

SUPPORTING INFORMATION.

Synthetic procedures.

Pentaerythrityl tetrathioacetate. Potassium thioacetate (31.8g, 0.278mol) was dissolved in DMF (150 mL) and pentaerythrityl tetrabromide (12.1g, 0.031mol) was added to this solution. Reaction mixture was stirred under nitrogen atmosphere for 60 hours at 25°C. The solvent was removed in vacuo, residue was dissolved in CH₂Cl₂ (150 mL) and washed three times with water (3x100 mL). The organic phase was dried with MgSO₄, and solvent was then removed with rotary evaporator. The crude product was recrystallized from methanol to give yellow crystals (m.p. 124°C), (10.1g, 87%). ¹H NMR (400 MHz, CDCl₃) δ 3.038 (s, 8H), 3.356 (s, 12H); ¹³C NMR (400 MHz, CDCl₃) δ 30.72, 34.91, 42.66, 193.98; MS *m/z* (relative intensity) 325 ([M-CH₃CO]⁺, 100), 283 (40), 241 (90), 223 (45), 119 (30).

2,4,8,10-tetrathiaspiro[5.5]undecane (1). Pentaerythrityl tetrathioacetate (3g, 8.15mmol) was suspended in formaline-HCl mixture (53g, 0.652mol of the formaline, 8ml of 37% HCl). Reaction mixture was refluxing for 16 hours. Reaction mixture was neutralized with Na₂CO₃ saturated solution, then product was extracted with CH₂Cl₂ (50mL). Organic layer was dried with MgSO₄, and solvent evaporated in vacuo. Crude product was recrystallized from chloroform-methanol mixture. Obtained yellow crystals was then boiled with activated carbon in chloroform-methanol mixture (70:30) for 1 hour, charcoal was filtered off, solvent removed with rotary evaporator to give white crystals (**1**) (m.p. 164°C), (1.39g, 76%): ¹H NMR (400 MHz, CDCl₃) δ 2.948 (s, 8H), 3.656 (s, 4H); ¹³C NMR (400 MHz, CDCl₃) δ 24.94, 32.16, 38.6; MS *m/z* (relative intensity) 224 (M⁺, 100), 177 (30), 131 (40), 99 (60), 85 (50); Calcd. for C₇H₁₂S₄: C, 37.46; H, 5.39. Found: C, 37.28; H, 5.53.

Bis-calixarene (3). A solution of 2,4,8,10-tetrathiaspiro[5.5]undecane **1** (50 mg, 0.22 mmol) in 10mL of freshly distilled THF was cooled to -78°C under nitrogen. Then n-butyllithium (1.6M solution in hexanes, 0.80 mmol, 0.50 mL) was added dropwise upon stirring. The resulting mixture was stirred for 2h at -25°C. The temperature was then lowered to -78°C, and 5-formyl-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]-arene **2** (330 mg, 0.45 mmol) dissolved in 5 mL of THF was added to the vigorously stirred solution of the anion. The reaction mixture was stirred for 1h at this temperature and then stored in a freezer at -25°C overnight. The subsequent aqueous workup included quenching the reaction mixture with saturated solution of ammonium chloride, extracting twice with 10 mL of diethyl ether, and drying the combined organic extracts over magnesium sulfate. The solvent was then removed with a rotary evaporator, and the residue was purified by a silica gel column, eluted with ethyl acetate/hexane (1:2), to give **3** (0.27 mg, 71% as a colorless oil): ¹H NMR (400 MHz, CDCl₃) δ 1.15-1.25 (m, 24H), 1.92-2.02 (m, 2H), 2.57-2.90 (m, 6H), 3.06-3.18 (m, 10H), 3.49-3.57 (m, 16H), 3.80-3.86 (m, 16H), 3.87-3.93 (m, 2H), 4.04-4.18 (m, 16H), 4.39-4.52 (m, 10H), 6.42-6.70 (m, 22H); HRMS [MH-H₂O]⁺calcd for C₉₇H₁₂₃O₁₇S₄ 1687.7640, found 1687.7696 (~3 ppm).

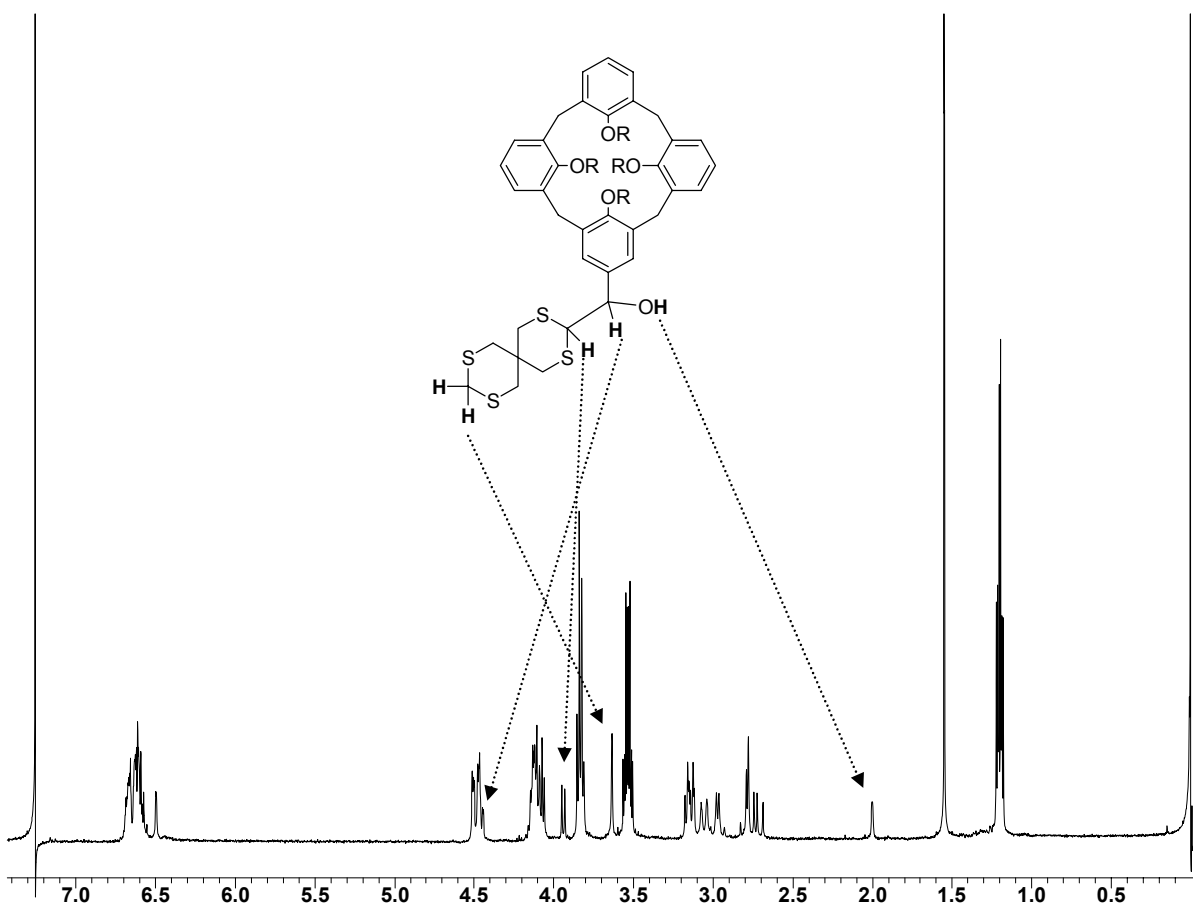
Mono-adduct (4). A solution of 2,4,8,10-tetrathiaspiro[5.5]undecane **1** (430 mg, 1.92 mmol) in 20mL of freshly distilled THF was cooled to -78°C under nitrogen. Then n-butyllithium (1.6M solution in hexanes, 1.92 mmol, 1.20 mL) was added dropwise upon stirring. The resulting mixture was stirred for 2h at -25°C. The temperature was then lowered to -78°C, and 5-formyl-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]-arene **2** (370 mg, 0.5 mmol) dissolved in 2 mL of THF and 0.5 ml of HMPA was added to the vigorously stirred solution of the anion. The reaction mixture was stored in a freezer at -25°C overnight. The subsequent aqueous workup included quenching the reaction mixture with saturated solution of ammonium chloride, extracting twice with 10 mL of chloroform, and drying the combined organic extracts over sodium sulfate. The solvent was then removed with a rotary evaporator, and the residue was purified by a silica gel column, eluted with ethyl acetate/hexane (1:3), to give **4** (416 mg, 86% as a glass solid): ¹H NMR (400 MHz, CDCl₃) δ 1.16-1.25 (m, 12H), 1.92-2.02 (s, 1H), 2.68-3.18 (m, 12H), 3.51-3.58 (m, 8H), 3.64 (s, 2H), 3.81-3.86 (m, 8H), 3.93-3.96 (d, 1H), 4.05-4.17 (m, 8H), 4.43-4.53 (m, 5H), 6.48-6.70 (m, 11H). Calcd. For C₅₂H₆₈O₉S₄: C, 64.70; H, 7.10. Found: C, 64.83; H, 7.24.

Bis-calixarene - 24-crown-8 adduct (5). A solution of carbinol **4** (387 mg, 0.4 mmol) in 20mL of freshly distilled THF was cooled to -78°C under nitrogen. Then n-butyllithium (1.6M solution in hexanes, 0.93 mmol, 0.58 mL) was added dropwise upon stirring. The resulting mixture was stirred for 0.5h at -25°C, 0.2 ml of HMPA was added and the mixture was stirred for 1.5h at -25°C. The temperature was then lowered to -78°C, and diformyl-24-crown-8 (67 mg, 0.133 mmol) dissolved in 1 ml of HMPA and 1 mL of THF was added to the vigorously stirred solution of the anion. The reaction mixture was stored in a freezer at -25°C overnight. The subsequent aqueous workup included quenching the reaction mixture with saturated solution of ammonium chloride, extracting twice with 10 mL of chloroform, and drying the combined organic extracts over sodium sulfate. The solvent was then removed with a rotary evaporator, and the residue was boiled with methanol to remove HMPA, the residue was separated from the solution and was purified by a silica gel column, eluted with acetonitrile/chloroform (1:2), to give **5** (87mg, 27% as a glassy solid): ¹H NMR (400 MHz, CDCl₃) δ 1.17-1.25 (m, 24H), 1.96-2.01 (m, OH), 2.60-3.19 (m, 24H), 3.48-3.57 (m, 16H), 3.78-4.13 (m, 60H), 4.41-4.53 (m, 10H), 4.72-4.79 (m, 2H), 6.46-6.70 (m, 22H), 6.78-6.92 (m, 6H).

NMR SPECTRA AND EXPERIMENTS.

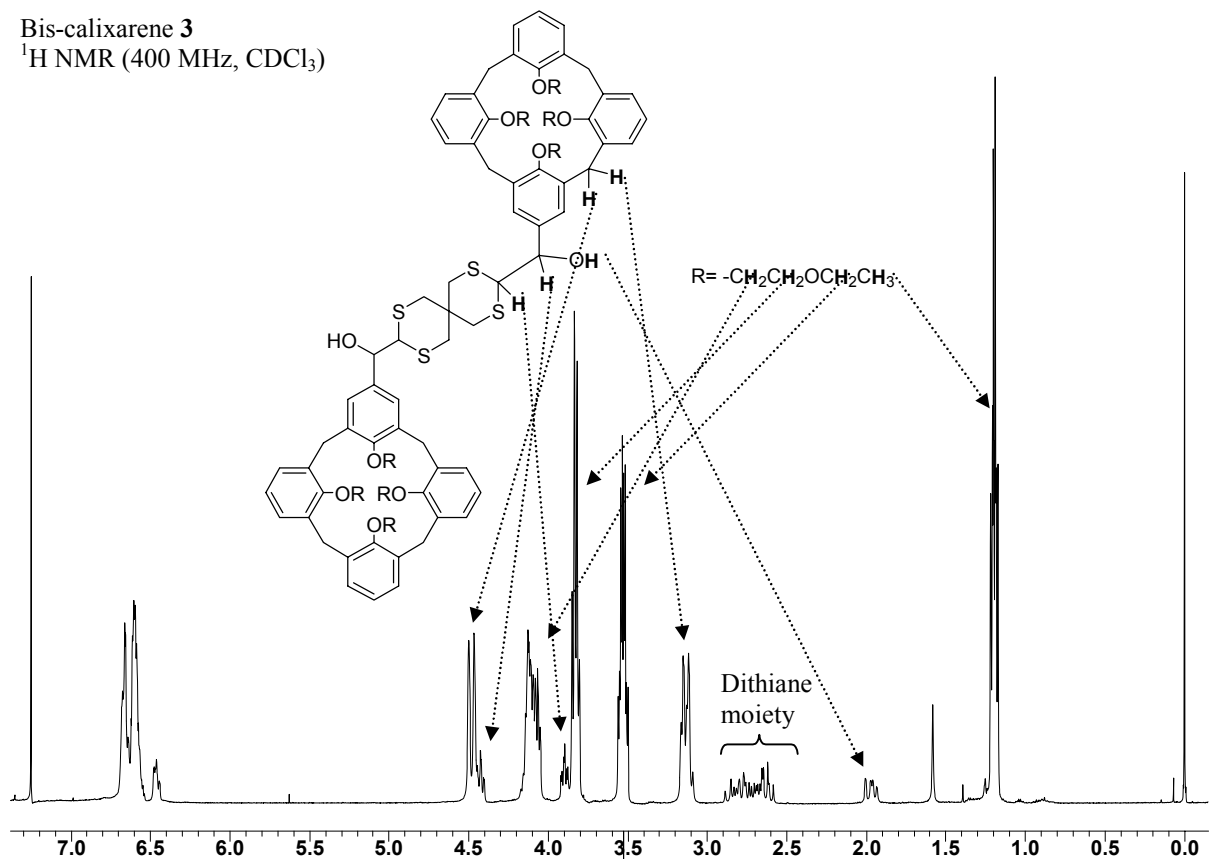
Mono-adduct **4**

¹H NMR (400MHz, CDCl₃)



Bis-calixarene **3**

^1H NMR (400 MHz, CDCl_3)



3, ^{13}C NMR (100 MHz, CDCl_3)

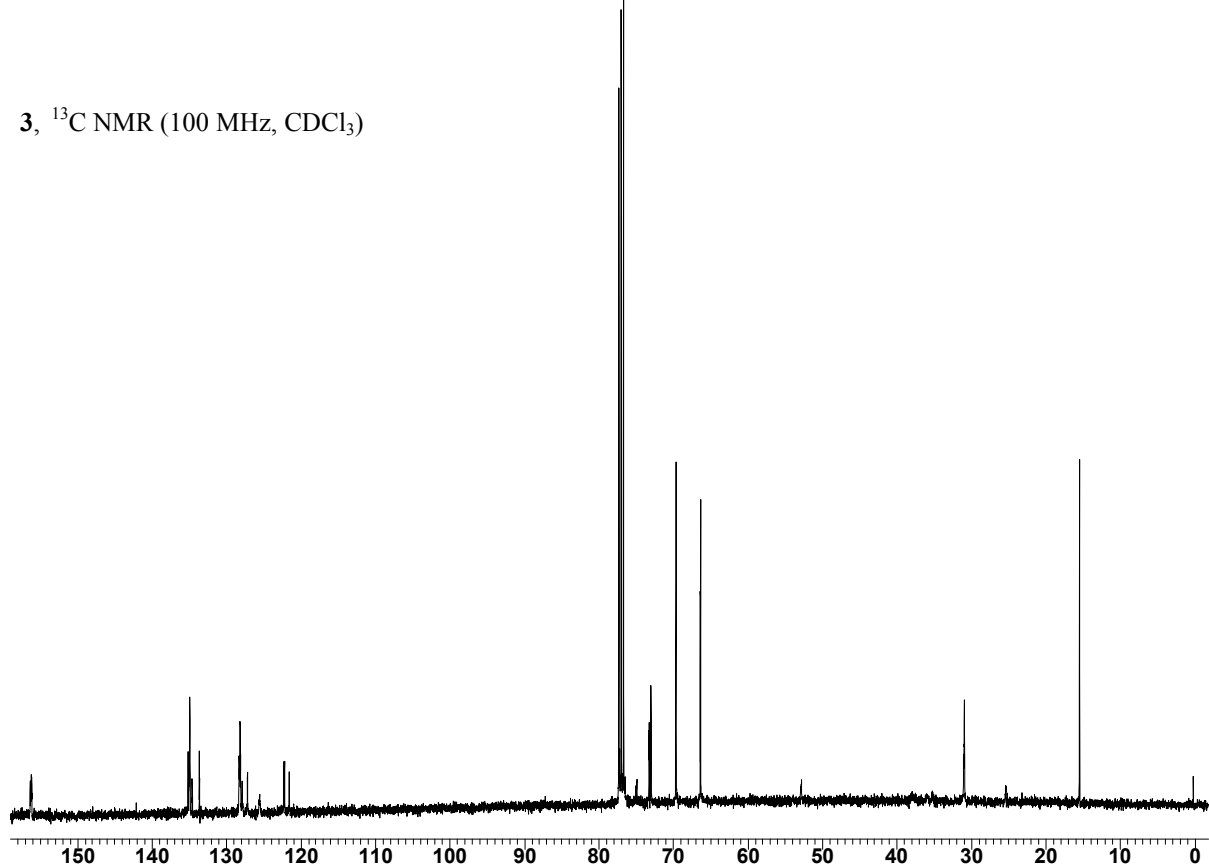
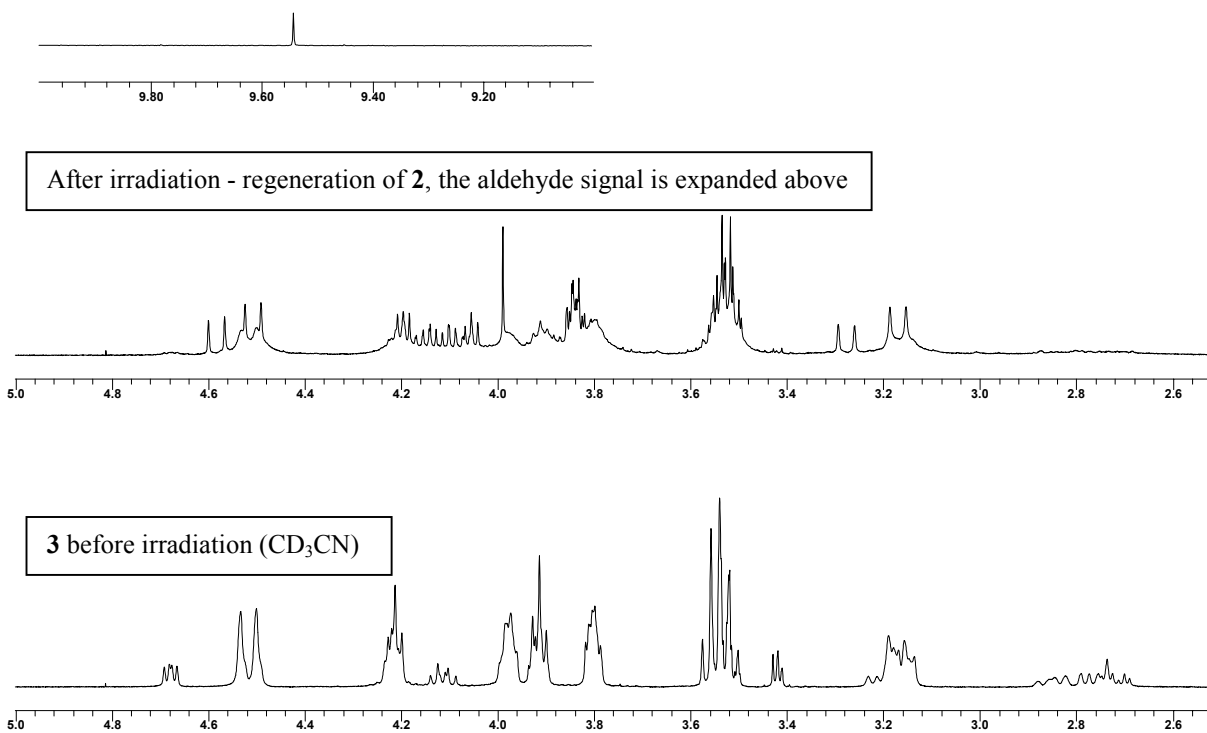
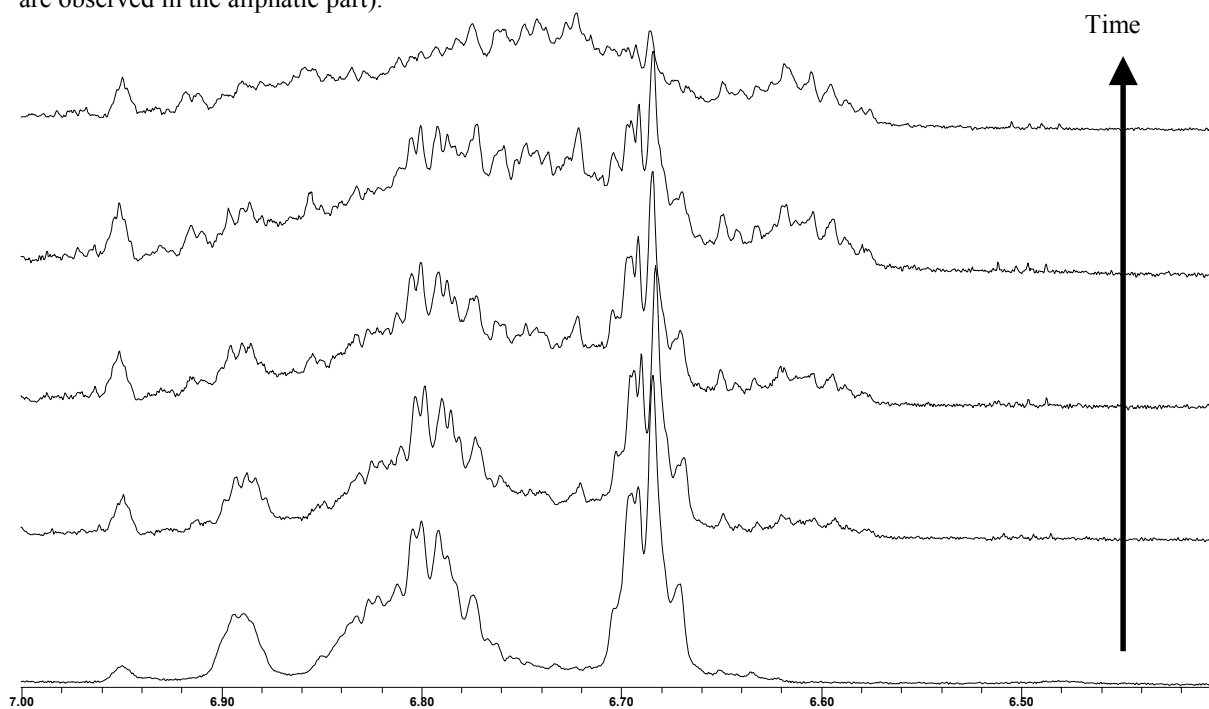


Photo-disassembly of **3** (~80% conversion is shown):

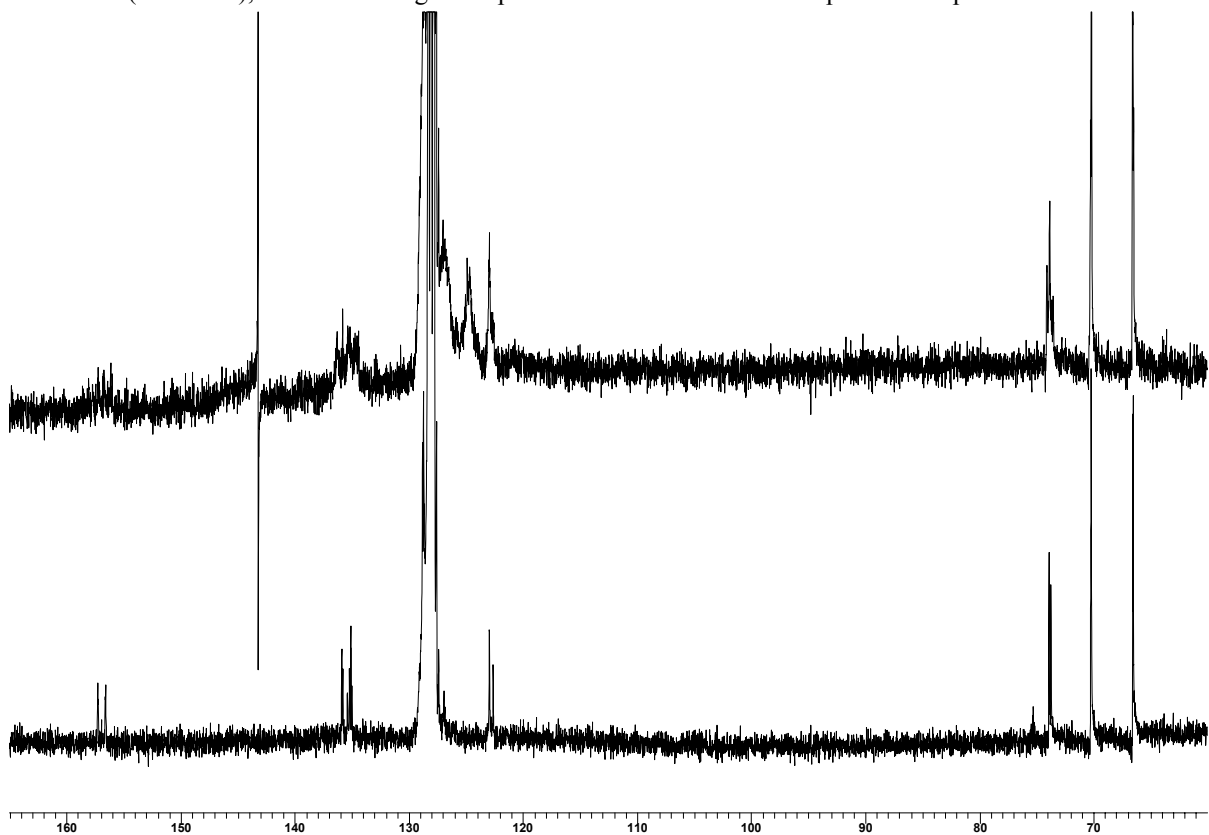


C_{60} added to **3** in C_6D_6

1H NMR (400 MHz), changes in the aromatic part of the host (- most dramatic. Although some changes are observed in the aliphatic part).



^{13}C NMR (100 MHz), most visible signal dispersion occurs in the aromatic part of the spectrum:



DIFFUSION COEFFICIENT MEASUREMENTS

The diffusion measurements (PFG-LED technique) were carried out with Varian Mercury 400MHz spectrometer equipped with Performa I PFG module and PFG-capable, 4 nuclei auto-switchable probe. The PFG module is capable of forming PFG pulses up to 21 G/cm strength, which was sufficient to drive the signal amplitude to zero for all cases studied.

We used slightly modified watersLED sequence (with water-suppression turned off completely). This is a stimulated spin-echo technique. The strength of the PFG pulse is increased in successive experiments. The echo amplitude is then differentially attenuated in each spectrum due to translational diffusion. The echo amplitude is related to the diffusion coefficient by the following expression:

$$A = A_0 \exp[-(\gamma\delta G)^2(\Delta - \delta/3)D_s] \text{ (see reference 9 of the text)}$$

γ - gyromagnetic ratio, 2.6752×10^4 1/G s

δ - length of pulsed field gradient (s)

G - gradient strength (G)

Δ - diffusion time = δ + gstab1 + pulse width + diff

D_s - diffusion coefficient

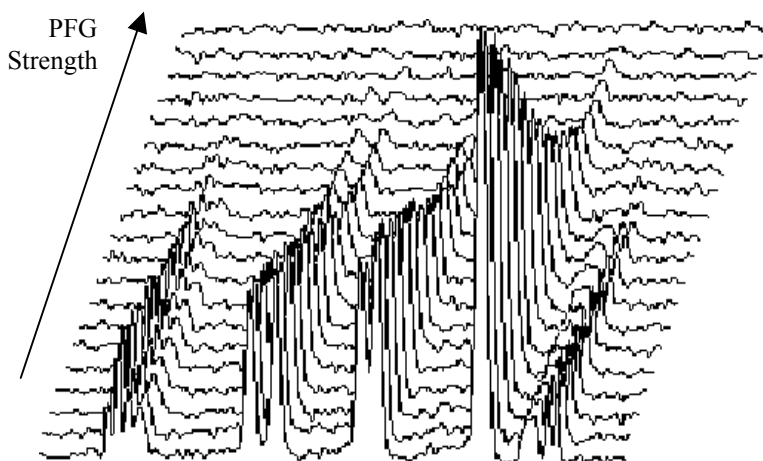
In our runs we arrayed the PFG strength from 100 to 2000 DAC units (variable gzlvl1), which corresponds to the maximum strength of 21 G/cm.

Other relevant parameters:

gt1 = 0.005 (= δ), pw = 8.75, led = 0.02, diff = 0.2, gstab1 = 0.0005

Every spectrum was recorded with 8 transients (at=0.128) delayed by 6.5 seconds.

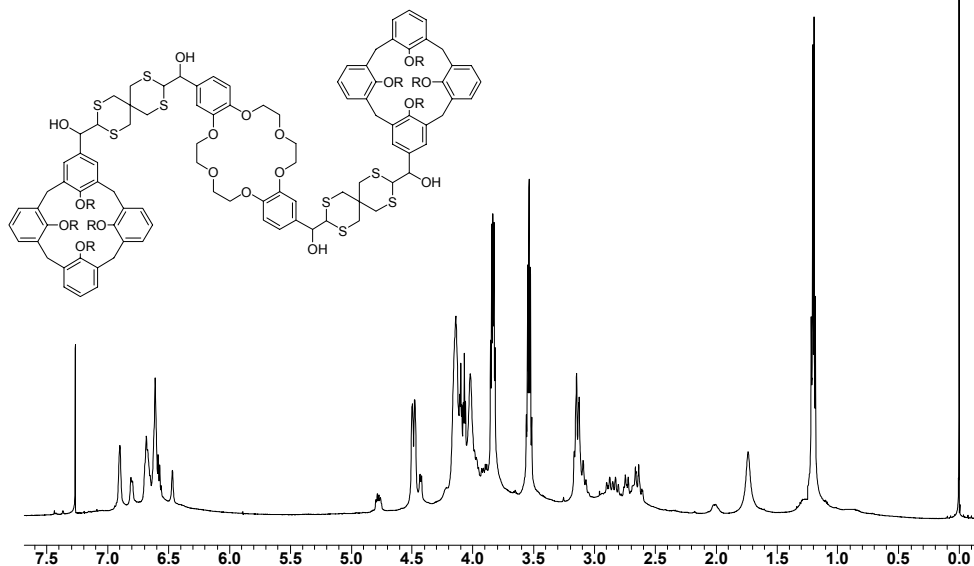
A typical array of PFG spectra



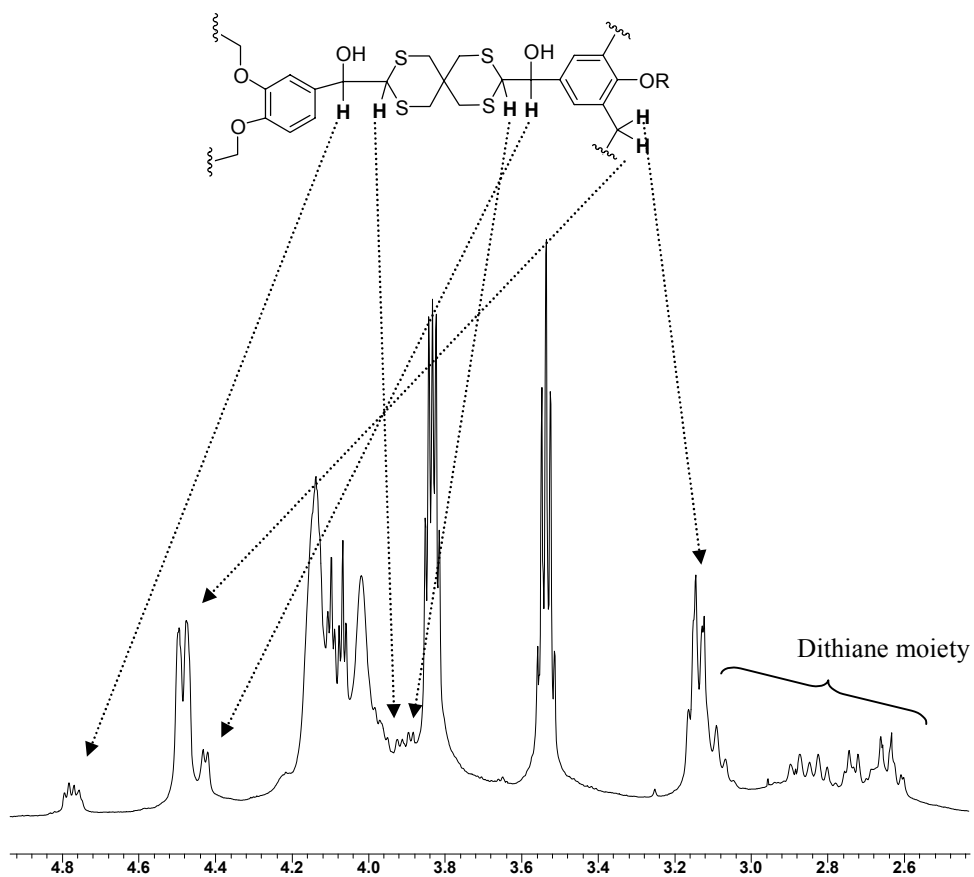
The logarithms of integrated intensities of the attenuated signals were then plotted against G^2 . The slope corrected for $-(\gamma\delta)^2(\Delta - \delta/3)$ gave the diffusion coefficient.

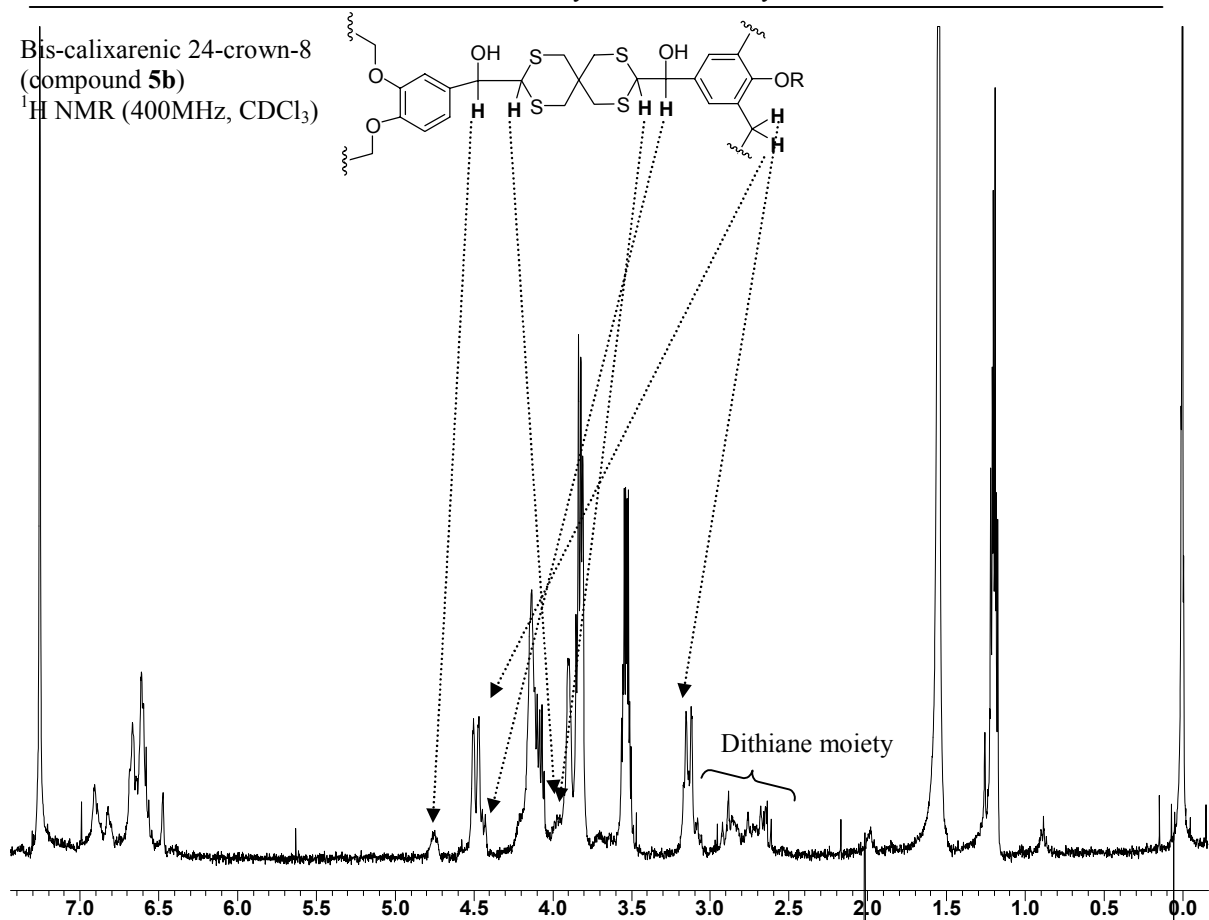
These measurements were repeated for half- and quarter-concentrated solutions. Interpolation to the infinite dilution (Y-intercept) gave the value of the diffusion coefficients at infinite dilution, which are reported in the communication.

Bis-calixarenic 18-crown-6 (compound **5a**)
 ^1H NMR (600MHz, CDCl_3)

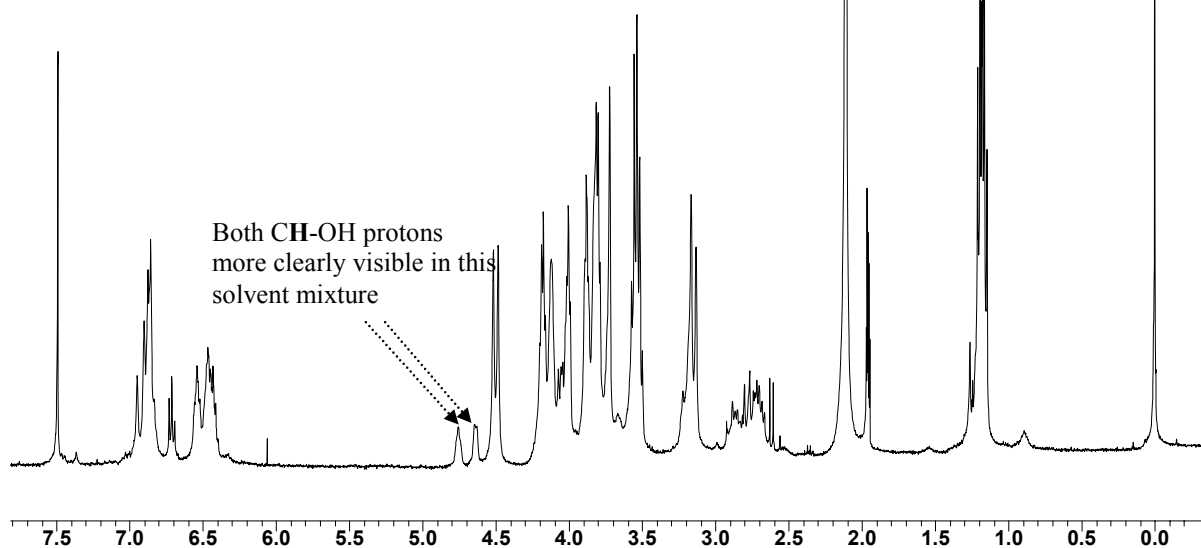


2.4-5 ppm region expanded:





400MHz ^1H NMR of **5b** in
 CD_3CN and C_6D_6 mixture



Photodisassembly of **5b** (~60% conversion is shown)

