Supporting Information

Title: Structure and Thermodynamics of a Multimeric Cavitand Assembly

Authors: Christer B. Aakeröy,* Prashant D. Chopade, Colette F. Quinn, and John Desper

Department of Chemistry, Kansas State University, Manhattan, KS 66503.

aakeroy@ksu.edu

Table of contents

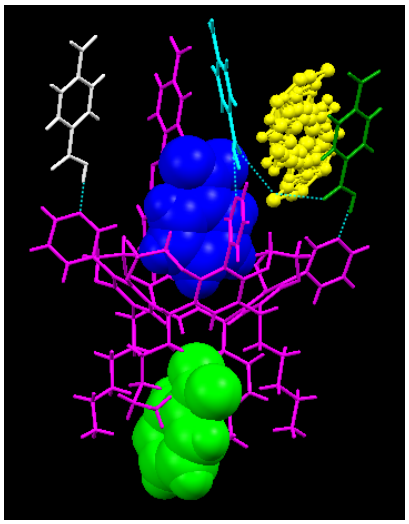

Figure S1. **2•(3)$_4$** colour coded for clarity (disordered 2,6-dimethyl naphthalene guest molecule is shown in yellow ball stick model)

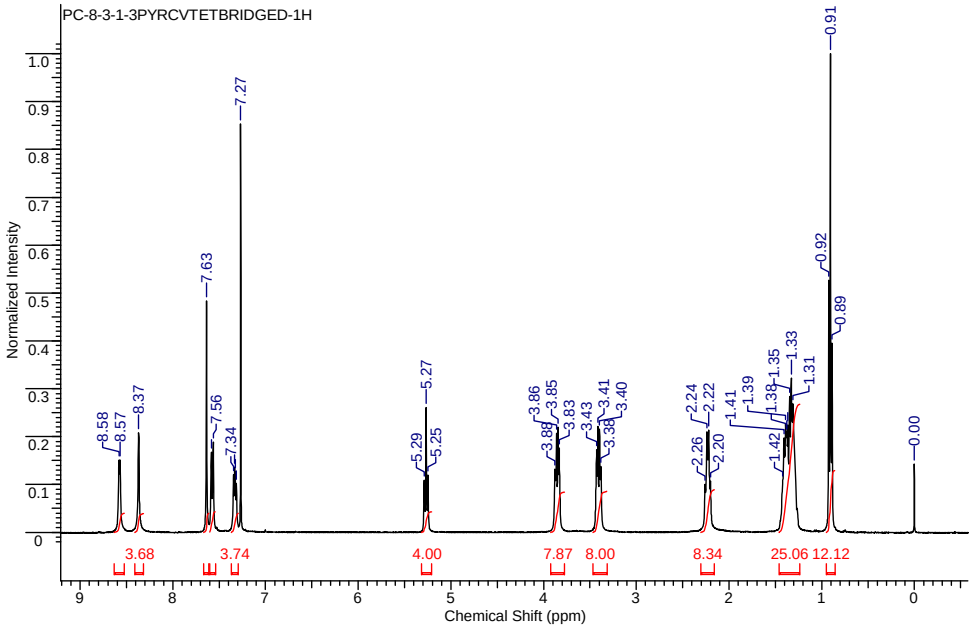

Figure S2. ^{1}H NMR spectrum of **2.**

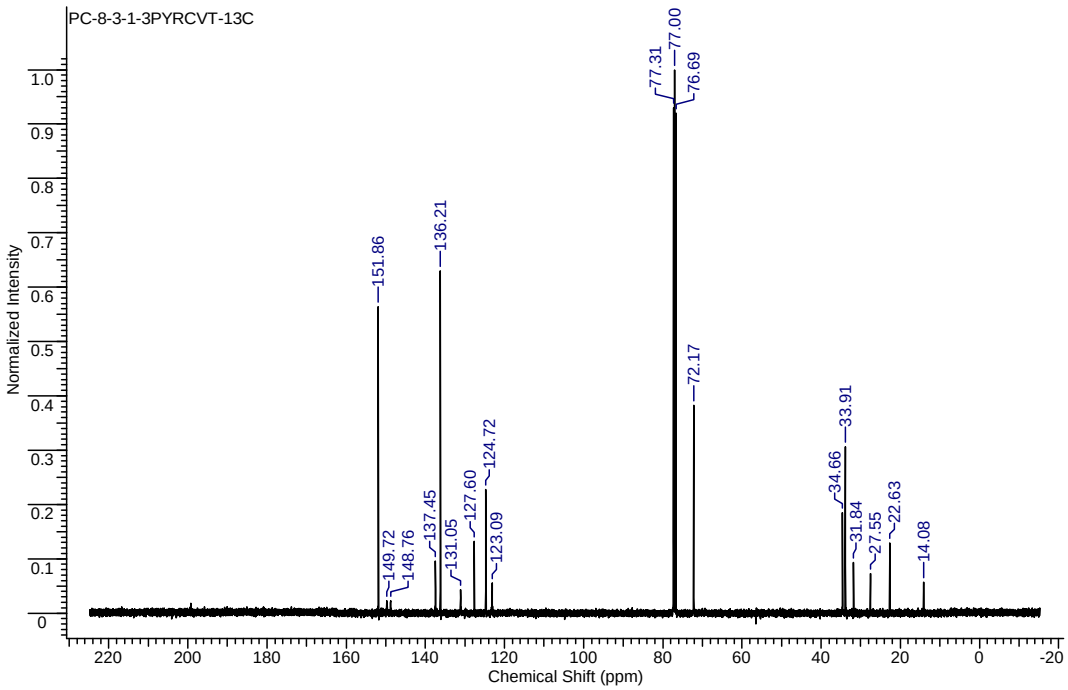

Figure S3. ^{13}C NMR spectrum of **2.**

ITC Data

ITC titration data were fitted using the independent model from the software *NanoAnalyze* resulting in information about enthalpy change (ΔH), association constant (K_a), and stoichiometry (N), Fig. 1. Since N was estimated to be 0.25, the numerical value of N was allowed to vary in the range of 0.2 to 0.3. ΔH and K_a were allowed to vary freely. The number of moles of both titrant (syringe) and titrate (cell) change. The independent model uses Equation 1 and 2 to account for the cell volume staying the same while moles of both titrant and titrate leave the active cell volume during the assay.

moles of Titrate after injection = (moles of Titrate before injection / cell volume) * (cell volume – injection volume) .....Equation 1

moles Titrant after injection = injected moles + ((moles Titrant before injection * (cell volume – injection volume)) / cell volume) .....Equation 2

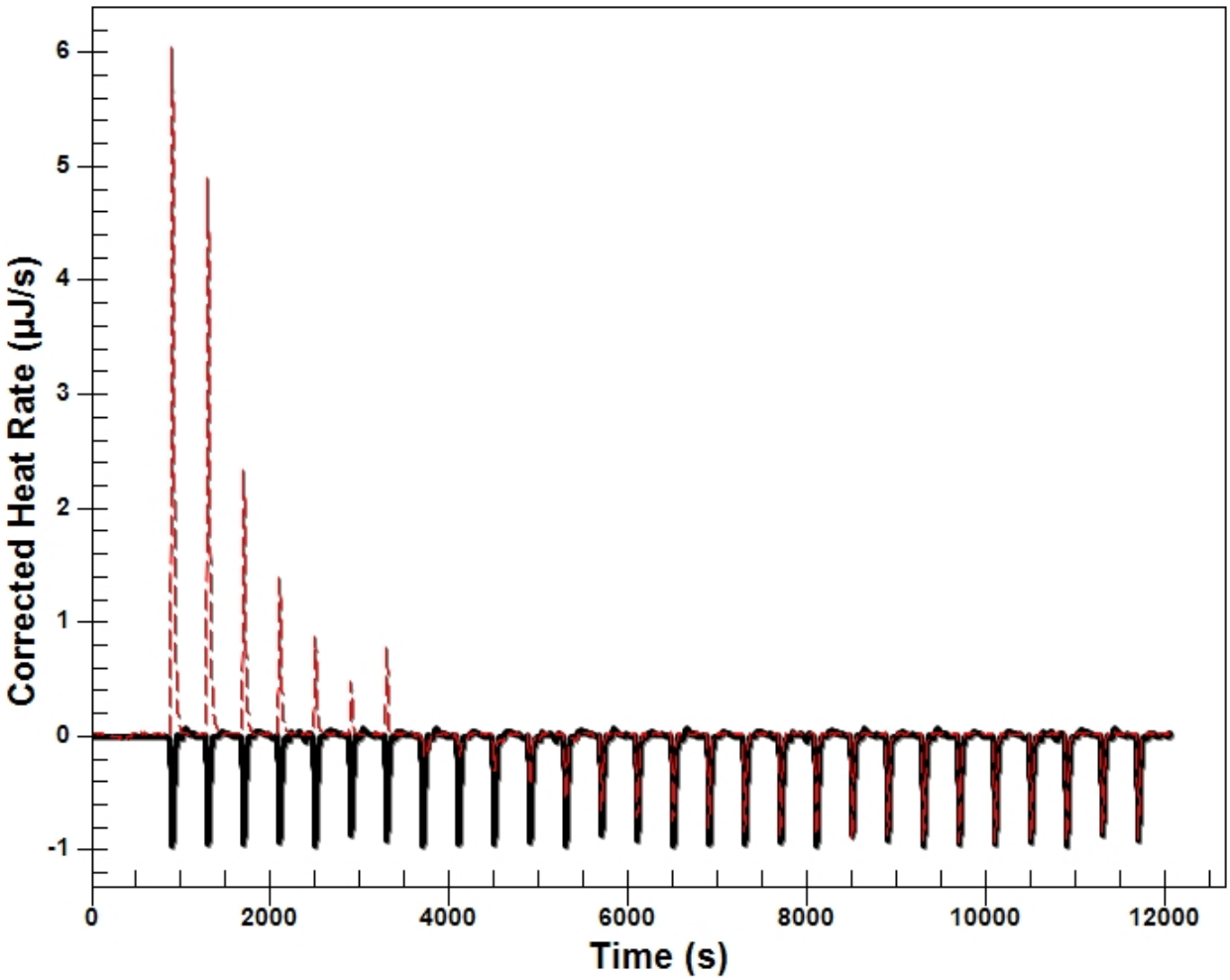

Figure S4 ITC titration curve of C-pentyltetra(3-pyridyl)cavitand vs. 4-nitrobenzoic acid for the first experiment; overlay of the binding titrations with a background generated from the last few data points (black curve represents the heat of dilution of the C-pentyltetra(3-pyridyl)cavitand)

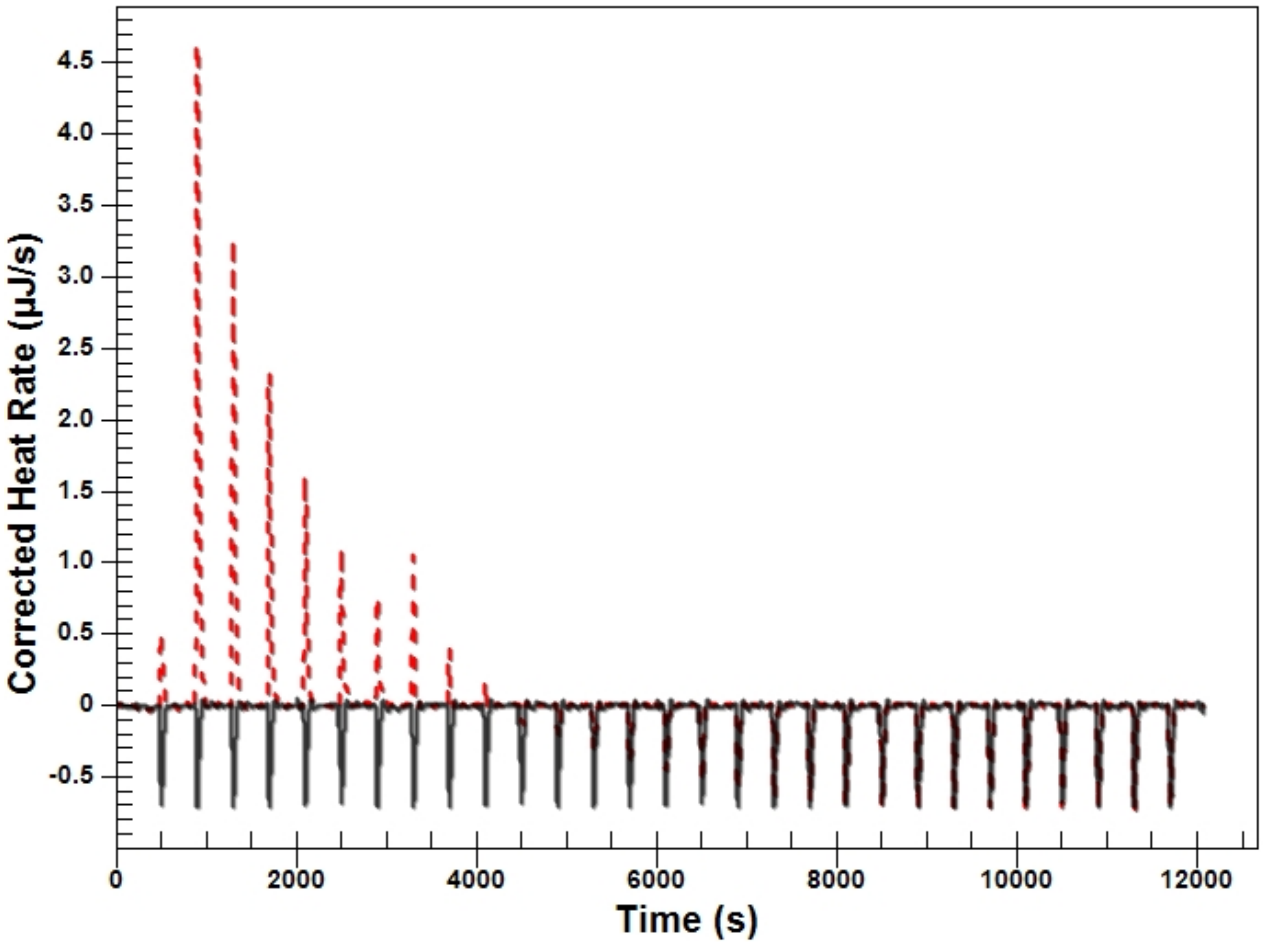

Figure S5 ITC titration curve of C-pentyltetra(3-pyridyl)cavitand vs. 4-nitrobenzoic acid for the duplicate experiment; overlay of the binding titrations with a background generated from the last few data points (black curve represents the heat of dilution of the C-pentyltetra(3-pyridyl)cavitand)

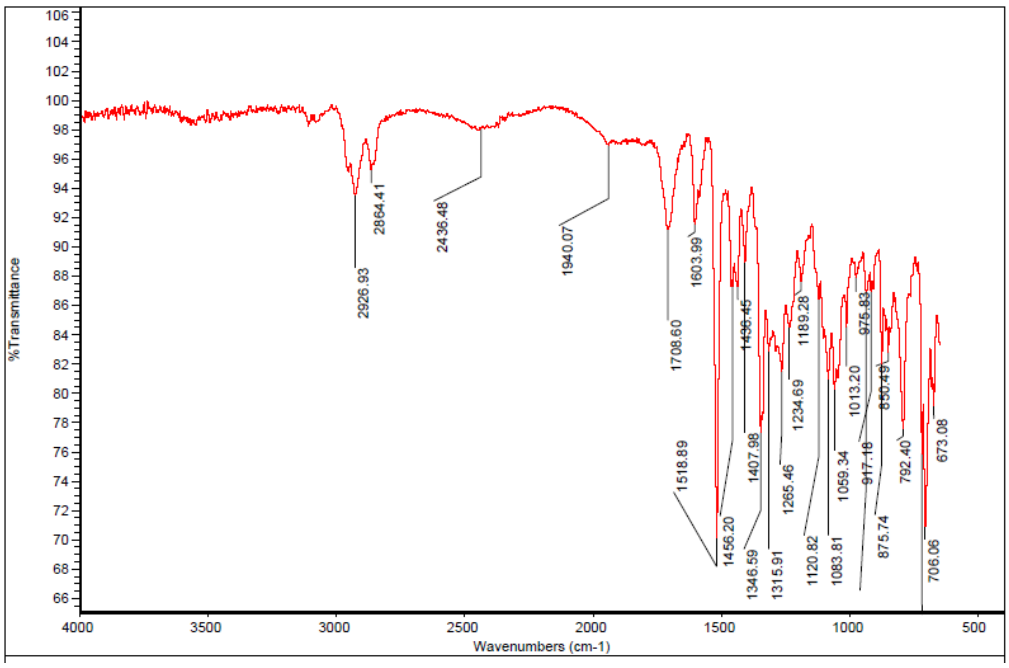

Figure S6. IR spectrum of a single crystal of **2•(3)$_4$**.

Table S1. Crystal data for **1**, **2** and **2•(3)$_4$**

	1	**2**	**2•(3)$_4$**
Empirical formula	$C_{122}H_{151}Br_8N_5O_{16}$	$C_{170}H_{222}N_8O_{25}$	$C_{238}H_{237}N_{21}O_{60}$
Molecular weight	2582.76	2777.56	4351.49
Color, Habit	orange prism	colourless prism	yellow prism
Crystal system	Triclinic	Triclinic	Monoclinic
Space group, Z	P-1, 2	P-1, 1	P2(1)/n, 2
a, Å	14.9430(6)	12.7536(6)	13.3210(9)
b, Å	17.0436(7)	13.7525(7)	52.697(4)
c, Å	26.1853(11)	24.5901(12)	16.3401(11)
α, °	101.948(2)	105.279(2)	90.00
β, °	97.566(2)	95.784(2)	109.773(3)
γ, °	111.014(2)	102.120(2)	90.00
Volume, Å^3	5933.7(4)	4011.7(3)	10794.1(13)
X-ray wavelength	0.71073	0.71073	1.54178
μ, mm^{-1}	2.768	0.076	0.805
Crystal size, mm x mm x mm	0.30 x 0.25 x 0.20	0.30 x 0.25 x 0.20	0.30 x 0.22 x 0.14
Absorption corr	multi-scan	multi-scan	multi-scan
Reflections			

collected	136124	59661	71066
independent	44792	25761	19052
observed	36074	15075	15436
Threshold expression	>2σ (I)	>2σ (I)	>2σ (I)
R_1 (observed)	0.0337	0.0963	0.0629
wR_2 (all)	0.0906	0.3349	0.1806
S	0.989	1.046	1.092
Δρ max / min	2.271 / -1.507	1.428 / -0.934	0.725 / -0.665
Θ_{full}, °	30.00	31.54	67.50
Completeness to Θ_{full}	0.995	0.964	0.964