Electronic Supplementary Information

for

A four-unit [c2]daisy chain connected by hydrogen bonds

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Table of Contents

Contents

1. General information

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiple, br = broad), coupling constants (Hz). ^{13}C NMR data were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. The two-dimensional NMR spectra (HMBC, COSY, HSQC, DOSY, NOESY) were recorded on commercial instruments (400 MHz). HRMS was recorded on a commercial apparatus (ESI Source). Single crystal X-ray data were obtained on commercial instruments. Melting points (m. p.) were determined using on commercial apparatus and were not corrected. All reagents were commercially available and most of them were used without further purification, except that some solvents were dried by standard methods.

2. General procedure for the synthesis and characterization of pillar[5]arene H, guest G and compound R.
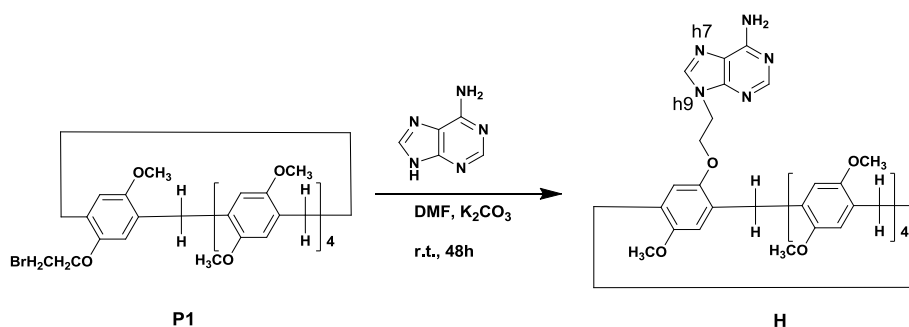

Scheme S1. Synthetic route for pillar[5]arene **H**

P1 was synthesized according to the reported method[S1]. To the solution of **P1** (0.5 mmol) in 20 mL DMF, anhydrous K_2CO_3 (3.0 mmol) and adenine (3.0 mmol)

were added sequentially. The mixtures were stirred 48 h at room temperature. After the reaction finished, 50 mL water was added and the mixtures were extracted with CH_2Cl_2. The combined organic phase was washed with saturated brine, dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (CH_2Cl_2/ methanol= 60: 1) to yield **H** as a white powder (218mg, 25%). HMBC spectroscopy of **H** was performed and the results showed that **P1** reacted with adenine at h9 location (for details, see Fig. S10).
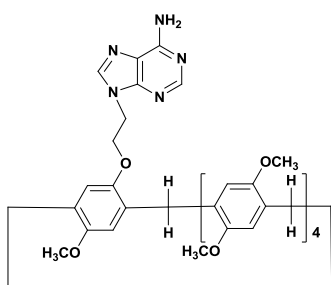

White powder. 25%, m. p. 108-110 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.04 (s, 1H), 6.52 - 6.79 (m, 10H), 5.68 (s, 2H), 4.49 (t, J = 4.4 Hz, 2H), 4.13 (t, J= 4.4 Hz, 2H), 3.78 - 3.50 (m, 37H). ^{13}C NMR (100MHz, $CDCl_3$): δ 155.4, 152.9, 151.6, 151.1, 150.9, 150.9, 150.8, 150.8, 150.8, 148.9, 141.4, 128.6, 125.9, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 127.9, 115.2, 114.5, 114.4, 114.2, 114.1, 114.1, 114.0, 66.8, 56.0, 55.9, 55.8, 55.7, 43.5, 30.45, 29.9, 29.8, 29.7, 29.4. HRMS: exact mass calcd for $C_{51}H_{55}N_5O_{10}Na$ [M+Na]$^+$ requires m/z 898.3982, found m/z 898.4020.
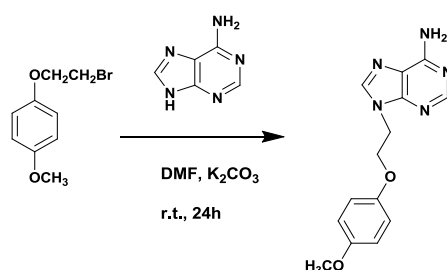

Scheme S2. Synthetic route for compound **R**

**R** was synthesized according to the similar procedure with **H**.
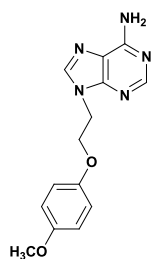
White powder. 85%, m. p.180-183 ℃; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.36 (s, 1H), 7.99 (s, 1H), 6.79 (d, J = 0.8 Hz, 4H), 5.76 (br, 2H), 4.57 (t, J = 4.9 Hz, 2H), 4.26 (t, J = 4.9 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (100MHz, CDCl$_3$) δ 155.4, 154.4, 152.9 , 152.0, 150.0 , 141.5 , 119.5 , 115.5, 114.7, 66.6 , 55.7 , 43.3. HRMS: exact mass calcd for C$_{14}$H$_{16}$N$_5$O$_2$ [M+H]$^+$ requires m/z 286.1259, found m/z 286.1248.
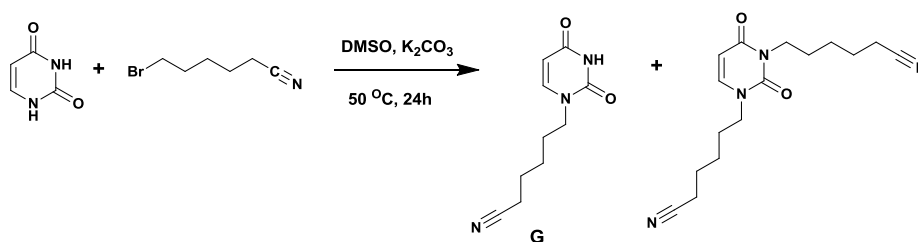
Scheme S3. Synthetic route for guest **G**

To the solution of uracil (1.0 mmol) in 25 mL DMSO, anhydrous K$_2$CO$_3$ (1.0 mmol) and 6-bromohexanenitrile (1.0 mmol) were added sequentially. The mixtures were stirred at 50℃ for about 24 hours. After the reaction was completed, 50 mL water was added and the mixtures were extracted with CH$_2$Cl$_2$. The combined organic phase was washed with saturated brine, dried over anhydrous Na$_2$SO$_4$, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (CH$_2$Cl$_2$/ Ethyl acetate) to afford **G** and another byproduct.
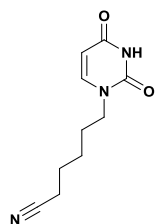
White powder. 54%, m. p. 92-93 ℃; ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.86 (s, 1H),

7.18 (d, J =7.9 Hz, 1H), 5.72 (dd, J = 7.9 Hz, 2.3Hz, 1H), 3.75 (t, J = 7.3 Hz, 2H), 2.37 (t, J= 7.0 Hz, 2H), 1.78-1.48 (m, 6H). ^{13}C NMR (400 MHz, CDCl₃): δ 163.5, 150.8, 144.2, 119.3, 102.4, 48.5, 28.3, 25.4, 24.8, 17.1. HRMS: exact mass calcd for $C_{10}H_{13}N_3O_2Na$ [M+Na]$^+$ requires m/z 230.0906, found m/z 230.0891.
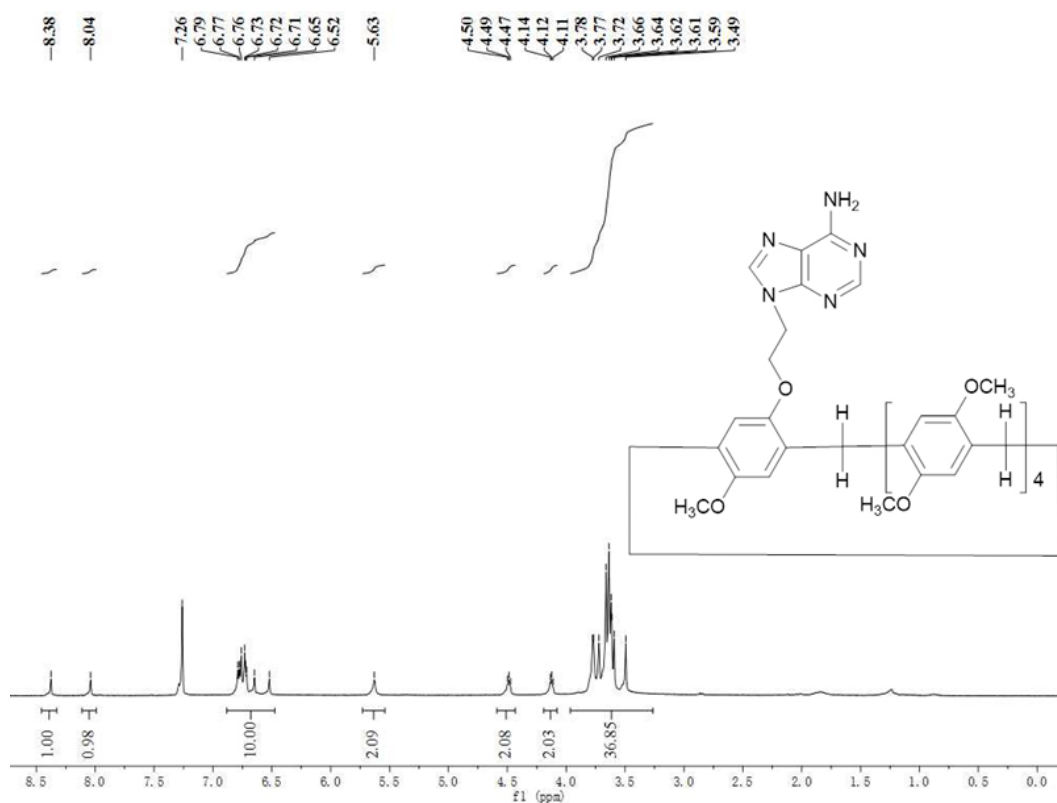

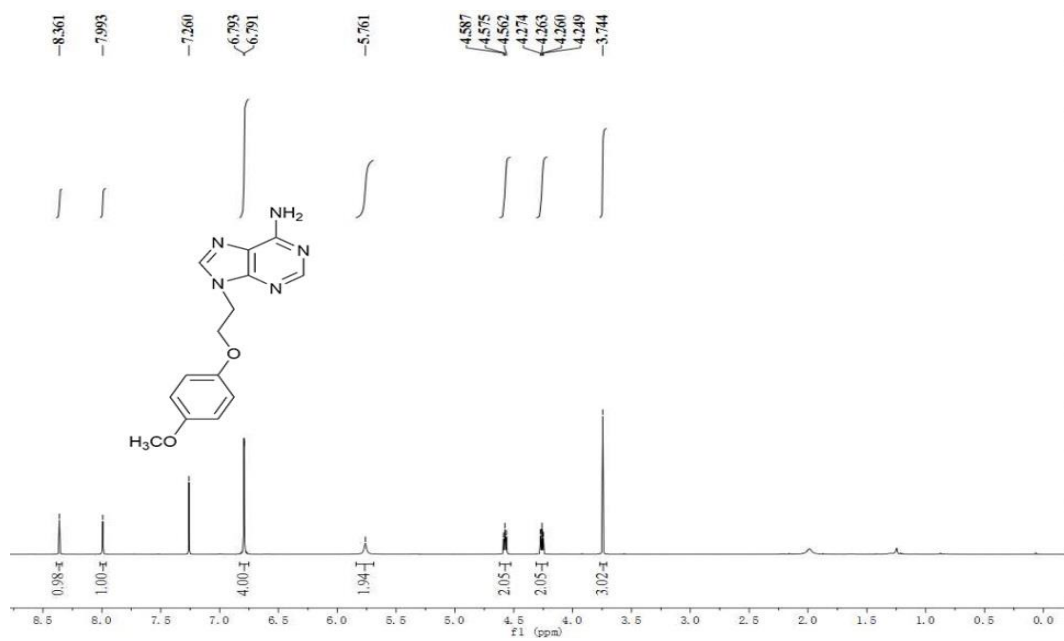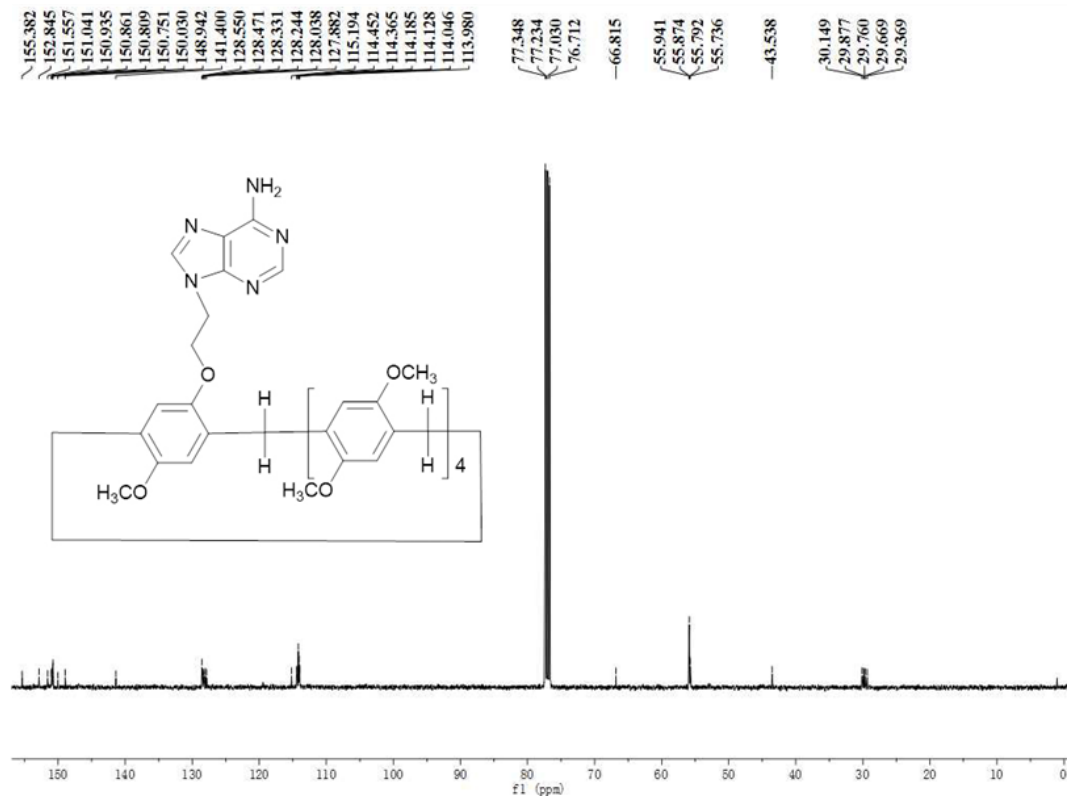Fig. S1 ^{1}H NMR spectrum of **H**

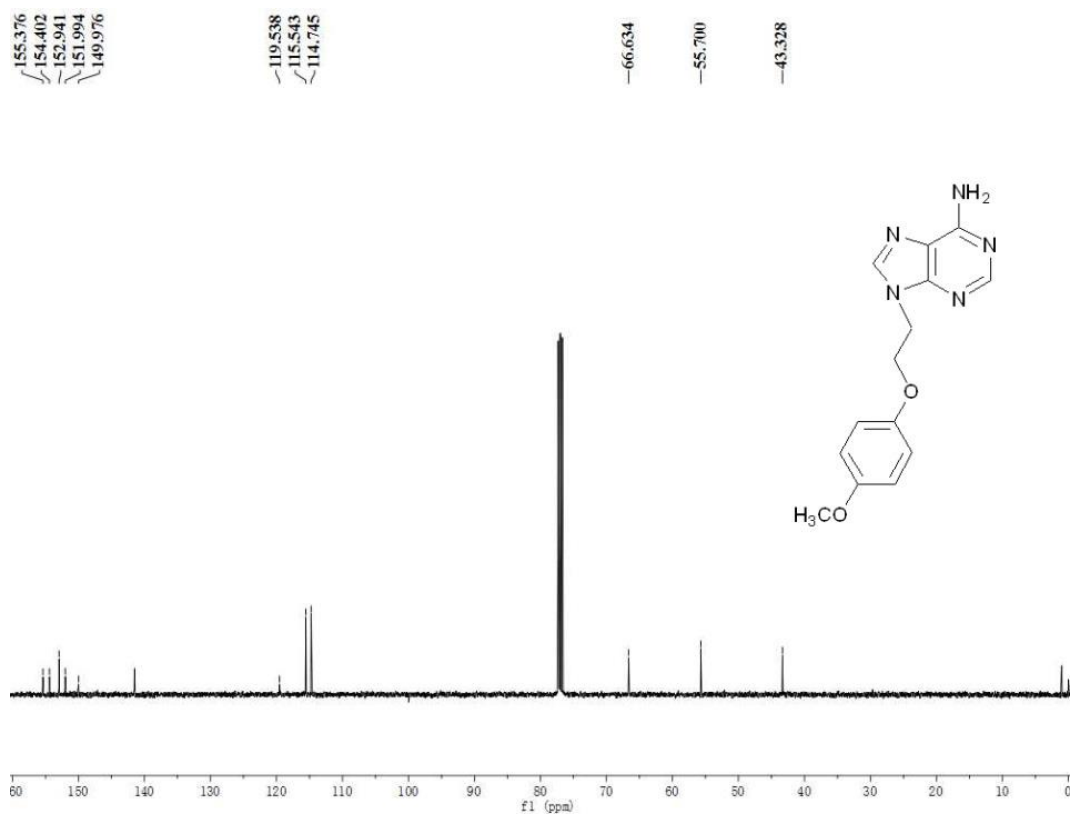Fig.S2 ^{13}C NMR spectrum of **H**

Fig. S3 ^{1}H NMR spectrum of **R**

Fig. S4 ^{13}C NMR spectrum of **R**
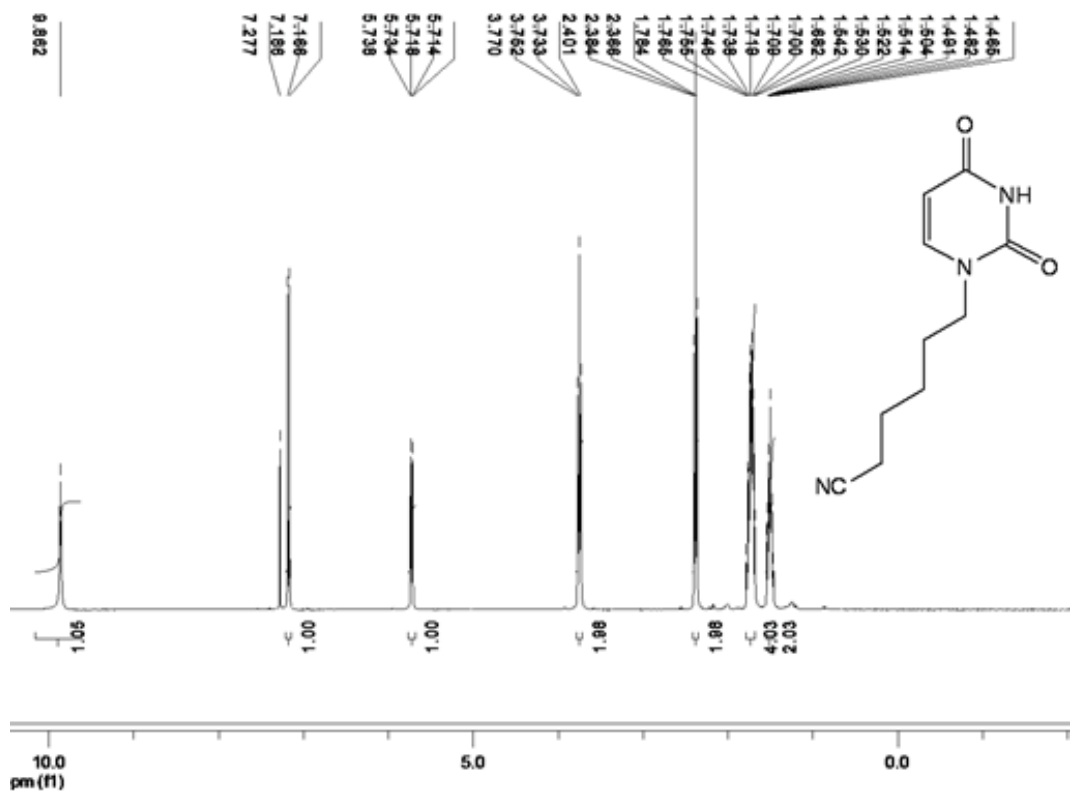
Fig. S5 ^{1}H NMR spectrum of **G**
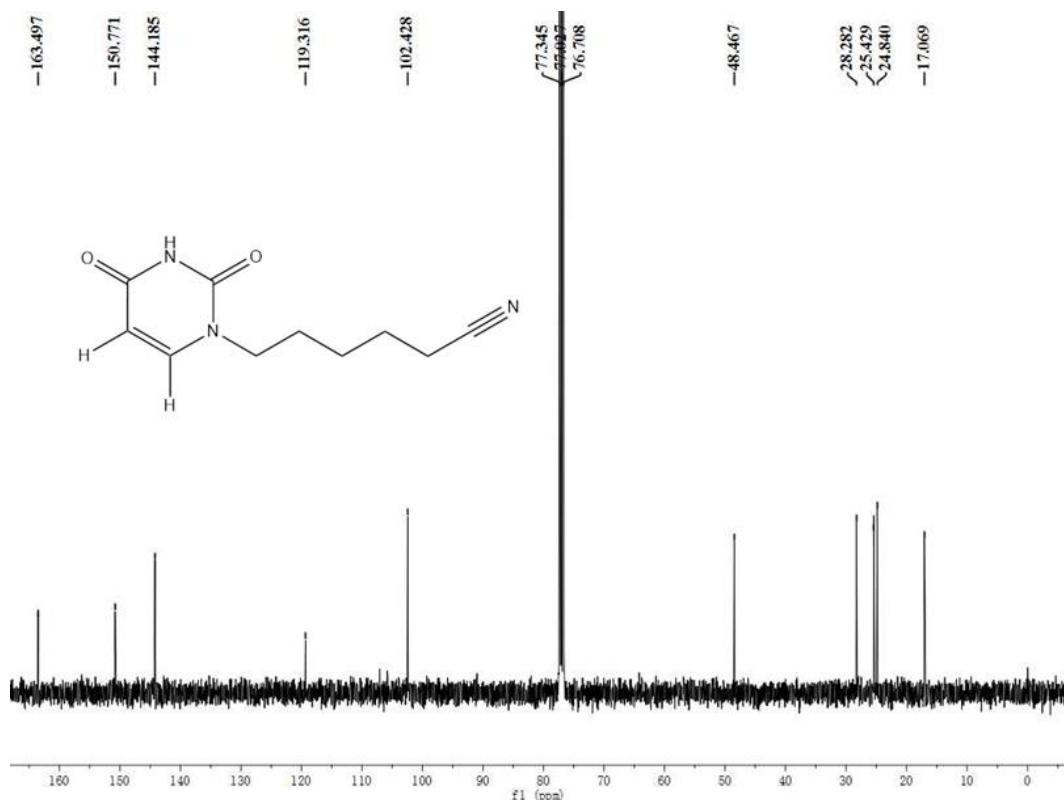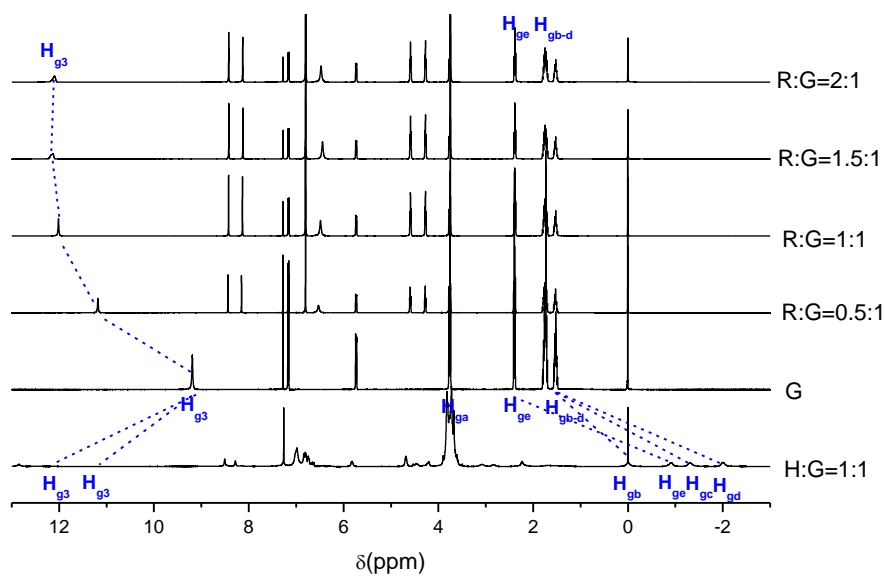
Fig. S6 ^{13}C NMR spectrum of **G**

3 ^{1}H NMR experiment

Fig. S7 ^{1}H NMR spectra (400 MHz, CDCl$_3$, 298K) of **G** (20 mM) in the presence of

1.0 equivalent of **H** and different equivalents of **R.**

4 Determination of the association constant

For G⊂H host-guest complex, chemical exchange is slow on the NMR time scale and peaks are observed for both complexed and uncomplexed species in the NMR spectra. So association constant for this complex could be determined by integration from a 1:1 mixture using the ^{1}H NMR single point method[S2].
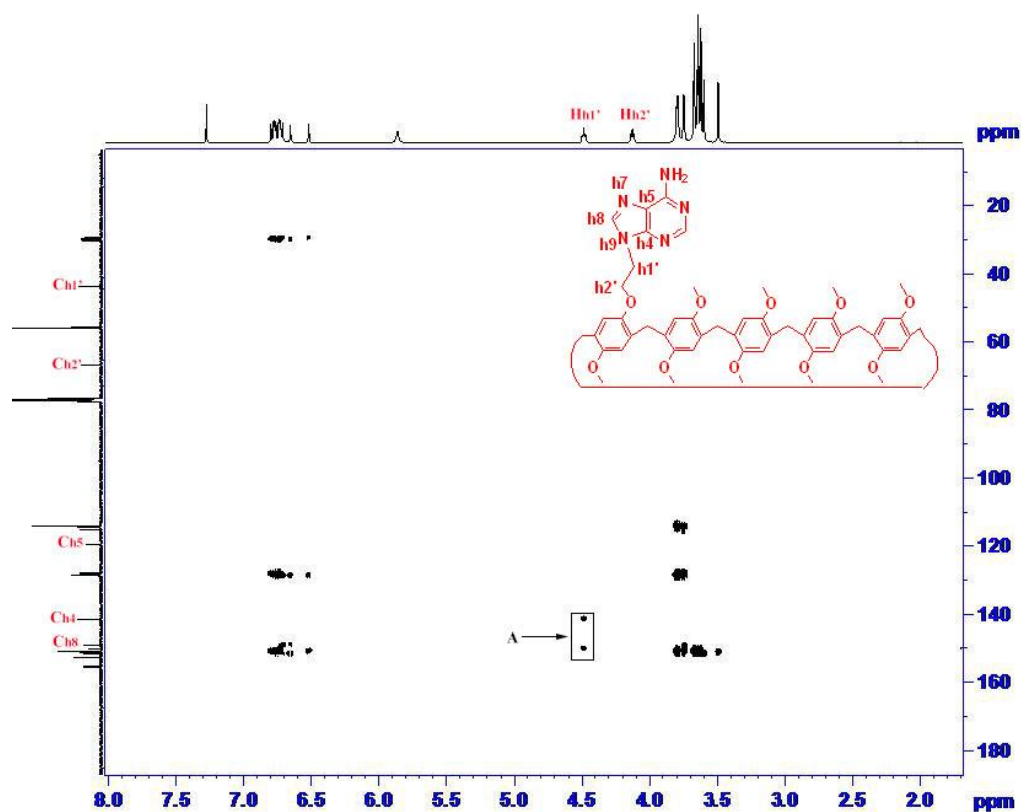
$$K_a = \frac{[H \cdot G]_c}{[H]_{uc}\,[G]_{uc}}$$

5. 2D NMR experiments

Fig. S8 HMBC spectrum of **H**. As shown in this figure, C_{h4} and C_{h8} exhibit the ^3J correlation with $H_{h1'}$ (peaks A) while C5 shows no correlation with $H_{h1'}$, indicating that **P1** reacted with adenine at h9 location.
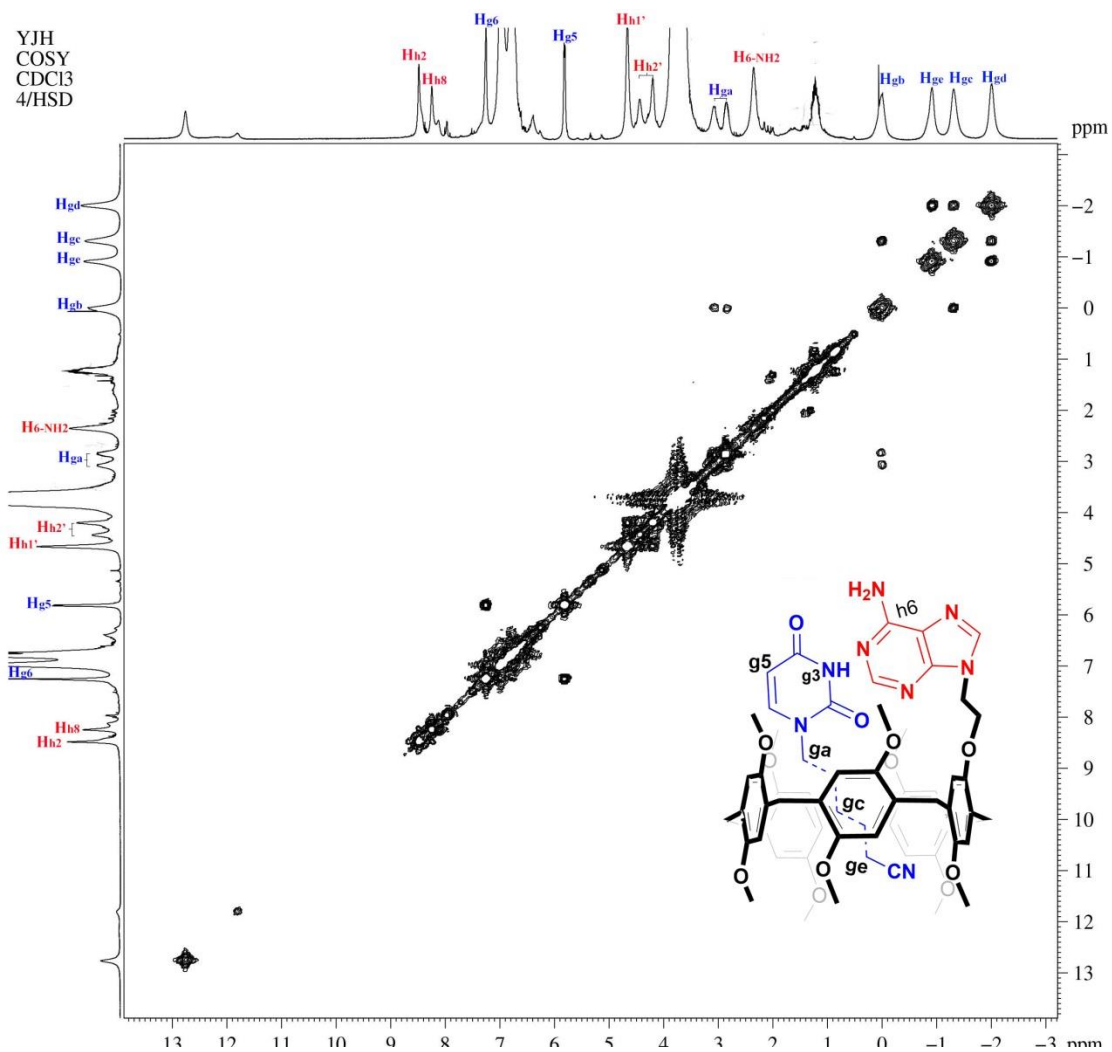
Fig. S9 2D COSY spectrum (400 MHz, CDCl₃) of the aggregate of G⊂H in CDCl₃ (100 mM). The illustration shows the possible structure of [2]pseudorotaxane .

Fig. S10 HSQC spectrum (400 MHz, CDCl₃) of the aggregate of G⊂H in CDCl₃ (100 mM). The illustration shows the possible structure of [2]pseudorotaxane .
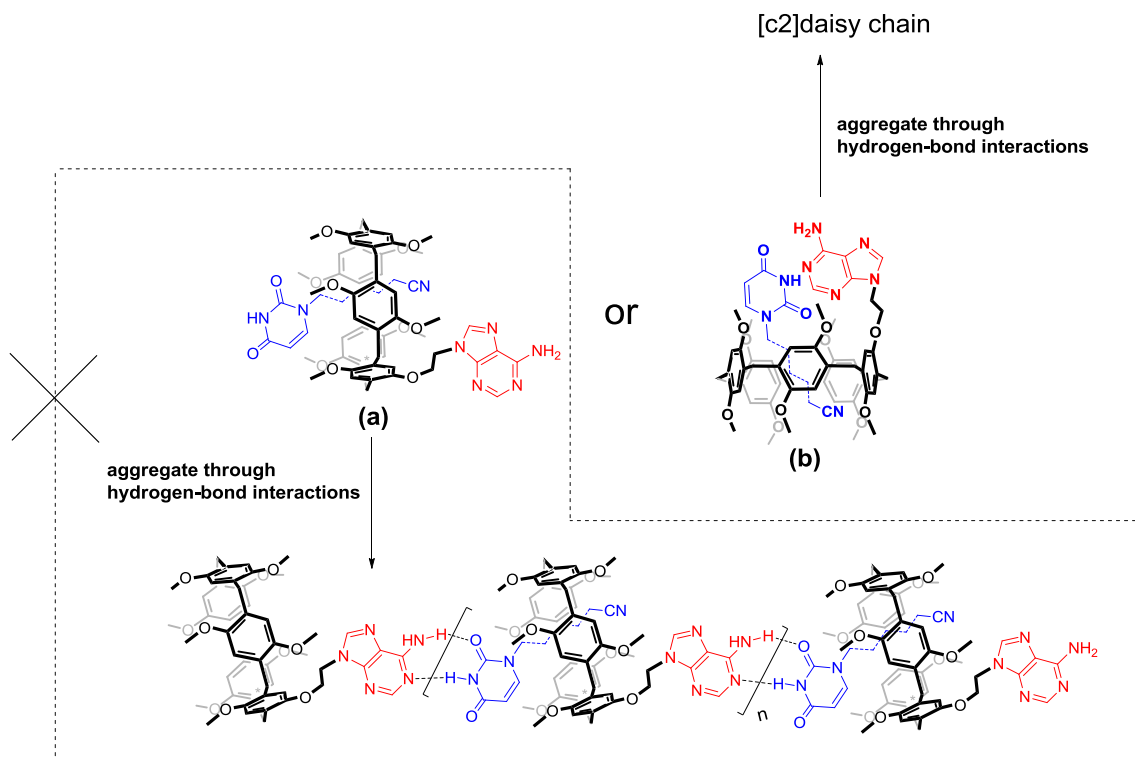
Fig. S11 Possible structures of [2]pseudorotaxane and their aggregates through hydrogen-bond interactions.

As can be seen in Fig.S11a and Fig. 4, in supramolecular polymer three monomers are stabilized by two supramolecular interactions and two hydrogen-bond interactions exist between two [2]pseudorotaxanes. In [c2]daisy chain, two monomers are stabilized by two supramolecular interactions. At the same time, sextuple hydrogen-bond interactions exist between two [2]pseudorotaxanes. Then [c2] daisy chain seems to be thermodynamically more stable than supramolecular polymer systems. So **H** and **G** does not form supramolecular polymer but form [c2]daisy chain.

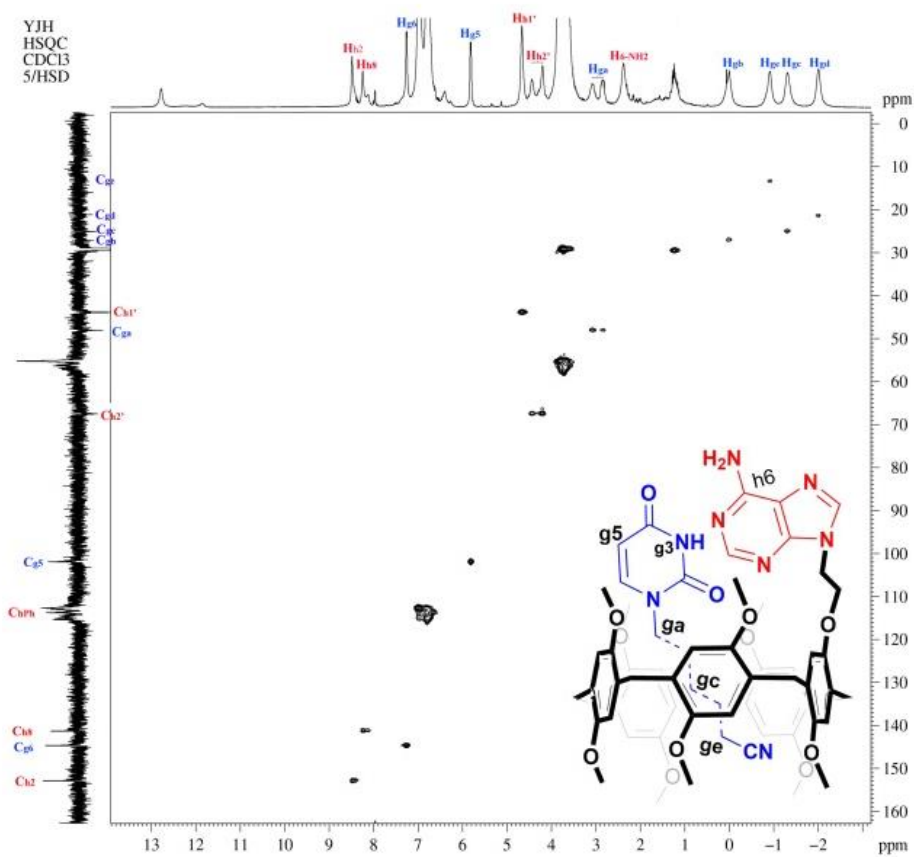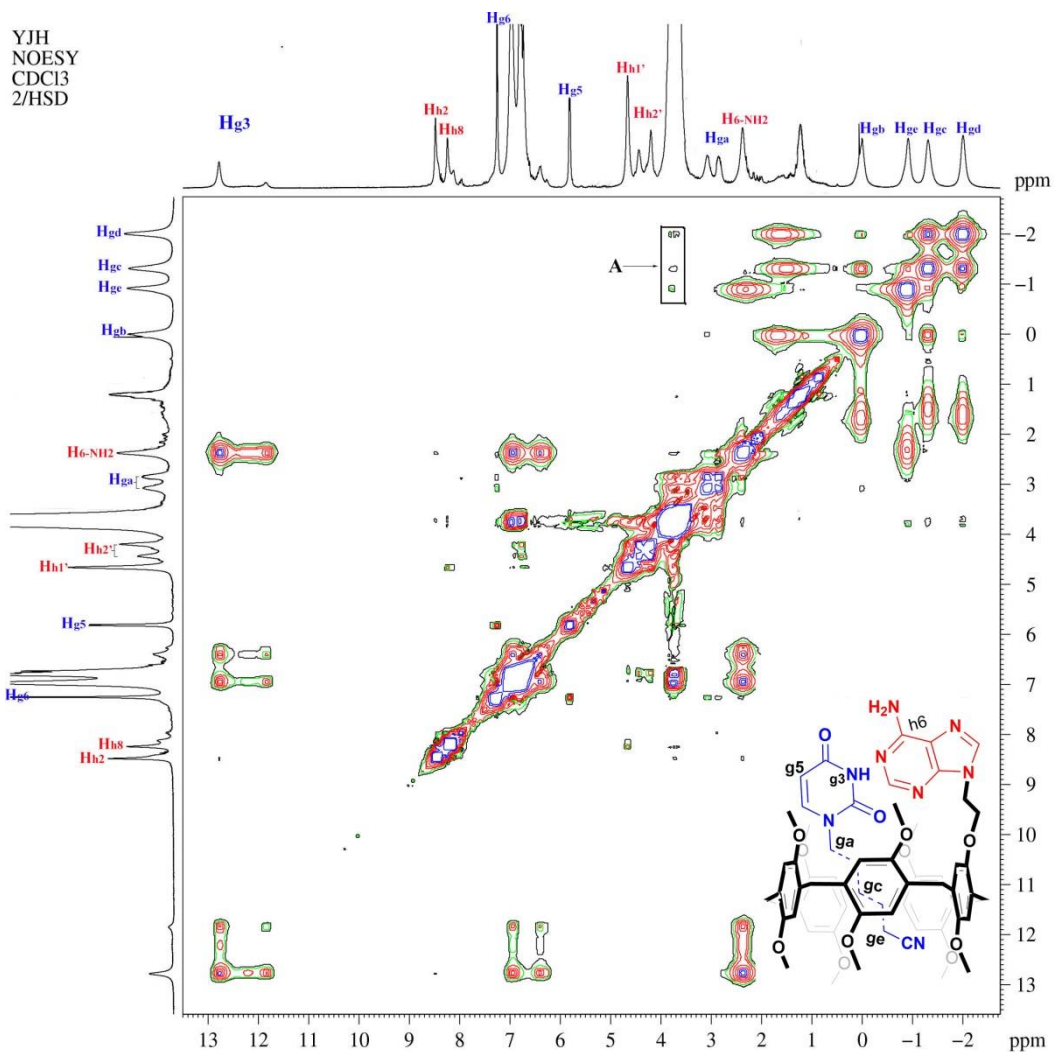Fig. S12 2D NOESY spectrum (400 MHz, CDCl$_3$) of the aggregate of G⊂H in CDCl$_3$ (100 mM). The illustration show the possible structure of [2]pseudorotaxane. Peak A represents the correlation signals of methylene protons g$_c$-g$_d$ with methyl protons of **H**.
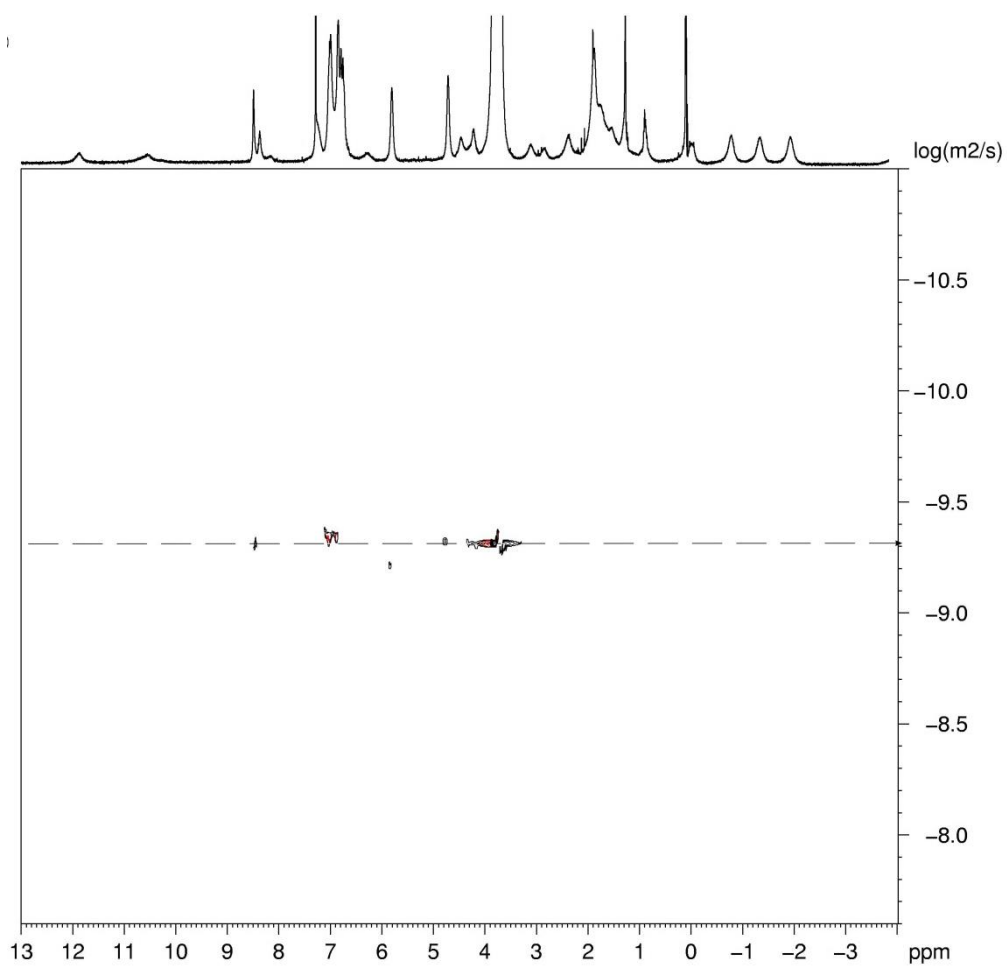
Fig. S13 DOSY spectrum (400 MHz, CDCl$_3$, 298K) of the aggregate of G⊂H in CDCl$_3$ (M_H+M_G = 1082 g/mol, 2(M_H+M_G) = 2164 g/mol) at a concentration of 10 mM. Only one set of signals of G⊂H could be observed from the DOSY spectrum (D= 4.90 ×10^{-10} m^2 S^{-1}).
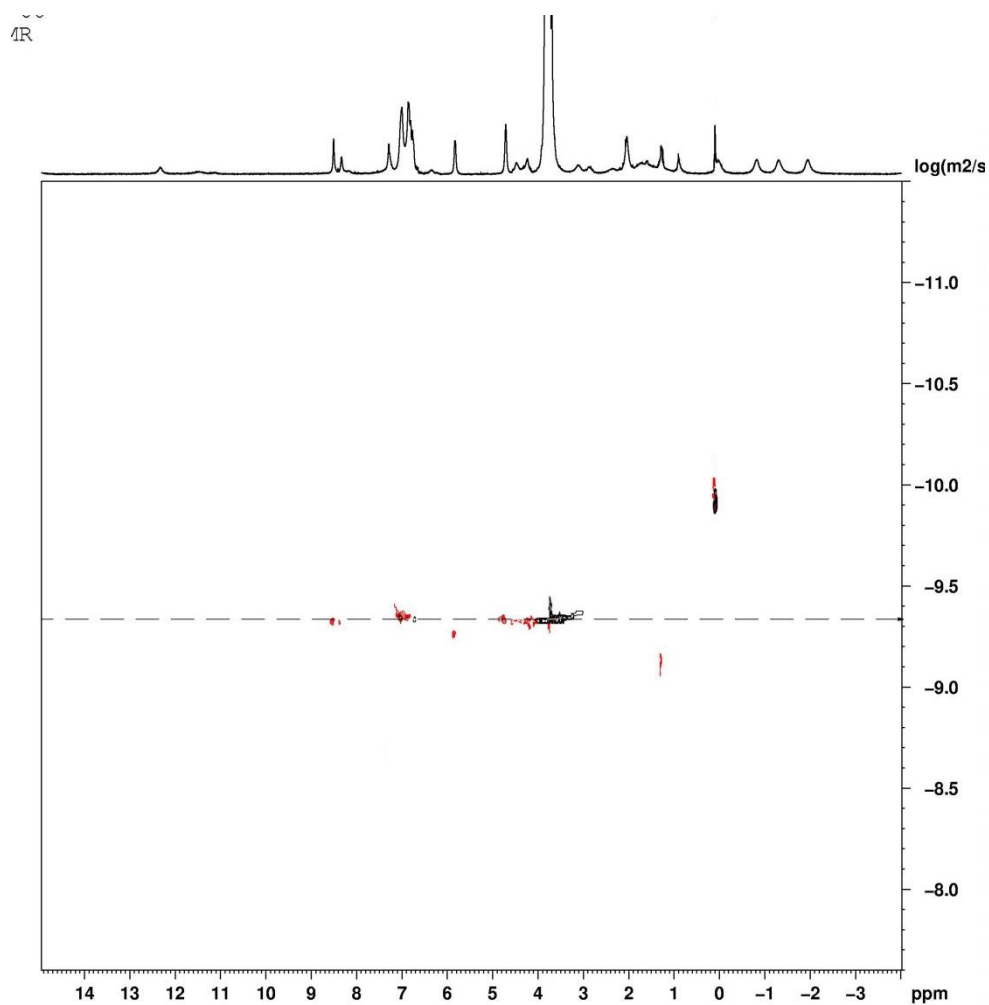
Fig. S14 DOSY spectrum (400 MHz, CDCl$_3$, 298K) of the aggregateof G⊂H in CDCl$_3$ ($M_H+M_G = 1082$ g/mol, 2 (M_H+M_G) = 2164 g/mol) at a concentration of 60 mM. Only one set of signals of G⊂H could be observed from the DOSY spectrum (D= 4.57 ×10^{-10} m^2 S^{-1}).

Fig. S15 DOSY spectrum (400 MHz, CDCl$_3$, 298K) of the aggregate of G⊂H in chloroform ($M_H+M_G = 1082$ g/mol, 2 (M_H+M_G) = 2164 g/mol) at a concentration of 150 mM. Only one set of signals of G⊂H could be observed from the DOSY spectrum (D= 3.31 ×10^{-10} m^2 S^{-1}).
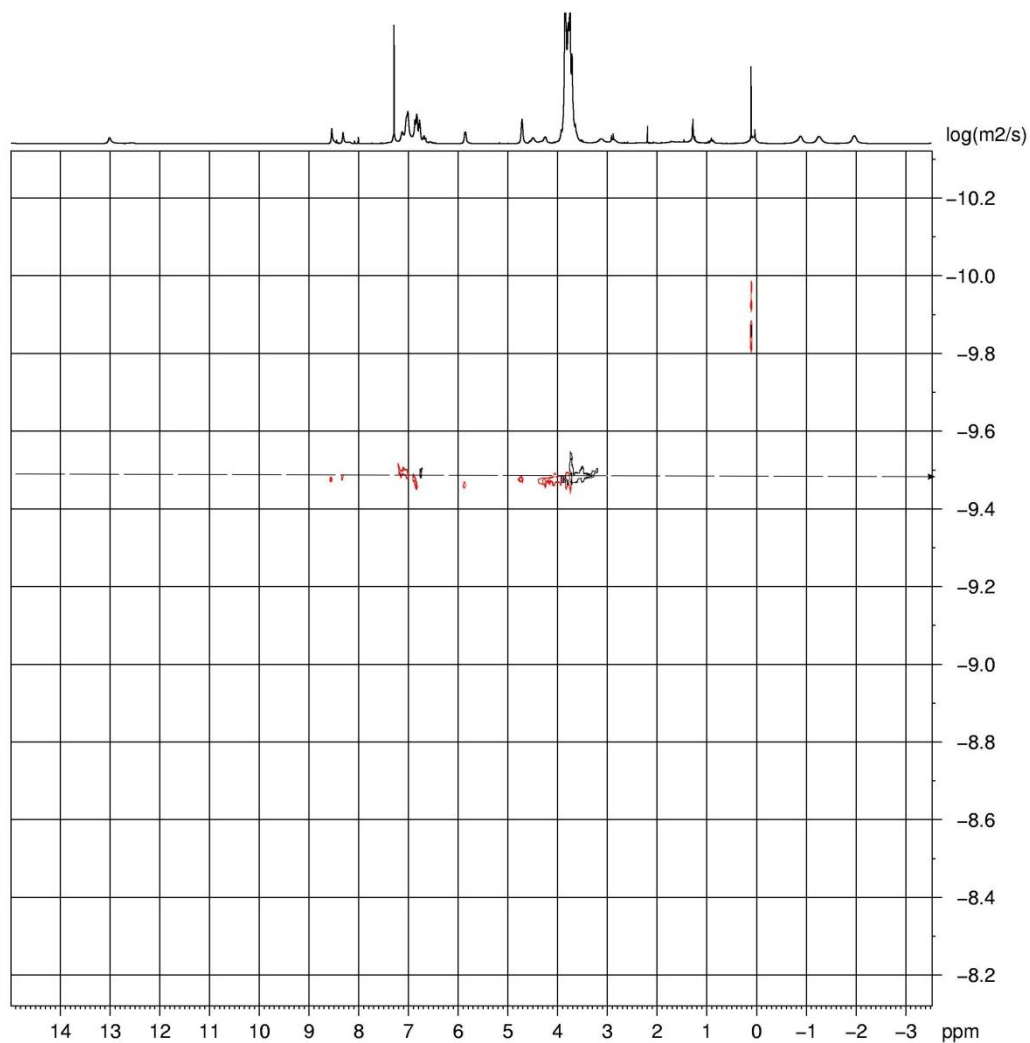
Fig. S16 DOSY spectrum (400 MHz, CDCl$_3$, 298K) of the aggregate of G⊂H in chloroform (M_H+M_G = 1082 g/mol, *2* (M_H+M_G) = 2164 g/mol) at a concentration of 200 mM. Only one set of signals of G⊂H could be observed from the DOSY spectrum (D= 2.51 ×10^{-10} m^2 ·S^{-1}).
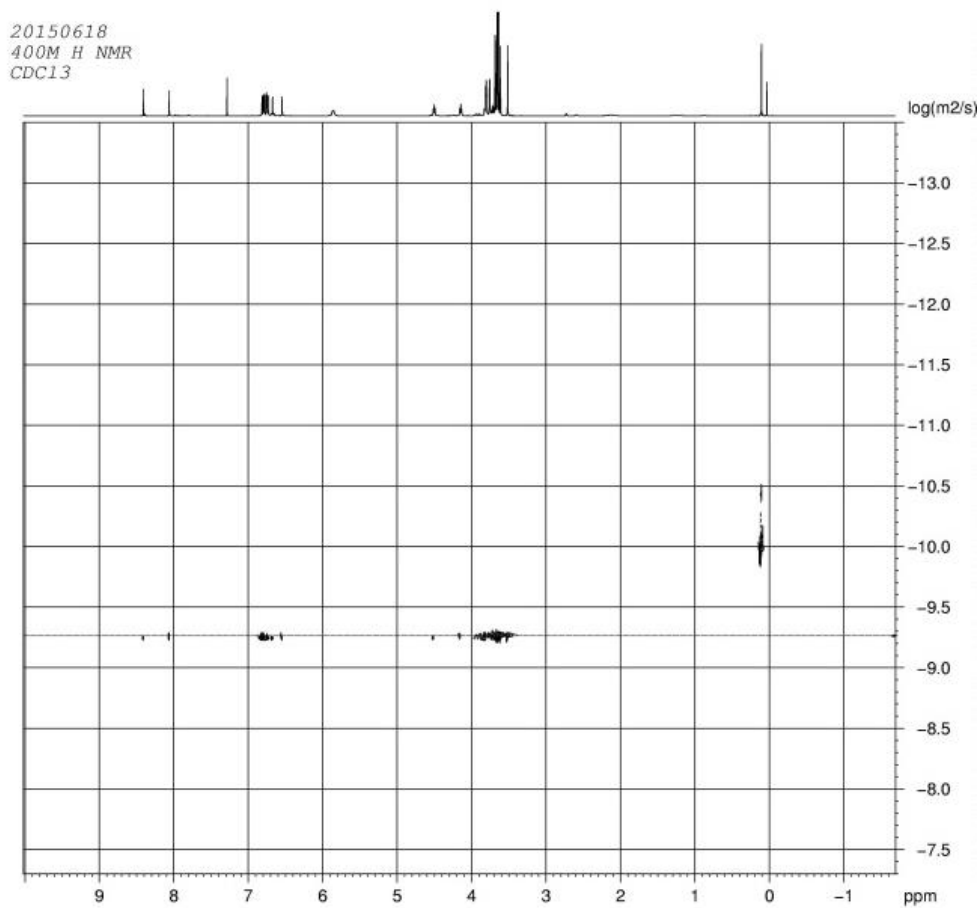
Fig. S17 DOSY spectrum (400 MHz, CDCl$_3$, 298K) of **H** in chloroform (*M* = 875 g/mol) at a concentration of 60 mM. Only one set of signals of H could be observed from the DOSY spectrum (D= 5.62×10^{-10} m$^2 \cdot$S^{-1}).
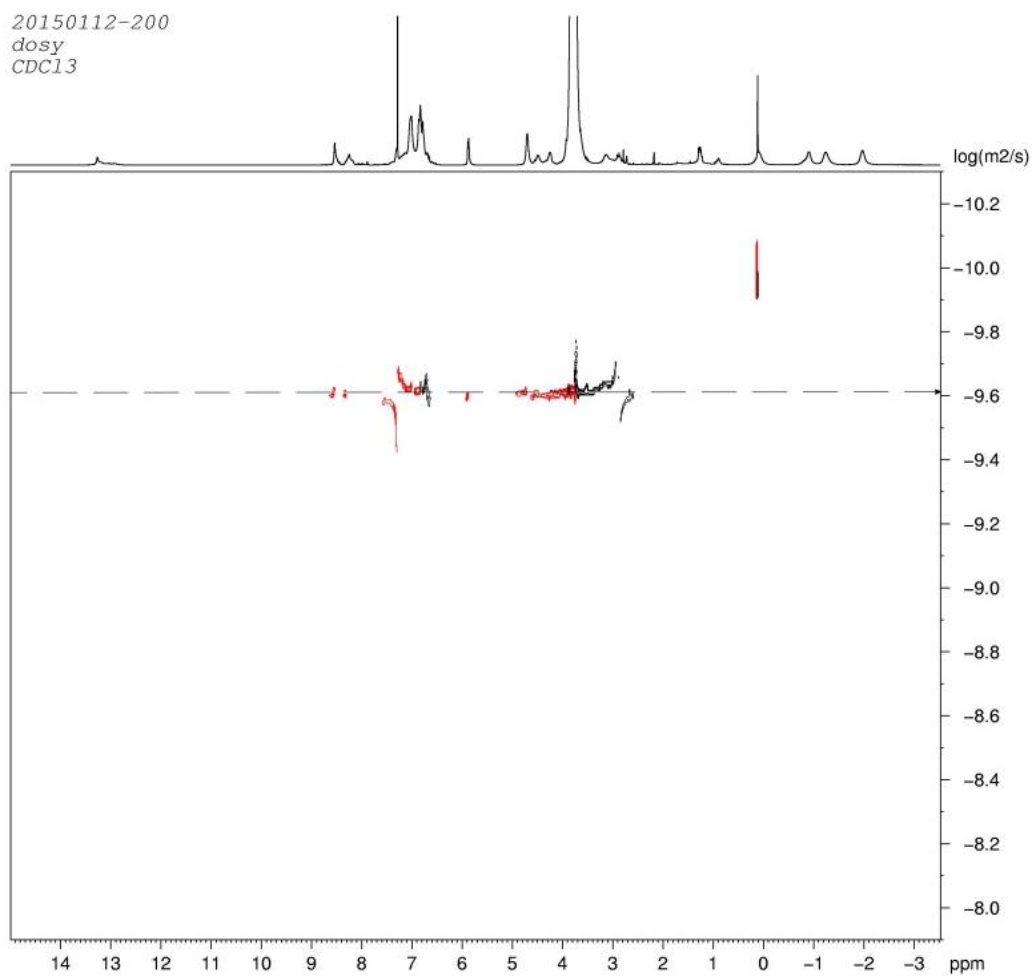
6. ESI-MS spectra of equal molar mixtures of H and G in CHCl₃

Fig. S18 ESI-MS spectrum of the equal molar mixtures of **H** and **G** in chloroform in the positiveion mode. The peak at m/z = 208.1085 is corresponding to the [G+H]⁺ and m/z = 898.4069 is corresponding to the [H+Na]⁺ respectively. No peak for the [2]pseudorotaxane or daisy chain could be found.

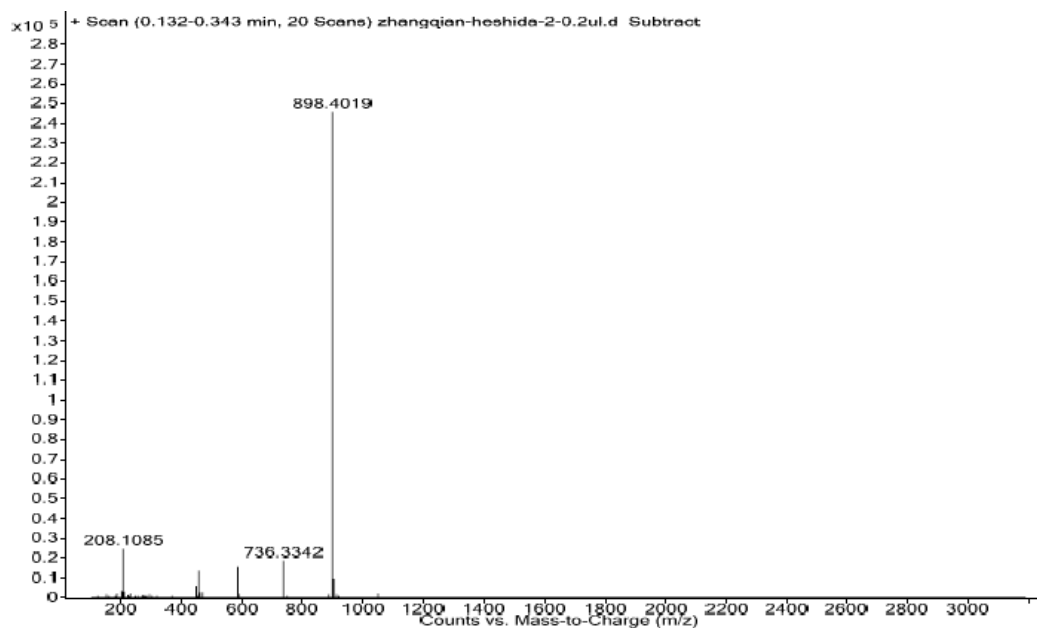# 7. Crystal structure and crystal data of G⊂H
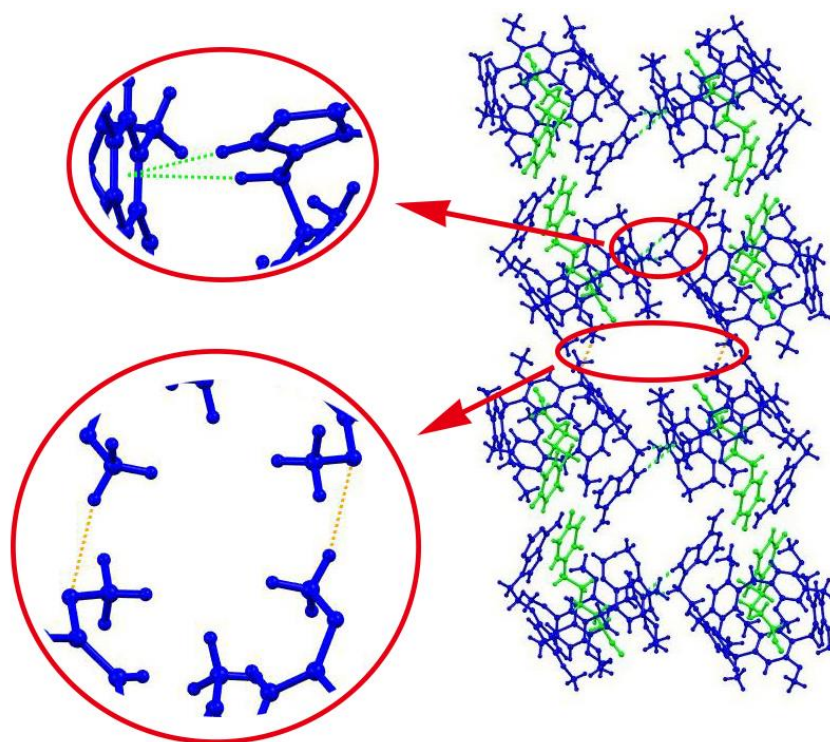
Fig. S19 Packing plot of G⊂H in the solid state showing the C-H···π (green dotted lines) and C-H···o (orange dotted lines) interactions between [c2]daisy chains. The distances of c-H···π-plane distances were 2.894-2.959 Å and that of H···O were 2.555 Å. Solvent molecules are omitted for clarity.

Table S1 Crystal data and structure refinement for G⊂H

CCDC number	1412888
Empirical formula	$C_{51}H_{55}N_5O_{10}; C_{10}H_{13}N_3O_2$
Formula weight	875 g/mol; 229 g/mol
Temperature	160 K
Wavelength	1.54178
Crystal system	monoclinic
Space group	C 2/C
a	48.4242 (10) Å
b	11.8956 (2) Å

c	22.5531 (4) Å
α	90.00 °
β	94.643 (2) °
γ	90.00 °
Volume	12946.1 (4) Å^3
Z	48
Density (calculated)	1.13407 g/cm^3
Absorption coefficient	0.653
F(000)	4688
Crystal size	0.33 x 0.25 x 0.22 nm^3
Theta range for data collection	3.915 to 76.167 °
Index ranges	−45<=h<=60, −14<=k<13, −28<=l<=28
Reflections collected	13293
Independent reflections	9718 [R(int) = 0.041]
Completeness to theta = 26.00 °	0.975
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F2
Goodness-of-fit on F^2	1.14
Final R indices [I > 2sigma(I)]	R1=0.0897,wR2= 0.2701
R indices (all data)	R1= 0.1067,wR2= 0.2915
Largest diff. peak and hole	1.21 and -1.06 e Å^{-3}

S1 N. L. Strutt, R. S. Forgan, J. M. Spruell, Y. Y. Botros and J. F. Stoddart, *J. Am. Chem. Soc.*, 2011, **133**, 5668-5671.

S2 Association constants determined using the ^{1}H NMR single point methods. See: (a) A. B. Braunschweig, C. M. Ronconi, J.-Y. Han, F. Arico, S. J. Cantrill, J. F. Stoddart, S. I. Khan, A. J. P. White and D. J. Williams, *Eur. J. Org. Chem.* 2006, 1857-1866; b) S. J. Loeb and J. A. Wisner, *Angew. Chem. Int. Ed.* 1998, **37**, 2838-2840; c) S. J. Loeb, J. Tiburcio and S. J. Vella, *Org. Lett.* 2005, **7**, 4923-4926; d) J.-M. Zhao, Q.-S. Zong, T. Han, J.-F. Xiang and C.-F. Chen, *J. Org. Chem.* 2008, **73**, 6800-6806; e) C. Li, S. Chen, J. Li, K. Han, M. Xu, B. Hu, Y. Yu and X. Jia, *Chem. Commun.*, 2011, **47**, 11294-11296.