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Supporting Information

An Imine-Based Molecular Cage with Distinct Binding Sites for Small and Large Alkali Metal Cations

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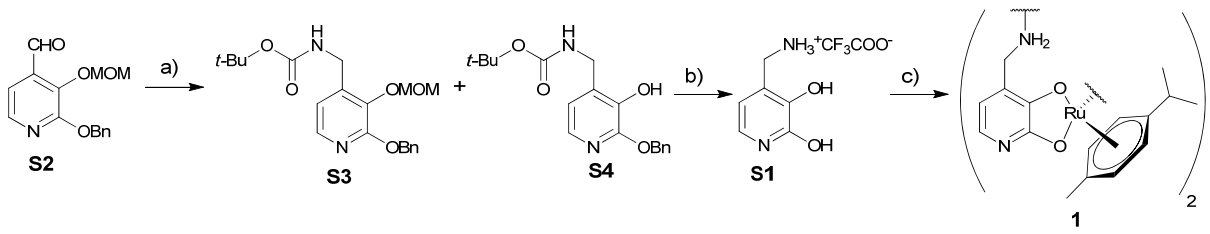
1. Syntheses



Compounds (S2) and (S3): to a solution of **S1** (1.50 g, 5.49 mmol) and *tert*-Butyl carbamate (2.00 g, 17.1 mmol) stirred in 50 mL degassed acetonitrile under N_2 were added Et_3SiH (2.70 mL, 17.1 mmol) and CF_3COOH (1.31 mL,17.1 mmol). The resulting solution was stirred for 3 days at r.t. The solvent was then evaporated under reduced pressure and the residue was dissolved in 50 ml DCM and the organic phase was washed with 50 mL sat. aq. $NaHCO_3$ and 50 mL H_2O, then dried over anhyd. Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography (Al_2O_3 neutral deactivated with 5 w/w % H_2O; eluent: DCM to DCM/acetone 1:1) to give one fraction of **S2** (493 mg, 24 %) and one fraction of **S3** (922 mg, 51 %) as pale-yellow oils. **(S2)** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 (s, 9H, CH_3), 3.52 (s, 3H, CH_3), 4.38 (d, 2H, ^3J = 5.6 Hz, CH_2), 5.14 (s, 2H, CH_3), 5.42 (s, 2H, CH_2), 6.89 (d, 1H, ^3J = 5.1 Hz, Ar-H), 7.30-7.46 (m, 5H, Ar-H), 7.88 (d, 1H, ^3J = 5.1 Hz, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.4 (CH_3), 39.1 (CH_2), 57.6 (CH_3), 67.9 (CH_2), 79.6 (C_q), 98.5 (CH_2), 117.3 (CH), 127.8 (CH), 127.9 (CH), 128.4 (CH), 137.1 (C_q), 138.8 (C_q), 141.2 (C_q), 141.5 (CH), 155.9 (C_q), 156.4 (C_q); HRMS (ESI$^+$): *m/z* = 375.1916 [*M* + H]$^+$; calcd. for [$C_{20}H_{26}N_2O_5$ + H]$^+$: 375.1920. **(S3)** ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.44 (s, 9H, CH_3), 4.26 (d, 2H, ^3J = 6.1 Hz, CH_2), 5.38 (s, 2H, CH_2), 6.73 (d, 1H, ^3J = 4.9 Hz, Ar-H), 7.26-7.40 (m, 5H, Ar-H), 7.61 (d, 1H, ^3J = 4.9 Hz, Ar-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 28.4 (CH_3), 39.1 (CH_2), 68.1 (CH_2), 80.1 (C_q), 117.6 (CH), 127.9 (CH), 128.2 (CH), 128.4 (CH), 132.6 (C_q), 136.3 (CH), 136.9 (C_q), 138.9 (C_q), 152.8 (C_q), 156.9 (C_q); HRMS (ESI$^+$): *m/z* = 331.1667 [*M* + H]$^+$; calcd. for [$C_{18}H_{22}N_2O_4$ + H]$^+$: 331.1658.

Ligand (2): a solution of **S2** (493 mg, 1.31 mmol) and **S3** (922 mg, 2.79 mmol) in 40 mL of a 1:1 v/v mixture of DCM and CF_3COOH was stirred at r.t overnight. The solvent was then evaporated under reduced pressure and the residue was co-evaporated with 5 x 20 mL of toluene. The resulting powder was suspended in 5 mL DCM, filtered, washed with Et_2O and dried under vacuum to afford **2** (956 mg, 92%) as an off-white powder. ^{1}H NMR (400 MHz, d_4-MeOD): δ = 4.08 (s, 2H, CH_2), 6.33 (d, 1H, ^3J = 6.9 Hz, Ar-H), 7.00 (d, 1H, ^3J = 6.8Hz, Ar-H); ^{13}C NMR (100 MHz, d_4-MeOD): δ = 37.2 (CH_2), 107.2 (CH), 115.6 (C_q), 118.0 (C_q), 121.8 (C_q), 123.6 (CH), 145.9 (C_q), 158.3 (C_q); ^{19}F NMR (376 MHz, d_4-MeOD): δ = -77.0 (CF_3); HRMS (ESI$^+$): *m/z* = 141.0661 [*M*]$^+$; calcd. for [$C_6H_9N_2O_2$]$^+$: 141.0664.

2. Crystallographic data for compounds 4·CsCl and 4·$(LiCl)_2$.

Complex	**4**·CsCl·$(CHCl3)_3$	**4**·$(LiCl)_2$
Empirical formula	$C_{99}H_{108}Cl_9CsN_9O_{12}Ru_6$	$C_{96}H_{105}Cl_2Li_2N_9O_{12}Ru_6$
Formula weight	2674.32	2268.09
Temperature [K]	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a [Å]	32.273(9)	18.7149(10) Å
b [Å]	21.362(3)	23.060(3) Å
c [Å]	36.5880(18)	26.181(4) Å
a [°]	90	90
b [°]	90.267(17)	108.343(9)
g [°]	90	90
Volume [$Å^3$]	25224(8)	10725(2)
Z	8	4
Density (calculated) [g/cm^3]	1.408	1.405
Absorption coefficient [mm^{-1}]	1.227	0.93
F(000)	10664	4576
Crystal size [mm^3]	0.56 x 0.37 x 0.34	0.48 x 0.33 x 0.17
Theta range for data collection	3.01 to 25.00°.	3.03 to 25.00°.
Index ranges	-38 ≤ h ≤ 38	-21 ≤ h ≤ 22
	0 ≤ k ≤ 25	-27 ≤ k ≤ 27
	0 ≤ l ≤ 43	-31 ≤ k ≤ 31
Reflections collected	21558	55785
Independent reflections *(R_{int})*	21558 (0.0000)	9335 (0.0500)
Completeness to theta = 25.00°	97.1%	98.6%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max./min. transmission	0.7452 / 0.6278	0.7452 / 0.4902
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	21558 / 840 / 1236	9335 / 276 / 574
Goodness-of-fit on F^2	1.045	1.069
Final *R* indices [I>2s(I)] R_1, wR_2	0.1057, 0.2813	0.0835, 0.2215
R indices (all data) R_1, wR_2	0.1335, 0.3002	0.1041, 0.2365
Largest diff. Peak/hole [e $Å^{-3}$]	1.945/-2.139	1.890/-1.245

2. ^{1}H and ^{13}C NMR spectra of 3 and 4

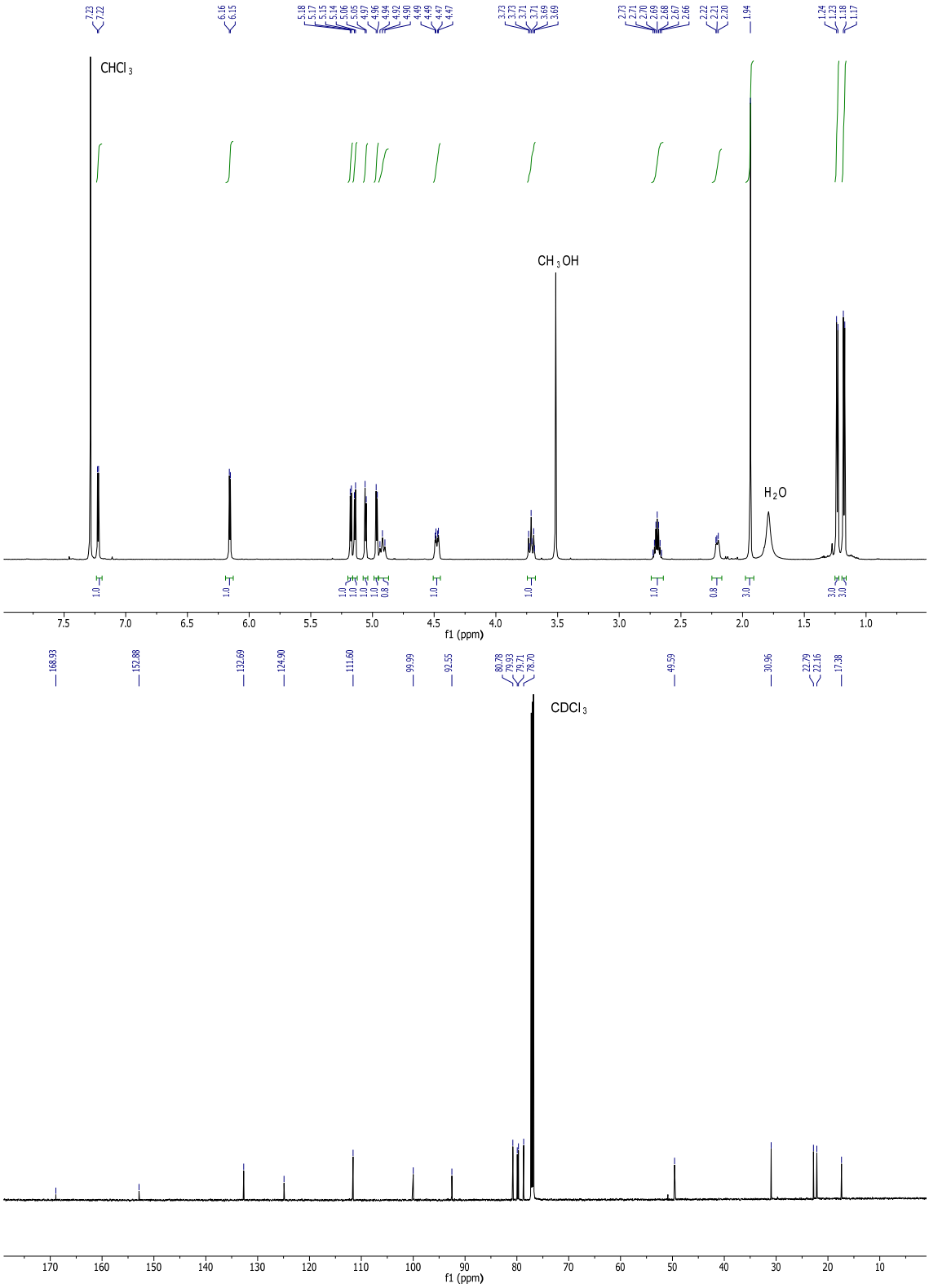


Figure S1: ^{1}H (top panel, 600 MHz) and ^{13}C (bottom panel, 150 MHz) NMR spectra of dimer **3** in $CDCl_3$.

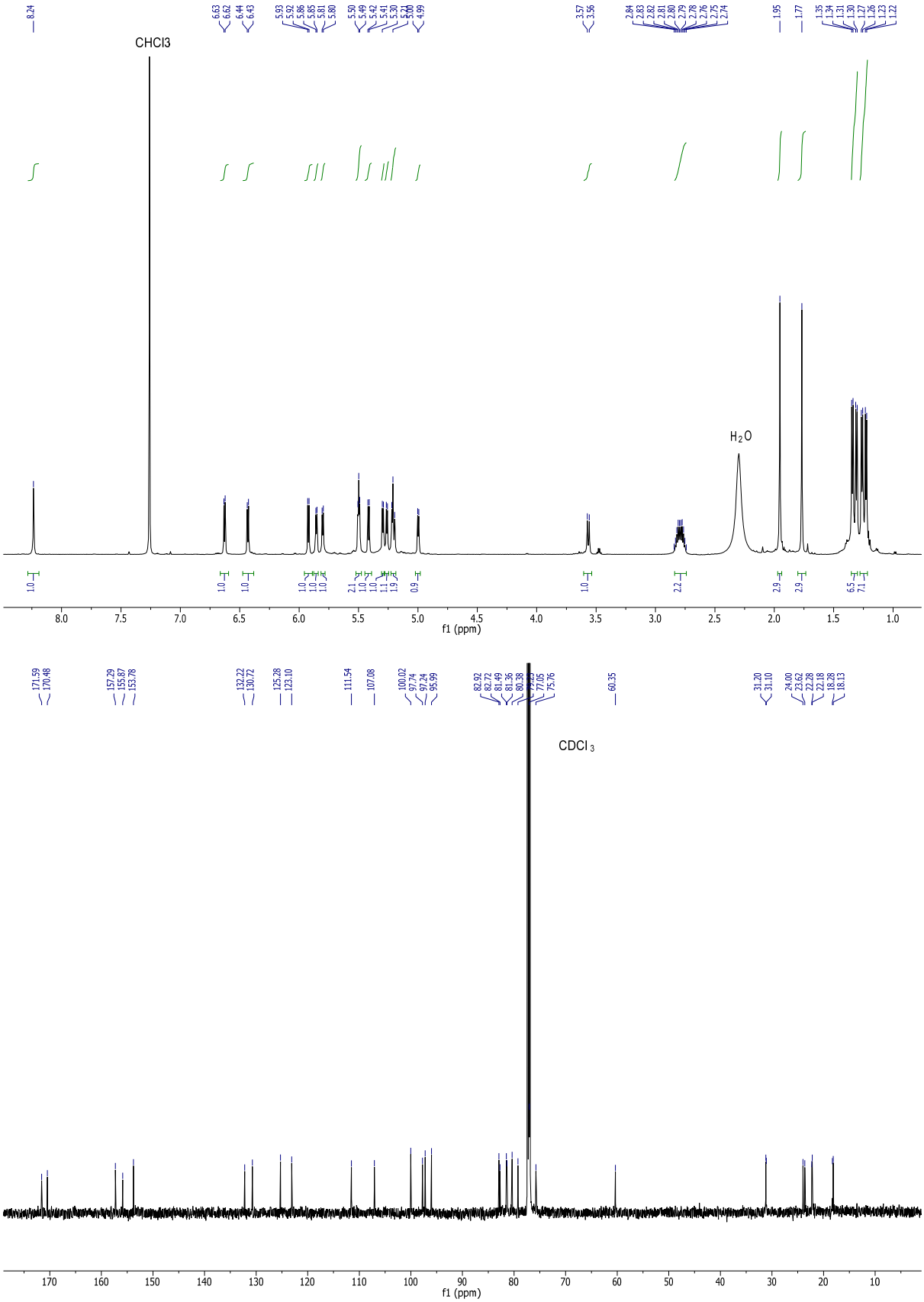


Figure S2: ^{1}H (top panel, 600 MHz) and ^{13}C (bottom panel, 150 MHz) NMR spectra of cage **4** in $CDCl_3$.

3. High-resolution ESI$^+$-MS spectra of 3 and 4

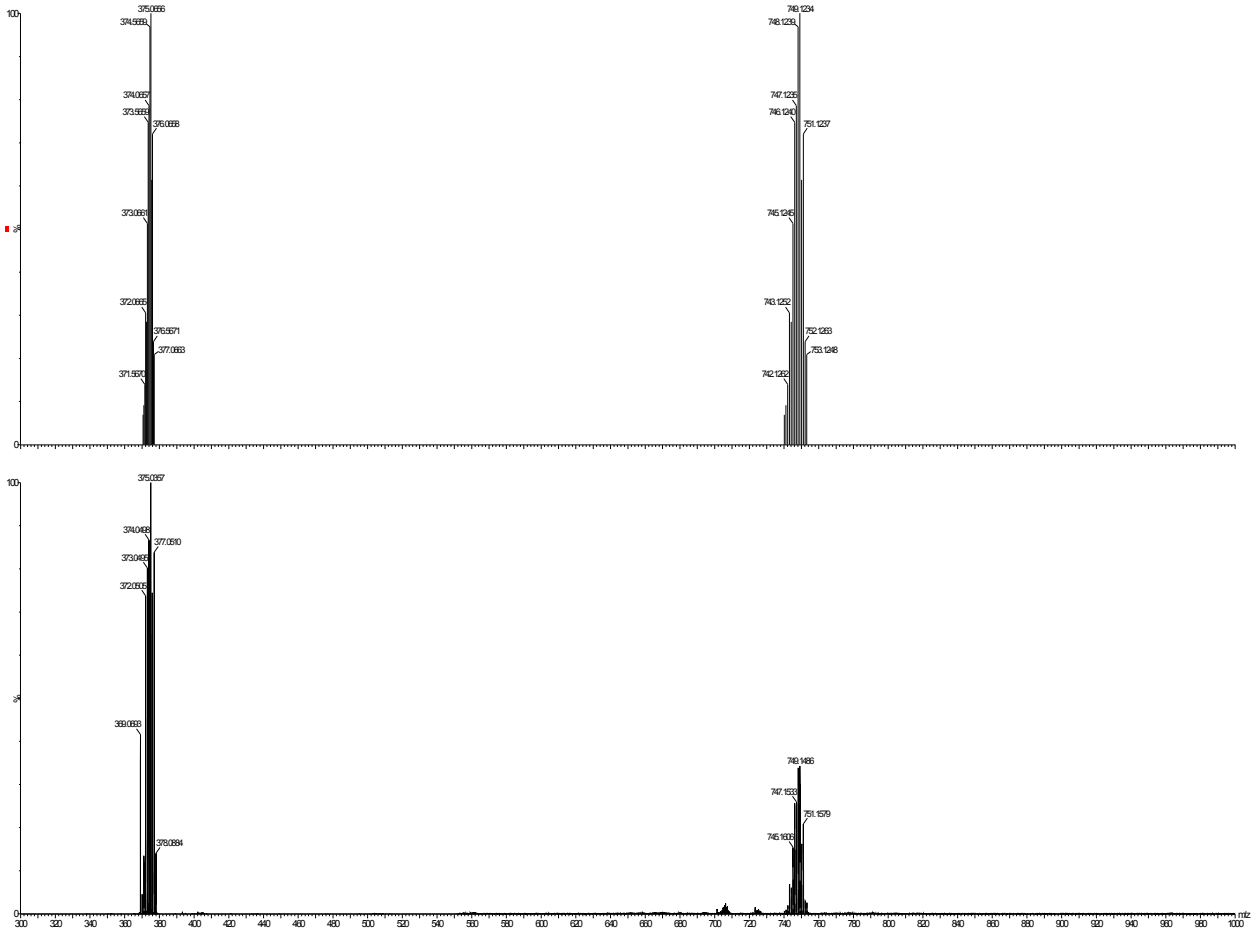


Figure S3: high-resolution (ESI$^+$) mass spectrum (top panel: calculated isotopic distribution of charged series, bottom panel: experimental data) of **3** in MeOH.

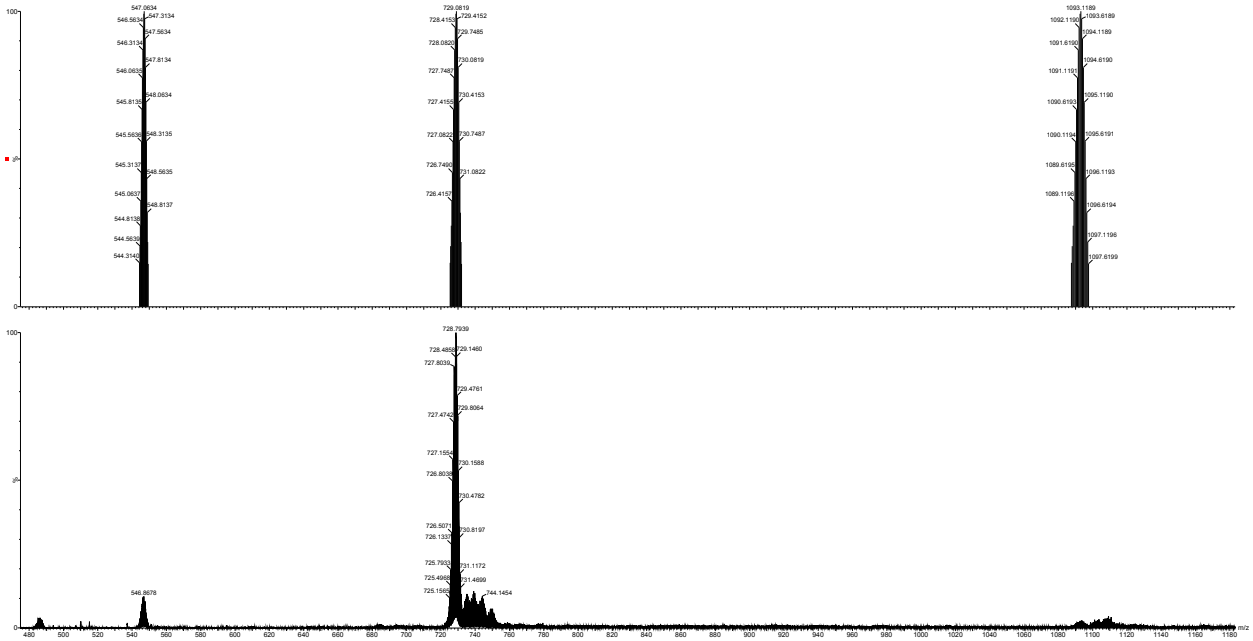


Figure S4: high-resolution (ESI^+) mass spectrum (top panel: calculated isotopic distribution of charged series, bottom panel: experimental data) of **4** in MeOH. Minor peaks correspond to singly hydrolysed product, MeOH adduct or K^+ adduct.

4. Supplementary ^{1}H NMR data

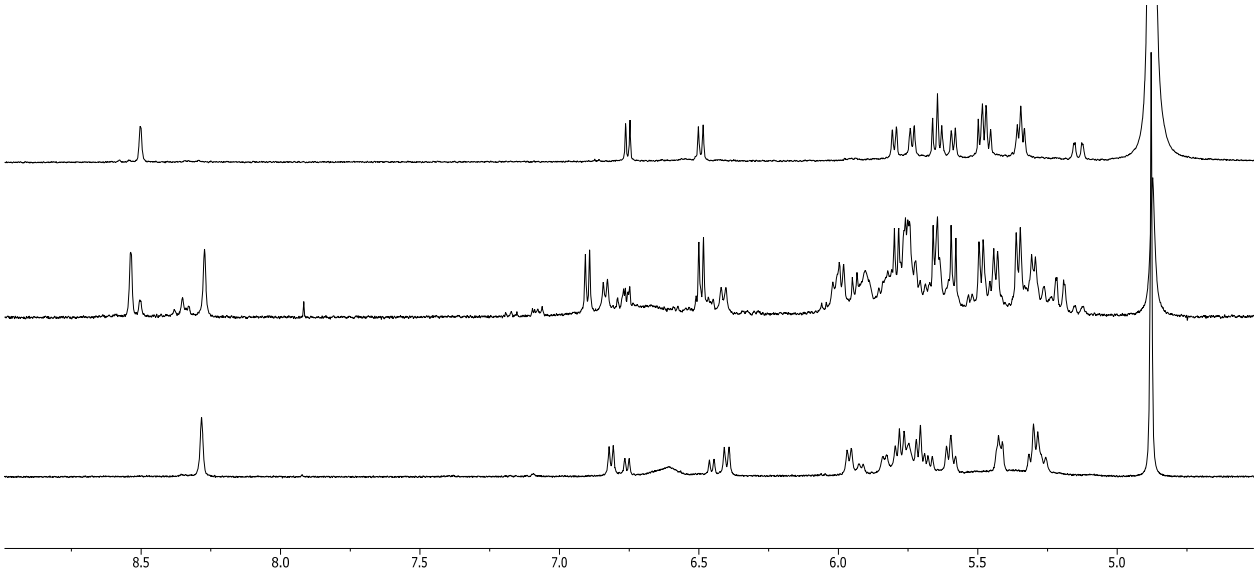


Figure S5: ^{1}H NMR of a 1 mM solution of **4** in CD_3OD with 10 eq. of RbCl (top); 1 eq of LiCl and X eq of RbCl, major products are Rb^{+}@LiCl·**4**, LiCl·**4** and CD_3OD@LiCl·**4**, minor products are Rb^{+}@**4**, $(LiCl)_2$·**4** and CD_3OD@$(LiCl)_2$·**4** (middle); 1eq of LiCl (bottom).

5. UV-VIS titrations

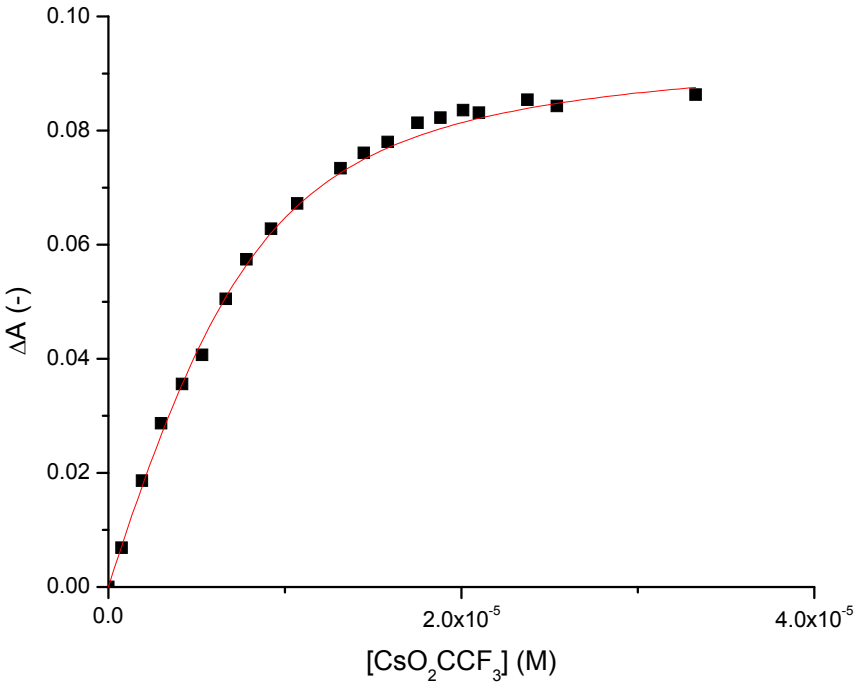


Figure S6: UV-VIS titration data (black) and calculated binding isotherm (red) of cage **4** in MeOH.

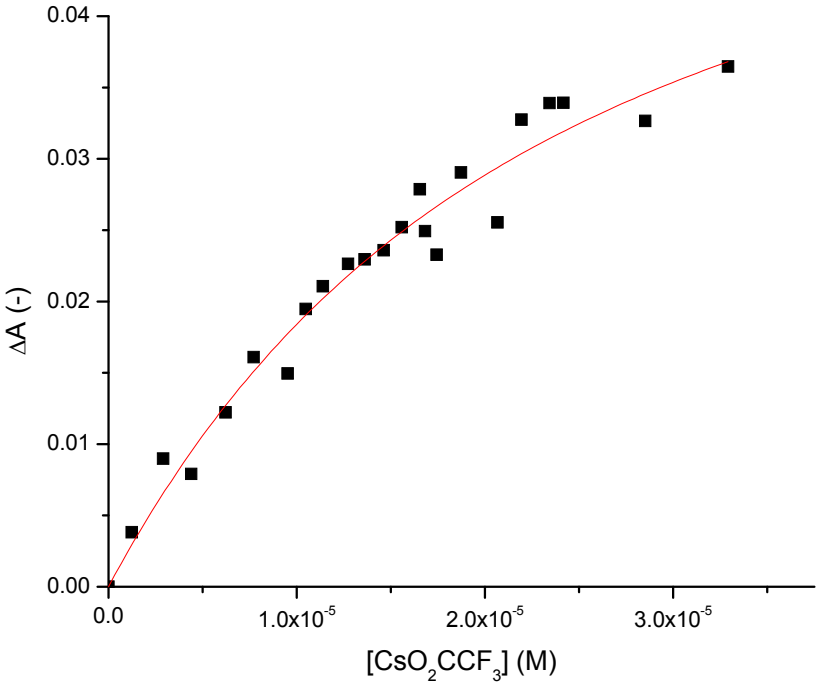


Figure S7: UV-VIS titration data (black) and calculated binding isotherm (red) of cage **4** in MeOH in the presence of 2.2 eq. of LiCl.

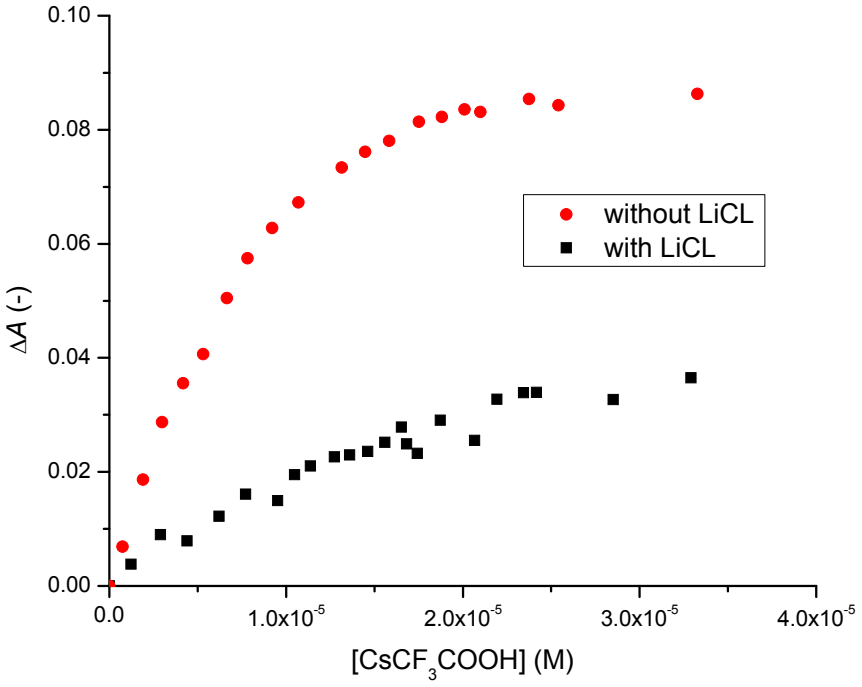


Figure S8: UV-VIS titration data of cage **4** in MeOH without (red circles) and with (black squares) 2.2 eq of LiCL.