Three-dimensional supramolecular polymerization based on pillar[*n*]arenes (*n* = 5, 6) and halogen bonding interactions

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Electronic Supplementary Information (14 pages)

1. Materials and Methods:

Pillar[*n*]arenes[S1a] and 1,4-di(1*H*-imidazol-1-yl)butane (**G1**)[S1b] were synthesized according to literature procedures. The guest molecules 1,4-diazabicyclo[2.2.2]octane (**G2**) and linker molecule 1,4-diiodotetrafluorobenzene (**L**) were purchased from Shanghai Aladdin Bio-Chem Company and used without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. ^{1}H NMR spectra were collected on a Bruker Ascend™ 400 MHz spectrometer. ^{13}C NMR spectra were recorded on a Bruker Ascend™ 400 MHz spectrometer at 100 MHz. ^{19}F NMR spectra were recorded on a Bruker Ascend™ 400 MHz spectrometer at 396 MHz.

*2. [1]H NMR investigation of **(DEP5⊃G1•L)** at different concentrations of **L***

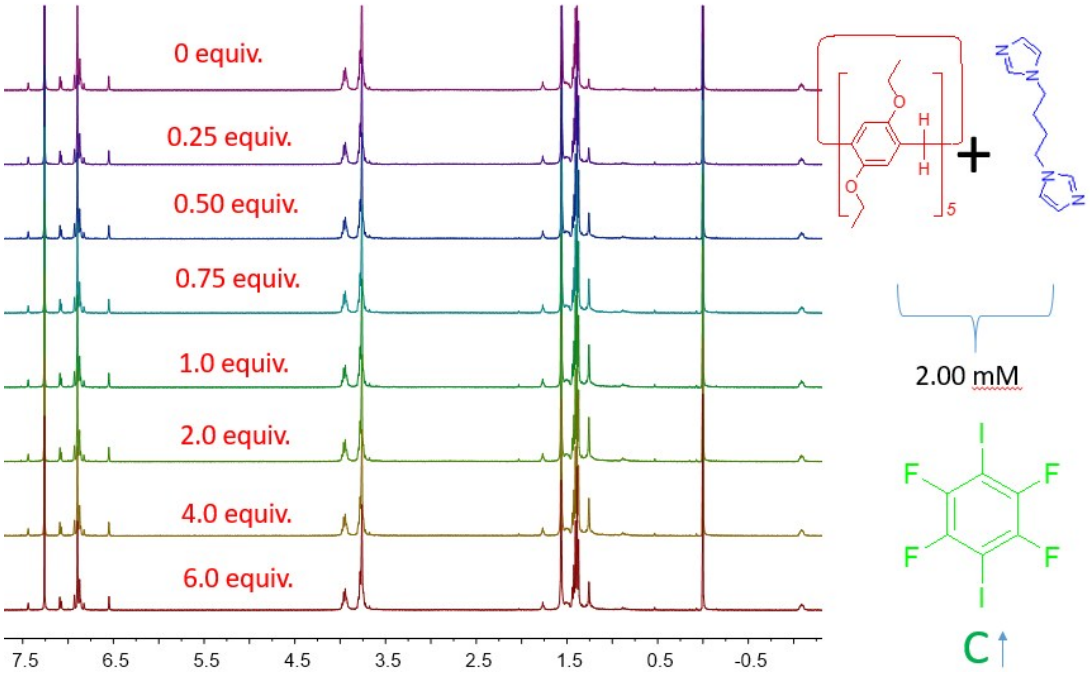


Fig.S1 Partial [1]H NMR spectra (400 MHz, $CDCl_3$, 22 °C) of **(DEP5⊃G1•L)** with **L** at different concentrations: 0.00 mmol; 0.50 mmol; 1.00 mmol; 1.50 mmol; 2.00 mmol; 4.00 mmol; 8.00 mmol; 12.0 mmol. (**DEP5⊃G1** was kept as constant at 2.00 mM)

*3. [19]F NMR investigation of **(DEP5⊃G1•L)** at different concentrations of **DEP5⊃G1***

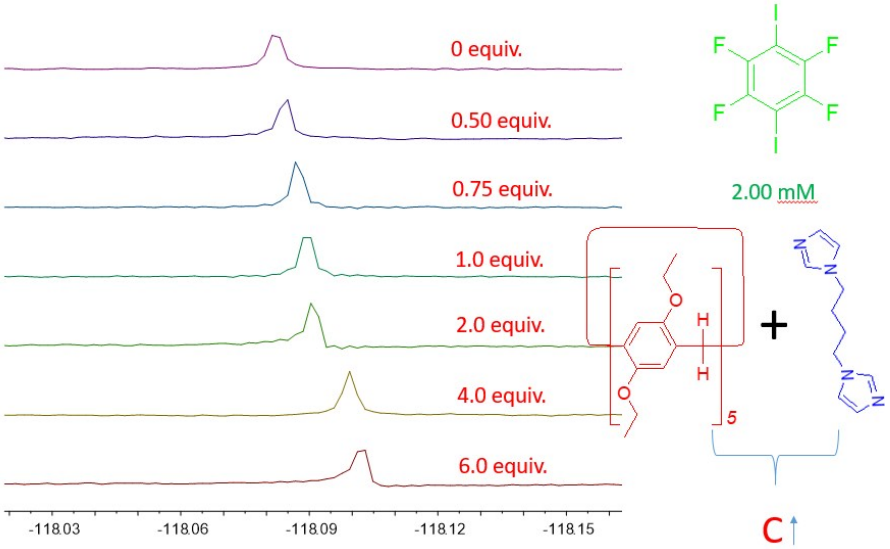


Fig.S2 Partial [19]F NMR spectra (396 MHz, $CDCl_3$, 22 °C) of **(DEP5⊃G1•L)** with ***DEP5⊃G1*** at different concentrations: 0.00 mmol; 1.00 mmol; 1.50 mmol; 2.00 mmol; 4.00 mmol; 8.00 mmol; 12.0 mmol. (**L** was kept as constant at 2.00 mM)

*4. [1]H NMR investigation of **(DPP5⊃G1•L)** at different concentrations*

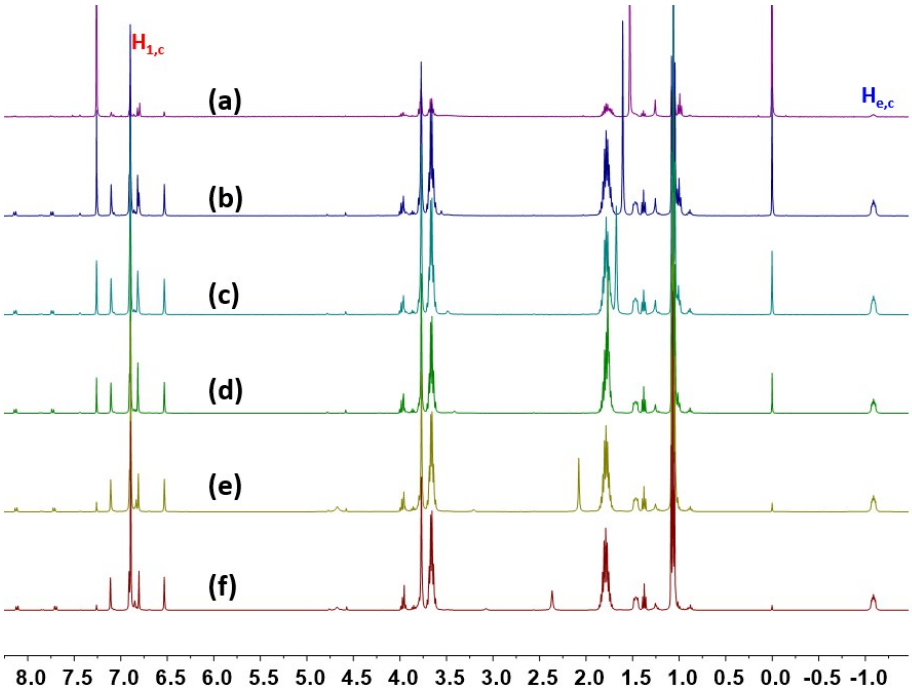


Fig.S3 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 22 °C) of **(DPP5⊃G1•L)** (1/1/1) at different concentrations: (a) 1.00 mmol; (b) 8.00 mmol; (c) 16.0 mmol; (d) 32.0 mmol; (e) 62.5 mmol; (f) 125 mmol.

*5. [19]F NMR investigation of **(DPP5⊃G1•L)** at different concentrations*

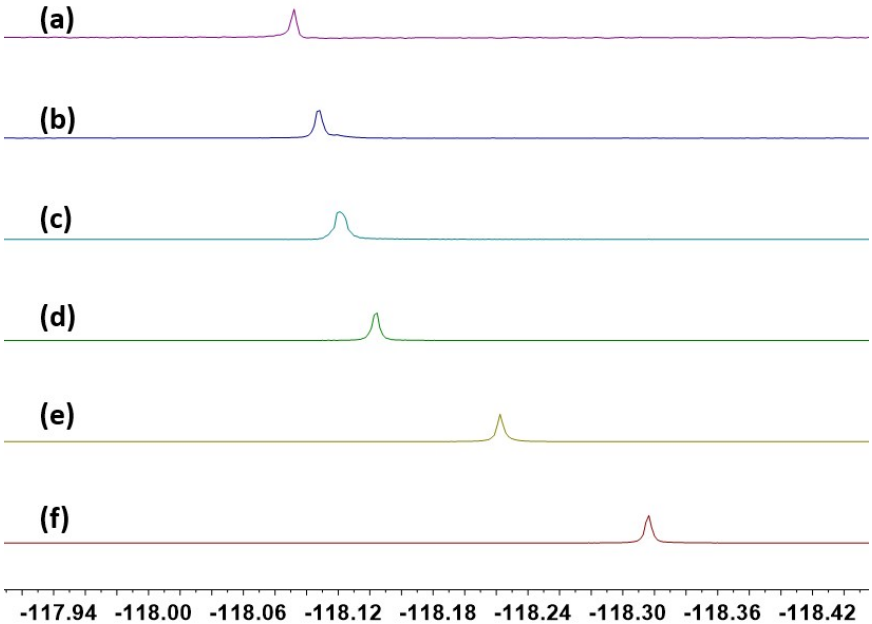


Fig.S4 Partial ^{19}F NMR spectra (396 MHz, $CDCl_3$, 22 °C) of **(DPP5⊃G1•L)** (1/1/1) at different concentrations: (a) 1.00 mmol; (b) 8.00 mmol; (c) 16.0 mmol; (d) 32.0 mmol; (e) 62.5 mmol; (f) 125 mmol.

6. X-ray crystal data of ***(DEP5⊃G1•L)***

Crystal data of **(DEP5⊃G1•L)**: white, $C_{55}H_{70}O_{10}$•$C_{10}H_{14}N_4$•$C_6F_4I_2$, FW 1483.22, triclinic, space group P-1, a = 14.2852(6), b = 15.3486(7), c = 16.0133(7) Å, α = 87.769(4)° , β = 85.092(4)°, γ = 79.626(4)°, V = 3440.0(3) $Å^3$, Z = 2, D_c = 1.432 g cm^{-3}, T = 140(2) K, μ = 7.765 mm^{-1}, 23749 measured reflections, 12272 independent reflections, 841 parameters, 1410 restraints, F(000) = 1520, R_1 = 0.1031, wR_2 = 0.2747 (all data), R_1 = 0.0967, wR_2 = 0.2607 [I > 2σ(I)], max. residual density 2.902 e•$Å^{-3}$, and goodness-of-fit (F2) = 1.041. CCDC-1865312.

7. ^{19}*F NMR investigation of* ***(DEP5⊃G1•L)*** *at different concentrations*

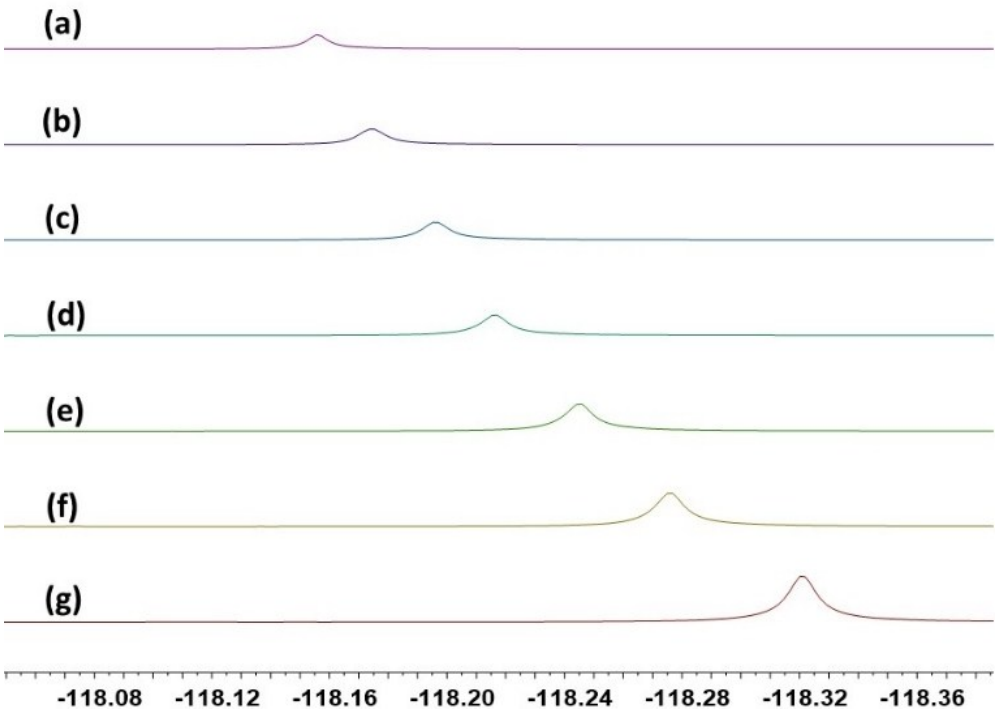


Fig.S5 Partial ^{19}F NMR spectra (376 MHz, $CDCl_3$, 22 °C) of **(DEP5⊃G1)•L** (1/1/1) at different concentrations: (a) 45.0 mmol; (b) 55.0 mmol; (c) 70.0 mmol; (d) 90.0 mmol; (e) 115 mmol; (f) 145 mmol; (g) 200 mmol.

8. The π•••π stacking interactions of ***(DEP5⊃G1•L)***

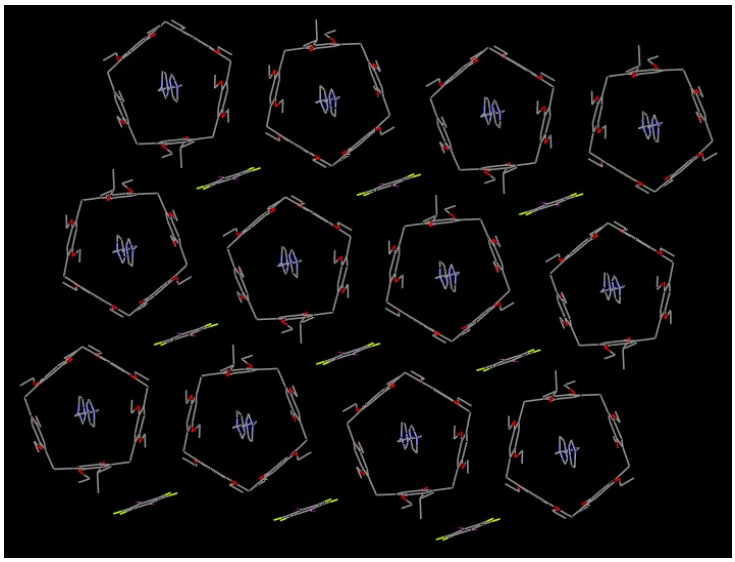
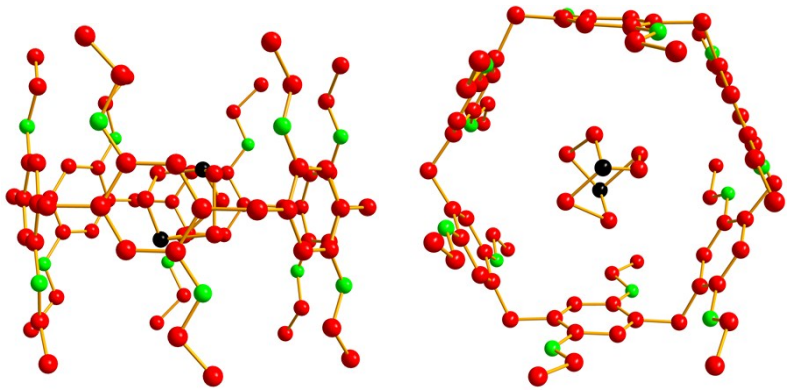


Fig.S6 Top view of the π•••π stacking pattern in the crystal structure.

9. The crystal structure of ***(DEP6⊃G2)*** *in solid state*



(A) Side View (B) Top View

Fig.S7 The crystal structure of **(DEP6⊃G2)**.

10. ***(DEP6⊃G2•L)*** *in different solvents*

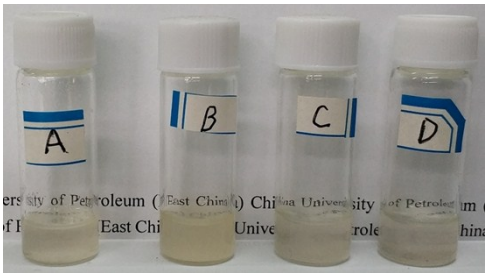


Fig.S8 (DEP6⊃G2•L) in different solvents: (A) $CHCl_3$; (B) acetone; (C) DMF; (D) DMSO.

11. The proposed π•••π stacking pattern of ***(DPP6⊃G2•L)*** *in solid state*

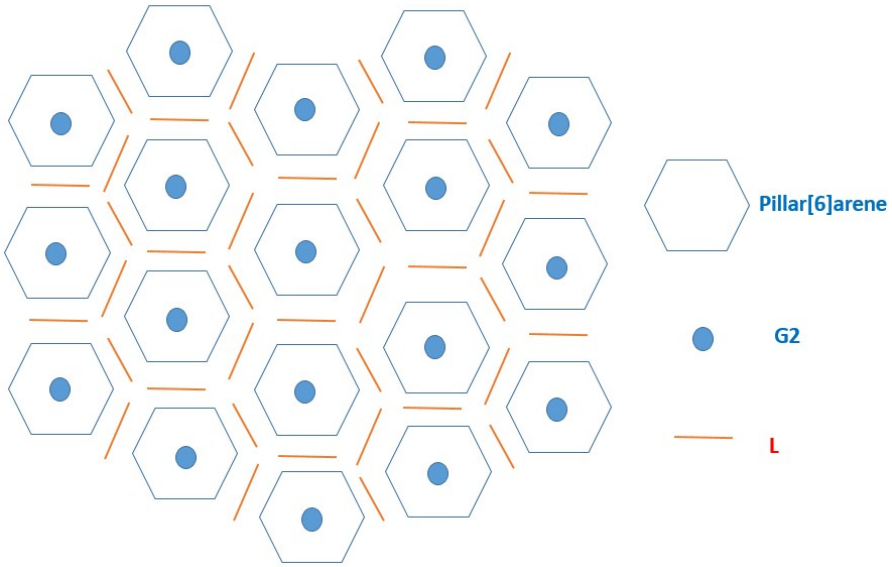


Fig.S9 Top view of the proposed π•••π stacking pattern *of* **(DPP6⊃G2•L)** in the solid state.

12. Variable temperature ^{1}*H NMR spectra of* ***(DPP6⊃G2•L)***

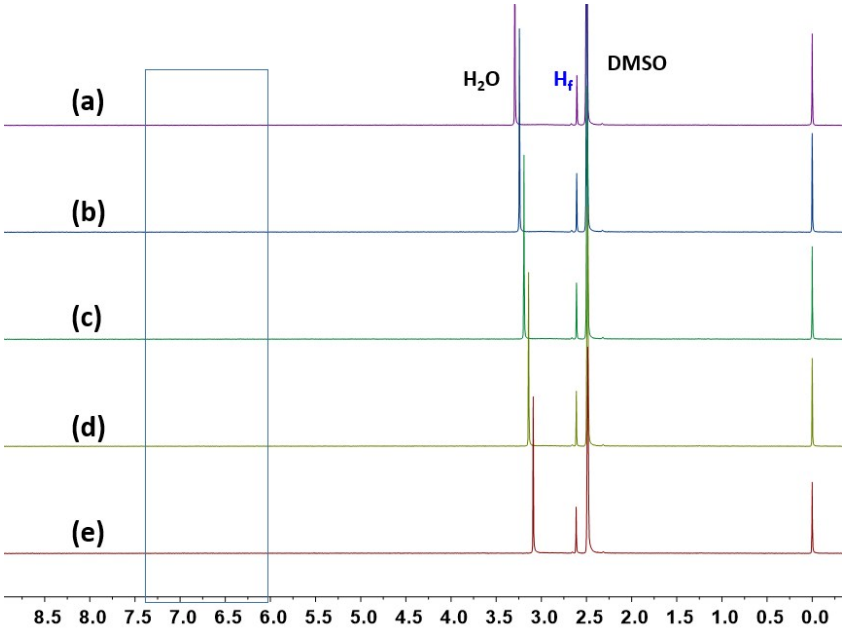


Fig.S10 Variable temperature ^{1}H NMR spectra (400 MHz, DMSO-d_6) of **(DPP6⊃G2•L)** (**G2•L** is slightly excess) at different temperatures: (a) 30 °C; (b) 40 °C; (c) 50 °C; (d) 60 °C; (e) 70 °C. (**No trace of DPP6 even at 70 °C**).

*13. [1]H NMR tube of **DPP6⊃G2** and **DEP5⊃G1** mixture with adding of **L***

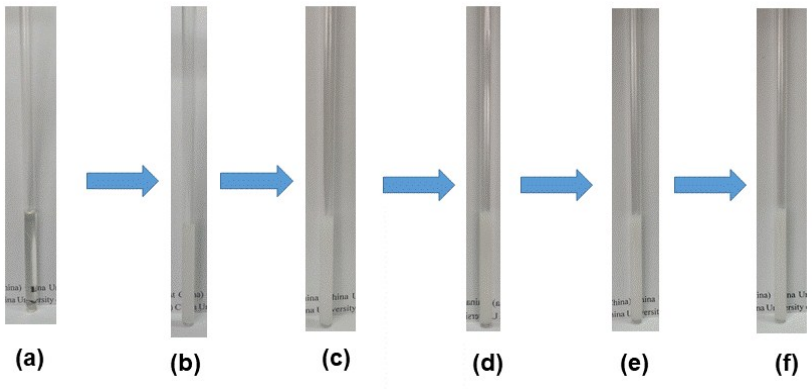


Fig.S11 Photos of [1]H NMR tube of **DPP6⊃G2** (**DPP6** is slight excess) and **DEP5⊃G1** mixture at 10 mM with adding of **L** (a) 0 equiv.; (b) 0.5 equiv.; (c) 1.0 equiv.; (d) 2.0 equiv.; (e) 3.0 equiv.; (f) 4.0 equiv.

*14. The determination of the association constants of **DEP6/DPP6⊃G2***

(1) To determine the association constant for the complexation between **DEP6** and guest molecule (**G2**), NMR titrations were done with solutions which had a constant concentration of **DEP6** (3.00 mM) and varying concentrations of **G2**. By a non-linear curve-fitting method, the association constant (K_a) of **DEP6⊃G2** was estimated to be about 61.6 (± 4.8) M^{-1}.

The non-linear curve-fitting was based on the equation [S2]:

$$\Delta\delta = (\Delta\delta_\infty/[H]_0)\ (0.5[G]_0 + 0.5([H]_0+1/K_a)-(0.5\ ([G]_0^2+(2[G]_0(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5})) \quad \text{(Eq. S1)}$$

Where $\Delta\delta$ is the chemical shift change of H_2 on **DEP6** at $[G]_0$, $\Delta\delta_\infty$ is the chemical shift change of H_1 when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the host, and $[G]_0$ is the initial concentration of **G2**.

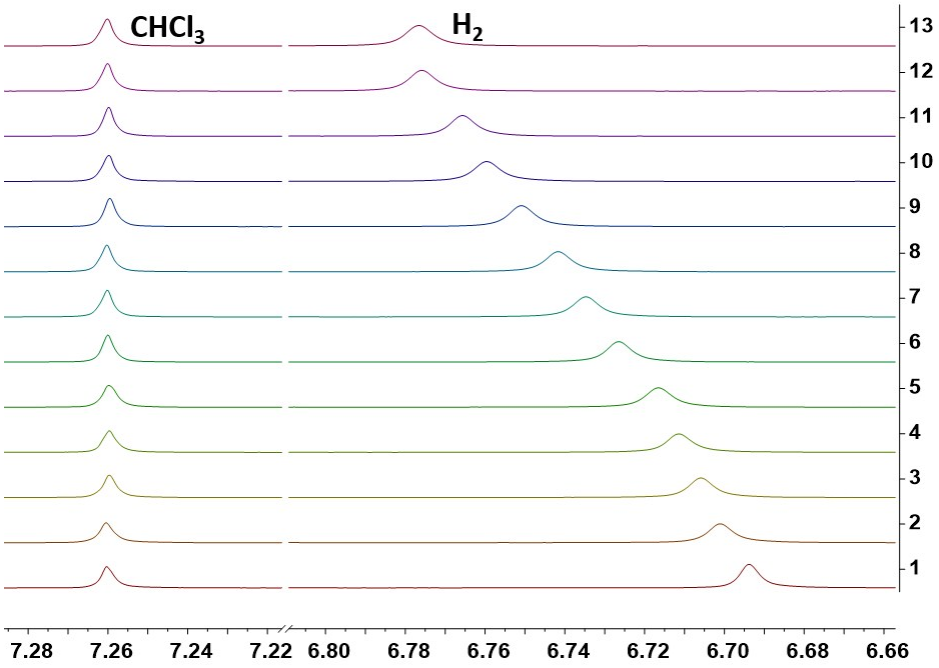


Fig. S12. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, room temperature) of **DEP6** at a concentration of 3.00 mM upon addition of **G2** (15 mM): (1) 0.00 μL, (2) 10.0 μL to (1), (3) 10.0 μL to (2), (4) 10.0 μL to (3), (5) 10.0 μL to (4), (6) 25.0 μL to (5), (7) 25.0 μL to (6), (8) 25.0 μL to (7), (9) 50.0 μL to (8), (10) 50.0 μL to (9), (11) 50.0 μL to (10), (12) 100 μL to (11), (13) 100 μL to (12).

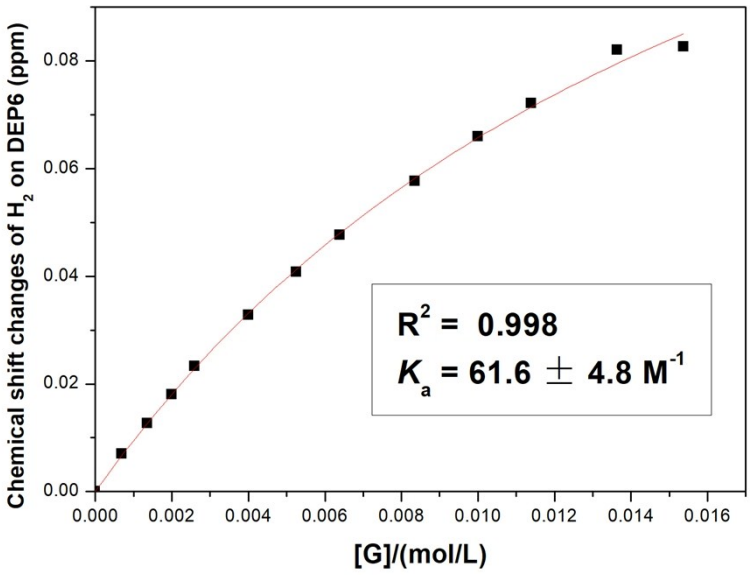


Fig. S13. The chemical shift change of H_1 on **DEP6** upon addition of **G2**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

(2) To determine the association constant for the complexation between **DPP6** and guest molecules (**G2**), NMR titrations were done with solutions which had a constant concentration of **DPP6** (3.90 mM) and varying concentrations of **G2**. By a non-linear curve-fitting method, the association constant (K_a) of **DPP6⊃G2** was estimated to be about 27.8 (± 0.4) M^{-1}.

The non-linear curve-fitting was based on the above equation S1.

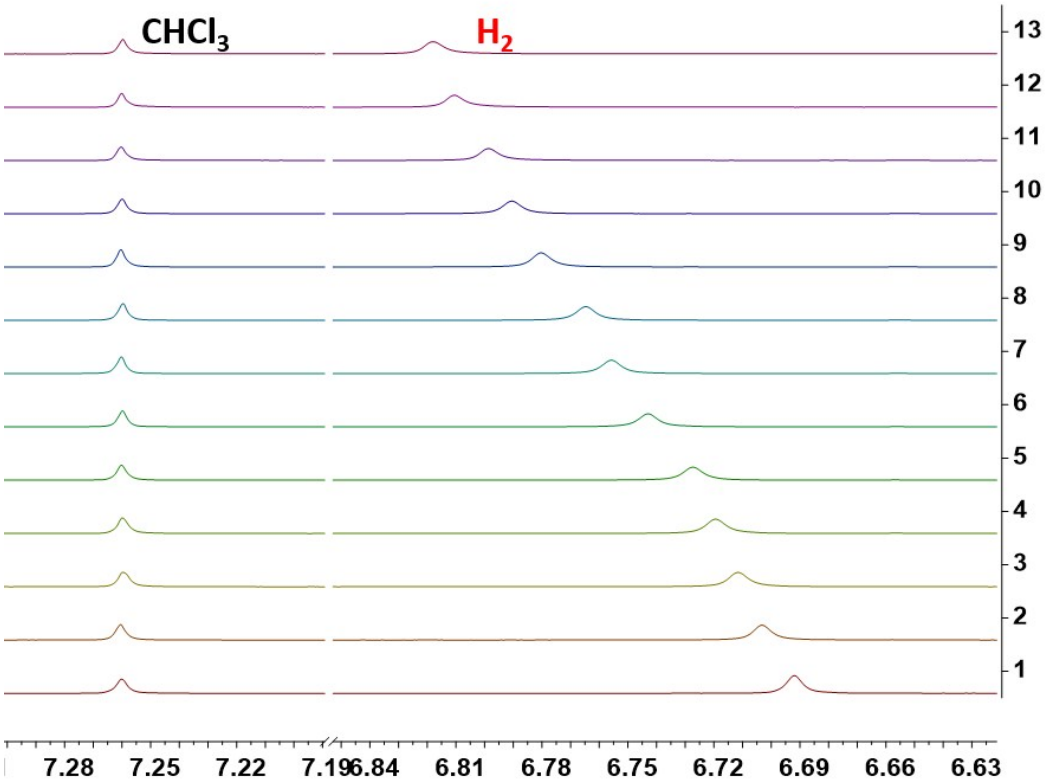


Fig. S14. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, room temperature) of **DPP6** at a concentration of 2.00 mM upon addition of **G2** (15 mM): (1) 0.00 μL, (2) 10.0 μL to (1), (3) 10.0 μL to (2), (4) 10.0 μL to (3), (5) 10.0 μL to (4), (6) 25.0 μL to (5), (7) 25.0 μL to (6), (8) 25.0 μL to (7), (9) 50.0 μL to (8), (10) 50.0 μL to (9), (11) 50.0 μL to (10), (12) 100 μL to (11), (13) 100 μL to (12).

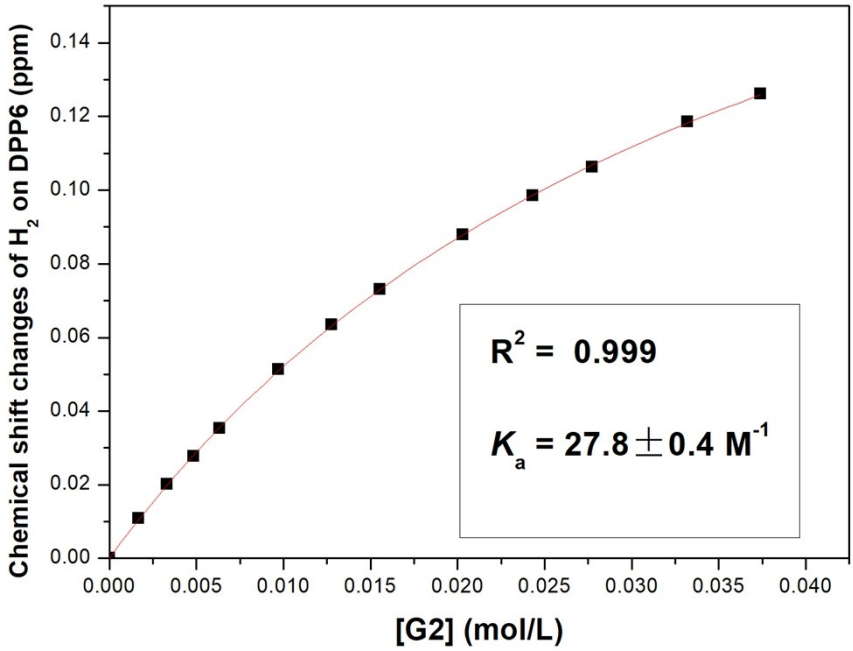


Fig. S15 The chemical shift change of H_2 on **DPP6** upon addition of **G2**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

15. Chemical shift changes of $H_{a,c}$ and $H_{b,c}$ at different concentrations of ***(DEP5⊃G1•L)***

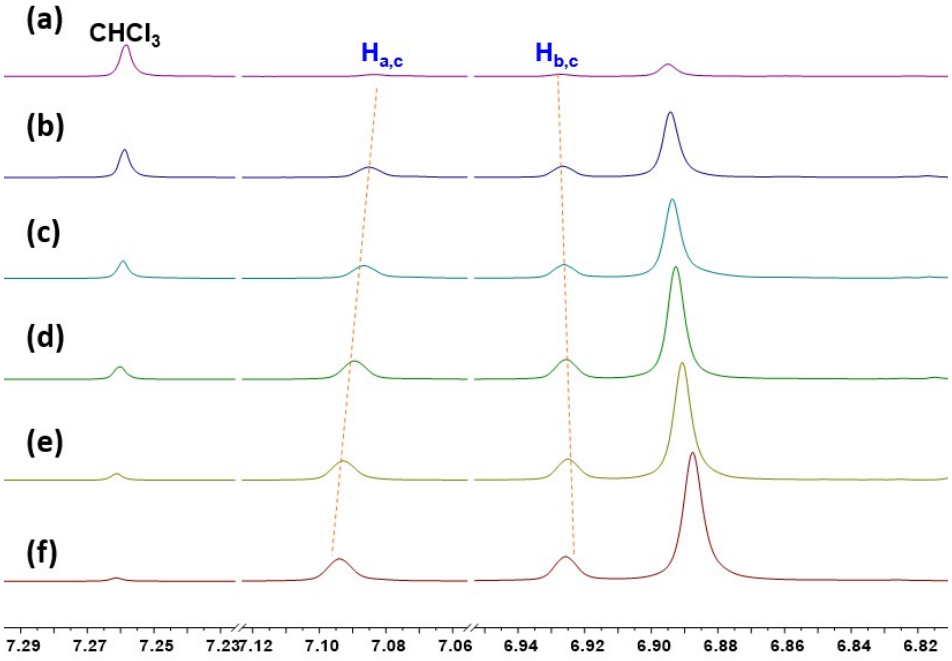


Fig. S16 Chemical shift changes of $H_{a,c}$ and $H_{b,c}$ at different concentrations of **(DEP5⊃G1•L)** (1/1/1) (400 MHz, $CDCl_3$, 22 °C): (a) 1.00 mmol; (b) 8.00 mmol; (c) 16.0 mmol; (d) 32.0 mmol; (e) 62.5 mmol; (f) 125 mmol.

*16. ^1H NMR spectra (400 MHz, $CDCl_3$, 22 °C) of **DPP6**, toluene and their mixing solution*

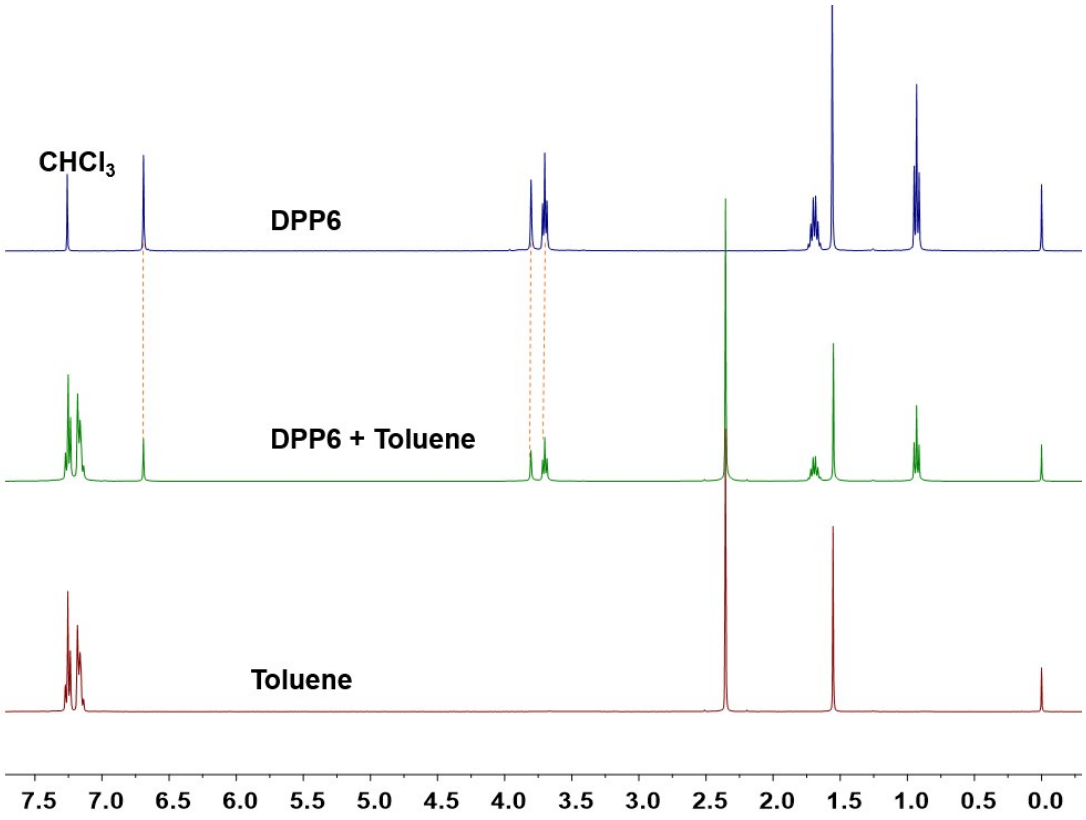


Fig. S17 ^1H NMR spectra (400 MHz, $CDCl_3$, 22 °C) of **DPP6**, toluene and their mixing solution.

*17. **G2** and **L** in $CHCl_3$ solution*

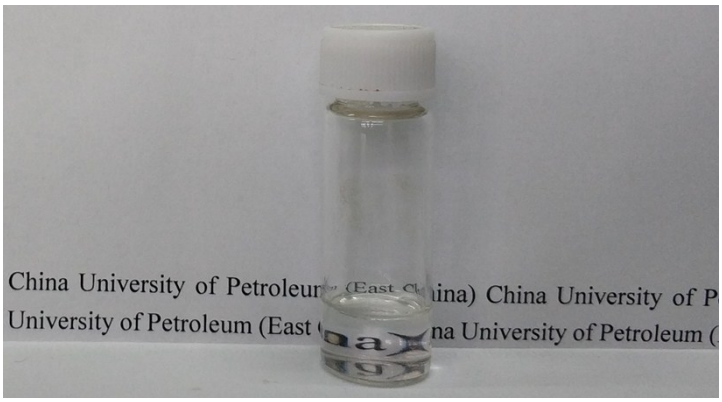


Fig. S18 G2 and **L** in $CHCl_3$ solution.

*18. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 22 °C) of **DPP6** and **DPP6•L** mixing solution*

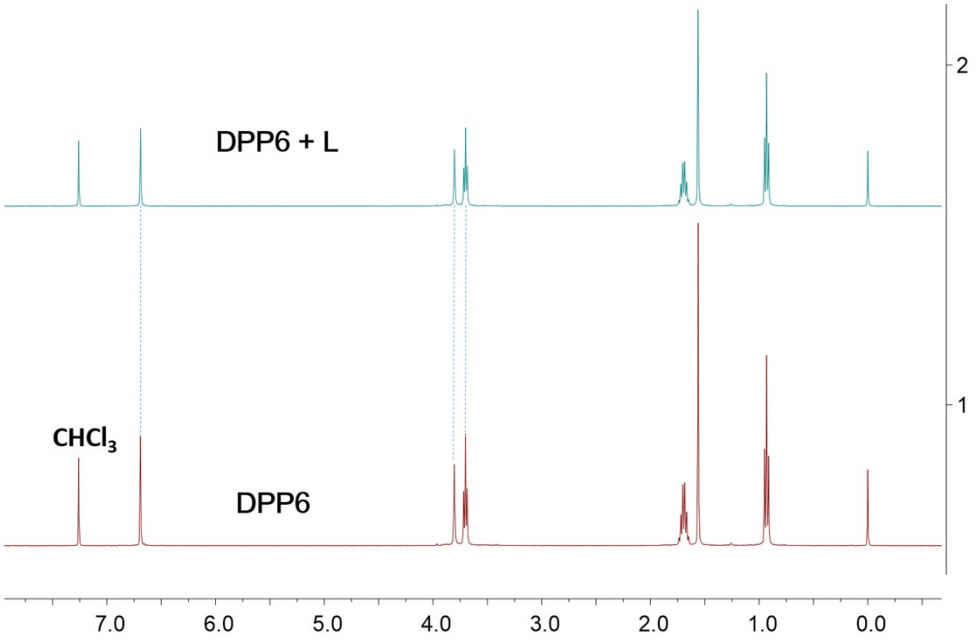


Fig. S19 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 22 °C) of **DPP6** and **DPP6•L** mixing solution. (No chemical shift changes were observed)

*19. ^{19}F NMR spectra (376 MHz, $CDCl_3$, 22 °C) of **L** and **DPP6•L** mixing solution*

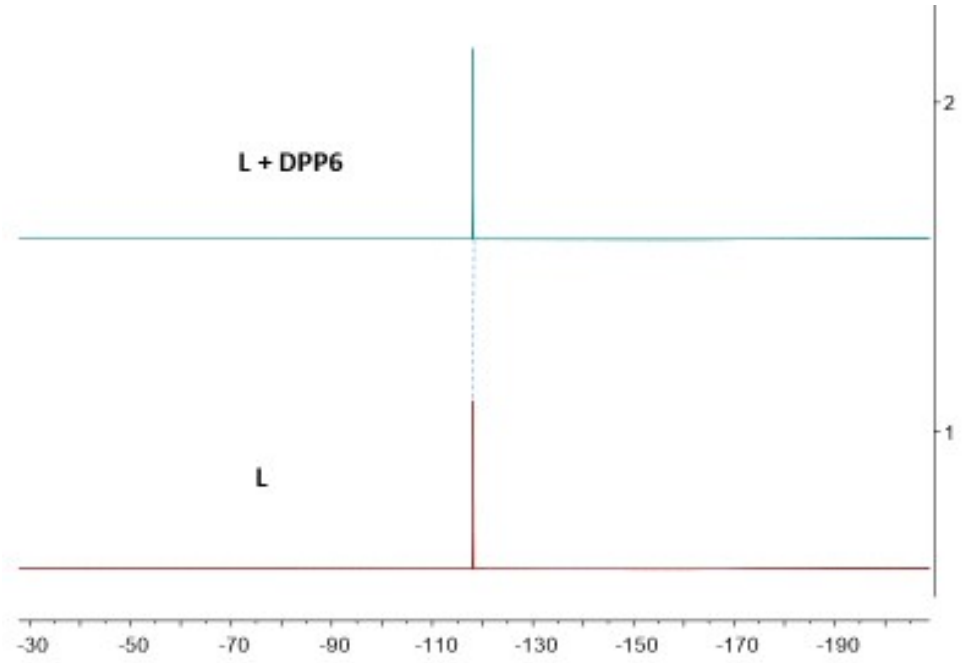


Fig. S20 ^{19}F NMR spectra (376 MHz, $CDCl_3$, 22 °C) of **L** and **DPP6•L** mixing solution. (No chemical shift changes were observed)

References:

S1. (a) H. Tao, D. Cao, L. Liu, Y. Kou, L. Wang and H. Meier, *Sci. China Chem.*, 2012, **55**, 223; (b) J.-F. Ma, J. Yang, G.-L. Zheng, L. Li and J.-F. Liu, *Inorg. Chem.*, 2003, **42**, 7531.

S2. 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.