Supplementary Material (ESI) for Chemical Communications

Supplementary Information: Enhanced control over metal composition in mixed Ga/Zn and Ga/Cu coordinated pyrogallol[4]arene nanocapsules

Synthesis of PgC4 Ga-MONC, 1

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).

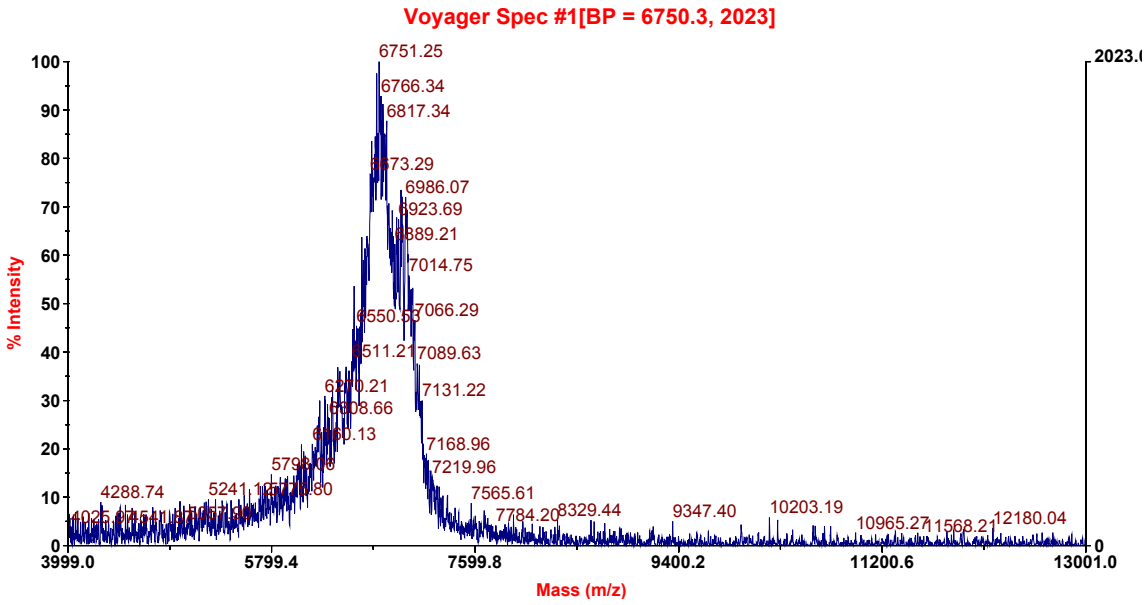
^{1}H NMR (500MHz, CD_3CN): δ = 0.98 (m, 72H, -CH_3); 1.40 (m, 96H, β-CH_2, γ-CH_2); 2.26 (m, 48H, α-CH_2, encapsulated water/acetone); 4.36 (m, 24H, -CH); 6.79, 6.82, 6.91, 6.95 (m, 24H, Ar), 7.38, 7.76, 8.33 (brs, partial OH); 1H NMR of 1 (CD_3CN + D_2O): the peaks at δ = 7.38, 7.76, 8.33ppm disappear.
^{13}C NMR (500MHz, [D_6]acetone): δ = 14.52 (s, -CH_3), 23.32 (m, γ -CH_2), 23.72 (m, β -CH_2), 31.56 (m, α-CH_2), 35.87 (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/Zn-MONC (14 Ga + 10 Zn), 2

Ethanolic zinc (II) nitrate (excess) was added to an acetone solution of **1** (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 (105 mg, 80% yield based on dried **1**).

Theoretical molecular mass:
Basic skeleton (6 PgC4 + 14 Ga +10 Zn): 6224g/mol
Basic skeleton + 48 metal ligand water: 7088g/mol

Experimental Molecular Mass:
MALDI-TOF shows there to be a mass range of ~ 6000 - 7200 Da, with two sharp peaks at 6751 (equal to basic skeleton plus 30 metal ligand water) and 6986 (equal to basic skeleton plus 42 metal aquo ligands) Da, respectively. The reason for this broad mass range may be because of varied levels of encapsulation of solvent molecules / metal ligation of water molecules.



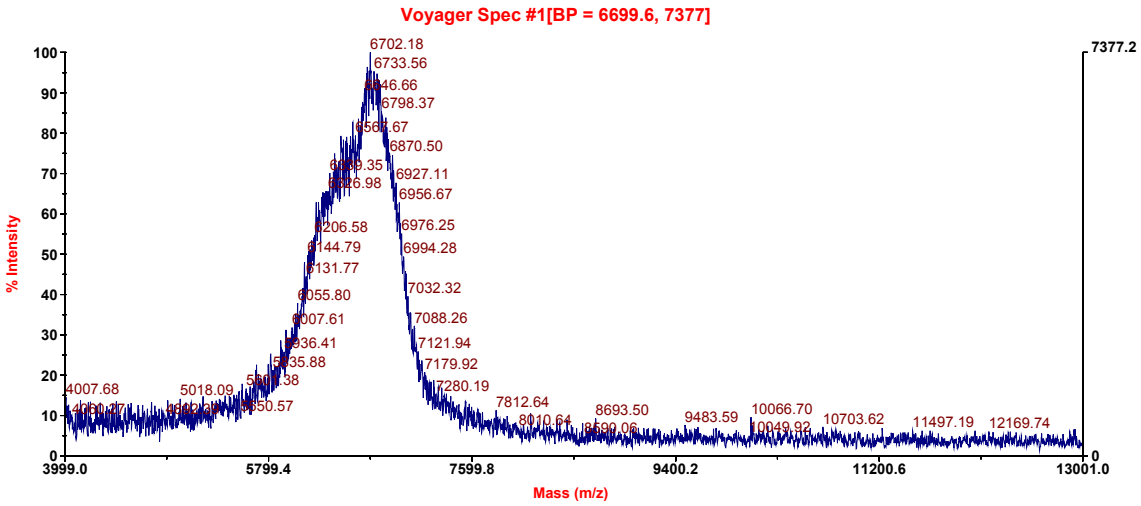
^{1}H NMR (500MHz, CD_3CN): δ = -1.75 (brs, -CH_3 of encapsulated ethanol); -0.25 (brs, encapsulated acetone); 1.00 (m, 72H, -CH_3 containing –CH_2 of encapsulated ethanol); 1.39, 1.48 (m, 96H, β-CH_2, γ-CH_2); 2.36 (m, 48H, α-CH_2); 4.31(m, 24H, -CH); 6.70, 6.78, 6.87, 6.92 (m, 10OH + 24ArH).
^{13}C NMR (500MHz, CD_3CN): δ = 14.41 (s, -CH_3), 23.19 (m, γ -CH_2), 23.56 (m, β -CH_2), 31.32 (m, α-CH_2), 36.37 (s, -CH), 109.46, 113.80 (m, ArH), 123.42, 126.77, 129.00, 134.08, 138.27, 143.46 (m, Ar)

Synthesis of PgC4 Ga/Cu-MONC (13 Ga + 11 Cu), 3

A methanolic solution containing a vast excess of copper (II) nitrate hemi-pentahydrate was added to an acetone solution of **2** resulting in a colour change from colourless to dark red. Upon slow evaporation, single red crystals suitable for synchrotron diffraction studies formed.

Theoretical molecular mass:
Basic skeleton (6 PgC4 + 13 Ga +10 Cu): 6220g/mol
Basic skeleton + 48 metal ligand water: 7084g/mol

Experimental Molecular Mass:
MALDI-TOF MS also shows a mass range of ~ 5800 - 7200 Da, with one sharp peak at 6702 Da (equal to basic skeleton plus 27 metal aquo ligands). Again this broad mass range may be due to varied levels of solvent encapsulation / metal ligation of water molecules.



Crystallography

Single crystal X-ray data for **1** were collected on a Bruker APEX II CCD system using synchrotron radiation with a wavelength of 0.6907 Å. Single crystal X-ray data for **2** and **3** were collected on a Bruker APEX II CCD system using synchrotron radiation with a wavelength of 0.7749 Å. Absorption corrections in all cases were performed using SADABS (Bruker, 2004). Structure solution and refinement of **1** – **3** were performed using the SHELX-97 software package. The routine SQUEEZE was applied to the datasets for **1**-**3** in order to remove diffuse electron density attributable to badly disordered solvent.[1] Crystals of **1** were extremely solvent dependent and required the use of a microscope stage cooling device during crystal mounting to prevent solvent loss upon removal of crystals from the mother liquor.

Supplementary references

1. A. L. Spek, *Acta Cryst. A46* 1990, C34.