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Electronic Supplementary Information

Systems chemistry: Logic gates based on the stimuli-responsive gel-sol transition of a crown-ether-functionalized bis-urea gelator

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1. General Methods

All reagents were commercially available and used as supplied without further purification. *N*,*N*′′-(*p*-xylylene) bis(*N*′-benzylurea) **1**,[1] hexa-(ethylene glycol) ditosylate,[2] monovalent guest **5**,[3] divalent guest **6**,[4] and di-*tert*-butyl tricarbonate **10**[5] were prepared according to published procedures. Solvents were either employed as purchased or dried prior to use by usual laboratory methods. Melting points were determined on a BUCHI 510 heating stage and are uncorrected. ^{1}H NMR, ^{13}C NMR, and ^{1}H-^{1}H COSY NMR spectra were recorded on Bruker ECX 400 MHz, Jeol Eclipse 500 MHz, or Bruker AVANCE III 700 MHz NMR spectrometers. All FTIR spectra were recorded on a Nicolet Avatar 320 FT-IR.

Gelation test of organic fluids: The gelator and the solvents were put into a capped test-tube sonicated for 5 min to aid the dissolution process. The sample vial was left for 12 h at ambient condition. The state was evaluated by the "stable to inversion of a test tube" method. In the gel-sol transition test, the sample vial was left for 15 min before inversion test. The critical gelation concentration (cgc) was defined as the lowest concentration of the gelator which leads to a stable gel.

Guest-induced stimuli-responsive behavior: The guest compound was added to the test tube containing the already prepared gel. Subsequently, the capped test tube was sonicated for 5 min. The sample vial was left for 15 min at the ambient conditions. The state was evaluated as described above.

AFM measurements: The AFM measurements have been performed using a Nanoscope Multimode V (Veeco, now Bruker AXS, Mannheim). All images were flattened previous to height analysis using algorithms contained in the software NanoScope 8.10. Tip convolution makes lateral dimension analysis difficult. Measurements were performed in laboratory air at room temperature. The microscope was operated in the tapping mode (TM-AFM) using silicone probes NCL-W (NanoAndMore GmbH, Wetzlar) with a size of 225 μm and a tip radius of < 8 nm at resonance frequencies of 160 – 210 kHz under ambient conditions. The force constant was 31 – 71 N/m. The cantilever was forced to oscillate near its resonance frequency. The samples were prepared by spin coating (Spin Coater SCV-2) at 5.000 rpm for 20 min on freshly cleaved mica.

Gel-sol transition temperature measurements: T_{gs} was determined by a 'dropping-ball method',[6] a small ball (about 166 mg) was placed on top of the gel in a test tube (inner diameter 1.0 cm), which was slowly heated in a water bath at a rate of 1 °C·min^{-1}. T_{gs} is defined as the average value when the ball had reached the bottom of the test tube.

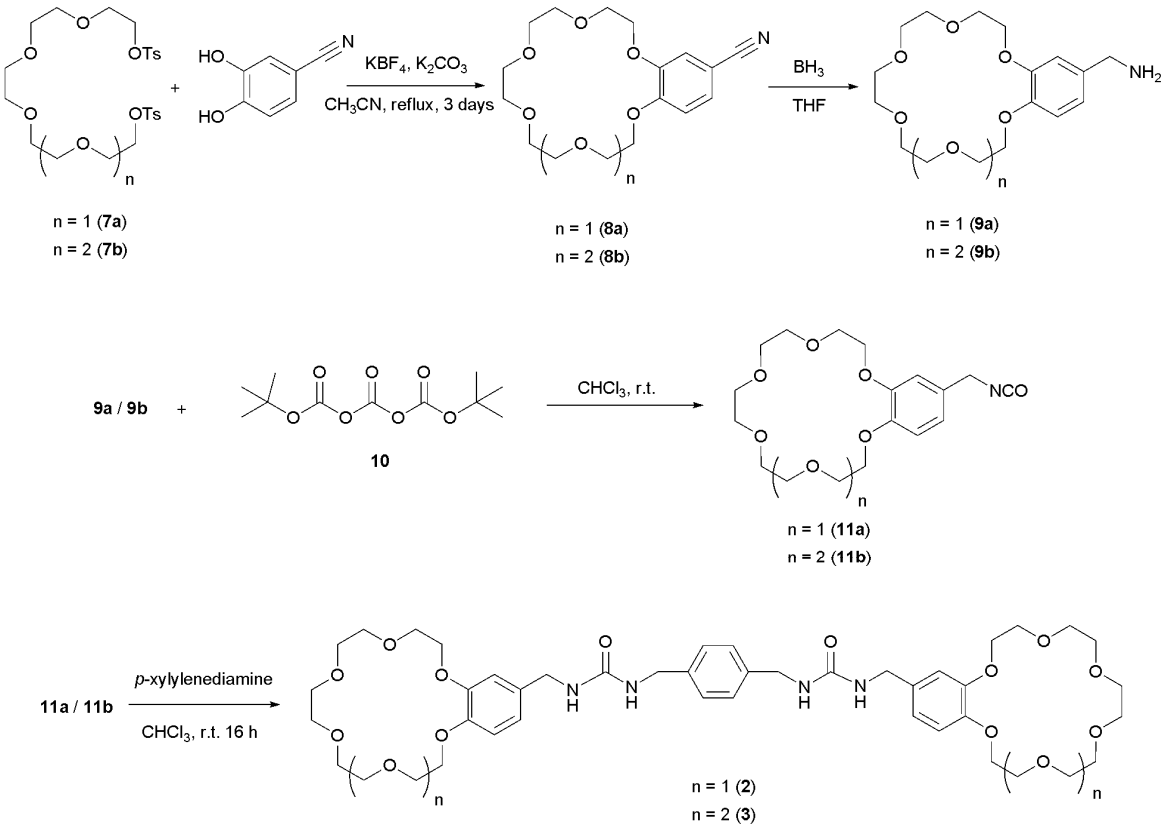
Dropping-ball experiments were carried out at least in duplicate, and the T_{gs} obtained were reproducible to within ± 1 °C.

Rheological measurements: Oscillatory measurements were performed using a Malvern (Bohlin) Gemini rheometer and employing a plate-plate geometry (40 mm diameter) at a constant temperature of 25°C with a fixed deformation of 0.01. If not noted otherwise, the experiments were done such that one started from the highest frequency and measurements were done in downward direction frequency-wise. As these gels are quite sensitive to deformations we also verified that the filling history of the samples did not affect the outcome of our rheological experiments.

Differential scanning calorimetry thermograms (DSC): Differencial scanning calorimetry measurements were performed with a Multi Cell DSC from TA Instruments. Three heating/cooling cycles from 0 to 80 °C were performed with a heating/cooling rate was 1 $K \cdot min^{-1}$. The heating curves were reproducible for the second and third cycle.

2. Syntheses of compounds

2.1 Synthesis of compounds 2 and 3



Scheme S1**. Synthesis of **2** and **3

2.1.1 Synthesis of compound 8a

While stirring vigorously under argon atmosphere, a suspension of K_2CO_3 (2.070 g, 15 mmol) and KBF_4 (0.944 g, 7.5 mmol) in anhydrous CH_3CN (100 mL) was heated to reflux. To the suspension, a solution of penta-(ethylene glycol) ditosylate (2.877g, 5.0 mmol) and 3,4-dihydroxybenzonitrile (675 mg, 5.0 mmol) in CH_3CN (100 mL) was added dropwise within 24 h. The resulting reaction mixture was stirred under reflux for another 3 days. After cooling to r.t., the suspension was filtered and washed with CH_2Cl_2 (100 mL). The filtrate was concentrated in vacuo. The residue was partitioned between CH_2Cl_2 (100 mL) and water (100 ml), and the aqueous phase was extracted twice by CH_2Cl_2 (50 mL). the combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude product, which was purified by column chromatography over silica gel (eluent: CH_2Cl_2/MeOH, 30:1 (*v*/*v*)) in 52 % yield as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ [ppm] = 3.67 (s, 4H), 3.69-3.71 (m, 4H), 3.75-3.76 (m, 4H), 3.90-3.94 (m, 4H), 4.13-4.19 (m, 4H), 6.87 (d, J = 8.0 Hz, 1H), 6.07 (d, J = 2.0 Hz, 1H), 7. 24 (dd, J = 10.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ [ppm] = 68.6, 68.9, 69.0, 70.4, 70.4, 70.5, 70.6, 70.7, 71.0, 103.8, 112.7, 115.8, 119.1, 126.6, 148.6, 152.6. ESI-TOF-HRMS: calcd. for $[M+Na]^+$ ($C_{17}H_{23}NO_6Na$) *m*/*z* 360.1423, found 360.1412.

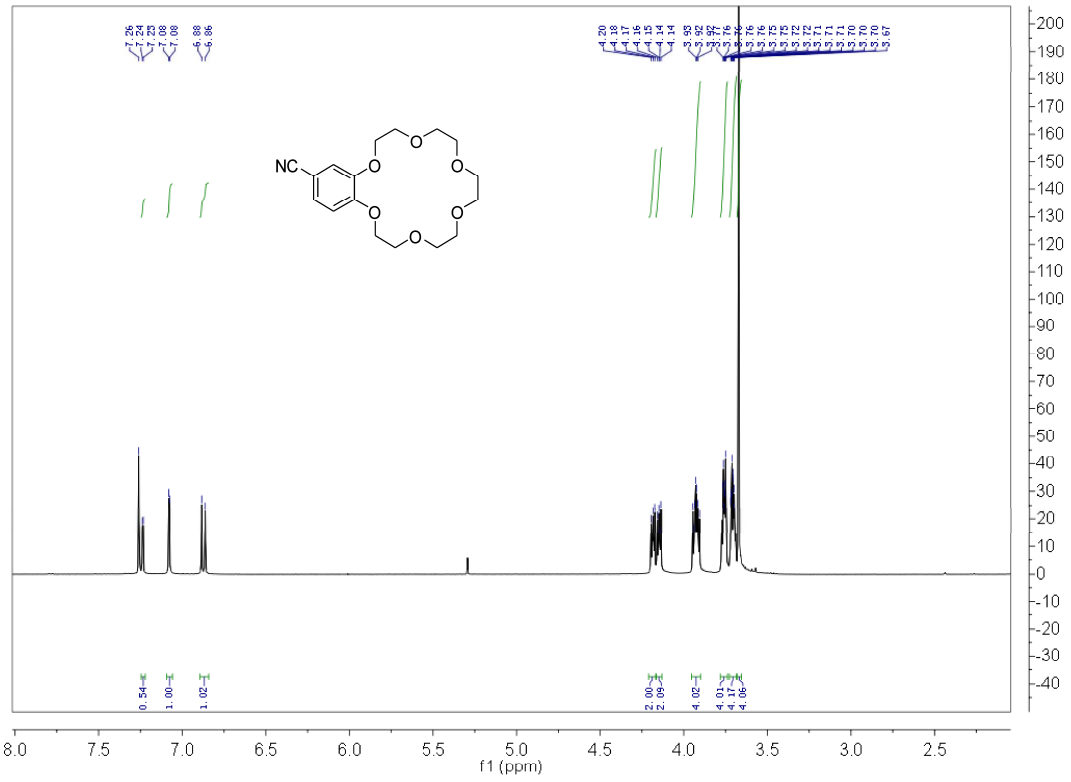


Figure S1. *^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of* ***8a***

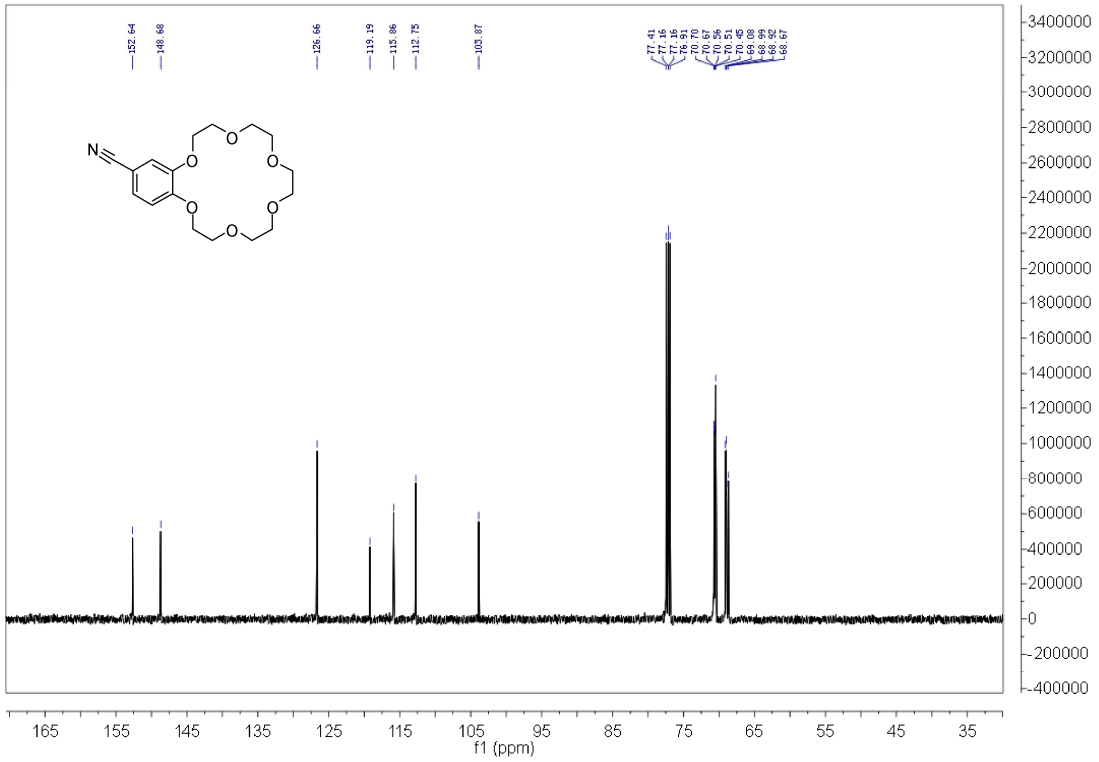


Figure S2. *^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298K) of* ***8a***

2.1.2 Synthesis of compound 8b

Compound **8b** was synthesized following the procedure described above for compound **8a**, using hexa-(ethylene glycol) ditosylate (2.953 g, 5.0 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ [ppm] = 3.62-3.66 (m, 8H), 3.69-3.72 (m, 4H), 3.75-3.78 (m, 4H), 3.89-3.92 (m, 4H), 4.12-4.18 (m, 4H), 6.69 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 2.0 Hz, 1H), 7.24 (dd, *J* = 10.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ [ppm] = 69.0, 69.2, 69.3, 69.4, 70.4, 70.4, 70.8, 70.9, 70.9, 71.0, 71.1, 71.2, 103.9, 113.0, 113.0, 116.4, 121.3, 126.6, 148.7, 152.7. ESI-TOF-HRMS: calcd. for $[M+K]^+$ ($C_{19}H_{27}NO_7K$) *m/z* 420.1425, found 420.1455.

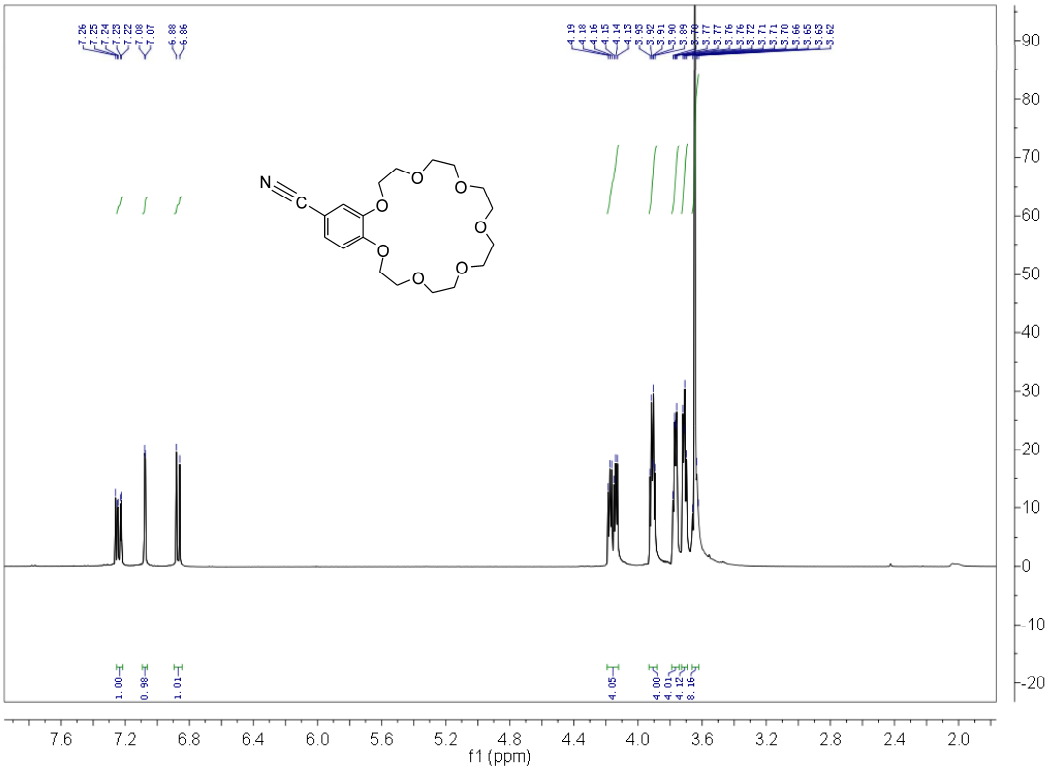


Figure S3. *^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of* ***8b***

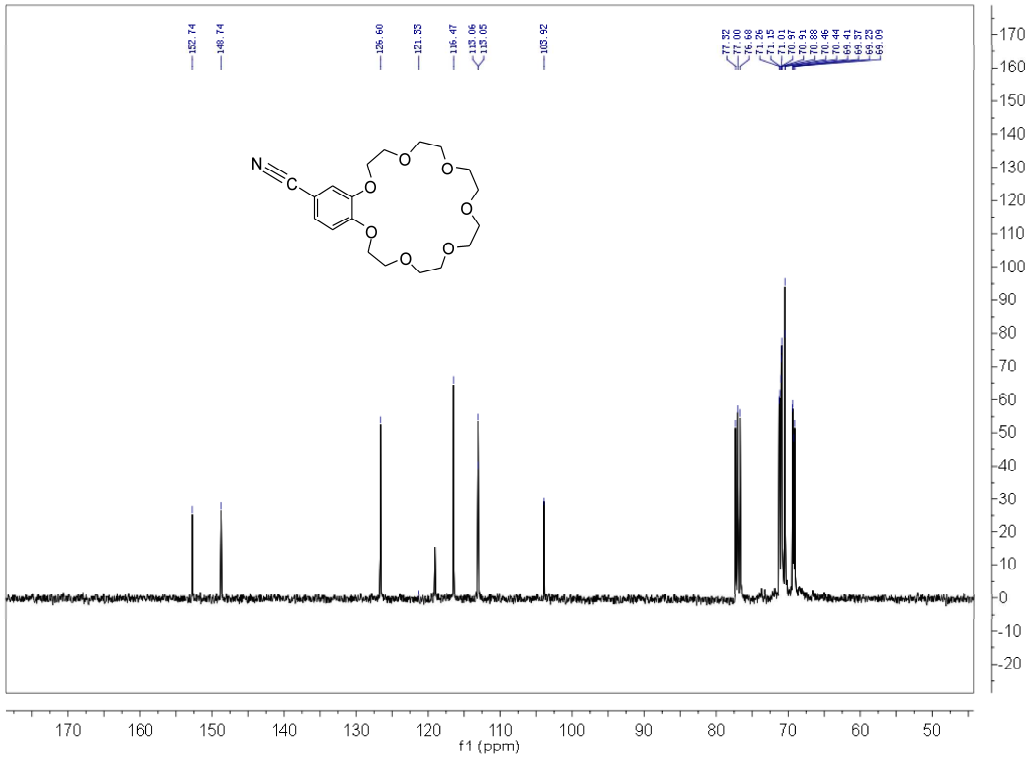


Figure S4. *^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298K) of* ***8b***

2.1.3 Synthesis of compound 9a

A solution of **8a** (177 mg, 0.52 mmol) dissolved in dry THF (10 mL) was added slowly to a solution of 1 M borane-tetrahydrofurane complex (5.2 mL, 5.2 mmol) in dry THF (15 mL) at 0 °C. The solution was stirred for 30 min at 0 °C, after which it was heated to reflux for 20 h. The reaction mixture was cooled to 0 °C, and methanol (6 mL) was added dropwise (caution: H_2 evolution). Hydrochloric acid (260 µL, 37% in water) was added slowly, and the reaction mixture was stirred for 1 h and subsequently evaporated to dryness under reduced pressure. Trimethyl borate was removed by three subsequent coevaporations with methanol (3 times 50 mL). Sodium hydroxide solution (80 mL, 1 M in water) was added to the viscous liquid, followed by extraction with CH_2Cl_2 (3 times 60 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the solvent was evaporated on a rotary evaporator yielding a yellow oil (186 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm] = 3.69 (s, 4H), 3.71- 3.73 (m, 4H), 3.76- 3.79 (m, 6H), 3.91-3.93 (m, 4H), 4.14-4.18 (m, 4H), 6.83- 6.88 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ [ppm] = 46.0, 69.1, 69.3, 69.7, 70.7, 70.8, 113.4, 114.3, 119.8, 147.8, 149.0. ESI-TOF-HRMS: calcd. for $[M+H]^+$ ($C_{17}H_{28}NO_6$) *m/z* 342.1919, found 342.1912.

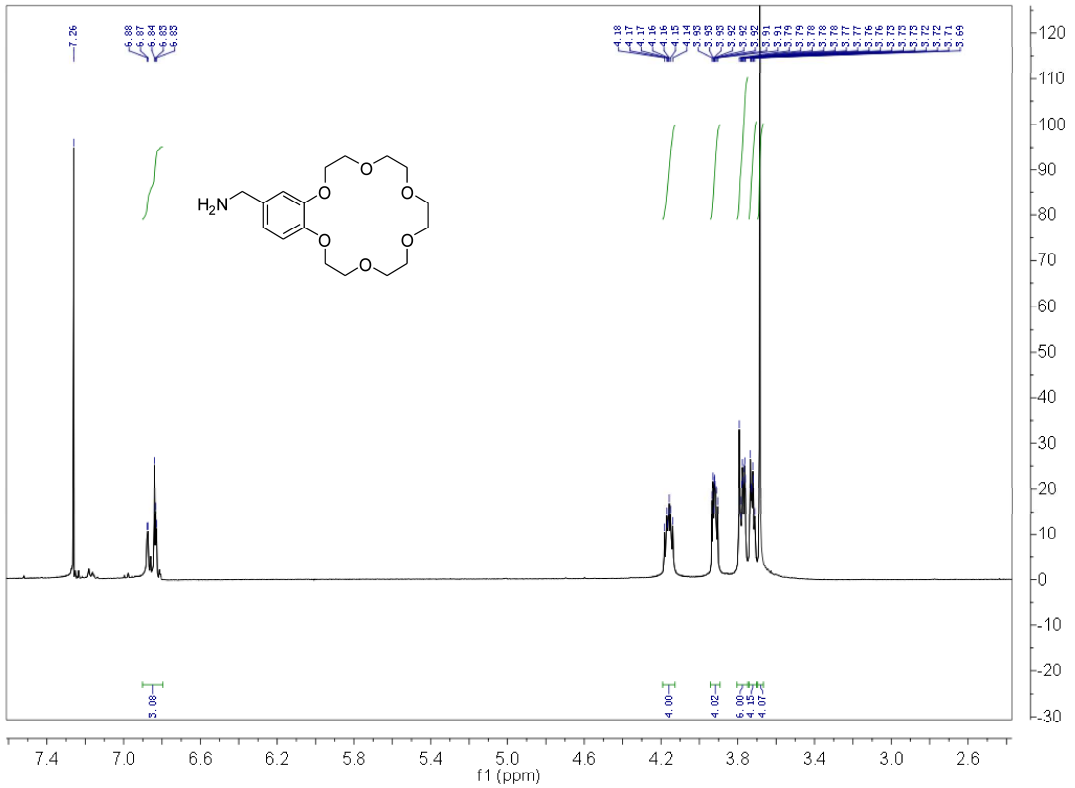


Figure S5. *^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of* ***9a***

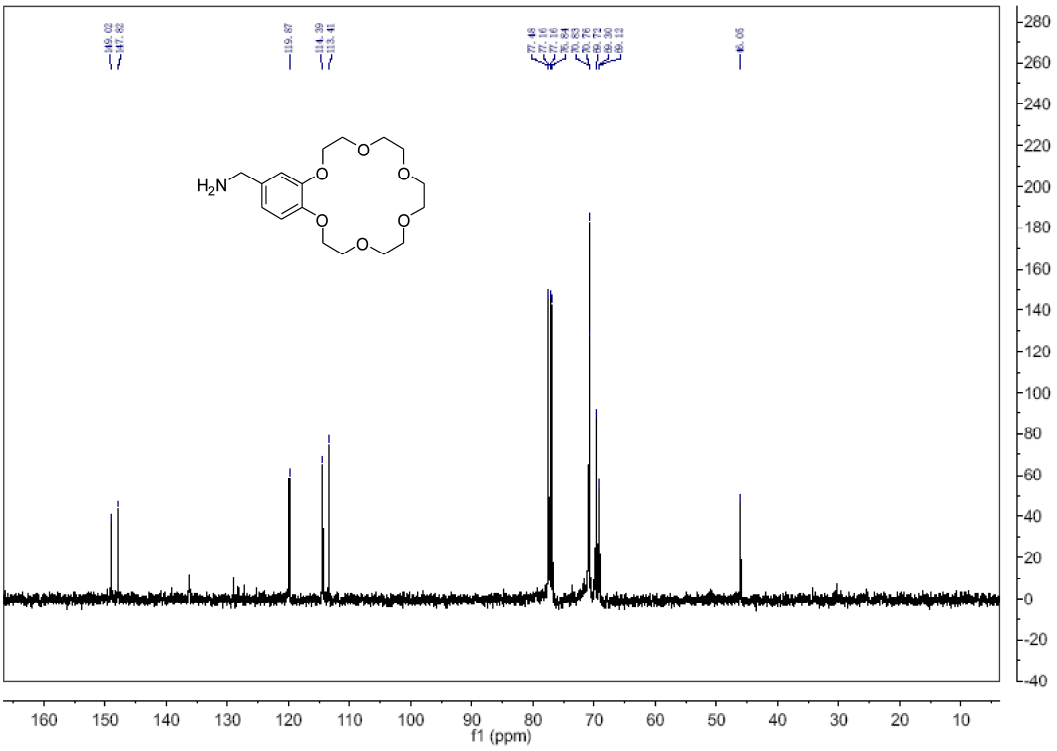


Figure S6. *^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298K) of* ***9a***

2.1.4 Synthesis of compound 9b

Compound **9b** was synthesized following the procedure described above for compound **9a**, using **8b** (200 mg, 0.52 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ [ppm] = 3.61 (s, 8H), 3.66-3.68 (m, 4H), 3.71 (m, br, 6H), 3.84-3.86 (m, 4H), 4.08-4.11 (m, 4H), 6.87-6.81 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ [ppm] = 45.9, 69.1, 69.2, 69.8, 70.4, 70.5, 70.8, 70.9, 71.0, 113.3, 114.2, 119.8, 147.6, 151.6. ESI-TOF-HRMS: calcd. for $[M+H]^+$ ($C_{19}H_{32}NO_7$) *m/z* 386.2179, found 386.2167.

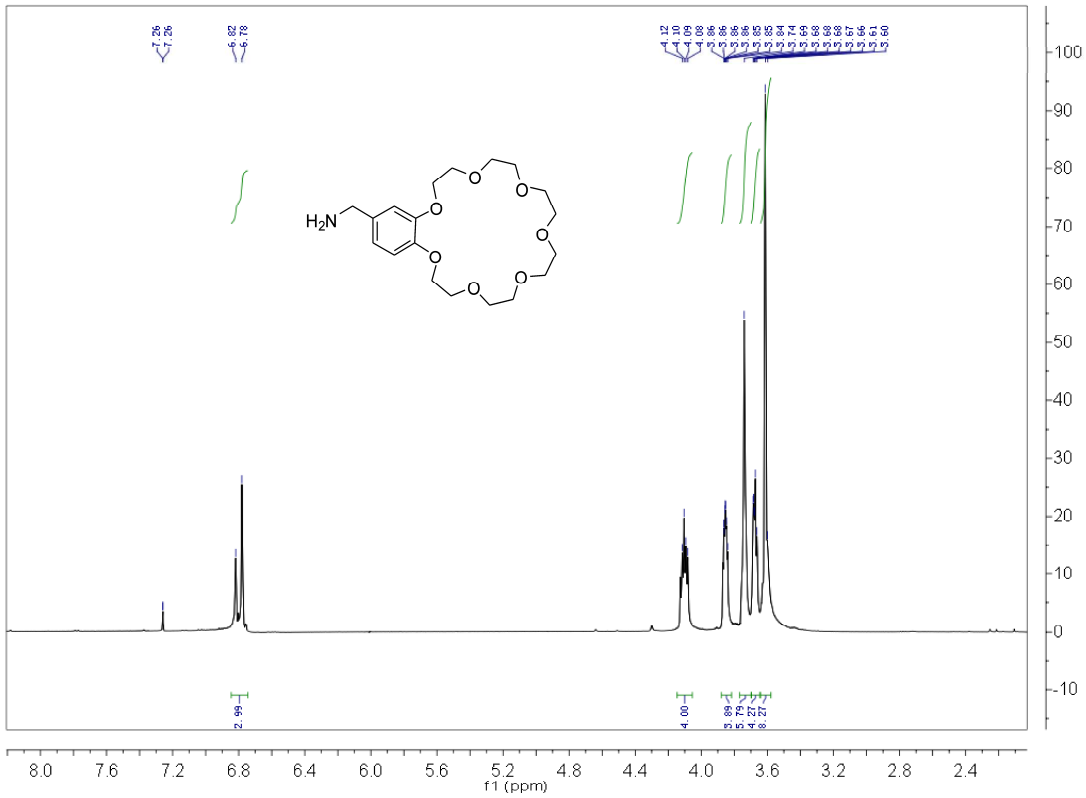


Figure S7. *^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of* ***9b***

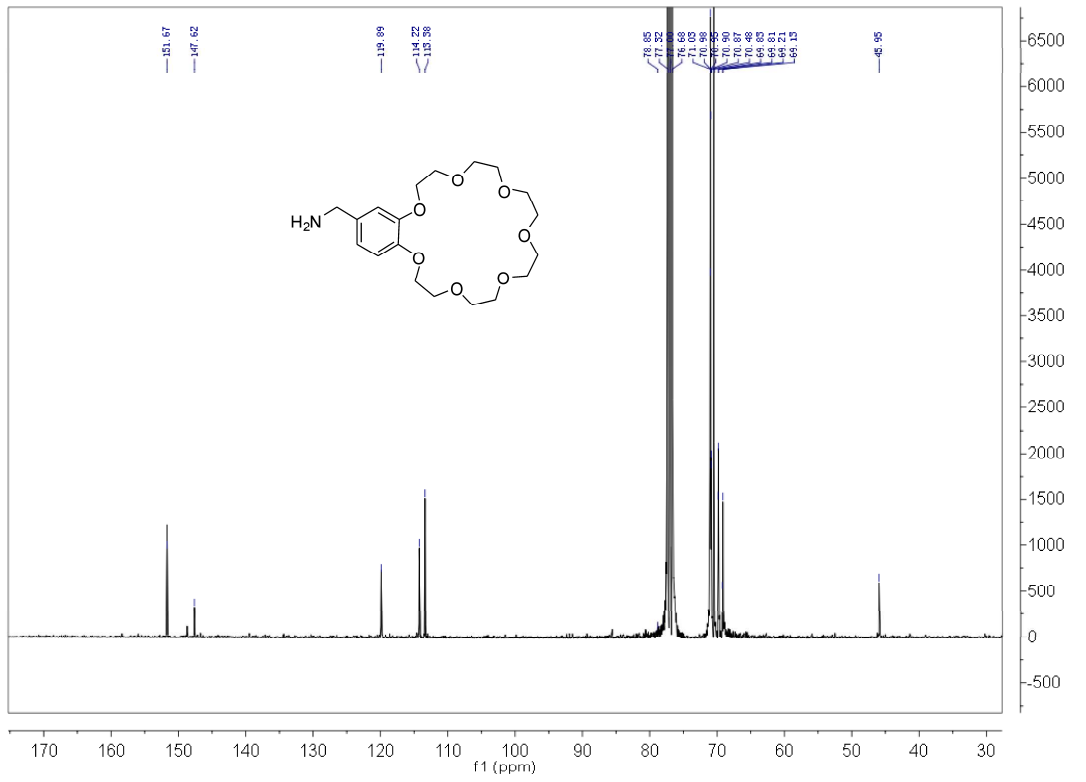


Figure S8. *^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of* ***9b***

2.1.5 Synthesis of compound 2

A solution of **9a** (178 mg, 0.516 mmol) in dry $CHCl_3$ (3 mL) was injected into a stirred solution of di-*tert*-butyl tricarbonate (135 mg, 0.64 mmol) in dry $CHCl_3$ (10 mL) under argon. After vigorously stirring for 40 min at room temperature, *p*-xylylenediamine (29.28 mg, 0.215 mmol) in dry $CHCl_3$ (3 mL) was added to the isocyanate solution. The solution was vigorously stirred overnight under argon. Then 24 mL of 1 M HCl were added to the reaction mixture and the organic layer was washed with 40 mL of brine twice and followed by 30 mL of deionized water twice. After drying the organic phase over anhydrous Na_2SO_4, the crude product was purified by column chromatography over neutral aluminum oxide with CH_2Cl_2 and MeOH (80:1 to 20:1 v/v) to afford a pale yellow solid (60% yield). Mp: 204-206 °C. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K) δ [ppm] = 3.52 (s, 8H), 3.55-3.56 (m, 8H), 3.59-3.61 (m, 8H), 3.72-3.76 (m, 8H), 4.01-4.04 (m, 8H), 4.13-4.14 (d, J = 5.6 Hz, 4H) 4.19-4.20 (d, J = 5.6 Hz, 4H), 6.31-6.36 (m, 4H), 6.74-6.76 (m, 2H), 6.85-6.88 (m, 4H), 7.18 (s, 4H); ^{13}C NMR (175 MHz, DMSO-d_6, 298 K) δ [ppm] = 42.6, 42.7, 68.1, 68.3, 68.7, 69.7, 69.8, 112.6, 113.3, 119.3, 126.8, 133.5, 139.1, 147.0, 148.1, 157.9. Elemental analysis calcd (%) for $C_{44}H_{62}N_4O_{14}$: C, 60.68; H, 7.17; N, 6.43; Found: C, 60.58; H, 7.17; N, 6.40. ESI-TOF-HRMS: calcd. for $[M+Na]^+$ ($C_{44}H_{62}N_4O_{14}Na$) *m*/*z* 893.4160, found 893.4129.

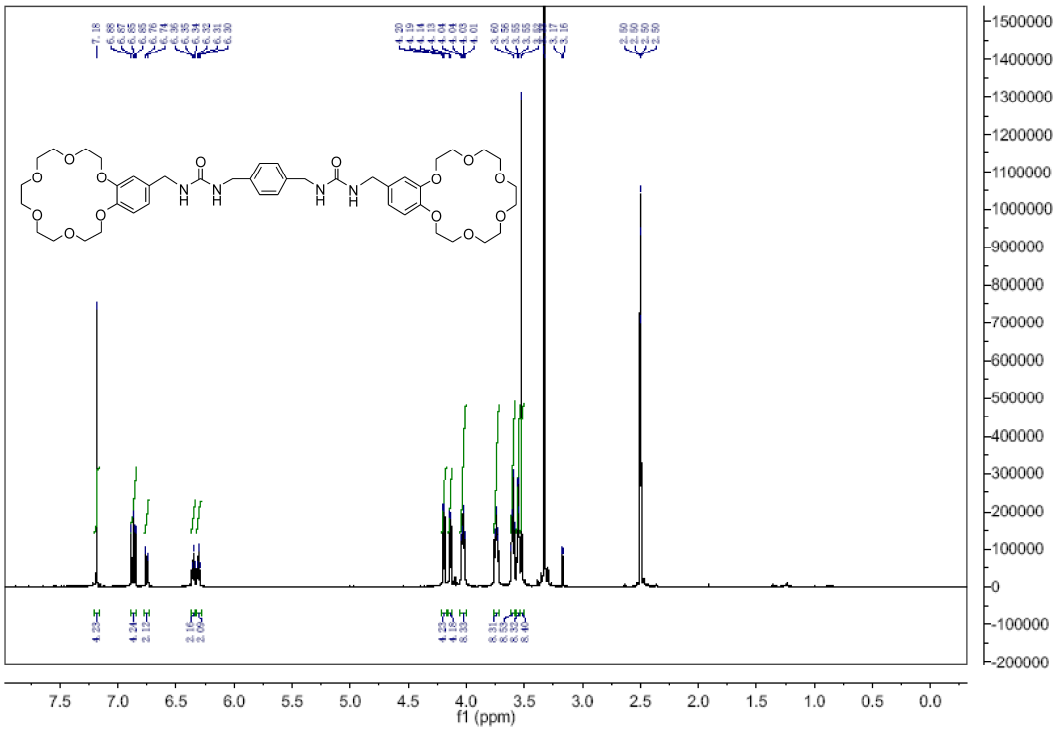


Figure S9. *^{1}H NMR spectrum (500 MHz, DMSO-d_6, 298 K) of* ***2***

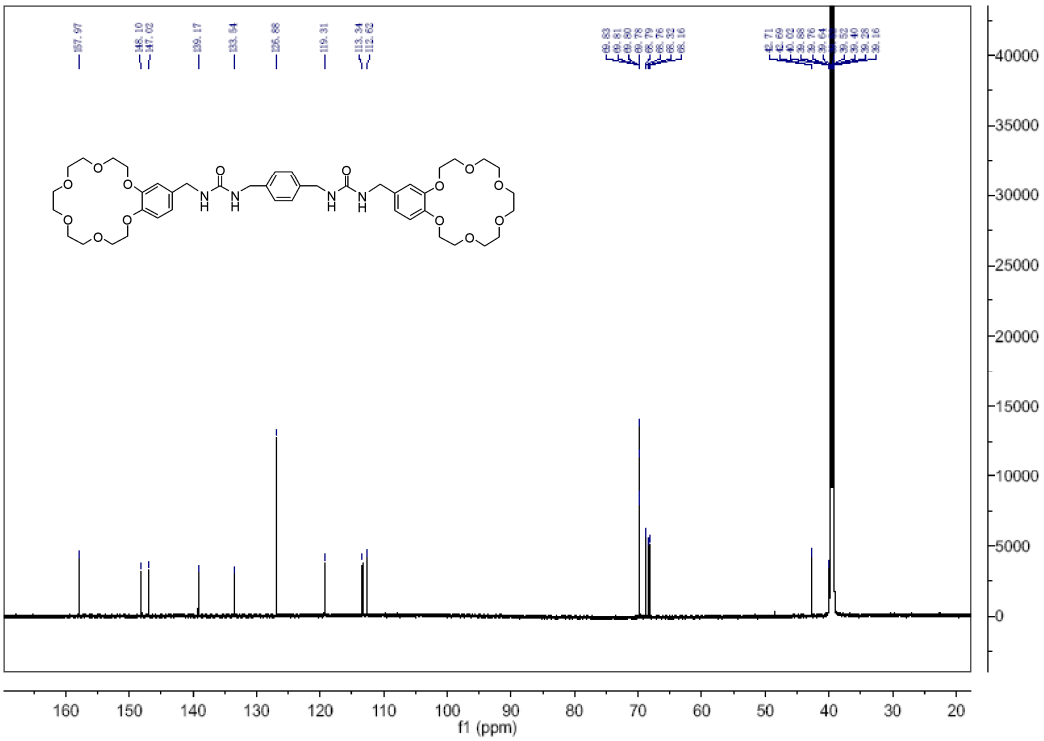


Figure S10. *^{13}C NMR spectrum (175 MHz, DMSO-d_6, 298 K) of* ***2***

2.1.6 Synthesis of compound 3

Compound **3** was synthesized following the procedure described above for compound **2**, using **9b** (200 mg, 0.516 mmol). Mp: 165-166 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ [ppm] = 3.51 (s, 16H), 3.55-3.56 (m, 8H), 3.59-3.61 (m, 8H), 3.72-3.75 (m, 8H), 4.02-4.04 (m, 8H), 4.13-4.14 (d, J = 5.6 Hz, 4H) 4.18-4.20 (d, J = 5.6 Hz, 4H), 6.31-6.36 (m, 4H), 6.74-6.77 (m, 2H), 6.85-6.89 (m, 4H), 7.18 (s, 4H); ^{13}C NMR (175 MHz, DMSO-d_6, 298 K): δ [ppm] = 42.6, 68.1, 68.3, 68.8, 69.8, 70.0, 70.1, 112.5, 113.2, 119.2, 126.8, 133.5, 139.1, 146.8, 147.9, 157.9. Elemental analysis calcd (%) for $C_{48}H_{70}N_4O_{16}$: C, 60.11; H, 7.36; N, 5.84; Found: C, 60.01; H, 7.32; N, 5.64. ESI-TOF-HRMS: calcd for $[M+Na]^+$ $C_{48}H_{70}O_{16}N_4Na$, m/z 981.4684, found 981.4676.

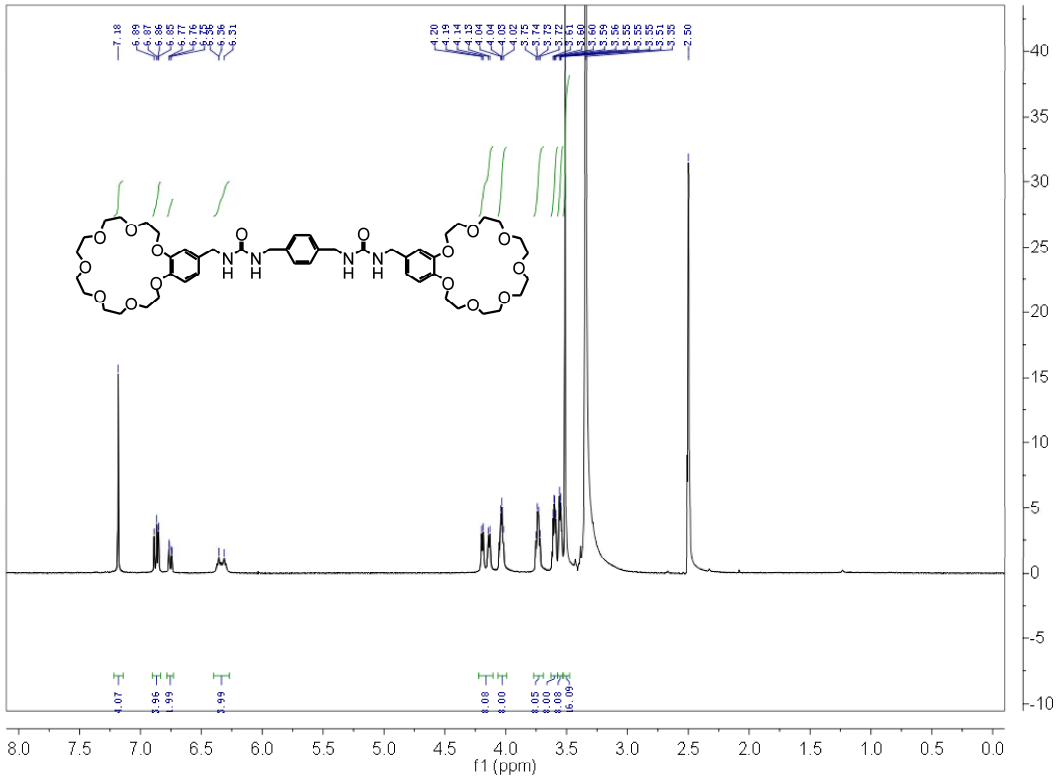


Figure S11. *^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of* ***3***

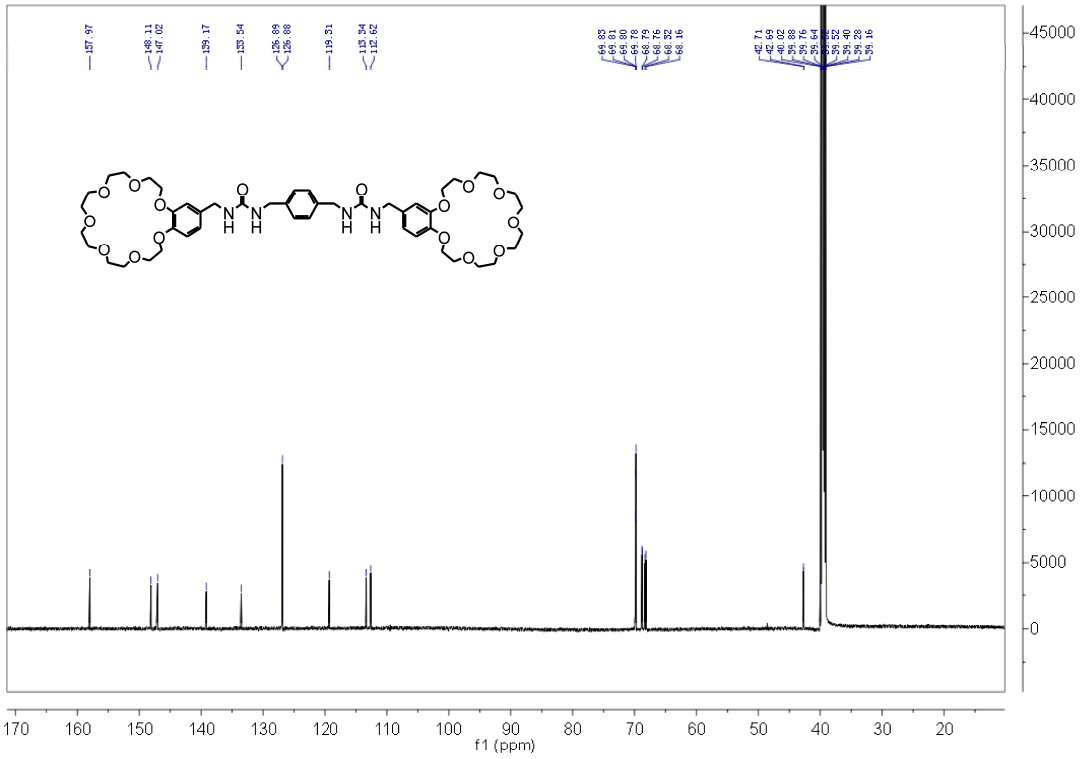
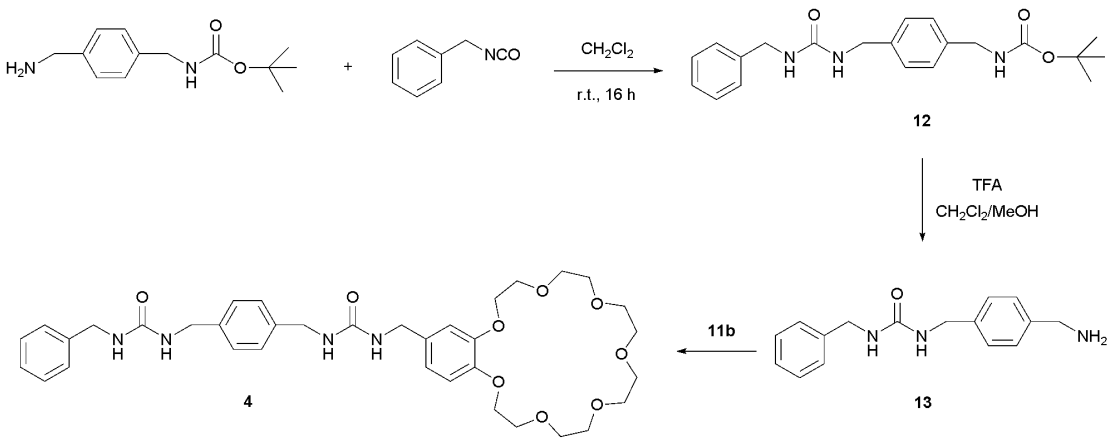


Figure S12. *^{13}C NMR spectrum (175 MHz, DMSO-d_6, 298 K) of* ***3***

2.2 Synthesis of compound 4



Scheme S2. *Synthesis of **4***

2.2.1 Synthesis of compound 12

A solution of *tert*-butyl-4-(aminomethyl)benzylcarbamate (214.8 mg, 0.91 mmol) and benzyl isocyanate (133.1 mg, 1.00 mmol) of in 30 mL of CH_2Cl_2 was stirred at room temperature for 12 h under argon. After the reaction, the reaction mixture was poured into diethyl ether (400 mL) and the precipitate was collected as a white solid 137 mg (40%). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ [ppm] = 1.38 (s, 9H), 4.07 (d, J = 6.0 Hz, 2H), 4.18-4.23 (m, 4H), 7.15-7.37 (m, 9H); ^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ [ppm] = 28.2, 42.7, 42.9, 43.0, 77.6, 126.4, 126.7, 126.8, 126.9, 128.1, 138.4, 139.1, 140.8, 155.7, 158.0. ESI-TOF-HRMS: calcd. for $[M+Na]^+$ ($C_{21}H_{27}N3O_3Na$), m/z 392.1950, found 392.1974.

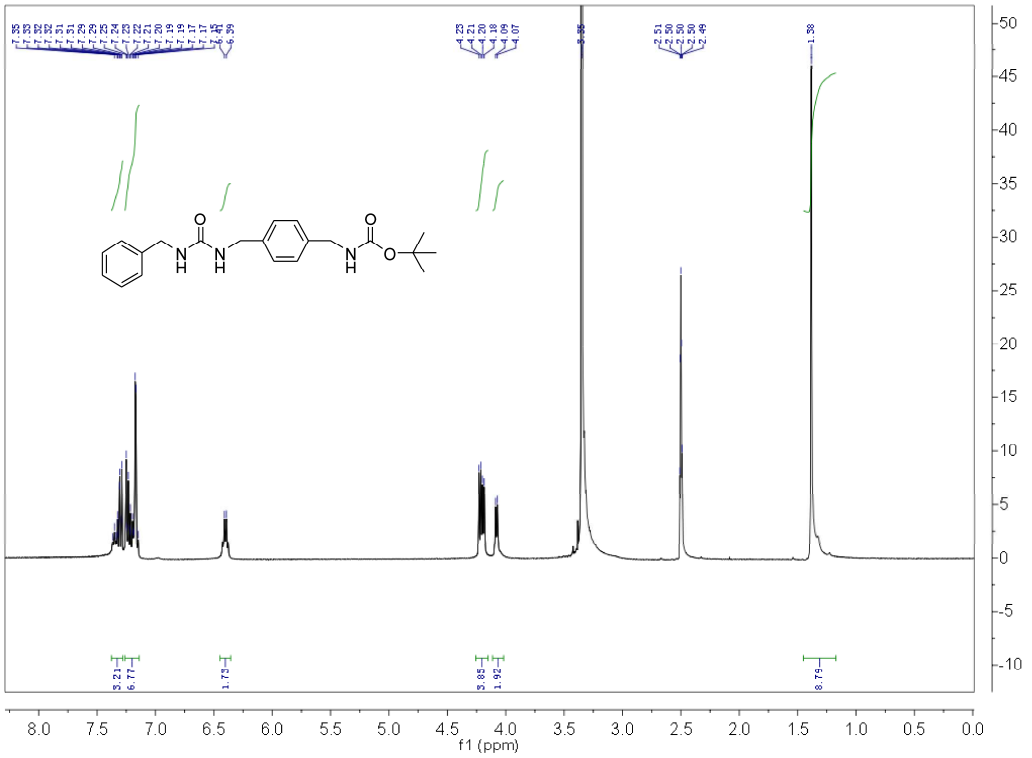


Figure S13. *^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298K) of* ***12***

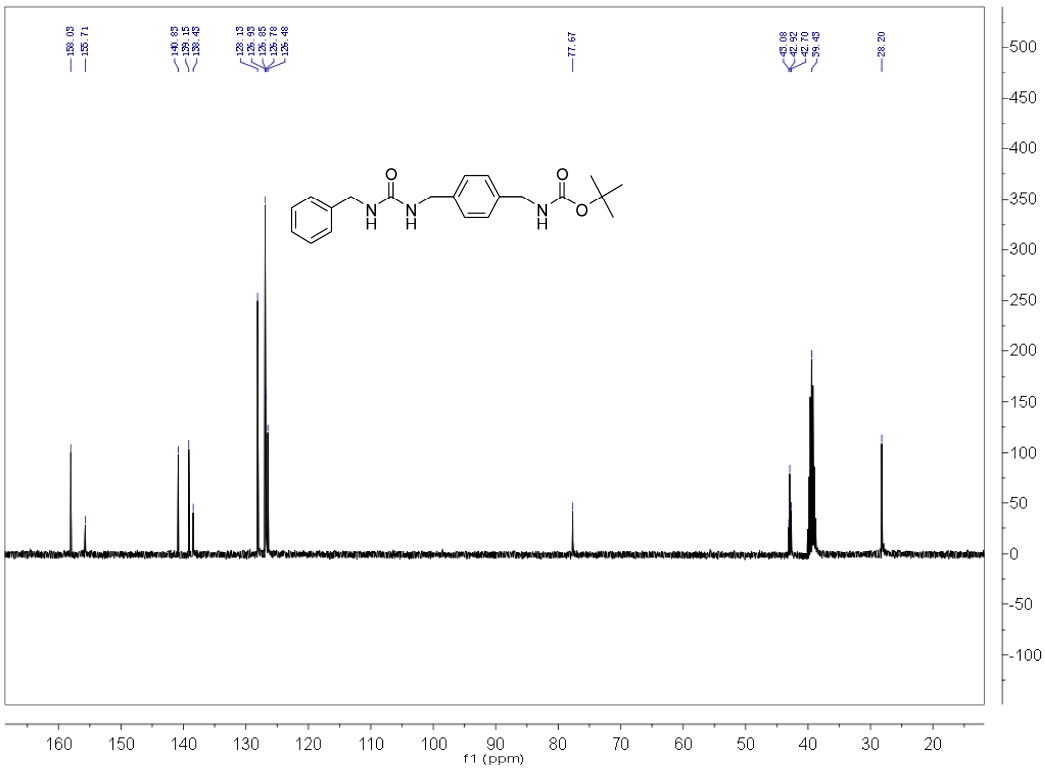


Figure S14. *^{13}C NMR spectrum (100 MHz, DMSO-d_6, 298K) of* ***12***

2.2.2 Synthesis of compound 13

Compound **12** (120 mg, 0.32 mmol) was dissolved in 10 mL of CH_2Cl_2/MeOH mixture (7:3 *v*/*v*) and 6 mL of trifluoroacetic acid (TFA, 78 mmol) were added. The reaction process was monitored by TLC. After 16 h stirring at room temperature, the solvent was removed and fresh dichloromethane was added. The organic layer was washed with 200 mL of 1 M sodium hydroxide solution. To increase the yield, the traces of product in the aqueous sodium hydroxide layer were re-extracted with CH_2Cl_2 (3 × 40 mL). The combined organic layer was dried over anhydrous Na_2SO_4. Solvent was evaporated to obtain the product (91% yield). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ [ppm] = 3.65 (s, 2H), 4.18-4.21 (d, 4H), 7.16-7.32 (m, 9H); ^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ [ppm] = 41.7, 42.9, 45.2, 126.5, 126.8, 126.9, 127.1, 128.2, 138.8, 141.0, 142.5, 158.2. ESI-TOF-HRMS: calcd. for $[M+H]^+$ ($C_{16}H_{20}N_3O$) *m*/*z* 270.1604, found 270.1612.

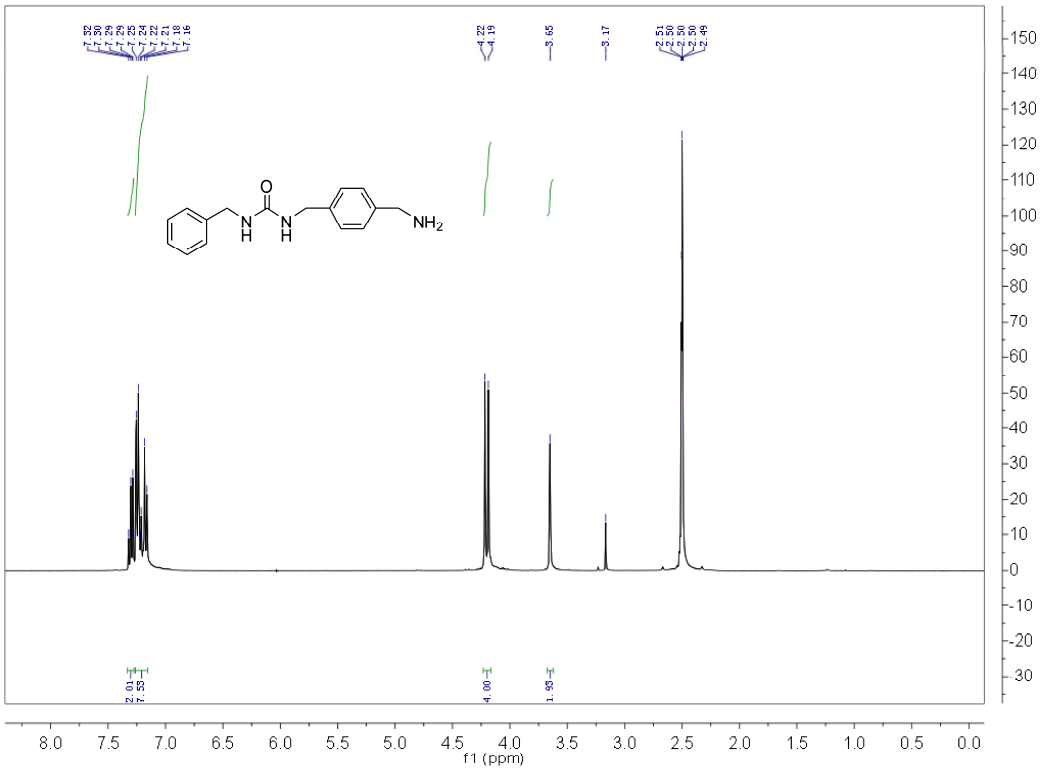


Figure S15. *^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298K) of* ***13***

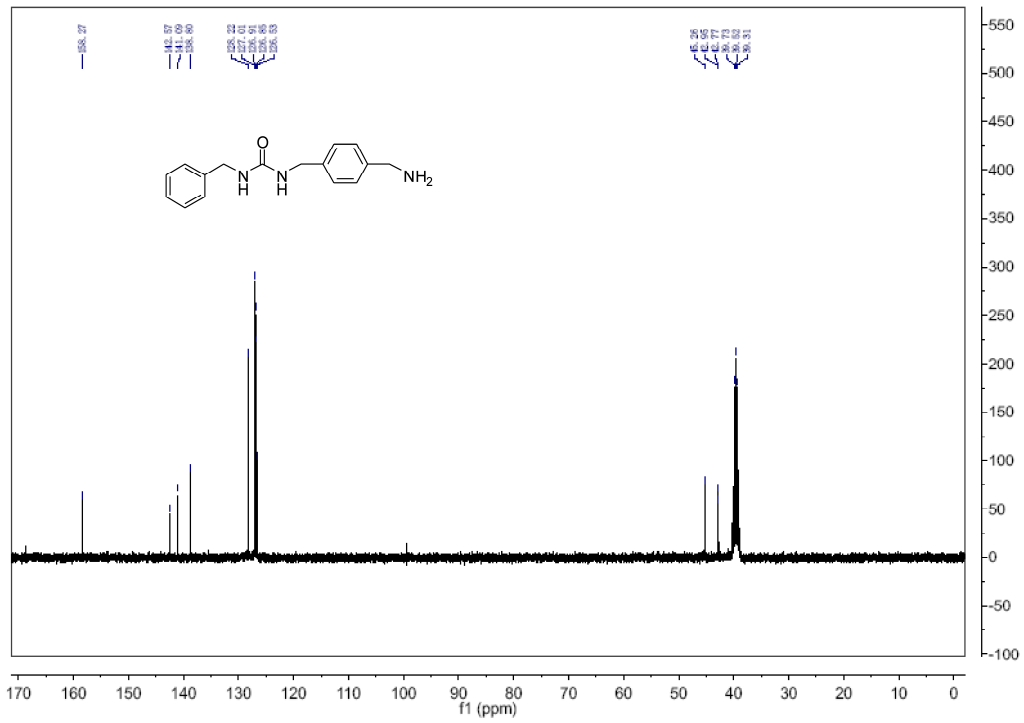


Figure S16. *^{13}C NMR spectrum (400 MHz, DMSO-d_6, 298K) of* ***13***

2.2.3 Synthesis of compound 4

Compound **4** was synthesized following the procedure described above for compound **2**. (Mp was not detected, since the decomposition before melting). ^{1}H-NMR (500 MHz, DMSO-d_6, 298 K): δ [ppm] = 3.52 (s, 8H), 3.55-3.57 (m, 4H), 3.59-3.63 (m, 4H), 3.72-3.75 (m, 4H), 4.03-4.05 (m, 4H), 4.13-4.15 (d, J = 10.0 Hz, 2H) 4.19-4.20 (d, J = 5.0 Hz, 4H), 4.22-4.23 (d, J = 5.0 Hz, 2H), 6.36-6.47 (m, 4H), 6.75-6.77 (m, 1H), 6.86-6.89 (m, 2H), 7.19-7.25 (m, 7H), 7.29-7.32 (m, 2H); ^{13}C NMR (175 MHz, DMSO-d_6, 298 K): δ [ppm] = 42.6, 42.7, 68.3, 68.4, 68.9, 69.0, 69.8, 70.1, 70.2, 112.7, 113.52, 119.3, 126.4, 126.8, 126.9, 128.1, 133.6, 139.0, 139.2, 140.8, 146.9, 148.0, 158.0. Elemental analysis calcd (%) for $C_{36}H_{48}N_4O_9$: C, 63.51; H, 7.11; N, 8.23; Found: C, 62.27; H, 6.97; N, 8.21. ESI-TOF-HRMS: calcd for $[M+K]^+$ $C_{48}H_{70}O_{16}N_4K$, m/z 719.3058, found 719.3103.

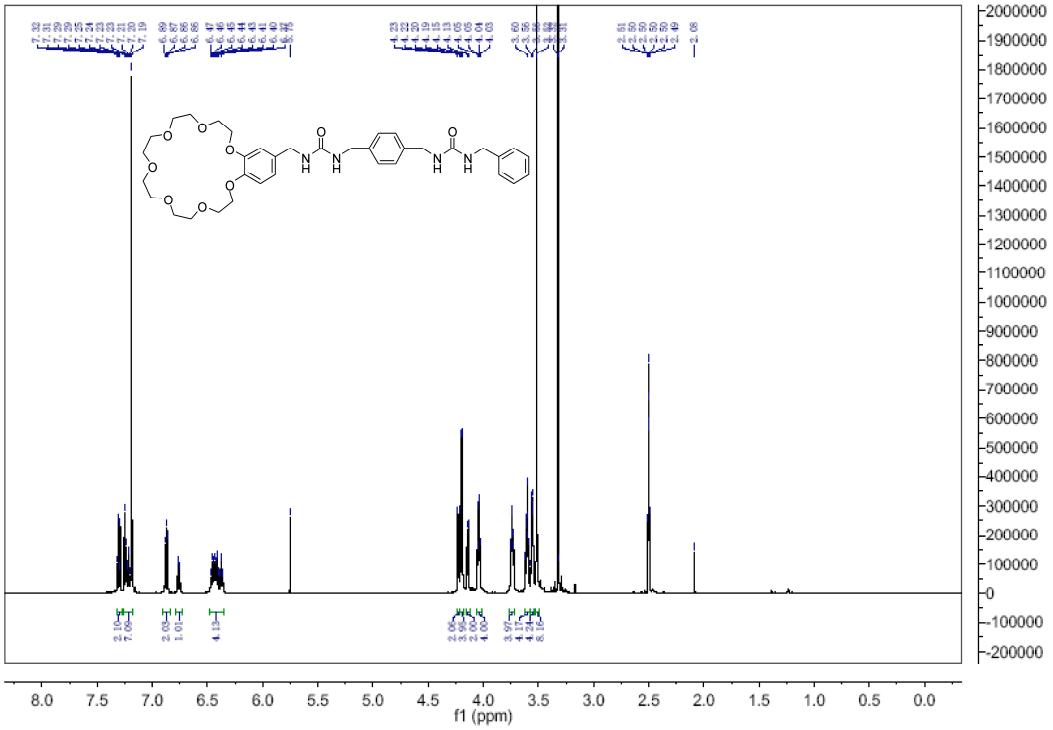


Figure S17. *^{1}H NMR spectrum (500 MHz, DMSO-d_6, 298 K) of* ***4***

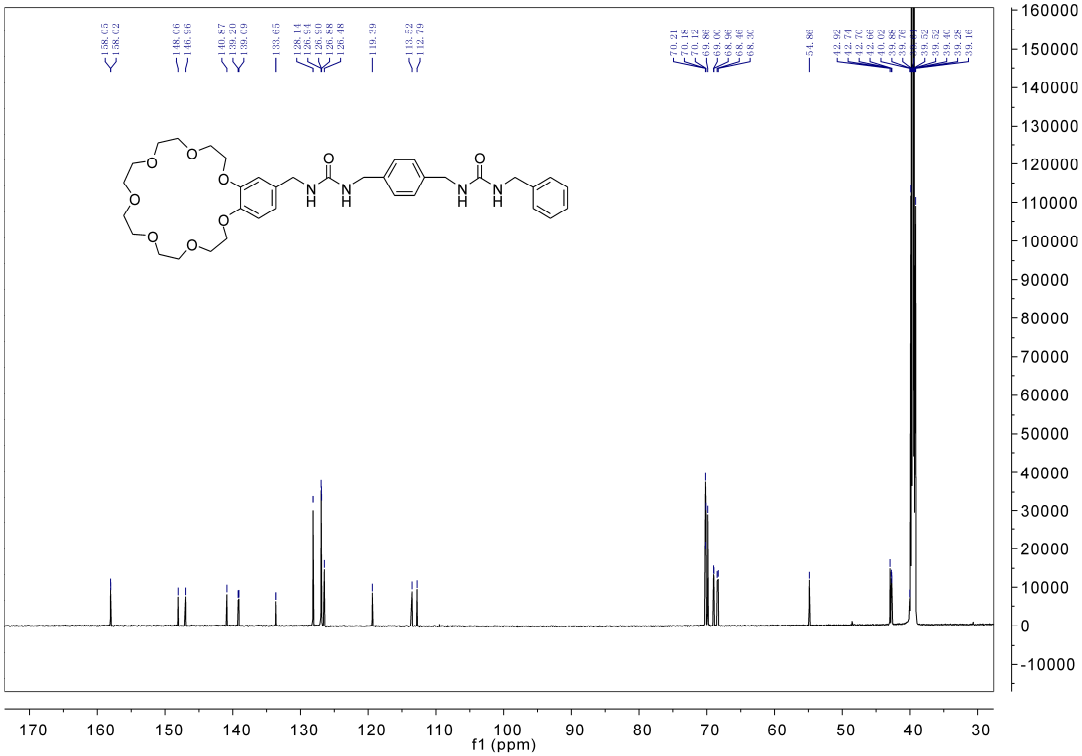


Figure S18. *^{13}C NMR spectrum (175 MHz, DMSO-d_6, 298 K) of* ***4***

3. IR measurements

Infrared spectroscopy is helpful for studying the extent of hydrogen bonding in the self-assembly of gelators. Previous studies indicated that the frequency of both the N-H and the C=O (amide I) vibration depend strongly on the hydrogen-bonding nature of the urea groups.[7] The free urea group exhibits N-H stretch and C=O (amide I) vibrations at 3400 cm^{-1} and 1690 cm^{-1} respectively. Table 1 shows the gel in acetonitrile to exhibit these two vibrations at significantly different wavenumbers (3319 and 1615 cm^{-1}, respectively). These wavenumbers match very well those obtained from solutions of gelator **3** in $CHCl_3$ and CH_2Cl_2 – solvents which are known to allow rather strong hydrogen bond formation. Consequently, we conclude the bifurcated hydrogen bonds between the urea groups in stacked gelators to prevail in the gel state in acetonitrile.

Table S1. FT-IR data for **3** in the solid state, in solution, and in the gel state.[a]

Solvent and concerntration	Absorptions [cm^{-1}]		
	NH-stretch	Amide-I	Amide-II
$CHCl_3$, 5.1 mM (S)	3324	1617	1566
$CHCl_3$, 20.8 mM (S)[b]	3318	1613	1562
CH_2Cl_2, 20.8 mM (PG)	3321	1614	1565
CH_3CN, 20.8 mM (Gel)	3319	1615	1566
Solid state	3314	1615	1561

[a] All spectra are recorded at RT; [b] The sample will become partial gel after 1 week.

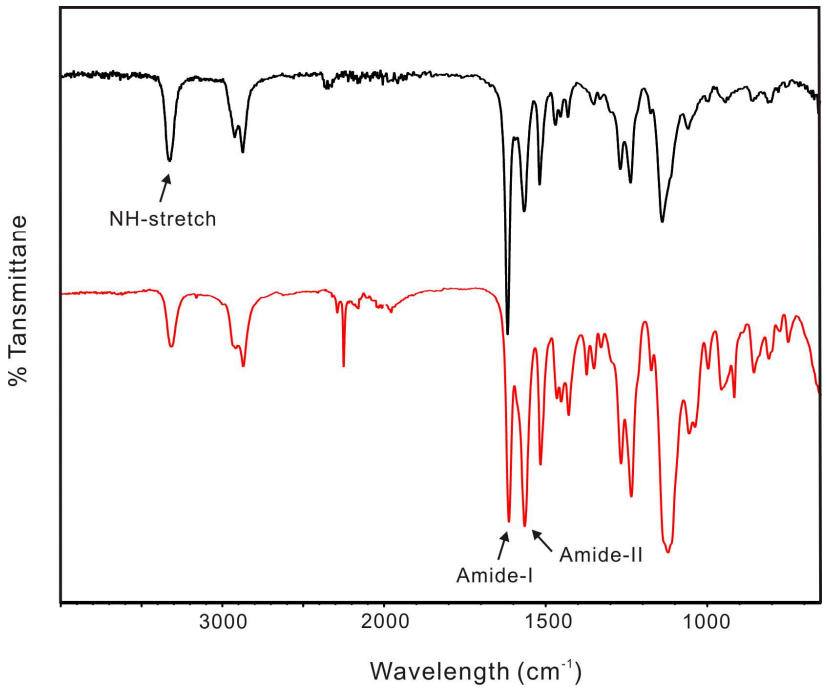


Figure S19. *FT-IR spectrum of* ***3*** *in $CHCl_3$ solution (5.1 mM, black line) and in CH_3CN in the gel state (20.8 mM, red line).*

4. Height and pitch profiles of isolated helical fibers of 3

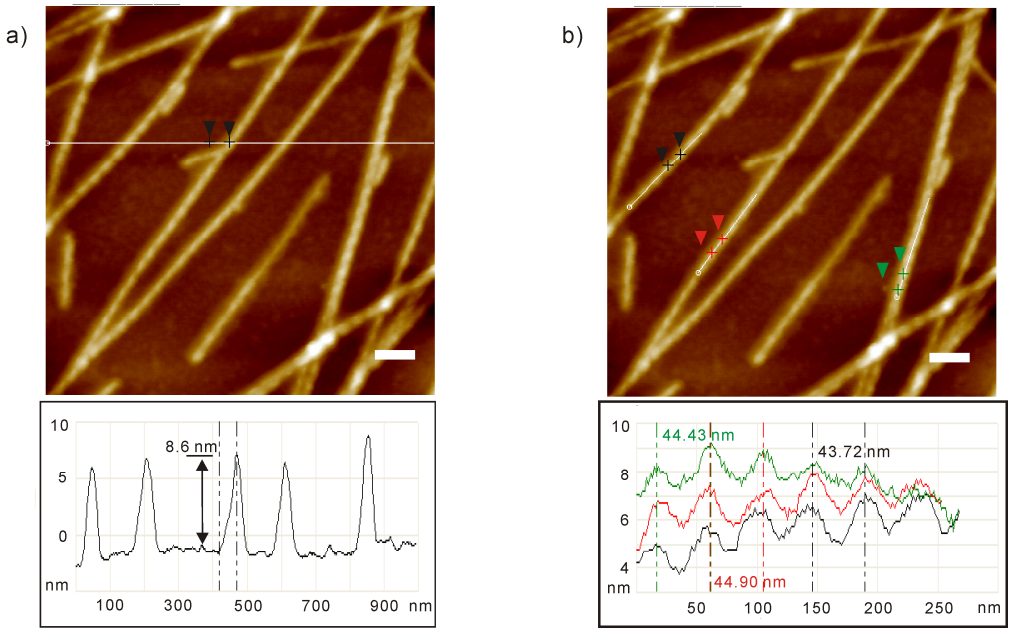


Figure S20. *AFM height analysis of the isolated fibers of* ***3****: a) the height profile; b) the pitch profile of the fibers. The scale bar is 100 nm.*

5. Gel-sol transition temperatures T_{gs}

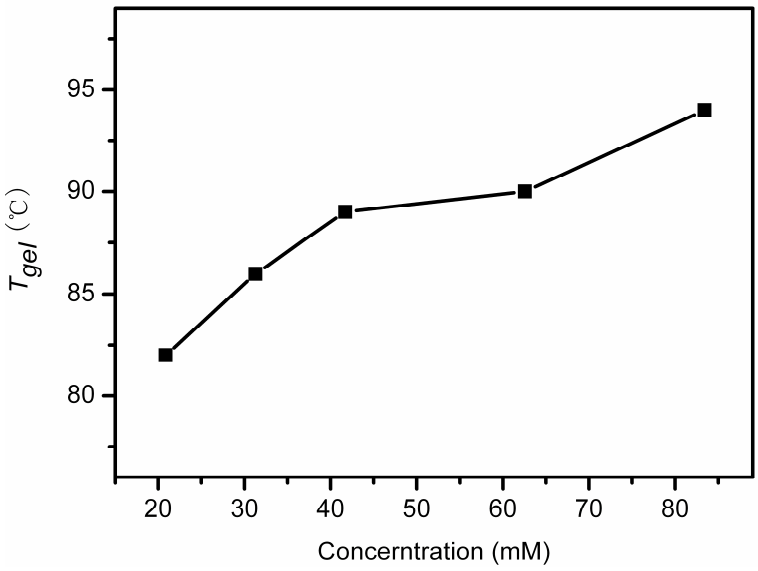


Figure S21. *Plot of T_{gs} versus concentration of* ***3*** *in acetonitrile.*

6. DSC measurement

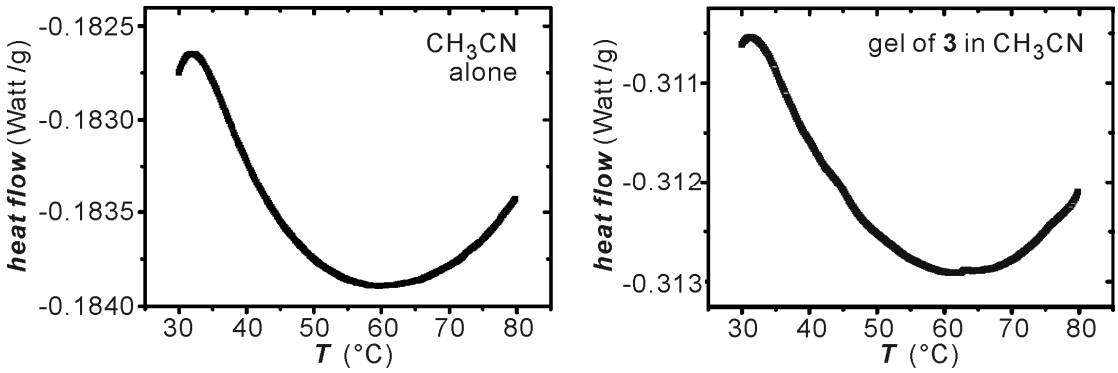


Figure S22. *DSC thermogram of (a) acetonitrile alone, (b) gelator* ***3*** *(20.8 mM in CD_3CN).*

7. Concentration-dependent ^{1}H NMR spectra of 3

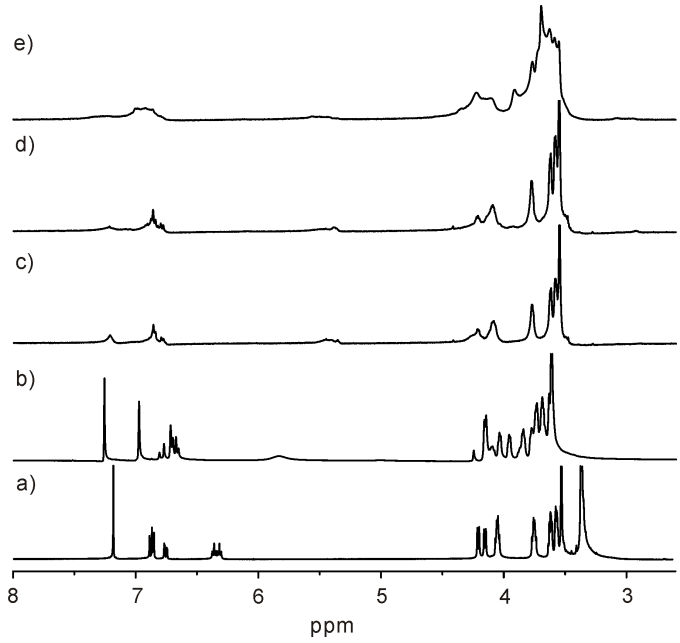


Figure S23. *Partial ^{1}H NMR spectra (500 MHz, 293 K) of* ***3*** *at a) 10.4 mM DMSO-d_6; b) 10.4 mM in $CDCl_3$; c) 2.6 mM, d) 5.2 mM, e) 10.4 mM in CD_3CN.*

The crown-bis(urea) **3** nicely dissolved in DMSO-d_6 upon warming the sample. It remained fully dissolved after cooling to room temperature as confirmed by well-resolved ^{1}H NMR peaks in spectrum (a). However, slight aggregation is observed in $CDCl_3$ as indicated by peak broadening in spectrum (b). From the concentration-dependent ^{1}H NMR spectra in CD_3CN (c-e), strong peak broadening was observed, when the concentration of **3** increased to more than 10.4 mM. Therefore, we fixed the concentration of **3** at 5.2 mM in CD_3CN for the following NMR measurements.

8. ^{1}H NMR spectral investigation of KPF_6 addition to 3

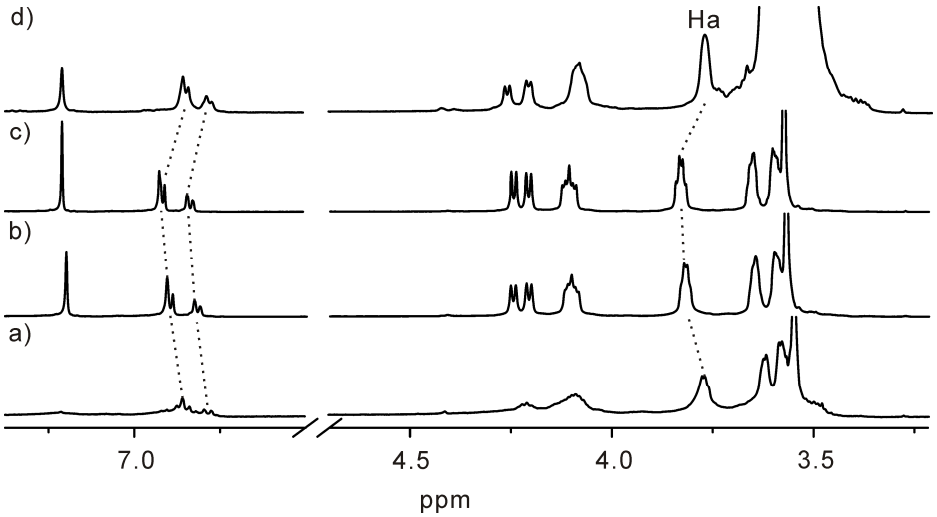


Figure S24. *Partial ^{1}H NMR spectra (500 MHz, CD_3CN, 298K) of a) 5.2 mM* ***3****, b) the mixture obtained after adding 1.0 eq. KPF_6, to solution (a), c) the mixture obtained after adding 1.0 eq. KPF_6 to the (b), d) the mixture obtained after adding 4.0 eq. of [2. 2. 2] cryptand to solution (c).*

9. Control experiment excluding PF_6^- as the trigger for the gel-sol transition

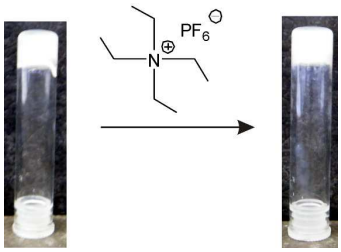


Figure S25. *Photographs of the gelator* ***3*** *(20.8 mM in CD_3CN) and the mixture obtained after adding 2.0 eq. tetraethylammonium hexafluorophosphate (NEt_4PF_6). The retained gel phase indicates the PF_6^- anion not to trigger the gel-sol transition.*

10. ^{1}H NMR spectral investigation of the addition of monovalent guest 5 to 3

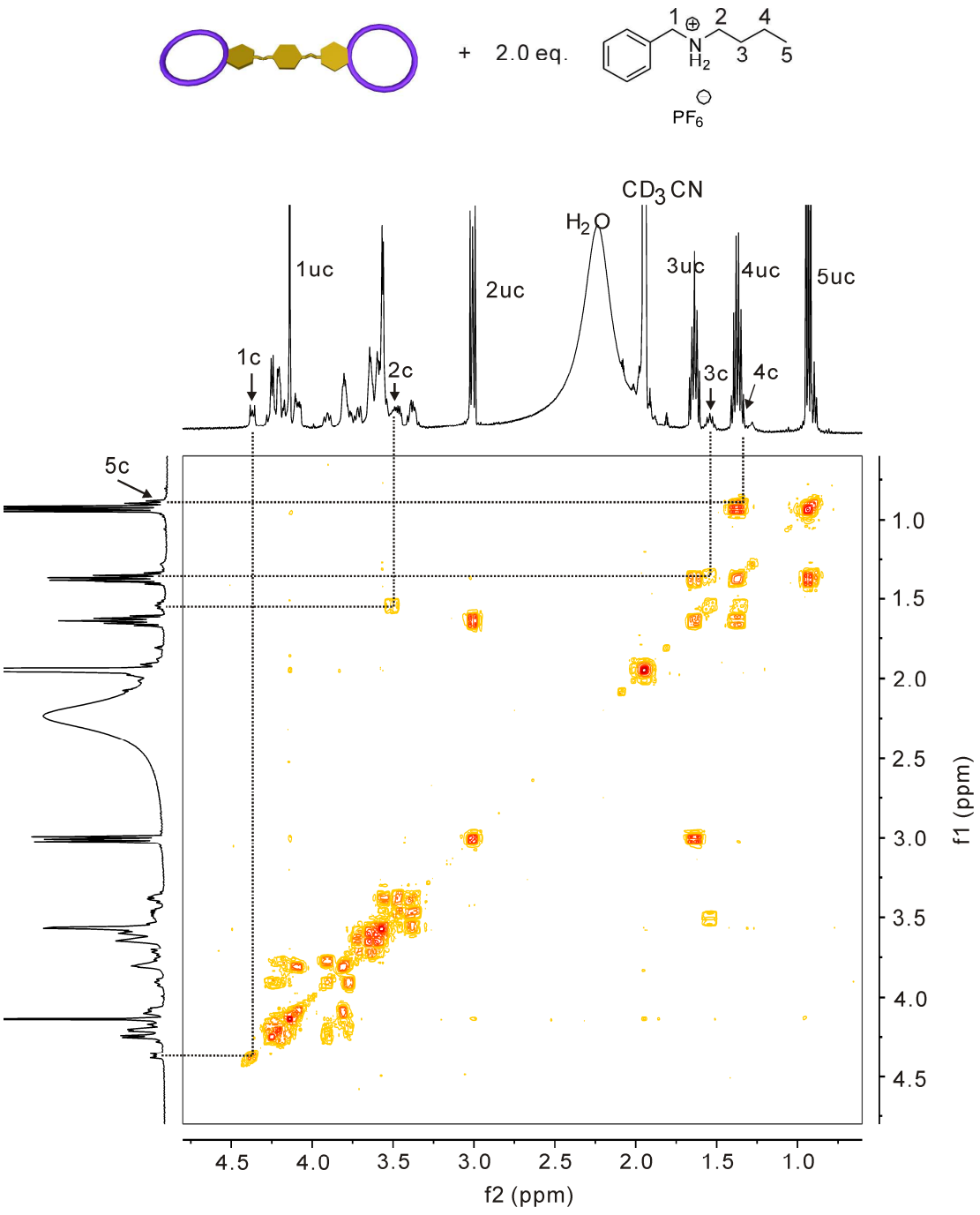


Figure S26. *^{1}H-^{1}H COSY NMR spectrum (500 MHz, 298 K, CD_3CN, 5.2 mM) of the 1:2 mixture of **3** and **5**. The protons are labeled with the number indicated above plus "c" for complexed" and "uc" for uncomplexed"*

11. ^{1}H NMR spectral investigation of the addition of divalent guest 6 to 3

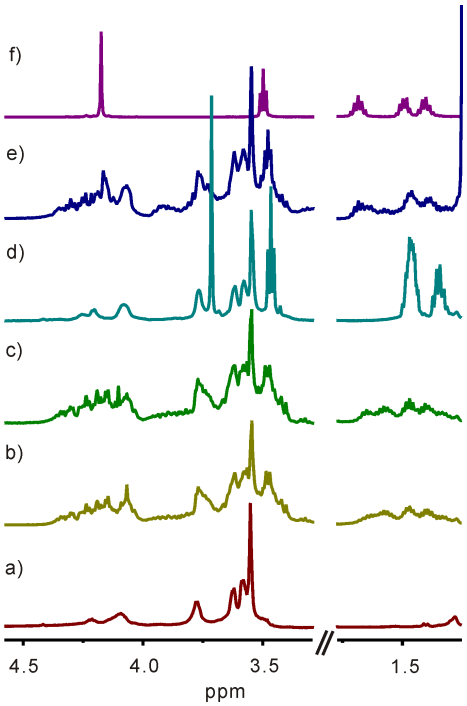


Figure S27. *Partial ^{1}H NMR spectra (500 MHz, CD_3CN, 298 K) of a) compound **3** (5 mM), b) the mixture obtained after adding **6** (0.5 eq.) to solution (a), c) the mixture obtained after adding **6** (0.5 eq.) to solution (b), d) the mixture obtained after addition of TEA (2.2 eq.) to solution (c), e) the mixture obtained after addition of TFA (2.0 eq.) to solution (d), and (f) compound **6** alone.*

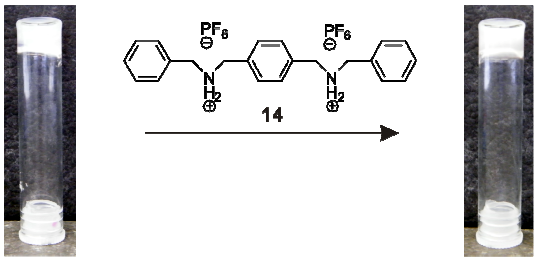


Figure S28. *Control experiment for divalent guest **6** supporting pseudorotaxane formation as the trigger for the gel-sol transition. Photographs of the gelator **3** (20.8 mM in CD_3CN) and the mixture obtained after adding 1.0 eq. divalent control guest **14**. Again, pseudorotaxane formation is required to break the gel.*

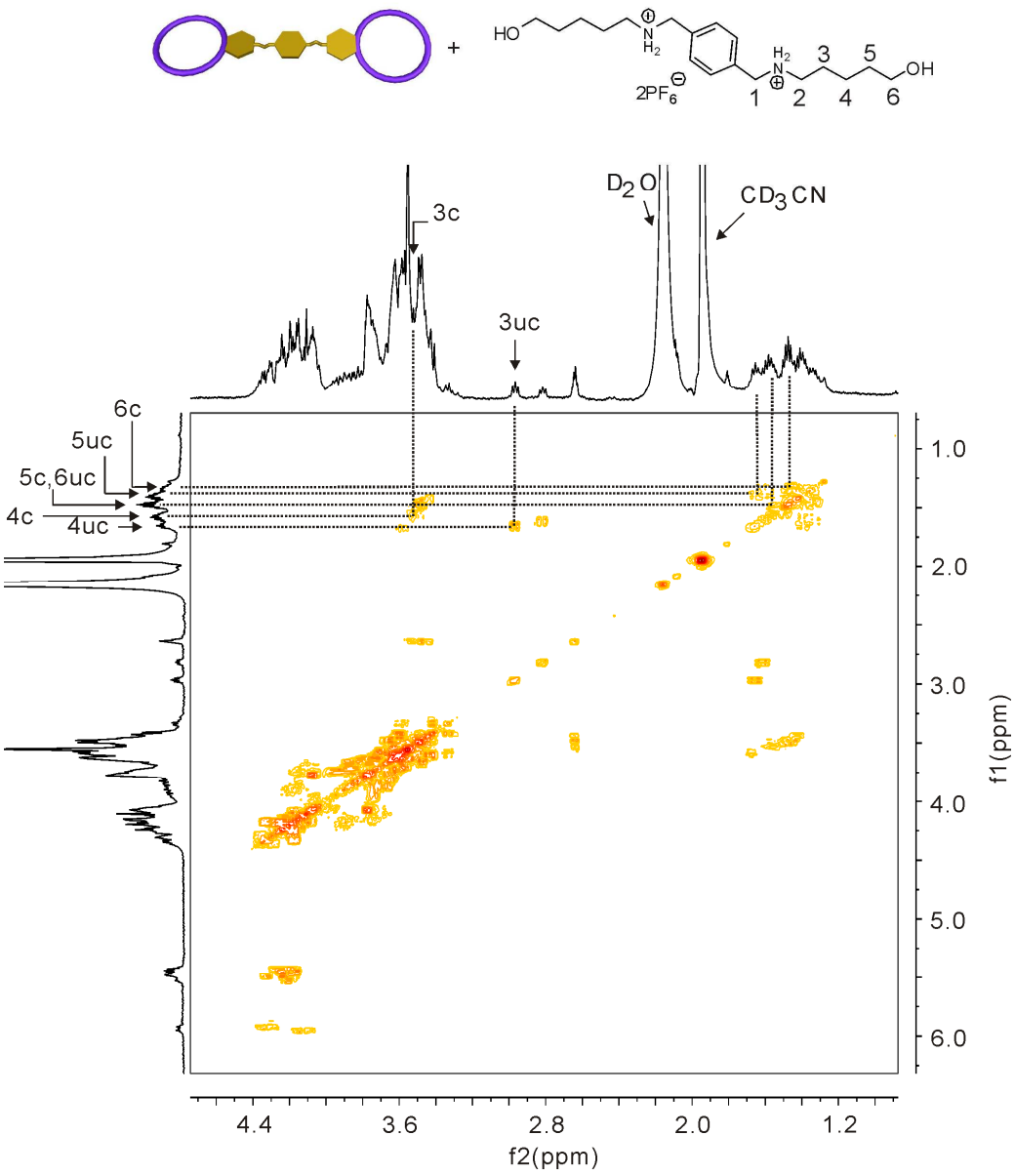


Figure S29. *^{1}H-^{1}H COSY NMR spectrum (500 MHz, 298 K, CD_3CN, 5.2 mM) of 1:1 of* ***3*** *and* ***6****. Peaks are labeled with their number indicated above and "c" for complexed or "uc" for uncomplexed cations.*

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