Electronic Supplementary Material (ESI) for New Journal of Chemistry.

A water-soluble hybrid[4]arene: synthesis, host–guest complexation and application in construction of a supra-amphiphile

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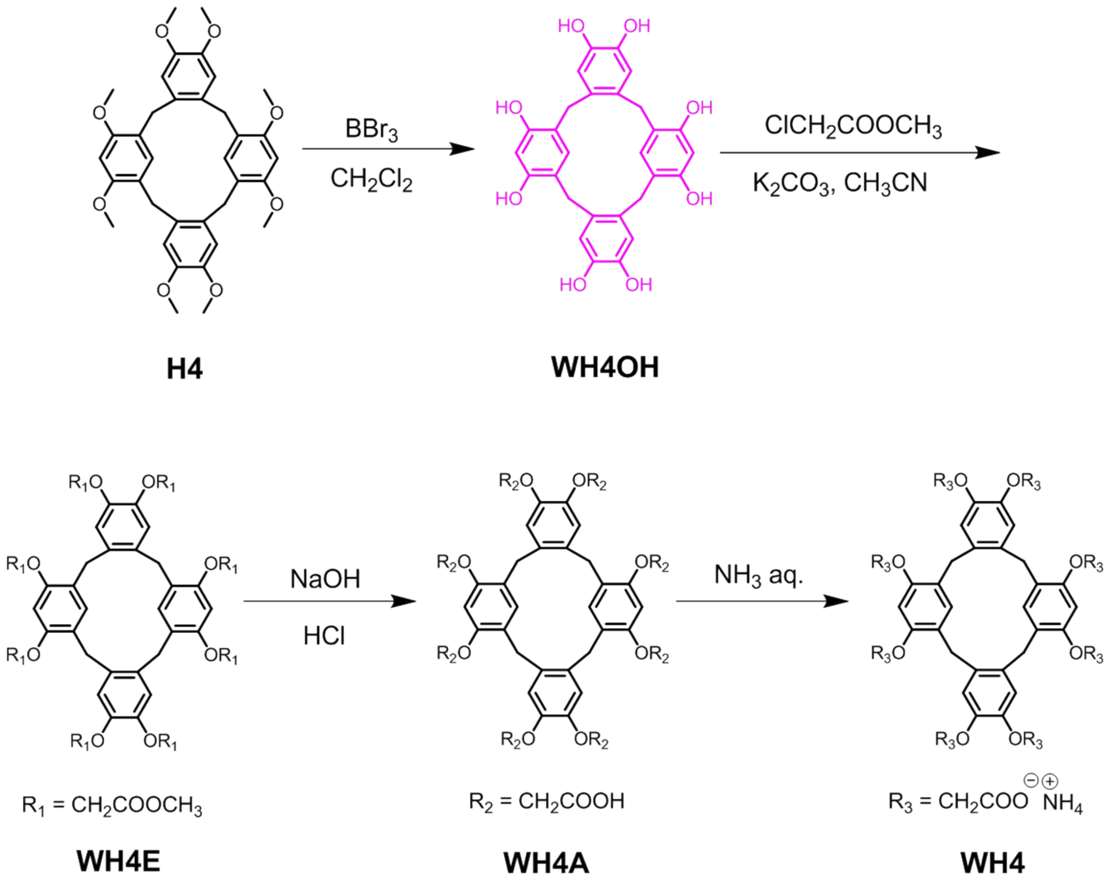
Electronic Supplementary Information (10 pages)

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. Compound **H4**[S1] was synthesized according to previous literature. NMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer or a Bruker Avance DMX 500 spectrophotometer with the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. 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). 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. The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. The ITC experiment was performed on a VP-ITC micro-calorimeter (Microcal, USA). The critical aggregation concentration (CAC) value of **WH4⊃G1** were determined on a DDS-307 instrument. Transmission electron microscopy (TEM) investigation was carried out on a JEM-1200EX instrument.

*2. Synthesis of water-soluble hybrid[4]arene **WH4***



Scheme S1. Synthetic route to water-soluble hybrid[4]arene **WH4**.

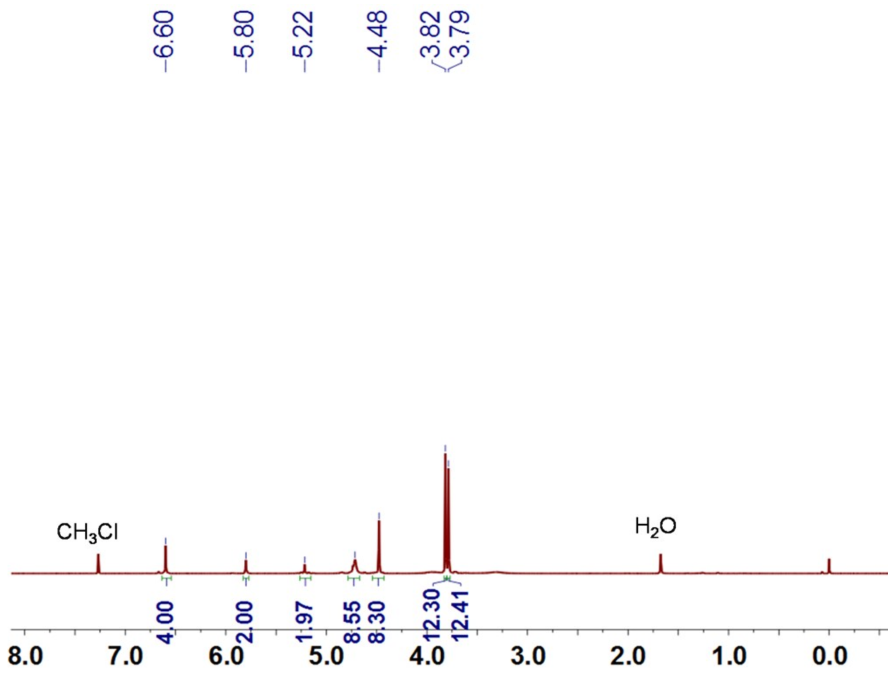


Fig. S1. ^{1}H NMR spectrum (400 MHz, chloroform-*d*, room temperature) of **WH4E**.

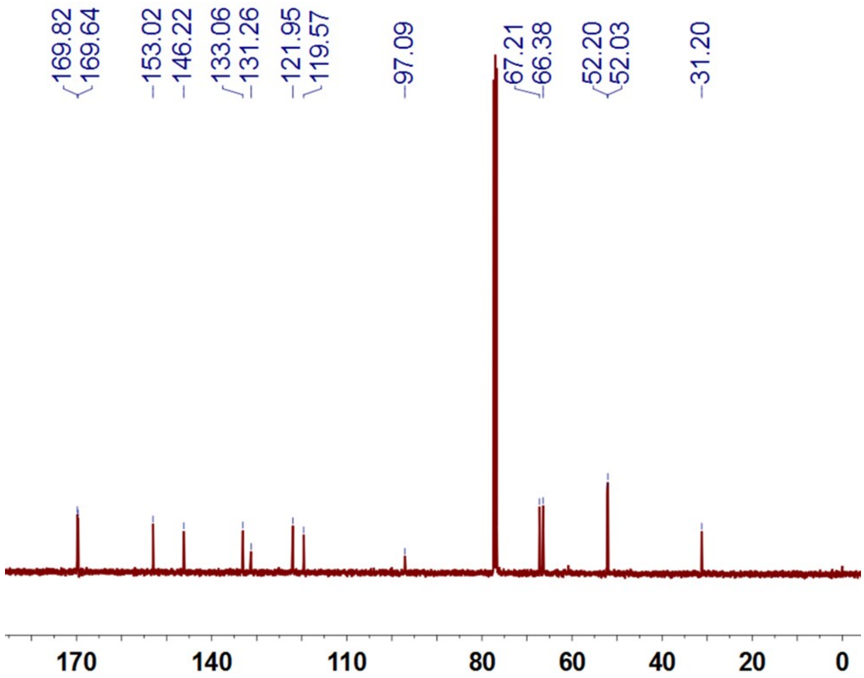


Fig. S2. ^{13}C NMR spectrum (100 MHz, chloroform-*d*, room temperature) of **WH4E**.

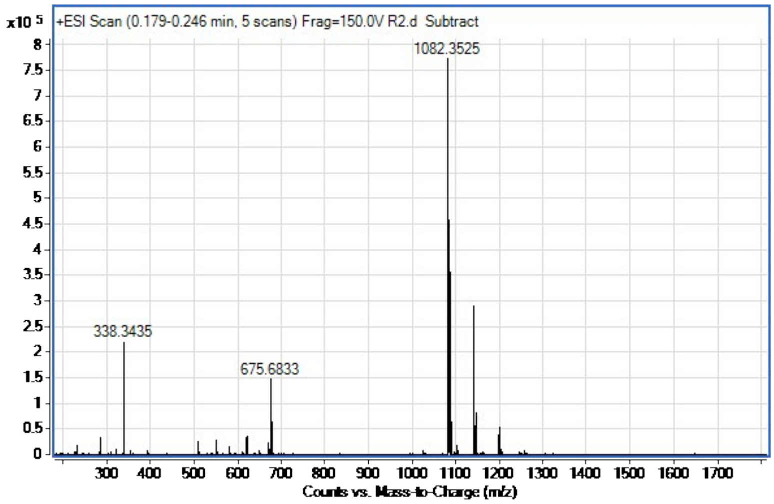


Fig. S3. Electrospray ionization mass spectrum of **WH4E**. Assignment of the main peak: *m*/*z* 1082.3525 $[M + NH_4]^+$.

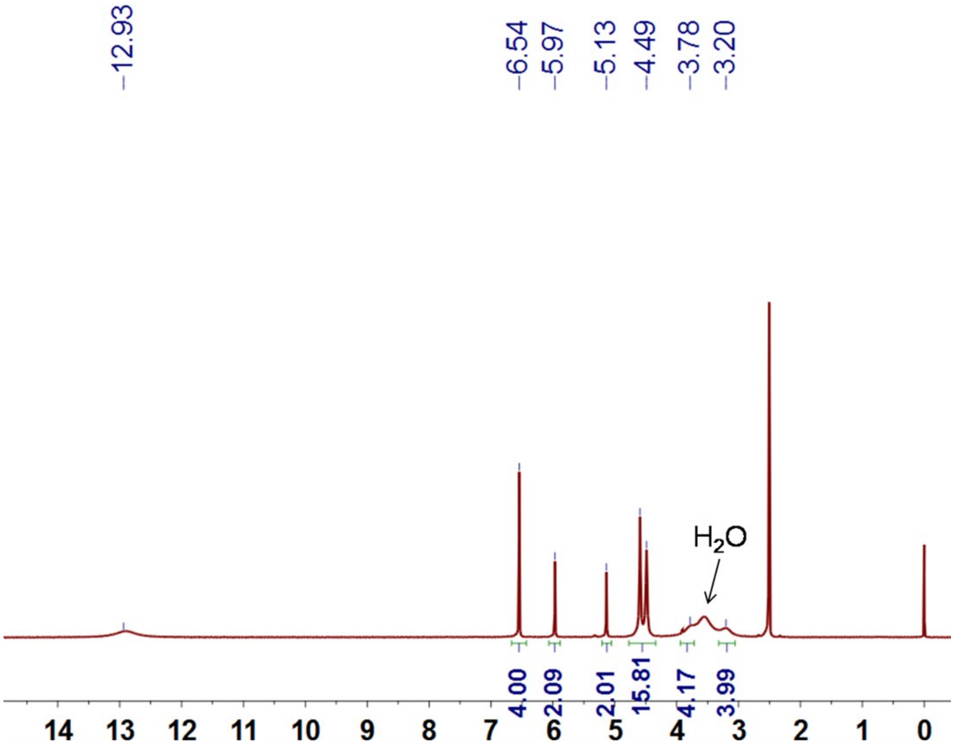


Fig. S4. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, room temperature) of **WH4A**.

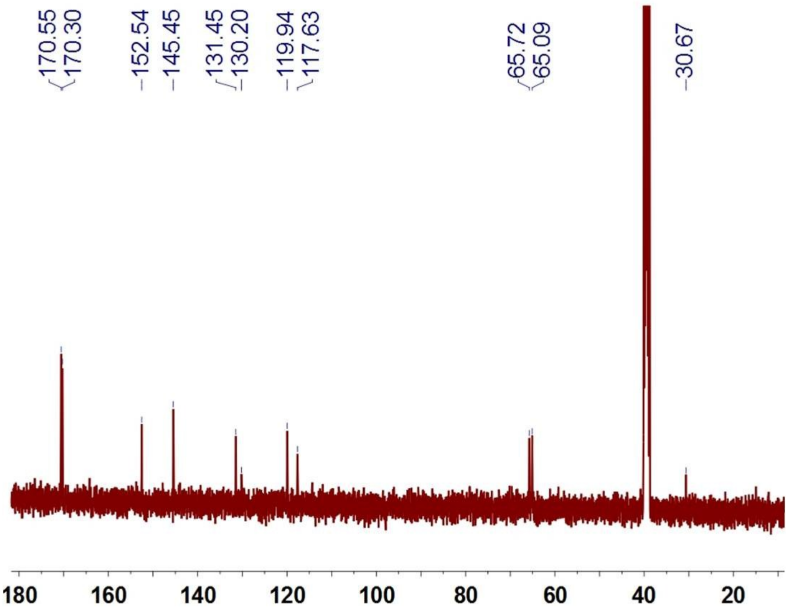


Fig. S5. ^{13}C NMR spectrum (100 MHz, DMSO-d_6, room temperature) of **WH4A**.

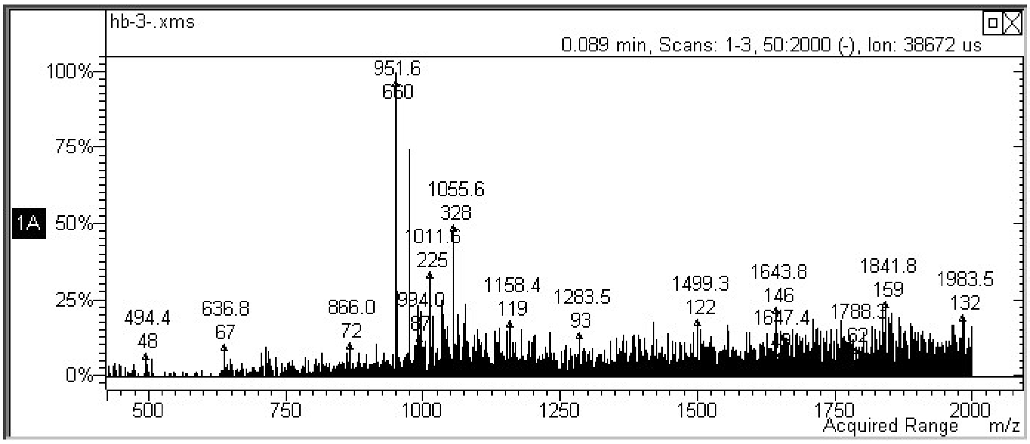


Fig. S6. Electrospray ionization mass spectrum of **WH4A**. Assignment of the main peak: *m*/*z* 951.6 $[M-H]^{-}$.

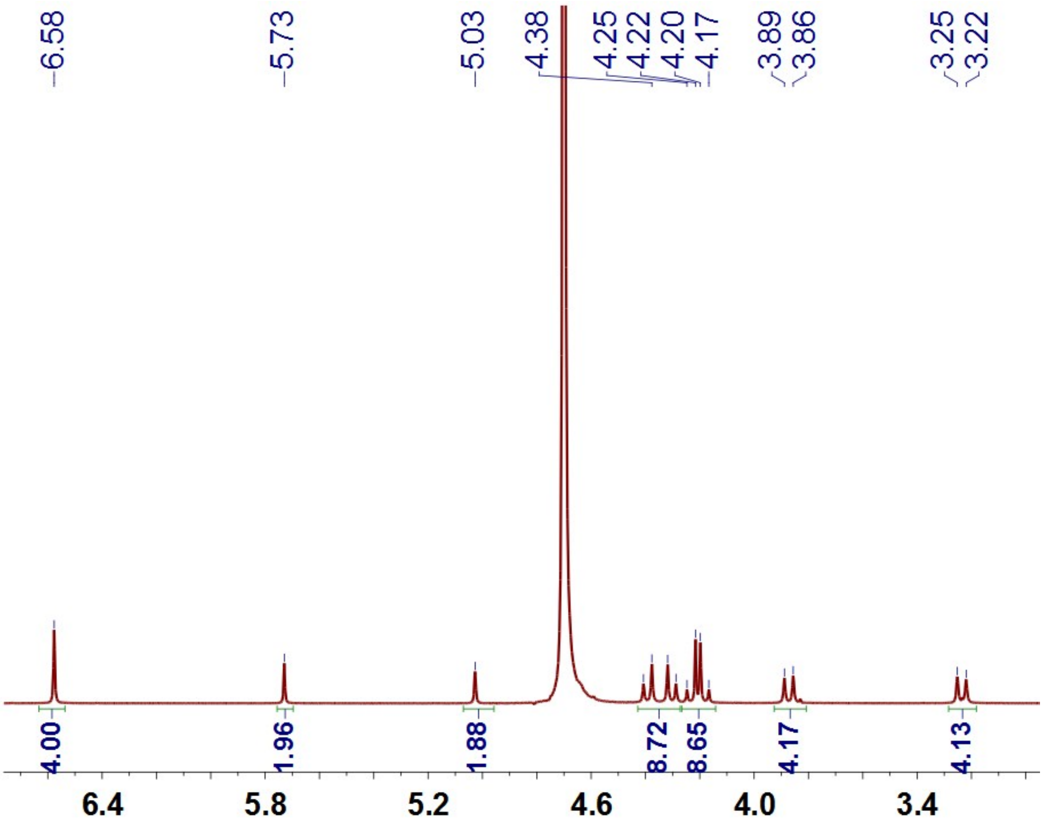


Fig. S7. ^{1}H NMR spectrum (400 MHz, D_2O, room temperature) of **WH4**.

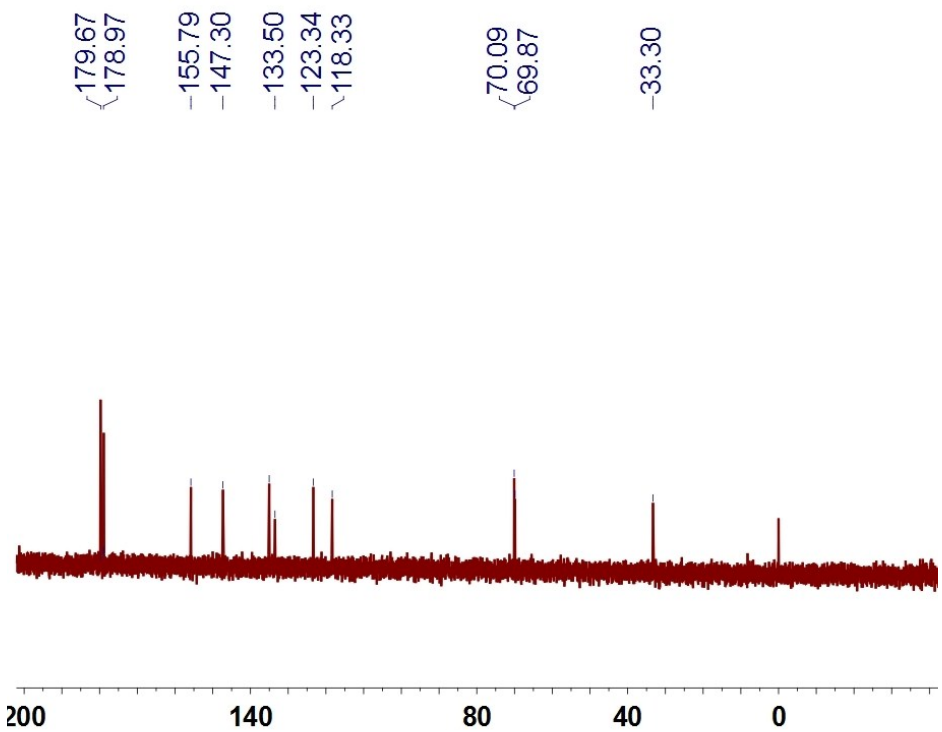


Fig. S8. ^{13}C NMR spectrum (100 MHz, D_2O, room temperature) of **WH4**.

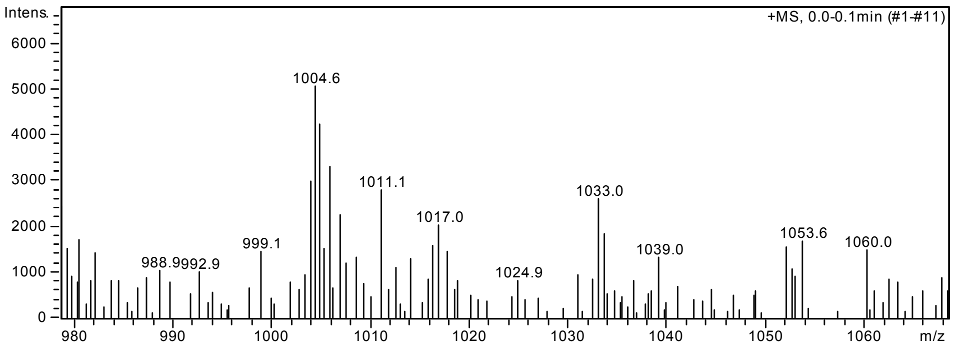


Fig. S9. Electrospray ionization mass spectrum of **WH4**. Assignment of the main peak: *m*/*z* 1004.6 $[M - 5NH_3 + H]^+$.

*3. Measurement of association constant between **WH4** and **G.***

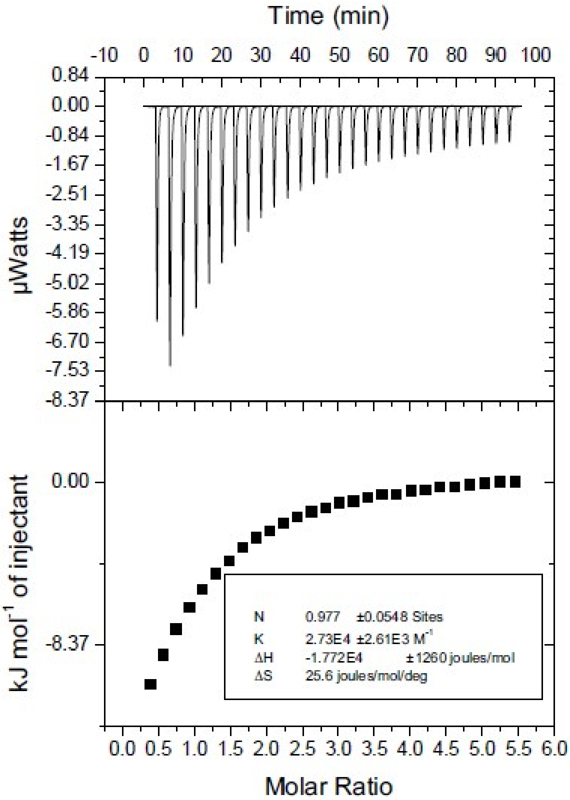


Fig. S10. Microcalorimetric titration of **G** with **WH4** in water at 303.15 K. (Top) Raw ITC data for 26 sequential injections (10 μL per injection) of a **WH4** solution (2.00 mM) into a **G** solution (0.100 mM). (Bottom) Net reaction heat obtained from the integration of the calorimetric traces.

*4. Critical aggregation concentration (CAC) determination of **G1** and **WH4⊃G1***

Some parameters such as the conductivity, fluorescence intensity, osmotic pressure and surface tension of the solution change sharply around the critical aggregation concentration. The dependence of the solution conductivity on the solution concentration is used to determine the critical aggregation concentration. Typically, the slope of conductivity versus the concentration below CAC is steeper than the slope above the CAC. Therefore, the junction of the conductivity-concentration plot represents the CAC value. To measure the CAC values of **WH4⊃G1**, the conductivity of the equimolar solutions of **WH4** and **G** at different concentrations (from 0 to 0.100 mM) was determined. By plotting the conductivity versus the concentration, we estimated the CAC value of **WH4⊃G1**.[S2]

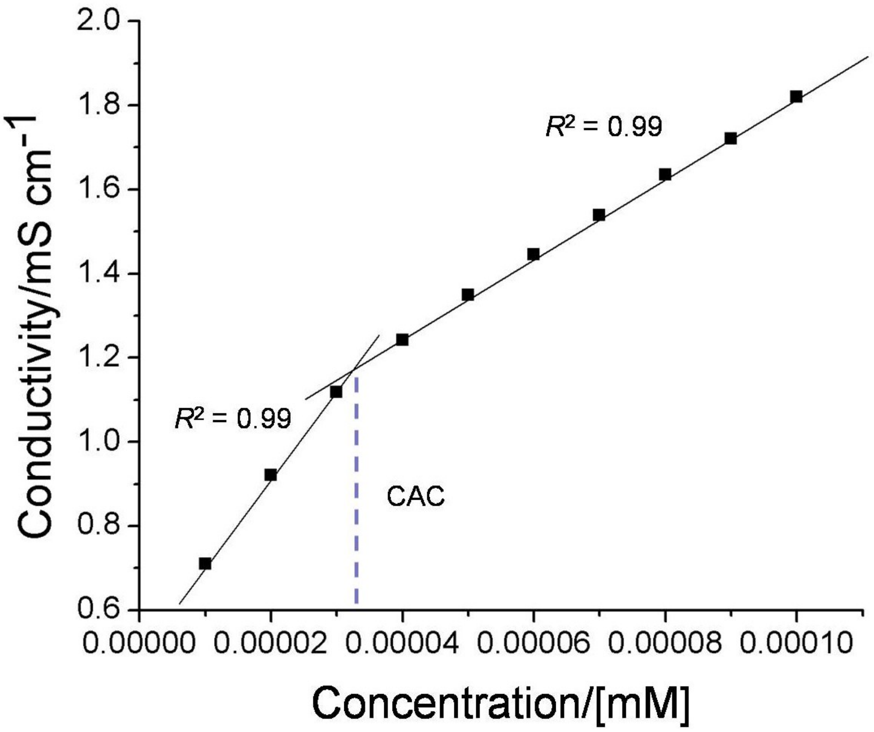


Fig. S11. The concentration-dependent conductivity of **WH4⊃G1**. The critical aggregation concentration (CAC) was determined to be 3.27×10^{-5} M.

*7. The color changes of the aqueous solutions upon complexation between **WH4** and **G**.*

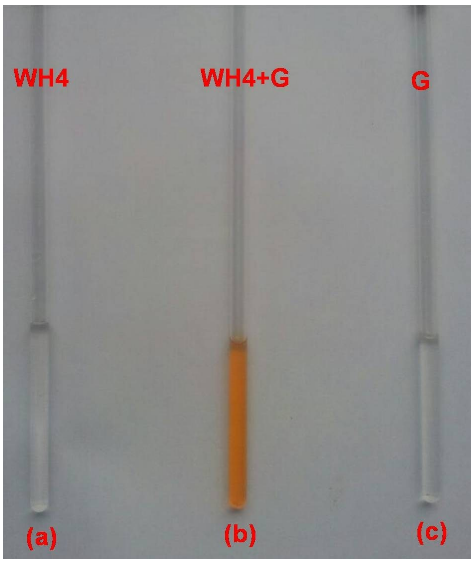


Fig. S12. The photograph to show the color changes of the aqueous solutions upon complexation between **WH4** and **G**: (a) **WH4**; (b) **WH4 + G**; (c) **G**.

References:

S1. T. Boinski, A. Cieszkowski, B. Rosa and A. Szumna, *J. Org. Chem*., 2015, **80**, 3488–3495.

S2 Z. Li, J. Yang, G. Yu, J. He, Z. Abliz and F. Huang, *Org. Lett*., 2014, **16**, 2066–2069.