Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information (ESI)

Recognition-Guided Sulfate Extraction and Transport Using Tripodal Hexaurea Receptors

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S1. General Information and Computational Studies

All starting materials and solvents were ordered from commercial sources (Beijing InnoChem, Aladdin, Macklin Science & Technology Co., Ltd.) and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE AV II-400/700 MHz spectrometer at 298 K. ^{1}H NMR chemical shifts were reported relative to residual solvent peaks (^{1}H NMR: 2.50 ppm for DMSO-d_6, 7.26 ppm for $CDCl_3$;^{13}C NMR: 39.52 ppm for DMSO-d_6, 77.1 ppm for $CDCl_3$). High resolution mass spectrometry data were obtained by Autoflex max MALDI-TOF/TOF. Single crystal X-ray data were measured on Bruker D8 Venture Photon II diffractometer. The anion concentration in aqueous solution was recorded by Shine ion chromatography (CIC-D100, China). All aqueous solutions were prepared by using ultrapure water (18.25 MΩ·cm).

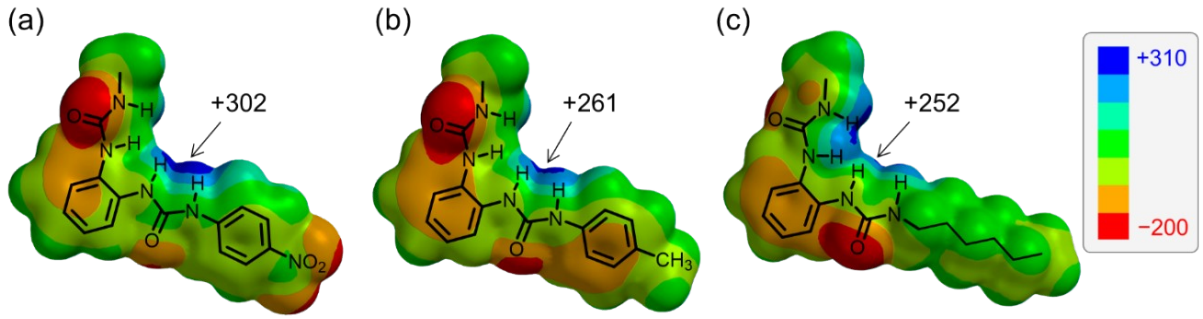


Fig. S1 Calculated electrostatic potential map (DFT, B3LYP/6-31+G(d)) showing terminal substitution dependent hydrogen bonding strength of lower urea unit.

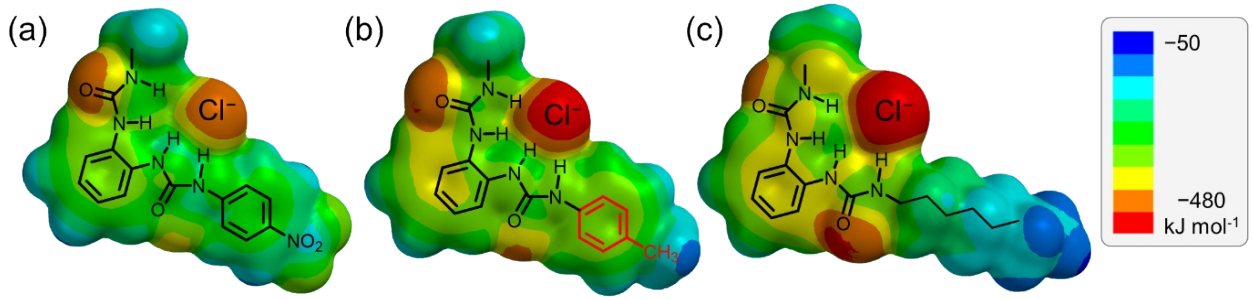
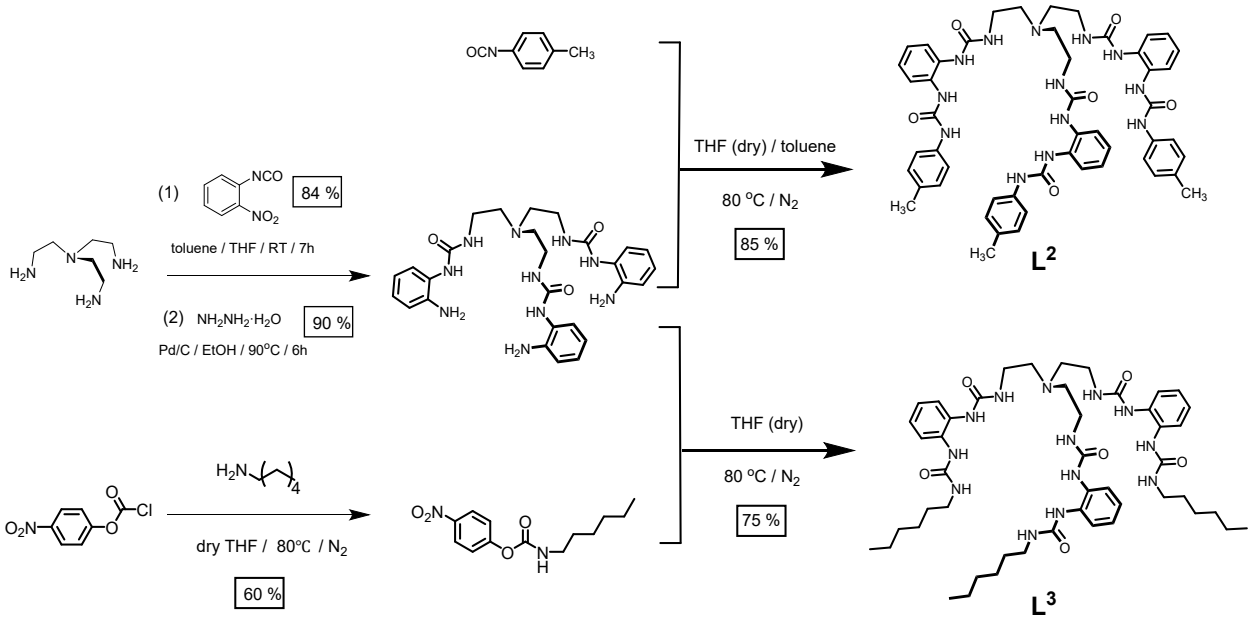
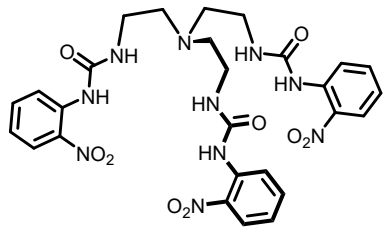


Fig. S2 Calculated electrostatic potential map (DFT, B3LYP/6-31+G(d)) when binding to chloride.

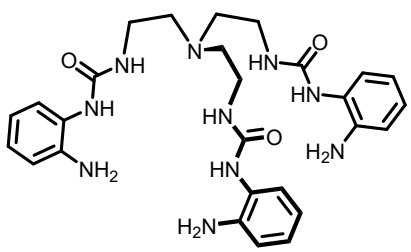
S2. Synthetic Procedures of Hexaurea Receptors L^2 and L^3



Scheme S1. Synthetic scheme of preparing tripodal hexaurea receptors $\mathbf{L^2}$ and $\mathbf{L^3}$. The synthesis of receptor $\mathbf{L^1}$ has been reported.

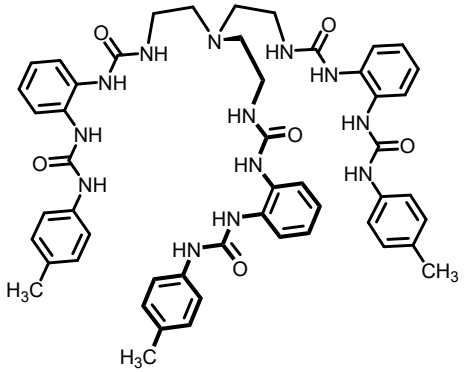


Compound **1**: *o*-nitrobenzene isocyanate (5.0 g, 30.5 mmol, 3.2 equiv.) was placed in a 250 mL round-bottomed flask and dissolved in toluene (80 mL). A solution of tris(2-aminoethyl)amine (tren, 1.4 g, 9.6 mmol, 1 equiv.) in THF (25 mL) was added into the flask by using a dropping funnel (2 seconds per droplet). Obvious precipitation occurred once tren react with isocyanate. The reaction was stirred at room temperature for 6 hours and monitored by TLC. The precipitates were separated by filtration and washed with toluene (10 mL × 3) and diethyl ether (10 mL × 3). The obtained yellow powder was further dried over vacuum dried and isolated as compound **1** (5.9 g). Yield, 98%. ^{1}H NMR (400 MHz, 298 K, DMSO-d_6, ppm): δ = 9.35 (s, 3H), 8.24 (d, 3H, J = 8.48 Hz), 7.99 (d, 3H, J = 9.84Hz), 7.57 (t, 3H, J = 8.6 Hz), 7.49 (s, 3H), 7.08 (t, 3H, J = 8.36Hz), 3.2 (m, 6H), 2.63 (t, 6H, J = 6.6 Hz).

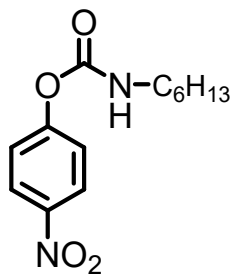


Compound **2**: Compound **1** (3.5 g, 5.5 mmol) was placed in double-necked, round-bottomed flask and suspended in ethanol (500 mL). Pd/C (0.7 g) was added into the flask. The reaction

mixture was heated to 90°C and stirred for 20 mins until all the starting material got dissolved. Hydrazine monohydrate (8.5 mL) was added dropwise using dropping funnel. The reaction mixture was further stirred at the same temperature for 4 hours until all the reactant was consumed. Before cooling to room temperature, the Pd/C was removed by filtration over celite. The obtained filtrate was concentrated by evaporation and white powder precipitated. The white powder was subsequently washed by cold ethanol (10 mL) and diethyl ether (10 mL × 3). Compound (10 mL × 3) was obtained as white powder, 2.4 g. Yield, 74%. ^{1}H NMR (400 MHz, 298 K, DMSO-d_6, ppm): δ = 7.61 (s, 3H), 7.21 (d, 3H, J = 7.84 Hz), 6.69 (t, 3H, J = 7.8 Hz), 6.51 (d, 3H, J = 8.56 Hz), 6.21 (t, 3H, J = 8.56 Hz), 4.69 (s, 6H), 3.18 (m, 6H), 2.58 (t, 6H, J = 6.32 Hz).

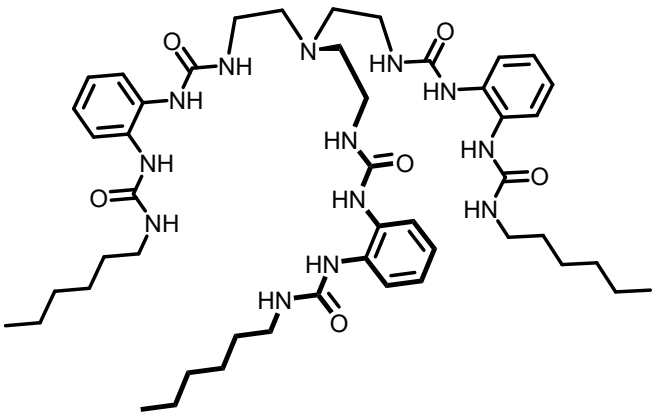


Receptor **L²**: Under N_2 atmosphere, compound **2** (1.44 g, 2.6 mmol, 1.0 equiv.) was placed in a 500 mL double-necked, round-bottomed flask and suspend in dry THF (20 ml) and toluene (180 mL). The reaction was heated to 110 °C, and *P*-methylbenzene isocyanate (1.2 mL, 9 mmol, 3.5 equiv.) in dry THF (20 ml) was added dropwise over 30 mins. The reaction mixture was stirred at the same temperature for 14 hours until compound **2** was consumed based on TLC (CH_2Cl_2:CH_3OH = 50:6). Cooled down to room temperature, and the precipitated solids was separated by filtration. The obtained yellow powder was further washed with THF (10mL × 3) and diethyl ether (10 mL × 3). A white solid powder was yielded as receptor **L³** (2 g), yield, 85%. ^{1}H NMR (400 MHz, 298 K, DMSO-d_6, ppm): δ = 8.96 (s, 1H), 7.96 (s, 1H), 7.91 (s, 1H), 7.57 (dd, J = 7.6, 2.0 Hz, 1H), 7.42 (dd, J = 7.6, 2.1 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.06 – 6.93 (m, 4H), 6.50 (t, J = 5.5 Hz, 1H), 3.19 (d, J = 6.4 Hz, 2H), 2.60 (t, J = 6.9 Hz, 2H), 2.22 (s, 3H). ^{13}C NMR (176 MHz, DMSO-d_6), 156.6 (CO), 153.6 (CO), 137.8 (C), 132.0 (C), 131.9 (C), 130.9 (C), 129.6 (CH), 124.4 (CH), 124.1 (CH), 118.7 (CH), 54.4 (CH_2), 38.3 (CH_2), 20.8 (CH_3). MS (MALDI-TOF) m/z: calcd. for $C_{51}H_{57}N_{13}O_6$ at $[M+H]^+$: 949.463; found: 949.315.



Compound **3**: Under N_2 atmosphere, 4-nitrochlorobenzoate (4.50 g, 22.4 mmol, 1.2 equiv.) was placed im a 250 mL three-necked, round-bottomed flask and dissolved in dry THF (60 mL). The solution was heated to 80°C, and hexamine (1.91 g, 18.8 mmol, 1.0 equiv.) in dry THF (60 mL) was added dropwise using a dropping funnel. The reaction mixture was stirred at 80°C for 14 hours before cooling down to room temperature. The white precipitates were removed by filtration. The obtained filtrate was concentrated by evaporation under reduced

pressure. The solid was suspended in petroleum ether (150mL), filtered, and further washed with petroleum ether (10mL × 3). A white solid powder was isolated as compound **3** (2.8 g), yield, 60%.^{1}H NMR (400 MHz, 298 K, $CDCl_3$, ppm): δ = 8.25 (dd, 2H, J = 4.0 Hz, 8.0 Hz), 7.33 (dd, 2H, J = 4.0 Hz, 8.0 Hz), 5.11 (t, 1H, J = 8.0 Hz), 3.28 (q, 2H, J = 8.0 Hz), 1.57 (m, 2H) ，1.34 (m, 6H), 0.90 (t, 3H, J = 6.76 Hz).



L^3: Under N_2 atmosphere, compound **2** (1.42 g, 2.6 mmol, 1.0 eq) was placed in a 500 mL double-necked, round-bottomed flask and suspend in dry THF (40 mL). The reaction was heated to 110 ^{o}C, and a solution of compound **3** (2.76 g, 10.4 mmol, 4.0 equiv.) and triethylamine (1.44 mL, 10.4 mmol, 4.0 equiv.) in dry THF (60 mL) was dropwise. The reaction mixture was stirred at the same temperature overnight until compound **2** was consumed based on TLC (CH_2Cl_2:CH_3OH = 50:3). Cooled down to room temperature, and the precipitated solids was separated by filtration. The obtained powder was further washed with THF (10mL × 3). A white solid powder was yielded as receptor **L^3** (1.9 g), yield, 75%. ^{1}H NMR (400 MHz, 298 K, DMSO-d_6, ppm): δ = 7.89 (s, 1H), 7.77 (s, 1H), 7.52 (d, 1H, J = 7.72 Hz), 7.37 (d, 1H, J = 7.76 Hz), 6.93 (m, 2H), 6.52 (m, 2H), 3.18 (m, 2H), 3.02 (q, 2H, J = 6.48 Hz), 2.60 (t, 2H, J = 6.44 Hz), 1.38 (m, 2H), 1.25 (m, 6H), 0.86 (t, 3H, J = 6.96 Hz). ^{13}C NMR (100 MHz, DMSO-d_6), 156.1 (CO), 155.7 (CO), 132.2 (C), 130.7 (C), 124.0 (CH), 123.5 (CH), 122.9 (CH), 122.8 (CH), 53.8 (CH_2), 37.9 (CH_2), 31.0 (CH_2), 29.6 (CH_2), 26.1 (CH_2), 22.0 (CH_2), 13.9 (CH_3). MS (MALDI-TOF) m/z: calcd. for $C_{48}H_{75}N_{13}O_6$ at $[M+Na]^+$: 952.585; found: 952.445.

S3. X-ray Crystallography Structures

$[K(18\text{-Crown-6})]_2SO_4$ (12 μL or 20μL, 0.4 mol/L, prepared by mixing K_2SO_4 with 2 equivalents of 18-Crown-6) was added to a suspension of **L^2** or **L^3** (5 mg) in acetonitrile (1 mL). After stirring overnight at room temperature, the solution was centrifugated. The obtained clear solution was used for crystal growing. Slow vapor diffusion of diethyl ether into above-mentioned solution provided white crystals of **L^2**•SO_4^{2-} or **L^3**•SO_4^{2-} within one week.

K(18-Crown-6) Cl (0.4 mol/L, prepared by mixing KCl with one equivalent of 18-Crown-6) was added to a suspension of **L^2** (15 mg) in acetonitrile (3 mL) and DMF (1mL). After stirring

overnight at room temperature, the solution was centrifugated. The obtained clear solution was used for crystal growing. Slow vapor diffusion of diethyl ether into above-mentioned solution produced white crystals of $\mathbf{L^2}$•Cl^- within one week.

X-ray diffraction data were collected on a Bruker D8 Venture Photon II diffractometer at 150 K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS was applied for all data. The structures were solved by the dual methods using the SHELXS program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by the use of the program SHELXL, and hydrogen atoms were included in idealized positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Some remaining solvents could not be successfully resolved despite numerous attempts at modeling, and consequently the SQUEEZE function of PLATON was used to account for these highly disordered solvents. The crystal data and refinement details are given in Table S1.

Table S1 Crystal data details for obtained structures.

Complex	$\mathbf{L^2}$•SO_4^{2-}	$\mathbf{L^3}$•SO_4^{2-}	$\mathbf{L^2}$•Cl^-
Empirical formula	$C_{81}H_{115}K_2N_{14}O_{23}S$	$C_{144}H_{244}K_4N_{26}O_{44}S_2$	$C_{67}H_{87}ClKN_{15}O_{12}$
CCDC	2206148	2206147	2206150
Formula weight	1761.72	3259.12	1369.06
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.346(3)	17.4005(13)	13.8072(8)
b(Å)	14.677(4)	19.8555(18)	17.1399(10)
c(Å)	46.574(11)	28.573(3)	17.1959(11)
α(deg)	90.000	82.040(5)	96.900(2)
β(deg)	91.997(9)	89.664(4)	110.197(2)
γ(deg)	90.000	78.292(4)	101.987(2)
V (Å^3)	9117.3(40)	9570.7(14)	3653.5(4)
Z	4	2	2
T (K)	180.0	180.0	180.0
F(000)	3748	3490	1452
$D_{calc,}$g/cm^3	1.284	1.131	1.244

Total no. of data	128548	189166	50298
Crystal size (mm)	0.25×0.19×0.17	0.22×0.17×0.15	0.22×0.17×0.15
Completeness to θ	0.996	0.985	0.995
θ range	2.120-28.378	2.110-25.498	2.163-25.464
μ /mm^{-1}	0.204	0.188	0.177
Data/restraints/	22750/9	35103/95	13500/38
Parameters	1075	1990	870
GoF on F^2	1.022	1.021	1.007
$R1$	0.0686	0.1113	0.1031
$wR2$	0.1952	0.3183	0.3813

Table S2. Hydrogen bonding information in the crystal structure of $\mathbf{L^2}$•SO_4^{2-}.

D-H···*A*	d (*D*-H)	d (H···*A*)	d (D···*A*)	∠*D*H*A*
N2-H2···O7	0.88	2.11	2.979(3)	170
N3-H3···O10	0.88	2.16	2.979(3)	154
N4-H4···O10	0.88	2.01	2.873(3)	166
N5-H5···O8	0.88	2.11	2.980(3)	170
N6-H6···O7	0.88	2.11	2.977(3)	167
N7-H7···O8	0.88	2.12	2.954(3)	158
N8-H8···O8	0.88	2.01	2.882(2)	172
N9-H9···O9	0.88	2.09	2.907(2)	153
N10-H10···O7	0.88	2.16	3.009(3)	161
N11-H11···O9	0.88	2.10	2.942(3)	159
N12-H12···O9	0.88	2.10	2.947(3)	161

N13-H13···O10	0.88	2.11	2.956(3)	161
average	0.88	2.10	2.95	163

Table S3. Hydrogen bonding information in the crystal structure of $\mathbf{L^3}$•SO_4^{2-}.

D-H···*A*	d (*D*-H)	d (H···*A*)	d (D···*A*)	∠*D*H*A*
N2-H2···O44	0.88	2.08	2.930(4)	161
N3-H3···O41	0.88	2.22	3.065(4)	161
N4-H4···O41	0.88	2.18	3.004(5)	156
N4-H4···O43	0.88	2.58	3.320(5)	142
N5-H5···O43	0.88	2.09	2.906(5)	153
N6-H6···O44	0.88	2.11	2.950(5)	160
N7-H7···O42	0.88	2.06	2.917(5)	165
N8-H8···O42	0.88	2.12	2.905(6)	147
N9-H9···O41	0.88	2.21	3.074(8)	168
N10-H10···O44	0.88	2.1	2.969(5)	169
N11-H11···O43	0.88	2	2.825(5)	156
N12-H12···O42	0.88	2.47	3.259(5)	150
N12-H12···O43	0.88	2.28	3.035(5)	143
N13-H13···O42	0.88	2.05	2.894(5)	159
N15-H15···O40	0.88	2.12	2.985(4)	168
N16-H16···O39	0.88	1.98	2.812(4)	156
N17-H17···O38	0.88	2.44	3.225(5)	148
N17-H17···O39	0.88	2.25	3.022(5)	146

N18-H18···O38	0.88	2.06	2.895(6)	159
N19-H19···O40	0.88	2.14	2.959(4)	155
N20-H20···O38	0.88	2.07	2.926(4)	164
N21-H21···O38	0.88	2.09	2.862(4)	146
N22-H22···O37	0.88	2.24	3.056(5)	155
N23-H23···O40	0.88	2.06	2.906(4)	161
N24-H24···O37	0.88	2.19	3.037(4)	163
N25-H25···O37	0.88	2.16	2.987(4)	157
N25-H25···O39	0.88	2.08	2.885(5)	153
average	0.88	2.15	2.964	155

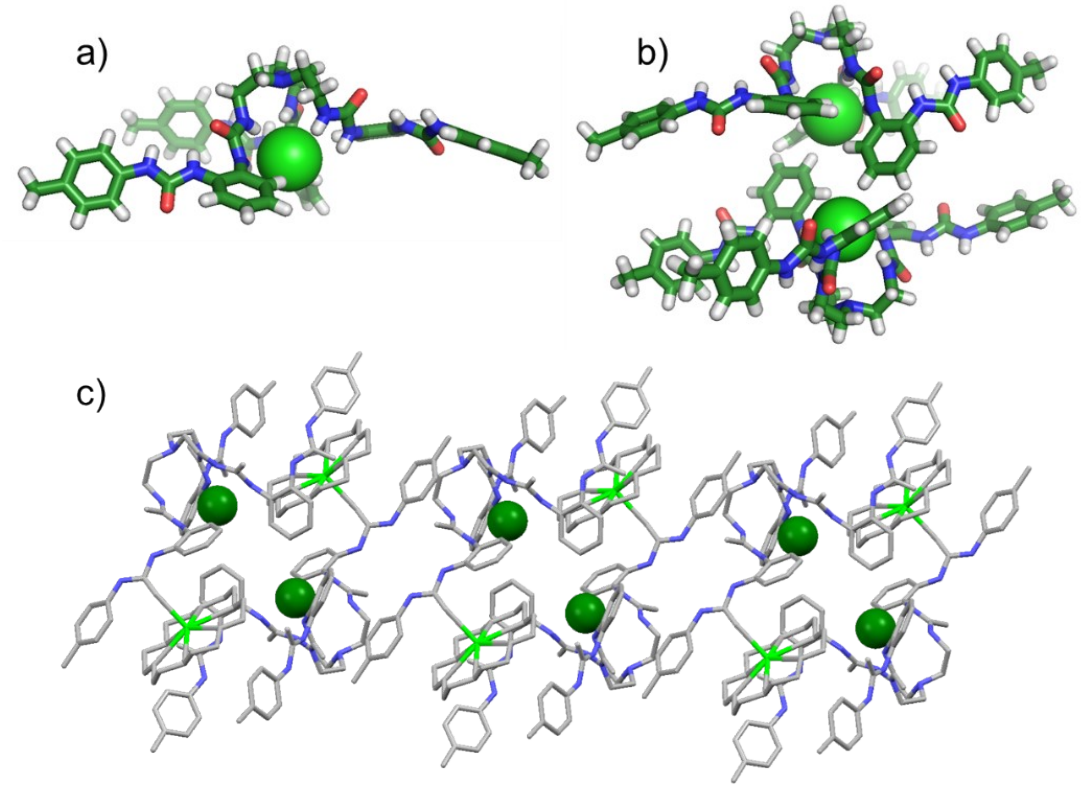


Fig. S3 a) X-ray structure for the complex of $\mathbf{L^2}$•Cl^- showing overall 1:1 stoichiometry. Packing for a b) dimeric and c) one dimensional arrangement of $\mathbf{L^2}$•Cl^- complex.

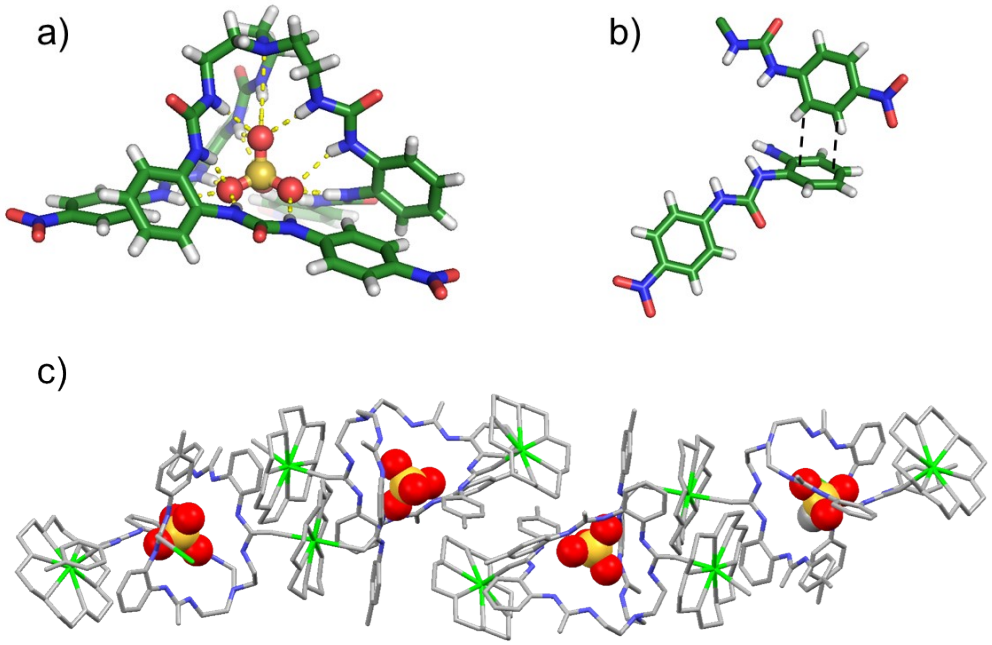


Fig. S4 a) X-ray structure for the complex of $\mathbf{L^2}$•SO_4 showing overall 1:1 stoichiometry. b) Secondary C-H•••π within phenyl spacer and C−H atoms of terminal phenyl ring. c) Crystal packing arrangement showing interactions among 18-crown 6 ether, K^+, and $\mathbf{L^2}$•SO_4 complex.

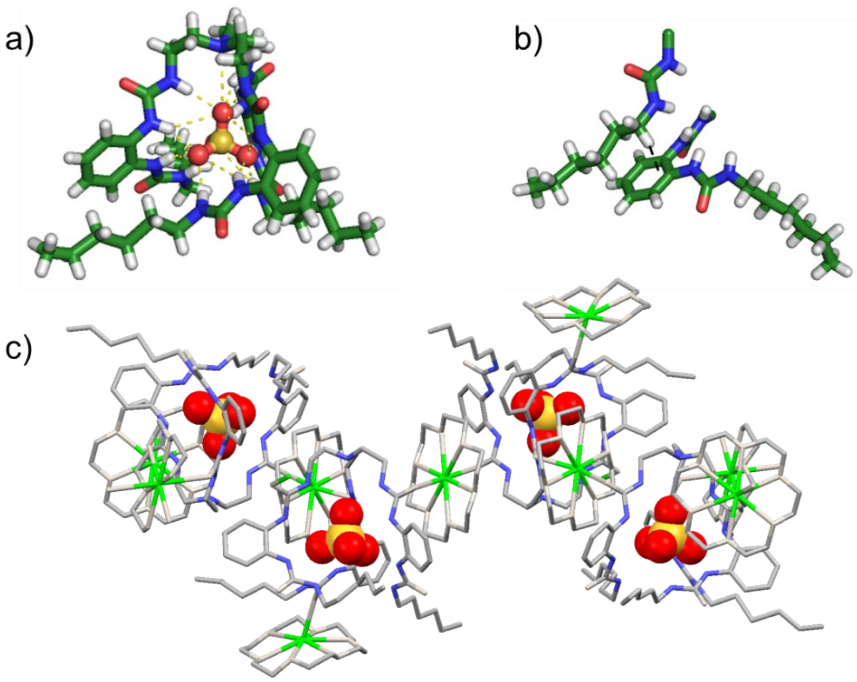


Fig. S5 a) X-ray structure for the complex of $\mathbf{L^3}$•SO_4 showing overall 1:1 stoichiometry. b) Secondary C-H•••π within phenyl spacer and C−H atoms of terminal hexyl chain. c) Crystal packing arrangement showing interactions among 18-crown 6 ether, K^+, and $\mathbf{L^3}$•SO_4 complex.

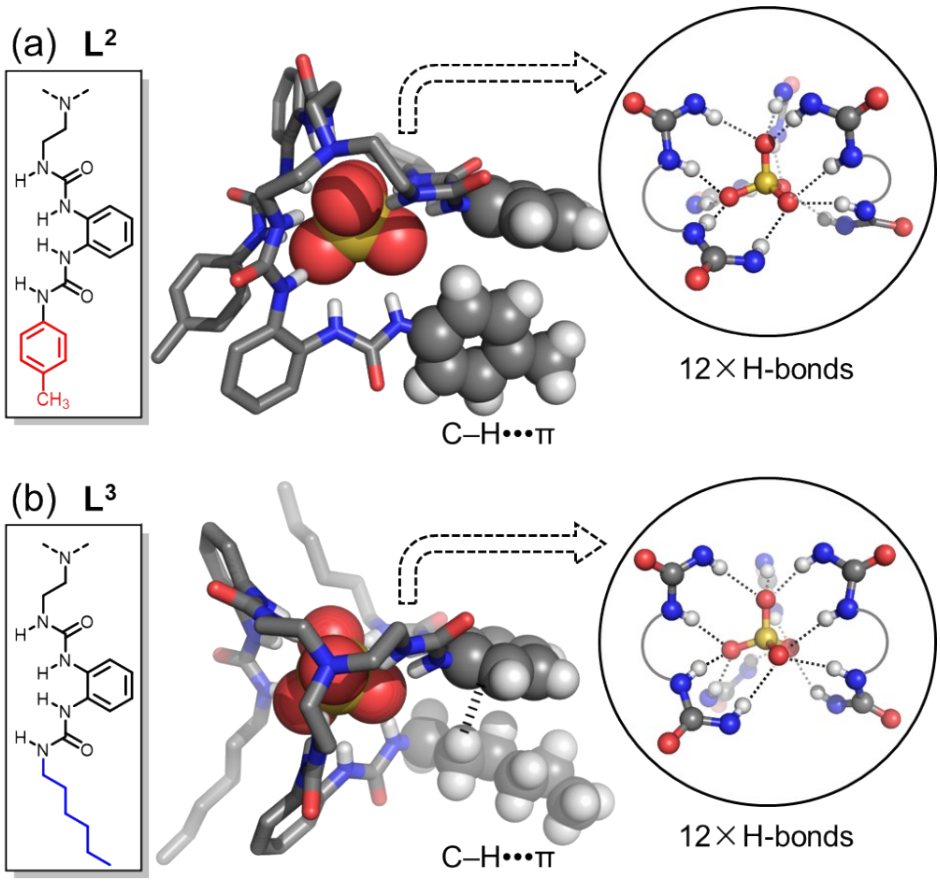


Fig. S6 X-ray crystal structures of the $\mathbf{L^2}$•SO_4^{2-} and $\mathbf{L^3}$•SO_4^{2-} complexes showing primary hydrogenb bonding and secondary C-H•••π interactions.

S4. ^{1}H NMR Titration Studies with Chloride Anion

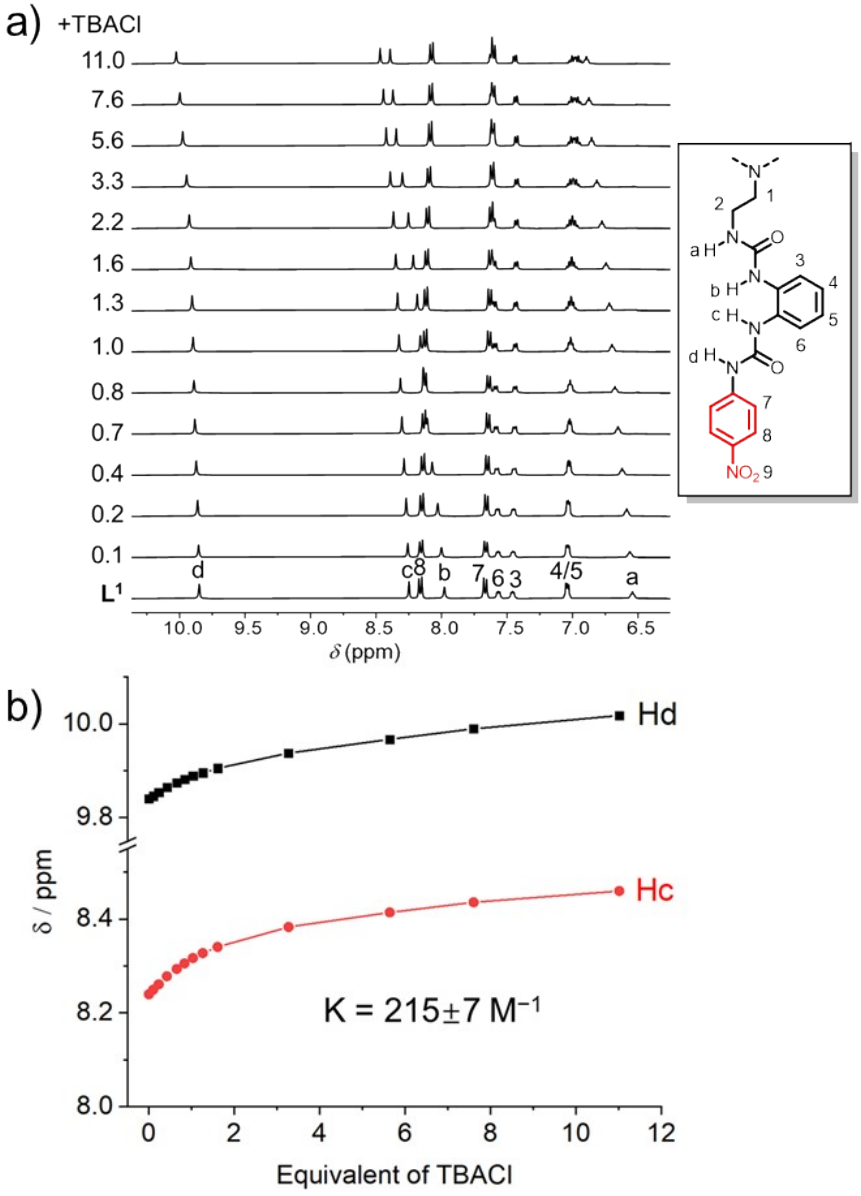


Fig. S7 a) Stacked partial ^{1}H NMR spectra (400 MHz, 298 K, DMSO-d_6) of receptor **L^1** by adding chloride as tetrabutylammonium salt (TBACl). ([**L^1**] = 2 mM, [TBACl] = 50 mM) b) Chemical shift changes of proton H_d and H_c during titration. The chloride binding affinity was determined to be 215 ± 7 M^{-1} using Bindfit (v0.5).
http://app.supramolecular.org/bindfit/view/02aeb51d-6d9c-4c2d-91ae-6e919970afd6

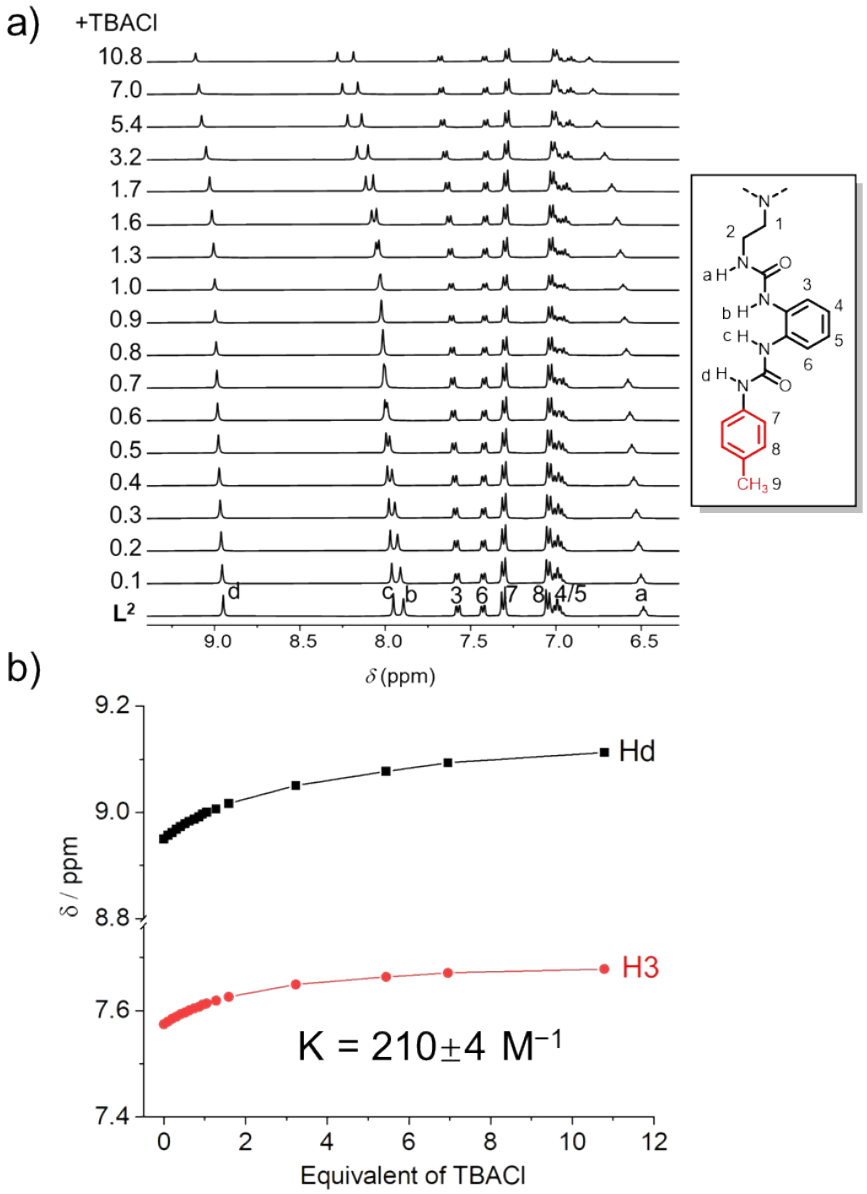


Fig. S8 a) Stacked partial ^{1}H NMR spectra (400 MHz, 298 K, DMSO-d_6) of receptor **L²** by adding chloride as tetrabutylammonium salt (TBACl). ([**L²**] = 2 mM, [TBACl] = 50 mM) b) Chemical shift changes of proton H_d and H_c during titration. The chloride binding affinity was determined to be 210 ± 4 M^{-1} using Bindfit (v0.5).

http://app.supramolecular.org/bindfit/view/73cb3e33-e5aa-40f2-9f20-ef4e86a50ab3

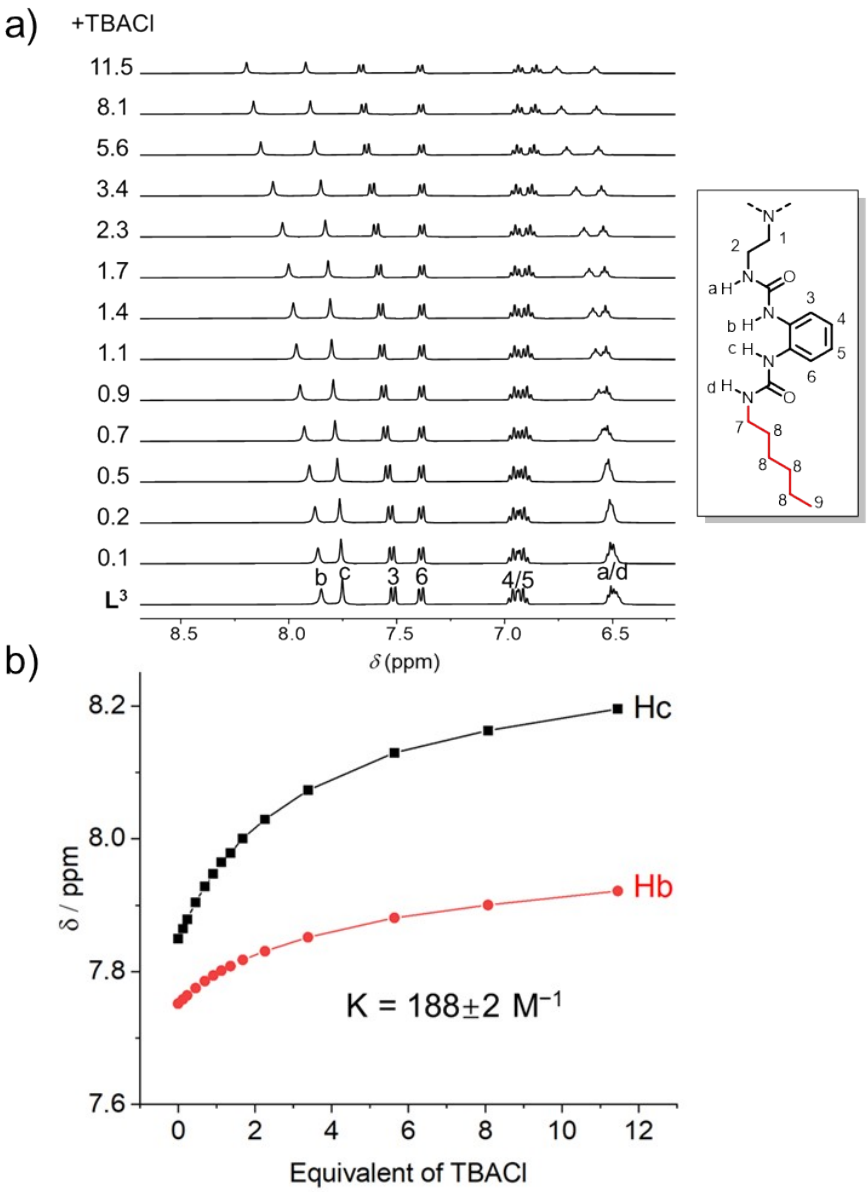


Fig. S9 a) Stacked partial ^{1}H NMR spectra (400 MHz, 298 K, DMSO-d_6) of receptor **L³** by adding chloride as tetrabutylammonium salt (TBACl). ([**L³**] = 2 mM, [TBACl] = 50 mM) b) Chemical shift changes of proton H_d and H_c during titration. The chloride binding affinity was determined to be 188 ± 2 M^{-1} using Bindfit (v0.5).

http://app.supramolecular.org/bindfit/view/786cc2bc-c040-4231-9338-987f3d9206cb

S5. ^{1}H NMR Titration Studies with Sulfate Anion

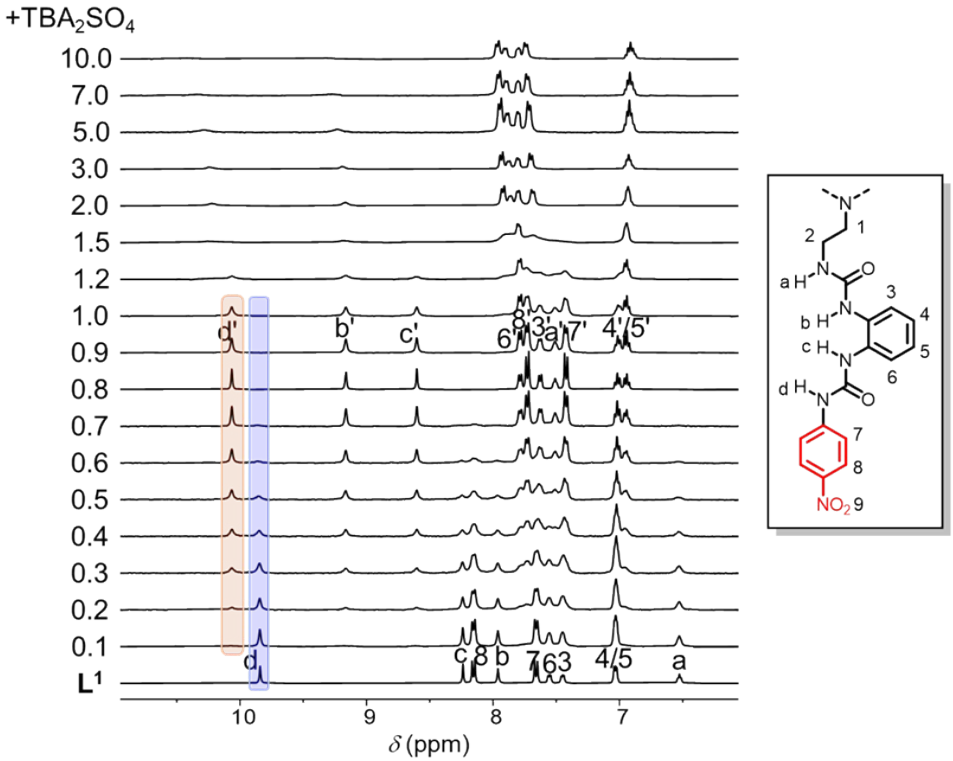


Fig. S10 Stacked partial ^{1}H NMR spectra (400 MHz, 298 K, DMSO-d_6) of receptor **L^1** (2 mM) by adding sulfate anion as tetrabutylammonium salt (TBA_2SO_4, 50 mM).

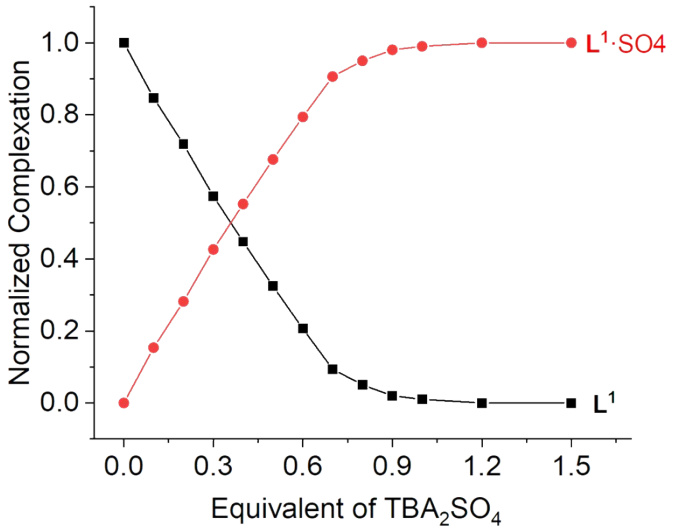


Fig. S11 Normalized complexation distribution for the free receptor **L^1** and sulfate complex **L^1**•SO_4^{2-} during the titration in **Fig. S7**.

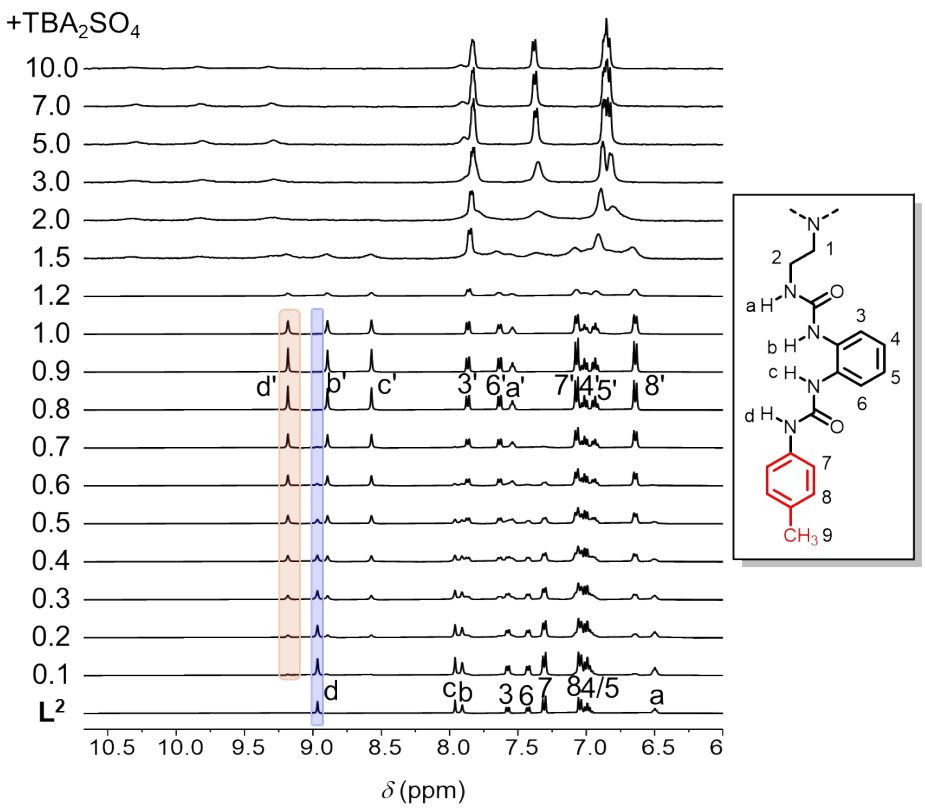


Fig. S12 Stacked partial ^{1}H NMR spectra (400 MHz, 298 K, DMSO-d_6) of receptor **L²** (2 mM) by adding sulfate anion as tetrabutylammonium salt (TBA_2SO_4, 50 mM).

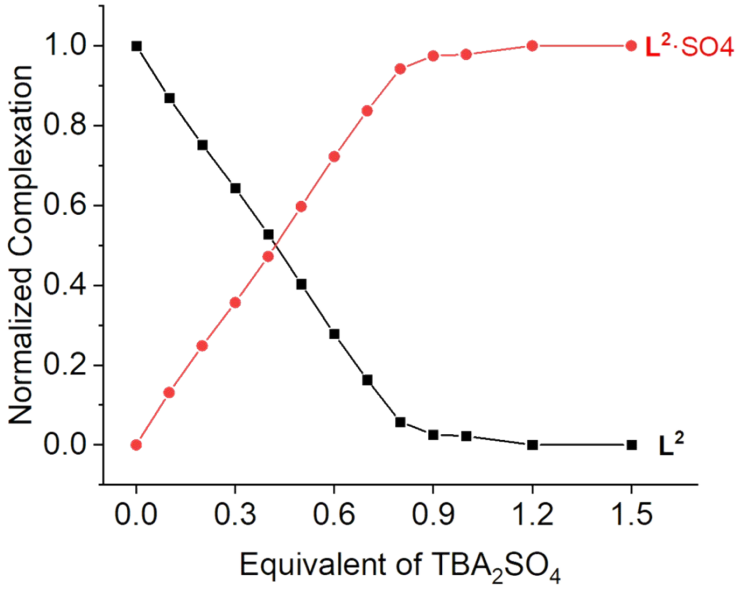


Fig. S13 Normalized complexation distribution for the free receptor **L²** and sulfate complex **L²**•SO_4^{2-} during the titration in **Fig. S9**.

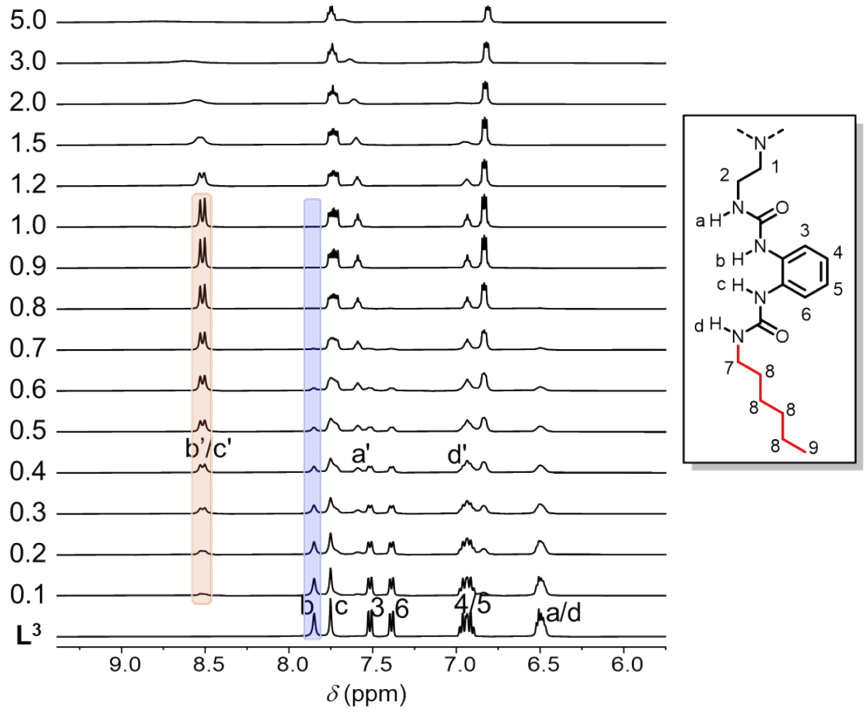


Fig. S14 Stacked partial ^{1}H NMR spectra (400 MHz, 298 K, DMSO-d_6) of receptor **L²** (2 mM) by adding sulfate anion as tetrabutylammonium salt (TBA_2SO_4, 50 mM).

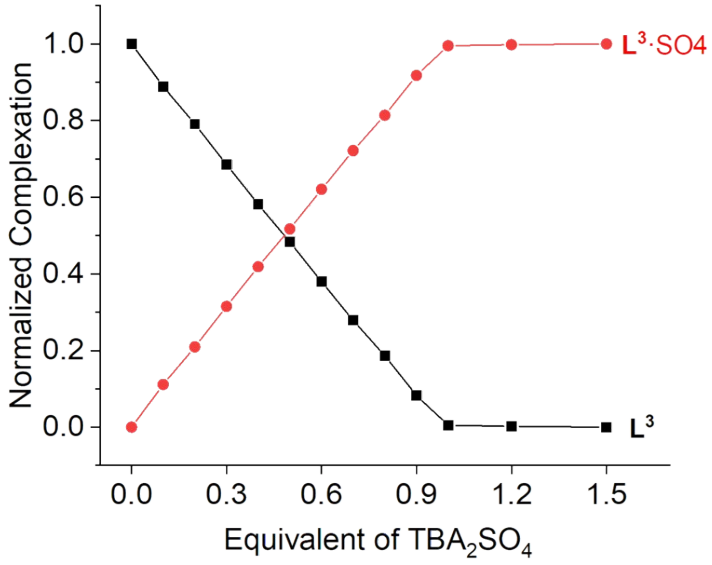


Fig. S15 Normalized complexation distribution for the free receptor **L³** and sulfate complex **L³**•SO_4^{2-} during the titration in **Fig. S11**.

For a typical competitive titration, e.g., titrating the complex of $\mathbf{L^3}\bullet SO_4^{2-}$ with receptor L1, the competitive equilibrium can be expressed as follow,

$$L^1 + L^3A \rightleftharpoons L^1A + L^3 \quad (1)$$

the competitive equilibrium constant K can be represented as

$$K = \frac{[L^1A] \times [L^3]}{[L^1] \times [L^3A]} = \frac{K(L^1(SO4))}{K(L^3(SO4))} = \frac{y^2}{(x-y) \times (a-y)} = \frac{y^2}{ax - xy - ay + y^2} \quad (2)$$

where the $K(\mathbf{L^1}SO_4)$ and $K(\mathbf{L^3}SO_4)$ indicate the binding constant of receptor $\mathbf{L^1}$ and $\mathbf{L^3}$ with sulfate anion, respectively. For the calculation, we define these:

$$x = [L^1] + [L^1A],\ y = [L^3] = [L^1A]$$

$$a = [L^3A] + [L^3],\ [L^3A] = a - y$$

$$a = [L^3A] + [L^1],\ [L^1A] = a - a + y = y$$

Thus, the competitive equilibrium constant K can be determined based on the following equation using Origin.

$$y = \frac{a + x \pm \sqrt{(a+x)^2 - 4ax \times (1 - \frac{1}{k})}}{2 \times (1 - \frac{1}{K})} \quad (3)$$

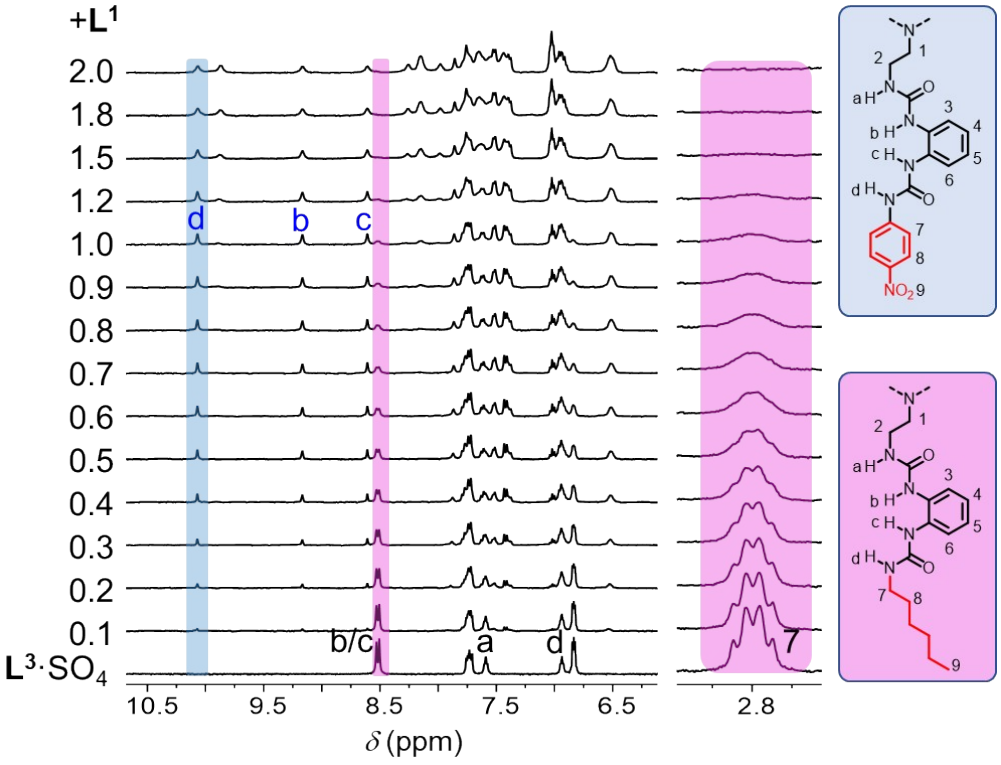


Fig. S16 Stacked partial ^{1}H NMR spectra (400 MHz, 298 K, DMSO-d_6) of $\mathbf{L^3}\bullet SO_4^{2-}$ complex (1 mM) by adding receptor $\mathbf{L^1}$ (25 mM).

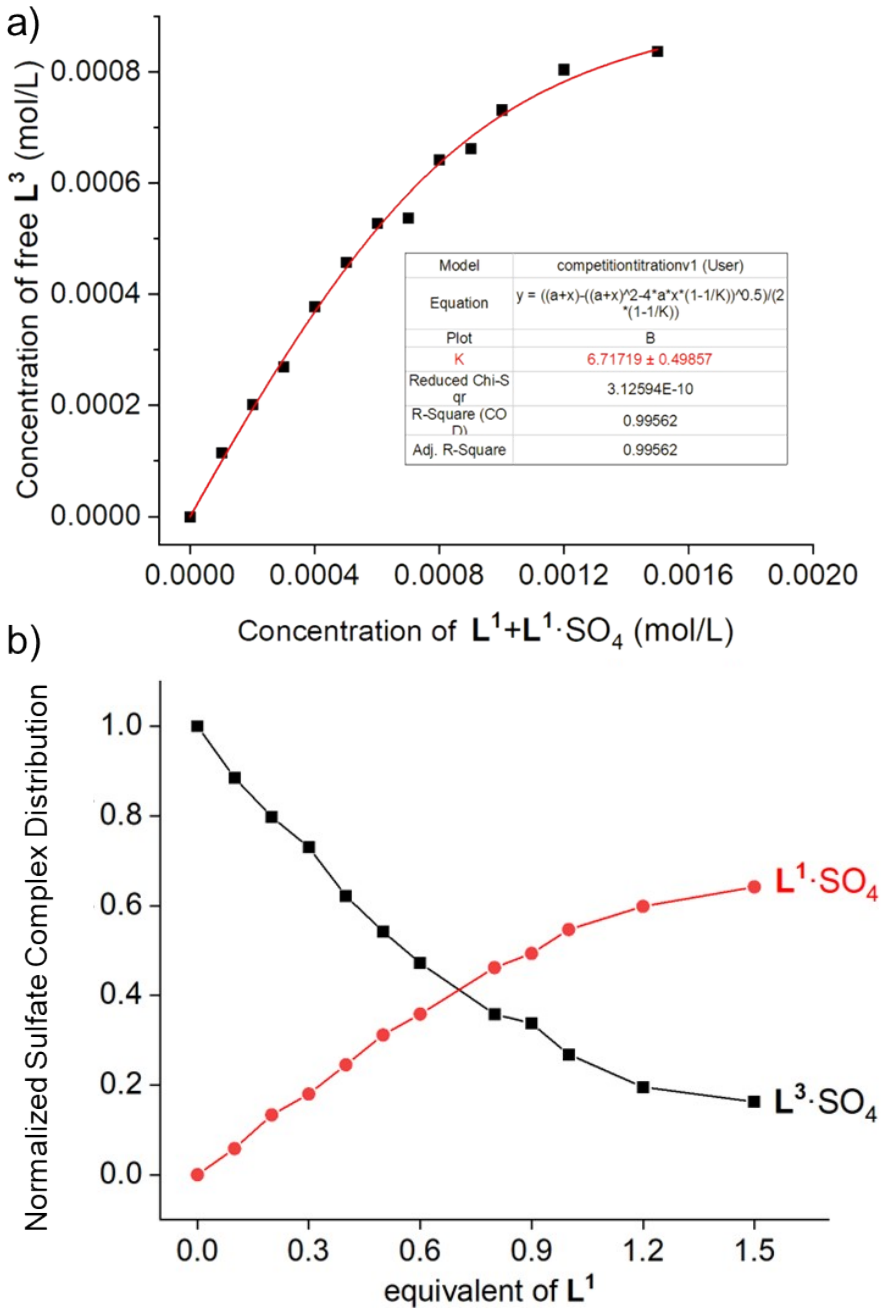


Figure S17. a) The fitting curve determined based on above-mentioned equation (3) using Origin. b) Normalized sulfate complex distribution of $\mathbf{L^1}\bullet SO_4^{2-}$ and $\mathbf{L^3}\bullet SO_4^{2-}$ during titration.

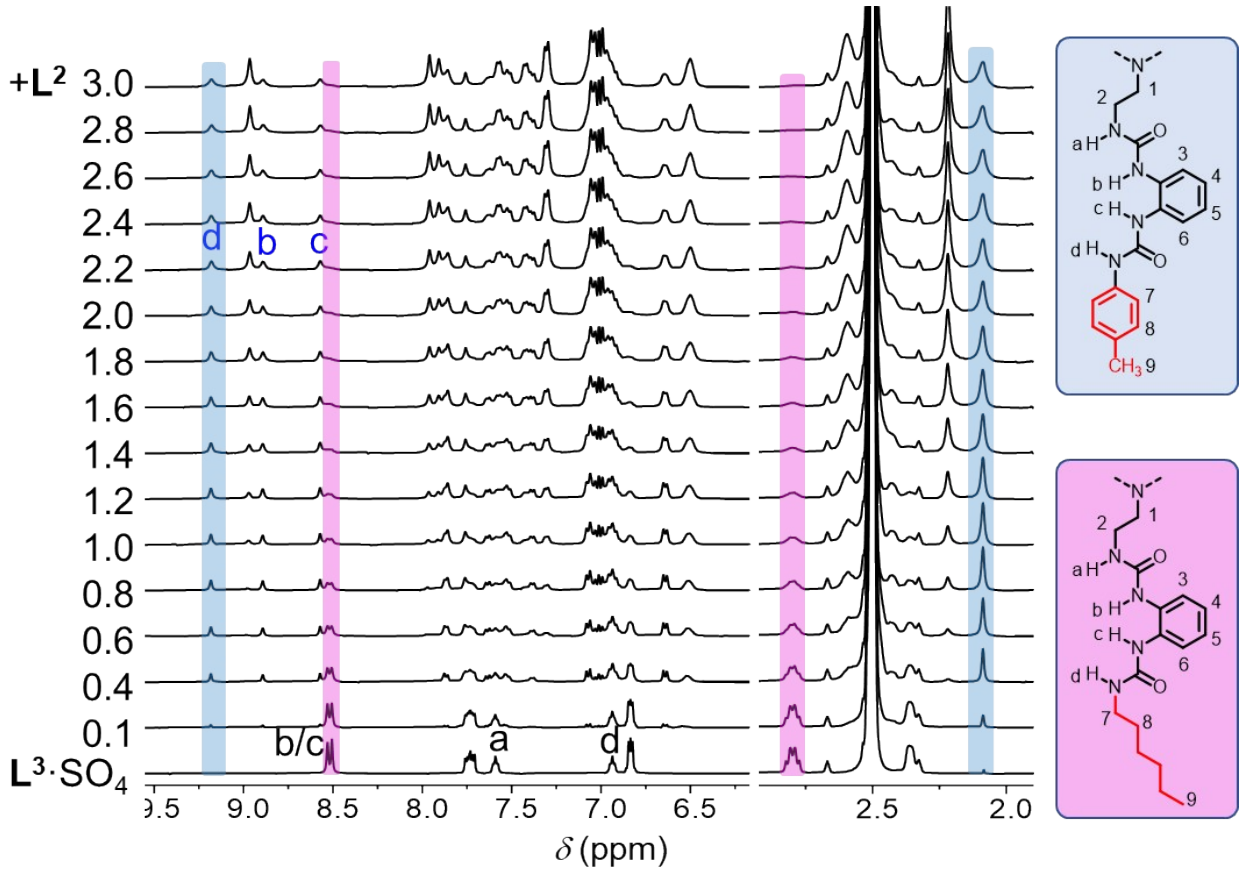


Fig. S18 Stacked partial ^{1}H NMR spectra (400 MHz, 298 K, DMSO-d_6) of $\mathbf{L^3}$•SO_4^{2-} complex (1 mM) by adding receptor $\mathbf{L^2}$ (25 mM).

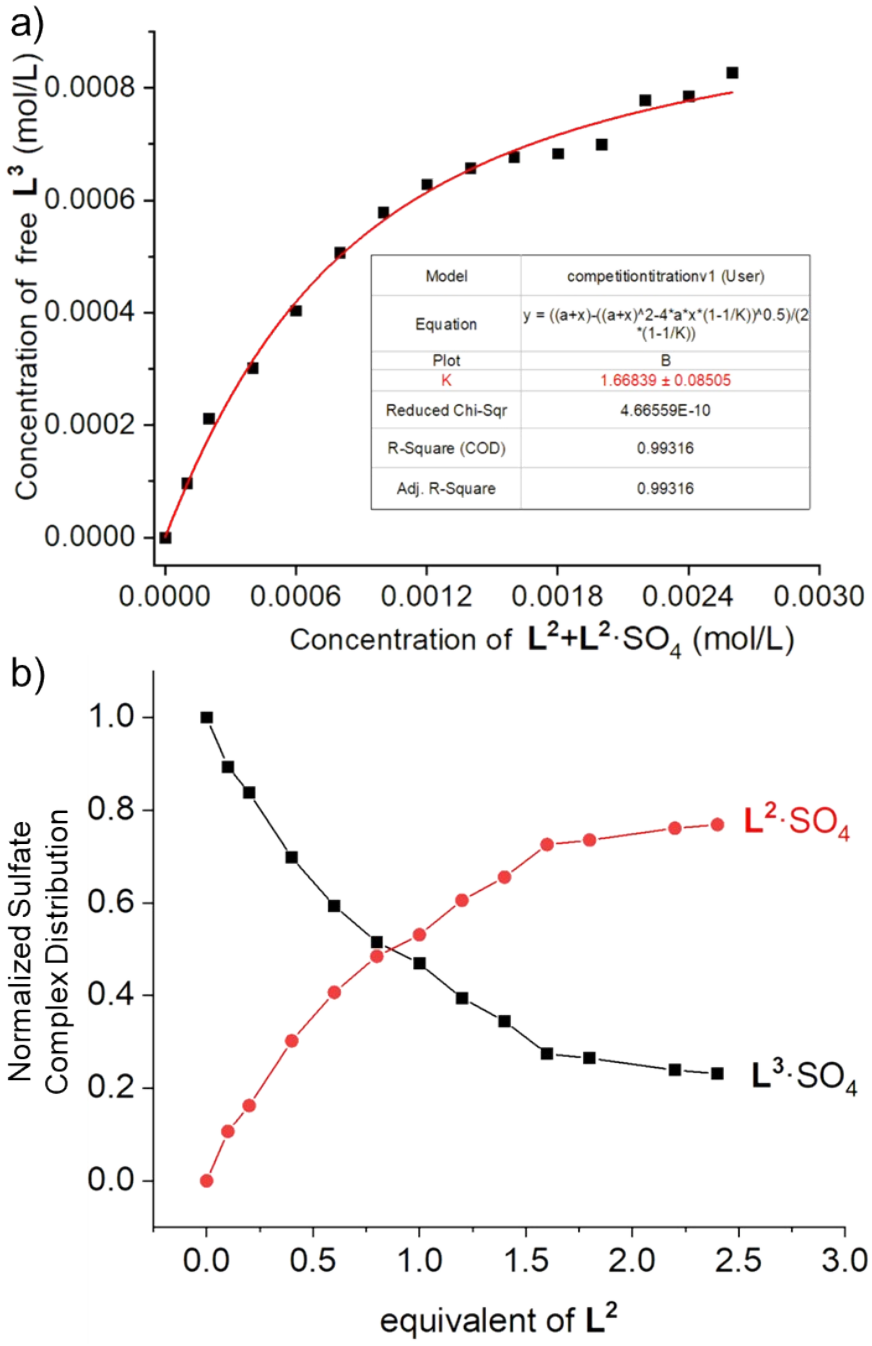


Figure S19. a) The fitting curve determined based on above-mentioned equation (3) using Origin. b) Normalized sulfate complex distribution of $\mathbf{L^2}$•SO_4^{2-} and $\mathbf{L^3}$•SO_4^{2-} during titration.

S6. Liquid-Liquid Extraction Studies

S6.1 General liquid-liquid extraction procedure for ^{1}H NMR and IC analyses.

An aqueous solution (2 mL) of the targeted anion salt (e.g., Na_2SO_4, 10 mM) was exposed to 2mL of extractant **L** (10 mM) with 2 equivalent A336Cl in $CHCl_3$. Extraction was then performed by violent shaking at room temperature for 5 seconds. The two phases of the solution were immediately stratified. The aqueous solutions layer (2 mL) was taken out and filtered through a 0.2 μM syringe filter, then determined by IC analyses. The organic layer (0.5 mL) was carefully removed, concentrated, and was recorded for NMR analyses.

Table S4 Summary for the sulfate concentration that is remaining in water after extraction. The results were determined by IC. Only sulfate is present in water before extraction, and the initial sulfate concentration is determined to be 9.59 mM.

Receptor	concentration of SO_4^{2-} remaining in water after extraction (mM)
L^1	0.97±0.07
L^2	1.19±0.11
L^3	2.11±0.03

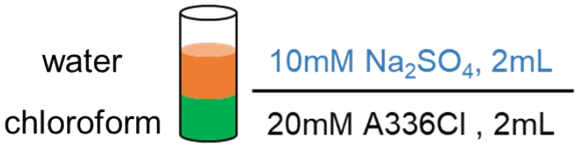
Table S5 Sulfate concentration remaining in water after extraction under different concentration of receptor and initial sulfate concentration.

mM	SO_4^{2-} before extraction	**L^1**	**L^2**	**L^3**
1	0.92	0.20±0.02	0.22±0.02	0.25±0.02
2	2.04	0.37±0.09	0.45±0.02	0.45±0.12
5	4.84	0.69±0.16	0.73±0.10	1.05±0.02
10	9.52	0.97±0.07	1.19±0.11	2.11±0.03
20	19.54	2.05±0.12	2.43±0.03	4.06±0.03

Table S6 Remaining sulfate concentration in water after extraction by using different equivalents of receptors.

Equivalents of receptors	**L¹**	**L²**	**L³**
1	0.97±0.07	1.19±0.11	2.11±0.03
1.1	0.47±0.04	0.60±0.06	1.43±0.05
1.2	0.21±0.04	0.26±0.00	0.79±0.03
1.3	-	0.19±0.01	0.75±0.12
1.4	-	-	0.54±0.05
1.5	-	-	0.33±0.02

(a)



(b)

Exp.	SO_4^{2-} before extraction (mM)	SO_4^{2-} after extraction (mM)
1		9.94
2	9.99	9.97
3		10.00

Fig. S20 Control liquid-liquid extraction experiment using A336Cl alone. (a) Schematic illustration of the control experiment, and (b) concentration of sulfate anion before and after extraction using A336Cl alone as determined by IC.

S6.2 Competitive extraction of common anions (Na_2SO_4、$NaNO_3$、KBr and NaH_2PO_4) or (Na_2SO_4、$NaNO_3$、KBr 、KI、$NaHCO_3$ and NaH_2PO_4).

Competitive experiment: To a solution of Ligand (10 mmol) and A336Cl (20 mmol) in $CHCl_3$ (2 mL) was added a solution of mixed salts solution consisting of Na_2SO_4、$NaNO_3$、KBr and NaH_2PO_4 (10 mM, respectively) or Na_2SO_4、$NaNO_3$、KBr 、KI、$NaHCO_3$ and NaH_2PO_4 (10 mM, respectively) in ultrapure H_2O (2 mL, 18.2 MΩ-cm). Manually vibrate up and down for 5 seconds and then stand for 20 seconds. Thus, 1 mL of the aqueous layer was taken out and filtered

through a 0.2 μM syringe filter, then determined by IC analyses. The organic layer (0.5 mL) was carefully removed, concentrated, was used for NMR analyses.

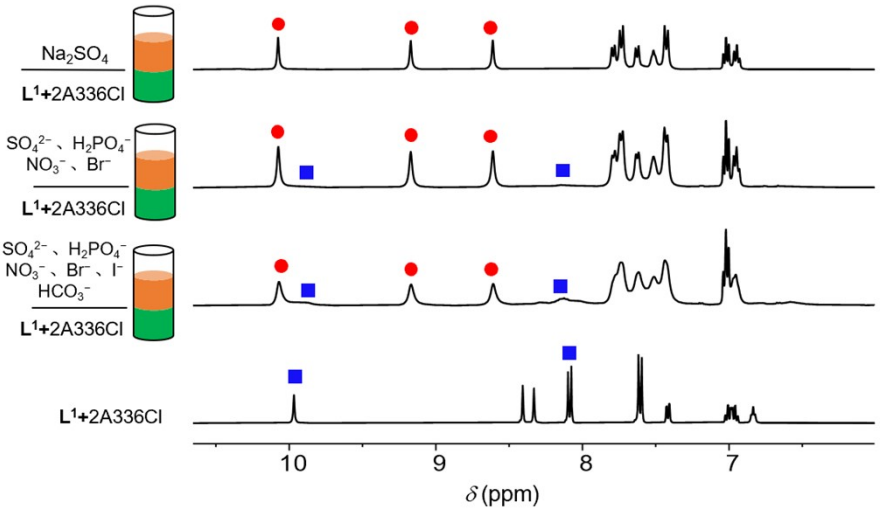


Fig. S21 Stacked partial ^{1}H NMR (400 MHz, 298 K, DMSO-d_6), from bottom to top: receptor **L^{1}** with two equivalents of A336Cl, obtained spectra after extraction with six different anions, obtained spectra after extraction with four different anions, after extraction with sodium sulfate (only). The blue squares denote the peaks assigned to **L^{1}**•Cl^{-} complex, the red circles denote the peaks assigned to **L^{1}**•SO_4^{2-} complex.

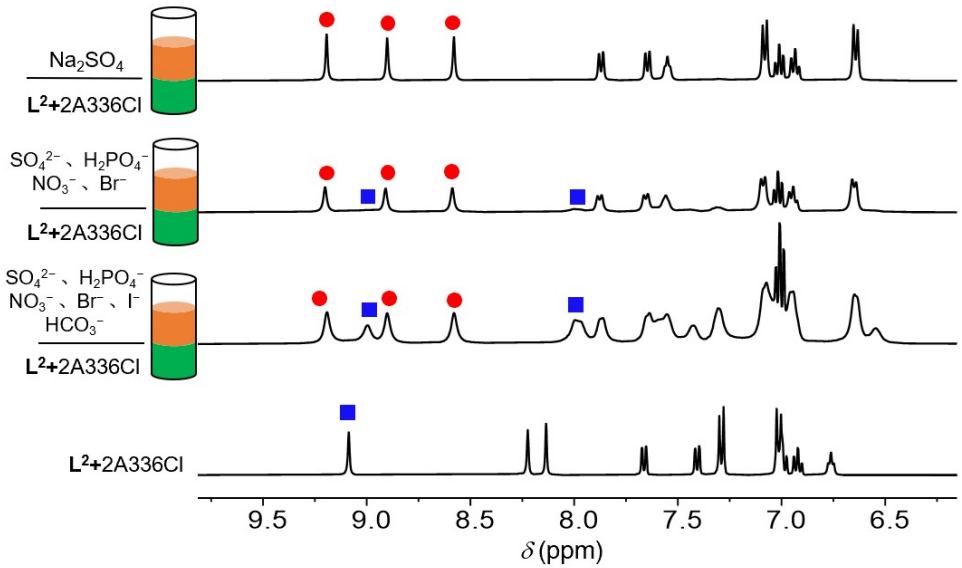


Fig. S22 Stacked partial ^{1}H NMR (400 MHz, 298 K, DMSO-d_6), from bottom to top: receptor **L^{2}** with two equivalents of A336Cl, obtained spectra after extraction with six different anions, obtained spectra after extraction with four different anions, after extraction with sodium sulfate

(only). The blue squares denote the peaks assigned to $\mathbf{L^2}$•Cl^- complex, the red circles denote the peaks assigned to $\mathbf{L^2}$•SO_4^{2-} complex.

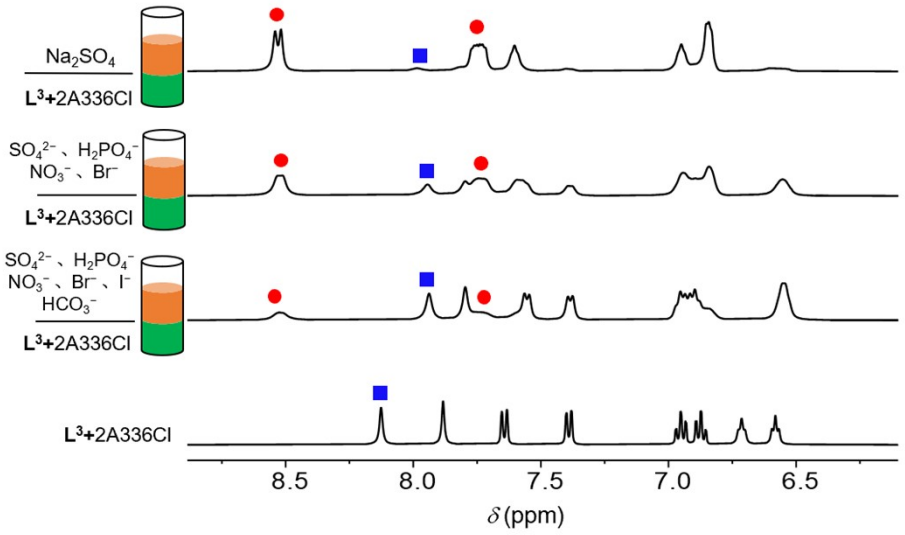


Fig. S23 Stacked partial ^{1}H NMR (400 MHz, 298 K, DMSO-d_6), from bottom to top: receptor $\mathbf{L^3}$ with two equivalents of A336Cl, obtained spectra after extraction with six different anions, obtained spectra after extraction with four different anions, after extraction with sodium sulfate (only). The blue squares denote the peaks assigned to $\mathbf{L^3}$•Cl^- complex, the red circles denote the peaks assigned to $\mathbf{L^3}$•SO_4^{2-} complex.

Table S7 Concentration of various anions remaining in water after extraction.

Run	SO_4^{2-} (mM)	NO_3^- (mM)	Br^- (mM)	$H_2PO_4^-$ (mM)
before	9.74	9.42	9.71	9.67
$\mathbf{L^1}$	1.33±0.01	8.84±0.05	8.99±0.04	9.70±0.09
$\mathbf{L^2}$	2.20±0.04	8.39±0.02	8.37±0.01	9.89±0.04
$\mathbf{L^3}$	4.62±0.06	7.04±0.11	6.59±0.04	9.99±0.12

S6.3 Analyses for the extraction equilibrium.

The extraction equilibrium equation for extraction can be represented as follows,

$$[\mathbf{L}\bullet Cl^-]_o + \mathbf{L}_o + 3Cl^-_o + 2SO_4^{2-}{}_w \rightleftharpoons 2\,[\mathbf{L}\bullet SO_4^{2-}]_o + 4\,Cl^-_w \qquad K_{ex} \quad (4)$$

$$K_{ex} = \frac{\left[L\cdot SO_4{}^{2-}\right]^2{}_o \times \left[Cl^-\right]^4{}_w}{\left[L\cdot Cl^-\right]_o \times [L]_o \times \left[Cl^-\right]^3{}_o \times \left[SO_4{}^{2-}\right]^2{}_w} \qquad (5)$$

where the subscript 'o' denotes the species present in organic phase, and the subscript 'w' denotes the species present in aqueous phase. $[\mathbf{L}\bullet Cl^-]_o$ denotes chloride complex, $[L\bullet SO_4^{2-}]_o$ denotes sulfate complex, $\mathbf{L}_o$ denotes free receptor in organic phase, $SO_4^{2-}{}_w$ denotes sulfate in water phase, Cl^-_o and Cl^-_w denote chloride in organic and water phase, respectively. Concentrations of anions can be directly determined using ion chromatography.

For the chloride binding equilibrium in organic phase, it can be represented as follows,

$$L_o + Cl^-_o \rightleftharpoons [L\cdot Cl^-]_o \qquad K_{Cl} \qquad (6)$$

$$K_{Cl} = \frac{\left[L\cdot Cl^-\right]_o}{[L]_o \times \left[Cl^-\right]_o} \qquad (7)$$

Based on the chloride binding constant K_{Cl} determined by ^{1}H NMR titrations (Figs. S4-S6), we can calculate the concentration of free chloride and receptor bound chloride anion in organic phase. Thus, the K_{ex} can be determined based on the principle of overall charge neutrality.

S6.4 Repeatable sulfate extraction and release

A solution of ligand **L³** (15 mM) with 2 equivalent A336Cl in $CHCl_3$ (2 mL) was placed in a centrifuge tube and mixed with an aqueous solution of Na_2SO_4 (10 mM). The solutions were handshake over five seconds, and the aqueous solution was carefully removed for IC analysis. The left organic solution was re-mixed with an aqueous solution of HCl (0.4 M, 2 mL). The new mixed solutions were handshake over five seconds, the aqueous solution was separated for IC analysis. The extraction and back-extraction process was repeated over eight cycles, and the IC results were summarized in Table S8.

Table S8 Aqueous phase concentration after cyclic extraction of sulfate. (before extraction [Na_2SO_4] = 9.59 mM, sulfate: receptor = 1:1)

Cycles	L^1		L^2		L^3	
	After extraction	After HCl	After extraction	After HCl	After extraction	After HCl
1	0.70±0.19	8.29±0.24	0.38±0.16	9.12±0.14	0.28±0.05	9.05±0.07
2	1.49±0.20	7.87±0.04	0.82±0.17	9.07±0.31	1.48±0.06	8.88±0.01
3	1.94±0.24	7.93±0.15	0.93±0.16	9.02±0.27	1.56±0.09	8.70±0.16
4	2.16±0.25	7.99±0.95	1.74±0.22	8.46±0.21	1.57±0.09	8.54±0.50
5	1.86±0.15	8.12±0.12	2.72±0.28	7.79±0.32	1.57±0.21	8.77±0.26
6	2.36±0.30	8.05±0.06	2.89±0.42	7.27±0.38	1.67±0.26	8.69±0.10
7	2.47±0.02	8.26±0.55	3.13±0.36	6.97±0.27	1.82±0.30	8.70±0.76
8	2.80±0.09	7.66±0.16	3.24±0.33	6.99±0.25	1.83±0.19	8.50±0.42

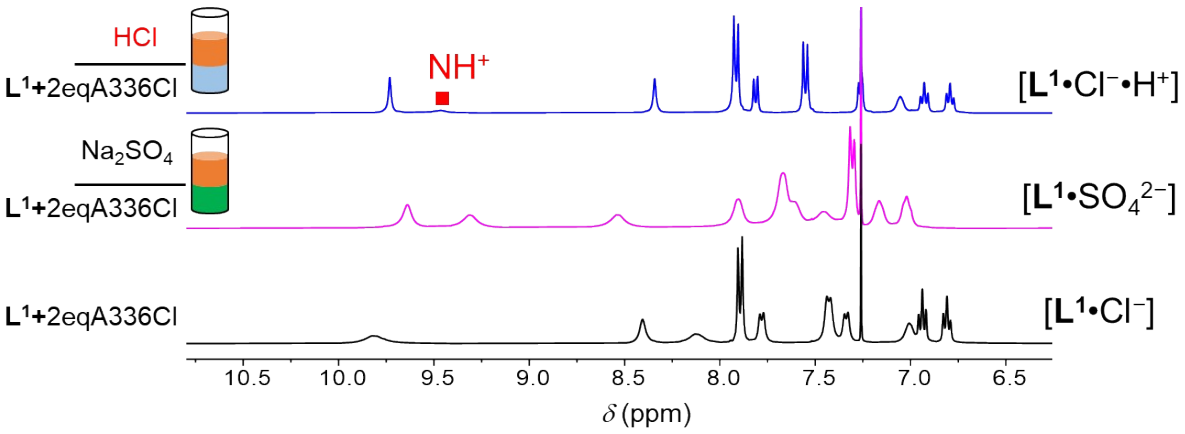


Fig. S24 Stacked partial ^{1}H NMR (400 MHz, 298 K, $CDCl_3$), from bottom to top: receptor **L^1** with

two equivalents of A336Cl, obtained spectra after extraction with sodium sulfate, obtained spectra after back-extraction with HCl solution. The spectra indicates that central N atom (NR_3) is partially protonated after back extraction.

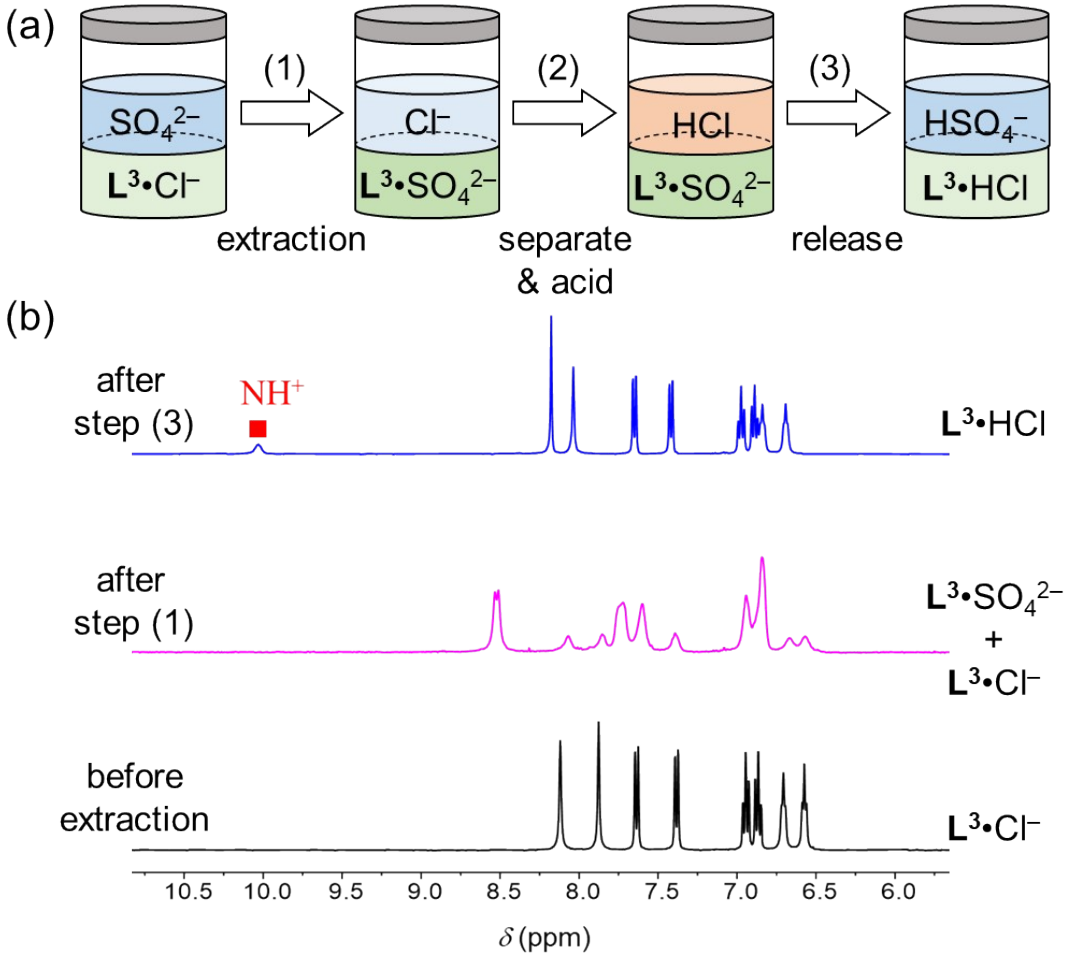


Fig. S25 (a) Schematic illustration for sulfate extraction and release process using aqueous HCl solution ($[Na_2SO_4]_w$ = 10 mM, $[\mathbf{L^3}]_o$ = 15 mM, $[HCl]_w$ = 0.4 M). (b) Stacked partial ^{1}H NMR (400 MHz, 298 K, DMSO-d_6), from bottom to top: receptor $\mathbf{L^3}$ with two equivalents of A336Cl, obtained spectra after extraction with sodium sulfate, obtained spectra after acidifying with HCl solution. The spectra indicates that central N atom (NR_3) is protonated.

S7 U-tube Transport Studies experiments:

A solution of L^3 with two equivalents of A336Cl in $CHCl_3$ (3 mL) was placed in a U-tube cell with a magnetic stir bar on the bottom. A solution of Na_2SO_4 (100 mM) as the source phase

and a solution of hydrochloride acid (0.6 M) were carefully placed into the tube, respectively. The whole tube was placed in oil bath (25±1 °C) and stirred (1000 rpm). An aliquot (10 μL) of the source and receiving phase were taken and monitored by ion chromatography. Each experiment was repeated at least three times and averaged data was recorded.

Table S9 Conditions for U-tube transport experiments.

Expe.	Source phase	Organic phase	Receiving phase
A	100 mM Na_2SO_4	5 mM **L³** and 10 mM A336Cl in $CDCl_3$	600 mM HCl
B		10 mM **L³** and 20 mM A336Cl in $CDCl_3$	
C		20 mM **L³** and 40 mM A336Cl in $CDCl_3$	
D		40 mM A336Cl in $CDCl_3$	

Table S10 Sulfate concentration changes in the source phase. Experiments A-B refer to the setup in Table S9.

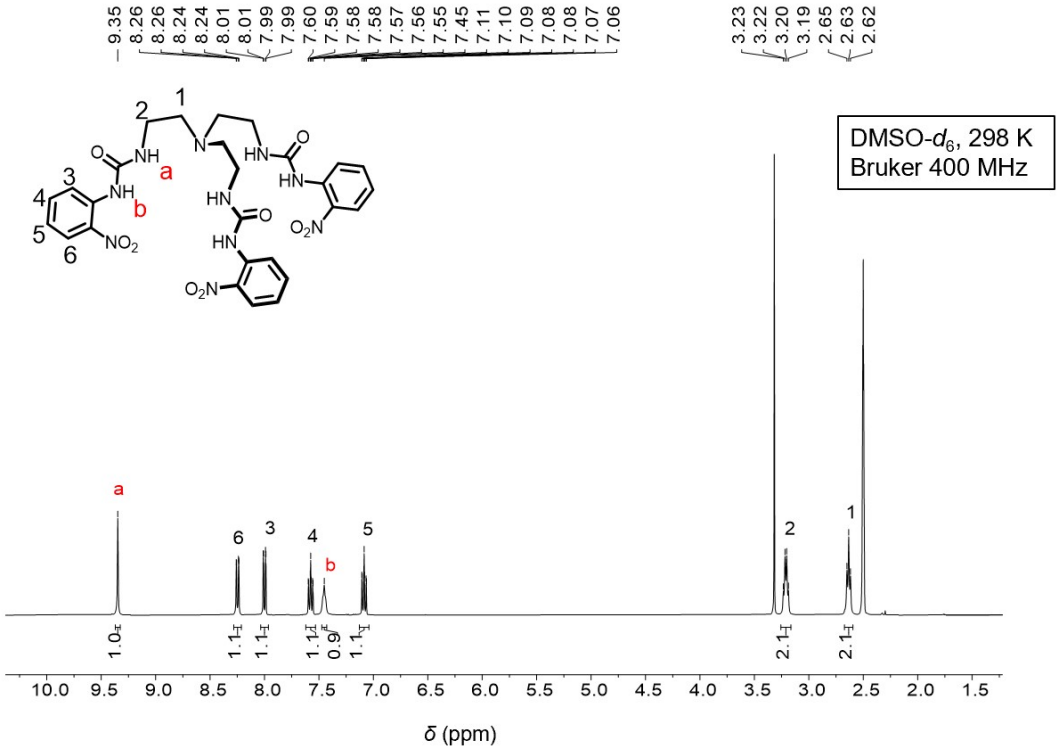
Time (h)	A	B	C	D
0	100.8	100.8	100.8	100.8
6	81.5±1.8	63.3±4.1	46.8±6.8	97.3±2.7
12	68.2±1.6	51.9±2.5	37.0±3.0	98.4±3.4
24	52.9±3.6	36.7±2.8	32.6±2.3	97.2±2.7
34	44.6±2.9	33.6±2.0	29.0±1.7	97.0±3.1
46	38.4±2.1	29.2±2.8	26.8±0.7	96.4±0.7
58	35.1±0.7	27.3±0.9	26.6±0.7	97.6±3.1

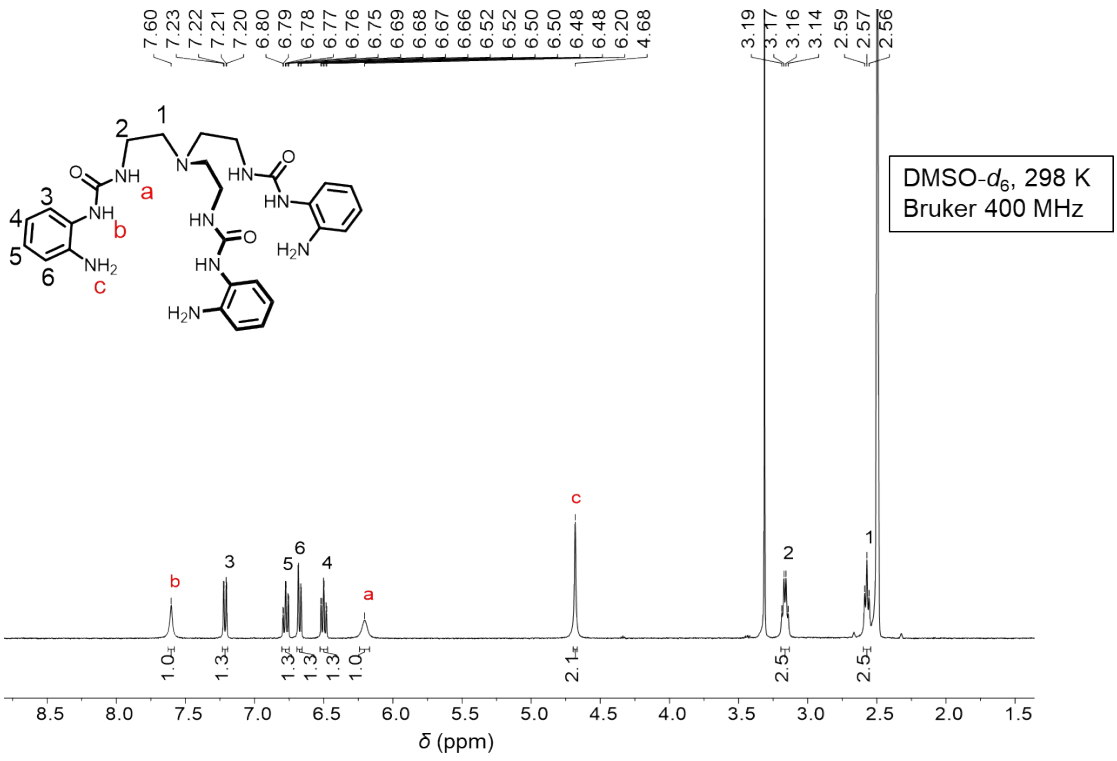
70	32.3±0.9	26.0±1.4	27.5±0.8	100.1±4.0

Table S11 Sulfate concentration changes in the receiving phase. Experiments A-B refer to the setup in Table S9.

Time (h)	A	B	C	D
0	0.0	0.0	0.0	0.0
6	9.9±0.3	12.0±2.2	12.8±1.1	0.0
12	14.6±1.0	17.4±1.4	24.5±2.6	0.0
24	30.1±1.3	42.1±0.8	49.8±4.0	0.0
34	45.3±1.6	55.6±2.3	58.4±2.9	0.0
46	56.3±1.6	64.5±2.6	62.1±2.7	0.0
58	66.2±2.4	70.8±1.8	63.5±2.7	0.0
70	69.2±2.1	70.9±0.7	64.0±0.8	0.0

S8. ^{1}H and ^{13}C NMR Spectra

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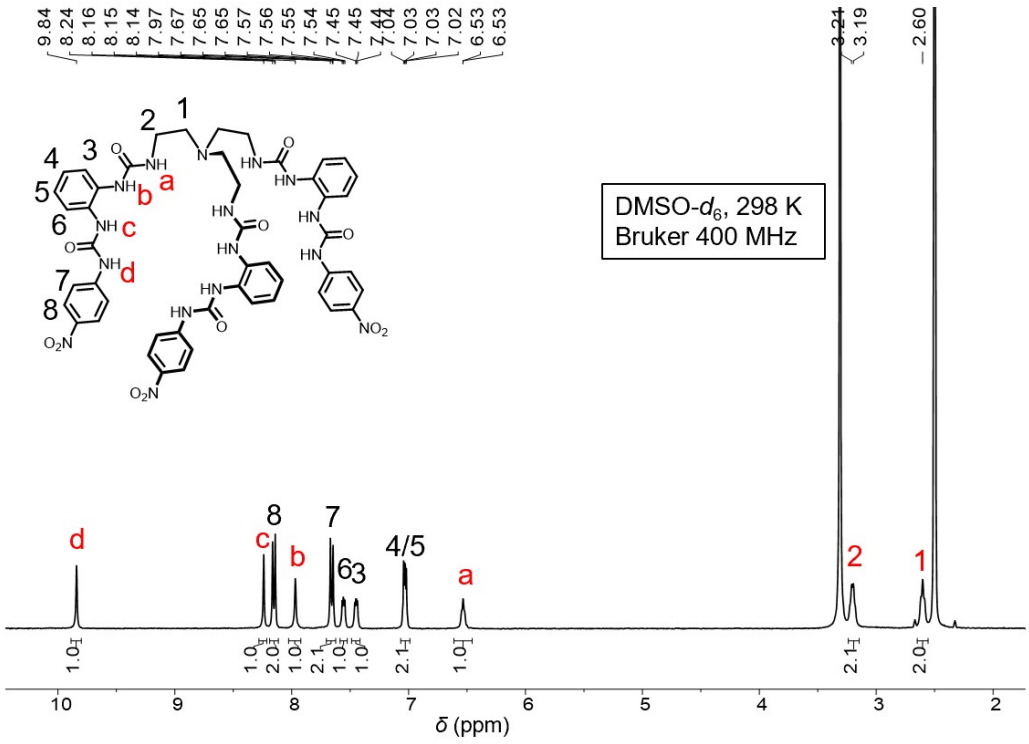
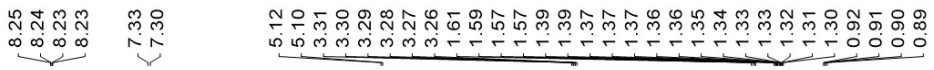
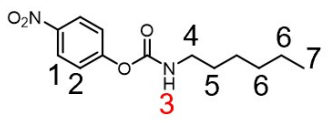
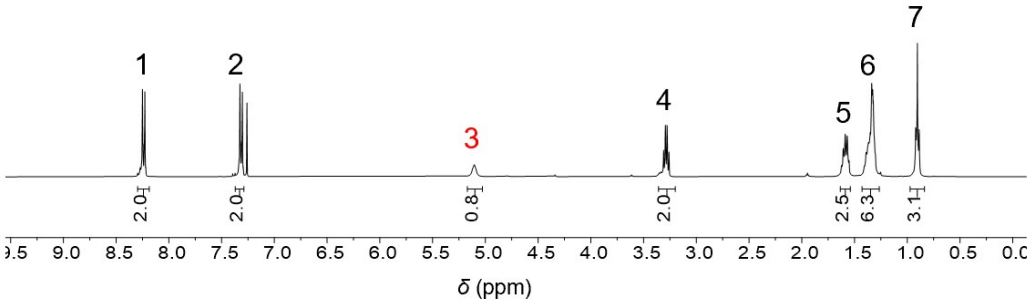
Bruker 400 MHz
δ (ppm)

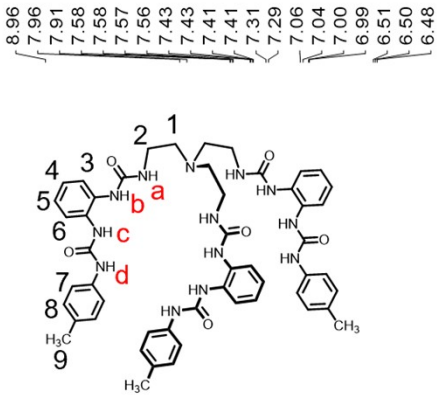

DMSO-d_6, 298 K
Bruker 400 MHz
δ (ppm)



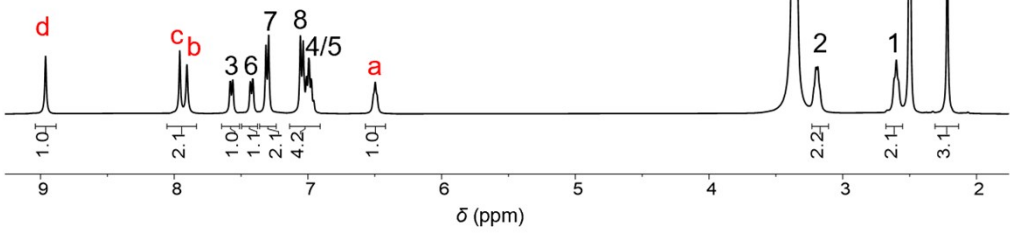


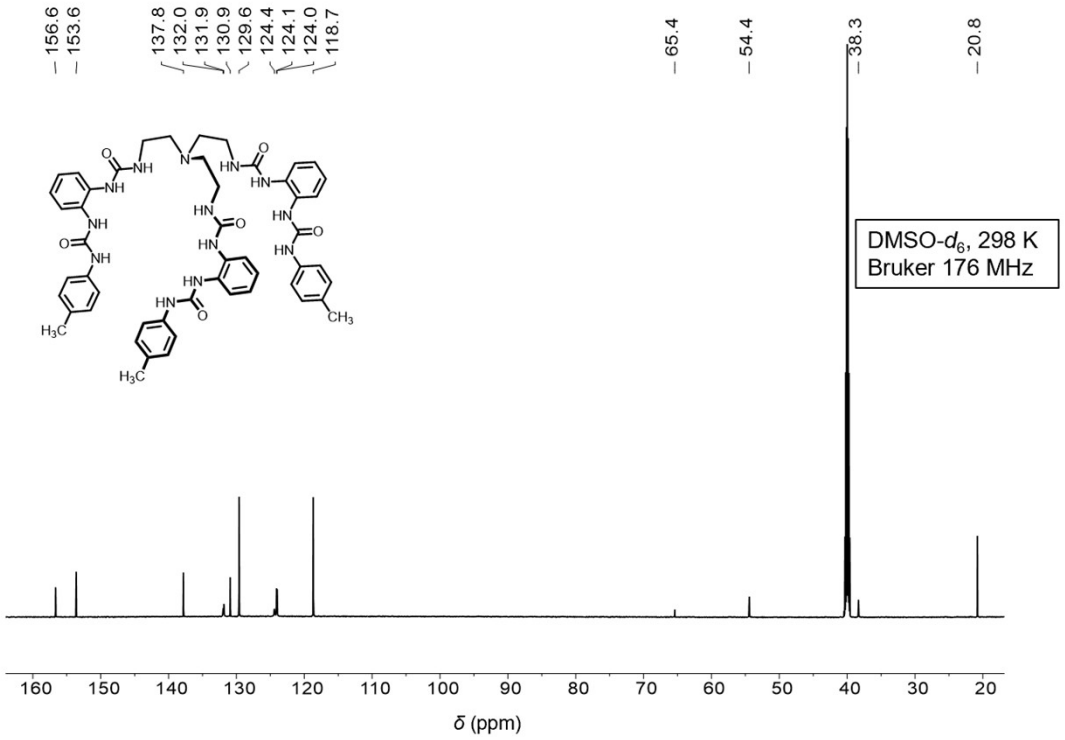
$CDCl_3$, 298 K
Bruker 400 MHz

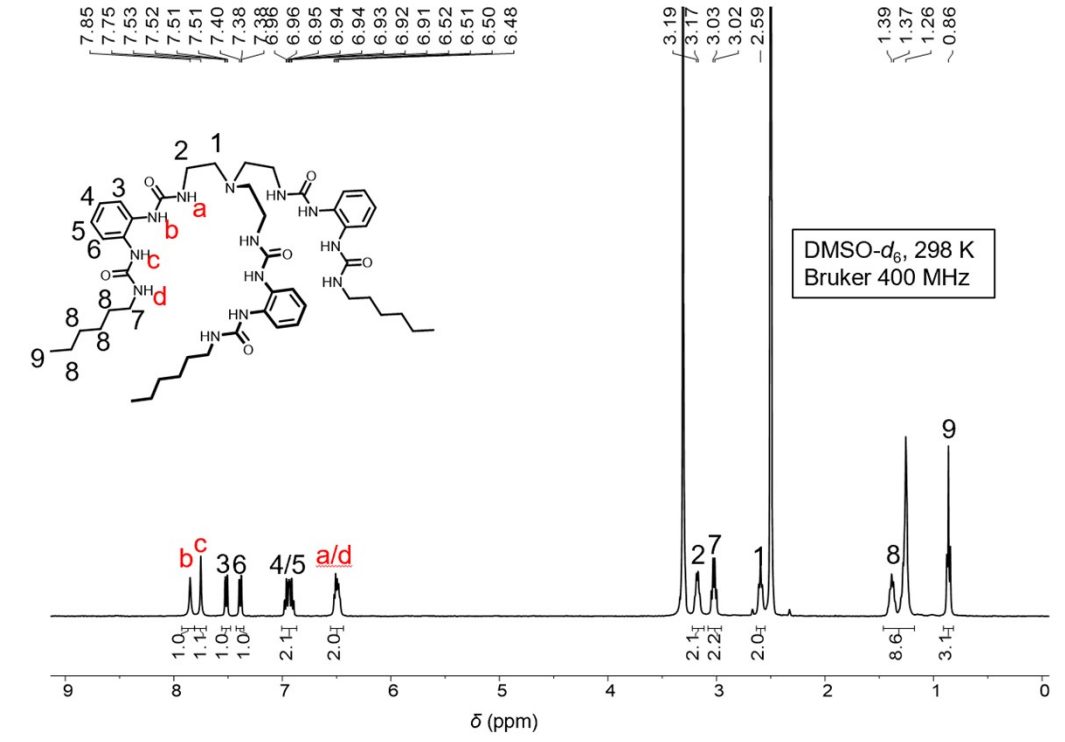


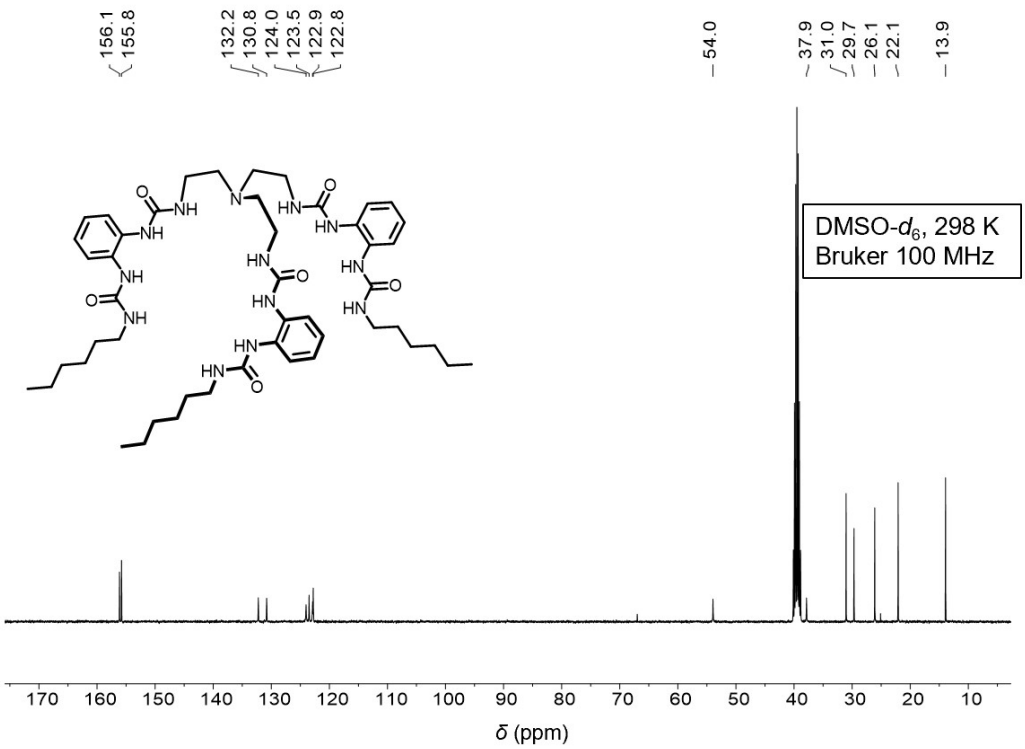


DMSO-d_6, 298 K
Bruker 400 MHz




156.6
153.6
137.8
132.0
131.9
130.9
129.6
124.4
124.1
124.0
118.7
65.4
54.4
38.3
20.8
DMSO-d_6, 298 K
Bruker 176 MHz
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
δ (ppm)


7.85
7.75
7.53
7.52
7.51
7.51
7.40
7.38
6.96
6.95
6.94
6.94
6.93
6.92
6.91
6.52
6.51
6.50
6.48
3.19
3.17
3.03
3.02
2.59
1.39
1.37
1.26
0.86
DMSO-d_6, 298 K
Bruker 400 MHz
b c 3 6 4/5 a/d
2 7 1 8 9
1.0 1.1 1.0 1.0 2.1 2.0
2.1 2.2 2.0 8.6 3.1
9 8 7 6 5 4 3 2 1 0
δ (ppm)


156.1
155.8
132.2
130.8
124.0
123.5
122.9
122.8
54.0
37.9
31.0
29.7
26.1
22.1
13.9
DMSO-d_6, 298 K
Bruker 100 MHz
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
δ (ppm)