Electronic Supplementary Information

Recognition of naphthoflavone by Calix[4]pyrrole[2]phenanthrene

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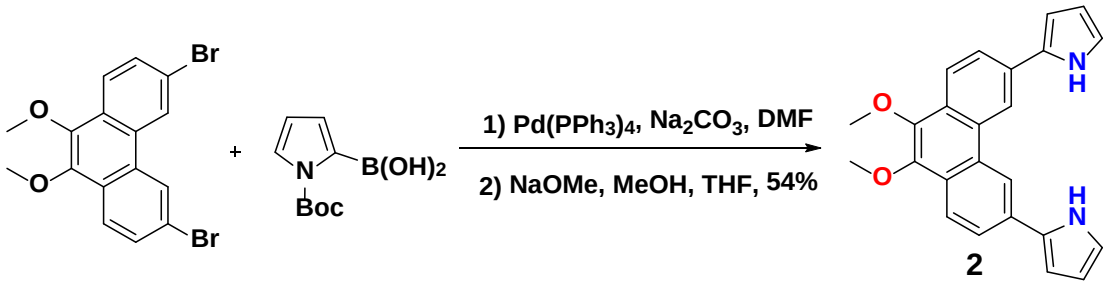
Contents

1. Materials and Methods.

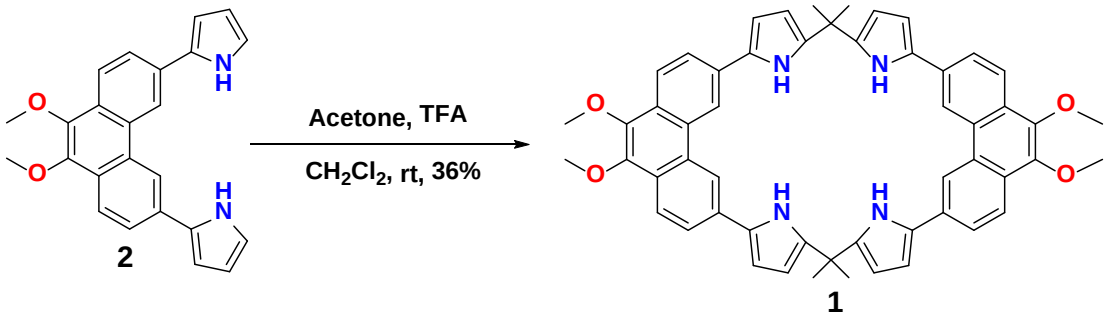
All reactions were carried out with oven-dried glassware. Commercial reagents were used without further purification. Flash column chromatography was performed on 100-200 mesh silica gel. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker DMX400 NMR spectrometer. Melting points were determined using WRR melting point apparatus and were uncorrected. High Resolution atmospheric-pressure chemical ionization mass spectra (APCI-MS) were determined by Bruker Daltonics. Inc, APEX II. FT-ICRMS. Electrospray ionization mass spectra (ESI-MS) were recorded on the Thermo Fisher® Exactive LC-MS spectrometer.

2. Synthesis of New Compounds.



Compound 2: A mixture of 3,6-dibromo-9,10-dimethoxyphenanthrene[S1] (3.94 g, 10 mmol), Na_2CO_3 (2.96 g, 28 mmol), N-Boc-2-pyrroleboronic acid (4.00 g, 22 mmol) and tetrakis(triphenylphosphine)palladium (0.23 g, 0.2 mmol) in 100 mL DMF in a flask was stirred at 90 ^{o}C for 24 h under N_2. After evaporating the solvents, resulting mixture was extracted with dichloromethane (3 × 50 mL) and then washed with water and brine successively. The organic layer was dried over anhydrous Na_2SO_4 and evaporated. Then, the residue was dissolved in 100 mL THF/MeOH (V/V = 5:1) and sodium methanolate (3.50g, 64.8mmol) was added. The resulting mixture was stirred at room temperature for 20 h under N_2. Then the reaction was quenched by the addition of 50 mL water. The organic layer was separated and dried with anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was separated by column chromatography on silica gel (eluent: 1:2 DCM/Petroleum ether) to give compound **2**

(1.99 g, yield 54%) as gray solid. M.p.: 172-174 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (s, 2H), 8.64 (s, 2H), 8.18 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 6.97 (s, 2H), 6.73 (s, 2H), 6.40 (q, *J* = 2.7 Hz, 2H), 4.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 132.5, 130.3, 128.8, 127.8, 123.8, 122.9, 119.3, 117.2, 110.4, 106.6, 61.0. HRMS (APCI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}N_2O_2^+$, 369.1598; found, 369.1579.



Compound 1: To a mixture of **2** (184 mg, 0.5 mmol) and acetone (180 mg, 0.52 mmol) in dichloromethane (10 mL) was added trifluoroacetic acid (28.5 mg, 0.25 mmol). The mixture was stirred at room temperature for 20 h under N_2. Then the reaction was quenched by the addition of 10 mL water. The organic layer was separated and dried with anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was separated by column chromatography on silica gel (eluent: 2:1 DCM/Petroleum ether) to give **1** (73.5 mg, 36%) as a gray solid. M.p.: 218-220 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (s, 2H), 8.42 (s, 2H), 8.13 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 2H), 6.81 (s, 2H), 6.50 (s, 2H), 4.06 (s, 6H), 1.93 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.49, 140.30, 131.49, 129.58, 128.58, 127.58, 122.80, 122.69, 116.17, 106.18, 105.78, 60.99, 36.01, 28.91. HRMS (APCI) m/z: $[M+H]^+$ calcd for $C_{54}H_{49}N_4O_4^+$, 817.3748; found, 817.3753.

3. ^{1}H NMR and ^{13}C NMR Spectral of New compounds.

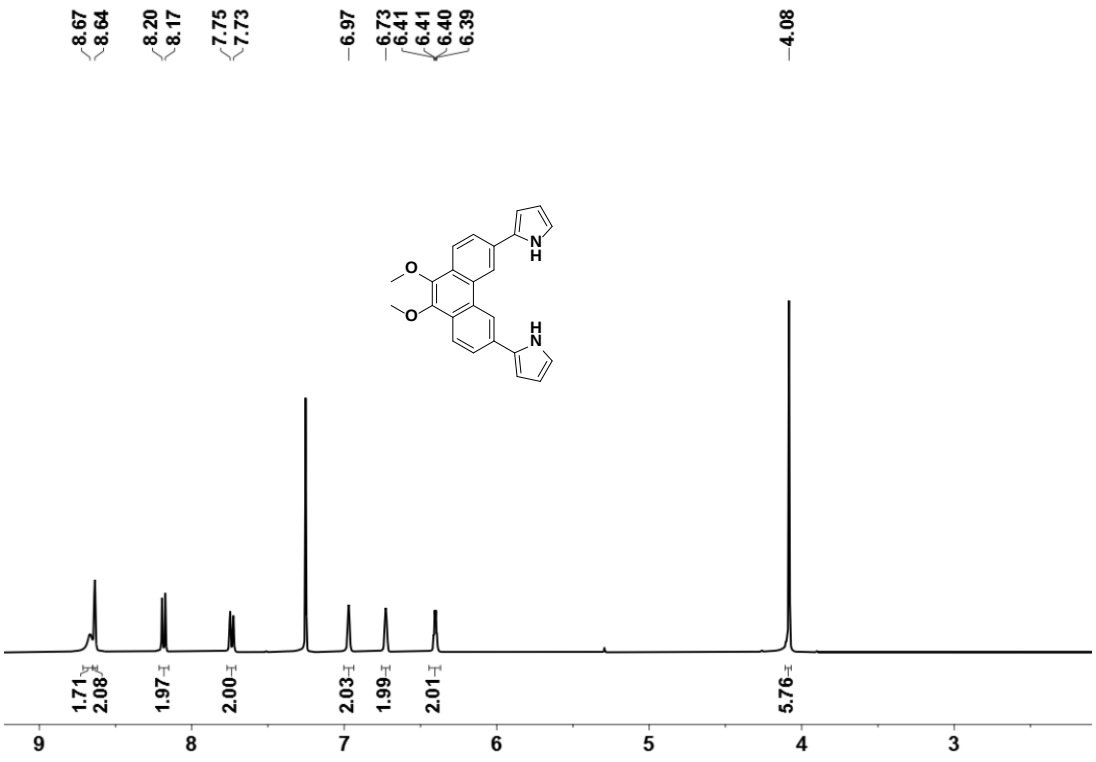


Figure S1.^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **2**

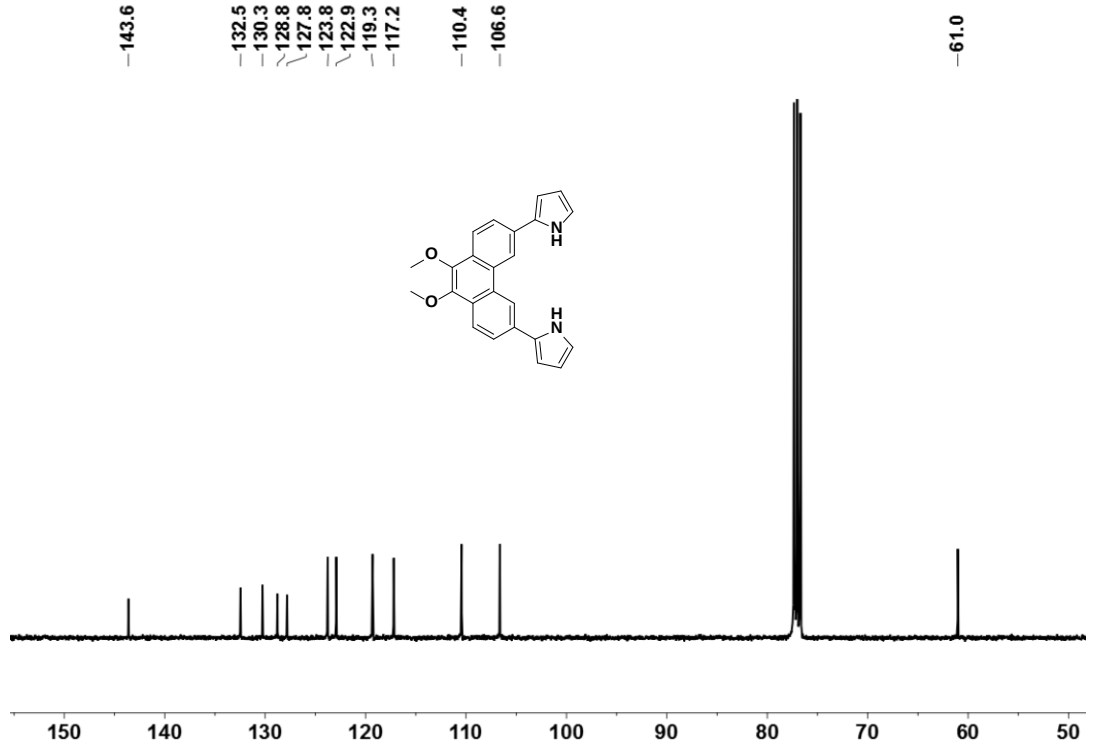


Figure S2.^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298K) of **2**

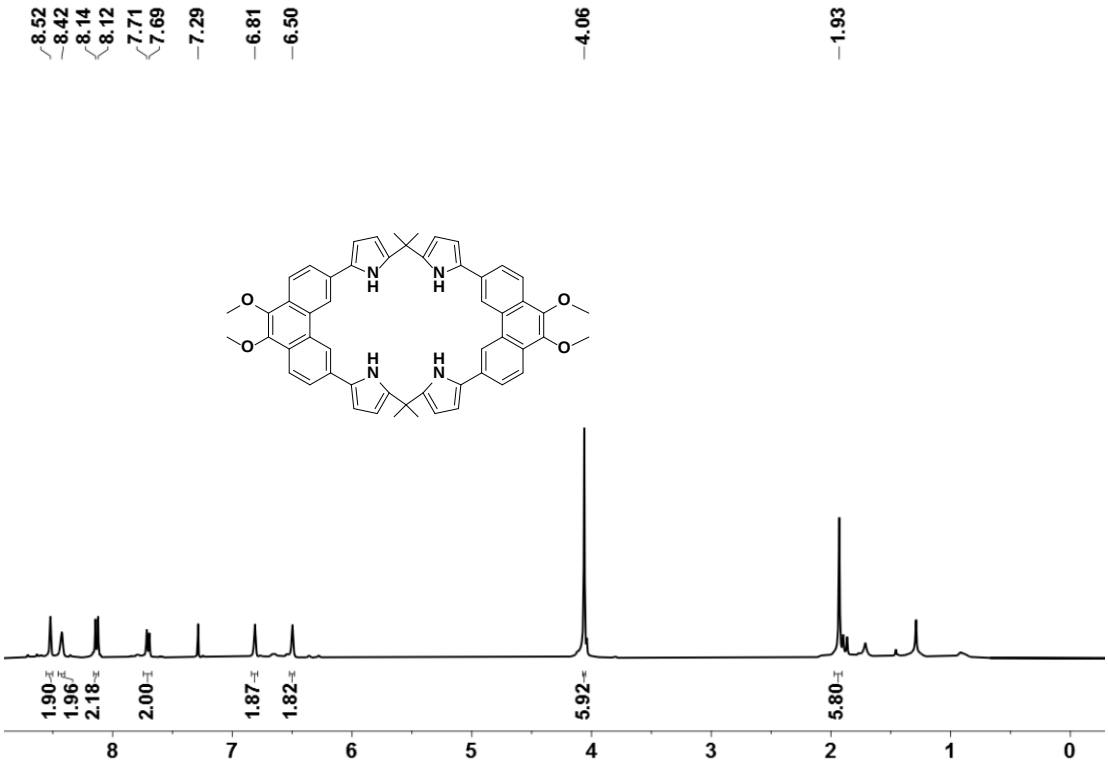


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **1**

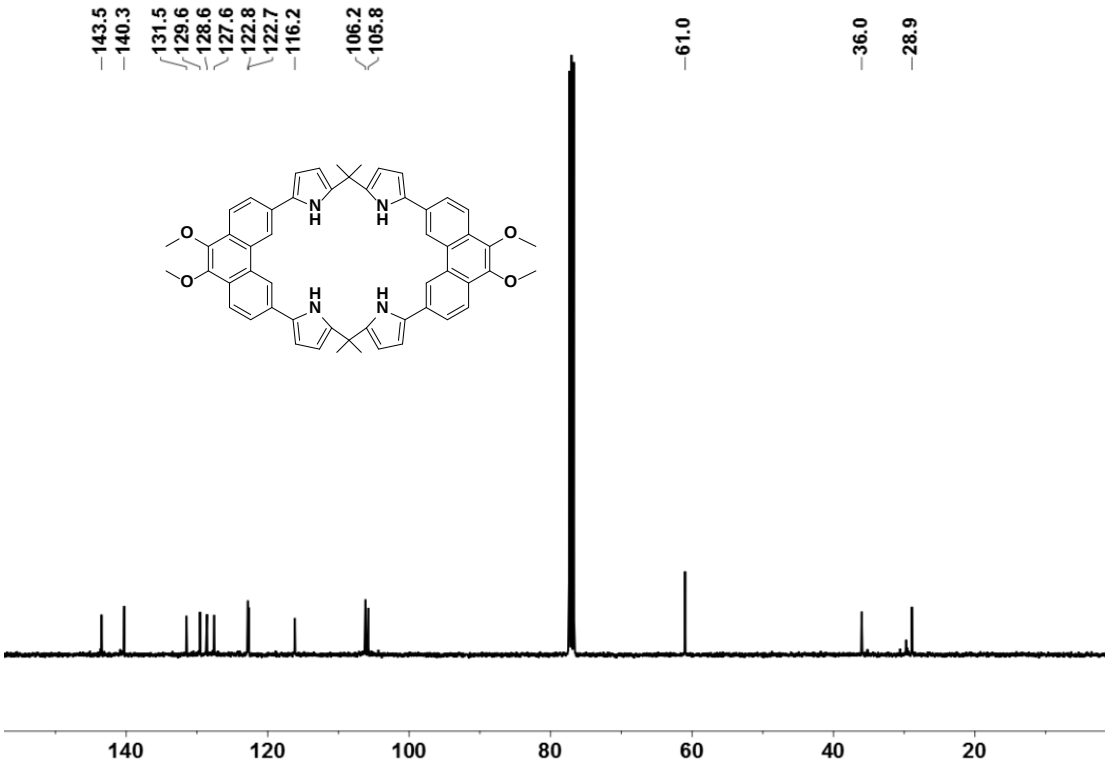


Figure S4. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298K) of **1**

4. ^{1}H NMR studies of Complexation of the Host and Guest

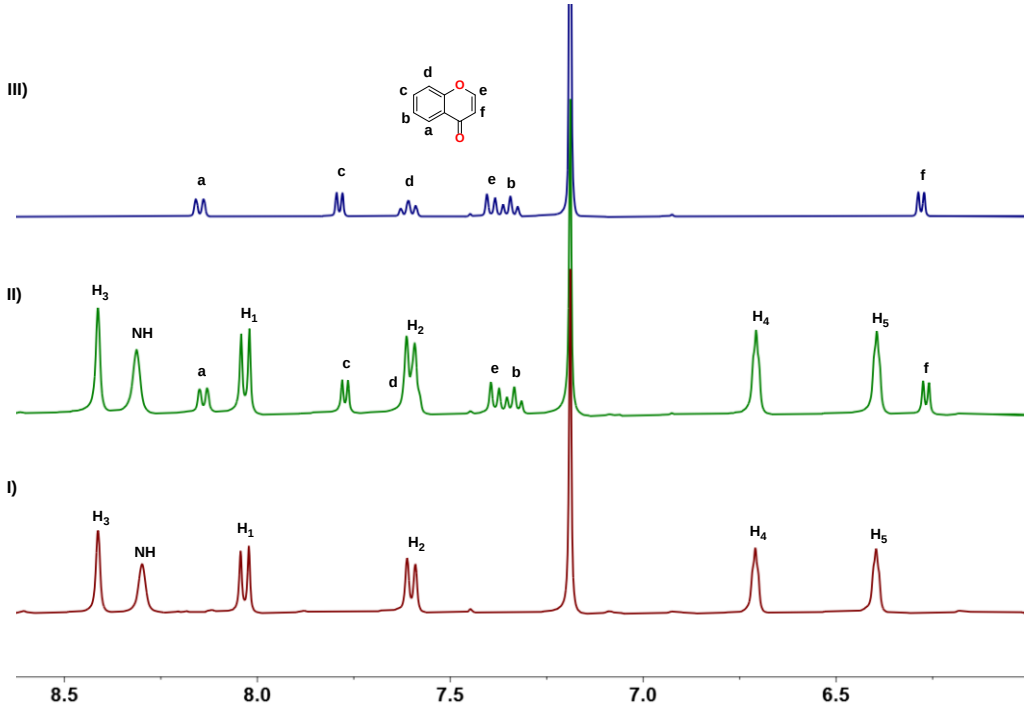


Figure S5. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (I) free **1**, (II) **1** and 1.0 equiv. of **G1**, and (III) free **G1**. $[\mathbf{1}]_0$ = 4.0 mM.

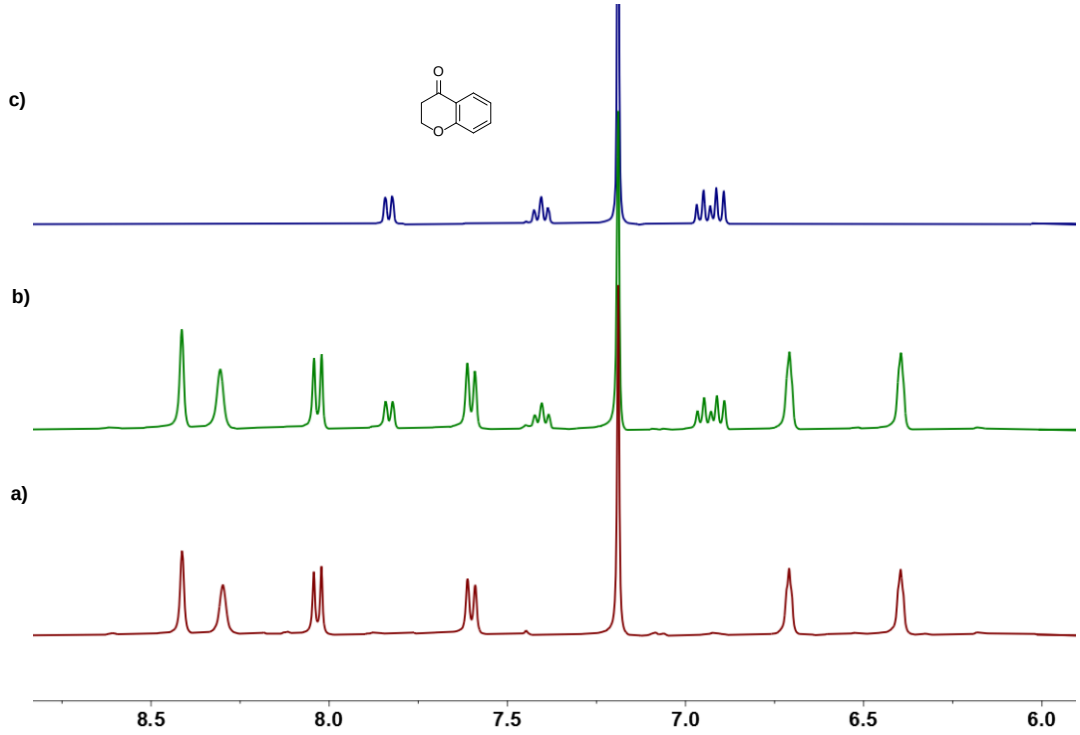


Figure S6. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (a) free **1**, (b) **1** and 1.0 equiv. of **G2**, and (c) free **G2**. $[\mathbf{1}]_0$ = 4.0 mM.

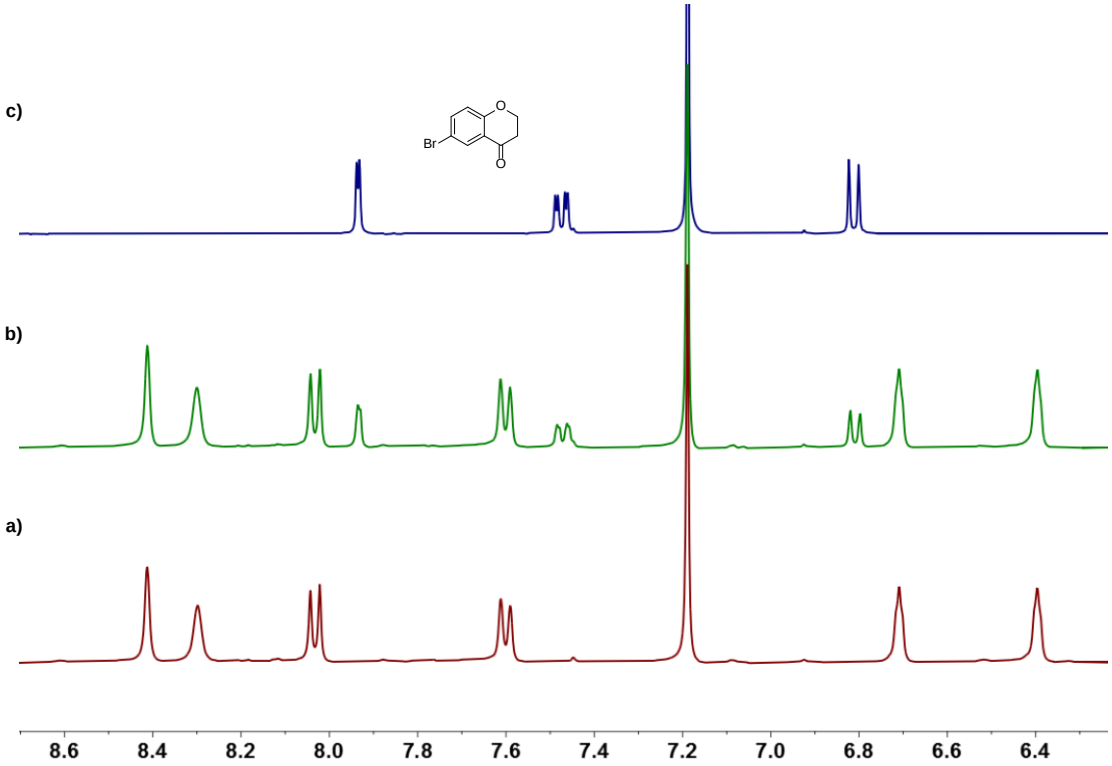


Figure S7. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (a) free **1**, (b) **1** and 1.0 equiv. of **G3**, and (c) free **G3**. $[\mathbf{1}]_0$ = 4.0 mM.

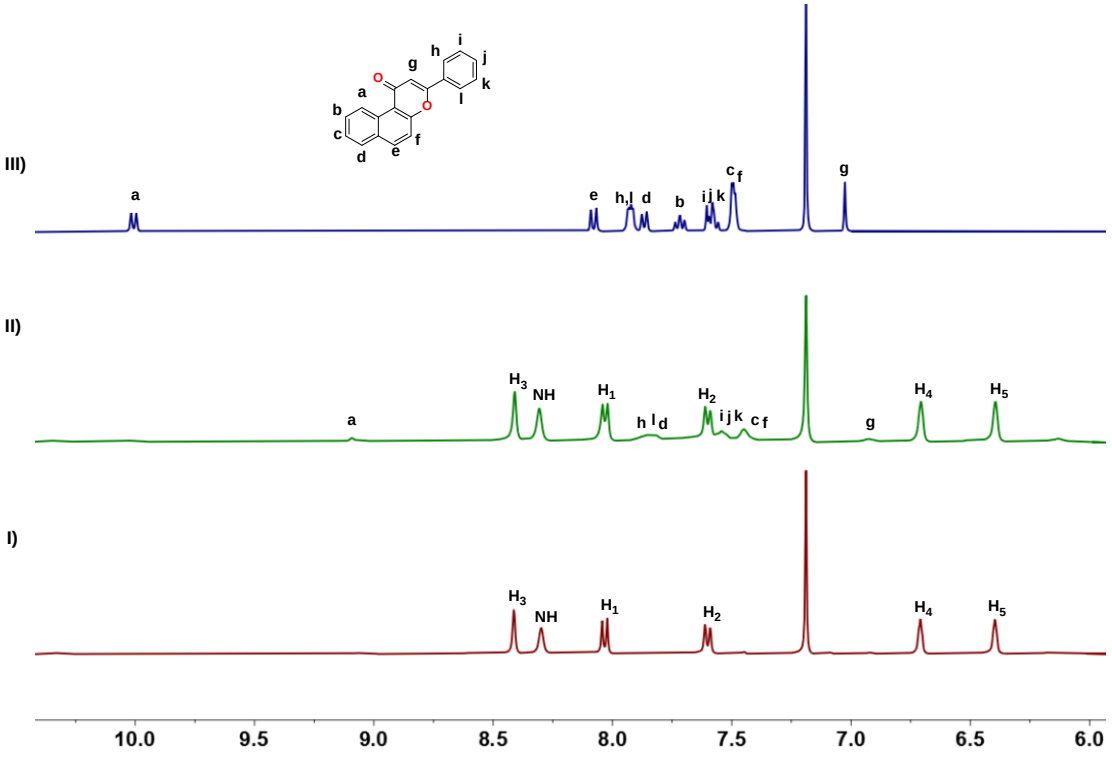


Figure S8. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (I) free **1**, (II) **1** and 1.0 equiv. of **G5**, and (III) free **G5**. $[\mathbf{1}]_0$ = 4.0 mM.

5. Determination of the Association Constants of the Complexes

In the ^{1}H NMR titrations, $CDCl_3$ was chosen to dissolve the host and the guests. Chemical shifts were reported in parts per million (*ppm*). By a mole ratio plot, each stoichiometry was determined. Titration curve-fitting and association constant values were calculated by employing the BindFit program developed by Prof. Pall Thordarson of UNSW. 1:1 Binding stoichiometry was chosen in the BindFit program. This program employs a nonlinear least-squares regression analysis and is available free of cost online through the following link: http://supramolecular.org.

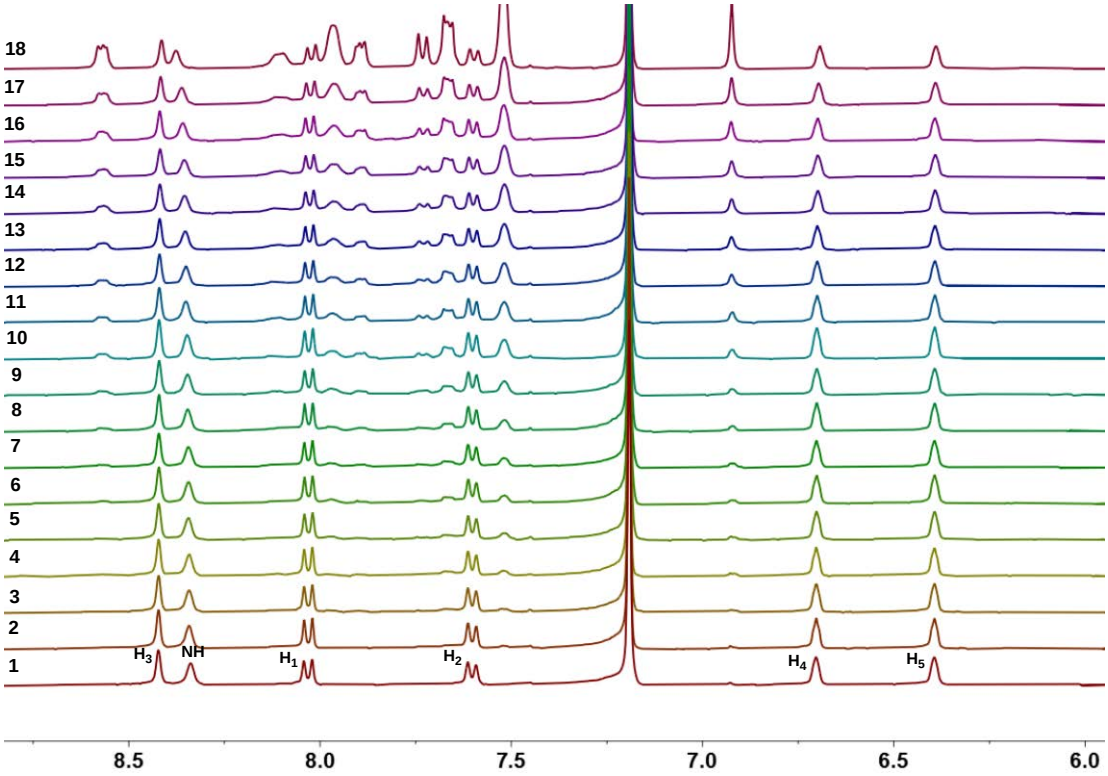


Figure S9. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of **1** at a concentration of 1.0 mM with different concentrations of **G4**: (1) 0.00 mM; (2) 0.2 mM; (3) 0.3 mM; (4) 0.4 mM; (5) 0.5 mM; (6) 0.6 mM; (7) 0.7 mM; (8) 0.8 mM; (9) 1.0 mM; (10) 1.2 mM; (11) 1.4 mM; (12) 1.6 mM; (13) 1.8 mM; (14) 2.0 mM; (15) 2.2 mM; (16) 2.4 Mm; (17) 3.0 mM; (18) 10.0 mM.

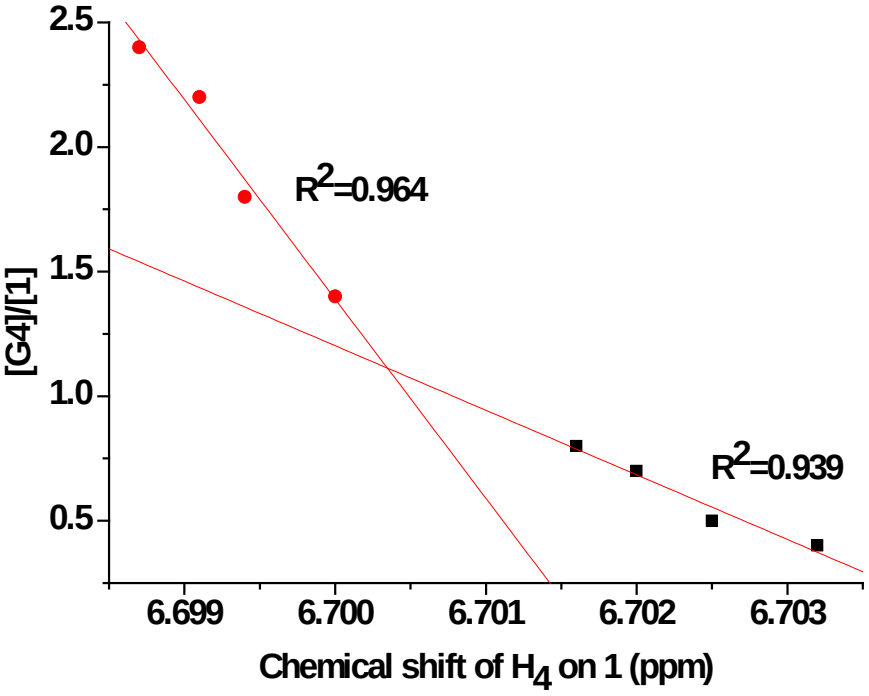


Figure S10. Mole ratio plot of the complexation of **1** and **G4** in $CDCl_3$ at 298 K.

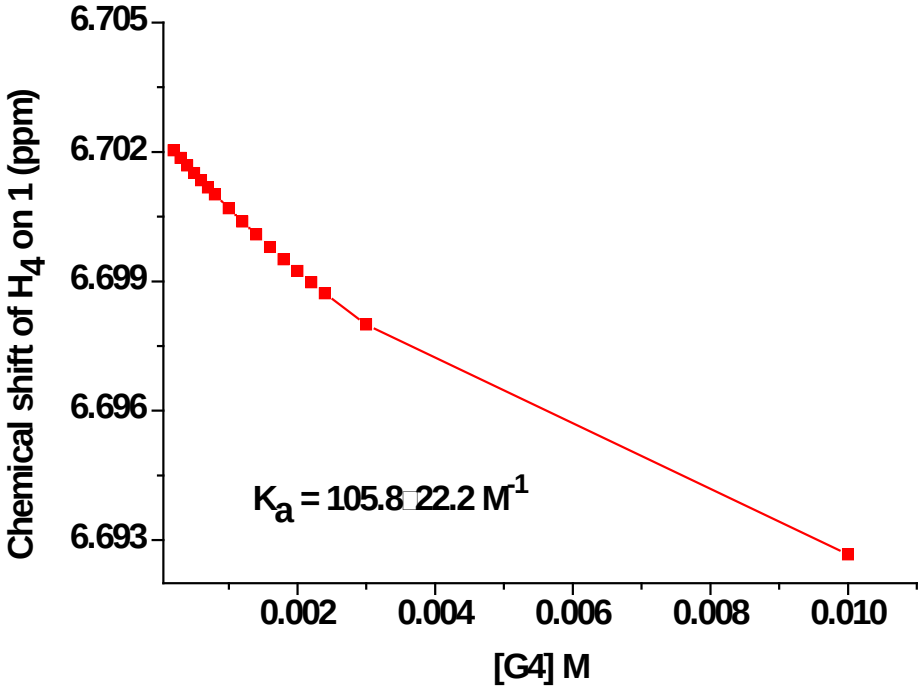


Figure S11. Plot of chemical shift (ppm) for the H_4 of **1** and **G4** in $CDCl_3$ at 298 K.

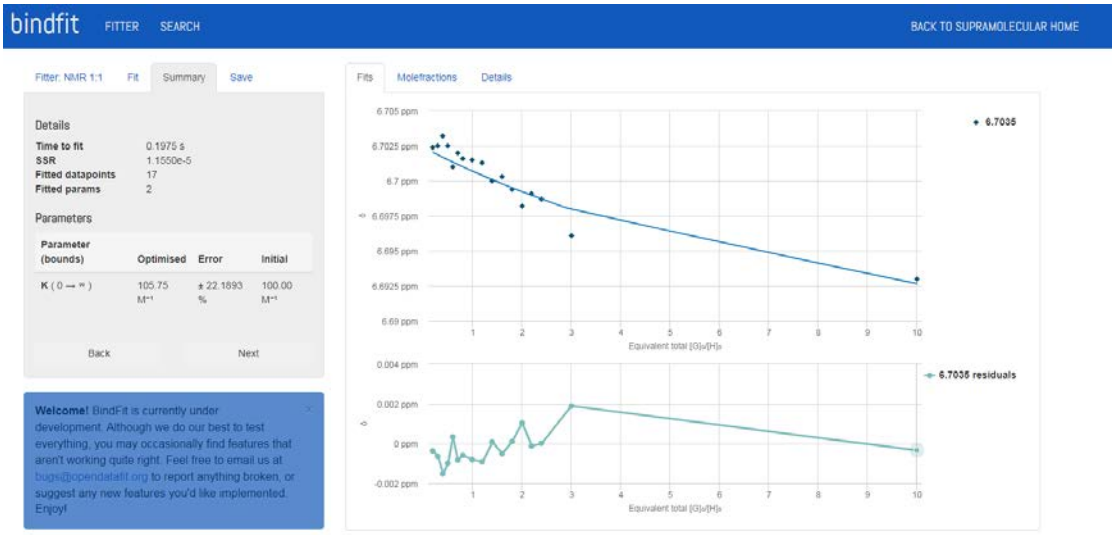


Figure S12. Nonlinear least-square analysis of the ^{1}H NMR binding data corresponding to the formation of [**1•G4**] complex. The data were fitted to a 1:1 binding model to give K_a = 105.8 ± 22.2 M^{-1}. The residual distribution is shown below the binding isotherm. All solid lines were obtained from non-linear curve-fitting to a 1:1 binding model using the www.supramolecular.org web applet.

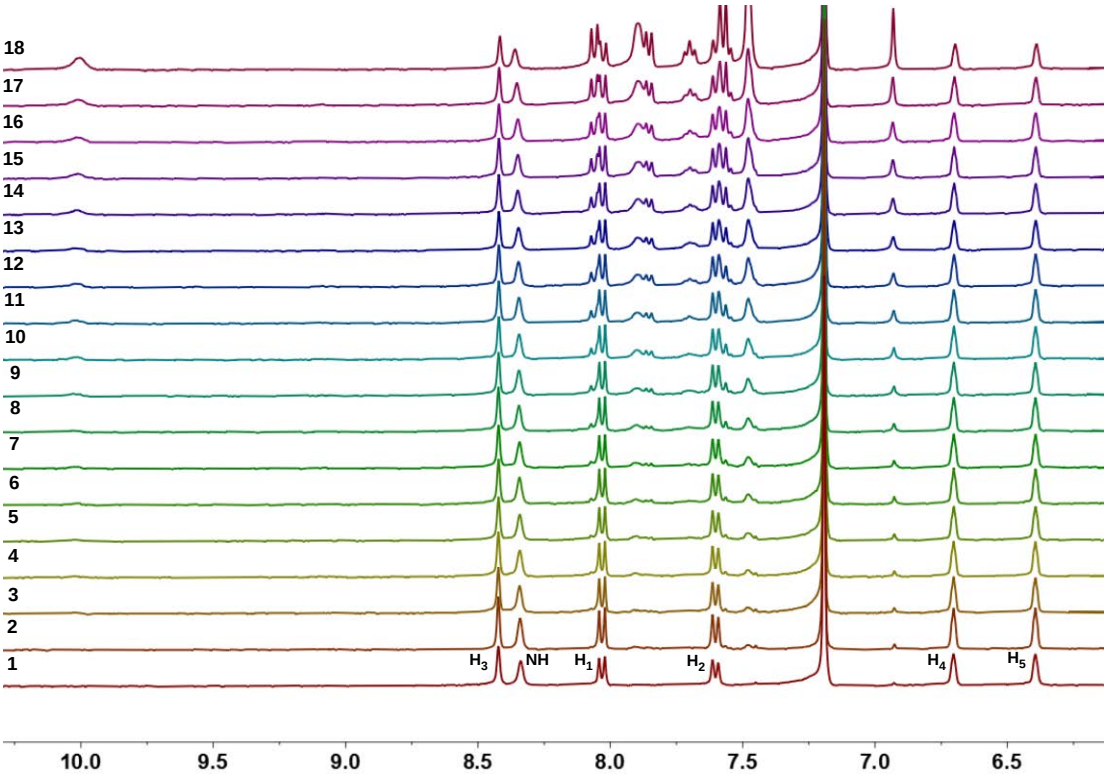


Figure S13. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of **1** at a concentration of 1.0 mM with different concentrations of **G5**: (1) 0.00 mM; (2) 0.2 mM; (3) 0.3 mM; (4) 0.4 mM; (5) 0.5 mM; (6) 0.6 mM; (7) 0.7 mM; (8) 0.8 mM; (9) 1.0 mM; (10) 1.2 mM;

(11) 1.4 mM; (12) 1.6 mM; (13) 1.8 mM; (14) 2.0 mM; (15) 2.2 mM; (16) 2.4 Mm; (17) 3.0 mM; (18) 10.0 mM.

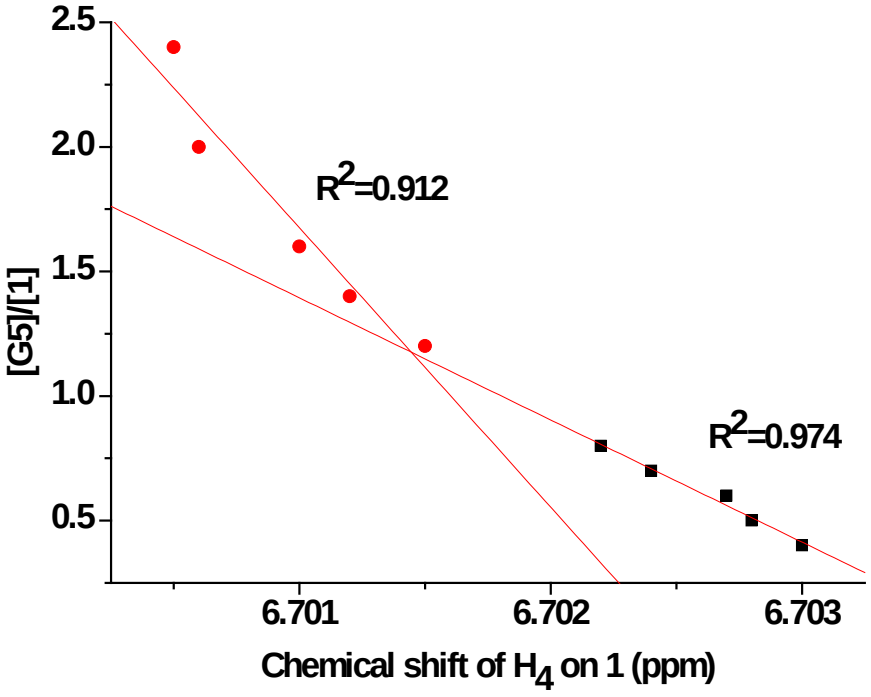


Figure S14. Mole ratio plot of the complexation of **1** and **G5** in $CDCl_3$ at 298 K.

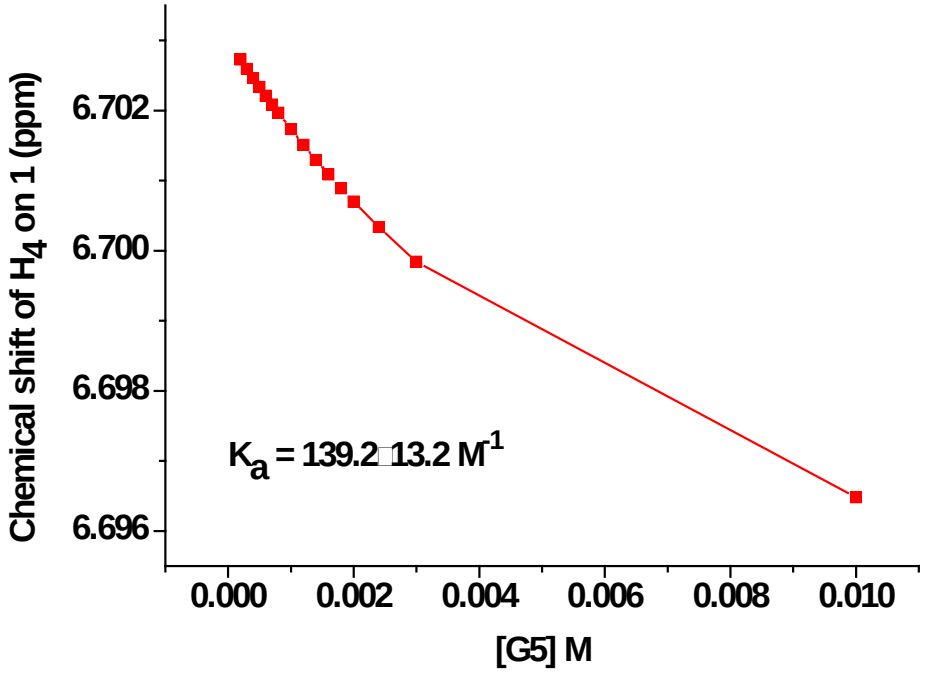


Figure S15. Plot of chemical shift (ppm) for the H_4 of **1** and **G5** in $CDCl_3$ at 298 K.

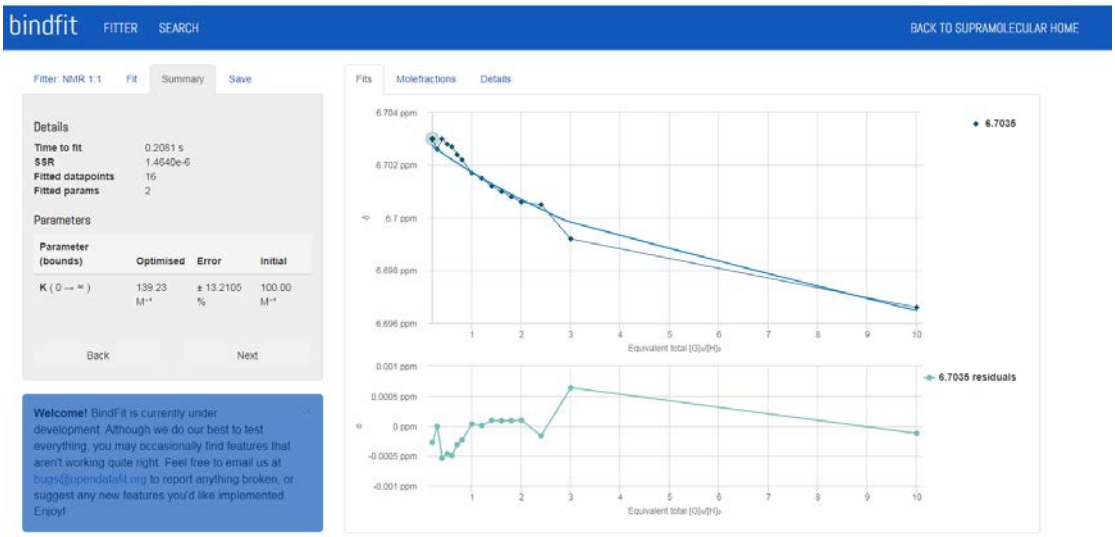


Figure S16. Nonlinear least-square analysis of the ^{1}H NMR binding data corresponding to the formation of [**1•G5**] complex. The data were fitted to a 1:1 binding model to give K_a = 139.2 ± 13.2 M^{-1}. The residual distribution is shown below the binding isotherm. All solid lines were obtained from non-linear curve-fitting to a 1:1 binding model using the www.supramolecular.org web applet.

6. ESI MS Studies of the new compounds and complexes

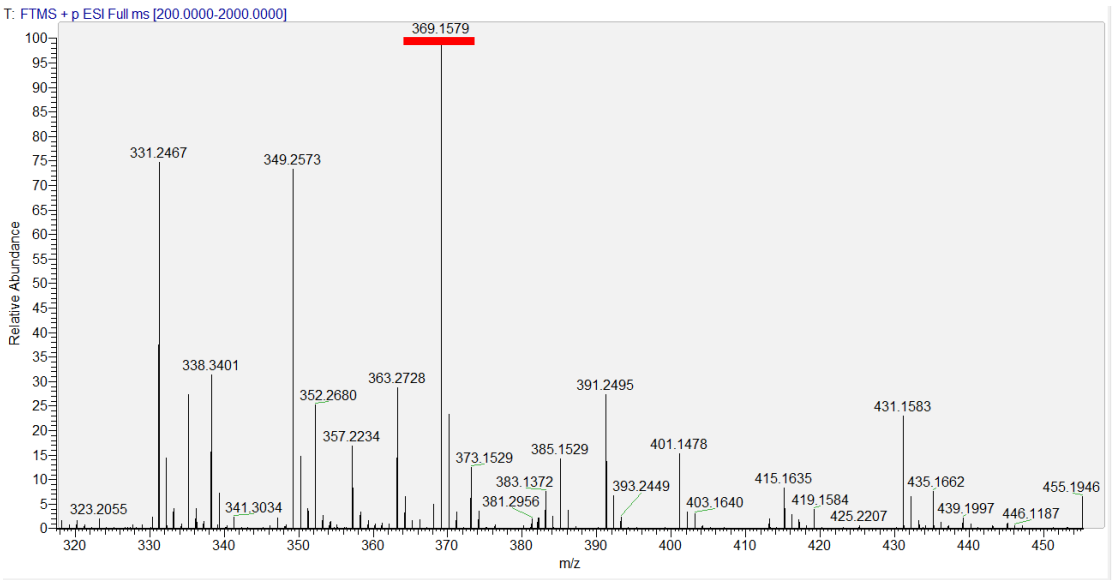


Figure S17. ESI Spectrum of **2**

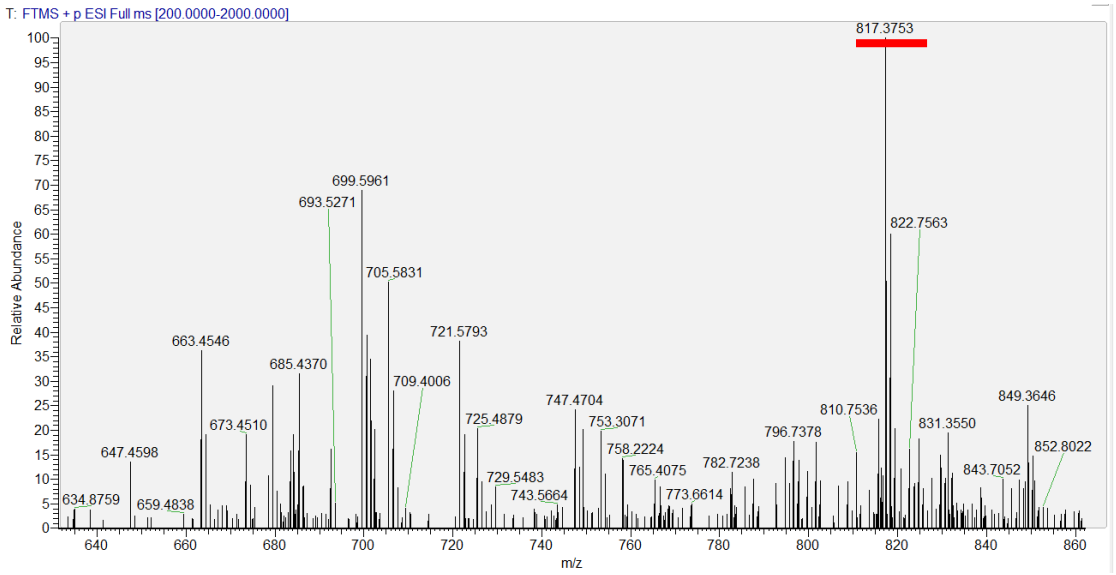


Figure S18. ESI Spectrum of host **1**

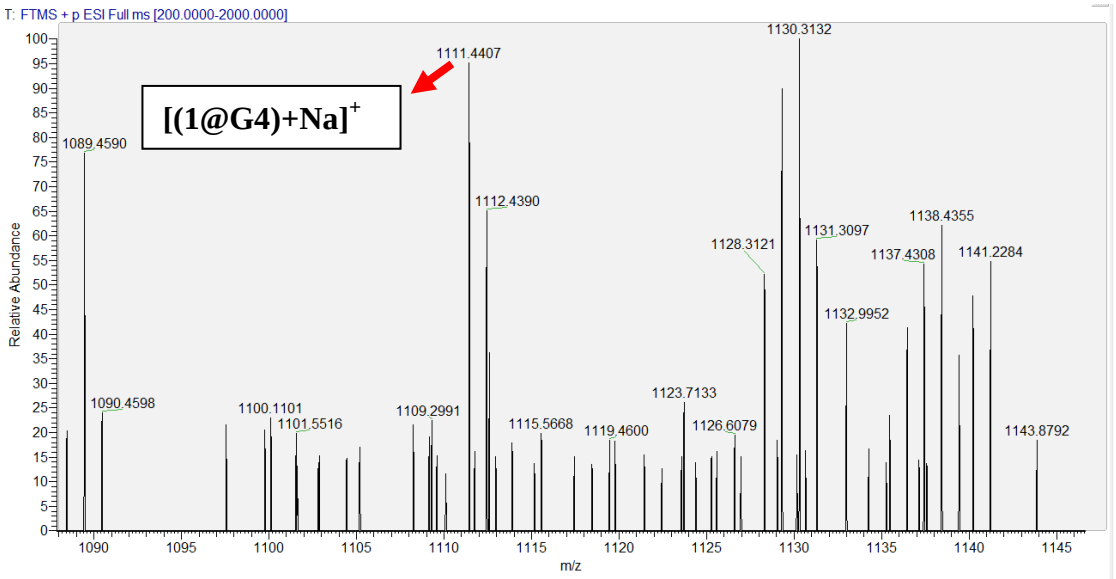


Figure S19. ESI Spectrum of complex **1@G4**

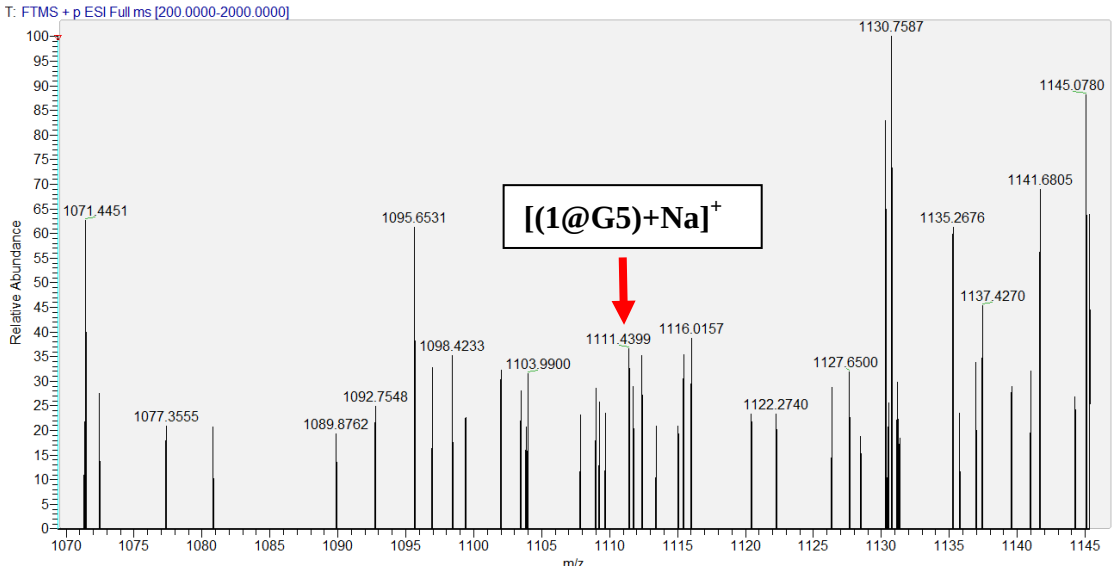


Figure S20. ESI Spectrum of complex **1@G5**

7. ^{1}H-^{1}H ROESY spectral of the complexes

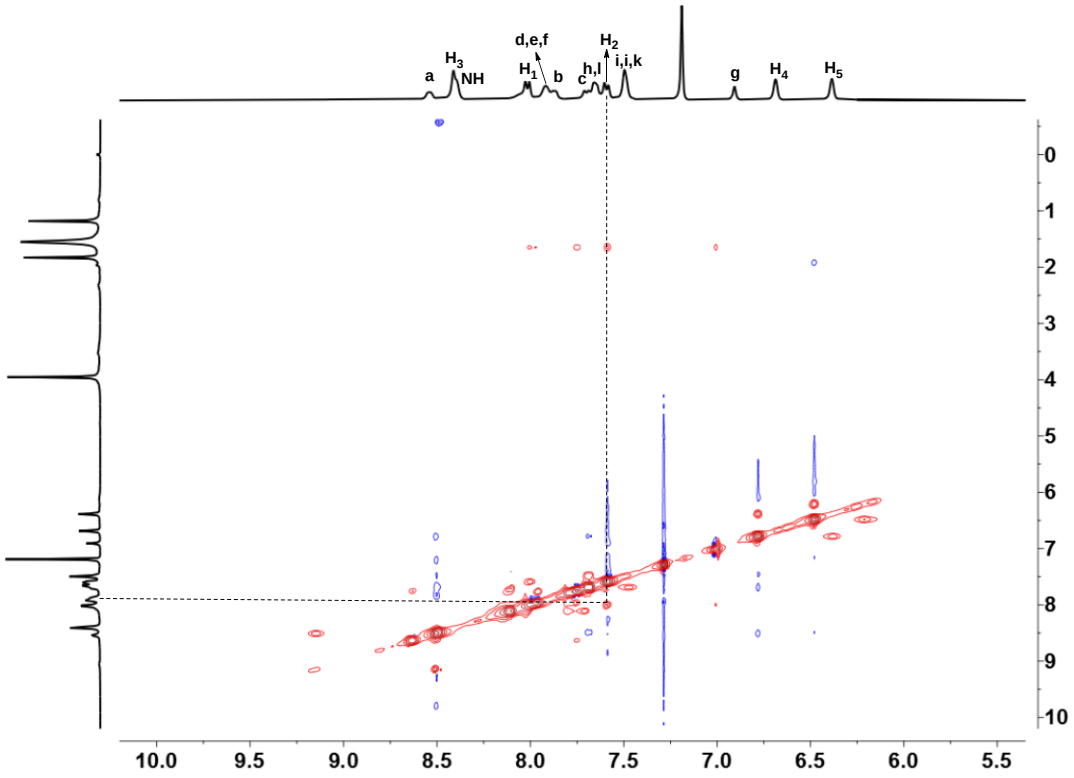


Figure S21. ^{1}H-^{1}H ROESY spectrum (400 MHz, $CDCl_3$, 298 K) of **1@G4**

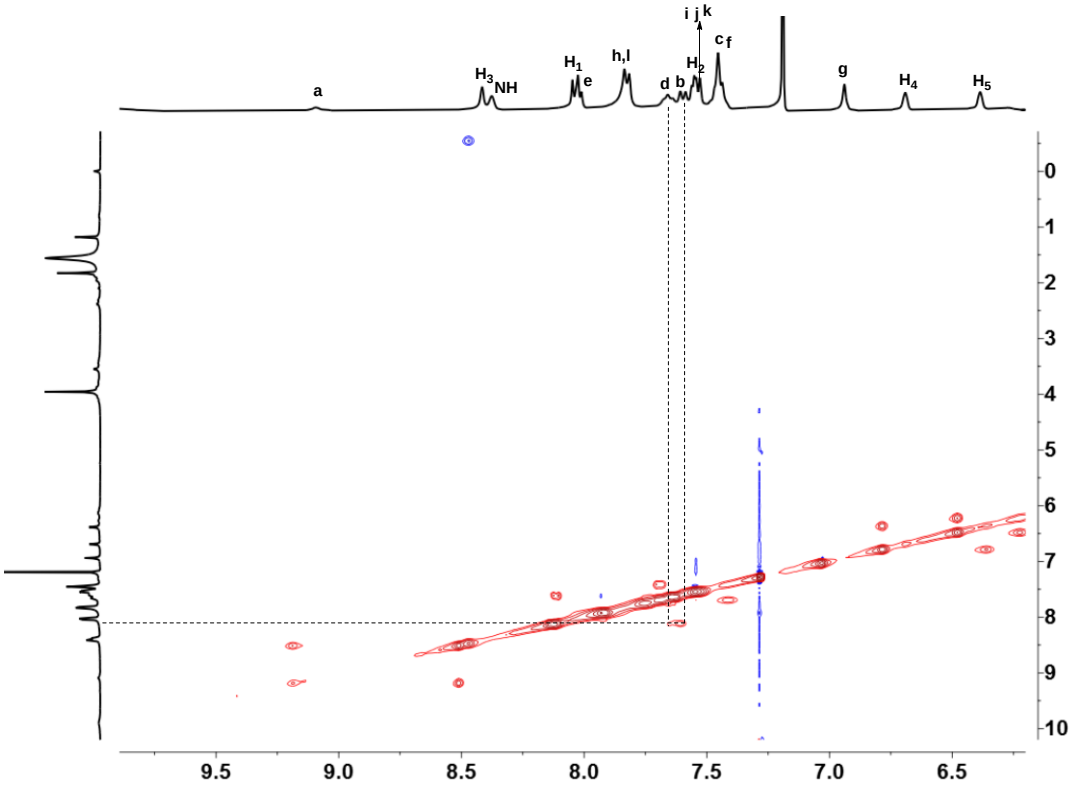


Figure S22. ^{1}H-^{1}H ROESY spectrum (400 MHz, $CDCl_3$, 298 K) of **1@G5**

8. References

S1. B. V. Phulwale, S. K. Mishra, M. Nečas and C. Mazal, Phenanthrylene-butadiynylene and phenanthrylenethienylene macrocycles. Synthesis, structure and properties, *J. Org. Chem.*, 2016, **81**, 6244.