

Electronic Supplementary Information

Sandwich phosphate complexes of macrocyclic tris(urea) ligands and the rotation around the anion

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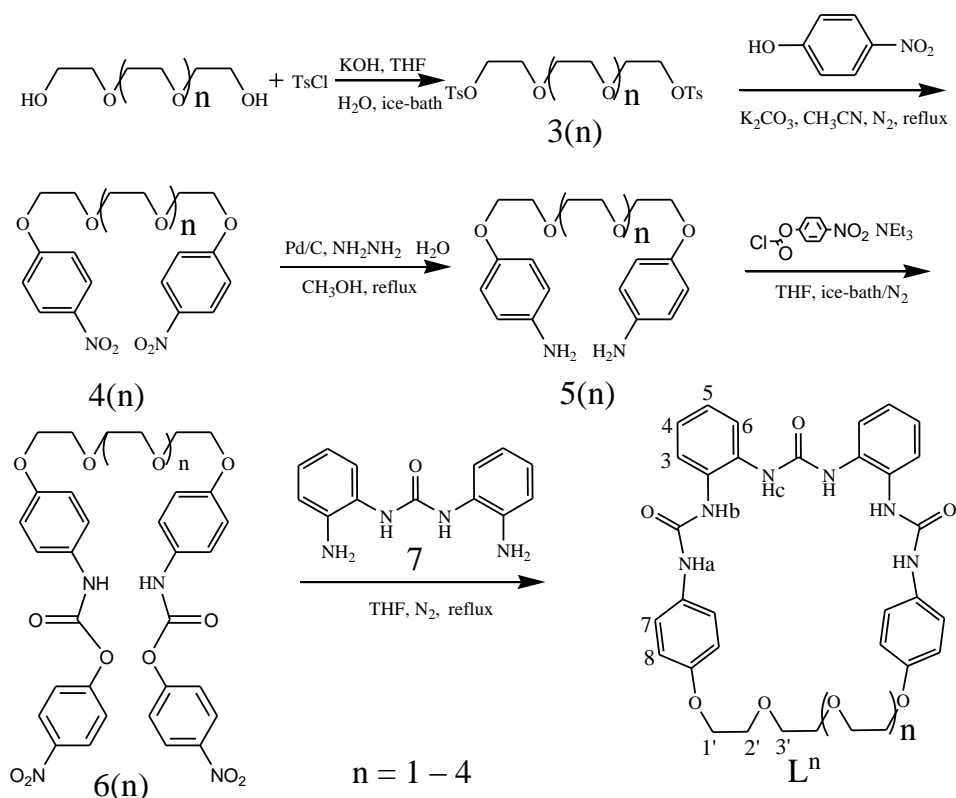
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S1. General

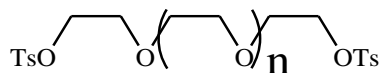
All solvents and reagents were of reagent grade quality. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE III-400 spectrometer at 400 and 100 MHz, respectively, with TMS as an internal standard. ³¹P NMR spectra were measured in acetone-*d*₆/0.5% water by using PPh₃ as the internal reference (which was calibrated to be at $\delta = -4.15$ ppm relative to 85% aqueous phosphoric acid). All ¹H NMR titrations were performed in DMSO-*d*₆/0.5% water or acetone-*d*₆/0.5% water. Elemental analyses were performed on an Elementar VarioEL instrument. IR spectra were recorded on a Bruker IFS 120HR spectrometer. ESI-MS measurements were carried out using a Bruker micrOTOF-Q II Electrospray Ionization Mass Spectrometer in THF or THF/DMF. Melting points were detected on an X-4 Digital Vision MP Instrument.

S2. Synthesis of ligands **L¹–**L**⁴**



Scheme S1. Synthesis of the heteroditopic macrocyclic receptors L^n ($n = 1-4$).

1,8-Bis(tosyloxy)-3,6-dioxaoctane [TsO(CH₂CH₂)₃OTs, **3(1)**].



3(1) was prepared following a similar procedure to that of the previous literature.^{S1} A solution of triethylene glycol (5.0 g, 0.033 mol) in THF (35 mL) was added to a solution of KOH (7.5 g, 0.13 mol) in water (18 mL) under stirring with an ice/water bath, and then a solution of *p*-toluenesulfonyl chloride (13.3 g, 0.07 mol) in THF (35 mL) was added dropwise to the mixture over 2 h with continuous stirring and cooling. The solution was further stirred vigorously for an additional 5 h before being poured into ice-water (35 mL). The ditosylate was isolated by extracting twice with CH₂Cl₂ (35 mL). The combined organic extracts were washed twice with H₂O (20 mL) and once with saturated aqueous sodium chloride solution (20 mL) and then dried (MgSO₄). Removal of MgSO₄ and solvent afforded **3(1)** as a white solid (13.5 g, 88%): ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.78 (d, 4H), 7.34 (d, 4H), 4.13 (t, 4H), 3.65 (t, 4H), 3.52 (s, 4H), 2.44 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm), 144.9 (C), 132.9 (C), 129.8 (CH), 127.9 (CH), 70.6 (CH₂), 69.2 (CH₂), 68.7 (CH₂), 21.6 (CH₃). M.p. 82–83 °C (Ref. S1: 80–81 °C).

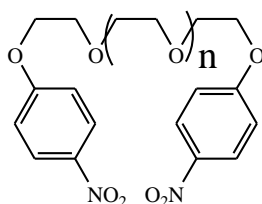
Ditosylates of $n = 2-4$ [Ts(OCH₂CH₂) _{$n+2$} OTs, **3(n)].** Ditosylates **3(n)** ($n = 2-4$) were prepared in the same way as **3(1)**. After removal of MgSO₄ and solvent, a clear, colorless viscous liquid was obtained. The product was pure enough for further use.

1,11-Bis(tosyloxy)-3,6,9-trioxaundecane [Ts(OCH₂CH₂)₄OTs, 3(2)]: Yield 93%. ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, 4H), 7.34 (d, 4H), 4.15 (t, 4H), 3.68 (t, 4H), 3.58 (m, 8H), 2.44 (s, 6H). ¹³C NMR (100 MHz, CDCl₃), 144.8 (C), 132.9 (C), 129.8 (CH), 127.9 (CH), 70.5 (CH₂), 69.3 (CH₂), 68.6 (CH₂), 21.6 (CH₃).

1,14-Bis(tosyloxy)-3,6,9,12-tetraoxatetradecane [Ts(OCH₂CH₂)₅OTs, 3(3)]: Yield 92%. ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, 4H), 7.34 (d, 4H), 4.14 (t, 4H), 3.68 (t, 4H), 3.59 (m, 12H), 2.44 (s, 6H). ¹³C NMR (100 MHz, CDCl₃), 144.8 (C), 132.9 (C), 129.8 (CH), 127.9 (CH), 70.6 (CH₂), 69.3 (CH₂), 68.6 (CH₂), 21.6 (CH₃).

1,17-Bis(tosyloxy)-3,6,9,12,15-pentaoxaheptadecane [Ts(OCH₂CH₂)₆OTs, 3(4)]: Yield 95%. ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, 4H), 7.34 (d, 4H), 4.15 (t, 4H), 3.68 (t, 4H), 3.60 (m, 16H), 2.45 (s, 6H). ¹³C NMR (100 MHz, CDCl₃), 144.8 (C), 132.9 (C), 129.8 (CH), 127.9 (CH), 70.5 (CH₂), 69.3 (CH₂), 68.6 (CH₂), 21.6 (CH₃).

1,8-Bis(4-nitrophenoxy)-3,6-dioxaoctane, 4(1).



4(1) can be prepared by nucleophilic displacement of the tosyl group of ditosylate by 4-nitrophenoxide ion. A solution of 4-nitrophenol (3.18 g, 0.023 mol), K₂CO₃ (9.50 g, 0.069 mol), and **3(1)** (5.00 g, 0.011 mol) in dry acetonitrile (40 mL) was refluxed under N₂ for 8 hours. The reaction mixture was then allowed to cool to room temperature, filtered and the solvent removed in vacuo. The crude product was purified by extracting twice with CH₂Cl₂/H₂O (v/v 30 mL/15 mL). The combined organic extracts were washed twice with H₂O (15 mL) and once with saturated aqueous sodium chloride solution (15 mL) and then dried (MgSO₄). Removal of MgSO₄ and solvent afforded **4(1)** as a pale yellow solid, which is recrystallized from dichloromethane/n-hexane/ethyl acetate (v/v 10:5:1) (3.7 g, 86%): ¹H NMR (400 MHz, CDCl₃): δ 8.18 (d, 4H), 6.97 (d, 4H), 4.22 (t, 4H), 3.91 (t, 4H), 3.77 (s, 4H). ¹³C NMR (100 MHz, CDCl₃), 163.8 (C), 141.6 (C), 125.9 (CH), 114.6 (CH), 70.9 (CH₂), 69.5 (CH₂), 68.2 (CH₂). M.p. 97–98 °C (Ref. S2: 96.5–97.5 °C).

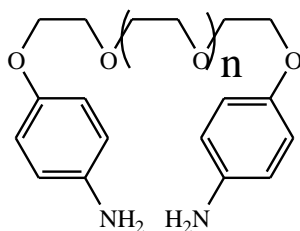
4(n) (*n* = 2–4) were prepared in the same way as **4(1)**.

1,11-Bis(4-nitrophenoxy)-3,6,9-trioxaundecane, 4(2): Yield 81%. ¹H NMR (400 MHz, CDCl₃): δ 8.17 (d, 4H), 6.98 (d, 4H), 4.23 (t, 4H), 3.90 (t, 4H), 3.72 (m, 8H). ¹³C NMR (100 MHz, CDCl₃), 163.9 (C), 141.5 (C), 125.8 (CH), 114.6 (CH), 70.8 (CH₂), 69.4 (CH₂), 68.2 (CH₂). M.p. 75–76 °C (Ref. S2: 76–77 °C).

1,14-Bis(4-nitrophenoxy)-3,6,9,12-tetraoxatetradecane, 4(3): Yield 78%. ^1H NMR (400 MHz, CDCl_3): δ 8.10 (d, 4H), 6.90 (d, 4H), 4.14 (t, 4H), 3.82 (t, 4H), 3.58 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3), 162.8 (C), 140.5 (C), 124.8 (CH), 113.6 (CH), 69.7 (CH_2), 68.4 (CH_2), 67.2 (CH_2). M.p. 92–93 °C (Ref. S2: 91–92 °C).

1, 17-Bis(4-nitrophenoxy)-3,6,9,12,15-pentaoxaheptadecane, 4(4): Yield 74%. ^1H NMR (400 MHz, CDCl_3): δ 8.20 (d, 4H), 6.98 (d, 4H), 4.22 (t, 4H), 3.89 (t, 4H), 3.67 (m, 16H). ^{13}C NMR (100 MHz, CDCl_3), 163.9 (C), 141.6 (C), 125.8 (CH), 114.6 (CH), 70.6 (CH_2), 69.4 (CH_2), 68.2 (CH_2). M.p. 63–64 °C (Ref. S2: 63–64 °C).

1,8-Bis(4-aminophenoxy)-3,6-dioxaoctane, 5(1).



Hydrazine monohydrate (8.0 mL) was added dropwise to a suspension of **4(1)** (2.50 g, 6.4 mmol) and Pd/C 10% (0.20 g, cat.) in methanol (300 mL). After refluxing under intensive stirring for 10 hours, the Pd/C was filtered off *via* suction filtration through celite, and then the solvent removed in vacuo. The crude product was purified by washing several times with water, small volumes of methanol, diethyl ether and dried over vacuum. The product **5(1)** was isolated as an off-white solid (1.7 g, 80%). ^1H NMR (400 MHz, CDCl_3): δ 6.75 (d, 4H), 6.60 (d, 4H), 4.03 (t, 4H), 3.81 (t, 4H), 3.73 (s, 4H), 3.39 (s, 4H, NH_2). ^{13}C NMR (100 MHz, CDCl_3), 151.9 (C), 140.2 (C), 116.3 (CH), 115.8 (CH), 70.8 (CH_2), 69.9 (CH_2), 68.1 (CH_2). M.p. 94–95 °C (Ref. S2: 92.2–92.6 °C).

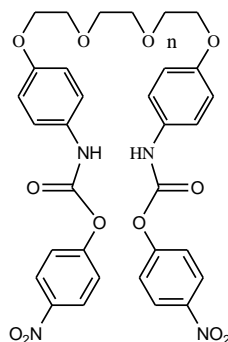
5(n) ($n = 2-4$) were prepared by the similar method as **5(1)**. After removing the solvent, the crude product was purified by extracting twice with $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ (v/v 30 mL/15 mL). The combined organic extracts were washed twice with H_2O (15 mL) and once with saturated aqueous sodium chloride solution (15 mL) and then dried (MgSO_4). Removal of MgSO_4 and solvent afforded **5(n)** as a pale white solid.

1,11-Bis(4-aminophenoxy)-3,6,9-trioxaundecane, 5(2): Yield 82%. this product was obtained as a viscous oil as reported in Ref. S2. ^1H NMR (400 MHz, CDCl_3): δ 6.74 (d, 4H), 6.60 (d, 4H), 4.03 (t, 4H), 3.80 (t, 4H), 3.69 (m, 8H), 3.30 (s, 4H, NH_2). ^{13}C NMR (100 MHz, CDCl_3), 151.8 (C), 140.2 (C), 116.3 (CH), 115.8 (CH), 70.7 (CH_2), 69.9 (CH_2), 68.1 (CH_2).

1,14-Bis(4-aminophenoxy)-3,6,9,12-tetraoxatetradecane, 5(3): Yield 83%. ^1H NMR (400 MHz, CDCl_3): δ 6.74 (d, 4H), 6.60 (d, 4H), 4.03 (t, 4H), 3.79 (t, 4H), 3.65 (m, 12H), 3.36 (s, 4H, NH_2). ^{13}C NMR (100 MHz, CDCl_3), 151.8 (C), 140.2 (C), 116.3 (CH), 115.8 (CH), 70.6 (CH_2), 69.8 (CH_2), 68.1 (CH_2). M.p. 55–56 °C (Ref. S2: 54–55 °C).

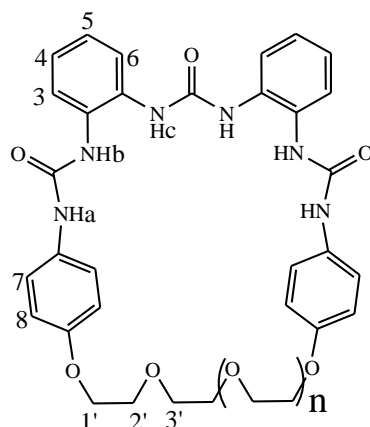
1,17-Bis(4-aminophenoxy)-3,6,9,12,15-pentaoxaheptadecane, 5(4): Yield 85%. ^1H NMR (400 MHz, CDCl_3): δ 6.74 (d, 4H), 6.60 (d, 4H), 4.03 (t, 4H), 3.79 (t, 4H), 3.65 (m, 16H), 3.43 (s, 4H, NH_2). ^{13}C NMR (100 MHz, CDCl_3), 151.8 (C), 140.3 (C), 116.3 (CH), 115.8 (CH), 70.6 (CH_2), 69.9 (CH_2), 68.1 (CH_2). M.p. 57–58 °C (Ref. S2: 56–57 °C).

Oligomeric ethylene glycol di(4-nitrophenyl-N-(4-phenyl)-carbamate), 6(*n*).



To a solution of 4-nitrophenyl chloroformate (0.24 g, 1.2 mmol) in dry THF (50 mL) was slowly added a solution of **5(1)** (0.2 g, 0.6 mmol) in dry THF (50 mL) over a period of 30 min under a dry nitrogen atmosphere and ice-cooling. After being stirred for an additional 2 h at room temperature, the reaction mixture was filtered and the filtrate was used immediately in the next step without any purification or characterization.

1,3-Bis(2-(4-(1,4,7,10-tetraoxa-decane-1,10-diyl)phenyl)urea-phenyl)urea, (L¹)



A solution of **6(1)** in dry THF (100 mL) prepared in the step above and a solution of 1,3-bis(2-aminophenyl)urea (**7**, 0.15 g, 0.6 mmol) in dry THF (150 mL), which was prepared by literature method,^{S3} were added dropwise simultaneously to a flask containing 0.8 L dry THF under stirring, refluxing and inert atmosphere over 2 h. After that, triethyl amine (1.0 mL) was added to this solution, and the mixture was stirred for an additional 3 h. Then the solvent was evaporated and the crude product was purified by column chromatography using 10 % MeOH/ CH_2Cl_2 as the eluent to give the pure product as a white solid (0.12 g, 31%): M.p.: 234–235 °C. Anal. Calc. for $\text{C}_{33}\text{H}_{34}\text{N}_6\text{O}_7$ (M = 626.7): C, 63.25; H, 5.47;

N, 13.41. Found: C, 63.12; H, 5.39; N, 13.56. ^1H NMR (400 MHz, DMSO- d_6 , ppm): δ 8.73 (s, 2H, Hb), 8.53 (s, 2H, Hc), 8.06 (s, 2H, Ha), 7.61 (m, 2H, H6), 7.51 (m, 2H, H3), 7.24 (d, $J = 8.8$ Hz, 4H, H7), 7.08 (m, 4H, H4 + H5), 6.72 (d, $J = 8.8$ Hz, 4H, H8), 3.97 (t, $J = 4.8$ Hz, 4H, H1'), 3.72 (t, $J = 4.8$ Hz, 4H, H2'), 3.60 (s, 4H, H3'). ^{13}C NMR (100 MHz, DMSO- d_6): δ 153.9 (CO), 153.4 (CO), 132.7 (C), 131.5 (C), 131.4 (C), 124.0 (CH), 123.9 (CH), 120.2 (CH), 114.6 (CH), 70.2 (CH $_2$), 68.9 (CH $_2$), 67.5 (CH $_2$). IR (KBr, v/cm^{-1}): 3282 (N-H), 2925, 2869, 1644 (C=O), 1557, 1510, 1452, 1300, 1241. ESI-MS (m/z): $[\text{M}-\text{H}]^-$ 625.2525, $[\text{M}+\text{Cl}]^-$ 661.2291.

L^n ($n = 2-4$) were prepared in the same way as L^1 .

1,3-Bis(2-(4-(1,4,7,10,13-pentaoxa-tridecane-1,13-diyl)phenyl)urea-phenyl)urea, (L^2): Yield 27%. M.p.: 210–211 °C. Anal. Calc. for $\text{C}_{35}\text{H}_{38}\text{N}_6\text{O}_8$ ($M = 670.7$): C, 62.68; H, 5.71; N, 12.53. Found: C, 62.84; H, 5.79; N, 12.41. ^1H NMR (400 MHz, DMSO- d_6 , ppm): δ 8.76 (s, 2H, Hb), 8.53 (s, 2H, Hc), 7.98 (s, 2H, Ha), 7.61 (m, 2H, H6), 7.51 (m, 2H, H3), 7.29 (d, $J = 8.8$ Hz, 4H, H7), 7.08 (m, 4H, H4 + H5), 6.77 (d, $J = 8.8$ Hz, 4H, H8), 3.96 (m, 4H, H1'), 3.71 (m, 4H, H2'), 3.55 (m, 8H, H3'). ^{13}C NMR (100 MHz, DMSO- d_6): δ 153.9 (CO), 153.3 (CO), 132.8 (C), 131.6 (C), 131.1 (C), 124.4 (CH), 123.8 (CH), 119.7 (CH), 114.2 (CH), 69.9 (CH $_2$), 69.0 (CH $_2$), 67.2 (CH $_2$). IR (KBr, v/cm^{-1}): 3283 (N-H), 2922, 2870, 1640 (C=O), 1557, 1509, 1451, 1299, 1240. ESI-MS (m/z): $[\text{M}-\text{H}]^-$ 669.2747, $[\text{M}+\text{Cl}]^-$ 705.2488.

1,3-Bis(2-(4-(1,4,7,10,13,16-hexaoxa-hexadecane-1,16-diyl)phenyl)urea-phenyl) urea, (L^3): Yield 25%. M.p.: 203–204 °C. Anal. Calc. for $\text{C}_{37}\text{H}_{42}\text{N}_6\text{O}_9$ ($M = 714.8$): C, 62.17; H, 5.92; N, 11.76. Found: C, 62.04; H, 5.80; N, 11.91. ^1H NMR (400 MHz, DMSO- d_6 , ppm): δ 8.76 (s, 2H, Hb), 8.51 (s, 2H, Hc), 7.98 (s, 2H, Ha), 7.62 (m, 2H, H6), 7.52 (m, 2H, H3), 7.29 (d, $J = 8.8$ Hz, 4H, H7), 7.07 (m, 4H, H4 + H5), 6.78 (d, $J = 8.8$ Hz, 4H, H8), 3.98 (t, $J = 4.8$ Hz, 4H, H1'), 3.71 (t, $J = 4.8$ Hz, 4H, H2'), 3.55 (m, 12H, H3'). ^{13}C NMR (100 MHz, DMSO- d_6): δ 153.9 (CO), 153.4 (CO), 132.8 (C), 131.6 (C), 131.1 (C), 124.3 (CH), 123.8 (CH), 119.8 (CH), 114.4 (CH), 70.0 (CH $_2$), 69.0 (CH $_2$), 67.2 (CH $_2$). IR (KBr, v/cm^{-1}): 3292 (N-H), 2922, 1647 (C=O), 1558, 1510, 1454, 1302, 1216. ESI-MS (m/z): $[\text{M}-\text{H}]^-$ 713.3108, $[\text{M}+\text{Cl}]^-$ 749.2862.

1,3-Bis(2-(4-(1,4,7,10,13,16,19-heptaoxa-nonadecane-1,19-diyl)phenyl)urea-phenyl) urea, (L^4): Yield 20%. M.p.: 207–208 °C. Anal. Calc. for $\text{C}_{39}\text{H}_{46}\text{N}_6\text{O}_{10}$ ($M = 758.8$): C, 61.73; H, 6.11; N, 11.08. Found: C, 61.54; H, 6.02; N, 11.16. ^1H NMR (400 MHz, DMSO- d_6 , ppm): δ 8.77 (s, 2H, Hb), 8.49 (s, 2H, Hc), 7.97 (s, 2H, Ha), 7.64 (m, 2H, H6), 7.52 (m, 2H, H3), 7.31 (d, $J = 8.8$ Hz, 4H, H7), 7.07 (m, 4H, H4 + H5), 6.80 (d, $J = 8.8$ Hz, 4H, H8), 3.99 (t, $J = 4.8$ Hz, 4H, H1'), 3.70 (t, $J = 4.8$ Hz, 4H, H2'), 3.54 (m, 16H, H3'). ^{13}C NMR (100 MHz, DMSO- d_6): δ 153.9 (CO), 153.4 (CO), 132.8 (C), 131.6 (C), 130.9 (C), 123.9 (CH), 123.7 (CH), 119.8 (CH), 114.5 (CH), 69.9 (CH $_2$), 69.0 (CH $_2$), 67.2 (CH $_2$). IR (KBr, v/cm^{-1}): 3287 (N-H), 2872, 1646 (C=O), 1552, 1510, 1452, 1300, 1238. ESI-MS (m/z): $[\text{M}-\text{H}]^-$ 757.3434, $[\text{M}+\text{Cl}]^-$ 793.3189.

S3. X-ray crystallography

Diffraction data of the complexes were collected on a Bruker SMART APEX II diffractometer at 100 or 150 K with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). An empirical absorption correction using SADABS was applied for all data. The structures were solved by direct 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 SHELXL program. Hydrogen atoms bonded to carbon and nitrogen were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. CCDC 1456031–1456038.

Table S1. Crystal data and refinement details for complexes **1–4**.

| | 1 | 2 | 3 | 4 |
|---|---|---|---|--|
| Formula | C ₁₀₅ H ₁₄₃ N ₁₂ O ₃₇ PK ₂ | C ₉₈ H ₁₂₈ N ₁₆ O ₂₈ PK | C ₁₁₆ H ₁₇₄ N ₁₇ O ₂₇ P | C ₃₆₀ H ₄₉₀ K ₈ N ₄₈ O ₁₃₃ S ₄ |
| <i>M</i> | 2274.48 | 2048.23 | 2269.69 | 8059.04 |
| Crystal system | Triclinic | Triclinic | Triclinic | Monoclinic |
| Space group | <i>P</i> -1 | <i>P</i> -1 | <i>P</i> -1 | <i>P</i> 2 ₁ / <i>c</i> |
| <i>a</i> /Å | 16.775(3) | 14.990(4) | 14.782(2) | 16.6867(18) |
| <i>b</i> /Å | 19.152(4) | 16.270(4) | 19.415(3) | 19.400(2) |
| <i>c</i> /Å | 20.418(4) | 25.088(6) | 21.552(3) | 32.767(3) |
| α /° | 93.782(3) | 99.668(4) | 85.538(2) | 90 |
| β /° | 113.688(2) | 100.824(4) | 85.989(2) | 112.755(4) ° |
| γ /° | 106.847(3) | 105.587(4) | 89.867(2) | 90 |
| <i>V</i> /Å ³ | 5623.5(18) | 5632(2) | 6151.5(17) | 9781.8(17) |
| <i>Z</i> | 2 | 2 | 2 | 1 |
| <i>T</i> /K | 296(2) | 296(2) | 188(2) | 100(2) |
| <i>F</i> (000) | 2412 | 2172 | 2446 | 4266 |
| <i>D</i> _{calc} /g cm ⁻³ | 1.343 | 1.208 | 1.225 | 1.368 |
| μ /mm ⁻¹ | 0.187 | 0.138 | 0.100 | 0.207 |
| <i>R</i> (int) | 0.1138 | 0.0743 | 0.0689 | 0.0357 |
| Data/restraints/ parameters | 19321/1464/ 1417 | 19655/2162/ 1282 | 24370/1200/ 1429 | 24420/2344/ 1473 |
| GOF | 1.186 | 1.093 | 1.095 | 1.143 |
| <i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)] | 0.1465 | 0.1228 | 0.1300 | 0.0523 |
| <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)] | 0.2739 | 0.2519 | 0.2572 | 0.1332 |

Table S2. Crystal data and refinement details for complexes **5–8**.

| | 5 | 6 | 7 | 8 |
|--|---|--|---|--|
| Formula | C ₉₇ H ₁₃₂ N ₁₃ O ₃₅ K ₂ S | C ₅₀ H ₇₅ N ₁₀ O ₁₄ Cl | C ₅₁ H ₇₈ N ₉ O ₁₄ Cl | C ₅₁ H ₆₈ I ₂ N ₁₀ O ₁₀ |
| <i>M</i> | 2150.42 | 1075.65 | 1070.63 | 1234.95 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | <i>P2(1)/c</i> | <i>Cc</i> | <i>P2(1)/c</i> | <i>P-1</i> |
| <i>a</i> /Å | 18.0761(18) | 20.611(5) | 18.572(5) | 12.2750(16) |
| <i>b</i> /Å | 21.110(2) | 31.842(8) | 34.162(8) | 13.0629(17) |
| <i>c</i> /Å | 32.803(3) | 8.872(2) | 8.774(2) | 19.863(3) |
| <i>α</i> /° | 90 | 90 | 90 | 71.072(2) |
| <i>β</i> /° | 122.130(4) | 104.307(5) | 94.732(4) | 78.8600(10) |
| <i>γ</i> /° | 90 | 90 | 90 | 70.582(2) |
| <i>V</i> /Å ³ | 10600.1(18) | 5642(2) | 5548(2) | 2828.3(6) |
| <i>Z</i> | 4 | 4 | 4 | 2 |
| <i>T</i> /K | 173(2) | 296(2) | 173(2) | 173(2) |
| <i>F</i> (000) | 4556 | 2296 | 2304 | 1260 |
| <i>D</i> _{calc} /g cm ⁻³ | 1.347 | 1.266 | 1.289 | 1.450 |
| <i>μ</i> /mm ⁻¹ | 0.197 | 0.138 | 0.140 | 1.175 |
| <i>R</i> (int) | 0.1498 | 0.0408 | 0.0783 | 0.0236 |
| Data/restraints/ parameters | 18839/1408/ 1333 | 7028/2/ 683 | 9855/1032/ 657 | 9664/24/ 650 |
| GOF | 1.157 | 1.028 | 1.179 | 1.156 |
| <i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)] | 0.1846 | 0.0474 | 0.1890 | 0.0685 |
| <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)] | 0.3121 | 0.1296 | 0.3684 | 0.1542 |

Table S3. Hydrogen bonds [Å and °] in the crystal structure of complex **1**.

| D–H···A | <i>d</i> (D–H) (Å) | <i>d</i> (H···A) (Å) | <i>d</i> (D···A) (Å) | ∠(DHA) (°) |
|--------------|--------------------|----------------------|----------------------|------------|
| N1–H1···O27 | 0.860 | 1.893 | 2.735 | 166 |
| N2–H2···O27 | 0.860 | 2.146 | 2.93 | 151 |
| N3–H3A···O26 | 0.860 | 2.145 | 2.959 | 157 |
| N4–H4A···O26 | 0.860 | 2.246 | 3.035 | 152 |
| N5–H5A···O25 | 0.860 | 2.207 | 3.025 | 158 |
| N6–H6A···O27 | 0.860 | 2.294 | 2.868 | 124 |

| | | | | |
|----------------|-------|-------|-------|-----|
| N7–H7 ..O26 | 0.860 | 1.97 | 2.794 | 160 |
| N8–H8 ..O25 | 0.860 | 2.107 | 2.941 | 163 |
| N9–H9 ..O25 | 0.860 | 1.897 | 2.736 | 165 |
| N10–H10A ..O25 | 0.860 | 2.488 | 3.231 | 145 |
| N11–H11A ..O28 | 0.860 | 2.177 | 3.005 | 161 |
| N12–H12 ..O26 | 0.860 | 1.974 | 2.813 | 165 |
| O28–H28 ..O1* | 0.820 | 1.873 | 2.683 | 169 |

* [-x+1, -y+1, -z+2]

Table S4. Hydrogen bonds [\AA and $^\circ$] in the crystal structures of complex **2**

| D–H...A | $d(\text{D–H})$ (\AA) | $d(\text{H...A})$ (\AA) | $d(\text{D...A})$ (\AA) | $\angle(\text{DHA})$ ($^\circ$) |
|------------------|----------------------------------|------------------------------------|------------------------------------|-----------------------------------|
| N1–H1 ..O28 | 0.860 | 2.012 | 2.816 | 155 |
| N2–H2 ..O25 | 0.860 | 1.945 | 2.804 | 178 |
| N3–H3A ..O25 | 0.860 | 2.23 | 2.936 | 139 |
| N4–H4A ..O26 | 0.860 | 1.941 | 2.798 | 174 |
| N5–H5A ..O28 | 0.860 | 2.233 | 2.987 | 146 |
| N6–H6A ..O28 | 0.860 | 1.938 | 2.733 | 153 |
| N7–H7 ..O25 | 0.860 | 1.997 | 2.777 | 150 |
| N8–H8 ..O26 | 0.860 | 2.062 | 2.88 | 158 |
| N9–H9 ..O26 | 0.860 | 1.922 | 2.766 | 167 |
| N10–H10I ..O27 | 0.860 | 1.975 | 2.795 | 159 |
| N11–H11A ..O27 | 0.860 | 1.967 | 2.825 | 175 |
| N12–H12 ..O25 | 0.860 | 1.935 | 2.782 | 168 |
| C89–H89...O5* | 0.93 | 2.44 | 3.358(10) | 167 |
| C90–H90B...O7* | 0.97 | 2.36 | 3.07(2) | 130 |
| C90–H90B...O6* | 0.97 | 2.59 | 3.37(2) | 138 |
| C91–H91A...O17* | 0.96 | 2.52 | 3.46(2) | 165 |
| C91–H91B...O8* | 0.96 | 2.58 | 3.40(2) | 144 |
| C88–H88...O17* | 0.93 | 2.45 | 3.045(10) | 122 |
| C88–H88...O16* | 0.93 | 2.06 | 2.949(10) | 159 |
| C113–H11C...O13* | 0.96 | 2.60 | 3.01(2) | 106 |

* [x, y, 1+z]

Table S5. Hydrogen bonds [\AA and $^\circ$] in the crystal structure of complex **3**.

| D–H \cdots A | $d(\text{D–H})$ (\AA) | $d(\text{H}\cdots\text{A})$ (\AA) | $d(\text{D}\cdots\text{A})$ (\AA) | $\angle(\text{DHA})$ ($^\circ$) |
|-------------------------|----------------------------------|--|--|-----------------------------------|
| N1–H1 \cdots O22* | 0.880 | 1.951 | 2.821 | 170 |
| N2–H2 \cdots O21* | 0.880 | 2.266 | 2.799 | 119 |
| N3–H3A \cdots O21* | 0.880 | 2.004 | 2.846 | 160 |
| N4–H4A \cdots O23* | 0.880 | 1.86 | 2.734 | 172 |
| N5–H5A \cdots O23* | 0.880 | 1.849 | 2.72 | 170 |
| N6–H6A \cdots O22* | 0.880 | 2.443 | 3.062 | 128 |
| N7–H7 \cdots O21 | 0.880 | 2 | 2.841 | 160 |
| N8–H8 \cdots O22 | 0.880 | 2.163 | 2.796 | 128 |
| N9–H9 \cdots O24 | 0.880 | 2.12 | 2.918 | 150 |
| N10–H10T \cdots O24 | 0.880 | 1.883 | 2.725 | 160 |
| N11–H11W \cdots O24 | 0.880 | 1.95 | 2.79 | 159 |
| N12–H12 \cdots O24 | 0.880 | 2.113 | 2.914 | 151 |
| C94–H94 \cdots O18 | 0.95 | 2.48 | 3.331(11) | 149 |
| C94–H94 \cdots O17 | 0.95 | 2.7 | 3.345(11) | 126 |
| C104–H10L \cdots O18 | 0.99 | 2.63 | 3.516(17) | 149 |
| C104–H10M \cdots O15 | 0.99 | 2.18 | 3.11(2) | 155 |
| C105–H10N \cdots O14 | 0.98 | 2.85 | 3.695(18) | 145 |
| C95–H95 \cdots O13 | 0.95 | 2.75 | 3.606(13) | 151 |
| C96–H96 \cdots O7** | 0.95 | 2.38 | 3.212(10) | 146 |
| C103–H10J \cdots O6** | 0.98 | 2.74 | 3.591(15) | 146 |
| C103–H10L \cdots O2** | 0.98 | 2.54 | 3.298(16) | 134 |

* $[x+1, y, z]$; ** $[x-1, y, z]$ **Table S6.** Hydrogen bonding parameters (\AA , $^\circ$) for SO_4^{2-} binding in complex **4**.

| N–H \cdots O | H \cdots O | N \cdots O | $\angle\text{N–H}\cdots\text{O}$ |
|-------------------|--------------|--------------|----------------------------------|
| N1–H1 \cdots O1 | 2.11 | 2.936(3) | 155 |
| N2–H2 \cdots O1 | 2.21 | 3.036(3) | 157 |
| N3–H3 \cdots O2 | 2.17 | 2.960(3) | 150 |
| N4–H4 \cdots O4 | 2.26 | 3.054(3) | 150 |
| N5–H5 \cdots O1 | 2.21 | 3.029(3) | 156 |
| N6–H6 \cdots O1 | 2.11 | 2.922(3) | 154 |

| | | | |
|----------------|------|----------|------|
| N7–H7···O3 | 2.16 | 2.911(3) | 143 |
| N8–H8···O4 | 2.13 | 2.917(3) | 148. |
| N9–H9···O4 | 2.10 | 2.968(3) | 169 |
| N10–H10···O2 | 2.13 | 2.993(3) | 167 |
| N11–H11···O2 | 2.04 | 2.903(3) | 168 |
| N12–H12···O3 | 2.03 | 2.903(3) | 169 |
| C63–H63B···O15 | 2.43 | 3.153(3) | 130 |
| C64–H64A···O18 | 2.52 | 3.206(3) | 126 |

Table S7. The parameters (Å, °) of C–H··· π interactions involved in complex **4**.

| C–H··· π | D(H··Cg*) | D(C··Cg) | D(H··plane) | \angle C–H··Cg |
|-----------------|-----------|----------|-------------|------------------|
| C6–H6A·· π | 3.26 | 3.87 | 3.04 | 124 |
| C26–H26·· π | 3.16 | 3.73 | 2.99 | 120 |
| C39–H39·· π | 3.01 | 3.80 | 2.93 | 142 |
| C59–H59·· π | 2.96 | 3.60 | 2.90 | 126 |

* Cg represents the centroid of the aryl ring.

Table S8. Hydrogen bonds [\AA and °] in the crystal structure of complex **5**.

| D–H···A | $d(\text{D–H})$ (\AA) | $d(\text{H··A})$ (\AA) | $d(\text{D··A})$ (\AA) | $\angle(\text{DHA})$ (°) |
|-----------------|----------------------------------|-----------------------------------|-----------------------------------|--------------------------|
| N1–H1···O20 | 0.88 | 2.488 | 3.316 | 157 |
| N2–H2···O19 | 0.88 | 2.011 | 2.873 | 166 |
| N3–H3A···O22 | 0.88 | 2.418 | 3.188 | 146 |
| N4–H4A···O22 | 0.88 | 2.000 | 2.871 | 170 |
| N5–H5A···O22 | 0.88 | 2.187 | 2.954 | 145 |
| N6–H6A···O20 | 0.88 | 2.07 | 2.941 | 170 |
| N7–H7···O20* | 0.88 | 2.051 | 2.883 | 157 |
| N8–H8···O19* | 0.88 | 2.365 | 3.08 | 139 |
| N9–H9···O19* | 0.88 | 2.152 | 2.982 | 157 |
| N10–H10A···O21* | 0.88 | 2.024 | 2.901 | 174 |
| N11–H11A···O21* | 0.88 | 2.017 | 2.876 | 165 |
| N12–H12···O21* | 0.88 | 2.455 | 3.235 | 148 |
| C61–H61A···O7* | 0.99 | 2.33 | 3.25(3) | 153 |

*[$x, -y+1/2, z+1/2$]

Table S9. Hydrogen bonds [\AA and $^\circ$] in the crystal structure of complex **6**.

| D–H \cdots A | $d(\text{D–H})$ (\AA) | $d(\text{H}\cdots\text{A})$ (\AA) | $d(\text{D}\cdots\text{A})$ (\AA) | $\angle(\text{DHA})$ ($^\circ$) |
|----------------------|----------------------------------|--|--|-----------------------------------|
| N1–H1 \cdots O1* | 0.86 | 2.101 | 2.839 | 144 |
| N2–H2 \cdots O1* | 0.86 | 2.199 | 2.921 | 141 |
| N3–H3A \cdots Cl1* | 0.86 | 2.657 | 3.445 | 153 |
| N4–H4A \cdots Cl1* | 0.86 | 2.255 | 3.102 | 168 |
| N5–H5A \cdots Cl1* | 0.86 | 2.567 | 3.363 | 154 |
| N6–H6A \cdots Cl1* | 0.86 | 2.440 | 3.231 | 153 |

*[x, -y, z+1/2]

Table S10. Hydrogen bonds [\AA and $^\circ$] in the crystal structure of complex **7**.

| D–H \cdots A | $d(\text{D–H})$ (\AA) | $d(\text{H}\cdots\text{A})$ (\AA) | $d(\text{D}\cdots\text{A})$ (\AA) | $\angle(\text{DHA})$ ($^\circ$) |
|--------------------|----------------------------------|--|--|-----------------------------------|
| N1–H1 \cdots Cl1 | 0.88 | 2.601 | 3.400 | 151 |
| N2–H2 \cdots Cl1 | 0.88 | 2.290 | 3.148 | 169 |
| N3–H3 \cdots Cl1 | 0.88 | 2.317 | 3.166 | 170 |
| N4–H4 \cdots Cl1 | 0.88 | 2.601 | 3.381 | 151 |
| N5–H5 \cdots O9* | 0.88 | 2.131 | 2.869 | 146 |
| N6–H6 \cdots O9* | 0.88 | 2.249 | 2.959 | 140 |

*[x, -y+1/2, z-1/2]

Table S11. Hydrogen bonds [\AA and $^\circ$] in the crystal structure of complex **8**.

| D–H \cdots A | $d(\text{D–H})$ (\AA) | $d(\text{H}\cdots\text{A})$ (\AA) | $d(\text{D}\cdots\text{A})$ (\AA) | $\angle(\text{DHA})$ ($^\circ$) |
|---------------------|----------------------------------|--|--|-----------------------------------|
| N1–H1...I2 | 0.88 | 2.829 | 3.671 | 161 |
| N2–H2...I2 | 0.88 | 2.753 | 3.611 | 165 |
| N5–H5A...I1* | 0.88 | 2.927 | 3.72 | 151 |
| N4–H4A...I1* | 0.88 | 2.797 | 3.662 | 168 |
| N6–H6A...I1* | 0.88 | 2.959 | 3.801 | 161 |
| N3–H3A...I1* | 0.88 | 2.87 | 3.708 | 160 |
| C(51)–H(51C)...O(8) | 0.98 | 2.69 | 3.373(12) | 127 |
| C(51)–H(51C)...O(7) | 0.98 | 2.48 | 3.434(14) | 165 |
| C(54)–H(54A)...O(6) | 0.99 | 2.64 | 3.537(19) | 151 |
| C(54)–H(54B)...O(4) | 0.99 | 2.60 | 3.459(18) | 145 |

*[-x+1, -y+1, -z+1]

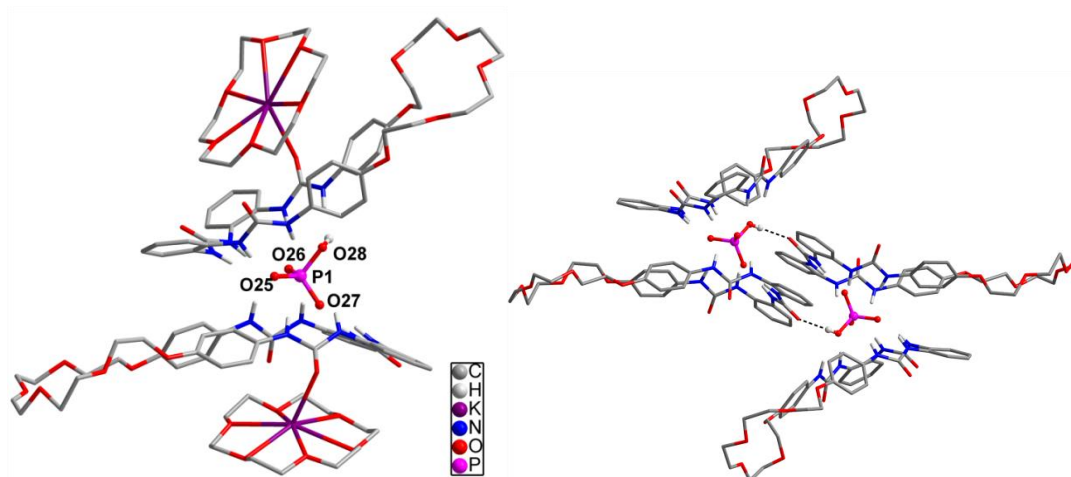


Fig. S1. Crystal structure of the HPO_4^{2-} complex **1** including $[\text{K}([\text{18}]\text{-crown-6})]^+$ counterions (left); the dimeric structure of complex **1** linked by two $\text{O}-\text{H}\cdots\text{O}$ bonds from HPO_4^{2-} ion to $\text{C}=\text{O}$ (right). Non-interacting hydrogen atoms and solvents are omitted for clarity.

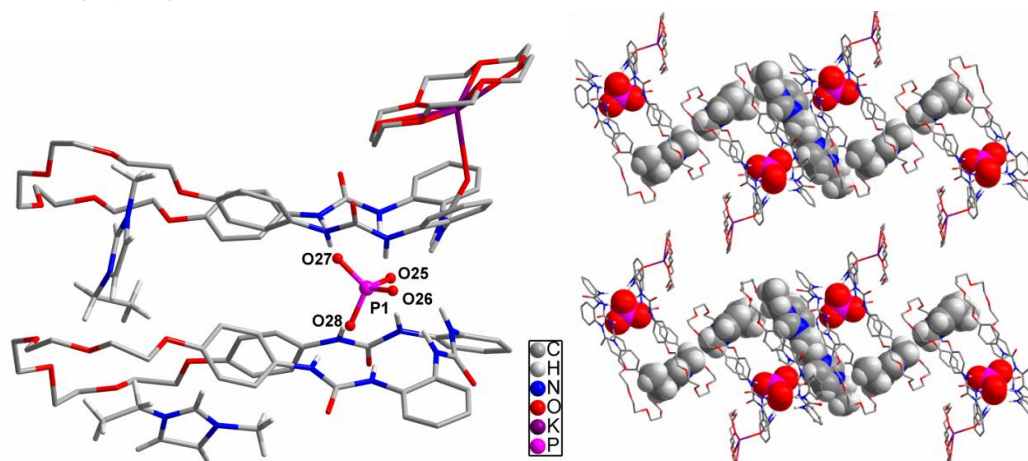


Fig. S2. Crystal structure of the PO_4^{3-} complex **2** including $[\text{K}([\text{18}]\text{-crown-6})]^+$ and Emim^+ counterions (left), and packing mode of the Emim^+ cation and PO_4^{3-} anion in complex **2** (right). Non-interacting hydrogen atoms and solvents are omitted for clarity.

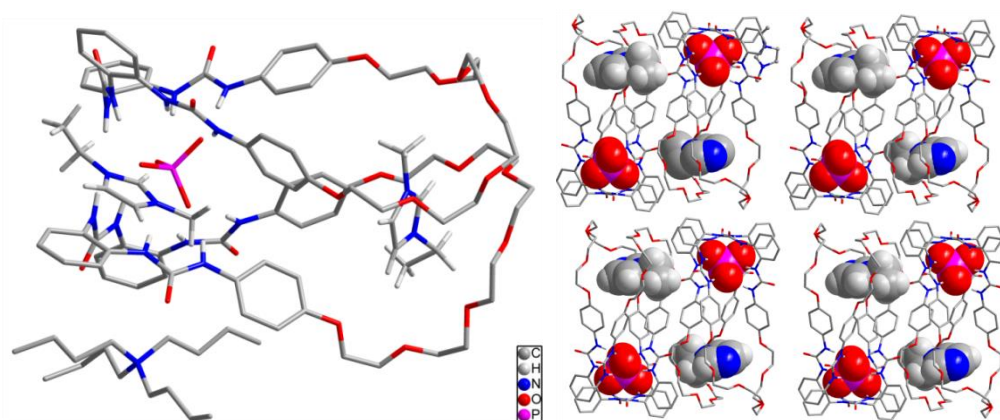


Fig. S3. Crystal structure of the PO_4^{3-} complex **3** including $[\text{K}([\text{18}]\text{-crown-6})]^+$ and Emim^+ counterions (left); b) packing mode of the Emim^+ cation and PO_4^{3-} anion (right). Non-interacting hydrogen atoms and solvents are omitted for clarity.

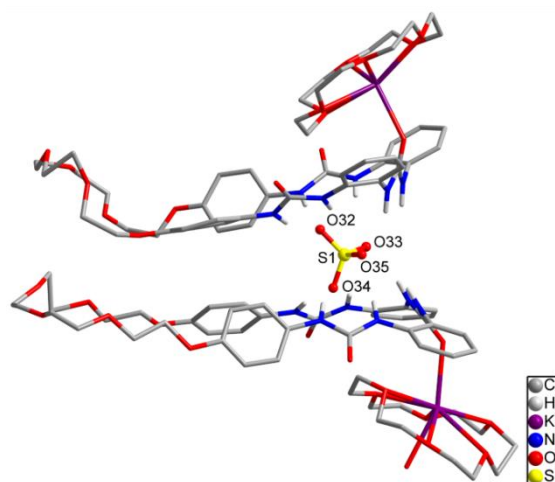


Fig. S4. Crystal structure of the SO_4^{2-} complex **5** including $[\text{K}([18]\text{-crown-6})]^+$ counteranions. Non-interacting hydrogen atoms and solvents are omitted for clarity.

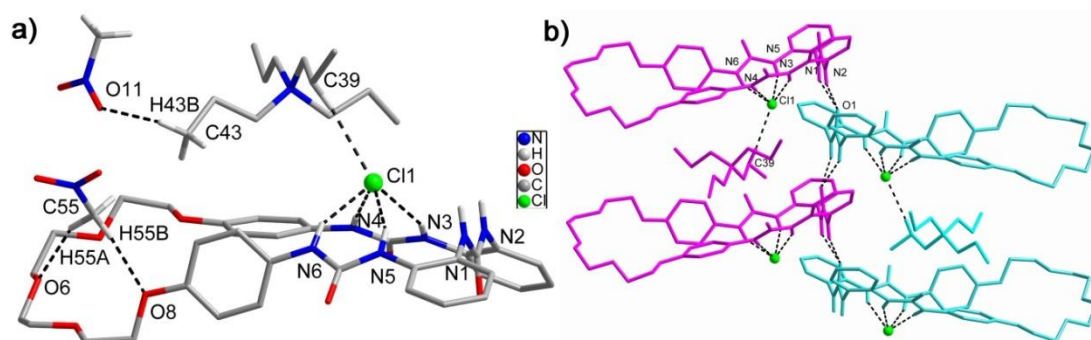


Fig. S5. a) Crystal structure of the chloride complex **6** including TPA^+ counteranions; b) the herringbone packing structure formed by L^2 and Cl^- ion. Non-interacting hydrogen atoms and solvents are omitted for clarity.

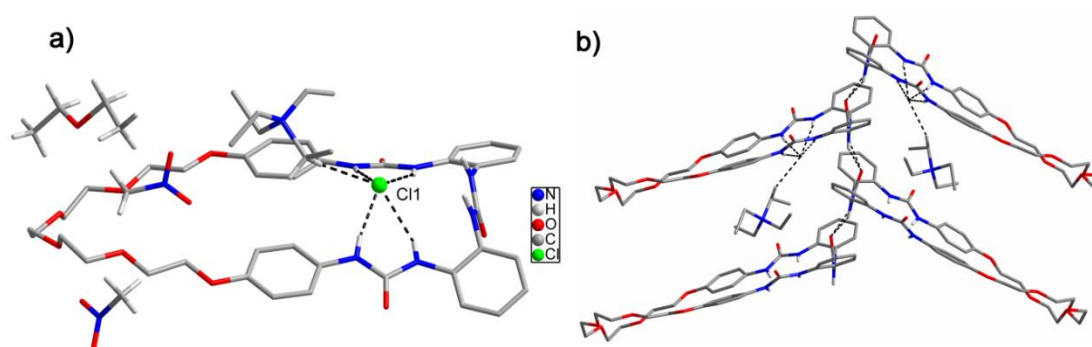


Fig. S6. a) Crystal structure of the chloride complex **7** including TEA^+ counteranions; b) the herringbone packing structure formed by L^3 and Cl^- ion. Non-interacting hydrogen atoms and solvents are omitted for clarity.

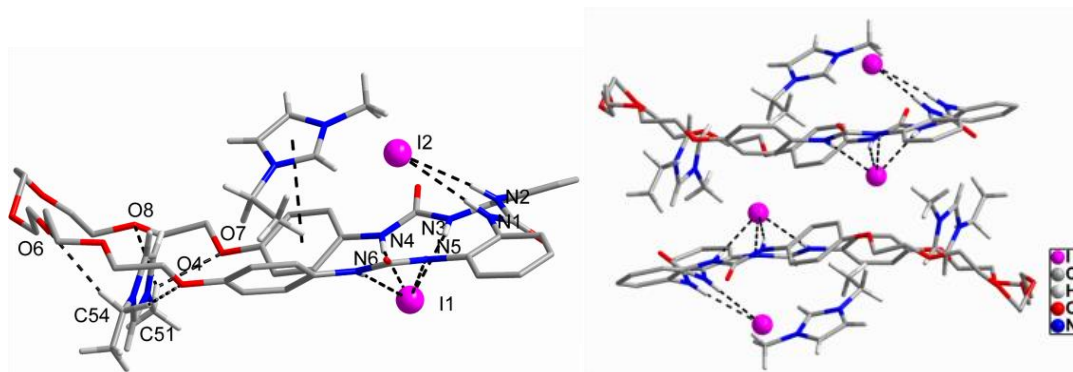


Fig. S7. Crystal structure of the iodide complex **8** including Emim⁺ counteranions and the “head-to-tail” packing mode. Non-interacting hydrogen atoms and solvents are omitted for clarity.

S4. ¹H NMR studies

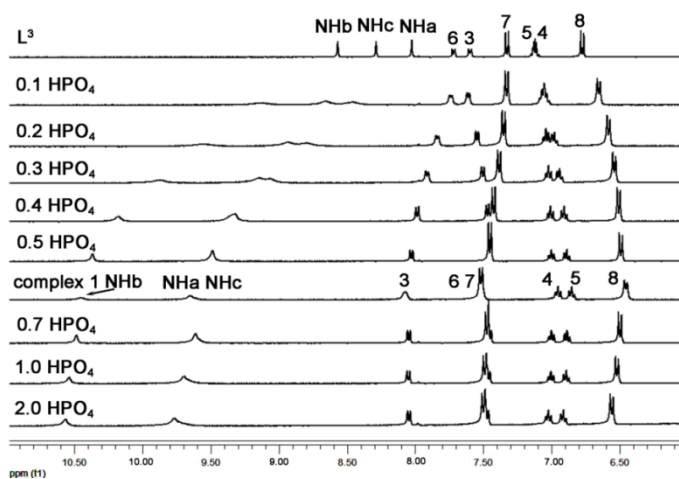


Fig. S8. ¹H NMR titration of **L³** (5×10^{-3} M) with $[K([18]\text{-crown-}6)_2\text{HPO}_4]$ and the spectrum of complex **1** in acetone-*d*₆/5% H₂O (400 MHz, 298 K)

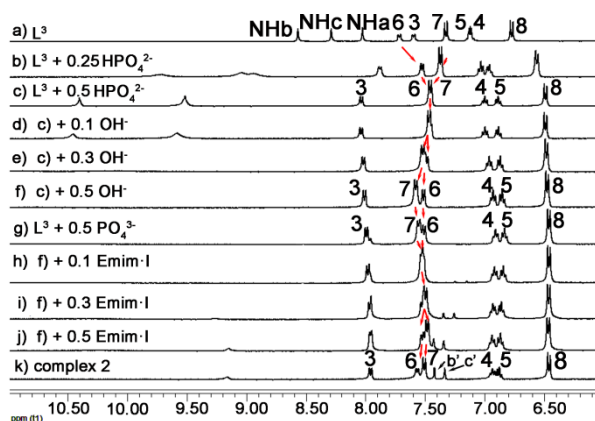


Fig. S9. ¹H NMR titration of complex **1** (**L³** + 0.5 equ HPO₄²⁻) (5×10^{-3} M) with TMAOH and Emim-I and the spectrum of complex **2** in acetone-*d*₆/5% H₂O (400 MHz, 298 K)

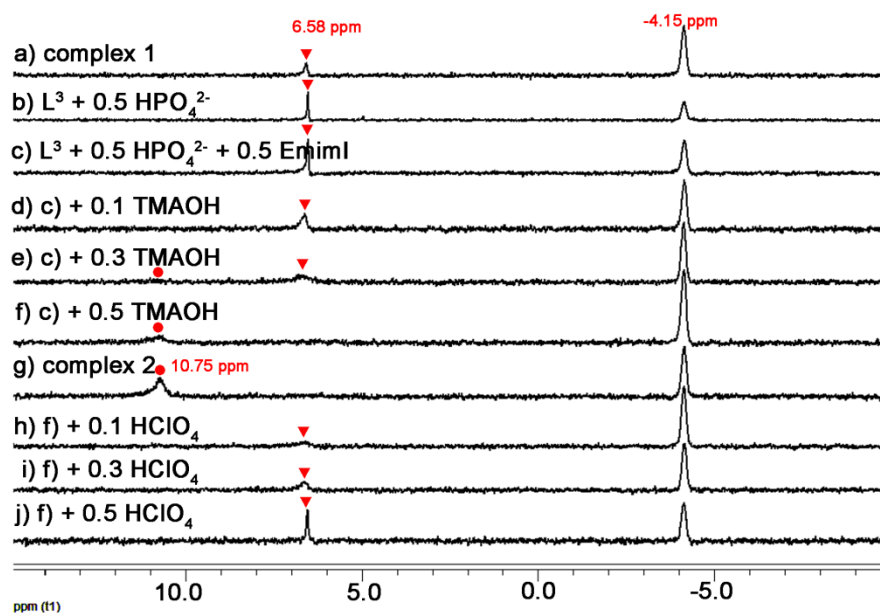


Fig. S10. Details of ^{31}P NMR detection of the reversible interconversion of **1** and **2** upon acid/base and cation modulation and the ^{31}P NMR spectra of complexes **1** and **2** in acetone- d_6 /5% H_2O (162 MHz, 298 K, PPh_3 as an internal standard).

(1) ^1H NMR titrations

A stock solution of L^n ($n = 1-5$) (5.0 mM) in $\text{DMSO-}d_6$ -10% H_2O (v/v) (0.5 mL) was prepared for the ^1H NMR titrations. Stock solutions of anion as $[\text{K}(18\text{-crown-6})]_2\text{SO}_4$ (1 mL, 0.05–1 M) were prepared in $\text{DMSO-}d_6$ -40% H_2O (v/v). Small portions (2–5 μL) of the anion solution were added to the 0.5 mL host solution of L^n in 5 mm-o.d. NMR tube, and the spectrum was recorded after each addition. The association constants (K) were determined by WinEQNMR^{S4} as shown below.

(2) Job's plots:

^1H NMR spectroscopy: Stock solutions of host (5.0 mM) and guest (5.0 mM) in $\text{DMSO-}d_6$ -10% H_2O (v/v) (5.0 mL) were prepared in separate volumetric flasks. Ten 5 mm-o.d. NMR tubes were separately filled with a total of 500 μL solution of the host and guest in the following ratios (μL , host/guest) at 297 K: 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9. The ^1H NMR spectra were obtained for each tube and the NHa signals were used to calculate the complex concentration, $[\text{HG}] = [\text{H}]_t \times (\delta_{\text{obsd}} - \delta_{\text{free}}) / (\delta_{\text{com}} - \delta_{\text{free}})$, where $[\text{H}]_t$ is the total concentration of the host, δ_{obsd} is the chemical shift observed on every point, δ_{free} and δ_{com} corresponds to the chemical shifts of the free ligand and the complex. This value was plotted against the molar fraction of the host.

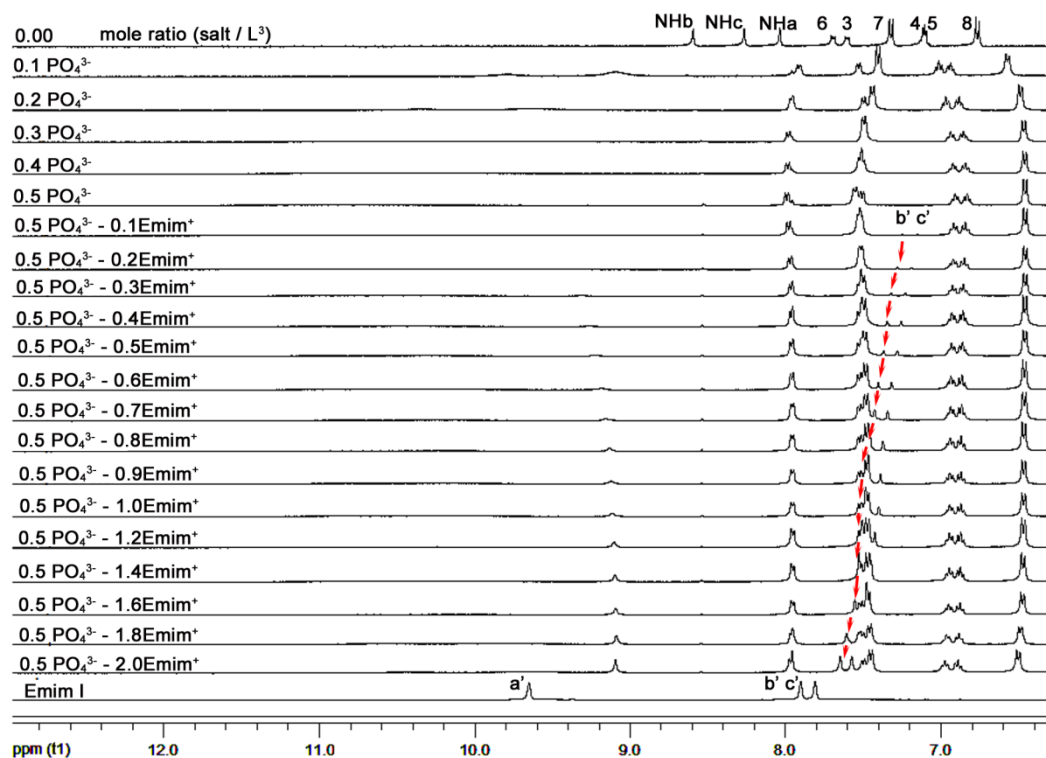
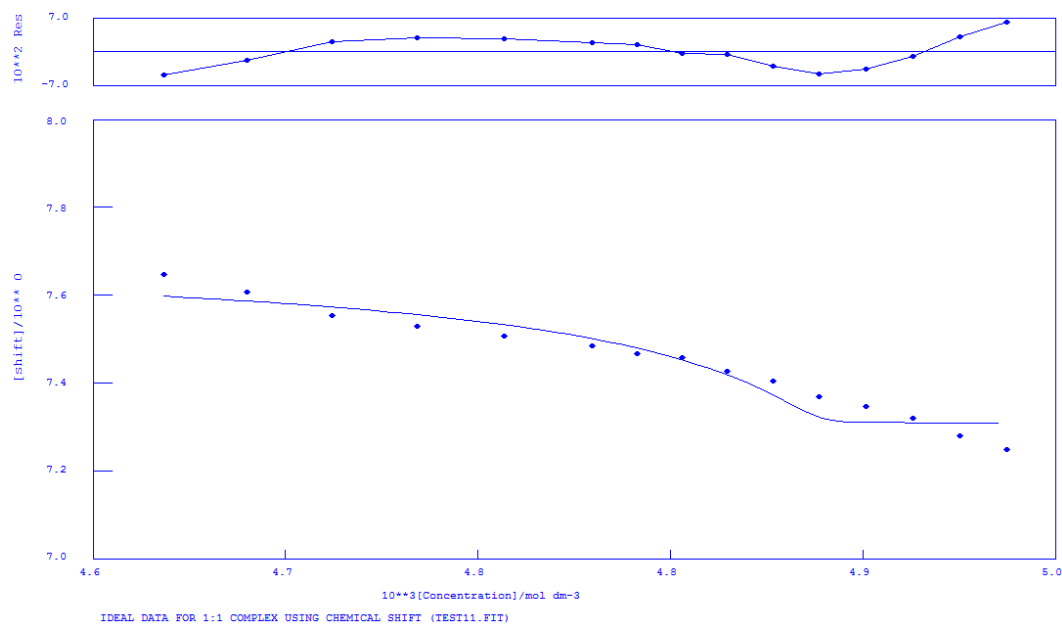


Fig. S11. (a) Experimental binding isotherms for ^1H NMR titration of L^3 and 0.5 equiv of PO_4^{3-} (as 18-C-6-K^+ salt) with Emim^+ (as Γ^- salt) and the corresponding fit using WinEQNMR. (b) The corresponding ^1H NMR spectra (acetone- d_6 -5% H_2O (v/v), 400 MHz).

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
 Program run at 10:13:05 on 08/02/2015

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)

Reaction: $\text{M} + \text{L} = \text{ML}$

FILE: TEST11.FIT

IDEAL DATA: $\text{K}_1 = 175000$; $\text{DELTA M} = 7.901$; $\text{DELTA ML} = 7.20$

| NO. | A | PARAMETER | DELTA | ERROR | CONDITION | DESCRIPTION |
|-----|---|-------------|-----------|-----------|-----------|-------------|
| 1 | 1 | 1.64808E+05 | 2.000E-01 | 1.238E+04 | 1.292E+00 | K1 |
| 2 | 1 | 7.69410E+00 | 2.000E-01 | 2.301E-02 | 1.352E+00 | SHIFT M |
| 3 | 1 | 7.30734E+00 | 1.000E+00 | 1.596E-02 | 1.637E+00 | SHIFT ML |

ORMS ERROR = 3.44E-02 MAX ERROR = 5.96E-02 AT OBS.NO. 15

RESIDUALS SQUARED = 1.42E-02

RFACTOR = 0.4129 PERCENT

The binding of L^n with SO_4^{2-} anion in solution was investigated by 1H NMR in acetone- d_6 /5% H_2O , which demonstrated a 2:1 binding mode for L^3 and SO_4^{2-} (Fig. S11) as in complex **5**. Furthermore, when 0.5 equiv of Emim-I salt was added, some upfield shifts of the CH protons b' and c' on Emim $^+$ can be observed (Fig. S12), implying the encapsulation of Emim $^+$ cation (log K = 4.80, Fig. S13). This result indicates that the sulfate sandwich complex **5** can also accommodate the Emim $^+$ cation in the "pre-organized" space of the polyether moieties.

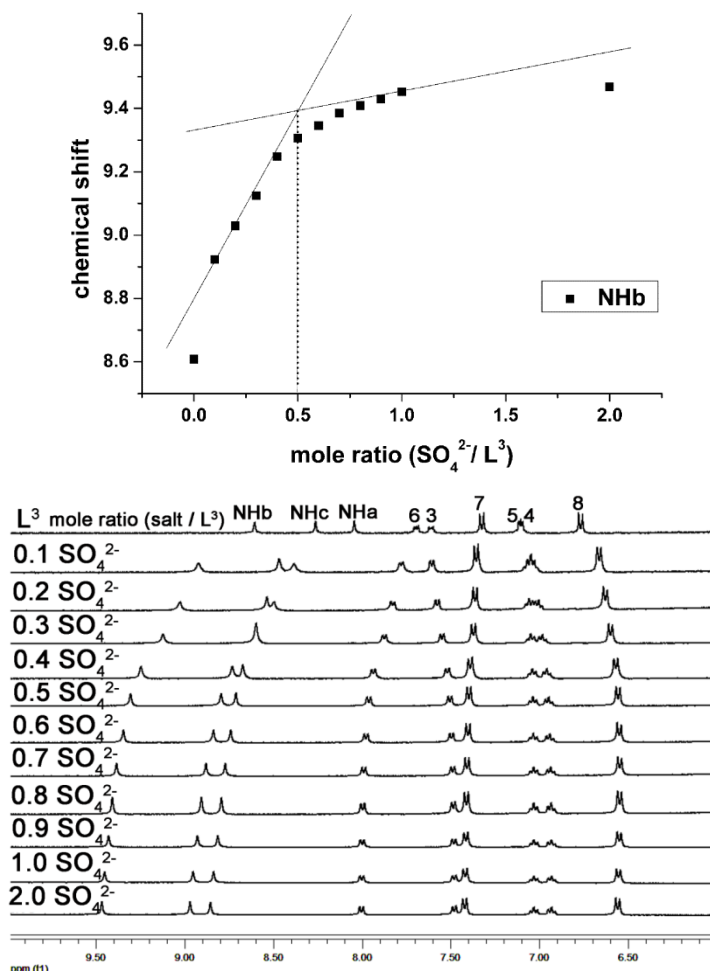


Fig. S12. The 2:1 binding mode of L^3 and SO_4^{2-} (as 18-C-6- K^+ salt) and the corresponding 1H NMR titration spectra (acetone- d_6 -5% H_2O (v/v), 400 MHz)

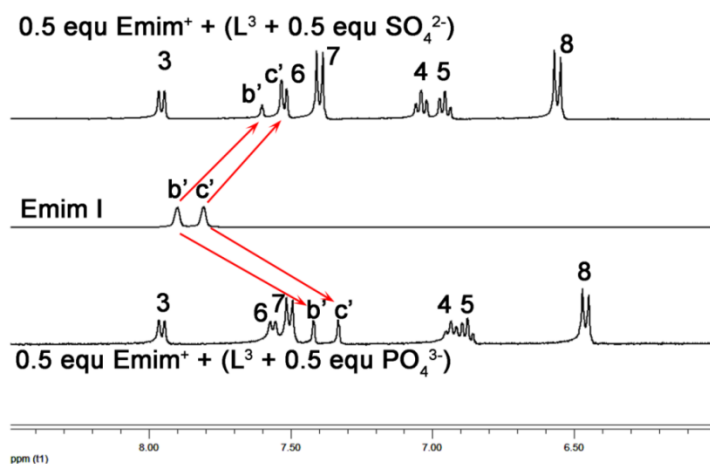


Fig. S13. The upfield shift of the protons b' and c' in Emim⁺ ring in SO₄²⁻ sandwich complex **5** and PO₄³⁻ sandwich complex **2** (acetone-*d*₆-5% H₂O (v/v), 400 MHz).

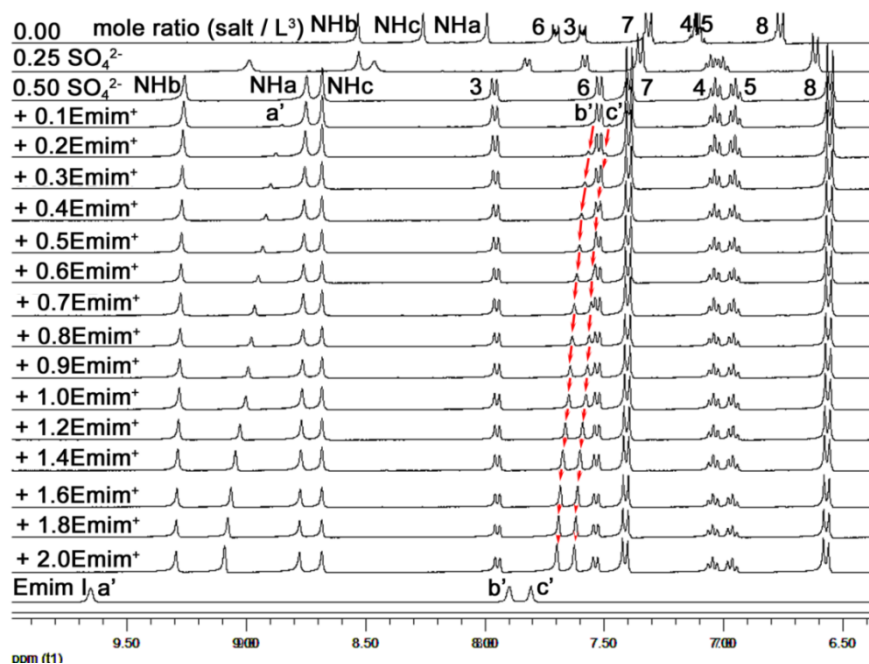
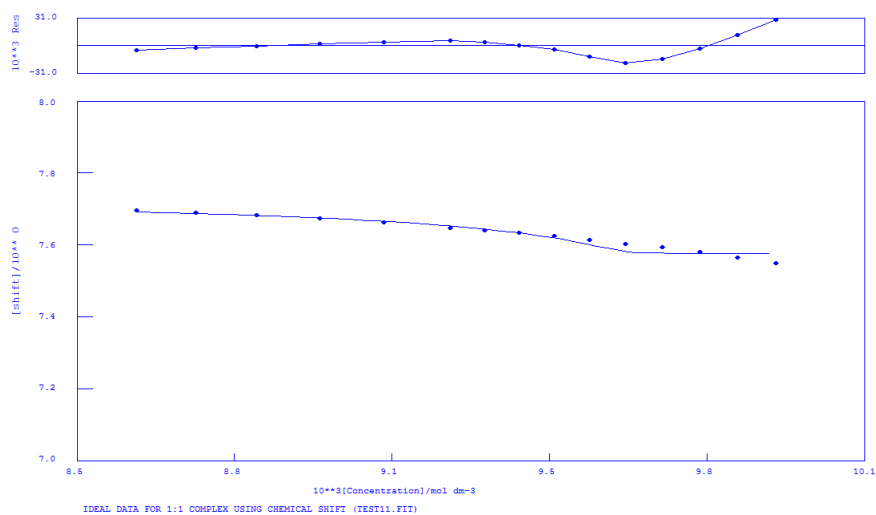


Fig. S14. (a) Experimental binding isotherms for ^1H NMR titration of L^3 and 0.5 equiv SO_4^{2-} (as 18-C-6- K^+ salt) with Emim^+ (as I^- salt) and the corresponding fit using WinEQNMR. (b) The corresponding ^1H NMR spectra (acetone- d_6 -5% H_2O (v/v), 400 MHz).

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes

Program run at 15:22:20 on 08/02/2015

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)

Reaction: $\text{M} + \text{L} = \text{ML}$

FILE: TEST11.FIT

IDEAL DATA: $\text{K1} = 50000$; $\text{DELTA M} = 7.901$; $\text{DELTA ML} = 7.5$

File prepared by M. J. Hynes, October 22 2000

| NO. | A | PARAMETER | DELTA | ERROR | CONDITION | DESCRIPTION |
|-----|---|-------------|-----------|-----------|-----------|-------------|
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| 2 | 1 | 7.73068E+00 | 2.000E-01 | 8.134E-03 | 1.278E+00 | SHIFT M |
| 3 | 1 | 7.57487E+00 | 1.000E+00 | 5.384E-03 | 1.403E+00 | SHIFT ML |

ORMS ERROR = 1.25E-02 MAX ERROR = 2.79E-02 AT OBS.NO. 15

RESIDUALS SQUARED = 1.87E-03

RFACTOR = 0.1465 PERCENT

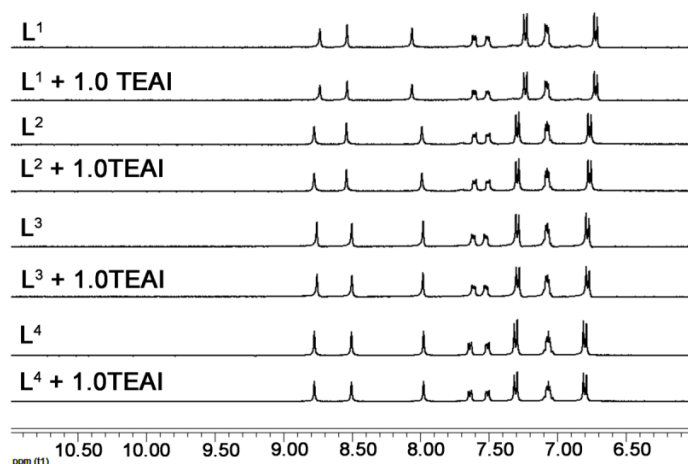


Fig. S15. ^1H NMR of 1.0 equiv of I^- ion (as TEA^+ salt, TEA = tetramethylammonium) added into L^n (5×10^{-3} M) in $\text{DMSO}-d_6$ (400 MHz, 298 K)

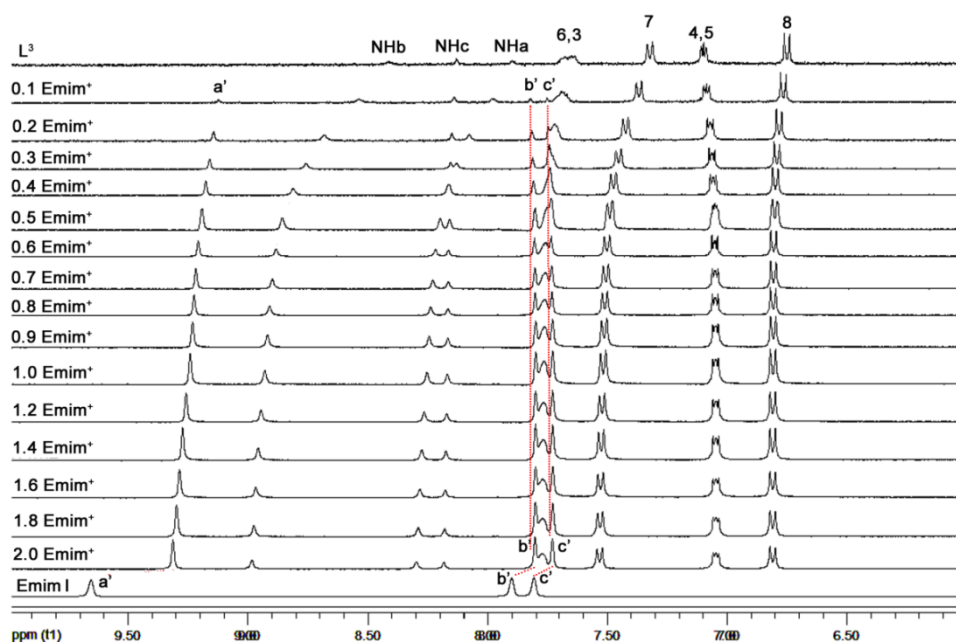


Fig. S16. ^1H NMR titration of L^3 (5×10^{-3} M) with Emim-I in acetone- d_6 /5% H_2O (400 MHz, 298 K).

Table S12 Binding constants for L^n ($n = 1-4$) with Cl^- (as TEA^+ salt) in $\text{DMSO}-d_6$ -0.5% H_2O (v/v).

| | L^1 | L^2 | L^3 | L^4 |
|-------------------------|--------------|--------------|--------------|--------------|
| log K (Cl^-) | 3.20 | 3.60 | 3.36 | 3.19 |

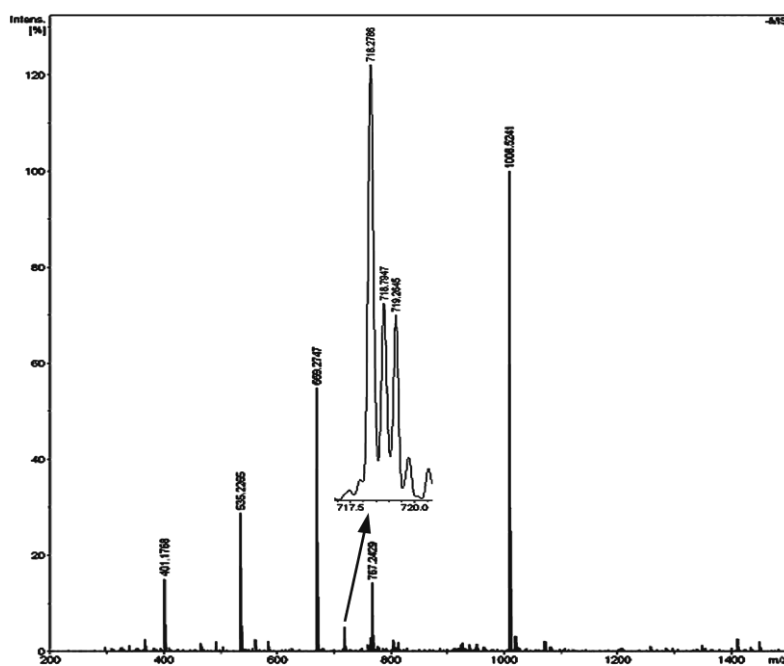


Fig. S17. Negative-ion mode ESI-MS spectrum for L^2 and $(\text{TBA})_2\text{SO}_4$ in THF (TBA = tetrabutylammonium). $[\text{M} - \text{H}]^-$ 669.2747, $[2\text{M} + \text{SO}_4]^{2-}/2$ 718.2786, $[\text{M} + \text{HSO}_4]^-$ 767.2429, $[\text{M} + \text{TBASO}_4]^-$ 1008.5241.

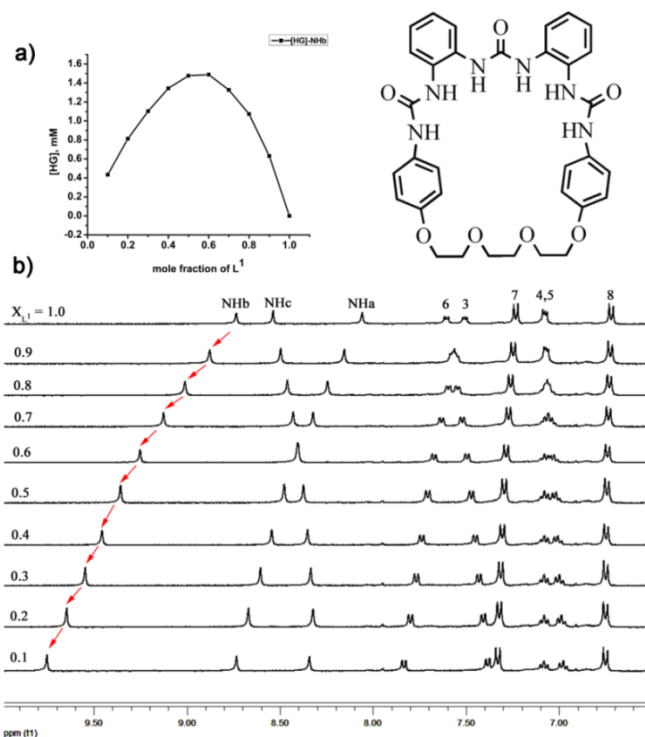


Fig. S18. a) Job's plot of L^1 with Cl^- (as TEA^+ salt); b) the corresponding 1H NMR spectra (DMSO- d_6 -0.5% H_2O (v/v), 400 MHz).

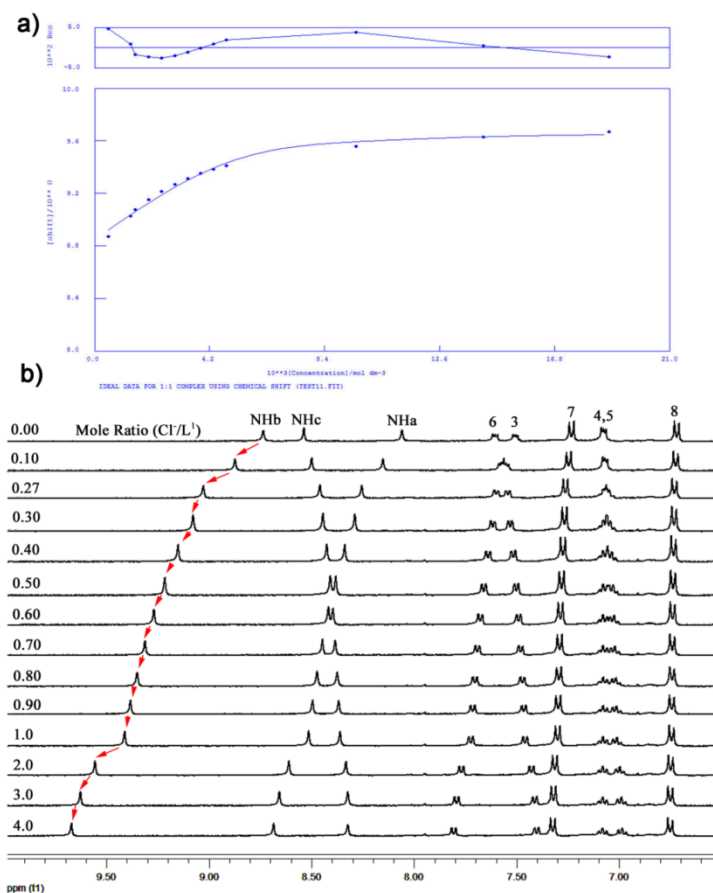


Fig. S19. a) Experimental binding isotherms for 1H NMR titration of L^1 with Cl^- (as TEA^+ salt) and the fit by WinEQNMR. b) The corresponding 1H NMR spectra (DMSO- d_6 -0.5% H_2O (v/v), 400 MHz).

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
 Program run at 15:26:10 on 02/04/2015

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)

Reaction: $M + L = ML$

FILE: TEST11.FIT

IDEAL DATA: $K1 = 50000$; $\Delta M = 8.736$; $\Delta ML = 13.0$

File prepared by M. J. Hynes, October 22 2000

| NO. | A | PARAMETER | DELTA | ERROR | CONDITION | DESCRIPTION |
|-----|---|-------------|-----------|-----------|-----------|-------------|
| 1 | 1 | 1.59517E+03 | 2.000E-01 | 1.292E+02 | 1.176E+00 | K1 |
| 2 | 1 | 8.84621E+00 | 2.000E-01 | 1.742E-02 | 1.615E+00 | SHIFT M |
| 3 | 1 | 9.67962E+00 | 1.000E+00 | 1.419E-02 | 1.423E+00 | SHIFT ML |

ORMS ERROR = 2.61E-02 MAX ERROR = 4.62E-02 AT OBS.NO. 1

RESIDUALS SQUARED = 6.82E-03

RFACTOR = 0.2461 PERCENT

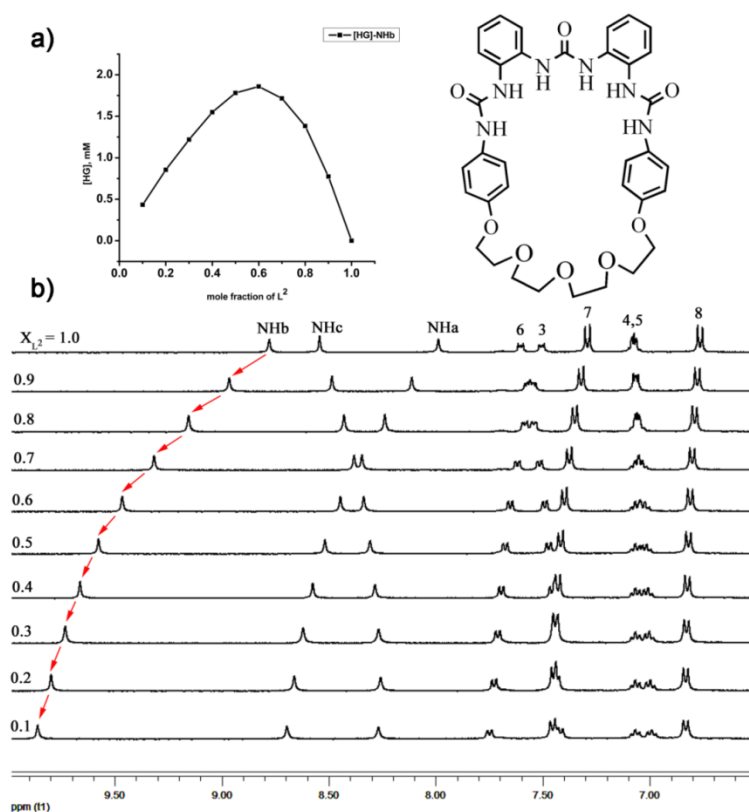


Fig. S20. a) Job's plot of L^2 with Cl^- (as TEA^+ salt); b) the corresponding 1H NMR spectra ($DMSO-d_6$ -0.5% H_2O (v/v), 400 MHz).

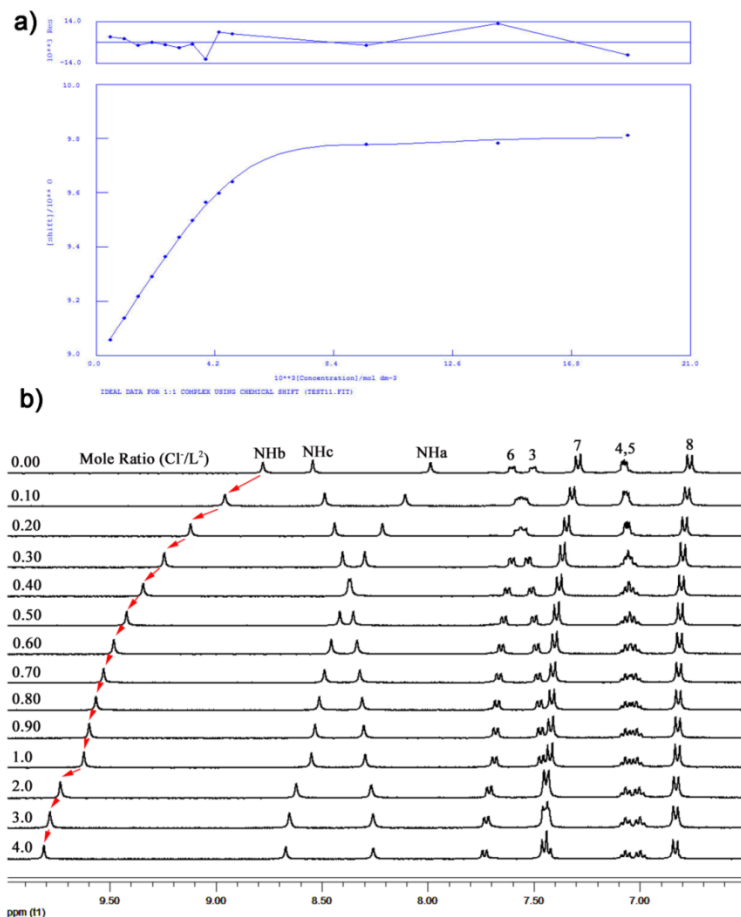


Fig. S21. a) Experimental binding isotherms for ^1H NMR titration of L^2 with Cl^- (as TEA^+ salt) and the corresponding fit using WinEQNMR. b) The corresponding ^1H NMR spectra ($\text{DMSO-}d_6$ -0.5% H_2O (v/v), 400 MHz).

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes

Program run at 14:22:34 on 01/05/2015

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)

Reaction: $\text{M} + \text{L} = \text{ML}$

FILE: TEST11.FIT

IDEAL DATA: $K_1 = 4000$; $\Delta M = 8.777$; $\Delta \text{ML} = 10.0$

File prepared by M. J. Hynes, October 22 2000

| NO. | A | PARAMETER | DELTA | ERROR | CONDITION | DESCRIPTION |
|-----|---|-------------|-----------|-----------|-----------|-------------|
| 1 | 1 | 3.95148E+03 | 2.000E-01 | 3.599E+02 | 4.771E+00 | K_1 |
| 2 | 1 | 8.98167E+00 | 2.000E-01 | 4.463E-03 | 1.342E+00 | SHIFT M |
| 3 | 1 | 9.81604E+00 | 1.000E+00 | 6.340E-03 | 4.680E+00 | SHIFT ML |

ORMS ERROR = 6.95E-03 MAX ERROR = 1.25E-02 AT OBS.NO. 12

RESIDUALS SQUARED = 4.83E-04

RFACTOR = 0.0643 PERCENT

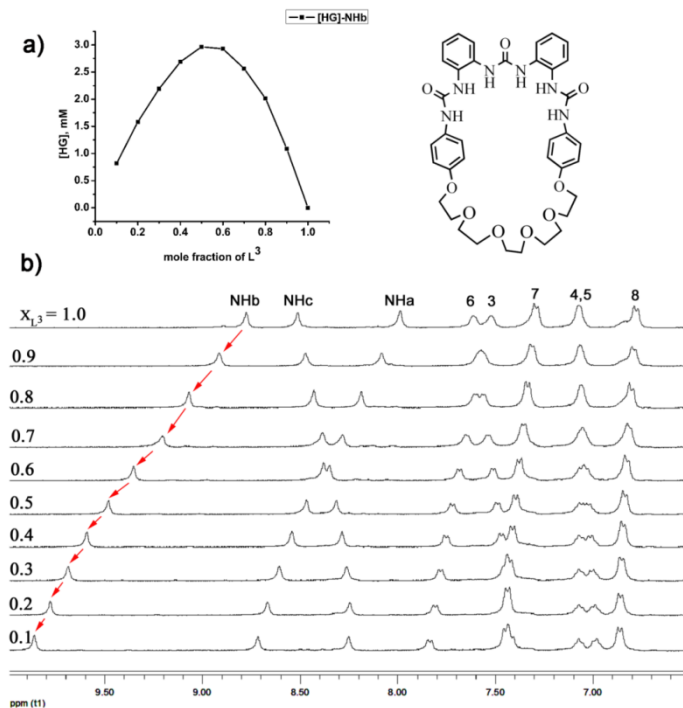


Fig. S22. a) Job's plot of L³ with Cl⁻ (as TEA⁺ salt); b) the corresponding ¹H NMR spectra (DMSO-*d*₆-0.5% H₂O (v/v), 400 MHz).

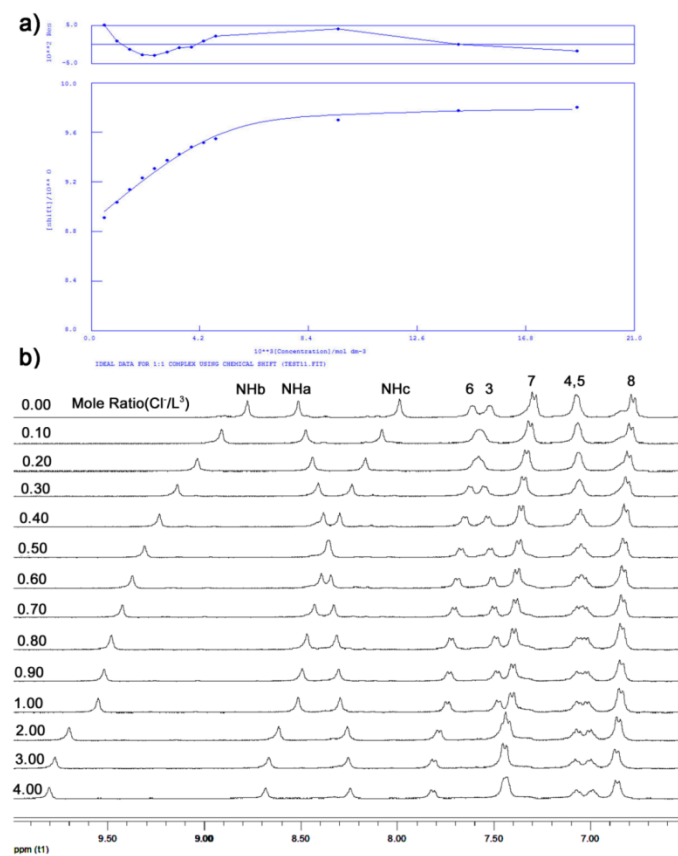


Fig. S23. a) Experimental binding isotherms for ¹H NMR titration of L³ with Cl⁻ (as TEA⁺ salt) and the corresponding fit using WinEQNMR; b) The corresponding ¹H NMR spectra (DMSO-*d*₆-0.5% H₂O (v/v), 400 MHz).

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
 Program run at 18:08:12 on 12/29/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)

Reaction: $M + L = ML$

FILE: TEST11.FIT

IDEAL DATA: $K1 = 2500$; $\Delta M = 8.776$; $\Delta ML = 10.0$

File prepared by M. J. Hynes, October 22 2000

| NO. | A | PARAMETER | DELTA | ERROR | CONDITION | DESCRIPTION |
|-----|---|-------------|-----------|-----------|-----------|-------------|
| 1 | 1 | 2.29039E+03 | 2.000E-01 | 1.800E+02 | 1.716E+00 | K1 |
| 2 | 1 | 8.87522E+00 | 2.000E-01 | 1.709E-02 | 1.381E+00 | SHIFT M |
| 3 | 1 | 9.81195E+00 | 1.000E+00 | 1.660E-02 | 1.919E+00 | SHIFT ML |

ORMS ERROR = 2.72E-02 MAX ERROR = 4.94E-02 AT OBS.NO. 1

RESIDUALS SQUARED = 7.40E-03

RFACTOR = 0.2537 PERCENT

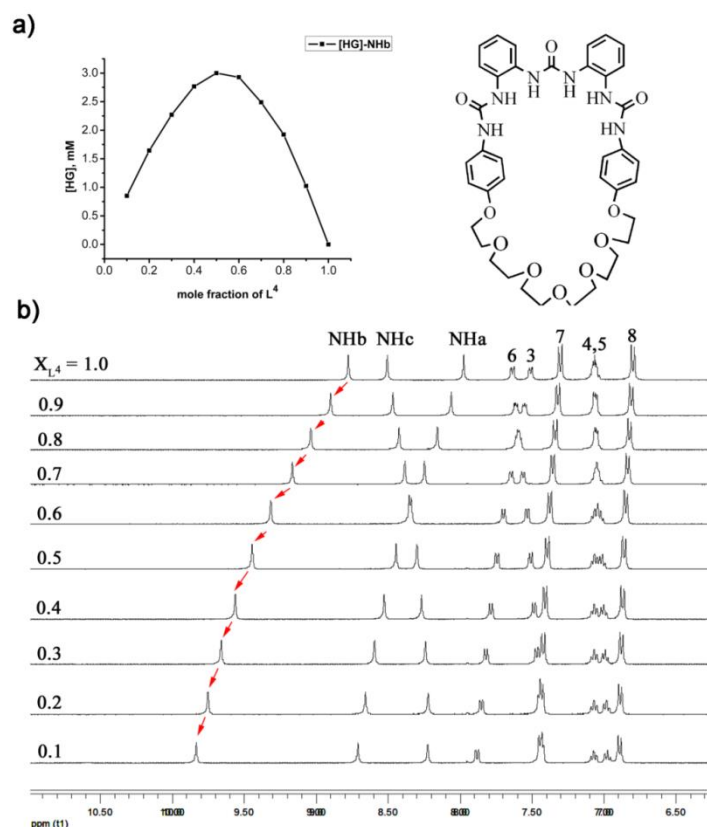


Fig. S24. a) Job's plot of L⁴ with Cl⁻ (as TEA⁺ salt); b) the corresponding ¹H NMR spectra (DMSO-*d*₆-0.5% H₂O (v/v), 400 MHz).

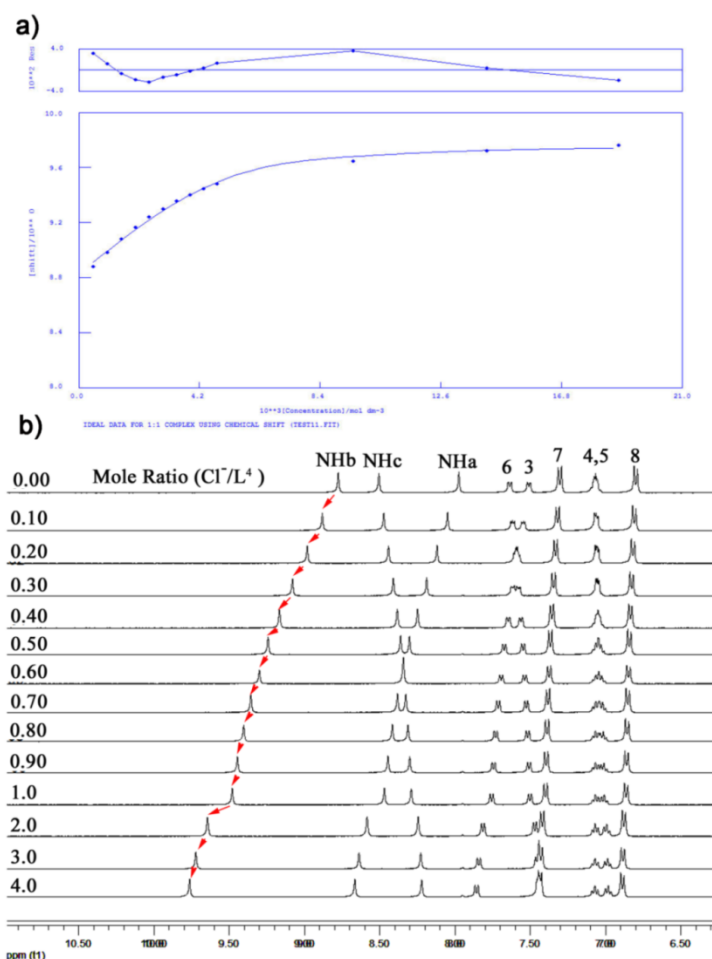


Fig. S25. a) Experimental binding isotherms for ^1H NMR titration of L^4 with Cl^- (as TEA^+ salt) and the corresponding fit using WinEQNMR; b) The corresponding ^1H NMR spectra ($\text{DMSO-}d_6$ -0.5% H_2O (v/v), 400 MHz).

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes

Program run at 08:55:14 on 12/26/2014

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)

Reaction: $\text{M} + \text{L} = \text{ML}$

FILE: TEST11.FIT

IDEAL DATA: $\text{K1} = 47500$; $\text{DELTA M} = 8.775$; $\text{DELTA ML} = 11.0$

File prepared by M. J. Hynes, October 22 2000

| NO. | A | PARAMETER | DELTA | ERROR | CONDITION | DESCRIPTION |
|-----|---|-------------|-----------|-----------|-----------|-------------|
| 1 | 1 | 1.53944E+03 | 2.000E-01 | 1.063E+02 | 2.177E+00 | K1 |
| 2 | 1 | 8.82800E+00 | 2.000E-01 | 1.268E-02 | 1.447E+00 | SHIFT M |
| 3 | 1 | 9.78248E+00 | 1.000E+00 | 1.419E-02 | 2.304E+00 | SHIFT ML |

ORMS ERROR = 2.04E-02 MAX ERROR = 3.50E-02 AT OBS.NO. 11

RESIDUALS SQUARED = 4.16E-03

RFACTOR = 0.1914 PERCENT

References

- S1. (a) D. Marquis, J.-P. Desvergne and H. Bouas-Laurent, *J. Org. Chem.* 1995, **60**, 7984–7996; (b) Y. Chen and G. L. Baker, *J. Org. Chem.* 1999, **64**, 6870–6873.
- S2. G. C. Eastmond and J. Paprotny, *Polymer* 2002, **43**, 3455–3468.
- S3. (a) S. J. Brooks, P. A. Gale and M. E. Light, *Chem. Commun.* 2006, 4344–4346; (b) C. Jia, B. Wu, S. Li, Z. Yang, Q. Zhao, J. Liang, Q.-S. Li and X.-J. Yang, *Chem. Commun.* 2010, **46**, 5376–5378.