Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Novel magnesium-seamed organic nanocapsules with hierarchical structural complexity

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Materials and characterization. All solvents and chemicals were purchased from commercial sources and used without further purification. The single crystal X-ray diffraction (XRD) data was collected on a Bruker Apex II CCD diffractometer at 100 (2) K using CuKα (1.5406Å) radiation with Inco-tech Microfocus tube.

Synthesis of *C*-alkylpyrogallol[4]arene (PgC_n). *C*-Alkylpyrogallol[4]arene were synthesized according to literature procedures.[1, 2] Butyraldehyde (7.21 mL, 0.08 mol), and pyrogallol (0.08 mol, 10 g) were mixed in 40 mL of methanol followed by the addition of 3.5 mL of concentrated HCl. Thereafter, the mixture was refluxed at 110 °C for 24 hours. After cooling to room temperature, the precipitate was filtered, washed with cold methanol and dried in vacuum, resulting in 5.4 g of white solid, PgC_3 (38% yield). Pentanal, and 2,3-dihydrofuran were used for the synthesis of PgC_4 and PgC_3OH, respectively. The yield was 45% for PgC_4 and 35% for PgC_3OH.

Preparation of 1, $[Mg_{24}(PgC_3)_6(Pro)_6(DMF)_2(H_2O)_{30}]$. *C*-Propylpyrogallol[4]arene (PgC_3, 0.1 mmol, 72.0 mg), $Mg(NO_3)_2{\cdot}6H_2O$ (0.4 mmol, 102.6 mg) and L-proline (0.2 mmol, 23 mg) were dissolved in 1 mL of DMF and 1 mL of MeCN in a 4 mL glass vial. The mixture was sonicated for 5 minutes and then heated at 100 °C overnight. Blue crystals were formed and collected for single crystal X-ray analysis. The yield was 35% based on $Mg(NO_3)_2$. *Crystallographic data*: $C_{276}H_{282}Mg_{24}N_8O_{116}$, *M* = 6150.52, monoclinic, space group *C*2, *a* = 28.6297(8), *b* = 35.3408(10), *c* = 21.5450(6),

α = 90°, β = 119.007(2)°, γ = 90°, V = 19064.7(10) Å^3, T = 173(2) K, Z = 2, calculated density = 1.071 g/cm^3, θ range of data collection = 2.48° – 64.43°, 9060 total unique reflections, goodness of fit = 1.027, R1 after merging = 0.116, R(int) = 0.065, wR2 = 0.274, CCDD 1550207.

Preparation of 2, $[Mg_{24}(PgC_4)_6(Pro)_6(DMF)_4(H_2O)_{28}]$. *C*-Butylpyrogallol[4]arene (PgC_4, 0.1 mmol, 77.6 mg), $Mg(NO_3)_2{\cdot}6H_2O$ (0.4 mmol, 102.6 mg) and L-proline (0.2 mmol, 23 mg) were dissolved in 1 mL of DMF and 1 mL of MeCN in a 4 mL glass vial. The mixture was sonicated for 5 minutes and then heated at 100 °C overnight. Blue crystals were formed and collected for single crystal X-ray analysis. The yield was 38% based on $Mg(NO_3)_2$. *Crystallographic data*: $C_{306}H_{342}Mg_{24}N_{10}O_{116}$, M = 6599.32, monoclinic, space group $C2$, a = 28.261(6), b = 36.059(7), c = 21.798(4), α = 90°, β = 117.95(3) °, γ = 90°, V = 19623(8) Å^3, T = 173(2) K, Z = 2, calculated density = 1.117 g/cm^3, θ range of data collection = 2.45° – 65.10°, 9212 total unique reflections, goodness of fit = 1.77, R1 after merging = 0.1267, R(int) = 0.032, wR2 = 0.362, CCDD 1550206.

Preparation of 3, $[Mg_{24}(PgC_3OH)_6(Pro)_6(DMF)_2(H_2O)_{30}]$. *C*-Propan-3-olpyrogallol[4]arene (PgC_3OH, 0.1 mmol, 78.4 mg), $Mg(NO_3)_2{\cdot}6H_2O$ (0.4 mmol, 102.6 mg) and L-proline (0.2 mmol, 23 mg) were dissolved in 1 mL of DMF and 1 mL of MeCN in a 4 mL glass vial. The mixture was sonicated for 5 minutes and then heated at 100 °C overnight. Blue crystals were formed and collected for single crystal X-ray analysis. The yield was 40% based on

$Mg(NO_3)_2$. *Crystallographic data*: $C_{276}H_{258}Mg_{24}N_8O_{140}$, M = 6510.33, monoclinic, space group $C2$, a = 28.887(1), b = 35.560(1), c = 21.8751(9), α = 90°, β = 119.007(2)°, γ = 90°, V = 19655(1) Å^3, T = 173(2) K, Z = 2, calculated density = 1.100 g/cm^3, θ range of data collection = 2.31° – 69.95°, 9228 total unique reflections, goodness of fit = 1.478, $R1$ after merging = 0.139, R(int) = 0.054, w$R2$ = 0.357, CCDD 1550208.

Supplementary Data

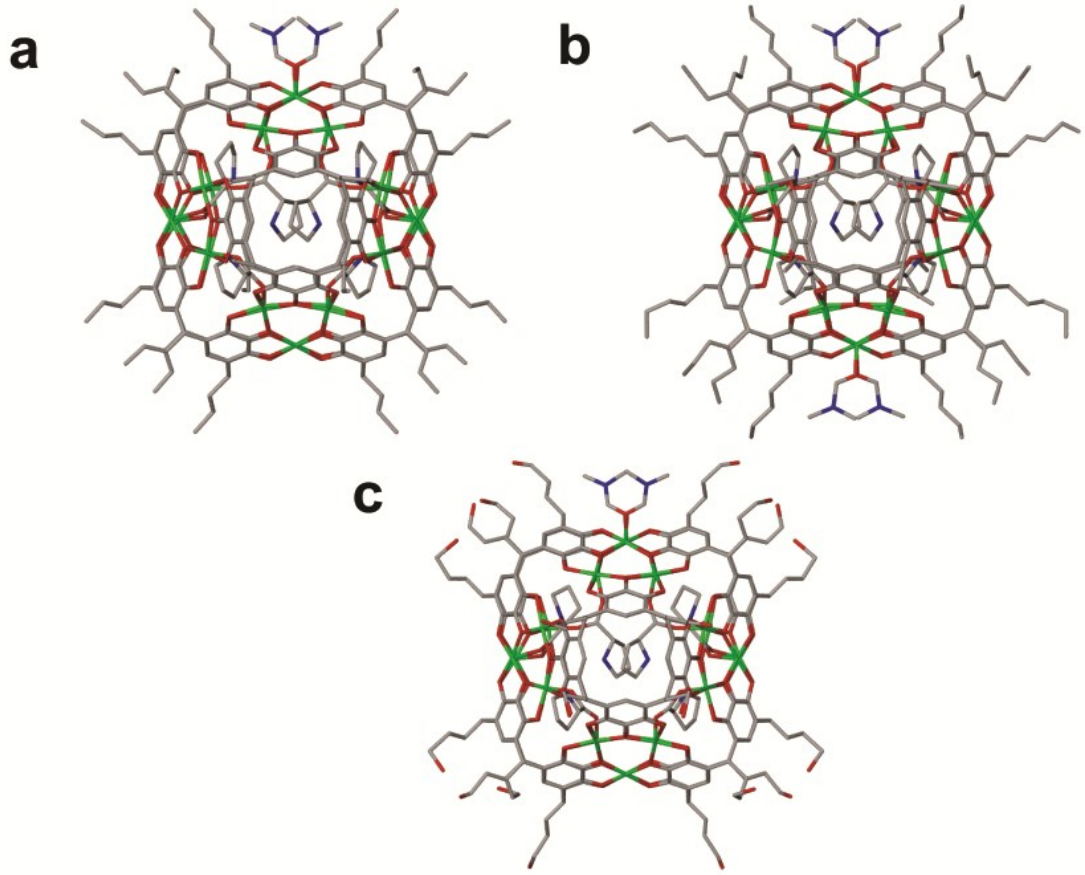

Figure S1 | Crystal structure of magnesium-seamed *C*-alkylpyrogallol[4]arene nanocapsule. Functionalized nanocapule **1**, **2**, and **3** are shown in (**a**) – (**c**). All the hydrogen atoms and axial water ligands have been omitted for clarity. Colour codes: carbon, grey; oxygen, red; nitrogen, blue; magnesium, green.

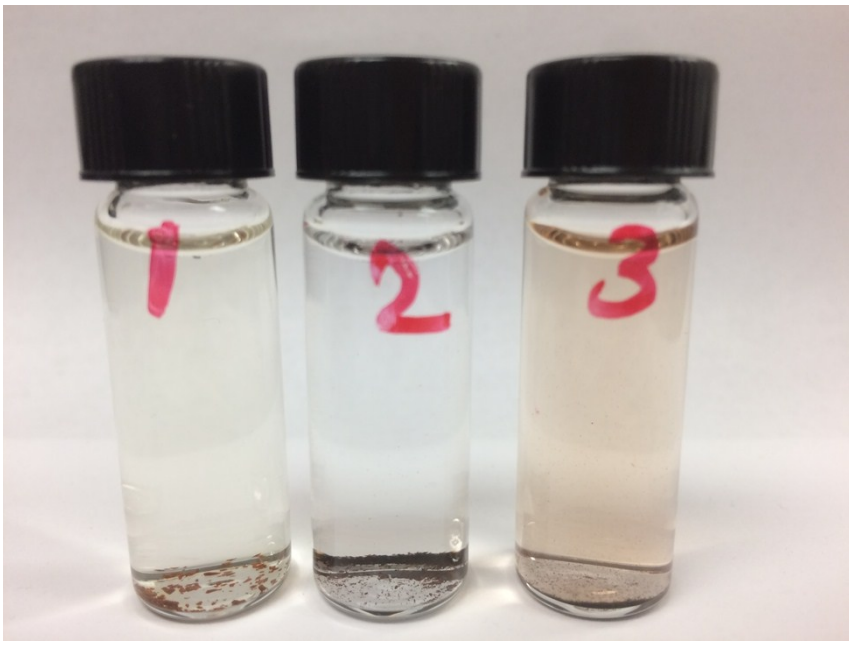

Figure S2 | Solubility test in water. The brown color of **3** indicates improved water solubility compared to **1** and **2**.

References:

1. C. Zhang, R. S. Patil, T. Li, C. L. Barnes, S. J. Teat and J. L. Atwood, *Chem. Eur. J.*, 2017, **23**, 8520-8524.
2. R. M. McKinlay, P. K. Thallapally, G. W. V. Cave and J. L. Atwood, *Angew. Chem. Int. Ed.*, 2005, **44**, 5733-5736.