Supporting Information

Hierarchical 2D honeycomb-like network from barium-seamed nanocapsules

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Materials and Methods

Materials

Pyrogallol (Chem-Impex, 22779), butyraldehyde (Sigma-Aldrich, 538191), concentrated hydrochloric acid (Fisher chemicals, A144S-212), barium bromide dihydrate (Fisher Laboratory Chemicals, B-27), pyridine 99+% (Acros organics, AC13178-0025) and methanol (Fisher chemicals, A452SK-4).

Synthesis of *C*-propylpyrogallol[4]arene, PgC$_3$

In a 100 mL round bottom flask containing magnetic stir bar, pyrogallol (10 g, 0.08 mol), butyraldehyde (7.21 ml, 0.08 mol), and 30 ml of methanol were taken sequentially. The reaction mixture was heated at 110 ºC in an oil bath and upon reflux, 3.5 mL of concentrated HCl was added. The reflux was continued for about 24 hours resulting in formation of solid suspension. The reaction mixture be cooled to room temperature and the product was filtered and washed with cold methanol followed by vacuum drying resulting in a solid white product (4.25 g, yield: 29.51 %).[1]

Synthesis of *C*-pentylpyrogallol[3]resorcinol[1]arene, mmC$_5$

In a 100 mL round bottom flask containing magnetic stir bar, pyrogallol (5 g, 0.04 mol), resorcinol (4.4 g, 0.04 mol), 30 mL of methanol, and hexanal (7.21 mL, 0.08 mol) were taken sequentially. The reaction mixture was heated at 110 ºC in an oil bath and upon reflux, 3.5 mL of concentrated HCl was added. The reflux was continued for about 24 hours resulting in formation of solid suspension. The reaction mixture be cooled to room temperature and the product was filtered and washed with cold methanol followed by vacuum drying resulting in a solid white

product (5.0 g, yield: 45.90 %).[2] The resulting white product was used directly for crystallization experiments without further purification.[3]

Preparation of a 2D-honeycomb like coordination network 2 [Ba$_{16}$(PgC$_3$)$_{12}$(OH$_2$)$_{16}$(DMF)$_{21}$]

PgC$_3$ (0.1 mmol, 72.0 mg) and barium bromide (dihydrate, 0.4 mmol, 133.3 mg) were dissolved in 1:1 DMF:methanol mixture (2 mL each) taken in an 8 mL glass vial. The solution was sonicated for 90 minutes. Later, pyridine (1.2 mmol, 97μl) was added, and the resulting solution mixture was heated to 120 °C for 24 hours and red colored plate-like crystals were formed and collected for single crystal X-ray analysis. The yield was found to be 0.071 g or 31.00% based on barium bromide.

Preparation of Coordination network 4

mmC$_5$ (0.1 mmol, 81.7 mg) and barium bromide (dihydrate, 0.4 mmol, 133.3 mg) were dissolved in 1:1 DMF:ethanol mixture (2 mL each) taken in an 8 mL glass vial. The solution was sonicated for 90 minutes. Later, pyridine (1.2 mmol, 97μl) was added and the resulting solution mixture was heated to 120°C for 96 hours and later, left for 24 h at room temperature until red colored plate-like crystals were formed and these are then collected for single crystal X-ray analysis. The yield was found to be 0.020 g.

Single crystal X-ray diffraction (SCXRD) and crystal structure refinement

The SCXRD data were measured on a Bruker SMART Diffractometer equipped with an APEX II CCD area detector and a D8 3-circle goniometer (Bruker AXS, Madison, WI, USA) using Mo-Kα radiation from a sealed source with focusing optics. The crystals were mounted on Kapton loops with heavy hydrocarbon oil and cooled to the collection temperatures under a stream of cold N$_2$ gas using a Cryostream 700 cryostat (Oxford Cryosystems, Oxford, UK). A hemisphere of

unique data was collected out to 0.80 Å using strategies of scans about the omega and phi axes. The Bruker Apex3 software suite was used for unit cell determination, data collection, data reduction, absorption correction and scaling, and space group determination.[4]

Data for **2** was truncated to 1.00 Å during integration (R_{int} for the 1.01-1.00 Å shell was 83% and the average I/σ is 2.16). The crystal structure was solved by an iterative dual space method as implemented in SHELXT,[5] and the structure were refined by full-matrix least squares refinement against $|F^2|$ using SHELXL,[6] implemented within Olex[2] as an interface for model-building. Two of the unique Ba atoms refined with anomalously large thermal ellipsoids and with unusually large nearby difference map peaks. When these were refined as a barium atom disordered over two positions, a set of difference map peaks consistent with a unique, endocyclic DMF ligand emerged from the difference map. This confirmed that all sites were occupied by Ba atoms and that the Ba atoms could be either exocyclic with respect to the capsule, coordinating to ligands protruding from the capsule, or endocyclic and coordinating to ligands inside the capsule. Additional peaks appeared collinear with the pairs of Ba atoms along what would be 3-fold axes of symmetry for an ideal, isolated capsule; these were not in chemically reasonable positions and are attributed to unmodeled twin domains where crystallographic 3-fold axes do point in those directions. The two disordered Ba atoms had their occupancies refined separately with the sums of both positions constrained to 100%. For Ba2 the major position refined to 64.8(9)% and for Ba3 it refined to 64.9(8)%.

For Ba3, the disordered Ba atom not residing on a 3-fold axis, the entire coordination sphere could not be located from the difference map. One coordinating atom, modeled as a water ligand, and several peaks possibly corresponding to overlapping positions of disordered DMF ligands could be located from the difference map. The occupancies of these were constrained to

be equal to that of the major occupancy Ba atom. The minor occupancy ligands were not located, and in the calculation of the formula these ligands were assumed to have 100% total occupancy.

Two of the propyl tails of the PgC_3 ligands were found to be disordered over two conformations; in both cases the disordered atoms were the terminal two carbon atoms of the chain and could be refined with reasonably similar thermal parameters with their occupancies constrained to be 50% each. One of the DMF ligands bonded to Ba1 was found to be disordered by symmetry over two positions and had its occupancy constrained to 50%. Some of these half occupancy light atoms could not refine to convergence anisotropically and were constrained to have isotropic thermal motion. All other atoms were refined with anisotropic thermal parameters using restraints for rigid bond behavior. A correction for the contribution of disordered matter located in solvent-accessible void volume was applied using PLATON SQUEEZE,[7] which found 7,764 e⁻/unit cell disordered across a volume of 28,858 $Å^3$. The disordered matter has been tentatively assigned to 23 H_2O molecules and 26.5 DMF molecules per capsule, in agreement with both the electron count and the two-step mass loss observe in the TGA which suggests *ca.* 3 weight percent H_2O (Fig. S6).

Hydrogen atoms were placed in calculated positions and constrained to ride on the carrier atoms. For full occupancy methyl atoms, the methyl group hydrogen atoms were allowed to rotate about the C–C bond axis, while for partial occupancy atoms they were constrained to an ideal staggered geometry.

The attempted refinement of **4** produced a partial solution but due to generally weaker diffraction data quality it became clear that only the Ba atoms could be resolved at the atomic level. Its assignment as an isomorphous structure is based on the similarities of the unit cell and space groups as well their similar powder diffraction patterns.

Thermogravimetric analysis (TGA)

TGA was conducted with a TA Instruments TGA Q50 under a nitrogen atmosphere (40 mL min^{-1}) with platinum pan, scanning from room temperature to 500 ºC at a heating rate of 20 ºC min^{-1}.

Transmission Fourier-transform infrared (FTIR) spectroscopy

FTIR spectroscopy was performed using a Thermo Scientific Nicolet Summit Pro FTIR spectrometer with potassium bromide (KBr) pellets, averaging 24 scans with a resolution of 4 cm-^{1}.

Scanning electron microscope (SEM)–Energy-dispersive X-ray spectroscopy (EDS)

SEM-EDS was performed using an FEI Quanta 600F Environmental Scanning Electron Microscope equipped with a Bruker Quantax 200 silicon drift detector at 10 kV. Powdered samples were mounted directly onto carbon adhesive and analyzed using low-vacuum mode to mitigate charging. Backscatter and secondary electron images were collected to generate chemical phase and topographical contrast, respectively. EDS spectra were collected from representative particles to perform quantitative analysis.
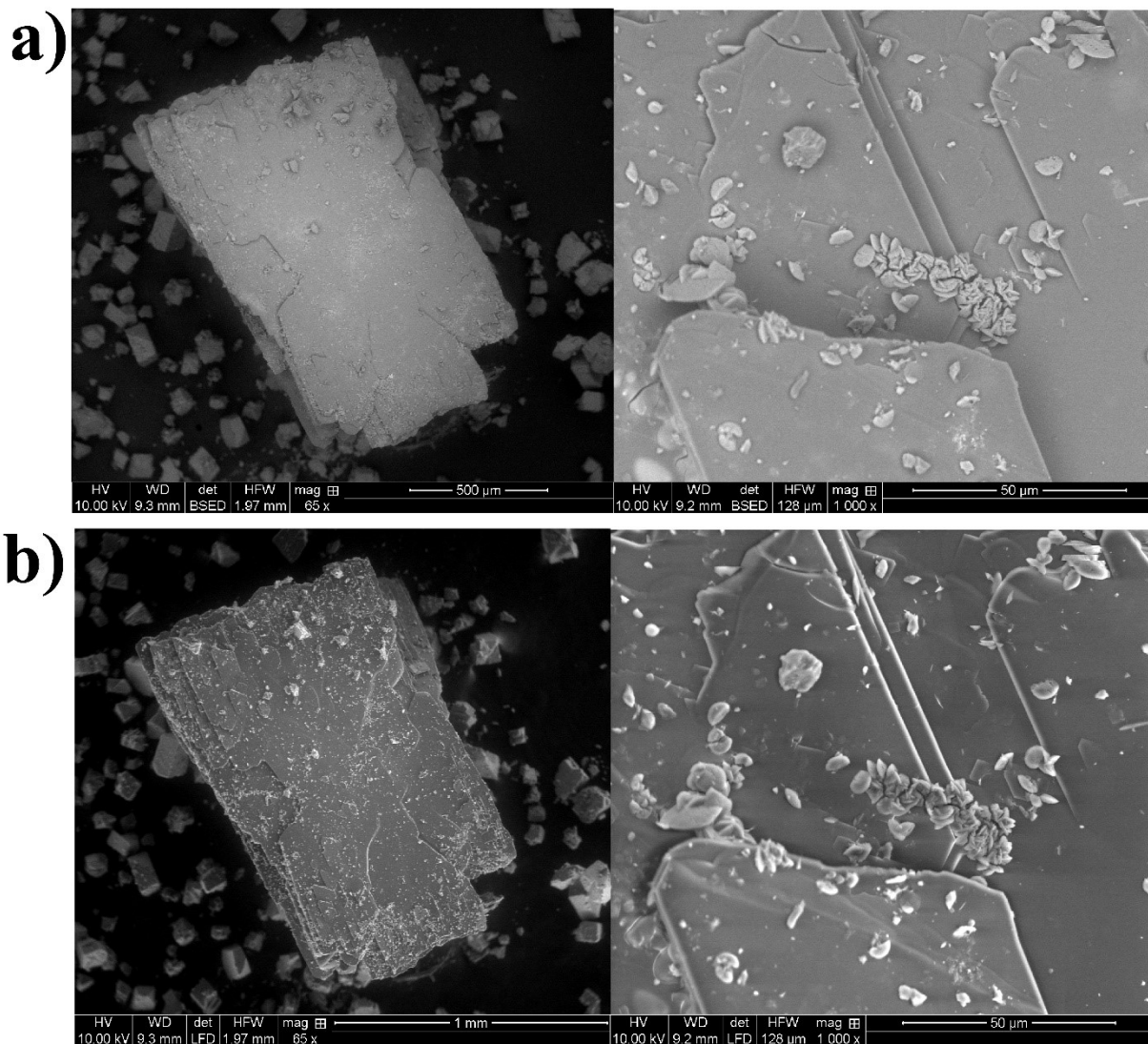
Fig. S1 SEM images of crystals of the coordination network **2**. a) background electron image and b) secondary electron image of the crystal.
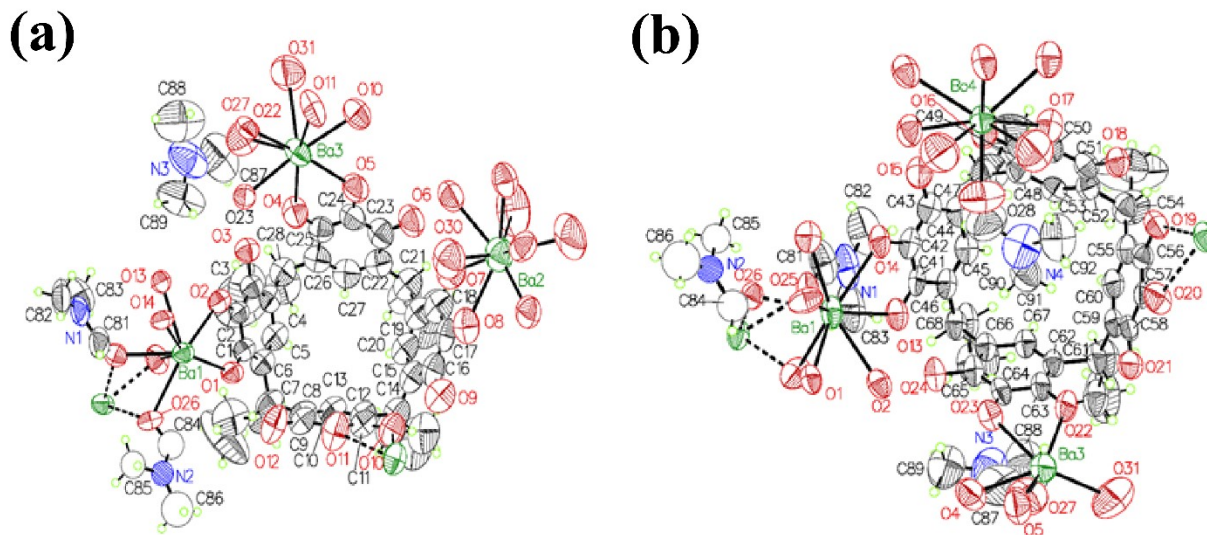
Fig. S2 50% probability ellipsoid plot of the two unique PgC$_3$ ligands in the coordination network **2**. (a) C1–C40 and (b) C41–C80 with all bonded Ba atoms. Dashed lines indicate extension of coordination network. Propyl carbon atom labels (C29–C40 and C69-C80) are omitted for clarity, all other unlabeled atoms are symmetry equivalents of labeled atoms. Isotropic atoms are drawn as circles. Color codes: barium (green), carbon (black), hydrogen (green circles), oxygen (red), and nitrogen (blue).
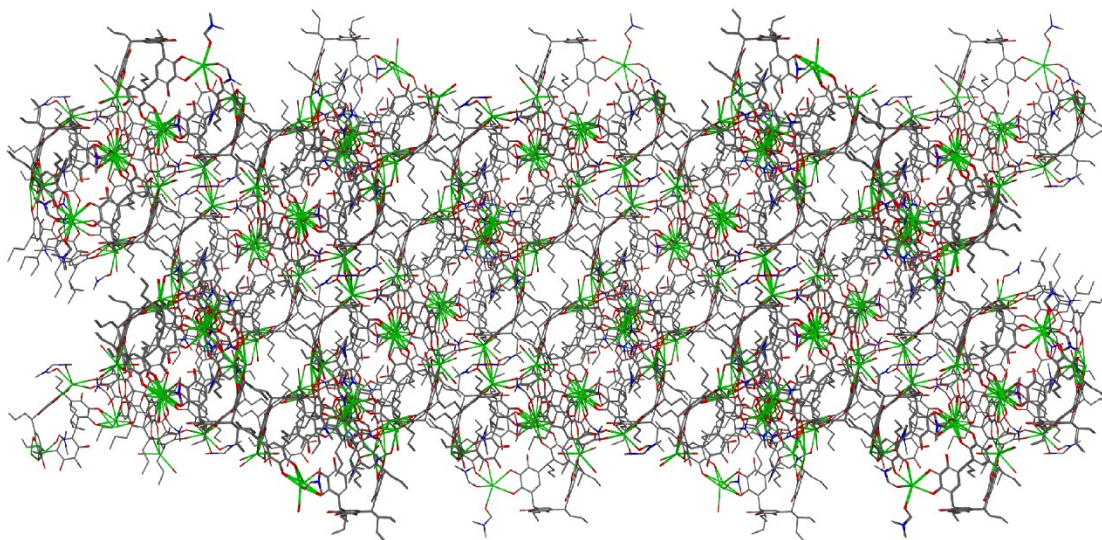
Fig. S3 Packing plot of **2**. Color codes: barium (green), carbon (gray), nitrogen (blue), and oxygen (red). Hydrogen atoms are omitted for clarity.

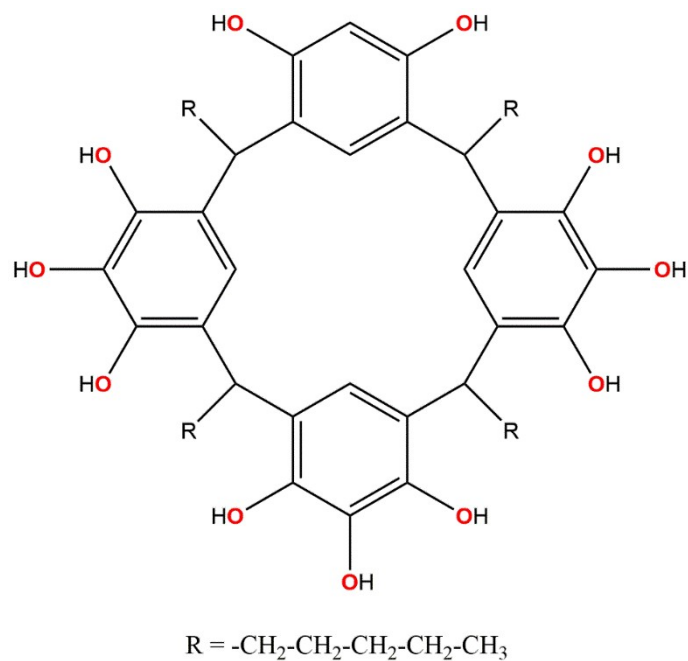

$R = -CH_2-CH_2-CH_2-CH_2-CH_3$

Fig. S4 Structural representation of the ligand *C*-pentylpyrogallol[3]resorcin[1]arene macrocycle (mmC$_5$) **3**.
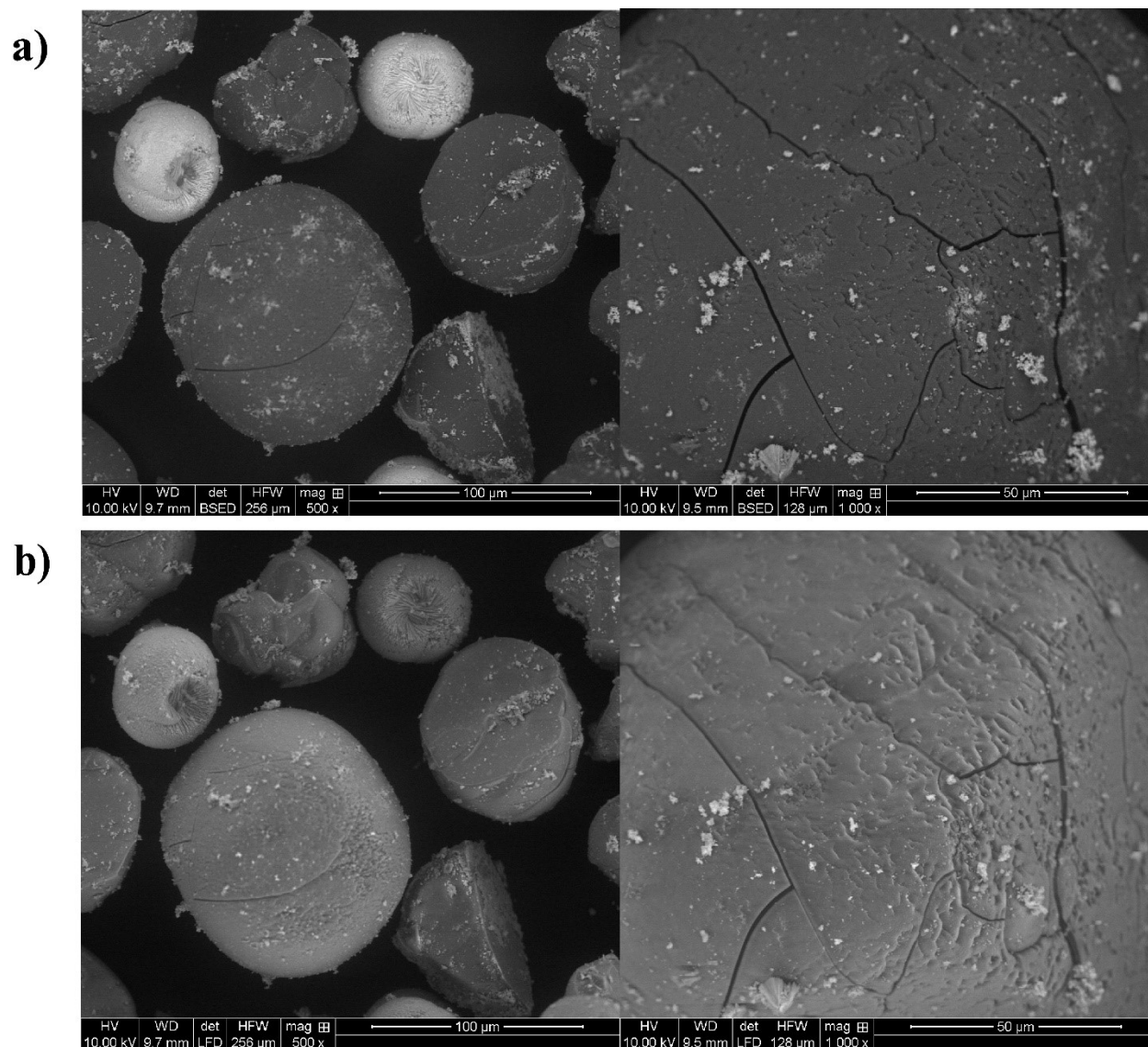
a)

b)

Fig. S5 SEM images of crystals of Framework **4**. a) background electron image and b) Secondary electron image of the crystal.

Thermogravimetric Analysis (TGA): TGA of **2** shows a slow mass loss event with an approximate T_{onset} of 108 °C leading into a second, more rapid event with a T_{onset} of 158 °C. These values are close to the boiling points of liquid H_2O and dimethylformamide, respectively. These events combine to a total mass loss of 5.0%, which is far smaller than the total estimated mass of the disordered solvent (32.35 DMF molecules corresponding to 16.65% of the total mass). While the largest voids in the crystal structure are isolated (either by being included in the structure or being blocked by the positioning of the adjacent honeycomb sheets), a small fraction of the void volume does form continuous channels parallel to the *ab* face diagonals. These first two mass loss events most likely correspond to the evaporation of relatively unbound H_2O and DMF molecules which escape through these channels. Following these events, a third step occurs with $T_{onset} = 183$ °C which overlaps with multiple other mass loss events at higher temperatures. These are most likely the simulatenous thermal decomposition of the framework itself and release of solvent of crystallization trapped in isolated voids. The temperature range of these later decomposition steps overlaps with the known decomposition temperature of metal-free pyrogallol[4]arene crystalline hydrates.[8]

TGA of **4** shows mass loss beginning at room temperature and proceeding to *ca.* 10 weight percent before overlapping with further mass loss events beginning around 200 °C. Similar thermal profiles have been observed in crystalline Mg_{24} pyrogallol[4]arene hexamers.[9] The greater interlayer spacing implied by the longer *c* axis in **4** likely results in larger surface-accessible solvent channels and possibly the inclusion of a wider range of solvent species in the crystal, both of which account for more rapid mass loss compared to **2**.
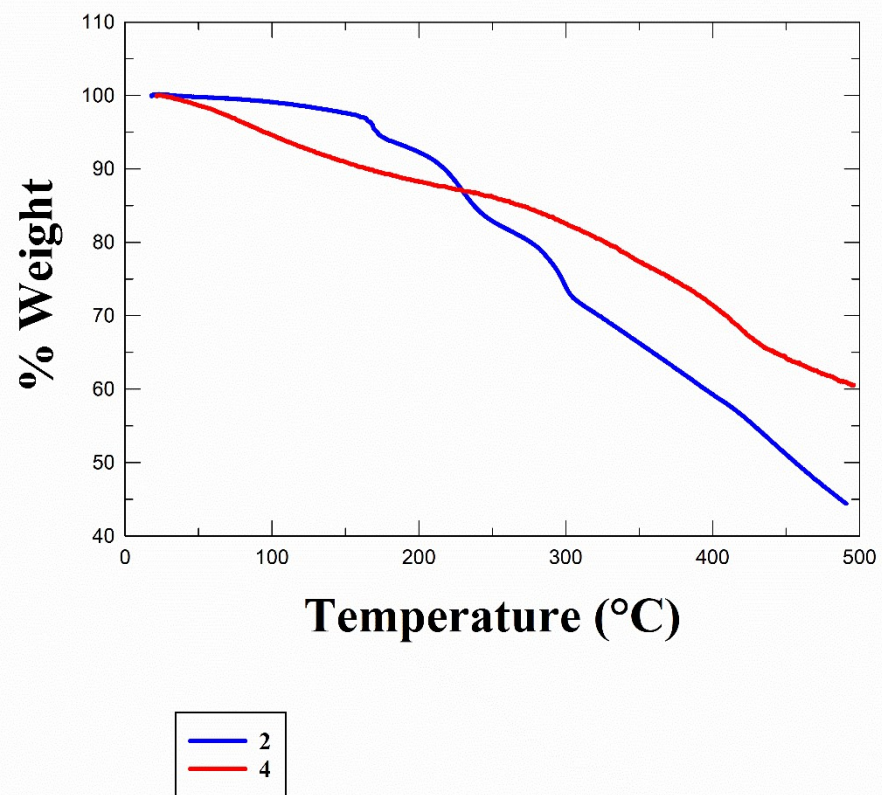
Fig. S6 TGA thermogram of the coordination networks **2** and **4.**
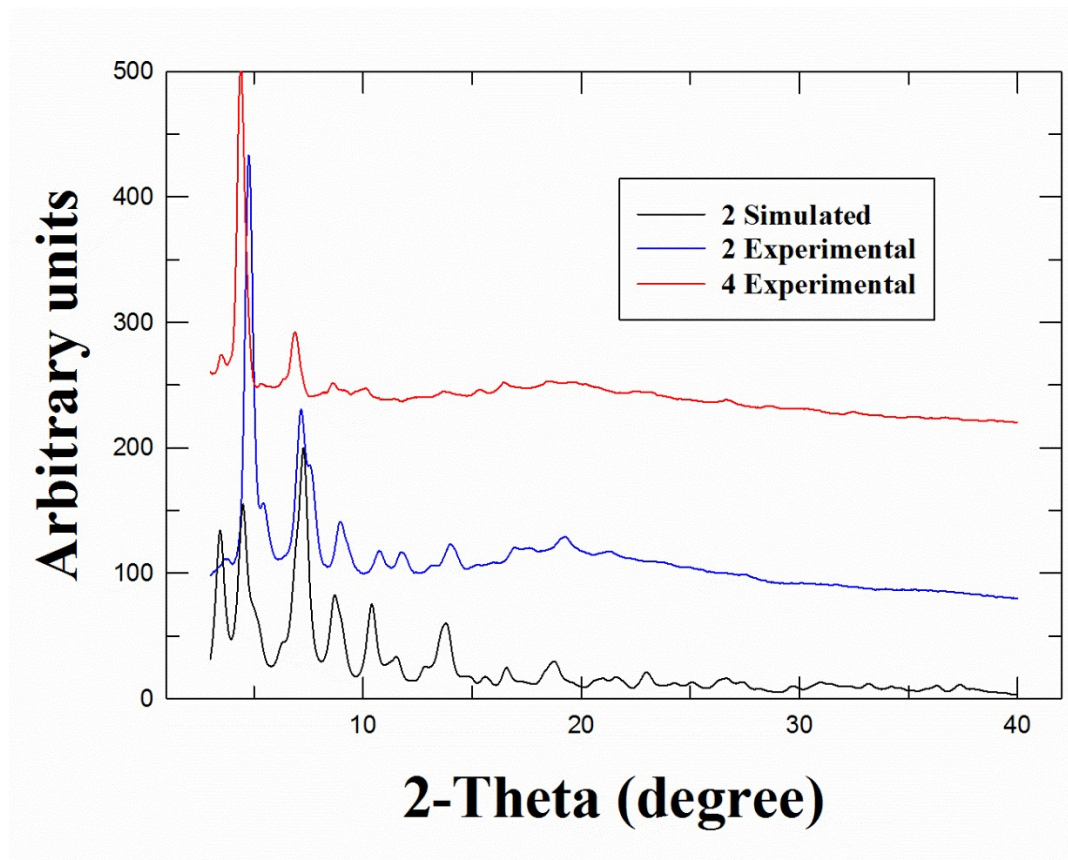
Fig. S7 PXRD of the coordination networks **2** and **4**.
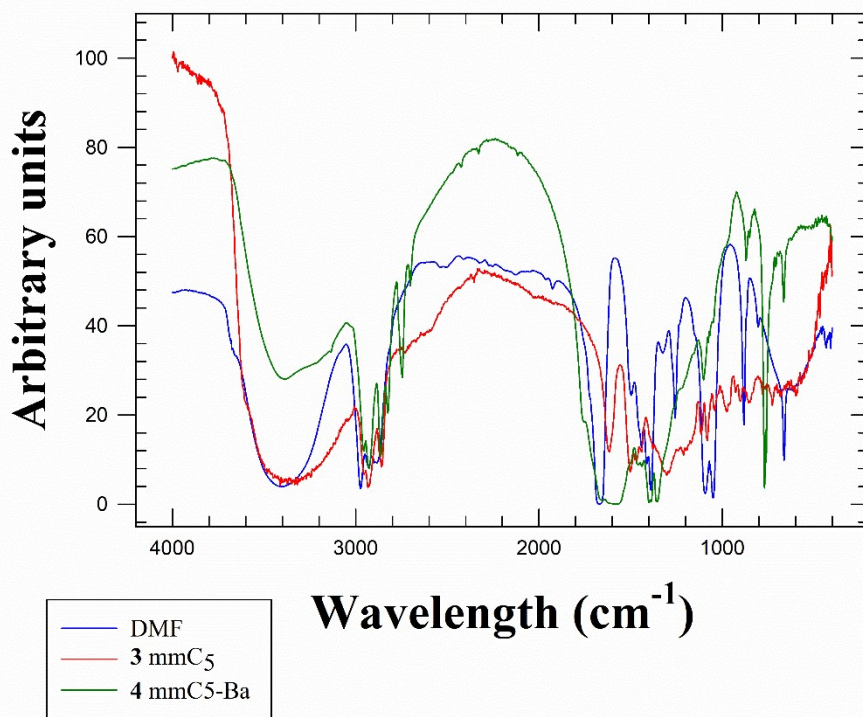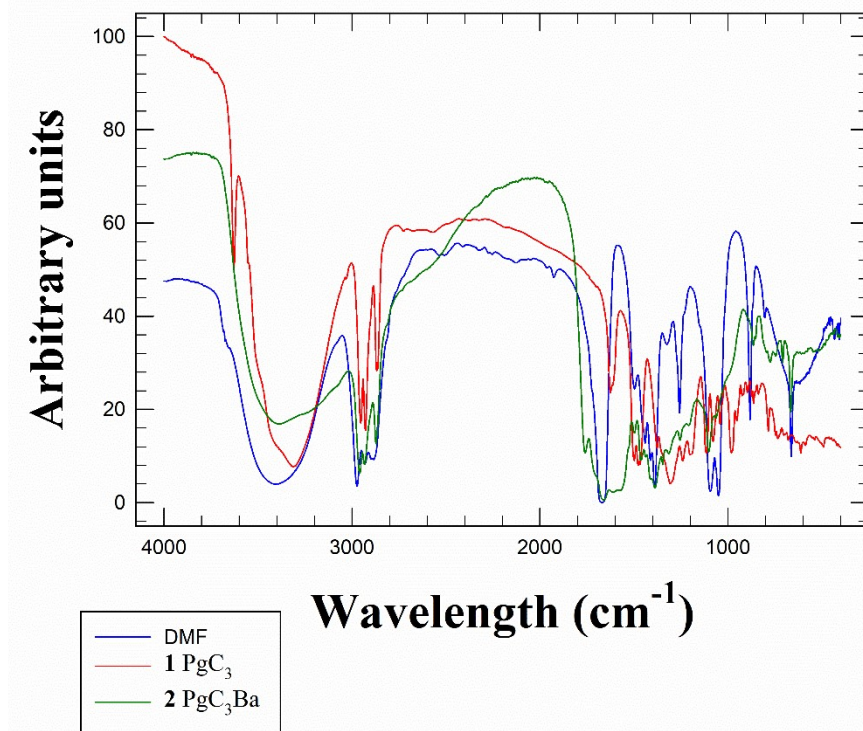
Fig. S8 FTIR of Framework **2** (top) and **4** (bottom) along with the DMF and the ligands.

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (3 sigma)	rel. error [%] (3 sigma)
Carbon	6	2494512	57.76	57.76	71.79	6.13	10.60
Nitrogen	7	39910	3.76	3.76	4.01	0.61	16.30
Oxygen	8	612857	24.22	24.22	22.60	3.09	12.75
Barium	56	167066	13.65	13.65	1.48	1.10	8.05
Bromine	35	19749	0.57	0.57	0.11	0.12	21.13
Silicon	14	2576	0.04	0.04	0.02	0.00	7.78
		Sum	100.00	100.00	100.00		

Fig. S9 SEM-EDS of **2**.

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (3 sigma)	rel. error [%] (3 sigma)
Carbon	6	2323820	57.48	57.48	73.55	6.13	10.66
Nitrogen	7	32406	3.31	3.31	3.63	0.55	16.54
Oxygen	8	510754	21.58	21.58	20.73	2.75	12.74
Silicon	14	2451	0.04	0.04	0.02	0.00	7.82
Bromine	35	22840	0.71	0.71	0.14	0.13	18.63
Barium	56	192985	16.78	16.78	1.88	1.33	7.95
Chlorine	17	1122	0.02	0.02	0.01	0.00	7.53
Sulfur	16	4017	0.07	0.07	0.04	0.08	108.07
		Sum	100.00	100.00	100.00		

Fig. S10 SEM-EDS of **4**.

Table S1. Crystallographic Information

Crystal Structure	2
CCDC Number	2267032
Empirical formula	$C_{542}H_{719}Ba_{16}N_{21}O_{131}$
Formula weight (g/mol)	11821.78
Temperature (K)	150.0 K
Wavelength (Å)	0.71073 Å
Crystal system	Trigonal
Space group	R-3c
a (Å)	33.701(4)
b (Å)	33.701(4)
c (Å)	106.519(12)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	104770(25)
Z	6
Calculated density (Mg/m^3)	1.124
Absorption Coefficient (mm^{-1})	0.949
F (000)	36372
Crystal Size (mm^3)	0.28 x 0.2 x 0.12
Θ range of data collection(°)	1.035 to 20.923
Index ranges	$-33<=h<=33$ $-33<=k<=33$ $-106<=l<=106$
Reflections collected	255726
Independent reflections	12371
Completeness to Theta= 67.679°	99.8
Absorption Correction	Semi-empirical from

	equivalents
Max. to min. transmission	0.7446–0.6083
Refinement Method	Full-matrix least squares on F^2
Data / restraints / parameters	12371 / 1727 / 1187
Goodness of fit	1.079
Final R Indices [I>2sigma(I)]	$R1 = 0.1348$ $wR2 = 0.3178$
R indices (all data)	$R1 = 0.2112$ $wR2 = 0.3906$
Extinction Coefficient	n/a
Largest diff. peak and hole	3.142 and –0.795 e.Å^{-3}

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