# A dual redox-responsive supramolecular amphiphile fabricated by selenium-containing pillar[6]arene-based molecular recognition

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### 1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. Compounds 1,<sup>S1</sup> G1,<sup>S2</sup> and G2<sup>S2</sup> were prepared according to published procedures. <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>77</sup>Se NMR spectra were recorded with a Bruker AVANCE III 400, Bruker AVANCE III 500 spectrometer, or Agilent DD2-600 spectrometer using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Transmission electron microscopy (TEM) investigations were carried out on a HITACHI HT-7700 instrument. Scanning electron microscopy (SEM) investigations were carried out on a JEOL 6390LV instrument. Dynamic light scattering (DLS) was carried out on a Malvern Nanosizer S instrument at room temperature. The isothermal titration calorimetry (ITC) experiment was performed on a VP-ITC micro-calorimeter (Microcal, USA). Mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. Elemental analyses were carried out on a VarioMICRO V 1.9.5 instrument. Scanning Probe Microscope (Veeco Company, USA) in the tapping mode. Elemental analyses were carried out on a varioMICRO V 1.9.5 instrument.

#### 2. Synthesis of pillar[6] arene H1

Scheme S2. Synthetic route to H1.



## 2.1 Synthesis of pillar[6] arene H2

Pillar[6]arene **1** was synthesized according to literature.<sup>S1</sup> To a solution of diphenyldiselane (312 mg, 1.00 mmol) in THF (10.0 mL) under N<sub>2</sub> protection, 2 mL of a NaBH<sub>4</sub> (152 mg, 4.00 mmol) aqueous solution was injected. Pillar[6]arene **1** (407 mg, 0.22 mmol) was then added. The mixture was stirred for 24 h at 50 °C. Then the solvent was removed and the mixture was purified by column chromatography (silica gel, dichloromethane/petroleum ether = 1:5). Evaporation of the solvent gave **H2** as a pale yellow oil (258 mg, 88%). The <sup>1</sup>H NMR spectrum of **H2** is shown in Fig. S1. <sup>1</sup>H NMR (400 MHz, chloroform-*d*, 293 K)  $\delta$  (ppm): 7.42–7.38 (m, 24 H, SePh, the twenty-four terminal benzene ring protons that are closer to selenium), 7.16–7.14 (t, *J* = 8 Hz, 36 H, SePh, the thirty-six terminal benzene ring protons that are far away from selenium), 6.59 (s, 12 H, Ph), 4.00–3.97 (m, 24H, OCH<sub>2</sub>), 3.74 (s, 12H, PhCH<sub>2</sub>), 3.05–3.01 (m, 24H, SeCH<sub>2</sub>). The <sup>77</sup>Se NMR spectrum of **H2** is shown in Fig. S2. <sup>77</sup>Se NMR (600 MHz, chloroform-*d*, 293 K)  $\delta$  (ppm): 268.01. The <sup>13</sup>C NMR spectrum of **H2** is shown in Fig. S3. <sup>13</sup>C NMR (100 MHz, chloroform-*d*, 293 K)  $\delta$  (ppm): 150.27, 132.46, 130.12, 129.21, 128.07, 126.97, 115.61, 88.24, 29.78, 29.40, 27.44, 26.90. LRESIMS is shown in Fig. S4: *m/z* 653.8 [**H2** + CH<sub>3</sub>OH + 5CH<sub>3</sub>COO<sup>-</sup>]<sup>5–</sup>. Anal. Calcd for C<sub>138</sub>H<sub>132</sub>O<sub>12</sub>Se<sub>12</sub>: C, 56.57; H, 4.54. Found: C, 56.60; H, 4.49.



*Fig. S1* <sup>1</sup>H NMR spectrum (400 MHz, chloroform-*d*, 298 K) of pillar[6]arene H2.



*Fig. S2* <sup>77</sup>Se NMR spectrum (114 MHz, chloroform-*d*, 293 K) of pillar[6]arene H2.



*Fig. S3* <sup>13</sup>C NMR spectrum (100 MHz, chloroform-*d*, 293 K) of pillar[6]arene H2.



*Fig. S4* Electrospray ionization mass spectra of H2. Assignment of the main peak: m/z 653.8 [H2 + CH<sub>3</sub>OH + 5CH<sub>3</sub>COO<sup>-</sup>]<sup>-</sup>.

#### 2.2 Oxidation of pillar[6] arene H2

To a solution of pillar[6]arene H2 (293 mg, 0.10 mmol) in a mixture of MeCN (5 mL) and H<sub>2</sub>O (5 mL), 58 µL of 30% H<sub>2</sub>O<sub>2</sub> was added. The mixture was stirred at room temperature for 12 h. MeCN was removed under vacuum and H<sub>2</sub>O was removed by freeze-drying to give H1 (273 mg, 95 %) as an oil. <sup>1</sup>H NMR spectrum of H1 is shown in Fig. S5. <sup>1</sup>H NMR (400 MHz, acetone- $d_6$ , 298 K)  $\delta$  (ppm): 7.99–7.98 (t, J = 4 Hz, 24H, SeOPh), 7.71–7.64 (m, 36H, SeOPh), 6.36 (s, 12H, Ph), 4.07 (s, 24H, PhCH<sub>2</sub>), 3.90 (s, 12H, OCH<sub>2</sub>), 3.58 (s, 24H, SeOCH<sub>2</sub>). The <sup>77</sup>Se NMR spectrum of H1 is shown in Fig. S6. <sup>77</sup>Se NMR (600 MHz, acetone- $d_6$ , 293 K)  $\delta$  (ppm): 864.96. The <sup>13</sup>C NMR spectrum of H1 is shown in Fig. S7. <sup>13</sup>C NMR (100 MHz, acetone- $d_6$ , 293 K)  $\delta$  (ppm): 143.48, 133.49, 130.63, 129.68, 128.87, 127.35, 126.05, 63.54, 53.57, 31.24, 30.96, 21.93, 12.95. LRESIMS is shown in Fig. S8: m/z 670.5 [H1 + 5HCOO<sup>-</sup>]<sup>5-</sup>. Anal. Calcd for C<sub>138</sub>H<sub>132</sub>O<sub>24</sub>Se<sub>12</sub>: C, 53.09; H, 4.26. Found: C, 53.15; H, 4.21.



*Fig. S5* <sup>1</sup>H NMR spectrum (400 MHz, acetone- $d_6$ , 298 K) of H1.



*Fig. S6* <sup>77</sup>Se NMR spectrum (114 MHz, acetone- $d_6$ , 293 K) of pillar[6]arene H1.



*Fig.*  $S7^{13}$ C NMR spectrum (100 MHz, acetone- $d_6$ , 293 K) of H1.



Fig. S8 Electrospray ionization mass spectra of H1. Assignment of the main peak: m/z 670.5 [H1 + 5HCOO<sup>-</sup>]<sup>5-</sup>.

#### 3. Host-guest complexation between H1 and G1



Fig. S9 2D NOESY spectrum (500 MHz, D<sub>2</sub>O/CD<sub>3</sub>COCD<sub>3</sub> (5:1, v/v), 293 K) of H1 (10.0 mM) and G1 (10.0 mM).

*4. ITC experiment of*  $H1 \supset G1$  *in water* 



*Fig. S10* Microcalorimetric titration of G1 with H1 in water at 298 K. (Top) Raw ITC data for 29 sequential injections (10.0  $\mu$ L per injection) of a G1 solution (2.00 mM) into a H1 solution (0.100 mM). (Bottom) Net reaction heat obtained from the integration of the calorimetric traces.

5. Redox responsive host-guest complexation between H1 and G1 controlled by GSH and FeCl<sub>3</sub>



*Fig. S11* Partial <sup>1</sup>H NMR spectra (400 MHz,  $D_2O/CD_3COCD_3$  (5:1, v/v), 293 K): (a) **G1** (1.00 mM); (b) **H1** (1.00 mM) and **G1** (1.00 mM); (c) **H1** (1.00 mM); (d) b after addition of 1.2 molar equiv. of GSH; (e) d after further addition of 1.5 molar equiv. of FeCl<sub>3</sub>.

6. Critical aggregation concentration (CAC) determination of G2



*Fig. S12* The concentration-dependent conductivity of G2 in water. The critical aggregation concentration was determined to be  $1.72 \times 10^{-6}$  M.

7. Critical aggregation concentration (CAC) determination of  $H1 \supset G2$ 



*Fig. S13* The concentration-dependent conductivity of H1 $\supset$ G2 in water. The critical aggregation concentration was determined to be  $2.53 \times 10^{-5}$  M.



*Fig. S14* (a) AFM result of the self-assembled vesicles; (b) the height measured from the AFM experiment is the height of two walls of the vesicles. It means that the wall thickness of the vesicles is 7.05 nm, which is equal to half of the vertical distance, 14.09 nm.

References

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