# Formation of a pillar[5]arene-based [3]pseudorotaxane in solution and in the solid state

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## Electronic Supplementary Information (10 pages)

*1. Materials and methods*

All reagents were commercially available and used as supplied without further purification. 1,4-Dipropoxybenzene **1** and 1,4-bis(4-bromobutoxy)benzene **2** were synthesized according to literature procedures.[S1] ^{1}H NMR spectra were collected on a temperature-controlled 400 MHz or 500 MHz spectrometer. ^{13}C NMR spectra were recorded on a Bruker AVANCE DMX-500 spectrometer at 125 MHz. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with a ESI interface and an ion trap analyzer.

*2. Syntheses of 3 and 4*

A mixture of 1,4-dipropoxybenzene (4.40 g, 26.3 mmol), 1,4-bis(4-bromobutoxy)benzene (1.00 g, 2.60 mmol), paraformaldehyde (2.45 g, 79.0 mmol) and $FeCl_3$ (0.800 g, 4.94 mmol) was stirred in dichloromethane under nitrogen atmosphere at room temperature for 8 h. The solution was evaporated under vacuo and the residue was purified by flash column chromatography on silica gel (petroleum ether/dichloromethane = 40/1, *v/v*) to afford **3** as a white solid (1.00 g, 32%) and [3]pseudorotaxane **4** (100 mg). Melting point of **3**: 127.7–129.6 °C. ^{1}H NMR of **3** (400 MHz, CDCl₃, 295 K) $\delta$ (ppm): 6.82–6.81 (8H, m), 6.76 (2H, s), 3.89 (4H, *J* = 6.0 Hz, t), 3.86–3.73 (26H, m), 3.42 (4H, *J* = 6.5 Hz, t), 2.05–1.98 (4H, m), 1.92–1.86 (4H, m), 1.83–1.71 (16H, m), 1.08–1.00 (24H, m). ^{13}C NMR of **3** (125 MHz, CDCl₃, 295 K) $\delta$ (ppm): 149.88, 149.84, 149.74, 128.54, 128.39, 128.31, 128.29, 128.01, 115.04, 70.08, 70.04, 69.96, 69.93, 67.21, 33.67, 29.70, 29.51, 28.39, 23.08, 23.04, 10.92, 10.79. LRESIMS: *m/z* 1234.4 [M + H₂O + H]$^+$ (100%). HRESIMS: *m/z* calcd for [M + Na]$^+$ $C_{67}H_{92}Br_2NaO_{10}{}^+$, 1237.4949; found 1237.4938; error –0.9 ppm. ^{1}H NMR of **4** (400 MHz, CDCl₃, 295 K, 8.00 mM) $\delta$ (ppm): 6.89 (16H, s), 6.84 (4H, s), 6.80 (4H, s), 3.89–3.77 (60H, m), 3.48–3.45 (8H, t), 2.04 (8H, m), 1.93 (8H, m), 1.84–1.81 (32H, m), 1.07–1.03 (48H, m). ^{13}C NMR of **4** (125 MHz, CDCl₃, 295 K, 15.0 mM) $\delta$ (ppm): 148.84, 148.81, 148.67, 127.51, 127.45, 127.33, 127.26, 127.22, 127.05, 126.98, 113.89, 113.83, 69.10, 69.04, 69.03, 68.97, 68.90, 66.34, 66.27, 66.23, 66.20, 32.67, 32.65, 27.39, 22.09, 22.06, 21.90, 9.91, 9.78.
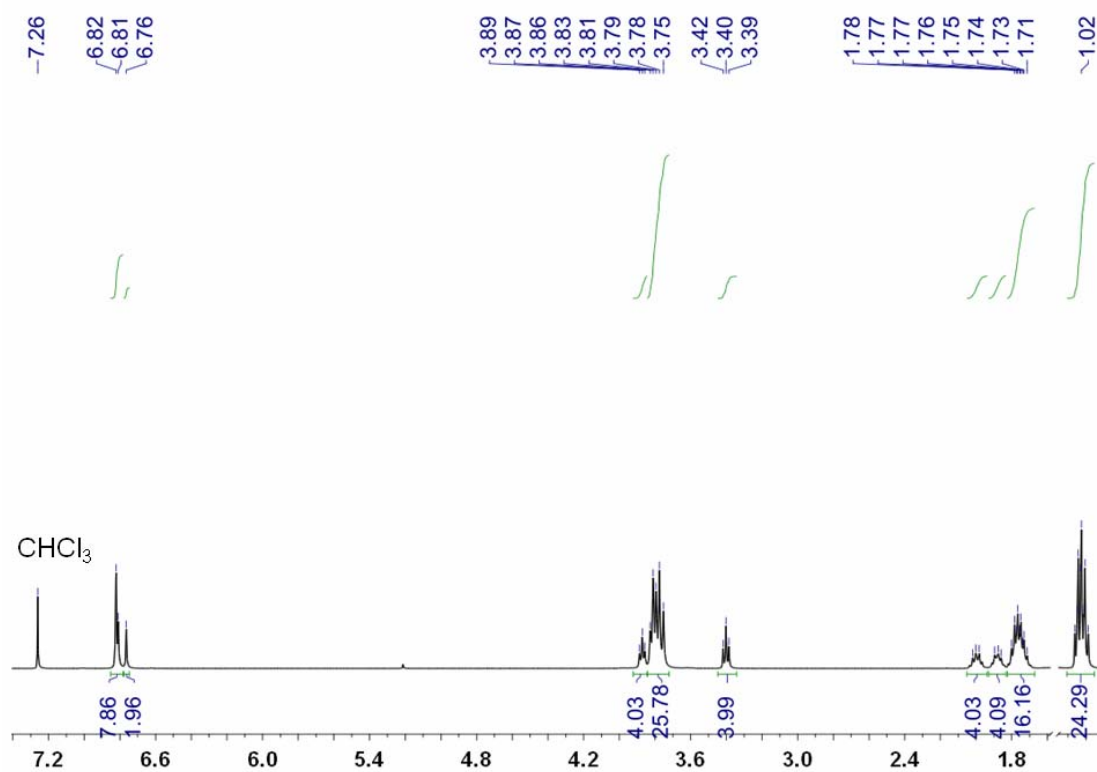
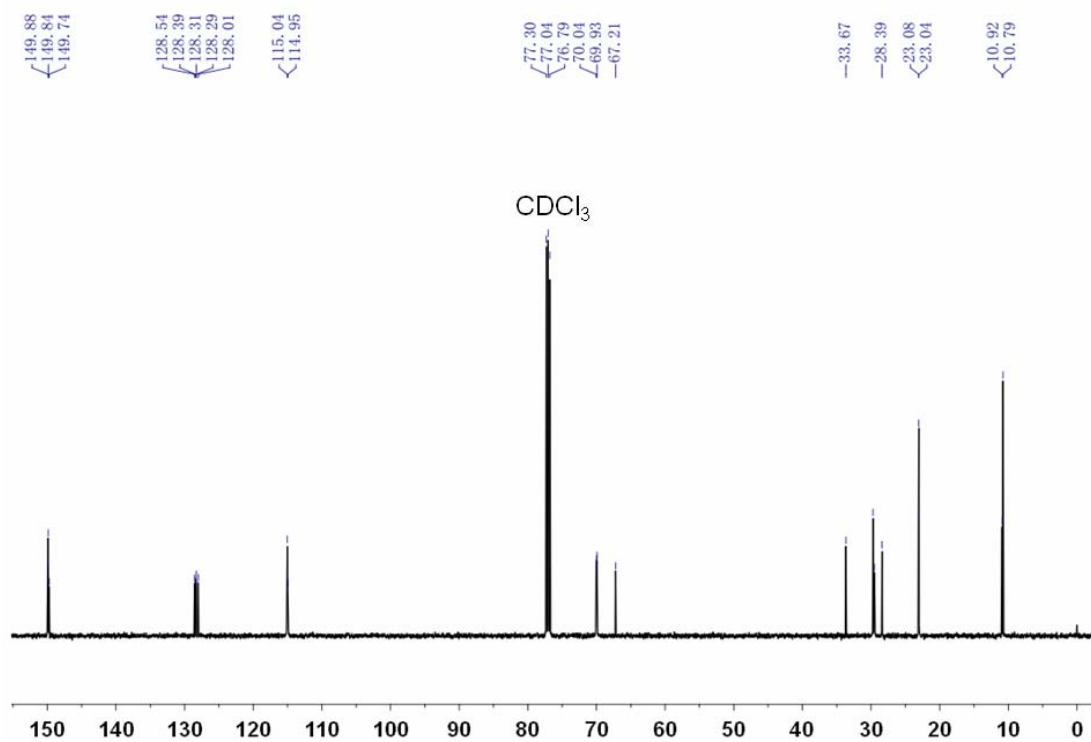**Fig. S1** $^1$H NMR spectrum (400 MHz, chloroform-*d*, 22 °C) of **3**.

**Fig. S2** $^{13}$C NMR spectrum (125 MHz, chloroform-*d*, 22 °C) of **3**.
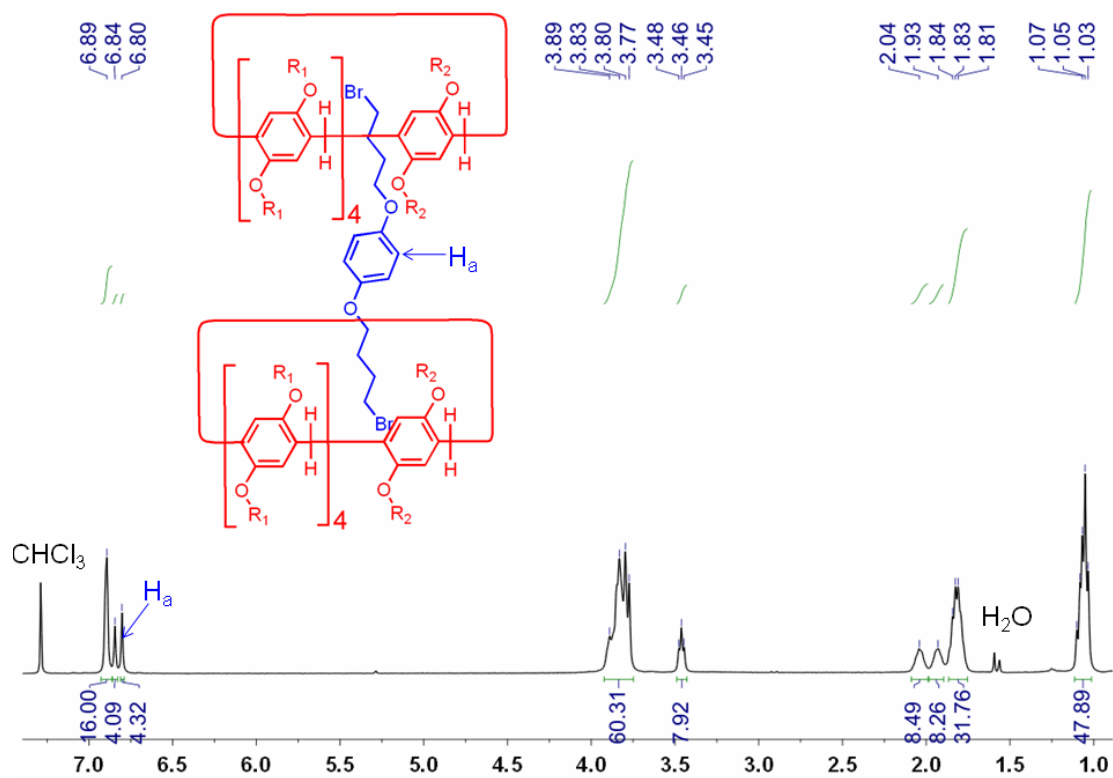
***Fig. S3*** $^1$H NMR spectrum (400 MHz, chloroform-*d*, 22 °C, 8.00 mM) of **4**.
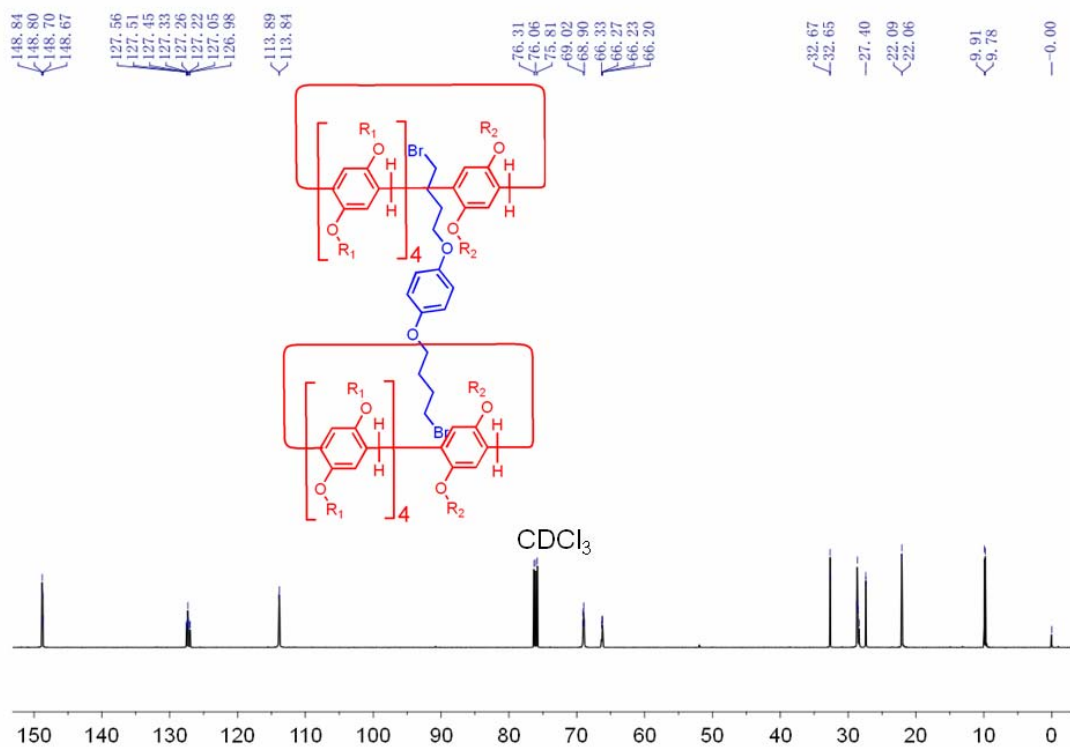


***Fig. S4*** $^{13}$C NMR spectrum (125 MHz, chloroform-*d*, 22 °C, 15.0 mM) of **4**.
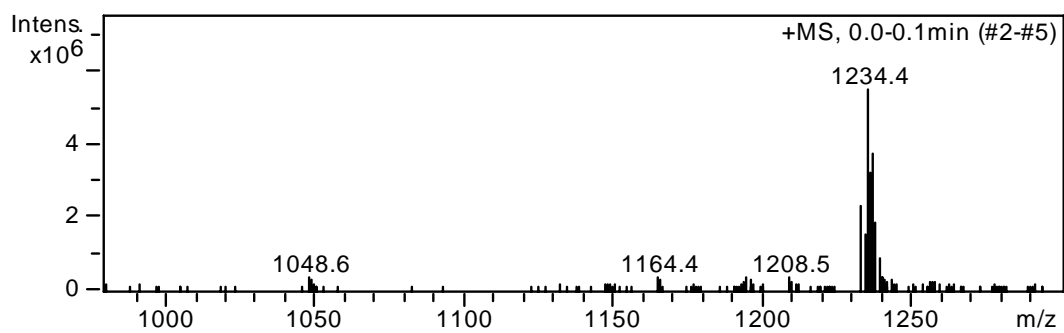
***Fig. S5*** LRESI mass spectrum of **3**. Main peak: *m/z* 1234.4 $[M + H_2O + H]^+$ (100%).



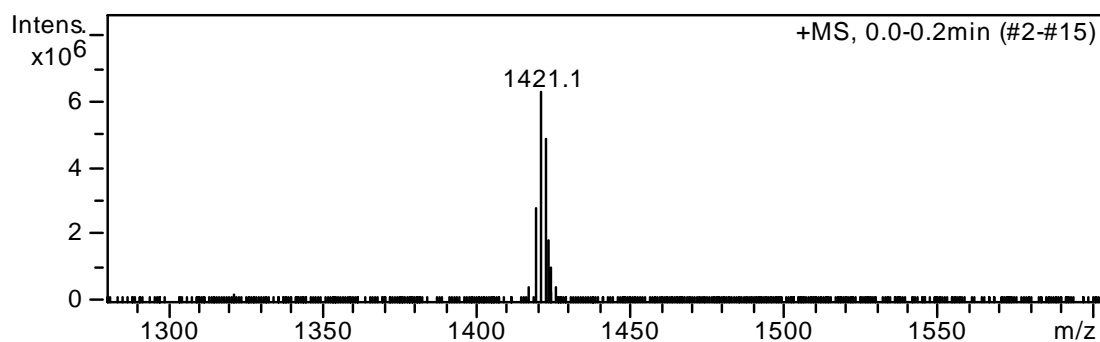***Fig. S6*** LRESI mass spectrum of a solution of **3** and **2**. Main peak: *m/z* 1421.1 $[M + 2H_3O]^{2+}$ (100%).

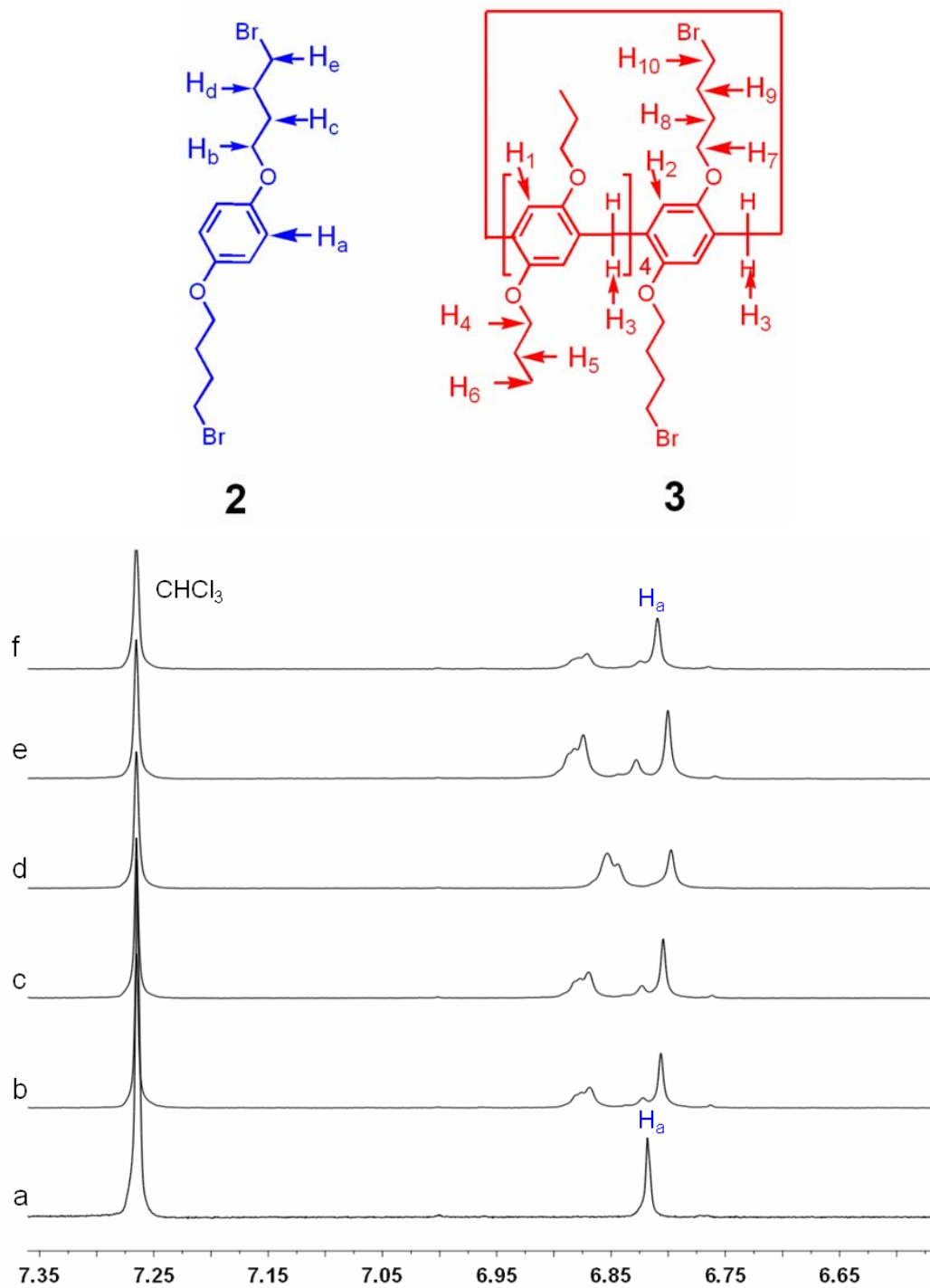*3. Stoichiometry and association constant determination for the complexation between 3 and 2*



**Fig. S7** Partial $^1$H NMR spectra (500 MHz, chloroform-*d*, 22 °C): (a) 4.00 mM **2**; (b) 1.00 mM **3** and 3.00 mM **2**; (c) 2.67 mM **3** and 1.33 mM **2**; (d) 2.00 mM **3** and 2.00 mM **2**; (e) 1.33 mM **3** and 2.67 mM **2**; (d) 3.00 mM **3** and 1.00 mM **2**.
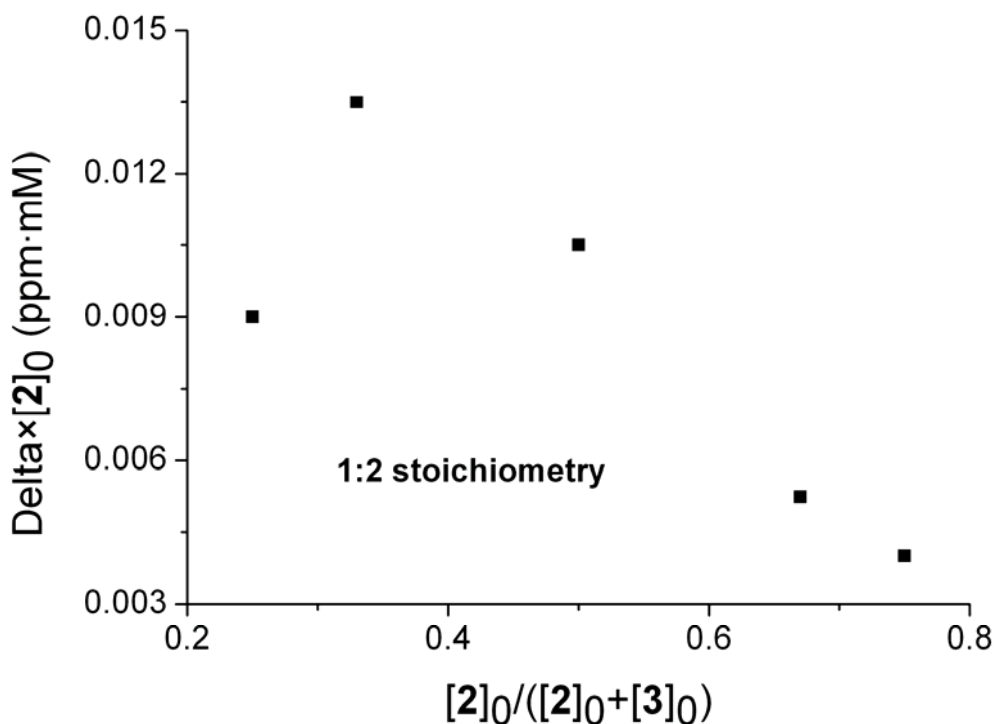
**Fig. S8** Job plot showing the 1:2 stoichiometry of the complexation between **2** and **3** in chloroform-*d* using the proton NMR data for $H_a$. Delta is the chemical shift change of $H_a$. $[2]_0 + [3]_0 = 4.00$ mM. $[2]_0$ and $[3]_0$ are initial concentrations of **2** and **3**.
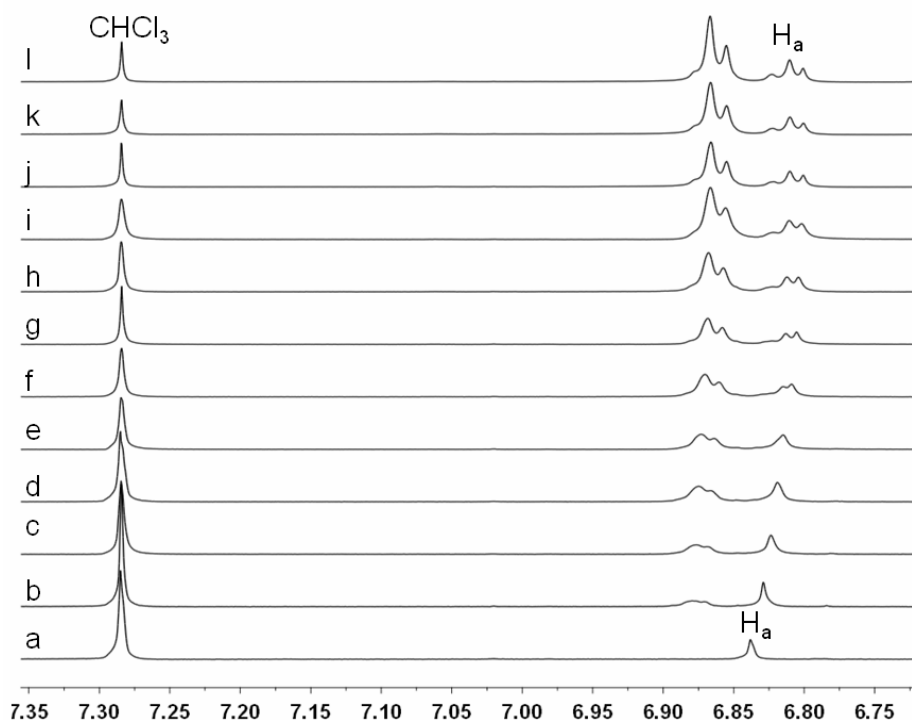


**Fig. S9** Partial $^1$H NMR spectra (500 MHz, chloroform-*d*, 22 °C) of **2** at the concentration of 1.50 mM upon addition of **3**: (a) 0 mM; (b) 0.880 mM; (c) 1.73 mM; (d) 2.55 mM; (e) 3.33 mM; (f) 5.18 mM; (g) 6.86 mM; (h) 8.41 mM; (i) 11.2 mM; (j) 13.5 mM; (k) 17.4 mM; (l) 20.0 mM.

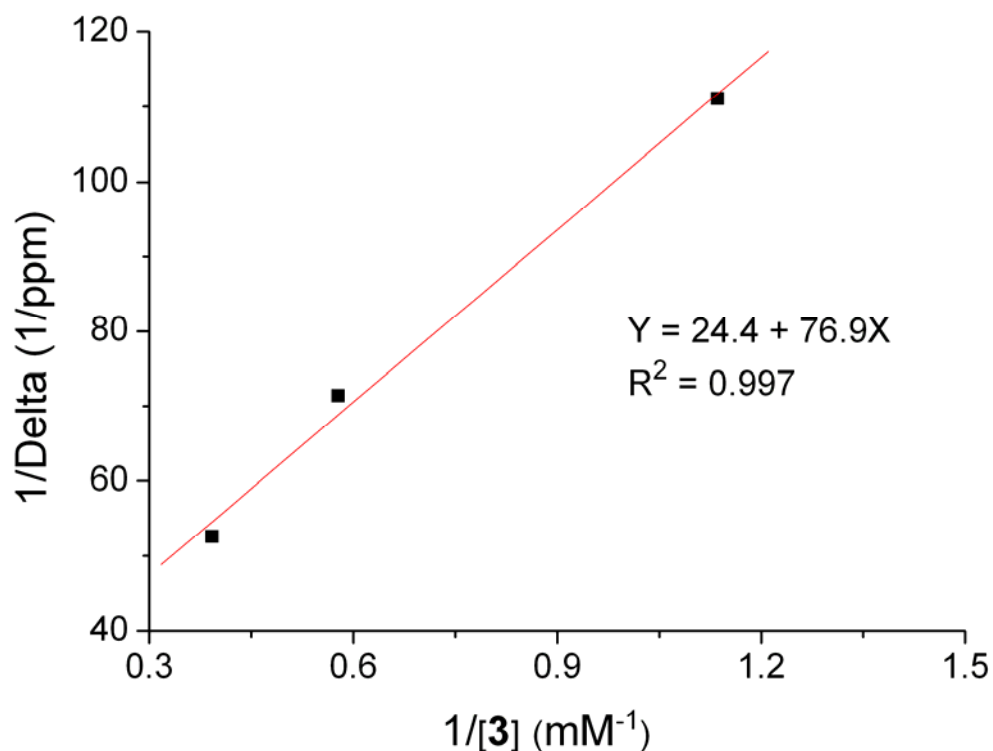Treatment of chemical shifts of $H_a$ on **2** by Benesi-Hildebrand method[S2]



$$Y = 24.4 + 76.9X$$
$$R^2 = 0.997$$

**Fig. S10** Benesi-Hildebrand plot for the complexation of host **3** with guest **2**. $\Delta_0$, the difference in $\delta$ values for $H_a$ of **2** in the uncomplexed and fully complexed species, was determined as the y-intercept of a plot of $\Delta = \delta - \delta_u$ versus $1/[2]_0$ in the high initial concentration range of **2**. $\Delta_0 = 1/24.4 = 0.0401$ ppm.
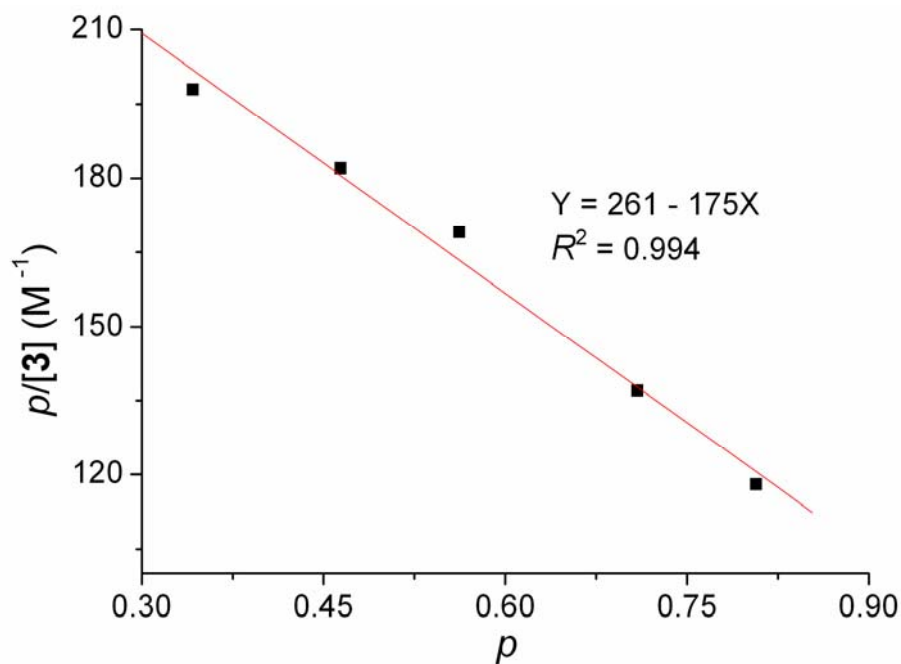


$$Y = 261 - 175X$$
$$R^2 = 0.994$$

**Fig. S11** Scatchard plot for the complexation of host **3** with guest **2** in chloroform-*d* at 22 °C. $p$ = fraction of alkyl chains unit on **2** bound. Error bars in $p$: ±0.03 absolute; error bars in $p/[\textbf{3}]$: ±0.06 relative.

## 4. The $^1$H NMR of a solution of 2 and 3 in different organic solvents
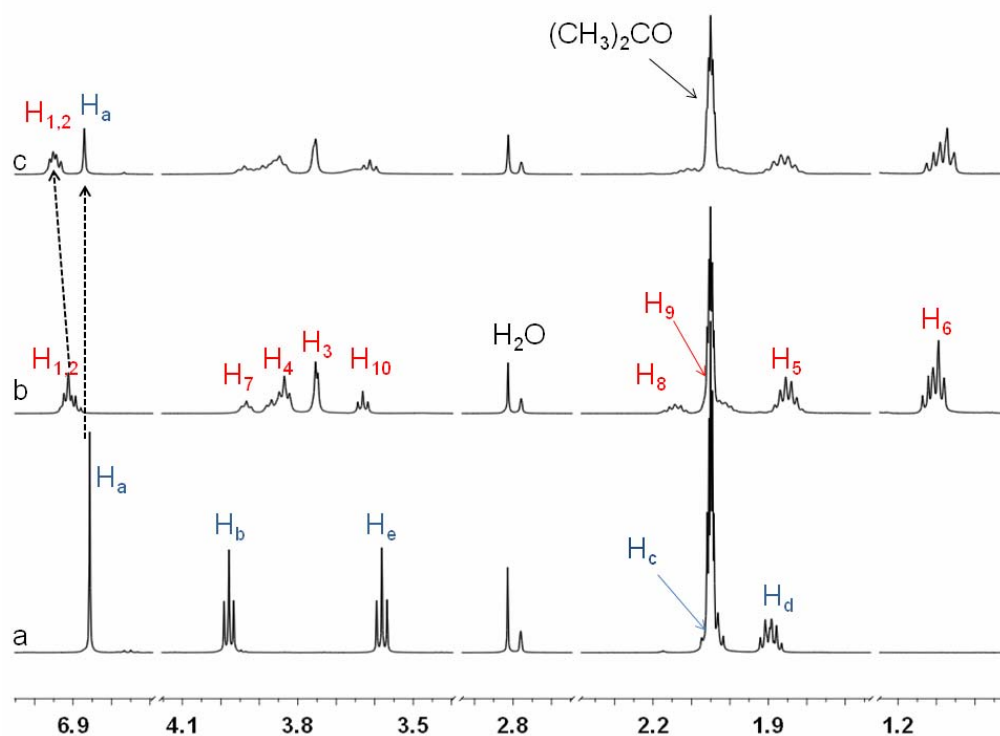


**Fig. S12** Partial $^1$H NMR spectra (500 MHz, acetone-$d_6$, 22 °C): (a) 4.00 mM **2**; (b) 4.00 mM **3**; (c) 4.00 mM **3** and 2.00 mM **2**.
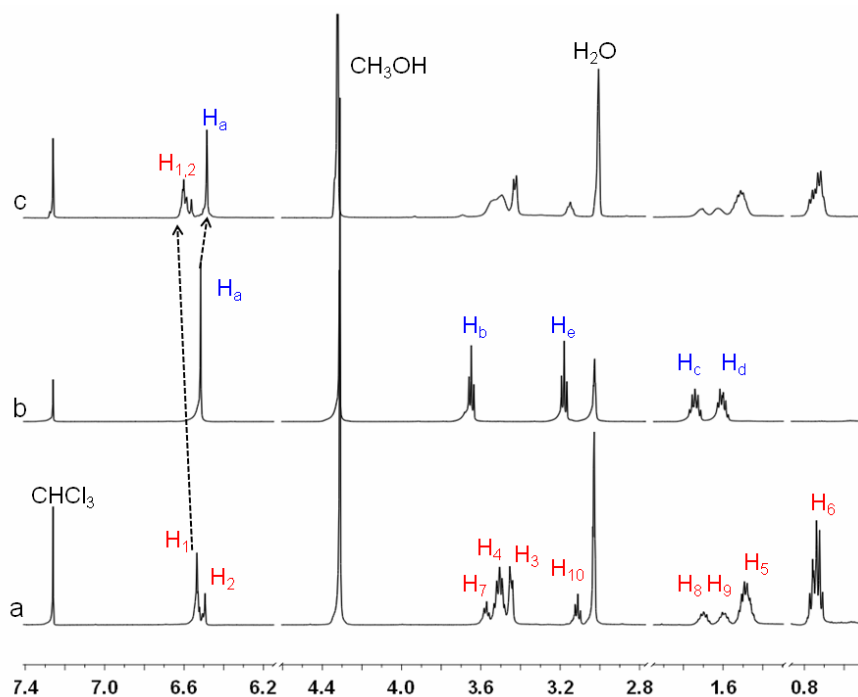


**Fig. S13** Partial $^1$H NMR spectra [500 MHz, methanol-$d_4$/chloroform-$d$ (1:1, v/v), 22 °C]: (a) 4.00 mM **3**; (b) 4.00 mM **2**; (c) 4.00 mM **3** and 2.00 mM **2**.

## 5. Variable-temperature ¹H NMR spectra of a solution of 2 and 3 in toluene-d₈

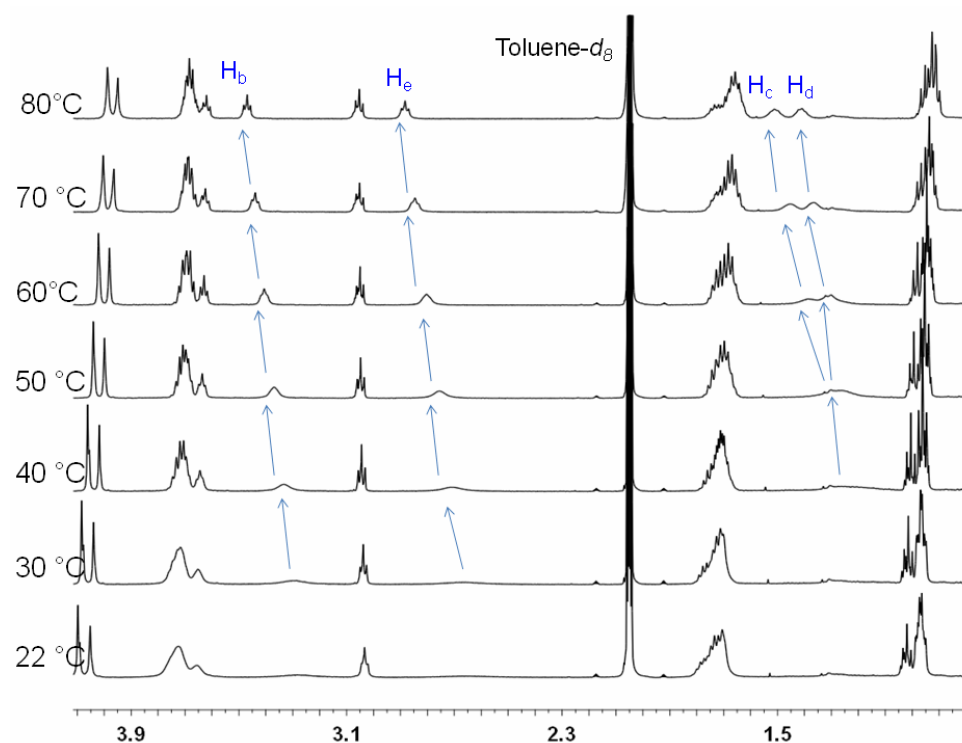*5. Variable-temperature $^1H$ NMR spectra of a solution of 2 and 3 in toluene-d₈*



**Fig. S14** Partial variable-temperature $^1H$ NMR spectra (500 MHz, toluene-$d_8$) of a solution of 4.00 mM **3** and 2.00 mM **2**.

## 6. X-ray crystal data of 4

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Crystal data of **4**: colorless, $C_{74}H_{102}Br_3O_{11}$, *FW* 1407.29, monoclinic, space group *C*2/*c*, *a* = 32.807(3), *b* = 20.7165(10), *c* = 27.943(3) Å, $\alpha$ = 90.00°, $\beta$ = 130.180(17)°, $\gamma$ = 90.00°, *V* = 14510(2) Å³, *Z* = 8, $D_c$ = 1.288 g cm⁻³, *T* = 140(2) K, $\mu$ = 1.724 mm⁻¹, 28619 measured reflections, 13256 independent reflections, 931 parameters, 472 restraints, *F*(000) = 5912, $R_1$ = 0.1805, $wR_2$ = 0.2659 (all data), $R_1$ = 0.0843, $wR_2$ = 0.2048 [$I > 2\sigma(I)$], max. residual density 0.569 e•Å⁻³, and goodness-of-fit ($F^2$) = 1.004. CCDC-900315.

*References:*

S1. (*a*) S. A. Caldarelli, J.-F. Duckert, S. Wein, M. Calas, C. Périgaud, H. Vial and S. Peyrottes, *ChemMedChem*, 2010, **5**, 1102–1109; (*b*) R. Castro, K. R. Nixon, J. D. Evanseck and A. E. Kaifer, *J. Org. Chem.*, 1996, **61**, 7298–7303.

S2. Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.*, 1949, **71**, 2703–2707.