Supporting Information

For

Rapid Metal Ion Shuttling Through 1,3-Alternate Thiacalix[4]crown Tubes

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Data S1: IR, ^{1}H, ^{13}C NMR data for **1**.

IR (KBr, cm^{-1}): 2942, 2880, 1436, 1235, 1150. ^{1}H NMR (400 MHz, $CDCl_3$): • 7.44-7.42 (d, 4 H, Ar-H_m, J = 8.00Hz), 7.35-7.33 (d, 4 H, Ar-H_m, J = 7.60 Hz), 6.93-6.84 (m, 4 H, Ar-H_p, J = 8.00 Hz), 4.03-3.99 (t, 4 H, -OCH_2CH_2O-, J = 8.00 Hz), 3.87-3.83 (t, 4 H, -OCH_2CH_2CH_3-, J = 8.00 Hz), 3.51 (s, 8 H, -OCH_2CH_2O-), 3.20-3.17 (t, 4 H, -OCH_2CH_2O-, J = 8.00 Hz), 1.20-1.11 (m, 4 H, -OCH_2CH_2CH_3, J = 8.00 Hz), 0.64-0.60 (t, 6 H, -OCH_2CH_2CH_3, J = 8.00 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 160.4, 159.8, 132.2, 132.1, 129.5, 123.9, 123.8, 72.9, 71.5, 70.3, 67.9 ppm.

Data S2: IR, ^{1}H, ^{13}C NMR data for **2**.

IR (KBr, cm^{-1}): 2943, 2872, 1445, 1360, 1243, 1142. ^{1}H NMR (400 MHz, $CDCl_3$): • 7.42-7.37 (q, 8 H, Ar-H_m, J = 8.00 Hz), 6.91-6.82 (m , 4 H, Ar-H_p, J = 8.00 Hz), 4.07-4.04 (t, 4 H, -OCH_2CH_2O-, J = 4.00 Hz), 3.86-3.83 (t, 4 H, -OCH_2CH_2 CH_3-, J = 8.00 Hz), 3.66 (s, 4 H, -OCH_2CH_2O-), 3.66-3.57 (t, 4 H, -OCH_2CH_2O-, J = 4.00 Hz), 3.43-3.40 (t, 4 H, -OCH_2CH_2O-, J = 8.00 Hz), 3.35-3.33 (t, 4 H, -OCH_2CH_2O-, J = 8.00 Hz), 1.26-1.15 (m, 4 H, -OCH_2CH_2CH_3-, J = 8.00 Hz), 0.69-0.65 (t, 6 H, -OCH_2CH_2 CH_3, J = 8.00 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 160.7, 160.5, 133.3, 132.6, 129.8, 129.4, 123.8, 123.7, 71.7, 71.5, 71.3, 70.3, 70.0, 22.9, 10.6 ppm.

Data S3: IR, ^{1}H, ^{13}C NMR data for **3**.

IR (KBr, cm^{-1}): 2943, 2881, 1437, 1231, 1152. ^{1}H NMR (600 MHz, $CDCl_3$): • 7.84-7.82 (d, 1 H, Ar-H_m, J = 6.00 Hz), 7.72-7.70 (d, 1 H, Ar-H_m, J = 7.80 Hz), 7.52-7.50 (t, 4 H, Ar-H_m, J = 5.40 Hz), 7.02-6.99 (t, 1 H, Ar-H_p, J = 7.80 Hz), 6.93-6.90 (t, 1 H, Ar-H_p, J = 7.20 Hz), 6.72-6.68 (q, 2 H, Ar-H_m, J = 7.32 Hz), 6.56-6.50 (m, 2 H, Ar-H_p, J = 7.20 Hz), 4.34-4.30 (m, 1 H, -OCH_2CH_2O-), 4.15-3.55 (m, 24 H, -OCH_2CH_2O-diethyleneglycol spacers; 4 H -OCH_2CH_2CH_3), 2.09-2.05 (m, 2 H, -

$OCH_2CH_2CH_3$) 1.93-1.90 (m, 2 H, -$OCH_2CH_2CH_3$) 1.15-1.08 (m, 6 H, -$OCH_2CH_2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): 163.5, 161.1, 160.8, 160.6, 138.5, 138.3, 138.2, 136.1, 136.0, 135.9, 133.4, 133.0, 131.6, 131.4, 130.8, 130.7, 128.4, 128.3, 123.7, 123.4, 123.3, 76.3, 75.8, 71.5, 71.3, 71.2, 71.1, 71.0, 70.3, 69.7, 24.6, 24.2, 11.4 ppm.

Data S4: IR, ^{1}H, ^{13}C NMR data for **5**.

IR (KBr, cm^{-1}): 2943, 2881, 1436, 1231, 1151. ^{1}H NMR (400 MHz, $CDCl_3$): • 7.48-7.46 (d, 4 H, Ar-H_m, J = 8.00 Hz), 7.42-7.40 (d, 4 H, Ar-H_m, J = 8.00 Hz), 6.95-6.91 (t, 4 H, Ar-H_p, J = 8.00 Hz), 4.09-4.01 (m, 8 H, -OCH_2CH_2O-, J = 6.04 Hz), 3.67 (s, 4 H, -OCH_2CH_2O-), 3.56-3.52 (t, 12 H, -OCH_2CH_2O-, J = 3.14 Hz), 3.42-3.39 (t, 4 H, -CH_2OCH_2O-, J = 6.00 Hz), 3.31 (s, 4 H, -OCH_2CH_2O-), 3.19-3.16 (t, 4 H, -OCH_2CH_2O-, J = 6.27 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 160.5, 159.6, 133.0, 132.1, 129.8, 129.2, 124.3, 124.1, 73.0, 71.7, 71.5, 71.4, 70.2, 67.7 ppm.

Data S5: IR, ^{1}H, ^{13}C NMR data for **7**.

IR (KBr, cm^{-1}): 2945, 2879, 1431, 1228, 1149. ^{1}H NMR (400 MHz, $CDCl_3$): • 7.57-7.53 (t, 8 H, Ar-H_m, J = 7.60 Hz), 6.97-6.91(m, 4 H, Ar-H_p), 4.17-4.10 (m, 4 H, -OCH_2CH_2O-), 3.71-3.65 (m, 24 H, -$CH_2OCH_2CH_2O$-), 3.55 (m, 16 H, -$CH_2CH_2OCH_2CH_2$-). ^{13}C NMR (100 MHz, $CDCl_3$): 160.7, 159.6, 135.3, 129.5, 124.0, 71.5, 71.5, 71.4, 71.2, 70.8, 70.3 ppm.

Table S1. Crystallographic Data and Structure Refinement Parameters for **5** · $K^+ClO^-_4$ and **6** · $2Cs^+ClO^-_4$.

parameters	**5** · $K^+ClO^-_4$	**6** · $2Cs^+ClO^-_4$.
Empirical formula	C_{42} H_{48} Cl K O_{15} S_4	C_{44} H_{52} Cl_2 Cs_2 O_{20} S_4
Formula weight	995.59	1365.82
Temperature	295(2) K	298(2) K
Wavelength	0.71073 Å	0.71069 Å
Crystal system	Orthorhombic	Triclinic
Unit cell dimensions	a = 19.493(5) Å α= 90°.	a = 14.012(5) Å α= 94°.
	b = 10.283(3) Å β= 90°.	b = 17.389(5) Å β=109.55(5)°.
	c = 23.164(7) Å γ = 90°.	c = 12.931(5) Å γ = 111°.
Volume	4644(2) $Å^3$	2681.7(16) $Å^3$
Z	4	2
Density (calculated)	1.424 g/cm^3	1.691 g/cm^3
Absorption coefficient	0.418 mm^{-1}	1.688 mm^{-1}
F(000)	2080	1368
Crystal size	0.26 x 0.24 x 0.22 mm^3	
θ data collection	1.98 to 25.00°	1.30 to 24.97°
Index ranges	0<=h<=23, 0<=k<=12, 0<=l<=27	-16<=h<=15, -20<=k<=20, 0<=l<=15
Independent reflections	4201 [R(int) = 0.0000]	9897 / 9439 [R(int) = 0.0157]
Completeness to theta	100.00%	100.00%
Absorption correction	Empirical	Empirical
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4201 / 1 / 569	9439 / 0 / 702
Goodness-of-fit on F_2	1.021	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0637, wR2 = 0.1089	R1 = 0.0419, wR2 = 0.1138
R indices (all data)	R1 = 0.1561, wR2 = 0.1426	R1 = 0.0604, wR2 = 0.1239
Extinction coefficient	0.0006(3)	0.0001(2)

Largest diff. peak and hole	0.275 and -0.250 e.Å^{-3}	1.168 and -0.813 e Å^{-3}

Table S2. Bond lengths [Å] for **5** · $K^+ClO^-_4$ and **6** · $2Cs^+ClO^-_4$.

5 · $K^+ClO^-_4$		**6** · $2Cs^+ClO^-_4$			
atom	distance Å	atom	distance Å	atom	distance Å
K(1)-O(7)	2.816(7)	Cs(1)-O(45)	3.407(3)	Cs(2)-O(4)	3.493(3)
K(1)-O(8)	2.851(8)	Cs(1)-O(48)	3.148(3)	Cs(2)-O(7)	3.071(4)
K(1)-O(9)	2.851(8)	Cs(1)-O(51)	3.389(3)	Cs(2)-O(10)	3.049(4)
K(1)-O(10)	2.842(7)	Cs(1)-O(54)	3.260(3)	Cs(2)-O(13)	3.227(4)
K(1)-O(11)	2.816(7)	Cs(1)-O(57)	3.263(4)	Cs(2)-O(16)	3.108(4)
K(1)-C(3)	3.387(10)	Cs(1)-O(60)	3.497(3)	Cs(2)-O(19)	3.265(3)
K(1)-C(4)	3.294(9)	Cs(1)-C(22)	3.902(3)	Cs(2)-C(28)	3.561(5)
K(1)-C(5)	3.341(9)	Cs(1)-C(23)	3.649(5)	Cs(2)-C(29)	3.363(5)
K(1)-C(9)	3.468(11)	Cs(1)-C(24)	3.816(4)	Cs(2)-C(30)	3.646(6)
K(1)-C(10)	3.469(12)	Cs(1)-C(34)	3.586(5)	Cs(2)-C(40)	3.631(5)
K(1)-C(11)	3.511(11)	Cs(1)-C(35)	3.334(5)	Cs(2)-C(41)	3.382(5)
		Cs(1)-C(36)	3.516(5)	Cs(2)-C(42)	3.530(5)

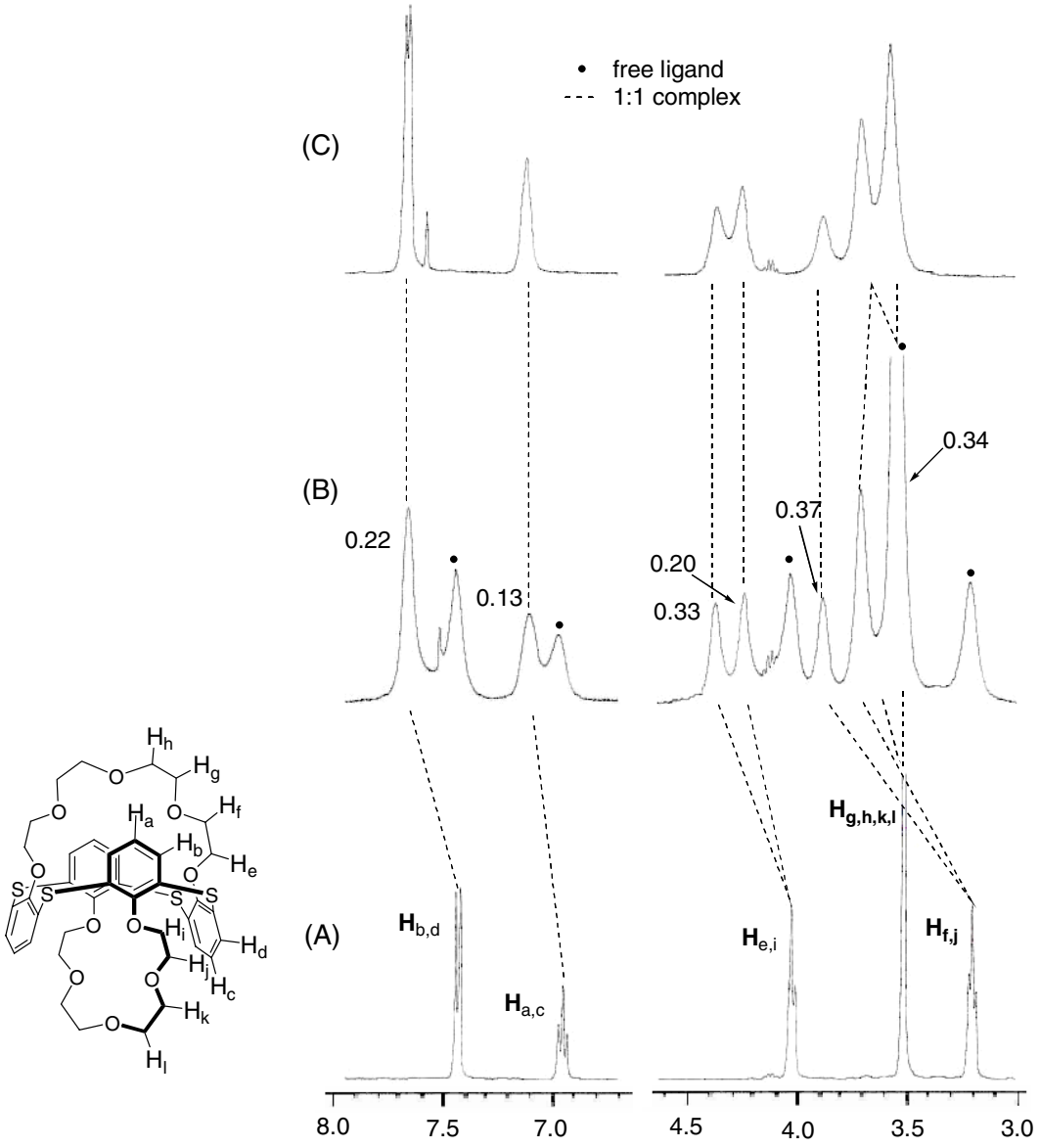

Figure S1. ^{1}H-NMR spectra of. (A): free ligand **4**, (B): **4** + 0.5 equiv and (C): **4** + 1 equiv of $K^+ClO_4^-$. The numbers denote chemical shift change upon K^+ ion complexation.