Supporting Information

Phase dependent structural perturbation of a robust multicomponent assembled icosahedral array

Irene Ling*,[a,b] Harshita Kumari,[c] Marzieh Mirzamani,[c] Alexandre N. Sobolev,[d] Christopher J. Garvey,[e] Jerry L. Atwood[f] and Colin L. Raston*[b]

Syntheses

Single crystals of complex **3** were obtained at room temperature by slow evaporation of a solution of **1**, **2** and Y^{3+} in basic aqueous solution (pH 10-11) in a 2:1:2 molar ratio. Single crystals for complex **4** were obtained at room temperature by slow evaporation of **1**, **2** and Y^{3+} in a 2:1:1 molar ratios. The structure of both complexes were resolved with CuKα radiation (Oxford Diffraction Gemini-R and Bruker APEX-II CCD diffractometers) at T = 100(2)K and solved by direct methods, and refined against F^2 with full-matrix least-squares using the SHELXL-97[1] crystallographic package. Lp and absorption corrections applied.

Crystal data for complex 3: $C_{63}H_{97}NNa_2O_{64}S_8Y_2$, M = 2376.73, brownish plate, 0.28 x 0.18 x 0.12 mm^3, trigonal, space group R $\bar{3}$ (No. 148), $a = b = 47.5183(6)$, $c = 25.9584(2)$ Å, $V = 50761.6(8)$ Å^3, $Z = 18$, $D_c = 1.399$ g/cm^3, $\mu = 3.688$ mm^{-1}. $F_{000} = 22068$, $\lambda = 1.54178$ Å, $2\theta_{max} = 134.8°$, 352139 reflections collected, 20234 unique ($R_{int} = 0.0541$). Final GooF = 1.319, $R1 = 0.0979$, $wR2 = 0.2801$, R indices based on 16861 reflections with $I>2\sigma(I)$, $|\Delta\rho|_{max}$= 2.1(1) eÅ^{-3}, 1236 parameters, 146 restraints. CCDC: 1480640

Crystal data for complex **4**: $C_{56}H_{106}Na_2O_{65}S_8Y_2$, M = 2299.69, colorless needle, 0.50 x 0.15 x 0.12 mm^3, triclinic, space group P $\bar{1}$ (No. 2), $a = 12.1783(5)$, $b = 13.4788(6)$, $c = 27.6293(11)$ Å, $\alpha = 89.078(1)$, $\beta = 80.089(1)$, $\gamma = 88.413(1)°$, $V = 4465.6(3)$ Å^3, $Z = 2$, $D_c = 1.710$ g/cm^3, $\mu = 4.636$ mm^{-1}. $F_{000} = 2380$, $2\theta_{max} = 144.9°$, 46897 reflections collected, 16320 unique ($R_{int} = 0.0215$). Final GooF = 1.179, $R1 = 0.0682$, $wR2 = 0.1559$, R indices based on 16025 reflections with $I>2\sigma(I)$, $|\Delta|\rho_{max}$= 2.96(13) eÅ^{-3}, 1219 parameters, 12 restraints. CCDC: 1480641

Hirshfeld surface analyses

Molecular calculation related to Hirshfeld surface and fingerprint plots were generated from

CrystalExplorer version 3.2.[2]

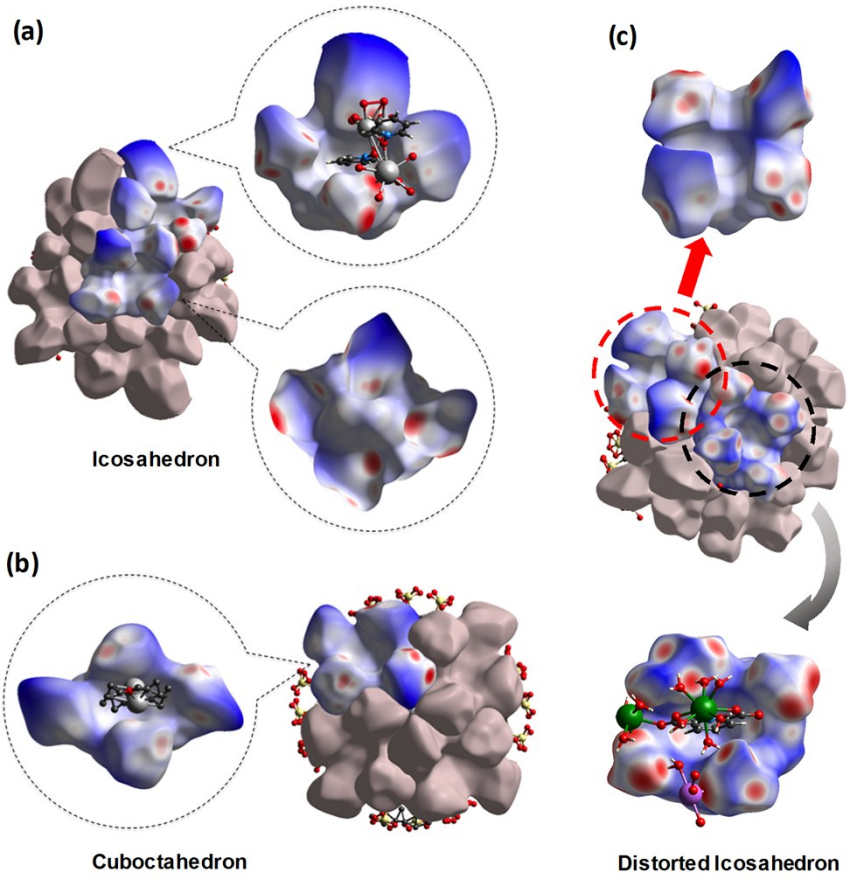

Figure S1. Polyhedra Hirshfeld surface analysis. (a) Icosahedral arrangement, where one independent calixarene has pyridine N-oxide included, the other devoid of guest molecules. (b) Cuboctahedral arrangement, which has an included sodium crown-ether complex. (c) Distorted icosahedron in 3, which has two crystallographically independent calixarenes, one accommodating a dipicolinate molecule.

Solution and particle studies

DLS analysis was performed using Malvern Zetasizer Nanoseries. TEM images were obtained by drop casting method on a copper grid carbon film (300 mesh) with Leo Libra 120 microscope operating at an accelerating voltage of 120 kV.

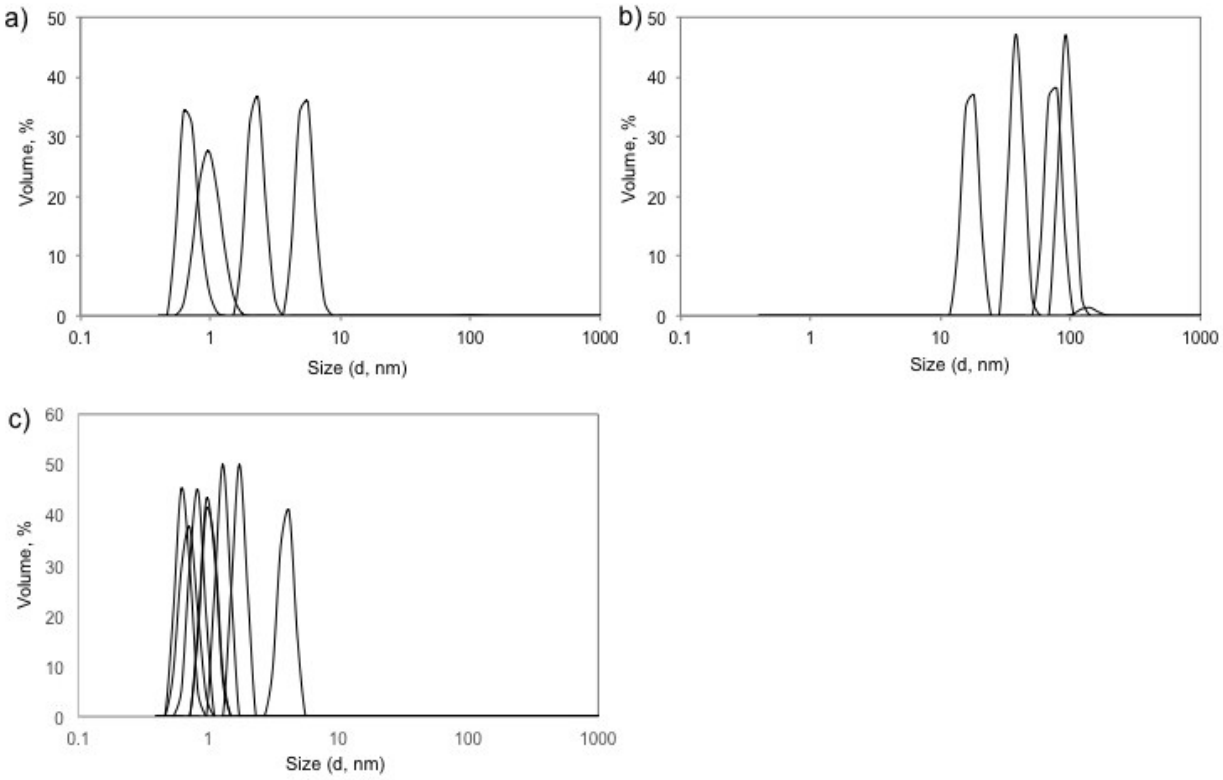

Figure S2. Particle size distribution (volume distribution) for monomeric spherical assembly (a) and super self-assembly (b) of Complex 3. (c) Particle size distribution (volume distribution) of Complex 3 after addition of dilute NaCl (0.01M).

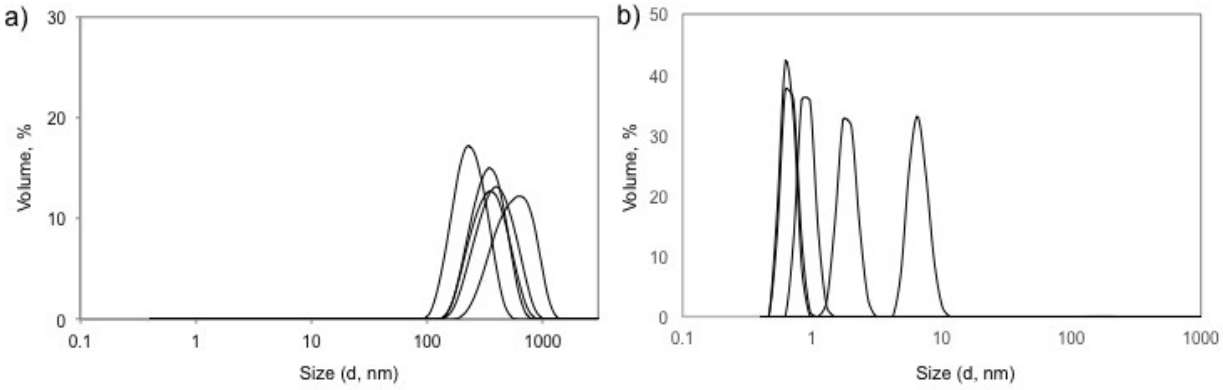

Figure S3. (a) Monomodal distribution (volume distribution) for white precipitates of Complex 3. (c) Particle size distribution (volume distribution) of Complex 3 (white precipitates) after addition of dilute NaCl (0.01M).

Small-angle Neutron Scattering (SANS)

SANS measurements were conducted at 25 °C with neutrons of wavelength λ = 5 Å and a wavelength distribution $\Delta\lambda/\lambda$ = 10%. Three sample to detector distances were used (1.3 m and 4.5 m, counting time 4000s and 7000s respectively) to cover the q range of 0.013 Å^{-1}<q< 0.534 Å^{-1}, where $q = (4\pi/\lambda) \sin(\theta/2)$ (q=scattering vector; λ = neutron wavelength; θ=scattering angle), with the scattered data for the samples corrected for the dark current, empty cell scattering and the sensitivity of the individual detector pixels. The corrected data were then placed on an absolute scale after normalization to the empty beam flux and structures were determined by comparing the data with that modeled using IGORPro[3] software smeared by an instrument resolution function.

Small-angle neutron scattering (SANS) data for the yttrium-seamed *p*-sulfonatocalix[4]arene complex **3**, in D_2O been reduced and fitted to elliptical and spherical models. The quality of the fit and physical plausibility of the structural parameters was used to evaluate which structure was the most likely solution structure. The scattering length densities (SLDs) for the nanostructure and solvent were calculated as constraints for the analyses done with macro's for the IgorPro[3] software provided by NIST. The scattering length density (SLD) of the nanostructure was calculated based on the molecular formula and number densities of the constituent nuclei obtained from the crystal structure. The SLDs for the nanostructure and the solvent D_2O were held fixed at the calculated values and the structural parameters were adjusted to provide the best fit. The deuterated solvent enhances the coherent scattering and increases the contrast between the solvent and the solute. Scattering curve for the nanostructure was fitted to spheroidal and elliptical models. The scattering data for yttrium-seamed *p*-sulfonatocalix[4]arene fitted best to the sphere model indicating the presence of only one spherical assembly in solution. The resultant nanoassembly has rearranged from a distorted icosahedron in solid state to a symmetric spherical icosahedron in solution.

Scattering length density (SLD):

Sample	Molecular formula	Density	wavelength (Å)	SLD
Yttrium-seamed *p*-sulfonatocalix[4]arene, **3**	$C_{63}H_{101}NNa_2O_{64}S_8Y_2$	1.447	5	1.714E-06

Yttrium-seamed *p*-sulfonatocalix[4]arene, 3, in solution

Sphere Model:

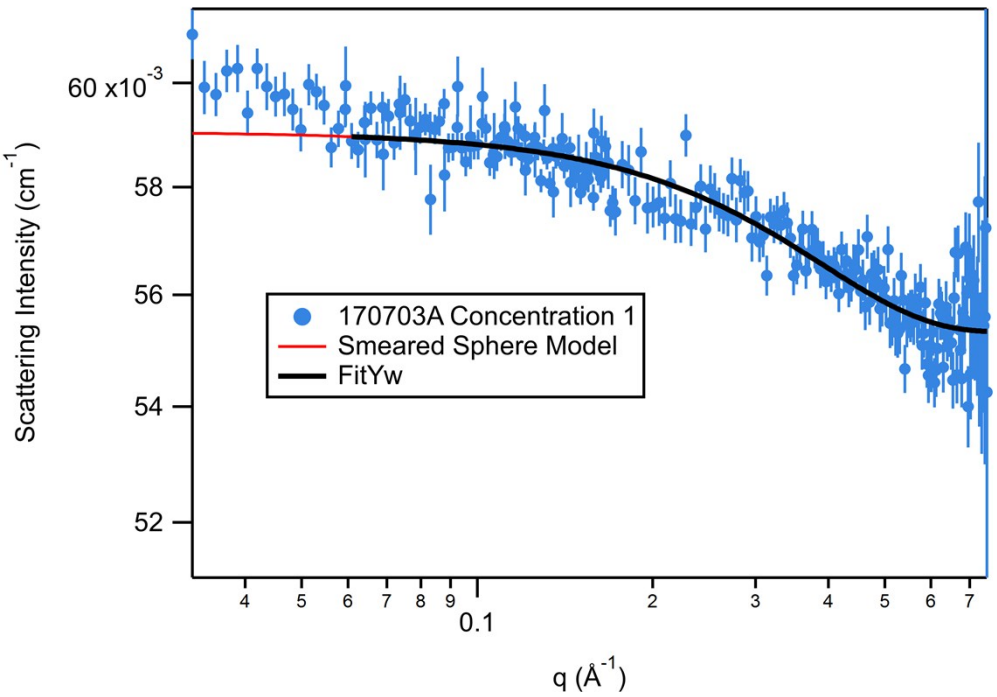

Figure S4. Smeared Sphere Model Fit

scale	0.00208921	±	0.000252303
Radius (Å)	5.79012	±	0.198018
SLD sphere ($Å^{-2}$)	1.714e-06	±	0
SLD solvent ($Å^{-2}$)	6.393e-06	±	0
bkgd (cm^{-1})	0.0553327	±	9.95346e-05
Sqrt(Chi^2/N)	1.12855		
Fitted Range	.060918	< Q <	0.7487

This model has small error bars for the fitted values and a small sqrt(Chi^2/N) value, and the visually the fit is good. There is a small low q tail at 0.06 $Å^{-1} < q$, indicative of slight aggregation of the particles, which was not included in the fit.

170630B Concentration 2—Sphere Model:

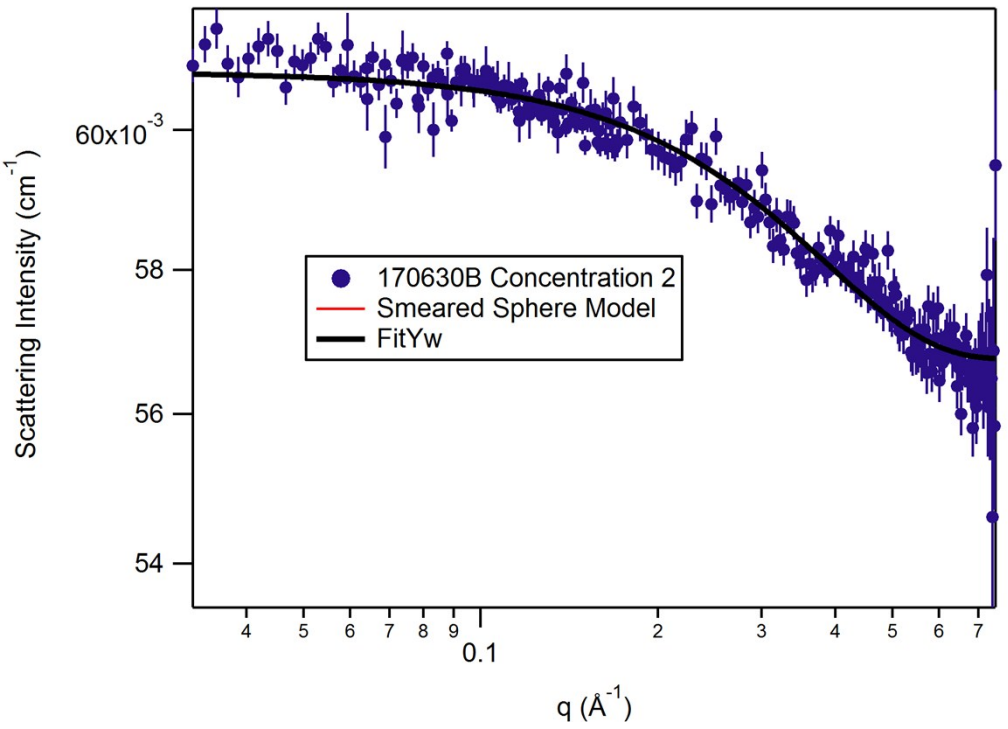

Figure S5. Smeared Sphere Model Fit

scale	0.00219717	±	0.000147854
Radius (Å)	5.87773	±	0.111922
SLD sphere ($Å^{-2}$)	1.714e-06	±	0
SLD solvent ($Å^{-2}$)	6.393e-06	±	0
bkgd (cm^{-1})	0.0567584	±	6.08113e-05
Sqrt(Chi^2/N)	1.15839		
Fitted Range	.032457	< Q <	0.7487

This model fits well visually, has a very small sqrt(Chi^2/N) value, and the error bars are very small compared to the fitted values. For these reasons, this model was chosen.

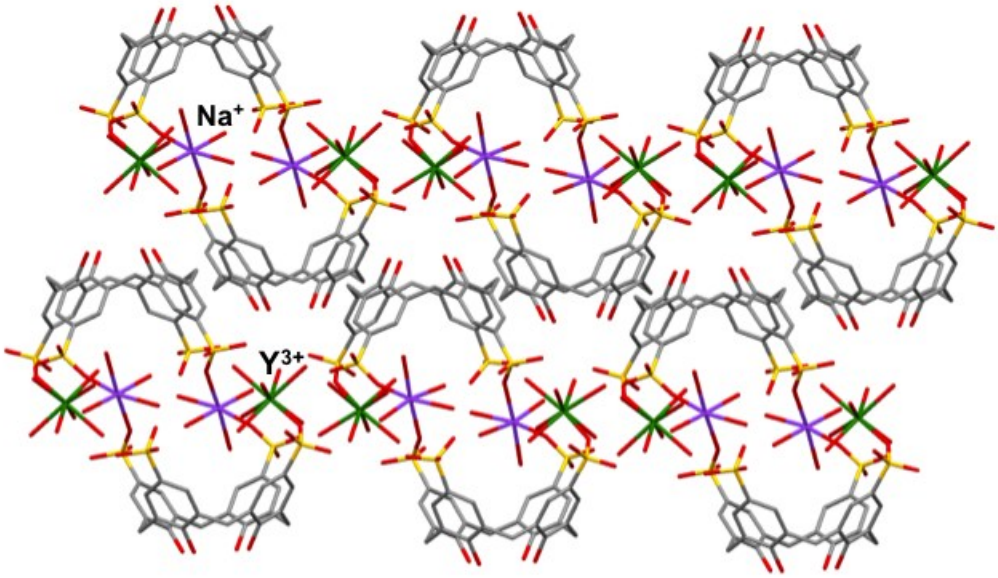

Figure S6. The bilayer arrangement of *p*-sulfonatocalixarenes devoid of dipicolinate inclusion, in the complex formed from a solution containing a 2:1:1 mixture of calixarene, dipicolinic acid, and yttrium(III) chloride.

Reference

[1] Sheldrick, G. M. *Acta Crystallog*., **2008**, *A64*, 112.

[2] Spackman, M. A.; Jayatilaka, D. *CrystEngComm*, **2009**, *11*, 19.

[3] Kline, S. R. *J. Appl. Crystallogr.*, **2006**, *39*, 895.