Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Stimuli-responsive supramolecular gel constructed by pillar[5]arene-based pseudo[2]rotaxanes via orthogonal metal-ligand coordination and hydrogen bonding interaction

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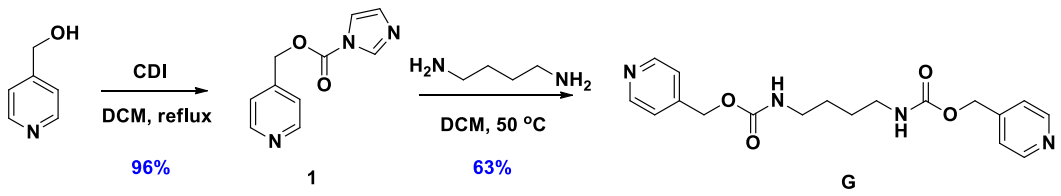
Table of Contents

1. General information

All reactions were performed in air atmosphere unless otherwise stated. The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literature. Column chromatography was performed with silica gel (200-300 mesh) produced by Qingdao Marine Chemical Factory, Qingdao (China). All yields were given as isolated yields. NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer (or Bruker DPX400 MHz spectrometer) with internal standard tetramethylsilane (TMS) and solvent signals as internal references at 298 K, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan Mat TSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion. Melting points (M.p.) were determined using a Focus X-4 apparatus (made in China) and were not corrected. Rheological properties were tested on a HAAKE Rheo-Stress 600 instrument with a 20 mm diameter parallel plate. All rheological experiments were carried out at 25 ℃. Scanning electron microscopy (SEM) images were recorded on a SHIMADZU SSX-550 device. Viscosity measurements were carried out in $CHCl_3$ using a micro-Ubbelohde viscometer at the surrounding temperature of 25 ^{o}C. Dynamic light scattering (DLS) measurements were carried out on a Brookhaven BI-9000AT system (Brookhaven Instruments Corporation, USA), using a 200-mW polarized laser source (λ = 514 nm).

2. Experimental procedure



Scheme S1. The synthesis route of **G**

Compound 1: 4-Hydroxymethylpyridine (1.09 g, 10 mmol) and N,N'-Carbonyldiimidazole (CDI) (3.24 g, 20 mmol) were dissolved in anhydrous dichloromethane (50 mL) and this solution was stirred and refluxed for 12 h under nitrogen. Then, dichloromethane (60 mL) was added to the reaction mixture and the organic layer was washed with water (2 × 30 mL), and followed by brine (40 mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo resulting in a light yellow solid (1.93 g, 9.6 mmol, 96% yield). M.p. 97−99 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.65 (d, J = 6.0 Hz, 2H, Ar*H*), 8.15 (s, 1H, C*H*), 7.43 (t, J = 6.0 Hz, 1H, C*H*), 7.30 (d, J = 6.0 Hz, 2H, Ar*H*), 7.07 (s, 1H, C*H*), 5.41 (s, 2H, OCH_2). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 150.4, 148.4, 142.8, 137.1, 131.0, 122.0, 117.1, 67.6. HR-ESI-MS: *m/z* Calcd. For $C_{10}H_{10}N_3O_2^+$ $[M+H]^+$ 204.0768, found 204.0767.

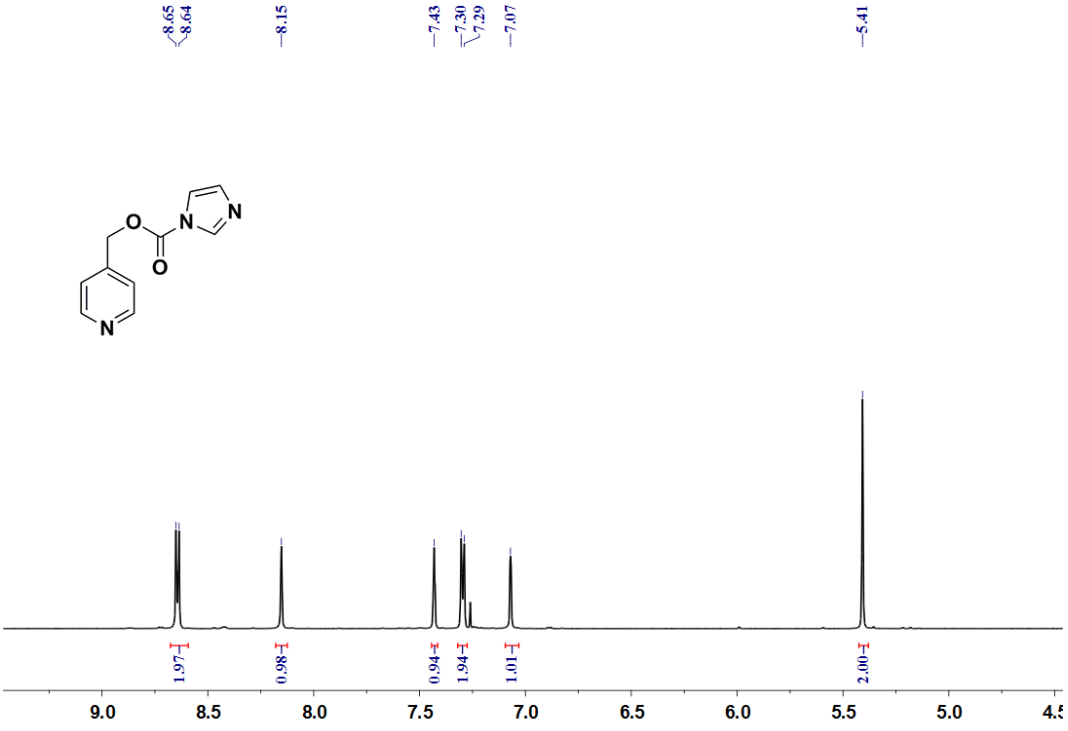


Fig. S1 ^{1}H NMR spectrum of **1** (400 MHz, $CDCl_3$, 298 K).

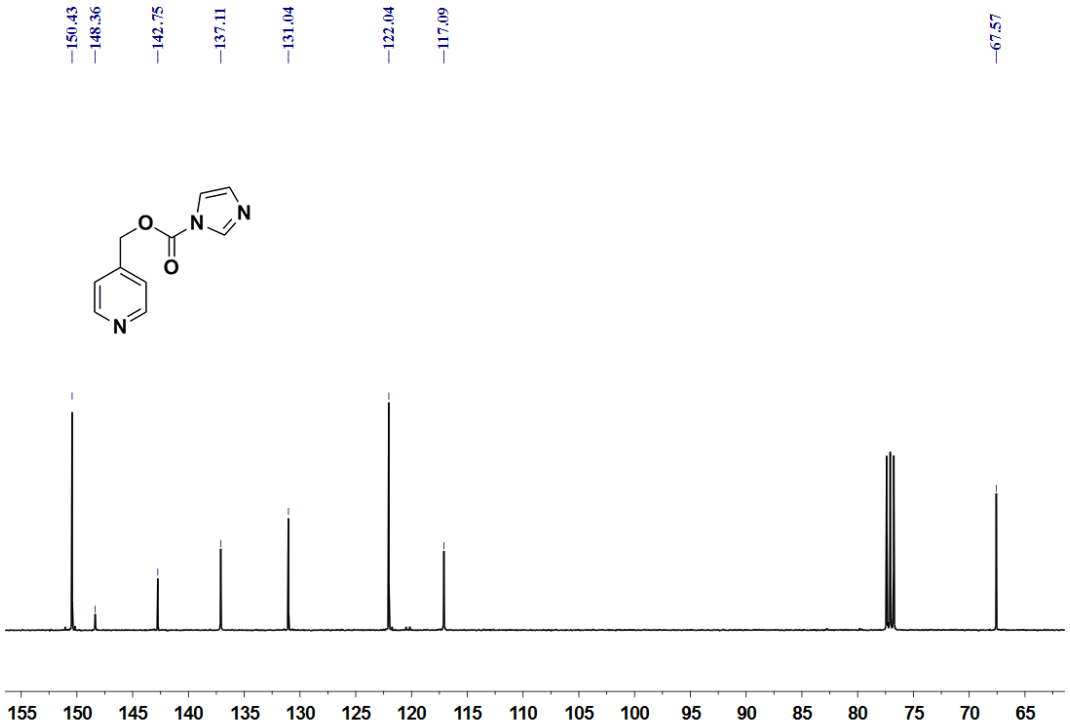


Fig. S2 ^{13}C NMR spectrum of **1** (100 MHz, $CDCl_3$, 298 K).

G: compound **1** (2.23 g, 10.0 mmol) and 1,4-butanediamine (0.35 g, 4.0 mmol) were dissolved in anhydrous dichloromethane (50 mL) and the solution was stirred for 12 h under nitrogen at 50 ^{o}C. Then, dichloromethane (50 mL) was added to the reaction mixture and the organic layer was washed with 1N HCl (40 mL), saturated $NaHCO_3$ (40 mL), and brine (40 mL), respectively. After drying with Na_2SO_4, the organic layer was concentrated under vacuum, and subjected to silica gel chromatography (dichloromethane/MeOH = 100:1, *v/v*) to give the target guest **G** (2.65 g, 2.5 mmol, 63% yield) as a white solid. M.p. 133−135 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.59 (d, J = 5.9 Hz, 4H, Ar*H*), 7.24 (d, J = 5.9 Hz, 4H, Ar*H*), 5.20–4.98 (m, 6H, OCH_2 and N*H*), 3.38–3.10 (m, 4H, NHCH_2), 1.68–1.49 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 156.1, 149.8, 145.9, 135.0, 121.7, 64.5, 40.7, 27.2. HR-ESI-MS: *m/z* Calcd. For $C_{18}H_{23}N_4O_4^+$ $[M+H]^+$ 359.1714, found 359.1717.

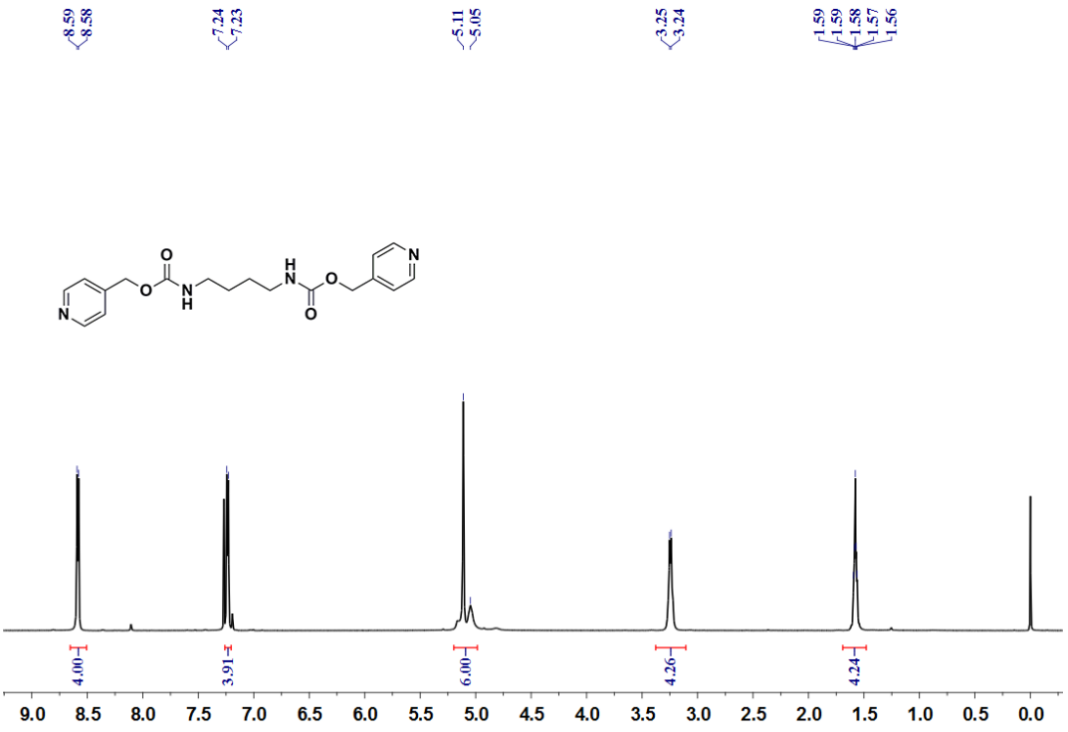


Fig. S3 ^{1}H NMR spectrum of **G** (400 MHz, $CDCl_3$, 298 K).

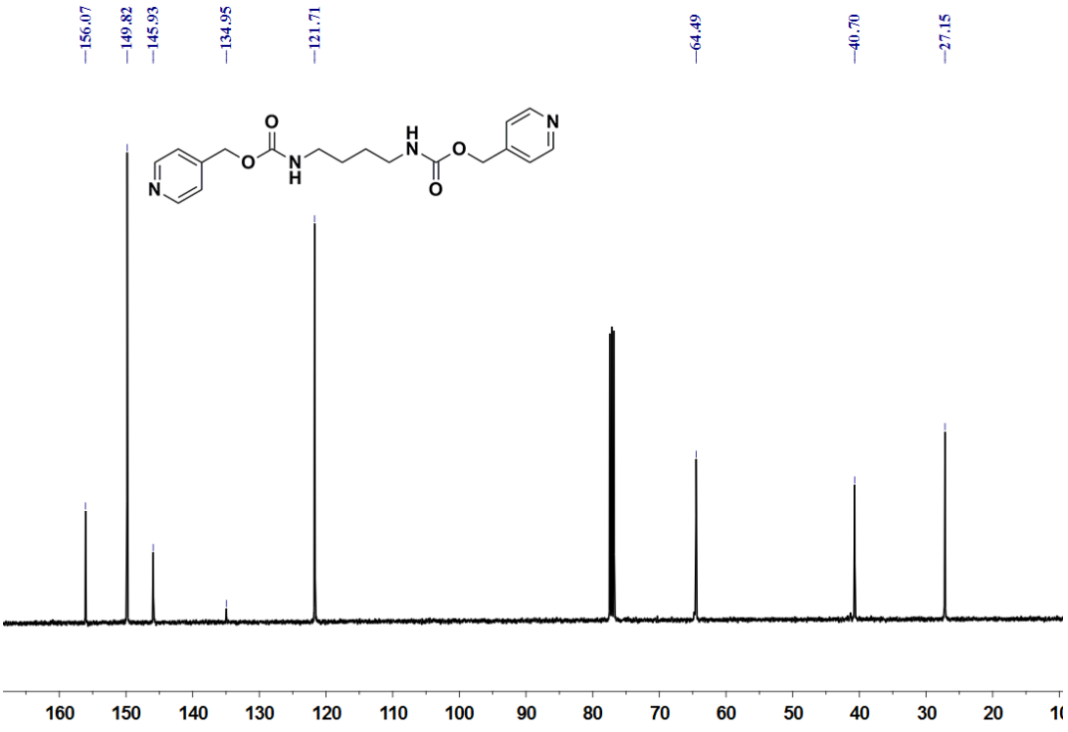


Fig. S4 ^{13}C NMR spectrum of **G** (100 MHz, $CDCl_3$, 298 K).

3. 2D NOESY spectrum of DMP5⊃G

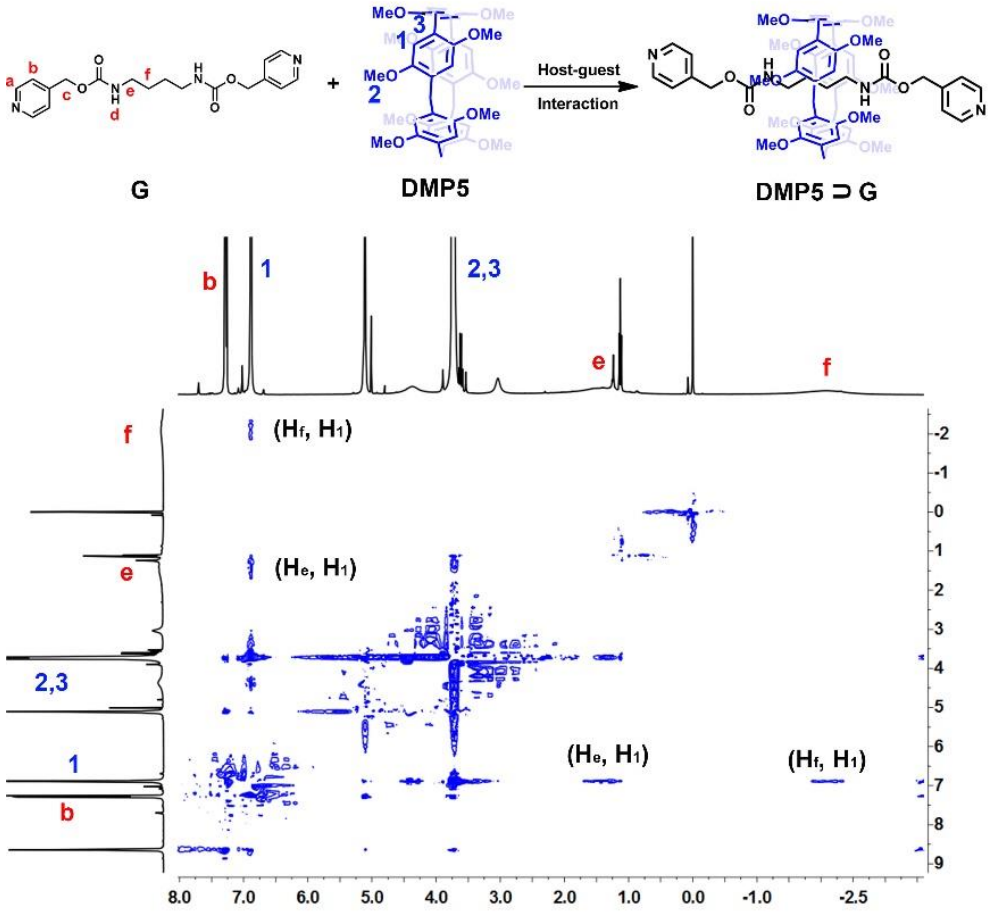


Fig. S5 Partial 2D NOESY spectrum of **DMP5⊃G** (400 MHz, $CDCl_3$, 298 K).

4. Determination of the binding constant

To determine the binding constant between **G** and **DMP5**, the Job's plot experiment was first carried out to determine the stoichiometry of complexation by the means of ^{1}H NMR spectroscopy. Accordingly, the ^{1}H NMR spectra were recorded by varying the mole fractions of host and guest compounds with a fixed total concentration of the host and guest. And the resulted Job's plot indicated that 1:1 binding stoichiometry was formed between the **G** and **DMP5**.

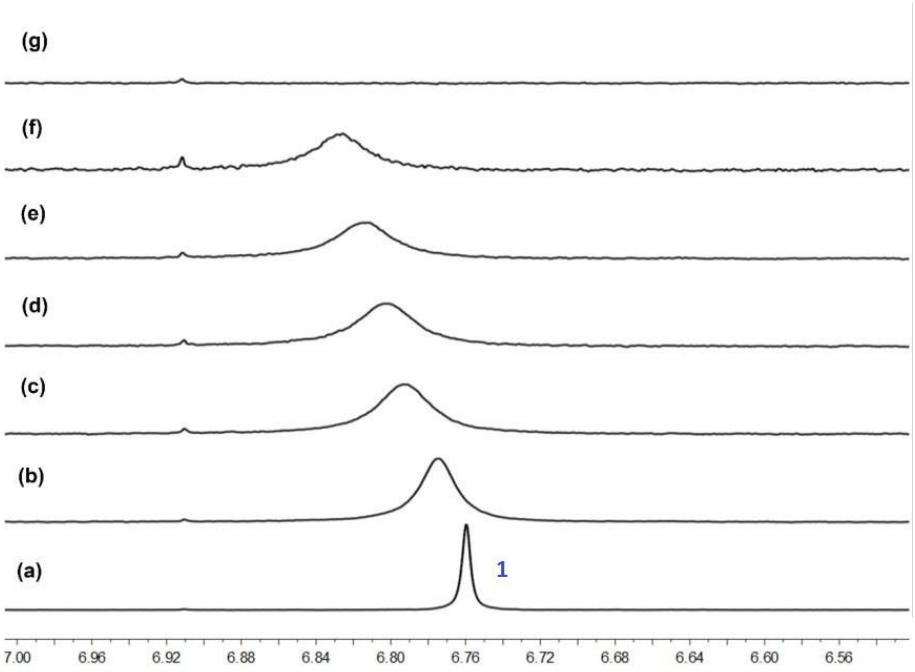


Fig. S6 Partial ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K) of **DMP5** and **G** at different molar ratios while [**DMP5**] + [**G**] = 4 × 10^{-3} M. (a) [**DMP5**]/[**G**] = 10:0, (b) [**DMP5**]/[**G**] = 8:2, (c) [**DMP5**]/[**G**] = 6:4, (d) [**DMP5**]/[**G**] = 5:5, (e) [**DMP5**]/[**G**] = 4:6, (f) [**DMP5**]/[**G**] = 2:8, (g) [**DMP5**]/[**G**] = 0:10.

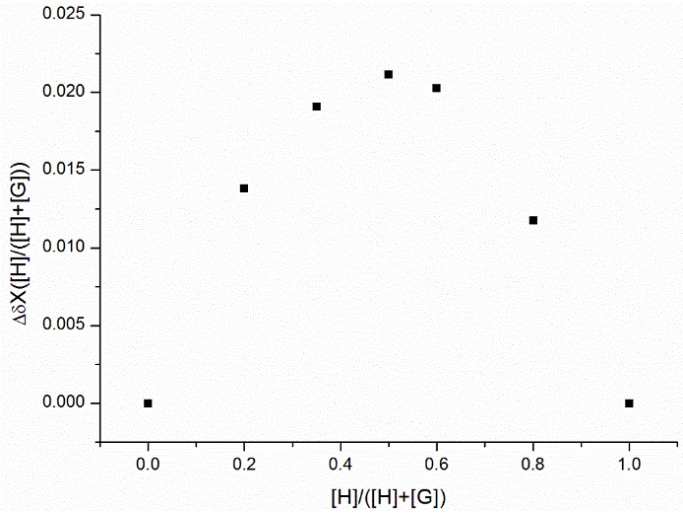


Fig. S7 Job's Plot showing 1:1 stoichiometry of the complexation between **DMP5** and **G** by plotting the difference on chemical shift changes of the aromatic protons H_1 on **DMP5** against the molar fractions of **DMP5** at an invariant total concentration of 4 × 10^{-3} M ([**DMP5**] + [**G**]) in $CDCl_3$.

Fig. S8 ESI-MS spectrum of the host−guest complex formed between **DMP5** and **G**.

To determine the binding constant, ^{1}H NMR titration experiments were carried out in $CDCl_3$ which had a constant concentration of **DMP5** (4×10^{-3} M) and varying concentration of **G**. A nonlinear curve-fitting method was applied to calculate the association constant for the complexation between **DMP5** host and **G** guest, which was based on the following equation:

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

Where $\Delta\delta$ is the chemical shift change of the aromatic protons H_1 on **DMP5** host 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 varying concentrations of the guest. By non-linear fitting the spectrum data with equation, the binding constant K_a was determined to be $(3.62 \pm 0.04) \times 10^2$ M^{-1}.

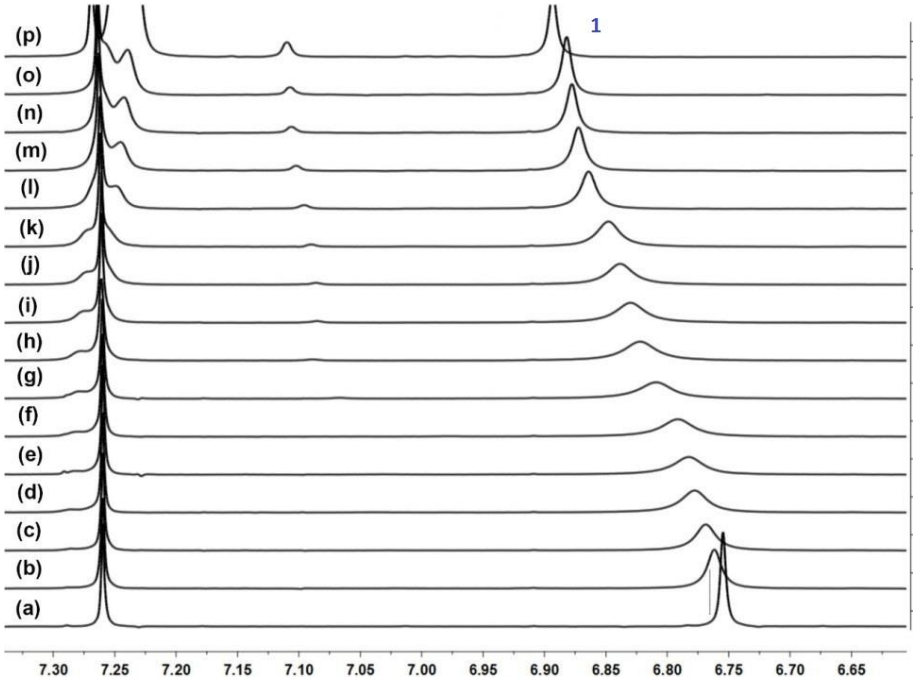


Fig. S9 Partial ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K) of **DMP5** at a concentration of 4.0 mM upon the addition of **G**: (a) 0 mM, (b) 0.4 mM, (c) 0.8 mM, (d) 1.2 mM, (e) 1.6 mM, (f) 2.0 mM, (g) 3.2 mM, (h) 4.0 mM, (i) 4.8 mM, (j) 5.6 mM, (k) 6.4 mM, (l) 9.6 mM, (m) 12.8 mM, (n) 16 mM, (o) 20 mM, and (p) 40 mM.

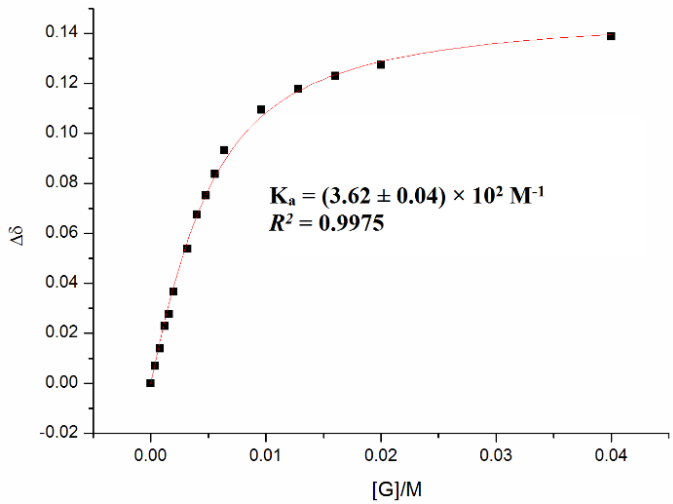


Fig. S10 The chemical shift changes of H_1 on **DMP5** (4.0 mM) upon the addition of **G** (0−40 mM). The red solid line was obtained from the nonlinear curve-fitting (K_a = (3.62 ± 0.04) × 10^2 M^{-1}, R^2 = 0.9975).

5. The coordination interaction of the host-guest complexation with $Pd(OAc)_2$

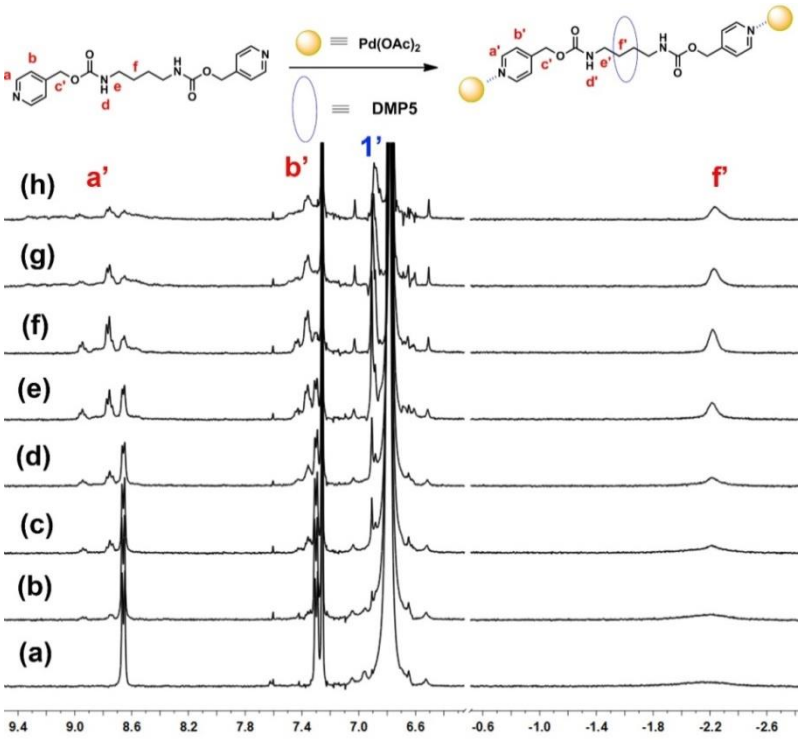


Fig. S11 ^{1}H NMR spectra (300 MHz, 298 K) of the mixture solution of **DMP5** and **G** ([**G**] = 4 mM, [**DMP5**] = 20 mM) in $CDCl_3$ with varying molar ratios of $Pd(OAc)_2$: (a) 0 mM, (b) 0.4 mM, (c) 0.8 mM (d) 1.6 mM, (e) 2.4 mM, (f) 3.2 mM, (g) 4.0 mM, and (h) 6 mM.

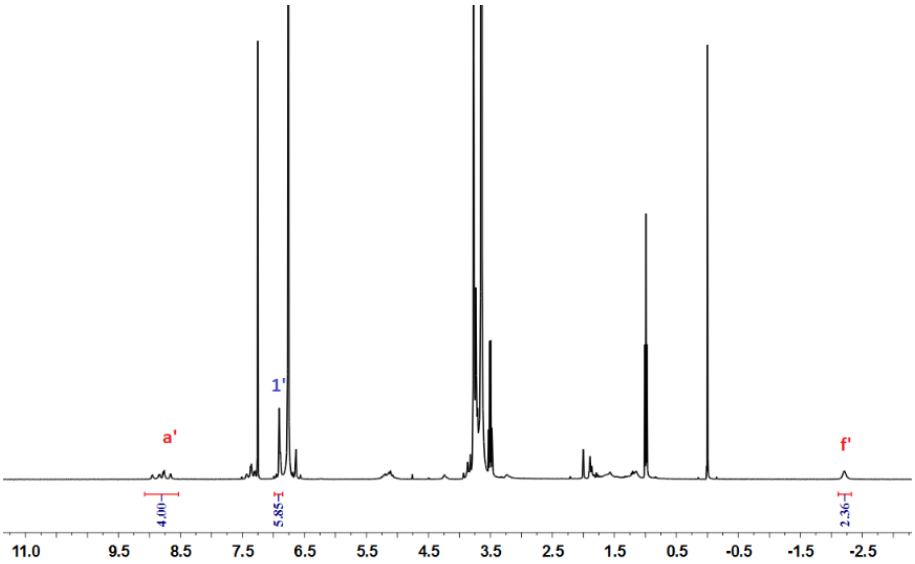


Fig. S12 ^{1}H NMR spectra (400 MHz, 298 K) of the mixed solution of **DMP5**, **G** and $Pd(OAc)_2$ ([**G**] = 2 mM, [**DMP5**] = 10 mM, and [$Pd(OAc)_2$] = 2 mM) in $CDCl_3$.

6. Variant concentration ^{1}H NMR spectroscopy of G

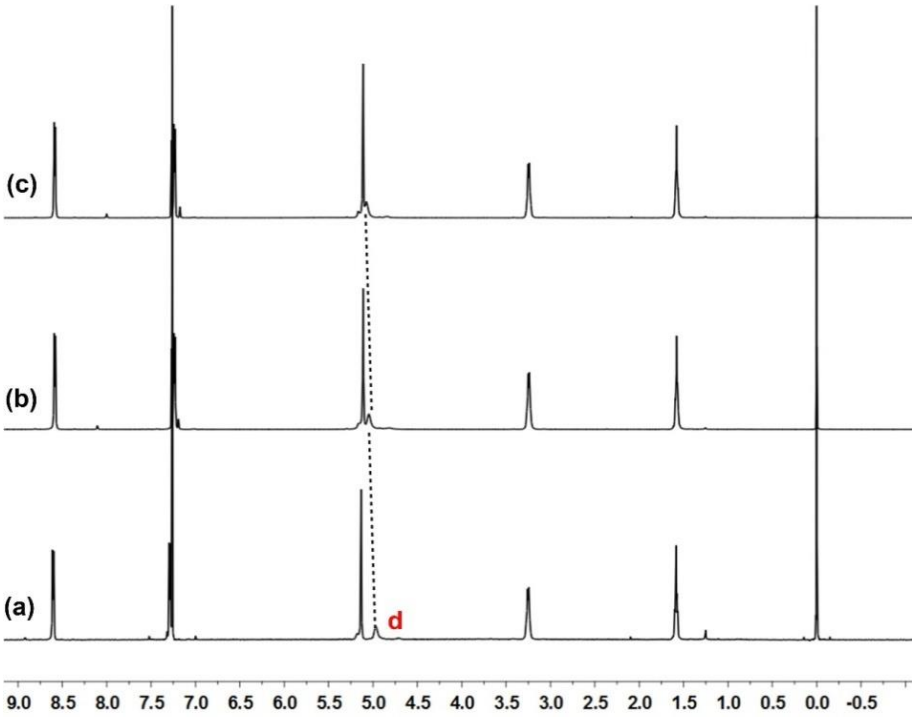


Fig. S13 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of **G** at variant concentrations: (a) 5 mM, (b) 15 mM, and (c) 25 mM.