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Construction of a pillar[6]arene based water-soluble supramolecular pseudopolyrotaxane driven by cucurbit[8]uril-enhanced π - π interaction

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Electronic Supplementary Information (12 pages)

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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. Water-soluble pillar[6]arene (**WP6**) was synthesized according to literature procedures.^{S1 1}H NMR and ¹³C NMR spectra were recorded on a Bruker Avance III-400 spectrometry. The 2D DOSY NMR spectrum was collected on a Bruker Avance DMX-500 spectrometer with internal standard TMS. 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 WATERS GCT Premier mass spectrometer. The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus.

2. Synthesis of compounds G, DIMBr and Np

Scheme S1. Synthetic route to G



1,4-Di(1H-imidazol-1-yl)butane (1.90 g, 10.0 mmol) and 2-(bromomethyl)naphthalene (6.60 g, 30.0 mmol) were added to acetonitrile (100 mL) and heated at reflux overnight under N₂ atmosphere. After the completion of the reaction, the cooled reaction mixture was filtered and washed with acetonitrile to afford **G** as a white solid (5.20 g, 83%). The ¹H NMR spectrum of **G** is shown in Fig. S1. ¹H NMR (400 MHz, DMSO- d_6 , 293 K) δ (ppm): 9.46 (s, 2H), 7.93 (m, 12H), 7.56 (m, 6H), 5.62 (s, 4H), 4.25 (s, 4H), 1.82 (s, 4H). The ¹³C NMR spectrum of **G** is shown in Fig. S2. ¹³C NMR (100 MHz, CDCl₃-d, 293 K) δ (ppm): 136.34, 132.16, 128.79, 127.85, 127.68, 127.61, 126.79, 126.76, 125.71, 52.14, 48.20, 26.06. LRESIMS is shown in Fig. S3: m/z 551.1 [M – Br]⁺. HRESIMS: m/z calcd for [M – Br]⁺ C₃₂H₃₂BrN₄, 551.1799; found 551.1792; error –1 ppm.



Fig. S1 ¹H NMR spectrum (400 MHz, DMSO- d_6 , 293 K) of **G**.



Fig. S3 Electrospray ionization mass spectrum of G. Assignment of the main peak: m/z 551.1 [M – Br]⁺.



1,4-Di(1H-imidazol-1-yl)butane (1.90 g, 10.0 mmol) and bromoethane (10.9 g, 100 mmol) were added to acetonitrile (100 mL) and heated at reflux overnight under N₂ atmosphere. After the completion of the reaction, the cooled reaction mixture was filtered and washed with acetonitrile to afford **DIMBr** as a white solid (3.80 g, 93%). The ¹H NMR spectrum of **DIMBr** is shown in Fig. S4. ¹H NMR (400 MHz, D₂O, 293 K) δ (ppm): 8.71 (s, 2H), 7.44 (t, *J* = 4 Hz, 2H), 7.40 (t, *J* = 4 Hz, 2H), 4.15 (m, 8H), 1.82 (m, 4H), 1.41 (t, *J* = 4 Hz, 6H). The ¹³C NMR spectrum of **DIMBr** is shown in Fig. S5. ¹³C NMR (100 MHz, D₂O, 293 K) δ (ppm): 134.94, 122.22, 122.16, 48.75, 44.91, 26.23, 14.41. LRESIMS is shown in Fig. S6: m/z 327.1 [M – Br]⁺. HRESIMS: m/z calcd for [M – Br]⁺ C₁₄H₂₄BrN₄, 327.1179; found 327.1183; error 1 ppm.





Fig. S6 Electrospray ionization mass spectrum of **G**. Assignment of the main peak: m/z 327.1 $[M - Br]^+$.

Scheme S3. Synthetic route to Np



2-(Bromomethyl)naphthalene (2.21 g, 10.0 mmol) and 1-methylimidazole (2.46 g, 30.0 mmol) were added to acetonitrile (100 mL) and heated at reflux overnight under N₂ atmosphere. After the completion of the reaction, the solvent was removed and the residue was washed with methylbenzene to afford **Np** as a yellow solid (2.78 g, 92%). The ¹H NMR spectrum of **Np** is shown in Fig. S7. ¹H NMR (400 MHz, D₂O, 293 K) δ (ppm): 8.69 (s, 1H), 7.90 (m, 3H), 7.85 (s, 1H), 7.55 (m, 2H), 7.49 (d, J = 4 Hz, 2H), 7.36 (s, 1H), 5.45 (s, 2H), 3.80 (s, 3H). The ¹³C NMR spectrum of **Np** is shown in Fig. S8. ¹³C NMR (100 MHz, D₂O, 293 K) δ (ppm): 135.98, 132.90, 132.82, 131.02, 129.11, 127.94, 127.71, 127.12, 126.99, 125.52, 123.75, 123.70, 122.20, 122.25, 52.81, 35.65. LRESIMS is shown in Fig. S9: m/z 223.1 [M – Br]⁺. HRESIMS: m/z calcd for [M – Br]⁺ C₁₅H₁₅N₂, 223.1230; found 223.1232; error 1 ppm.





Fig. S9 Electrospray ionization mass spectrum of Np. Assignment of the main peak: m/z 223.1 [M – Br]⁺.

3. Isothermal titration calorimetry (ITC) experiments



Fig. S10 Microcalorimetric titration of Np with WP6 in water at 298.15 K. Top: raw ITC data for 29 sequential injections (10 μ L per injection) of a Np solution (10.0 mM) into a WP6 solution (0.50 mM); Bottom: net reaction heat obtained from the integration of the calorimetric traces.



Fig. S11 Microcalorimetric titration of Np with CB[8] in water at 298.15 K. Top: raw ITC data for 29 sequential injections (10 μ L per injection) of a Np solution (10.0 mM) into a CB[8] solution (0.50 mM); Bottom: net reaction heat obtained from the integration of the calorimetric traces.



Fig. S12 Microcalorimetric titration of **DIMBr** with **WP6** in water at 298.15 K. Top: raw ITC data for 29 sequential injections (10 μ L per injection) of a **DIMBr** solution (10.0 mM) into a **WP6** solution (0.50 mM); Bottom: net reaction heat obtained from the integration of the calorimetric traces.

4. Reference:

S1. T. Ogoshi, M. Hashizume, T.-a. Yamagishi and Y. Nakamoto, Chem. Commun., 2010, 46, 3708-3710.