# A bola-type supra-amphiphile constructed from a water-soluble pillar[5]arene and a rod-coil molecule for dual fluorescent sensing

Yong Yao, Xiaodong Chi, Yujuan Zhou, and Feihe Huang\*

State Key Laboratory of Chemical Engineering, Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China; Email: <u>fhuang@zju.edu.cn</u>.

## **Supporting Information**

1.	Materials and methods	S2
2.	Syntheses of rod-coil molecule $m{1}$ and model compound $m{2}$	<b>S</b> 3
3.	Self-assembly of rod-coil molecule <b>1</b> in water	S15
4.	Host-guest complexation of <b>WP5</b> with <b>1</b> and <b>2</b>	S16
5.	References	S20

#### 1. Materials and methods

Hydroquinone, 1,10-dibromodecane, K<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>CN, I<sub>2</sub>, HIO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH, 4-biphenylboronic acid, tetrakis(triphenylphosphine)palladium(0), and 1-methylimidazole were reagent grade and used as received. Solvents were either employed as purchased or dried according to procedures described in the literatures. Water-soluble pillar[5]arene **WP5** was prepared according to the literature.<sup>S1 1</sup>H NMR spectra were collected on a Varian Unity INOVA-400 spectrometer (Bruker) with internal standard TMS. <sup>13</sup>C NMR spectra were recorded on a Varian Unity INOVA-400 spectrometry at 100 MHz. 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. HRMS were obtained on a Bruker 7-Tesla FT-ICRMS equipped with an electrospray source (Billerica, MA, USA). The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. The TEM images were obtained using a HITACHI instrument with an accelerating voltage of 80 kV. Dynamic light scattering (DLS) was carried out on a Malvern Nanosizer S instrument at room temperature. The fluorescence titration experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan).

2. Syntheses of rod-coil molecule  ${\bf 1}$  and model compound  ${\bf 2}$ 

2.1 Synthesis of rod-coil molecule 1





#### Scheme S2. Synthetic route to compound A



A solution of hydroquinone (11.0 g, 100 mmol) and 1,10-dibromodecane (120 g, 400 mmol) in dry acetonitrile (250 mL) was made. Under vigorous stirring, K<sub>2</sub>CO<sub>3</sub> (46.4 g, 400 mmol) was added. The mixture was refluxed for 12 hours under nitrogen atmosphere. After removal of the inorganic salt, the solvent was evaporated and the residue was purified by chromatography on silica gel (petroleum ether/ dichloromethane, v/v 10:1) to give compound **A** as a white solid (46.7 g, 85%). The <sup>1</sup>H NMR spectrum of **A** is shown in Fig. S1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, rt)  $\delta$  (ppm): 7.02 (s, 4H), 4.05 (t, J = 6.0 Hz, 4H), 3.44 (t, J = 6.0 Hz, 4H), 1.88–1.81 (m, 4H), 1.78–1.75 (m, 4H), 1.50 (s, 4H), 1.35–1.28 (m, 20H).



*Fig. S1.* <sup>1</sup>H NMR spectrum (400 Hz, CDCl<sub>3</sub>, rt) of **A**.

2.1.2 Synthesis of compound **B** 





Compound **A** (19.8 g, 36.2 mmol), I<sub>2</sub> (8.30 g, 32.6 mmol), and HIO<sub>3</sub> (3.82 g, 21.7 mmol) were dissolved in a mixture of H<sub>2</sub>SO<sub>4</sub> (30%, 10.8 mL), CCl<sub>4</sub> (15 mL) and CH<sub>3</sub>COOH (50 mL). The above mixture was stirred at room temperature for 30 minutes and then stirred at 75 °C for 3 hours. The reaction mixture was cooling to 0 °C to give white precipitate. The solvent was filtrated to provide a crude product, which was purified by column chromatography (eluent: petroleum ether/dichloromethane, 100:1) to afford a white solid (17.2 g, 61%). Mp: 53.2–54.3 °C. The <sup>1</sup>H NMR spectrum of **B** is shown in Fig. S2. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, rt)  $\delta$  (ppm): 7.17 (s, 2H), 3.92 (t, *J* = 6.0 Hz, 4H), 3.41 (t, *J* = 6.0 Hz, 4H), 1.86–1.78 (m, 8H), 1.44–1.37 (m, 8H), 1.32 (s, 16H). The <sup>13</sup>C NMR spectrum of **B** is shown in Fig. S3. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, rt)  $\delta$  (ppm): 152.8, 122.7, 86.3, 70.3, 34.1, 32.9, 29.4, 29.3, 29.2, 29.1, 28.8, 28.2, 26.0. LRESIMS is shown in Fig. S4: *m*/*z* 798.2 [**B**]<sup>+</sup>. HRESIMS: *m*/*z* calcd for [**B** + Na]<sup>+</sup> C<sub>26</sub>H<sub>42</sub>Br<sub>2</sub>I<sub>2</sub>NaO<sub>2</sub>, 820.9539, found 820.9542; error 0.3 ppm.



*Fig.* S2. <sup>1</sup>H NMR spectrum (400 MHz,  $CDCl_3$ , rt) of **B**.



Fig. S3. <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, rt) of **B**.



*Fig. S4.* Electrospray ionization mass spectrum of **B**. Assignment of the main peak: m/z 798.2 [**B**]<sup>+</sup>.

#### Scheme S4. Synthetic route to compound C



A mixture of **B** (8.00 g, 10.0 mmol), 4-biphenylboronic acid (8.00 g, 40.0 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.115 g, 0.100 mmol) in DMF (50 mL) was stirred in a 100 mL round-bottom flask at 100 °C for 24 hours. After cooling, the inorganic salt was removed, the solvent was evaporated, and the residue was purified by chromatography on silica gel (petroleum ether/ dichloromethane, v/v 10:1) to give compound **C** as a white solid (6.7 g, 79%). Mp: 120.3–121.5 °C. The <sup>1</sup>H NMR spectrum of **C** is shown in Fig. S5. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, rt)  $\delta$  (ppm): 7.82–7.80 (m, 4H), 7.620 (s, 2H), 7.52–7.41 (m, 14H), 4.14 (t, J = 6.0 Hz, 4H), 3.44 (t, J = 6.0 Hz, 4H), 1.89–1.84 (m, 8H), 1.54–1.50 (m, 4H), 1.39–1.32 (m, 20H). The <sup>13</sup>C NMR spectrum of **C** is shown in Fig. S6. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, rt)  $\delta$  (ppm): 153.50, 140.39, 138.49, 130.49, 130.00, 128.92, 128.34, 127.29, 117.44, 70.34, 33.04, 31.49, 30.59, 28.95, 28.71, 26.49. LRESIMS is shown in Fig. S7: m/z 873.4 [**C** + Na]<sup>+</sup>. HRESIMS: m/z calcd for [**C** + Na]<sup>+</sup> C<sub>50</sub>H<sub>60</sub>Br<sub>2</sub>NaO<sub>2</sub>, 873.2858, found 873.2844; error –0.9 ppm.







Fig. S6. <sup>13</sup>C NMR spectrum (100MHz, CDCl<sub>3</sub>, rt) of C.



*Fig.* S7. Electrospray ionization mass spectrum of compound C. Assignment of the main peak: m/z 873.4  $[C + Na]^+$ .

### 2.1.4 Synthesis of rod-coil molecule 1



Scheme S5. Synthetic route to rod-coil molecule 1

A mixture of **C** (1.74 g, 2.00 mmol) and *N*-methylimidazole (1.64 g, 20.0 mmol) in toluene (25 mL) was stirred in a 100 mL round-bottom flask at 120 °C for 24 h. After cooling, the solvent was removed and the residue was recrystallized from ethanol/diethyl ether (1:2) to give a white solid (1.66 g, 82%). Mp: 198.3–199.1 °C. The <sup>1</sup>H NMR spectrum of compound **1** is shown in Fig. S8. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , rt)  $\delta$  (ppm): 9.01 (s, 2H), 7.73–7.52 (m, 16H), 7.50–7.48 (m, 4H), 7.41–7.39 (m, 2H), 7.11 (s, 2H), 4.10 (t, J = 6.4Hz, 4H), 4.01 (t, J = 6.4Hz, 4H), 3.84 (s, 6H), 1.71–1.61 (m, 8H), 1.35 (s, 4H), 1.21 (s, 20H). The <sup>13</sup>C NMR spectrum of **1** is shown in Fig. S9. <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ , rt)  $\delta$  (ppm): 149.87, 139.95, 138.75, 137.05, 136.53, 128.69, 127.14, 126.37, 125.95, 123.44, 122.10, 115.48, 68.74,

48.77, 39.50, 39.08, 38.66, 35.48, 25.52, 25.43. LRESIMS is shown in Fig. S10: m/z 428.2  $[1 - 2Br]^{2+}$ . HRESIMS: m/z calcd for  $[1 - 2Br]^{2+} C_{58}H_{72}N_4O_2$ , 428.2822, found 428.2822; error 0 ppm.



*Fig.* S8. <sup>1</sup>H NMR spectrum (400MHz, DMSO- $d_6$ , rt) of **1**.



*Fig.* S9. <sup>13</sup>C NMR spectrum (100MHz, DMSO- $d_6$ , rt) of **1**.



*Fig. S10.* Electrospray ionization mass spectrum of **1**. Assignment of the main peak: m/z 428.2  $[1 - 2Br]^{2+}$ .

Scheme S6. Synthetic route to compound 2



A mixture of 1-bromododecane (24.9 g, 100 mmol) and *N*-methylimidazole (1.64 g, 20.0 mmol) in toluene (25 mL) was stirred in a 100 mL round-bottom flask at 120 °C for 24 h. After cooling, the solvent was removed and the residue was recrystallized from ethanol/diethyl ether (1:2) to give a white solid (3.0 g, 88%). Mp: 38.7–39.4 °C. The <sup>1</sup>H NMR spectrum of compound **2** is shown in Fig. S11. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, rt)  $\delta$  (ppm): 7.60 (s, 2H), 7.37 (s, 2H), 4.30 (t, J = 8Hz, 2H), 3.97 (s, 3H), 1.92 (s, 2H), 1.37–1.27 (m, 18H), 0.86 (t, J = 8Hz, 2H). The <sup>13</sup>C NMR spectrum of **2** is shown in Fig. S12. <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O, rt)  $\delta$  (ppm): 136.08, 123.58, 121.84, 49.51, 31.97, 29.90, 29.67, 29.21, 22.62, 13.72. LRESIMS is shown in Fig. S13: m/z 251.2 [**2** – Br]<sup>+</sup>. HRESIMS: m/z calcd for [**2** – Br]<sup>+</sup> C<sub>16</sub>H<sub>31</sub>N<sub>2</sub>, 251.2487, found 251.2482; error –0.2 ppm.



*Fig. S11*. <sup>1</sup>H NMR spectrum (400MHz,  $D_2O$ , rt) of **2**.



*Fig. S12*. <sup>13</sup>C NMR spectrum (100MHz, D<sub>2</sub>O, rt) of **2**.



*Fig. S13*. Electrospray ionization mass spectrum of **2**. Assignment of the main peak: m/z 251.2 [**2** – Br]<sup>+</sup>.

3. Self-assembly of rod-coil molecule 1 in water



*Fig. 14.* Surface tension of water as a function of the rod-coil **1** concentration. There are two linear segments in the curve and a sudden reduction of the slope, implying that the CAC of **1** is approximately  $1.62 \times 10^{-4}$  M in water.



*Fig. S15*. Model of the rod-coil molecule **1** (carbon atoms are gray, oxygen atoms are red, and hydrogen atoms are white). It was estimated by ChemBio3D Ultra 13.0.



*Fig. S16*. Small-angle X-ray scattering (SAXS) scan of 1.  $\lambda = 0.01548$  nm, and  $2\theta = 2.85^{\circ}$ .<sup>S3</sup>

4. Host-guest complexation of WP5 with 1 and 2



*Fig. S17.* Partial <sup>1</sup>H NMR (400 Hz, D<sub>2</sub>O, rt) spectra: (a) model compound **2** (1.00 mM); (b) **WP5** (1.00 mM) and **2** (3.00 mM); (c) **WP5** (1.00 mM).

To determine association constant for the complexation between **WP5** and model compound **2**, fluorescence titration experiments were done with solutions which had a constant concentration of **WP5** (2.50 × 10<sup>-4</sup> M) and varying concentrations of **2**. The non-linear curve-fitting was based on the equation:  $\Delta F = (\Delta F_{\infty}/[H]_0) (0.5[G]_0 + 0.5([H]_0+1/K_a)-(0.5 ([G]_0^2+(2[G]_0(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5}))$ . Where  $\Delta F$  is the fluorescence intensity changes at 330 nm at  $[H]_0$ ,  $\Delta F_{\infty}$  is the fluorescence intensity changes at 330 nm when **WP5** is completely complexed,  $[G]_0$  is the initial concentration of **2**, and  $[H]_0$  is the fixed initial concentration of **WP5**.<sup>S4</sup>



Fig. S18. Fluorescence emission spectra of WP5 with different concentrations of 2.



Fig. S19. Mole ratio plot for WP5 and 2, indicating a 1:1 stoichiometry.



*Fig. S20*. The fluorescence intensity changes at 330 nm upon addition of **2**. The red solid line was obtained from the non-linear curve-fitting using the above equation.



*Fig. S21*. Fluorescence spectra of mixtures of **1** and **WP5** with different molar ratios. Inset: fluorescent photographs of **1** (left) and (**WP5**)<sub>2</sub> $\supset$ **1** (right) aqueous solutions upon irradiation with a 354 nm light source. The concentration of **1** is fixed at 2.00 × 10<sup>-5</sup> M.



*Fig. S22.* Electrospray ionization mass spectrum of  $(WP5)_2 \supset 1$ . Assignment of the main peaks: m/z 662.8  $[WP5 - 2NH_4]^{2-}$ ; 867.6  $[(WP5)_2 \supset 1 - 2Br - 6NH_4]^{4-}$ ; 1162.8  $[(WP5)_2 \supset 1 - 2Br - 5NH_4]^{3-}$ ; 1342.4  $[WP5 - NH_4]^{-}$ .



*Fig. S23*. Partial <sup>1</sup>H NMR (400 Hz, D<sub>2</sub>O, rt) spectra: (a) **WP5** + 2 + paraquat; (b) **WP5**; (c) **WP5** + 2; (d) paraquat.



*Fig. S24*. Photographs: (a) WP5; (b) 1; (c) WP5 and 1; (d) WP5, 1 and paraquat.

- 5. References
- S1. (a) T. Ogoshi, S. Kanai, S. Fujinami, T. A. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.*, 2008, 130, 5022; (b) G. Yu, M. Xue, Z. Zhang, J. Li, C. Han and F. Huang, *J. Am. Chem. Soc.*, 2012, 134, 13248.
- S2. K. Liu, Y. Yao, C. Wang, X. Zhang, Y. Liu and Z. Li, Chem-Eur. J., 2012, 18, 8622.
- S3. J.-K. Kim, E. Lee, Y.-H. Jeong, J.-K. Lee, W.-C. Zin and M. Lee, J. Am. Chem. Soc., 2007, 129, 6082.
- S4. P. R. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi and D. J. Williams, *J. Am. Chem. Soc.*, 1996, **118**, 4931.