Supporting Information

Real-time determination of chloride anion concentration in aqueous-DMSO using a pyrrole-strapped calix[4]pyrrole anion receptor

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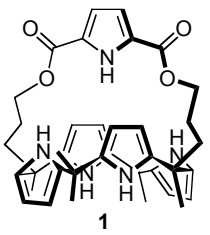
General Experimental Procedures

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Mercury 400 MHz NMR spectrometers using the residual peaks of deuterated solvents as internal standards.

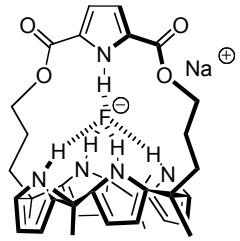


1

Strap Pyrrolic N-H = 11.58 ppm

Calix[4]pyrrole Pyrrolic N-H = 9.43 ppm

Calix[4]pyrrole Pyrrolic β-H = 5.76-5.74 ppm

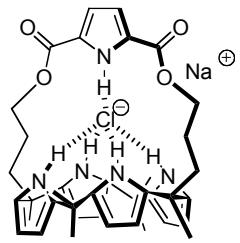


1•F^-

Strap Pyrrolic N-H = 15.20 ppm (d, J = 50 Hz)

Calix[4]pyrrole Pyrrolic N-H = 12.20 ppm (d, J = 33 Hz)

Calix[4]pyrrole Pyrrolic β-H = 5.51-5.49 ppm



1•Cl^-

Strap Pyrrolic N-H = 12.87 ppm

Calix[4]pyrrole Pyrrolic N-H = 10.92 ppm

Calix[4]pyrrole Pyrrolic β-H = 5.48-5.45 ppm

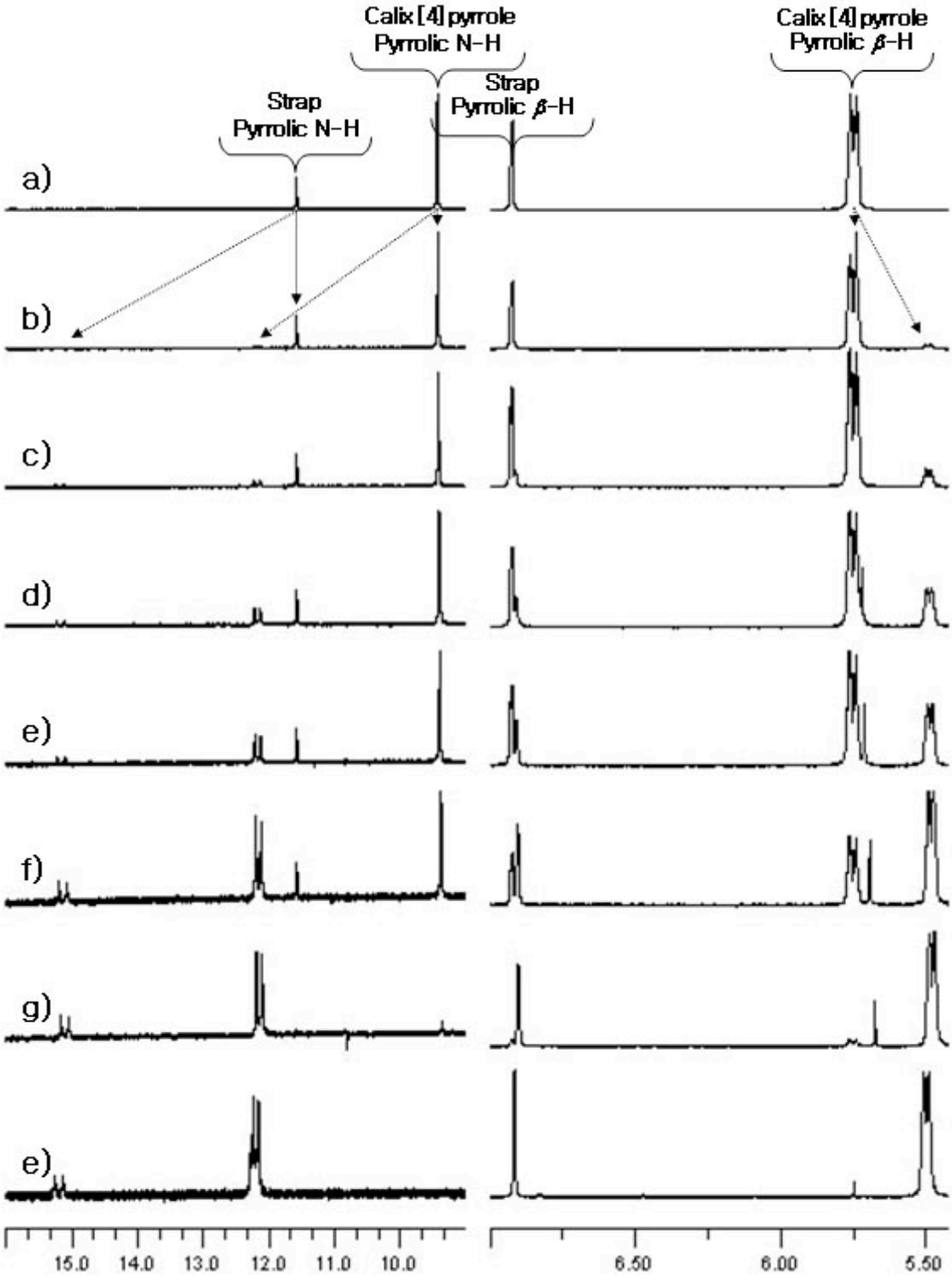


Figure 1. Proton NMR spectra of a) pyrrole-strapped calix[4]pyrrole (**1**) ([**1**] = 14.74 mM, DMSO-d_6 = 0.800 mL), b) after adding 0.10 equiv. of aq. NaF (0.010 mL, 1.2% H_2O by volume), c) 0.40 equiv. of aq. NaF (0.040 mL, 4.8%), d) 0.60 equiv. of aq. NaF (0.060 mL, 7.0%). e) 0.70 equiv. of aq. NaF (0.070 mL, 8.0%). f) 0.8 equiv. of aq. NaF (0.080 mL, 9.1%). g) 0.90 equiv. of aq. NaF (0.090 mL, 10%), e) 1.10 equiv. of aq. NaF (1.10 mL, 12.1%)

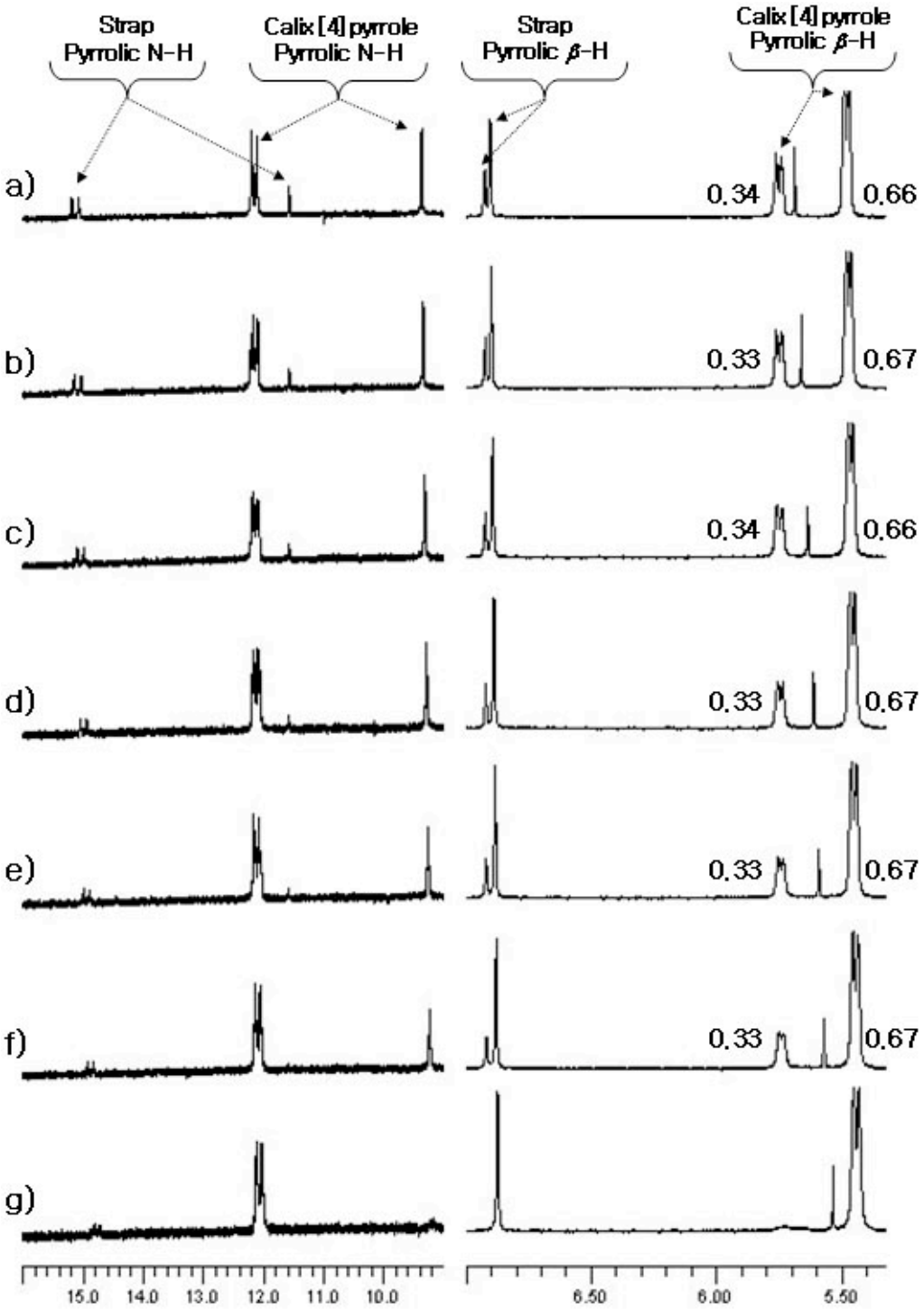


Figure 2. Water dependent proton NMR spectral titration of the pyrrole-strapped calix[4]pyrrole (**1**) fluoride complex. In this study, compound **1** was dissolved in 1.00 mL of DMSO-d_6 (19.50 mM) containing 80 uL of aq. NaF solution (0.68 equiv.). The percent water in each of the spectra was as follows: a) 7%, b) 11%, c) 14%, d) 17%, e) 19%, f) 22%, and g) 24%. The numbers on the spectra are the integrated ratios for the sets of peaks in question. Note that precipitation occurs under the conditions of spectrum g).

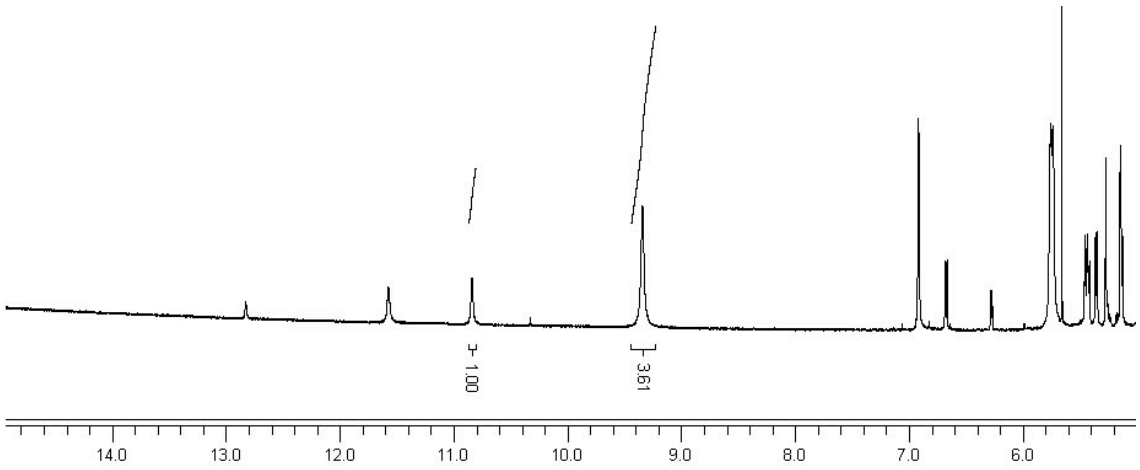


Figure 3. Proton NMR spectrum of pyrrole-strapped calix[4]pyrrole (**1**) dissolved in 1.0 mL of DMSO-d_6 after adding 100 uL of a high-ion sports drink (Pocari Sweat^{TM}).

(Pyrrole-strapped calix[4]pyrrole **1**) = 635.7950 g/mol

(5.2 mg of **1**) = 8.2×10^{-6} mole

The integrated proton NMR ratio => [**1**·Cl^-] / [**1**] = 1.00 / 3.61

(The sum of **1**·Cl^- and **1**) = 8.2×10^{-6} mole

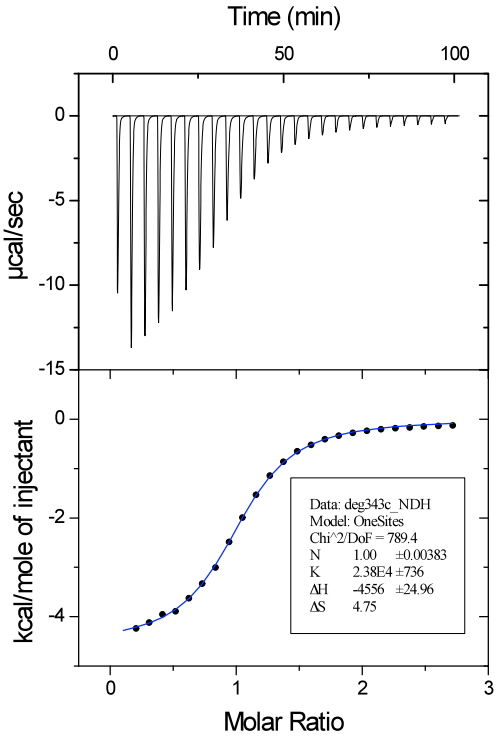
$\therefore$ **1**·Cl^- = 8.2×10^{-6} mole × (1.00/(1.00+3.61)) = 1.77×10^{-6} mol

Thus, 0.100 mL of sports drink contained 1.77×10^{-6} mol of chloride anions

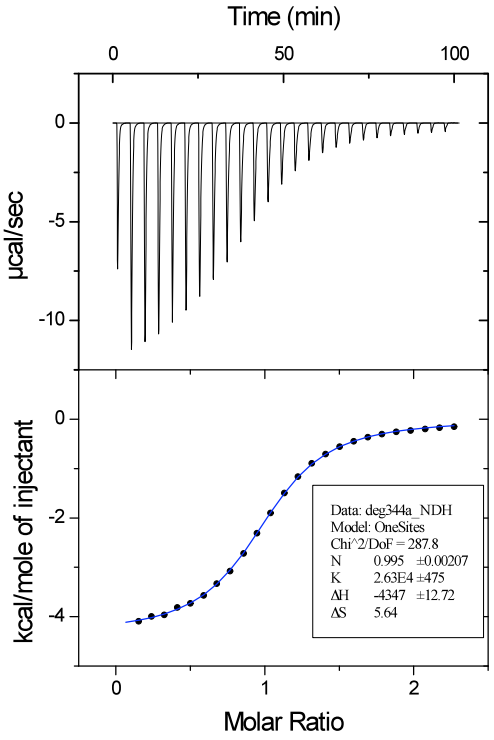
[Cl^-] = 1.77×10^{-6} mole / 0.100 mL = 17.7 mmol/L

ITC Titrations with salts in DMSO/H_2O (4:1 v/v)

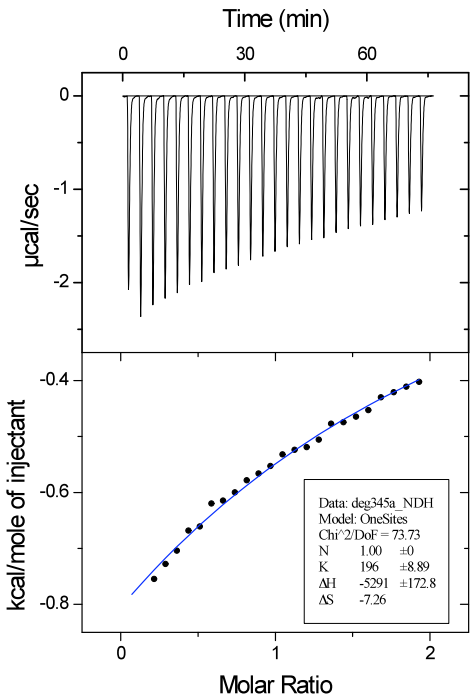
A. NaCl



B. TBACl



C. $TBAH_2PO_4$



D. TBAOBz

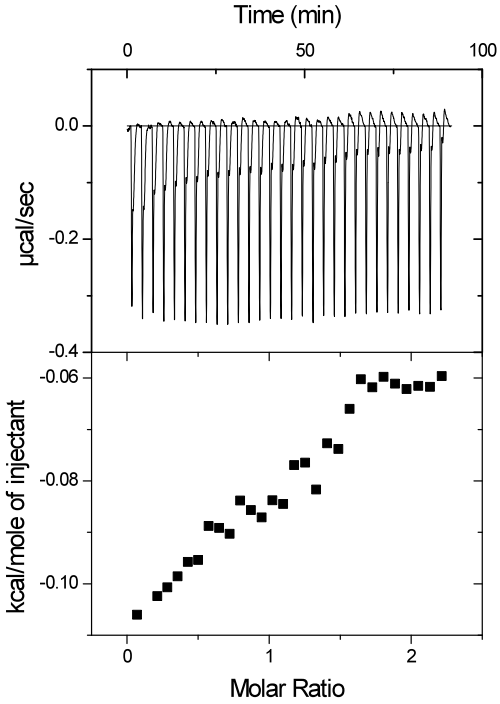


Table S1. Titration data for the interaction of strapped calix[4]pyrrole **1** with chloride salts in DMSO/H_2O (4:1 v/v) at 298 K.

Titration	salt	[salt]	[CP]	$T\Delta S$	ΔH	ΔG	K_a
		mM	mM	kcal/mol	kcal/mol	kcal/mol	M^{-1}
A	NaCl	15.0	0.72	1.42	-4.56	-5.97	24 000
B	TBACl	10.0	0.72	1.68	-4.35	-6.03	26 000
C	$TBAH_2PO_4$	10.2	0.72	Affinity is too low to allow for K_a determination at this concentration			
D	TBAOBz	11.1	0.72	No binding detected			