Formation of a [2]pseudorotaxane based on a pillar[5]arene and a rigid guest in solution and in the solid state

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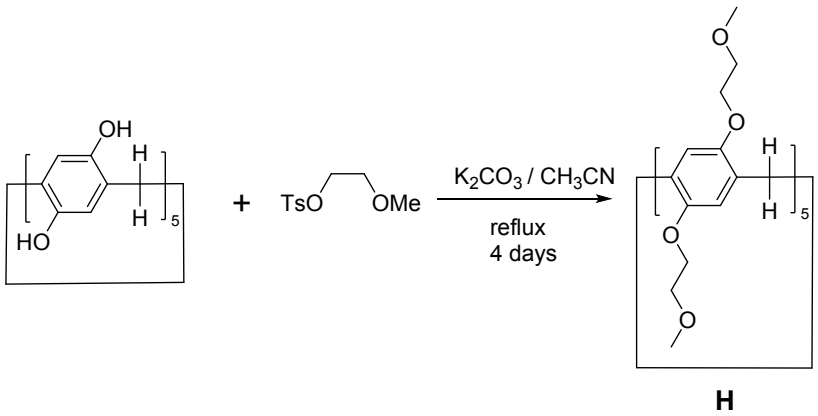
Electronic Supplementary Information (13 pages)

1. Materials and methods

Pillar[5]arene **H**[S1] and guest **G1**[S2] were synthesized according to the literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. ^{1}H NMR spectra were collected on a temperature-controlled 400 MHz spectrometer. Low-resolution electrospray ionization (LRESI) 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. The crystals data were collected on an Oxford Diffraction Xcalibur Atlas Gemini ultra. The crystal structures were solved by SHELXS-97 and refined by SHELXL-97. The fluorescence experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan).

*2. Synthetic route to pillar[5]arene **H***



Scheme S1 Synthetic route to pillar[5]arene **H**.

*3. Synthesis of pillar[5]arene **H***

per-Hydroxylated pillar[5]arene (0.42 g, 0.68 mmol) was dissolved in CH_3CN (50 mL). K_2CO_3 (2.25 g, 16.30 mmol) was added and the reaction mixture was stirred. Then 2-methoxyethyl *p*-toluenesulfonate (4.10 g, 21.30 mmol) was added and the reaction mixture was stirred under N_2 at reflux for 5 days. The solvent was evaporated and the residue was dissolved in CH_2Cl_2. The resultant solution was washed with H_2O and brine. The organic phase was collected, dried over anhydrous Na_2SO_4 and concentrated to give a crude solid. Column chromatography (silica gel; CH_2Cl_2 : CH_3OH =50 : 1) afforded a light yellow solid (150 mg, 18.46%).The ^1H NMR spectrum of pillar[5]arene **H** is shown in Figure S1. ^1H NMR (400 MHz, CD_3CN, room temperature) δ (ppm): 6.96 (10 H, s), 4.00 (20 H, s), 3.74 (20 H, d, J = 4.2 Hz), 3.72 (10 H, s), 3.38 (30 H, s).

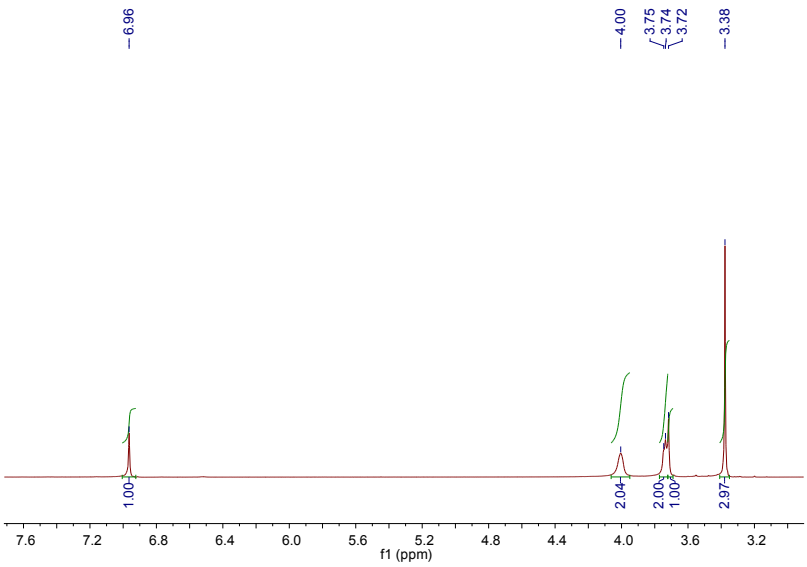


Fig. S1 ^{1}H NMR spectrum (400 MHz, $CDCN_3$, room temperature) of pillar[5]arene **H**.

4. X-ray crystal data of ***H⊃G1***

Crystal data of **H⊃G1**: red, $C_{168}H_{217}F_{24}O_{40}N_7P_4$, *FW* 3554.37, triclinic, space group *P-1*, a = 12.6852(6), b = 17.3581(6), c = 21.7669(9) Å, α = 104.590(3)°, β = 100.420(4)°, γ = 95.616(3)°, V = 4509.7(3) Å^3, Z = 1, D_c = 1.309 g cm^{-3}, T = 170 K, μ = 0.141 mm^{-1}, 11015 measured reflections, 18372 independent reflections, 384 parameters, 3 restraints, F(000) = 1870.0, R_1 = 0.1206, wR_2 = 0.0708 (all data), R_1 = 0.2313, wR_2 = 0.1904 [$I > 2\sigma(I)$], max. residual density 1.309 e·Å^{-3}, and goodness-of-fit (F^2) = 1.042. CCDC-1001509.

5. Electrospray ionization mass spectrometry of an equimolar solution of ***H*** *and* ***G1***

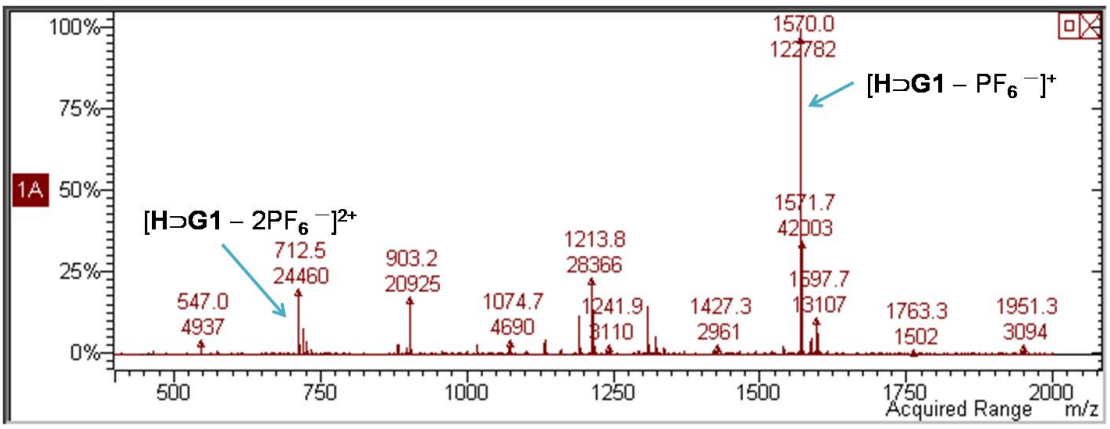


Fig. S2 Electrospray ionization mass spectrometry of an equimolar solution of **H** and **G1**.

*6. NOESY NMR analysis of **H⊃G1***

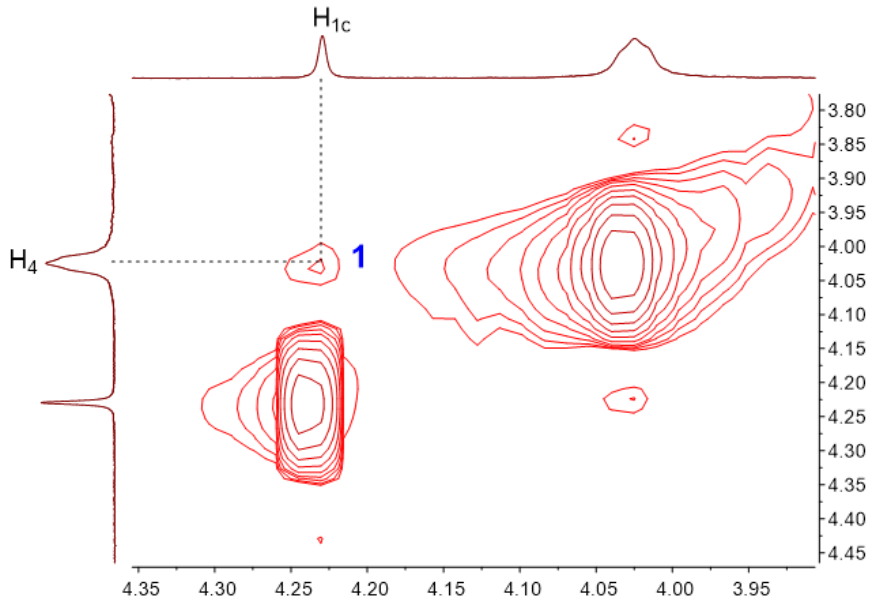


Fig. S3 Partial NOESY NMR analysis of **H⊃G1**(3.00 mM) in CD_3CN with a mixing time of 800 ms (500 MHz, 298 K).

7. A photo showing color changes after host–guest complexation

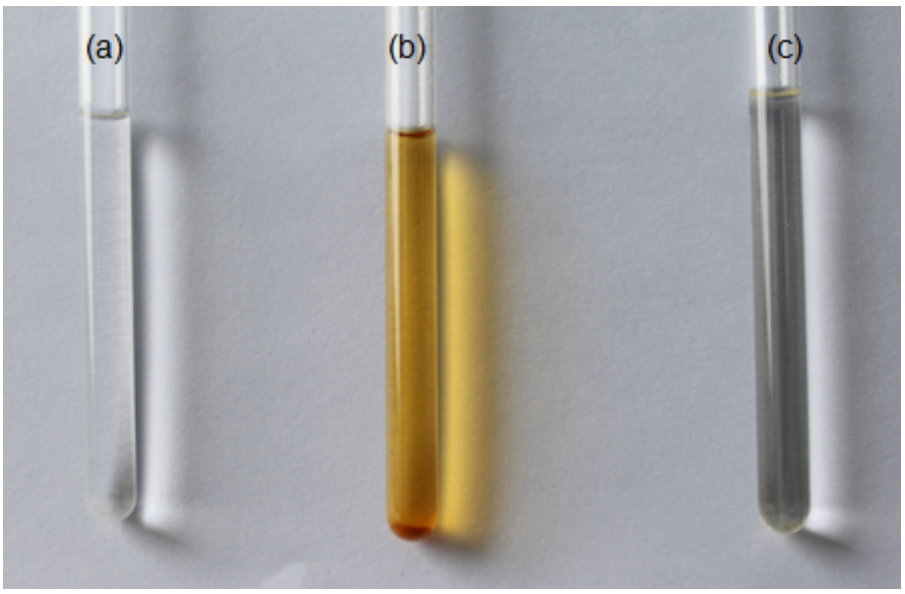


Fig. S4 A photo showing color changes after host–guest complexation in acetonitrile: (a) **H** alone; (b) an equimolar solution of **H** and **G1**; (c) **G1** alone;

*8. Fluorescence titration experiments of **H**, **G1** and **G2** in acetonitrile*[S3]

To determine the stoichiometry and association constant for the complexation between **H** and **G1** (or **G2**), fluorescence titration experiments were done with solutions which had a constant concentration of **H** (1.00×10^{-5} M) and varying concentrations of **G1** (or **G2**). By a non-linear curve-fitting method, the association constant (K_a) of **H⊃G1** or **H⊃G2** was determined. By a mole ratio plot, 1:1 stoichiometry was obtained for the complexations between **H** and **G1**, and between **H** and **G2**.

The non-linear curve-fittings were 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 ΔF is the fluorescence intensity changes at 326 nm at $[G]_0$, ΔF_∞ is the fluorescence intensity changes at 294 nm when **H** is completely complexed, $[G]_0$ is the initial concentration of **G1** (or **G2**), and $[H]_0$ is the fixed initial concentration of **H**.

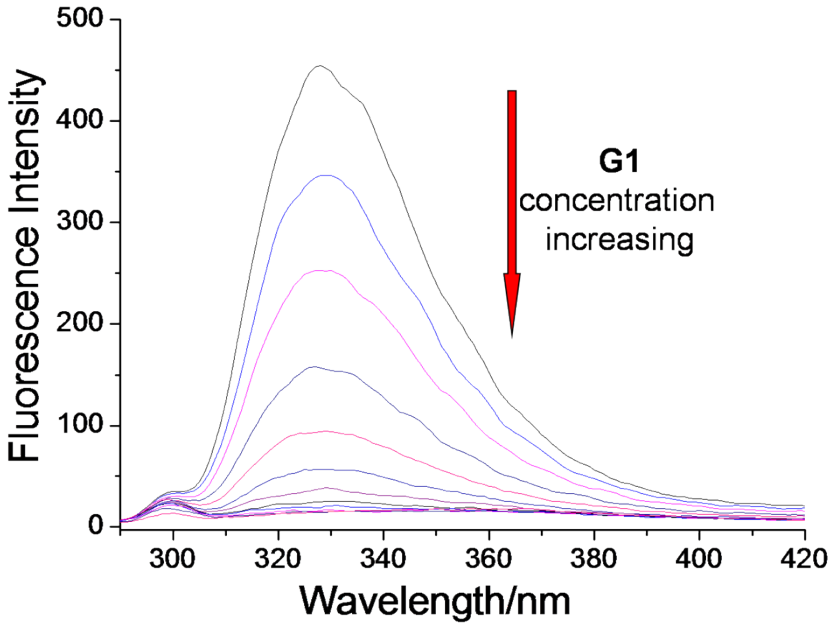


Fig. S5 Fluorescence spectra of **H** at a concentration of 1.00×10^{-5} M in acetonitrile solution at room temperature with different concentrations of **G1**: 0, 0.249, 0.498, 0.744, 0.990, 1.23, 1.48, 1.72, 1.96, 2.44, 3.38, 6.10 and 10.3×10^{-5} M in acetonitrile solution.

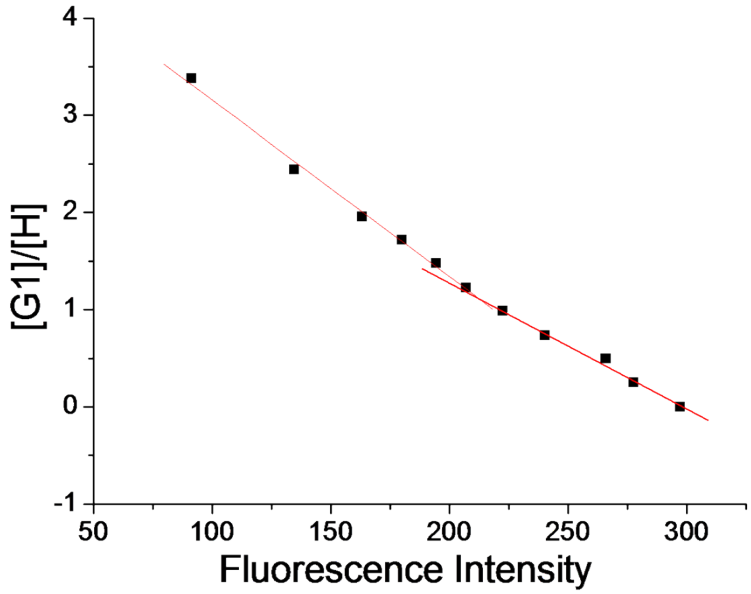


Fig. S6 Mole ratio plot for **H** and **G1**, showing a 1:1 complexation stoichiometry.

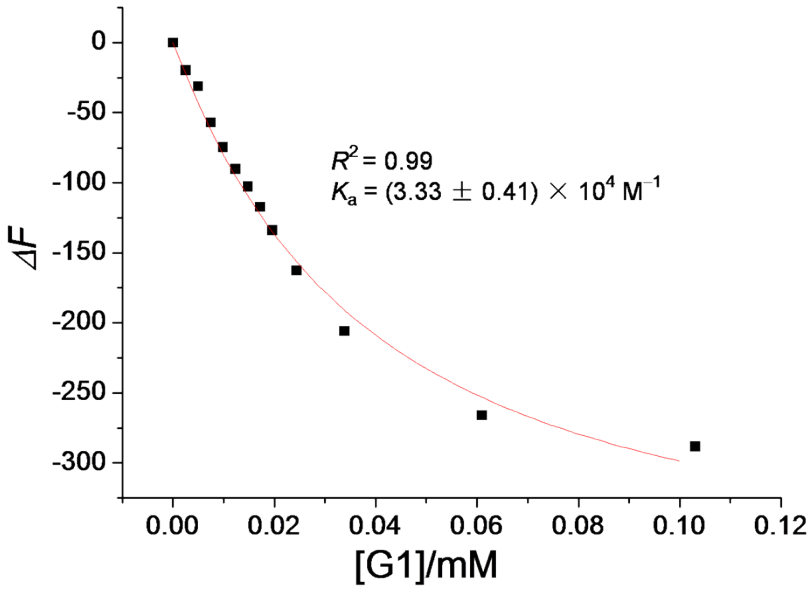


Fig. S7 The fluorescence intensity changes of **H** upon addition of **G1**. The red solid line was obtained from the non-linear curve-fitting method based on the above equation.

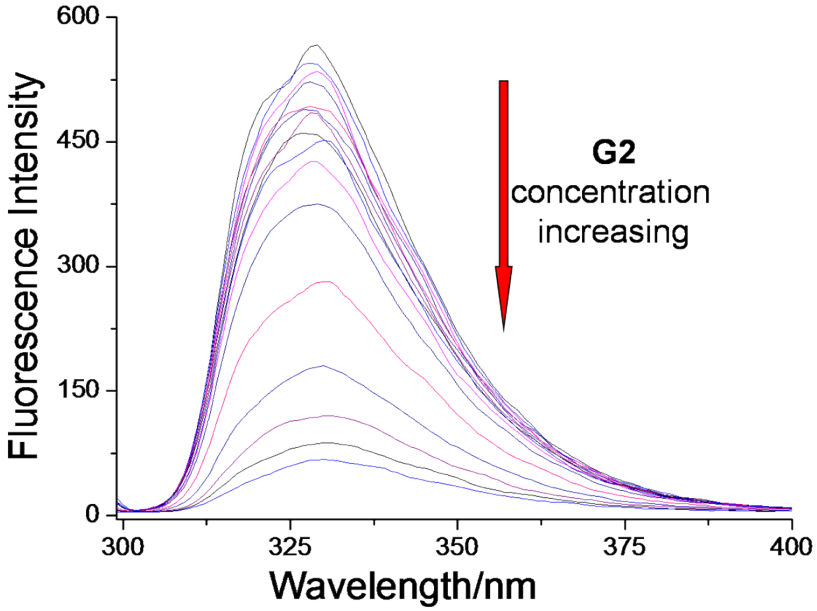


Fig. S8 Fluorescence spectra of **H** at a concentration of 1.00×10^{-5} M in acetonitrile solution at room temperature with different concentrations of **G2**: 0, 0.249, 0.498, 0.744, 0.990, 1.23, 1.48, 1.72, 1.96, 2.44, 3.38, 6.10 and 10.3×10^{-5} M in acetonitrile solution.

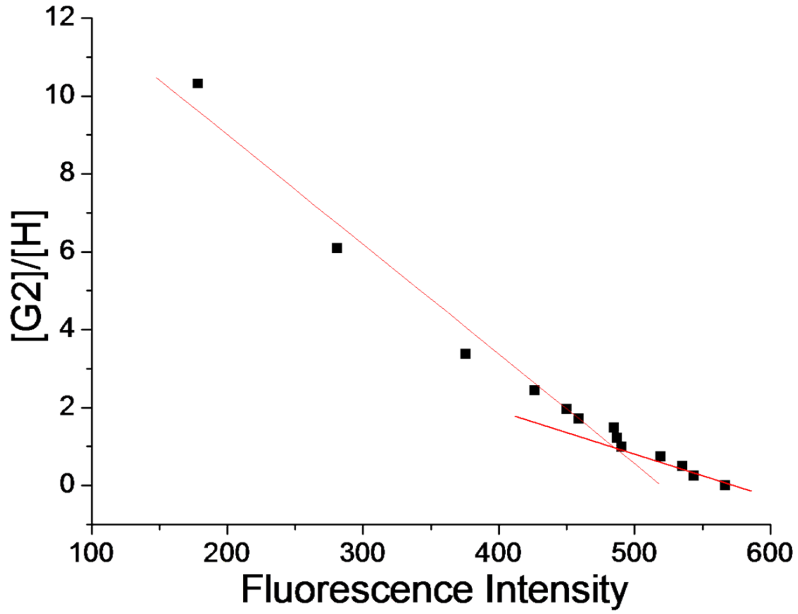


Fig. S9 Mole ratio plot for **H** and **G2**, showing a 1:1 complexation stoichiometry.

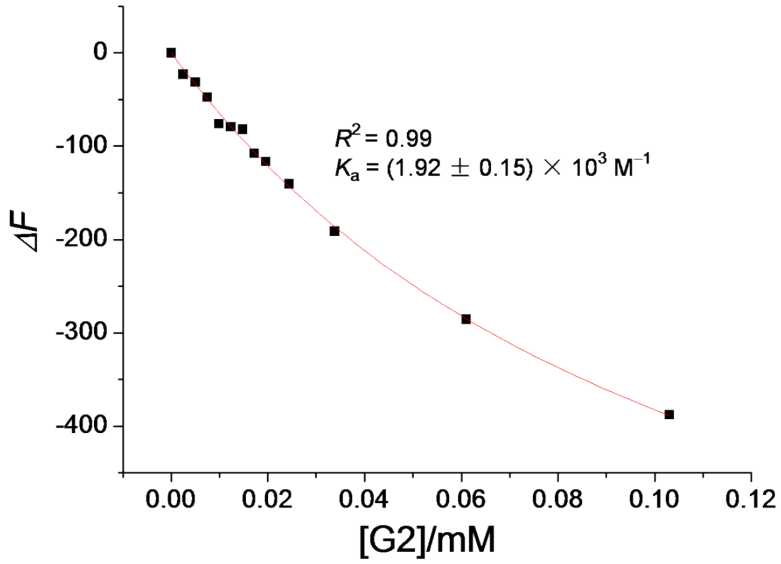


Fig. S10 The fluorescence intensity changes of **H** upon addition of **G2**. The red solid line was obtained from the non-linear curve-fitting method based on the above equation.

*9. Investigation on the complexation between pillar[5]arene **H** and **G2**.*

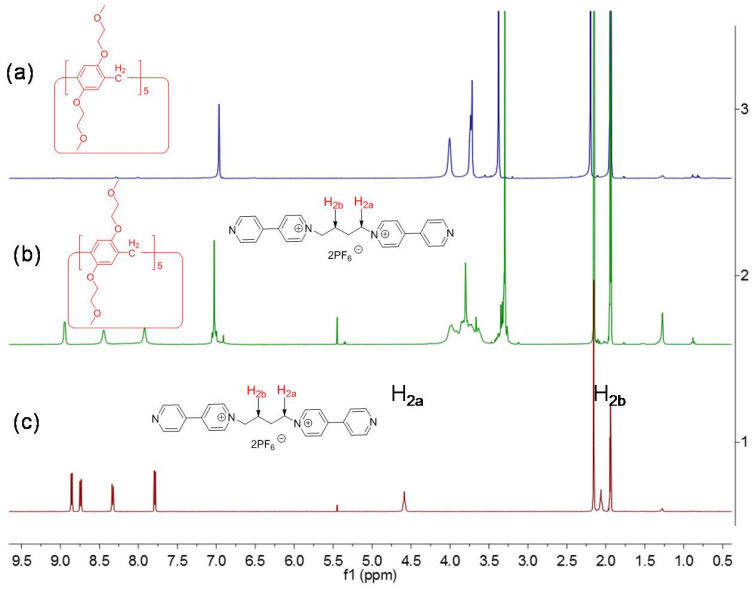


Fig. S11 Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 25 °C): (a) 1.00 mM **H**; (b) 1.00 mM **H** and **G2**; (c) 1.00 mM **G2**.

*10. Electrospray ionization mass spectrometry of an equimolar solution of **H** and **G2***

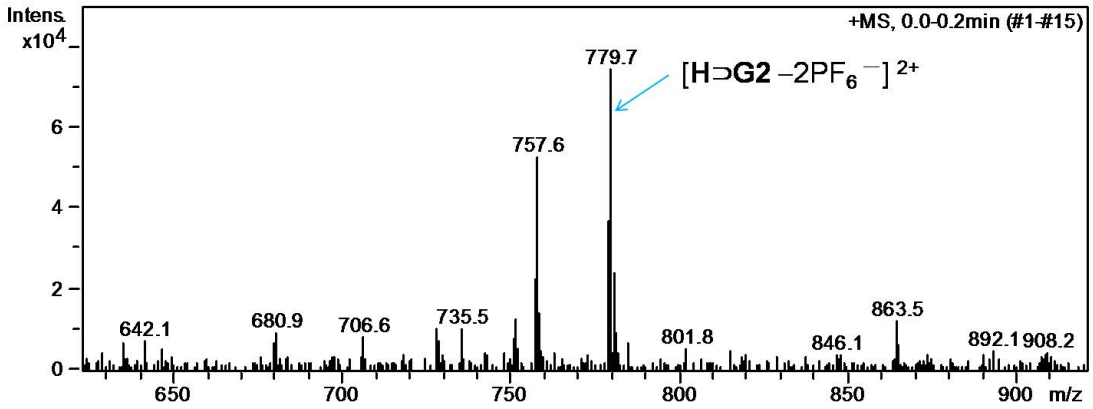
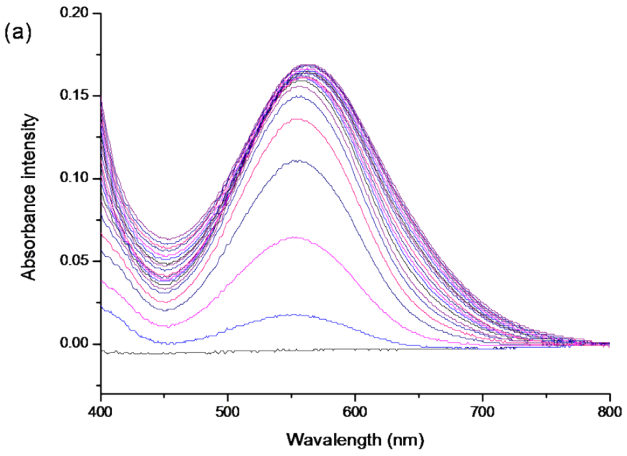


Fig. S12 Electrospray ionization mass spectrometry of an equimolar solution of **H** and **G2**.

*11. Determination of association constants of complexes **H⊃G1** in acetonitrile*

The association constants (Ka) of complexes **H⊃G1** were determined by probing the charge-transfer band of the complexes by UV-vis spectroscopy and employing a titration method. Progressive addition of an acetonitrile solution with high guest concentration and low host concentration to an acetonitrile solution with the same host concentration resulted in an increase of the intensity of the charge-transfer band of the complex. Treatment of the collected absorbance data with a non-linear curve-fitting program afforded the association constants (Ka): 5.0 (±0.8) $\times 10^4$ M^{-1}



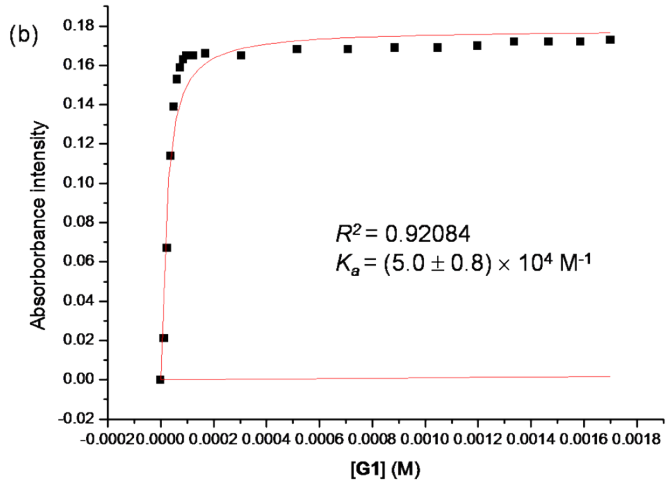


Fig. S13 (a) The absorption spectral changes of **H**(0.05 mM) upon addition of **G1** and (b) the absorbance intensity changes at λ= 560 nm upon addition of **G1**(from 0 to 1.7 mM). The red solid line was obtained from the non-linear curve-fitting.

*12. ^{1}H NMR titration of **H** with **G2***

^{1}H NMR titration was done with solutions which had a constant concentration of **G2** (1.00 mM) and varying concentrations of **H**. By a non-linear curve-fitting method, the association constant between the guest **G2** and host **H** was calculated.

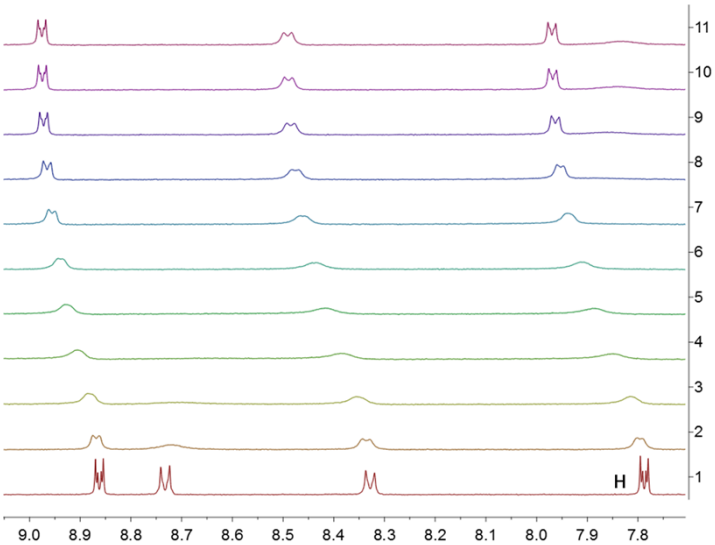


Fig. S14 ^{1}H NMR spectra (acetonitrile-d_3) of **G2** at a concentration of 1.0 mM with different concentrations of **H**.

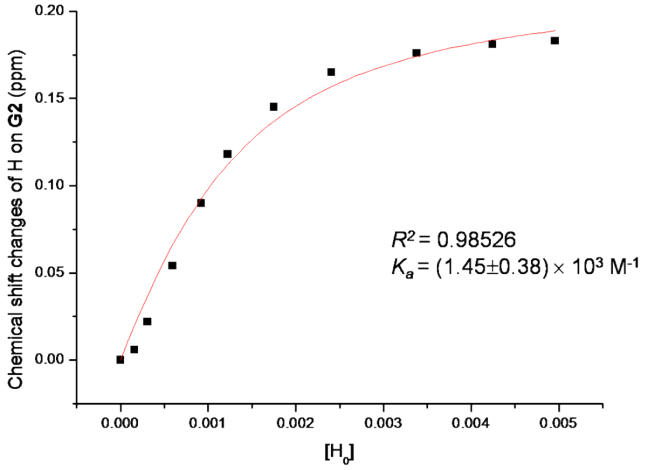


Fig. S15 The chemical shift changes of H on **G2** upon addition of **H**. The red solid line was obtained from the non-linear curve-fitting.

*13. Job plots of **H**⊃**G1** based on UV-vis spectroscopy data in acetonitrile*

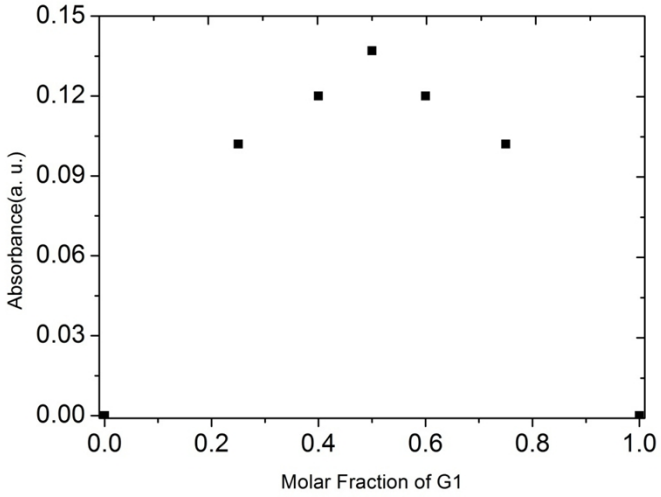


Fig. S16 Job plots showing the 1:1 stoichiometries of the complexes between **H** and **G1** in acetonitrile.([**H**]+[**G1**]=2.00 Mm)

14. Partial [1]H NMR spectra

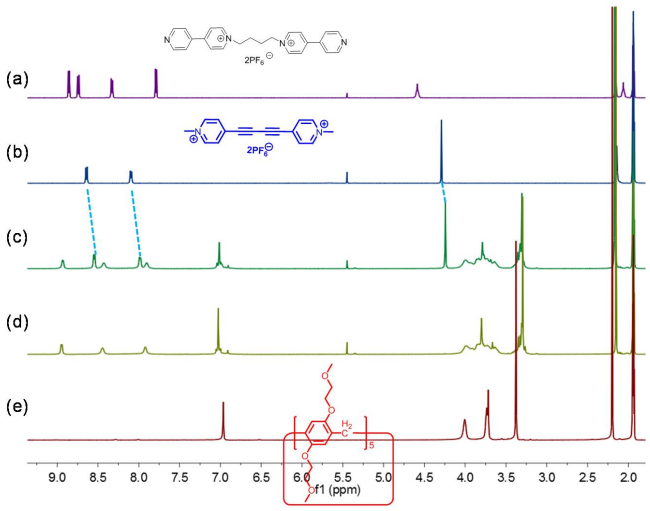


Fig. S17 Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 25 °C): (a) 1.00 mM **G2**; (b) 1.00 mM **G1**; (c) 0.500 mM **H**, **G2** and **G1**; (d) 0.500 mM **H** and **G2;** (e) 1.00 mM **H.**

References:

S1. T. Ogoshi, R. Shiga and T. Yamagishi, *J. Am. Chem. Soc.*, 2012, **134**, 4577–4580.

S2. E. Merkul, D. Urselmann and T. J. J. Müller, *Eur. J. Org. Chem.*, 2011, **2,** 238–242.

S3. K. A. Connors, *Binding Constants*; Wiley: New York, 1987; P. S. Corbin, Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, IL, 1999; 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**, 4931–4951.