of $\text{M}_0$. Assignment of main peak: $m/z$ 394.4 [$\text{M} + \text{H}]^+$.  

Synthesis of $\text{M}$: Excess bromoethane (2.60 g, 23.9 mmol) was added into a toluene solution of $\text{M}_0$ (4.00 g, 7.96 mmol). The mixture was heated in a flask under nitrogen atmosphere at reflux for 24 h. The product was filtered and dried under vacuum to get a red solid $\text{M}$ (5.57 g, 87%) M.p. 261.4–262.1 °C. The proton NMR spectrum of $\text{M}$ is shown in Fig. S10. $^1\text{H}$ NMR (400 MHz, D$_2$O, room temperature) $\delta$ (ppm): 8.47–8.37 (m, 4H), 4.52 (t, $J$ = 8.0 Hz, 2H), 3.92 (d, $J$ = 8.0 Hz, 2H), 3.50 (m, 4H), 3.19 (s, 6H), 1.56 (m, 2H), 1.40 (t, $J$ = 8.0 Hz, 3H), 1.32 (m, 2H), 0.88 (t, $J$ = 8.0 Hz, 3H). The $^{13}\text{C}$ NMR spectrum of $\text{M}$ is shown in Fig. S11. $^{13}\text{C}$ NMR (100 MHz, DMSO-$d_6$, room temperature) $\alpha$ (ppm): 162.69, 162.55, 130.50, 130.41, 126.56, 126.24, 126.16, 126.13, 58.95, 58.23, 49.75, 33.16, 29.52, 19.82, 13.66, 7.79. LRESIMS is shown in Fig. S12: $m/z$ 422.2 [$\text{M} – \text{Br}]^+$ (100%). HRESIMS: $m/z$ calcd for [$\text{M} – \text{Br}]^+$ C$_{24}$H$_{28}$N$_3$O$_4^+$, 422.2080; found 422.2063; error –4.0 ppm.
Fig. S10 $^1$H NMR spectrum (400 MHz, D$_2$O, room temperature) of M.

Fig. S11 $^{13}$C NMR spectrum (125 MHz, DMSO-$d_6$, room temperature) of M.
**Fig. S12** Electrospray ionization mass spectrum of M. Assignment of main peaks: $m/z$ 422.2 $[M-Br]^+$. 

4. **2D COSY spectrum of M in $D_2O$**

**Fig. S13** 2D $^1H-^1H$ COSY spectrum (400 MHz, $D_2O$, 298 K) of M.


From previous work,$^{S2}$ the diameters of the internal cavities of pillar[5]arenes, pillar[6]arenes and pillar[7]arenes were calculated to be ~4.7, ~6.7 and ~8.7 Å, respectively, by treating pillar[5]arenes, pillar[6]arenes and pillar[7]arenes as regular pillars and ignoring the influence of the substituents on the oxygen atoms (Scheme
S3). On the other hand, the size of G in its energy-minimized structure was calculated by using Chem 3D (Scheme S4).

**Scheme S3.** The cavity sizes of pillar[5]arenes (a), pillar[6]arenes (b) and pillar[7]arenes (c). We used the van der Waals radii of the atoms to calculate the sizes.

**Scheme S4.** The size (Å) of the NDI group. We used the van der Waals radii of the atoms to calculate the size.
6. $^1$H NMR spectroscopic investigations of WP7$\rightarrow$M, WP6$\rightarrow$M and WP5$\rightarrow$M

**Fig. S14** Partial $^1$H NMR spectra (400 MHz, D$_2$O, room temperature): (a) WP7 (2.00 mM); (b) M (2.00 mM) and WP7 (2.00 mM); (c) M (2.00 mM).

**Fig. S15** Partial $^1$H NMR spectra (400 MHz, D$_2$O, room temperature): (a) WP6 (2.00 mM); (b) M (2.00 mM) and WP6 (2.00 mM); (c) M (2.00 mM).
**Fig. S16** Partial $^1$H NMR spectra (400 MHz, D$_2$O, room temperature): (a) WP5 (2.00 mM); (b) M (2.00 mM) and WP5 (2.00 mM); (c) M (2.00 mM).

7. **Critical aggregation concentration (CAC) determinations of G and WP7=G**

**Fig. S17** The concentration-dependent conductivity of G. The critical aggregation concentration (CAC) was determined to be $4.02 \times 10^{-7}$ M.
Fig. S18 The concentration-dependent conductivity of equimolar WP7 and G. The critical aggregation concentration (CAC) was determined to be $4.49 \times 10^{-5}$ M.

8. Dynamic light scattering (DLS) results of WP7$\rightarrow$G in the absence and presence of 1 equiv. $\alpha$-CD

![Graph showing conductivity vs. concentration for WP7 and G](image)

Fig. S19 DLS result of WP7 (3.57 $\times$ 10$^{-5}$ M) and G (5.00 $\times$ 10$^{-5}$ M). The average diameter of the nanospheres was determined to be 87 nm.

![Histogram showing size distribution of WP7 and G](image)

Fig. S20 DLS result of WP7 (3.57 $\times$ 10$^{-5}$ M) and G (5.00 $\times$ 10$^{-5}$ M) in the presence of 1 equiv. $\alpha$-CD. The average diameter of the nanospheres was determined to be 23 nm. The
diameter of the nanoparticles determined by DLS was larger than that determined by TEM, because the nanoparticles might aggregated together to form larger aggregates in solution state.

9. The $^1$H NMR of WP7$\rightarrow$M with different molar ratios

![Partial $^1$H NMR spectra (400 MHz, D$_2$O, room temperature): (a) WP7 (2.00 mM); (b) WP7 (2.00 mM) and M (2.00 mM); (c) WP7 (2.00 mM) and M (6.00 mM); (d) M (2.00 mM).](image)

10. Enlarged TEM images of WP7$\rightarrow$G in the presence of 1 equiv. α-CD.

![Enlarged TEM images of WP7$\rightarrow$G in the presence of 1 equiv. α-CD.](image)
11. ITC investigations of host–guest complexation between WP7 and M, WP6 and M, WP5 and M, M and α-CD, WP7⇒M and α-CD.

**Figure S23.** 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.

**Figure S24.** Microcalorimetric titration of WP6 (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 WP6 solution (2.00 mM) into an M solution (0.100 mM); bottom: net reaction heat obtained from the integration of the calorimetric traces.
**Figure S25.** Microcalorimetric titration of WP5 (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 WP5 solution (2.00 mM) into an M solution (0.100 mM); bottom: net reaction heat obtained from the integration of the calorimetric traces.

**Figure S26.** Microcalorimetric titration of α-CD (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 an α-CD solution (2.00 mM) into an M solution (0.100 mM); bottom: net reaction heat obtained from the integration of the calorimetric traces.
12. Fluorescence spectroscopy studies of $M$ and $WP7\rightarrow M$ after the addition of $\alpha$-CD

**Figure S27.** Fluorescence spectra of $M$ (2.00 $\times$ 10$^{-4}$ M) in aqueous solution at room temperature with different concentrations of $\alpha$-CD: 0, 0.080, 0.100, 0.200, 1.00, 2.00, 3.00, 4.00, 5.00 and 6.00 $\times$ 10$^{-4}$ M.

**Figure S28.** Fluorescence spectra of $WP7\rightarrow M$ (5.00 $\times$ 10$^{-5}$ M) in aqueous solution at room temperature with different concentrations of $\alpha$-CD: 0, 1.00, 2.00, 3.00, 4.00, 5.00, 6.00, 7.00, 8.00, 9.00 and 10.00 $\times$ 10$^{-4}$ M.
13. 2D NOESY NMR spectrum of $M$ and $\alpha$-CD in $D_2O$

**Figure S29.** Partial NOESY NMR spectrum (400 MHz, $D_2O$, room temperature) of $M$ (10.0 mM) and $\alpha$-CD (10.0 mM).

**References:**
