Supplementary Information: Synthesis of mixed Ga/Cd coordinated pyrogallol[4]arene nano-capsule presents a novel spherical template

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Information includes:

- Experimental details for synthesis of 1
- ¹H NMR Spectral comparison between the PgC₄ Ga-MONC and 1.
- Mass Spectrometry
- Elemental analyses: ICP (inductively coupled plasma) analyses

Synthesis of PgC₄ Ga-MONC: An aqueous solution of gallium nitrate (excess) was added to an acetone solution of C-butylpyrogallol[4]arene (200 mg, 0.26 mmol). Single crystals of the metal-organic nanocapsule that were suitable for synchrotron diffraction study formed upon standing overnight with slow evaporation. The crystalline material was harvested and dried to afford 131 mg (45% yield based on PgC₄). ¹H NMR (500MHz, CD₃CN): $\delta = 0.98$ (m, 72H, -CH₃); 1.40 (m, 96H, β-CH₂, γ-CH₂); 2.26 (m, 48H, α-CH₂, encapsulated water/acetone); 4.36 (m, 24H, -CH); 6.79, 6.82, 6.91, 6.95 (m, 24H, Ar), 7.38, 7.76, 8.33 (brs, partial OH); 1H NMR of 1 (CD₃CN + D₂O): the peaks at $\delta = 7.38$, 7.76, 8.33ppm disappear. ¹³C NMR (500MHz, [D₆]acetone): $\delta = 14.59$ (s, -CH₃); 23.32, 23,72 (m, γ -CH₂); 31.29, 31.56, 32.20, 32.85, 33.55(m, β-CH₂, α-CH₂), 34.91, 35.87, 36.32, 38.48 (m, -CH), 112.96, 114.27 (m, ArH), 123.03, 125.71, 133.67, 138.36, 140.13, 141.35 (m, Ar).

Synthesis of PgC4 Ga/Cd-MONC, **1:** Methanol cadmium (II) nitrate (excess) was added to an acetone solution of PgC₄ Ga-MONC (100 mg, 0.015 mmol, pre-dried and crystalline). Slow evaporation of the colourless solution afforded single crystals that were suitable for synchrotron diffraction studies (42 mg, 46% yield based on dried **1**). ¹H **NMR (500MHz, [D₆]acetone):** $\delta = 0.92$ (m, 72H, -CH₃); 1.32, 1.40, 1.48 (m, 96H, β-CH₂, γ -CH₂); 2.35 (m, 48H, α -CH₂); 4.37(m, 24H, -CH); 6.82, 6.94, 7.00 (m, 24ArH); 7.40, 7.92, 8.78(m, 2H, remaining –OH). ¹³C **NMR (500MHz, [D₆]acetone):** $\delta = 14.12$ (s, -CH₃); 23.26, 23,30 (m, γ -CH₂); 30.85, 31.14, 31.72, 32.99(m, β-CH₂, α-CH₂), 34.48, 35.00, 35.35, 35.88(m, -CH), 112.94, 113.59 (m, ArH), 117.65, 122.85, 126.34, 133.82, 140.96, 145.85, 145.35 (m, Ar)

NOTE: ¹³C **NMR** spectra for PgC₄Ga and PgC₄GaCd differs due to difference in hydroxyl environments around the metal centers. For example,

- difference in linker carbon environment: 38.5 ppm for PgC₄ Ga versus 35 ppm for PgC₄GaCd
- difference in aromatic carbon environment: 141 ppm for PgC₄ Ga versus 145 ppm for PgC₄GaCd



NOTE: For both PgC₄GaCd and PgC₄GaZn, multiple aromatic (at about 7 ppm) and – CH (at about 4.3 ppm) protons of linker carbon are observed, which indicates that these protons are experiencing multiple environments. (Phenolic –OH at 6 ppm)

The ¹H NMR of PgC₄GaZn shows following signals that are different from that of PgC₄GaCd:

- Proton of encapsulated molecule at 0 and -1.7 ppm (could be acetone or ethanol).
- There are no peaks below 0 ppm in the spectrum of the PgC_4 Ga/Cd MONCs while the spectrum of the PgC_4 Ga/Zn MONCs contain two peaks below 0 ppm representing two solvent molecules encapsulated permanently inside the capsule.
- Ethanol signal at 1.1 and 3.6 ppm (ethanol was present in the sample preparation).
- Because of the difference in solvents employed, at 4 ppm we see broader peak for PgC₄GaCd . This is due to the linker carbon environment which is affected by the aromatic rings.
- 7 ppm: not symmetrical aromatic region for both hexamers.

Theoretical Molecular Masses:

Basic skeleton (6 PgC4 + 16 Ga + 4Cd): 6161 g mol⁻¹ Basic skeleton (6 PgC4 + 18 Ga + 2Cd): 6078 g mol⁻¹

Basic skeleton + 40 aquo ligands (6 PgC4 + 16 Ga + 4Cd): 6881 g mol⁻¹ Basic skeleton + 40 aquo ligands (6 PgC4 + 18 Ga + 2Cd): 6798 g mol⁻¹

Experimental Molecular Mass:

MALDI-TOF MS spectra shows mass in a range of 5900~6200 Da



Elemental Analyses: Inductively coupled plasma / ICP elemental analysis is reported below. The atomic percentage of C, O, Ga,Cd is calculated from this analyses to deduce the Ga/Cd ratios per nanocapsule.



Mon Mar 02 12:11:36 2009 Filter Fit Chi Squared:6.450 Errors: +/- 1 Sigma Correction Method: Proza (Phi-Rho-Z) Acc.Voltage: 20.0 kV Take Off Angle: 38.2 deg. Detector: Pioneer

Quantitative Results for: gacd(5)													
Element Line	Net Counts	Net	Counts Error	K-Ratio	Weight %	Weight % Error	Atom %	Atom % Error					
C K	51489	+/-	294	0.91	78.97	+/- 0.45	85.61	+/- 0.49					
O K	2695	+/-	80	0.04	16.77	+/- 0.50	13.65	+/- 0.41					
Ga K	1279	+/-	112	0.04	3.44	+/- 0.30	0.64	+/- 0.06					
Cd L	1100	+/-	166	0.01	0.82	+/- 0.12	0.10	+/- 0.01					
Total					100.00		100.00						





Live Time: 90.0 sec.

Mon Mar 02 12:13:33 2009 Filter Fit Chi Squared:4.856 Errors: +/- 1 Sigma Correction Method: Proza (Phi-Rho-Z) Acc.Voltage: 20.0 kV Take Off Angle: 38.2 deg. Detector: Pioneer

Quantitative Results for: gacd(6)

Element	Net	Net Counts		K-Ratio	Weight %	Weight %	Atom %	Atom %
Line	Counts		Error			Error		Error
C K	34961	+/-	220	0.87	76.69	+/- 0.48	84.91	+/- 0.53
O K	2112	+/-	70	0.04	16.76	+/- 0.56	13.93	+/- 0.46
Ga K	1513	+/-	119	0.07	5.25	+/- 0.41	1.00	+/- 0.08
Cd L	1328	+/-	165	0.02	1.29	+/- 0.16	0.15	+/- 0.02
Total					100.00		100.00	