

Electronic Supplementary Information (ESI)

Selective lithium ion recognition in self-assembly of columnar liquid crystals based on a lithium receptor

Yuan Luo, Nicolas Marets and Takashi Kato*

Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

E-mail: kato@chiral.t.u-tokyo.ac.jp

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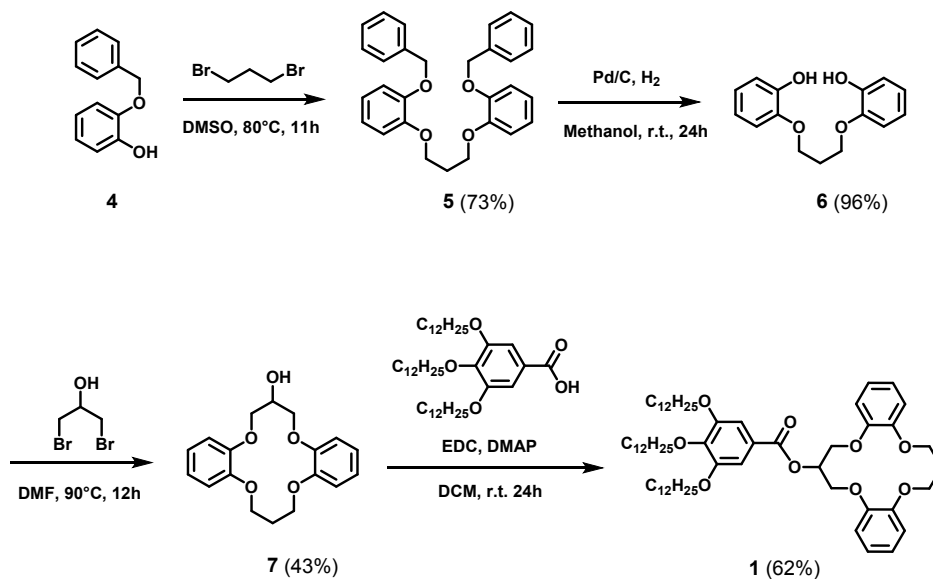
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1. Materials and methods

Phase transition behaviour was examined by differential scanning calorimetry (DSC) by using a NETZCH DSC 204 Phoenix system. Polarizing optical microscope (POM) observation was conducted with an Olympus BX-51 polarizing optical microscope equipped with a Linkam LTS350 hot-stage. NMR spectra were recorded at 400 MHz for ^1H and 100 MHz for ^{13}C in CDCl_3 , CD_3CN or CD_3CD using a JEOL JNM-ECX400 NMR spectrometer. Chemical shifts of ^1H and ^{13}C NMR signals were quoted to internal standard Me_4Si ($\delta = 0.00$) and CDCl_3 ($\delta = 77.00$) respectively, and expressed by chemical shifts in ppm (δ), multiplicity, coupling constant (Hz), and relative intensity. Fourier-transform infrared (FT-IR) measurements were conducted with a JASCO FT/IR-6100 spectrometer. Matrix-associated laser desorption ionization time-of-flight mass spectra (MALDI-TOF MS) were recorded on a Bruker Daltonics Autoflex Speed using dithranol as the matrix. X-ray diffraction (XRD) patterns were recorded using a Rigaku RINT-2500 diffractometer with Ni-filtered CuK_α radiation, and the samples were placed in a heating stage. All alkali metal salts were dried at 40°C under vacuum for at least 6 hours before use. All other materials of the highest quality were purchased from Aldrich, Kanto, TCI, and Wako, and were used as received. Unless otherwise noted, all of the reactions were carried out under an argon atmosphere in a dry solvent purchased from Kanto.

2. Synthetic procedures

Synthesis of compound 1



Scheme 1 Synthetic route of compound 1

1,3-Bis(2-(benzyloxy) phenoxy) propane (5): To a stirred solution of 2-(benzyloxy) phenol (**4**) (10.4 g, 52 mmol) in DMSO (80 ml) was added 4.0 N NaOH aqueous solution (13 ml), followed by 1,3-dibromopropane (5.06 g, 25 mmol), and the mixture was stirred at 80 °C for 11 h. The cooled solution was poured into 0.5 N NaOH aqueous solution (100 ml) and extracted with CH₂Cl₂ (3 times). The organic phase was washed with water and brine, then dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo. The crude product was purified by recrystallization from MeOH to obtain **5** (8.40 g, 73 %) as a colorless solid.

¹H NMR (400 MHz, CDCl₃, δ): 7.42-7.25 (m, 10H, ArH), 6.94-6.84 (m, 8H, ArH), 5.09 (s, 4H, CH₂), 4.27 (t, 4H, *J*=6.3 Hz, CH₂), 2.33 (dd, 2H, *J*=18.4, 6.1 Hz, CH₂). ¹³C NMR (100 MHz, CDCl₃, δ): 149.48, 148.93, 137.64, 128.66, 127.91, 127.41, 121.95, 121.38, 115.32, 114.35, 71.43, 66.01, 29.64. MS (MALDI-TOF): [M + Na]⁺ calcd. for C₂₉H₂₈O₄Na, 463.54; found, 463.20.

2,2'-(Propane-1,3-diylbis(oxy)) diphenol (6): A solution of compound **5** (8.40 g, 19 mmol) in THF (200 ml) was diluted with as much MeOH (200 ml) as could be added while still maintaining a clear solution. A slurry of 10% Pd/C (0.84 g) in the minimum

amount of THF was added, and the mixture was hydrogenated with H₂ at room temperature for 24h. After the uptake of H₂ had stopped, the mixture was filtered through Celite, and the filtrate was concentrated in vacuo. Recrystallization of the residual material from hexane afforded pure **6** (4.75 g, 96 %) as light brown needles.

¹H NMR (400 MHz, CDCl₃, δ): 6.96-6.82 (m, 8H, ArH), 5.64 (s, 2H, OH), 4.27 (t, 4H, *J*=6.1 Hz, CH₂), 2.35 (dd, 2H, *J*=18.1, 6.1 Hz, CH₂).

¹³C NMR (100 MHz, CDCl₃, δ): 146.03, 145.77, 122.20, 120.49, 115.14, 112.32, 66.11, 29.44. MS (MALDI-TOF): [M + Na]⁺ calcd. for C₁₅H₁₆O₄Na, 283.29; found, 283.16.

Hydroxydibenzo-14-crown-4 (7): A mixture of compound **6** (2.00 g, 7.7 mmol) and LiOH (0.59 g, 24 mmol) in DMF (130 ml) was stirred at 80 °C for 30 min. 1,3-dibromo-2-propanol (1.68 g, 7.7 mmol) was added to the reaction mixture. After the addition, the reaction mixture was stirred at 90 °C for 12 h. The reaction solution was poured into 5 wt % HCl aqueous solution (100 ml) and extracted with CH₂Cl₂ (3 times). The organic phase was washed with water and brine, then dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, eluent: diethyl ether) and then further purified by recrystallization in ethyl acetate to give **7** (1.05 g, 43 %) as a white solid.

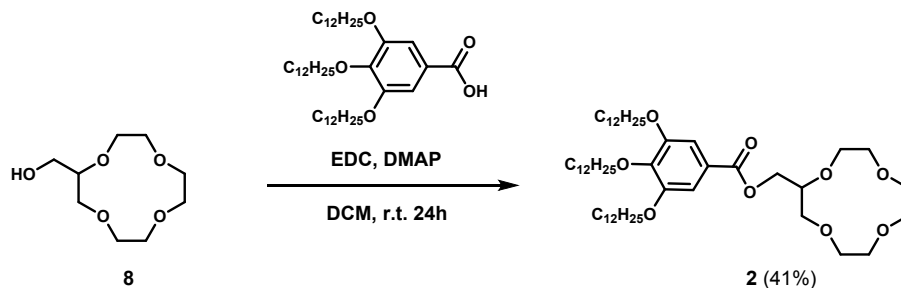
¹H NMR (400 MHz, CDCl₃, δ): 6.98-6.90 (m, 8H, ArH), 4.33-4.16 (m, 9H, CH, CH₂), 3.18 (d, 1H, *J*=6.0 Hz, OH), 2.37-2.23 (m, 2H, CH₂).

¹³C NMR (100 MHz, CDCl₃, δ): 149.84, 149.23, 122.81, 122.11, 117.14, 115.55, 71.46, 69.07, 67.64, 29.54. MS (MALDI-TOF): [M + Na]⁺ calcd. for C₁₈H₂₀O₅Na, 339.35; found, 339.19. Elemental analysis: calcd (%) for C₁₈H₂₀O₅: C 68.34, H 6.37, O 25.29. Found C 68.17, H 6.37.

Compound 1: A mixture of 3,4,5-tris(dodecyloxy)benzoic acid (0.256 g, 0.38 mmol), compound **7** (0.100 g, 0.32 mmol), EDC (0.121 g, 0.64 mmol), and DMAP (0.008 g, 0.06 mmol) in CH₂Cl₂ (40 mL) was stirred overnight at ambient temperature. The reaction mixture was added to NaHCO₃ (aq.) and extracted with CH₂Cl₂. The organic phase was washed with water and brine, then dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo. The residue was purified by flash column chromatography (silica gel, eluent: hexane : ethyl acetate 95:5) to give **1** (0.191 g, 62 %) as a white waxy solid.

¹H NMR (400 MHz, CDCl₃, δ): 7.30 (s, 2H, ArH), 6.99-6.88 (m, 8H, ArH), 5.62 (t, 1H, *J*=15.8 Hz, CH), 4.49 (m, 4H, CH₂), 4.27 (t, 4H, *J*=5.4 Hz, CH₂), 4.01 (m, 6H, CH₂), 2.40-2.24 (m, 2H, CH₂), 1.85-1.71 (m, 6H, CH₂), 1.48 (m, 6H, CH₂), 1.22-1.35 (m, 48H, CH₂), 0.88 (t, 9H, *J*=6.8 Hz, CH₃). ¹³C NMR (100 MHz, CDCl₃, δ): 153.09, 150.21, 148.88, 123.22, 122.19, 118.23, 116.04, 108.55, 73.76, 71.21, 69.47, 68.71, 67.54, 32.15, 30.55, 29.93, 29.87, 29.79, 29.59, 29.54, 26.30, 22.91, 14.33. MS (MALDI-TOF): [M + Na]⁺ calcd. for C₆₁H₉₆O₉Na, 996.43; found, 996.95. Elemental analysis: calcd (%) for C₆₁H₉₆O₉: C 75.27, H 9.94, O 14.79. Found C 75.49, H 10.07.

Synthesis of compound 2

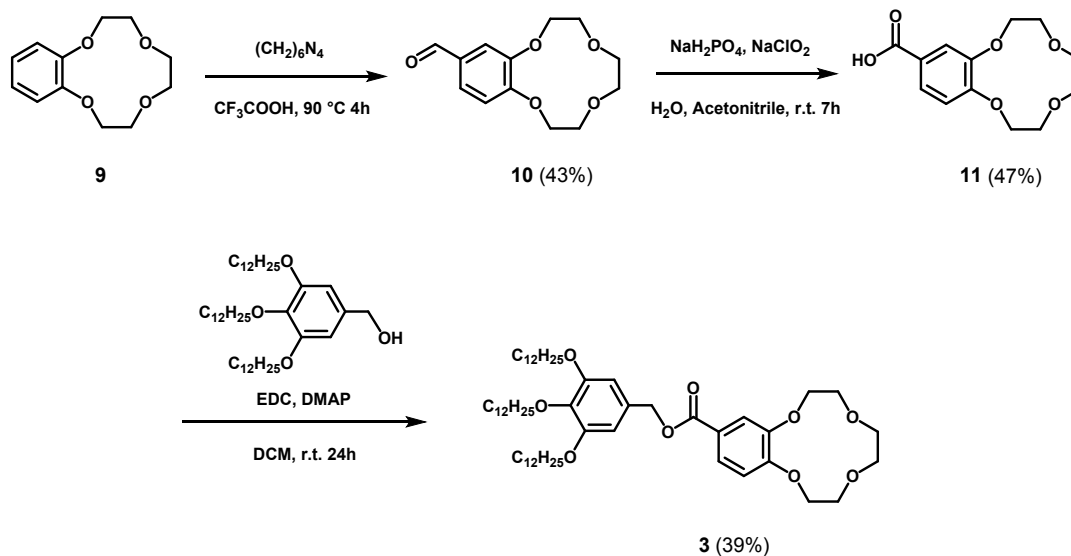


Scheme 2 Synthetic route of compound 2

Compound 2: A mixture of 3,4,5-tris(dodecyloxy)benzoic acid (0.393 g, 0.59 mmol), 2-hydroxymethyl-12-crown-4 (**8**) (0.100 g, 0.49 mmol), EDC (0.186 g, 0.98 mmol), and DMAP (0.012 g, 0.10 mmol) in CH₂Cl₂ (20 mL) was stirred overnight at ambient temperature. The reaction mixture was added to NaHCO₃ (aq.) and extracted with CH₂Cl₂. The organic phase was washed with water and brine, then dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo. The residue was purified by flash column chromatography (silica gel, eluent: hexane : ethyl acetate 80:20) to give **2** (0.173 g, 41 %) as a white waxy solid.

¹H NMR (400 MHz, CDCl₃, δ): 7.25 (s, 2H, ArH), 4.36-4.25 (m, 2H, CH₂), 4.03-3.61 (m, 21H, CH, CH₂), 1.83-1.71 (m, 6H, CH₂), 1.47 (m, 6H, CH₂), 1.22-1.35 (m, 48H, CH₂), 0.88 (t, 9H, *J*=6.7 Hz, CH₃). ¹³C NMR (100 MHz, CDCl₃, δ): 166.46, 153.06, 142.84, 124.69, 108.39, 77.85, 73.74, 71.70, 71.28, 71.12, 71.03, 70.96, 70.63, 69.46, 64.68, 32.15, 30.55, 29.93, 29.86, 29.79, 29.62, 29.59, 29.54, 26.31, 22.91, 14.33. MS (MALDI-TOF): [M + Na]⁺ calcd. for C₅₂H₉₄O₉Na, 886.32; found, 886.87. Elemental analysis: calcd (%) for C₅₂H₉₄O₉: C 72.35, H 10.98, O 16.68. Found C 72.57, H 11.02.

Synthesis of compound 3



Scheme 3 Synthetic route of compound 3

2, 3, 5, 6, 8, 9-Hexahydro-1, 4, 7, 10-benzotetraoxacyclodo decin-12-carboxaldehyde (10): At a solution of 2, 3, 5, 6, 8, 9-hexahydro-1, 4, 7, 10-benzotetraoxacyclodo decin (**9**) (1.40 g, 6.24 mmol, 1 eq) in 10ml of trifluoroacetic acid was added hexamethylenetetramine (0.875 g, 6.24 mmol, 1 eq). The mixture was refluxed (90 °C) under argon. After 4h, 20 ml of water was poured into the red solution and the reaction mixture was stirred for another 90 min at 90 °C. After cooling at room temperature, the acid mixture was neutralized until pH 7 with saturated aqueous NaHCO_3 solution. The compound was extracted with dichloromethane (3 x 50 ml) and the combined organic solution was dried over MgSO_4 and evaporated. The crude oil was purified by flash chromatography (SiO_2) with ethyl acetate/hexane (85/15) to give **10** as a white solid (0.678 g, 2.68 mmol, 43%).

^1H NMR (400 MHz, CDCl_3 , δ): 3.78 (s, 4H, CH_2), 3.84 (m, 2H, CH_2), 3.91 (m, 2H, CH_2); 4.26 (m, 4H, CH_2), 7.06 (d, $J=7.9\text{Hz}$, 1H, ArH), 7.54 (m, 2H, CH_2), 9.86 (s, 1H, CH). ^{13}C NMR (100 MHz, CDCl_3 , δ): 69.70, 69.80, 70.92, 71.09, 71.52, 72.88, 116.16, 118.23, 127.44, 131.24, 150.87, 156.64, 190.87. MS (MALDI-TOF): $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_5\text{Na}$, 275.10; found, 275.99.

2,3,5,6,8,9-Hexahydro-1,4,7,10-benzotetraoxacyclododecin-12-carboxylic acid (11): At a solution of compound **10** (0.505 g, 2 mmol, 1 eq) and NaH_2PO_4 (0.072 g, 0.6 mmol, 0.3 eq) in a mixture of 10 ml of water, 20 ml of acetonitrile and 3 ml of H_2O_2 (35%) at 0°C, was added dropwise a solution of NaClO_2 (0.271 g, 3 mmol, 1.5 eq) in 2ml of water. After complete addition, the reaction mixture was allowed to warm up to room temperature under argon. After 7h, the excess of NaClO_2 was quenched with 20ml of

an aqueous solution of Na₂SO₃ (15%). Then the solution was acidified until pH3 with a HCl solution (5%) and extracted with ethyl acetate (3 x 50 ml). The combined organic solution was evaporated and the crude oil was recrystallized in acetone to yield **11** as white needles crystals (0.250 g, 0.96 mmol, 47%).

¹H NMR (400 MHz, Acetone-d₆, δ): 3.70 (s, 4H, CH₂), 3.77 (m, 2H, CH₂), 3.83 (m, 2H, CH₂); 4.22 (m, 4H, CH₂), 7.10 (d, J=8.4Hz, 1H, ArH), 7.64 (d, J=2.0Hz, 1H, ArH), 7.70 (dd, J=2.0Hz, J=8.4Hz, 1H, ArH). ¹³C NMR (100 MHz, Acetone-d₆, δ): 70.19, 70.37, 71.72, 71.77, 72.10, 73.72, 116.86, 120.86, 124.95, 125.92, 151.04, 156.19, 167.17. MS (MALDI-TOF): [M + Na]⁺ calcd. for C₁₃H₁₆O₆Na, 291.09; found, 290.99.

Compound 3: At a solution of compound **11** (0.120 g, 0.45 mmol, 1 eq), 3,4,5-tris(dodecyloxy)benzenemethanol (0.444 g, 0.67 mmol, 1.5 eq) and DMAP (0.080 g, 0.66 mmol, 1.5 eq) in 10 ml of dry CH₂Cl₂ under argon was added DCC (0.138 g, 0.67 mmol, 1.5 eq). The mixture was stirred under argon at room temperature for 24 h. After complete reaction, the reaction mixture was poured in a saturated aqueous solution of NaHCO₃ (20 ml). The organic layer was separated, washed with water (2x50 ml), brine (50 ml), dried over MgSO₄, filtered and evaporated under reduced pressure. The crude product was purified by flash chromatography (SiO₂) with CH₂Cl₂ then CH₂Cl₂/MeOH (1%), recrystallized in ethyl acetate to yield **3** as a white solid (0.158 g, 0.17 mmol, 39%).

¹H NMR (400 MHz, CDCl₃, δ): 0.88 (t, J=7.0Hz, 9H, CH₃), 1.26 (m, 48H, CH₂), 1.47 (m, 6H, CH₂), 1.78 (m, 6H, CH₂), 3.77 (s, 4H, CH₂), 3.82 (m, 2H, CH₂), 3.97 (m, 6H, CH₂), 4.37 (t, J=4.3Hz, 6H, CH₂), 5.23 (s, 2H, CH₂), 6.62 (s, 2H, ArH), 7.07 (d, J=8.4Hz, 1H, ArH), 7.77 (d, J=1.8Hz, 1H, ArH), 7.84 (dd, J=1.8Hz, J=8.4Hz, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃, δ): 14.20, 22.78, 25.07, 25.73, 26.21, 26.23, 29.46, 29.49, 29.50, 29.53, 29.71, 29.74, 29.75, 29.80, 29.83, 29.85, 30.44, 32.02, 32.04, 34.05, 67.08, 69.24, 69.75, 69.87, 70.79, 71.03, 71.05, 72.83, 73.52, 107.09, 115.90, 120.42, 124.12, 125.57, 131.14, 138.28, 149.95, 153.29, 155.24, 166.04. MS (MALDI-TOF): [M + Na]⁺ calcd. for C₅₆H₉₄O₉Na, 933.69; found, 933.95. Elemental analysis: calcd (%) for C₅₆H₉₄O₉: C 73.80, H 10.40, O 15.80. Found C 73.81, H 10.36.

3. Thermal and liquid-crystalline properties

Summary of thermal properties

Table S1. Thermal properties of compounds **1–3** and equimolar mixtures of **1–3** with LiClO₄ or NaClO₄.

Sample	Phase transition behaviour ^[a]											
	1st cooling cycle					2nd heating cycle						
1	Iso	-10	Cr			Cr ₁	1	Cr ₂	58	Iso		
1/Li⁺	Iso	109	Col _r ^[b]	73	G	G	73	Col _r	117	Cr ^[d]	151	Iso
1/Na⁺		Phase separation ^[c]						Phase separation ^[c]				
2	Iso	2	Cr			Cr	28	Iso				
2/Li⁺	Iso	156	Col _h	22	Cr	Cr	74	Col _h	158	Iso		
2/Na⁺		Phase separation ^[c]						Phase separation ^[c]				
3	Iso	14	Cr			Cr	71	Iso				
3/Li⁺	Iso	-10	Cr			Cr	2	Iso				
3/Na⁺		Phase separation ^[c]						Phase separation ^[c]				

[a] Transition temperatures (°C) were determined by DSC on a first cooling cycle at a scan rate of 10 K min⁻¹. G, glassy; Cr, crystal; Iso, isotropic; Col_r, columnar rectangular phase; Col_h, columnar hexagonal phase. [b] The sample shows monotropic liquid-crystalline Col_r phase upon cooling from isotropic state. [c] Observed by POM measurements above the isotropization temperature of the single component compounds **1–3**. [d] Cold crystallization occurs in the heating process at around 137 °C. A Col_r to Cr phase transition was observed.

Compound 1, 1/Li⁺ and 1/Na⁺

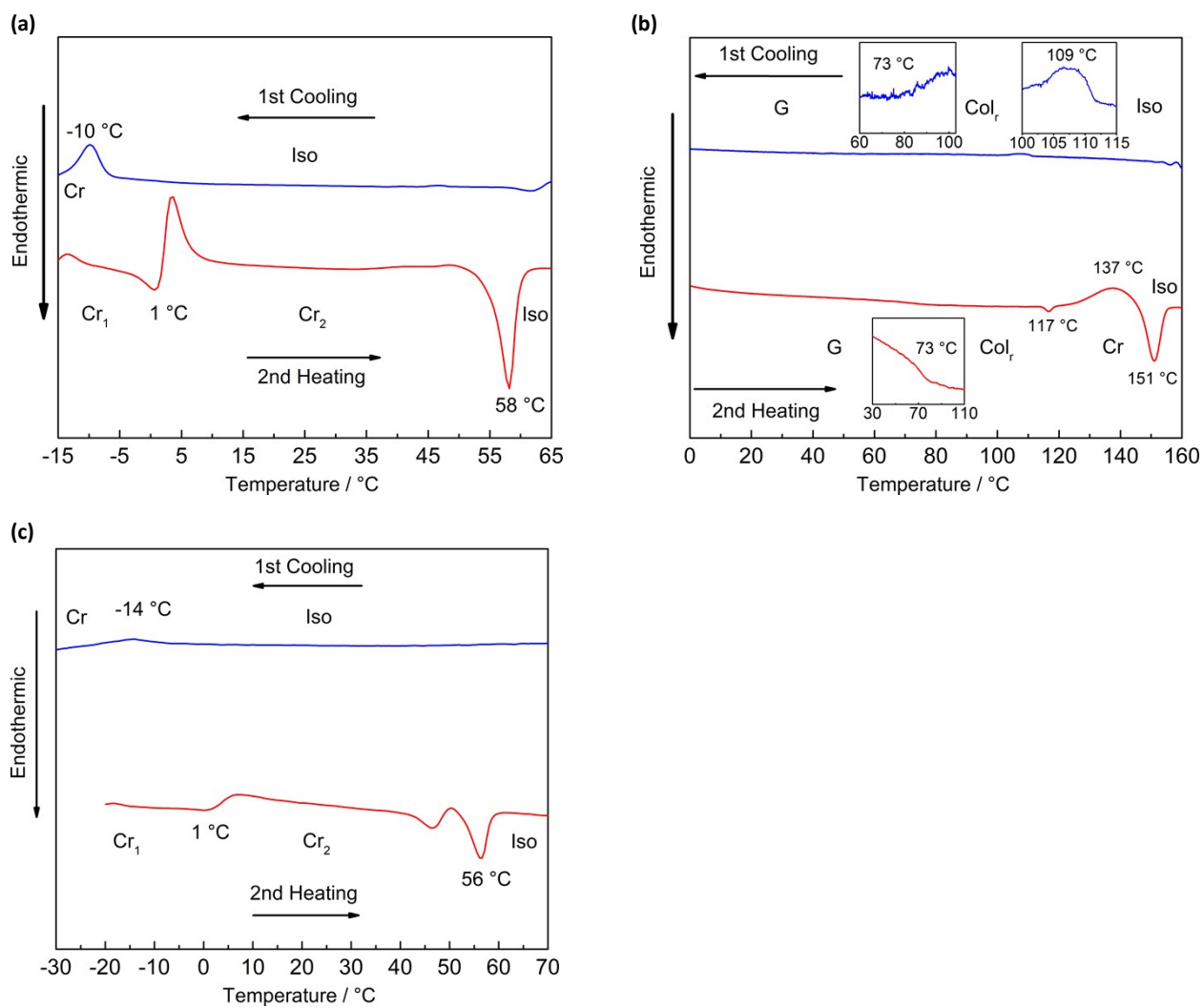


Fig. S1 DSC thermograms of (a) compound 1, (b) 1/Li⁺ and (c) 1/Na⁺ at a scan rate of 10 k min⁻¹.

X-ray diffraction pattern of 1/Li⁺ at 95 °C

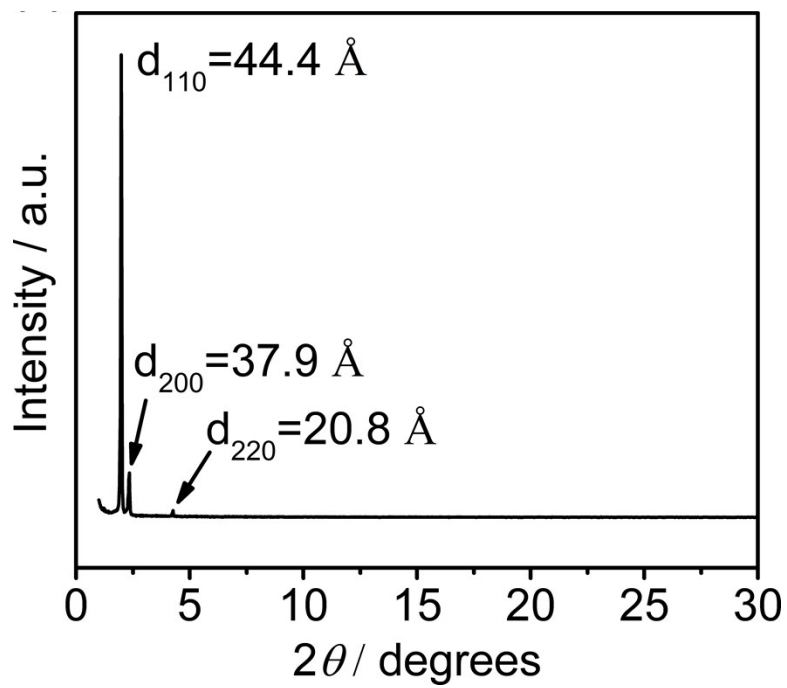


Fig. S2 X-ray diffraction pattern of 1/Li⁺ at 95 °C.

Compound 2, 2/Li⁺ and 2/Na⁺

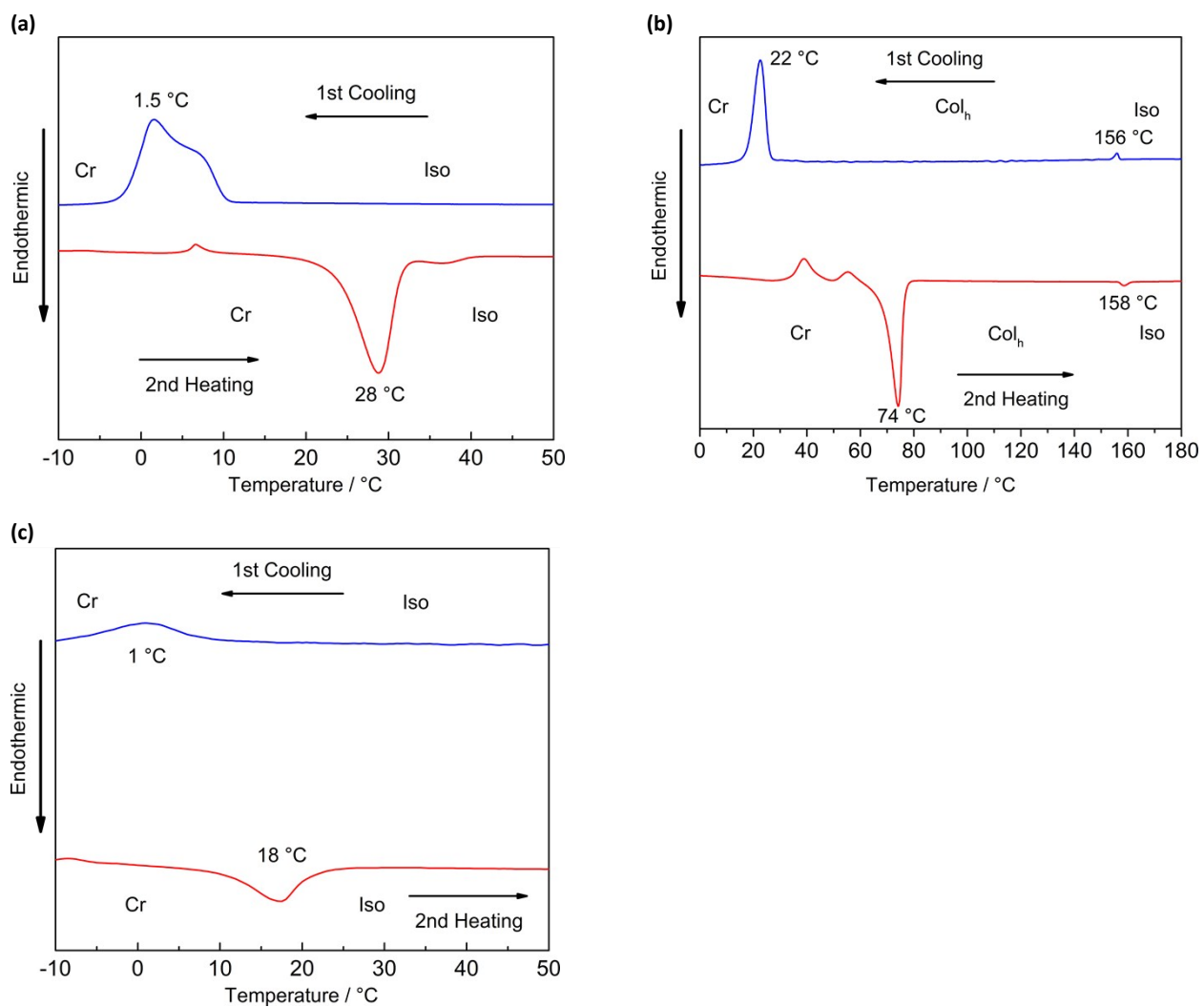


Fig. S3 DSC thermograms of (a) compound 2, (b) 2/Li⁺ and (c) 2/Na⁺ at a scan rate of 10 k min⁻¹.

X-ray diffraction pattern of 2/Li⁺ at 130 °C

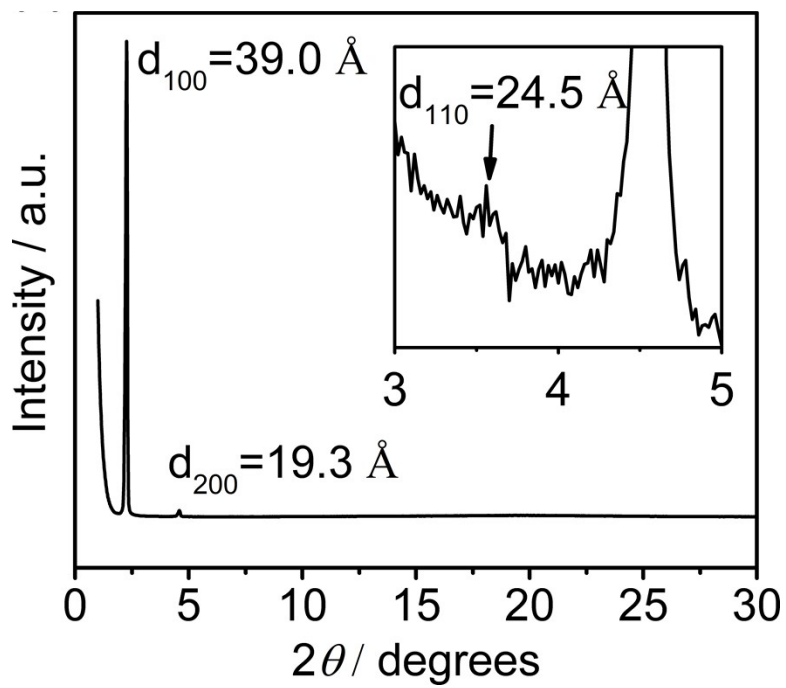


Fig. S4 X-ray diffraction pattern of 2/Li⁺ at 130 °C.

Compound 3, 3/Li⁺ and 3/Na⁺

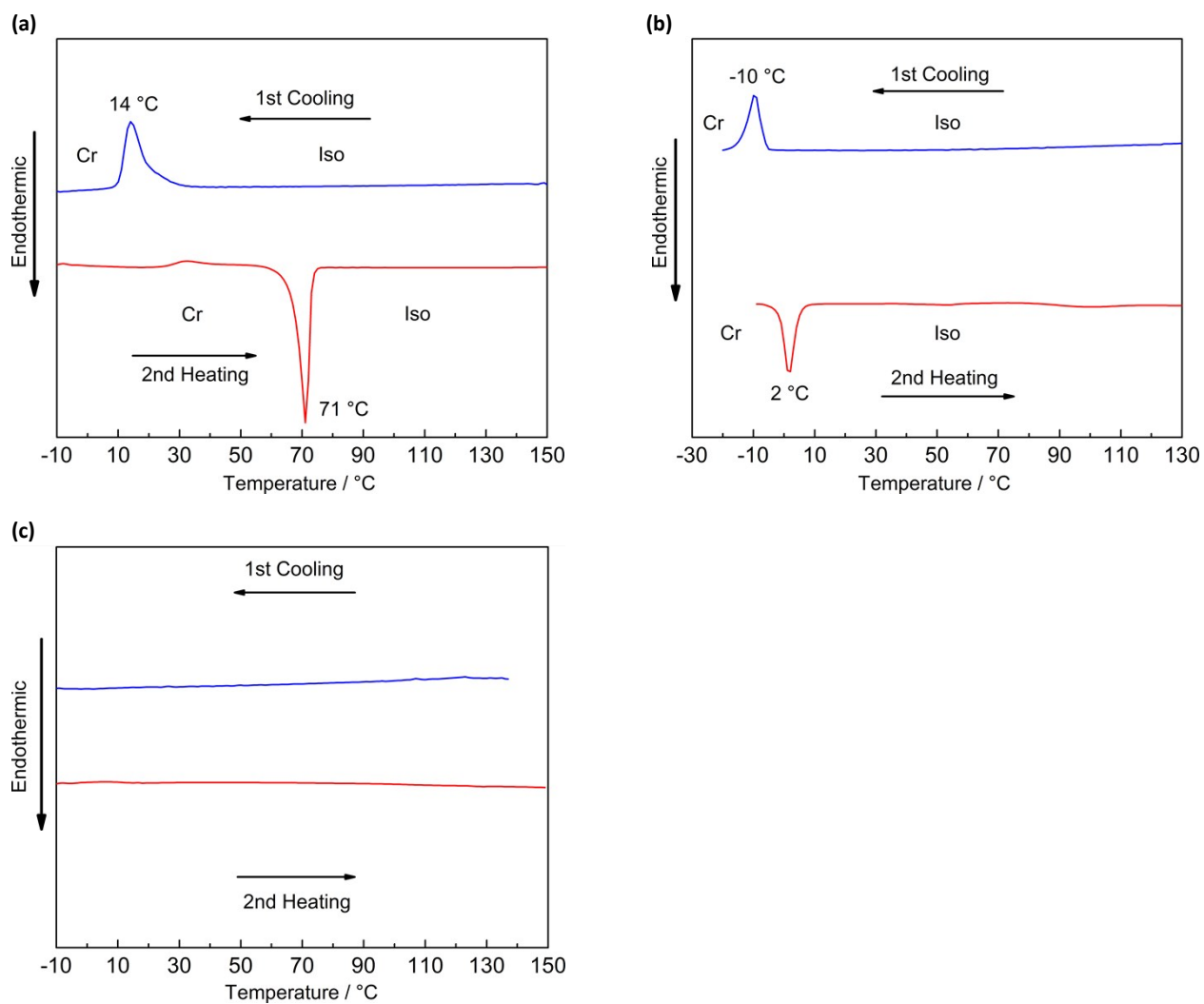
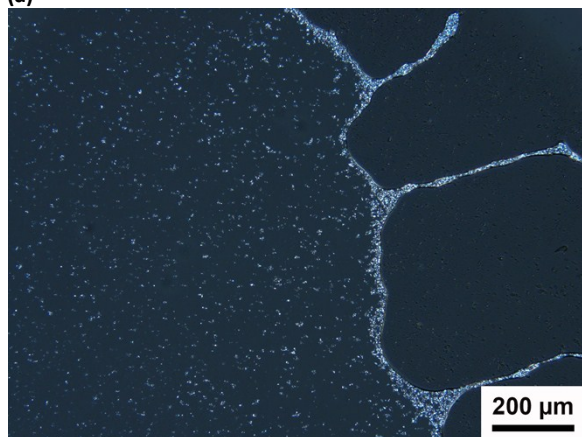


Fig. S5 DSC thermograms of (a) compound 3, (b) 3/Li⁺ and (c) 3/Na⁺ at a scan rate of 10 k min⁻¹.

Mixture of **2**/ Na^+ and mixture of **3**/ Na^+

(a)



(b)



Fig. S6 POM images of (a) mixture of **2** and NaClO_4 after isotropization of **2** at 130 °C and (b) mixture of **3** and NaClO_4 after isotropization of **3** at 150 °C.

4. NMR spectra

¹H NMR spectrum of 1

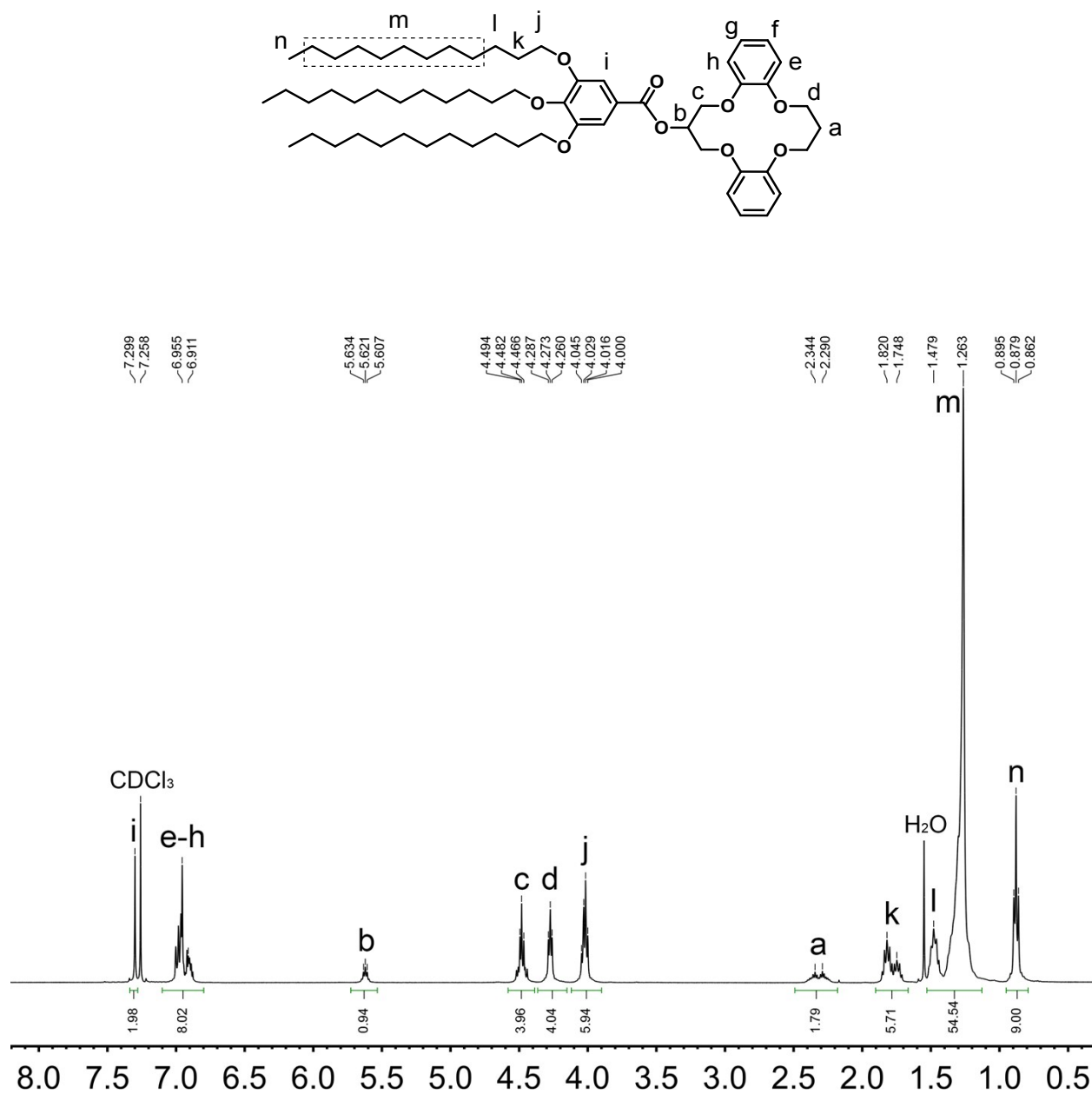


Fig. S7 ¹H NMR spectrum (400MHz, 298K) of 1 in CDCl₃.

¹H COSY spectrum of **1**

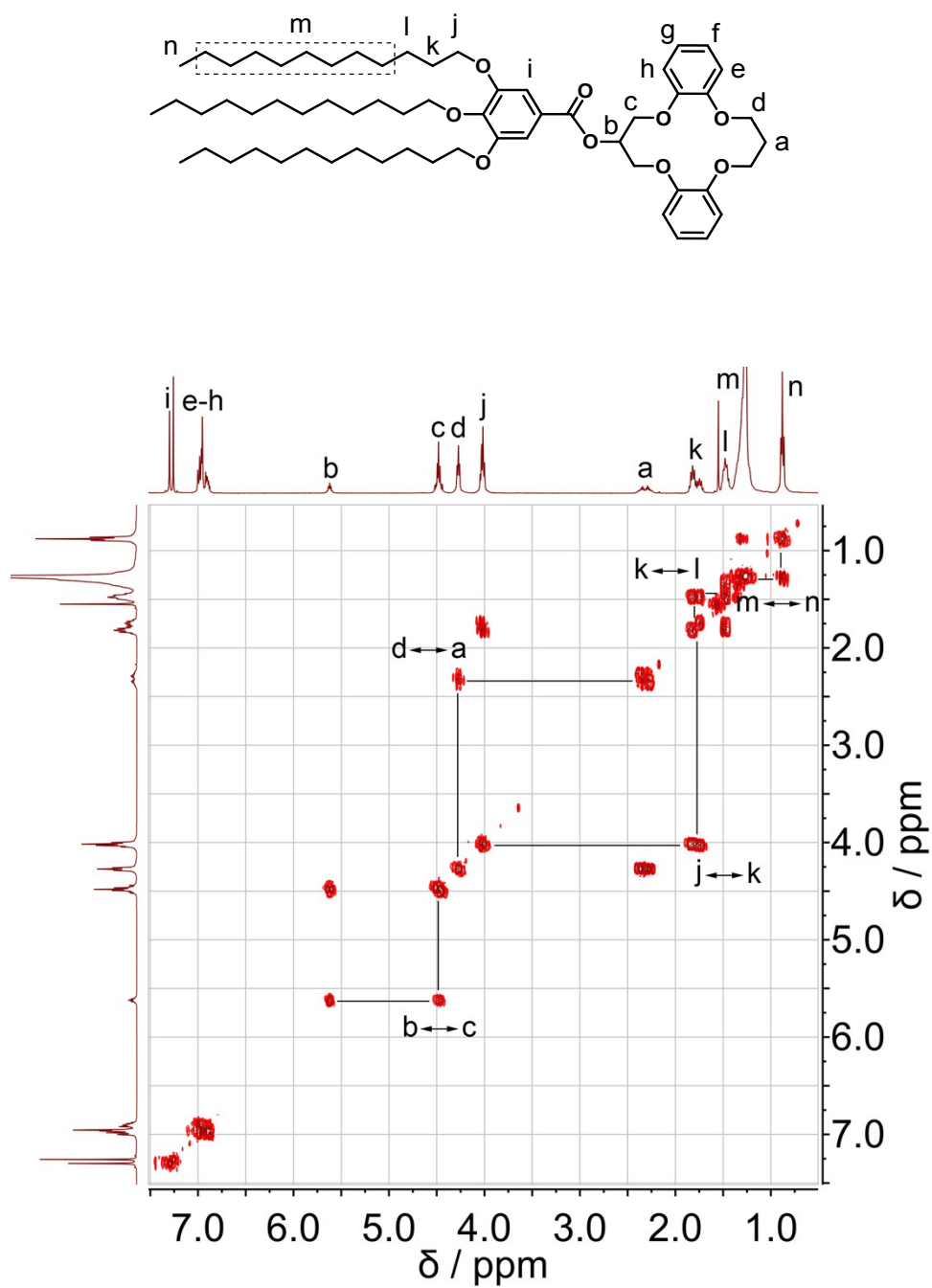


Fig. S8 ¹H COSY spectrum (400MHz, 298K) of **1** in CDCl₃.

¹H NMR spectrum of 2

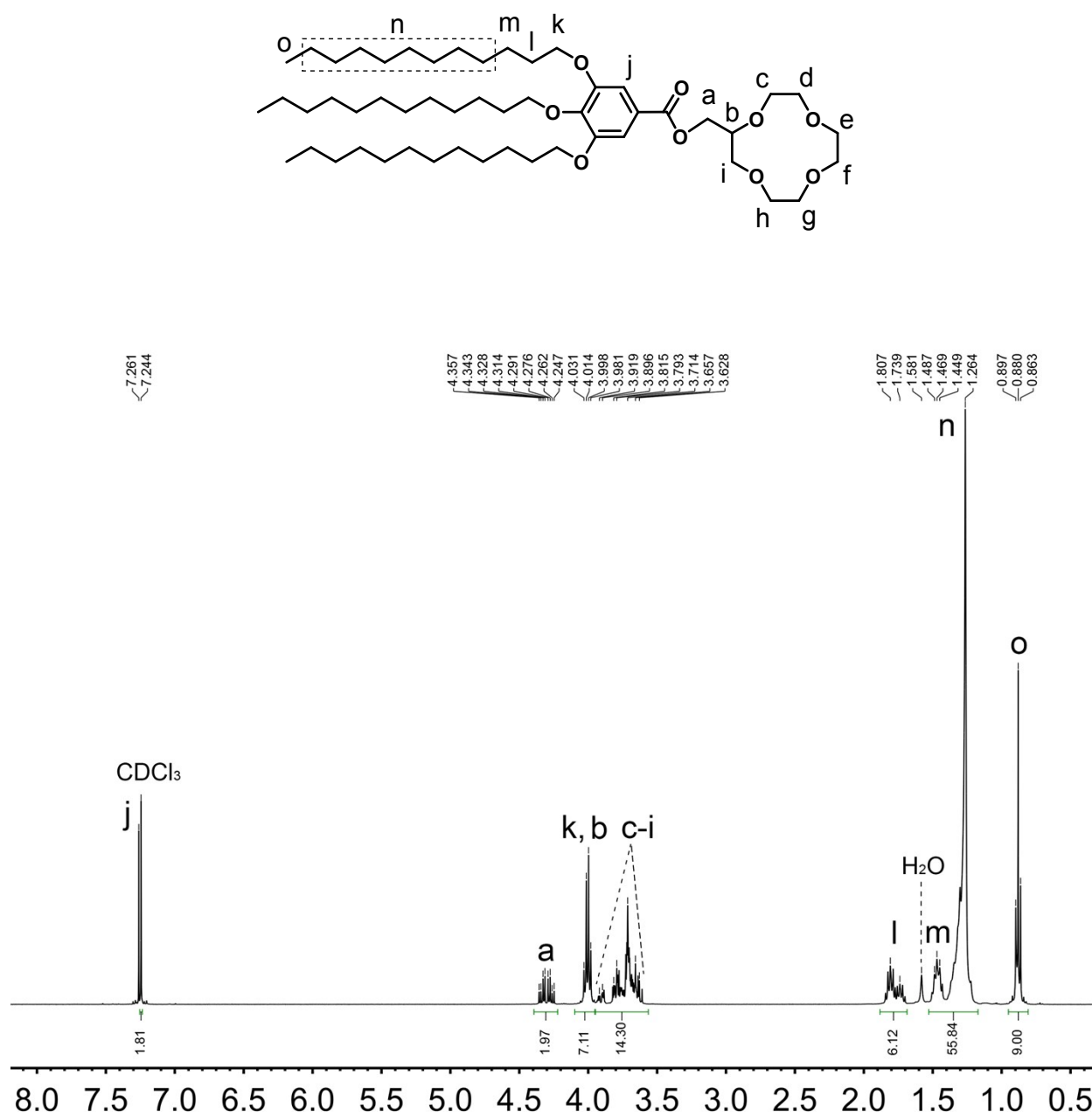


Fig. S9 ¹H NMR spectrum (400MHz, 298K) of 2 in CDCl₃.

¹H NMR spectrum of 3

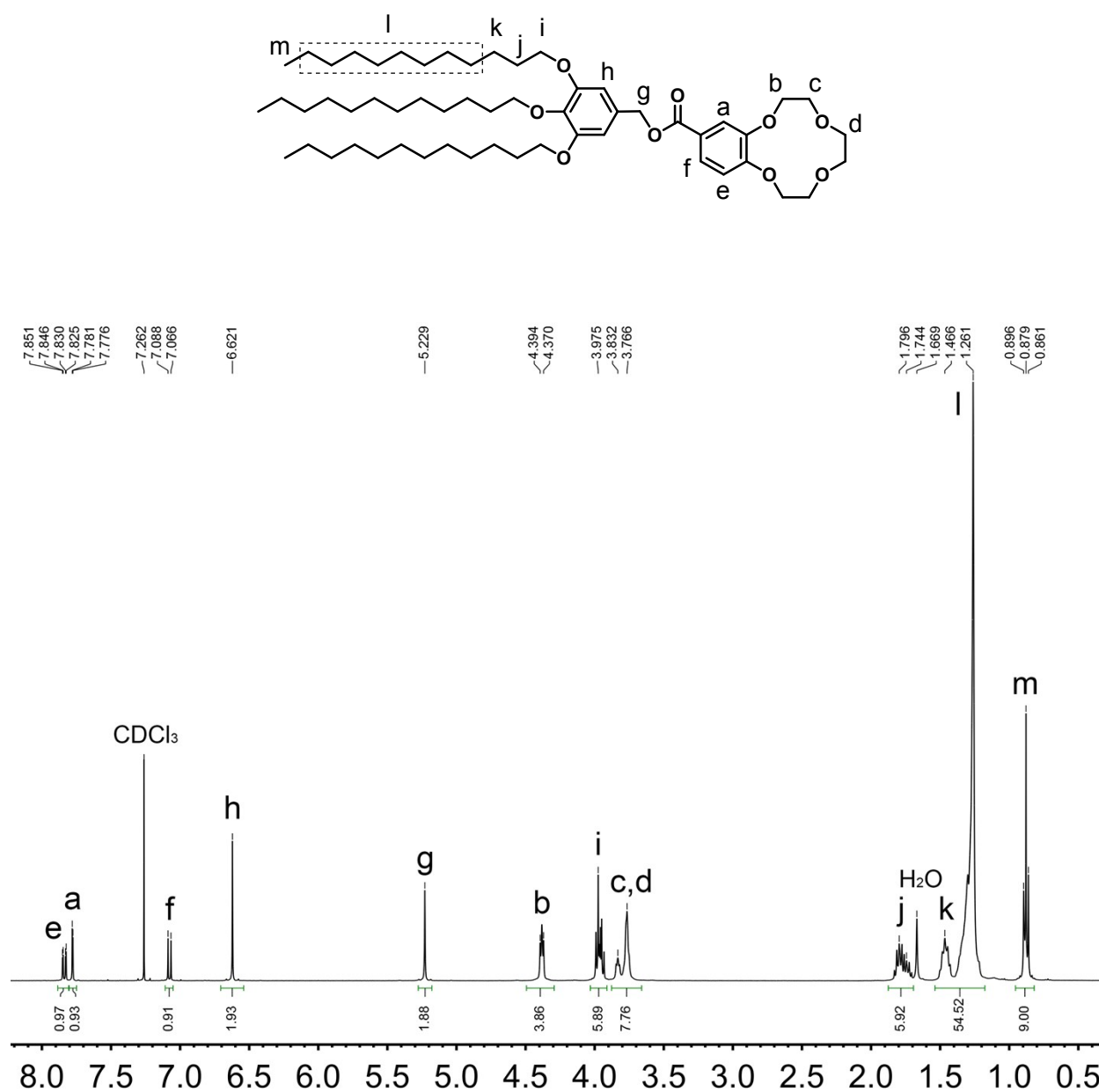


Fig. S10 ¹H NMR spectrum (400MHz, 298K) of 3 in CDCl₃.

^1H NMR spectra of **3** showing shifts of crown ether proton resonances in the presence of excess Li^+ and Na^+

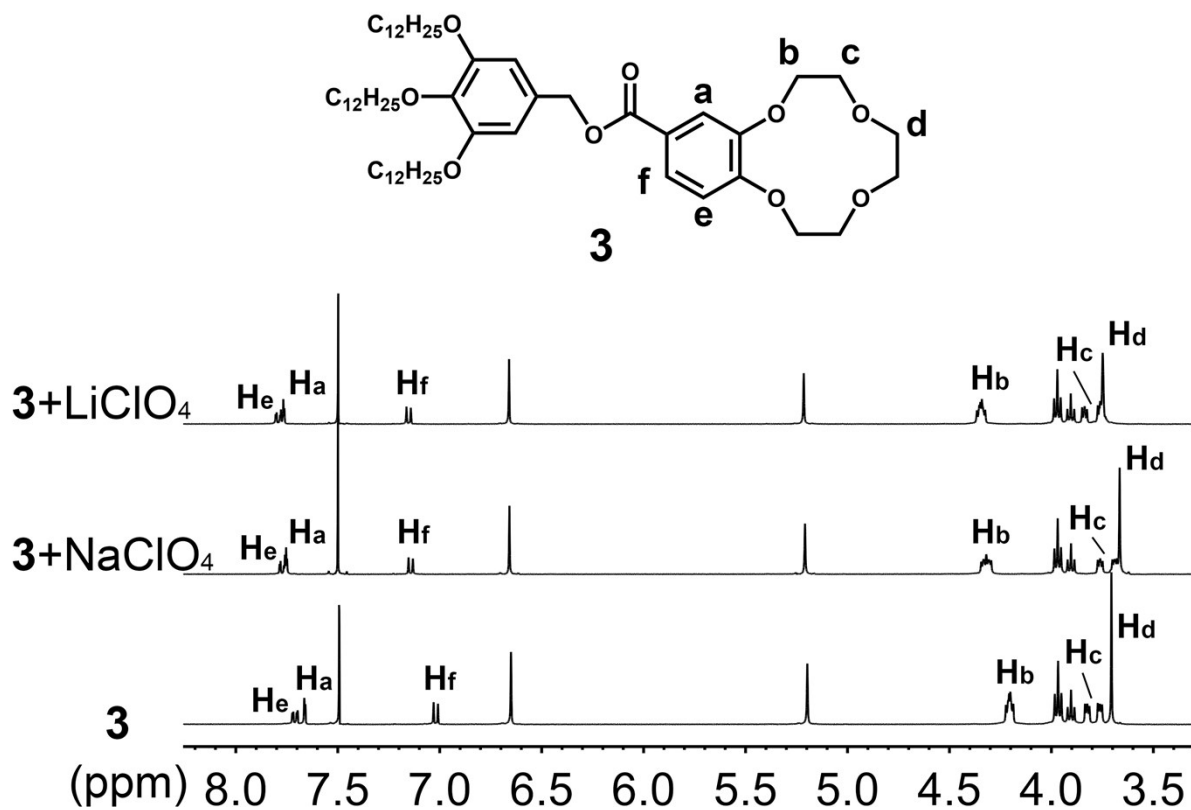


Fig. S11 Partial ^1H NMR spectra (400MHz, 1:1 $\text{CDCl}_3/\text{CD}_3\text{CN}$, 298K) of **3** show shifts crown ether proton resonances in the presence of excess of Li^+ and Na^+ .

5. ^1H NMR spectroscopic titrations

Compound 1 titration with LiClO_4

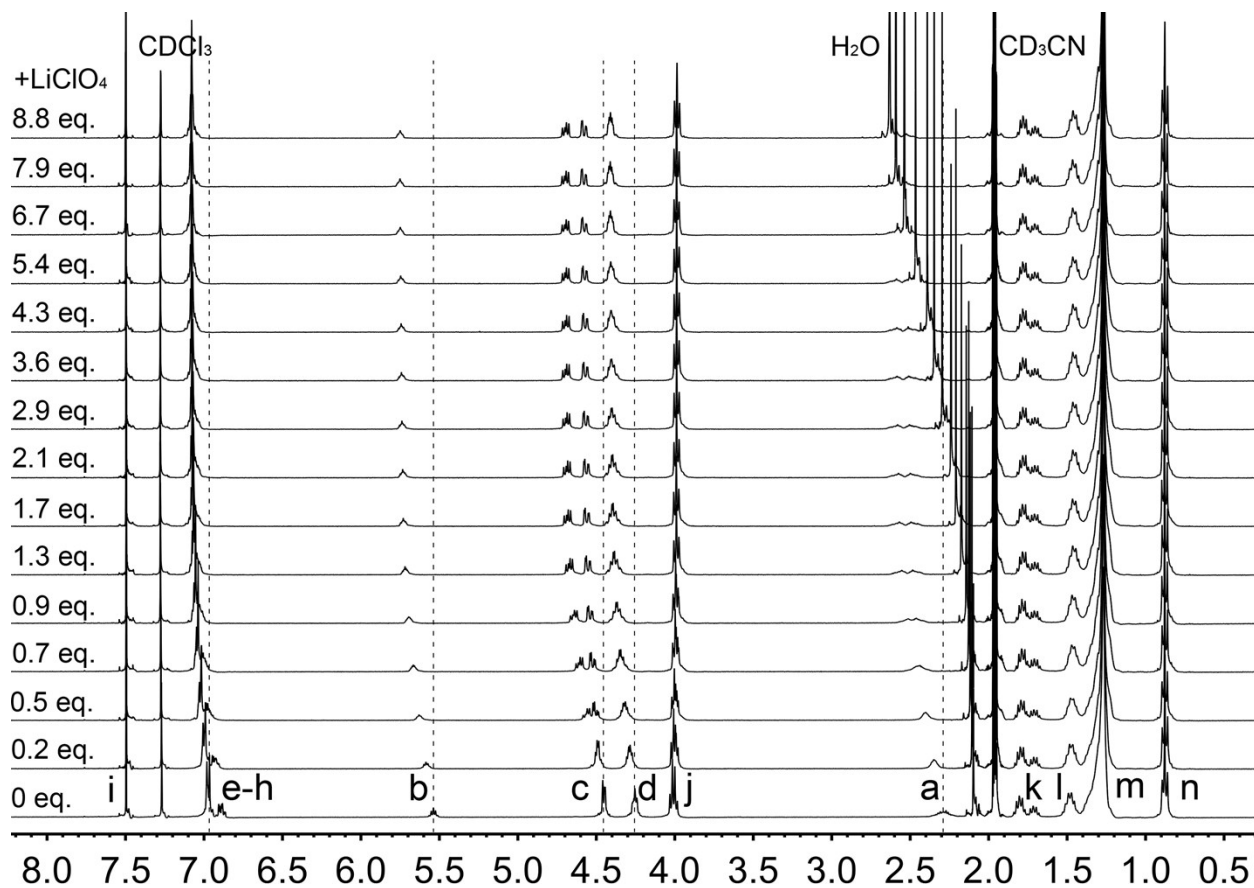


Fig. S12 Representative ^1H NMR titration (400MHz, 1:1 $\text{CDCl}_3/\text{CD}_3\text{CN}$, 298K) spectra of compound 1 (5 mM) with LiClO_4 .

Compound 1 titration with NaClO₄

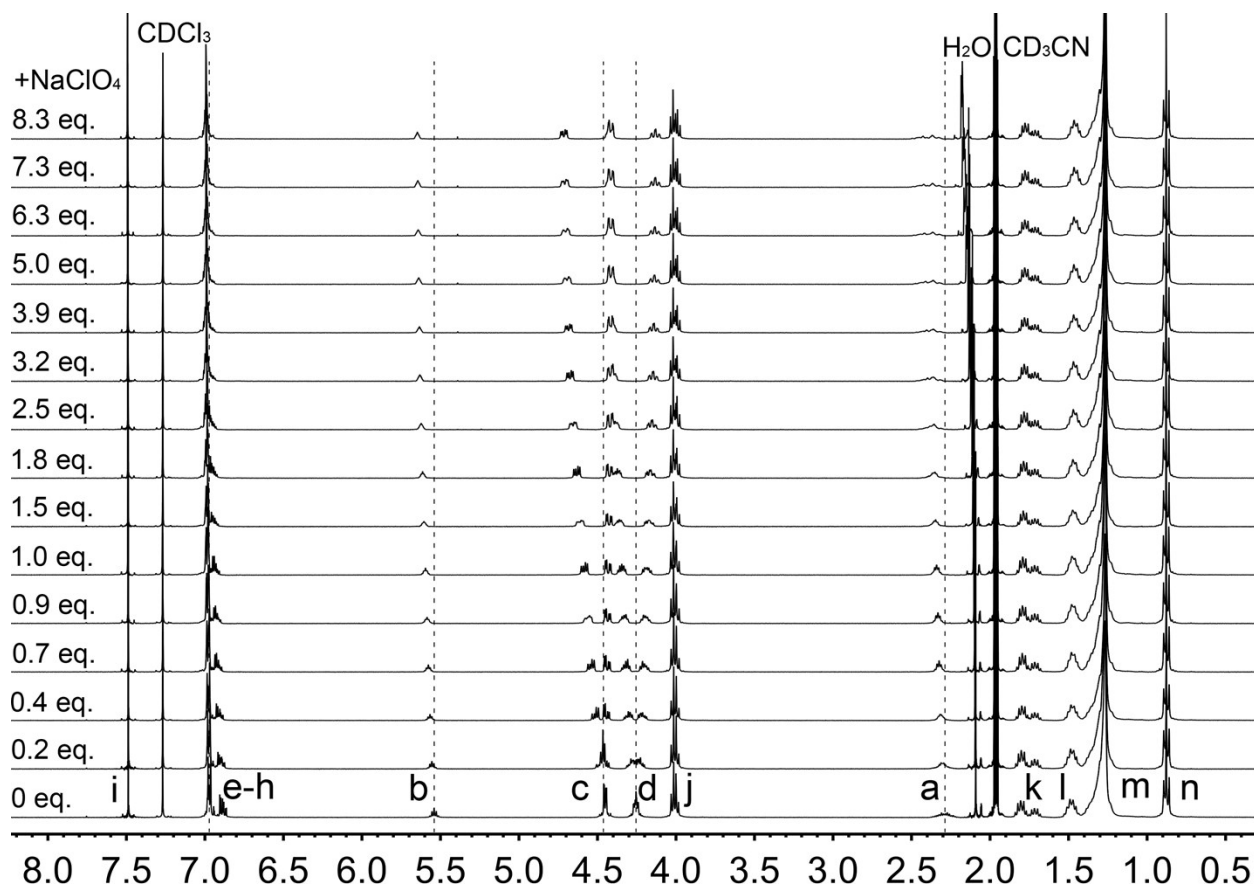


Fig. S13 Representative ¹H NMR titration (400MHz, 1:1 CDCl₃/CD₃CN, 298K) spectra of compound 1 (5 mM) with NaClO₄.

Compound 2 titration with LiClO₄

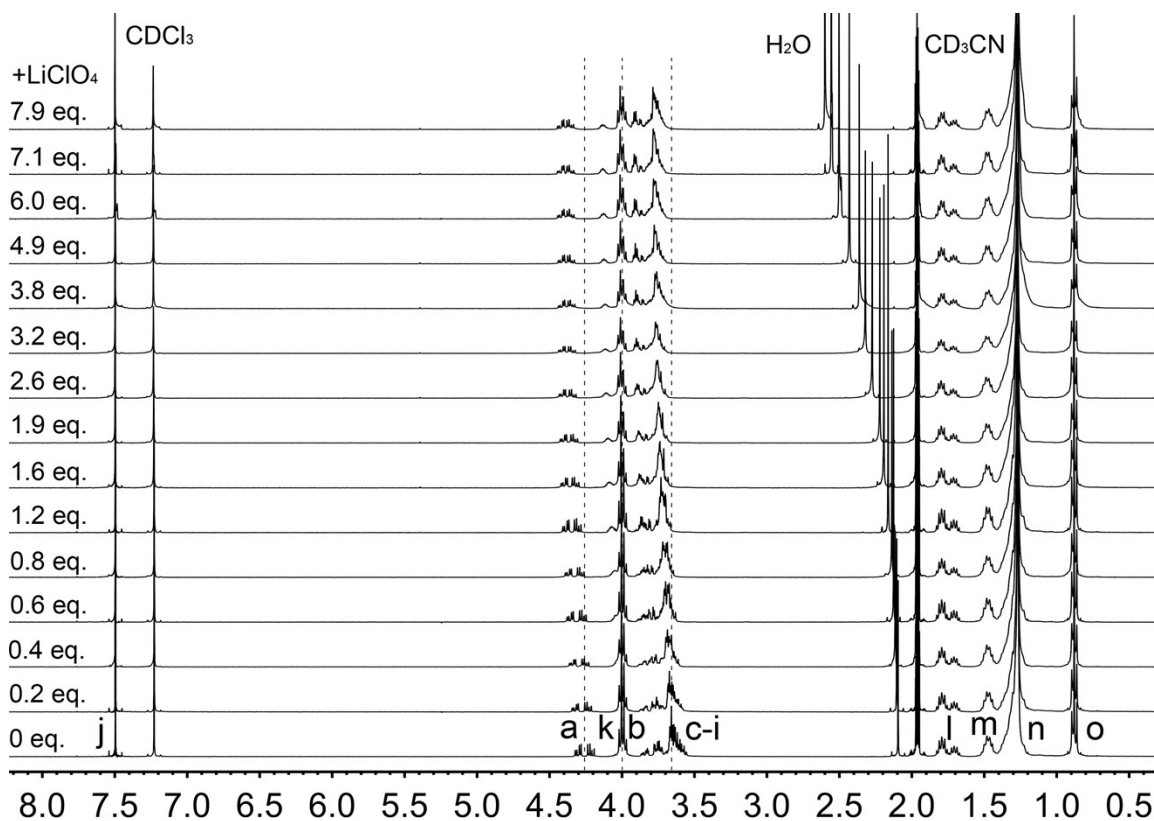


Fig. S14 Representative ¹H NMR titration (400MHz, 1:1 CDCl₃/CD₃CN, 298K) spectra of compound **2** (5 mM) with LiClO₄.

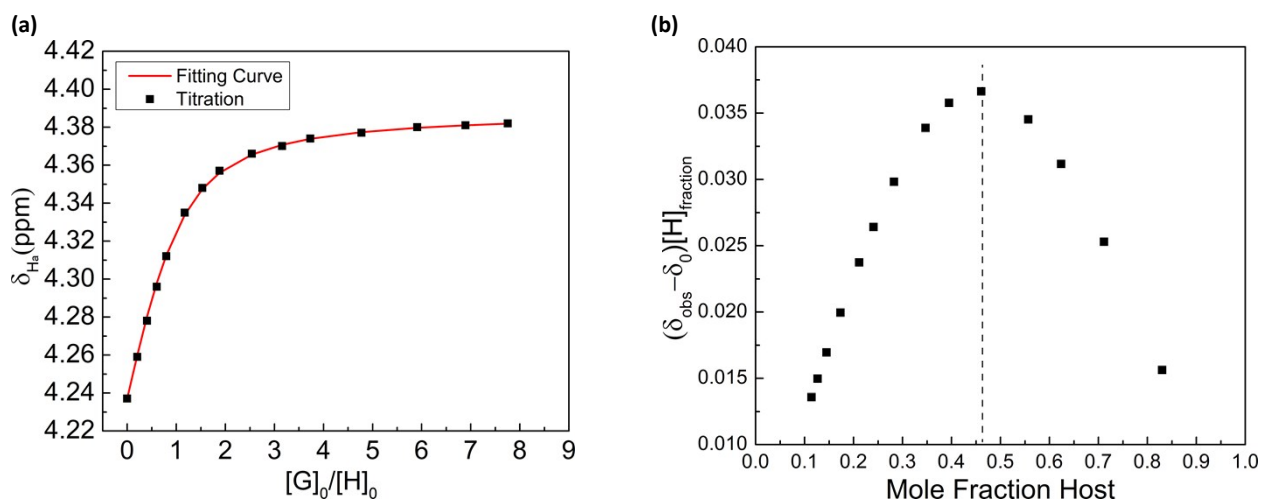


Fig. S15 (a) Representative binding curve obtained by fitting the shift of the H_a proton resonance against [Guest]₀/[Host]₀ from the titration of **2** with LiClO₄. (b) Representative Job plots of **2** with LiClO₄.

Compound 2 titration with NaClO₄

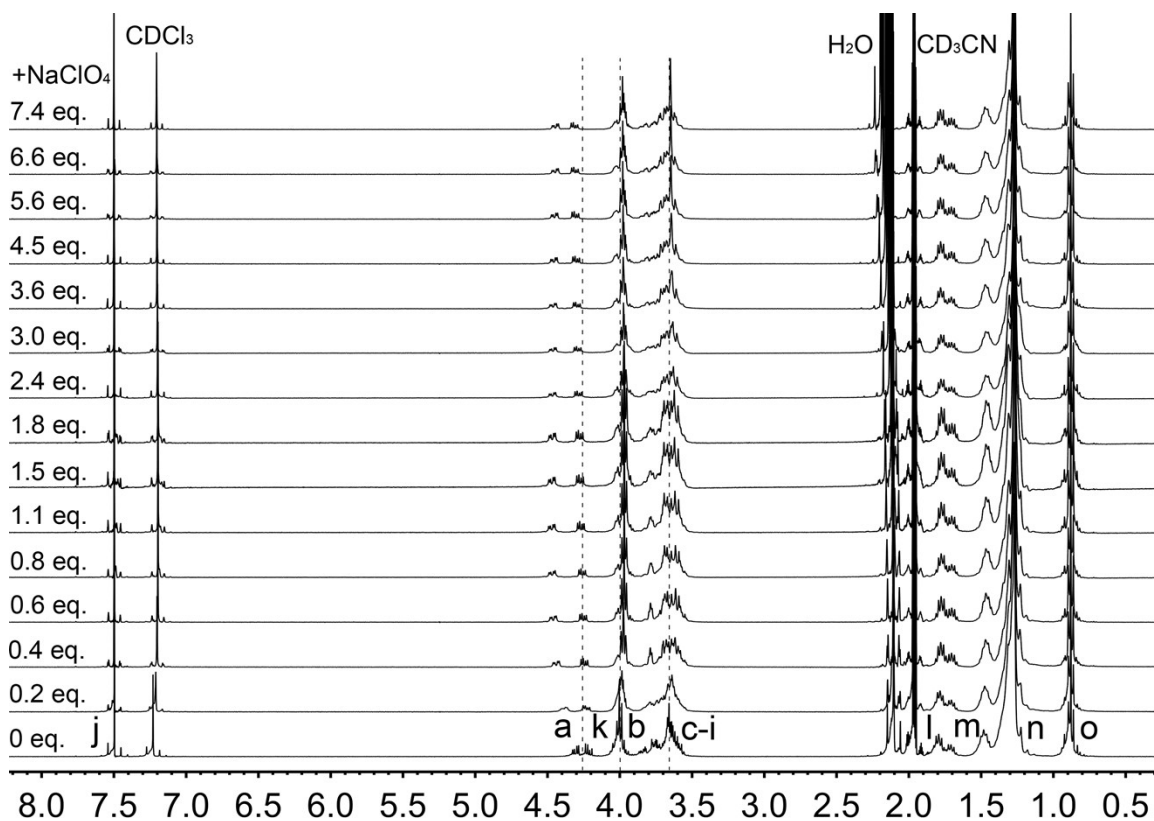


Fig. S16 Representative ¹H NMR titration (400MHz, 1:1 CDCl₃/CD₃CN, 298K) spectra of compound **2** (5 mM) with NaClO₄.

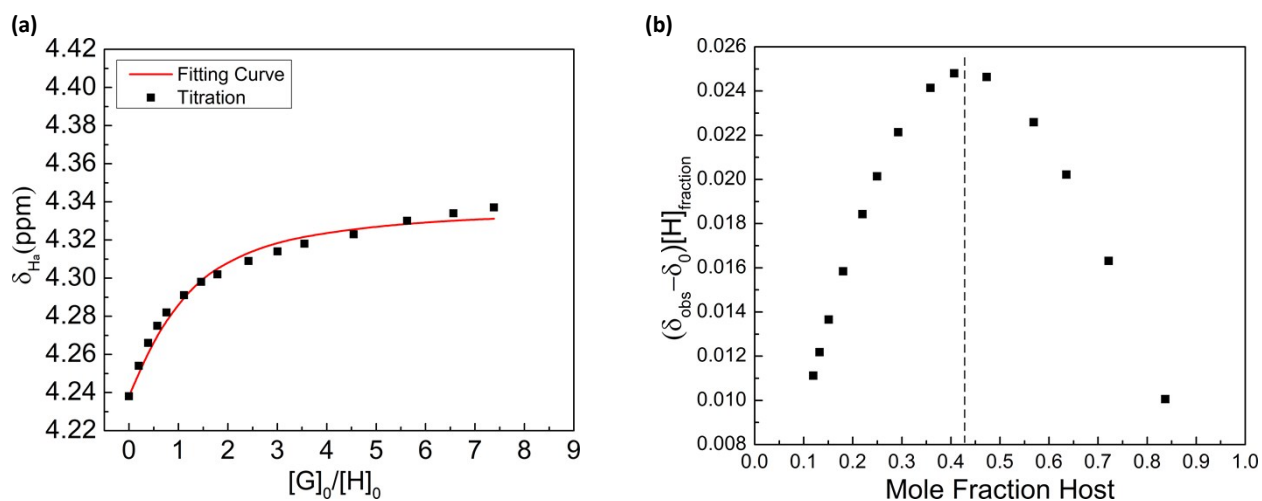


Fig. S17 (a) Representative binding curve obtained by fitting the shift of the H_a proton resonance against [Guest]₀/[Host]₀ from the titration of **2** with NaClO₄. (b) Representative Job plots of **2** with NaClO₄.

Compound 3 titration with LiClO₄

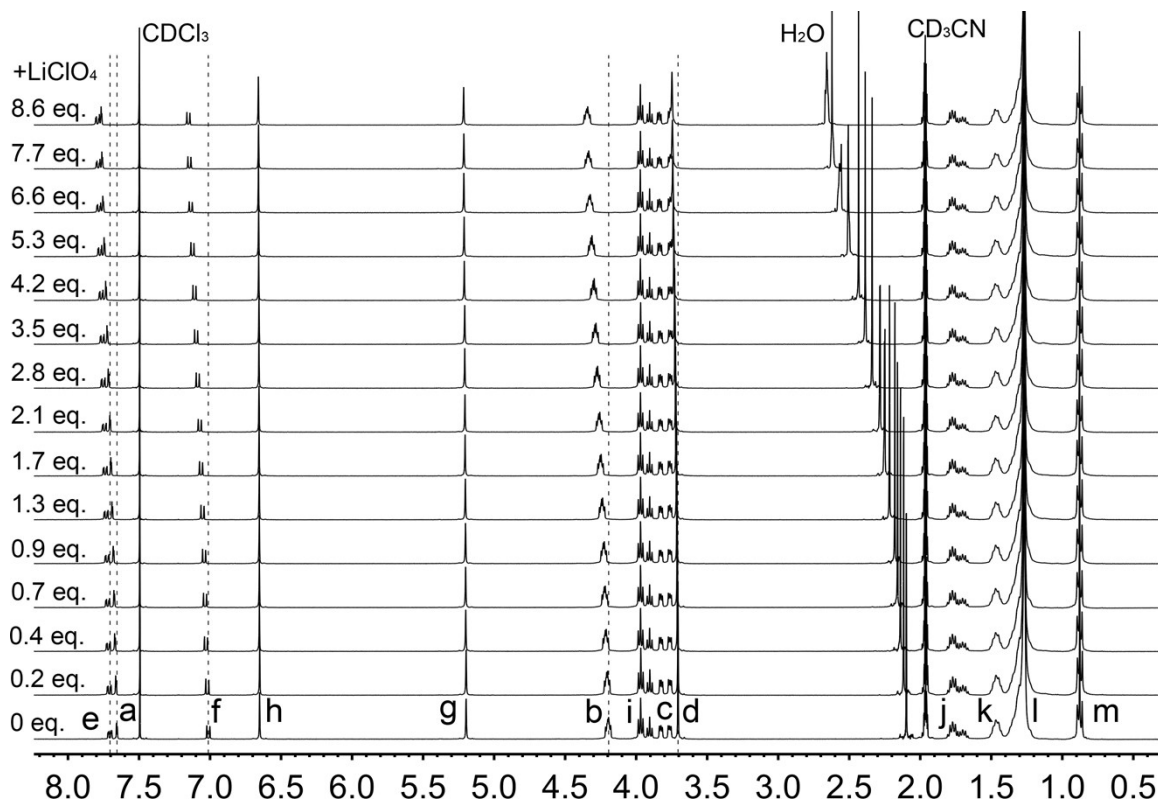


Fig. S18 Representative ¹H NMR titration (400MHz, 1:1 CDCl₃/CD₃CN, 298K) spectra of compound 3 (5 mM) with LiClO₄.

(a)

(b)

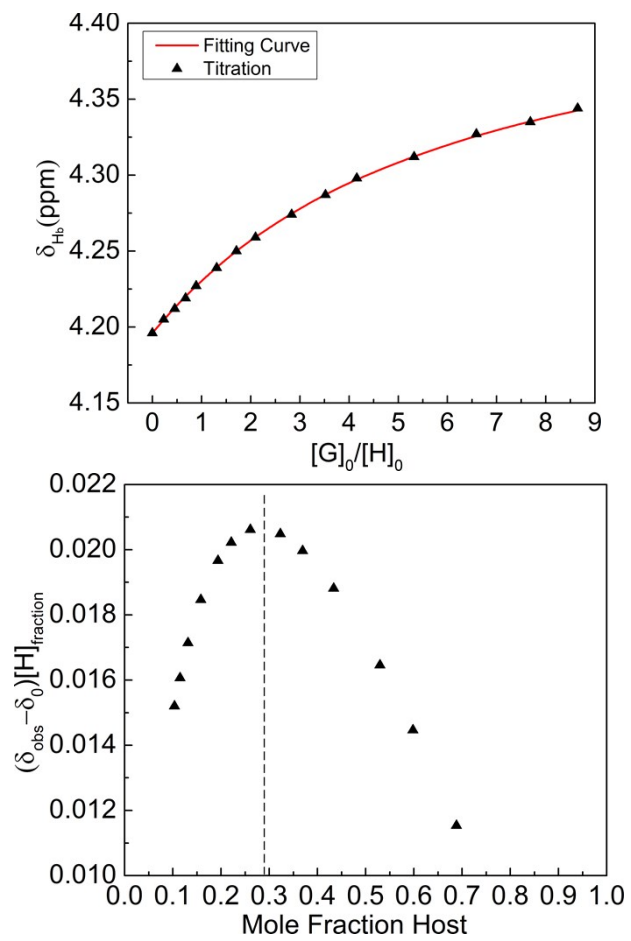


Fig. S19 (a) Representative binding curve obtained by fitting the shift of the H_b proton resonance against $[Guest]_0/[Host]_0$ from the titration of **3** with $LiClO_4$. (b) Representative Job plots of **3** with $LiClO_4$.

Compound 3 titration with NaClO₄

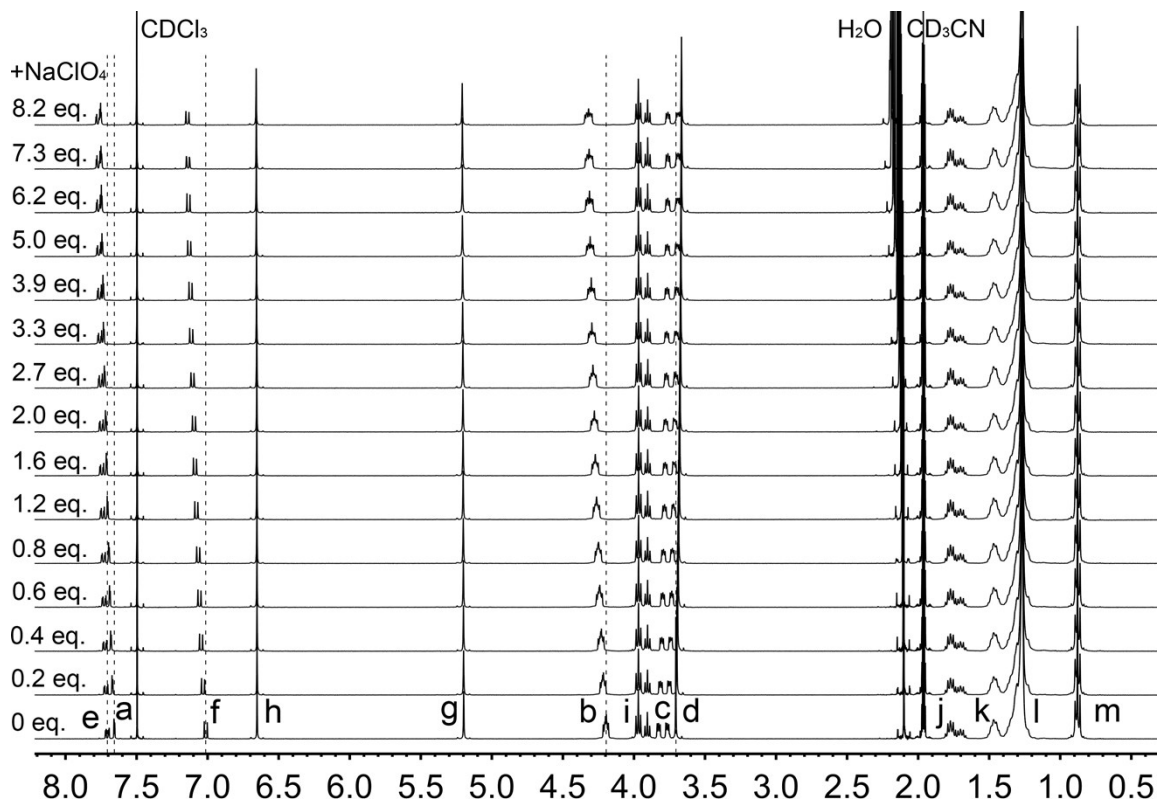


Fig. S20 Representative ¹H NMR titration (400MHz, 1:1 CDCl₃/CD₃CN, 298K) spectra of compound **3** (5 mM) with NaClO₄.

(a)

(b)

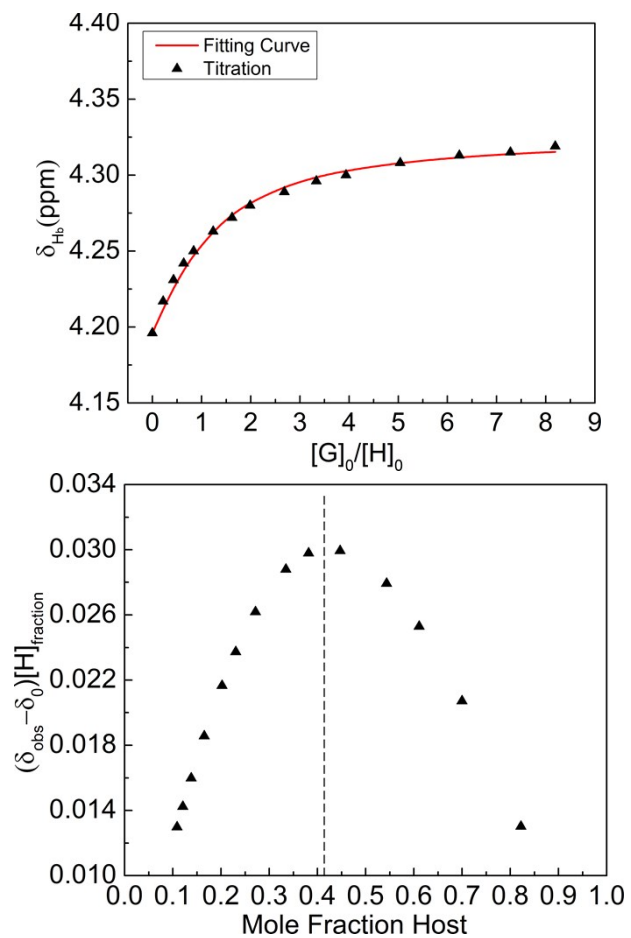


Fig. S21 (a) Representative binding curve obtained by fitting the shift of the H_b proton resonance against $[Guest]_0/[Host]_0$ from the titration of **3** with $NaClO_4$. (b) Representative Job plots of **3** with $NaClO_4$.