Electronic Supplementary Material (ESI) for RSC Advances.

Pillar[7]arene-based host–guest complex in water: dual-responsiveness and application in controllable self-assembly†

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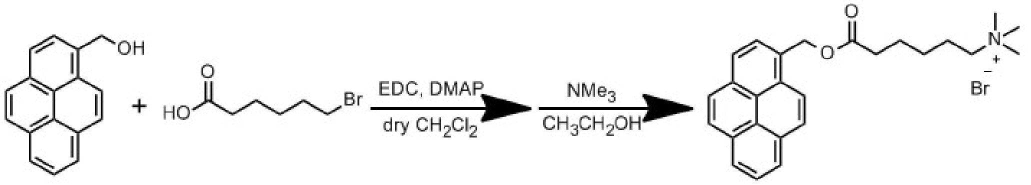
Electronic Supplementary Information (8 pages)

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.[S1] 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 spectrophotometerora Bruker Avance DMX 500 spectrophotomete. 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. Transmission electron microscopy investigations were carried out on a HITACHI HT-7700 instrument. 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. Synthesis of **G***



Scheme S1. Synthetic route to **G**.

To a solution of 1-pyrenemethanol (3.00 g, 0.0130 mol) and 6-bromohexanoic acid (2.50 g, 0.0130 mol) in dry CH_2Cl_2 (300 mL), 4-dimethylaminopyridine (DMAP, catalytic amount) and 1-(3'-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 4.60 g, 0.026mol) were added under nitrogen atmosphere. The mixture was stirred overnight at room temperature. The solution was evaporated under vacuum and the residue was purified by flash column chromatography on silica gel (dichloromethane/petroleum ether = 2:1, *v*/*v*) to get an intermediate product. Then the intermediate was dissolved in ethanol. After treatment with excess trimethylamine (4 equiv), a colorless solid was obtained. Then the colorless solid was recrystallized in CH_3CN to afford **G** (2.86 g, 47%), m.p. 217.9–218.4 ºC. The proton NMR spectrum of **G** is shown in Fig. S1. ^1H NMR (400 MHz, DMSO-d_6, room temperature) δ (ppm): 8.38–8.31 (m, 5H), 8.25–8.20 (m, 2H), 8.15–8.11 (m, 2H), 5.85 (s, 2H), 3.21–3.17 (m, 2H), 2.99 (s, 9H), 2.44 (t, J = 8 Hz,2H), 1.65–1.57 (m, 4H), 1.29–1.22 (m, 2H). The ^{13}C NMR spectrum of **G** is shown in Fig. S2. ^{13}C NMR (100 MHz, DMSO-d_6, room temperature) δ (ppm): 172.71, 131.03, 130.67, 130.16, 129.42, 128.81, 128.03, 127.85, 127.72, 127.30, 126.47, 125.64, 125.51, 124.69, 123.91, 123.69, 123.10, 64.96, 63.92, 52.00, 33.13, 25.06, 23.83, 21.66. LRESIMS is shown in Fig. S3: *m*/*z* 388.2 [M –Br]$^+$ (100%). HRESIMS: *m*/*z* calcd for [M – Br]$^+$ $C_{26}H_{30}NO_2^+$, 388.2277; found 388.2280; error 0.8 ppm.

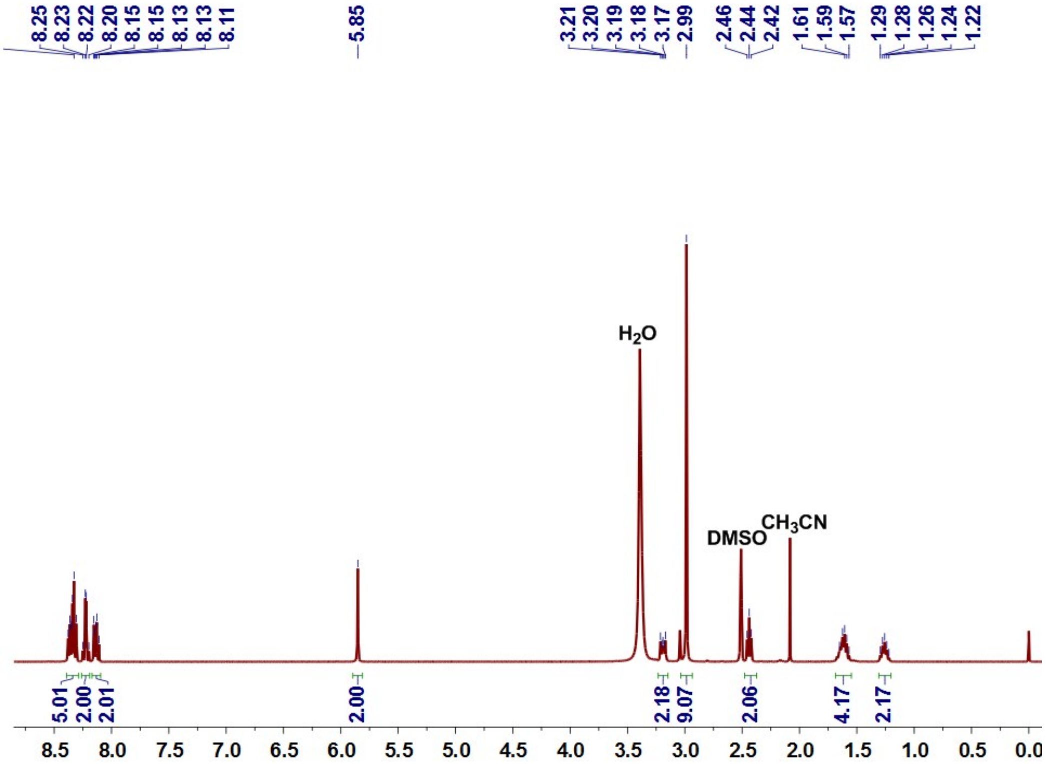


Fig. S1 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, room temperature) of **G**.

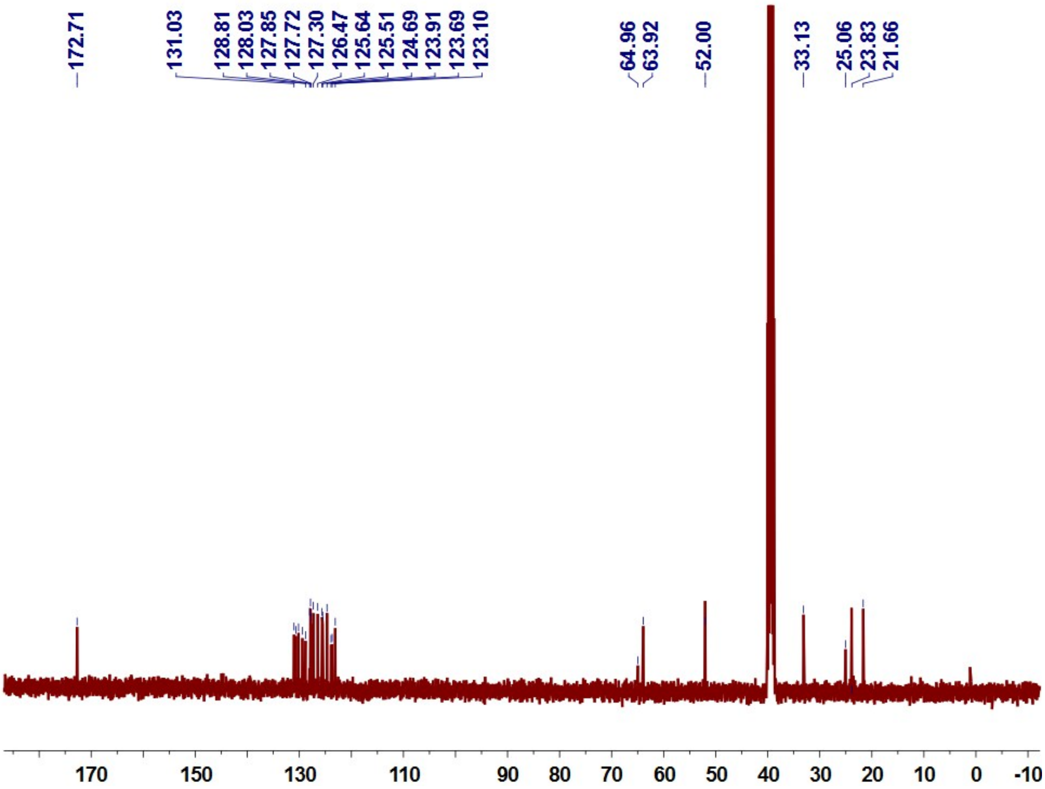


Fig. S2 ^{13}C NMR spectrum (100 MHz, DMSO-d_6, room temperature) of **G**.

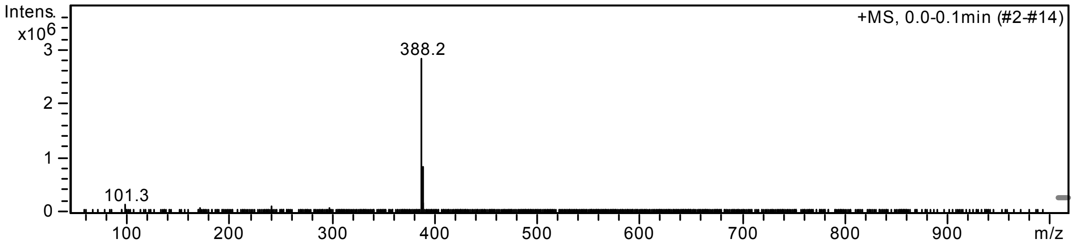


Fig. S3 Electrospray ionization mass spectrum of **G**. Assignment of main peaks: *m*/*z* 388.2 [M – Br]$^+$.

*3. ITC investigations of the host–guest complexation between **WP7** and **M***

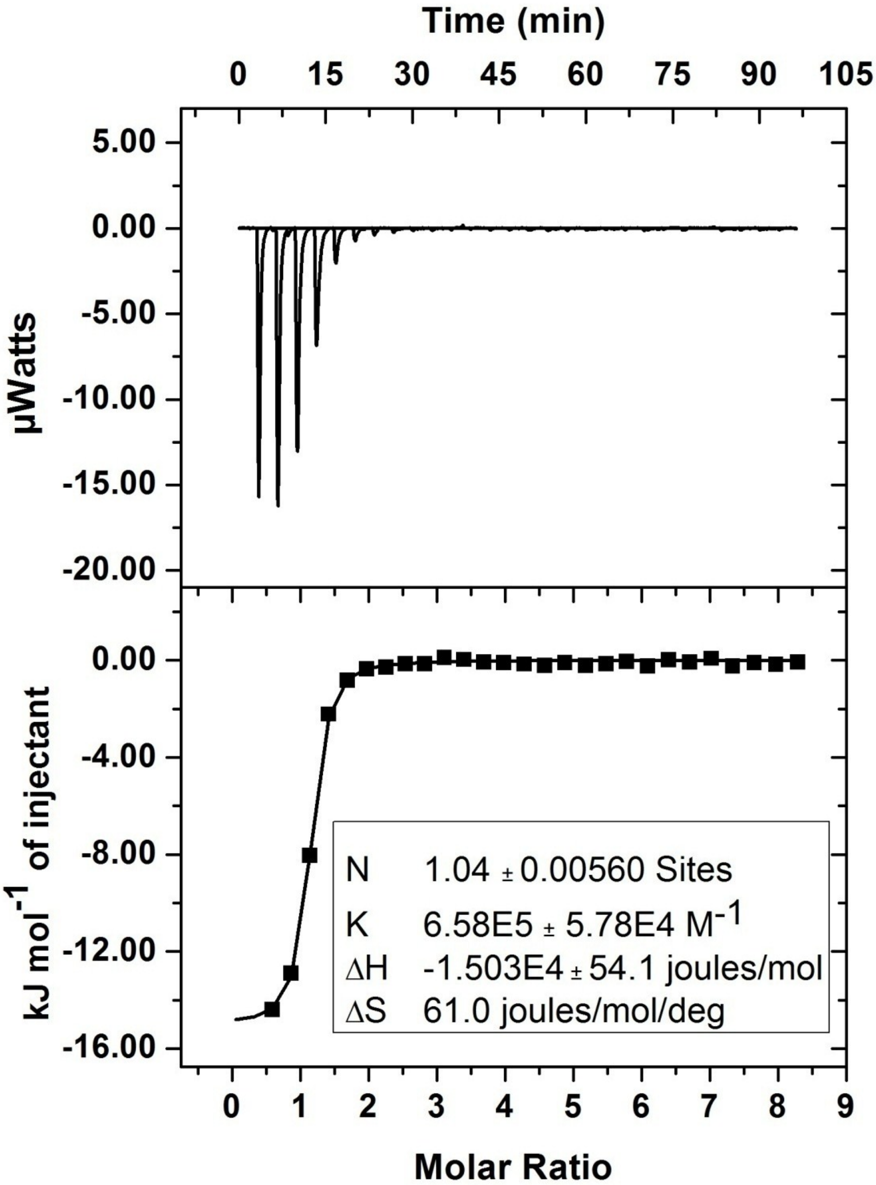


Fig. S4 Microcalorimetric titration of **M** (2.00 mM, 10 μL per injection) with **WP7** (0.100 mM) in water at 298.15 K.

*4. The color change of **G** with the UV irradiation*

Fig. S5 A photo to show the color change of **G** with the UV irradiation: (a) **G** after UV irradiation at 365 nm for 10 min; (b) **G** after UV irradiation at 365 nm for 1 min; (c) **G** after UV irradiation at 365 nm for 30 s; (d) **G**.

*5. Critical aggregation concentration (CAC) determinations of **G** and **WP7⊃G***

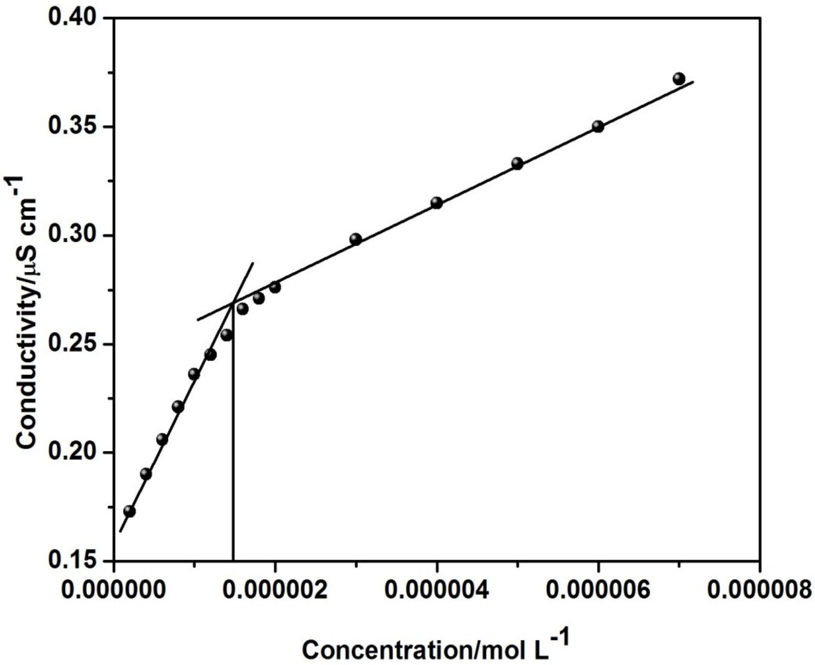


Fig. S6 The concentration-dependent conductivity of **G**. The critical aggregation concentration (CAC) was determined to be 1.48× 10^{-6} M.

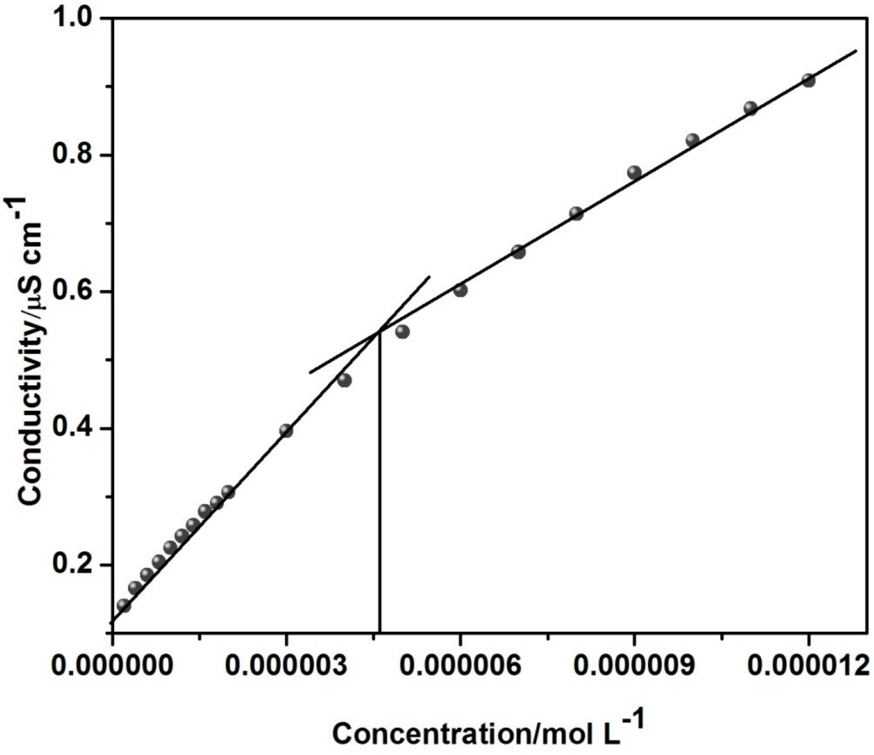


***Fig. S**7* The concentration-dependent conductivity of equimolar **WP7** and **G**. The critical aggregation concentration (CAC) was determined to be 4.65 × 10^{-6} M.

*6. Dynamic light scattering (DLS) results of **WP7⊃G***

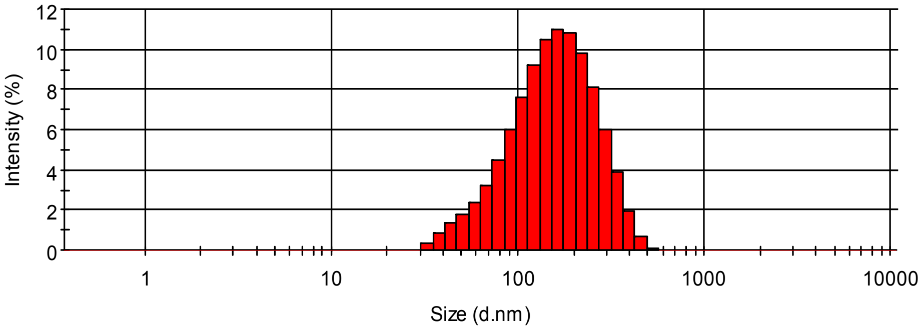


Fig. S8 DLS result of **WP7** (5.00× 10^{-5} M) and **G** (5.00 × 10^{-5} M). The average diameter of the vesicles was determined to be 172 nm.

*7. TEM image of **PyOH***

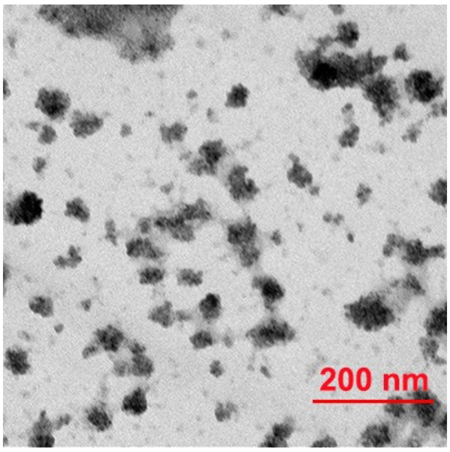


Fig. S9 Nanoparticles self-assembled from **PyOH**.

*8. ITC investigation of the host–guest complexation between **WP6** and **M***

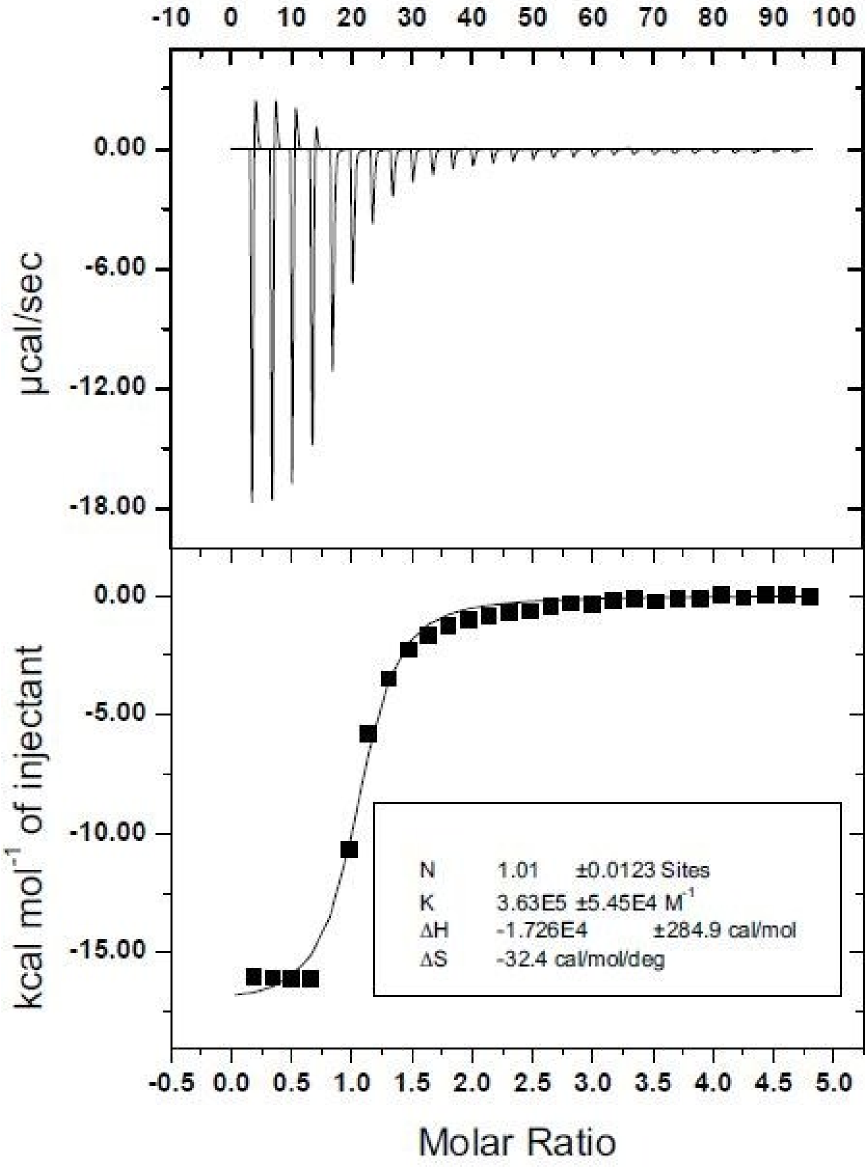


Fig. S10 Microcalorimetric titration of **M** (2.00 mM, 10 µL per injection) with **WP6** (0.100 mM) in water at 298.15 K.

9. Reference:

S1. Z. Li, J. Yang, G. Yu, J. He, Z. Abliz and F. Huang, *Org. Lett.*, 2014, **16**, 2066−2069.