Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Bis-cation salt complexation by *meso*-octamethylcalix[4]pyrrole: linking complexes in solution and in the solid state

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Supplementary Information

NMR Experiments:

NMR spectra used to create the stack plot were collected on a Varian Mercury 400 instrument. All spectra were referenced to CH_3CN-d_3. Spectroscopic grade CH_3CN-d_3 was purchased in 0.75 ml ampules from Cambridge Isotope Laboratories. Due to the limited solubility of calix[4]pyrrole in CH_3CN-d_3 as noted above, a saturated solution (~3 mM) of **1** in CH_3CN-d_3 was obtained via sonication. The saturated supernatant was decanted into an NMR tube (0.70 mL). A solution of **5** (~ 10 mM) in CH_3CN-d_3 was also produced. NMR spectra of various ratios of C4P:**5** were obtained by adding aliquots (10 µL) of the salt solution to **1** CH_3CN-d_3 in the NMR tube. To ensure complete mixing the tube was inverted several times before running the NMR. The ratio of **1**:**5** was calculated by integration of the β-pyrrolic (~ 5.6 ppm) peaks of **1** and comparing it to that of the protons at the 4 and 5 positions (~ 7.3-7.8 ppm) of imidazolium **5**.

ITC Experiments:

Solvents used for the ITC experiments were purchased commercially of reagent grade and further dried over a column of molecular sieves (CH_3CN) or calcium hydride (CH_2Cl_2) before each titration. Calix[4]pyrrole (**1**) has a maximum solubility of approximately 3 mM in CH_3CN whereas salts **4** and **5** have a much higher solubility. Fresh solutions of **1** were prepared daily. Using a VP-ITC calorimeter made by MicroCal the salt solution was injected from the syringe into a solution of **1** in the cell. All ITC titrations were run at 25 °C with a stir rate of 307 rpm. The calorimeter reference power was set at 70 µCal/sec. In general syringe injection volumes ranged from 6 µL to 8 µL, however depending on the system and the concentrations of the species present some titrations were limited to 2 µL injections. Titrations were run until a minimum 1.5 equivalents of the salt were added. Data was analyzed using the Origin software provided by MicroCal.

Crystal data were collected on a Bruker Nonius KappaCCD with a Mo rotating anode generator; standard data collection and processing procedures were followed.

Crystal data for $\mathbf{1}_2\cdot\mathbf{2}$: $2(C_{28}H_{36}N_4)\bullet C_{14}H_{18}N_2\bullet 2(CH_2Cl_2)\bullet 2(Br)$, M = 1401.19, Monoclinic, a = 10.4058(2), b = 19.7769(4), c = 18.4439(2) Å, β = 97.8800(10)°, U = 3759.81(11) Å^3, T = 120(2) K, space group $P2(1)/c$, Z = 2, μ(MoK\α) = 1.266 mm^{-1}, 64143 reflections measured, 8589 unique reflections (R_{int} = 0.0754). The final R_1 values were 0.0501 ($I>2\sigma(I)$). The final $wR(F_2)$ values were 0.1137 ($I>2\sigma(I)$). The final R_1 values were 0.0673 (all data). The final $wR(F_2)$ values were 0.1213 (all data).

Crystal data for $\mathbf{1}_2\cdot\mathbf{3}$: $2(C_{28}H_{36}N_4)\bullet C_{16}H_{22}N_2\bullet 2(Br)$, M = 1259.39, Monoclinic, a = 10.8396(2), b = 16.6349(3), c = 18.3543(4) Å, β = 105.0800(10)°, U = 3195.60(11) Å^3, T = 120(2) K, space group $P2(1)/n$, Z = 2, μ(MoK\α) = 1.319 mm^{-1}, 36877 reflections measured, 7293 unique reflections (R_{int} = 0.0739). The final R_1 values were 0.0630 ($I>2\sigma(I)$). The final $wR(F_2)$ values were 0.1066 ($I>2\sigma(I)$). The final R_1 values were 0.0970 (all data). The final $wR(F_2)$ values were 0.1200 (all data).

Crystal data for $\mathbf{1}_2\cdot\mathbf{5}$: $2(C_{28}H_{36}N_4)\bullet C_{14}H_{24}N_4\bullet 2(Br),2(C_{28}H_{36}N_4)\bullet C_{14}H_{24}N_4\bullet 2(Br)$, M = 1265.41, Monoclinic, a = 10.8915(7), b = 16.6068(12), c = 18.2330(11) Å, β = 103.519(4)°, U = 3206.5(4) Å^3, T = 120(2) K, space group $P2(1)/n$, Z = 2, μ = 1.316 mm^{-1}, 31608 reflections measured, 5659 unique reflections (R_{int} = 0.1655). The final R_1 values were 0.0618 ($I>2\sigma(I)$). The final $wR(F_2)$ values were 0.1107 ($I>2\sigma(I)$). The final R_1 values were 0.1118 (all data). The final $wR(F_2)$ values were 0.1274 (all data).

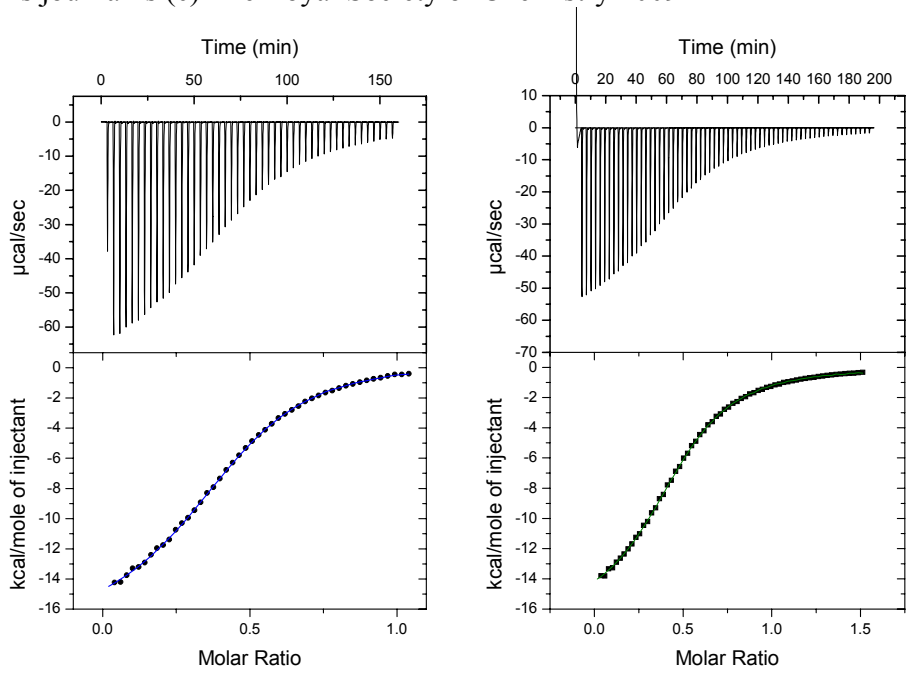

Figure S1. Left: sequential binding fit of 1,4-bis-(3-methylimidazolium)butane dibromide salt **4** [15.8 mM] titrated into calix[4]pyrrole **1** [3.3 mM] and right: sequential binding fit of 1,4-bis-(3-methylimidazolium)hexane dibromide salt **5** [19.9 mM] titrated into calix[4]pyrrole **1** [2.6 mM].

Several titrations of varying concentrations were run for both salt **4** and **5**. For the sequential fitting equation, the data for the titrations is summarized in table S1. The thermodynamic data from some representative titrations can be seen in Figure S1.

Table S1. ITC titration data for **1** and imidazolium salts **4** and **5** (sequential fit; two binding sites)

salt	[salt]	[CP]		ΔG	ΔH	$T\Delta S$	K_a
	mM	mM		kcal/mol	kcal/mol	kcal/mol	M^{-1}
4	11.84	1.26	*K1*	-3.83	-5.25	-1.42	640
			K2	-5.24	-15.34	-10.10	6820
4	6.32	1.26	*K1*	-4.33	-7.61	-3.28	1500
			K2	-4.73	-9.80	-5.07	2810
4	31.5	3.32	*K1*	-3.83	-6.41	-2.58	642
			K2	-4.41	-12.10	-7.69	1690
4	15.75	3.32	*K1*	-4.73	-5.91	-1.18	2950
			K2	-4.06	-11.90	-7.84	961
4	14.7	3.38	*K1*	-3.88	-12.22	-8.34	678
			K2	-4.60	-5.01	-0.41	2370
4	14.7	3.38	*K1*	-4.86	-6.14	-1.28	3640
			K2	-3.99	-12.30	-8.31	802
5	4.65	0.98	*K1*	-4.62	-9.00	-4.38	2460
			K2	-4.59	-5.85	-1.26	2300
5	19.85	2.6	*K1*	-4.99	-7.45	-2.46	4570
			K2	-4.16	-9.43	-5.27	1080
5	34.65	3.31	*K1*	-4.97	-7.80	-2.83	4390
			K2	-4.20	-8.04	-3.84	1190
5	17.3	3.31	*K1*	-4.72	-7.27	-2.55	4230
			K2	-4.18	-8.41	-4.23	1050
5	21.4	2.52	*K1*	-4.80	-7.90	-3.10	3390
			K2	-4.19	-9.35	-5.16	1150

Titrations run in acetonitrile at 298 K; Calix[4]pyrrole **1** (in the cell) titrated with salt (in the syringe). All errors are estimated to be less than 15%

The onesites equation was also used to fit the data for comparison. Some of the salt concentrations were adjusted (assuming a 2:1 C4P to salt interaction) following the titration to compensate for measuring errors and the hygroscopic nature of the salt. The pertinent data is displayed in Table S2.

Table S2: ITC titration data for **1** and imidazolium salts **4** and **5** (one site binding equation)

salt	2x[salt] mM	[CP] mM	N	ΔG kcal/mol	Δ*H* kcal/mol	*T*Δ*S* kcal/mol	K_a M^{-1}
4	34.2	1.26	.99	-4.58	-7.92	-3.34	2300
4	16.8	1.26	1.00	-4.49	-7.28	-2.79	1960
4	85.0	3.32	1.01	-4.26	-7.27	-3.01	1290
4	35.9	3.32	1.00	-4.42	-7.97	-3.55	1700
4	33.8	3.38	.99	-4.41	-7.96	-3.35	1700
4	33.2	3.38	1.01	-4.40	-7.98	-3.58	1720
5	10.94	0.98	1.01	-4.53	-7.30	-2.77	2070
5	45.3	2.6	1.01	-4.49	-7.36	-2.87	1940
5	69.3	3.31	0.98	-4.57	-8.00	-3.43	2280
5	40.75	3.31	1.00	-4.47	-6.97	-2.50	1890
5	34.6	1.68	0.95	-4.65	-8.40	-3.75	2530
5	42.8	2.52	0.96	-4.63	-8.15	-3.52	2510

Titrations run in acetonitrile at 298 K; Calix[4]pyrrole **1** (in the cell) titrated with salt (in the syringe). All errors are estimated to be less than 15%

Crystallographic Data:

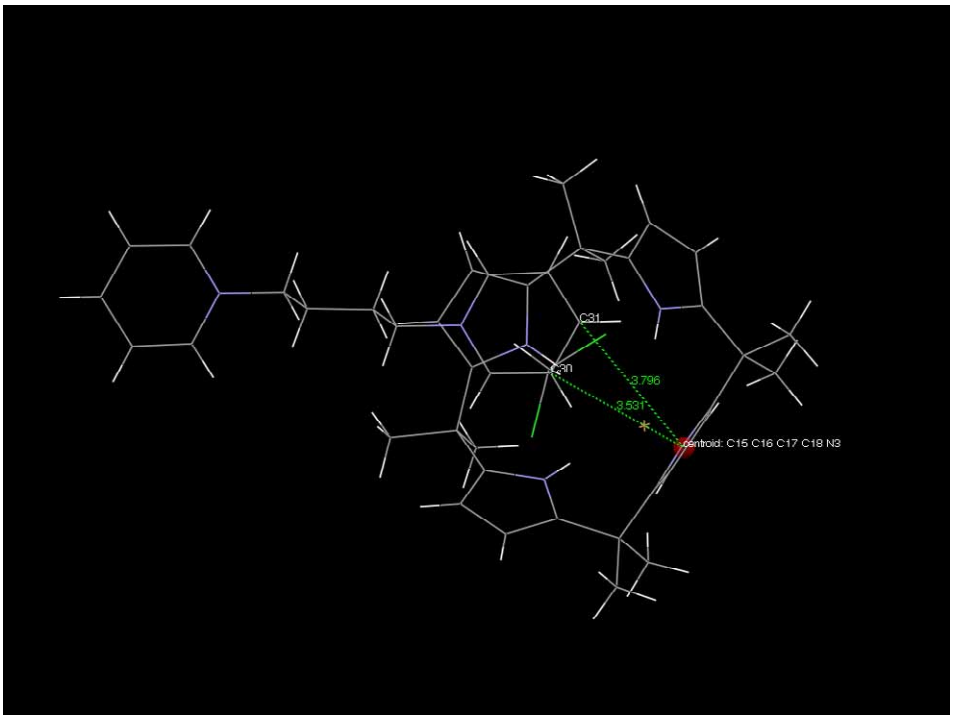

Figure S2 Figure showing degree of encapsulation of pyridinium ring in calixpyrrole cavity in $\mathbf{1}_2.\mathbf{2}$

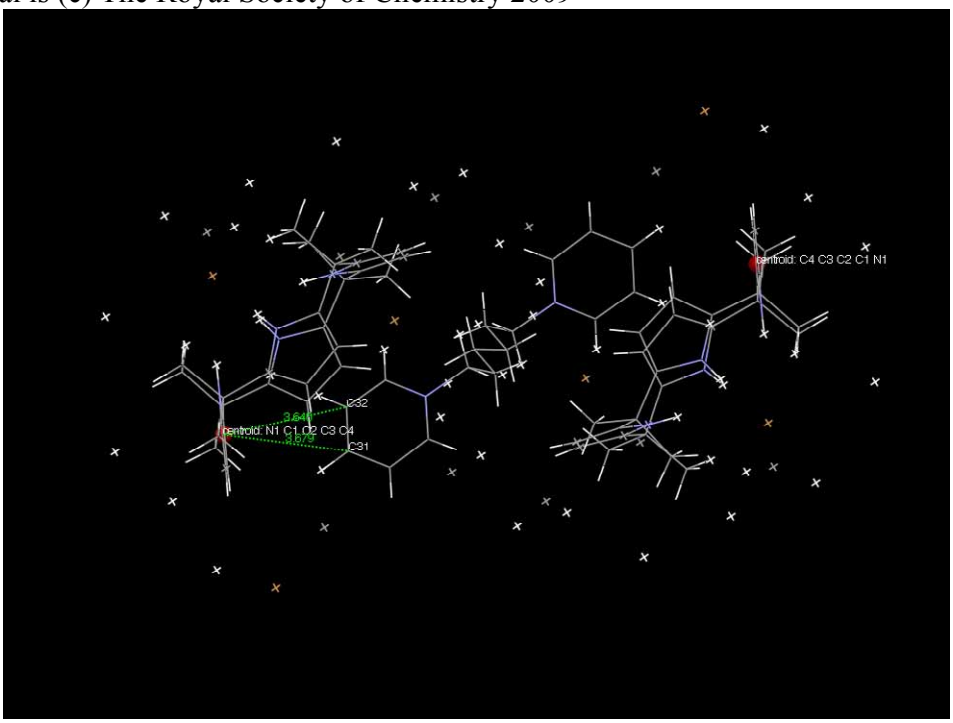

Figure S3 Figure showing degree of encapsulation of pyridinium ring in calixpyrrole cavity in **1**$_2$.**3**

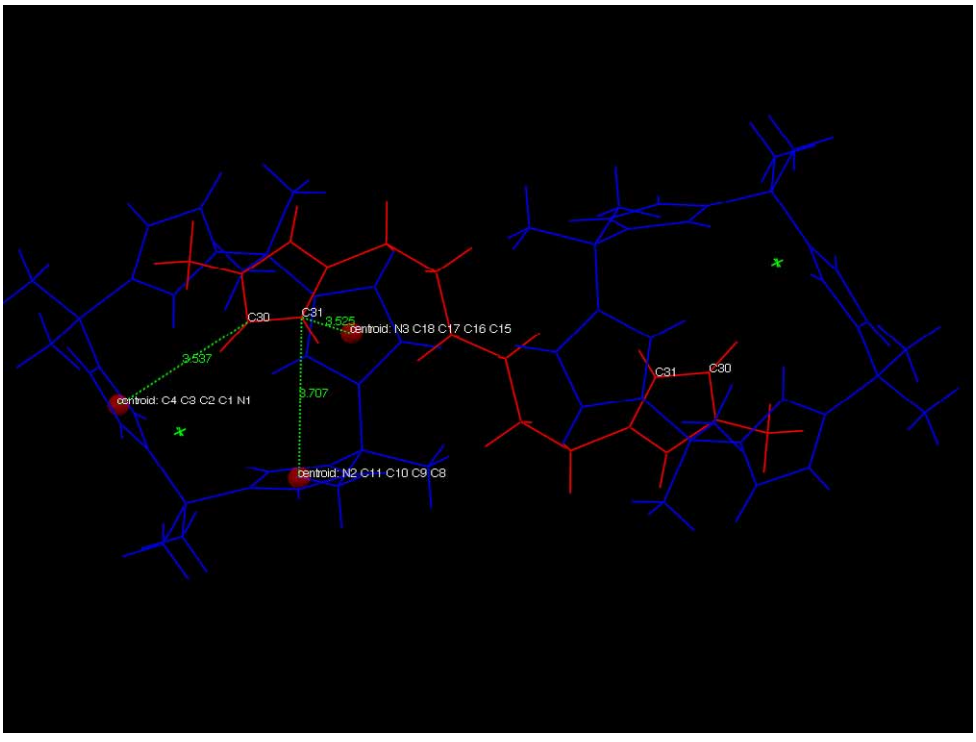

Figure S4 Figure showing degree of encapsulation of imidazolium ring in calixpyrrole cavity in **1**$_2$.**5**