Supporting Information

Anion-templated synthesis of a switchable fluorescent [2]catenane with sulfate sensing capability

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Contents

1. General Information

1.1 Materials

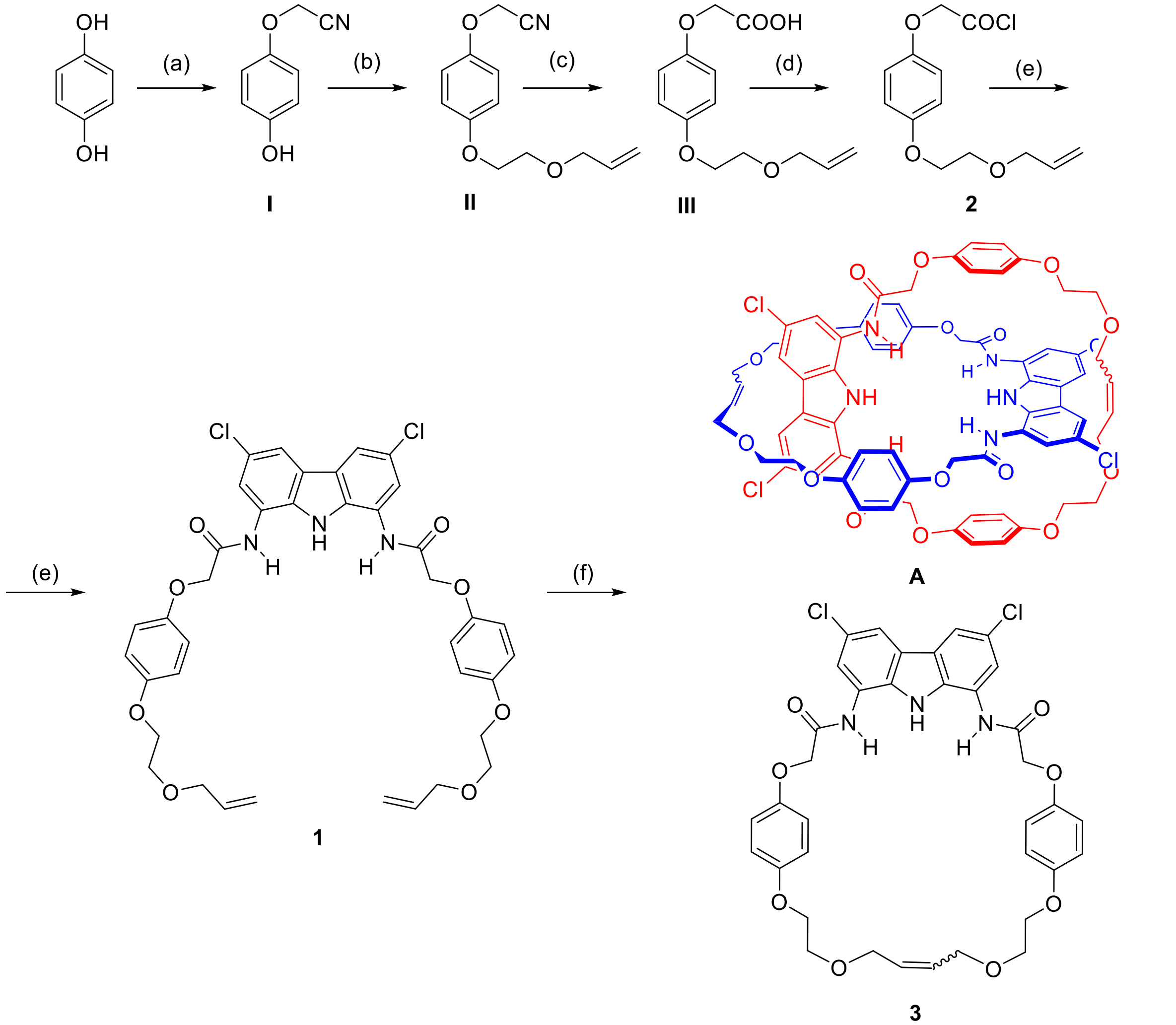
All reagents were purchased from Alfa Aesar or Sigma-Aldrich and used without further purification. Deuterated solvents were purchased from Euriso-top. TLC was carried out on Merck silica gel 60 F254 plates. Preparative chromatography was done using Merck Silica Gel 60 (230-400 mesh) or Teledyne Isco CombiFlash system with RediSep Normal-phase Silica Flash Columns.

Tetrabutylammonium sulfate was purchased from Alfa Aesar as a 50% aqueous solution. Before drying, the pH of this solution was checked and found to be neutral (pH=7.3 upon dilution to 1 M concentration), confirming that the sample is essentially free from hydrogensulfate. Anhydrous salt was obtained in the following way: *ca.* 2 g of the 50% solution was transferred to a 50 ml round-bottom flask and most of the water was removed on a rotary evaporator with gentle heating over a few hours. Viscous residue was then further dried under high vacuum over KOH to a constant mass (in total *ca.* 47% loss of weight was reached). The resulting white crystalline solid was stored in a vacuum desiccator over KOH and used for titrations. Tetrabutylammonium chloride, tetrabutylammonium benzoate and tetrabutylammonium dihydrogen phosphate were obtained from Sigma-Aldrich and used as received.

1.2 Instruments and Methods

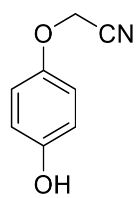
NMR spectra were recorded using Agilent 400 MHz or Bruker Avance 500 MHz spectrometers at ambient temperature in DMSO-d_6. Chemical shifts are reported in parts per million (ppm) and coupling constants *J* are given in hertz (Hz). Data are reported as follows: chemical shift, multiplicity (s-singlet, bs – broad singlet, d – doublet, dd – doublet of doublets), coupling constant and integration. The residual signal of DMSO-d_6 solvent was used as an internal reference standard (δH = 2.500 ppm and δC = 39.50 ppm). The HR-ESI mass spectra were obtained using a Quattro TOF mass spectrometer with methanol as a spray solvent. Elemental analysis was performed using a CHN analyser model Vario EL III Elementar Analyser. Chlorine content in all analysed samples was determined according to the Schöniger method.

2. Synthetic Procedures and Characterization of New Compounds



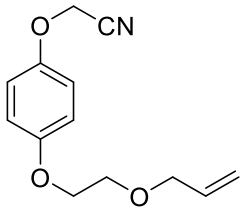
Scheme S1. Synthetic pathway leading to catenane **A**. (a) NaOH/$BrCH_2CN$, H_2O/1,4-dioxane 1:1, 1h, 49%; (b) K_2CO_3/2-allyloxyethyl-*p*-toluene sulfonate, acetonitrile, reflux, 20h, 80%; (c) NaOH, H_2O/MeOH 1:1, reflux, 24h, 94%; (d) $SOCl_2$, DCM, reflux, 24h, assumed quantitative; (e) 1,8-diamino-3,6-dichlorocarbazole/Et_3N, acetonitrile, RT, 40h, 80%; (f) TBA_2SO_4/ tetrafluoro-1,4-benzoquinone/nitro-Grela SiPr catalyst, DCM, RT, 26% for **1**, 14% for **5**, 10% for **6**.

Synthesis of I



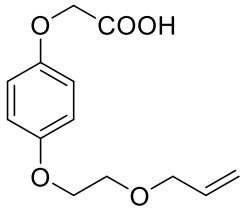
Prepared according to the previously published procedure.[1]

Synthesis of II



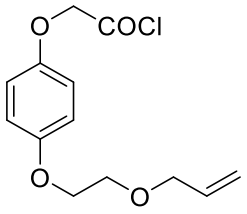
To a 250 ml two-neck round-bottom flask equipped with a magnetic stirrer, 2-(4-hydroxyphenoxy)acetonitrile (4.474 g, 30.00 mmol) and acetonitrile (75 ml) were added. The flask was equipped with a reflux condenser connected to a check-valve bubbler and argon was bubbled through the solution for 15 min. Afterwards, 2-allyloxyethyl-*p*-toluene sulfonate (7.690 g, 30.00 mmol) and solid potassium carbonate (4.561 g, 33.0 mmol) were added in a counterstream of argon. Argon inlet was removed and the reaction mixture was heated at reflux for 20 h under an argon atmosphere. After this time, reaction mixture was cooled down to room temperature, filtered, and washed with acetonitrile. The solvent was removed on a rotary evaporator. The product was purified by column chromatography using hexane/AcOEt mixture (9:1 – 8:2 v/v). Fractions containing pure product were combined and evaporated to yield a brown oil (5.617 g, 24.08 mmol, 80.3%). ^{1}H NMR in accordance with previously published data.[2]

Synthesis of III



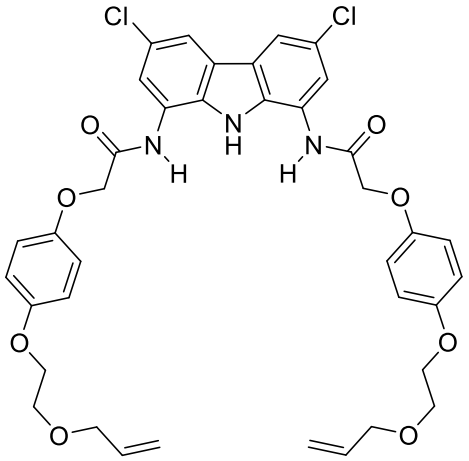
To a 250 ml one-neck round-bottom flask equipped with a magnetic stirrer, 2-(4-(2-(allyloxy)ethoxy)phenoxy)acetonitrile (Compound **II**) (2.333 g, 10.0 mmol) and methanol (45 ml) were added, forming clear solution. Next, aqueous solution of NaOH (20%) was added (45 ml). The flask was equipped with a reflux condenser connected to a check-valve bubbler. Reaction mixture was heated at reflux for 24 h and then cooled down in an ice bath causing precipitation of a white solid. Mixture was acidified to pH 7 by the addition of 3 M aqueous HCl. Afterwards, solid was filtered, washed with water (3×15 ml) and dried in vacuo to give a pure white product (2.378 g, 9.427 mmol, 94.3%).**^{1}H NMR** (400 MHz, DMSO-d_6) δ_{DMSO}: 12.95 (bs; 1H); 6.85 (m; *J* = 6.4 Hz; 2H); 5.90 (ddt; *J* = 17.3; 10.6; 5.4 Hz; 1H); 5.27 (ddd; *J* = 17.3; 3.7; 1.7 Hz; 1H); 5.15 (ddd; *J* = 10.4; 3.4; 1.4 Hz; 1H); 4.58 (s; 1H); 4.03 (m; 1H); 4.00 (dt; *J* = 5.4; 1.5 Hz; 1H); 3.68 (m; 1H) (Figure S1); **^{13}C NMR** (101 MHz, DMSO-d_6) δ_{DMSO}: 170.84; 153.26; 152.28; 135.58; 116.93; 115.77; 115.69; 71.54; 68.65; 67.92; 65.49 (Figure S2) **HR MS** (ESI): m/z calcd. for $C_{13}H_{16}O_5Na$ $[M+Na]^+$: 275.0895; found: 275.0883. **Elemental Analysis** calcd. for $C_{13}H_{16}O_5$: C 61.90; H 6.39; found: C 61.90; H 6.30.

Synthesis of 2



To a 100 ml single-neck round-bottom flask equipped with a magnetic stirrer, 2-(4-(2-(allyloxy)ethoxy)phenoxy)acetic acid (2.000 g, 7.928 mmol), DCM (SPS, 30 ml) and thionyl chloride (1.800 ml, 23.78 mmol) were added. The flask was equipped with a reflux condenser connected to a check-valve bubbler. Reaction mixture was heated at reflux for 24 h. After that time, it was cooled down to room temperature and solvent was removed on a rotary evaporator. Product was dried *in vacuo* at 60°C, and used in the next synthetic step without further purification and characterization.

Synthesis of 1

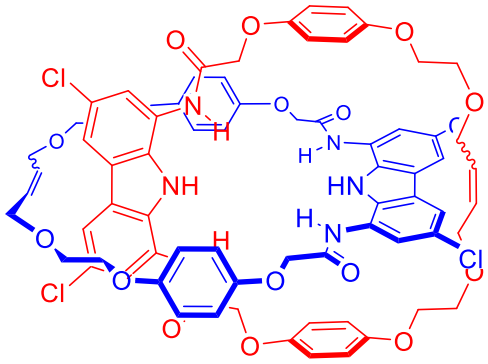


A 100 ml two-neck round-bottom flask was dried in a stream of hot air and then cooled down in vacuo. After that, it was equipped with a magnetic stirrer and 1,8-diamino-3,6-dichlorocarbazole (0.950 g, 3.568 mmol) was added. The flask was closed with rubber septum and purged with argon. Next, acetonitrile (40 ml) and triethylamine (1.2 ml, 8.7 mmol) were added. A single-neck round bottom flask with 2-(4-(2-(allyloxy)ethoxy)phenoxy)acetyl chloride (Compound **2**) obtained in the previous synthetic step was closed with a septum, purged with argon, and then acetonitrile (10 ml) was added. The solution of acetyl chloride was added dropwise to the solution of 1,8-diamino-3,6-dichlorocarbazole. Reaction mixture was left in room temperature for 40 h. After that, white solid was filtered, suspended in MeOH (50 ml) and placed in ultrasonic bath. Afterwards, it was filtered again and dried in vacuo, yielding pure precursor **1** of catenane (2.111 g, 2.873 mmol, 80%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ_{DMSO}: 10.81 (s; 1H); 10.32 (s; 2H); 8.19 (d; *J* = 1.9 Hz; 2H); 7.75 (d; *J* = 1.4 Hz; 2H); 7.02 (d; *J* = 9.1 Hz; 4H); 6.92 (d; *J* = 9.1 Hz; 4H); 5.89 (ddt; *J* = 17.2; 10.6; 5.4 Hz; 2H); 5.27 (ddd; *J* = 17.3; 3.6; 1.7 Hz; 2H); 5.15 (ddd; *J* = 10.5; 3.3; 1.4 Hz; 2H); 4.78 (s; 4H); 4.04 (m; 4H); 4.00 (dt; *J* = 5.3; 1.5 Hz; 4H); 3.69 (m; 4H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ_{DMSO}: 167.97; 153.55; 152.18; 135.57; 132.08; 124.65; 123.78; 123.75; 120.70; 117.60; 116.92; 116.23; 115.78; 71.55; 68.65; 68.22; 67.91;

HR MS (ESI): m/z calcd. for $C_{38}H_{36}N_3O_8Cl_2$ $[M-H]^-$: 732.1879; found: 732.1877.

Elemental Analysis calcd. for $C_{38}H_{37}N_3O_8Cl_2$: C 62.13; H 5.08; Cl 9.65; N 5.72; found: C 62.01; H 5.16; Cl 9.40; N 5.70.

Synthesis of catenane A



A 100 ml two-neck round-bottom flask was dried in an oven and cooled down *in vacuo.* Then the flask was equipped with a magnetic stirrer and acyclic precursor **1** (50 mg, 0.068 mmol) was added. The flask was closed with a rubber septum, purged with argon and dry DCM (SPS, 65 ml) was added. Nitro-Grela SiPr catalyst (2.48 mg, 0.00328 mmol, 5% mol), dried tetrabutylammonium sulfate (20.87 mg, 0.0359 mmol, 0.5 equiv.) and tetrafluoro-1,4-benzoquinone (1.17 mg, 0.0065 mmol, 10% mol) were weighed out in three separate vials, which were then filled with argon. DCM (SPS, 2 ml + 2 ml for vial washing) was added to the vial with tetrabutylammonium sulfate. This solution was then added to the reaction mixture causing immediate dissolution of the precursor. Dry DCM (SPS, 1 ml) was added to the vial with tetrafluoro-1,4-benzoquinone. This solution was then used to dissolve catalyst. The mixture of catalyst and quinone was added dropwise to the reaction mixture using a syringe pump (100 µL/h). Reaction was left overnight at room temperature. Next day, 1,4-piperazinedipropanenitrile (3.268 mg, 0.017 mmol, as 1 mg/ml DCM solution) was added to the reaction mixture and stirred for 30 min. to quench the reaction. After that, silica gel (0.5 g) was added and solvent was removed on a rotary evaporator (dry loading). The crude product was purified by a flash column chromatography (CombiFlash) on 4 g cartridge using gradient elution with DCM/MeOH mixtures (0 to 5% MeOH). Fractions containing pure products were combined and evaporated to yield catenane **A** (12.5 mg, 0.0088 mmol, 25.9%) and macrocycle **3** (4.1 mg, 0.0058 mmol).

Catenane A ^{1}H NMR (500 MHz, DMSO-d_6) δ_{DMSO}: 10.82 (bs, 1H), 10.29 (bs, 2H), 8.18 (bd, 2H), 7.76 (bd, 2H), 7.03 (d, *J* = 9.0 Hz, 4H), 6.90 (d, *J* = 9.0 Hz, 4H), 5.77 (bt, 2H), 4.75 (s, 4H), 4.04 – 3.96 (8H), 3.66 (m, 4H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ_{DMSO}: 167.41, 153.09, 151.65, 131.59, 128.92, 124.22, 123.32, 120.13, 117.16, 115.80, 115.29, 70.08, 68.09, 67.84, 67.45. **HR MS** (ESI-): m/z calcd. for $C_{72}H_{64}N_6O_{16}Cl_4$ $[M-2H]^{2-}$: 704.1561; found: 704.1562.

Macrocycle 3 ^{1}H NMR (500 MHz, DMSO-d_6) δ_{DMSO}: 11.02 (bs, 1H), 10.24 (bs, 2H), 8.19 (bd, 2H), 7.83 (bd, 2H), 7.08 (d, *J* = 7.5 Hz, 4H), 6.91 (d, *J* = 7.7 Hz, 4H), 5.78 (bs, 2H), 4.74 (bs, 4H), 4.01 (8H), 3.67 (bs, 4H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ_{DMSO}: 167.36, 153.20, 151.57, 131.47, 128.84, 124.26, 123.37, 119.89, 117.13, 115.88, 115.30, 69.73, 68.02, 67.92, 67.64. **HR MS** (ESI): m/z calcd. for $C_{36}H_{33}N_3O_8Cl_2Na$ $[M+Na]^{+}$: 728.1530; found: 728.1542.

3. NMR Spectra

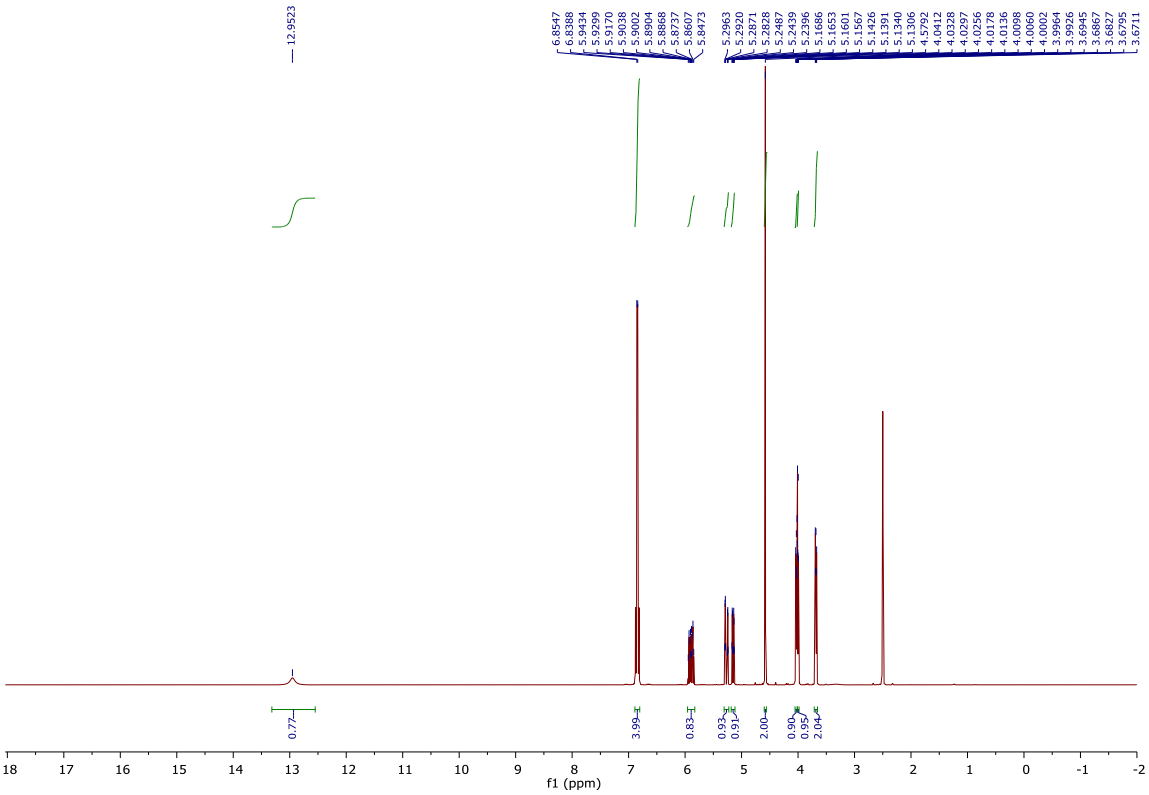


Figure S1. ^{1}H NMR spectrum of compound **III** in DMSO-d_6.

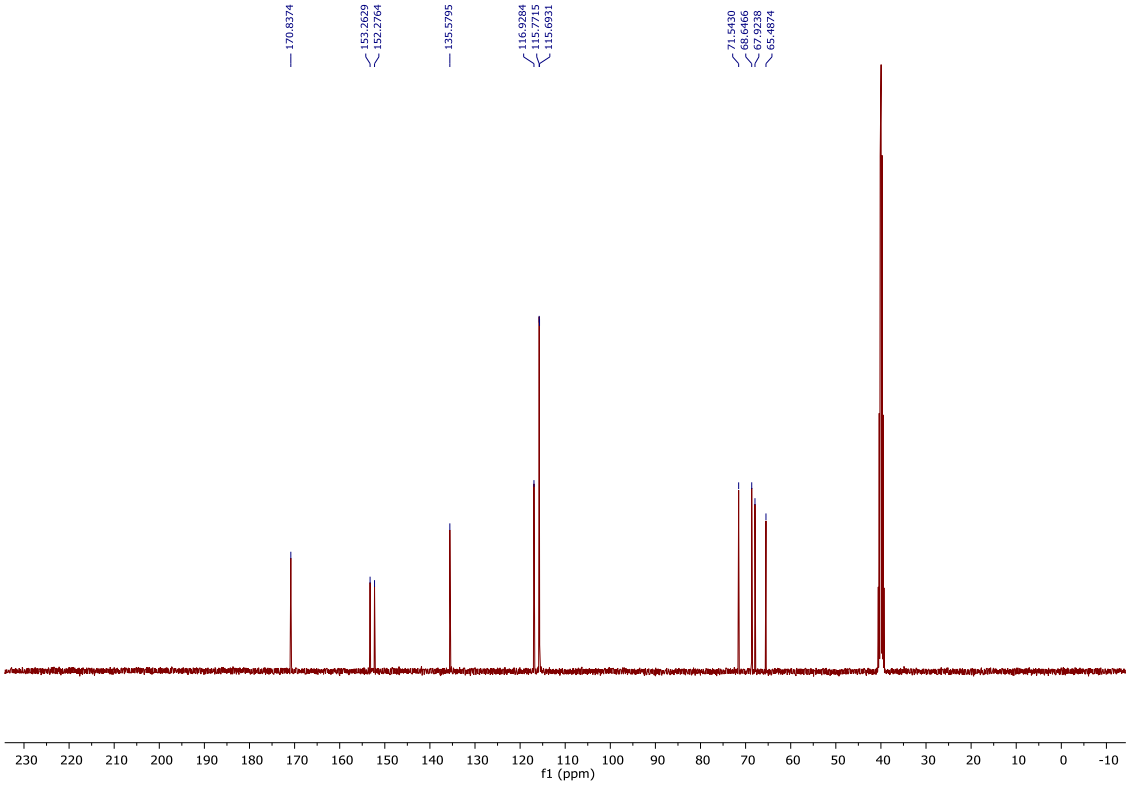


Figure S2. ^{13}C NMR spectrum of compound **III** in DMSO-d_6.

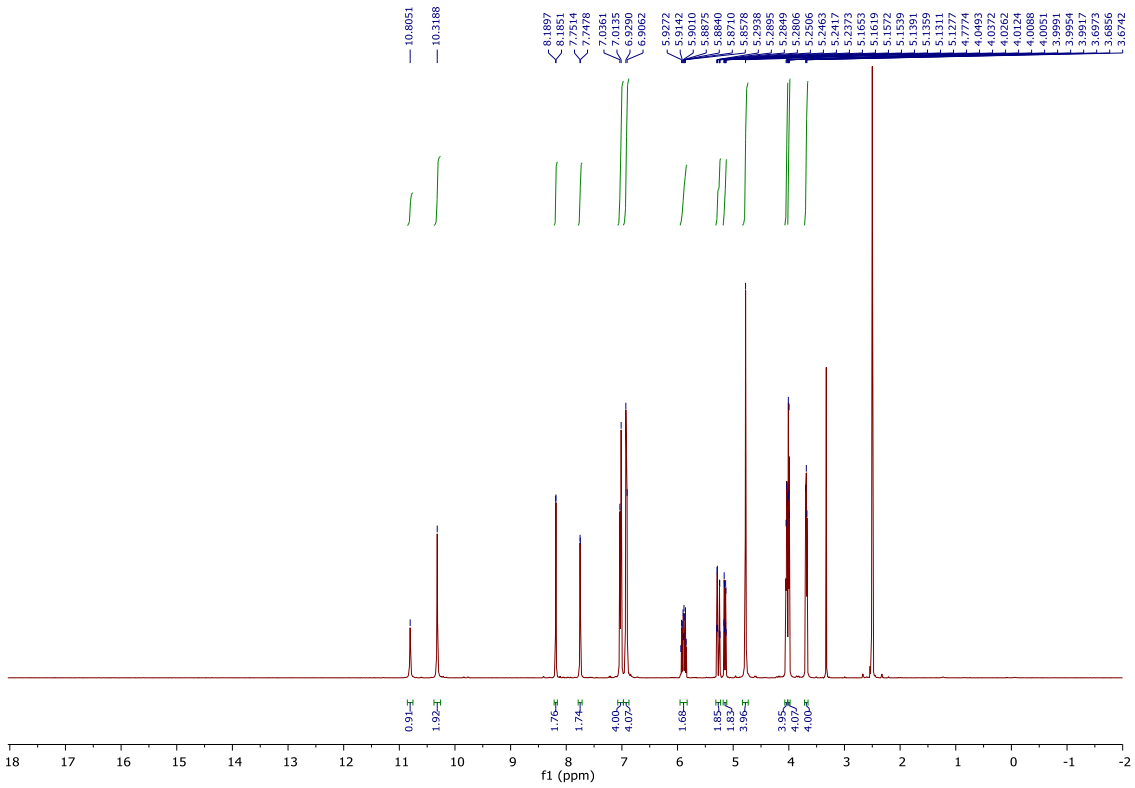


Figure S3. ^{1}H NMR spectrum of precursor **1** in DMSO-d_6.

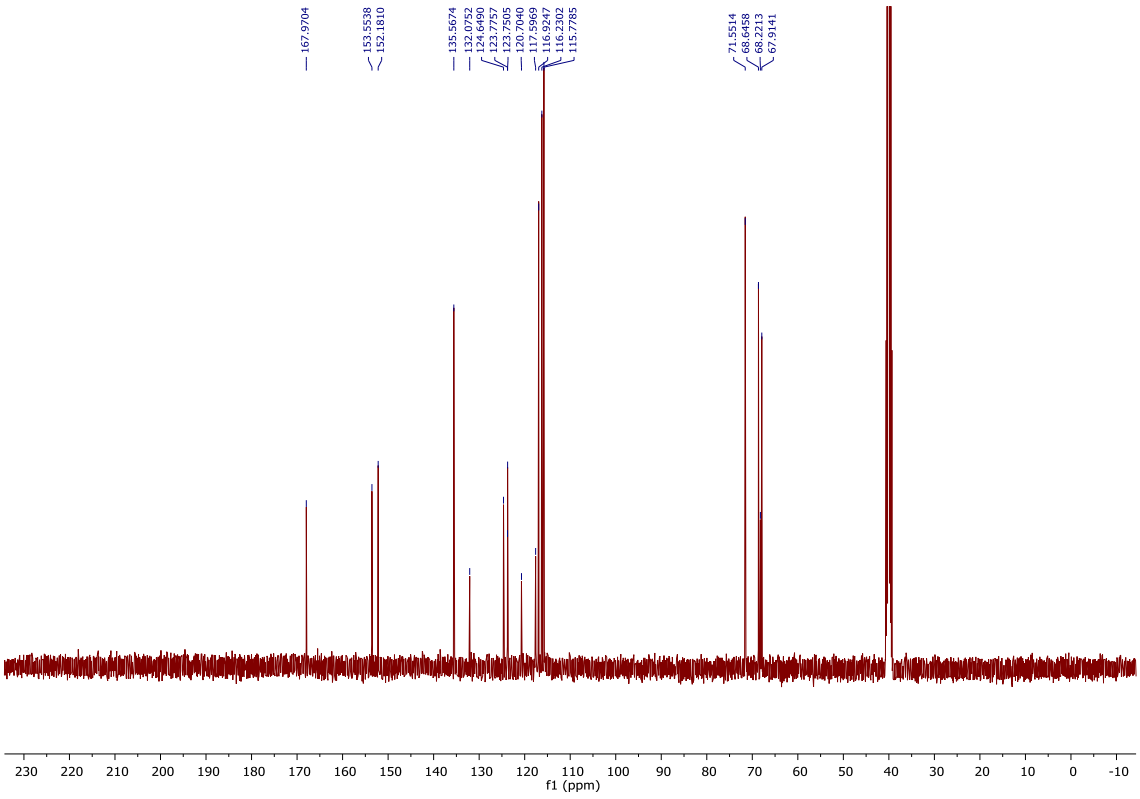


Figure S4. ^{13}C NMR spectrum of precursor **1** in DMSO-d_6.

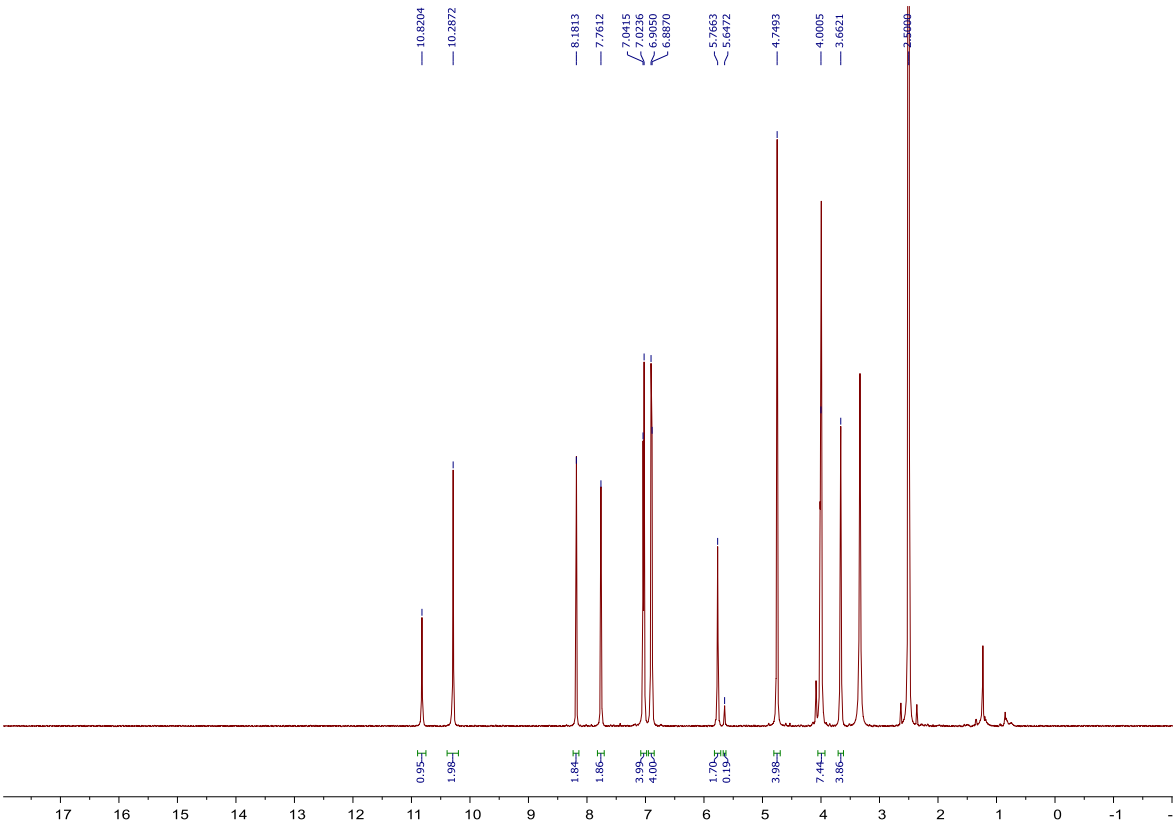


Figure S5. ^{1}H NMR spectrum of catenane **A** in DMSO-d_6.

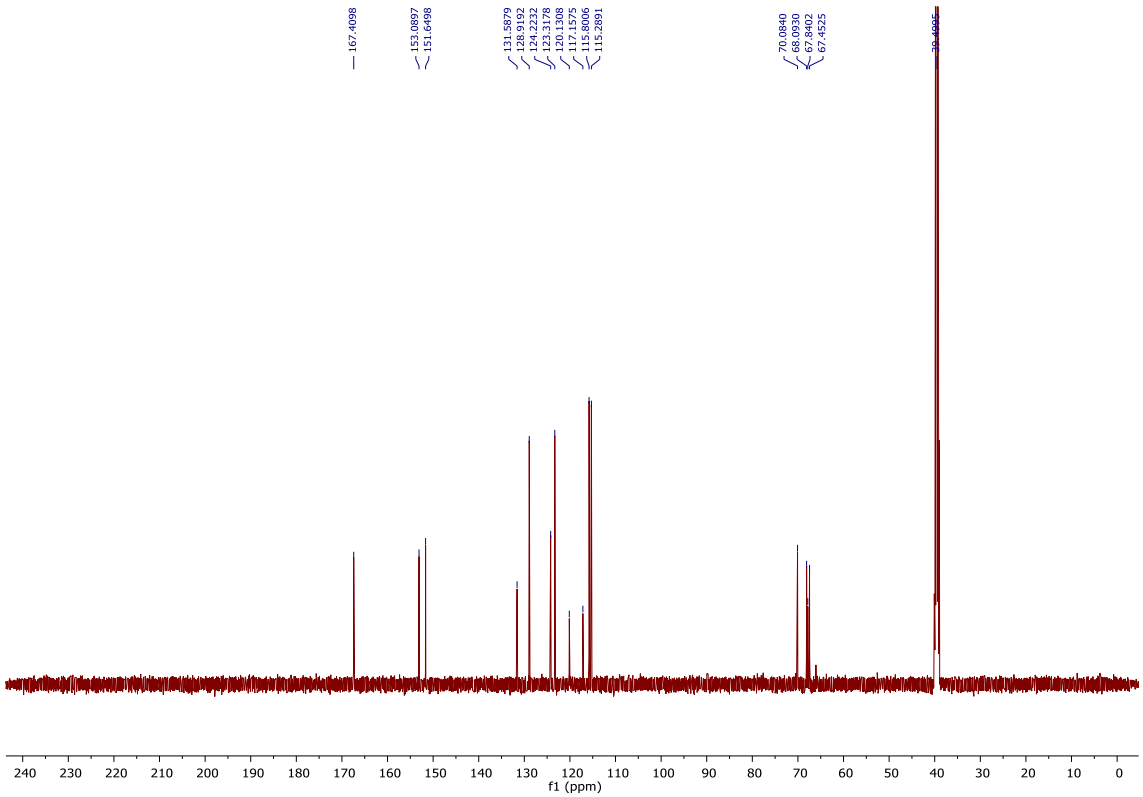


Figure S6. ^{13}C NMR spectrum of catenane **A** in DMSO-d_6.

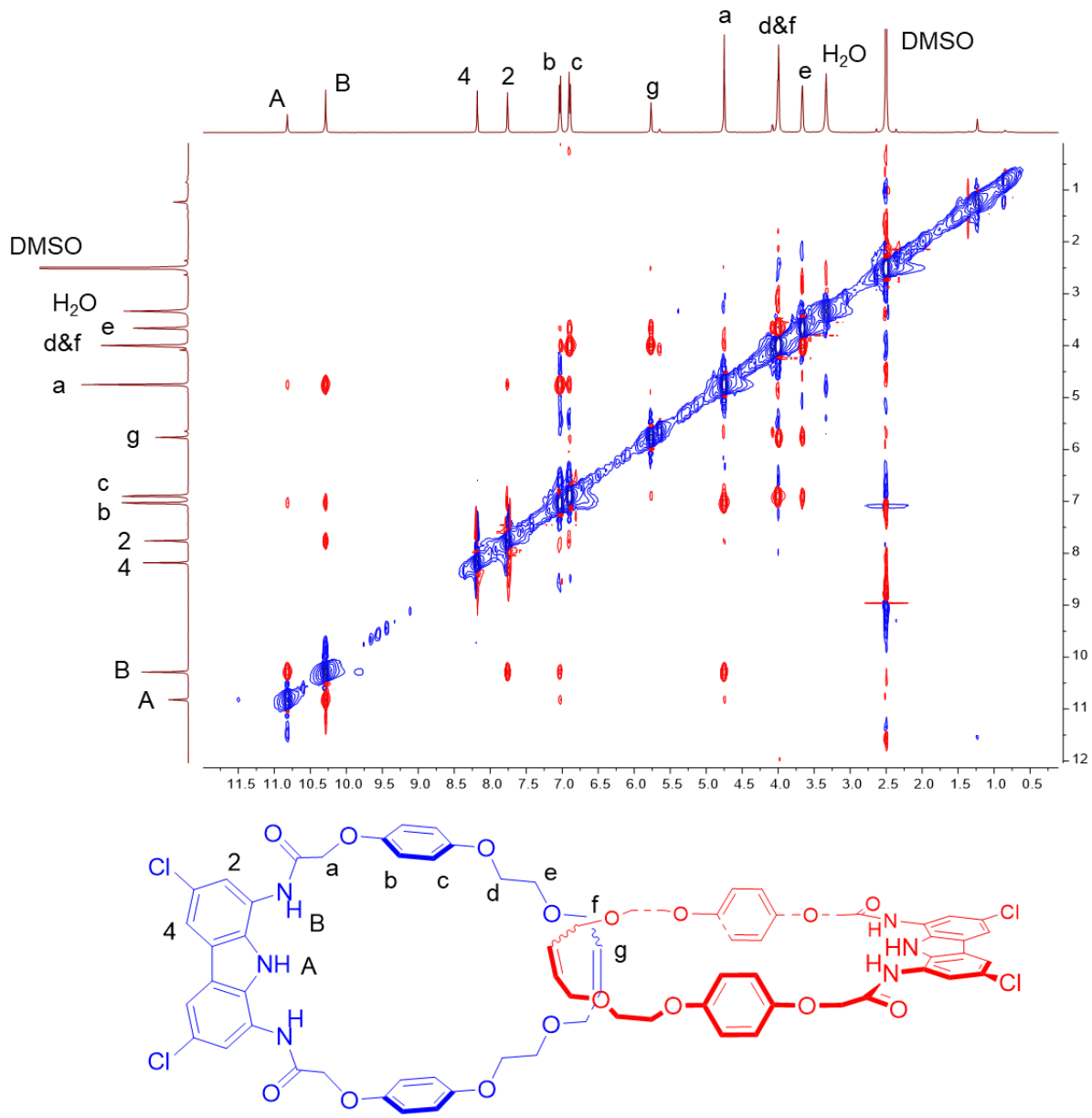


Figure S7. 2D ^{1}H-^{1}H ROESY spectrum of catenane **A** in DMSO-d_6. No cross signals characteristic for an interlocked architecture were found.

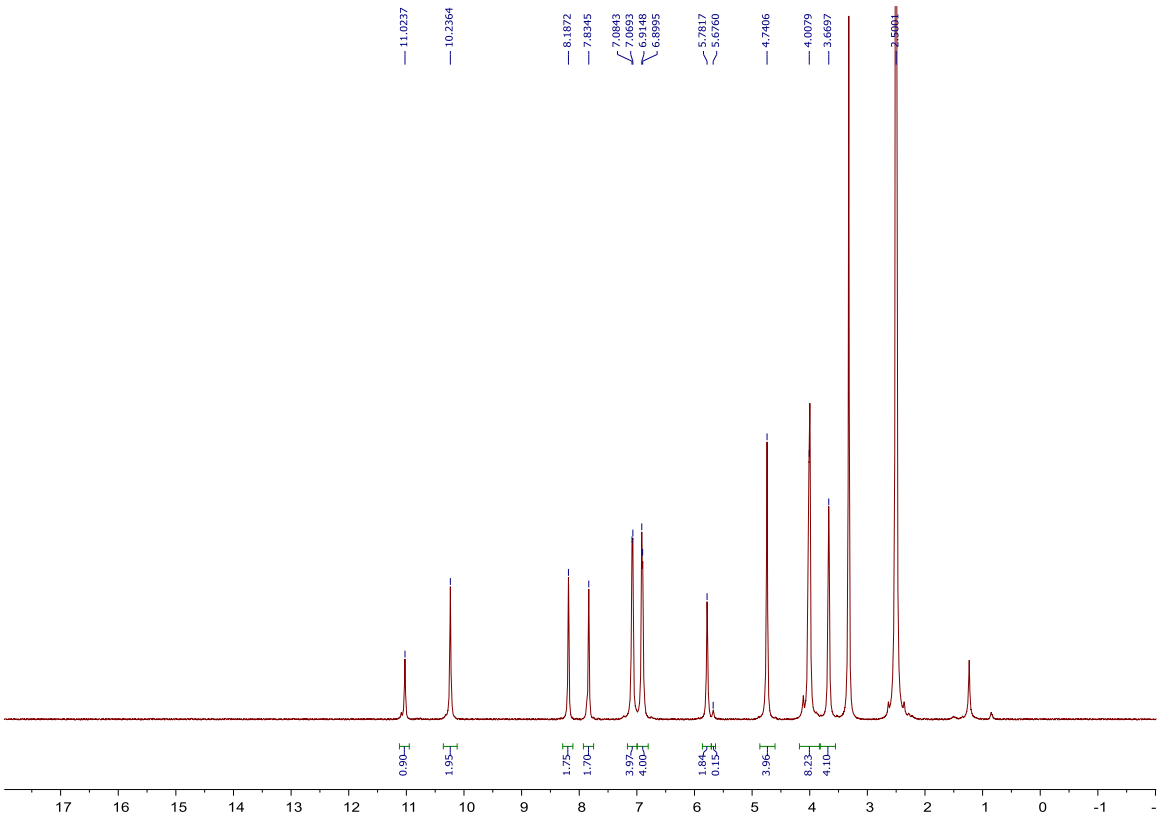


Figure S8. ^{1}H NMR spectrum of macrocycle **3** in DMSO-d_6.

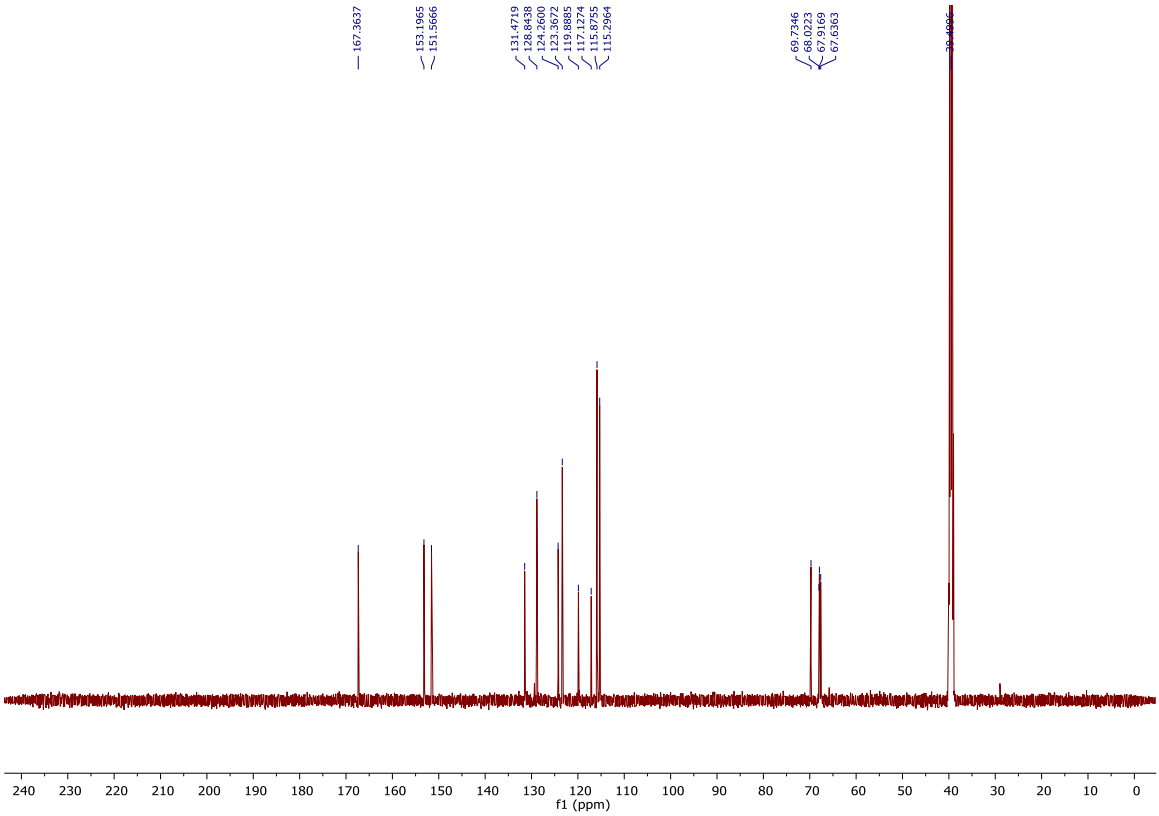


Figure S9. ^{13}C NMR spectrum of macrocycle **3** in DMSO-d_6.

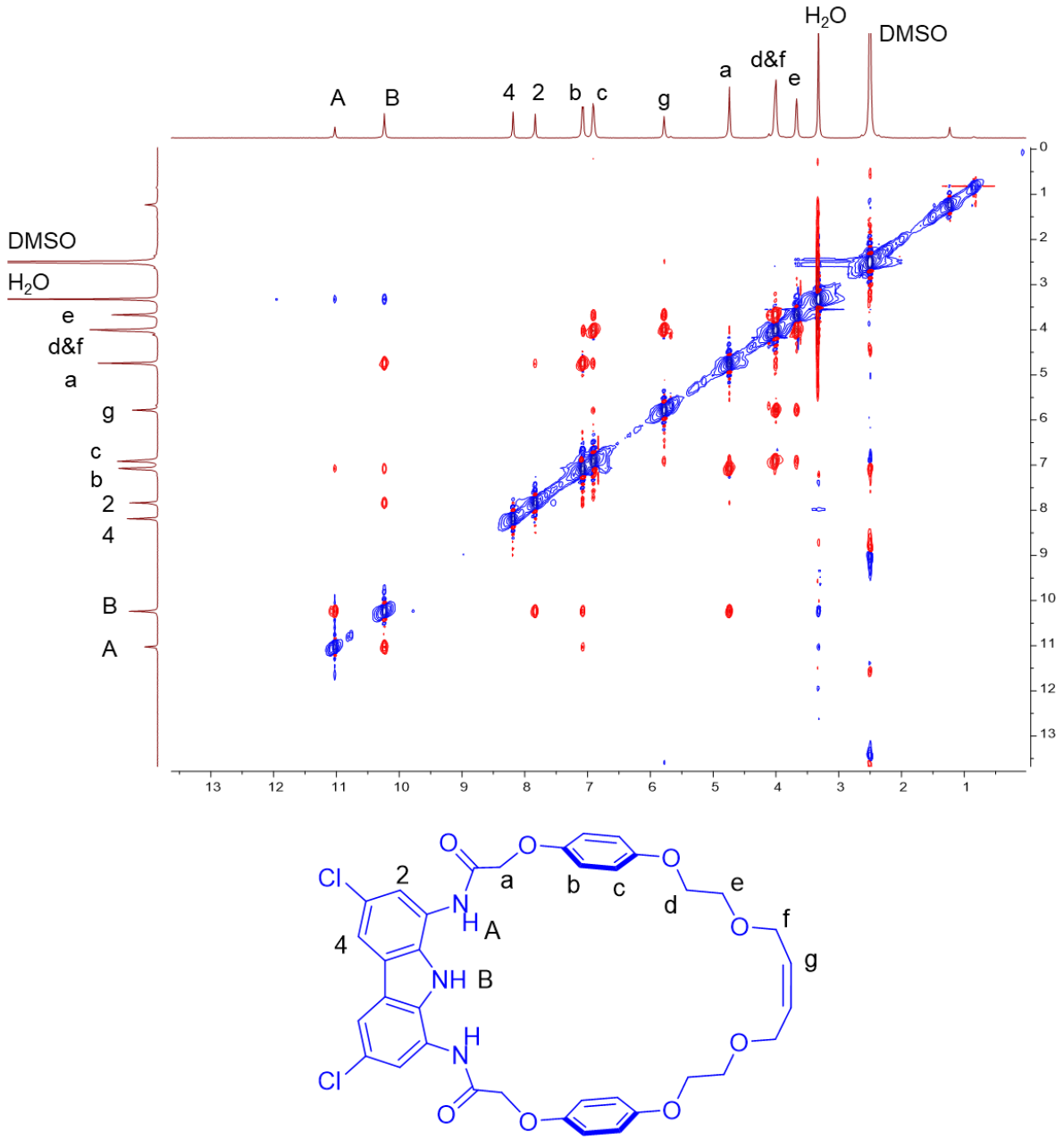


Figure S10. 2D ^{1}H-^{1}H ROESY spectrum of macrocycle **3** in DMSO-d_6. Similar pattern of cross peaks were observed as in the case of catenane **A** (Fig. S7)

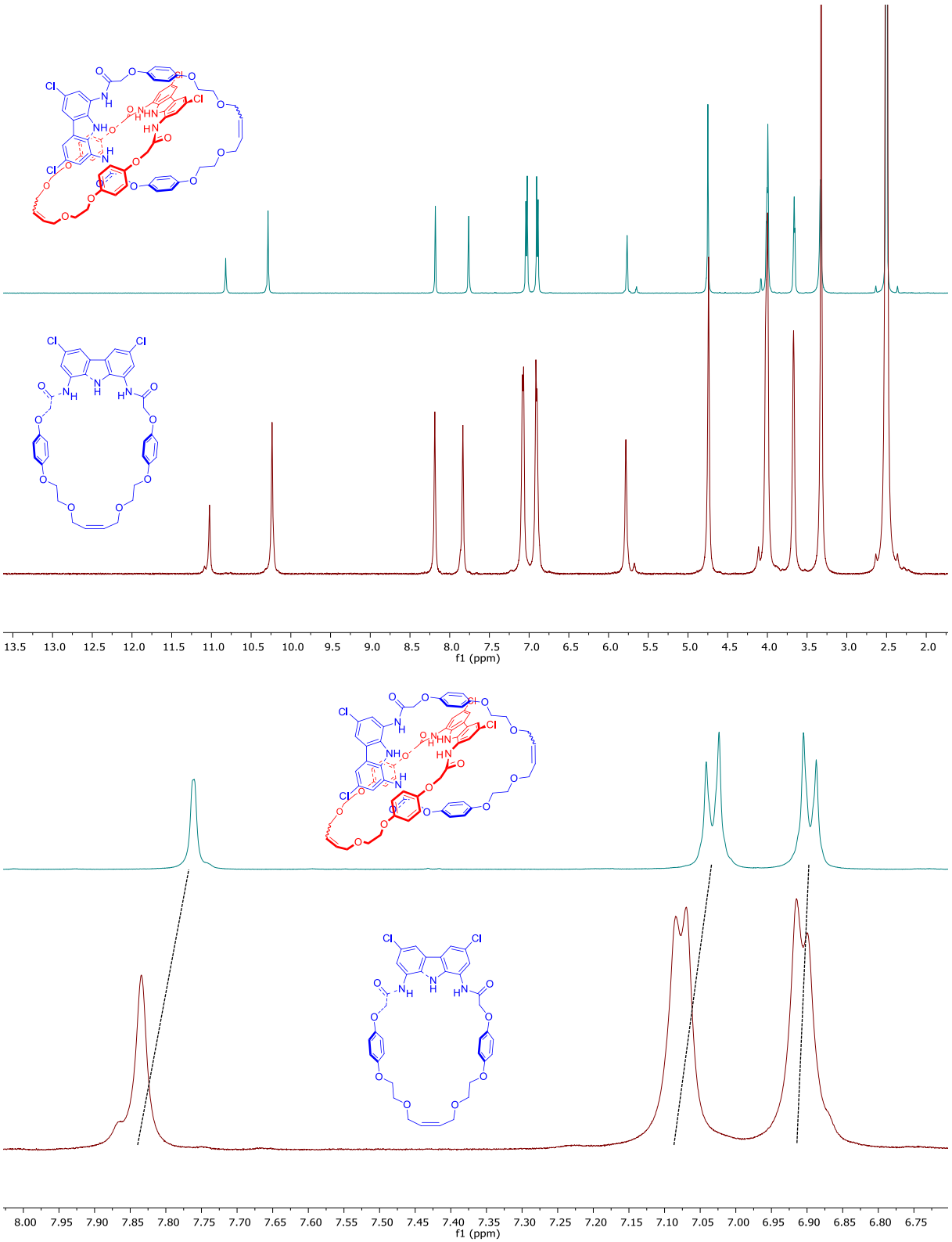


Figure S11. Comparison of ^{1}H NMR spectra of catenane **A** and macrocycle **3**. Lower stack presents zoom of aromatic 6.70-8.00 ppm region. Signals of carbazole CH-*2* proton and hydroquinone protons *B* & *C* are slightly shifted downfield as a result of shielding effect in the interlocked architecture.

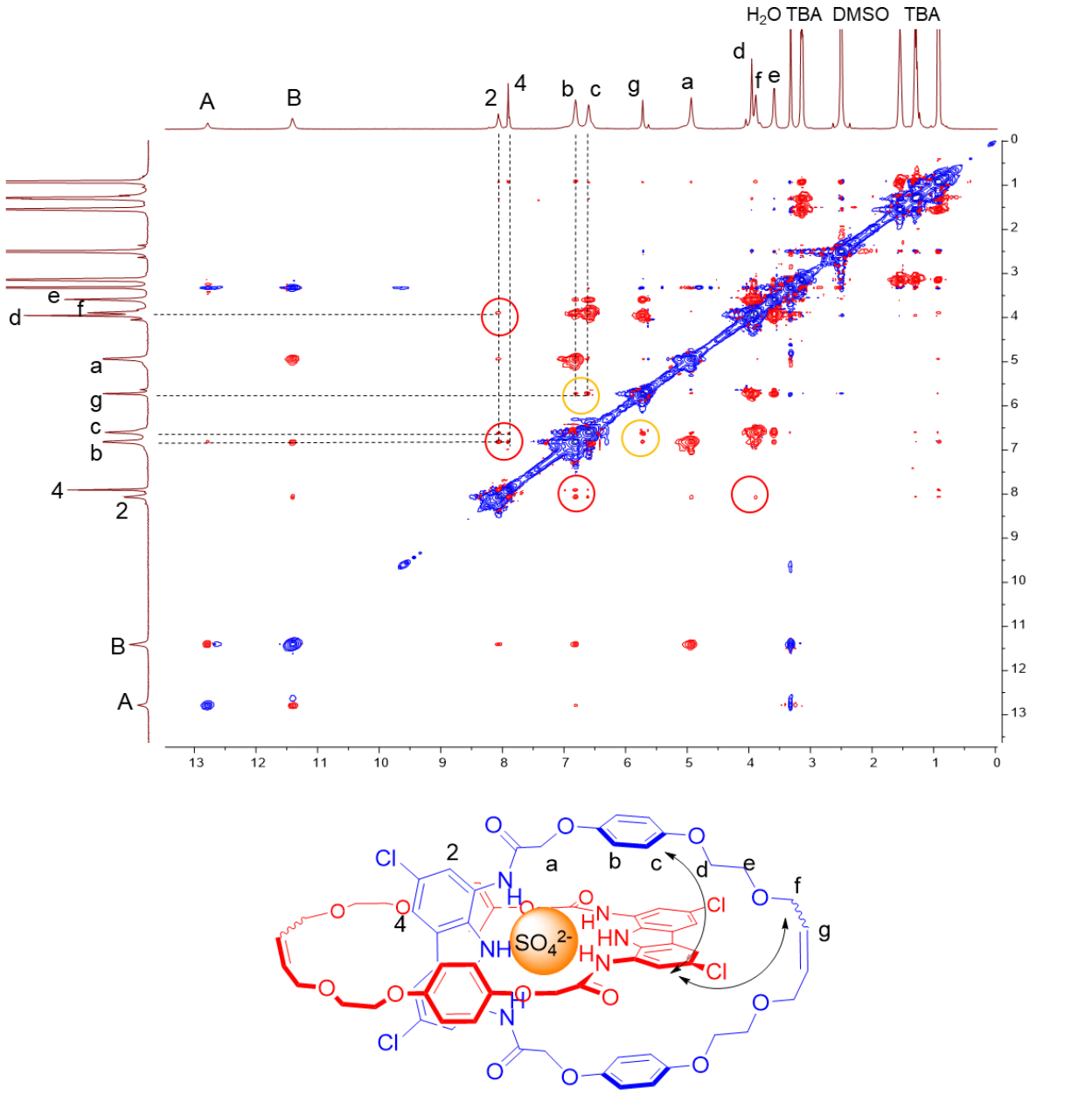


Figure S12. 2D ^{1}H-^{1}H ROESY spectrum of catenane **A** in the presence of 1 equivalent of TBA_2SO_4 recorded in DMSO-d_6. Sulfate binding rigidifies the structure of catenane leading to appearance of the specific cross peaks (encircled), e.g. between protons b/c and 2/4 or g and b/c, characteristic for the interlocked structure.

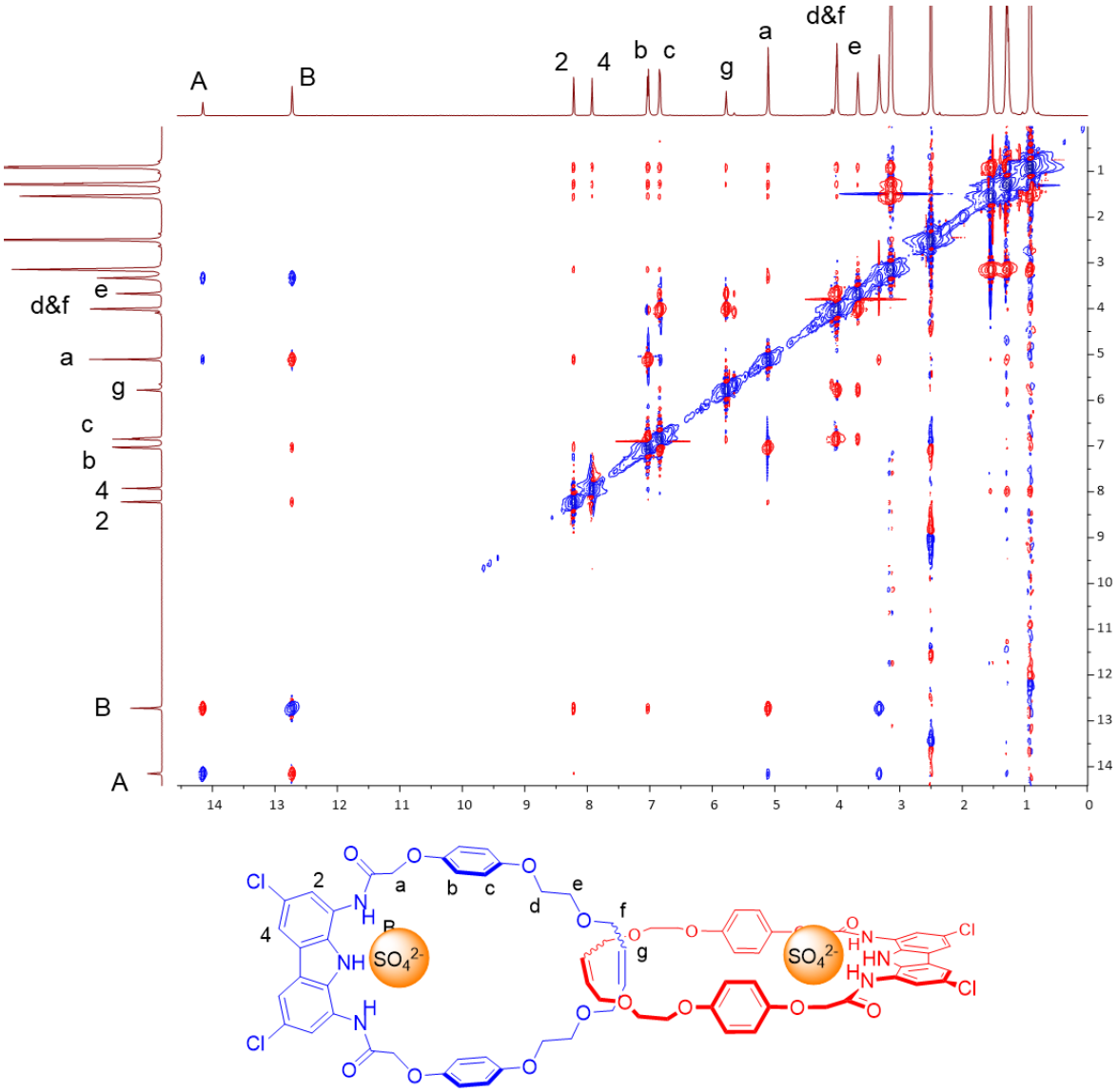


Figure S13. 2D ^{1}H-^{1}H ROESY spectrum of catenane **A** in presence of 2.5 equivalents of TBA_2SO_4 recorded in DMSO-d_6. In excess of sulfate characteristic cross peaks present in ROESY spectrum of catenane **A** in presence of 1 equivalent of TBA_2SO_4 disappeared, suggesting the catenane drastically changes its co-conformation in 1:2 complex.

4. DOSY Experiments

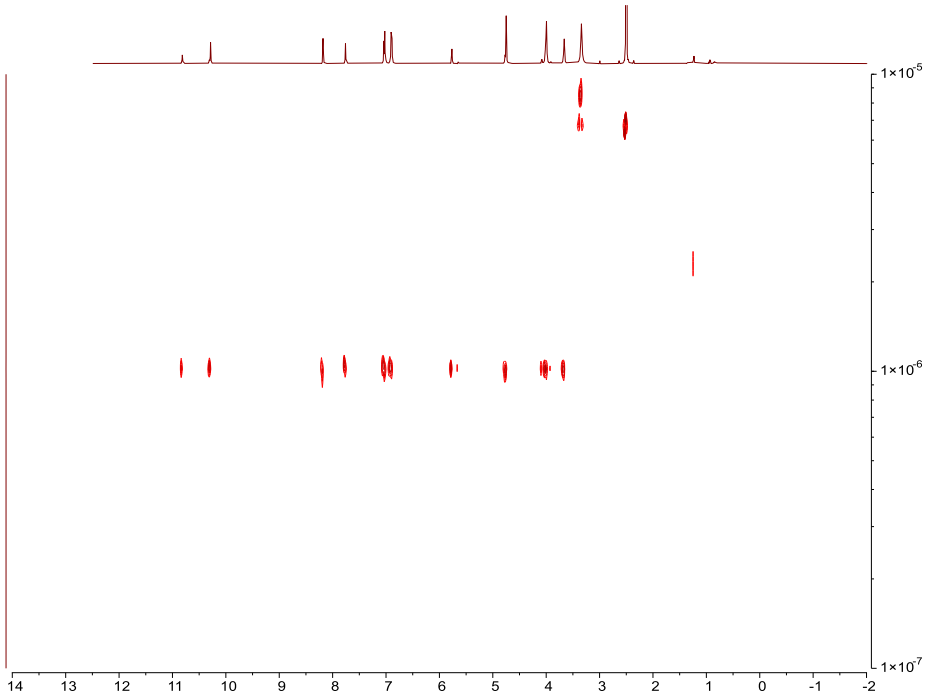


Figure S14. DOSY spectrum of catenane **A** in DMSO-d_6. Concentration of **A**: 0.002 M. Temperature: 298 K. The calculated diffusion coefficient equals to: $D_{\mathbf{A}} = 1.03 \cdot 10^{-6}$ cm^2/s.

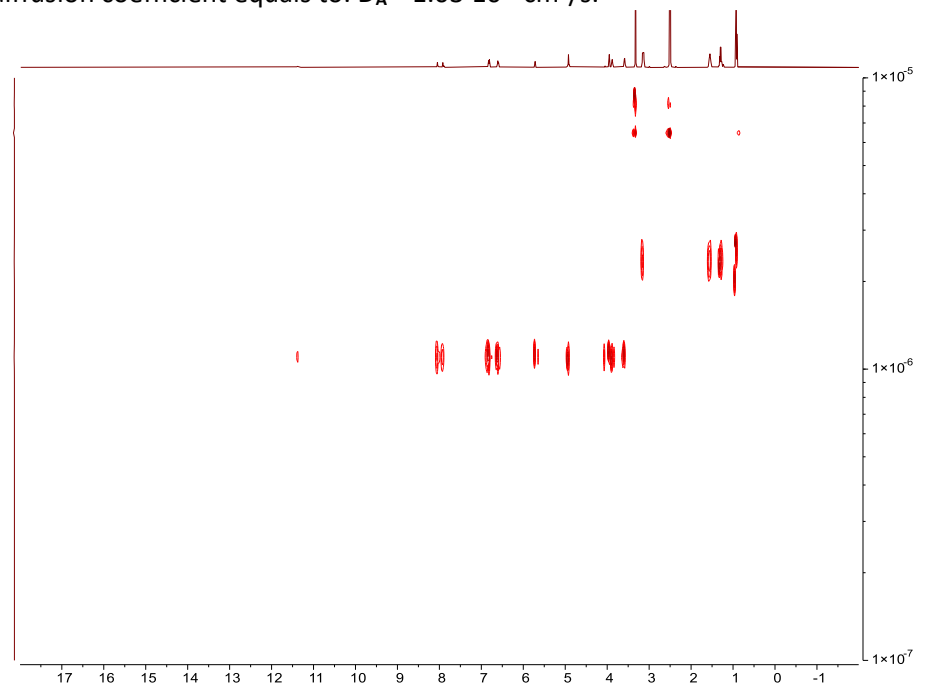


Figure S15. DOSY spectrum of catenane **A** in the presence of 1 equivalent of TBA_2SO_4 in DMSO-d_6. Concentration of **A**: 0.002 M. Temperature: 298 K. The calculated diffusion coefficient equals to: $D_{\mathbf{A}\times SO4} = 1.11 \cdot 10^{-6}$ cm^2/s.

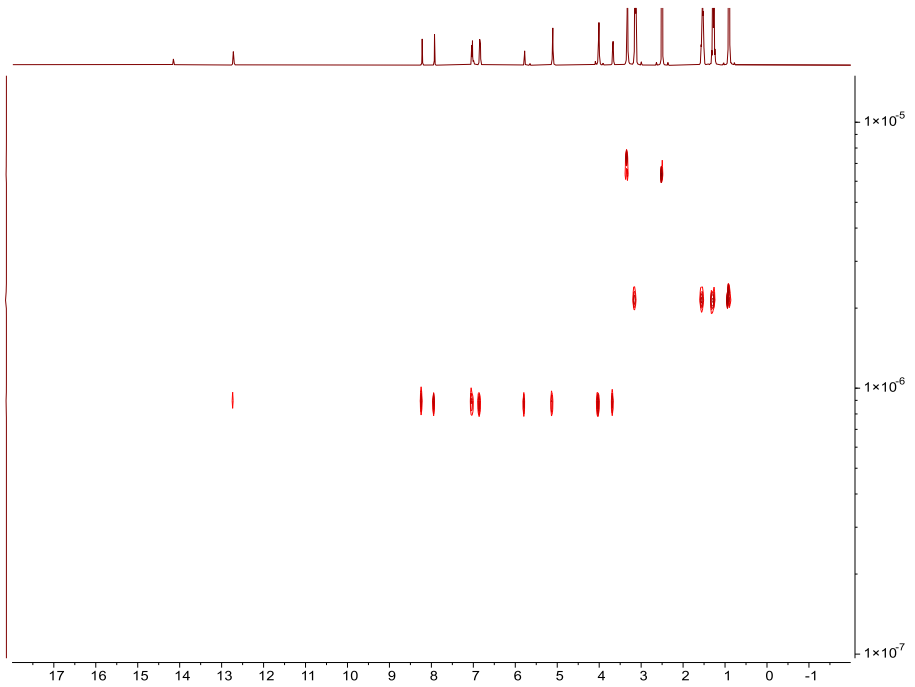


Figure S16. DOSY spectrum of catenane **A** in the presence of 2.5 equivalent of TBA_2SO_4 in DMSO-d_6. Concentration of **A**: 0.002 M. Temperature: 298 K. The calculated diffusion coefficient equals to: $D_{SO4×A×SO4} = 0.89 \cdot 10^{-6}$ cm^2/s.

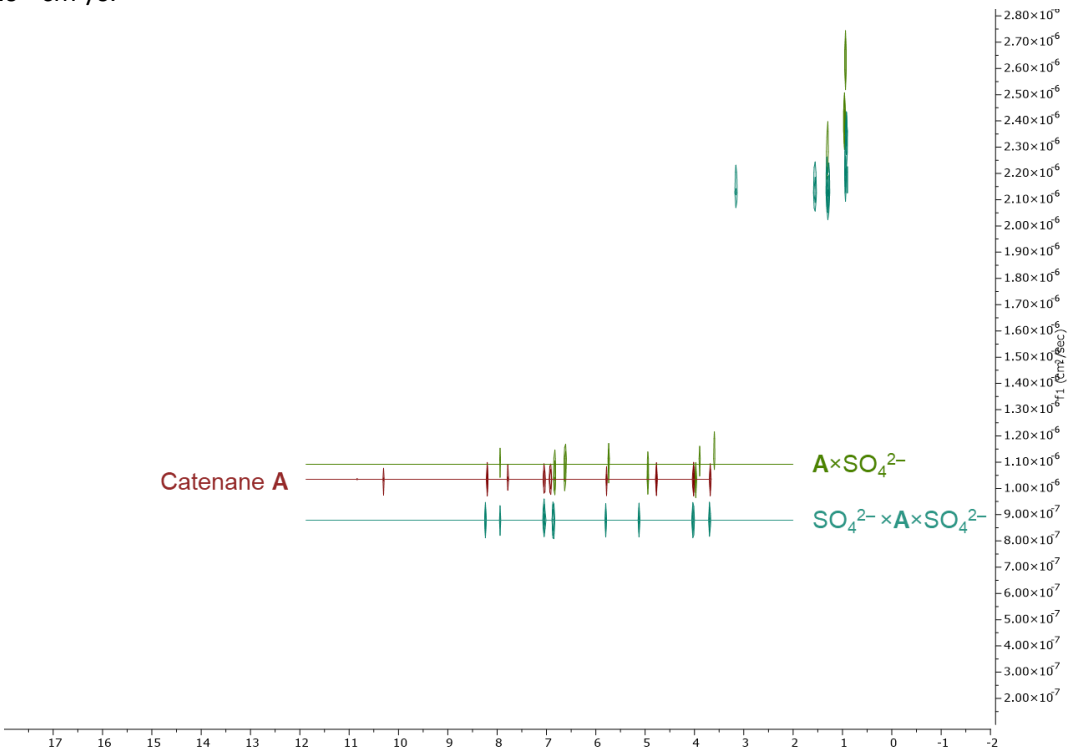


Figure S17. Superimposed DOSY spectra of catenane **A** in the presence of 0, 1, or 2.5 equivalent of TBA_2SO_4 in DMSO-d_6. Concentration of **A**: 0.002 M. Temperature: 298 K.

5. Binding Studies

5.1 ^{1}H NMR Titrations

General Procedure

All the reagents were weighted separately on a Mettler Toledo Excellence XA105DU analytical balance (readability 0.01 mg) in screw-capped vials sealed with Teflon-covered septa. DMSO/H_2O mixtures were obtained using Milli-Q H_2O and their concentrations were expressed as weight-weight percentage. All the solvent/solution manipulations were done using gas-tight Hamilton glass syringes. Titrants were prepared by dissolving appropriate salts in the solution of the receptor (unless specified otherwise), in order to avoid dilution of the receptor during titration. Titrations were performed in screw-capped NMR tubes sealed with Teflon-covered septa, by adding aliquots of the titrant solution to the receptor solution (0.600 mL, 2 mM) and recording ^{1}H NMR spectra after each addition. The NMR spectra were measured on Agilent 400 MHz spectrometer. The ^{1}H NMR titration data were fitted with WinEQNMR2 software when possible. Association constants and chemical shifts of both 1:1 and 1:2 complexes were set as free parameters for fitting, whereas chemical shifts of free ligands were constrained to be equal to experimentally measured values.

5.1.1 ^{1}H NMR titration of 0.001 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.015 M $(TBA)_2SO_4$.

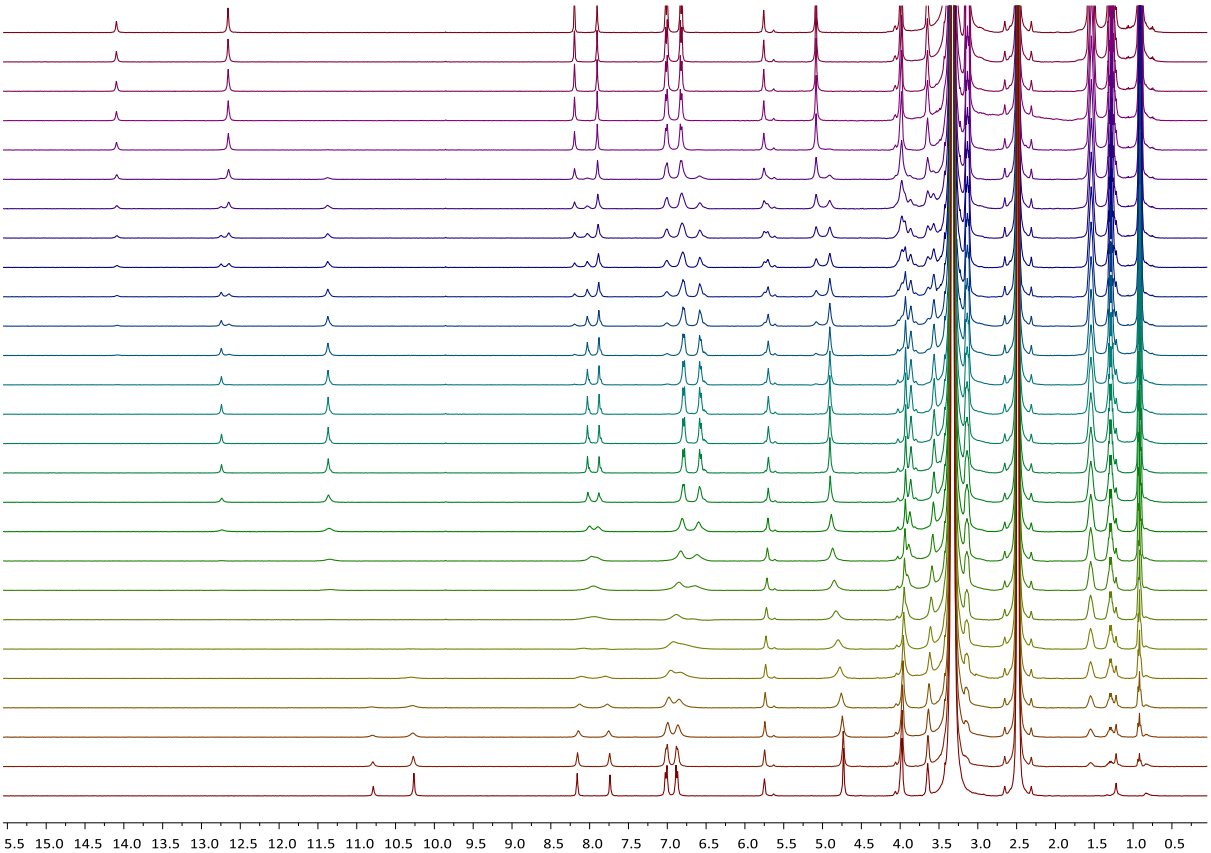


Figure S18. Stack of ^{1}H NMR spectra obtained during titration of 0.001 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.015 M $(TBA)_2SO_4$.

5.1.2 ^{1}H NMR titration of 0.0001 M solution of catenane **A** in DMSO-d_6/H_2O 9:1 with 0.0015 M $(TBA)_2SO_4$. Water suppression (wet1D) was used.

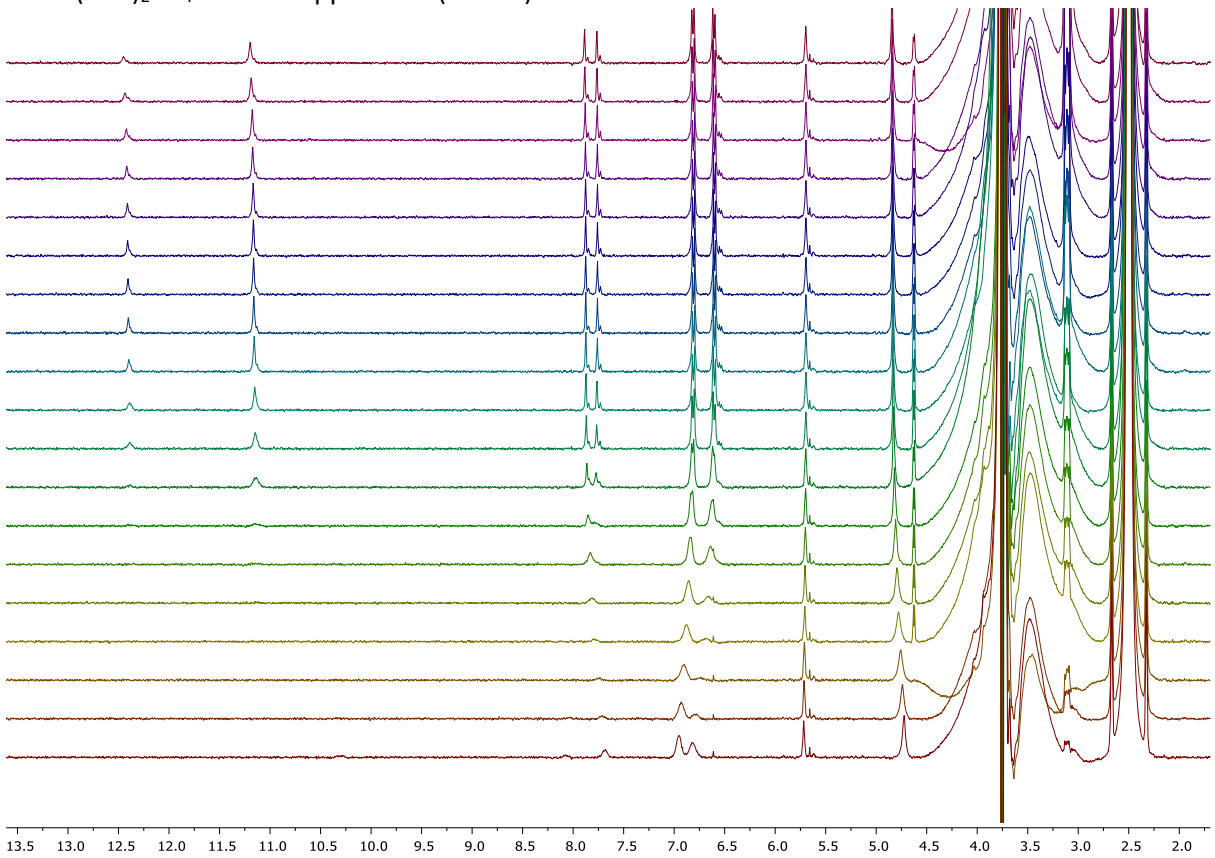
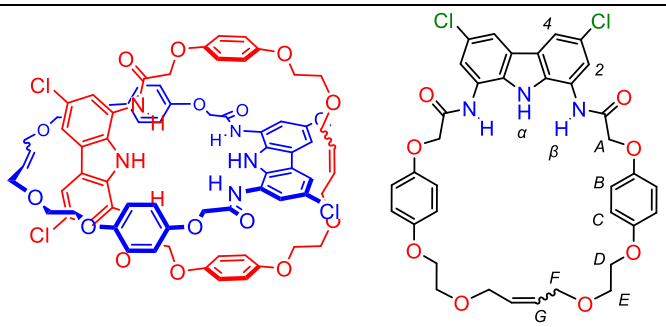


Figure S19. Stack of ^{1}H NMR (wet 1D supression) spectra obtained during titration of 0.0001 M solution of catenane **A** in DMSO-d_6/H_2O 9:1 with 0.0015 M $(TBA)_2SO_4$.

Table S1. Chemical shifts of proton signals obtained during titration of 0.0001 M solution of catenane **A** in DMSO-d_6/H_2O 9:1 with 0.0015 M $(TBA)_2SO_4$.



Equivalents of $(TBA)_2SO_4$	α	β	2	4	A	B	C	G
0.00	10.6893	10.2962	7.6607	8.0934	4.7078	6.9746	6.8409	5.7218
0.10	10.6946	10.307	7.6839	8.0674	4.7238	6.9522	6.8175	5.7181
0.20	10.7041	10.3501	7.7106	8.0354	4.7399	6.9296	6.7902	5.7135
0.29	11.027	10.3504	7.7559	7.9674	4.7572	6.8962	6.7489	5.7116
0.40	broad	broad	7.7881	overlap	4.7786	6.8750	6.6887	5.7074

0.50	broad	broad	7.8122	overlap	4.7917	6.8567	6.6650	5.7046
0.60	broad	11.1379	7.8285	overlap	4.8082	6.8391	6.6368	5.7015
0.70	12.3811	11.1324	7.8529	7.7859	4.8201	6.8261	6.6221	5.699
0.80	12.3938	11.1418	7.8694	7.7735	4.8276	6.8169	6.6113	5.6971
0.90	12.3835	11.1461	7.8696	7.7682	4.8318	6.8121	6.6049	5.6965
1.00	12.3884	11.1509	7.8727	7.7629	4.8336	6.8101	6.6025	5.696
1.20	12.3982	11.1572	7.8748	7.761	4.8351	6.8089	6.6008	5.6959
1.40	12.4029	11.1605	7.8763	7.7602	4.8355	6.8085	6.6002	5.6959
1.60	12.406	11.1629	7.8767	7.7603	4.836	6.8085	6.6001	5.6956
1.80	12.41	11.1652	7.8771	7.76	4.8365	6.8087	6.6004	5.6961
2.00	12.4117	11.167	7.8778	7.7599	4.8369	6.8090	6.6007	5.6961
2.50	12.4175	11.1714	7.8798	7.7609	4.8382	6.8098	6.6016	5.6961
3.00	12.4225	11.1771	7.8811	7.7608	4.8393	6.8106	6.6026	5.6962
4.00	12.4368	11.1884	7.8849	7.7639	4.8419	6.8126	6.6050	5.6969
5.00	12.4491	11.1974	7.8881	7.7655	4.8447	6.8148	6.6077	5.6975

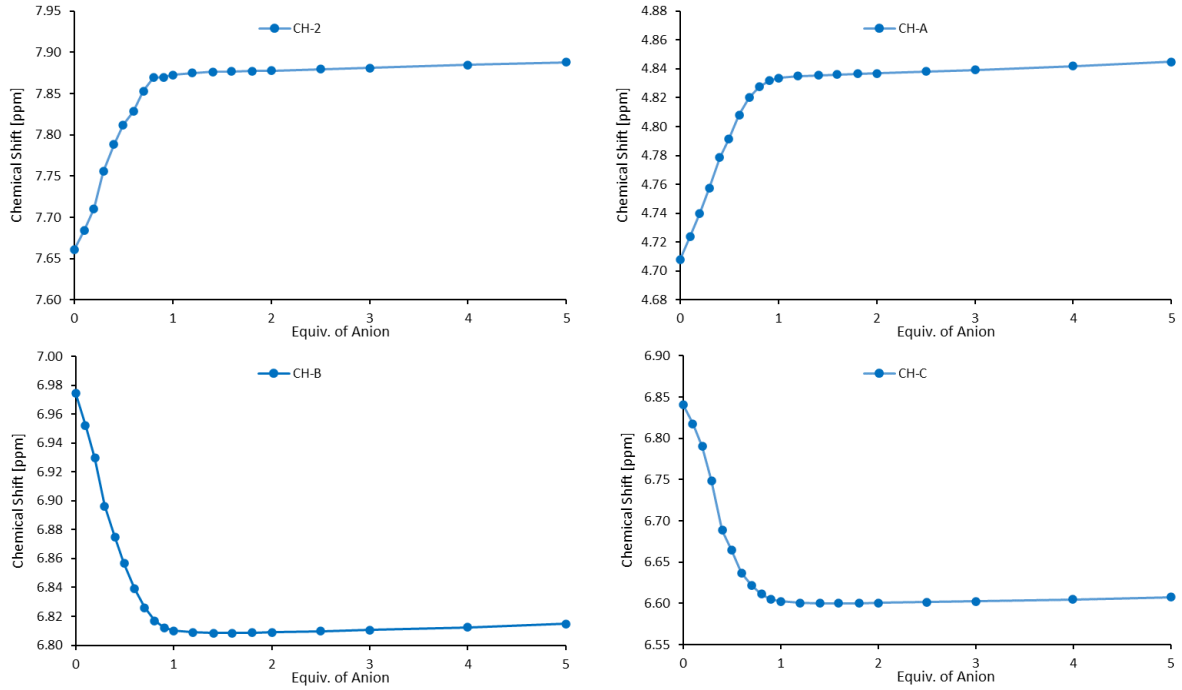


Figure S20. Binding isotherms obtained during titration of 0.0001 M solution of catenane **A** in DMSO-d_6/H_2O 9:1 with 0.0015 M $(TBA)_2SO_4$. No fitting was performed.

5.1.3 ^{1}H NMR titration of 0.0005 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.0075 M $TBAH_2PO_4$.

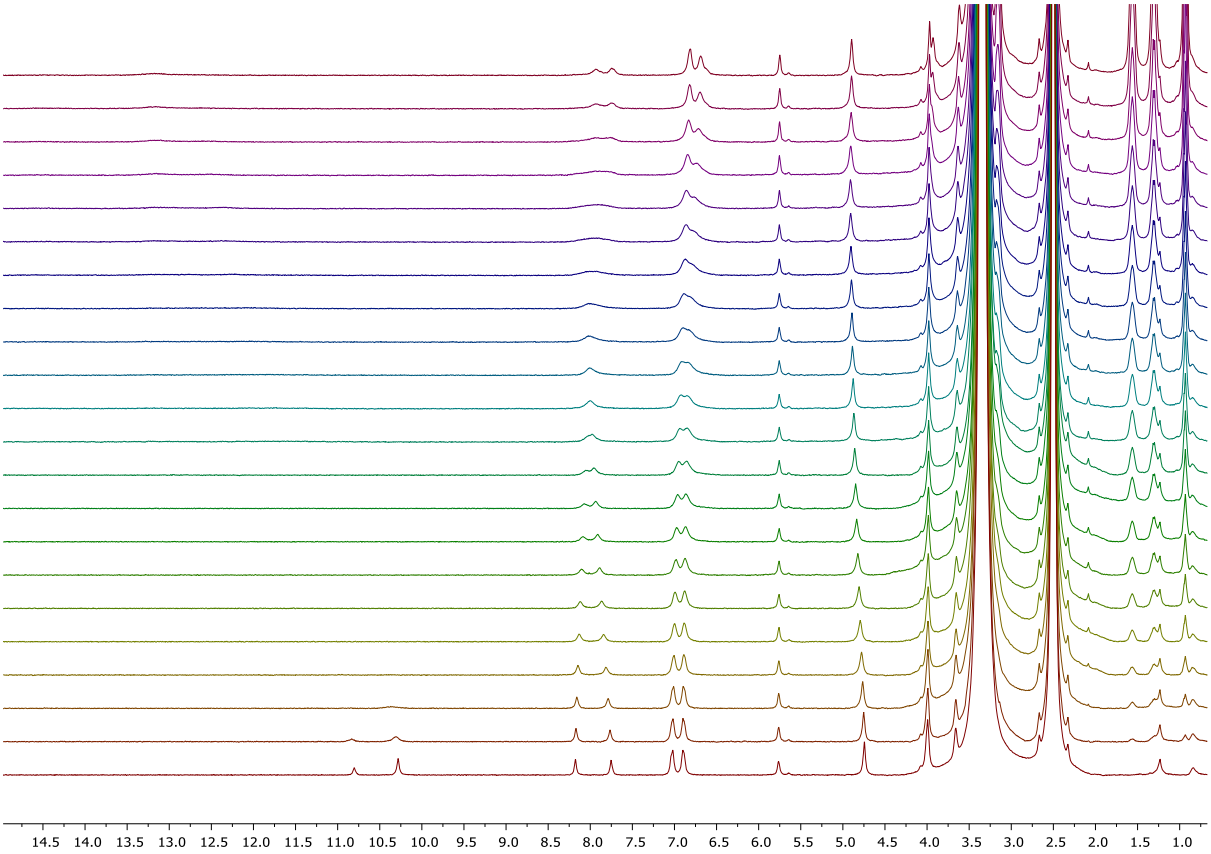


Figure S21. Stack of ^{1}H NMR spectra obtained during titration of 0.0005 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.0075 M $TBAH_2PO_4$.

Table S2. Chemical shifts of proton signals obtained during titration of 0.0005 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.0075 M $TBAH_2PO_4$.

Equivalents of TBA_2HPO_4	α	β	2	4	A	B	C	D&F	E	G
0.00	10.8034	10.2819	7.7524	8.1765	4.7446	7.027	6.8938	3.9921	3.6596	5.7634
0.10	10.8323	10.31	7.7644	8.1698	4.752	7.023	6.8916	3.9905	3.6583	5.7619
0.20	10.8753	10.3704	7.7886	8.1583	4.7649	7.0164	6.8881	3.9893	3.6567	5.7613
0.29	10.9696	10.4453	7.8138	8.146	4.7784	7.0095	6.8861	3.9877	3.6555	5.7593
0.40	broad	broad	7.8406	8.1308	4.7935	6.9996	6.8824	3.9866	3.6524	5.7595
0.50	broad	broad	7.8636	8.1197	4.8076	6.9913	6.8783	3.9852	3.6509	5.7585
0.60	broad	broad	7.8894	8.1018	4.8213	6.9822	6.8737	3.9841	3.6496	5.7575
0.70	broad	broad	7.9127	8.0875	4.8352	6.9699	6.867	3.983	3.6484	5.7562
0.80	broad	broad	7.9342	8.0717	4.8476	6.961	6.8628	3.9822	3.6459	5.7565
0.90	broad	broad	7.9563	8.0449	4.8583	6.9503	6.8571	3.9809	3.6447	5.756
1.00	broad	broad	7.9769	8.0168	4.8683	6.9329	6.849	3.9809	3.6429	5.7553
1.10	broad	broad	7.9996	7.9996	4.8777	6.9245	6.8482	3.9802	3.6426	5.755

1.20	broad	broad	overlap	overlap	4.885	6.9047	6.8351	3.9793	3.6409	5.7546
1.30	broad	broad	overlap	overlap	4.8927	6.897	6.831	3.9787	3.6385	5.7549
1.40	broad	broad	8.0179	7.9573	4.8971	6.8848	6.8186	3.9777	3.6371	5.7546
1.60	broad	broad	8.0139	7.927	4.9043	6.8714	broad	3.9769	3.6359	5.7543
1.80	broad	broad	broad	broad	4.9069	6.8649	6.7867	3.9764	3.6337	5.753
2.00	broad	broad	8.0047	7.8684	4.9083	6.8554	6.7639	3.9756	3.6324	5.7527
2.50	broad	broad	7.967	7.8206	4.9068	6.8414	6.7336	3.9744	3.6295	5.7522
3.00	broad	broad	7.9375	7.76	4.9018	6.832	6.7111	3.973	3.6252	5.7512
4.00	broad	broad	7.9286	7.7418	4.897	6.8175	6.6948	3.9719	3.6206	5.7493
5.00	broad	broad	7.9306	7.7405	4.8956	6.815	6.687	3.9702	3.6162	5.7494

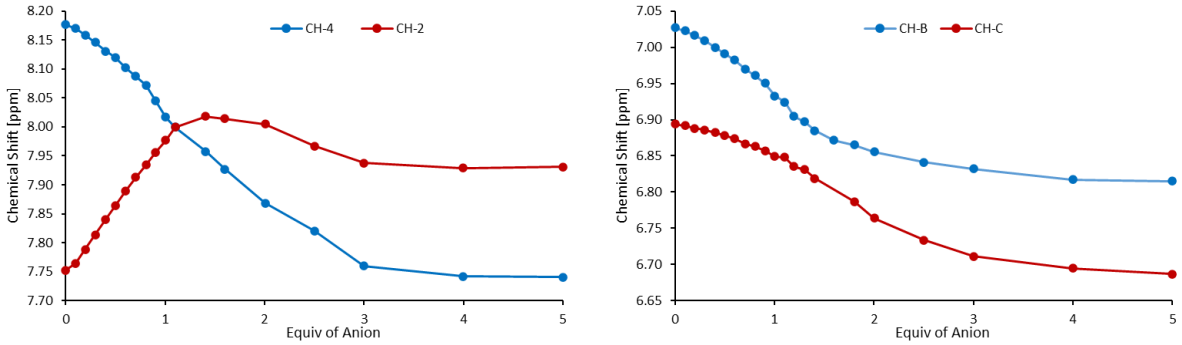


Figure S22. Binding isotherms obtained during titration of 0.0005 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.0075 M $TBAH_2PO_4$. No fitting was performed.

5.1.4 ^{1}H NMR titration of 0.0005 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.0075 M TBAPhCOO.

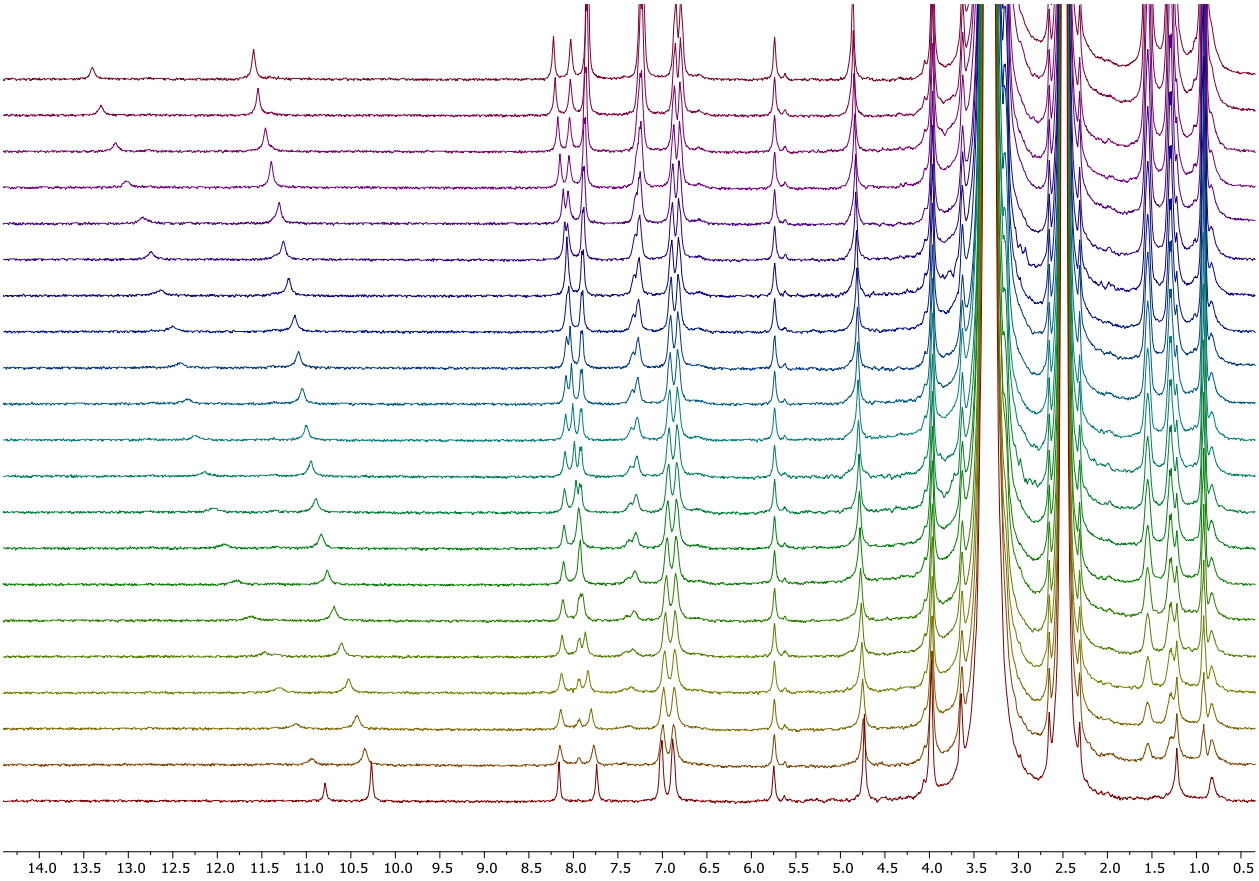


Figure S23. Stack of ^{1}H NMR spectra obtained during titration of 0.0005 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.0075 M TBAPhCOO.

Table S3. Chemical shifts of proton signals obtained during titration of 0.0005 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.0075 M TBAPhCOO.

Equivalents of TBAPhCOO	α	β	2	4	A	B	C	D&F	E	G
0.00	10.8045	10.2822	7.7528	8.1759	4.7452	7.0262	6.8933	3.9912	3.6587	5.7623
0.10	10.9508	10.3564	7.7839	8.1647	4.7572	7.0119	6.8857	3.9854	3.6493	5.7575
0.20	11.1228	10.4475	7.8162	8.1564	4.7644	7.0016	6.8794	3.9846	3.648	5.757
0.30	11.3225	10.5383	7.8492	8.146	4.7739	6.992	6.8727	3.9833	3.647	5.7559
0.40	11.4857	10.6215	7.88	8.1388	4.7807	6.9807	6.8674	3.9822	3.6467	5.7552
0.50	11.636	10.7015	7.914	8.1324	4.7874	6.972	6.8615	3.9813	3.6449	5.7531
0.60	11.7966	10.7807	7.9362	8.1257	4.7952	6.9615	6.8573	3.9817	3.6449	5.7541
0.70	11.9353	10.8479	7.9538	8.1189	4.801	6.9556	6.8534	3.9821	3.6443	5.7558
0.80	12.0549	10.9093	7.9846	8.1132	4.806	6.9482	6.8487	3.9803	3.646	5.7534
0.90	12.1556	10.9621	8.0037	8.1083	4.8111	6.9414	6.8443	3.9803	3.6447	5.7555
1.00	12.267	11.0153	8.0216	8.1022	4.8165	6.936	6.8422	3.9798	3.644	5.7533

1.10	12.3436	11.06	8.0358	8.0968	4.821	6.931	6.839	3.9798	3.6443	5.7537
1.20	12.436	11.1014	8.0521	8.0926	4.8242	6.9262	6.8365	3.9795	3.6414	5.7544
1.35	12.5209	11.147	8.0672	8.0852	4.8283	6.9212	6.8319	3.9799	3.6439	5.754
1.60	12.6491	11.212	8.087	8.087	4.8348	6.914	6.8298	3.9794	3.6448	5.7537
1.80	12.7595	11.2713	8.1112	8.0805	4.8417	6.9081	6.8243	3.9789	3.6417	5.755
2.00	12.855	11.3198	8.1302	8.0736	4.8457	6.9022	6.8211	3.9789	3.6406	5.7549
2.50	13.0388	11.4094	8.1653	8.0647	4.8555	6.8916	6.8155	3.9782	3.64	5.755
3.00	13.1584	11.4728	8.1895	8.0581	4.8619	6.8841	6.8107	3.9794	3.6401	5.7552
4.00	13.3215	11.5571	8.2192	8.0497	4.8704	6.8734	6.8074	3.9778	3.6404	5.755
5.00	13.4205	11.6067	8.2383	8.0448	4.8755	6.8674	6.8028	3.979	3.6415	5.7538

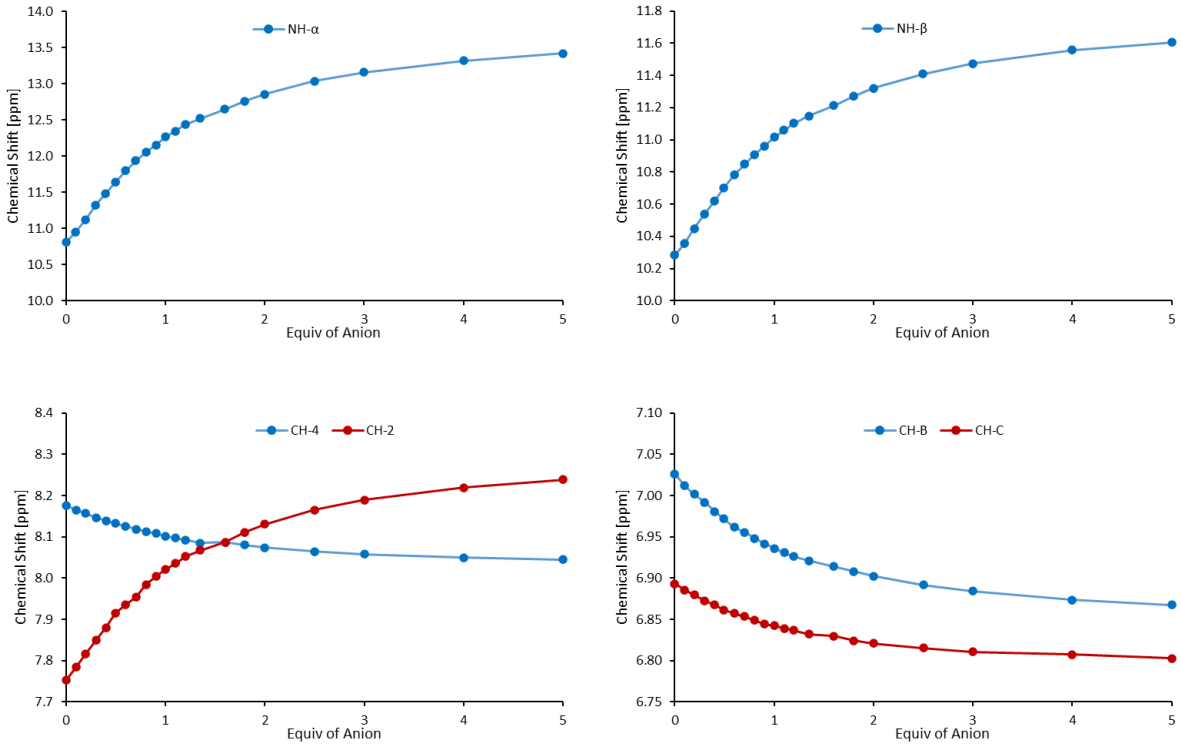


Figure S24. Binding isotherms obtained during titration of 0.0005 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.0075 M TBAPhCOO. No fitting was performed.

5.1.5 ^{1}H NMR titration of 0.001 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.015 M TBACl.

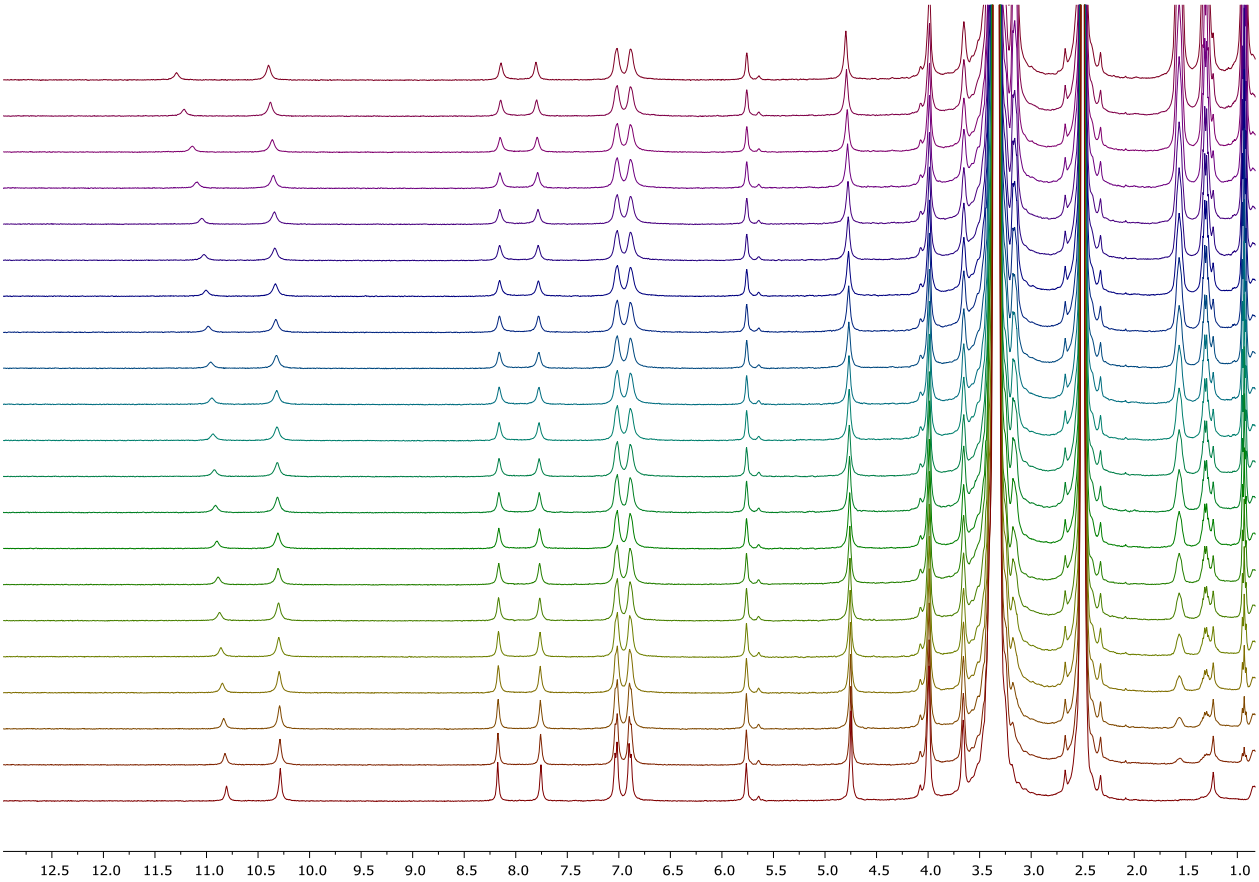


Figure S25. Stack of ^{1}H NMR spectra obtained during titration of 0.001 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.015 M TBACl.

Table S4. Chemical shifts of proton signals obtained during titration of 0.001 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.015 M TBACl.

Equivalents of TBACl	α	β	2	4	A	B	C	D&F	E	G
0.00	10.8059	10.2837	7.7555	8.1746	4.7468	7.0277	6.8904	3.9905	3.659	5.7627
0.10	10.821	10.2872	7.7585	8.1721	4.7498	7.0251	6.88905	3.9901	3.6581	5.7623
0.20	10.8341	10.2903	7.7611	8.1706	4.7514	7.02455	6.88825	3.9887	3.6571	5.7622
0.29	10.8461	10.2942	7.763	8.1695	4.7539	7.02325	6.8871	3.989	3.6572	5.762
0.40	10.8601	10.2971	7.7641	8.1673	4.7556	7.0208	6.8872	3.9883	3.6553	5.7613
0.50	10.8728	10.3008	7.7668	8.1662	4.7572	7.0212	6.8868	3.9886	3.6556	5.7613
0.60	10.8852	10.3042	7.7679	8.165	4.7594	7.0195	6.8858	3.9871	3.655	5.7607
0.70	10.8996	10.3073	7.7698	8.1642	4.7608	7.0199	6.8848	3.9877	3.6558	5.7605
0.80	10.913	10.3102	7.7716	8.1634	4.7623	7.0191	6.885	3.9874	3.6551	5.7605
0.90	10.9233	10.3129	7.7725	8.1612	4.764	7.0172	6.8836	3.9869	3.6547	5.7599
1.00	10.9368	10.3156	7.7737	8.1609	4.7654	7.0186	6.8837	3.987	3.6546	5.7599
1.10	10.9484	10.319	7.7751	8.1601	4.7671	7.0183	6.8839	3.9871	3.654	5.7592
1.20	10.9584	10.3218	7.776	8.1588	4.7681	7.0185	6.8835	3.986	3.6536	5.7592

1.40	10.9822	10.3271	7.7781	8.1581	4.7703	7.018	6.8827	3.9863	3.6531	5.7584
1.60	11.0036	10.3321	7.7801	8.1562	4.7723	7.0172	6.8833	3.9862	3.6527	5.7586
1.80	11.024	10.3373	7.7827	8.1563	4.7747	7.0175	6.8853	3.9856	3.6528	5.7588
2.00	11.0472	10.3428	7.784	8.1552	4.7766	7.0178	6.8845	3.9861	3.6527	5.7582
2.50	11.0948	10.3537	7.7878	8.1527	4.781	7.0187	6.8831	3.9859	3.652	5.7588
3.00	11.1371	10.3619	7.7917	8.1502	4.784	7.0179	6.8832	3.9858	3.6519	5.7583
4.00	11.2188	10.3801	7.7974	8.1462	4.7911	7.0201	6.8827	3.9853	3.6519	5.7579
5.00	11.2896	10.3968	7.8037	8.1426	4.7971	7.0194	6.8847	3.9855	3.6525	5.7577

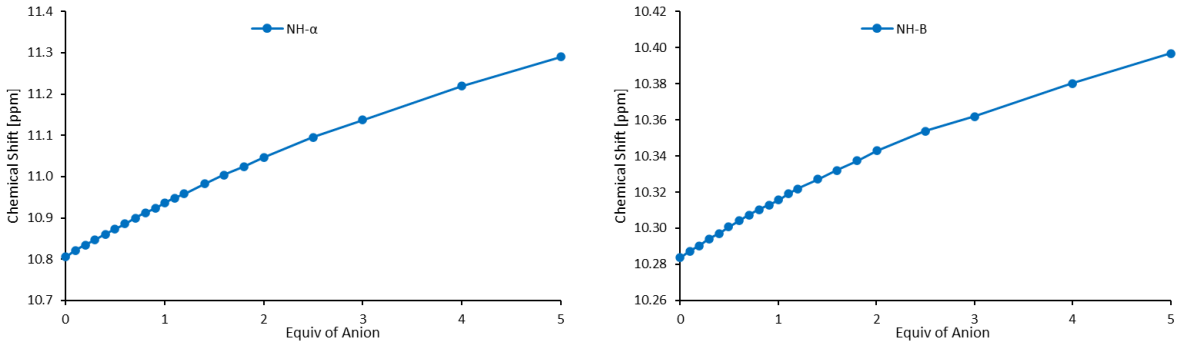


Figure S26. Binding isotherms obtained during titration of 0.001 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.015 M TBACl. No fitting was performed.

5.1.6 ^{1}H NMR titration of 0.001 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.015 M $TBAHSO_4$.

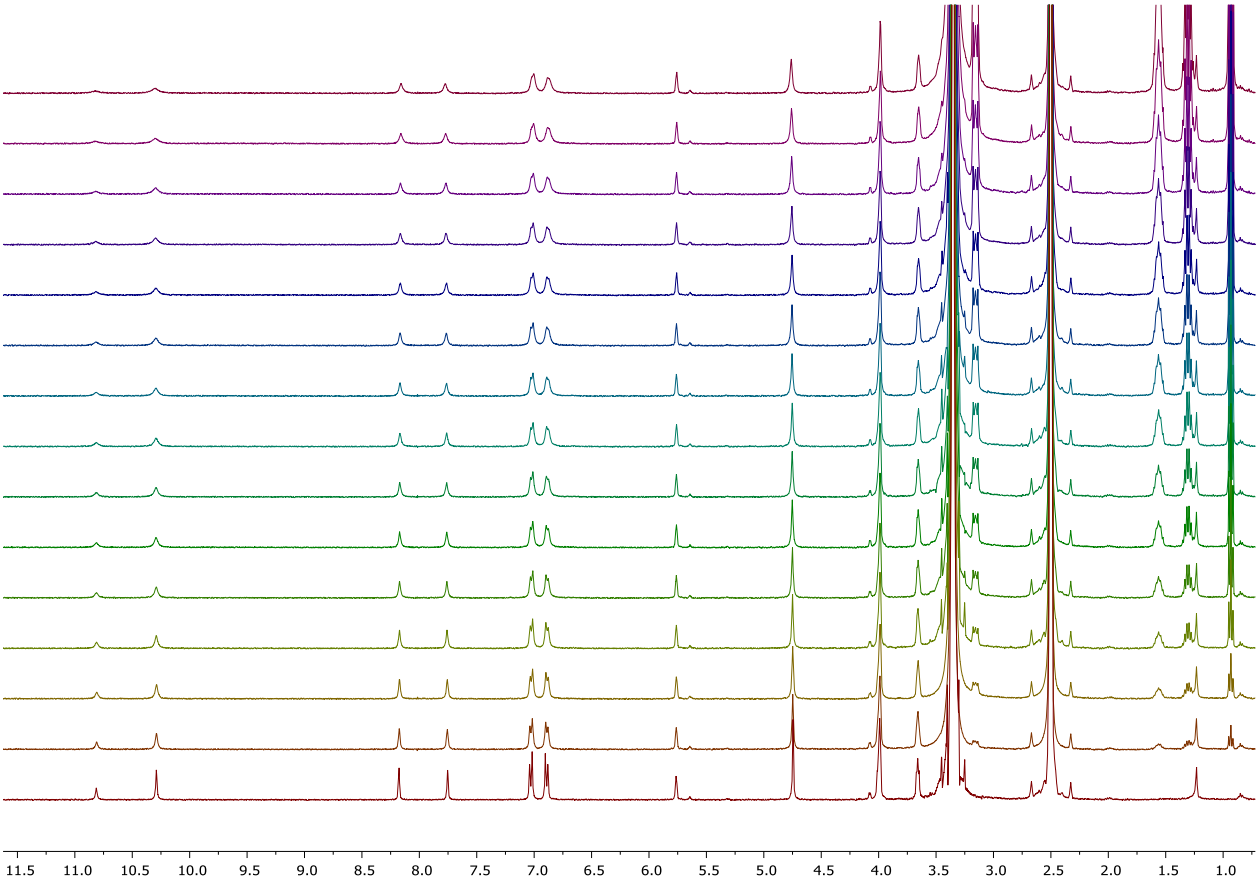


Figure S27. Stack of ^{1}H NMR spectra obtained during titration of 0.001 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.015 M $TBAHSO_4$.

Table S5. Chemical shifts of proton signals obtained during titration 0.001 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.015 M $TBAHSO_4$.

Equivalents of $TBAHSO_4$	α	β	2	4	A	B	C	D&F	E	G
0.00	10.8128	10.29	7.7538	8.1774	4.7456	7.0286	6.89205	3.9949	3.6592	5.7632
0.20	10.8093	10.288	7.7562	8.1748	4.7478	7.02625	6.8891	3.9923	3.6568	5.7619
0.40	10.8089	10.2886	7.7564	8.173	4.7479	7.02395	6.8876	3.993	3.6557	5.7609
0.60	10.8112	10.2906	7.7583	8.1723	4.7493	7.02345	6.88715	3.9922	3.6555	5.7613
0.80	10.8116	10.2912	7.7597	8.1717	4.7502	7.02235	6.8856	3.9925	3.6558	5.7611
1.00	10.8114	10.2917	7.7606	8.1709	4.7514	7.02125	6.88515	3.9916	3.6552	5.7605
1.20	10.8108	10.2913	7.7615	8.17	4.7523	7.0202	6.88415	3.9906	3.655	5.7608
1.40	10.8127	10.2905	7.7614	8.168	4.7521	7.01945	6.88325	3.9905	3.653	5.76
1.60	10.8126	10.2917	7.7631	8.167	4.7536	7.0184	6.88335	3.9919	3.654	5.7603
1.80	10.8139	10.2925	7.7635	8.1665	4.7535	7.0178	6.883	3.9917	3.6535	5.7601
2.00	10.8147	10.2935	7.7645	8.1657	4.7551	7.0168	6.88205	3.9918	3.653	5.7595
2.50	10.8131	10.2939	7.7675	8.1643	4.7556	7.0169	6.88175	3.99	3.6528	5.7594

3.00	10.8135	10.2925	7.7681	8.163	4.7573	7.01445	6.87745	3.9881	3.652	5.7593
4.00	10.8189	10.2987	7.7698	8.1593	4.7585	7.01195	6.8745	3.9888	3.6521	5.7591
5.00	10.8186	10.3016	7.7743	8.1591	4.7599	7.0111	6.8759	3.9873	3.6505	5.7583

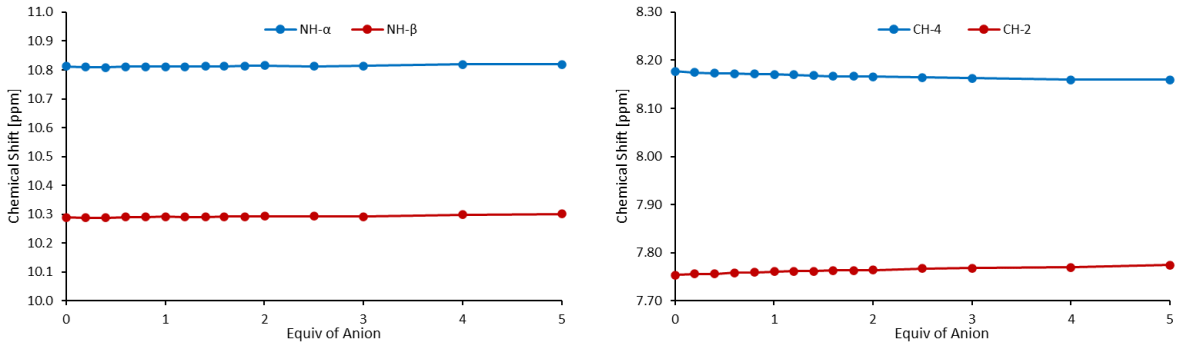


Figure S28. Binding isotherms obtained during titration of 0.001 M solution of catenane **A** in DMSO-d_6 + 0.5% H_2O with 0.015 M $TBAHSO_4$.

5.1.7 ^{1}H NMR titration of 0.001 M solution of macrocycle **3** in DMSO-d_6 + 0.5% H_2O with 0.015 M TBA_2SO_4.

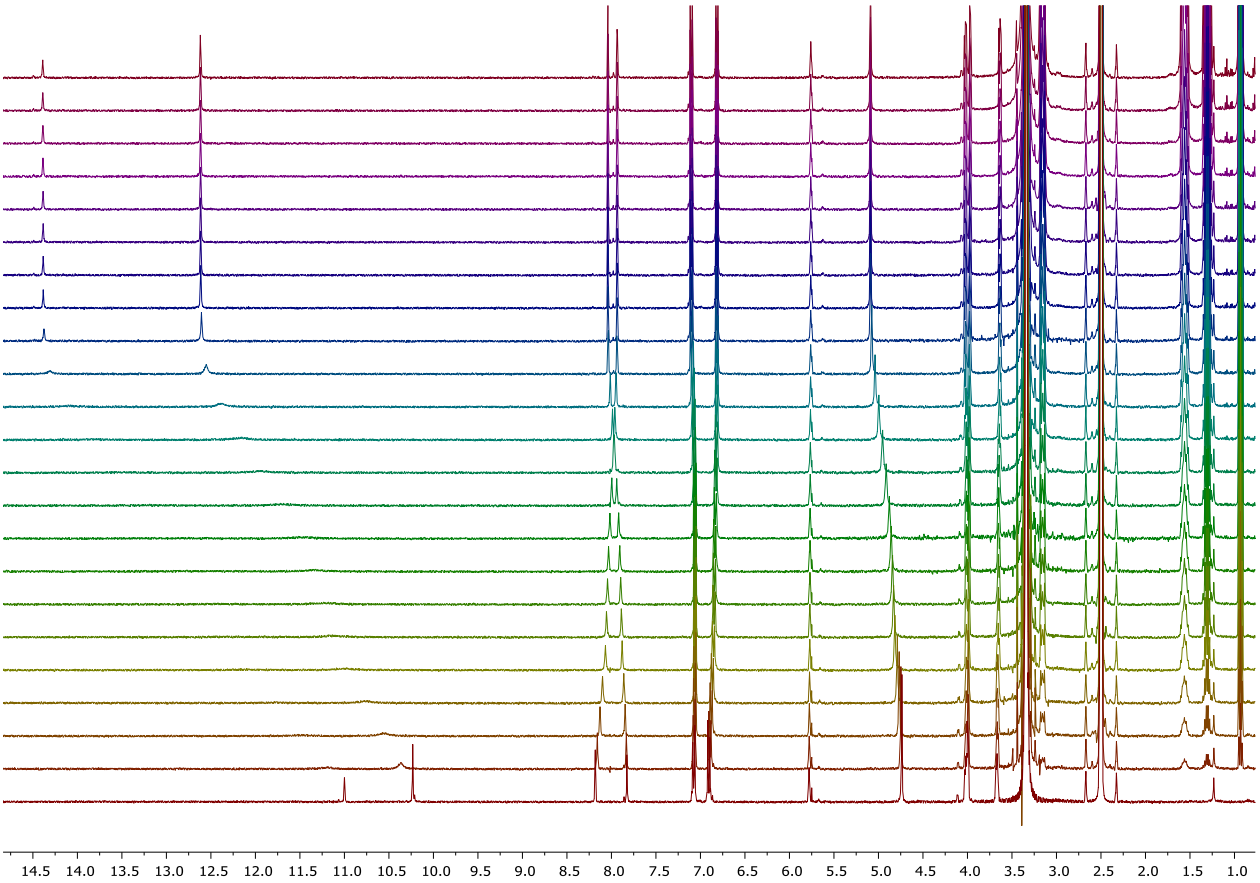


Figure S29. Stack of ^{1}H NMR spectra obtained during titration of 0.001 M solution of macrocycle **3** in DMSO-d_6 + 0.5% H_2O with 0.015 M TBA_2SO_4.

Table S6. Chemical shifts of proton signals obtained during titration of 0.001 M solution of macrocycle **3** in DMSO-d_6 + 0.5% H_2O with 0.015 M TBA_2SO_4.

Equivalents of TBA_2SO_4	α	β	2	4	A	B	C	D	E	F	G
0.00	10.9997	10.2326	7.82535	8.18415	4.7371	7.0749	6.9054	4.0185	3.6691	3.9972	5.7799
0.10	11.1967	10.3669	7.8346	8.1605	4.7483	7.07	6.8938	4.0163	3.665	3.9941	5.7773
0.20	11.4771	10.562	7.8473	8.12895	4.7667	7.06515	6.879	4.0141	3.6615	3.9917	5.7756
0.29	11.7863	10.7703	7.8616	8.0989	4.7874	7.062	6.86565	4.0127	3.6578	3.9887	5.7734
0.40	12.1407	11.0073	7.8789	8.0683	4.8152	7.06045	6.85245	4.0118	3.6543	3.9861	5.7711
0.45	12.2759	11.1359	7.8878	8.0553	4.829	7.06045	6.8472	4.0118	3.6524	3.9849	5.7706
0.50	12.4256	11.2122	7.8961	8.0437	4.8421	7.0606	6.8425	4.0116	3.6512	3.9838	5.7695
0.54	broad	11.3339	7.9057	8.0318	4.8571	7.06135	6.838	4.0114	3.6496	3.9836	5.7687
0.60	broad	11.4617	7.9182	8.0176	4.8772	7.06285	6.83275	4.0115	3.6479	3.982	5.7677
0.70	13.1603	11.7011	7.941	7.9953	4.9137	7.06705	6.82545	4.0127	3.6445	3.9803	5.7661
0.80	13.4814	11.9441	7.9676	7.9737	4.9536	7.07315	6.82	4.0144	3.6421	3.9778	5.7646
0.90	13.813	12.1583	7.989	7.9613	4.9953	7.0809	6.81645	4.0166	3.6392	3.9756	5.7635

1.00	14.097	12.3854	8.0142	7.9481	5.0378	7.09015	6.81475	4.0194	3.6372	3.9739	5.7626
1.10	14.3085	12.5538	8.0358	7.93795	5.0747	7.09955	6.81455	4.0224	3.6355	3.972	5.7616
1.20	14.3749	12.6067	8.04145	7.93515	5.0875	7.1033	6.81455	4.0236	3.6339	3.9715	5.7616
1.40	14.3838	12.614	8.04195	7.93475	5.089	7.104	6.8146	4.0235	3.634	3.9712	5.7614
1.60	14.3844	12.6148	8.04185	7.9346	5.089	7.10395	6.81455	4.0238	3.6341	3.9706	5.7613
1.80	14.3847	12.6151	8.0419	7.93475	5.0892	7.10415	6.81465	4.0237	3.634	3.971	5.7613
2.00	14.3853	12.6151	8.04185	7.93465	5.089	7.1041	6.8146	4.0236	3.634	3.9707	5.7612
2.50	14.3864	12.616	8.0419	7.9346	5.089	7.1042	6.8146	4.0239	3.6341	3.9708	5.7612
3.00	14.3869	12.6169	8.0419	7.93465	5.0894	7.1043	6.81465	4.0236	3.6341	3.971	5.7611
4.00	14.3891	12.6177	8.0418	7.93465	5.0891	7.10435	6.8146	4.0235	3.6338	3.9708	5.7609
5.00	14.39	12.6185	8.04175	7.93455	5.089	7.1044	6.8145	4.0236	3.6336	3.9708	5.7607

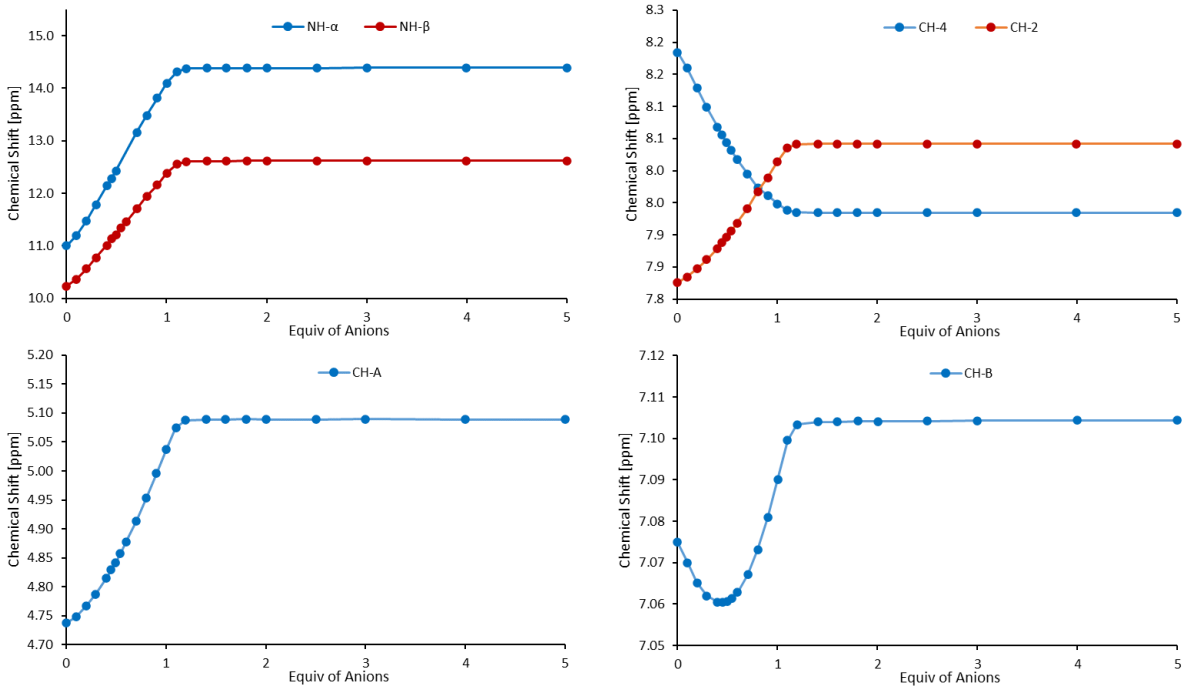


Figure S30. Binding isotherms obtained during titration of 0.001 M solution of macrocycle **3** in DMSO-d_6 + 0.5% H_2O with 0.015 M TBA_2SO_4.

5.1.8 ^{1}H NMR titration of 0.0001 M solution of macrocycle **3** in DMSO-d_6/D_2O 9:1 with 0.0015 M TBA_2SO_4.

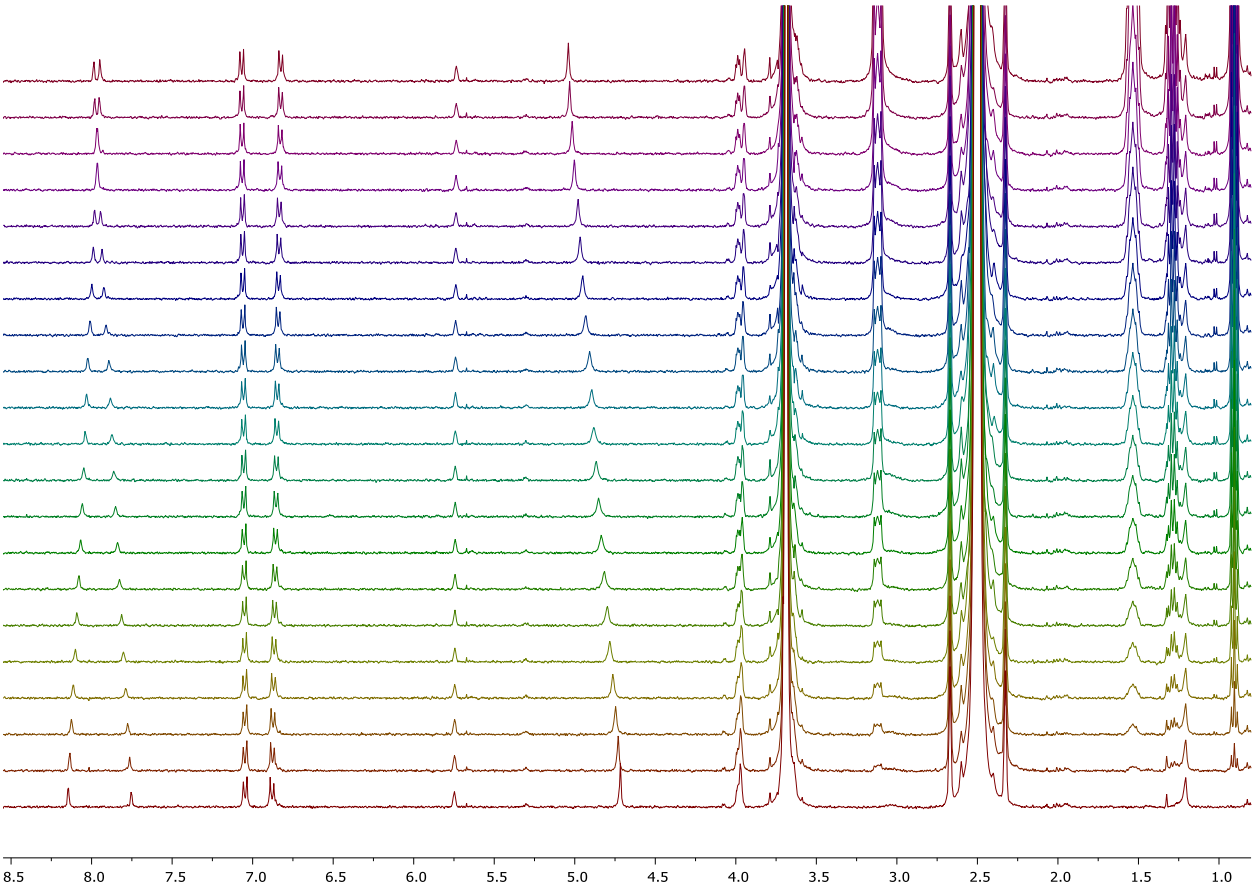


Figure S31. Stack of ^{1}H NMR spectra obtained during titration of 0.0001 M solution of macrocycle **3** in DMSO-d_6/D_2O 9:1 with 0.0015 M TBA_2SO_4.

Table S7. Chemical shifts of proton signals obtained during titration of 0.0001 M solution of macrocycle **3** in DMSO-d_6/D_2O 9:1 with 0.0015 M TBA_2SO_4.

Equivalents of TBA_2SO_4	2	4	A	B	C	D	E	F	G
0.00	7.7528	8.1454	4.7164	7.0461	6.8797	3.9877	3.6427	3.9684	5.7475
0.10	7.7631	8.1353	4.7299	7.0468	6.8766	3.9886	3.6382	3.9684	5.7446
0.20	7.7752	8.1245	4.7458	7.0476	6.8737	3.9876	3.6392	3.9676	5.7457
0.29	7.7872	8.113	4.7631	7.0488	6.8705	3.9875	3.6376	3.9648	5.7443
0.40	7.8018	8.1003	4.7821	7.0497	6.8667	3.9858	3.6366	3.964	5.7447
0.50	7.8129	8.0909	4.7982	7.0505	6.8643	3.9854	3.6341	3.963	5.7431
0.60	7.8261	8.0782	4.8177	7.0517	6.8610	3.9863	3.6327	3.961	5.7432
0.70	7.8379	8.067	4.8346	7.0532	6.8575	3.9874	3.6361	3.9602	5.7418
0.80	7.8506	8.0578	4.8513	7.0540	6.8547	3.9867	3.6312	3.9585	5.742
0.90	7.8612	8.0484	4.8665	7.0552	6.8521	3.9866	3.6296	3.9586	5.7418
1.00	7.8723	8.0393	4.881	7.0560	6.8496	3.9854	3.627	3.9566	5.7411
1.10	7.882	8.0309	4.8943	7.0571	6.8476	3.9864	3.6274	3.9558	5.7401

1.20	7.8921	8.0233	4.9075	7.0581	6.8454	3.9858	3.6271	3.9555	5.7403
1.40	7.9101	8.0084	4.9322	7.0594	6.8417	3.9847	3.6257	3.9538	5.7393
1.60	7.9233	7.9979	4.9503	7.0605	6.8386	3.986	3.6266	3.9519	5.7367
1.80	7.9348	7.9886	4.9663	7.0618	6.8363	3.9868	3.6239	3.951	5.7378
2.00	7.9438	7.9811	4.9785	7.0630	6.8345	3.9866	3.623	3.9507	5.7374
2.50	7.962	7.9661	5.0021	7.0647	6.8308	3.9862	3.6218	3.9483	5.7362
3.00	7.9681	7.9622	5.0156	7.0658	6.8288	3.9864	3.6197	3.9471	5.7353
4.00	7.9808	7.9517	5.0312	7.0670	6.8267	3.9859	3.6197	3.9467	5.735
5.00	7.9867	7.9462	5.0394	7.0675	6.8253	3.9875	3.6193	3.945	5.7354

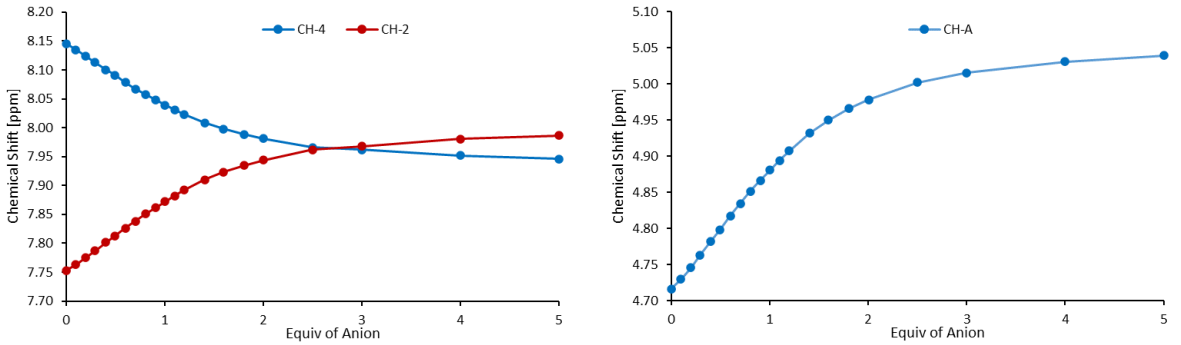


Figure S32. Binding isotherms obtained during titration of 0.0001 M solution of macrocycle **3** in DMSO-d_6/D_2O 9:1 with 0.0015 M TBA_2SO_4.

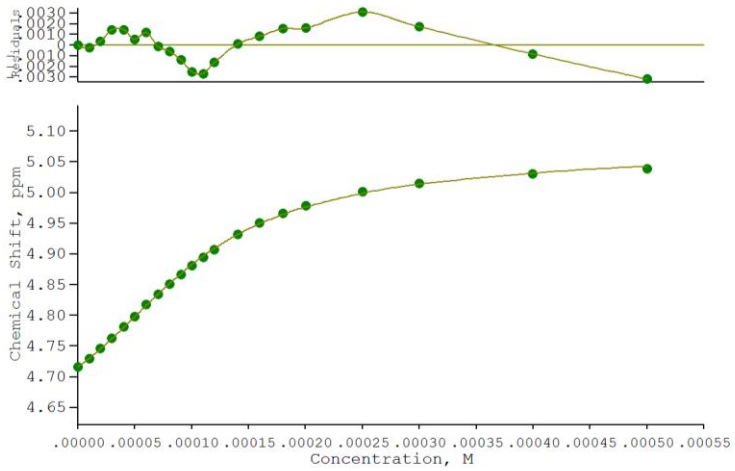


Figure S33. Fitting of 2:1 & 1:1 (receptor:anion) model to results of titration of 0.0001 M solution of macrocycle **3** in DMSO-d_6/D_2O 9:1 with 0.0015 M TBA_2SO_4 for CH-a protons using WinEQNMR.

Binding constants K derived from averaging the results from fitting of 2:1 & 1:1 (receptor:anion) model to titration results for CH-2, CH-4 and CH-a protons using WinEQNMR:

log $K_{1:1}$ = 4.55, Std Dev. = 0.01

log $K_{1:2}$ = 3.00, Std Dev. = 0.06

5.1.9 ^{1}H NMR titration of 0.0002 M solution of macrocycle **3** in DMSO-d_6/D_2O 9:1 with 0.006 M $TBAH_2PO_4$.

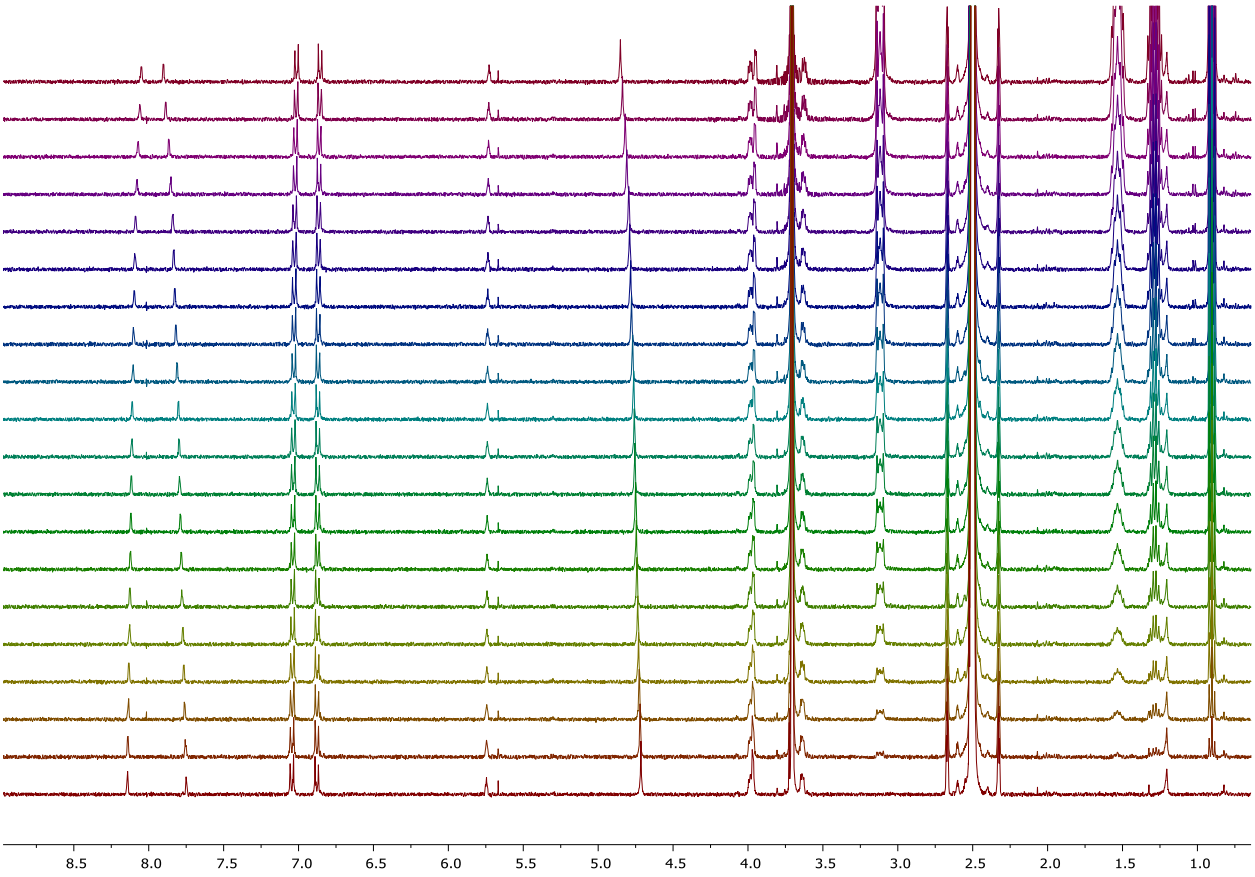


Figure S34. Stack of ^{1}H NMR spectra obtained during titration of 0.0002 M solution of macrocycle **3** in DMSO-d_6/D_2O 9:1 with 0.006 M $TBAH_2PO_4$.

Table S8. Chemical shifts of proton signals obtained during titration of 0.0002 M solution of macrocycle **3** in DMSO-d_6/D_2O 9:1 with 0.006 M $TBAH_2PO_4$.

Equivalents of $TBAH_2PO_4$	2	4	A	B	C	D	E	F	G
0.00	7.7479	8.1430	4.7141	7.0444	6.8785	3.985	3.6375	3.9675	5.7451
0.20	7.7537	8.1390	4.7198	7.0429	6.8775	3.9844	3.6372	3.9669	5.7442
0.39	7.7599	8.1356	4.7252	7.0419	6.8765	3.986	3.6368	3.9669	5.7433
0.59	7.7655	8.1323	4.7303	7.0408	6.8755	3.9853	3.6362	3.9658	5.7429
0.80	7.7716	8.1285	4.7355	7.0393	6.8749	3.985	3.6363	3.9647	5.7419
0.99	7.7769	8.1253	4.7401	7.0383	6.8742	3.9857	3.6351	3.9642	5.7416
1.20	7.7824	8.1220	4.7448	7.0372	6.8733	3.9849	3.6351	3.9625	5.741
1.41	7.7876	8.1189	4.7498	7.0361	6.8726	3.9854	3.6344	3.9627	5.7407
1.61	7.7925	8.1156	4.7544	7.0350	6.8721	3.985	3.6339	3.9618	5.74
1.81	7.7972	8.1132	4.7585	7.0343	6.8714	3.9856	3.6341	3.9614	5.7396
2.01	7.8015	8.1102	4.7623	7.0334	6.8707	3.9848	3.634	3.9612	5.7388

2.39	7.8100	8.1055	4.7695	7.0315	6.8695	3.9853	3.6327	3.9598	5.7378
2.81	7.8184	8.1001	4.7771	7.0298	6.8683	3.9842	3.632	3.9587	5.7375
3.19	7.8253	8.0957	4.7836	7.0283	6.8673	3.984	3.6309	3.9579	5.7363
3.61	7.8326	8.0915	4.7896	7.0268	6.8663	3.9824	3.6319	3.9569	5.7357
4.01	7.8388	8.0876	4.7956	7.0255	6.8652	3.9848	3.6314	3.9567	5.7349
5.00	7.8533	8.0785	4.8084	7.0225	6.8632	3.9849	3.6295	3.9548	5.7334
6.00	7.8654	8.0711	4.8193	7.0199	6.8614	3.9855	3.6277	3.9537	5.7318
8.00	7.8857	8.0588	4.8372	7.0159	6.8585	3.9859	3.6255	3.9509	5.7297
10.00	7.9013	8.0492	4.8515	7.0126	6.8562	3.9852	3.6248	3.9493	5.7281

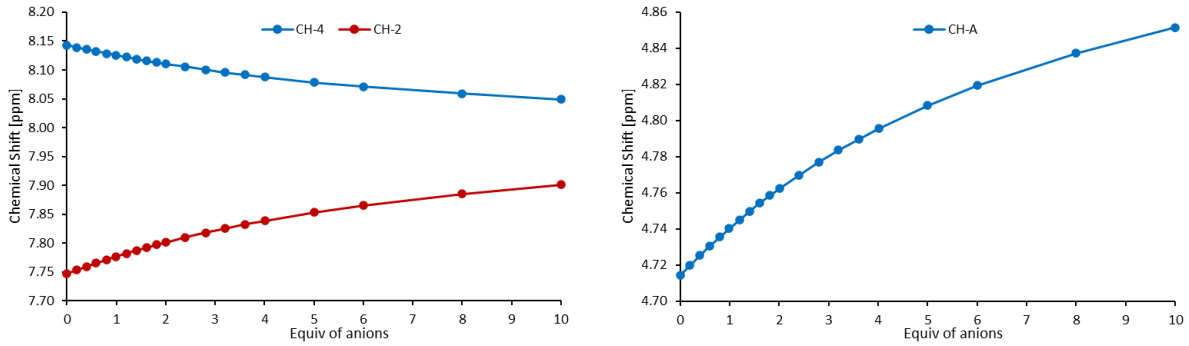


Figure S35. Binding isotherms obtained during titration of 0.0002 M solution of macrocycle **3** in DMSO-d_6/D_2O 9:1 with 0.006 M $TBAH_2PO_4$.

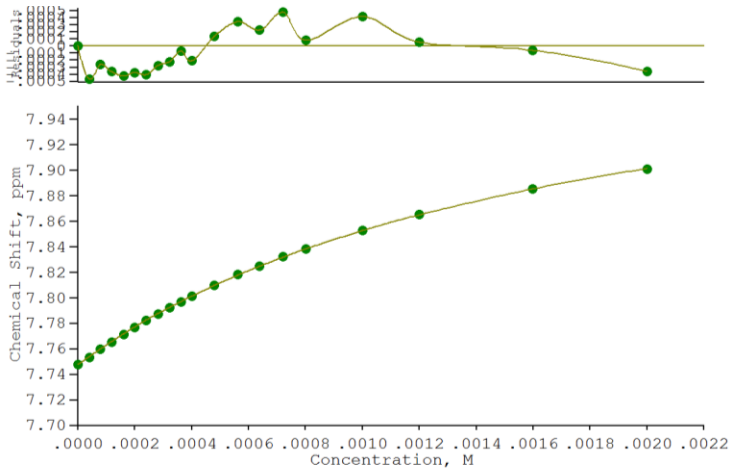


Figure S36. Fitting of 1:1 (receptor:anion) model to results of titration of 0.0001 M solution of macrocycle **3** in DMSO-d_6/D_2O 9:1 with 0.0015 M TBA_2SO_4 for CH-a protons using WinEQNMR.

Binding constants K derived from averaging the results from fitting of 1:1 (receptor:anion) model to titration results for CH-2, CH-4, CH-a, CH-b and CH-c protons using WinEQNMR:

log $K_{1:1}$ = 2.84, Std Dev. = 0.03

5.1.10 ^{1}H NMR titration of 0.0002 M solution of macrocycle **3** in DMSO-d_6/D_2O 9:1 with 0.03 M TBAPhCOO.

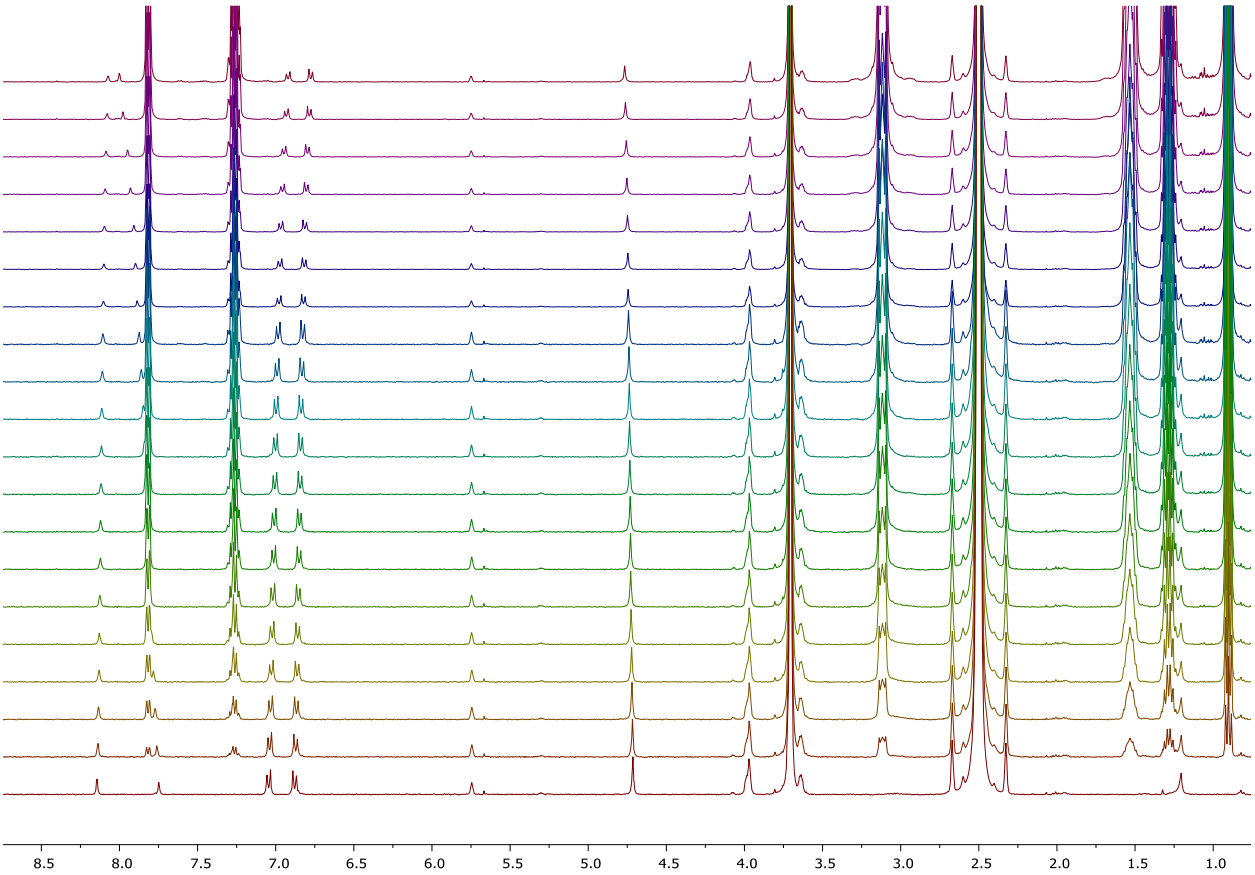


Figure S37. Stack of ^{1}H NMR spectra obtained during titration of 0.0002 M solution of macrocycle **3** in DMSO-d_6/D_2O 9:1 with 0.03 M TBAPhCOO.

Table S9. Chemical shifts of proton signals obtained during titration of 0.0002 M solution of macrocycle **3** in DMSO-d_6/D_2O 9:1 with 0.03 M TBAPhCOO.

Equivalents of TBAPhCOO	2	4	A	B	C	D	E	F	G
0.00	7.7468	8.1442	4.7132	7.0446	6.8789	3.9844	3.6375	3.9684	5.7450
0.99	7.7602	8.1386	4.7174	7.0387	6.8730	3.9832	3.6390	3.9673	5.7453
1.97	7.7722	8.1348	4.7200	7.0333	6.8682	3.9835	3.6378	3.9668	5.7451
2.94	7.7829	8.1310	4.7225	7.0279	6.8639	3.9831	3.6356	3.9669	5.7450
4.01	7.7941	8.1276	4.7251	7.0227	6.8591	3.9822	3.6351	3.9663	5.7461
4.96	overlap	8.1255	4.7273	7.0179	6.8554	3.9821	3.6353	3.9664	5.7455
6.00	overlap	8.1233	4.7292	7.0133	6.8514	3.9816	3.6350	3.9656	5.7462
6.92	overlap	8.1201	4.7310	7.0093	6.8479	3.9814	3.6357	3.9659	5.7461
8.04	overlap	8.1175	4.7332	7.0045	6.8439	3.9814	3.6345	3.9654	5.7459
9.04	7.8401	8.1151	4.7347	7.0005	6.8410	3.9805	3.6360	3.9648	5.7463
10.03	7.8478	8.1131	4.7365	6.9970	6.8380	3.9810	3.6342	3.9651	5.7466

11.96	7.8611	8.1096	4.7387	6.9903	6.8322	3.9795	3.6338	3.9643	5.7466
14.05	7.8751	8.1054	4.7416	6.9834	6.8267	3.9789	3.6344	3.9648	5.7473
15.97	7.8857	8.1020	4.7439	6.9776	6.8223	3.9783	3.6323	3.9639	5.7472
18.04	7.8972	8.0988	4.7459	6.9722	6.8174	3.9784	3.6326	3.9636	5.7474
20.04	7.9073	8.0961	4.7483	6.9670	6.8136	3.9776	3.6326	3.9636	5.7477
25.00	7.9293	8.0911	4.7524	6.9560	6.8044	3.9762	3.6317	3.9630	5.7481
30.00	7.9478	8.0860	4.7560	6.9466	6.7971	3.9756	3.6310	3.9629	5.7483
39.98	7.9771	8.0787	4.7618	6.9311	6.7851	3.9751	3.6301	3.9624	5.7492
50.00	7.9996	8.0732	4.7659	6.9199	6.7760	3.9746	3.6291	3.9619	5.7493

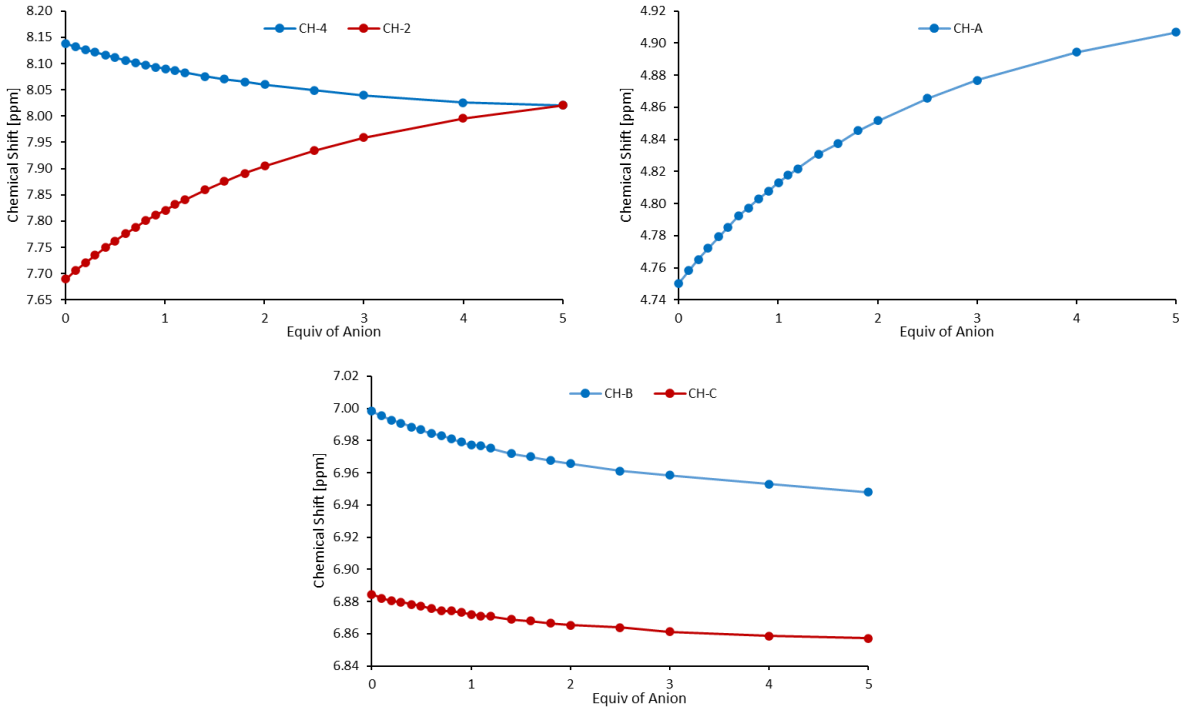


Figure S38. Binding isotherms obtained during titration of 0.0002 M solution of macrocycle **3** in DMSO-d_6/D_2O 9:1 with 0.03 M TBAPhCOO.

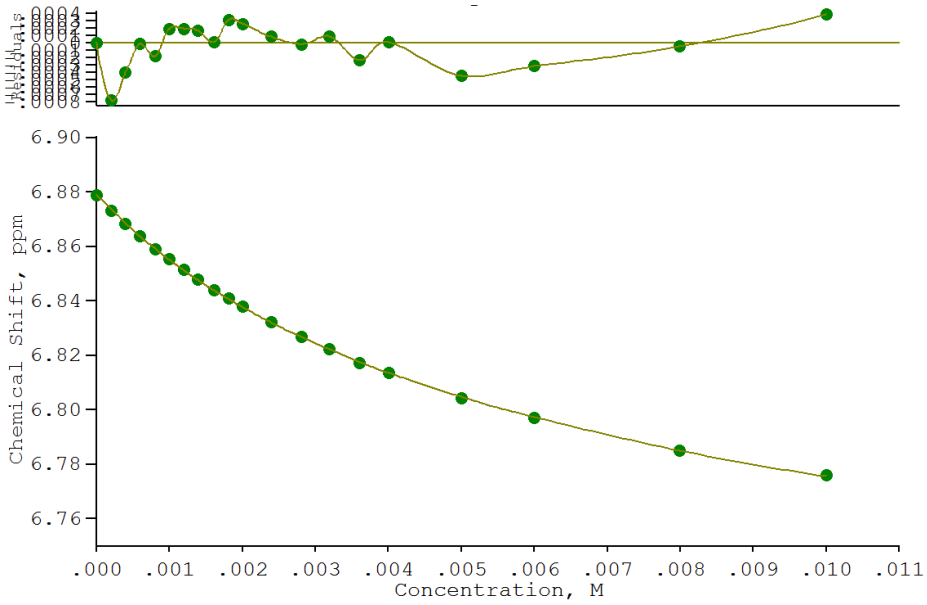


Figure S39. Fitting of 2:1 & 1:1 (receptor:anion) model to results of titration of 0.0002 M solution of macrocycle **3** in DMSO-d_6/D_2O 9:1 with 0.03 M TBAPhCOO for CH-c protons using WinEQNMR.

Binding constants K derived from averaging the results from fitting of 2:1 & 1:1 (receptor:anion) model to titration results for CH-2, CH-a, CH-b and CH-c protons using WinEQNMR:

log $K_{1:1}$ = 2.45, Std Dev. = 0.04

log $K_{2:1}$ = 3.48, Std Dev. = 0.07

5.1.11 ^{1}H NMR titration of 0.002 M solution of precursor **1** in DMSO-d_6 + 0.5% H_2O with 0.03 M TBA_2SO_4.

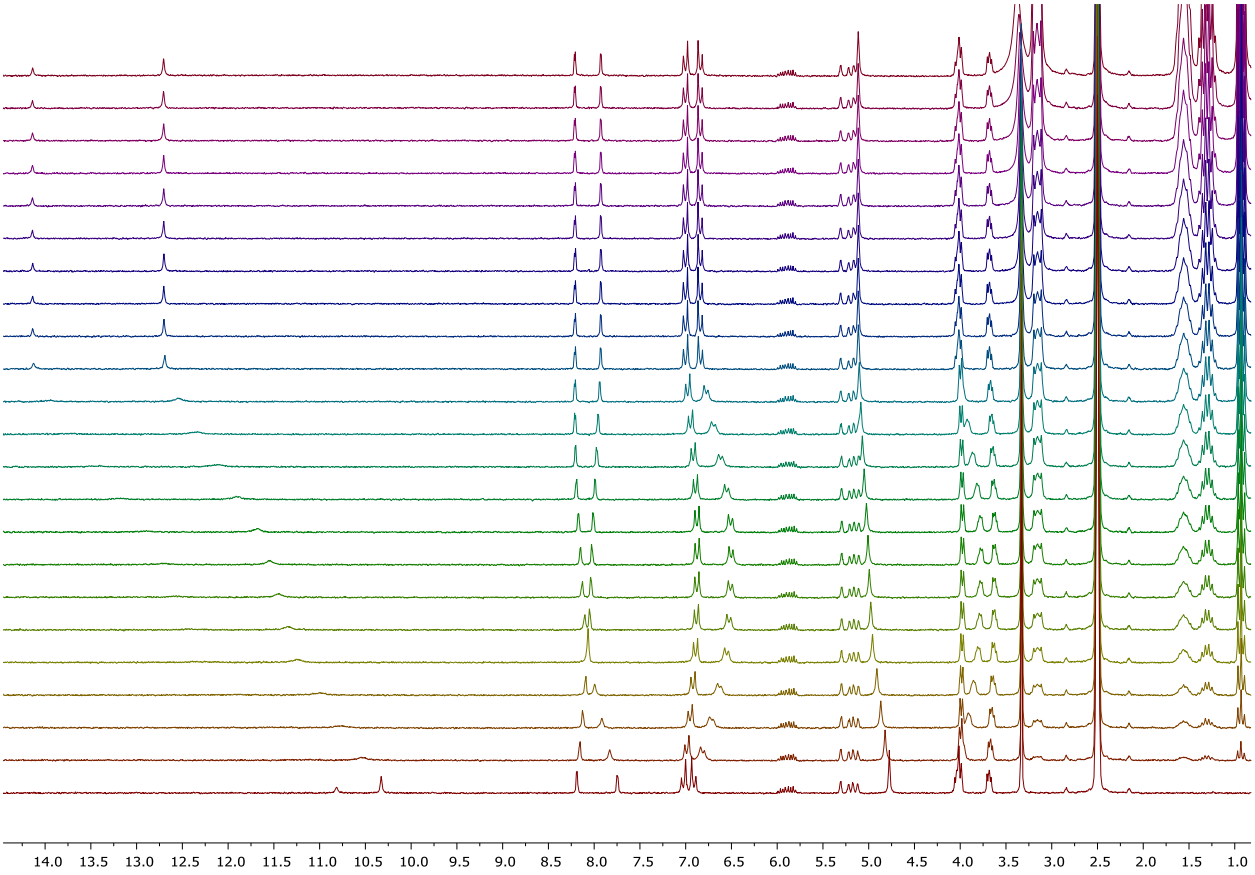
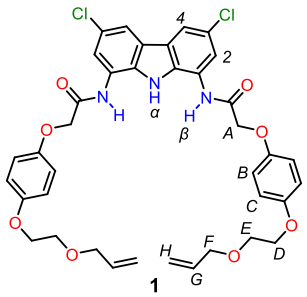


Figure S40. Stack of ^{1}H NMR spectra obtained during titration of 0.002 M solution of precursor **1** in DMSO-d_6 + 0.5% H_2O with 0.03 M TBA_2SO_4.

Table S10. Chemical shifts of proton signals obtained during titration of 0.002 M solution of precursor **1** in DMSO-d_6 + 0.5% H_2O with 0.03 M TBA_2SO_4.



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Equiv. of $(TBA)_2SO_4$	α	β	2	4	A	B	C	D	E	F	G	H
0.00	10.8142	10.3269	7.7467	8.1895	4.7749	7.0234	6.9116	4.0369	3.6841	4.0015	5.8948	5.3066
0.10	11.1520	10.5309	7.8302	8.1568	4.8212	6.9864	6.8158	overlap	3.6695	3.9951	5.8922	5.3037
0.20	11.4305	10.7661	7.9158	8.1249	4.8683	6.9510	6.7184	3.9141	3.6546	3.9890	5.8892	5.3009
0.29	broad	10.9948	7.9950	8.0944	4.9114	6.9203	6.6341	3.8574	3.6422	3.9837	5.8870	5.2987
0.40	12.2865	11.2411	8.0656	8.0656	4.9582	6.8918	6.5533	3.8110	3.6299	3.9788	5.8850	5.2968

0.45	12.3863	11.3479	8.1037	8.0481	4.9771	6.8831	6.5279	3.7921	3.6264	3.9774	5.8841	5.2961
0.50	12.5649	11.4479	8.1299	8.0348	4.9934	6.8775	6.5126	3.7850	3.6225	3.9765	5.8838	5.2959
0.54	12.6857	11.5487	8.1510	8.0246	5.0080	6.8747	6.5051	3.7820	3.6226	3.9761	5.8841	5.2954
0.60	12.8952	11.6808	8.1732	8.0098	5.0257	6.8770	6.5104	3.7857	3.6232	3.9767	5.8842	5.2956
0.70	13.1866	11.9086	8.1947	7.9893	5.0497	6.8933	6.5535	3.8220	3.6316	3.9801	5.8863	5.2977
0.80	13.4333	12.1090	8.2045	7.9716	5.0695	6.9178	6.6189	3.8683	3.6415	3.9850	5.8886	5.2997
0.90	13.7264	12.3412	8.2087	7.9553	5.0860	6.9467	6.6972	3.9314	3.6551	3.9905	5.8913	5.3026
1.00	13.9408	12.5429	8.2097	7.9393	5.1020	6.9773	6.7774	overlap	3.6690	3.9967	5.8951	5.3052
1.10	14.1258	12.6923	8.2091	7.9283	5.1132	7.0011	6.8391	4.0300	3.6790	4.0015	5.8968	5.3075
1.20	14.1351	12.7002	8.2091	7.9269	5.1140	7.0026	6.8420	4.0321	3.6791	4.0015	5.8973	5.3078
1.40	14.1368	12.7023	8.2091	7.9270	5.1139	7.0026	6.8421	4.0331	3.6797	4.0012	5.8972	5.3078
1.60	14.1356	12.7010	8.2090	7.9269	5.1133	7.0022	6.8420	4.0319	3.6795	4.0012	5.8967	5.3075
1.80	14.1386	12.7028	8.2095	7.9267	5.1145	7.0026	6.8425	4.0323	3.6811	4.0013	5.8965	5.3081
2.00	14.1384	12.7033	8.2095	7.9271	5.1141	7.0025	6.8424	4.0327	3.6821	4.0012	5.8973	5.3076
2.50	14.1370	12.7038	8.2099	7.9269	5.1145	7.0026	6.8423	4.0317	3.6803	4.0012	5.8966	5.3071
3.13	14.1367	12.7045	8.2102	7.9270	5.1144	7.0022	6.8421	4.0331	3.6793	4.0009	5.8966	5.3072
4.00	14.1375	12.7061	8.2105	7.9269	5.1148	7.0023	6.8421	4.0317	3.6800	4.0010	5.8961	5.3068
5.00	14.1365	12.7050	8.2106	7.9267	5.1144	7.0019	6.8416	4.0321	3.6796	4.0006	5.8958	5.3065

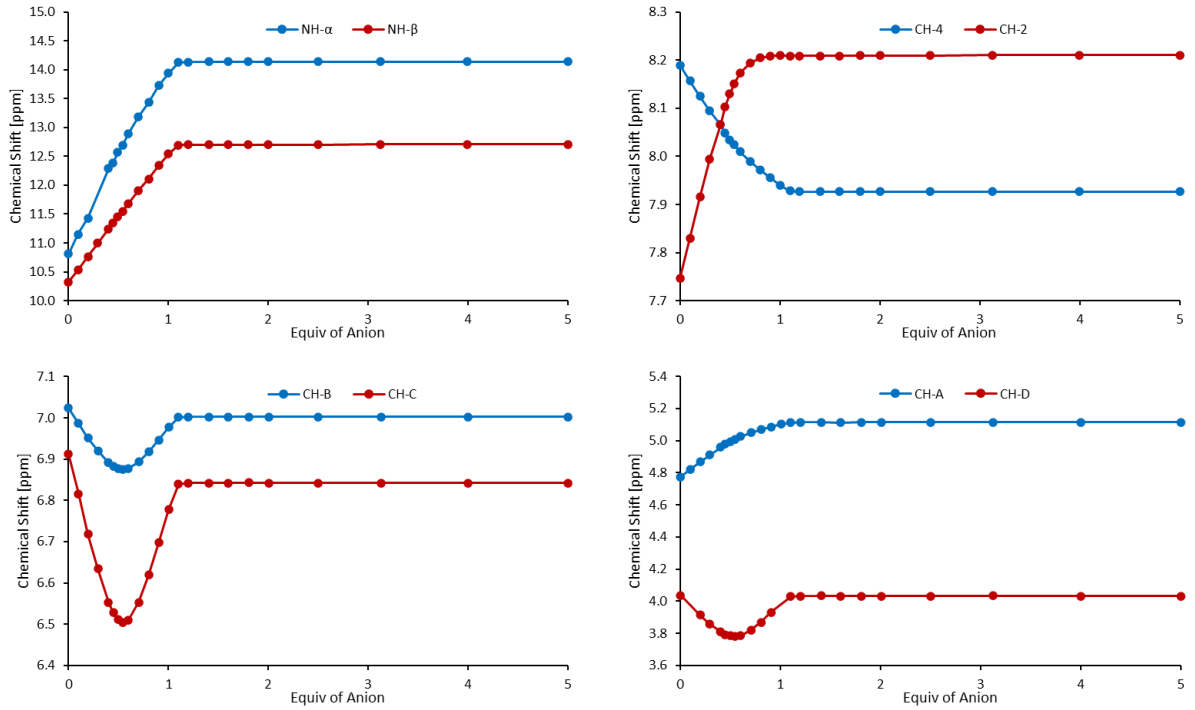

Figure S41. Binding isotherms obtained during titration of 0.002 M solution of precursor **1** in DMSO-d_6 + 0.5% H_2O with 0.03 M TBA_2SO_4.

5.1.12 ^{1}H NMR titration of 0.002 M solution of precursor **1** in $CDCl_3$ with 0.03 M TBA_2SO_4.

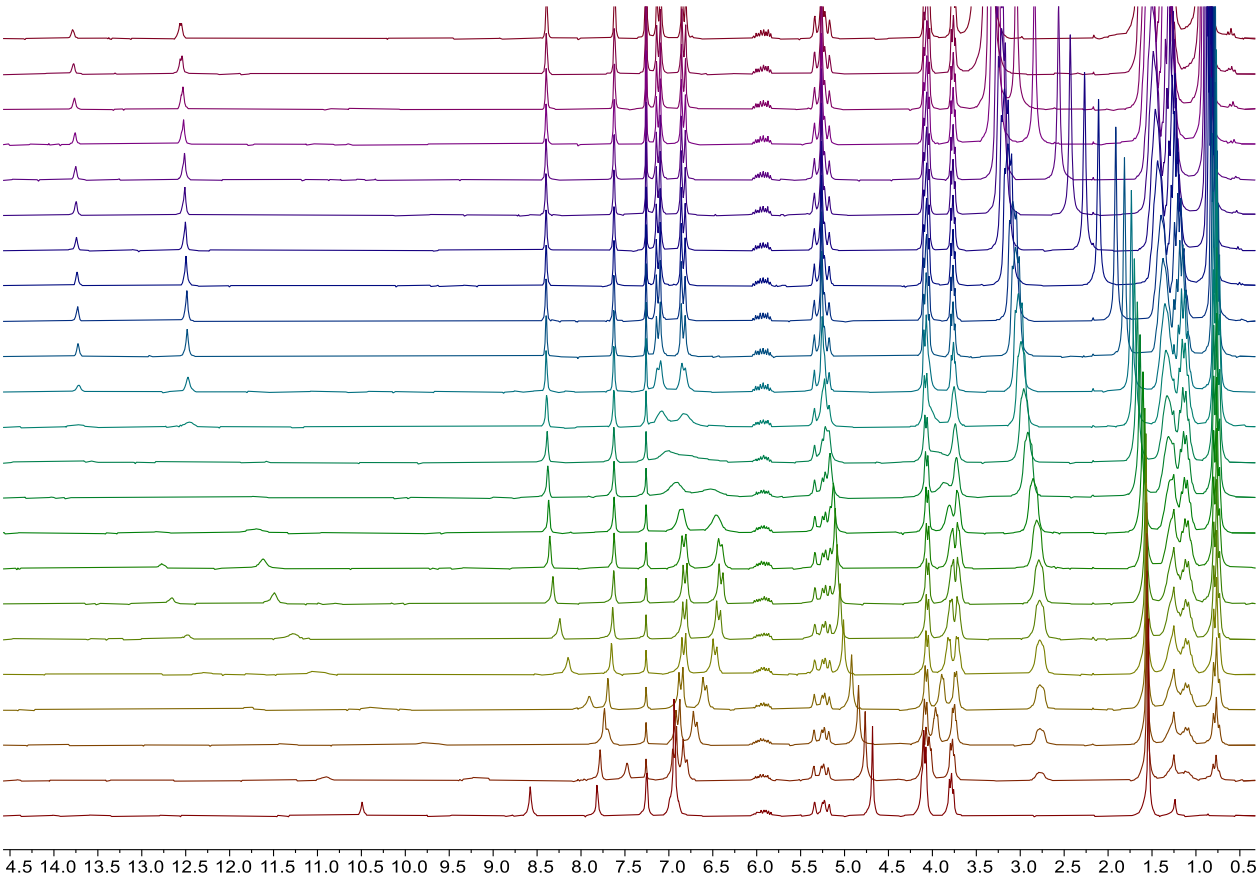

Figure S42. Stack of ^{1}H NMR spectra obtained during titration of 0.002 M solution of precursor **1** in $CDCl_3$with 0.03 M TBA_2SO_4.

Table S11. Chemical shifts of proton signals obtained during titration of 0.002 M solution of precursor **1** in $CDCl_3$with 0.03 M TBA_2SO_4.

Equiv of $(TBA)_2SO_4$	α	β	2	4	A	B	C	D	E	F	G	H
0.00	10.4918	8.578	7.2485	7.8162	4.6818	6.9647	6.9153	4.0965	3.7867	4.0965	5.935	5.3414
0.10	10.9023	9.1543	7.4754	7.7819	4.7652	6.9355	6.8161	4.04	3.7751	4.04	5.943	5.3511
0.20	11.3392	9.7588	7.6962	7.7349	4.8413	6.8967	6.7003	3.9609	3.7535	3.9609	5.9382	5.3466
0.29	11.7991	10.3588	7.9053	7.6928	4.9195	6.8626	6.5900	3.89	3.7305	3.89	5.9282	5.3424
0.40	12.2803	10.9989	8.1475	7.6515	5.0119	6.8306	6.4754	3.8159	3.7146	3.8159	5.9282	5.3394
0.45	12.4779	11.274	8.2414	7.6369	5.05	6.8198	6.4335	3.7894	3.7089	3.7894	5.9306	5.3378
0.50	12.658	11.4956	8.3214	7.6255	5.0845	6.8158	6.4058	3.7723	3.706	3.7723	5.9337	5.3372
0.54	12.7716	11.6179	8.3535	7.6216	5.1055	6.8275	6.4141	3.7777	3.7051	3.7777	5.9305	5.3363
0.60	12.8528	11.6922	8.3661	7.6209	5.1265	6.8589	6.4571	3.8061	3.7127	3.8061	5.926	5.3373
0.70	broad	broad	8.3759	7.6216	5.1657	6.9144	6.5230	3.8649	3.7262	3.8649	5.9324	5.3402
0.80	13.6615	12.4104	8.3837	7.6240	5.1996	6.9922	6.7846	3.9714	3.738	3.9714	5.9449	5.3432

0.90	13.7158	12.4558	8.3897	7.6247	5.2287	7.0829	6.8200	4.0407	3.7509	4.0407	5.9403	5.3450
1.00	13.7174	12.4759	8.3951	7.6258	5.256	7.1132	6.8315	4.0581	3.7624	4.0581	5.9383	5.3470
1.10	13.7257	12.4828	8.3967	7.6256	5.2604	7.1202	6.8370	4.072	3.7663	4.072	5.9339	5.3474
1.20	13.7288	12.4873	8.3967	7.6256	5.2621	7.1209	6.8375	4.0721	3.7671	4.0721	5.9387	5.3474
1.40	13.7368	12.4978	8.3969	7.6253	5.2632	7.1214	6.8373	4.0721	3.7677	4.0721	5.9315	5.3472
1.60	13.7444	12.504	8.3971	7.6248	5.2634	7.1214	6.8369	4.072	3.7652	4.072	5.9345	5.3470
1.80	13.7492	12.5084	8.3966	7.6244	5.2637	7.1211	6.8364	4.0715	3.7663	4.0715	5.9431	5.3466
2.00	13.7518	12.5141	8.3961	7.6236	5.2636	7.1206	6.8356	4.0712	3.7641	4.0712	5.9331	5.3463
2.50	13.7584	12.5237	8.3956	7.6225	5.2635	7.1198	6.8342	4.0703	3.7635	4.0703	5.9313	5.3453
3.13	13.7661	12.5319	8.3946	7.6214	5.2633	7.1191	6.8332	4.0696	3.7631	4.0696	5.9357	5.3446
4.00	13.7793	12.542	8.3931	7.6192	5.263	7.1173	6.8309	4.0679	3.7626	4.0679	5.9342	5.3427
5.00	13.784	12.5565	8.3910	7.6165	5.2619	7.1151	6.8283	4.0656	3.7598	4.0656	5.9348	5.3404

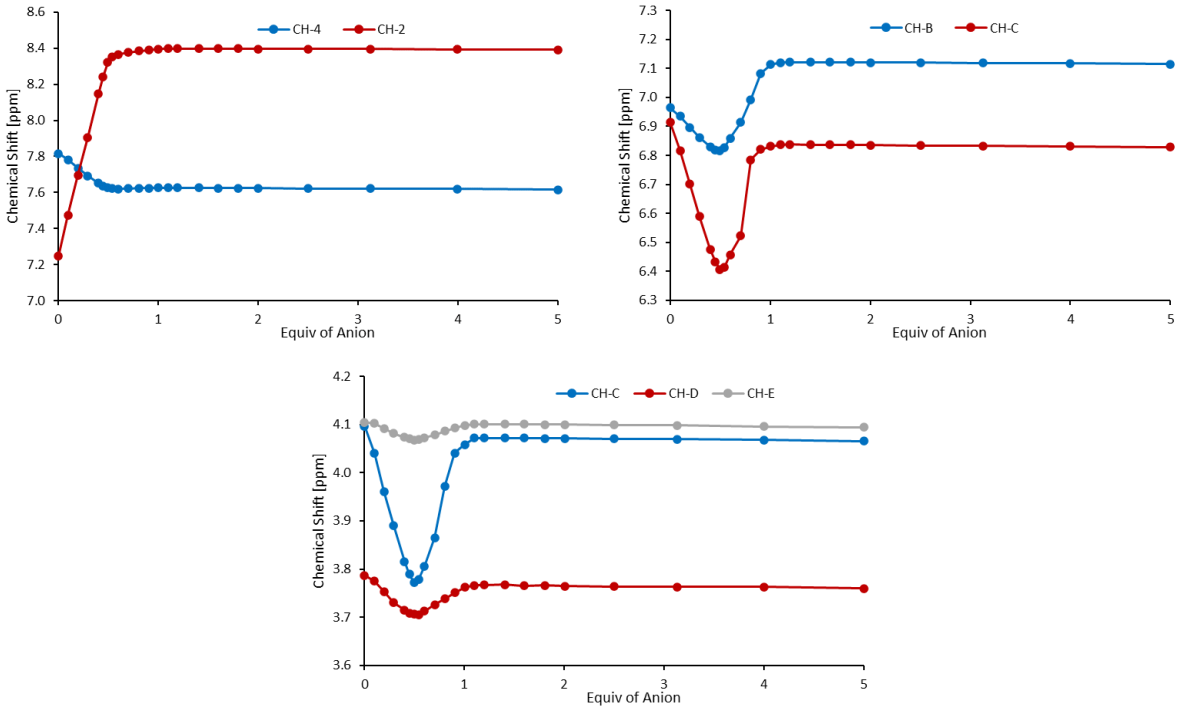

Figure S43. Binding isotherms obtained during titration of 0.002 M solution of precursor **1** in $CDCl_3$with 0.03 M TBA_2SO_4.

5.1.13 ^{1}H NMR titration of 0.0002 M solution of precursor **1** in DMSO-d_6/D_2O 9:1 with 0.003 M TBA_2SO_4.

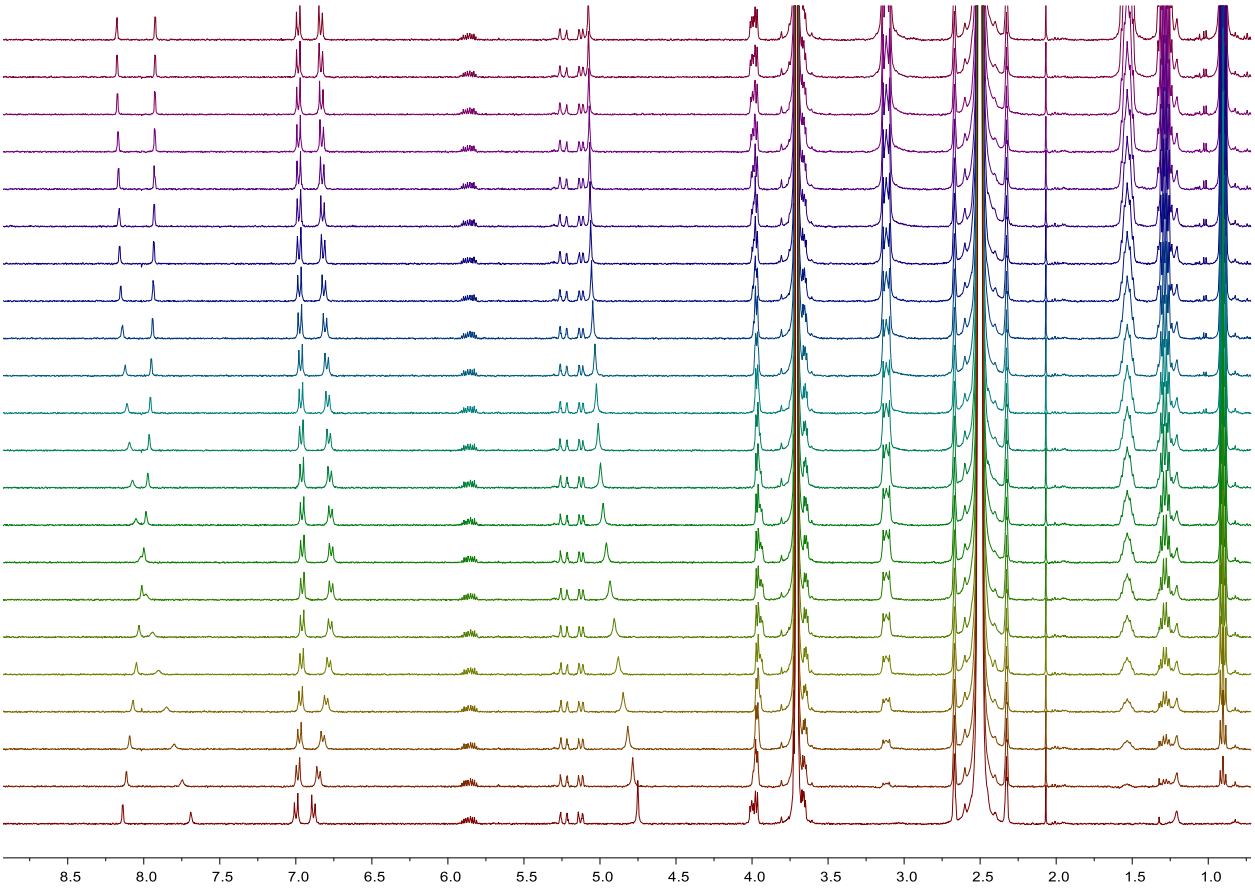

Figure S44. Stack of ^{1}H NMR spectra obtained during titration of 0.0002 M solution of precursor **1** in DMSO-d_6/D_2O 9:1 with 0.003 M TBA_2SO_4.

Table S12. Chemical shifts of proton signals obtained during titration of 0.0002 M solution of precursor **1** in DMSO-d_6/D_2O 9:1 with 0.003 M TBA_2SO_4.

Equiv of $(TBA)_2SO_4$	2	4	A	B	C	D	E	F	G	H
0.00	7.6895	8.1376	4.7510	6.9980	6.8840	4.0016	3.6612	3.9777	5.8564	5.2379
0.10	7.7459	8.1141	4.7839	6.9858	6.8504	3.9823	3.6546	3.9758	5.8579	5.2371
0.20	7.8000	8.0923	4.8160	6.9759	6.8228	overlap	3.6506	3.9744	5.8564	5.2366
0.29	7.8516	8.0704	4.8466	6.9680	6.8011	overlap	3.6475	3.9733	5.8581	5.2363
0.40	7.9028	8.0483	4.8793	6.9617	6.7832	3.9457	3.6451	3.9724	5.8598	5.2362
0.45	7.9427	8.0305	4.9059	6.9585	6.7739	3.9421	3.6439	3.9723	5.8570	5.2363
0.50	7.9855	8.0121	4.9337	6.9569	6.7687	3.9407	3.6439	3.9724	5.8597	5.2367
0.54	8.0166	7.9991	4.9575	6.9570	6.7683	3.9430	3.6443	3.9728	5.8582	5.2371
0.60	8.0499	7.9850	4.9794	6.9586	6.7717	3.9474	3.6453	3.9734	5.8561	5.2376
0.70	8.0739	7.9726	4.9962	6.9609	6.7772	3.9527	3.6468	3.9741	5.8606	5.2381
0.80	8.0940	7.9640	5.0110	6.9635	6.7839	overlap	3.6482	3.9747	5.8637	5.2386
0.90	8.1099	7.9563	5.0234	6.9662	6.7908	overlap	3.6498	3.9755	5.8598	5.2392

1.00	8.1213	7.9504	5.0326	6.9687	6.7969	overlap	3.6510	3.9761	5.8636	5.2396
1.10	8.1408	7.9413	5.0472	6.9731	6.8080	overlap	3.6534	3.9772	5.8576	5.2403
1.20	8.1510	7.9364	5.0555	6.9760	6.8154	overlap	3.6552	3.9780	5.8612	5.2407
1.40	8.1583	7.9330	5.0611	6.9780	6.8205	3.9881	3.6558	3.9784	5.8604	5.2411
1.60	8.1627	7.9308	5.0646	6.9793	6.8241	3.9908	3.6557	3.9788	5.8630	5.2413
1.80	8.1658	7.9292	5.0673	6.9804	6.8267	3.9934	3.6571	3.9790	5.8607	5.2414
2.00	8.1693	7.9280	5.0698	6.9815	6.8293	3.9945	3.6577	3.9792	5.8612	5.2415
2.50	8.1720	7.9261	5.0728	6.9826	6.8322	3.9969	3.6582	3.9793	5.8614	5.2417
3.13	8.1759	7.9246	5.0752	6.9837	6.8352	3.9997	3.6584	3.9797	5.8635	5.2418
4.00	8.1776	7.9241	5.0769	6.9842	6.8364	4.0002	3.6595	3.9798	5.8577	5.2420
5.00	7.6895	8.1376	4.7510	6.9980	6.8840	4.0016	3.6612	3.9777	5.8564	5.2379

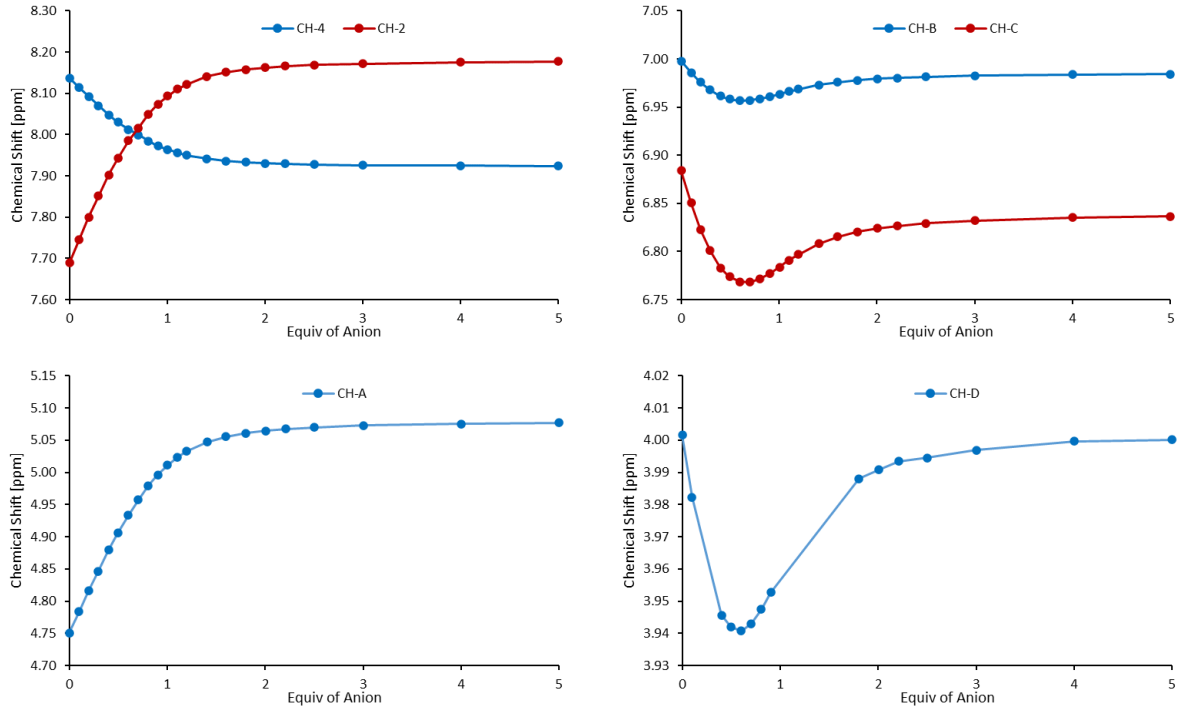

Figure S45. Binding isotherms obtained during titration of 0.0002 M solution of precursor **1** in DMSO-d_6/D_2O 9:1 with 0.003 M TBA_2SO_4.

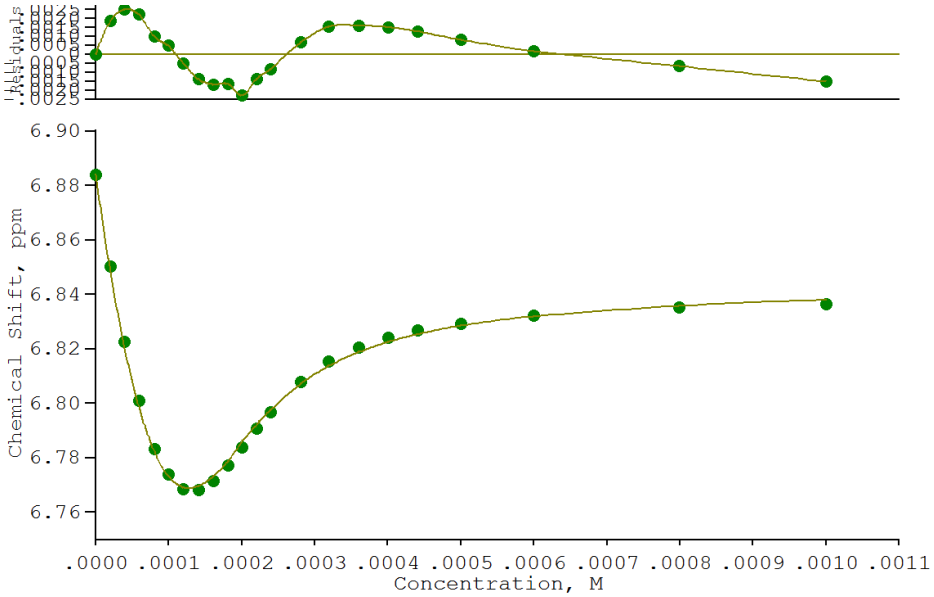

Figure S46. Fitting of 2:1 & 1:1 (receptor:anion) model to results of titration of 0.0002 M solution of precursor **1** in DMSO-d_6/D_2O 9:1 with 0.003 M TBA_2SO_4 for CH-c protons using WinEQNMR. $logK_{1:1}$ = 4.87 ± 0.01, $logK_{2:1}$ = 3.21 ± 0.11; δ(1:1)= 6.8441± 0.0013 ppm, δ (2:1)= 6.1089± 0.1464 ppm

Binding constants K derived from averaging the results from fitting of 2:1 & 1:1 (receptor:anion) model to titration results for CH-2, CH-4, CH-b and CH-c protons using WinEQNMR:

log $K_{1:1}$ = 4.91, Std Dev. = 0.02

log $K_{1:2}$ = 3.10, Std Dev. = 0.08

5.1.14 ^{1}H NMR titration of 0.0002 M solution of precursor **1** in DMSO-d_6/D_2O 9:1 with 0.003 M $TBAH_2PO_4$.

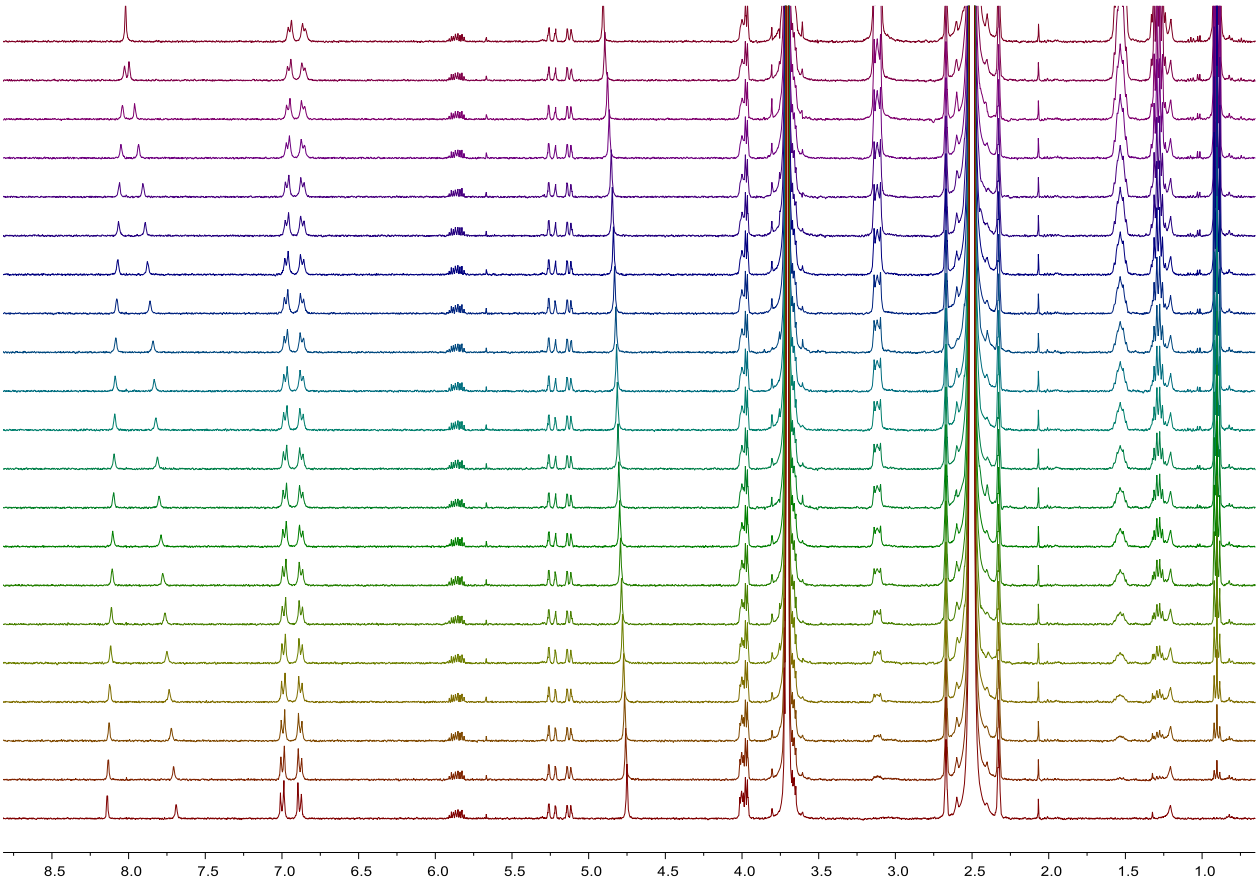

Figure S47. Stack of ^{1}H NMR spectra obtained during titration of 0.0002 M solution of precursor **1** in DMSO-d_6/D_2O 9:1 with 0.003 M $TBAH_2PO_4$.

Table S13. Chemical shifts of proton signals obtained during titration of 0.0002 M solution of precursor **1** in DMSO-d_6/D_2O 9:1 with 0.003 M TBA_2SO_4.

Equiv. of $TBAHPO_4$	2	4	A	B	C	D	E	F	G	H
0.00	7.6895	8.1388	4.7502	6.9984	6.8844	4.0023	3.6599	3.9712	5.8681	5.2381
0.10	7.7059	8.1321	4.7583	6.9955	6.8822	4.0016	3.6595	3.9711	5.8561	5.2381
0.20	7.7206	8.1267	4.7651	6.9929	6.8805	4.0010	3.6591	3.9711	5.8576	5.2381
0.29	7.7349	8.1219	4.7720	6.9908	6.8797	4.0008	3.6595	3.9710	5.8574	5.2381
0.40	7.7493	8.1166	4.7792	6.9886	6.8782	4.0002	3.6586	3.9710	5.8547	5.2382
0.50	7.7618	8.1113	4.7853	6.9868	6.8772	4.0012	3.6586	3.9710	5.8676	5.2382
0.60	7.776	8.1063	4.7922	6.9844	6.8756	4.0000	3.6586	3.9710	5.8573	5.2383
0.70	7.7877	8.1020	4.7973	6.9831	6.8743	4.0006	3.6588	3.9710	5.8560	5.2383
0.80	7.8009	8.0971	4.8031	6.9811	6.8742	4.0008	3.6587	3.9710	5.8548	5.2384
0.90	7.8111	8.0931	4.8077	6.9791	6.8732	4.0009	3.6586	3.9709	5.8589	5.2383
1.00	7.8206	8.0902	4.8131	6.9773	6.8719	3.9999	3.6588	3.9710	5.8584	5.2384
1.10	7.8319	8.0871	4.8177	6.9770	6.8711	4.0009	3.6581	3.9710	5.8568	5.2385

1.20	7.8403	8.0824	4.8217	6.9753	6.8707	4.0002	3.6581	3.9710	5.8592	5.2384
1.40	7.8598	8.0757	4.8307	6.9720	6.8690	4.0009	3.6589	3.9709	5.8592	5.2386
1.60	7.8756	8.0704	4.8374	6.9701	6.8678	4.0000	3.6582	3.9709	5.8602	5.2386
1.80	7.8908	8.0650	4.8455	6.9676	6.8665	3.9987	3.6590	3.9709	5.8553	5.2386
2.00	7.9052	8.0602	4.8517	6.9656	6.8653	3.9999	3.6603	3.9709	5.8615	5.2387
2.50	7.9344	8.0488	4.8656	6.9610	6.8638	4.0000	3.6582	3.9709	5.8621	5.2388
3.00	7.9588	8.0397	4.8768	6.9586	6.8612	3.9995	3.6598	3.9710	5.8598	5.2388
4.00	7.9956	8.0259	4.8942	6.9530	6.8586	3.9994	3.6591	3.9711	5.8586	5.2390
5.00	8.0202	8.0202	4.9068	6.9480	6.8572	4.0001	3.6561	3.9712	5.8583	5.2391

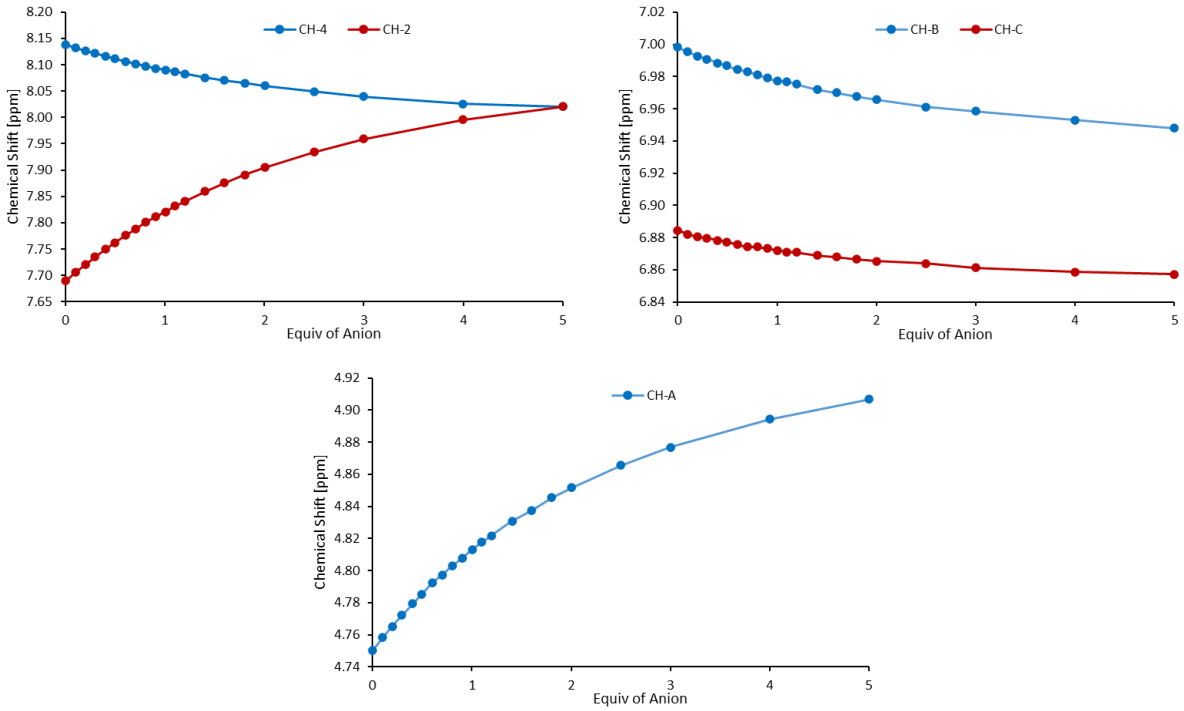

Figure S48. Binding isotherms obtained during titration of 0.0002 M solution of precursor **1** in DMSO-d_6/D_2O 9:1 with 0.003 M $TBAH_2PO_4$.

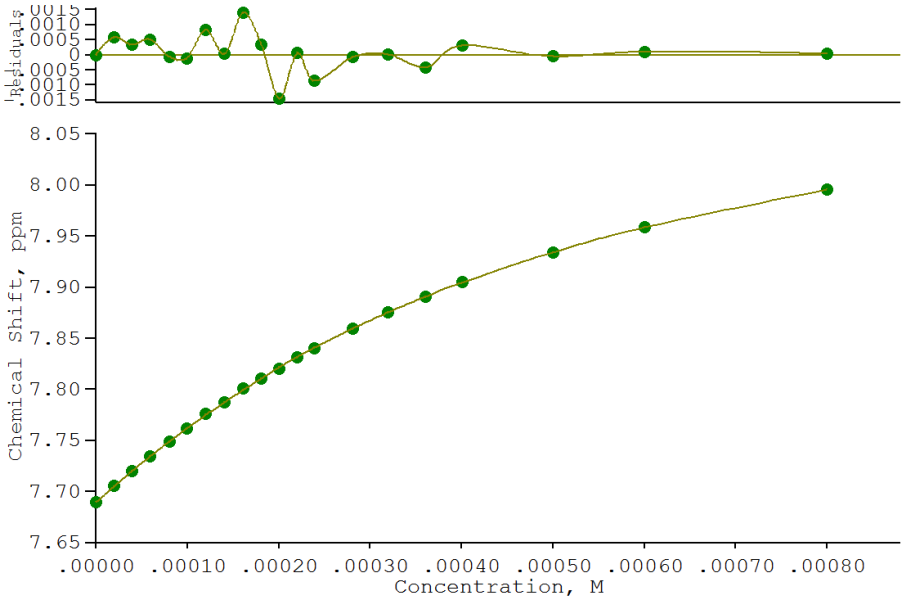

Figure S49. Fitting of 1:1 (receptor:anion) model to results of titration of 0.0002 M solution of precursor **1** in DMSO-d_6/D_2O 9:1 with 0.003 M $TBAH_2PO_4$ for CH-2 protons using WinEQNMR. $logK_{1:1}$ = 3.41 ± 0.01; δ(1:1)= 8.1697±0.0.0029 ppm.

Binding constants K derived from averaging the results from fitting of 1:1 (receptor:anion) model to titration results for CH-2, CH-4, CH-a and CH-b protons using WinEQNMR:

log $K_{1:1}$ = 3.42, Std Dev. = 0.04

5.2 UV-Vis Titrations

General Procedure

All the reagents were weighted separately on a Mettler Toledo Excellence XA105DU analytical balance (readability 0.01 mg) in screw-capped vials sealed with Teflon-covered septa. DMSO/H_2O mixtures were obtained using Milli-Q H_2O and their concentrations were expressed as weight-weight percentage. All the solvent/solution manipulations were done using gas-tight Hamilton glass syringes. Titrants were prepared by dissolving appropriate salts in the solution of the receptor, in order to avoid dilution of the receptor during titration. Titrations were performed in a septum-sealed screw-cap precision cell made of Quartz SUPRASIL (light path: 10 mm, by adding aliquots of the titrant solution to the receptor solution (2.5 mL, $1 \cdot 10^{-5}$ - $1 \cdot 10^{-4}$M) and recording UV-Vis spectra after each addition. UV spectra were obtained on Thermo Scientific Evolution 300 spectrometer at 25°C Association constants were calculated from absorbance changes at fixed wavelength. Nonlinear curve fit was carried out using the HypSpec software. Association constants and molar absorption coefficients of receptor and complexes were set as free parameters for fitting

5.2.1 UV-Vis titration of 10^{-4} M solution of catenane **A** in DMSO/H_2O 9:1 with 0.00625 M solution of $TBAH_2PO_4$ (dissolved in the solution of catenane **A**).

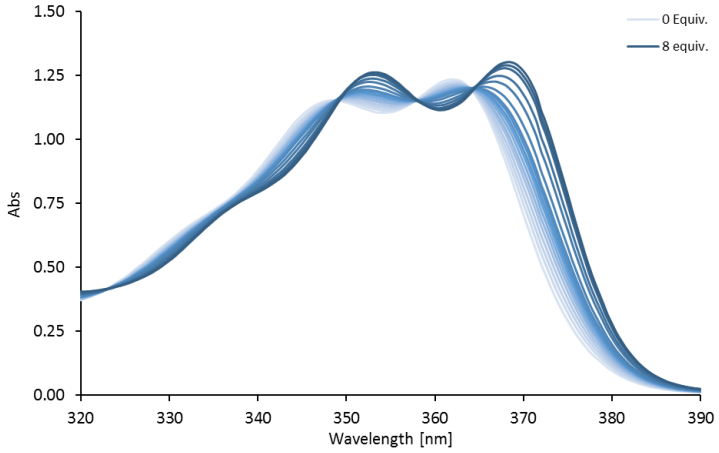

Figure S50. UV spectra obtained during titration of 10^{-4} M solution of catenane **A** in DMSO/H_2O 9:1 with 0.00625 M solution of $TBAH_2PO_4$ (dissolved in the solution of receptor **A**).

Table S14. Absorbance values for selected wavelentghts recorded during titration of 10^{-4} M solution of catenane **A** in DMSO/H_2O 9:1 with 0.00625 M solution of $TBAH_2PO_4$.

Added volume of titrant solution [µL]	Equivalents of $TBAH_2PO_4$	Wavelength [nm]									
		352	353	354	367	368	369	370	371	372	373
		Absorbance									
0.0	0.00	1.121	1.110	1.105	1.004	0.912	0.810	0.706	0.608	0.512	0.429
4.0	0.10	1.125	1.115	1.110	1.013	0.926	0.828	0.726	0.629	0.534	0.450
8.0	0.20	1.131	1.121	1.115	1.026	0.943	0.847	0.747	0.650	0.554	0.469
12.0	0.30	1.136	1.126	1.120	1.036	0.954	0.861	0.763	0.668	0.571	0.486
16.0	0.40	1.140	1.131	1.125	1.046	0.968	0.877	0.782	0.686	0.589	0.503

20.0	0.50	1.145	1.137	1.129	1.055	0.981	0.893	0.799	0.705	0.608	0.521
24.0	0.59	1.149	1.140	1.134	1.065	0.993	0.908	0.816	0.723	0.625	0.537
28.5	0.70	1.154	1.146	1.139	1.075	1.007	0.924	0.834	0.742	0.643	0.555
32.5	0.80	1.158	1.150	1.143	1.085	1.020	0.939	0.851	0.759	0.661	0.572
36.5	0.90	1.161	1.154	1.146	1.093	1.030	0.953	0.866	0.776	0.677	0.588
40.5	1.00	1.163	1.157	1.150	1.099	1.039	0.964	0.879	0.790	0.692	0.603
45.0	1.11	1.167	1.161	1.154	1.108	1.050	0.978	0.895	0.807	0.709	0.619
49.0	1.20	1.171	1.166	1.158	1.117	1.061	0.992	0.910	0.823	0.723	0.632
53.0	1.30	1.175	1.170	1.163	1.123	1.070	1.002	0.922	0.835	0.736	0.644
57.5	1.41	1.179	1.174	1.167	1.132	1.082	1.016	0.939	0.853	0.753	0.661
61.5	1.50	1.181	1.177	1.169	1.138	1.090	1.026	0.950	0.865	0.766	0.674
65.5	1.60	1.184	1.180	1.172	1.143	1.098	1.036	0.960	0.875	0.777	0.684
70.0	1.70	1.188	1.184	1.176	1.152	1.109	1.049	0.975	0.892	0.793	0.699
74.0	1.80	1.191	1.188	1.180	1.157	1.116	1.057	0.985	0.902	0.803	0.709
78.5	1.90	1.194	1.191	1.183	1.164	1.125	1.070	0.998	0.916	0.817	0.723
82.5	2.00	1.195	1.192	1.184	1.167	1.129	1.075	1.005	0.924	0.824	0.731
91.0	2.20	1.200	1.198	1.190	1.176	1.142	1.091	1.024	0.943	0.844	0.749
104.0	2.50	1.207	1.206	1.199	1.191	1.163	1.117	1.054	0.976	0.876	0.780
126.0	3.00	1.216	1.217	1.210	1.211	1.191	1.152	1.094	1.020	0.919	0.823
148.5	3.50	1.224	1.225	1.217	1.226	1.212	1.178	1.125	1.053	0.953	0.857
171.0	4.00	1.230	1.232	1.225	1.240	1.231	1.203	1.153	1.084	0.984	0.887
194.0	4.50	1.234	1.239	1.232	1.249	1.245	1.222	1.176	1.110	1.009	0.913
217.0	4.99	1.238	1.244	1.237	1.257	1.258	1.238	1.196	1.133	1.032	0.935
267.0	6.03	1.247	1.253	1.246	1.272	1.279	1.265	1.228	1.167	1.068	0.971
317.0	7.03	1.250	1.258	1.252	1.280	1.291	1.282	1.248	1.190	1.090	0.993
367.0	8.00	1.252	1.263	1.259	1.287	1.302	1.298	1.268	1.212	1.114	1.018

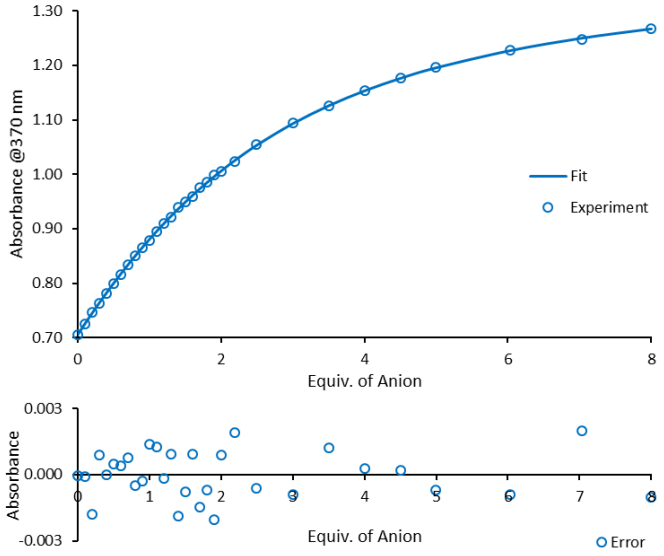

Figure S51. Fitting of 1:1 and 1:2 (receptor:anion) model to results of titration of of 10^{-4} M solution of catenane **A** in DMSO/H_2O 9:1 with 0.00625 M solution of $TBAH_2PO_4$.

Binding constants K derived from simultaneous fitting of 1:1 and 1:2 model to ten selected wavelengths using HypSpec:

log $K_{1:1}$ = 4.0326, Std Dev. 0.0083
log $K_{1:2}$ = 3.4995, Std Dev. Beta 0.0101

Table S15. Molar absorption coefficients derived from simultaneous fitting of 1:1 and 1:2 model to ten selected wavelengths using HypSpec.

	Wavelength [nm]									
	352	353	354	367	368	369	370	371	372	373
L [$M^{-1}cm^{-1}$]	11203	11097	11047	10019	9110	8093	7057	6077	5122	4297
L×H_2PO_4 [$M^{-1}cm^{-1}$]	12316	12285	12157	12529	12340	11935	11312	10491	9445	8404
L×($H_2PO_4)_2$ [$M^{-1}cm^{-1}$]	12766	12940	12926	13304	13720	13932	13851	13461	12492	11552

Binding constants K derived from two experiments repeated according to the same methodology:

log $K_{1:1}$ = 3.8189, Std Dev. 0.0179
log $K_{1:2}$ = 3.3998, Std Dev. Beta 0.029

log $K_{1:1}$ = 4.2769, Std Dev. 0.0152
log $K_{1:2}$ = 3.6565, Std Dev. Beta 0.0153

Binding constants averaged from the above three experiments:

log $K_{1:1}$ = 4.043, Std Dev. 0.187
log $K_{1:2}$ = 3.519, Std Dev. 0.106

5.2.2 UV-Vis titration of 10^{-4} M solution of catenane **A** in DMSO/H_2O 9:1 with 0.0625 M solution of TBAPhCOO (dissolved in the solution of catenane **A**).

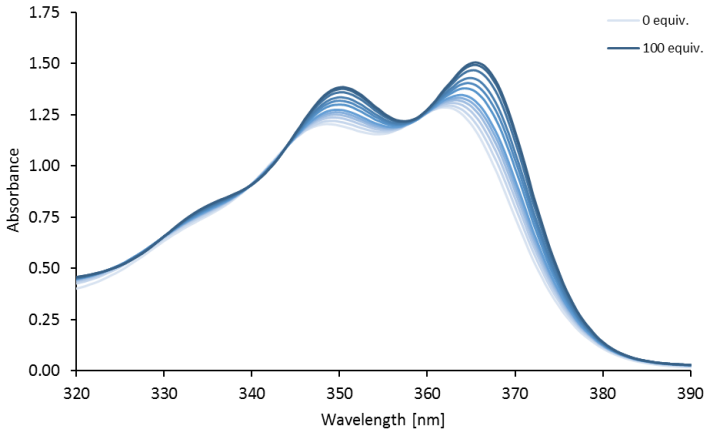

Figure S52. UV spectra obtained during titration of 10^{-4} M solution of catenane **A** in DMSO/H_2O 9:1 with 0.0625 M solution of TBAPhCOO (dissolved in the solution of catenane **A**).

Table S16. Absorbance values for selected wavelentghts recorded during titration of 10^{-4} M solution of catenane **A** in DMSO/H_2O 9:1 with 0.0625 M solution of TBAPhCOO.

Added volume of titrant solution [µL]	Equivalents of TBAPhCOO	Wavelength [nm]									
		350	351	352	353	364	365	366	367	368	369
		Absorbance									
0	0.0	1.197	1.186	1.172	1.162	1.251	1.204	1.138	1.054	0.961	0.856
8	2.0	1.207	1.196	1.182	1.170	1.263	1.221	1.159	1.078	0.988	0.885
16	4.0	1.216	1.206	1.192	1.179	1.274	1.236	1.178	1.101	1.012	0.909
24	5.9	1.227	1.217	1.202	1.188	1.286	1.253	1.197	1.121	1.035	0.931
32.5	8.0	1.235	1.225	1.210	1.195	1.297	1.266	1.214	1.141	1.055	0.952
40.5	10.0	1.243	1.233	1.217	1.201	1.307	1.279	1.230	1.158	1.074	0.970
49	12.0	1.250	1.241	1.225	1.208	1.316	1.292	1.246	1.176	1.092	0.988
57.5	14.1	1.256	1.248	1.232	1.214	1.324	1.302	1.257	1.190	1.107	1.002
65.5	16.0	1.262	1.253	1.237	1.218	1.331	1.312	1.270	1.205	1.123	1.020
74	18.0	1.268	1.260	1.243	1.224	1.339	1.322	1.282	1.218	1.136	1.033
82.5	20.0	1.274	1.266	1.250	1.230	1.347	1.332	1.294	1.231	1.151	1.048
104	25.0	1.287	1.280	1.263	1.241	1.363	1.354	1.321	1.261	1.183	1.080
126	30.0	1.300	1.294	1.275	1.252	1.379	1.374	1.344	1.288	1.211	1.107
148.5	35.0	1.310	1.303	1.285	1.261	1.390	1.390	1.365	1.312	1.237	1.133
171	40.0	1.319	1.312	1.293	1.269	1.400	1.403	1.380	1.329	1.254	1.151
194	45.0	1.328	1.322	1.303	1.277	1.411	1.417	1.398	1.349	1.275	1.172
217	49.9	1.336	1.330	1.310	1.284	1.420	1.430	1.413	1.366	1.292	1.189
265.5	60.0	1.349	1.344	1.324	1.296	1.435	1.450	1.437	1.394	1.323	1.220
315.5	70.0	1.360	1.355	1.335	1.307	1.448	1.467	1.458	1.418	1.348	1.245
367	80.0	1.369	1.364	1.344	1.314	1.458	1.480	1.475	1.436	1.368	1.266
420.5	90.0	1.376	1.372	1.351	1.321	1.467	1.491	1.488	1.452	1.385	1.282
476	100.0	1.384	1.380	1.360	1.329	1.475	1.502	1.501	1.467	1.401	1.298

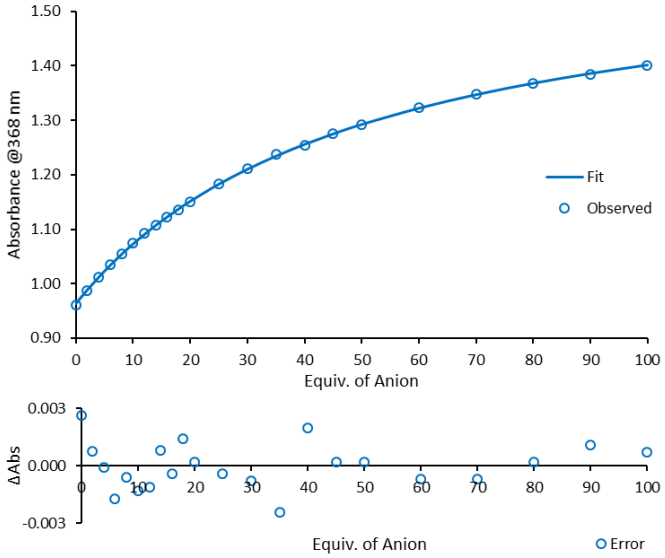

Figure S53. Fitting of 1:1 model to results of titration of 10^{-4} M solution of catenane **A** in DMSO/H_2O 9:1 with 0.0625 M solution of TBAPhCOO.

Binding constants K derived from simultaneous fitting of 1:1 model to ten selected wavelengths using HypSpec:

$$\log K_{1:1} = 2.3106, \text{ Std Dev. } 0.0004$$

Table S17. Molar absorption coefficients derived from simultaneous fitting of 1:1 model to ten selected wavelengths using HypSpec.

	Wavelength [nm]									
	350	351	352	353	364	365	366	367	368	369
L [$M^{-1}cm^{-1}$]	11955	11844	11707	11597	12503	12042	11386	10549	9636	8597
L×PhCOO [$M^{-1}cm^{-1}$]	14743	14738	14493	14079	15866	16505	16817	16715	16174	15153

Binding constants K derived from two experiments repeated according to the same methodology :

$$\log K_{1:1} = 2.4200, \text{ Std Dev. } 0.0009$$

$$\log K_{1:1} = 2.3862, \text{ Std Dev. } 0.0010$$

Binding constants averaged from the above three experiments:

$$\log K_{1:1} = 2.3723, \text{ Std Dev. } 0.0457$$

5.2.3 UV-Vis titration of 10^{-5} M solution of catenane **A** in DMSO/H_2O 9:1 with 0.000625 M solution of TBA_2SO_4 (dissolved in the solution of receptor **A**).

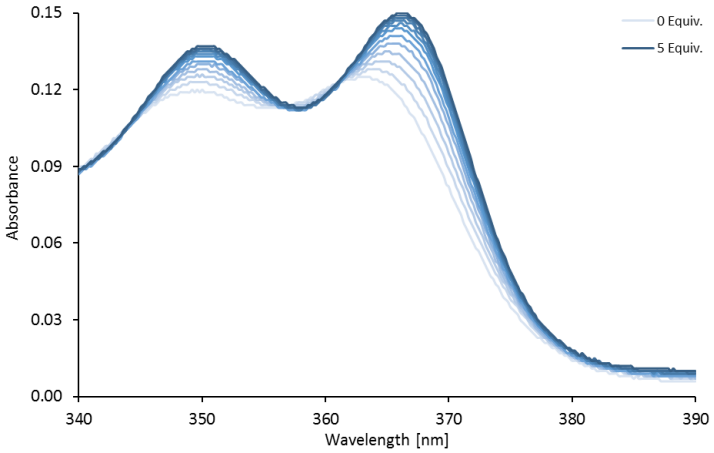

Figure S54. UV spectra obtained during titration of 10^{-5} M solution of catenane **A** in DMSO/H_2O 9:1 with 0.000625 M solution of TBA_2SO_4.

Table S18. Absorbance values for selected wavelentghts recorded during titration of 10^{-5} M solution of catenane **A** in DMSO/H_2O 9:1 with 0.000625 M solution of TBA_2SO_4.

Added volume of titrant solution [µL]	Equivalents of TBA_2SO_4	Wavelength [nm]									
		350	351	352	353	365	366	367	368	369	370
		Absorbance									
0	0.00	0.120	0.119	0.117	0.115	0.122	0.117	0.110	0.102	0.092	0.082
4	0.10	0.121	0.120	0.119	0.117	0.124	0.120	0.114	0.106	0.096	0.085
8	0.20	0.123	0.122	0.120	0.118	0.127	0.123	0.118	0.110	0.100	0.089
12	0.30	0.124	0.123	0.121	0.119	0.129	0.126	0.121	0.113	0.103	0.092
16	0.40	0.126	0.125	0.123	0.120	0.131	0.129	0.124	0.117	0.107	0.095
20	0.50	0.126	0.126	0.124	0.121	0.133	0.132	0.127	0.120	0.110	0.098
24	0.59	0.128	0.127	0.125	0.122	0.135	0.134	0.129	0.123	0.113	0.101
28.5	0.70	0.129	0.128	0.126	0.123	0.137	0.136	0.132	0.126	0.116	0.103
32.5	0.80	0.130	0.130	0.127	0.124	0.138	0.138	0.135	0.128	0.118	0.106
36.5	0.90	0.131	0.130	0.128	0.124	0.139	0.139	0.136	0.130	0.120	0.107
40.5	1.00	0.131	0.131	0.128	0.125	0.140	0.141	0.138	0.132	0.122	0.109
45	1.11	0.132	0.132	0.129	0.126	0.142	0.143	0.140	0.134	0.124	0.111
49	1.20	0.133	0.133	0.130	0.126	0.143	0.144	0.141	0.135	0.125	0.113
53	1.30	0.134	0.133	0.131	0.127	0.143	0.145	0.143	0.137	0.127	0.114
57.5	1.41	0.134	0.134	0.131	0.128	0.144	0.146	0.143	0.138	0.127	0.114
65.5	1.60	0.135	0.134	0.132	0.127	0.145	0.146	0.144	0.139	0.128	0.116
74	1.80	0.135	0.135	0.132	0.128	0.145	0.147	0.146	0.139	0.129	0.116
82.5	2.00	0.136	0.135	0.133	0.128	0.146	0.148	0.146	0.140	0.130	0.117
91	2.20	0.136	0.135	0.133	0.129	0.146	0.148	0.147	0.141	0.131	0.118
104	2.50	0.136	0.136	0.133	0.129	0.147	0.149	0.147	0.142	0.132	0.119
126	3.00	0.136	0.136	0.133	0.129	0.147	0.149	0.148	0.142	0.132	0.119

171	4.00	0.137	0.136	0.134	0.130	0.147	0.150	0.148	0.143	0.133	0.119
217	4.99	0.137	0.137	0.134	0.130	0.147	0.150	0.148	0.143	0.133	0.120

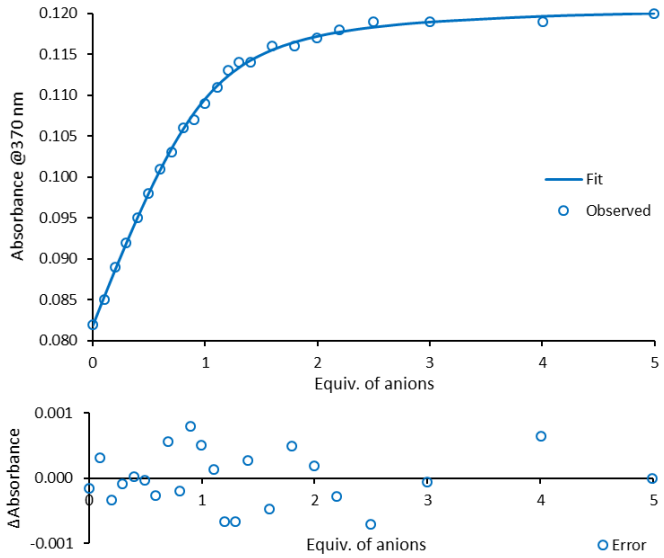

Figure S55. Fitting of 1:1 model to results of titration of 10^{-5} M solution of catenane **A** in DMSO/H_2O 9:1 with 0.000625 M solution of TBA_2SO_4

Binding constants K derived from simultaneous fitting of 1:1 model to ten selected wavelengths using HypSpec:

$$\log K_{1:1} = 5.9070, \text{ Std Dev. } 0.0022$$

Table S19. Molar absorption coefficients derived from simultaneous fitting of 1:1 model to ten selected wavelengths using HypSpec.

	Wavelength [nm]									
	350	351	352	353	365	366	367	368	369	370
L [$M^{-1}cm^{-1}$]	11952	11852	11686	11510	12215	11730	11061	10244	9248	8185
L×SO_4 [$M^{-1}cm^{-1}$]	13721	13689	13415	12985	14841	15132	14998	14471	13455	12118

Binding constants K derived from three experiments repeated according to the same methodology and different receptor concentrations:

$\log K_{1:1} = 6.0432$, Std Dev. 0.0056, concentration: 1e-5 M
$\log K_{1:1} = 5.8622$, Std Dev. 0.0025, concentration 2.5e-5 M
$\log K_{1:1} = 5.9815$, Std Dev. 0.0045, concentration 2.5e-5 M

Binding constants averaged from the above four experiments:

$$\log K_{1:1} = 5.9485, \text{ Std Dev. } 0.0693$$

5.2.4 UV-Vis titration of $2 \cdot 10^{-4}$ M solution of macrocycle **3** in DMSO/H_2O 9:1 with 0.025 M solution of $TBAH_2PO_4$ (dissolved in the solution of receptor **3**).

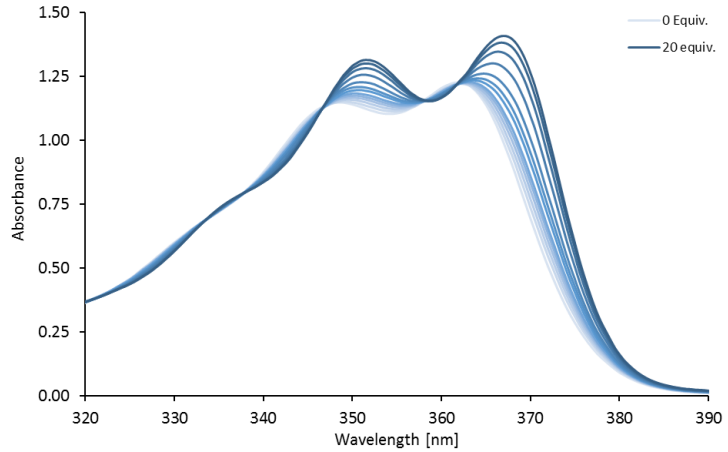

Figure S56. UV spectra obtained during titration of $2 \cdot 10^{-4}$ M solution of macrocycle **3** in DMSO/H_2O 9:1 with 0.025 M solution of $TBAH_2PO_4$.

Table S20. Absorbance values for selected wavelentghts recorded during titration of $2 \cdot 10^{-4}$ M solution of macrocycle **3** in DMSO/H_2O 9:1 with 0.025 M solution of $TBAH_2PO_4$.

Added volume of titrant solution [µL]	Equivalents of $TBAH_2PO_4$	Wavelength [nm]									
		351	352	353	354	366	367	368	369	370	371
		Absorbance									
0	0	1.129	1.117	1.107	1.103	1.072	0.989	0.898	0.796	0.694	0.596
4	0.20	1.135	1.123	1.114	1.108	1.084	1.006	0.919	0.819	0.717	0.619
8	0.40	1.140	1.130	1.120	1.114	1.094	1.019	0.934	0.836	0.736	0.638
12	0.60	1.147	1.137	1.126	1.119	1.104	1.032	0.949	0.854	0.754	0.656
16	0.79	1.152	1.142	1.132	1.124	1.113	1.044	0.963	0.870	0.770	0.671
20	0.99	1.157	1.148	1.137	1.129	1.123	1.057	0.979	0.887	0.788	0.689
24	1.19	1.163	1.154	1.143	1.134	1.133	1.069	0.993	0.903	0.804	0.704
28.5	1.41	1.168	1.160	1.149	1.139	1.143	1.082	1.008	0.919	0.821	0.721
32.5	1.60	1.172	1.164	1.153	1.143	1.150	1.092	1.019	0.932	0.834	0.734
36.5	1.80	1.178	1.170	1.159	1.148	1.159	1.103	1.033	0.946	0.850	0.749
40.5	1.99	1.181	1.174	1.163	1.152	1.165	1.110	1.042	0.956	0.860	0.759
49	2.40	1.189	1.183	1.172	1.159	1.181	1.132	1.067	0.985	0.889	0.787
57.5	2.81	1.196	1.190	1.179	1.166	1.194	1.148	1.087	1.006	0.911	0.809
65.5	3.19	1.204	1.197	1.185	1.171	1.208	1.166	1.108	1.029	0.935	0.832
74	3.59	1.208	1.202	1.190	1.176	1.216	1.177	1.121	1.044	0.951	0.847
82.5	3.99	1.216	1.210	1.198	1.182	1.228	1.191	1.138	1.062	0.969	0.865
104	4.99	1.227	1.223	1.210	1.193	1.248	1.217	1.168	1.097	1.005	0.900
126	6.00	1.239	1.235	1.222	1.203	1.269	1.245	1.201	1.132	1.042	0.936
171	8.00	1.256	1.253	1.240	1.219	1.300	1.284	1.247	1.183	1.094	0.987
217.5	10.00	1.269	1.267	1.254	1.231	1.323	1.315	1.283	1.224	1.136	1.030
267.5	12.08	1.280	1.280	1.267	1.243	1.345	1.342	1.316	1.259	1.172	1.064
317.5	14.09	1.290	1.291	1.277	1.252	1.361	1.364	1.341	1.287	1.202	1.093
367.5	16.02	1.298	1.299	1.284	1.259	1.375	1.381	1.362	1.310	1.227	1.117

467.5	19.69	1.311	1.313	1.299	1.272	1.396	1.408	1.394	1.346	1.263	1.153

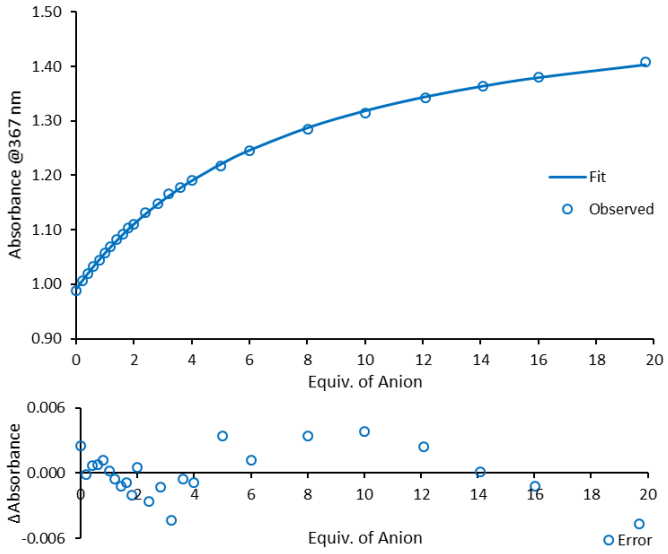

Figure S57. Fitting of 1:1 model to results of titration of $2 \cdot 10^{-4}$ M solution of macrocycle **3** in DMSO/H_2O 9:1 with 0.025 M solution of $TBAH_2PO_4$.

Binding constants K derived from simultaneous fitting of 1:1 model to ten selected wavelengths using HypSpec:

log $K_{1:1}$ 2.8878, Std Dev. 0.0007

Table S21. Molar absorption coefficients derived from simultaneous fitting of 1:1 model to ten selected wavelengths using HypSpec.

	Wavelength [nm]									
	351	352	353	354	366	367	368	369	370	371
L [$M^{-1}cm^{-1}$]	5645	5587	5538	5514	5364	4958	4507	4004	3494	3006
L×H_2PO_4 [$M^{-1}cm^{-1}$]	6843	6873	6793	6619	7506	7720	7773	7618	7234	6661

Binding constants K derived from an experiment repeated according to the same methodology:

log $K_{1:1}$ = 2.8651, Std Dev. 0.0005

Binding constants averaged from the above two experiments:

log $K_{1:1}$ = 2.87645, Std Dev. --

5.2.5 UV-Vis titration of $2 \cdot 10^{-4}$ M solution of macrocycle **3** in DMSO/H_2O 9:1 with 0.125 M solution of TBAPhCOO (dissolved in the solution of receptor **3**).

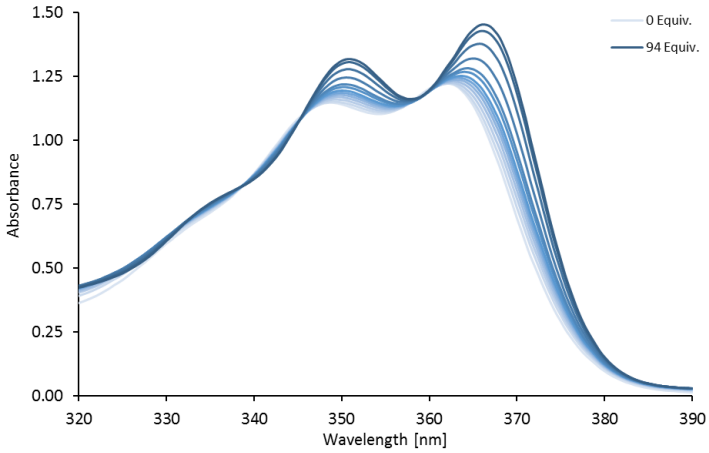

Figure S58. UV spectra obtained during titration of $2 \cdot 10^{-4}$ M solution of macrocycle **3** in DMSO/H_2O 9:1 with 0.125 M solution of TBAPhCOO.

Table S22. Absorbance values for selected wavelentghts recorder during titration of $2 \cdot 10^{-4}$ M solution of macrocycle **3** in DMSO/H_2O 9:1 with 0.125 M solution of TBAPhCOO.

Added volume of titrant solution [µL]	Equivalents of TBAPhCOO	Wavelength [nm]									
		316	317	318	319	320	321	366	367	368	369
		Absorbance									
0	0.00	0.340	0.341	0.345	0.353	0.364	0.377	1.071	0.989	0.900	0.799
4	1.00	0.363	0.362	0.365	0.373	0.383	0.395	1.083	1.005	0.918	0.819
8	1.99	0.374	0.372	0.376	0.383	0.392	0.404	1.094	1.019	0.935	0.837
12	2.99	0.382	0.380	0.383	0.390	0.399	0.411	1.108	1.036	0.953	0.857
16	3.97	0.389	0.387	0.389	0.396	0.405	0.416	1.119	1.049	0.968	0.873
20	4.96	0.393	0.391	0.393	0.400	0.408	0.420	1.132	1.064	0.985	0.889
24	5.94	0.395	0.393	0.395	0.402	0.410	0.421	1.143	1.078	1.000	0.905
28.5	7.04	0.400	0.397	0.399	0.406	0.414	0.425	1.155	1.090	1.015	0.921
32.5	8.02	0.403	0.400	0.402	0.408	0.417	0.428	1.165	1.103	1.028	0.936
36.5	8.99	0.406	0.402	0.404	0.411	0.419	0.430	1.174	1.114	1.039	0.947
40.5	9.96	0.407	0.404	0.406	0.412	0.420	0.431	1.183	1.125	1.052	0.960
45	11.05	0.409	0.406	0.408	0.414	0.422	0.432	1.194	1.138	1.066	0.975
49	12.01	0.410	0.407	0.409	0.414	0.422	0.433	1.202	1.147	1.076	0.985
57.5	14.05	0.412	0.409	0.411	0.416	0.424	0.435	1.219	1.167	1.098	1.008
65.5	15.96	0.415	0.411	0.413	0.419	0.426	0.437	1.232	1.183	1.116	1.027
74	17.97	0.418	0.413	0.415	0.420	0.428	0.438	1.246	1.199	1.133	1.045
82.5	19.97	0.418	0.414	0.415	0.421	0.428	0.438	1.256	1.211	1.146	1.059
104	24.96	0.421	0.416	0.417	0.422	0.430	0.440	1.284	1.245	1.184	1.098
126	29.99	0.422	0.417	0.418	0.424	0.431	0.441	1.310	1.275	1.217	1.132
171	40.01	0.423	0.417	0.418	0.423	0.430	0.440	1.348	1.320	1.266	1.183
217.5	50.02	0.426	0.419	0.419	0.424	0.431	0.440	1.377	1.354	1.304	1.222

267.5	60.41	0.425	0.418	0.418	0.422	0.429	0.438	1.401	1.382	1.336	1.255
342.5	75.31	0.424	0.416	0.416	0.420	0.426	0.435	1.428	1.415	1.371	1.291
442.5	93.99	0.424	0.416	0.415	0.418	0.424	0.433	1.453	1.444	1.403	1.325

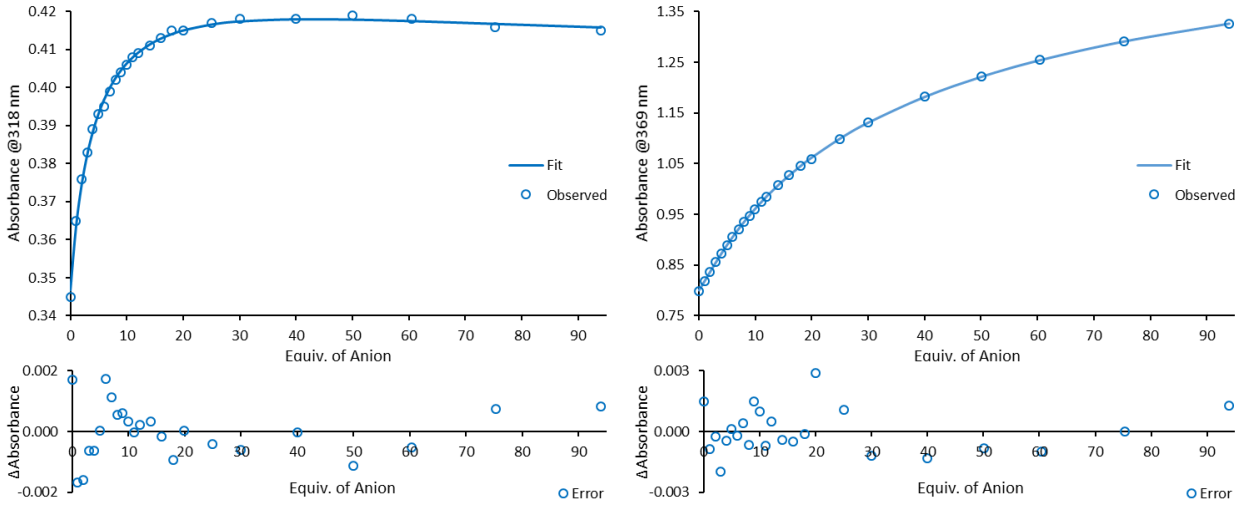

Figure S59. Fitting of 1:1 1 & 2:1 model to results of titration of $2 \cdot 10^{-4}$ M solution of macrocycle **3** in DMSO/H_2O 9:1 with 0.125 M solution of TBAPhCOO.

Binding constants K derived from simultaneous fitting of 1:1 & 2:1 (receptor:anion) model to ten selected wavelengths using HypSpec:

log $K_{1:1}$ = 2.5210, Std Dev. 0.0015

log $K_{2:1}$ = 3.5842, Std Dev. Beta 0.005

Table S23. Molar absorption coefficients derived from simultaneous fitting of 1:1 model to ten selected wavelengths using HypSpec.

	Wavelength [nm]									
	316	317	318	319	320	321	366	367	368	369
L [$M^{-1}cm^{-1}$]	1716	1715	1734	1773	1826	1889	5355	4949	4507	4003
L×PhCOO[$M^{-1}cm^{-1}$]	2086	2032	2023	2035	2065	2104	8177	8293	8192	7839
L_2×PhCOO [$M^{-1}cm^{-1}$]	5331	5336	5372	5449	5503	5612	8099	6901	5785	4777

Binding constants K derived from an experiment repeated according to the same methodology:

log $K_{1:1}$ = 2.4568, Std Dev. 0.0024

log $K_{2:1}$ = 3.7229, Std Dev. Beta 0.0065

Binding constants averaged from the above two experiments:

log $K_{1:1}$ = 2.4889, Std Dev. -

log $K_{2:1}$ = 3.6536, Std Dev. –

5.2.6 UV-Vis titration of $2 \cdot 10^{-4}$ M solution of macrocycle **3** in DMSO/H_2O 9:1 with 0.0125 M solution of TBA_2SO_4 (dissolved in the solution of receptor **3**).

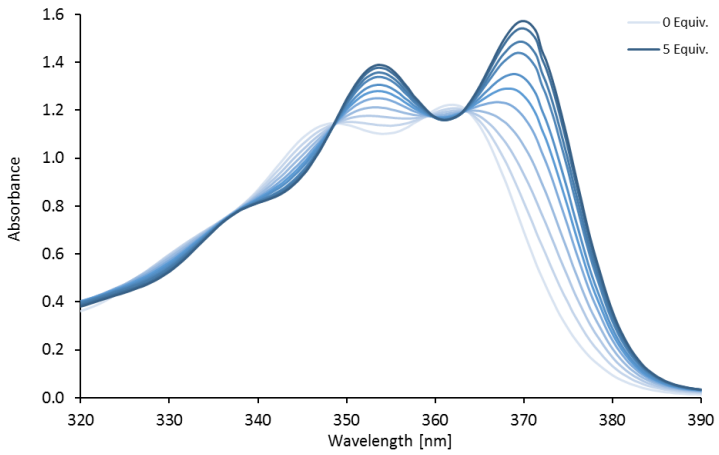

Figure S60. UV spectra obtained during titration of $2 \cdot 10^{-4}$ M solution of macrocycle **3** in DMSO/H_2O 9:1 with 0.0125 M solution of TBA_2SO_4.

Table S24. Absorbance values for selected wavelentghts recorded during titration of $2 \cdot 10^{-4}$ M solution of macrocycle **3** in DMSO/H_2O 9:1 with 0.125 M solution of TBAPhCOO.

Added volume of titrant solution [µL]	Equivalents of TBA_2SO_4	Wavelength [nm]									
		319	320	321	322	323	324	325	326	357	358
		Absorbance									
0	0.00	0.351	0.362	0.375	0.390	0.409	0.431	0.453	0.479	1.131	1.154
4	0.10	0.367	0.377	0.389	0.404	0.422	0.442	0.463	0.489	1.136	1.154
8	0.20	0.377	0.386	0.399	0.413	0.430	0.449	0.469	0.493	1.147	1.159
12	0.30	0.384	0.393	0.405	0.419	0.435	0.454	0.472	0.495	1.155	1.163
16	0.40	0.388	0.397	0.409	0.422	0.438	0.456	0.474	0.495	1.165	1.168
20	0.50	0.392	0.400	0.411	0.425	0.440	0.457	0.474	0.495	1.175	1.173
24	0.59	0.394	0.402	0.414	0.427	0.442	0.458	0.474	0.494	1.185	1.179
28.5	0.70	0.394	0.403	0.414	0.427	0.441	0.457	0.472	0.491	1.197	1.185
32.5	0.80	0.395	0.403	0.414	0.427	0.441	0.456	0.471	0.488	1.206	1.191
36.5	0.90	0.395	0.403	0.414	0.427	0.440	0.455	0.469	0.486	1.215	1.196
40.5	1.00	0.394	0.402	0.413	0.425	0.439	0.453	0.467	0.483	1.223	1.201
45	1.11	0.392	0.400	0.411	0.424	0.437	0.451	0.464	0.480	1.232	1.206
49	1.20	0.391	0.399	0.410	0.422	0.435	0.449	0.462	0.477	1.239	1.210
57.5	1.41	0.389	0.397	0.408	0.420	0.433	0.446	0.459	0.473	1.250	1.217
65.5	1.60	0.389	0.398	0.408	0.420	0.433	0.446	0.458	0.472	1.258	1.221
74	1.80	0.387	0.395	0.406	0.417	0.430	0.443	0.455	0.468	1.264	1.225
82.5	2.00	0.386	0.394	0.405	0.417	0.429	0.442	0.453	0.467	1.269	1.229
104	2.50	0.381	0.389	0.400	0.412	0.425	0.437	0.448	0.461	1.276	1.233
126	3.00	0.379	0.387	0.398	0.410	0.422	0.434	0.445	0.458	1.282	1.237
171	4.00	0.376	0.384	0.395	0.407	0.419	0.431	0.442	0.455	1.286	1.240
217.5	5.00	0.373	0.381	0.392	0.404	0.416	0.428	0.439	0.452	1.290	1.243

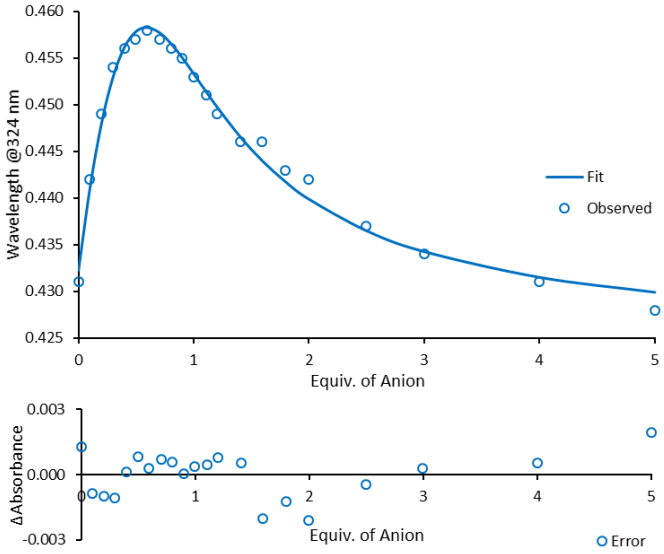

Figure S61. Fitting of 1:1 & 2:1 model to results of titration of $2 \cdot 10^{-4}$ M solution of macrocycle **3** in DMSO/H_2O 9:1 with 0.0125 M solution of TBA_2SO_4.

Binding constants K derived from simultaneous fitting of 1:1 & 2:1 (receptor:anion) model to ten selected wavelengths using HypSpec:

log $K_{1:1}$ = 4.5410, Std Dev. 0.005
log $K_{2:1}$ = 3.4175, Std Dev. Beta 0.0294

Table S25. Molar absorption coefficients derived from simultaneous fitting of 1:1 model to ten selected wavelengths using HypSpec.

	Wavelength [nm]									
	319	320	321	322	323	324	325	326	357	358
L [$M^{-1}cm^{-1}$]	1766	1819	1884	1959	2054	2161	2272	2406	5650	5765
L×SO_4[$M^{-1}cm^{-1}$]	1849	1890	1945	2003	2063	2120	2171	2229	6530	6262
L_2× SO_4 [$M^{-1}cm^{-1}$]	5518	5545	5626	5740	5839	5975	6110	6286	10682	10870

Binding constants K derived from an experiment repeated according to the same methodology:

log $K_{1:1}$ = 4.3964, Std Dev. 0.0045
log $K_{2:1}$ = 3.2794, Std Dev. Beta 0.0322

Binding constants averaged from the above two experiments:

log $K_{1:1}$ = 4.4687, Std Dev. -
log $K_{2:1}$ = 3.3485, Std Dev. -

5.2.7 UV-Vis titration of $2 \cdot 10^{-4}$ M solution of precursor **1** in DMSO/H_2O 9:1 with 0.0125 M solution of $TBAH_2PO_4$ (dissolved in the solution of receptor **1**).

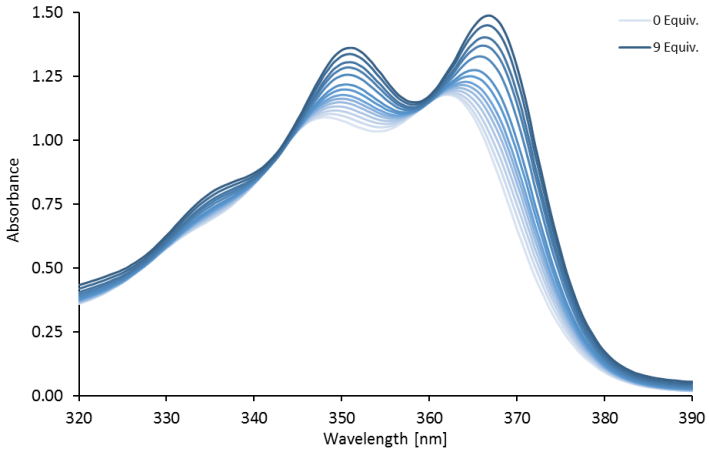

Figure S62. UV spectra obtained during titration of $2 \cdot 10^{-4}$ M solution of precursor **1** in DMSO/H_2O 9:1 with 0.0125 M solution of $TBAH_2PO_4$.

Table S26. Absorbance values for selected wavelentghts recorded during titration of $2 \cdot 10^{-4}$ M solution of precursor **1** in DMSO/H_2O 9:1 with 0.0125 M solution of $TBAH_2PO_4$.

Added volume of titrant solution [µL]	Equivalents of $TBAH_2PO_4$	Wavelength [nm]									
		350			350			350			350
		Absorbance									
0	0.00	1.076	0	0.00	1.076	0	0.00	1.076	0	0.00	1.076
4	0.10	1.086	4	0.10	1.086	4	0.10	1.086	4	0.10	1.086
8	0.20	1.096	8	0.20	1.096	8	0.20	1.096	8	0.20	1.096
12	0.30	1.105	12	0.30	1.105	12	0.30	1.105	12	0.30	1.105
16	0.40	1.113	16	0.40	1.113	16	0.40	1.113	16	0.40	1.113
20	0.50	1.122	20	0.50	1.122	20	0.50	1.122	20	0.50	1.122
24	0.59	1.131	24	0.59	1.131	24	0.59	1.131	24	0.59	1.131
28.5	0.70	1.139	28.5	0.70	1.139	28.5	0.70	1.139	28.5	0.70	1.139
32.5	0.80	1.148	32.5	0.80	1.148	32.5	0.80	1.148	32.5	0.80	1.148
36.5	0.90	1.155	36.5	0.90	1.155	36.5	0.90	1.155	36.5	0.90	1.155
40.5	1.00	1.162	40.5	1.00	1.162	40.5	1.00	1.162	40.5	1.00	1.162
45	1.11	1.170	45	1.11	1.170	45	1.11	1.170	45	1.11	1.170
49	1.20	1.177	49	1.20	1.177	49	1.20	1.177	49	1.20	1.177
57.5	1.41	1.186	57.5	1.41	1.186	57.5	1.41	1.186	57.5	1.41	1.186
65.5	1.60	1.198	65.5	1.60	1.198	65.5	1.60	1.198	65.5	1.60	1.198
74	1.80	1.207	74	1.80	1.207	74	1.80	1.207	74	1.80	1.207
82.5	2.00	1.216	82.5	2.00	1.216	82.5	2.00	1.216	82.5	2.00	1.216
104	2.50	1.236	104	2.50	1.236	104	2.50	1.236	104	2.50	1.236
126	3.00	1.252	126	3.00	1.252	126	3.00	1.252	126	3.00	1.252
148.5	3.50	1.267	148.5	3.50	1.267	148.5	3.50	1.267	148.5	3.50	1.267
171	4.00	1.279	171	4.00	1.279	171	4.00	1.279	171	4.00	1.279

194	4.50	1.290	194	4.50	1.290	194	4.50	1.290	194	4.50	1.290
217	4.99	1.299	217	4.99	1.299	217	4.99	1.299	217	4.99	1.299
265.5	6.00	1.315	265.5	6.00	1.315	265.5	6.00	1.315	265.5	6.00	1.315
315.5	7.00	1.329	315.5	7.00	1.329	315.5	7.00	1.329	315.5	7.00	1.329
365.5	7.97	1.340	365.5	7.97	1.340	365.5	7.97	1.340	365.5	7.97	1.340
440.5	9.36	1.352	440.5	9.36	1.352	440.5	9.36	1.352	440.5	9.36	1.352

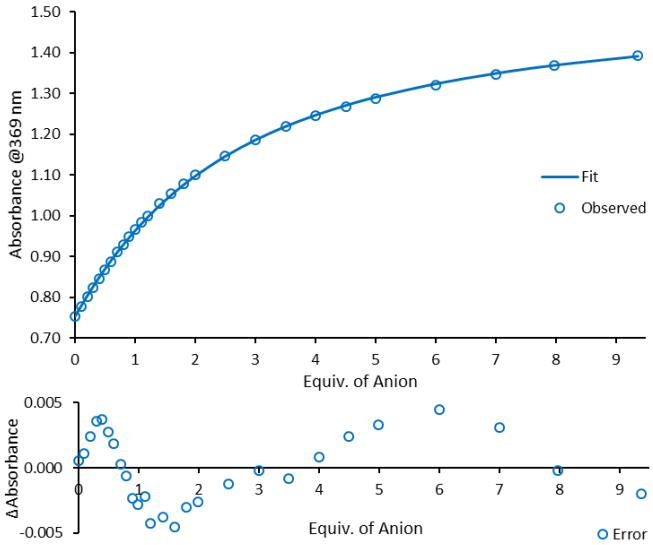

Figure S63. Fitting of 1:1 model to results of titration of $2 \cdot 10^{-4}$ M solution of precursor **1** in DMSO/H_2O 9:1 with 0.0125 M solution of $TBAH_2PO_4$.

Binding constants K derived from simultaneous fitting of 1:1 (receptor:anion) model to ten selected wavelengths using HypSpec:

log $K_{1:1}$ = 3.3953, Std Dev. 0.0007

Table S27. Molar absorption coefficients derived from simultaneous fitting of 1:1 model to ten selected wavelengths using HypSpec.

	Wavelength [nm]									
	350	351	352	353	365	366	367	368	369	370
L [$M^{-1}cm^{-1}$]	5364	5303	5232	5178	5433	5105	4698	4257	3768	3273
L×H_2PO_4[$M^{-1}cm^{-1}$]	7037	7111	7057	6887	7588	7906	8062	8005	7705	7172

Binding constants K derived from two experiments repeated according to the same methodology at different concentrations:

log $K_{1:1}$ = 3.4974 Std Dev. 0.0003
log $K_{1:1}$ = 3.4464 Std Dev. 0.0008, concentration: 1e-4 M

Binding constant averaged from the above three experiments:

log $K_{1:1}$ = 3.4464, Std Dev. 0.0417

5.2.8 UV-Vis titration of $2 \cdot 10^{-4}$ M solution of precursor **1** in DMSO/H_2O 9:1 with 0.0125 M solution of TBAPhCOO (dissolved in the solution of receptor **1**).

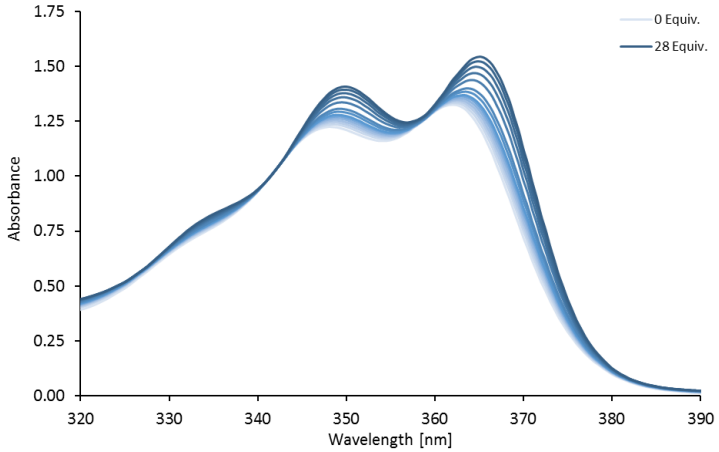

Figure S64. UV spectra obtained during titration of $2 \cdot 10^{-4}$ M solution of precursor **1** in DMSO/H_2O 9:1 with 0.0125 M solution of TBAPhCOO.

Table S28. Absorbance values for selected wavelentghts recorded during titration of $2 \cdot 10^{-4}$ M solution of precursor **1** in DMSO/H_2O 9:1 with 0.0125 M solution of TBAPhCOO.

Added volume of titrant solution [µL]	Equivalents of TBAPhCOO	Wavelength [nm]									
		348	349	350	351	364	365	366	367	368	369
		Absorbance									
0	0.00	1.225	1.222	1.211	1.195	1.281	1.224	1.145	1.049	0.945	0.834
4	0.40	1.231	1.229	1.219	1.203	1.291	1.237	1.161	1.067	0.964	0.853
8	0.80	1.235	1.235	1.225	1.210	1.298	1.247	1.173	1.081	0.978	0.867
12	1.19	1.240	1.239	1.231	1.215	1.306	1.257	1.184	1.093	0.992	0.880
16	1.59	1.244	1.245	1.236	1.221	1.313	1.267	1.196	1.106	1.005	0.893
20	1.98	1.248	1.250	1.241	1.227	1.320	1.276	1.208	1.119	1.018	0.905
24	2.38	1.252	1.254	1.246	1.232	1.326	1.283	1.216	1.129	1.027	0.916
28.5	2.82	1.256	1.260	1.253	1.238	1.333	1.293	1.227	1.141	1.041	0.929
32.5	3.21	1.259	1.264	1.257	1.242	1.339	1.301	1.238	1.152	1.053	0.941
36.5	3.60	1.264	1.268	1.262	1.248	1.346	1.309	1.248	1.164	1.064	0.951
40.5	3.99	1.267	1.272	1.266	1.252	1.352	1.317	1.256	1.173	1.074	0.961
45	4.42	1.270	1.277	1.271	1.257	1.357	1.324	1.265	1.183	1.085	0.970
49	4.81	1.273	1.279	1.274	1.260	1.361	1.330	1.273	1.192	1.094	0.980
57.5	5.62	1.278	1.287	1.283	1.269	1.371	1.343	1.288	1.208	1.112	0.999
65.5	6.38	1.284	1.294	1.290	1.277	1.381	1.355	1.303	1.226	1.130	1.017
74	7.19	1.290	1.301	1.298	1.284	1.390	1.367	1.317	1.241	1.145	1.032
82.5	7.99	1.295	1.307	1.304	1.291	1.399	1.378	1.331	1.256	1.161	1.047
104	9.98	1.308	1.321	1.321	1.308	1.419	1.405	1.362	1.291	1.196	1.082
126	12.00	1.319	1.335	1.335	1.322	1.438	1.429	1.391	1.322	1.230	1.114
148.5	14.02	1.329	1.346	1.347	1.335	1.453	1.447	1.412	1.347	1.255	1.139
171	16.01	1.338	1.356	1.359	1.347	1.467	1.466	1.435	1.372	1.281	1.165
217	19.97	1.352	1.374	1.378	1.366	1.491	1.497	1.472	1.413	1.323	1.206
267	24.12	1.364	1.389	1.394	1.383	1.512	1.523	1.503	1.447	1.358	1.241

317	28.13	1.375	1.401	1.408	1.396	1.528	1.544	1.528	1.474	1.387	1.268

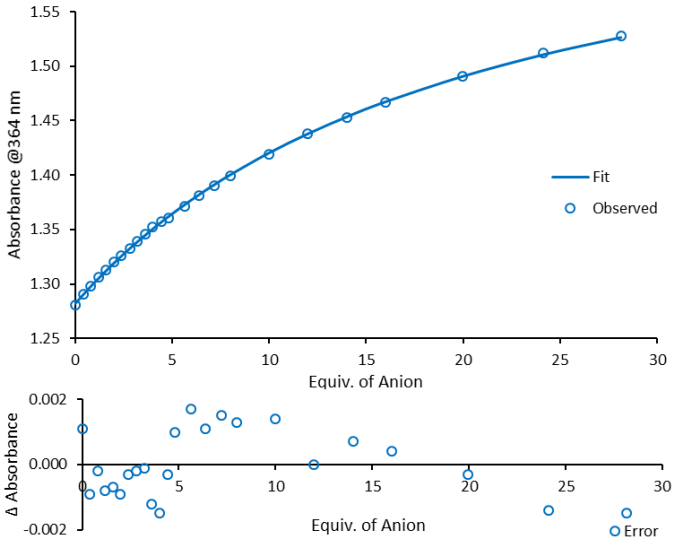

Figure S65. Fitting of 1:1 model to results of titration of $2 \cdot 10^{-4}$ M solution of precursor **1** in DMSO/H_2O 9:1 with 0.0125 M solution of TBAPhCOO.

Binding constants K derived from simultaneous fitting of 1:1 (receptor:anion) model to ten selected wavelengths using HypSpec:

log $K_{1:1}$ = 2.4092, Std Dev. 0.0005

Table S29. Molar absorption coefficients derived from simultaneous fitting of 1:1 model to ten selected wavelengths using HypSpec.

	Wavelength [nm]									
	348	349	350	351	364	365	366	367	368	369
L [$M^{-1}cm^{-1}$]	6147	6134	6080	6002	6434	6156	5764	5287	4768	4212
L×PhCOO[$M^{-1}cm^{-1}$]	7417	7650	7745	7705	8528	8865	9007	8890	8510	7893

Binding constants K derived from an experiment repeated according to the same methodology (KB460B):

log $K_{1:1}$ = 2.4070 Std Dev. 0.0009

Binding constant averaged from the above two experiments:

log $K_{1:1}$ = 2.4081, Std Dev. -

5.3 Fluorescence Titrations

General Procedure

To a solution of a host (2.5 mL, 10^{-5} M) in a screw-cap fluorescence cuvette made of Quartz SUPRASIL (light path: 10 mm) appropriate aliquot of titrant (dissolved in the solution of host to avoid dilution) were added using a 25 µl gas-tight microsyringe. Stream of argon was flushed through the solution of a host and the solution of titrant. Fluorescence spectra were obtained on Hitachi F-7000. Excitation wavelength: 350 nm, scan speed: 1200 nm/min, temperature: 25°C.

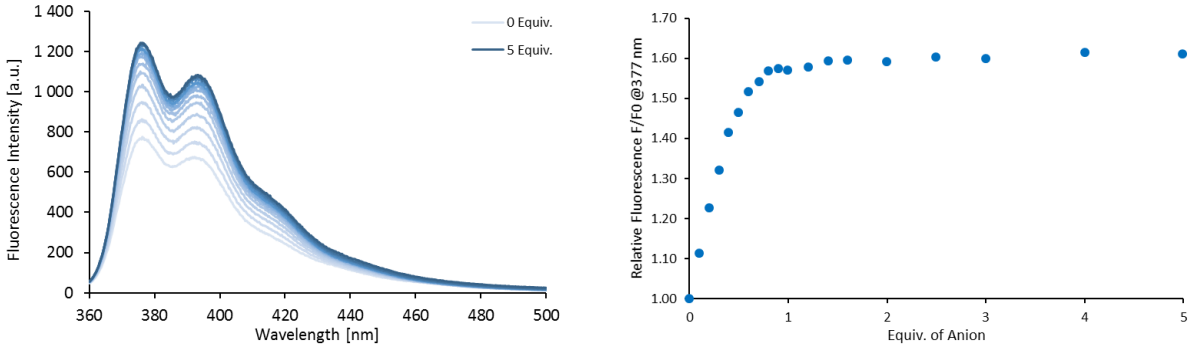

Figure S66. Emission spectra obtained during titration of 10^{-5} M solution of catenane **A** in DMSO/10% H_2O with $6.25 \cdot 10^{-4}$ M solution of TBA_2SO_4 (dissolved in the solution of catenane **A**).

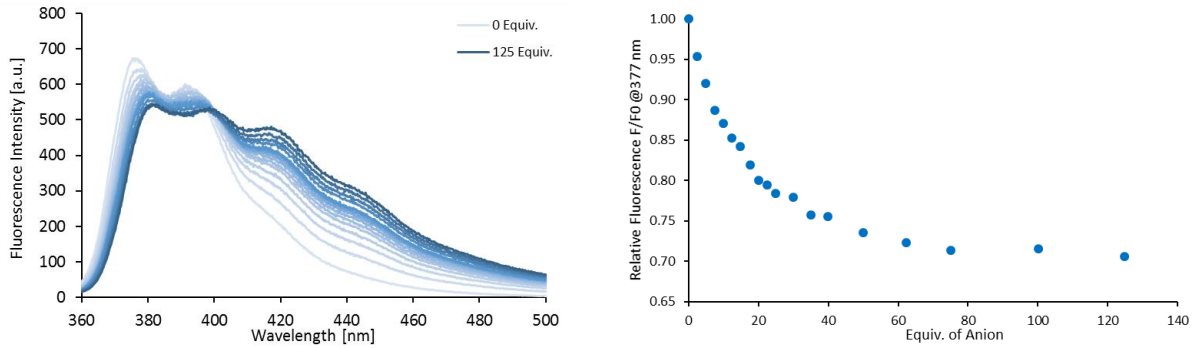

Figure S67. Emission spectra obtained during titration of 10^{-5} M solution of catenane **A** in DMSO/10% H_2O with 0.0156 M solution of $TBAH_2PO_4$ (dissolved in the solution of catenane **A**).

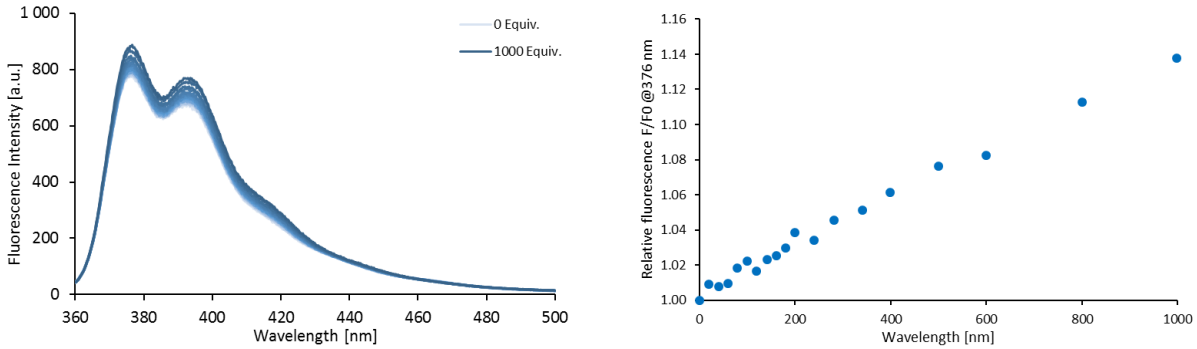

Figure S68. Emission spectra obtained during titration of 10^{-5} M solution of catenane **A** in DMSO/10% H_2O with 0.125 M solution of TBAPhCOO (dissolved in the solution of catenane **A**).

6. Computational Studies

6.1. Methods

Preparation of the starting structures for molecular dynamics simulations

The starting model of **A**×$SO_4^{2-}$was prepared on the basis of the crystal structure of the 2:1 (ligand:anion) complex of simple acyclic diamidocarbazoles bound to the sulfate anion.[3] Additional chains were manually added in Maestro software (Schrödinger Release 2017-1: Maestro, Schrödinger, LLC, New York, NY, 2017) and the entire system was minimized in OPLS 2005 force-field (with environment modelled as constant dielectric of DMSO) until energy convergence of 0.05 kJ/mol was obtained. The resulting structure was used as the starting point in conformational search and molecular dynamics (MD) simulations (see below). Next, we used the optimized structure of the 1:1 complex to obtain the initial conformation of the free catenane. More specifically, the sulfate ion was removed from the 1:1 complex, and the resulting free catenane was subjected to conformational sampling. For the 1:2 (catenane:sulfate) complex, the initial structure was a manually-built model with the two diamidocarbazole units positioned as far as possible from each other and sulfate ions added and minimized using the same approach as before.

Conformational search

The conformational sampling was performed in the Macromodel suite and OPLS 2015 force field using the following, non-standard search values: 50 kcal/mol energy window for saving structures, RMSD cutoff of 3 Å, 10000 simulation cycles, 10000 search steps in the low-scale low-mode conformational search and an enhanced torsion sampling protocol sampling all C-N and C-O single bonds.

Molecular dynamics simulations

The models of the free catenane and its 1:1 and 1:2 complexes obtained in the preparation step were subjected to molecular dynamics (MD) simulations. We used Charmm General Force Field v. 3.0.1 (CGenFF).[4] Catenanes and tetrabutylammonium ions (TBA) were parametrized using the CHARMM-GUI server, while the parameters and topologies for all other molecules were obtained directly from CGenFF. In all three cases (free catenane, 1:1 complex, 1:2 complex), the catenane/complex was immersed in the geometric center of the 50 × 50 × 50 Å periodic box of DMSO created using packmol software.[5] In the case of the 1:1 and 1:2 complexes, the appropriate number of TBA ions (two or four) were manually added to the box. In MD simulations, we used a standard, four-step approach. In the first step, the entire system was minimized for 1000 steps, while in the second step we performed 0.5 ns of NVT MD, both with the catenane/complex frozen. In the third step, we unfroze all coordinates and performed a 1000-step minimization, while the fourth step was a production run in the NPT ensemble for a variable amount of time. In all steps we used a 1 fs time step, a 12 Å cutoff of electrostatic and van der Waals interactions and a constant temperature of either 298.15 K (25^{o}C) or 373.15 K (100^{o}C, the increased temperature of 100^{o}C was used to speed up the evolution of the system), and maintained constant pressure of 1 atm using Langevin barostat. MD simulations were performed using the NAMD ver. 2.11.[6]

Interaction energy calculations

Sulfate-catenane interaction energies were estimated using the GFN2-xTB tight-binding approach, as implemented in xtb ver.6.4.1. program.[7,8]

6.2. Results

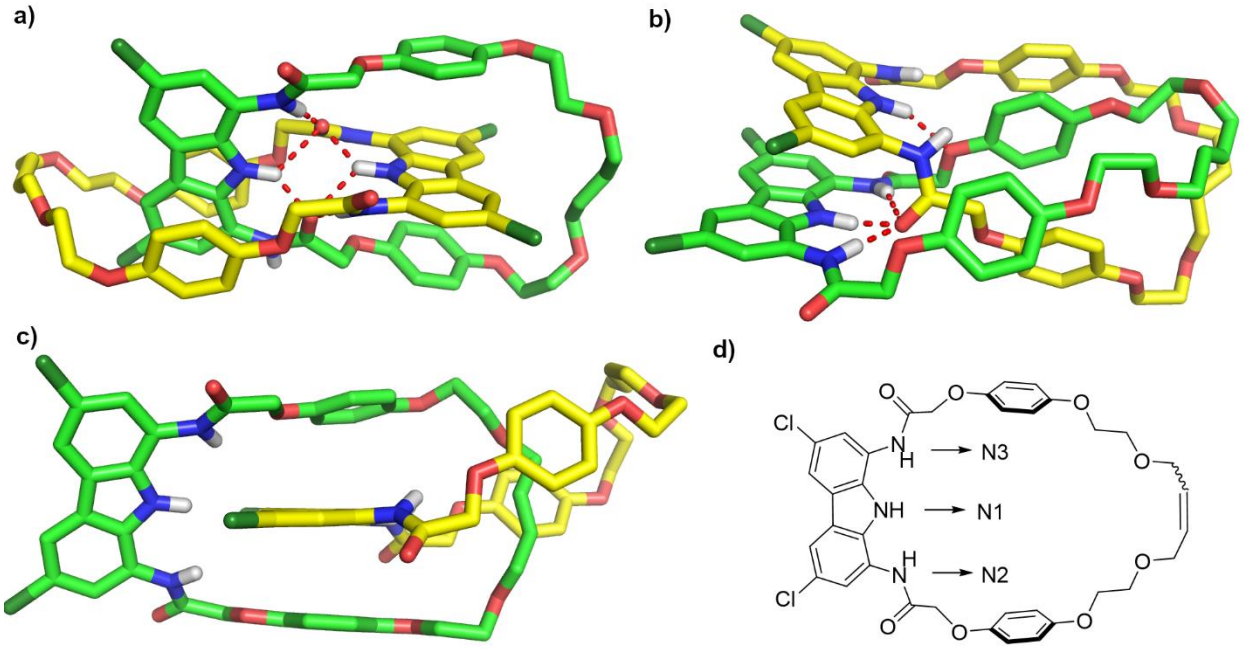

Figure S69. Low-energy conformations (a-c) of free catenene **A** obtained from conformational search and nitrogen atom naming scheme used throughout this study (d).

Molecular dynamics simulations of the three conformations revealed that the catenane is a very flexible system with multiple low-energy conformations occurring even during 100 ns simulations at 25°C. Conformation **a** is the most stable one with the average distance between the nitrogen atoms of diaminocarbazoles varying between 3.3 to 5.3 Å (average distance of 4.5 Å, see Figure S64). Interestingly, after 50 ns this conformation underwent a major change, breaking most of its hydrogen bonds and forming a new hydrogen bond network, which is almost identical to the original one, but formed by opposite C=O groups (Figure S65). The N1-N1 distance for conformation **b** does also not change much during the 100 ns simulation and has a similar average value of 4.6 Å. This conformation underwent, however, a major conformational change as the diamidocarbazoles switch from the π-π stacking arrangement to an orthogonal conformation similar to conformation **a** and stabilized by multiple hydrogen bonds. Conformation **c** was also not stable over the time of the simulation and underwent major conformational changes, including rotations of the macrocycles with respect to each other.

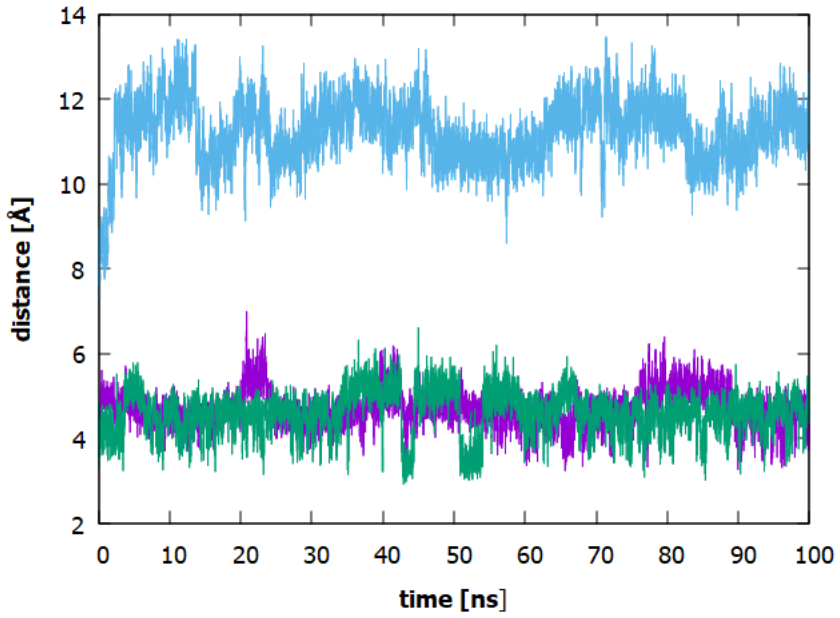

Figure S70. Plots of N1-N1 distances during 100 ns of MD simulation for catenane conformations **a** (purple), **b** (green) and **c** (cyan).

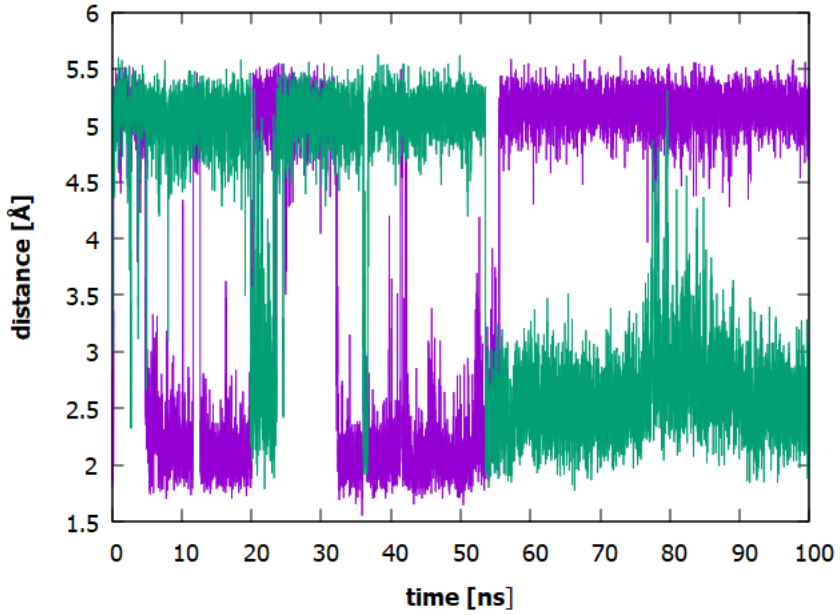

Figure S71. Selected O···H distances during 100 ns of MD simulation for a C=O oxygen atom forming a HB at the beginning of the MD simulation (purple) and for a C=O oxygen atom forming a HB at the end of the MD simulation (green) for catenane conformation **a**.

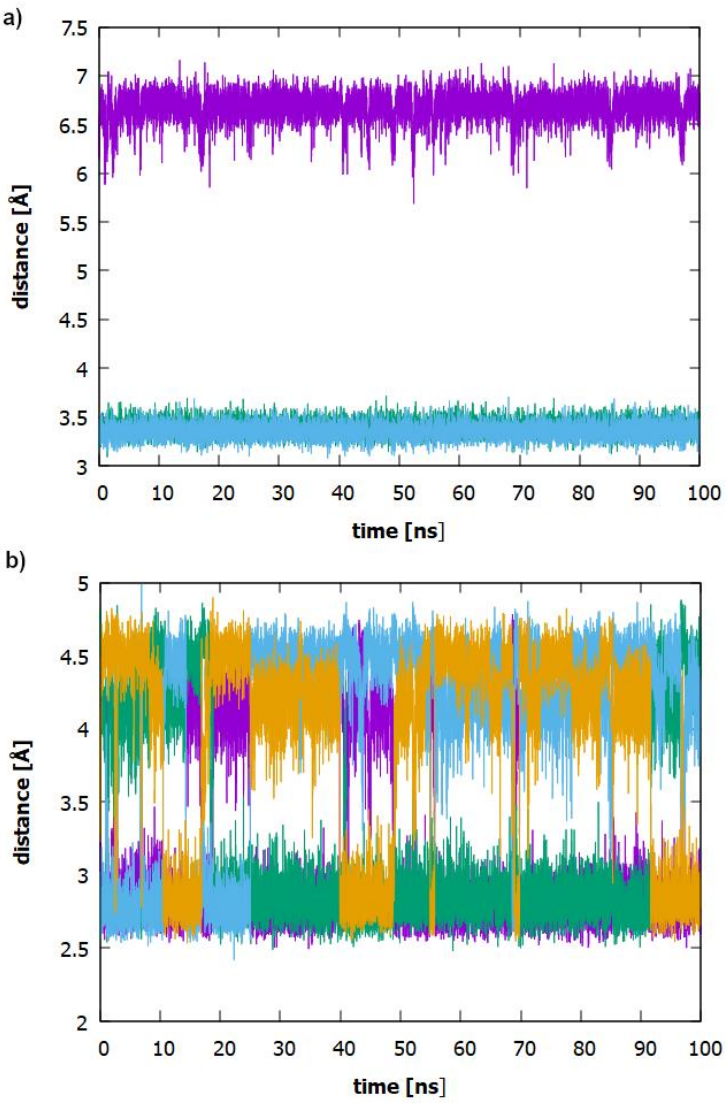

Figure S72. Plots of a) N1-N1 distance (purple) and N1-S distances (green and cyan) and b) N1-O(SO_4^{2-}) distances during 100 ns of MD simulation of the 1:1 complex.

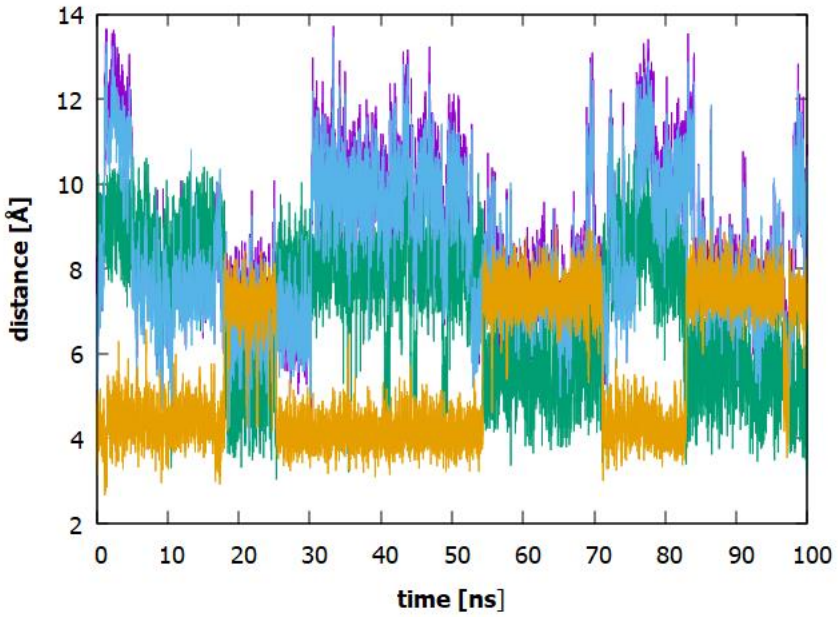

Figure S73. Plots of H-H distances during 100 ns of MD simulation of the 1:1 complex corresponding to expected contacts in the 2D ROESY spectra, as defined in Figure 4 of the manuscript: 2-B (purple), 2-C (green), 4-B (cyan) and 4-C (yellow).

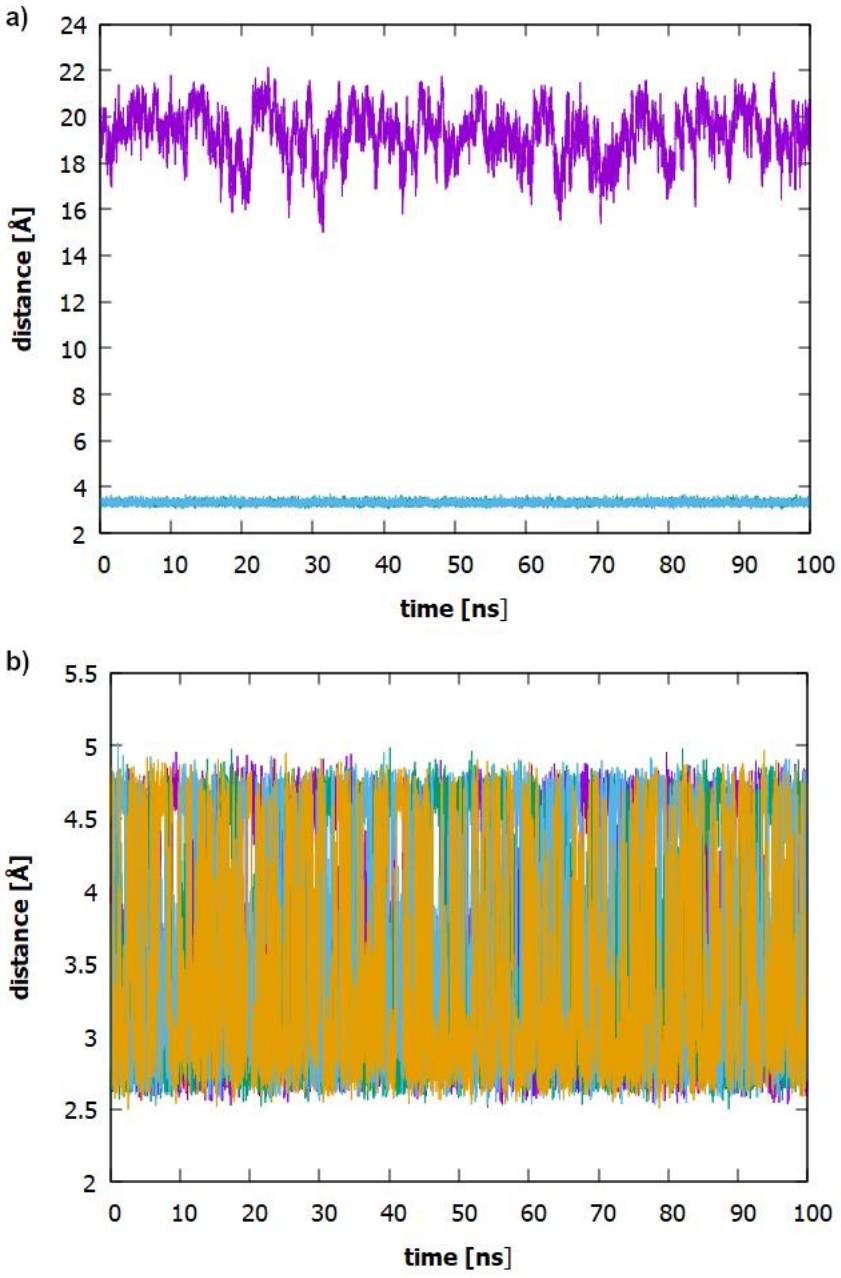

Figure S74. Plots of a) N1-N1 distance (purple) and N1-S distances (green and cyan) and b) N1-O(SO_4^{2-}) distances during 100 ns of MD simulation of the 1:2 complex.

Switching between the 1:2 and 1:1 complexes

To gain a better insight into the dynamics of sulfate binding, we also modelled switching between the 1:2 and 1:1 complex. First, we chose 10 different MD snapshots from the 100 ns run of the 1:2 complex (five with the lowest potential energy of the entire complex and five with the highest potential energy). To prepare the first set of 10 MD simulations, we removed one of the sulfate ions and two random TBA molecules, while in the second set we removed the other sulfate ion and the same two TBA molecules. We performed 50 ns MD on all 20 different sets. All MD runs were based on the same starting point, which was the lowest potential energy snapshot of the initial 1:2 100 ns MD run. Since the motions of the macrocycles were relatively slow at room temperature, we decided to perform the simulations at 100°C.

During these 20 different MD runs we observed two radically different macrocycle motions, leading to two different conformations of the 1:1 complex, which we analyze below.

The first set resulted in a very fast change in catenane conformation, which converged to the low-energy conformation of the 1:1 complex in less than 1 ns (Fig. S68 and S69). The plots of the N1-S distances show a drastic and very rapid change of one of these distances, from 17 Å to 3.5 Å, upon drastic co-conformational change driven by chelation of the sulfate by the second diamidocarbazole moiety. After switching to this low energy co-conformation, the system became very stable with respect to both its energy and geometry, similarly to the previously described 1:1 complex. However, we can observe a relatively large rotational freedom of the bound sulfate, manifested by the rapid changes in the N1/N1-O distance lengths.

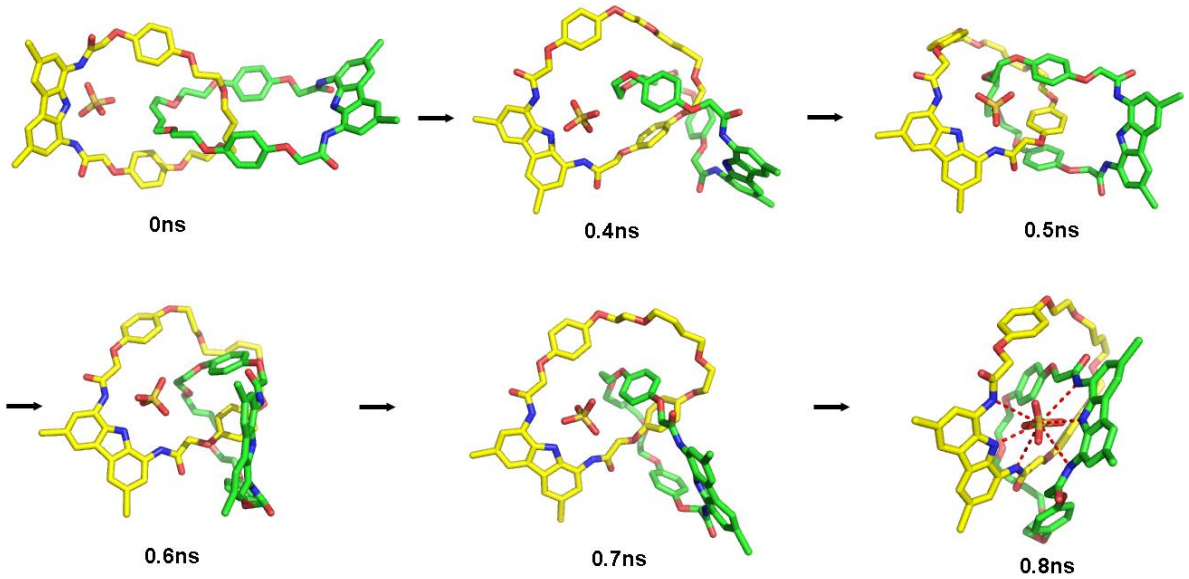

Figure S75. Evolution of the 1:2 catenane complex upon removal of one sulfate anion – simulation 1.

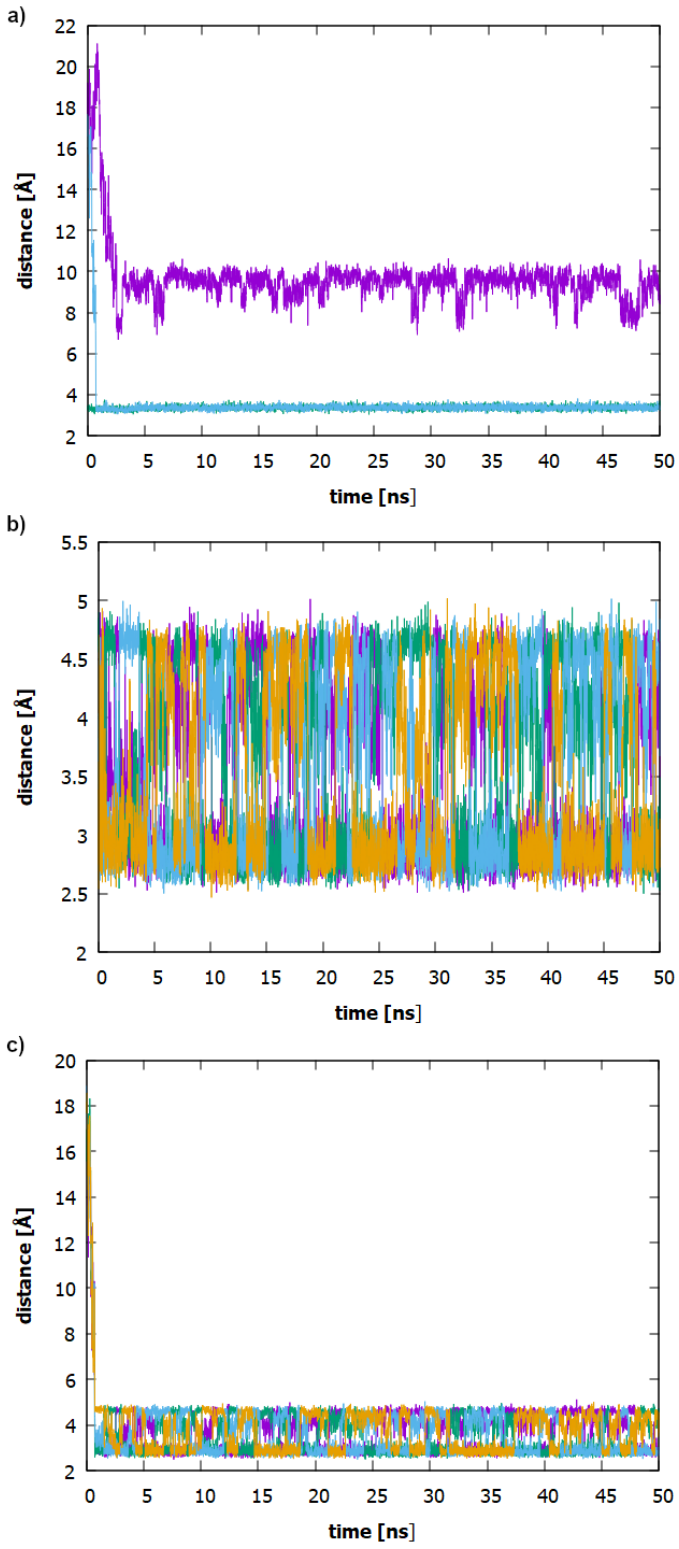

Figure S76. Plots of a) N1-N1 distance (purple) and N1-S distances (green and cyan) and b) and c) N1-O(SO_4^{2-}) distances during 50 ns of MD simulation of the 1:2 to1:1 switch – simulation 1.

The second set (with the other sulfate removed) also resulted in a fast change in the catenane co-conformation, but the final, metastable conformation was attained after 2.6 ns and was different from the lowest energy conformation of the 1:1 complex attained in the previous case (Fig. S70). Here the macrocycle that has no sulfate bound undergoes a number of rotations around the sulfate-bound macrocycle and finally ends up with the N2 amide nitrogen atom forming a hydrogen bond to the sulfate, while both N1 and N3 are positioned further away from the sulfate and with no direct interactions. As a result, the sulfate is bound more weakly than in the previous 1:1 complex and the N1'-S distance remains relatively large (on average 6.5 Å), while the N2-S distance varies similarly to the N1-S distance with an average of 3.5 Å (Fig. S71). Based on these results, we suggest that upon 1:2 to 1:1 switching it is likely that the 1:1 complex is temporarily trapped in this metastable conformation, with only four NHs interacting with the sulfate, but ultimately likely also converges to the lowest-energy conformation with all six NHs interacting with the sulfate.

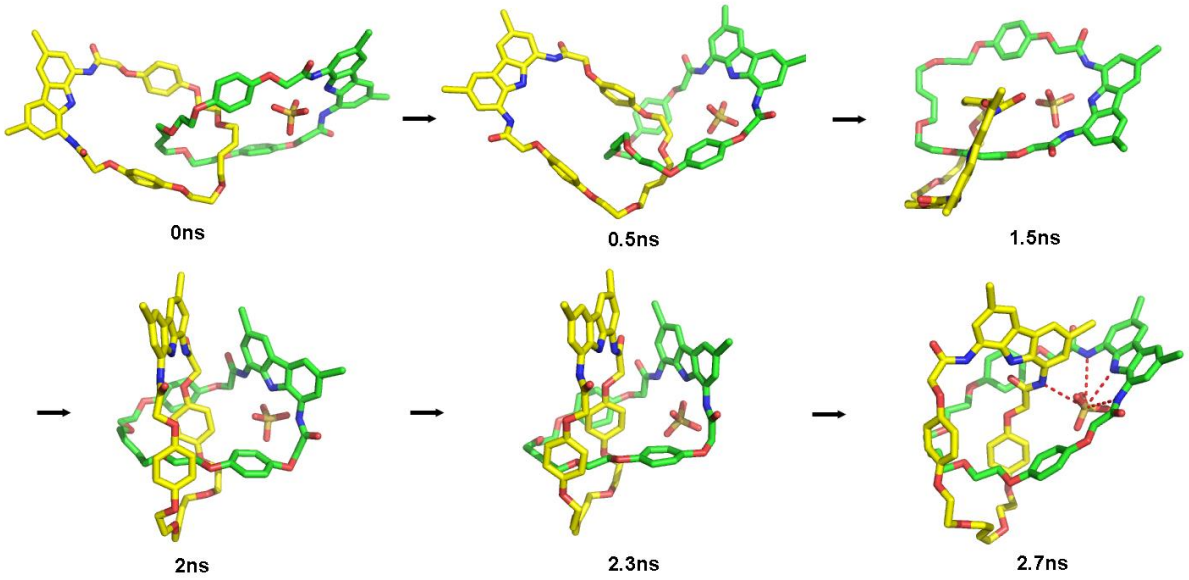

Figure S77. Evolution of the 1:2 catenane complex upon removal of one sulfate anion – simulation 2.

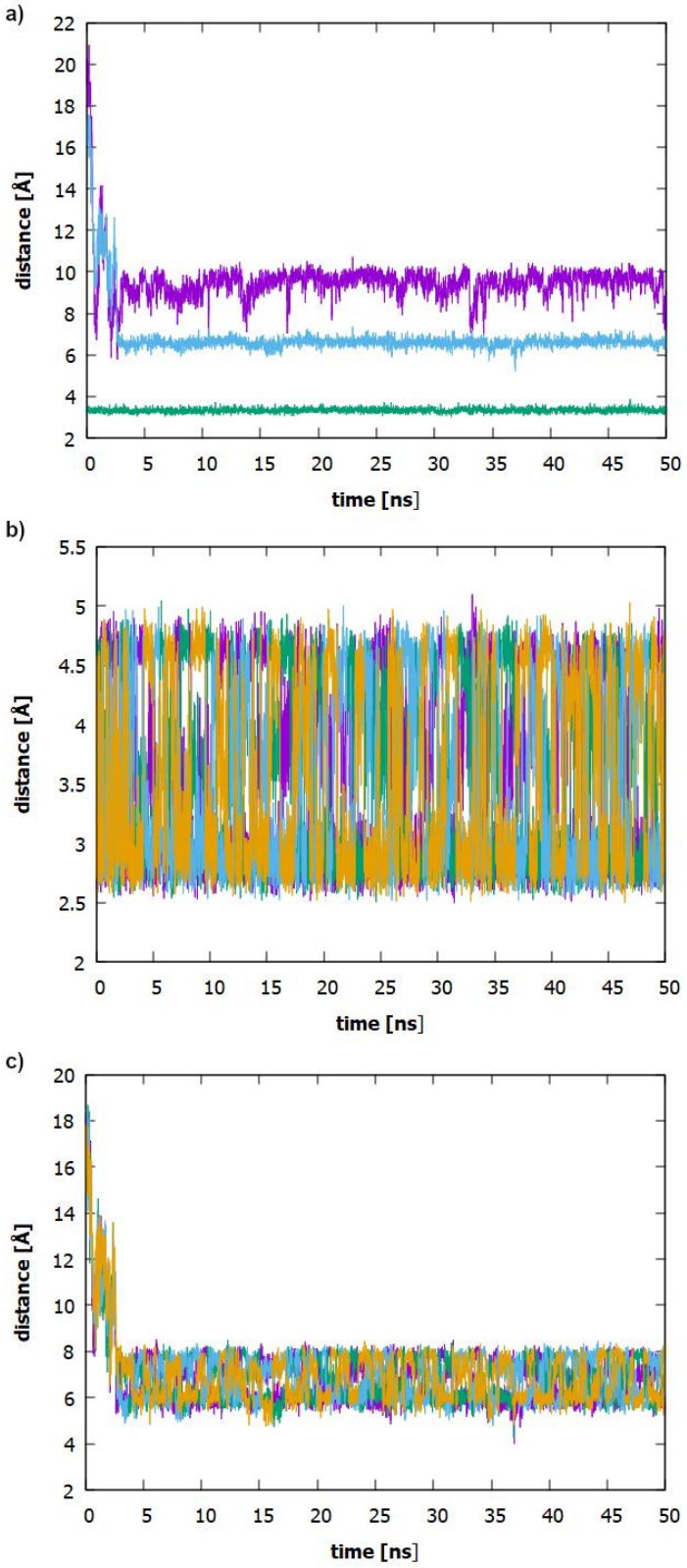

Figure S78. Plots of a) N1-N1 distance (purple) and N1-S distances (green and cyan) and b) and c) N1-O(SO_4^{2-}) distances during 50 ns of MD simulation of the 1:2 to1:1 switch – simulation 2.

6.3. Conformation Search for 2:1 Complexes of Macrocycle 3

A conformational search for 2:1 (receptor:anion) complexes of macrocycle **3** with sulfate has been performed using the Conformer–Rotamer Ensemble Sampling Tool with the GFN2-xTB approach (see 10.1039/C9CP06869D and 10.1021/acs.jctc.8b01176). We found that within a 6 kcal/mol window there are seven conformers with the sulfate bound by both macrocycles which are either in orthogonal-like arrangement or flat & sandwich-like arrangement.

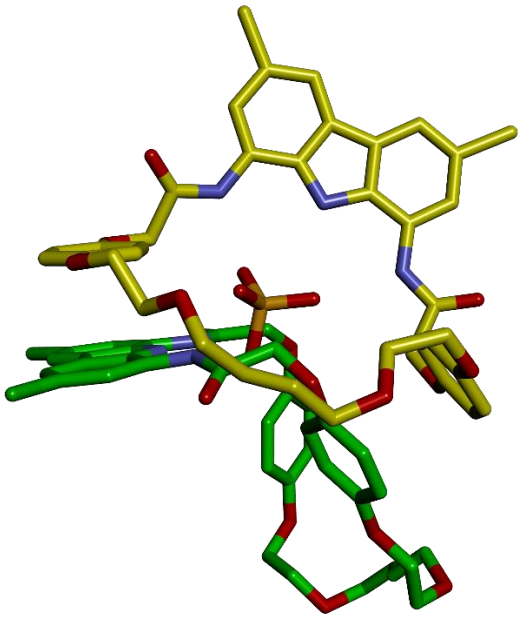

Figure S79. Example of an orthogonal arrangement of **3**×SO_4^{2-}×**3** complex. The lowest energy conformer.

Table S30. Cartesian coordinates of atoms in the lowest energy orthogonal arrangement of **3**×SO_4^{2-}×**3** complex.

169
-309.15636215

Cl	1.1613673975	-8.5402658011	0.3444451428
Cl	4.4063081719	-3.3347126028	-5.5594733633
O	1.7808349286	0.8329831520	-4.1487787015
O	-1.5580059548	-5.0661205513	2.9282689847
N	-0.5376226563	-3.7836867277	1.3331432585
H	-0.4585460488	-2.8112277747	1.0218926387
H	0.5494994843	-2.1076393324	-0.4208480225
N	1.7194798690	-0.4516039391	-2.2633243628
H	1.5364754939	-0.4155317356	-1.2483108284
C	1.1037913710	-6.8449089218	0.0039163329
C	1.8246637642	-6.3577975028	-1.0657990171
H	2.4125652941	-7.0135909206	-1.6857963810
C	1.7565675915	-4.9866443103	-1.3041402141

C	0.2348099483	-4.6852988978	0.6111536747
C	0.3112548600	-6.0511071208	0.8351629828
H	-0.2429880073	-6.4935947372	1.6460732190
C	-1.3250555987	-3.9888345725	2.4016658984
C	-1.9238657386	-2.6728165438	2.9193711921
H	-1.3001007774	-2.3397006338	3.7550986127
H	-1.8732490682	-1.9056277636	2.1389377082
C	1.8522354525	-2.8118334389	-1.9597608222
C	2.1845227698	-1.6855381746	-2.7169859775
C	2.9668333167	-1.8824021120	-3.8414154255
H	3.2367578805	-1.0471032455	-4.4649566119
C	3.4151274726	-3.1642690688	-4.1581401093
C	3.1200519987	-4.2852525986	-3.4126489466
H	3.4954588973	-5.2550985776	-3.6931378327
C	2.3142559777	-4.1063847604	-2.2913331124
C	1.6030081414	0.6966168696	-2.9478218945
C	1.2170910558	1.8845997535	-2.0485860086
H	0.8625483827	1.5287628588	-1.0753536175
H	2.1286807619	2.4741442555	-1.8896384580
O	-3.2181985920	-2.8248470120	3.4471882278
C	-6.3831115140	-4.0832181670	1.0433885212
C	-6.5187937862	-3.9058323528	2.4231648955
C	-5.4523582487	-3.4912635203	3.1858426322
C	-4.2119898031	-3.2358872964	2.5951036596
C	-4.0786355206	-3.3966833475	1.2239357733
C	-5.1547605743	-3.8184566513	0.4546095164
H	-7.4747950873	-4.1104127092	2.8769678502
H	-5.5478622225	-3.3600797459	4.2514907497
H	-3.1396548281	-3.1922761069	0.7325119671
H	-5.0038431406	-3.9312156644	-0.6076793501
O	-7.5031486119	-4.5197090007	0.3971917663
C	-7.4636835252	-4.7793956879	-0.9936463998
H	-6.5647469621	-5.3506067484	-1.2515354429
H	-8.3458032682	-5.3967923086	-1.1831885082
C	-7.5507207020	-3.5154648341	-1.8717110062
H	-6.9370399791	-2.7175649132	-1.4343311230
H	-7.1712540905	-3.7545907502	-2.8685982724
O	-8.8733639449	-3.0754347304	-2.0741477837
C	-9.4448396787	-2.3908700915	-0.9726137570
H	-9.2905803177	-2.9581257851	-0.0460272797
H	-10.5191413128	-2.3659842218	-1.1855029920
C	-8.9411616279	-0.9840097644	-0.7878562035
C	-8.2856650205	-0.2999833667	-1.7105838509
C	-7.7578341108	1.0932983610	-1.5319376569
H	-6.6645866985	1.0600871634	-1.4265901274
H	-8.1808463114	1.5469363223	-0.6314550300
H	-8.0985298383	-0.7558845978	-2.6733470538
H	-9.1472507326	-0.5521335095	0.1822048908
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C	-3.2033286145	3.0875404744	-3.4990470161
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C	-1.0114675398	2.4048804031	-2.7482020569
C	-1.5573972290	1.2217806998	-2.2624788517
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H	-1.4308184586	4.2490219391	-3.7357945680
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H	-3.3309232692	0.0640442096	-2.0138227904

O	-5.0682784917	1.5562968823	-3.1077609020
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N	1.0599996789	-2.8722169573	-0.8575434861
C	0.9782025283	-4.1669634537	-0.4545483112
S	0.3189693234	-0.5718791134	1.1944437771
O	0.7038257111	-1.4470170681	2.3175364774
O	-0.3129481052	0.6558174607	1.7170354335
O	1.5130634394	-0.1833562984	0.4186060651
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Cl	-0.5144678267	5.3839666232	7.5533465315
Cl	6.3438236386	0.6171813127	6.7186627279
O	5.3343153689	-1.5737999669	2.3879908327
O	-2.9193826726	4.1744188589	3.3602298176
N	-1.3510011325	2.5062672561	3.3993256567
H	-0.9918797415	1.7341052955	2.8328060928
H	0.8701977354	0.8100735772	3.0555369870
N	3.2301748736	-0.8417572532	2.9336306709
H	2.2399538410	-0.9621386443	2.6599635950
C	-0.0128832101	4.1575135033	6.4430955557
C	1.2069687526	3.5455003847	6.6234812641
H	1.8581790543	3.8158220232	7.4372047930
C	1.5607287625	2.5621375315	5.7029597417
C	-0.5325648548	2.8623035170	4.4702868450
C	-0.8747107215	3.8381070595	5.3957032229
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C	-2.4294299578	3.1550713659	2.9072810586
C	-3.0315851835	2.4369810060	1.6868480197
H	-2.2745715623	1.8070494458	1.2051444587
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C	4.6554095271	-0.0592257103	4.7534969312
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C	2.7263860410	1.7421638224	5.5636275108
C	4.1211219284	-1.5984708682	2.2596940275
C	3.4127854274	-2.5352706270	1.2749341462
H	2.9759717985	-3.3610481477	1.8473005005
H	2.5988150486	-1.9811410749	0.8013013555
O	-3.6368637356	3.3243162708	0.7803582637
C	-1.3812215477	6.0710845929	-1.4006166083
C	-2.7772198520	6.0336560560	-1.4598955647
C	-3.4885009797	5.1181471874	-0.7213322777
C	-2.8300809428	4.2019993298	0.1014474117
C	-1.4457197686	4.2394374526	0.1675125940
C	-0.7282749314	5.1694560368	-0.5722832782
H	-3.2801651408	6.7407029543	-2.0992696085
H	-4.5653014108	5.0869766493	-0.7607699533
H	-0.9001851397	3.5410840416	0.7848131337
H	0.3475098239	5.1619298980	-0.4885588141
O	-0.7915270650	7.0355935343	-2.1668896681

C	0.6133581816	7.1125180239	-2.2648751875
H	0.7940084838	8.0692431130	-2.7606162615
H	1.0788289885	7.1212732831	-1.2710841235
C	1.2414794514	5.9991668878	-3.1100974059
H	2.3363107379	6.0373659836	-2.9915631098
H	0.8929851981	5.0158016781	-2.7693264706
O	0.8823330175	6.1913843127	-4.4605139359
C	1.2051844021	5.0926512495	-5.2930230360
H	0.6939952804	5.3073255962	-6.2381029608
H	0.8076037556	4.1583361128	-4.8729698508
C	2.6787823155	4.9465030891	-5.5457428307
C	3.3360777336	3.8014264155	-5.4633137464
C	4.7951746254	3.6556683265	-5.7925152083
H	5.2483232477	4.6396625696	-5.9390704630
H	4.8943207789	3.0717325372	-6.7230461384
H	2.8218791486	2.8956318032	-5.1691187031
H	3.1867712751	5.8596028159	-5.8279581844
O	4.2737928934	-3.1304982156	0.3353026252
C	6.0174414594	-0.8698547718	-2.7008052759
C	6.2601227959	-2.2379799151	-2.5572609449
C	5.6671877393	-2.9535694036	-1.5434982002
C	4.8131087723	-2.3252143315	-0.6341153952
C	4.5670024204	-0.9679694187	-0.7778485224
C	5.1622324405	-0.2486081142	-1.8034179264
H	6.9201017046	-2.7188542292	-3.2608590877
H	5.8509290144	-4.0094206157	-1.4291221012
H	3.9010845346	-0.4506997895	-0.1061738324
H	4.9325584754	0.8026122685	-1.8843093368
O	6.6781355214	-0.2581621084	-3.7306169700
C	6.6373071963	1.1451180081	-3.8596735703
H	7.5369275727	1.4080632878	-4.4233685240
H	6.6806962801	1.6418427005	-2.8841024467
C	5.4175293369	1.6554417804	-4.6413122513
H	4.4836529161	1.3981301137	-4.1203431646
H	5.3940478074	1.1703480965	-5.6289902288
O	5.5748147681	3.0489427393	-4.7752976434
N	1.2848400614	1.2223459896	3.8889373220
C	0.6999473587	2.2096502040	4.6372380602

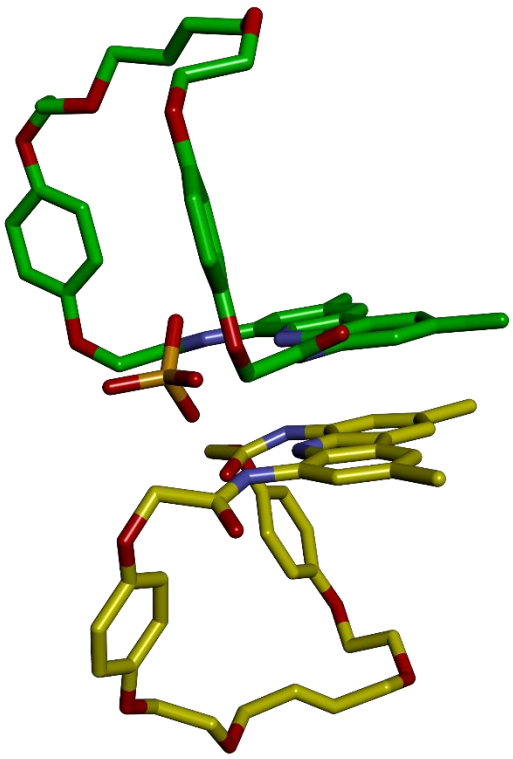


Figure S80. Example of an sandwich-like arrangement of **3**×SO_4^{2-}×**3** complex. The fifth lowest energy conformer.

Table S31. Cartesian coordinates of atoms in the fifth lowest energy arrangement of **3**×SO_4^{2-}×**3** complex (sandwich-like arrangement; ΔE = 5.1 kcal/mol in relation to the lowest energy arrangement).

169
-309.14822978

Cl	-2.9020197330	1.4687878888	5.5555806716
Cl	2.1380084932	-5.1030652682	4.2116278127
O	-0.9823181190	-2.6570023612	-1.5276055842
O	-4.5532011137	2.1284584379	0.8675170353
N	-2.6369177623	0.9514025026	0.4649740764
H	-1.9178209140	0.8120497091	-0.2718713765
H	-0.9680685934	-1.2258822677	-0.0909432165
N	0.7236248095	-3.7215015660	-0.4147909669
H	1.4404971631	-4.4142039488	-0.6054690163
C	-2.3191400543	0.6466915920	4.1519462502
C	-1.4795165023	-0.4340230346	4.3044716283
H	-1.1911474317	-0.7820333815	5.2816449117
C	-1.0286337051	-1.0469632682	3.1398052106
C	-2.2769124912	0.5288840185	1.7393876699
C	-2.7236410765	1.1263116421	2.9089675289
H	-3.3890301360	1.9713318568	2.8501664286
C	-3.6525900210	1.7595827432	0.1249691942
C	-3.6121489303	2.1702049204	-1.3514485269
H	-3.2792565089	3.2126339604	-1.3853087590

H	-2.8706088990	1.5838754964	-1.8993568955
C	-0.1253972380	-2.3429453982	1.4906261770
C	0.6099595780	-3.3998143858	0.9441248748
C	1.2921275239	-4.2327679085	1.8234187300
H	1.8832905535	-5.0466841144	1.4327148073
C	1.2395246424	-4.0352534887	3.1987612149
C	0.4967129865	-3.0223045973	3.7658969024
H	0.4557914050	-2.8806749546	4.8324883159
C	-0.1894834467	-2.1812781306	2.9005391671
C	-0.0393368387	-3.4309940745	-1.4892098249
C	0.4044498149	-4.2289235803	-2.7209923577
H	-0.4468896889	-4.3167956004	-3.4066266836
H	1.1947466388	-3.6535450656	-3.2171510060
O	-4.8823571869	2.1568917800	-1.9572170105
C	-6.8427701932	-1.4158234197	-2.8341937117
C	-7.4080952110	-0.1665211295	-3.1046820965
C	-6.7348552527	0.9908108079	-2.7925586733
C	-5.4684764385	0.9427546045	-2.2005810327
C	-4.9096400938	-0.2960232476	-1.9220502028
C	-5.5933317531	-1.4640325172	-2.2343593639
H	-8.3806471732	-0.1330886335	-3.5675334567
H	-7.1633219339	1.9577109476	-3.0004447755
H	-3.9333526391	-0.3700897750	-1.4684655641
H	-5.1154542601	-2.4019887683	-1.9991688644
O	-7.5945119305	-2.4895213252	-3.2192531785
C	-7.1308052476	-3.8058393480	-3.0056950836
H	-7.7307533276	-4.4223154261	-3.6818851472
H	-6.0736901749	-3.8968506787	-3.2821880364
C	-7.3922282005	-4.2940606032	-1.5639481962
H	-6.6141777784	-3.9323736661	-0.8806600715
H	-8.3528739823	-3.8833539215	-1.2412754562
O	-7.5435187512	-5.6913795855	-1.4948996161
C	-6.3494008853	-6.4639527797	-1.5152578544
H	-5.6531873412	-6.0776584387	-2.2714169448
H	-6.6788093760	-7.4634805014	-1.8088751175
C	-5.6737563391	-6.5230522679	-0.1720827050
C	-5.7372620948	-7.5748554114	0.6298098448
C	-5.1140254106	-7.6473347959	1.9934544786
H	-5.9097478423	-7.6332325380	2.7461407905
H	-4.4567579080	-6.7803953728	2.1589093339
H	-6.2713434997	-8.4648977575	0.3266242000
H	-5.1504095051	-5.6278794422	0.1422427971
O	0.9688700629	-5.4782948253	-2.4163729761
C	-1.3570742134	-8.5866707024	-0.8835633453
C	-0.0339457456	-8.7784503972	-1.2931547453
C	0.7020039616	-7.7350830817	-1.8052617319
C	0.1364324520	-6.4649288079	-1.9242578164
C	-1.1771164160	-6.2707049873	-1.5295958178
C	-1.9190339505	-7.3233566422	-1.0119285171
H	0.3944299403	-9.7622948836	-1.1968591734
H	1.7241000132	-7.8731590856	-2.1177373713
H	-1.6400482015	-5.2986102338	-1.6043901468
H	-2.9364266058	-7.1257498469	-0.7126777860
O	-1.9904153571	-9.6939217633	-0.4041492349
C	-3.2641632706	-9.5698402036	0.1944183382
H	-3.6501862636	-10.5899223351	0.2520255732
H	-3.9398457959	-8.9699497143	-0.4248037553
C	-3.1663062020	-8.9807446129	1.6152321186
H	-2.6461514149	-8.0129209046	1.5782384250

H	-2.5817438369	-9.6637880349	2.2380420835
O	-4.4152254042	-8.8507539802	2.2505626713
N	-0.8717660845	-1.3635738732	0.9042128771
C	-1.4170526687	-0.5686954992	1.8702301451
S	-0.3750025711	2.0730117164	-1.5995388797
O	-0.8793394395	2.9054475867	-0.4816533851
O	-0.8859655279	2.5511113810	-2.8863319682
O	1.1136068687	2.1899220826	-1.5742623995
O	-0.7709539093	0.6513067508	-1.3833023564
Cl	1.4522836727	1.2395183904	6.6210208551
Cl	4.7784815900	-3.7439614499	0.7183744574
O	2.4114638071	-1.8617274022	-3.3478947395
O	-0.5801553927	4.6569224645	3.7633618554
N	-0.3168727512	3.0303194487	2.1746925303
H	-0.4945830147	2.8400601827	1.1766839733
H	0.8136442533	1.3834492668	0.0666911869
N	1.8895771150	-0.3065781932	-1.7607527540
H	1.4281805781	0.6108907833	-1.6433446328
C	1.3789933306	1.1664361270	4.8984899231
C	2.0850350951	0.1899466483	4.2344543065
H	2.6912330035	-0.5256031299	4.7634302318
C	1.9738279074	0.1722217367	2.8488697446
C	0.4696476821	2.1051533606	2.8612458465
C	0.5923202071	2.1099600955	4.2441451491
H	0.0709572899	2.8552438364	4.8198774228
C	-0.8095100988	4.1905177118	2.6592142333
C	-1.7390655528	4.9129717217	1.6743704317
H	-1.5181321869	4.6063576507	0.6479473992
H	-2.7672419016	4.6144943760	1.9090683952
C	2.0533681839	-0.2084479129	0.6131436484
C	2.4103663842	-0.8294766518	-0.5903511714
C	3.2614636332	-1.9232282500	-0.5231052715
H	3.5525360221	-2.4255341484	-1.4305343098
C	3.7355056076	-2.3669466616	0.7101662614
C	3.4071547906	-1.7698332025	1.9069458239
H	3.7930047198	-2.1395927194	2.8419427763
C	2.5467240001	-0.6770416341	1.8506015707
C	1.8627029455	-0.8238824744	-2.9915945226
C	1.0089613747	0.0090776394	-3.9546208062
H	0.0849139828	-0.5553523645	-4.1281202409
H	0.7337140607	0.9638892210	-3.5005360315
O	-1.7084989442	6.3101830511	1.8300572370
C	1.7298388767	8.4990696212	0.9507052564
C	0.5672474698	9.0999821802	1.4401253732
C	-0.5489134201	8.3461880080	1.7207729533
C	-0.5430543666	6.9635676144	1.5190499756
C	0.6057194992	6.3658587814	1.0205402651
C	1.7324239753	7.1272869807	0.7427367632
H	0.5655508546	10.1669436762	1.5915215811
H	-1.4470558651	8.8024447994	2.1037723590
H	0.6398252805	5.3037649667	0.8292551753
H	2.6001609536	6.6188387606	0.3515895904
O	2.7678168136	9.3504612597	0.6878480066
C	4.0728898213	8.8414731253	0.4977032106
H	4.0967988893	8.0522781481	-0.2626630143
H	4.6505295904	9.6972082007	0.1391612618
C	4.6798403902	8.3522838937	1.8268543822
H	4.4886400943	9.1150622621	2.5872895557
H	4.1900639175	7.4172686800	2.1376165138

O	6.0755840716	8.1989530521	1.7964942712
C	6.5621502348	7.0323199484	1.1599895126
H	5.9565732051	6.1581645723	1.4386696884
H	7.5707626491	6.9042610102	1.5708028524
C	6.6638860906	7.1451036220	-0.3346400399
C	6.4077203392	6.1563114923	-1.1748000060
C	6.5958752188	6.2282968478	-2.6588311862
H	7.5047405146	5.6679824999	-2.9316639154
H	6.7197974718	7.2702331742	-2.9887809309
H	6.0442344284	5.2021523047	-0.8174139201
H	7.0148975227	8.1027620125	-0.6922480802
O	1.6030817120	0.1552141836	-5.2248872907
C	4.8081904117	2.7536280084	-5.8125284732
C	4.2521932140	2.6466005613	-4.5457127221
C	3.1929964365	1.7821932708	-4.3093999401
C	2.6660060679	1.0162500181	-5.3392510740
C	3.2326353806	1.1183728879	-6.6130566050
C	4.2866795434	1.9727667436	-6.8458424405
H	4.6054131477	3.2433366332	-3.7204882859
H	2.7693274230	1.7467961379	-3.3189191467
H	2.8193784922	0.5175952946	-7.4070830663
H	4.7226849234	2.0572113193	-7.8278500429
O	5.8525011547	3.5728355057	-6.1511514409
C	6.4579041224	4.3645634010	-5.1509221224
H	7.3804570470	4.7169188192	-5.6177380392
H	6.7080360094	3.7493293558	-4.2766525216
C	5.5748152352	5.5522617986	-4.6918542833
H	4.5559084127	5.3923526545	-5.0550661144
H	5.9506270206	6.4955055238	-5.1096976543
O	5.4647657734	5.6509756075	-3.2916752514
N	1.2337555410	0.8601284521	0.8205278302
C	1.1664899737	1.1114069743	2.1594512172

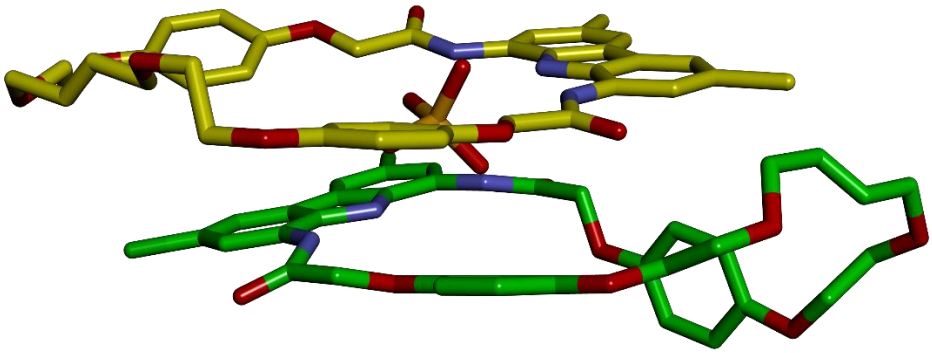


Figure S81. Example of an sandwich-like arrangement of **3**×SO_4^{2-}×**3** complex. The sixth lowest energy conformer.

Table S32. Cartesian coordinates of atoms in the sixth lowest energy arrangement of **3**×SO_4^{2-}×**3** complex (sandwich-like arrangement, ΔE = 5.6 kcal/mol in relation to the lowest energy arrangement).

169
-309.14751493

Cl	5.0807921707	-2.6368831172	4.9692400007
Cl	7.5068707385	-1.2806728732	-2.9748135029
O	3.0476313357	-1.1183546678	-5.1462294081
O	0.2008888938	-2.9575288142	4.2418778903
N	0.7716879512	-1.9018874989	2.2951663892
H	0.3794302999	-1.3760273064	1.4930964011
H	1.5520058927	-1.0674672941	-0.2792724466
N	2.4019816193	-0.8167330731	-2.9734420532
H	1.6359180977	-0.4761655016	-2.3861569224
C	4.2677717335	-2.3114354190	3.4803836645
C	5.0083215473	-2.1530092858	2.3296166410
H	6.0820650423	-2.2346644153	2.3385009418
C	4.3038354823	-1.8652357798	1.1640400413
C	2.1628653185	-1.9535987809	2.3479330573
C	2.8785731031	-2.2189213378	3.5073582372
H	2.3503779788	-2.3604456059	4.4347948043
C	-0.0917669217	-2.4266477186	3.1818787368
C	-1.5500537566	-2.3479862445	2.7153487832
H	-2.1568512509	-1.9859370682	3.5567877008
H	-1.6364318548	-1.6579272415	1.8700034607
C	3.5378807129	-1.3453480064	-0.9157235640
C	3.5930138968	-1.0534525505	-2.2843546162
C	4.8417080999	-1.0382041421	-2.8893490523
H	4.9178038380	-0.8347983622	-3.9437057995
C	5.9902541752	-1.3067831574	-2.1477900761
C	5.9658388625	-1.5913780313	-0.8001784159
H	6.8696194921	-1.7890935848	-0.2487700030
C	4.7187331167	-1.6095455007	-0.1841067192
C	2.1944178593	-0.9096667332	-4.2984359422
C	0.7270842849	-0.7384723109	-4.6984050266
H	0.4965067494	0.3368812877	-4.7322582117
H	0.6087685582	-1.1592455710	-5.7073650351
O	-1.9521541713	-3.6518330375	2.3504326274

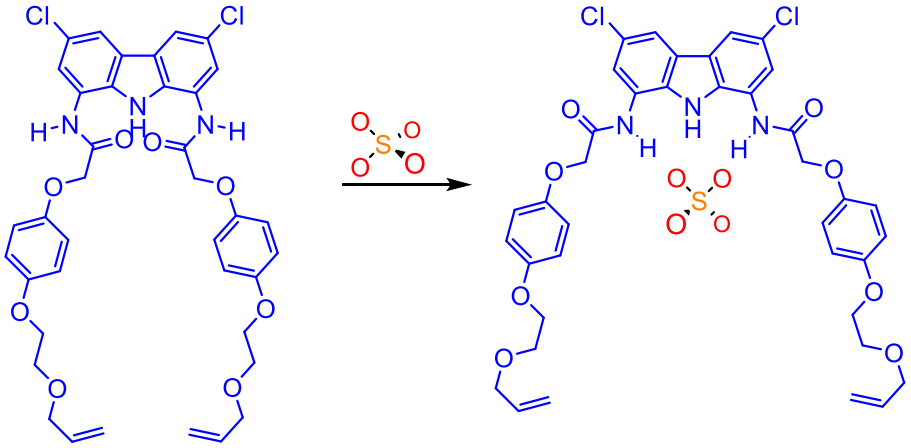
C	-5.9460464412	-4.4067081705	1.3999607413
C	-4.9896830318	-5.4255309302	1.4649306199
C	-3.6804377182	-5.1464108486	1.7828495814
C	-3.2800113203	-3.8337772203	2.0454268803
C	-4.2261665446	-2.8221012334	1.9829123262
C	-5.5475291440	-3.1049636283	1.6668891390
H	-5.3026127285	-6.4358354253	1.2575189790
H	-2.9403369483	-5.9286554615	1.8338501376
H	-3.9495663661	-1.7975038599	2.1698323889
H	-6.2458566578	-2.2839148724	1.6298511841
O	-7.2041125732	-4.8035182200	1.0557006854
C	-8.2388929169	-3.8488050310	0.9180078408
H	-7.8955028140	-2.9617599364	0.3752085035
H	-9.0044170691	-4.3534305239	0.3218984626
C	-8.8662048421	-3.4617025373	2.2723311287
H	-9.0175389435	-4.3802317141	2.8483634993
H	-8.1946319397	-2.7993085657	2.8351726736
O	-10.1397226241	-2.8797462847	2.1353723846
C	-10.1535020314	-1.4809135313	1.9047017251
H	-9.5912555906	-0.9613902832	2.6951134259
H	-11.2122689078	-1.2129577675	1.9851611804
C	-9.6324041525	-1.0701702847	0.5583005312
C	-8.7934215609	-0.0652790434	0.3696773020
C	-8.2470561360	0.3644865775	-0.9571368501
H	-7.1625318107	0.5057887411	-0.8621890092
H	-8.6738497662	1.3465891977	-1.2290697919
H	-8.4412282658	0.5266788647	1.2048439719
H	-9.9794607453	-1.6495301015	-0.2836563465
O	-0.0951367205	-1.3967307851	-3.7640164332
C	-4.2476785695	-1.1002015776	-3.9721678818
C	-3.4774185300	-0.6198391257	-5.0276665642
C	-2.0981917222	-0.6960978361	-4.9979068872
C	-1.4546240111	-1.2665599351	-3.9043113105
C	-2.2244812247	-1.7774316300	-2.8624188656
C	-3.6023045247	-1.6987322939	-2.8928668361
H	-3.9763754268	-0.1623665985	-5.8660864784
H	-1.5365228920	-0.2859682736	-5.8216836785
H	-1.7206257294	-2.2148087011	-2.0131549748
H	-4.1588506141	-2.0966122346	-2.0599458661
O	-5.5990164708	-0.9561104513	-4.0812125870
C	-6.3648989981	-1.1303929957	-2.9039261694
H	-5.8621032623	-0.6414763084	-2.0619311892
H	-6.4880723213	-2.1983847197	-2.6737569457
C	-7.7451594890	-0.4892265510	-3.1165929614
H	-8.2800434352	-1.0260574368	-3.9036458287
H	-7.6037429921	0.5551932512	-3.4250673530
O	-8.5528922936	-0.5804903571	-1.9687798803
N	2.4472572270	-1.4939925408	-0.0992474273
C	2.8943685178	-1.7564419928	1.1701194837
S	0.4007241024	0.7646718991	0.1339387750
O	-0.3957938630	-0.4727350383	0.3436107775
O	1.5419435217	0.8151197398	1.0695213708
O	0.8739060346	0.7875025822	-1.2598050594
O	-0.4250752575	1.9726491561	0.4060954499
Cl	0.0908737476	-0.3327841435	8.4209904405
Cl	-6.8437941244	0.1815473002	3.7067064099
O	-4.7296452541	1.0336681301	-0.8305974963
O	3.4489528836	1.2916883306	5.1840549934
N	1.7211049586	0.8888447500	3.7326395316

H	1.5201163007	0.8479728981	2.7184725873
H	-0.6010831189	1.0820433520	2.0223329857
N	-2.9182215377	1.1763183704	0.5636806633
H	-1.9012722242	1.3724891870	0.5302567107
C	-0.2343565477	0.0395339798	6.7670913195
C	-1.5374567039	0.0580484998	6.3262513587
H	-2.3590627065	-0.1504956364	6.9906491360
C	-1.7388825863	0.3519231902	4.9811309983
C	0.6654496913	0.6073263065	4.5946394907
C	0.8505010539	0.3073282418	5.9373884032
H	1.8491143288	0.2846429186	6.3392168785
C	3.0016132773	1.1771676200	4.0576587657
C	3.8452475238	1.3597996247	2.7982818735
H	3.8502329787	0.3976442271	2.2708795100
H	3.3438459333	2.0877247302	2.1458243920
C	-2.4932345470	0.7598841244	2.8761134450
C	-3.4116887259	0.8847999398	1.8225512268
C	-4.7571040420	0.7086727832	2.1174481620
H	-5.4870207021	0.7891472472	1.3298045814
C	-5.1583810544	0.4073458405	3.4179500832
C	-4.2781426904	0.2688084794	4.4679903580
H	-4.6192118724	0.0241467534	5.4601464428
C	-2.9251489800	0.4457117126	4.1839974420
C	-3.5435267342	1.2314036878	-0.6255239213
C	-2.5194571970	1.5722628683	-1.7042215482
H	-1.8820501855	2.3769685786	-1.3155779183
H	-1.8801144557	0.6846477943	-1.8263608681
O	5.1437844334	1.7742528063	3.1290615356
C	8.0056249112	2.3098546061	0.1433383329
C	8.2728769255	2.5741122208	1.4904929067
C	7.3072716526	2.3806085508	2.4502543512
C	6.0360379852	1.9187128301	2.0971697828
C	5.7691094601	1.6498315019	0.7619152242
C	6.7478944933	1.8410445516	-0.2050088645
H	9.2535813722	2.9322350102	1.7574271573
H	7.5050290790	2.5802048439	3.4907977825
H	4.8001850639	1.2918132370	0.4492133394
H	6.4979224139	1.6104457726	-1.2283281088
O	9.0430784187	2.5424817494	-0.7134481815
C	8.9102417705	2.2663161004	-2.0905416085
H	9.9338792246	2.2396458771	-2.4728237770
H	8.4473941631	1.2895440765	-2.2637613319
C	8.1561156936	3.3590071508	-2.8599342293
H	7.0697367714	3.2747353701	-2.7134481550
H	8.4735995345	4.3460398764	-2.4866899859
O	8.4909667063	3.2203674980	-4.2217762648
C	7.7866300653	4.0979494178	-5.0802501559
H	8.2906976057	3.9912894936	-6.0461423302
H	7.8844707814	5.1366186060	-4.7340147683
C	6.3377375252	3.7319367074	-5.2363695152
C	5.3338525526	4.5922326991	-5.2091214411
C	3.8932213234	4.2124161267	-5.3667160339
H	3.3834884801	4.3001535305	-4.3891584321
H	3.8106239032	3.1659816439	-5.6943890202
H	5.5053081468	5.6513736252	-5.0819038543
H	6.1552007893	2.6735187308	-5.3682934273
O	-3.1260418569	1.9493354261	-2.9129796401
C	-0.7164067227	3.2955109188	-6.0417942435
C	-0.1239280903	2.8367540075	-4.8744726161

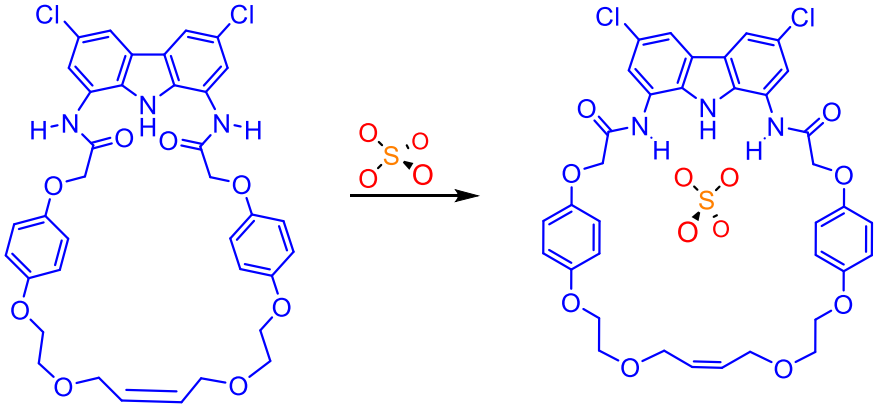
C	-0.8952749627	2.3774260906	-3.8148197941
C	-2.2809211399	2.3681018183	-3.9058275594
C	-2.8789178389	2.8283912013	-5.0826799324
C	-2.1111974305	3.2818206728	-6.1311047422
H	0.9485232520	2.8220283885	-4.7520061982
H	-0.3867305437	2.0213572876	-2.9318224922
H	-3.9544574347	2.8140853227	-5.1474329405
H	-2.5695188784	3.6344127775	-7.0404138226
O	-0.0513655118	3.7543387580	-7.1471078609
C	1.3589743590	3.8114319339	-7.1388309303
H	1.6481070430	3.9016330050	-8.1886922255
H	1.7864661556	2.8841472179	-6.7386327682
C	1.8861351126	5.0336085379	-6.3585322626
H	1.4501958834	5.0375816639	-5.3477825720
H	1.5747466040	5.9447145497	-6.8755286891
O	3.2893878901	5.0955496274	-6.2943155534
N	-1.1319223916	0.8756514522	2.8582012297
C	-0.6523618592	0.6186058002	4.1127752935

6.4. DFT Analysis of Sulfate Binding by Precursor 1 and Macrocycle 3.

To rationalize weaker anion binding by macrocycle **3** compared to precursor **1** we performed additional calculations (DFT level of theory, wb97x-d/6-31G** optimization and frequency calculations) of the precursor **1** and macrocycle **3** and estimated change in Gibbs free energy of the following hypothetical complexation reactions:



anti-anti



anti-anti

For both receptors the *anti-anti* conformation has the lowest energy. Anion binding switches the conformation of diamidocarbazoles to *syn-syn*, where three NH hydrogen bond donors point in the same direction. DFT results suggest that sulfate binding to the acyclic precursor is favoured by > 3 kcal/mol (ΔG = -21.8 kcal/mol for **1** versus -18.6 for **3**) over sulfate binding to the macrocycle. This difference likely stems from the fact that in order to bind sulfate both **1** and **3** have to change its conformation from *anti-anti* to *syn-syn* and due to structural differences between them this process requires more energy for **3** in comparison to **1**. The difference in Gibbs free energies between the *anti-anti* and *syn-syn* conformations is estimated at 20.2 kcal/mol for **1** and 23.2 kcal/mol for **3** (by single point estimation).

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