Supporting Information

Urea-based Macrocycle Selective for Sulfate and Structurally Sensitive to Water

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Table of Contents

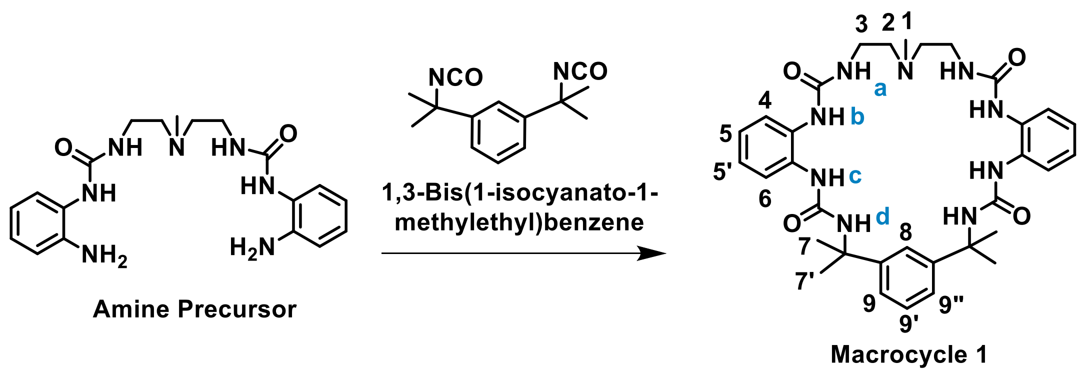
Experimental Procedures:

Reagents. All reagents, chemicals and deuterated solvents were purchased from commercial suppliers and used as such without further purification.

Instrumentation. All NMR spectra were recorded at 25°C and referenced according to the deuterated solvents. 1D ^{1}H NMRs spectra were recorded on Bruker AVIIIHD 400 and AVIII 500 MHz spectrometers. ^{13}C and 2D NMRs spectra were recorded in Avance AVIII 500 MHz spectrometer. HREIMS+ was recorded in Waters Micromass LCT Premier spectrometer.

NMR titration experiments. ^{1}H NMR titrations for macrocycles with anions (tetrabutylammonium salts) were conducted on Bruker 400 MHz spectrometer. Thr tetrabutylammonium (TBA) salt of SO_4^{2-} was purchased in a 50% H_2O solution (Sigma Aldrich) since sulfate dianion is not soluble in neat DMSO. A 5 mM solution of guest anions were titrated into 0.5 mL of 2 mM macrocyclic solution in 0.5% D_2O:DMSO-d_6 up to 20 spectra to examine anion binding. NMR titrations for $(TBA)_2SO_4$ were also recorded in DMSO-d_6 containing at 10, 25, and 50% D_2O. ^{1}H NMR titrations of a 1 mM macrocyclic solution with a 2.5 mM solution of $(TBA)_2SO_4$ in 0.5% D_2O:DMSO-d_6 to obtain a better binding curve and more accurate binding constant. Association constants, K for 1:1, K_1 and K_2 for 2:1 (host:anion), the latter when warranted, were obtained by fitting ^{1}H NMR titration data using the WinEQNMR software program.[1,2]

Synthesis and characterization of macrocycle 1:



To the solution of the amine precursor[3] (1.94 g, 5 mmol) in 400 mL anhydrous tetrahydrofuran (THF), 1,3-bis(1-isocyanato-1-methylethyl)benzene (1.15 mL, 5 mmol) in 200 mL THF were added through a dropping funnel within 1 hour. The reaction mixture was stirred at room temperature for 7 days. The solvent was removed by rotary evaporation followed by column chromatography on silica (230-400 mesh, gradient elution 40% v. CH_3OH in CH_2Cl_2) to isolate the product, which was recrystallized from ether to obtain the macrocycle **1** (0.8 g) in 25% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ_H = 7.84 (s, 2H, CONH_c), 7.72 (s, 2H, CONH_b), 7.54 (s, 1H, Ar), 7.46 (d, J = 10 Hz, 2H, Ar), 7.33 (d, J = 10 Hz, 2H, Ar), 7.24 (s, 3H, Ar), 6.97 (s, 2H, CONH_d), 6.92-6.87 (m, 4H, Ar), 6.14 (t, 2H, J = 5 Hz, CONH_a), 3.16 (q, J = 6.7 Hz, 4H, MeN$CH_2$$CH_2$), 2.44 (t, J = 7.5 Hz, 4H, MeN$CH_2$$CH_2$), 2.20 (s, 3H, N$CH_3$), 1.59 (s, 12H, C$CH_3$). ^{13}C NMR (125

MHz, DMSO-d_6) δ_c = 156.43 (C=O), 155.33 (C=O), 148.43, 133.25, 130.93, 127.97, 125.23, 124.31, 123.19, 122.96, 121.96, 57.33, 55.10, 42.42, 37.93, 30.43. Exact mass for [$C_{33}H_{43}N_9O_4$+H^+] = 630.3511, found (HREIMS+) 630.3344.

Crystallization Procedures

Crystallization of the macrocycle, 1·$CH_3CN·CH_3OH·H_2O$**:** 10 mg of **1** were added in MeOH:H_2O:ACN (1:1:2) followed by sonication under mild heat to dissolve completely. The clear solution was set up for slow evaporation at room temperature, and after 2 days single crystals suitable for X-ray crystallography were grown (CCDC No: 1974543).

Crystallization of [TBA^+][H**1**$^+$][SO_4^{2-}]**·**H_2O**:** 15 mg of **1** were first dissolved in 0.5 mL DMSO followed by addition of 0.5 mL H_2O, which resulted in a turbid solution. To this solution, excess $(TBA)_2SO_4$ was added to get the clear solution and set up for slow evaporation. After 4 weeks, single crystals suitable for X-ray crystallography developed (CCDC No: 1974544).

Crystallization of [TBA^+]$_2$[**1**]$_2$[$BPDC^{2-}$]**·**$2H_2O$**:** 10 mg of macrocycle **1** was added in 1 mL DMSO:H_2O (1:1) mixture followed by sonication under mild heating to get a turbid solution. To this, excess $(TBA)_2$BPDC (27 mg) was added, dissolved by sonication, and set for slow evaporation at room temperature. Single crystals suitable for X-ray crystallography were obtained after 1 week (CCDC No: 1974545).

Crystallization of [TMA^+][**1**][Cl^-]**·**$0.5H_2O$**:** To the turbid solution of macrocycle **1** (8 mg) in 0.5 mL DCM:MeOH (1:1), excess TMACl (10 mg) was added. The solution cleared and was kept for slow evaporation. Crystals suitable for X-ray crystallography were obtained after 3 days (CCDC No: 1974551).

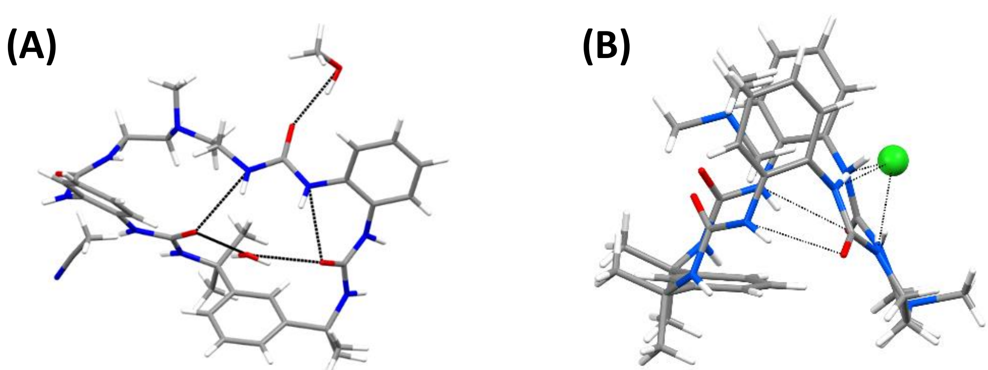
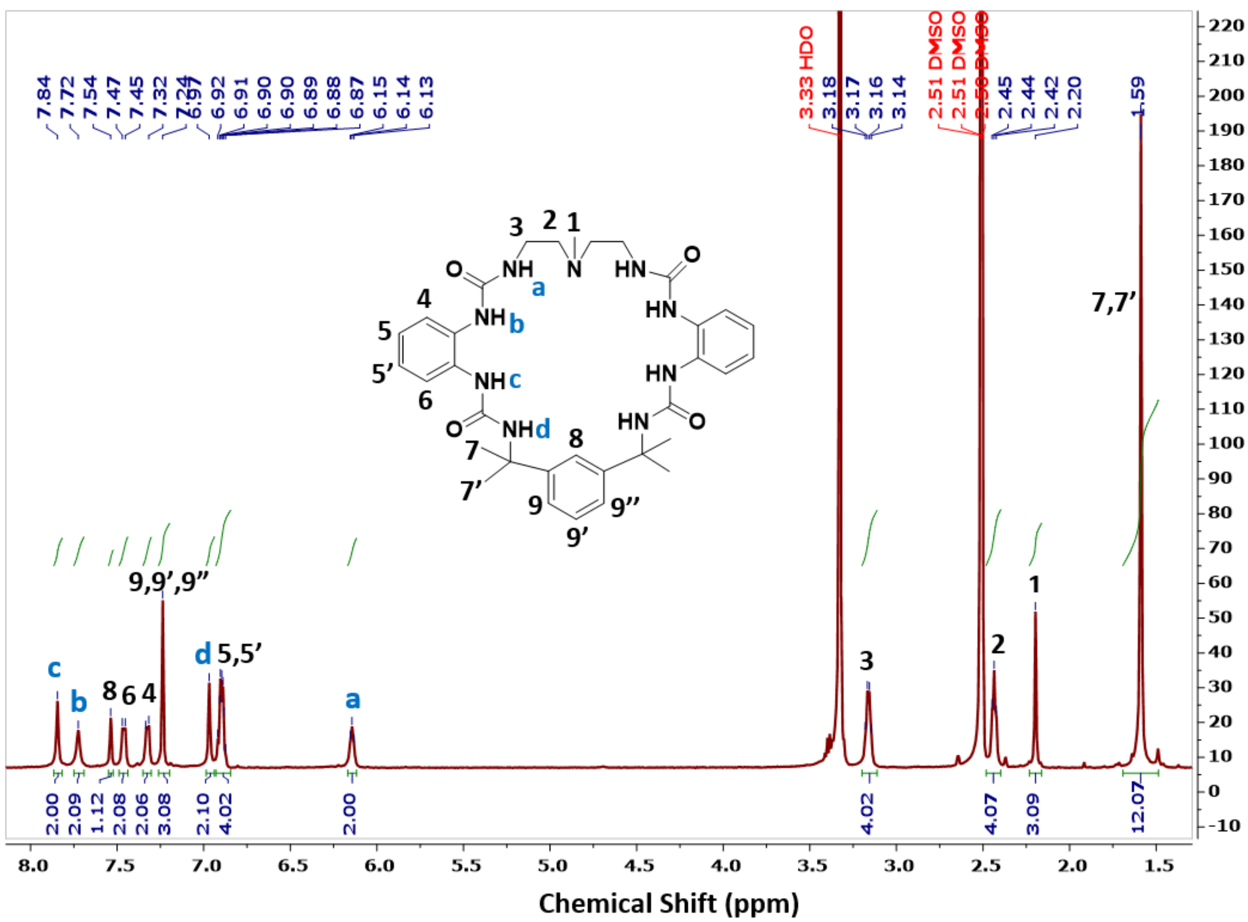


Figure S1. Perspective views of the structures of (A) macrocycle **1** with solvent molecules and (B) side view of the (TMA)Cl complex with **1**.

(A)



(B)

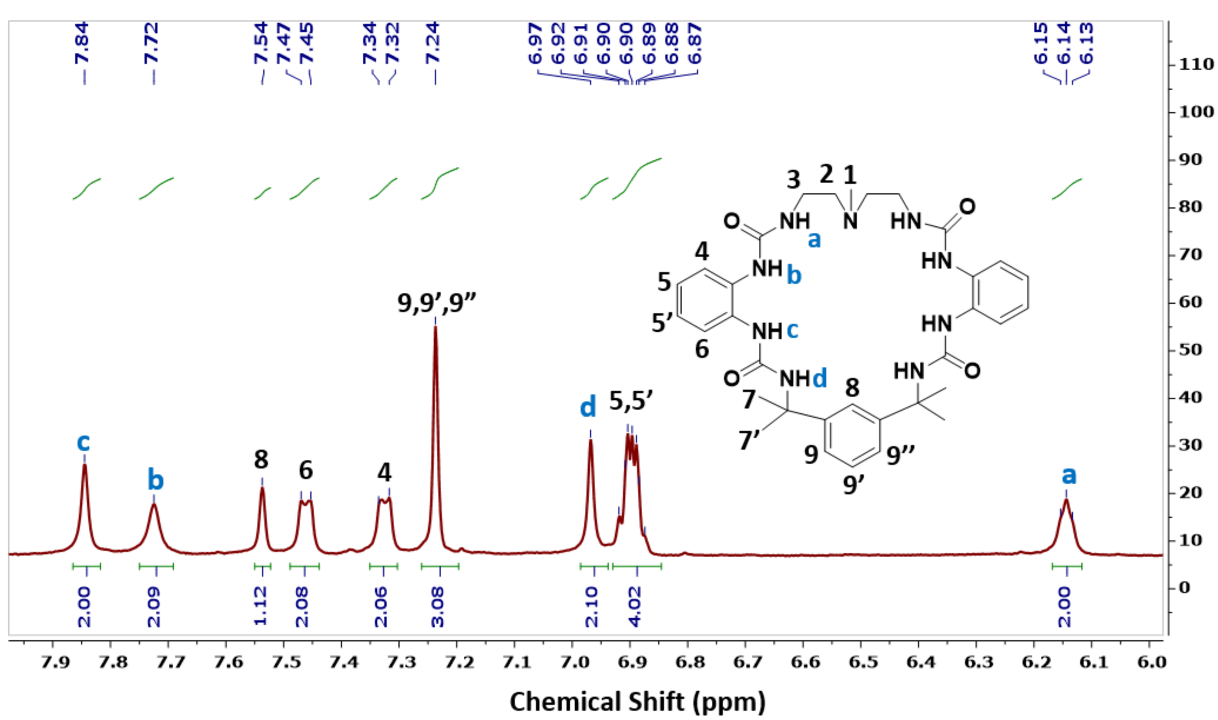


Figure S2. (A) Full and **(B)** expanded [1]H NMR (500 MHz, DMSO-d_6) of macrocycle **1**.

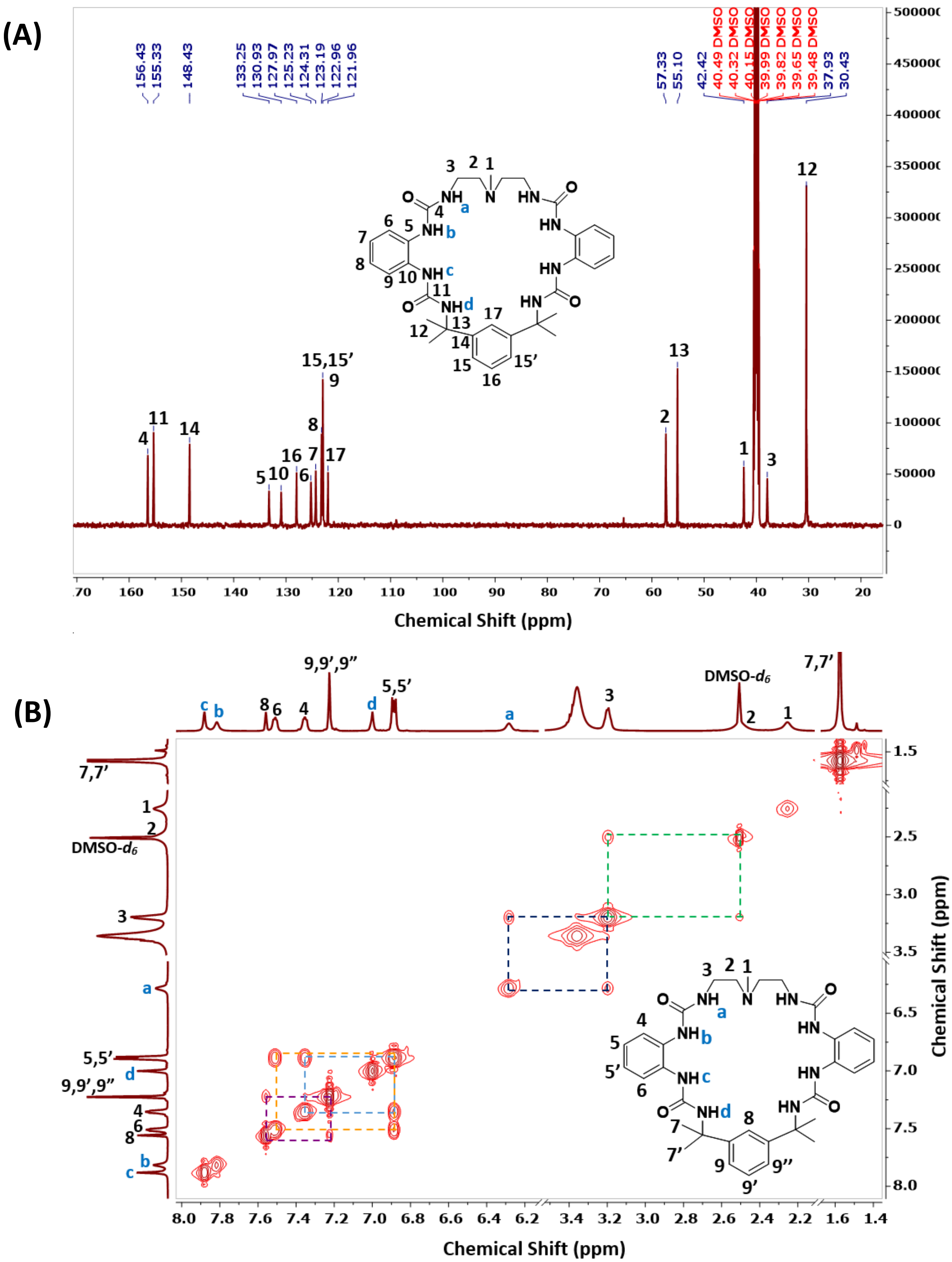


Figure S3. (A) ^{13}C (125 MHz, DMSO-d_6) and **(B)** ^{1}H-^{1}H COSY NMR spectrum (500 MHz, DMSO-d_6) of macrocycle **1**.

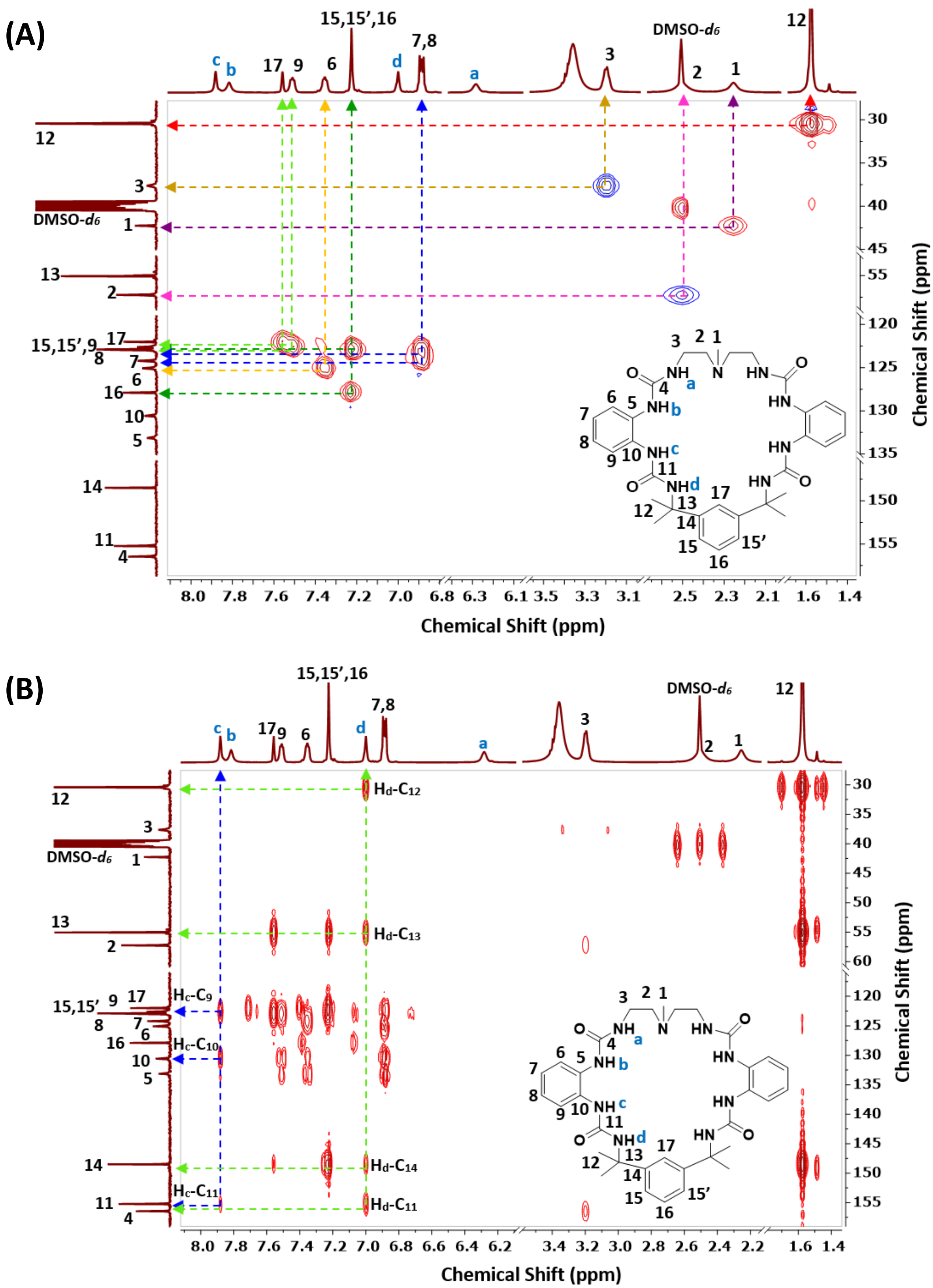


Figure S4. (A) ^{1}H-^{13}C HSQC and **(B)** ^{1}H-^{13}C HMBC NMR spectrum (500 MHz, DMSO-d_6) of macrocycle **1**.

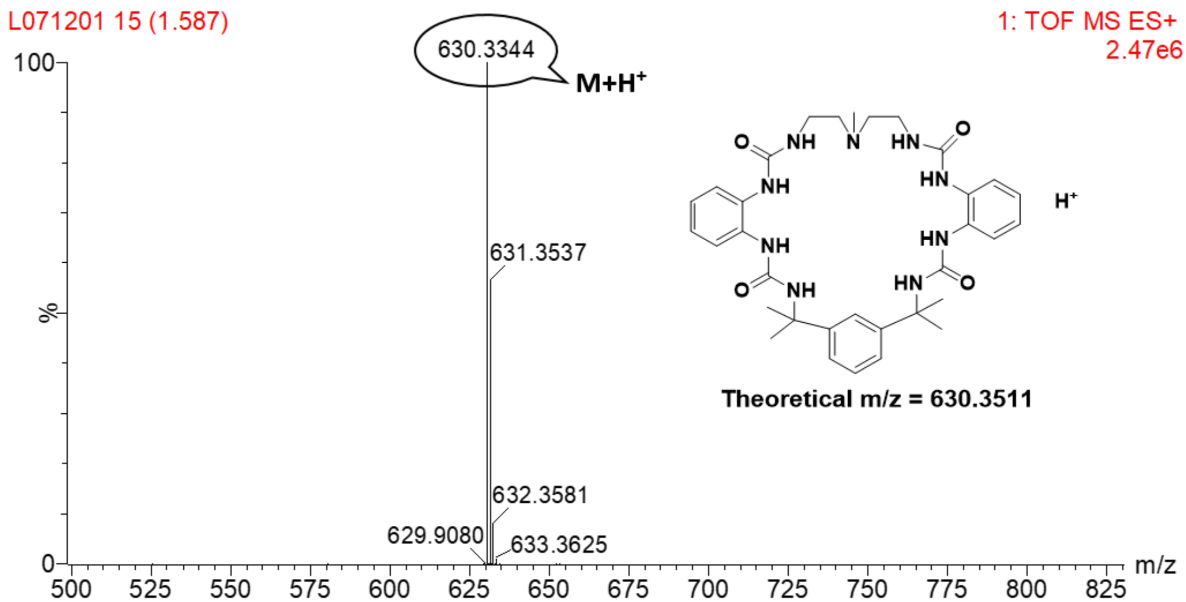
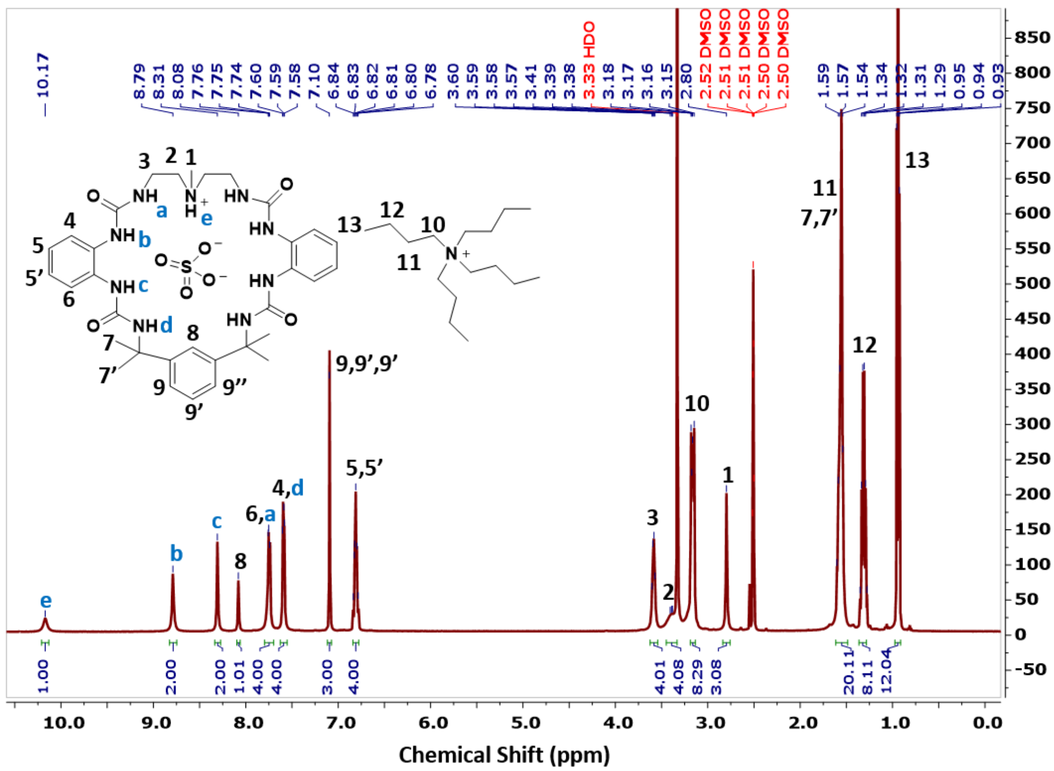


Figure S5. ESI-MS spectrum of macrocycle **1**.

(A)



(B)

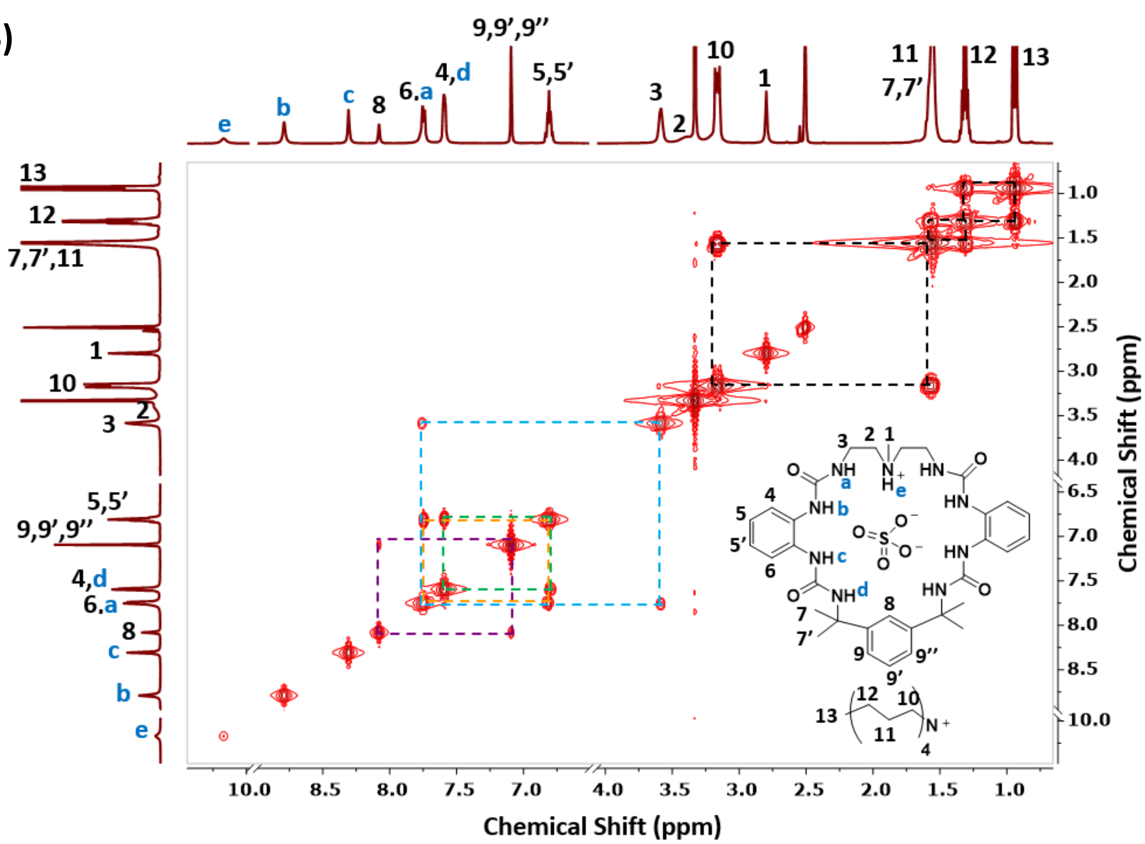
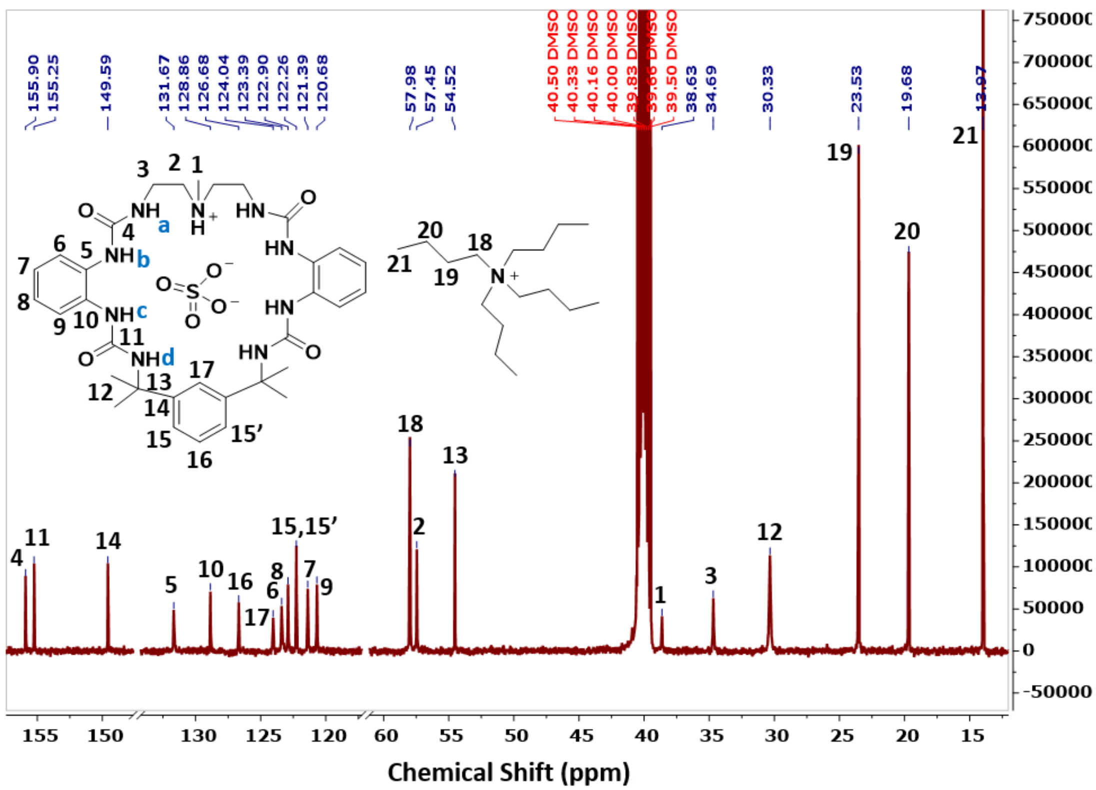


Figure S6. (**A**) ^{1}H NMR and (**B**) ^{1}H-^{1}H COSY spectrum of $[TBA^{+}][H\mathbf{1}^{+}][SO_4^{2-}]$ crystals (500 MHz, DMSO-d_6).

(A)



(B)

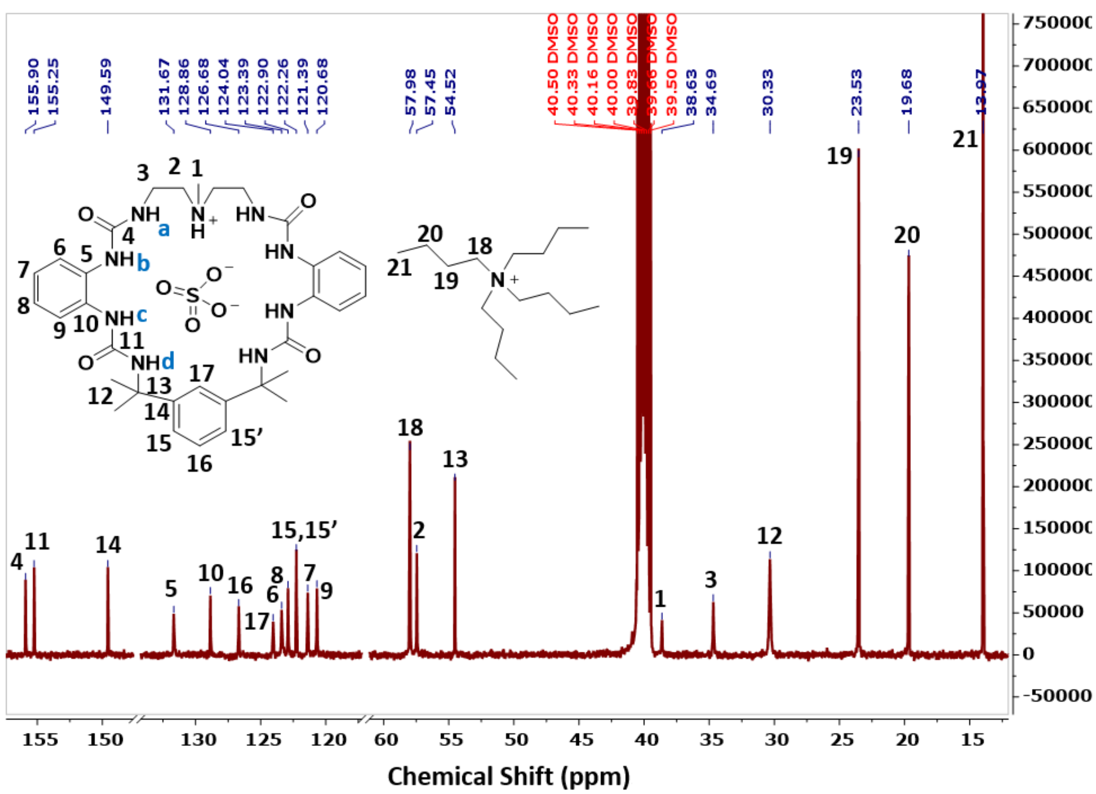


Figure S7. (**A**) ^{13}C NMR and (**B**) ^{1}H-^{13}C HSQC spectrum of [TBA^{+}][H**1**$^{+}$][SO_4^{2-}] crystals (500 MHz, DMSO-d_6).

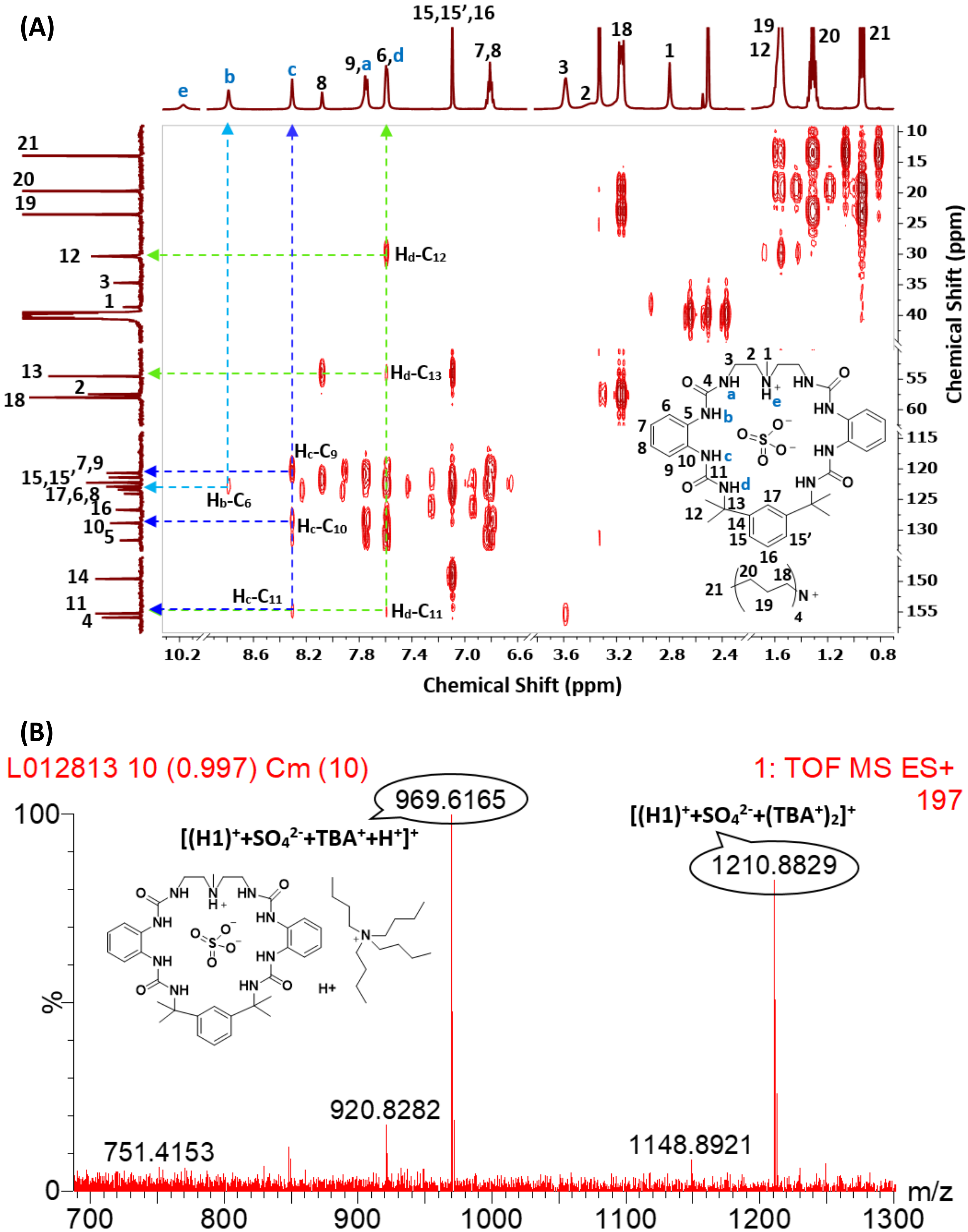


Figure S8. (**A**) ^{1}H-^{13}C HMBC NMR of [TBA$^+$][H**1**$^+$][SO_4^{2-}] crystals in DMSO-d_6 at 500 MHz and (**B**) ESI-MS spectrum.

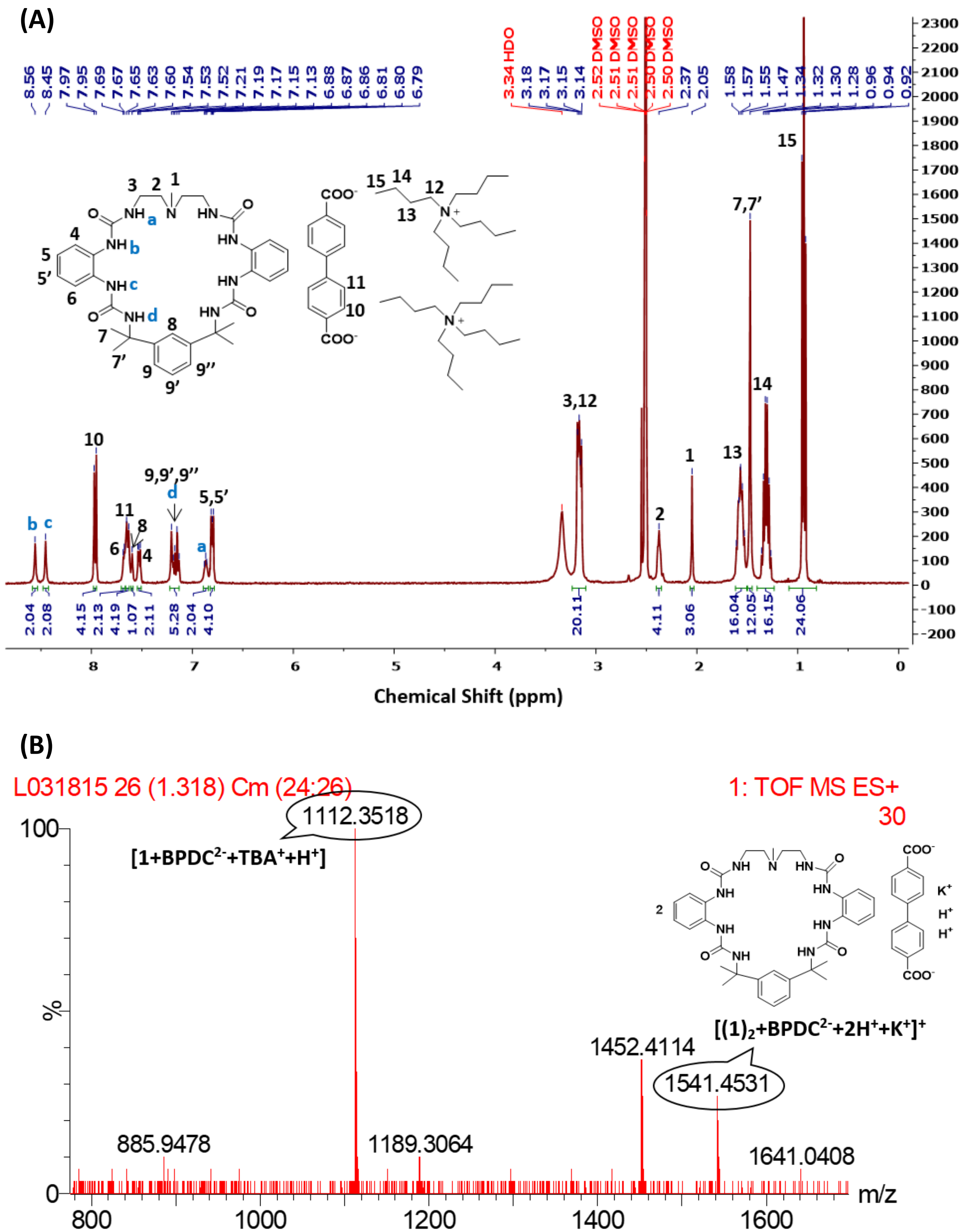


Figure S9. (**A**) ^{1}H NMR of $[TBA^+]_2[\mathbf{1}]_2[BPDC^{2-}]$ crystals in DMSO-d_6 and (**B**) ESI-MS spectrum.

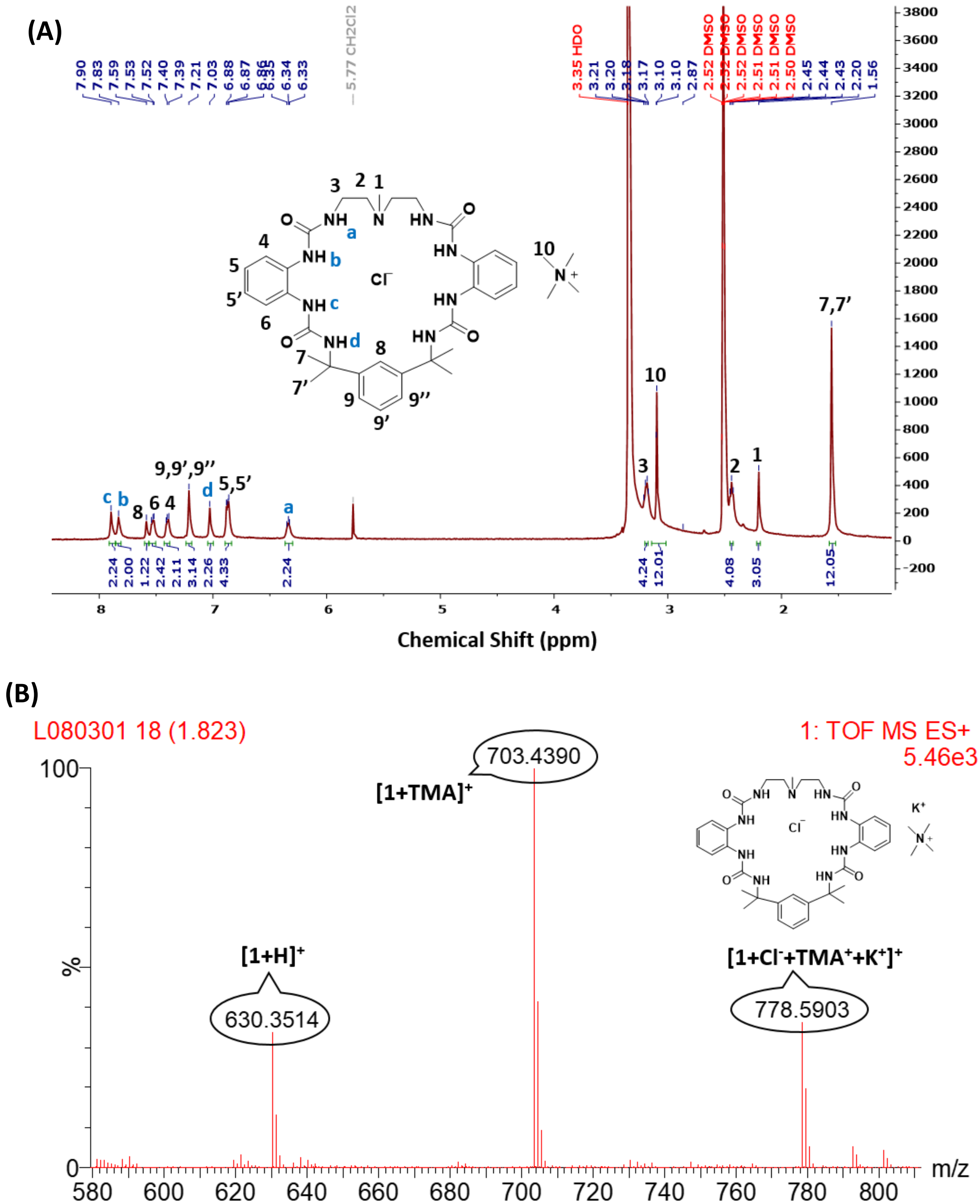


Figure S10. (**A**) ^{1}H NMR of [TMA$^+$][**1**][Cl$^-$] crystals in DMSO-d_6 and (**B**) ESI-MS spectrum.

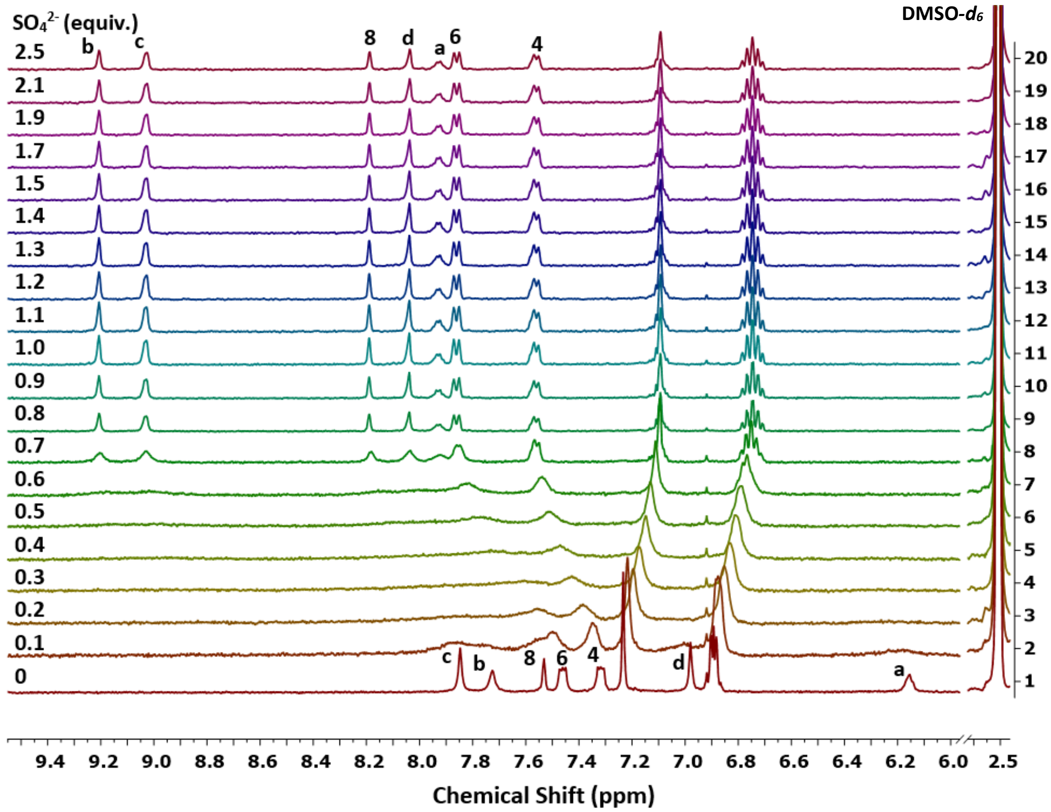


Figure S11. Quantitative ^{1}H NMR titration of macrocycle **1** (2mM) with $(TBA)_2(SO_4)$ (5mM) (400 MHz, 298 K, 0.5% D_2O:DMSO-d_6 mixture).

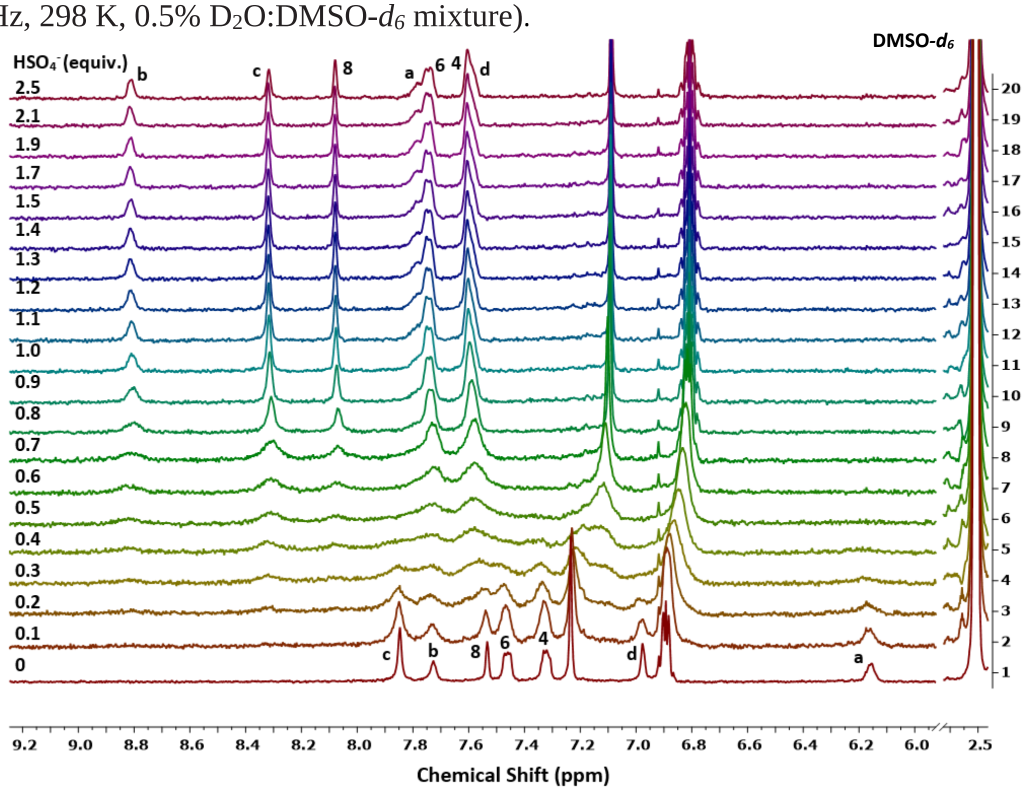


Figure S12. Quantitative ^{1}H NMR titration of macrocycle **1** (2mM) with $(TBA)(HSO_4)$ (5mM) (400 MHz, 298 K, 0.5% D_2O:DMSO-d_6 mixture).

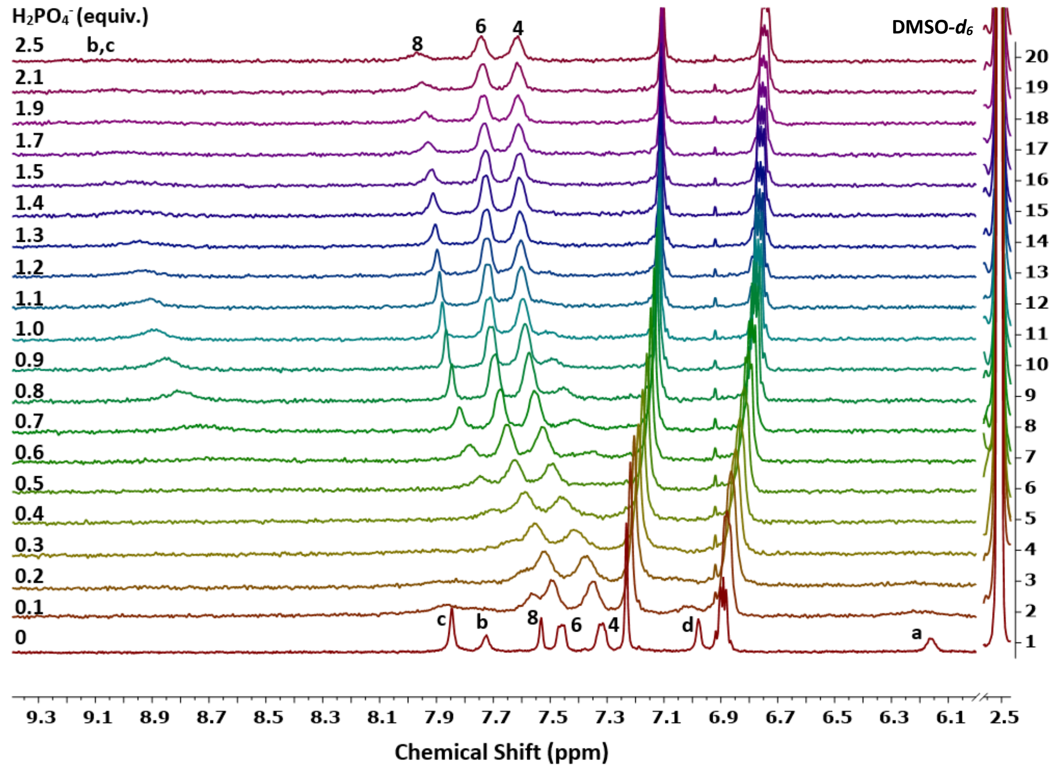


Figure S13. Quantitative ^{1}H NMR titration of macrocycle **1** (2mM) with (TBA)(H_2PO_4) (5mM) (400 MHz, 298 K, 0.5% D_2O:DMSO-d_6 mixture).

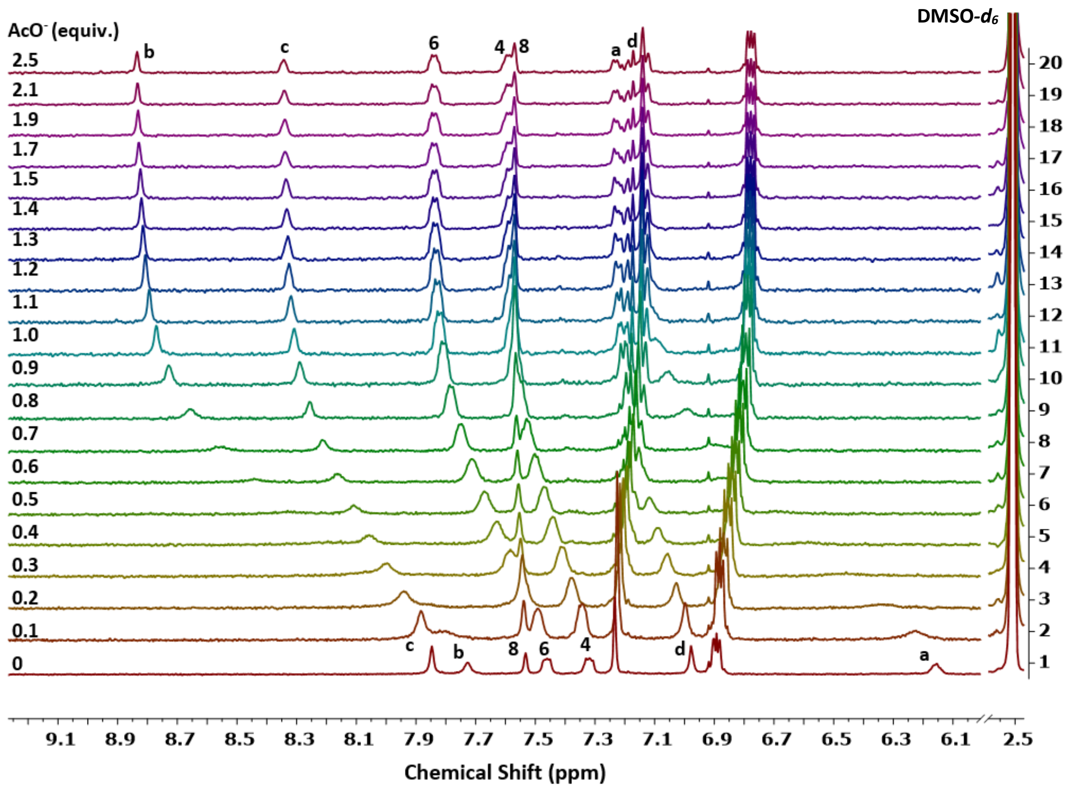


Figure S14. Quantitative ^{1}H NMR titration of macrocycle **1** (2mM) with (TBA)(OAc) (5mM) (400 MHz, 298 K, 0.5% D_2O:DMSO-d_6 mixture).

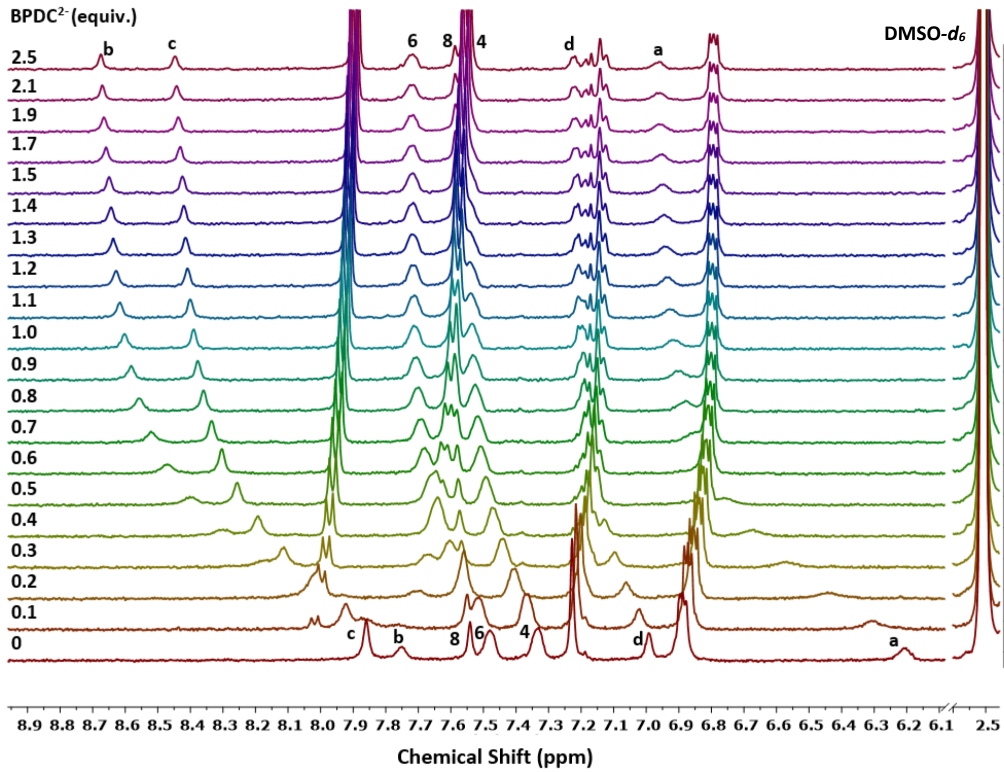


Figure S15. Quantitative ^{1}H NMR titration of macrocycle **1** (2mM) with $(TBA)_2(BPDC)$ (5mM) (400 MHz, 298 K, 0.5% D_2O:DMSO-d_6 mixture).

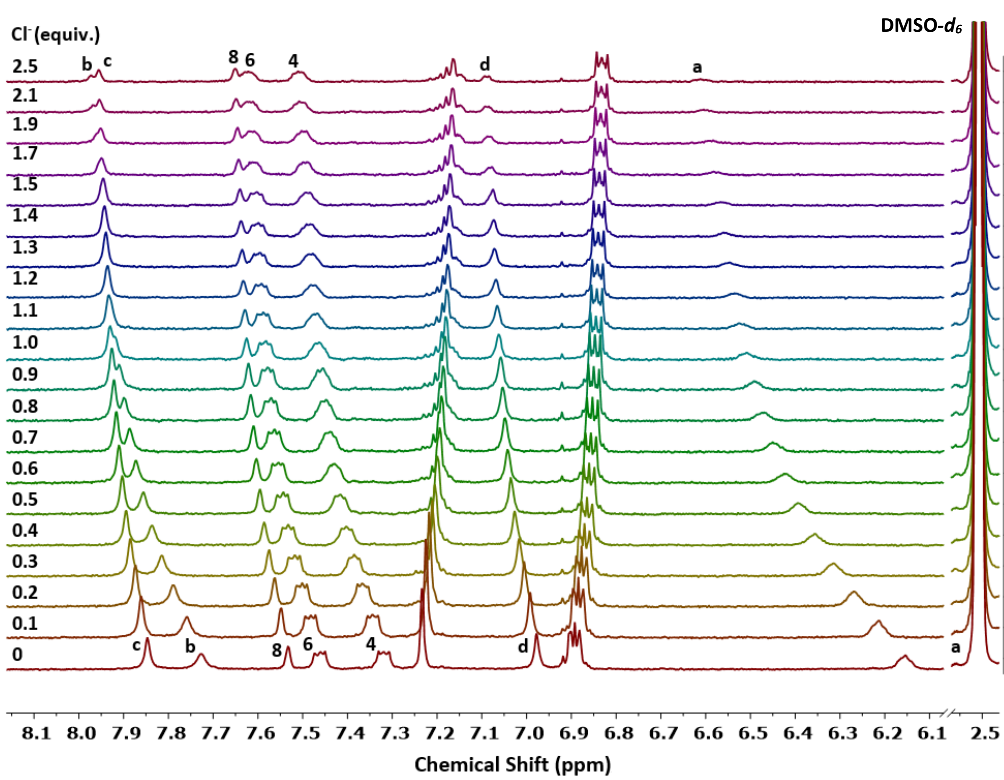


Figure S16. Quantitative ^{1}H NMR titration of macrocycle **1** (2mM) with (TBA)(Cl) (5mM) (400 MHz, 298 K, 0.5% D_2O:DMSO-d_6 mixture).

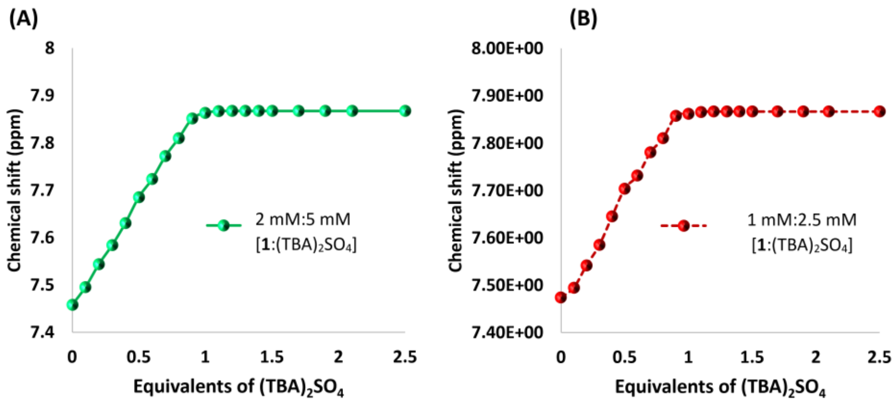


Figure S17. Chemical shift changes of the phenyl proton (C*H*$_6$) in **1** upon addition of $(TBA)_2SO_4$ in 0.5% D_2O:DMSO-d_6 at different concentrations (**A**) 2 mM of **1** with 5 mM $(TBA)_2SO_4$ and (**B**) 1 mM of **1** with 2.5 mM $(TBA)_2SO_4$.

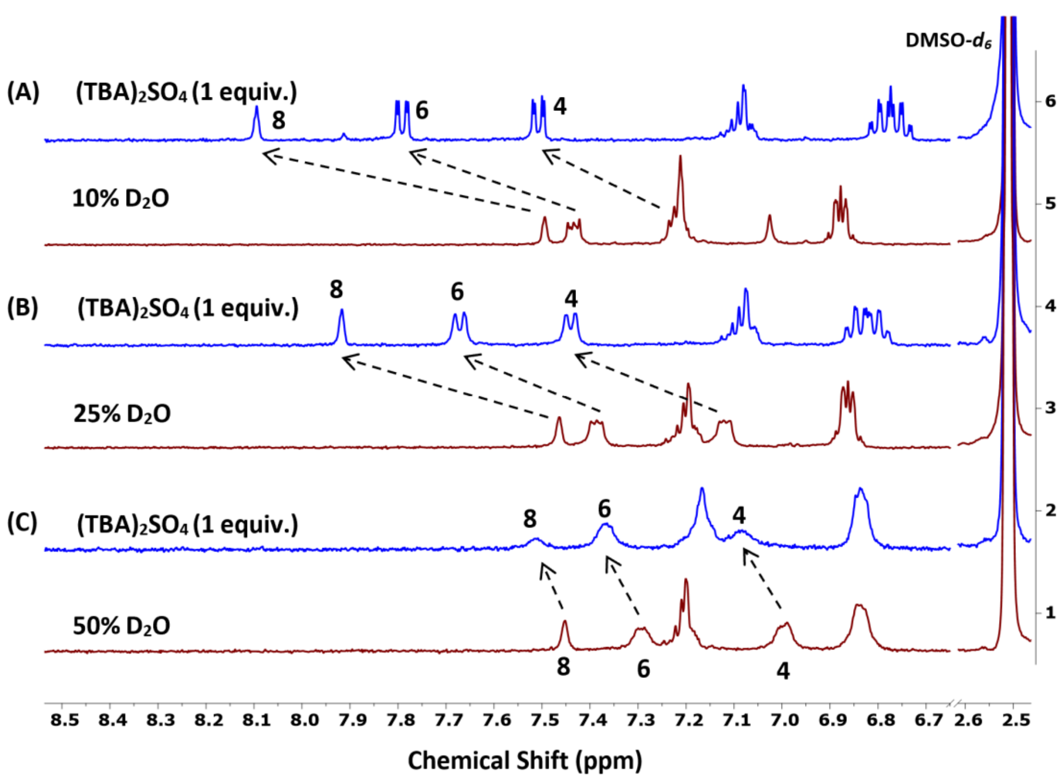


Figure S18. ^{1}H NMR spectra of macrocycle **1**, and **1** plus one equiv. $(TBA)_2SO_4$ in different D_2O:DMSO-d_6 mixtures (v/v) (**A**) 10% (**B**) 25%, and (**C**) 50% D_2O (400 MHz, 298 K).

DOSY diffusion experiment to determine solution complexation:

DOSY NMRs were recorded on a Bruker Avance AVIII 600 MHz NMR at 298 K and data were analyzed using MestreLab Mnova software. For DOSY NMR analysis of sandwich complex, **1**:[$(TBA)_2(SO_4^{2-})$] were prepared at different DMSO-*d*6:D_2O in 9.5:0.5, 9:1 and 7.5:2.5 ratios. Sample volumes were 500 μL and the concentration of all samples were 10 mM. Diffusion coefficients and hydrodynamic radii are correlated theoretically by the Stokes-Einstein relation:

$\boldsymbol{r_s = kT/(6\pi\eta D)}$ where

D is the diffusion coefficient,

k is the Boltzmann constant (1.38×10^{-23} m^2 kg s^{-2} K^{-1}),

T is the temperature in Kelvin (298K),

η is the viscosity of the solution,

η (DMSO-d_6) = 1.99×10^{-3} kg m^{-1} s^{-1},[4]

η (DMSO-d_6:D_2O, 9:1) = 2.70×10^{-3} kg m^{-1} s^{-1},[4]

η (DMSO-d_6:D_2O, 7.5:2.5) = 3.68×10^{-3} kg m^{-1} s^{-1},[4]

r_s is the hydrodynamic radius of molecular sphere, $2\times r_s$ is the hydrodynamic diameter.

Results are provided in Table S2 and spectral data Figure S19.

Table S2. DOSY results for solution sizes of **1**:[$(TBA)_2(SO_4^{2-})$] complexes in DMSO-d_6 with different D_2O percentages.

% D_2O	**Diffusion D ($\times10^{-6}$ cm^2 s^{-1})**	**r_s (Å)**	**DOSY Diameter (Å)**
0.5	2.07±0.1	5.30	10.60
10	1.30±0.2	6.22	12.44
25	0.96±0.2	6.17	12.35

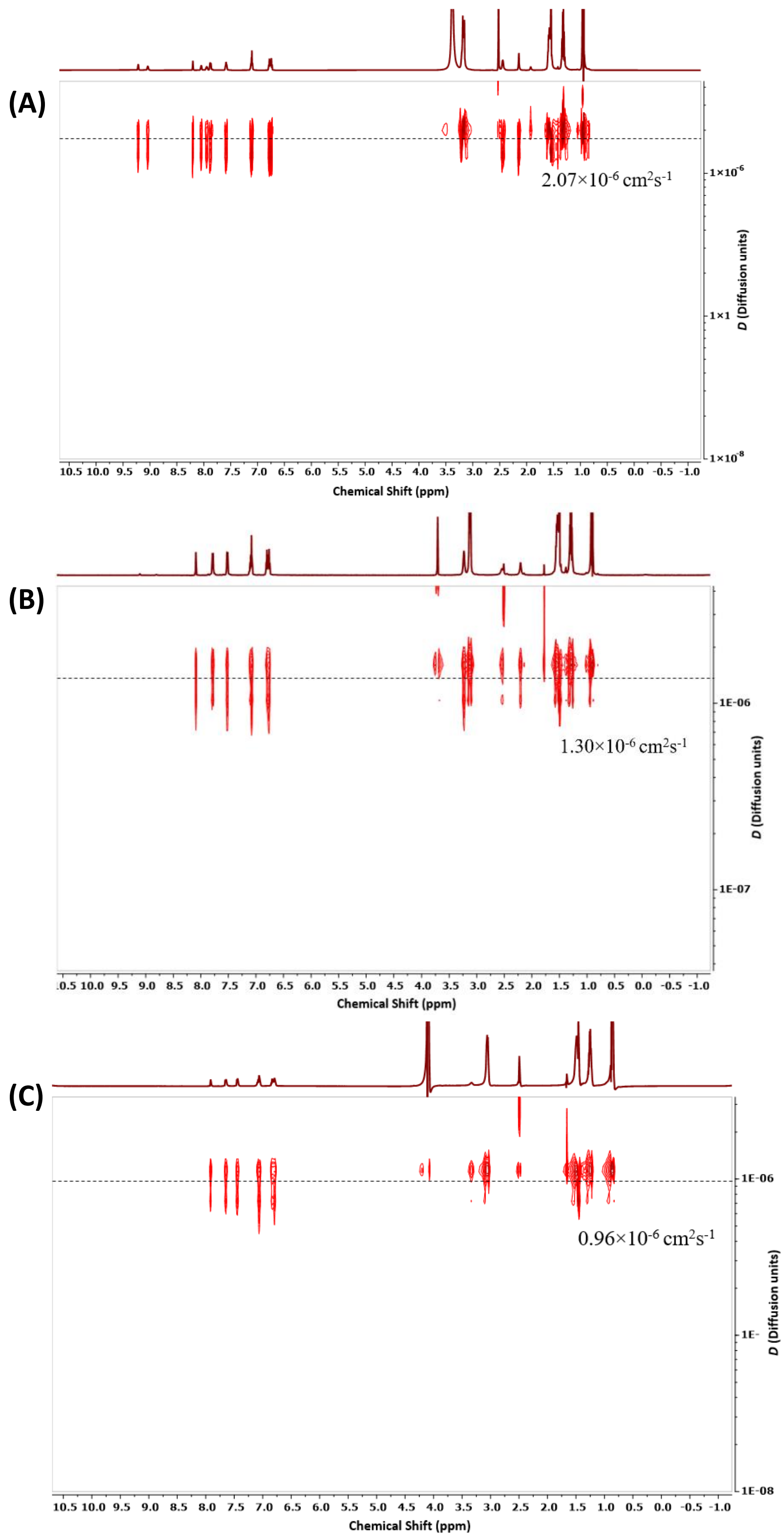


Figure S19. 2D DOSY NMR spectra of **1**:$(TBA)_2SO_4$ at different D_2O:DMSO-d_6 concentration (A) 0.5:9.5, (B) 1:9 and (C) 2.5:7.5 ratio.

X-ray Crystallographic Studies for (A) 1·CH_3CN·CH_3OH·H_2O, (B) [TBA^+][$H1^+$][SO_4^{2-}]·H_2O, (C) [TBA^+]$_2$[1]$_2$[$BPDC^{2-}$]·2H_2O, (D) [TMA^+][1][Cl^-]·0.5H_2O.

Complete sets of unique reflections were collected with monochromated CuKα radiation for single-domain crystals of all four compounds. Totals of 1314(**A**), 2102(**B**), 3886(**C**) and 2772(**D**) 1.0°-wide ω- or ϕ-scan frames with counting times of 4-6 seconds (**A**), 8-30 seconds (**B** and **C**) and 6-12 seconds (**D**) were collected on a Bruker APEX II (**A**) or Platinum 135 (**B, C** and **D**) CCD area detector. X-rays were provided by a Bruker MicroStar microfocus rotating anode operating at 45kV and 60 mA and equipped with Helios high-brilliance multilayer x-ray optics. Preliminary lattice constants were obtained with the Bruker program SMART.[5] Integrated reflection intensities for all four compounds were produced using the Bruker program SAINT.[6] Each data set was corrected empirically for variable absorption effects using equivalent reflections. The Bruker software package SHELXTL was used to solve each structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL v2014 software package.[7]

The final structural model for each compound incorporated anisotropic thermal parameters for all nonhydrogen atoms except the acetonitrile solvent molecule of crystallization present in **A**; isotropic thermal parameters were used for all included hydrogen atoms and the nonhydrogen atoms for the acetonitrile solvent molecule of crystallization present in **A**. The urea hydrogen atoms in all four structures (except H4N in **B**) were located in a difference Fourier and those for **A**, **B** and **C** were included in the structural model as independent isotropic atoms whose parameters were allowed to refine in least-squares refinement cycles. The urea hydrogen atoms for **D** were eventually fixed at idealized sp^2-hybridized riding model positions with a N-H distance of 0.88 Å and their isotropic thermal parameters were allowed to vary. The hydrogens on the water molecule (H1W1 and H1W2) in **A**, the methanol –OH (H1OS) in **A**, the amine proton (H1N) in **B** and both water protons (H1W1 and H1W2) in **C** were also located in a difference Fourier and refined as independent isotropic atoms. The remaining non-methyl hydrogen atoms in each structure (except water hydrogen atom H1W1 in **B** that was fixed at a calculated position from hydrogen bonding considerations) were fixed at idealized riding model sp^2- or sp^3-hybridized positions with C-H bond lengths of 0.95 - 0.99 Å. Methyl groups in all four structures were incorporated into their structural models as idealized sp^3-hybridized rigid rotors (with a C-H bond length of 0.98 Å) that were allowed to rotate freely about their C-C or N-C bonds in least-squares refinement cycles (**A**, **B** and **C**) or fixed at idealized "staggered" positions (**D**).The isotropic thermal parameters of idealized hydrogen atoms bonded to carbon in all four structures were fixed at values 1.2 (non-methyl) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded. The relevant crystallographic and structure refinement data for all four compounds are given in Table S3.

The carboxylate group in **C** is (80/20) rotationally-disordered about the C51-C52 bond, having two different hydrogen-bonded interactions with the macrocycle. The atoms bonded to amine nitrogen atom N1 in **D** initially refined to give a highly distorted geometry at N1. The C-N bond lengths and C-N-C bond angles were therefore restrained to have values that were appropriate sp^3-hybridized multiples of the C-N bond length that was included as a free variable in the least-squares refinement and refined to a final value of 1.436(9) Å. Mild restraints were applied to the anisotropic thermal parameters of C37 in **D**. The lone water molecule in the asymmetric unit of **D** (O1W) is only present 50% of the time and positions could not be calculated for its hydrogen atoms based on hydrogen-bonding considerations. This might be due to loss of additional solvent molecules of crystallization as indicated by a CheckCif A-alert specifying solvent VOIDS of 400 $Å^3$.

CCDC: 1974543 (**A**), 1974544 (**B**), 1974545 (**C**) and 1974551 (**D**)

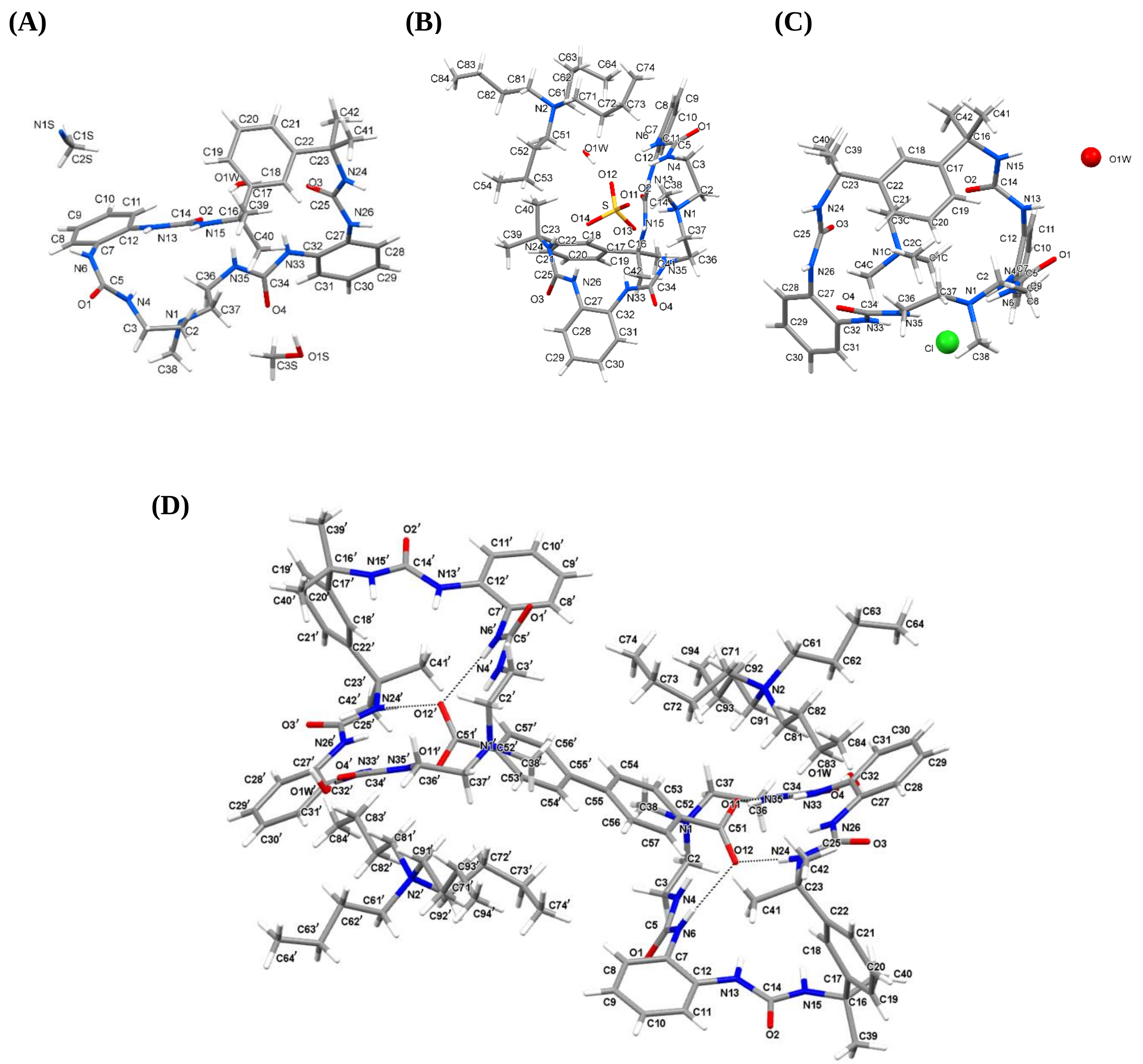


Figure S20. Perspective view with labelled plot of (A) macrocycle **1**$\cdot CH_3CN\cdot CH_3OH\cdot H_2O$, (B) $[TBA^+][H\mathbf{1}^+][SO_4^{2-}]\cdot H_2O$, (C) $[TMA^+][\mathbf{1}][Cl^-]\cdot 0.5H_2O$, and (D) $[TBA^+]_2[\mathbf{1}]_2[BPDC^{2-}]\cdot 2H_2O$.

Table S3. Crystal Data and Structure Refinement for (**A**) macrocycle **1**$\cdot CH_3CN\cdot CH_3OH\cdot H_2O$, (**B**) $[TBA^+][H1^+][SO_4^{2-}]\cdot H_2O$, (**C**) $[TBA^+]_2[$**1**$]_2[BPDC^{2-}]\cdot 2H_2O$, (**D**) $[TMA^+][$**1**$][Cl^-]\cdot 0.5H_2O$.

Content	**A**	**B**	**C**	**D**
Empirical formula	$C_{36}H_{52}N_{10}O_6$	$C_{49}H_{81}N_{10}O_9S$	$C_{112}H_{170}N_{20}O_{14}$	$C_{37}H_{55}ClN_{10}O_{4.50}$
Formula weight	720.87	986.29	2020.67	747.36
Temperature	200(2) K	200(2) K	200(2) K	200(2) K
Wavelength	1.54178 Å	1.54178 Å	1.54178 Å	1.54178 Å
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$C2/c$-C_{2h}^6(No. 15)	$P2_1/c$-C_{2h}^5(No. 14)	$P\overline{1}$-C_i^1(No. 2)	$P2_12_12_1$-D_2^4(No. 19)
a	24.1148(5) Å	13.5303(6) Å	12.2191(5) Å	11.1446(3) Å
b	13.7792(4) Å	22.4915(10) Å	13.3820(6) Å	19.6252(6) Å
c	23.4189(6) Å	17.1642(7) Å	19.0015(7) Å	21.5808(7) Å
α	90°	90°	75.900(2)°	90°
β	98.930(1)°	90.537(2)°	74.625(2)°	90°
γ	90°	90°	85.397(3)°	90°
Volume	7687.4(3) $Å^3$	5223.1(4) $Å^3$	2905.2(2) $Å^3$	4720.0(2) $Å^3$
Z	8	4	1	4
Density (calculated)	1.246 g/cm^3	1.254 g/cm^3	1.155 g/cm^3	1.052 g/cm^3
Absorption coefficient	0.710 mm^{-1}	1.064 mm^{-1}	0.616 mm^{-1}	1.076 mm^{-1}
F(000)	3088	2132	1094	1600
Crystal size (mm^3)	0.220 x 0.110 x 0.080	0.290 x 0.160 x 0.050	0.150 x 0.130 x 0.085	0.110 x 0.110 x 0.040
Theta range for data collection	3.711 to 70.319°	3.239 to 68.279°	6.950 to 68.445°	3.043 to 68.057°
Index ranges	$-28\leq h\leq 28$, $-11\leq k\leq 16$, $-26\leq l\leq 28$	$-15\leq h\leq 16$, $-22\leq k\leq 26$, $-20\leq l\leq 20$	$-14\leq h\leq 14$, $-12\leq k\leq 16$, $-22\leq l\leq 22$	$-11\leq h\leq 12$, $-15\leq k\leq 22$, $-24\leq l\leq 21$
Reflections collected	16881	33134	36032	23762
Independent reflections	6982 [R_{int} = 0.034]	9215 [R_{int} = 0.038]	9955 [R_{int} = 0.081]	7711 [R_{int} = 0.035]

Completeness to theta = 66.000°	98.3 %	98.8 %	96.4 %	96.8 %
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	1.000 and 0.803	1.000 and 0.831	1.000 and 0.857	1.000 and 0.905
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6982 / 0 / 505	9215 / 0 / 663	9955 / 0 / 726	7711 / 12 / 488
Goodness-of-fit on F^2	1.063	1.039	1.022	1.103
Final R indices [$I>2\sigma(I)$]	R_1 = 0.068, wR_2 = 0.202	R_1 = 0.098, wR_2 = 0.282	R_1 = 0.062, wR_2 = 0.165	R_1 = 0.088, wR_2 = 0.248
R indices (all data)	R_1 = 0.075, wR_2 = 0.215	R_1 = 0.115, wR_2 = 0.303	R_1 = 0.097, wR_2 = 0.199	R_1 = 0.091, wR_2 = 0.252
Absolute structure parameter	-	-	-	0.052(6)
Extinction coefficient	n/a	n/a	n/a	0.0025(6)
Largest diff. peak and hole	0.80 and -0.63 $e^-/Å^3$	0.64 and -0.56 $e^-/Å^3$	0.46 and -0.29 $e^-/Å^3$	1.28 and -0.35 $e^-/Å^3$

Table S4. Hydrogen bonds for free base **1**: $C_{33}H_{43}N_9O_4 \cdot CH_3CN \cdot CH_3OH \cdot H_2O$ [Å and °].

D-H···*A*	d(D-H)	d(H···*A*)	d(D···*A*)	∠(DH*A*)
N(6)-H(6N)···O(1S)#1	0.82(4)	2.10(4)	2.914(3)	174(3)
C(11)-H(11A)···O(2)	0.95	2.31	2.880(3)	118.2
N(13)-H(13N)···O(1)#2	0.92(3)	1.97(3)	2.850(3)	159(3)
N(15)-H(15N)···O(1)#2	0.89(3)	2.05(3)	2.876(2)	155(3)
N(24)-H(24N)···O(1W)#3	0.89(3)	2.25(3)	3.042(3)	149(3)
N(26)-H(26N)···O(1W)#3	0.90(4)	2.05(4)	2.930(3)	164(3)
N(33)-H(33N)···O(3)	0.78(3)	2.21(3)	2.839(3)	138(3)
N(35)-H(35N)···O(2)	0.81(3)	2.35(3)	3.018(3)	140(2)
N(35)-H(35N)···O(1W)	0.81(3)	2.57(3)	3.293(3)	150(2)
C(42)-H(42B)···O(3)	0.98	2.58	3.129(3)	115.1
C(2S)-H(2SB)···O(3)#4	0.98	2.12	3.100(11)	176.3
O(1S)-H(1OS)···O(4)	0.99(4)	1.79(5)	2.738(3)	158(4)
O(1W)-H(1W1)···O(2)	0.87(4)	1.97(4)	2.758(2)	150(3)
O(1W)-H(1W2)···O(3)	0.83(5)	1.99(5)	2.774(2)	157(4)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,y-1/2,z #2 -x+1,-y,-z #3 -x+1/2,y+1/2,-z+1/2 #4 -x+1/2,y-1/2,-z+1/2

Table S5. Hydrogen bonds for sulfate complex with **1**: $[N(C_4H_9)_4][C_{33}H_{44}N_9O_4][SO_4]{\cdot}H_2O$ [Å and °].

D-H···*A*	d(D-H)	d(H···*A*)	d(D···*A*)	∠(DH*A*)
N(1)-H(1N)···S	1.00(4)	2.93(4)	3.923(4)	171(3)
N(1)-H(1N)···O(11)	1.00(4)	1.70(4)	2.671(4)	161(4)
C(3)-H(3B)···O(1W)#1	0.99	2.59	3.316(19)	130.1
N(4)-H(4N)···O(11)	0.88	2.23	2.980(6)	143.2
N(6)-H(6N)···O(12)	0.71(4)	2.21(4)	2.866(6)	153(4)
C(11)-H(11)···O(2)	0.95	2.22	2.850(6)	123.1
N(13)-H(13N)···O(12)	0.89(4)	2.41(4)	3.139(5)	139(3)
N(15)-H(15N)···O(13)	0.76(4)	2.22(4)	2.971(5)	170(4)
N(24)-H(24N)···O(14)	0.75(4)	2.22(5)	2.919(5)	156(5)
N(26)-H(26N)···O(14)	0.76(5)	2.20(5)	2.888(6)	152(5)
C(31)-H(31)···O(4)	0.95	2.30	2.848(7)	115.7
N(33)-H(33N)···O(13)	0.79(5)	2.36(5)	3.112(8)	158(5)
N(35)-H(35N)···S	0.83(5)	3.01(5)	3.642(5)	135(4)
N(35)-H(35N)···O(13)	0.83(5)	2.15(5)	2.909(7)	153(5)
C(39)-H(39C)···O(3)	0.98	2.48	3.034(7)	115.8
C(40)-H(40B)···O(1W)	0.98	2.58	3.391(14)	139.9
C(41)-H(41C)···O(2)	0.98	2.33	2.936(6)	118.9
C(61)-H(61A)···O(1)#2	0.99	2.33	3.295(6)	166.0
C(61)-H(61B)···O(1W)	0.99	2.23	2.866(16)	120.7
O(1W)-H(1W1)···O(12)	0.87	1.74	2.613(13)	179.9

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z-1/2   #2 x,-y+3/2,z+1/2

Table S6. Hydrogen bonds for BPDC complex of **1**: $[N(C_4H_9)_4]_2[C_{33}H_{43}N_9O_4]_2[C_{14}H_8O_4]\cdot 2H_2O$ [Å and °].

D-H···*A*	d(D-H)	d(H···*A*)	d(D···*A*)	∠(DH*A*)
N(4)-H(4N)···O(12')	0.82(4)	1.95(4)	2.722(10)	155(4)
N(6)-H(6N)···O(12)	0.80(4)	2.22(4)	3.021(4)	175(3)
N(6)-H(6N)···O(12')	0.80(4)	2.37(4)	3.027(11)	140(3)
C(11)-H(11)···O(2)	0.95	2.24	2.857(4)	122.2
N(13)-H(13N)···O(1W)#2	0.91(3)	2.23(3)	3.061(3)	152(3)
N(15)-H(15N)···O(1W)#2	0.89(4)	2.09(4)	2.947(4)	162(3)
N(24)-H(24N)···O(12)	0.77(4)	2.31(5)	3.058(5)	163(4)
N(24)-H(24N)···O(11')	0.77(4)	2.16(5)	2.719(11)	130(4)
N(26)-H(26N)···O(11')	0.85(4)	1.93(4)	2.602(9)	135(4)
C(28)-H(28)···O(3)	0.95	2.20	2.836(4)	123.2
C(31)-H(31)···O(4)	0.95	2.34	2.856(4)	113.7
N(33)-H(33N)···O(11)	0.80(3)	2.00(3)	2.762(3)	159(3)
N(33)-H(33N)···O(11')	0.80(3)	2.44(3)	3.206(10)	161(3)
N(35)-H(35N)···O(11)	0.87(3)	2.21(3)	2.940(4)	142(3)
N(35)-H(35N)···O(12')	0.87(3)	2.47(3)	3.261(10)	153(3)
C(39)-H(39C)···O(2)	0.98	2.45	3.024(4)	117.0
C(42)-H(42C)···O(3)	0.98	2.43	3.033(5)	119.2
C(61)-H(61A)···N(13)#3	0.99	2.60	3.540(4)	159.3
C(61)-H(61B)···O(1)#3	0.99	2.48	3.287(3)	138.9
C(71)-H(71B)···O(1)#3	0.99	2.59	3.408(4)	139.5
C(91)-H(91B)···O(11)	0.99	2.46	3.216(4)	132.5
O(1W)-H(1W1)···O(4)	0.89(4)	1.88(4)	2.767(3)	173(4)
O(1W)-H(1W2)···O(12)#2	0.88(5)	1.92(5)	2.773(3)	164(4)
O(1W)-H(1W2)···O(12')#2	0.88(5)	2.19(5)	2.971(9)	148(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1 #2 -x+1,-y+1,-z #3 x,y+1,z

Table S7. Hydrogen bonds for $[C_{33}H_{43}N_9O_4][Cl][N(CH_3)_4]\cdot 0.5H_2O$ [Å and °].

D-H···*A*	d(D-H)	d(H···*A*)	d(D···*A*)	∠(DH*A*)
C(3)-H(3A)···N(26)#1	0.99	2.50	3.450(9)	161.3
N(4)-H(4N)···Cl	0.88	2.50	3.282(5)	149.1
N(6)-H(6N)···Cl	0.88	2.47	3.282(5)	154.3
N(13)-H(13N)···O(1)	0.88	2.41	2.862(7)	112.3
N(13)-H(13N)···O(4)#1	0.88	2.33	3.092(6)	144.3
N(15)-H(15N)···O(4)#1	0.88	2.09	2.848(6)	143.7
N(24)-H(24N)···O(1)#2	0.88	2.09	2.913(6)	154.8
N(26)-H(26N)···O(1)#2	0.88	2.39	3.154(7)	145.1
N(26)-H(26N)···O(4)	0.88	2.28	2.764(8)	114.6
N(33)-H(33N)···Cl	0.88	2.35	3.210(6)	164.3
N(35)-H(35N)···Cl	0.88	2.69	3.466(6)	147.9
C(40)-H(40B)···O(3)	0.98	2.43	3.050(9)	120.8
C(42)-H(42C)···O(2)	0.98	2.46	3.069(9)	120.0
C(1C)-H(1CA)···O(2)	0.98	2.60	3.418(8)	140.7
C(1C)-H(1CC)···Cl#3	0.98	2.94	3.804(7)	148.1
C(2C)-H(2CA)···O(2)	0.98	2.44	3.298(8)	145.3
C(2C)-H(2CB)···O(3)	0.98	2.46	3.287(8)	142.4
C(2C)-H(2CC)···Cl	0.98	2.84	3.767(7)	158.8
C(3C)-H(3CA)···O(2)	0.98	2.34	3.225(7)	149.1
C(3C)-H(3CB)···Cl#3	0.98	2.86	3.743(6)	150.7
C(3C)-H(3CC)···O(3)	0.98	2.30	3.173(7)	147.6
C(4C)-H(4CA)···O(3)	0.98	2.46	3.289(8)	142.3
C(4C)-H(4CB)···Cl#3	0.98	2.81	3.708(7)	152.6

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y+1/2,-z+1/2 #2 -x+1,y-1/2,-z+1/2 #3 x-1/2,-y+1/2,-z

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