Electronic Supplementary Material (ESI) for Chemical Communications

Versatile Self-assembled Molecular Capsule Formation of Resorcin[4]arene-based Benzamidoiminocavitand

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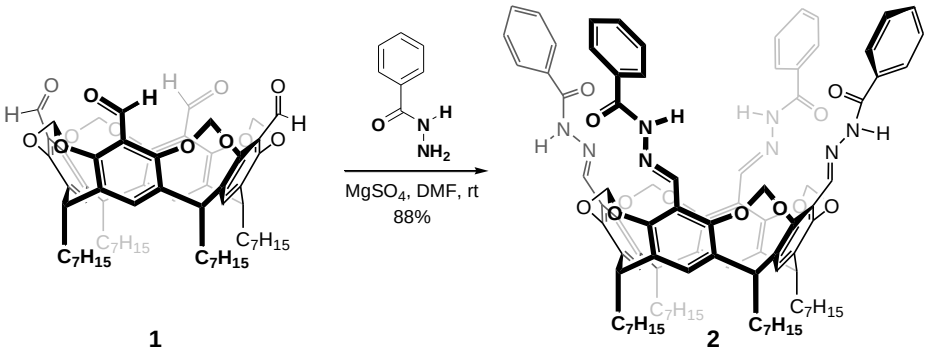
Supporting Information

1. Synthesis



1 **2**

Tetrakis(benzamidoimino)-cavitand **(2):** A mixture of tetraformyl cavitand **1** (1.00 g, 0.96 mmol), benzoic hydrazide (575 mg, 4.22 mmol), $MgSO_4$ (3 g), and anhydrous DMF (50 mL) was stirred for 4 days at room temperature under an argon atmosphere. The reaction mixture was concentrated under reduced pressure. The residue was dissolved with toluene (60 mL), filtered through a pad of celite. After removal of solvent, purification by short column chromatography on silica gel (CH_2Cl_2/EtOAc = 7:3) provided the product as a white solid (1.28 g, 88% yield): ^{1}H NMR (400 MHz, toluene-d_8) δ 12.65 (s, 4H, amide -N*H*), 8.80 (d, *J* = 7.6 Hz, 8H, Ar-*H*), 8.67 (s, 4H, imine -C*H*=N-), 7.35 (t, *J* = 7.6 Hz, 8H, Ar-*H*), 7.25 (t, *J* = 7.6 Hz, 4H, Ar-*H*), 7.24 (s, Ar-*H*), 6.09 (d, *J* = 7.6 Hz, 4H, -OCH_{out}H$_{in}$O-), 4.86 (t, *J* = 8.0 Hz, 4H, -C*H*-), 4.19 (d, *J* = 7.6 Hz, 4H, -OCH$_{out}$$H_{in}$O-), 2.13 (m, 4H, -C$H_2$-), 2.33 (m, 4H, -C$H_2$-), 1.28 - 1.13 (m, 40H, -(CH_2)$_5$-), 0.90 (t, *J* = 7.6 Hz, 12H, -CH_3); HRMS (MALD-TOF; [M + H]$^+$) calcd for $C_{92}H_{105}N_8O_{12}$ 1513.7852, found 1513.7877; Anal. Calcd for $C_{92}H_{104}N_8O_{12}$: C, 72.99; H, 6.92; N, 7.40. Found: C, 73.30; H, 6.80; N, 7.46.

2. ^{1}H NMR Spectrum of Molecular Capsule $\mathbf{2}_2$

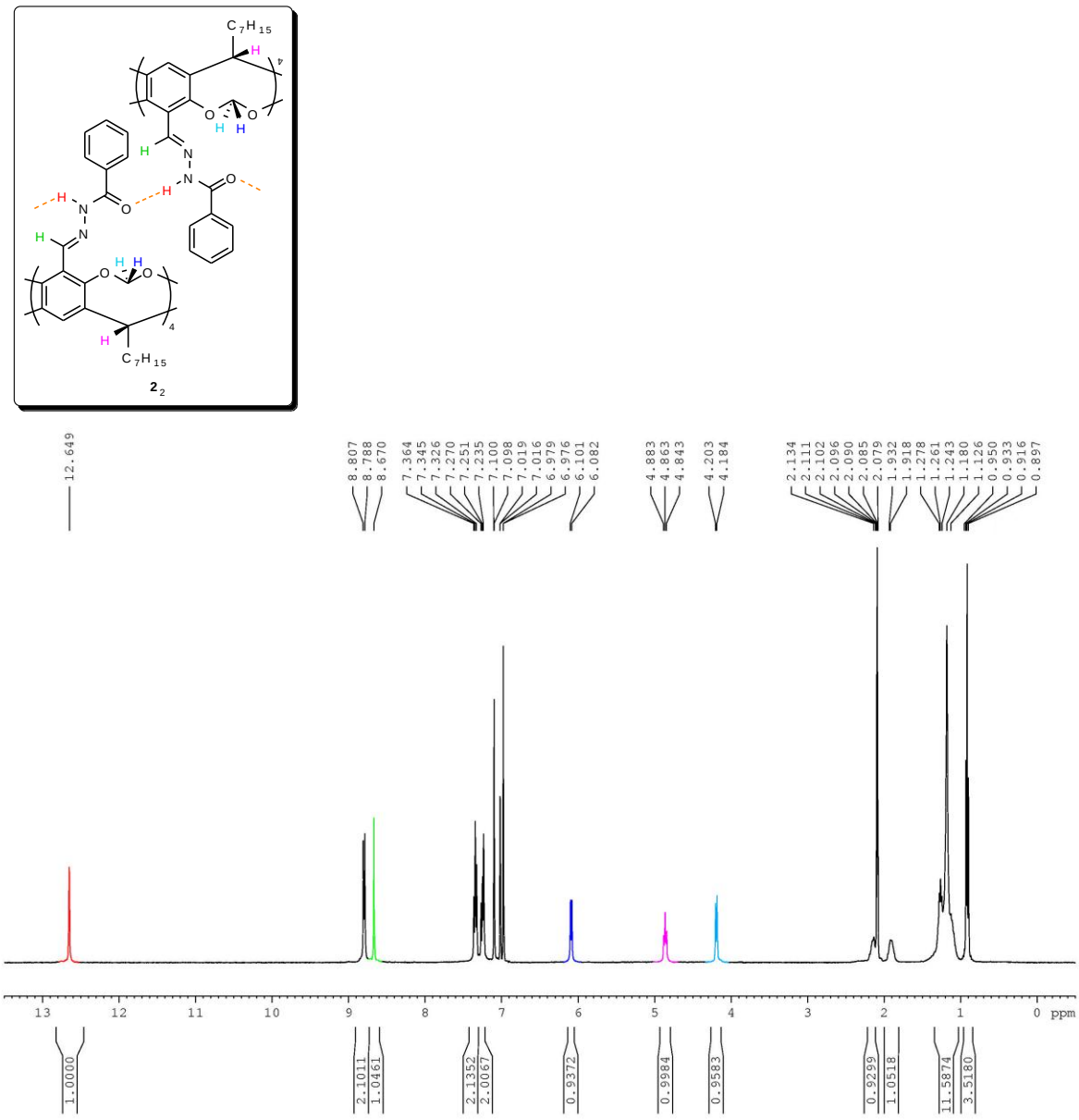


Fig. S2 ^{1}H NMR (400 MHz) spectrum of toluene-d_8@$\mathbf{2}_2$ in toluene-d_8.

3. Maldi-TOF Mass Spectrum

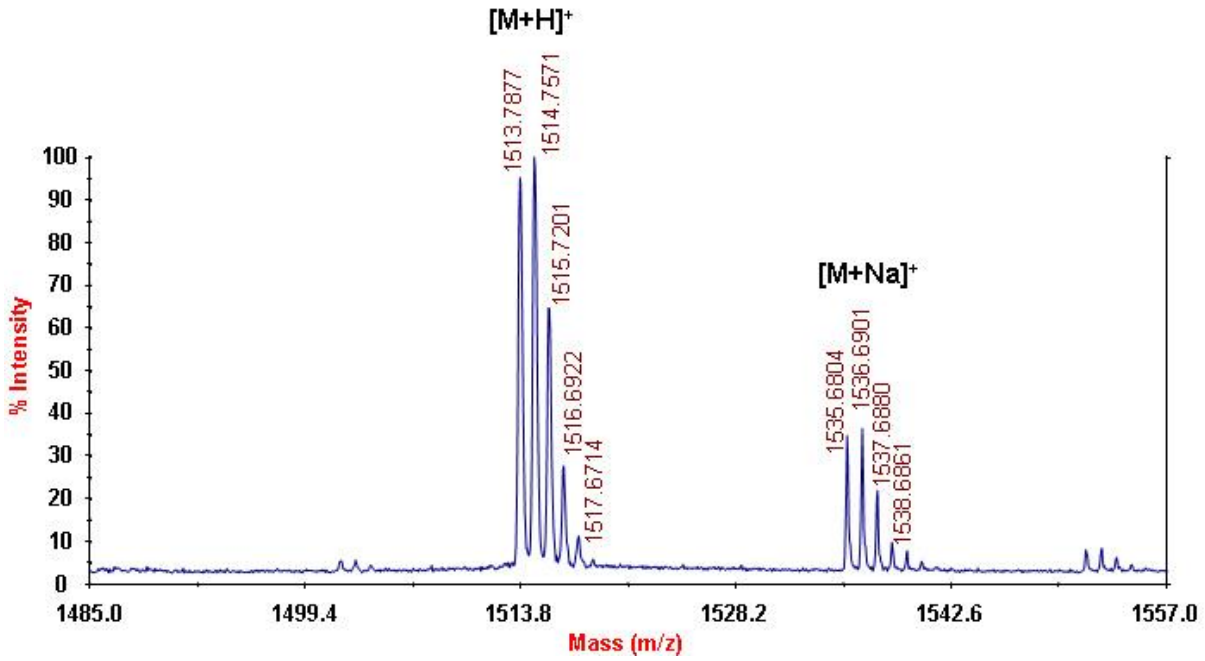
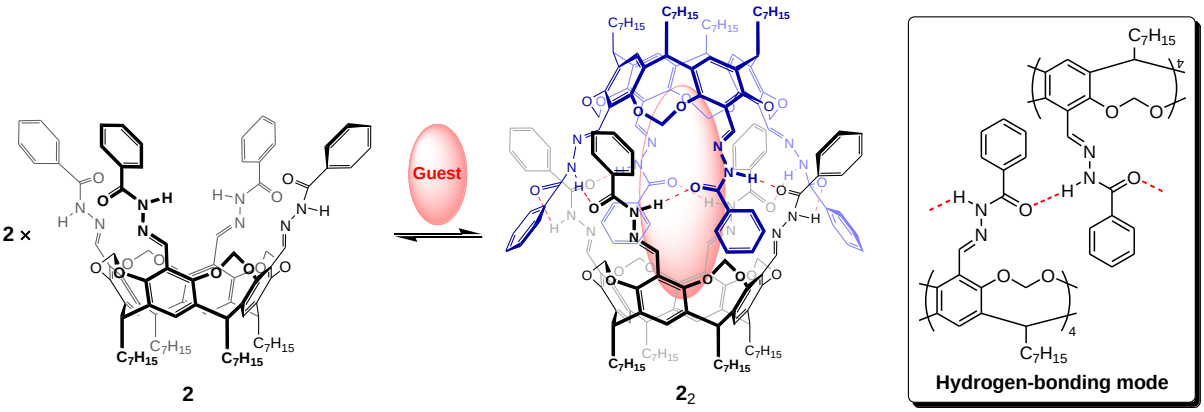


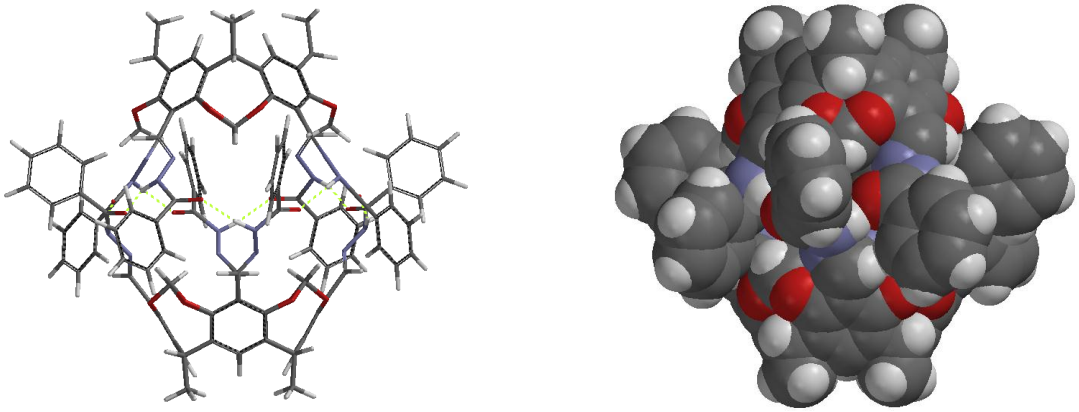
Fig. S3 High-resolution Maldi-TOF mass spectrum of cavitand **2**.

4. Molecular Modeling

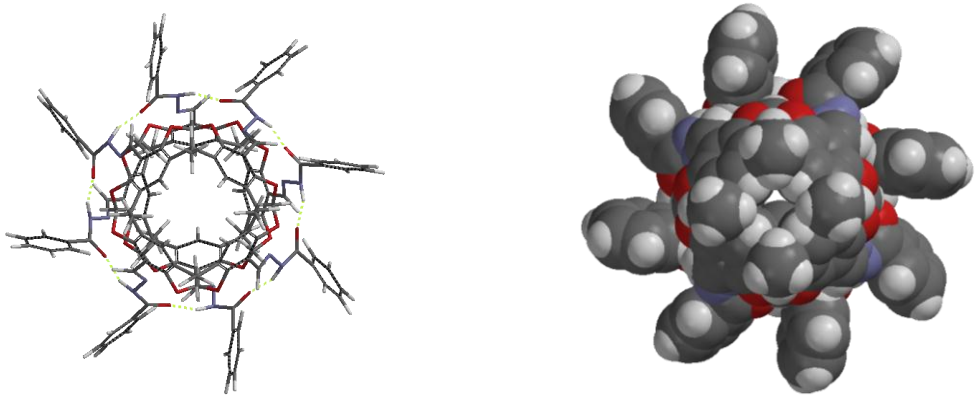
The structures of molecular capsule $\mathbf{2}_2$ are built and minimized Semi-Empirical PM3 level using the PC model program: Spartan'04 V1.03. The heptyl side chains in molecular capsule $\mathbf{2}_2$ are replaced to methyl groups.

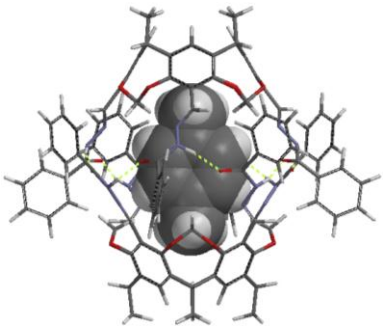


Side View

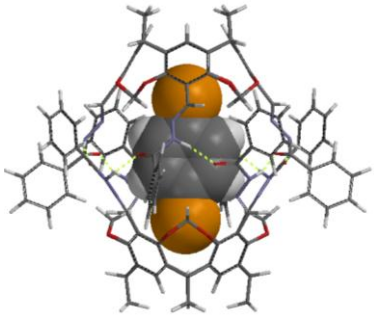


Top View

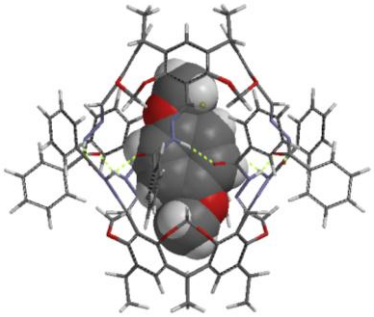




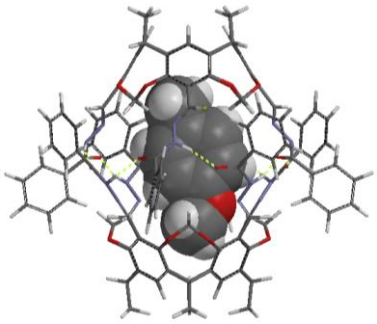
p-xylene@**2**$_2$



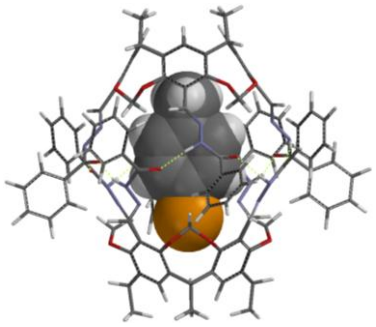
1,4-diiodobenzene@**2**$_2$



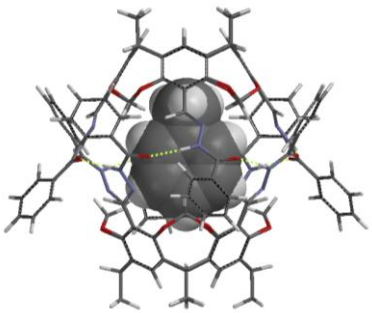
1,4-dimethoxybenzene@**2**$_2$



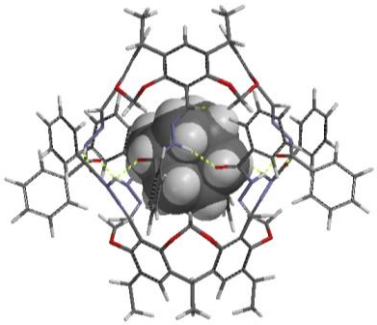
4-methylanisole@**2**$_2$



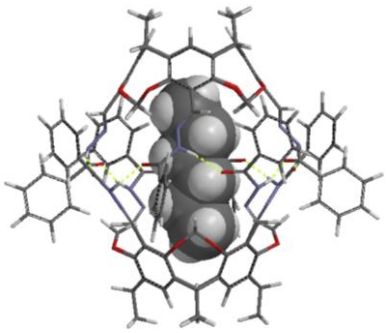
4-iodotoluene@**2**$_2$



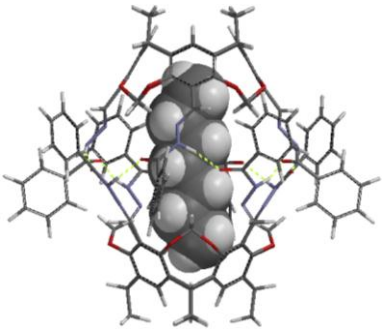
toluene@**2**$_2$



adamantane@**2**$_2$



n-hexane@**2**$_2$



n-heptane@**2**$_2$

Fig. S4 Energy minimized structures of **G**@**2**$_2$. Only the skeleton is shown for the molecular capsule, and the long alkyl chains and hydrogen atoms are omitted for clarity. Hydrogen bonds are represented by green lines.

5. ^{1}H NMR Spectra of Cavitand 2 in Various Solvents

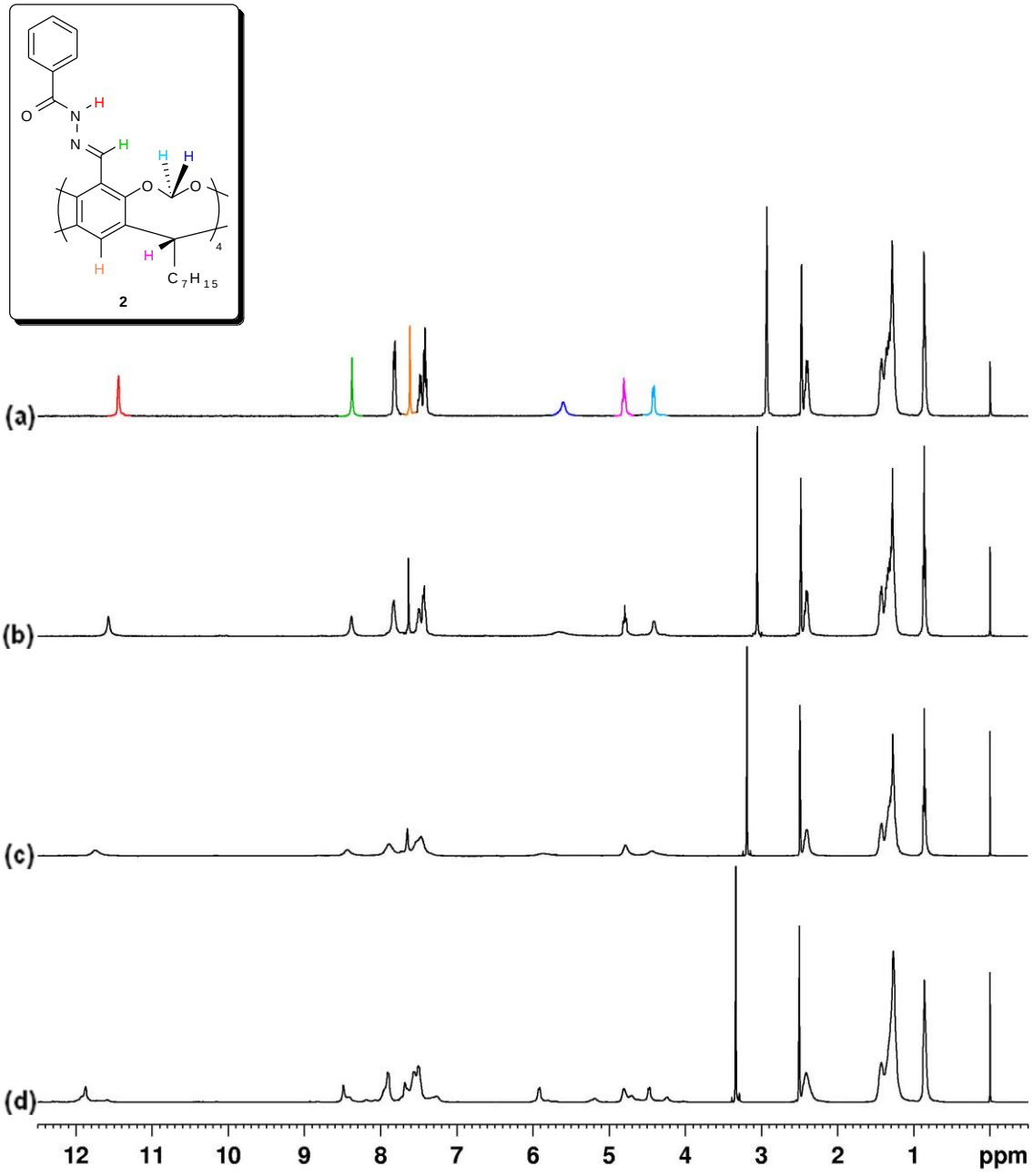


Fig. S5-1 ^{1}H NMR spectra of cavitand **2** in DMSO-d_6 at (a) 100 ^{o}C; (b) 75 ^{o}C; (c) 50 ^{o}C; (d) 25 ^{o}C.

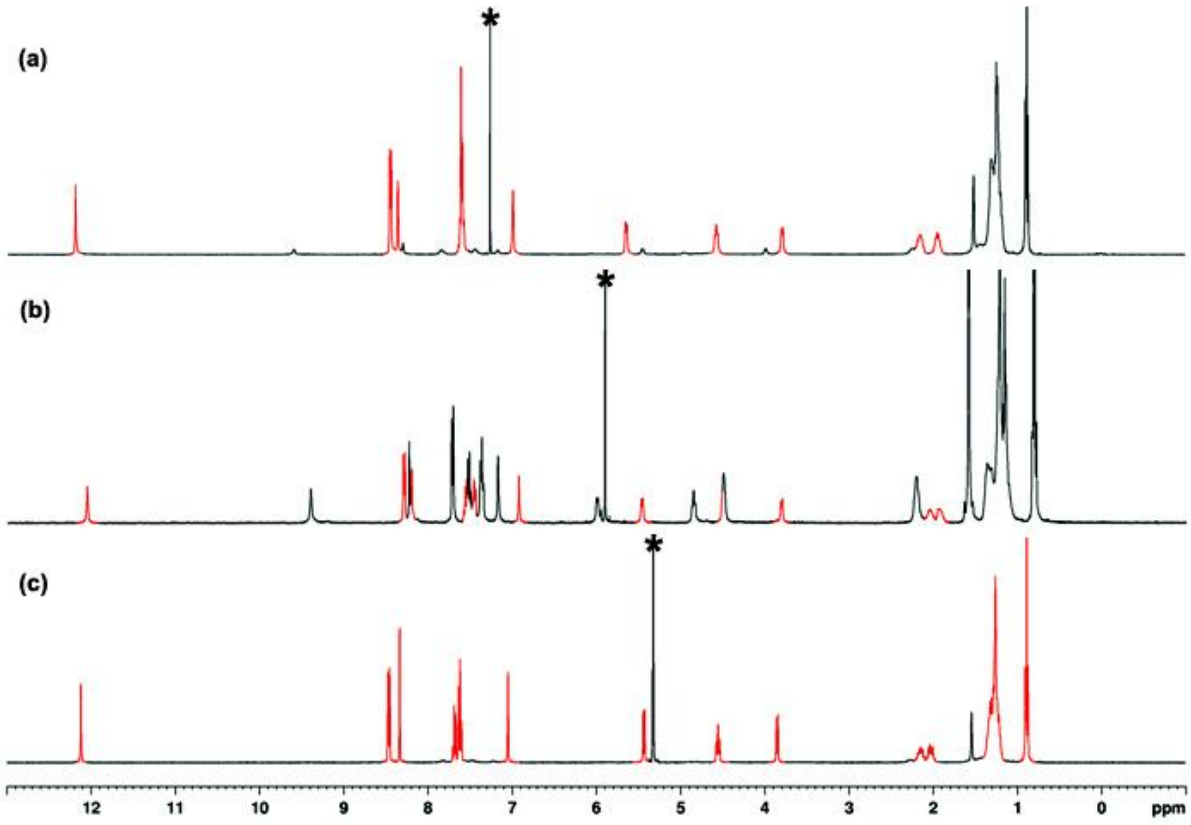


Fig. S5-2 ^{1}H NMR spectra (400 MHz) cavitand **2** at 25 ^{o}C in (a) $CDCl_3$; (b) $C_2D_2Cl_4$; (c) CD_2Cl_2. The signals of cavitand **2** (black) and molecular capsule $\mathbf{2}_2$ (red) are highlighted. The residual solvents are marked "*".

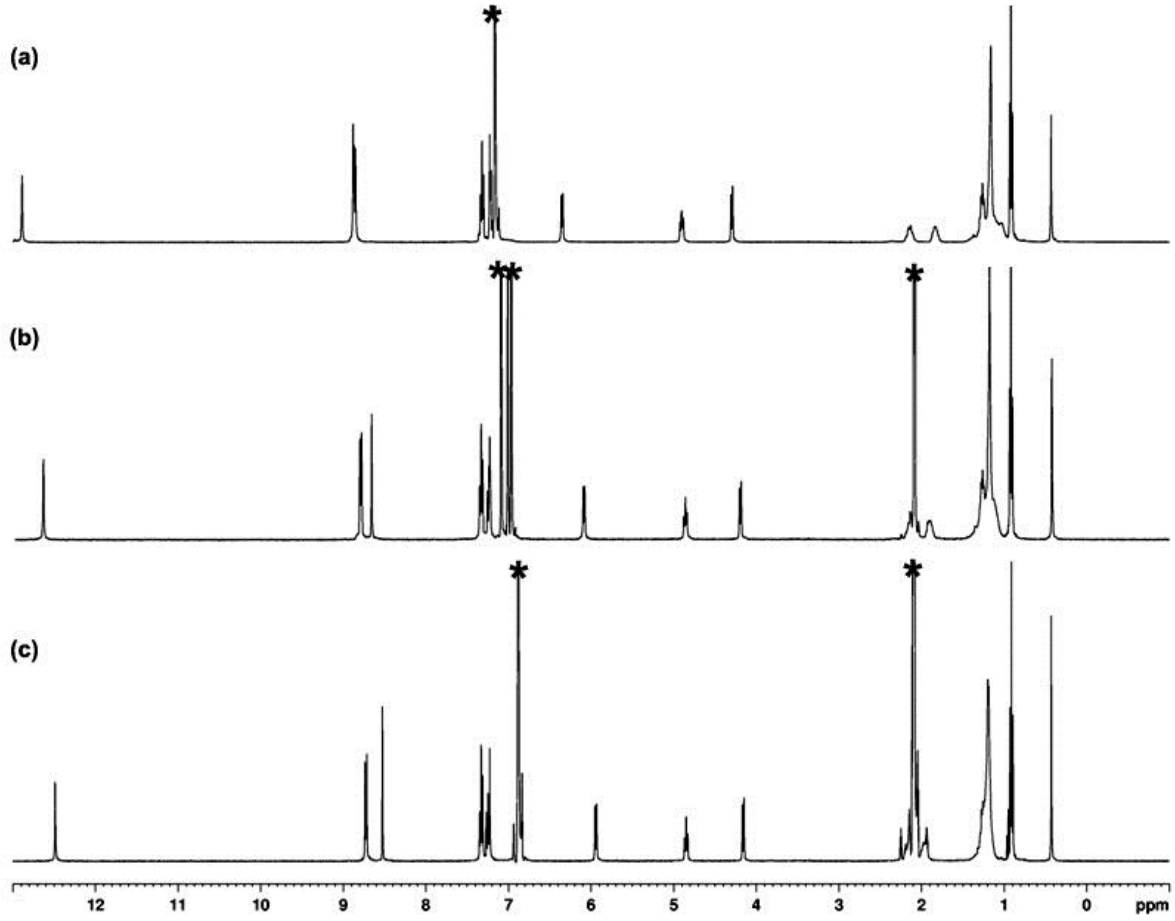


Fig. S5-3 ^{1}H NMR spectra (400 MHz) at 25 ^{o}C of (a) benzene-d_6@**2**$_2$ in benzene-d_6; (b) toluene-d_8@**2**$_2$ in toluene-d_8; (c) *p*-xylene-d_{10}@**2**$_2$ in *p*-xylene-d_{10}. The residual solvents are marked "✱".

6. The Encapsulation Properties of Molecular Capsule $\mathbf{2}_2$

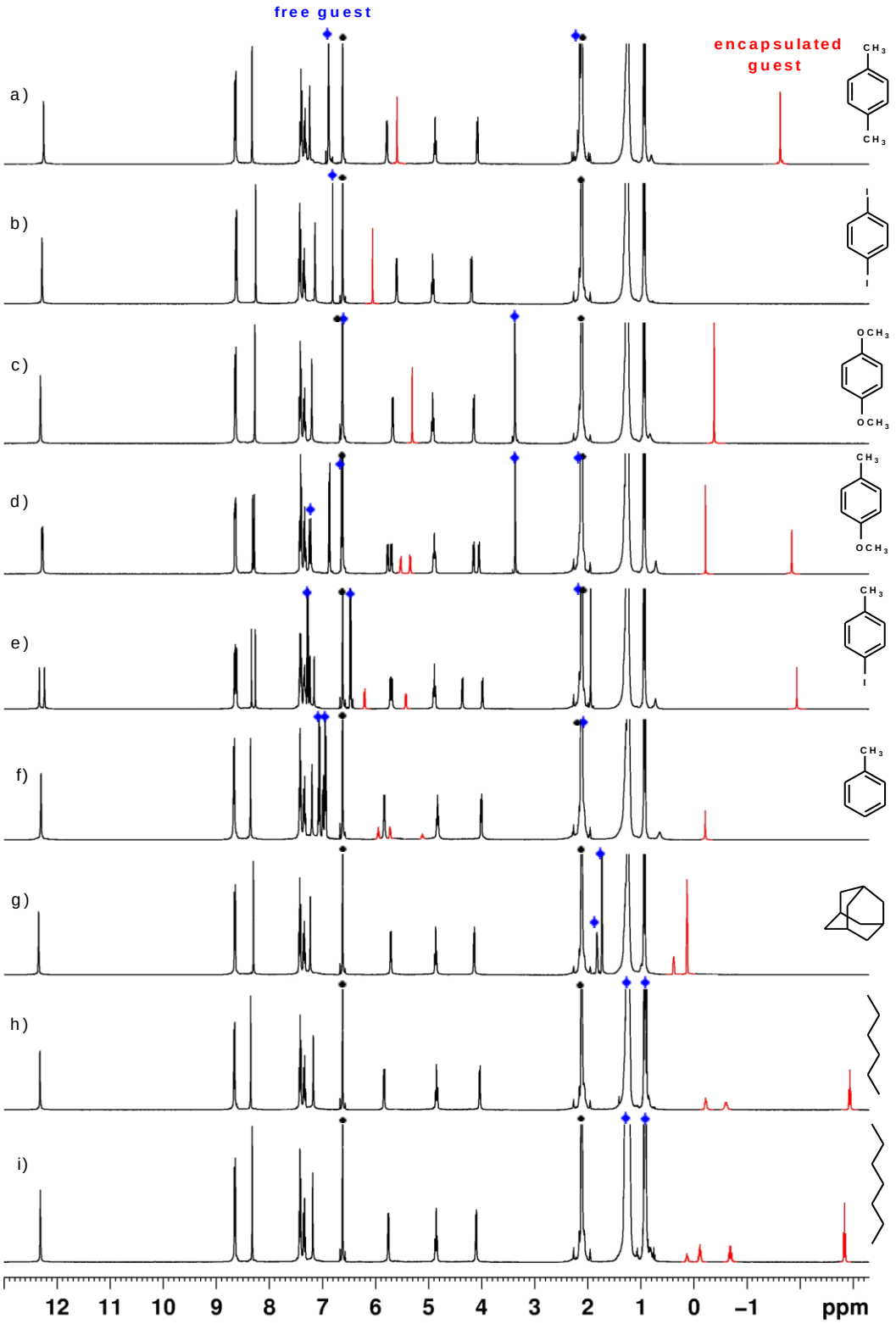


Fig. S6-1. ^{1}H NMR spectra (400 MHz) of **G**@$\mathbf{2}_2$ in mesitylene-d_{12} at 298 K: (a) *p*-xylene@$\mathbf{2}_2$; (b) 1,4-diiodobenzene@$\mathbf{2}_2$; (c) 1,4-dimethoxybenzene@$\mathbf{2}_2$; (d) 4-methylanisole@$\mathbf{2}_2$; (e) 4-iodotoluene@$\mathbf{2}_2$; (f) toluene@$\mathbf{2}_2$; (g) adamantane@$\mathbf{2}_2$; (h) *n*-hexane@$\mathbf{2}_2$; and (i) *n*-heptane@$\mathbf{2}_2$. [**2**] = 6 mM, [G] = 18 mM. The signals of the encapsulated guest (red) are highlighted. The signals of free guest and the residual solvent are marked "♦" and "•", respectively.

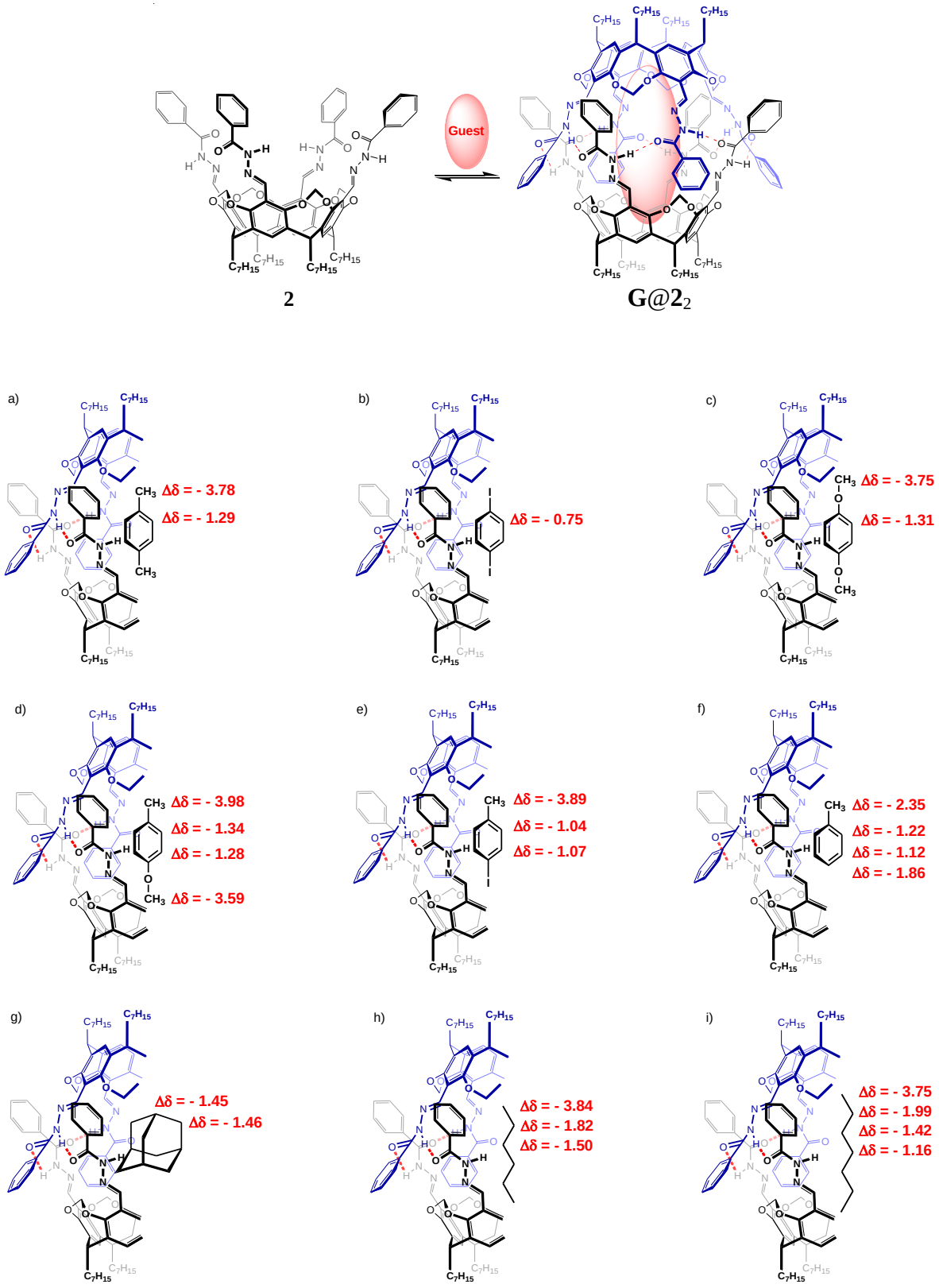


Fig. S6-2 Schematic representation of **G**@$\mathbf{2}_2$ and the chemical shift changes (Δδ, in ppm) of the encapsulated guest relative to the free guest monitored by ^{1}H NMR spectroscopy (400 MHz) in mesitylene-d_{12} at 298 K: (a) *p*-xylene@$\mathbf{2}_2$; (b) 1,4-diiodobenzene@$\mathbf{2}_2$; (c) 1,4-dimethoxybenzene@$\mathbf{2}_2$; (d) 4-methylanisole@$\mathbf{2}_2$; (e) 4-iodotoluene@$\mathbf{2}_2$; (f) toluene@$\mathbf{2}_2$, (g) adamantane@$\mathbf{2}_2$; (h) *n*-hexane@$\mathbf{2}_2$; and (i) *n*-heptane@$\mathbf{2}_2$.

7. The Conformational Stability of Capsular Complex at Various Temperatures

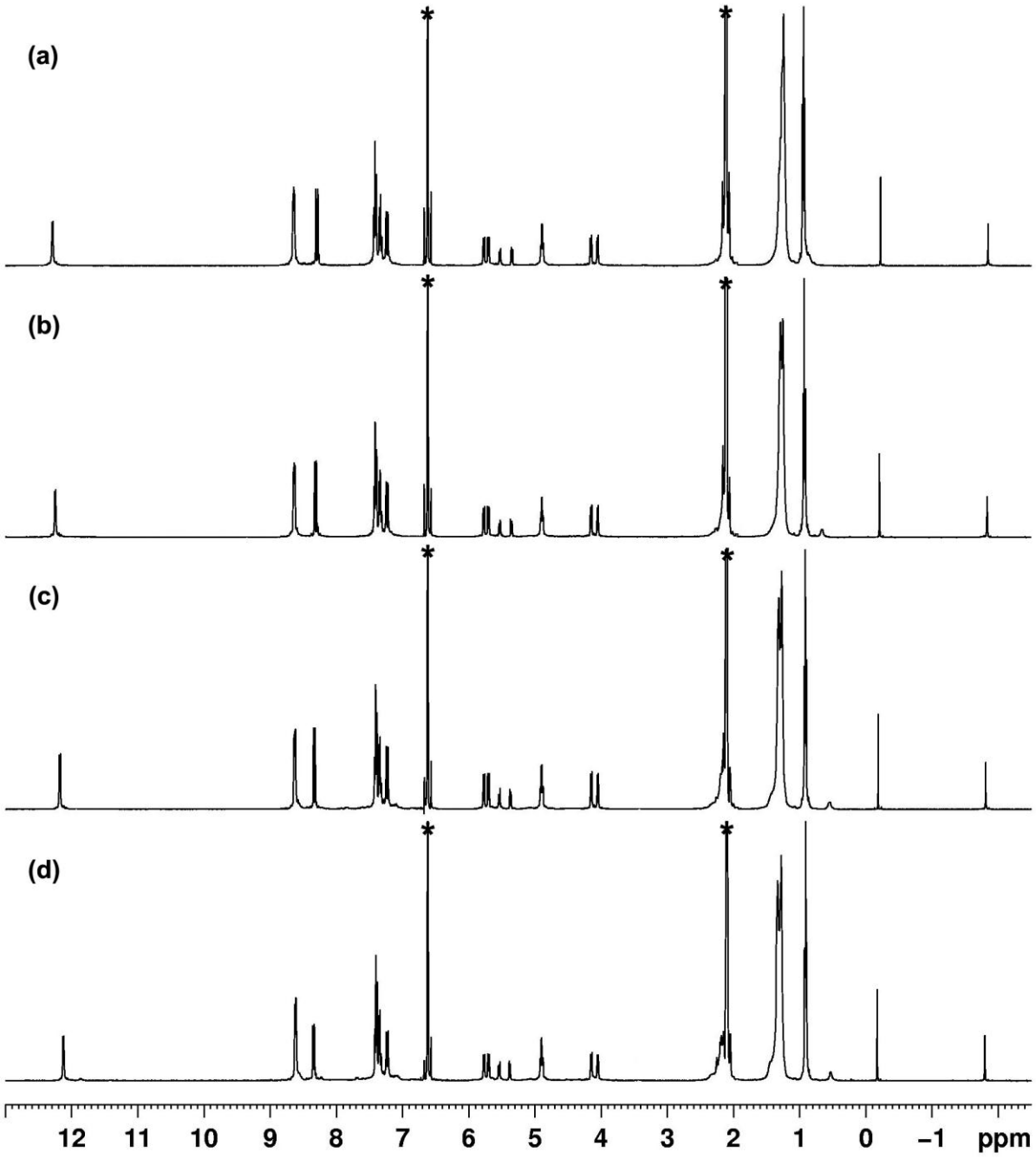


Fig. S7 ^{1}H NMR spectra of 4-methylanisole@**2**$_2$ in mesitylene-d_{12} at (a) 25 ^{o}C; (b) 50 ^{o}C; (c) 75 ^{o}C; (d) 100 ^{o}C. The residual solvents are marked "*".

8. Addition experiments with polar solvent (CD_3OD)

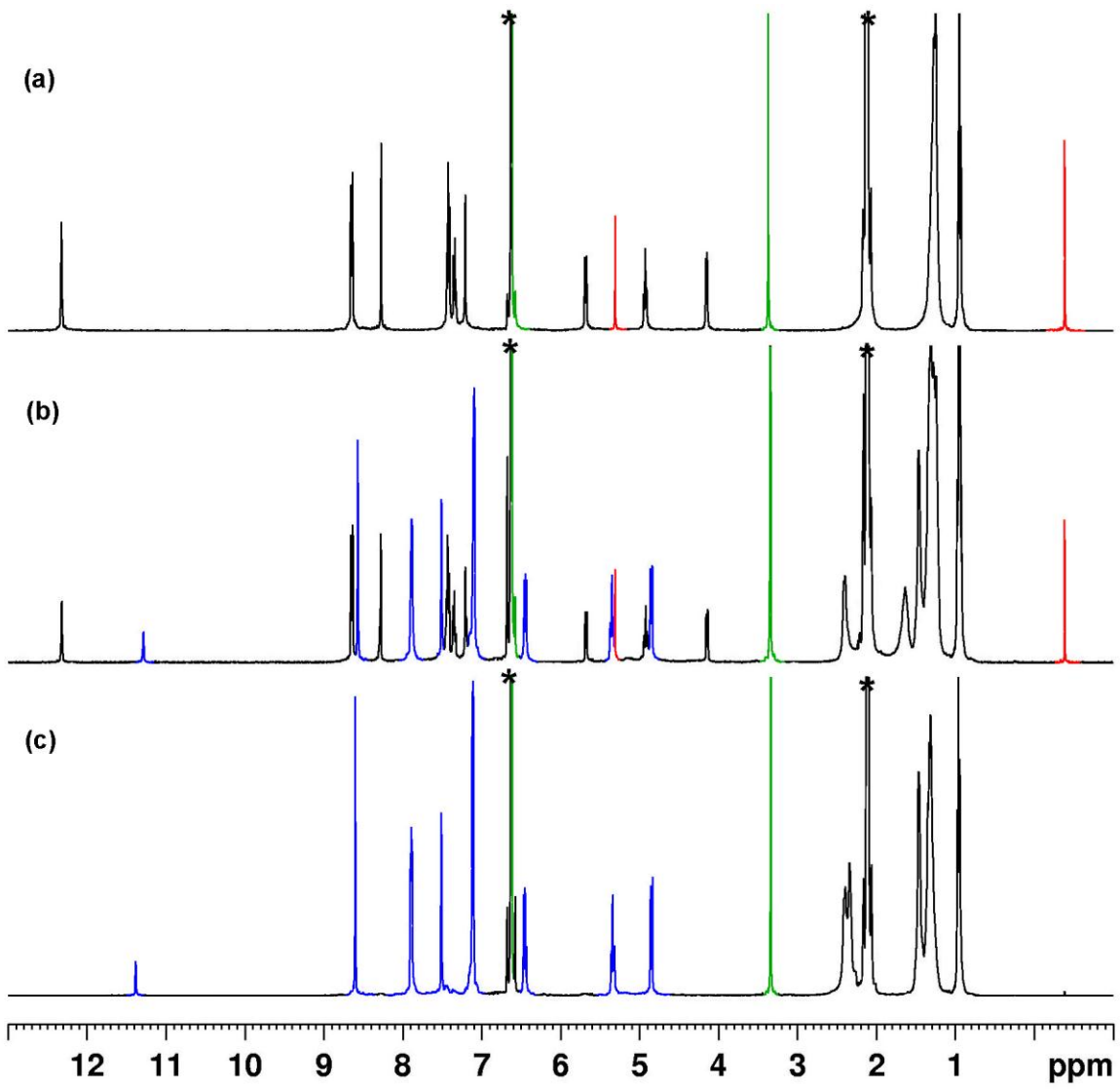


Fig. S8 ^{1}H NMR (400 MHz, 298 K) spectra of 4-methylanisole@$\mathbf{2}_2$ in (a) mesitylene-d_{12}; (b) 3% CD_3OD/mesitylene-d_{12}; (c) 10% CD_3OD/mesitylene-d_{12}. The signals of cavitand **2** (blue), molecular capsule $\mathbf{2}_2$ (black), the encapsulated guests (red), and free guests (green) are highlighted. The residual solvents are marked "*".

9. The Encapsulation of *n*-Alkanes

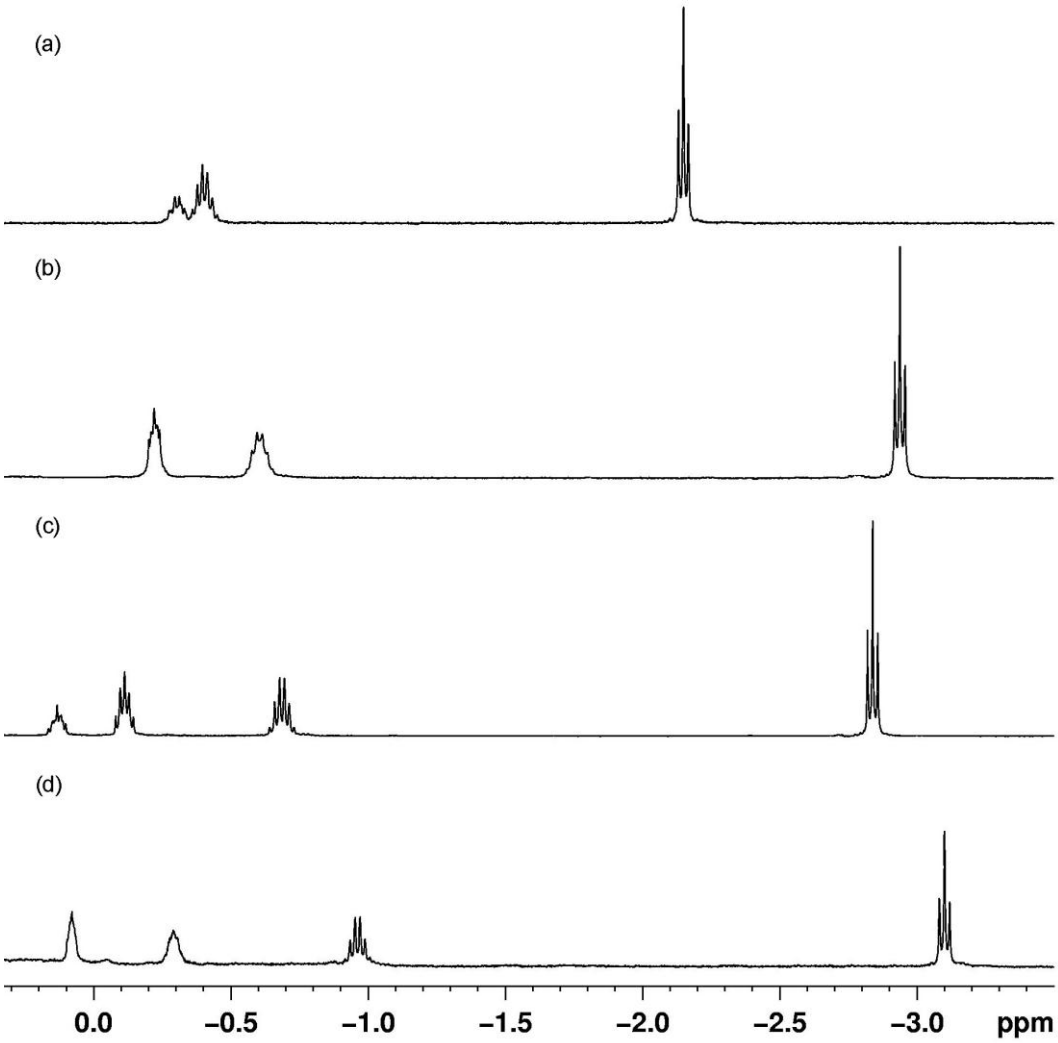
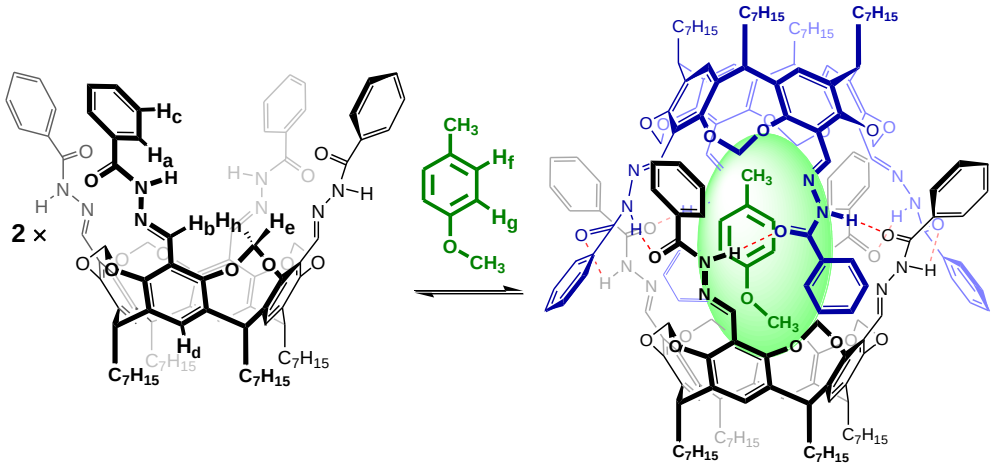


Fig. S9 Upfield region of ^{1}H NMR (400 MHz, 298 K) spectra in mesitylene-d_{12} of (a) *n*-pentane@**2**$_2$; (b) *n*-hexane@**2**$_2$; (c) *n*-heptane@**2**$_2$; (d) *n*-octane@**2**$_2$.

10. 2D-NOESY experiment



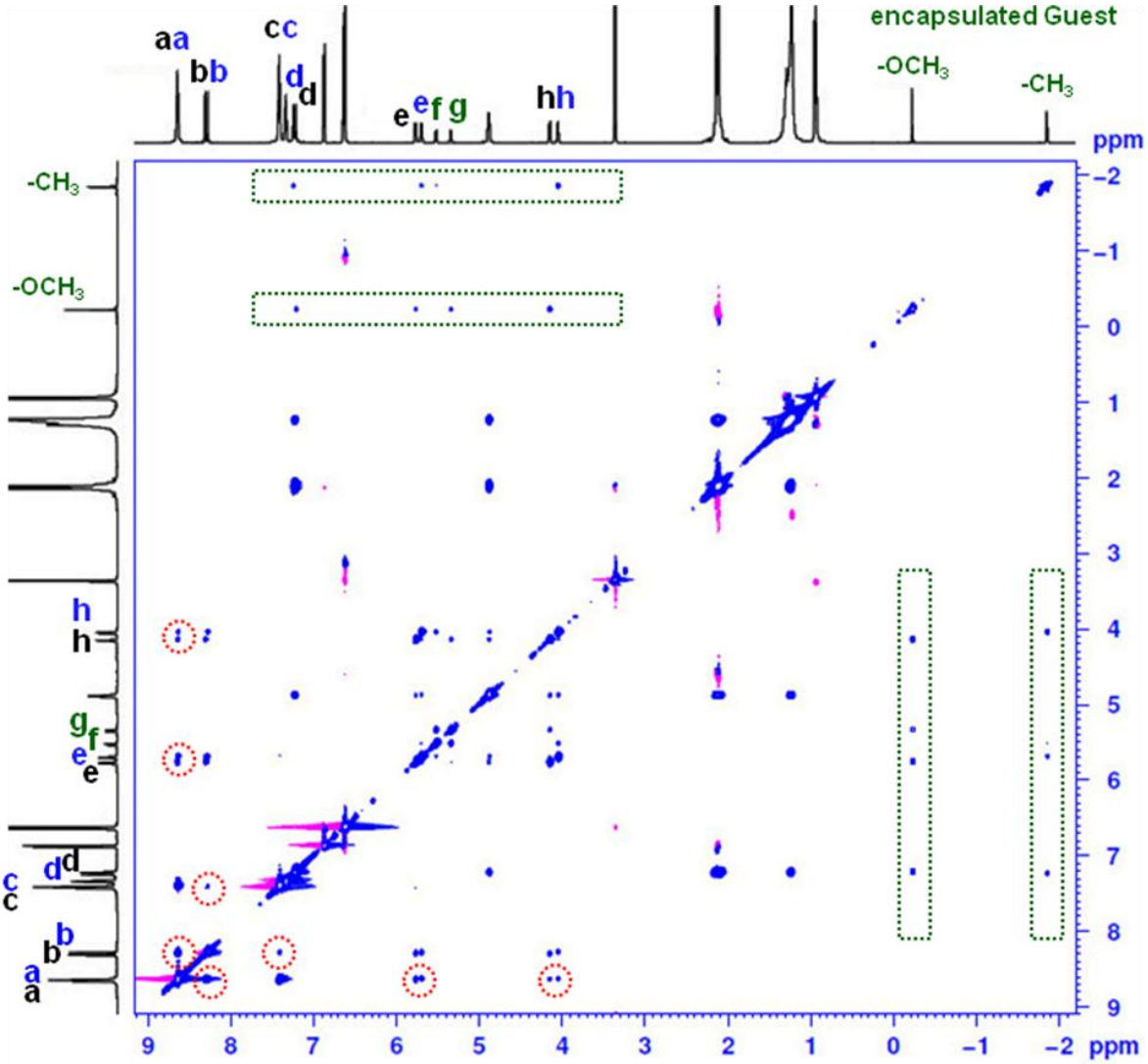


Fig. S10 Partial region of 2D-NOESY spectrum (400 MHz) of 4-methylanisole@**2**$_2$ in mesitylene-d_{12} at 298 K ([**2**] = 6 mM, [4-methylanisole] = 18 mM). The northern hemisphere and the southern hemisphere of the capsule, and the encapsulated guest are marked "blue", "black" and "green", respectively.

11. 2D-DOSY experiments

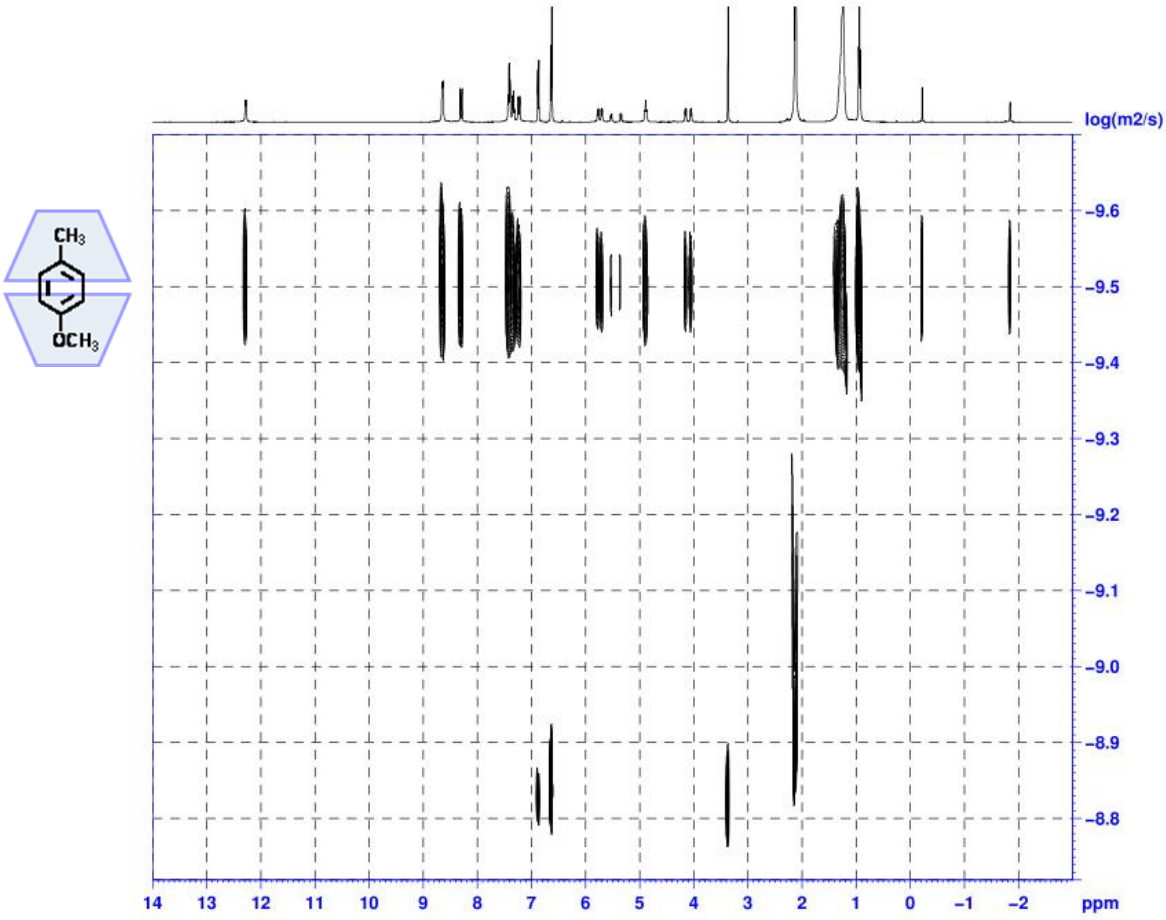


Fig. S11 2D-DOSY NMR (400 MHz) spectrum of 4-methylanisole@**2**$_2$ in mesitylene-d_{12} at 298 K ([**2**] = 6 mM and [4-methylanisole] = 18 mM).

Table S1. Diffusion coefficients of **2**, 4-methylanisole, and 4-methylanisole@**2**$_2$ measured by 2D-DOSY NMR.

entry	sample	Diffusion coefficient (m^2 s^{-1})
1	**2** [a]	5.06 (±0.14) × 10^{-10}
2	4-methylanisole	14.8 × 10^{-10}
3	4-methylanisole@**2**$_2$	3.14 (±0.08) × 10^{-10}

[a] in 10% CD_3OD/mesitylene-d_{12} at 298 K.