Supplementary Material (ESI) for New Journal of Chemistry

Specific Tetramethylammonium Recognition Drives General Anion Positioning in Tandem Sites of a Deep Cavitand

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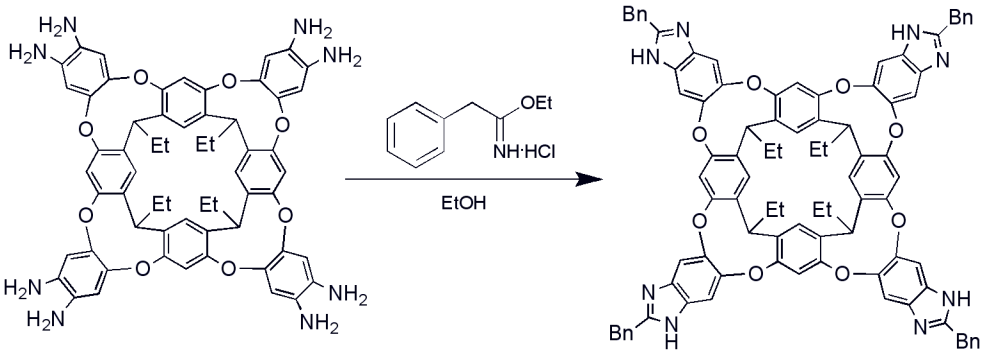
Electronic Supplementary Information

General procedure:

All manipulations were carried out under a nitrogen atmosphere. All glassware was oven dried immediately prior to use. All reagents and anhydrous solvents were obtained from commercial sources and used without further purification. ^{1}H NMR spectra were obtained at 500 MHz and recorded relative to residual protio-solvent. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, t = triplet, m = multiplet, coupling constant in Hz, integration).

Procedure for preparation of benzyl cavitand 1:



Octaamino cavitand[1] (500 mg, 0.49 mmol) and ethyl benzylimidate hydrochloride (515 mg, 2.58 mmol) were dissolved in anhydrous ethanol (25 mL) in a dry Schlenk tube flushed with nitrogen. The reaction mixture was heated at 80˚C for 20 h and then the product was filtered off and washed with methanol.

1: off-white solid, mp. > 300 ˚C; 75% yield (522 mg).

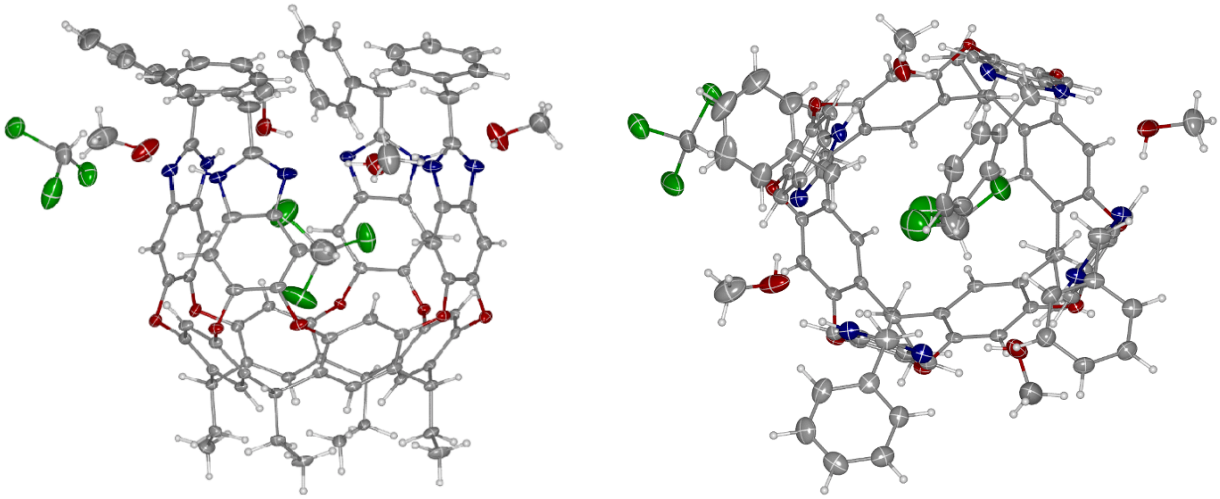
^{1}H NMR (500 MHz, $CDCl_3$+ 1% CD_3OD) δ = 7.49-6.98 (m, 36H), 5.62 (t, *J* = 8.3 Hz, 4H), 3.77 (s, 8H), 2.35-2.21 (m, 8H), 1.01 (t, *J* = 7.2 Hz, 12H).

IR υ_{max}(cm^{-1}): 3356, 3026, 2961, 2926, 2871, 1602, 1578, 1532, 1489, 1446, 1421, 1270, 1177, 1158, 1115, 1025, 905, 805.

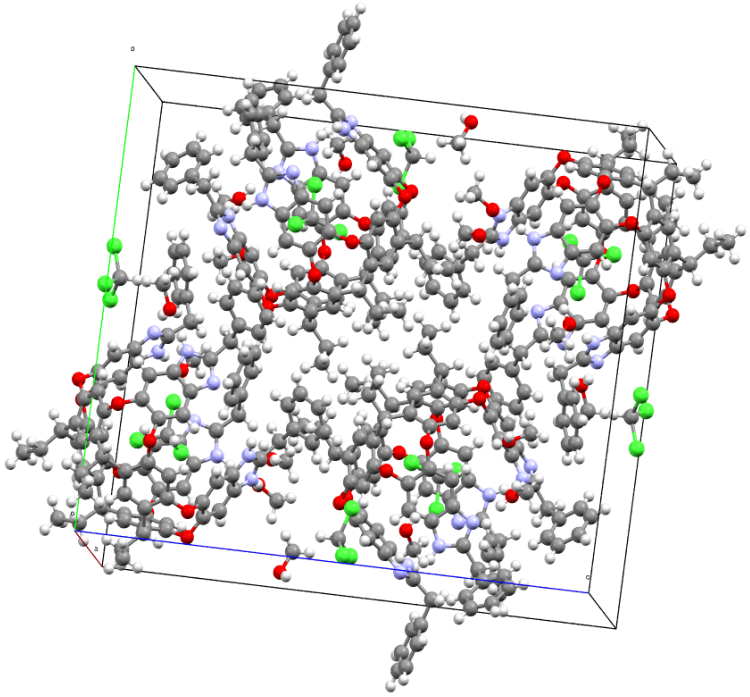
HRMS (ESI+) calcd for $C_{92}H_{73}N_8O_8$ ($[M+H]^+$): 1418.5578, Found: 1418.5552.

[1] A. R. Far, A. Shivanyuk and J. Rebek, *J. Am. Chem. Soc.*, 2002, **124**, 2854-2855.

Additional X-ray Structure Figures



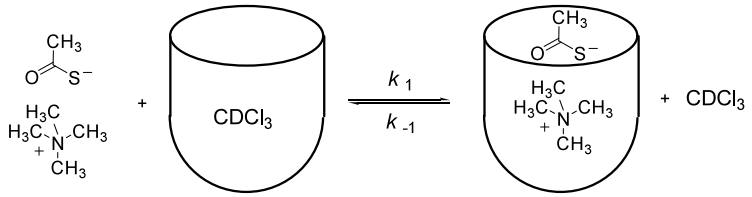
ORTEP plot (50% probability) of cavitand **1** with four molecules of methanol and two molecules of chloroform. One molecule of chloroform is bound in the cavitand as a guest. View from side (left) and from top (right).



Crystal unit cell of cavitand **1**.

Binding studies using EXSYCalc program

For these experiments we used the phase sensitive NOESY pulse sequence to measure the rate of quaternary ammonium cation exchange. Two NOESY spectra were taken sequentially, one with 300 ms mixing time and then with 0 ms mixing time.These experiments must be done under a consistent set of conditions that will allow for the direct comparison of the effect of different anions. An exchange equilibrium defines forward and reverse reaction rate constants that can be used to compare the effects of the anion on guest exchange.



We used the EXSYCalc program (Mestrelab Research, Santiago de Compostela) to calculate both exchange rate constants. NOESY measures first order forward and reverse magnetization transfer rate constants k_1' and k_{-1}', which are related to exchange rate constant k_1 and k_{-1} by

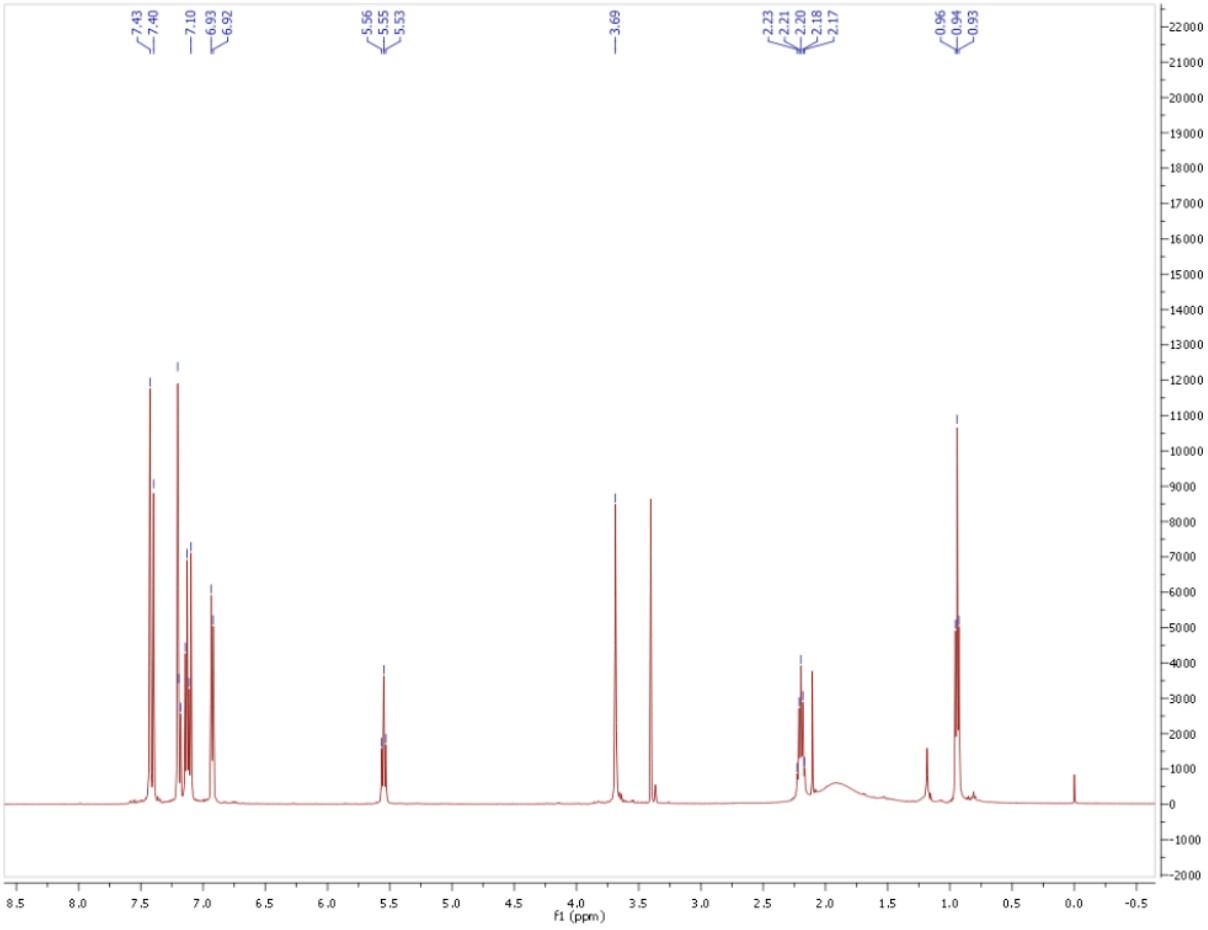
$k_1 = k_1'$/ [*quaternary ammonium salt*] and $k_{-1} = k_{-1}'$

According to the equation $K_a = k_1/k_{-1}$ we determined binding constants for NMe_4F, $NMe_4BH(OAc)_3$, and NMe_4SAc.

^{1}H NMR chemical shifts (ppm) of several hydrogens (benzylic, methine and tetramethylammonium guest) of cavitand complexes with different tetramethylammonium salts in $CDCl_3$ + 0.5% CD_3OD.

anion	benzyllic	methine	guest
-	3.69	5.55	-
F (without CD_3OD)	4.00	5.64	-1.73
F	4.16	5.68	-1.63
SAc	4.16	5.67	-1.64
OAc	4.17	5.69	-1.61
NO_3	4.17	5.68	-1.65
$BH(OAc)_3$	4.18	5.68	-1.63
Cl	4.18	5.66	-1.67
CH_2NO_2	4.20	5.69	-1.62
BF_4	4.28	5.66	-1.54
PF_6	4.28	5.67	-1.52
Br	4.46	5.65	-1.56
I	4.55	5.65	-1.39

^{1}H-NMR spectrum* of cavitand **1**(500 MHz, $CDCl_3$, 295 K)



* small amounts of methanol and acetone are present.