# Supplementary Information: Synthesis of mixed $\mathbf{G a} / \mathbf{C d}$ coordinated pyrogallol[4]arene nano-capsule presents a novel spherical template 

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Information includes:

- Experimental details for synthesis of 1
- ${ }^{1} \mathrm{H}$ NMR Spectral comparison between the $\mathrm{PgC}_{4}$ Ga-MONC and 1 .
- Mass Spectrometry
- Elemental analyses: ICP (inductively coupled plasma) analyses

Synthesis of $\mathrm{PgC}_{\mathbf{4}} \mathbf{G a - M O N C : ~ A n ~ a q u e o u s ~ s o l u t i o n ~ o f ~ g a l l i u m ~ n i t r a t e ~ ( e x c e s s ) ~ w a s ~ a d d e d ~ t o ~ a n ~}$ acetone solution of C-butylpyrogallol[4]arene ( $200 \mathrm{mg}, 0.26 \mathrm{mmol}$ ). Single crystals of the metalorganic 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 $\mathrm{mg}\left(45 \%\right.$ yield based on $\left.\mathrm{PgC}_{4}\right)$. ${ }^{\mathbf{1}} \mathbf{H}$ NMR ( $\mathbf{5 0 0 M H z}, \mathbf{C D}_{3} \mathbf{C N}$ ): $\delta=0.98\left(\mathrm{~m}, 72 \mathrm{H},-\mathrm{CH}_{3}\right) ; 1.40(\mathrm{~m}$, $\left.96 \mathrm{H}, \beta-\mathrm{CH}_{2}, \gamma-\mathrm{CH}_{2}\right) ; 2.26\left(\mathrm{~m}, 48 \mathrm{H}, \alpha-\mathrm{CH}_{2}\right.$, encapsulated water/acetone); $4.36(\mathrm{~m}, 24 \mathrm{H},-\mathrm{CH})$; $6.79,6.82,6.91,6.95(\mathrm{~m}, 24 \mathrm{H}, \mathrm{Ar}), 7.38,7.76,8.33$ (brs, partial OH$)$; 1 H NMR of $1\left(\mathrm{CD}_{3} \mathrm{CN}+\right.$ $\mathrm{D}_{2} \mathrm{O}$ ): the peaks at $\delta=7.38,7.76,8.33 \mathrm{ppm}$ disappear. ${ }^{13} \mathbf{C} \mathbf{N M R}\left(500 \mathbf{M H z}\right.$, [D $\left.\mathbf{D}_{6}\right]$ acetone): $\delta=$ $14.59\left(\mathrm{~s},-\mathrm{CH}_{3}\right) ; 23.32,23,72\left(\mathrm{~m}, \gamma-\mathrm{CH}_{2}\right) ; 31.29,31.56,32.20,32.85,33.55\left(\mathrm{~m}, \beta-\mathrm{CH}_{2}, \alpha-\mathrm{CH}_{2}\right)$, $34.91,35.87,36.32,38.48$ (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 $\mathrm{PgC}_{4} \mathrm{Ga}-\mathrm{MONC}(100 \mathrm{mg}, 0.015 \mathrm{mmol}$, pre-dried and crystalline). Slow evaporation of the colourless solution afforded single crystals that were suitable for synchrotron diffraction studies ( $42 \mathrm{mg}, 46 \%$ yield based on dried 1). ${ }^{\mathbf{1}} \mathbf{H} \mathbf{N M R}$ ( $\mathbf{5 0 0 M H z}$, [D $\left.\mathbf{D}_{6}\right]$ acetone): $\delta=$ $0.92\left(\mathrm{~m}, 72 \mathrm{H},-\mathrm{CH}_{3}\right) ; 1.32,1.40,1.48\left(\mathrm{~m}, 96 \mathrm{H}, \beta-\mathrm{CH}_{2}, \gamma-\mathrm{CH}_{2}\right) ; 2.35\left(\mathrm{~m}, 48 \mathrm{H}, \alpha-\mathrm{CH}_{2}\right) ; 4.37(\mathrm{~m}$, $24 \mathrm{H},-\mathrm{CH}) ; 6.82,6.94,7.00(\mathrm{~m}, 24 \mathrm{ArH}) ; 7.40,7.92,8.78(\mathrm{~m}, 2 \mathrm{H}$, remaining -OH$) .{ }^{13} \mathbf{C}$ NMR (500MHz, [D $\mathbf{D}_{6}$ acetone): $\delta=14.12\left(\mathrm{~s},-\mathrm{CH}_{3}\right) ; 23.26,23,30\left(\mathrm{~m}, \gamma-\mathrm{CH}_{2}\right) ; 30.85,31.14,31.72$, $32.99\left(\mathrm{~m}, \beta-\mathrm{CH}_{2}, \alpha-\mathrm{CH}_{2}\right), 34.48,35.00,35.35,35.88(\mathrm{~m},-\mathrm{CH}), 112.94,113.59(\mathrm{~m}, \mathrm{ArH}), 117.65$, $122.85,126.34,133.82,140.96,145.85,145.35$ (m, Ar)

NOTE: ${ }^{13} \mathbf{C}$ NMR spectra for $\mathrm{PgC}_{4} \mathrm{Ga}$ and $\mathrm{PgC}_{4} \mathrm{GaCd}$ differs due to difference in hydroxyl environments around the metal centers. For example,

- difference in linker carbon environment: 38.5 ppm for $\mathrm{PgC}_{4}$ Ga versus 35 ppm for $\mathrm{PgC}_{4} \mathrm{GaCd}$
- difference in aromatic carbon environment: 141 ppm for $\mathrm{PgC}_{4}$ Ga versus 145 ppm for $\mathrm{PgC}_{4} \mathrm{GaCd}$
${ }^{1} \mathrm{H}$ NMR - spectral comparison
A: Crystals of $\mathrm{PgC}_{4} \mathrm{Ga} / \mathrm{Cd}$ MONCs in [D $\mathrm{D}_{6}$ ]acetone
B: Crystals of $\mathrm{PgC}_{4} \mathbf{G a} / \mathbf{Z n}$ MONCs in $\mathrm{CD}_{3} \mathbf{C N}$


NOTE: For both $\mathrm{PgC}_{4} \mathrm{GaCd}$ and $\mathrm{PgC}_{4} \mathrm{GaZn}$, 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 ${ }^{1} \mathrm{H}$ NMR of $\mathrm{PgC}_{4} \mathrm{GaZn}$ shows following signals that are different from that of $\mathrm{PgC}_{4} \mathrm{GaCd}$ :

- 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 $\mathrm{PgC}_{4} \mathrm{Ga} / \mathrm{Cd}$ MONCs while the spectrum of the $\mathrm{PgC}_{4} \mathrm{Ga} / \mathrm{Zn}$ 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 $\mathrm{PgC}_{4} \mathrm{GaCd}$. 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 ( $6 \mathrm{PgC} 4+16 \mathrm{Ga}+4 \mathrm{Cd}$ ): $6161 \mathrm{~g} \mathrm{~mol}^{-1}$
Basic skeleton ( $6 \mathrm{PgC} 4+18 \mathrm{Ga}+2 \mathrm{Cd}$ ): $6078 \mathrm{~g} \mathrm{~mol}^{-1}$
Basic skeleton +40 aquo ligands ( $6 \mathrm{PgC} 4+16 \mathrm{Ga}+4 \mathrm{Cd}$ ): $6881 \mathrm{~g} \mathrm{~mol}^{-1}$
Basic skeleton +40 aquo ligands ( $6 \mathrm{PgC} 4+18 \mathrm{Ga}+2 \mathrm{Cd}$ ): $6798 \mathrm{~g} \mathrm{~mol}^{-1}$

## 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 $\mathrm{C}, \mathrm{O}, \mathrm{Ga}, \mathrm{Cd}$ is calculated from this analyses to deduce the $\mathrm{Ga} / \mathrm{Cd}$ ratios per nanocapsule.


Live Time: 90.0 sec .
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 <br> Line | Net <br> Counts | Net Counts <br> Error | K-Ratio | Weight \% | Weight \% <br> Error | Atom \% | Atom \% <br> Error |  |
| :---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| $\boldsymbol{C} \boldsymbol{K}$ | 51489 | $+/-$ | 294 | 0.91 | 78.97 | $+/-0.45$ | 85.61 | $+/-0.49$ |
| $\boldsymbol{O} \boldsymbol{K}$ | 2695 | $+/-$ | 80 | 0.04 | 16.77 | $+/-0.50$ | 13.65 | $+/-0.41$ |
| $\boldsymbol{G a} \boldsymbol{K}$ | 1279 | +- | 112 | 0.04 | 3.44 | $+/-0.30$ | 0.64 | $+/-0.06$ |
| $\boldsymbol{C d} \boldsymbol{L}$ | 1100 | +- | 166 | 0.01 | 0.82 | $+/-0.12$ | 0.10 | $+/-0.01$ |
| Total |  |  |  |  | 100.00 |  | 100.00 |  |

Full scale counts: 911


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: $\operatorname{gacd}(6)$

| Element <br> Line | Net <br> Counts | Net Counts <br> Error | K-Ratio | Weight \% | Weight \% <br> Error | Atom \% | Atom \% <br> Error |  |
| :---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| $\boldsymbol{C} \boldsymbol{K}$ | 34961 | $+/-$ | 220 | 0.87 | 76.69 | $+/-0.48$ | 84.91 | $+/-0.53$ |
| $\boldsymbol{O} \boldsymbol{K}$ | 2112 | $+/-$ | 70 | 0.04 | 16.76 | $+/-0.56$ | 13.93 | $+/-0.46$ |
| $\boldsymbol{G a} \boldsymbol{K}$ | 1513 | $+/-$ | 119 | 0.07 | 5.25 | $+/-0.41$ | 1.00 | $+/-0.08$ |
| $\boldsymbol{C d} \boldsymbol{L}$ | 1328 | $+/-165$ | 0.02 | 1.29 | $+/-0.16$ | 0.15 | $+/-0.02$ |  |
| Total |  |  |  |  | 100.00 |  | 100.00 |  |

