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Supporting Information

Ion Pair Complexes and Anion Binding in Solution of a Ditopic Receptor

Toni Mäkelä & Kari Rissanen*

University of Jyvaskyla, Department of Chemistry, Nanoscience Center, P.O. Box 35, FI-40014 University of Jyvaskyla, Finland.

Contents

1. Synthesis and Characterization

Synthesis of 2:

Commercial benzo-15-crown-5 (**1**) (2.24 g, 8.35 mmol) was dissolved in chloroform (50 ml) and the solution was cooled to 2 °C in ice bath. Concentrated nitric acid (10 ml) was added dropwise during 15 minutes keeping the temperature under 5 °C and 5 ml of concentrated sulfuric acid was added dropwise during 20 minutes keeping the temperature under 10 °C. The ice bath was removed and the mixture was stirred at room temperature overnight. Reaction mixture was diluted with chloroform (30 ml) and poured to ice water (100 ml). The organic phase was separated and washed with water (100 ml + 2 * 50 ml). Water phases were combined and washed with chloroform (60 ml). Organic phases were combined and dried with Na_2SO_4. Evaporation of the dried chloroform gave the product **2** as yellow solid. The product was recrystallized from chloroform and the filtered solid was washed with diethyl ether and dried in air; yield 77 %. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 3.69-3.75 (8H, m, CH_2), 3.91-3.93 (4H, dd, CH_2), 4.23-4.25 (4H, dd, CH_2), 7.30 (2H, s, ArH) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 303K): δ = 68.81, 69.80, 70.27, 71.26, 108.64, 136.87, 152.01 ppm. HRMS (ESI+): calcd. for $C_{14}H_{18}N_2O_9Na$, $[M + Na]^+$: *m/z* 381.0905; found: *m/z* 381.0899 (Δ = 0.6 mDa).

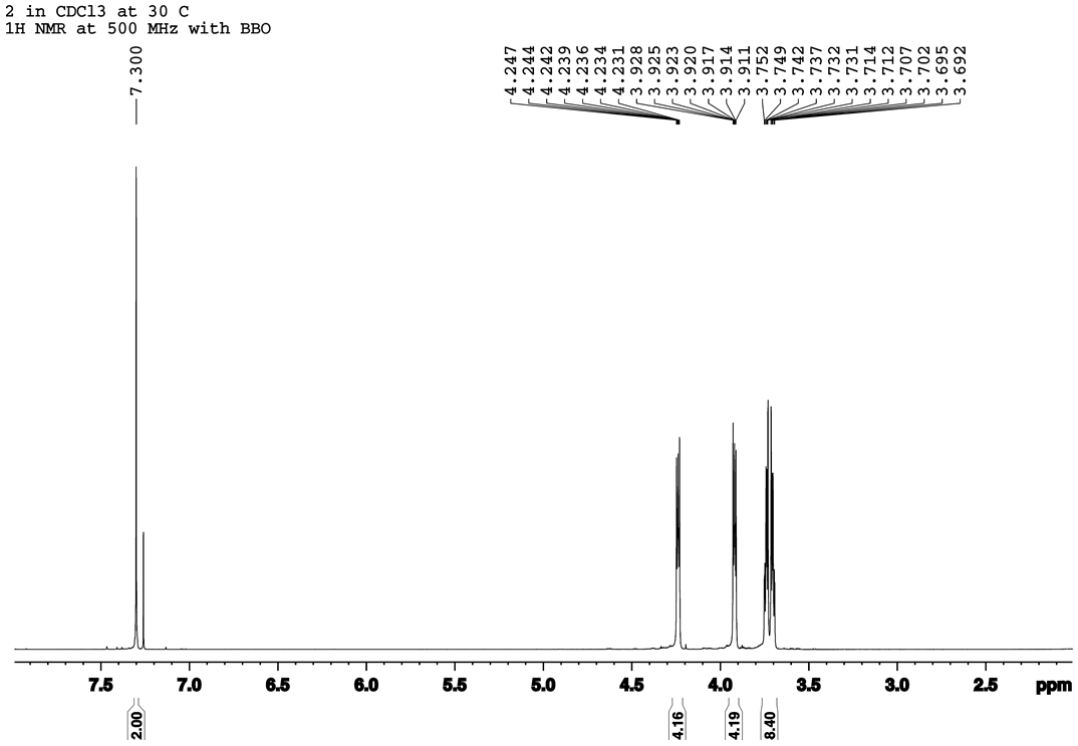


Figure S1. 500 MHz ^{1}H NMR spectrum of **2** in $CDCl_3$.

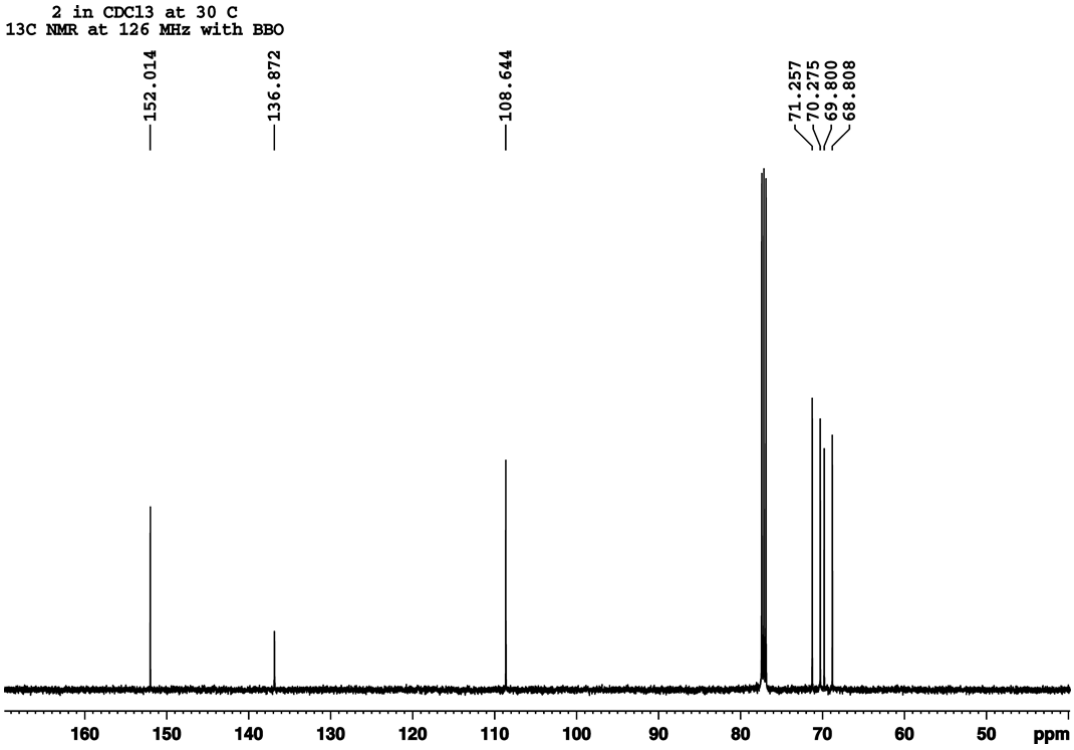


Figure S2. 126 MHz ^{13}C NMR spectrum of **2** in $CDCl_3$**.**

Synthesis of 3:

Ethanol and hydrazine monohydrate were degassed prior of use by sonication and simultaneous argon bubbling through the solution. Dinitrobenzo-15-crown-5 (**2**) (0.201 g, 0.561 mmol) and 10 % Pd/C (36 mg) were mixed in 20 ml of degassed ethanol under argon atmosphere, and degassed hydrazine monohydrate (0.30 ml) was added to the mixture. The mixture was heated at 90 °C in the dark for 1 hour, and then filtered quickly through Celite while hot to avoid exposure to air. The filtrate was evaporated close to dryness under reduced pressure. Resulting residue was dried under vacuum overnight giving a light brown solid which was used without purification in the next step. Due to the instability of the amine compound only ^{1}H NMR was recorded; yield 98%. ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 3.19 (4H, bs, NH_2), 3.74 (8H, s, CH_2) 3.86-3.89 (4H, dd, CH_2), 4.04-4.07 (4H, dd, CH_2), 6.37 (2H, s, ArH) ppm.

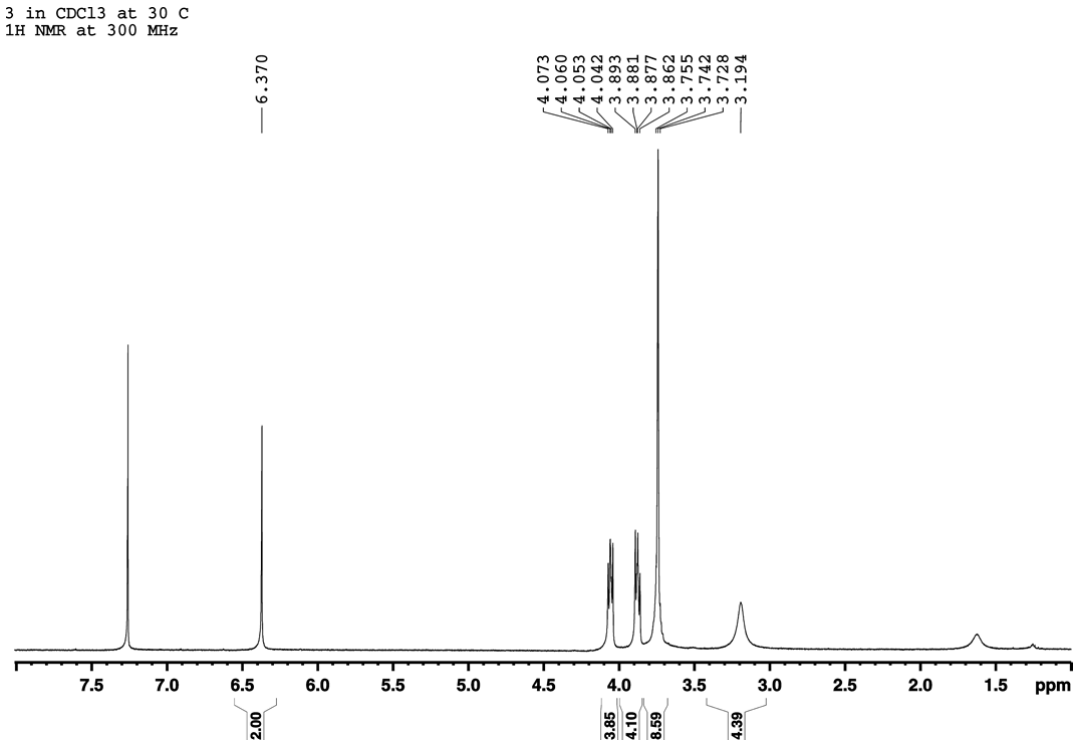


Figure S3. 300MHz ^{1}H NMR spectrum of **3** in $CDCl_3$**.**

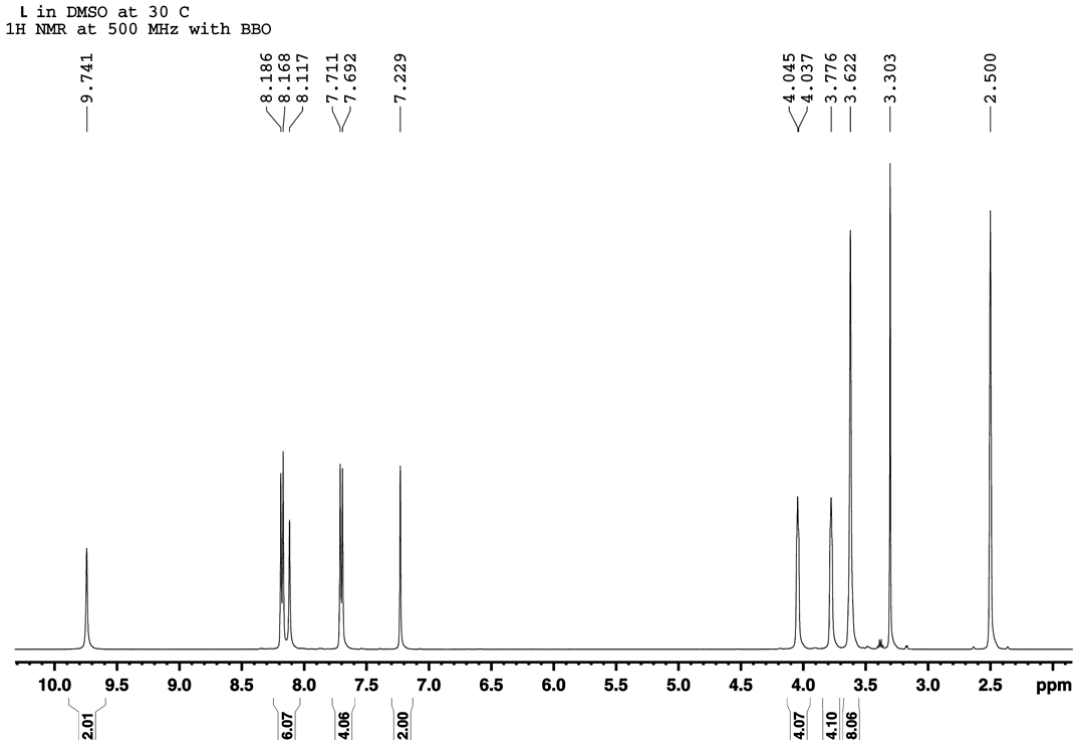


Figure S4. 500MHz ^{1}H NMR spectrum of **L** in DMSO**.**

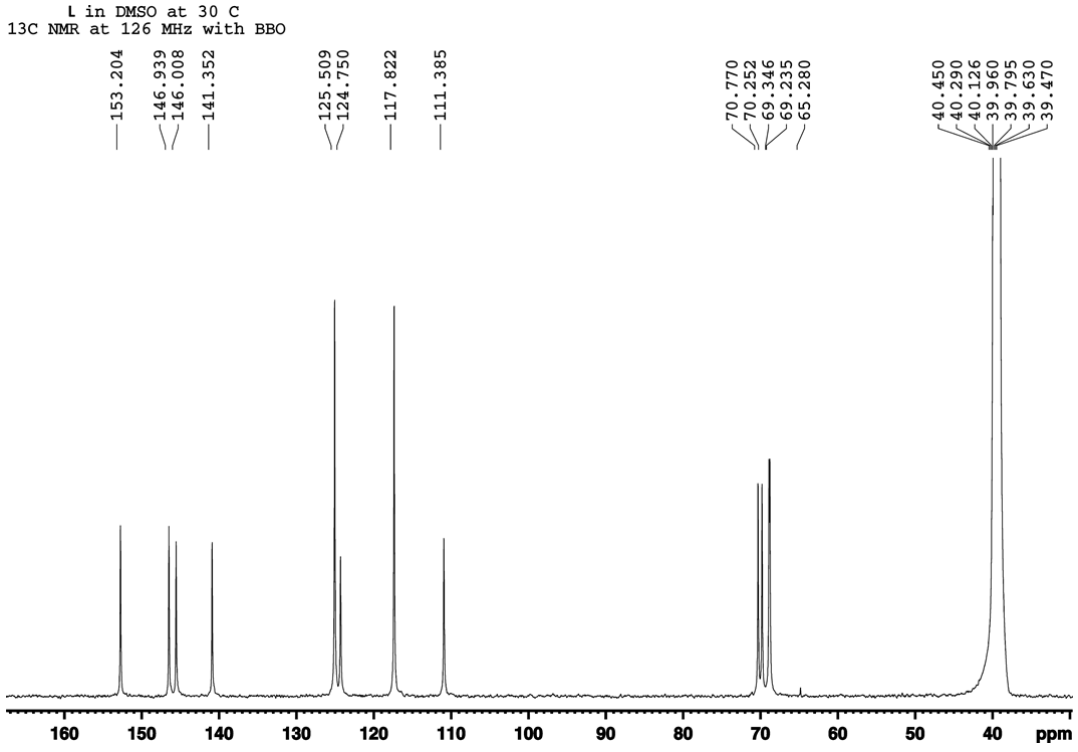


Figure S5. 126 MHz ^{13}C NMR spectrum of **L** in DMSO**.**

2. Crystallography

2.1 Crystal Data

Crystal data for **2**: Crystals were grown by slow evaporation of $CDCl_3$ solution. $C_{14}H_{18}N_2O_9$, M = 358.30, yellow block, 0.42 x 0.36 x 0.24 mm^3, monoclinic, space group $P2_1/c$, a = 11.6177(4) Å, b = 8.5331(3) Å, c = 17.2925(6) Å, α = 90°, β = 109.559(2)° , γ = 90°, V = 1615.37(10) $Å^3$, Z = 4, D_c = 1.473 g/cm^3, F000 = 752.0 , μ = 0.125 mm^{-1}, MoKα (λ = 0.71073), T = 173 K, $2\theta_{max}$ = 50.00°, 2843 reflections used, 2277 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0311, 226 parameters, 0 restraints, GoF = 1.065, R = 0.0369 [$I_o > 2\sigma(I_o)$], wR = 0.0903 (all reflections), 0.17 < Δρ < -0.20 e/$Å^3$. CCDC- 1425256

Crystal data for **L**: Crystals were grown by slow evaporation of acetone solution with NaF. $C_{62}H_{75.6}N_{12}O_{26}$, M = 1404.94, yellow block, 0.18 x 0.15 x 0.10 mm^3, monoclinic, space group $P2_1/n$, a = 15.41305(15) Å, b = 23.7285(2) Å, c = 18.50903(16) Å, α = 90°, β = 95.2966(9)° , γ = 90°, V = 6740.38(11) $Å^3$, Z = 4, D_c = 1.384 g/cm^3, F000 = 2958.0 , μ = 0.926 mm^{-1}, CuKα (λ = 1.54184), T = 123.0(1) K, $2\theta_{max}$ = 133.50°, 11832 reflections used, 10022 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0245, 1125 parameters, 488 restraints, GoF = 1.027, R = 0.0598 [$I_o > 2\sigma(I_o)$], wR = 0.1758 (all reflections), 0.76 < Δρ < -1.21 e/$Å^3$. CCDC-1425257

Crystal data for **L·DMF**: Crystals were grown by slow diffusion of methanol into DMF solution of **L**. $C_{34}H_{44}N_8O_{13}$, M = 772.77, yellow block, 0.40 x 0.20 x 0.20 mm^3, triclinic, space group P-1, a = 10.71590(10) Å, b = 11.3107(2) Å, c = 15.4992(3) Å, α = 101.4580(10)°, β = 95.3000(10)° , γ = 100.4910(10) °, V = 1794.18(5) $Å^3$, Z = 2, D_c = 1.430 g/cm^3, F000 = 816.0 , μ = 0.111 mm^{-1}, MoKα (λ = 0.71073), T = 120(2) K, $2\theta_{max}$ = 50.00°, 6315 reflections used, 5475 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0351, 500 parameters, 0 restraints, GoF = 1.028, R = 0.0422 [$I_o > 2\sigma(I_o)$], wR = 0.1088 (all reflections), 0.66 < Δρ < -0.35 e/$Å^3$. CCDC-1425258

Crystal data for **L·DMSO**: Crystals were grown by slow diffusion of methanol into acetone/DMSO solution of **L** with NaF. $C_{30}H_{36}N_6O_{12}S_1$, M = 704.71, yellow block, 0.32 x 0.16 x 0.08 mm^3, triclinic, space group P-1, a = 8.8481(3)Å, b = 10.1334(4) Å, c = 18.5466(6)Å, α = 86.562(3)°, β = 89.252(3)° , γ = 80.827(3)°, V = 1638.69(10) $Å^3$, Z = 2, D_c = 1.428 g/cm^3, F000 = 740.0, μ = 1.511 mm^{-1}, CuKα (λ = 1.54184), T = 134.41(10) K, $2\theta_{max}$ = 133.48°, 5740 reflections used, 5067 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0228, 468 parameters, 12 restraints, GoF = 1.065, R = 0.0591 [$I_o > 2\sigma(I_o)$], wR = 0.1657 (all reflections), 0.99 < Δρ < -0.95 e/$Å^3$. CCDC-1425259

Crystal data for **L·NaCl**: Crystals were grown by slow diffusion of diethyl ether into MeOH/DMSO solution of **L** with NaCl. $C_{56}H_{60}Cl_2N_{12}Na_2O_{10}$, M = 1370.04, yellow block, 0.36 x 0.23 x 0.18 mm^3, monoclinic, space group $P2_1/n$, a = 15.83850(18) Å, b = 23.7838(3) Å, c = 18.5462(2) Å, α = 90°, β = 90.8013(11)° , γ = 90°, V = 6985.69(14) $Å^3$, Z = 4, D_c = 1.303 g/cm^3, F000 = 2848.0 , μ = 1.638 mm^{-1}, CuKα (λ = 1.54184), T = 123.01(10) K, $2\theta_{max}$ = 133.50°, 12292 reflections used, 10679 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0201, 913 parameters, 28 restraints, GoF = 1.117, R = 0.0658 [$I_o > 2\sigma(I_o)$], wR = 0.2092 (all reflections), 2.11 < Δρ < -0.80 e/$Å^3$. CCDC-1425260

Crystal data for **L·NaBr**: Crystals were grown by slow diffusion of diethyl ether into acetonitrile solution of **L** with NaBr. $C_{30}H_{33}Br_1N_7Na_1O_{10}$, M = 786.53, yellow plate, 0.36 x 0.22 x 0.05 mm^3, triclinic, space group P-1, a = 9.4682(3) Å, b = 12.1247(3) Å, c = 16.1742(5) Å, α = 72.838(3)°, β = 87.307(2)° , γ = 87.437(2)°, V = 1771.21(9) $Å^3$, Z = 2, D_c = 1.475 g/cm^3, F000 = 808.0 , μ = 2.317 mm^{-1}, CuKα (λ = 1.54184), T = 123.0(1) K, $2\theta_{max}$ = 133.49°, 6209 reflections used, 5905 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0184, 476 parameters, 6 restraints, GoF = 1.033, R = 0.0309 [$I_o > 2\sigma(I_o)$], wR = 0.0843 (all reflections), 0.57 < Δρ < -0.43 e/$Å^3$. CCDC-1425261

Crystal data for **L·NaI**: Crystals were grown by slow diffusion of diethyl ether into acetone solution of **L** with NaI. $C_{29.5}H_{34}I_1N_6Na_1O_{11.75}$, M = 810.51, yellow needle, 0.54 x 0.06 x 0.04 mm^3, monoclinic, space

group *I*2/a, *a* = 22.1422(5) Å, *b* = 7.22931(19) Å, *c* = 42.6101(13) Å, α = 90°, β = 100.291(3)° , γ = 90°, V = 6711.0(3) Å^3, Z = 8, D_c = 1.604 g/cm^3, F000 = 3288.0 , μ = 8.240 mm^{-1}, CuKα (λ = 1.54184), T = 134.4(1) K, $2\theta_{max}$ = 133.45°, 5947 reflections used, 5434 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0499, 480 parameters, 3 restraints, GoF = 1.039, R = 0.0386 [$I_o > 2\sigma(I_o)$], wR = 0.1005 (all reflections), 0.98 < Δρ < -1.00 e/Å^3. CCDC-1425262

Crystal data for **2L·KF**: Crystals were grown by slow diffusion of diethyl ether into MeOH/DMF solution of **L** with KF. $C_{117.6}H_{140.8}F_2K_2N_{25.5}O_{52}$, M = 2858.20, yellow block, 0.20 x 0.19 x 0.13 mm^3, orthorombic, space group *F*dd2, *a* = 52.080(2) Å, *b* = 43.9225(8) Å, *c* = 27.7395(6) Å, α = 90°, β =90° , γ = 90°, V = 63453(3) Å^3, Z = 16, D_c = 1.197 g/cm^3, F000 = 23938.0 , μ = 1.277 mm^{-1}, CuKα (λ = 1.54184), T = 123.0(1) K, $2\theta_{max}$ = 133.50°, 19416 reflections used, 17270 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0186, 1958 parameters, 69 restraints, GoF = 1.064, R = 0.0823 [$I_o > 2\sigma(I_o)$], wR = 0.2316 (all reflections), 0.88 < Δρ < -0.57. Flack parameter 0.413(6). CCDC-1425263

Crystal data for **2L·KCl**: Crystals were grown by slow evaporation of acetone solution of **L** and KCl. $C_{56}H_{62}Cl_1K_1N_{12}O_{23}$, M = 1345.72, yellow block, 0.20 x 0.19 x 0.10 mm^3, triclinic, space group *P*-1, *a* = 10.5214(2) Å, *b* = 15.4120(4) Å, *c* = 21.1832(5) Å, α = 105.004(2)°, β = 97.408(2)°, γ = 109.292(2)°, V = 3043.69(14) Å^3, Z = 2, D_c = 1.468 g/cm^3, F000 = 1404.0 , μ = 1.957 mm^{-1}, CuKα (λ = 1.54184), T = 123.0(1) K, $2\theta_{max}$ = 133.50°, 10659 reflections used, 9612 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0360, 841 parameters, 0 restraints, GoF = 1.059, R = 0.0542 [$I_o > 2\sigma(I_o)$], wR = 0.1551 (all reflections), 0.55 < Δρ < -0.89 e/Å^3. CCDC-1425264

Crystal data for **2L·KBr**: Crystals were grown by slow evaporation of MeOH/DMF solution of **L** and KBr. $C_{59}H_{67}Br_1K_1N_{13}O_{23}$, M = 1445.26, yellow plate, 0.14 x 0.07 x 0.01 mm^3, monoclinic, space group $P2_1/c$, *a* = 14.9756(3) Å, *b* = 26.2676(5) Å, *c* = 16.2138(3) Å, α = 90°, β = 97.748(2)° , γ = 90°, V = 6319.8(2) Å^3, Z = 4, D_c = 1.519 g/cm^3, F000 = 3000.0 , μ = 2.265 mm^{-1}, CuKα (λ = 1.54184), T = 123.0(1) K, $2\theta_{max}$ = 133.48°, 11056 reflections used, 8742 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0457, 876 parameters, 0 restraints, GoF = 1.057, R = 0.0500 [$I_o > 2\sigma(I_o)$], wR = 0.1288 (all reflections), 0.80 < Δρ < -0.42 e/Å^3. CCDC-1425265

Crystal data for **2L·KI**: Crystals were grown by slow evaporation of acetone/$CHCl_3$ solution of **L** and KI. $C_{56}H_{60}I_1K_1N_{12}O_{22}$, M = 1419.16, yellow needle, 0.18 x 0.04 x 0.03 mm^3, monoclinic, space group $P2_1/c$, *a* = 15.5513(4) Å, *b* = 25.3840(6) Å, *c* = 16.1619(4) Å, α = 90°, β = 96.677(2)° , γ = 90°, V = 6336.7(3) Å^3, Z = 4, D_c = 1.488 g/cm^3, F000 = 2912.0 , μ = 5.299 mm^{-1}, CuKα (λ = 1.54184), T = 123.0(1) K, $2\theta_{max}$ = 133.47°, 11106 reflections used, 9271 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0383, 829 parameters, 0 restraints, GoF = 1.068, R = 0.0596 [$I_o > 2\sigma(I_o)$], wR = 0.1571 (all reflections), 1.52 < Δρ < -0.78 e/Å^3. CCDC-1425266

Crystal data for **2L·RbF**: Crystals were grown by slow diffusion of diethyl ether into MeOH/DMF solution of **L** with RbF. $C_{59.5}H_{71.5}F_1N_{12}O_{24.5}Rb_1$, M = 1451.25, yellow block, 0.25 x 0.24 x 0.12 mm^3, triclinic, space group *P*-1, *a* = 14.0458(3) Å, *b* = 15.7391(4) Å, *c* = 18.0442(4) Å, α = 83.6625(19)°, β = 71.3472(18)° , γ = 65.190(2)°, V = 3429.30(14) Å^3, Z = 2, D_c = 1.405 g/cm^3, F000 = 1509.0 , μ = 1.762 mm^{-1}, CuKα (λ = 1.54184), T = 123.0(1) K, $2\theta_{max}$ = 133.50°, 12028 reflections used, 11431 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0176, 934 parameters, 5 restraints, GoF = 1.043, R = 0.0362 [$I_o > 2\sigma(I_o)$], wR = 0.0965 (all reflections), 0.84 < Δρ < -0.60 e/Å^3. CCDC-1425267

Crystal data for **2L·RbCl**: Crystals were grown by slow slow diffusion of diethyl ether into MeOH/DMF solution of **L** with RbCl. $C_{57}H_{64}Cl_1N_{12}O_{23}Rb_1$, M = 1406.12, yellow block, 0.25 x 0.21 x 0.14 mm^3, triclinic, space group *P*-1, *a* = 10.38455(15) Å, *b* = 12.4289(2) Å, *c* = 25.4568(5) Å, α = 91.9928(15)°, β = 92.1858(14)° , γ = 91.3214(13)°, V = 3280.31(10) Å^3, Z = 2, D_c = 1.424 g/cm^3, F000 = 1456.0 , μ = 2.151 mm^{-1}, CuKα (λ = 1.54184), T = 123.0(1) K, $2\theta_{max}$ = 133.50°, 11512 reflections used, 10977 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0273, 891 parameters, 41 restraints, GoF = 1.125, R = 0.0608 [$I_o > 2\sigma(I_o)$], wR = 0.1552 (all reflections), 0.92 < Δρ < -0.83 e/Å^3. CCDC-1425268

Crystal data for **2L·RbI**: Crystals were grown by slow slow diffusion of diethyl ether into MeOH/DMF solution of **L** with RbI. $C_{57.5}H_{63.5}I_1N_{12.5}O_{22.5}Rb_1$, M = 1502.07, yellow plate, 0.28 x 0.09 x 0.04 mm^3,

monoclinic, space group $P2_1/c$, a = 15.4923(4) Å, b = 25.4062(6) Å, c = 16.2455(4) Å, α = 90°, β = 96.788(2)° , γ = 90°, V = 6349.4(3) $Å^3$, Z = 4, D_c = 1.571 g/cm^3, F000 = 3064.0 , μ = 5.652 mm^{-1}, CuKα (λ = 1.54184), T = 123.0(1) K, $2\theta_{max}$ = 133.49°, 15987 reflections used, 13164 with $I_o > 2\sigma(I_o)$, R_{int} =0.0320, 862 parameters, 4 restraints, GoF = 1.043, R = 0.0456 [$I_o > 2\sigma(I_o)$], wR = 0.1421 (all reflections), 1.17 < Δρ < -0.60 e/$Å^3$. CCDC-1425269

These data [CCDC 1425256 - 1425269] can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.2 Crystal Structures

2.2.1 Crystal Structure of 2

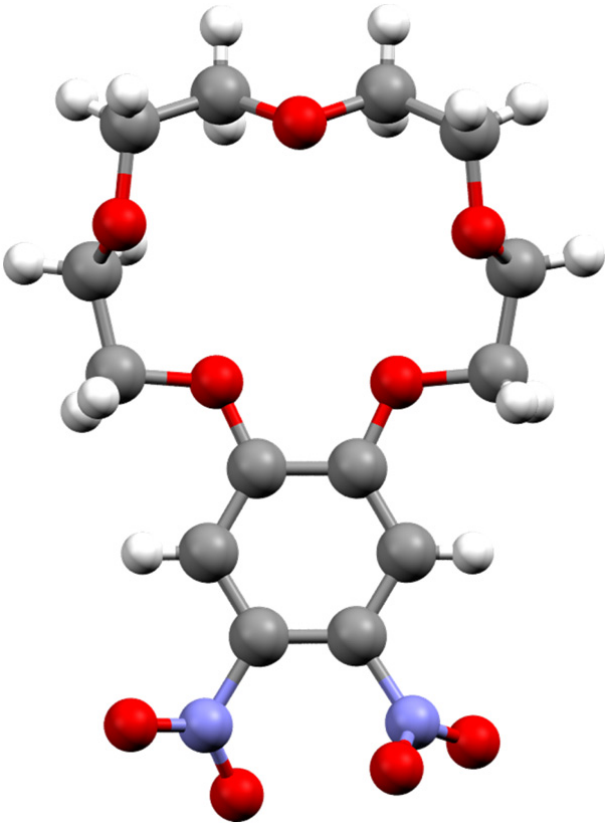


Figure S6. Crystal structure of **2**.

2.2.2 Crystal Structure of L

The hydrogen bond distances:

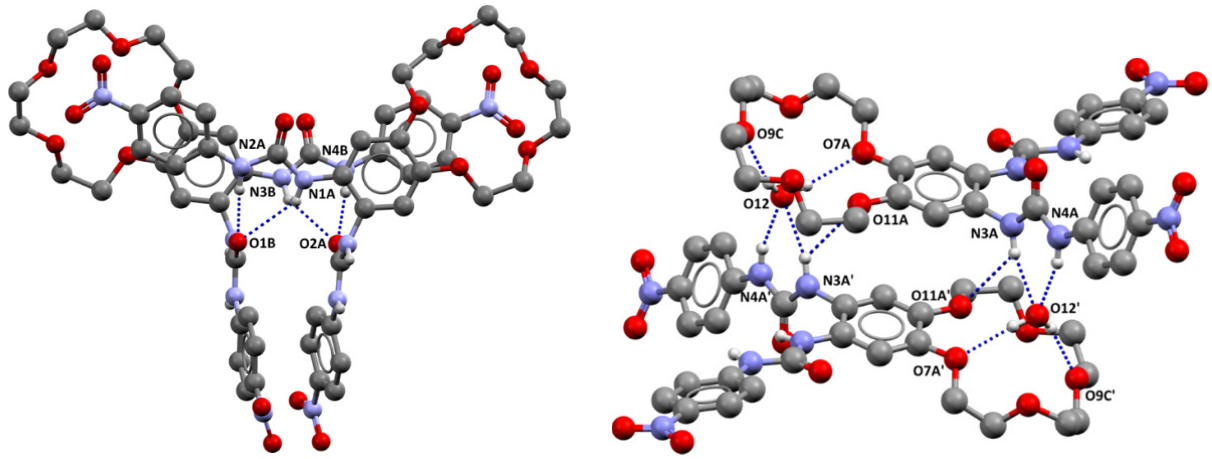
(a) N1A···O1B 3.393(3) Å, N2A···O1B 2.917(3) Å, N3B···O2A 3.219(3) Å, N4B···O2A 2.867(3) Å

(b) N3A···O11A' 3.331(3) Å, N3A···O12' 3.010(3) Å, N4A···O12' 2.821(3) Å, O12···O7A 2.926(2) Å, O12···O9C 2.783(9) Å

The hydrogen bond angles:

(a) N1A-H···O1B 148^{O}, N2A-H···O1B 174^{O}, N3B-H···O2A 150^{O}, N4B-H···O2A 171^{O};

(b) N3A-H···O11A' 128^{O}, N3A-H···O12' 152^{O}, N4A-H···O12' 163^{O}, O12-H···O7A 174^{O}, O12-H···O9C 155^{O}



(a) (b)

Figure S7. Crystal structure of **L**. (a) Dimerization of **L** results from hydrogen bonds between urea functionalities. (b) Water molecules form hydrogen bonds with the crown ether oxygens and urea group nitrogens. The heavy disorder of the crown ether parts, acetone solvate molecules and the nonbonding hydrogen atoms have been omitted from the figure.

2.2.3 Crystal Structure of L·DMF

The hydrogen bond distances:

N3···O13 2.970(2) Å, N4···O13 2.810(2) Å

The hydrogen bond angles:

N3-H···O13 156^{O}, N4-H···O13 163^{O}

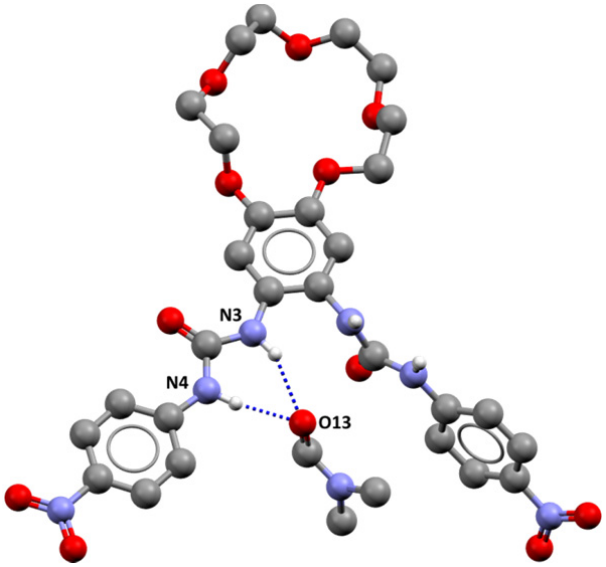


Figure S8. Crystal structure of **L·DMF**. The other DMF solvate molecules and the nonbonding hydrogen atoms have been omitted from the figure.

2.2.4 Crystal Structure of L·DMSO

The hydrogen bond distances:

N3···O12 2.882(3) Å, N4···O12 2.834(3) Å

The hydrogen bond angles:

N3-H···O12 153^{O}, N4-H···O13 158^{O}

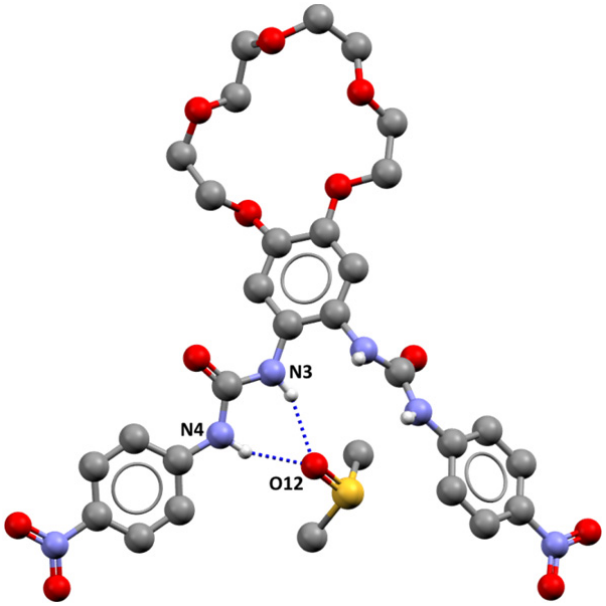


Figure S9. Crystal structure of **L·DMSO**. The disorder in the crown ether ring and the nonbonding hydrogen atoms have been omitted from the figure.

2.2.5 Crystal Structure of L·NaCl

The hydrogen bond distances:

N3A···Cl1 3.178(2) Å, N4A···Cl1 3.130(2) Å, N1B···Cl2 3.258(3) Å, N2B···Cl2 3.079(3) Å, N1A···O2A 3.084(3) Å, N3B···O2A 3.079(3) Å, N4B···O2A 2.789(3) Å, N1A···O1B 3.012(3) Å, N2A···O1B 2.786(3) Å, N3B···O1B 3.180(3) Å

The hydrogen bond angles:

N3A-H···Cl1 144^{O}, N4A-H···Cl1 162^{O}, N1B-H···Cl2 135^{O}, N2B-H···Cl2 161^{O}, N1A-H···O2A 126^{O}, N3B-H···O2A 149^{O}, N4B-H···O2A 167^{O}, N1A-H···O1B 147^{O}, N2A-H···O1B 164^{O}, N3B-H···O1B 122^{O},

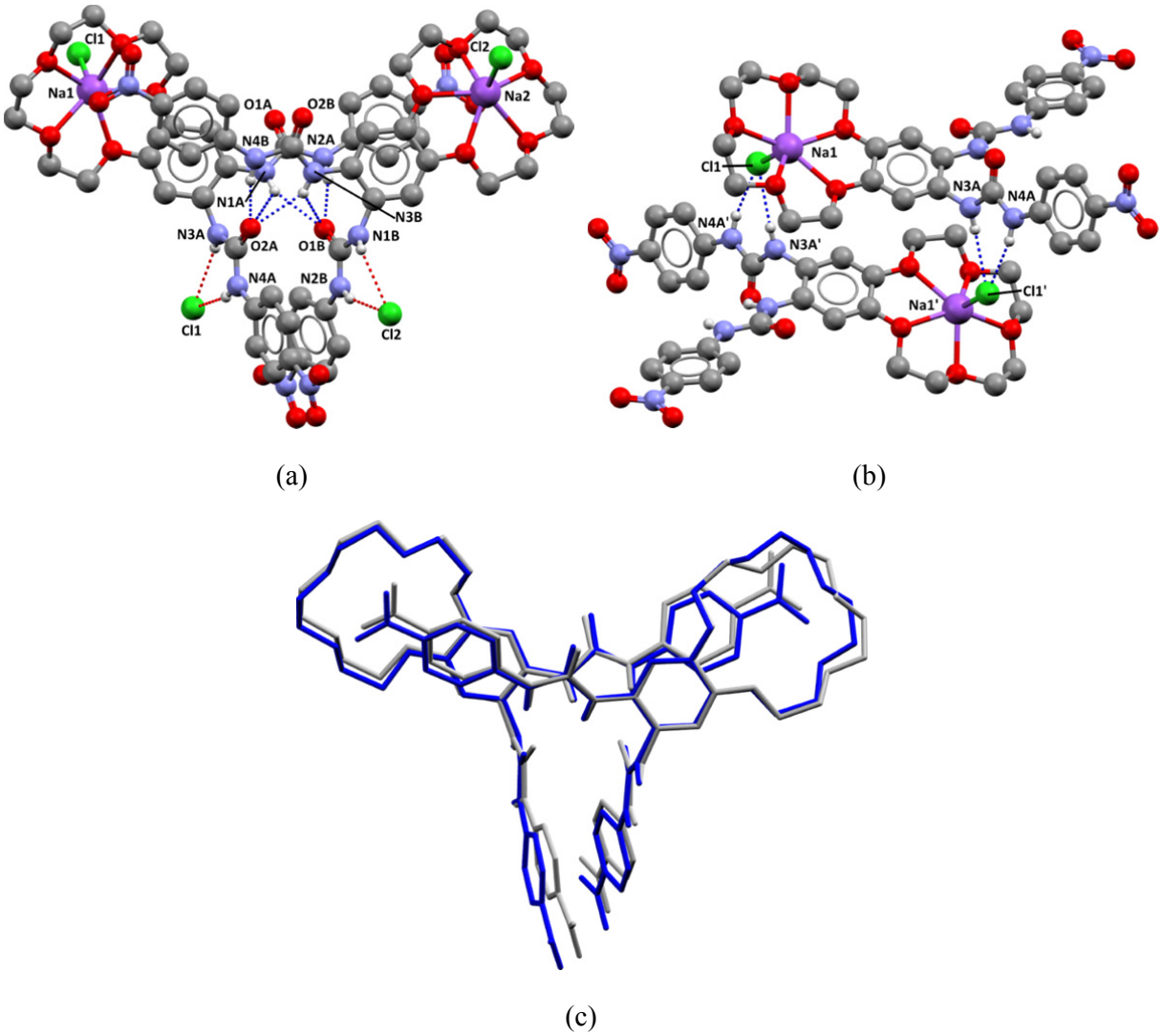


Figure S10. Crystal structure of **L·NaCl**. (a) Dimerization of the receptor molecules results from hydrogen bonding between the urea functionalities as in structure **L**. (b) Chloride anion forms a contact ion pair with the sodium cation. Chloride is further hydrogen bonded with the urea group of the adjacent receptor. (c) Structure overlay of crystal structures **L** (blue) and **L·NaCl** (grey). Disorder of one of the crown ethers and the nonbonding hydrogen atoms have been omitted from the figure.

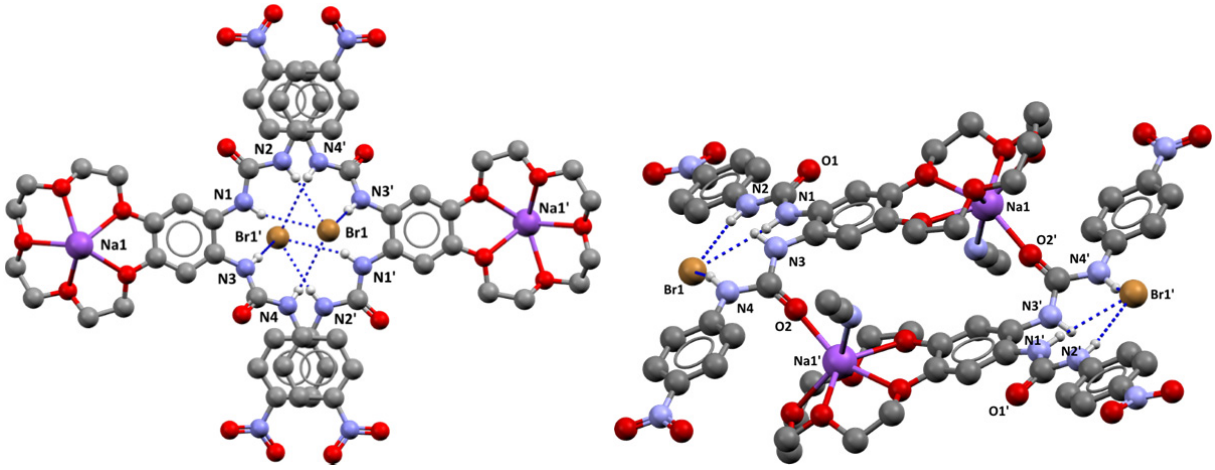
2.2.6 Crystal Structure of L·NaBr

The hydrogen bond distances:

N1···Br1 3.594(1) Å, N2···Br1 3.350(1) Å, N4···Br1 3.499(2) Å, N3···Br1’ 3.397(2) Å

The hydrogen bond angles:

N1-H···Br1 158^{O}, N2-H···Br1 171^{O}, N4-H···Br1 130^{O}, N3-H···Br1’ 156^{O}



(a) (b)

Figure S11. Crystal structure of **L·NaBr**. (a) **L** molecules form a urea proton-coated binding pocket for bromide anions. (b) Carbonyl oxygen O2 coordinates to sodium cation. The coordination sphere of sodium is filled with acetonitrile molecule. Disordered water solvate molecules and the nonbonding hydrogen atoms are omitted from the figure.

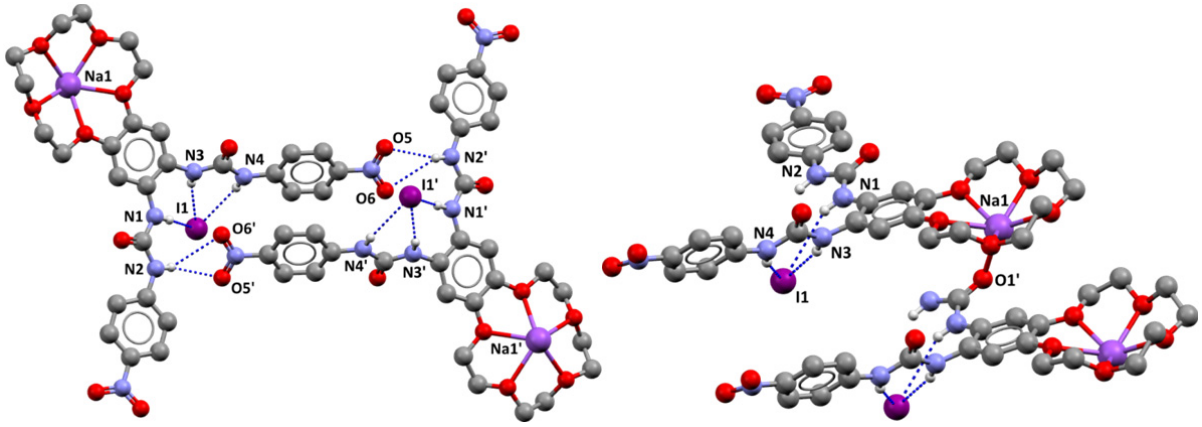
2.2.7 Crystal Structure of L·NaI

The hydrogen bond distances:

N1···I1 3.934(3) Å, N3···I1 3.515(3) Å, N4···I1 3.646(3) Å, N2···O5' 3.088(3) Å, N2···O6' 3.240(3) Å

The hydrogen bond angles:

N1-H···I1 154^{O}, N3-H···I1 162^{O}, N4-H···I1 159^{O}, N2-H···O5' 149^{O}, N2-H···O6' 121^{O}



(a) (b)

Figure S12. Crystal structure of **L·NaI**. (a) Iodide is hydrogen bonded with three urea nitrogens and there is hydrogen bonding between the urea nitrogen and the nitro group in the adjacent molecule. (b) Carbonyl oxygen O1 is coordinated to the sodium cation in the adjacent complex resulting in a 1D coordination polymer along the crystallographic b-axis. Disorder in the crown ether, water and acetone solvate molecules and the nonbonding hydrogen atoms have been omitted from the figure.

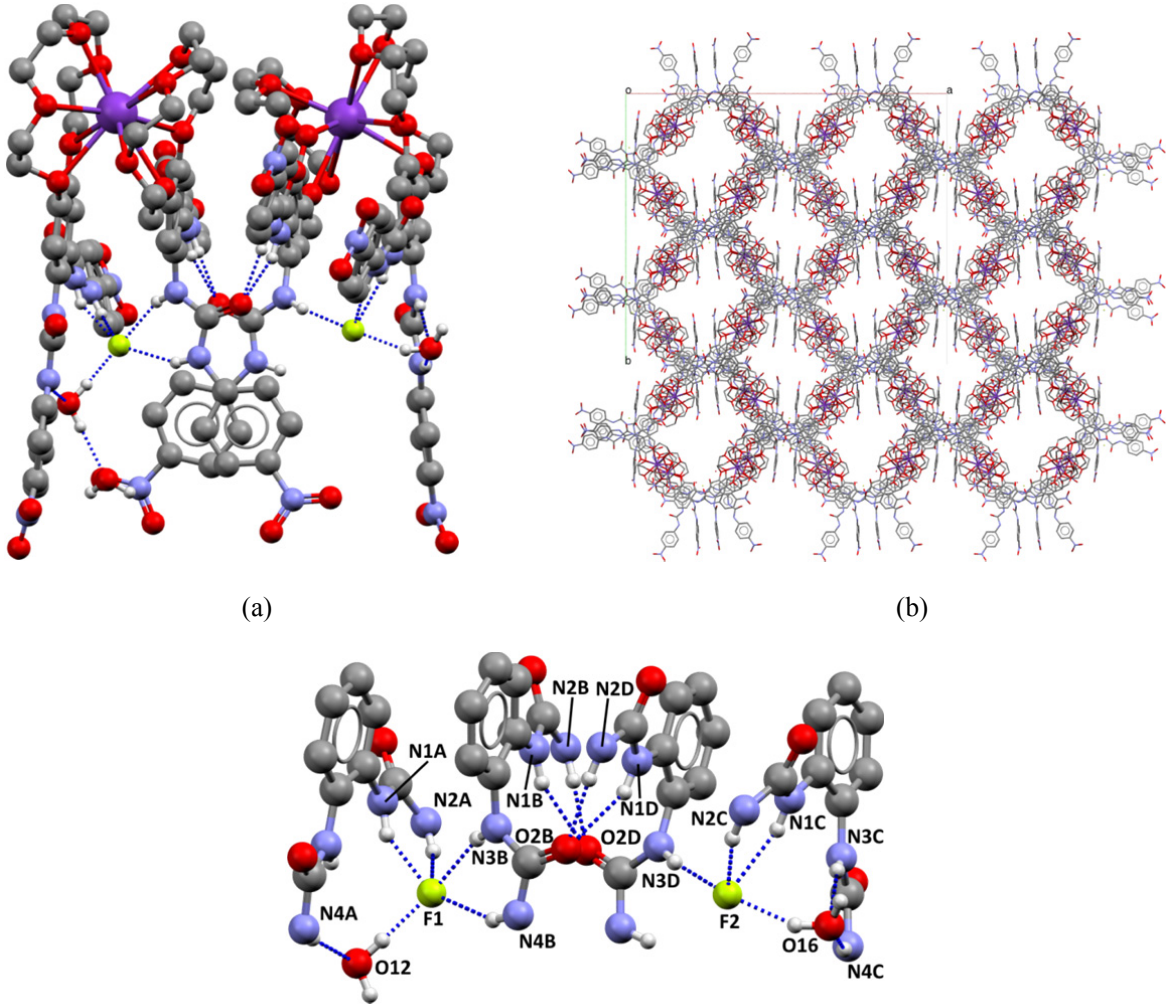
2.2.8 Crystal Structure of 2L·KF

The hydrogen bond distances:

N1A···F1 2.633(6) Å, N2A···F1 2.957(6) Å, N3B···F1 2.716(7) Å, N4B···F1 2.833(7) Å, O12···F1 2.557(8) Å, N1C···F2 2.871(6) Å, N2C···F2 2.707(6) Å, N3D···F2 2.785(6) Å, O16···F2 2.658(6) Å, N1D···O2B 3.017(6) Å, N2D···O2B 2.866(6) Å, N1B···O2D 3.039(6) Å, N2B···O2D 2.798(6) Å, N4A···O12 2.855(7) Å, N3C···O16 2.939(6) Å, N4C···O16 2.977(6) Å

The hydrogen bond angles:

N1A-H···F1 149^{O}, N2A-H···F1 147^{O}, N3B-H···F1 151^{O}, N4B-H···F1 152^{O}, O12-H···F1 169^{O}, N1C-H···F2 150^{O}, N2C-H···F2 159^{O}, N3D-H···F2 165^{O}, O16-H···F2 156^{O}, N1D-H···O2B 151^{O}, N2D-H···O2B 163^{O}, N1B-H···O2D 150^{O}, N2B-H···O2D 168^{O}, N4A-H···O12 160^{O}, N3C-H···O16 162^{O}, N4C-H···O16 159^{O}



(a) (b)

(c)

Figure S13. Crystal structure of **2L·KF**. (a) Dimer of **2L·KF** complexes are formed by hydrogen bonding between the urea groups in the adjacent dimers. (b) Crystal packing along the crystallographic c-axis. The structure has 8.6 % voids of the total volume. (c) More detailed figure of the hydrogen bonds responsible of the dimerization of the complexes and fluoride binding. All solvent molecules that are not interacting with the anions are omitted from the picture. Disorder in one of the crown ether rings is omitted for clarity.

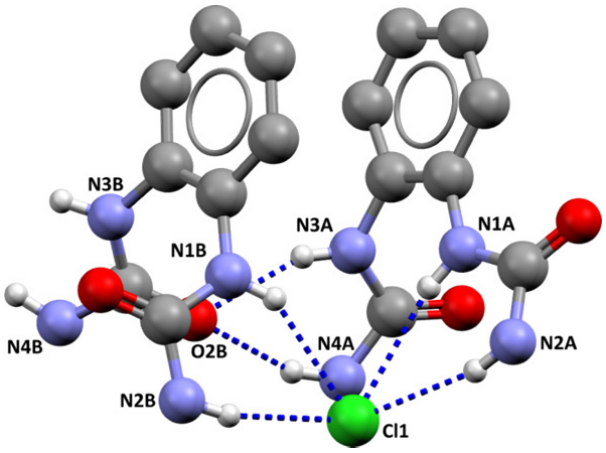
2.2.9 Crystal Structure of 2L·KCl

The hydrogen bond distances:

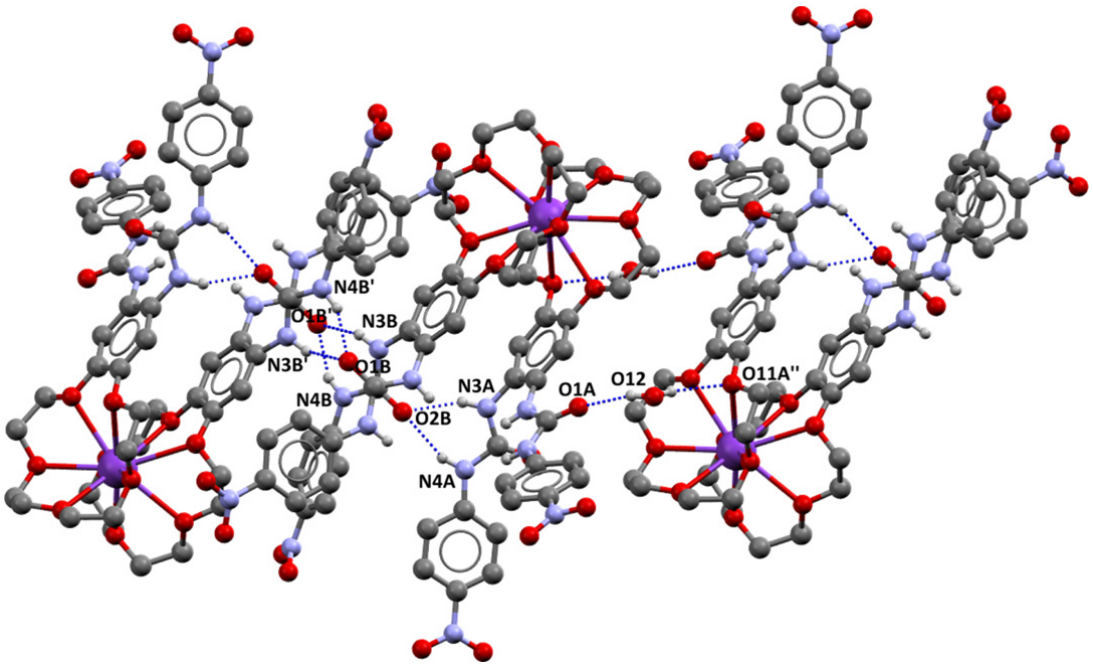
N1A···Cl1 3.389(2) Å, N2A···Cl1 3.171(2) Å, N1B···Cl1 3.264(2) Å, N2B···Cl1 3.194(2) Å, N3A···O2B 2.892(3) Å, N4A···O2B 2.942(3) Å, N3B···O1B' 2.891(2) Å, N4B···O1B' 2.750(3) Å, O12···O1A 2.829(3) Å, O12···O11A'' 2.941(4) Å

The hydrogen bond angles:

N1A-H···Cl1 156^{O}, N2A-H···Cl1 165^{O}, N1B-H···Cl1 148^{O}, N2B-H···Cl1 163^{O}, N3A-H···O2B 157^{O}, N4A-H···O2B 152^{O}, N3B···O1B' 144^{O}, N4B···O1B' 155^{O}, O12···O1A 166^{O}, O12···O11A'' 151^{O}



(a)



(b)

Figure S14. Crystal structure of **2L·KCl**. (a) Detailed image of the hydrogen bonds responsible for chloride binding. (b) Packing of three dimers. Chloride is omitted from the picture for clarity.

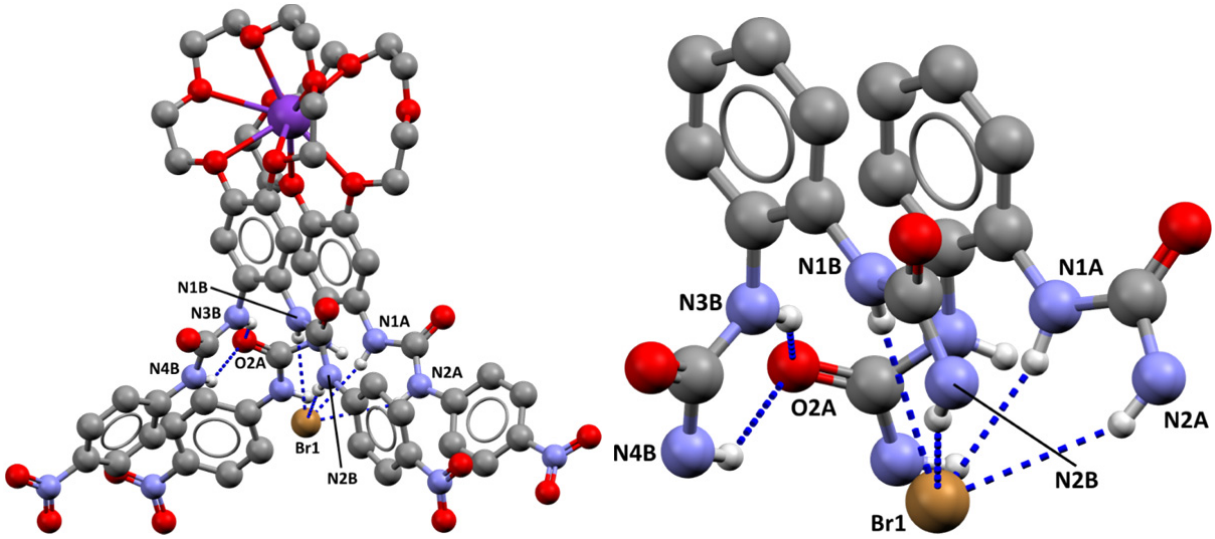
2.2.10 Crystal Structure of 2L·KBr

The hydrogen bond distances:

N1A···Br1 3.363(3) Å, N2A···Br1 3.692(3) Å, N1B···Br1 3.700(3) Å, N2B···Br1 3.339(3) Å, N3B···O2A 2.814(3) Å, N4B···O2A 2.988(4) Å

The hydrogen bond angles:

N1A-H···Br1 148^{O}, N2A-H···Br1 152^{O}, N1B-H···Br1 156^{O}, N2B-H···Br1 164^{O}, N3B-H···O2A 145^{O}, N4B-H···O2A 138^{O}



(a) (b)

Figure S15. Crystal structure of **2L·KBr**. (a) Structure of the dimer. (b) Detailed picture of the hydrogen bonding responsible for the dimerization and the bromide binding.

2.2.11 Crystal Structure of 2L·KI

The hydrogen bond distances:

N1A···I1 3.615(5) Å, N2A···I1 3.651(5) Å, N2B···I1 3.677(4) Å, N3B···O2A 2.776(6) Å, N4B···O2A 3.059(6) Å

The hydrogen bond angles:

N1A-H···I1 147^{O}, N2A-H···I1 151^{O}, N2B-H···I1 175^{O}, N3B-H···O2A 149^{O}, N4B-H···O2A 146^{O}

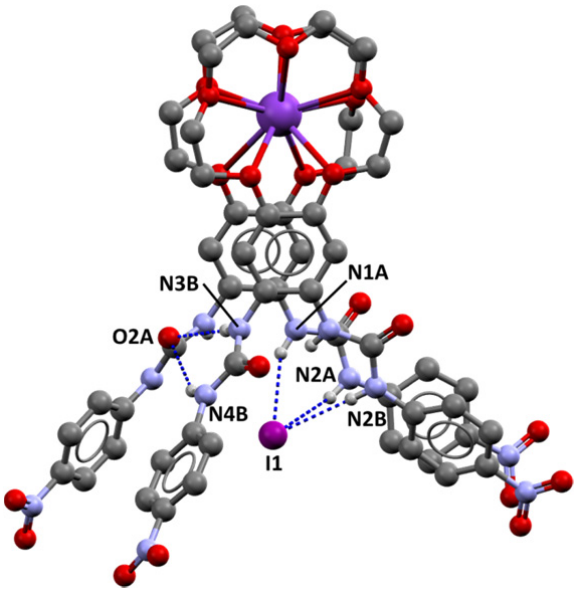


Figure S16. Crystal structure of **2L·KI**. The structure resembles complex **2L·KBr** (Figure S15) very closely.

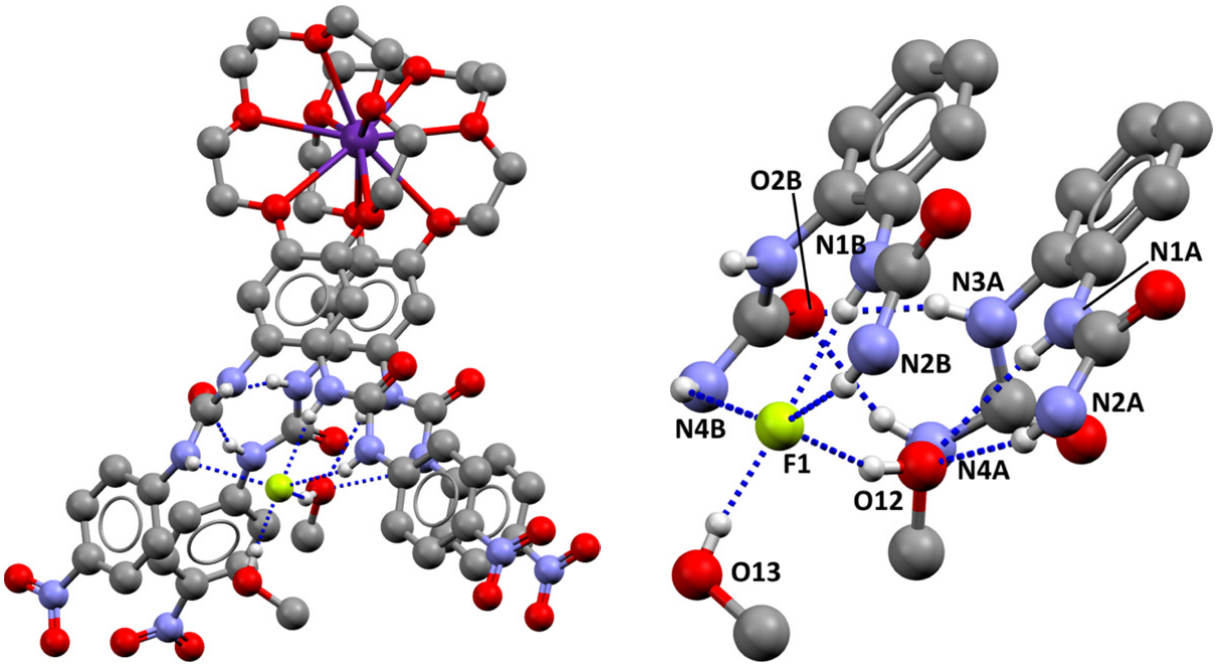
2.2.12 Crystal Structure of 2L·RbF

The hydrogen bond distances:

N1B···F1 2.803(2) Å, N2B···F1 2.835(2) Å, N4B···F1 2.941(3) Å, O12···F1 2.643(2) Å, O13···F1 2.566(2) Å, N3A···O2B 2.877(2) Å, N4A···O2B 2.950(2) Å, N1A···O12 3.090(2) Å, N2A···O12 2.822(3) Å

The hydrogen bond angles:

N1B···F1 160^{O}, N2B···F1 157^{O}, N4B···F1 122^{O}, O12···F1 157^{O}, O13···F1 171^{O}, N3A···O2B 158^{O}, N4A···O2B 157^{O}, N1A-H···O12 152^{O}, N2A···O12 161^{O}



(a) (b)

Figure S17. Crystal structure of **2L·RbF**. (a) Structure of the dimeric assembly. (b) Detailed image of the hydrogen bonding between the **L** molecules and the interactions responsible for fluoride binding.

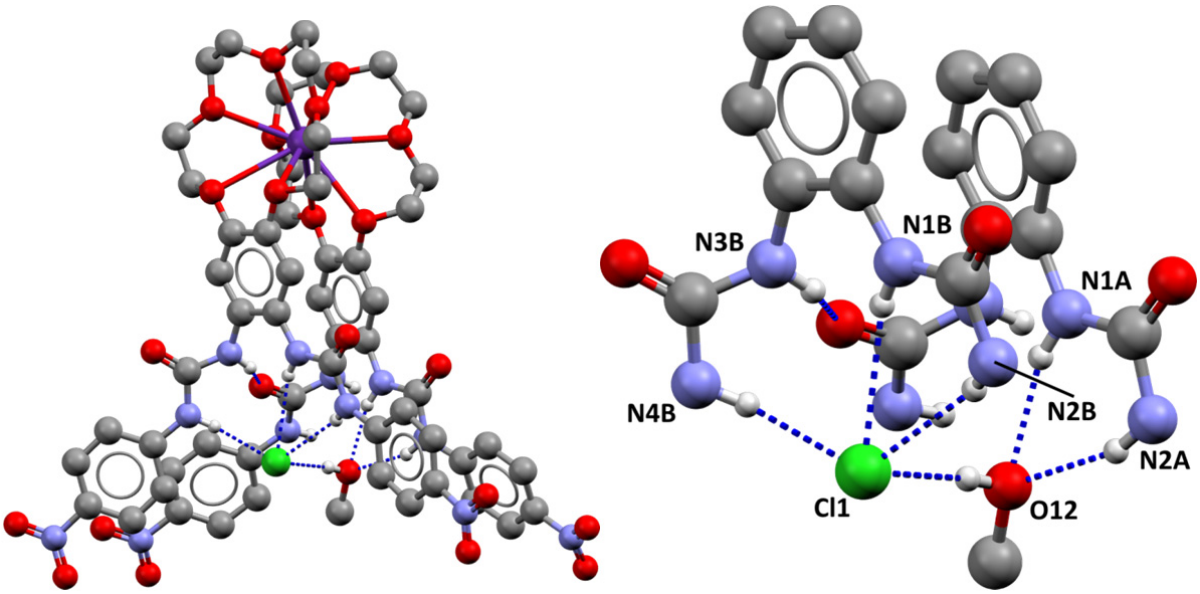
2.2.13 Crystal Structure of 2L·RbCl

The hydrogen bond distances:

N1B···Cl1 3.451(4) Å, N2B···Cl1 3.174(3) Å, N4B···Cl1 3.221(3) Å, O12···Cl1 3.066(4) Å, N3B···O2A 2.718(4) Å, N1A···O12 2.914(5) Å, N2A···O12 2.889(5) Å

The hydrogen bond angles:

N1B-H···Cl1 154^{O}, N2B-H···Cl1 150^{O}, N4B-H···Cl1 141^{O}, O12···Cl1 174^{O}, N3B-H···O2A 134^{O}, N1A-H···O12 158^{O}, N2A-H···O12 160^{O}



(a) (b)

Figure S18. Crystal structure of **2L·RbCl**. (a) The dimeric assembly of **2L·RbCl**. (b) Hydrogen bonds involved in the dimerization and chloride binding.

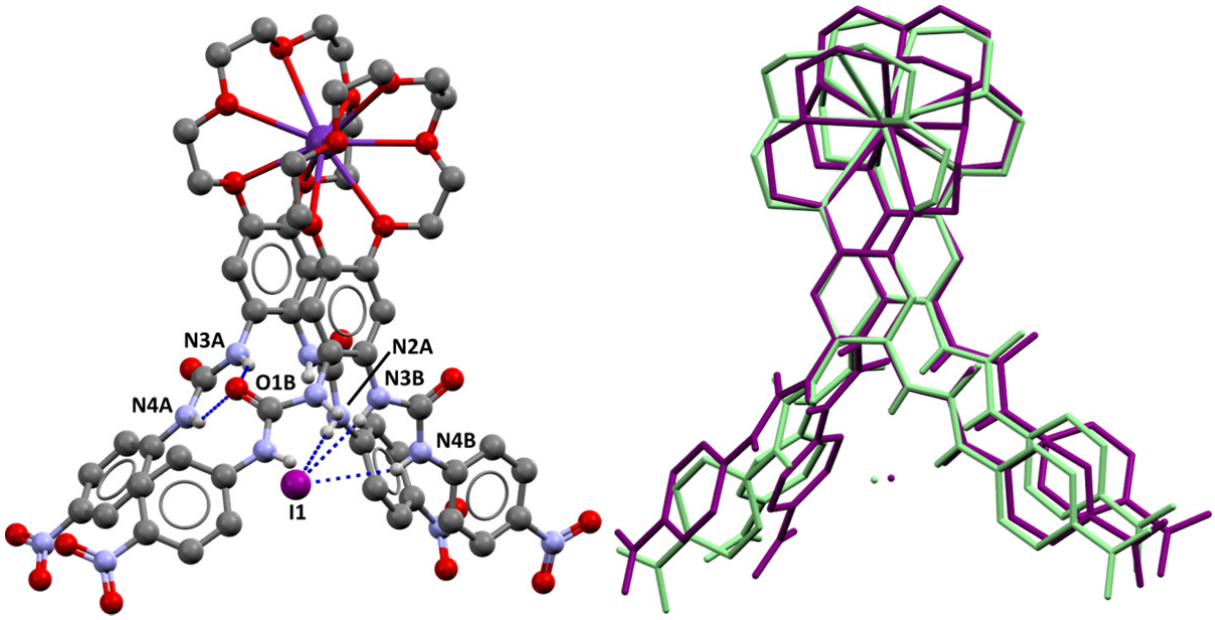
2.2.14 Crystal Structure of 2L·RbI

The hydrogen bond distances:

N2A···I1 3.665(5) Å, N3B···I1 3.588(5) Å, N4B···I1 3.664(5) Å, N3A···O1B 2.777(6) Å, N4A···O1B 3.029(6) Å

The hydrogen bond angles:

N2A-H···I1 176^{O}, N3B-H···I1 146^{O}, N4B-H···I1 149^{O}, N3A-H···O1B 149^{O}, N4A-H···O1B 146^{O}

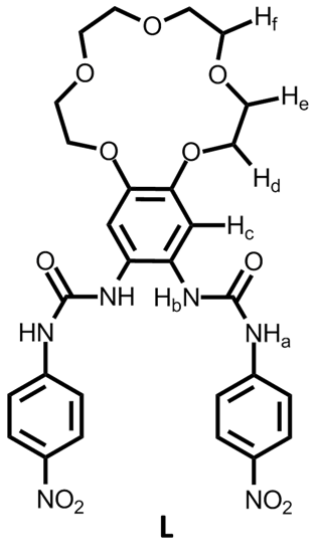


(a) (b)

Figure S19. Crystal structure of **2L·RbI**. (a) The structure of the dimeric assembly. (b) Structure overlay of **2L·RbF** (light green) and **2L·RbI** (purple).

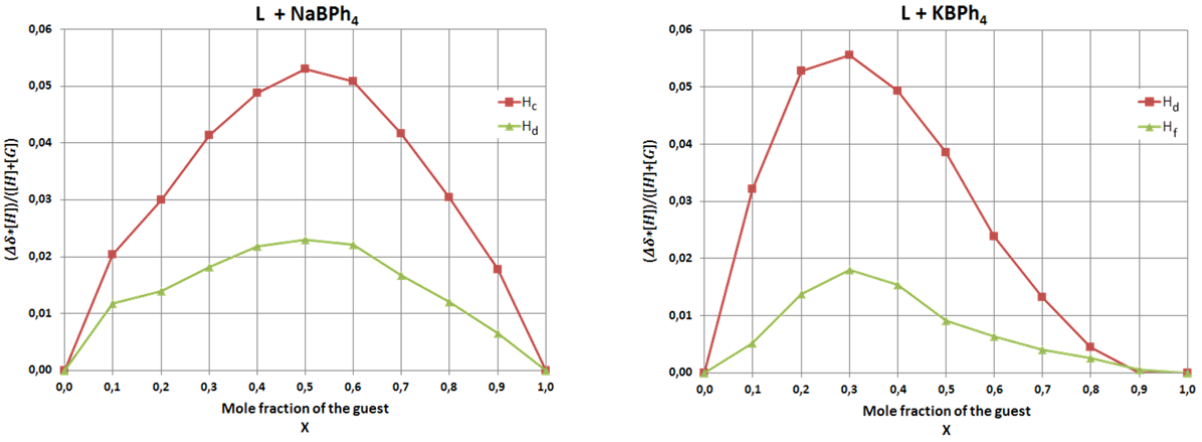
3. Solution Studies

3.1 Job's Plot Analysis



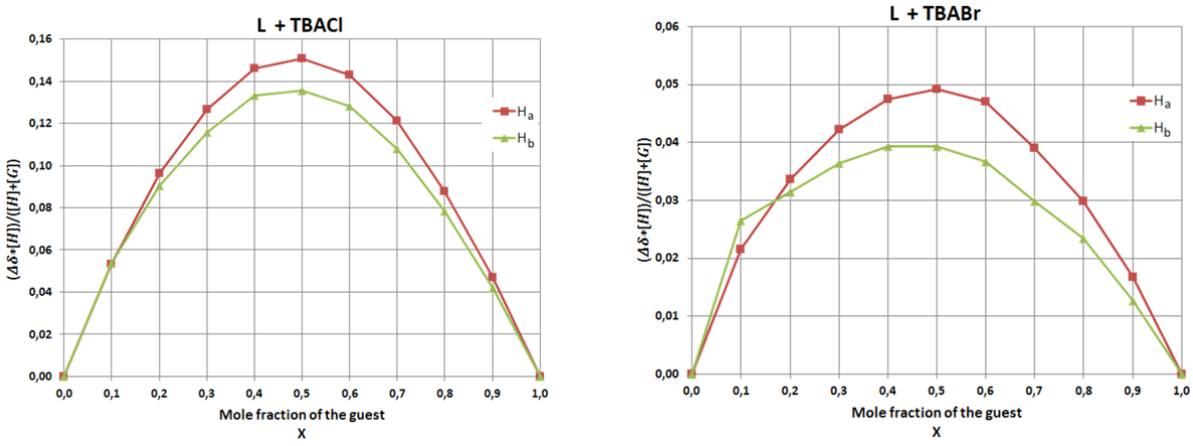
L

Figure S20. Proton assignment of **L** for Job's plot analysis and ^{1}H NMR titrations.



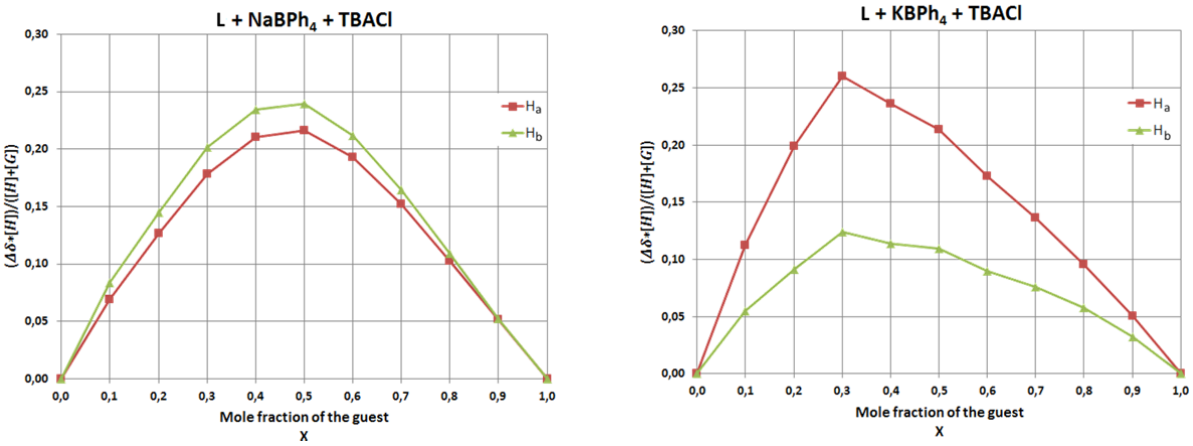
(a) (b)

Figure S21. Job's plot analysis for (a) **L** + $NaBPh_4$ and (b) **L** + $KBPh_4$.



(a) (b)

Figure S22. Job's plot analysis for (a) **L** + TBACl and (b) **L** + TBABr.



(a) (b)

Figure S23. Job's plot analysis for (a) **L** + $NaBPh_4$ + TBACl and (b) **L** + $KBPh_4$ + TBACl.

3.2 ^{1}H NMR Titrations

3.2.1 L + TBACl

L + TBACl

Species	Log beta	**L**	Cl	
1	2,9182	1	1	refine

Species concentrations/mol dm-3

Point	T(**L**)	T(Cl)	F(**L**)	F(Cl)	species 1
1	2,5537e-03	0,0000e00	2,5537e-03	1,9499e-90	4,1244e-90
2	2,5486e-03	2,5137e-04	2,3818e-03	8,4557e-05	1,6681e-04
3	2,5435e-03	5,0174e-04	2,2186e-03	1,7682e-04	3,2492e-04
4	2,5385e-03	7,5111e-04	2,0645e-03	2,7716e-04	4,7394e-04
5	2,5334e-03	9,9949e-04	1,9198e-03	3,8588e-04	6,1361e-04
6	2,5259e-03	1,3702e-03	1,7207e-03	5,6500e-04	8,0523e-04
7	2,5160e-03	1,8611e-03	1,4884e-03	8,3354e-04	1,0276e-03
8	2,5066e-03	2,3239e-03	1,3012e-03	1,1185e-03	1,2054e-03
9	2,4968e-03	2,8073e-03	1,1359e-03	1,4465e-03	1,3609e-03
10	2,4866e-03	3,3109e-03	9,9267e-04	1,8170e-03	1,4939e-03
11	2,4750e-03	3,8813e-03	8,6019e-04	2,2665e-03	1,6148e-03
12	2,4626e-03	4,4934e-03	7,4622e-04	2,7770e-03	1,7164e-03
13	2,4437e-03	5,4231e-03	6,1452e-04	3,5939e-03	1,8292e-03
14	2,4206e-03	6,5654e-03	4,9943e-04	4,6442e-03	1,9211e-03
15	2,3978e-03	7,6862e-03	4,1869e-04	5,7071e-03	1,9792e-03
16	2,3536e-03	9,8660e-03	3,1454e-04	7,8269e-03	2,0391e-03
17	2,2700e-03	1,3993e-02	2,0859e-04	1,1932e-02	2,0614e-03
18	2,1193e-03	2,1425e-02	1,2399e-04	1,9430e-02	1,9953e-03

Measured chemical shifts

Point	H_a	H_b	H_c
1	8,9964e00	7,5738e00	6,8384e00
2	9,0327e00	7,6049e00	6,8568e00
3	9,0683e00	7,6350e00	6,8758e00
4	9,1031e00	7,6664e00	6,8964e00
5	9,1435e00	7,7011e00	6,9178e00
6	9,1949e00	7,7463e00	6,9449e00
7	9,2601e00	7,8032e00	6,9821e00
8	9,3139e00	7,8501e00	7,0116e00
9	9,3618e00	7,8925e00	7,0375e00
10	9,4005e00	7,9269e00	7,0585e00
11	9,4379e00	7,9587e00	7,0781e00
12	9,4690e00	7,9858e00	7,0934e00
13	9,5045e00	8,0171e00	7,1115e00
14	9,5361e00	8,0445e00	7,1278e00
15	9,5555e00	8,0604e00	7,1352e00
16	9,5847e00	8,0858e00	7,1492e00
17	9,6133e00	8,1114e00	7,1622e00
18	9,6358e00	8,1303e00	7,1678e00

Calculated chemical shifts

Point	H_a	H_b	H_c
1	8,9817e00	7,5604e00	6,8330e00
2	9,0272e00	7,6001e00	6,8570e00
3	9,0705e00	7,6379e00	6,8798e00
4	9,1115e00	7,6736e00	6,9015e00
5	9,1501e00	7,7073e00	6,9218e00
6	9,2033e00	7,7538e00	6,9499e00
7	9,2656e00	7,8081e00	6,9828e00
8	9,3160e00	7,8521e00	7,0094e00
9	9,3606e00	7,8910e00	7,0329e00
10	9,3994e00	7,9248e00	7,0534e00

11	9,4353e00	7,9561e00	7,0723e00
12	9,4663e00	7,9831e00	7,0886e00
13	9,5021e00	8,0144e00	7,1076e00
14	9,5335e00	8,0418e00	7,1241e00
15	9,5556e00	8,0610e00	7,1358e00
16	9,5840e00	8,0859e00	7,1508e00
17	9,6131e00	8,1112e00	7,1661e00
18	9,6363e00	8,1315e00	7,1783e00

Chemical shifts for each nucleus

species	H_a	H_b	H_c
L	8,9817e00	7,5604e00	6,8330e00
(**L**)Cl	9,6770e00	8,1669e00	7,1998e00

Converged in 4 iterations with sigma = 5,267001

	value	standard deviation	Comments
1 log beta((**L**)Cl)	2.9182	0.0114	2.92(1)

Free energy of association at 303 K: ΔG = -16.931 kJ M^{-1}

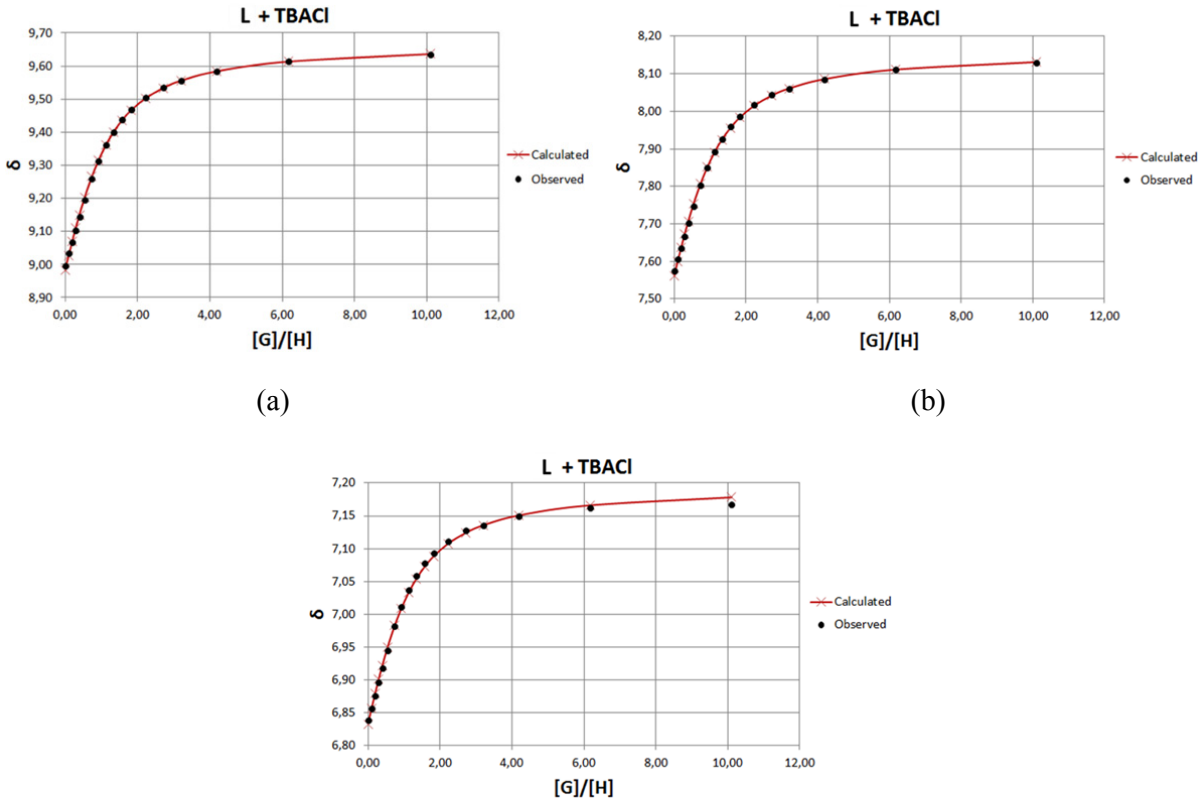


Figure S24. Binding isotherms of titration **L** + TBACl for (a) H_a, (b) H_b, and (c) H_c protons using 1:1 binding model.

3.2.2 L + TBABr

L + TBABr

Species	Log beta	**L**	Br	
1	2,2419	1	1	refine

Species concentrations/mol dm-3

Point	T(**L**)	T(Br)	F(**L**)	F(Br)	species 1
1	2,5537e-03	0,0000e00	2,5537e-03	3,4256e-90	1,5268e-90
2	2,5486e-03	2,4849e-04	2,4737e-03	1,7356e-04	7,4930e-05
3	2,5435e-03	4,9599e-04	2,3972e-03	3,4969e-04	1,4630e-04
4	2,5380e-03	7,6711e-04	2,3171e-03	5,4622e-04	2,2089e-04
5	2,5324e-03	1,0370e-03	2,2409e-03	7,4549e-04	2,9155e-04
6	2,5249e-03	1,4032e-03	2,1430e-03	1,0213e-03	3,8196e-04
7	2,5189e-03	1,6946e-03	2,0693e-03	1,2450e-03	4,4963e-04
8	2,5081e-03	2,2253e-03	1,9443e-03	1,6615e-03	5,6379e-04
9	2,4982e-03	2,7038e-03	1,8408e-03	2,0463e-03	6,5743e-04
10	2,4880e-03	3,2021e-03	1,7416e-03	2,4557e-03	7,4642e-04
11	2,4774e-03	3,7199e-03	1,6469e-03	2,8894e-03	8,3049e-04
12	2,4674e-03	4,2100e-03	1,5644e-03	3,3070e-03	9,0293e-04
13	2,4484e-03	5,1326e-03	1,4258e-03	4,1099e-03	1,0227e-03
14	2,4252e-03	6,2661e-03	1,2806e-03	5,1215e-03	1,1446e-03
15	2,4024e-03	7,3783e-03	1,1601e-03	6,1360e-03	1,2423e-03
16	2,3580e-03	9,5411e-03	9,7299e-04	8,1561e-03	1,3850e-03
17	2,2740e-03	1,3636e-02	7,3108e-04	1,2093e-02	1,5429e-03
18	2,1228e-03	2,1008e-02	4,8460e-04	1,9370e-02	1,6382e-03

Measured chemical shifts

Point	H_a	H_b	H_c
1	8,9973e00	7,5742e00	6,8383e00
2	9,0155e00	7,5866e00	6,8485e00
3	9,0317e00	7,5976e00	6,8574e00
4	9,0473e00	7,6079e00	6,8654e00
5	9,0616e00	7,6180e00	6,8741e00
6	9,0735e00	7,6262e00	6,8806e00
7	9,0874e00	7,6354e00	6,8882e00
8	9,1101e00	7,6514e00	6,9008e00
9	9,1286e00	7,6642e00	6,9111e00
10	9,1463e00	7,6772e00	6,9224e00
11	9,1639e00	7,6882e00	6,9300e00
12	9,1772e00	7,6982e00	6,9364e00
13	9,2032e00	7,7157e00	6,9493e00
14	9,2270e00	7,7338e00	6,9629e00
15	9,2484e00	7,7473e00	6,9741e00
16	9,2823e00	7,7716e00	6,9920e00
17	9,3264e00	7,8036e00	7,0151e00
18	9,3738e00	7,8371e00	7,0382e00

Calculated chemical shifts

Point	H_a	H_b	H_c
1	9,0024e00	7,5767e00	6,8426e00
2	9,0165e00	7,5865e00	6,8501e00
3	9,0300e00	7,5959e00	6,8573e00
4	9,0441e00	7,6057e00	6,8648e00
5	9,0575e00	7,6151e00	6,8720e00
6	9,0748e00	7,6272e00	6,8812e00
7	9,0879e00	7,6363e00	6,8882e00
8	9,1100e00	7,6517e00	6,9000e00
9	9,1284e00	7,6645e00	6,9098e00
10	9,1460e00	7,6769e00	6,9192e00
11	9,1629e00	7,6886e00	6,9282e00
12	9,1776e00	7,6989e00	6,9361e00
13	9,2024e00	7,7162e00	6,9493e00

14	9,2283e00	7,7343e00	6,9631e00
15	9,2500e00	7,7494e00	6,9746e00
16	9,2836e00	7,7728e00	6,9926e00
17	9,3272e00	7,8033e00	7,0159e00
18	9,3718e00	7,8344e00	7,0396e00

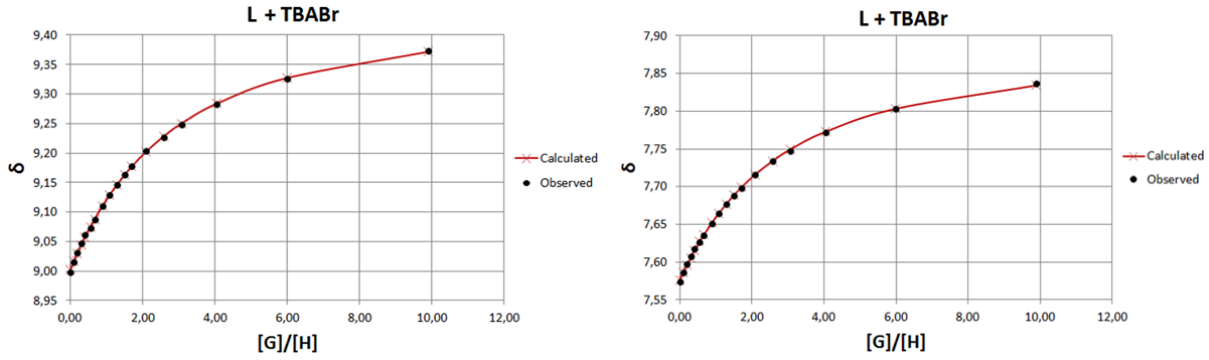
Chemical shifts for each nucleus

species	H_a	H_b	H_c
L	9,0024e00	7,5767e00	6,8426e00
(**L**)Br	9,4811e00	7,9106e00	7,0979e00

Converged in 4 iterations with sigma = 1,819593

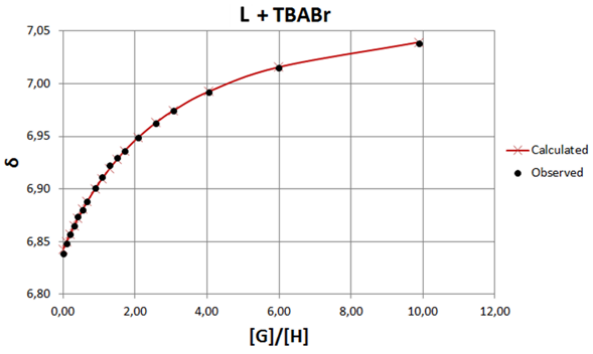
	value	standard deviation	Comments
1 log beta((**L**)Br)	2.2419	0.0076	2.242(8)

Free energy of association at 303 K: ΔG = -13.007 kJ M^{-1}



(a)

(b)



(c)

Figure S25. Binding isotherms of titration **L** + TBABr for (a) H_a, (b) H_b, and (c) H_c protons using 1:1 binding model.

3.2.3 L + TBAI

L + TBAI

Species	Log beta	**L**	I	
1	1,5033	1	1	refine

Species concentrations/mol dm-3

Point	T(**L**)	T(I)	F(**L**)	F(I)	species 1
1	2,5537e-03	0,0000e00	2,5537e-03	4,1045e-90	3,3396e-91
2	2,5486e-03	2,4822e-04	2,5301e-03	2,2970e-04	1,8516e-05
3	2,5435e-03	4,9544e-04	2,5069e-03	4,5880e-04	3,6645e-05
4	2,5380e-03	7,6626e-04	2,4818e-03	7,1011e-04	5,6151e-05
5	2,5329e-03	1,0114e-03	2,4594e-03	9,3793e-04	7,3497e-05
6	2,5279e-03	1,2556e-03	2,4374e-03	1,1651e-03	9,0485e-05
7	2,5229e-03	1,4989e-03	2,4158e-03	1,3917e-03	1,0712e-04
8	2,5130e-03	1,9825e-03	2,3736e-03	1,8431e-03	1,3938e-04
9	2,5031e-03	2,4623e-03	2,3328e-03	2,2919e-03	1,7035e-04
10	2,4934e-03	2,9383e-03	2,2933e-03	2,7382e-03	2,0008e-04
11	2,4837e-03	3,4107e-03	2,2550e-03	3,1820e-03	2,2862e-04
12	2,4740e-03	3,8793e-03	2,2180e-03	3,6233e-03	2,5605e-04
13	2,4550e-03	4,8059e-03	2,1473e-03	4,4982e-03	3,0774e-04
14	2,4316e-03	5,9443e-03	2,0647e-03	5,5774e-03	3,6691e-04
15	2,4087e-03	7,0611e-03	1,9881e-03	6,6405e-03	4,2063e-04
16	2,3641e-03	9,2329e-03	1,8501e-03	8,7189e-03	5,1396e-04
17	2,2797e-03	1,3344e-02	1,6234e-03	1,2687e-02	6,5625e-04
18	2,1277e-03	2,0743e-02	1,3017e-03	1,9917e-02	8,2604e-04

Measured chemical shifts

Point	H_a	H_b
1	9,0006e00	7,5796e00
2	9,0035e00	7,5796e00
3	9,0044e00	7,5796e00
4	9,0067e00	7,5803e00
5	9,0079e00	7,5806e00
6	9,0091e00	7,5812e00
7	9,0123e00	7,5821e00
8	9,0135e00	7,5835e00
9	9,0164e00	7,5847e00
10	9,0194e00	7,5859e00
11	9,0207e00	7,5866e00
12	9,0230e00	7,5880e00
13	9,0272e00	7,5904e00
14	9,0313e00	7,5925e00
15	9,0374e00	7,5957e00
16	9,0451e00	7,6004e00
17	9,0581e00	7,6083e00
18	9,0779e00	7,6202e00

Calculated chemical shifts

Point	H_a	H_b
1	9,0025e00	7,5777e00
2	9,0039e00	7,5785e00
3	9,0053e00	7,5792e00
4	9,0068e00	7,5800e00
5	9,0081e00	7,5808e00
6	9,0094e00	7,5815e00
7	9,0108e00	7,5822e00
8	9,0133e00	7,5836e00
9	9,0158e00	7,5849e00
10	9,0181e00	7,5862e00
11	9,0204e00	7,5874e00
12	9,0227e00	7,5887e00
13	9,0270e00	7,5910e00

14	9,0319e00	7,5937e00
15	9,0366e00	7,5962e00
16	9,0449e00	7,6007e00
17	9,0587e00	7,6082e00
18	9,0783e00	7,6188e00

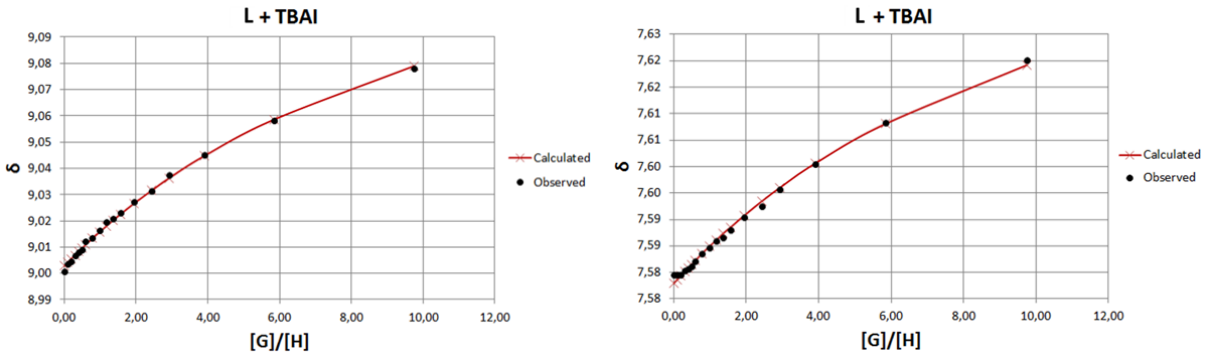
Chemical shifts for each nucleus

species	H_a	H_b
L	9,0025e00	7,5777e00
(**L**)I	9,1979e00	7,6835e00

Converged in 3 iterations with sigma = 0,830300

	value	standard deviation	Comments
1 log beta((**L**)I)	1.5033	0.0364	1.5(4)

Free energy of association at 303 K: ΔG = -8.722 kJ M^{-1}



(a) (b)

Figure S26. Binding isotherms of titration **L** + TBAI for (a) H_a and (b) H_b protons using 1:1 binding model.

3.2.4 L + $NaBPh_4$ + TBACl

L + NaBPh4 + TBACl_1

Species	Log beta	**L** + Na	TBACl	
1	3,8813	1	1	refine

Species concentrations/mol dm-3

Point	T(**L** + Na)	T(TBACl)	F(**L** + Na)	F(TBACl)	species 1
1	2,5336e-03	0,0000e00	2,5336e-03	6,2692e-91	1,2084e-89
2	2,5286e-03	2,5137e-04	2,2909e-03	1,3641e-05	2,3773e-04
3	2,5235e-03	5,0174e-04	2,0520e-03	3,0205e-05	4,7153e-04
4	2,5180e-03	7,7599e-04	1,7950e-03	5,2948e-05	7,2304e-04
5	2,5130e-03	1,0243e-03	1,5680e-03	7,9225e-05	9,4505e-04
6	2,5081e-03	1,2716e-03	1,3494e-03	1,1287e-04	1,1587e-03
7	2,5031e-03	1,5179e-03	1,1419e-03	1,5669e-04	1,3612e-03
8	2,4932e-03	2,0076e-03	7,7632e-04	2,9071e-04	1,7169e-03
9	2,4835e-03	2,4935e-03	5,0496e-04	5,1503e-04	1,9785e-03
10	2,4738e-03	2,9756e-03	3,3560e-04	8,3747e-04	2,1382e-03
11	2,4646e-03	3,4302e-03	2,4196e-04	1,2075e-03	2,2227e-03
12	2,4551e-03	3,9050e-03	1,8291e-04	1,6328e-03	2,2722e-03
13	2,4362e-03	4,8437e-03	1,2042e-04	2,5279e-03	2,3158e-03
14	2,4130e-03	5,9970e-03	8,3492e-05	3,6675e-03	2,3295e-03
15	2,3902e-03	7,1285e-03	6,3686e-05	4,8019e-03	2,3265e-03
16	2,3460e-03	9,3286e-03	4,3085e-05	7,0257e-03	2,3029e-03
17	2,2622e-03	1,3493e-02	2,6110e-05	1,1257e-02	2,2361e-03
18	2,1114e-03	2,0989e-02	1,4588e-05	1,8893e-02	2,0968e-03

Measured chemical shifts

Point	H_a	H_b	H_c
1	9,0439e00	7,6343e00	6,9524e00
2	9,0985e00	7,6939e00	6,9841e00
3	9,1574e00	7,7608e00	7,0192e00
4	9,2157e00	7,8244e00	7,0558e00
5	9,2714e00	7,8855e00	7,0896e00
6	9,3239e00	7,9440e00	7,1235e00
7	9,3711e00	7,9957e00	7,1526e00
8	9,4477e00	8,0802e00	7,2011e00
9	9,5115e00	8,1496e00	7,2426e00
10	9,5498e00	8,1890e00	7,2600e00
11	9,5740e00	8,2127e00	7,2769e00
12	9,5897e00	8,2284e00	7,2857e00
13	9,6109e00	8,2467e00	7,2954e00
14	9,6234e00	8,2572e00	7,3006e00
15	9,6317e00	8,2600e00	7,3005e00
16	9,6417e00	8,2630e00	7,2987e00
17	9,6473e00	8,2590e00	7,2917e00
18	9,6511e00	8,2391e00	

Calculated chemical shifts

Point	H_a	H_b	H_c
1	9,0429e00	7,6430e00	6,9545e00
2	9,0993e00	7,7023e00	6,9879e00
3	9,1550e00	7,7608e00	7,0209e00
4	9,2152e00	7,8240e00	7,0565e00
5	9,2685e00	7,8800e00	7,0881e00
6	9,3201e00	7,9342e00	7,1187e00
7	9,3692e00	7,9857e00	7,1477e00
8	9,4561e00	8,0770e00	7,1992e00
9	9,5210e00	8,1451e00	7,2376e00
10	9,5616e00	8,1877e00	7,2616e00
11	9,5841e00	8,2113e00	7,2750e00
12	9,5983e00	8,2263e00	7,2834e00
13	9,6133e00	8,2421e00	7,2923e00

14	9,6222e00	8,2514e00	7,2975e00
15	9,6270e00	8,2564e00	7,3004e00
16	9,6320e00	8,2616e00	7,3033e00
17	9,6361e00	8,2659e00	7,3057e00
18	9,6388e00	8,2689e00	

Chemical shifts for each nucleus

species	H_a	H_b	H_c
L + Na	9,0429e00	7,6430e00	6,9545e00
(**L** + Na)TBACl	9,6430e00	8,2732e00	7,3098e00

Converged in 3 iterations with sigma = 7,623075

	value	standard deviation	Comments
1 log beta((**L** + Na)Cl)	3.8813	0.032	3.88(3)

Free energy of association at 303 K: ΔG = -22.519 kJ M^{-1}

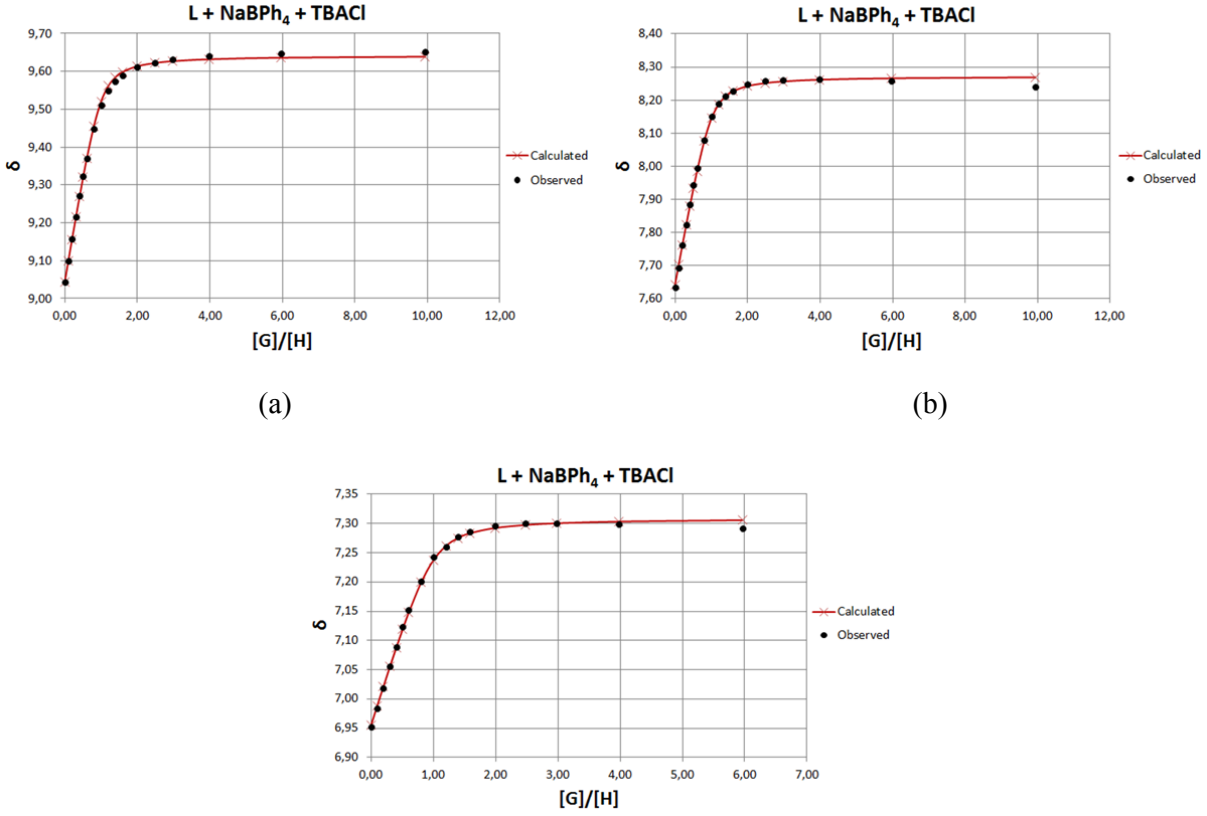


Figure S27. Binding isotherms of titration **L** + $NaBPh_4$ + TBACl for (a) H_a, (b) H_b, and (c) H_c using 1:1 binding model.

3.2.5 L + $NaBPh_4$ + TBABr

L + NaBPh4 + TBABr_1

Species	Log beta	**L** + Na	Br	
1	3,1494	1	1	refine

Species concentrations/mol dm-3

Point	T(**L** + Na)	T(Br)	F(**L** + Na)	F(Br)	species 1
1	2,5336e-03	0,0000e00	2,5336e-03	1,6036e-90	5,7313e-90
2	2,5286e-03	2,4973e-04	2,3370e-03	5,8122e-05	1,9161e-04
3	2,5230e-03	5,2329e-04	2,1304e-03	1,3065e-04	3,9263e-04
4	2,5180e-03	7,7093e-04	1,9524e-03	2,0535e-04	5,6558e-04
5	2,5125e-03	1,0422e-03	1,7685e-03	2,9822e-04	7,4399e-04
6	2,5076e-03	1,2878e-03	1,6129e-03	3,9319e-04	8,9462e-04
7	2,5026e-03	1,5324e-03	1,4690e-03	4,9880e-04	1,0336e-03
8	2,4928e-03	2,0188e-03	1,2170e-03	7,4307e-04	1,2757e-03
9	2,4825e-03	2,5253e-03	1,0029e-03	1,0458e-03	1,4796e-03
10	2,4723e-03	3,0278e-03	8,3489e-04	1,3903e-03	1,6374e-03
11	2,4618e-03	3,5497e-03	6,9917e-04	1,7871e-03	1,7626e-03
12	2,4522e-03	4,0203e-03	6,0349e-04	2,1716e-03	1,8487e-03
13	2,4334e-03	4,9508e-03	4,6706e-04	2,9844e-03	1,9663e-03
14	2,4102e-03	6,0939e-03	3,5955e-04	4,0432e-03	2,0507e-03
15	2,3875e-03	7,2155e-03	2,9045e-04	5,1184e-03	2,0971e-03
16	2,3434e-03	9,3964e-03	2,0842e-04	7,2614e-03	2,1349e-03
17	2,2598e-03	1,3525e-02	1,3232e-04	1,1397e-02	2,1274e-03
18	2,1093e-03	2,0957e-02	7,6162e-05	1,8924e-02	2,0331e-03

Measured chemical shifts

Point	H_a	H_b	H_c
1	9,0436e00	7,6331e00	6,9497e00
2	9,0755e00	7,6622e00	6,9692e00
3	9,1151e00	7,6991e00	6,9936e00
4	9,1453e00	7,7269e00	7,0127e00
5	9,1731e00	7,7545e00	7,0321e00
6	9,2000e00	7,7783e00	7,0496e00
7	9,2207e00	7,7985e00	7,0643e00
8	9,2608e00	7,8332e00	7,0871e00
9	9,2862e00	7,8591e00	7,1078e00
10	9,3103e00	7,8794e00	7,1215e00
11	9,3314e00	7,8983e00	7,1355e00
12	9,3465e00	7,9115e00	7,1455e00
13	9,3679e00	7,9286e00	7,1561e00
14	9,3876e00	7,9437e00	7,1660e00
15	9,3993e00	7,9541e00	7,1747e00
16	9,4176e00	7,9675e00	7,1840e00
17	9,4362e00	7,9794e00	7,1897e00
18	9,4524e00	7,9874e00	7,1925e00

Calculated chemical shifts

Point	H_a	H_b	H_c
1	9,0495e00	7,6433e00	6,9554e00
2	9,0800e00	7,6704e00	6,9744e00
3	9,1122e00	7,6989e00	6,9944e00
4	9,1400e00	7,7236e00	7,0117e00
5	9,1689e00	7,7491e00	7,0296e00
6	9,1933e00	7,7708e00	7,0448e00
7	9,2160e00	7,7909e00	7,0589e00
8	9,2558e00	7,8262e00	7,0836e00
9	9,2898e00	7,8563e00	7,1047e00
10	9,3165e00	7,8800e00	7,1213e00
11	9,3382e00	7,8992e00	7,1348e00
12	9,3535e00	7,9128e00	7,1443e00
13	9,3753e00	7,9321e00	7,1578e00

14	9,3926e00	7,9474e00	7,1685e00
15	9,4037e00	7,9572e00	7,1754e00
16	9,4169e00	7,9689e00	7,1836e00
17	9,4291e00	7,9798e00	7,1912e00
18	9,4382e00	7,9878e00	7,1969e00

Chemical shifts for each nucleus

species	H_a	H_b	H_c
L + Na	9,0495e00	7,6433e00	6,9554e00
(**L** + Na)Br	9,4527e00	8,0007e00	7,2059e00

Converged in 5 iterations with sigma = 5,252030

	value	standard deviation	Comments
1 log beta((**L** + Na)Br)	3.1494	0.0206	3.15(2)

Free energy of association at 303 K: ΔG = -18.273 kJ M^{-1}

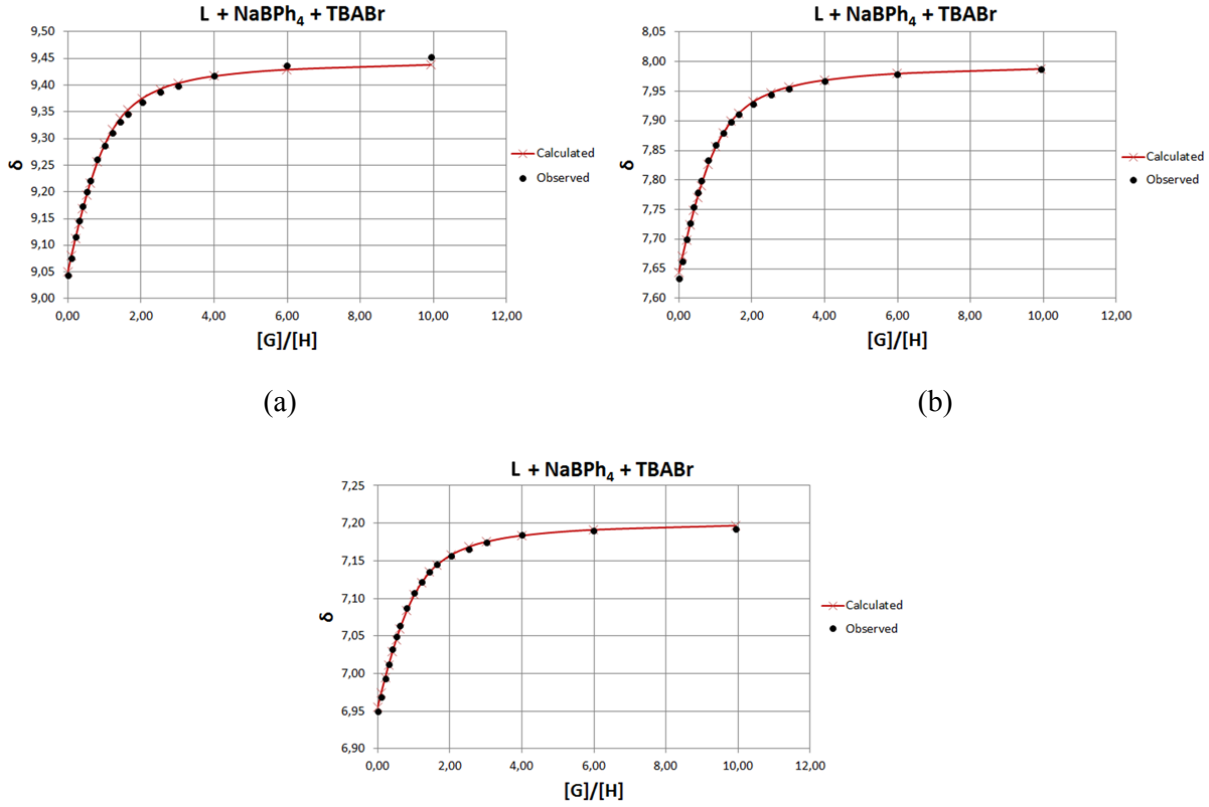


Figure S28. Binding isotherms of titration **L** + $NaBPh_4$ + TBABr for (a) H_a, (b) H_b, and (c) H_c using 1:1 binding model.

3.2.6 L + $NaBPh_4$ + TBAI

L + NaBPh4 + TBAI_1

Species	Log beta	**L** + Na	TBAI	
1	2,5727	1	1	refine

Species concentrations/mol dm-3

Point	T(**L** + Na)	T(I)	F(**L** + Na)	F(I)	species 1
1	2,5336e-03	0,0000e00	2,5336e-03	2,7564e-90	2,6111e-90
2	2,5286e-03	2,4894e-04	2,4106e-03	1,3093e-04	1,1800e-04
3	2,5235e-03	4,9688e-04	2,2941e-03	2,6747e-04	2,2941e-04
4	2,5175e-03	7,9311e-04	2,1629e-03	4,3850e-04	3,5461e-04
5	2,5125e-03	1,0389e-03	2,0605e-03	5,8682e-04	4,5207e-04
6	2,5066e-03	1,3326e-03	1,9454e-03	7,7143e-04	5,6112e-04
7	2,5011e-03	1,6005e-03	1,8473e-03	9,4667e-04	6,5384e-04
8	2,4913e-03	2,0847e-03	1,6854e-03	1,2789e-03	8,0588e-04
9	2,4815e-03	2,5652e-03	1,5430e-03	1,6267e-03	9,3848e-04
10	2,4718e-03	3,0419e-03	1,4179e-03	1,9880e-03	1,0539e-03
11	2,4622e-03	3,5149e-03	1,3079e-03	2,3605e-03	1,1543e-03
12	2,4527e-03	3,9842e-03	1,2110e-03	2,7425e-03	1,2417e-03
13	2,4343e-03	4,8890e-03	1,0531e-03	3,5078e-03	1,3812e-03
14	2,4112e-03	6,0293e-03	8,9696e-04	4,5151e-03	1,5142e-03
15	2,3884e-03	7,1482e-03	7,7788e-04	5,5376e-03	1,6105e-03
16	2,3442e-03	9,3238e-03	6,1081e-04	7,5903e-03	1,7334e-03
17	2,2606e-03	1,3442e-02	4,2342e-04	1,1605e-02	1,8371e-03
18	2,1100e-03	2,0855e-02	2,6030e-04	1,9006e-02	1,8497e-03

Measured chemical shifts

Point	H_a	H_b	H_c
1	9,0647e00	7,6585e00	6,9663e00
2	9,0708e00	7,6640e00	6,9691e00
3	9,0783e00	7,6699e00	6,9746e00
4	9,0872e00	7,6767e00	6,9789e00
5	9,0891e00	7,6811e00	6,9826e00
6	9,0978e00	7,6875e00	6,9858e00
7	9,0986e00	7,6904e00	6,9900e00
8	9,1073e00	7,6975e00	6,9956e00
9	9,1134e00	7,7038e00	7,0007e00
10	9,1197e00	7,7099e00	7,0045e00
11	9,1234e00	7,7132e00	7,0085e00
12	9,1289e00	7,7171e00	7,0106e00
13	9,1359e00	7,7247e00	7,0148e00
14	9,1436e00	7,7302e00	7,0191e00
15	9,1488e00	7,7370e00	7,0234e00
16	9,1598e00	7,7429e00	7,0292e00
17	9,1695e00	7,7488e00	7,0366e00
18	9,1813e00	7,7575e00	7,0419e00

Calculated chemical shifts

Point	H_a	H_b	H_c
1	9,0661e00	7,6606e00	6,9669e00
2	9,0720e00	7,6659e00	6,9709e00
3	9,0776e00	7,6708e00	6,9747e00
4	9,0839e00	7,6764e00	6,9790e00
5	9,0888e00	7,6807e00	6,9823e00
6	9,0944e00	7,6856e00	6,9861e00
7	9,0991e00	7,6898e00	6,9893e00
8	9,1070e00	7,6967e00	6,9946e00
9	9,1139e00	7,7028e00	6,9992e00
10	9,1200e00	7,7082e00	7,0034e00
11	9,1254e00	7,7129e00	7,0070e00
12	9,1301e00	7,7171e00	7,0102e00
13	9,1378e00	7,7239e00	7,0154e00

14	9,1455e00	7,7307e00	7,0206e00
15	9,1513e00	7,7358e00	7,0245e00
16	9,1596e00	7,7431e00	7,0301e00
17	9,1688e00	7,7513e00	7,0363e00
18	9,1769e00	7,7584e00	7,0418e00

Chemical shifts for each nucleus

species	H_a	H_b	H_c
L + Na	9,0661e00	7,6606e00	6,9669e00
(**L** + Na)I	9,1925e00	7,7722e00	7,0523e00

Converged in 6 iterations with sigma = 1,520847

	value	standard deviation	Comments
1 log beta((**L** + Na)I)	2.5727	0.0179	2.57(2)

Free energy of association at 303 K: ΔG = -14.927 kJ M^{-1}

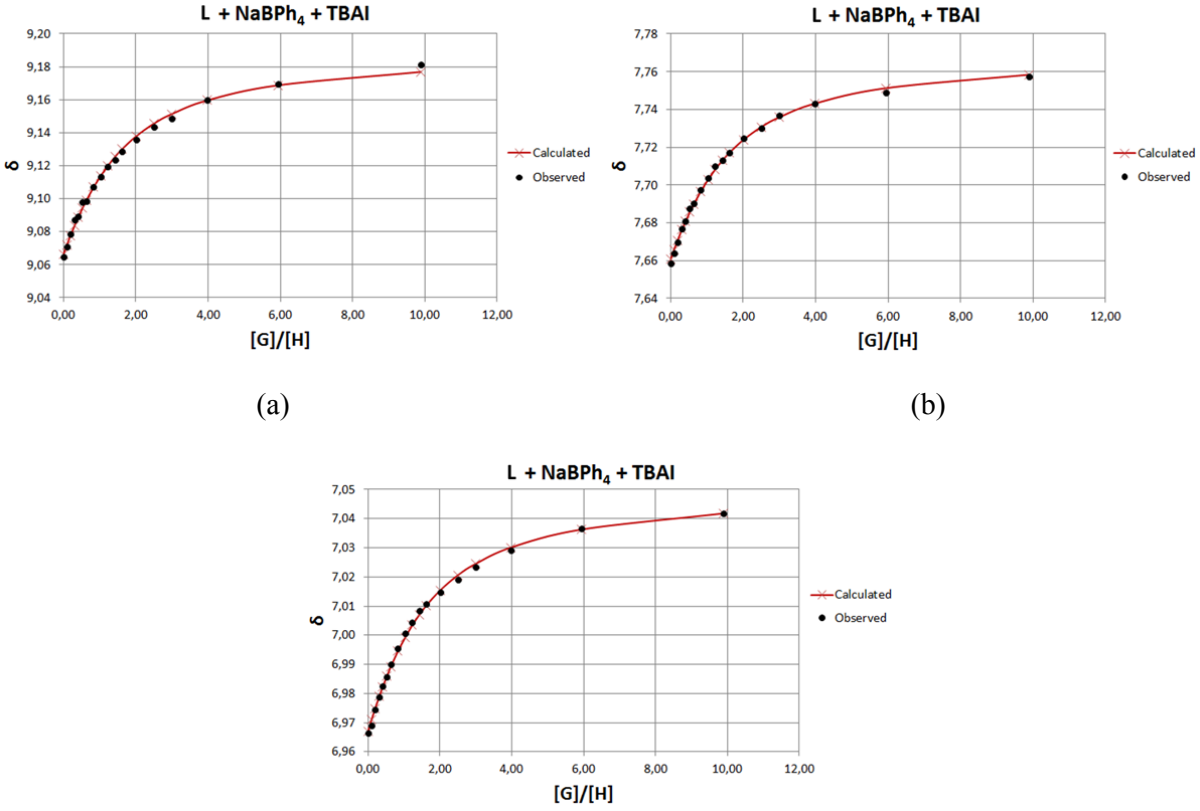


Figure S29. Binding isotherms of titration **L** + $NaBPh_4$ + TBAI for (a) H_a, (b) H_b, and (c) H_c protons using 1:1 binding model.

3.2.7 L + $KBPh_4$ + TBACl

L + KBPh4 + TBACl

Species	Log beta	**L** + K	Cl	
1	4,6258	1	1	refine
2	6,6095	1	2	refine

Species concentrations/mol dm-3

Point	T(**L** + K)	T(Cl)	F(**L** + K)	F(Cl)	species 1	species 2
1	2,5004e-03	0,0000e00	2,5004e-03	2,5932e-91	2,7391e-89	6,8414e-178
2	2,4954e-03	2,4945e-04	2,2486e-03	2,5974e-06	2,4673e-04	6,1728e-08
3	2,4904e-03	4,9791e-04	1,9986e-03	5,8218e-06	4,9154e-04	2,7563e-07
4	2,4845e-03	7,9476e-04	1,7014e-03	1,0883e-05	7,8224e-04	8,1999e-07
5	2,4786e-03	1,0902e-03	1,4082e-03	1,7962e-05	1,0685e-03	1,8487e-06
6	2,4732e-03	1,3598e-03	1,1443e-03	2,7417e-05	1,3254e-03	3,5000e-06
7	2,4673e-03	1,6525e-03	8,6515e-04	4,3654e-05	1,5955e-03	6,7085e-06
8	2,4576e-03	2,1374e-03	4,4614e-04	1,0565e-04	1,9912e-03	2,0263e-05
9	2,4470e-03	2,6664e-03	1,6532e-04	3,1702e-04	2,2141e-03	6,7609e-05
10	2,4370e-03	3,1670e-03	7,8711e-05	6,6646e-04	2,2161e-03	1,4226e-04
11	2,4266e-03	3,6872e-03	4,7102e-05	1,0829e-03	2,1548e-03	2,2475e-04
12	2,4163e-03	4,2029e-03	3,2493e-05	1,5155e-03	2,0802e-03	3,0364e-04
13	2,3973e-03	5,1524e-03	1,9651e-05	2,3378e-03	1,9407e-03	4,3699e-04
14	2,3745e-03	6,2903e-03	1,2609e-05	3,3520e-03	1,7855e-03	5,7645e-04
15	2,3504e-03	7,4953e-03	8,7171e-06	4,4509e-03	1,6390e-03	7,0267e-04
16	2,3071e-03	9,6632e-03	5,1807e-06	6,4770e-03	1,4175e-03	8,8434e-04
17	2,2249e-03	1,3768e-02	2,5157e-06	1,0431e-02	1,1086e-03	1,1138e-03
18	2,0771e-03	2,1158e-02	1,0198e-06	1,7772e-02	7,6558e-04	1,3105e-03

Measured chemical shifts

Point	H_a	H_b	H_c
1	8,8921e00	7,6106e00	6,7784e00
2	8,9335e00	7,6278e00	6,7794e00
3	8,9793e00	7,6403e00	6,7811e00
4	9,0319e00	7,6585e00	6,7826e00
5	9,0851e00	7,6711e00	6,7846e00
6	9,1344e00	7,6946e00	6,7865e00
7	9,1897e00	7,7146e00	6,7882e00
8	9,2694e00	7,7448e00	6,7909e00
9	9,3412e00	7,7783e00	6,7976e00
10	9,3696e00	7,7994e00	6,8073e00
11	9,3845e00	7,8141e00	6,8167e00
12	9,3956e00	7,8259e00	6,8236e00
13	9,4125e00	7,8452e00	6,8363e00
14	9,4290e00	7,8640e00	6,8480e00
15	9,4432e00	7,8806e00	6,8581e00
16	9,4667e00	7,9085e00	6,8772e00
17	9,4981e00	7,9442e00	6,8995e00
18	9,5466e00	7,9989e00	6,9422e00

Calculated chemical shifts

Point	H_a	H_b	H_c
1	8,8841e00	7,6049e00	6,7779e00
2	8,9313e00	7,6222e00	6,7794e00
3	8,9784e00	7,6395e00	6,7810e00
4	9,0347e00	7,6602e00	6,7828e00
5	9,0905e00	7,6808e00	6,7848e00
6	9,1411e00	7,6995e00	6,7865e00
7	9,1949e00	7,7196e00	6,7886e00
8	9,2773e00	7,7511e00	6,7925e00
9	9,3372e00	7,7777e00	6,7986e00
10	9,3629e00	7,7944e00	6,8061e00
11	9,3788e00	7,8084e00	6,8140e00
12	9,3911e00	7,8207e00	6,8215e00

13	9,4098e00	7,8410e00	6,8344e00
14	9,4285e00	7,8622e00	6,8480e00
15	9,4454e00	7,8817e00	6,8607e00
16	9,4702e00	7,9108e00	6,8797e00
17	9,5043e00	7,9511e00	6,9062e00
18	9,5419e00	7,9957e00	6,9355e00

Chemical shifts for each nucleus

species	H_a	H_b	H_c
L + K	8,8841e00	7,6049e00	6,7779e00
(**L** + K)Cl	9,3616e00	7,7801e00	6,7934e00
(**L** + K)Cl2	9,6477e00	8,1220e00	7,0187e00

Converged in 5 iterations with sigma = 4,778209

	value	standard deviation	Comments
1 log beta((**L** + K)Cl)	4.6258	0.1744	4.6(2)
2 log beta((**L** + K)Cl2)	6.6095	0.2055	6.6(2)

Correlation coefficients between stability constants. Numbering as above

2 0.9785
1

$\log K_{12} = 1.9837 \pm 0.1154$

Free energy of association for 1:1 complexation at 303 K: $\Delta G = -26.838$ kJ M^{-1}
Free energy of association for 1:2 complexation at 303 K: $\Delta G = -11.509$ kJ M^{-1}

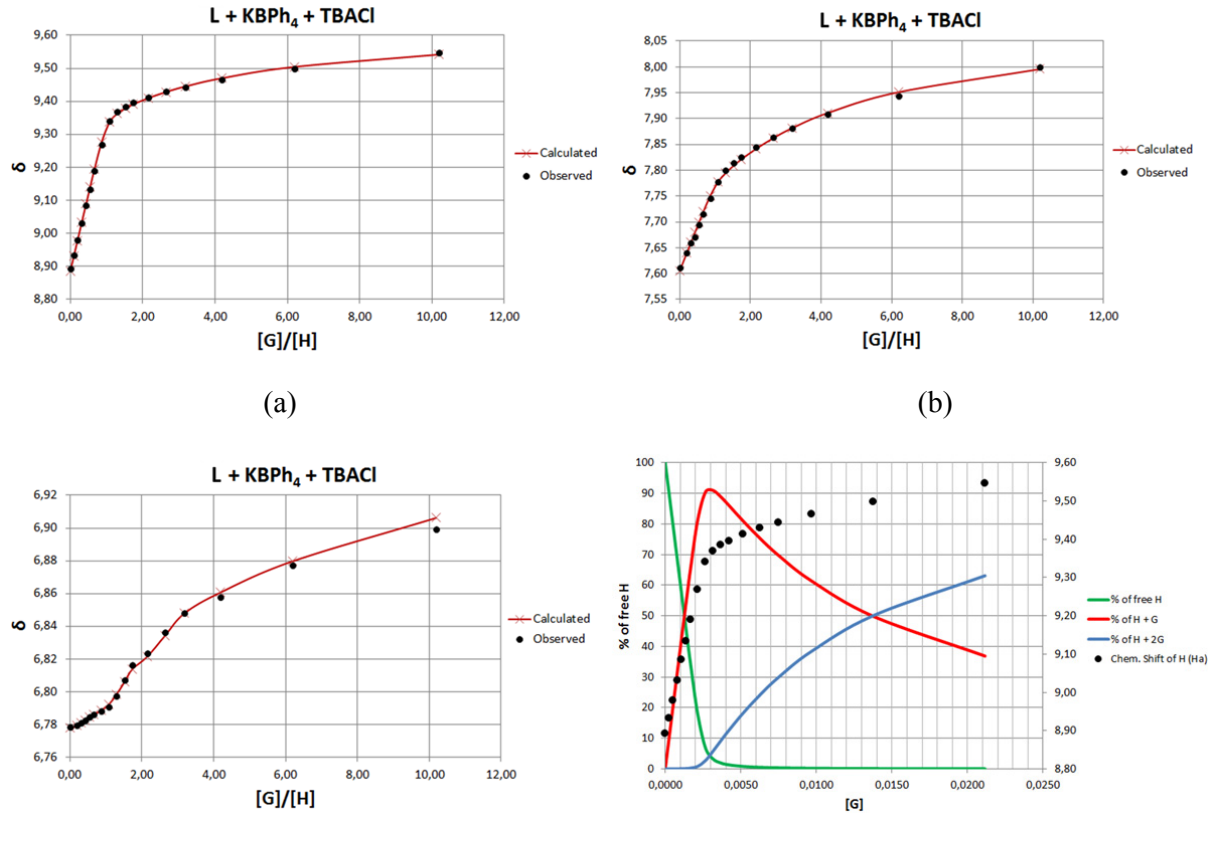


Figure S30. Binding isotherms of titration **L** + $KBPh_4$ + TBACl for (a) H_a, (b) H_b, and (c) H_c protons using 1:1 + 1:2 binding model. (d) Concentration plot using 1:1 + 1:2 binding model.

3.2.8 L + $KBPh_4$ + TBABr

L + KBPh4 + TBABr

Species	Log beta	**L** + K	Br	
1	4,1677	1	1	refine
2	5,8755	1	2	refine

Species concentrations/mol dm-3

Point	T(**L**+ K)	T(Br)	F(**L**+ K)	F(Br)	species 1	species 2
1	2,4956e-03	0,0000e00	2,4956e-03	4,1076e-91	1,5081e-89	3,1610e-178
2	2,4906e-03	2,4932e-04	2,2487e-03	7,3098e-06	2,4183e-04	9,0201e-08
3	2,4851e-03	5,2242e-04	1,9804e-03	1,7305e-05	5,0422e-04	4,4525e-07
4	2,4802e-03	7,6966e-04	1,7404e-03	2,8847e-05	7,3864e-04	1,0872e-06
5	2,4748e-03	1,0405e-03	1,4820e-03	4,5427e-05	9,9047e-04	2,2959e-06
6	2,4699e-03	1,2857e-03	1,2539e-03	6,5690e-05	1,2119e-03	4,0621e-06
7	2,4650e-03	1,5299e-03	1,0353e-03	9,3419e-05	1,4229e-03	6,7828e-06
8	2,4548e-03	2,0396e-03	6,2870e-04	1,9548e-04	1,8081e-03	1,8035e-05
9	2,4452e-03	2,5212e-03	3,5599e-04	3,9110e-04	2,0483e-03	4,0877e-05
10	2,4352e-03	3,0228e-03	2,0485e-04	7,1404e-04	2,1519e-03	7,8405e-05
11	2,4257e-03	3,4966e-03	1,3574e-04	1,0864e-03	2,1697e-03	1,2028e-04
12	2,4163e-03	3,9669e-03	9,8558e-05	1,4858e-03	2,1544e-03	1,6334e-04
13	2,3977e-03	4,8965e-03	6,1395e-05	2,3135e-03	2,0896e-03	2,4668e-04
14	2,3749e-03	6,0386e-03	4,0287e-05	3,3621e-03	1,9927e-03	3,4187e-04
15	2,3525e-03	7,1591e-03	2,9237e-05	4,4092e-03	1,8966e-03	4,2670e-04
16	2,3090e-03	9,3381e-03	1,8066e-05	6,4780e-03	1,7218e-03	5,6914e-04
17	2,2266e-03	1,3463e-02	9,3779e-06	1,0473e-02	1,4450e-03	7,7222e-04
18	2,0782e-03	2,0887e-02	4,1417e-06	1,7825e-02	1,0862e-03	9,8794e-04

Measured chemical shifts

Point	H_a	H_b	H_c
1	8,8877e00	7,6057e00	6,7927e00
2	8,9160e00	7,6145e00	6,7940e00
3	8,9481e00	7,6241e00	6,7957e00
4	8,9763e00	7,6339e00	6,7973e00
5	9,0076e00	7,6445e00	6,7986e00
6	9,0334e00	7,6534e00	6,8003e00
7	9,0598e00	7,6630e00	6,8029e00
8	9,1030e00	7,6789e00	6,8044e00
9	9,1341e00	7,6920e00	6,8088e00
10	9,1529e00	7,7018e00	6,8141e00
11	9,1640e00	7,7080e00	6,8171e00
12	9,1716e00	7,7125e00	6,8196e00
13	9,1827e00	7,7194e00	6,8232e00
14	9,1926e00	7,7265e00	6,8284e00
15	9,2006e00	7,7332e00	6,8347e00
16	9,2131e00	7,7423e00	6,8406e00
17	9,2323e00	7,7579e00	6,8531e00
18	9,2570e00	7,7775e00	6,8676e00

Calculated chemical shifts

Point	H_a	H_b	H_c
1	8,8913e00	7,6041e00	6,7915e00
2	8,9186e00	7,6140e00	6,7934e00
3	8,9484e00	7,6247e00	6,7955e00
4	8,9753e00	7,6344e00	6,7974e00
5	9,0043e00	7,6449e00	6,7995e00
6	9,0301e00	7,6542e00	6,8013e00
7	9,0550e00	7,6633e00	6,8032e00
8	9,1019e00	7,6806e00	6,8069e00
9	9,1347e00	7,6932e00	6,8102e00
10	9,1547e00	7,7018e00	6,8133e00
11	9,1657e00	7,7073e00	6,8160e00
12	9,1731e00	7,7116e00	6,8184e00

13	9,1836e00	7,7186e00	6,8230e00
14	9,1932e00	7,7258e00	6,8282e00
15	9,2011e00	7,7320e00	6,8328e00
16	9,2138e00	7,7424e00	6,8408e00
17	9,2324e00	7,7582e00	6,8530e00
18	9,2556e00	7,7782e00	6,8686e00

Chemical shifts for each nucleus

species	H_a	H_b	H_c
L+ K	8,8913e00	7,6041e00	6,7915e00
(**L**+ K)Br	9,1727e00	7,7053e00	6,8110e00
(**L**+ K)Br2	9,3481e00	7,8590e00	6,9323e00

Converged in 6 iterations with sigma = 1,614377

	value	standard deviation	Comments
1 log beta((**L**+ K)Br)	4.1677	0.0721	4.17(7)
2 log beta((**L**+ K) Br2)	5.8755	0.1279	5.9(1)

Correlation coefficients between stability constants. Numbering as above

2 0.9324
1

$\log K_{12} = 1.7078 \pm 0.1520$

Free energy of association for 1:1 complexation at 303 K: $\Delta G = -24.181$ kJ M^{-1}
Free energy of association for 1:2 complexation at 303 K: $\Delta G = -9.908$ kJ M^{-1}

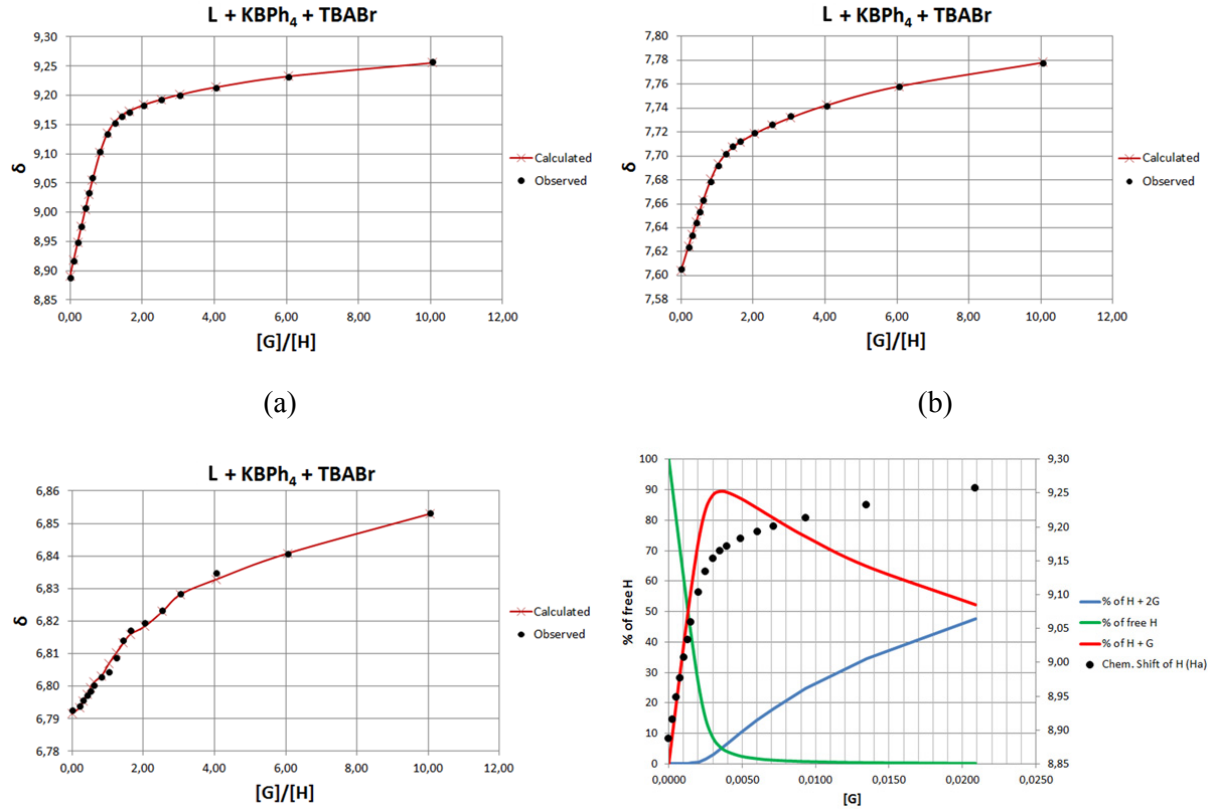


Figure S31. Binding isotherms of titration **L** + $KBPh_4$ + TBABr for (a) H_a, (b) H_b, and (c) H_c protons using 1:1 + 1:2 binding model. (d) Concentration plot using 1:1 + 1:2 binding model.

3.2.9 L + $KBPh_4$ + TBAI

L + KBPh4 + TBAI_1

Species	Log beta	**L** + K	TBAI	
1	2,8554	1	1	refine

Species concentrations/mol dm-3

Point	T(**L** + K)	T(TBAI)	F(**L** + K)	F(TBAI)	species 1
1	2,4956e-03	0,0000e00	2,4956e-03	2,0484e-90	3,6640e-90
2	2,4906e-03	2,5038e-04	2,3339e-03	9,3673e-05	1,5670e-04
3	2,4856e-03	4,9976e-04	2,1808e-03	1,9498e-04	3,0478e-04
4	2,4802e-03	7,7293e-04	2,0227e-03	3,1550e-04	4,5743e-04
5	2,4753e-03	1,0202e-03	1,8885e-03	4,3347e-04	5,8676e-04
6	2,4704e-03	1,2666e-03	1,7633e-03	5,5947e-04	7,0709e-04
7	2,4650e-03	1,5364e-03	1,6358e-03	7,0720e-04	8,2919e-04
8	2,4553e-03	2,0240e-03	1,4306e-03	9,9930e-04	1,0247e-03
9	2,4457e-03	2,5078e-03	1,2570e-03	1,3192e-03	1,1886e-03
10	2,4361e-03	2,9878e-03	1,1113e-03	1,6630e-03	1,3248e-03
11	2,4266e-03	3,4641e-03	9,8934e-04	2,0268e-03	1,4373e-03
12	2,4172e-03	3,9367e-03	8,8707e-04	2,4065e-03	1,5302e-03
13	2,3986e-03	4,8709e-03	7,2817e-04	3,2005e-03	1,6705e-03
14	2,3758e-03	6,0188e-03	5,8903e-04	4,2320e-03	1,7868e-03
15	2,3534e-03	7,1450e-03	4,9163e-04	5,2832e-03	1,8618e-03
16	2,3098e-03	9,3348e-03	3,6674e-04	7,3917e-03	1,9431e-03
17	2,2274e-03	1,3480e-02	2,4110e-04	1,1494e-02	1,9863e-03
18	2,0789e-03	2,0941e-02	1,4218e-04	1,9005e-02	1,9368e-03

Measured chemical shifts

Point	H_a	H_b
1	8,8871e00	7,6071e00
2	8,8950e00	7,6126e00
3	8,9016e00	7,6171e00
4	8,9082e00	7,6220e00
5	8,9137e00	7,6250e00
6	8,9188e00	7,6301e00
7	8,9233e00	7,6338e00
8	8,9309e00	7,6386e00
9	8,9362e00	7,6424e00
10	8,9410e00	7,6462e00
11	8,9452e00	7,6492e00
12	8,9482e00	7,6512e00
13	8,9528e00	7,6548e00
14	8,9574e00	7,6581e00
15	8,9610e00	7,6605e00
16	8,9668e00	7,6643e00
17	8,9732e00	7,6678e00
18	8,9822e00	7,6717e00

Calculated chemical shifts

Point	H_a	H_b
1	8,8901e00	7,6095e00
2	8,8960e00	7,6136e00
3	8,9016e00	7,6176e00
4	8,9073e00	7,6217e00
5	8,9122e00	7,6251e00
6	8,9168e00	7,6284e00
7	8,9215e00	7,6317e00
8	8,9290e00	7,6371e00
9	8,9354e00	7,6416e00
10	8,9408e00	7,6454e00
11	8,9453e00	7,6486e00
12	8,9491e00	7,6513e00
13	8,9550e00	7,6555e00

14	8,9602e00	7,6592e00
15	8,9638e00	7,6618e00
16	8,9685e00	7,6651e00
17	8,9732e00	7,6684e00
18	8,9769e00	7,6710e00

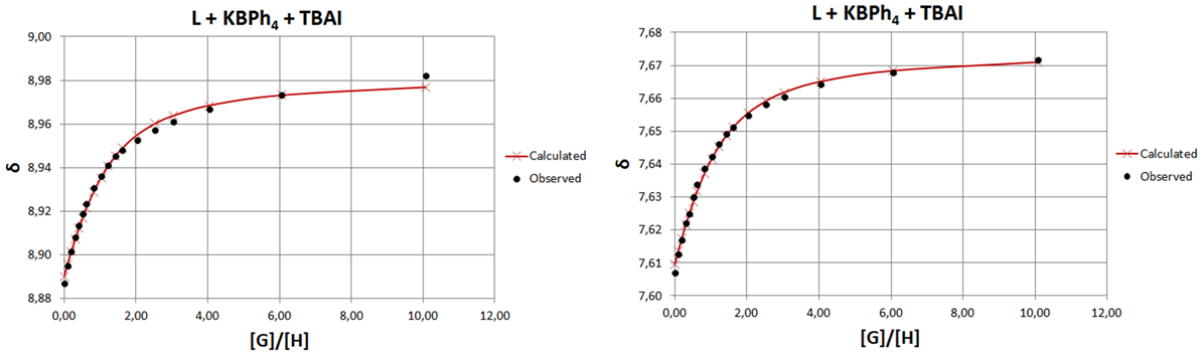
Chemical shifts for each nucleus

species	H_a	H_b
L + K	8,8901e00	7,6095e00
(**L** + K)TBAI	8,9833e00	7,6756e00

Converged in 5 iterations with sigma = 1,796534

	value	standard deviation	Comments
1 log beta((**L** + K)TBAI)	2.8554	0.0337	2.86(3)

Free energy of association at 303 K: ΔG = -16.567 kJ M^{-1}



(a) (b)

Figure S32. Binding isotherms of titration **L** + $KBPh_4$ + TBAI for (a) H_a and (b) H_b protons using 1:1 binding model.