Supporting Information

Ion Transport to the Interior of Metal-Organic Pyrogallol[4]arene Nano-Capsules.

Ping Jin,[†] Scott J. Dalgarno,*[₸] Charles Barnes,[†] Simon J. Teat,[Ж] Jerry L. Atwood[†,*]

[†] *Department of Chemistry, University of Missouri-Columbia, MO 65211, USA.*

[₸] *School of Engineering and Physical Sciences-Chemistry, Heriot-Watt University, Edinburgh, EH14 4AS, UK.*

[Ж] *Advanced Light Source, Berkeley Lab, 1 Cyclotron Rd., MS6R2100, Berkeley, CA 94720, USA.*

E-mail: S.J.Dalgarno@hw.ac.uk, AtwoodJ@missouri.edu

General X-ray Information

X-ray data was collected on an Bruker SMART 1000 CCD diffractometer. CCDC ????? and ????? contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk]. As both structures contained large amounts of disorder, it was necessary to apply numerous restraints to bond lengths. These were applied most to disordered pyrogallol[4]arene alkyl chains and disordered solvent molecules.

CsOH within Ga-PgC4 MONC, approximate formula {[$Ga_{12}(PgC4)_6(H_2O)_{23.5}(CH_3OH)_{0.5}$<(($(Cs_{0.46}\cdot(H_2O)_{0.65})_2$)$(H_2O)_5(CH_3OH)_4$)]$\cdot 4H_2O$}:

C-Butylpyrogallol[4]arene (PgC4) and the corresponding Ga-MONC were synthesized according to literature procedures, the latter being from an initial 1.0mmol amount of PgC4. Upon completion of PgC4 Ga-MONC crystal growth over a number of days, the mother liquid was decanted, and in order to preserve the Ga-MONC in crystalline form. Note that crystals of the precursor are sensitive to solvent loss upon exposure to air. Acetone (3 mL) was added and resulted in crystal dissolution. Addition of 0.60 mmol/L $CsOH\cdot H_2O$ in methanol solution (4 mL), with standing and slow evaporation over several days resulted in the formation of single crystals. Given that the occupancy of Cs within the capsule is

also around 50 % (obtained by structure refinement), this demonstrates the concept of Cs transport to the interior of the assembly while maintaining the metal-organic nano-capsule assembly. **Crystal data:** $C_{134.5}H_{193}O_{55}Cs_{0.46}Ga_6$, M = 3169.35, Monoclinic, a = 23.8435(11), b = 29.5489(14), c = 27.5426(13) Å, β = 100.9320(10)°, U = 19053.0(15) Å^3, μ = 1.105 mm^{-1}, T = 100(2) K, space group $P2_1/n$, Z = 4, synchrotron radiation (λ = 0.77490 Å), Final GOF = 1.718, R_1 = 0.0834, 168150 reflections measured, 28263 unique (R_{int} = 0.0490) which were used in all calculations. The final $\omega R(F^2)$ was 0.2450 (all data). The routine SQUEEZE was applied to the data in order to remove very diffuse electron density associated with exo-capsule solvent molecules.[1]

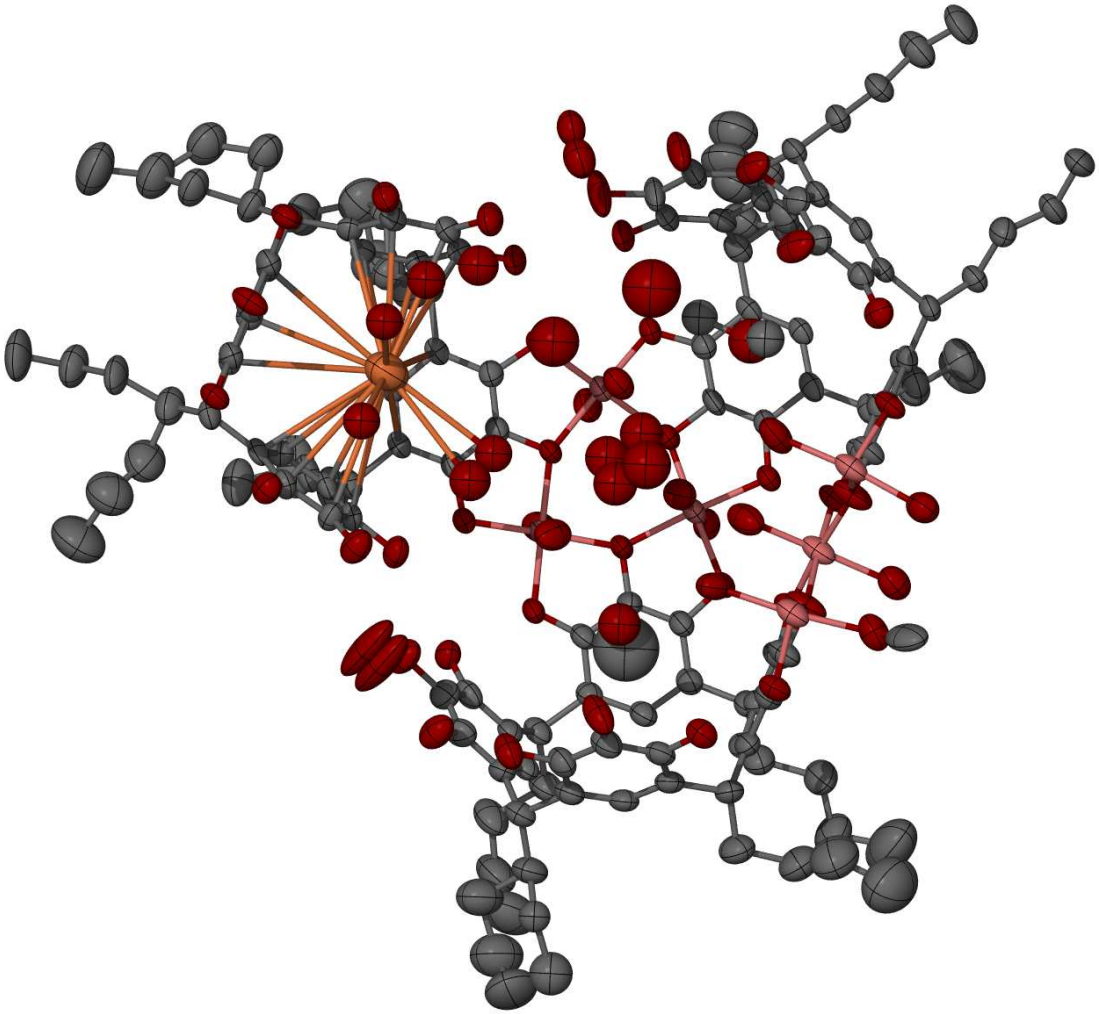

Figure S1. Thermal ellipsoid plot of the Cs/PgC4Ga metal organic nano-capsule showing Cs inclusion within the calixarene cavity.

$AgNO_3$ within Ga-PgC4 MONC, approximate formula {[$Ga_{12}(PgC4)_6(H_2O)_{24}$<(($AgNO_3$)($CH_3CN$)$_{1.5}$($H_2O$)$_3$($CH_3COCH_3$))]·5($CH_3CN$)·8.5($H_2O$)·8($CH_3COCH_3$)}:

C-Butylpyrogallol[4]arene (PgC4) and the corresponding Ga-MONC were synthesized according to literature procedures, the latter being from an initial 1.0mmol amount of PgC4. Upon completion of PgC4 Ga-MONC crystal growth over a number of days, the mother liquid was decanted, and in order to preserve the Ga-MONC in crystalline form. Note that crystals of the precursor are sensitive to solvent loss upon exposure to air. Acetone (3 mL) was added and resulted in crystal dissolution. Addition of 0.60 mmol/L $AgNO_3$ in acetonitrile solution (4 mL), with standing and slow evaporation over several days resulted in the formation of colourless single crystals. A yield was not obtained due to the step involving the removal of the mother liquor to preserve Ga-MONC formation. Given that the occupancy of Ag within the capsule is around 50% (obtained by structure refinement), this demonstrates the concept of Ag transport to the interior of the assembly while maintaining the metal-organic nano-capsule assembly. **Crystal data:** $C_{149.25}H_{217.75}N_{3.75}O_{59}Ga_6Ag_{0.5}$, M = 3480.78, triclinic, a = 21.960(4), b = 22.811(5), c = 24.091(5), α = 110.92(3), β = 106.34(3), γ = 107.66(3), Å, U = 9657(3) Å^3, μ = 1.203 mm^{-1}, T = 173(2) K, space group $P\bar{1}$, Z = 2, Mo-Kα radiation (λ = 0.71073 Å), Final GOF = 1.040, R_1 = 0.0845, 68759 reflections measured, 41525 unique (R_{int} = 0.0298) which were used in all calculations. The final $\omega R(F^2)$ was 0.26 (all data).

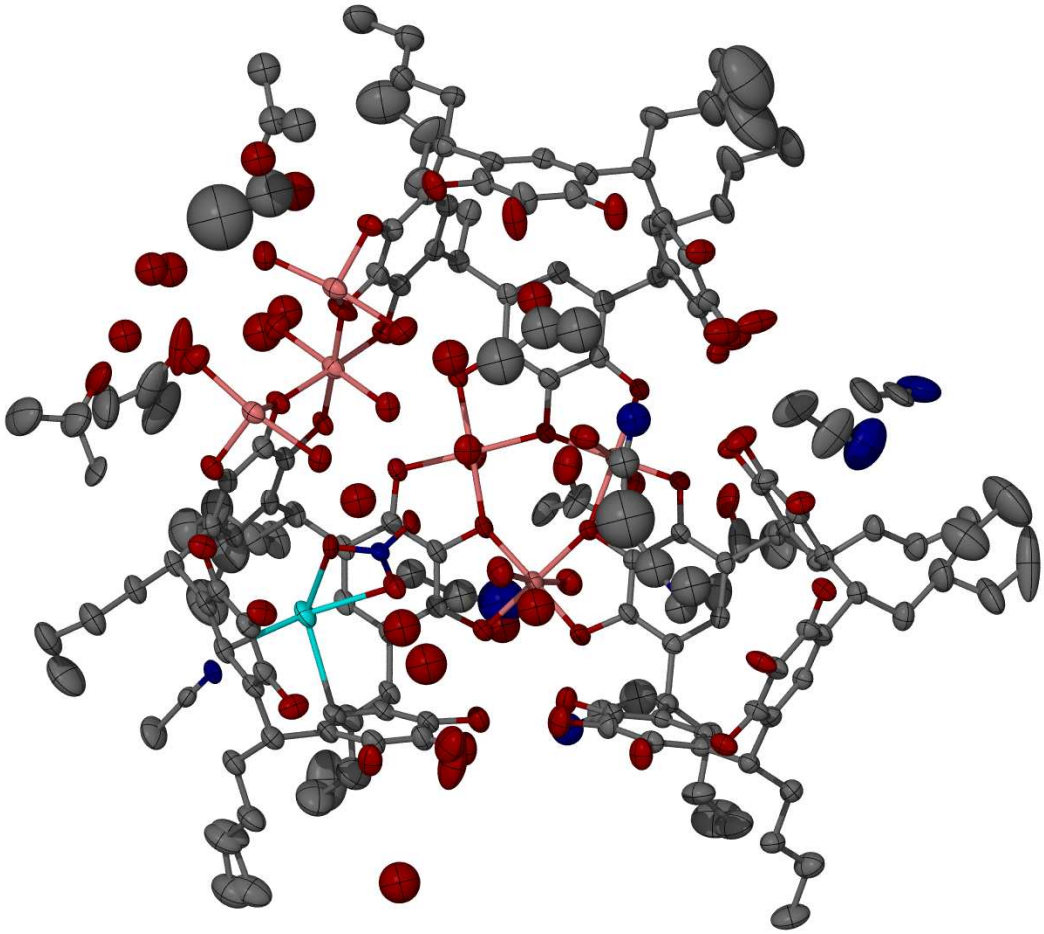

Figure S2. Thermal ellipsoid plot of the Ag/PgC4Ga metal organic nano-capsule showing $AgNO_3$ inclusion within the calixarene cavity.

References

1. Sluis, P. van der & Spek, A. L. (1990). Acta Cryst. A46, 194–201.