# A Cavitand With A Fluorous Rim Acts As An Amine Receptor

## Electronic Supplementary Information

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## 1. General Information

$^1$H and 2D spectra were recorded on a Bruker DRX-600 spectrometer with a 5mm QNP probe. Proton ($^1$H) chemical shifts are reported in parts per million (δ) with respect to tetramethylsilane (TMS, δ=0), and referenced internally with respect to the protio solvent impurity. $^{19}$F chemical shifts are reported in parts per million (δ) and referenced to $CFCl_3$ (δ=0). Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc., Andover, MA, and used without further purification. Guest molecules were obtained from Aldrich Chemical Company, St. Louis, MO and were used as received. Solvents were dried through a commercial solvent purification system (SG Water, Inc.). Molecular modeling (semi-empirical calculations) was carried out using the AMBER* force field using Maestro v7.0.2. Octaamine cavitand, HCl salt was synthesized according to the literature procedure.[1]

## 2. Synthesis of New Compounds

**Perfluoroacetate cavitand 1:**

To an oven-dried, 25 mL round-bottomed flask equipped with a magnetic stirrer was added octaamine cavitand, HCl salt (200 mg, 0.172 mmol). The mixture was placed under argon and dry DMF (5 mL) added, followed by trifluoroacetic anhydride (600 μL). The solution was stirred for 3h, then poured into water. The solid was isolated by filtration and purified by recrystallization from ethyl acetate, to yield cavitand **1** (227 mg, 85%) as an off-white solid. $^1$H NMR (600 MHz, $C_6D_6$) δ 0.96 (t, J = 7.8 Hz, 12H); 1.33 (m, 64H); 1.53 (m, 8H); 2.40 (q, J = 7.8 Hz, 8H); 6.24 (t, J = 7.8 Hz, 12H) 7.16 (s, 4 H); 7.27 (s, 4H); 7.64 (s, 8H); 13.66 (br s, 8H); $^{19}$F NMR (600 MHz, $C_6D_6$) δ -65.01(s); MALDIMS *m/z*: calcd for $C_{112}H_{120}F_{24}N_8O_{16}$ ($M+H^+$) 2290; found 2290. The cavitand

was not sufficiently soluble for a $^{13}C$ spectrum to be acquired in any reasonable amount of time.

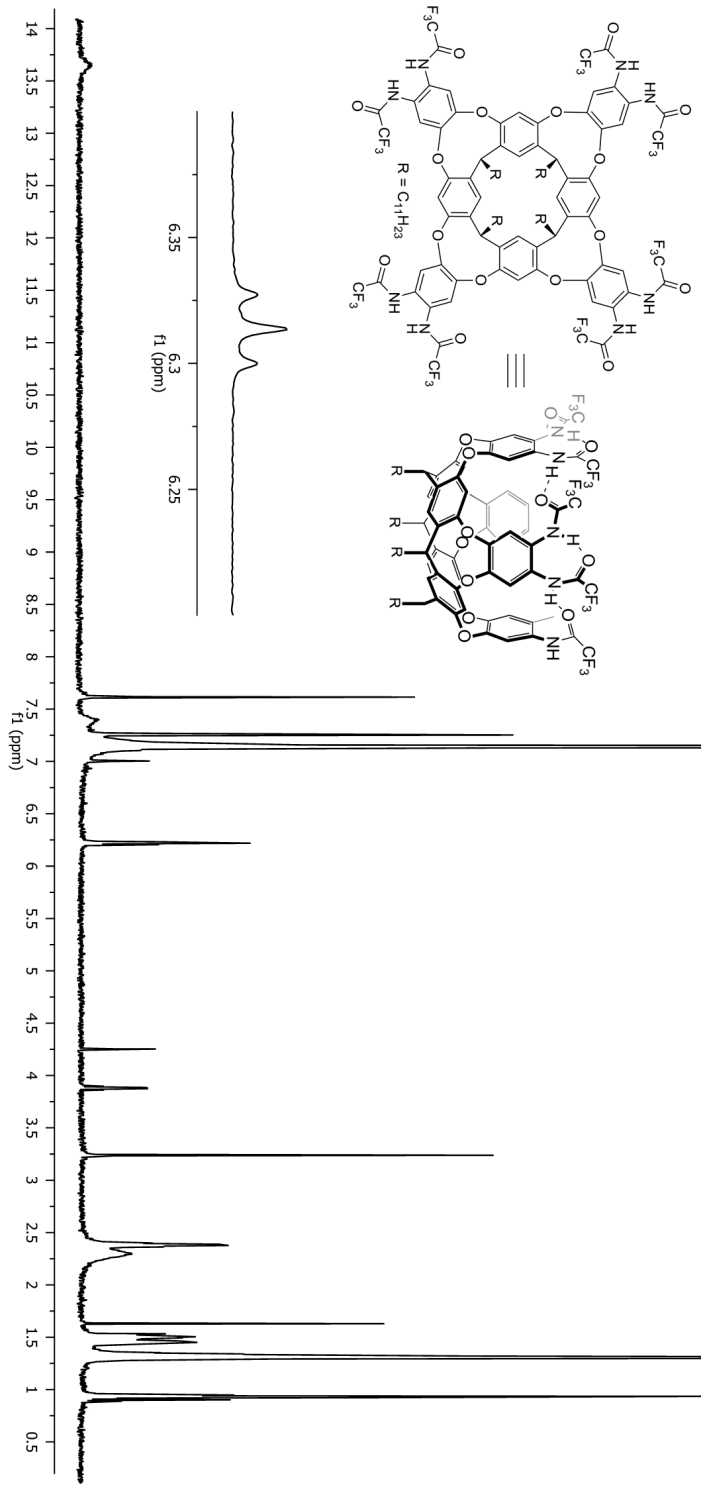


***Figure S-1.*** $^{1}H$ NMR spectrum of cavitand **1** (600 MHz, $C_6D_6$, 300K).

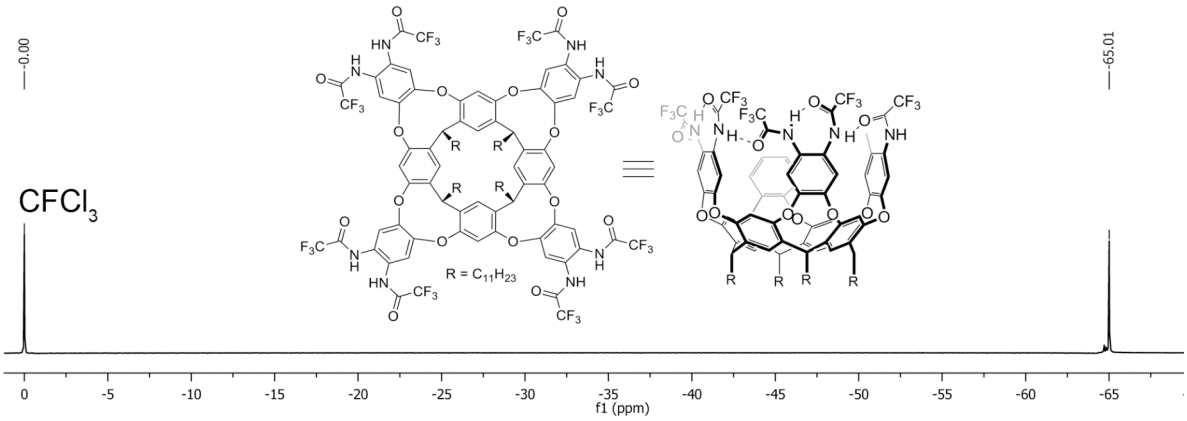


***Figure S-2.*** $^{19}$F NMR spectrum of cavitand **1** (600 MHz, $CDCl_3$, 300K).

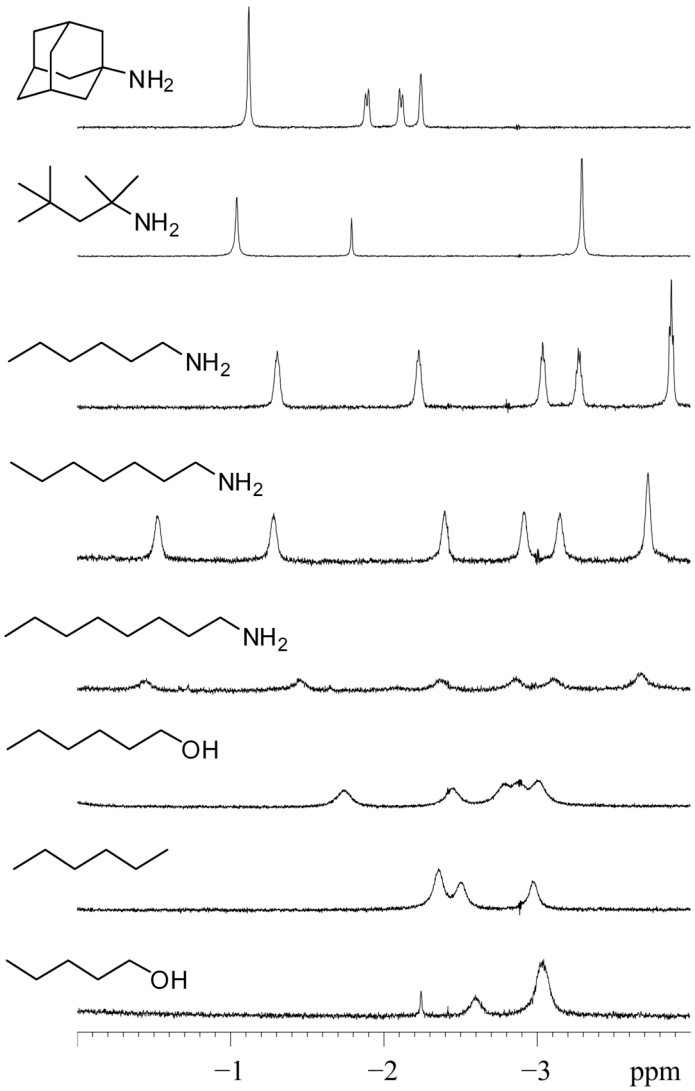


***Figure S-3.*** Upfield regions of the $^1$H NMR spectra of the complexes of cavitand **1** and various guests (600 MHz, mesitylene-$d_{12}$, 300K).

## 3. Binding Constant Determination

A solution of cavitand **1** and guest (2-10 mM) in mesitylene-$d_{12}$ was allowed to equilibrate for 4h at room temperature in an NMR tube, and then the $^1$H NMR spectrum was acquired. Integration of the bound and free peaks corresponding to suitable guest protons gave the equilibrium concentrations of bound and free guest, from which the binding constant was determined. The triplet at δ 6.24 ppm (cavitand methine proton) was used to calibrate the concentrations from a known concentration of cavitand **1**. The values in the Table are the averages of three separate experiments.

## 4. Procedure for 2D EXSY Experiment

A solution of cavitand **1** (2 mM) and tetrahydropyran (6 mM) in mesitylene-$d_{12}$ was allowed to equilibrate for 4h at room temperature in an NMR tube, the $^1$H NMR spectrum was acquired and then the 2D gNOESY spectrum was recorded at 600 MHz, 300K with the phase sensitive gradient NOESY pulse sequence supplied with the Bruker software. Each of the 512 F1 increments was the accumulation of 36 scans. Before Fourier transformation, the FIDs were multiplied by a 90° sine square function in both the F2 and the F1 domain. 1K _ 1K real data points were used, with a resolution of 1 Hz/point. Two gNOESY spectra were taken sequentially, one with 300 ms mixing time and then with 25 ms mixing time. The rate constant $k$ was calculated using the EXSYCALC program (Mestrelab Research, Santiago de Compostela)[2] and is the sum of the two dependent magnetization transfer rate constants $k_1$, $k_{-1}$ obtained from the calculations, an approximation due the system being in equilibrium.[3] The integral values of the peaks (both diagonal and exchange crosspeaks) seen in Figure *S4*, approximately δ 3.4, -0.8 ppm were used for the calculations. $\Delta G^{\ddagger}$ was obtained using the Eyring Equation.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$$k = k_1 + k_{-1}$$

$$k = \kappa\,(k_B T/h)e^{(-\Delta G\ddagger/RT)}$$

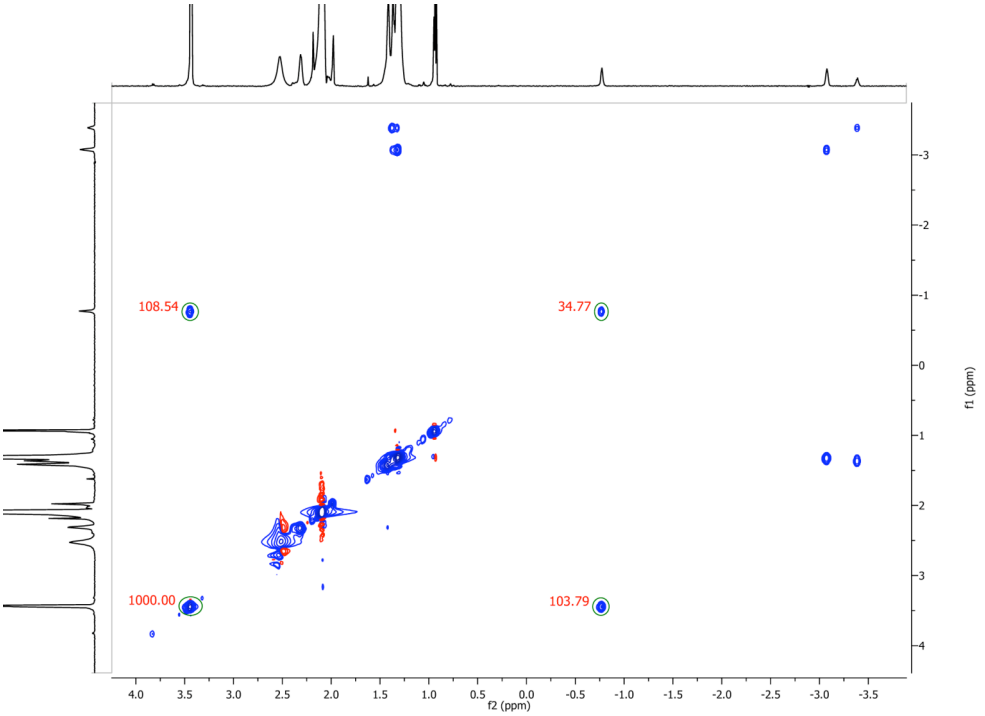


**Figure *S-4a*.** Upfield region of the 2D gNOESY NMR spectrum of complex **1**•tetrahydropyran (2 mM **1**, mesitylene-$d_{12}$, 300ms mixing time, 300K) illustrating in/out self-exchange peaks between the bound and free guest, and their corresponding integrals, used to calculate k and $\Delta G^{\ddagger}$.

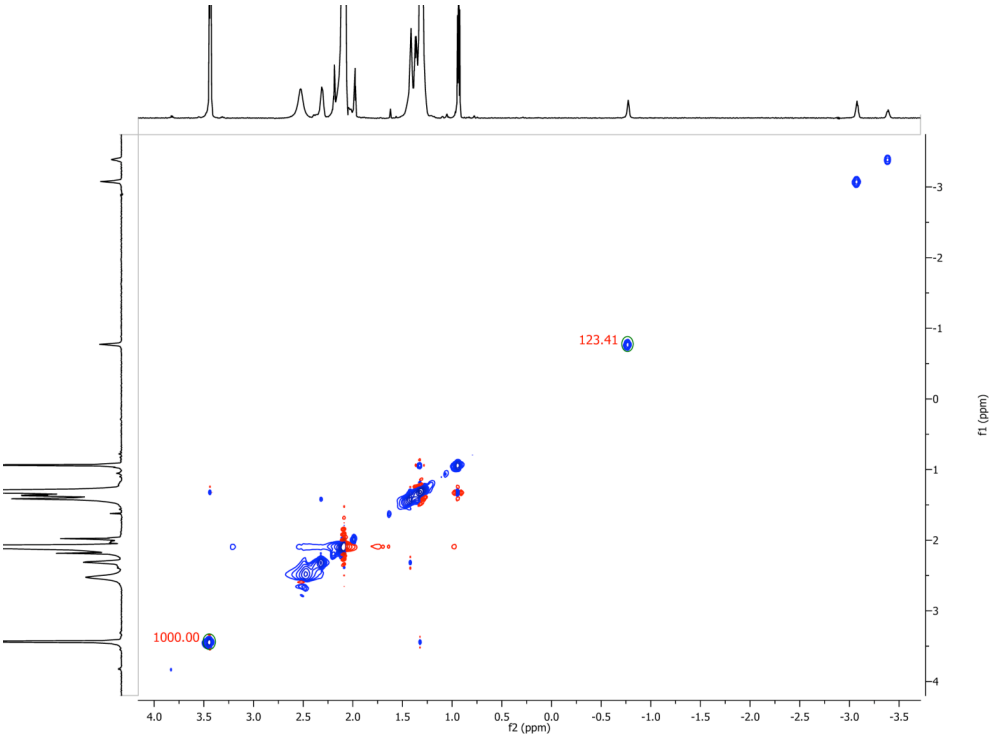


**Figure *S-4b*.** Upfield region of the 2D gNOESY NMR spectrum of complex **1**•tetrahydropyran (2 mM **1**, mesitylene-$d_{12}$, 25 ms mixing time, 300K) illustrating the lack of in/out self-exchange peaks between the bound and free guest. The diagonal integrals were used to calculate k and $\Delta G^{\ddagger}$.

## References:

1) A. Rafai Far, A. Shivanyuk and J. Rebek, Jr., *J. Am. Chem. Soc.,* 2002, **124**, 2854-2855.
2 a) C. L. Perrin and T. J. Dwyer, *Chem. Rev.,* 1990, **90**, 935-967; b) Z. Zolnai, N. Juranic, D. Vikic-Topic, and S. Macura, *J. Chem. Inf. Comput. Sci.,* 2000, **40**, 611-621.
3) E. V. Anslyn and D. A. Dougherty, in *Modern Physical Organic Chemistry*, University Science Books: Sausalito, CA, 2006, Ch. 10.