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Bis-Calix[4]arenes: From Ligand Design to the Directed Assembly of a Metal-Organic Trigonal Antiprism**

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Abstract: Calix[4]arenes (C[4]s) are versatile platforms for the construction of polymetallic clusters containing paramagnetic metal ions. Synthetic modification at the C[4] methylene bridge allows for the design of bis-C[4]s that, depending on the linker employed, can be used to either dictate which clusters can be formed or direct the assembly of a new metal-organic polyhedron (MOP). The assembly resulting from the latter approach displays thermal stability and uptake of N₂ or H₂ gas, confirming that this is viable route to the synthesis of new, functional supramolecular architectures.

The assembly of synthetically challenging metallosupramolecular systems is a rapidly expanding area of chemistry that continues to attract strong interest. This activity stems partly from the chemist's desire to understand the self-assembly of complex multi-component architectures,^[1] but also from the fact that the resulting assemblies can be discrete^[1] or polymeric^[2] in nature, possessing targeted physical properties^[3] or finding utility in a wide variety of areas such as catalysis,^[4] controlled guest uptake / release^[5] and novel crystallization media.^[6] Strategies for directed assembly typically rely on the use of both coordination templates and ligand design,^[7] the latter being the general focus of this contribution.

Calix[4]arenes (C[4]s) have featured prominently in supramolecular chemistry due to their conformational versatility, related topological directionality and ease of synthetic modification / functionalisation.^[8] In the cone conformation these versatile hosts possess cavities that are accessible to a range of suitably sized neutral or charged guests. We (amongst others) recently exploited the lower-rim polyphenolic character of methylene-bridged C[4]s in mapping out their transition (TM), lanthanide (Ln) metal and 3d-4f cluster-forming chemistry.^[9] In doing so we have reported a wide range of new clusters that are typically polygonal in nature, and can themselves be considered as building blocks; examples would be the [Mn^{III}₂Mn^{II}₂(C[4])₂]

and [Mn^{III}₄Ln^{III}₄(C[4])₄] cluster cores in Figures 1A and 1B respectively.^[9b,c] Analysis of our library of cluster types and conditions employed has allowed us to establish empirical C[4] metal ion binding rules that depend solely on the combination of metal ions present. An excellent example of this is the persistent incorporation of the [TM(C[4])] moiety within all 3d-4f clusters, as can be seen by comparing Figures 1A and 1B.^[9b,c]

We recently expanded our cluster forming chemistry with C[4] to focus on bis-C[4], a building block comprising two C[4]s linked directly *via* a methylene bridge. In doing so we found that when the constituent C[4] cavities are proximal the molecule behaves closely to how one would expect with respect to cluster formation.^[10] To illustrate this, the analogous reaction used to form the [Mn^{III}₂Mn^{II}₂(C[4])₂] cluster^[9b] (Fig. 1A) affords a new [Mn^{III}₄Mn^{II}₄(bis-C[4])₂] assembly (Fig. 1C) which is essentially 'double' the original cage (Fig. 1D). A number of structural parallels can therefore be drawn upon moving from C[4] to bis-C[4]. Based on the chemistry used to obtain bis-C[4] we anticipated that it should be possible to synthesise analogues containing linkers that possess varying degrees of rigidity, thereby giving rise to some level of control over the positioning of C[4]s relative to one another. This would then potentially allow us to either a) preferentially direct the formation of specific cluster types, b) force the formation of new cluster types or, most importantly, c) direct the formation of new structures / assemblies.

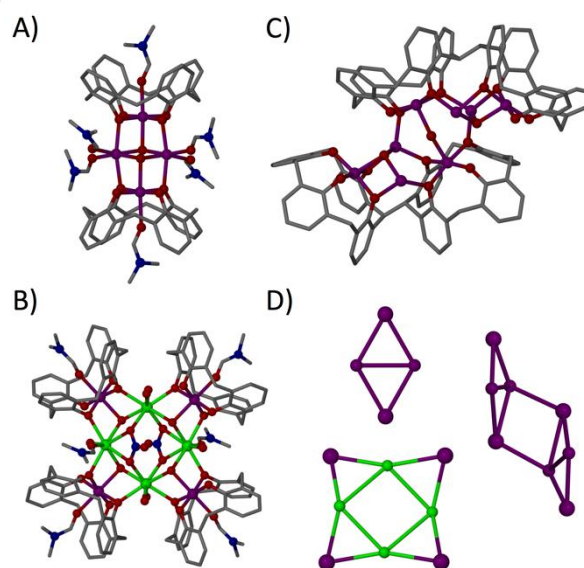


Figure 1. Structures of [Mn^{III}₂Mn^{II}₂(C[4])₂]^[9b] (A), [Mn^{III}₄Ln^{III}₄(C[4])₄]^[9c] (B) and [Mn^{III}₄Mn^{II}₄(bis-C[4])₂]^[10] (C) clusters showing persistence of the [Mn(C[4])] moiety. D) Cluster core topologies from A – C (rotated 90 degrees for the Mn₈ cluster in C) to show structural capping behaviour of the [Mn(C[4])] moiety and the relationship upon linking at the methylene bridge. Colour code: Mn – purple, Ln – green, C – grey, N – royal blue, O – red, Cl – yellow. H atoms and calix[4]arene ¹Bu groups omitted for clarity and not to scale.

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Here we report the use of computational chemistry to arrive at structures of *ortho*-, *meta*- and *para*-xylyl bis-C[4]s, subsequent ligand synthesis and their use in cluster formation. In the first of the results obtained we have directed the formation of a C[4]-supported $\text{Fe}^{\text{III}}_2\text{Ln}^{\text{III}}_2$ cluster with *meta*-xylyl bis-C[4], as well as a spectacular new trigonal antiprismatic metal-organic cage with the *para*- derivative. The latter is stable towards desolvation and its N_2 and CO_2 gas sorption has been studied.

Calculated structures were obtained for the *ortho*-, *meta*- and *para*-xylyl bis-C[4]s (**1** – **3** respectively) from DFT calculations using the B3LYP functional with added GD3 dispersion and 6-31G** basis set.^[11–13] There is inherent rotation freedom associated with the tether bonds to the methylene bridge. Although this is the case we undertook this work with a view to a) investigating conformational possibilities in the free ligand prior to synthesis and b) evaluating the likelihood of forming known C[4]-supported cluster types in the presence of target metal ions (based on the aforementioned empirical ion binding rules and cluster library). From these calculations it can be seen that, when the C[4] moieties in both the *ortho*- and *meta*-tethered bis-C[4]s are convergent (Fig. 2A and 2B), they are slightly offset with an eclipsed arrangement in which the lower-rim cavity...cavity distances are 3.081 Å and 3.177 Å, respectively (Figs. S1 and S2). In addition to this, calculations also showed that a divergent conformation for **3** was viable in which the molecule adopts the twisted conformation shown in Figure 2C (with lower-rim cavity...cavity distances of 12.679 Å, Fig. S3).

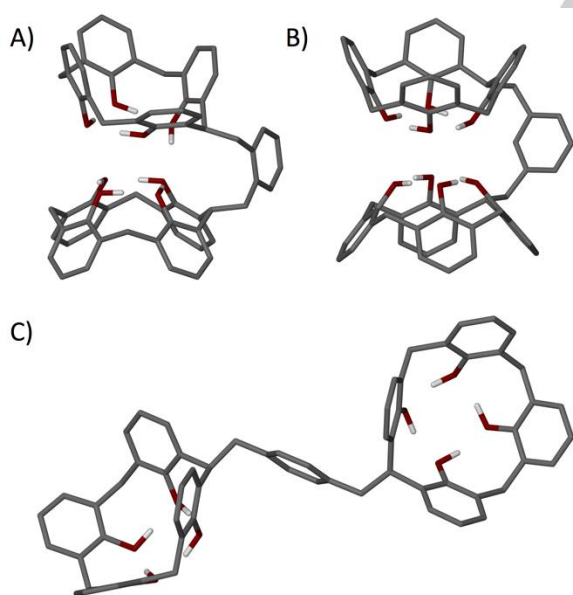


Figure 2. Calculated structures of **1** – **3**. A) Convergent *ortho*-xylyl bis-C[4] with H-bonding between the lower-rims. B) Convergent *meta*-xylyl bis-C[4] with less strained conformation. C) Divergent *para*-xylyl bis-C[4] with twisted conformation. H atoms except those at the C[4] lower-rims omitted for clarity.

From inspection it is clear that, due to constraints imposed by the *ortho*- and *meta*-xylyl linkers, compounds **1** and **2** would only be suitable to form analogues to C[4]-supported clusters that possess similar distances between either $[\text{TM}^{\text{III}}(\text{C}[4])]^{2-}$ or $[\text{Ln}^{\text{III}}(\text{C}[4])]$ moieties; the potentially divergent nature of **3** precludes formation of any reported C[4]-supported cluster type, unless it were (for example) to form a polymeric structure of

$[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{C}[4])_2]$ clusters. A survey of reported C[4]-supported clusters in which the C[4]s are most proximal returned two results.^[14] The first of these is the $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{C}[4])_2]$ cluster (Fig. 1A),^[9b] but it is clearly not possible to form this arrangement with either **1** or **2** as a) the lower-rim centroid...centroid distance is ~ 5.7 Å and b) the Mn^{II} ions / butterfly-like topology of the cluster forces the C[4] lower-rims to be drastically offset. The second was an $[\text{Fe}^{\text{III}}_2\text{Ln}^{\text{III}}_2(\text{C}[4])_2]$ cluster with a significantly closer lower-rim centroid...centroid distance of ~ 4.1 Å, and in which the C[4]s (binding the Fe^{III} ions) are tilted slightly to accommodate the incorporation of Ln^{III} ions (Fig. S4). This therefore suggested that from **1** and **2**, the latter would be most likely to form a cluster, in particular a $[\text{Fe}^{\text{III}}_2\text{Ln}^{\text{III}}_2(\text{2})]$ analogue to $[\text{Fe}^{\text{III}}_2\text{Ln}^{\text{III}}_2(\text{C}[4])_2]$; this is also likely when considering that **2** would have fewer steric constraints and or greater flexibility than **1**.

Prior to synthesising the xylyl-tethered bis-C[4]s and exploring their coordination chemistry, we first tested cluster formation / tolerance with a C[4] modified at one bridge with a benzyl group;^[15] this molecule was previously reported and was selected a logical starting point given the direct structural relationship to **1** – **3** (compare Figs. 2 and 3A), and that it would allow us to evaluate the effects (if any) of the methylene bridge substituent on cluster formation. The $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{C}[4])_2]$ SMM^[9b] was selected as the standard test system to see if this would form without the xylyl-tether constraints discussed above. Reaction between benzyl-C[4] and manganese (II) chloride hydrate in a dmf / MeOH mixture and in the presence of triethylamine afforded a dark purple solution from which single crystals grew upon vapour diffusion with acetonitrile. The crystals were in a triclinic cell and structural studies found them to be $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{benzyl-C}[4])_2(\text{OH})_2(\text{dmf})_6] \cdot (\text{MeOH})_{0.6}(\text{MeCN})_{1.4}$, **4**, with structure solution being performed in the space group *P*-1. The asymmetric unit (ASU) comprises one half of the expected $\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2$ butterfly-like cluster and symmetry generation around the inversion centre (located between the μ_3 -OH anions) produces the assembly in Figure 3A. The bridge substituents are positioned *trans* within the cluster framework, but this is to be expected when considering steric influence from the peripheral ligated solvent molecules of the general $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{C}[4])_2]$ assembly (Fig. 1A). As such it can be concluded that bridging groups have little or no effect on the introduction of secondary metal ions (Mn^{II} in this case) that are bridged to *via* the C[4] lower-rim.

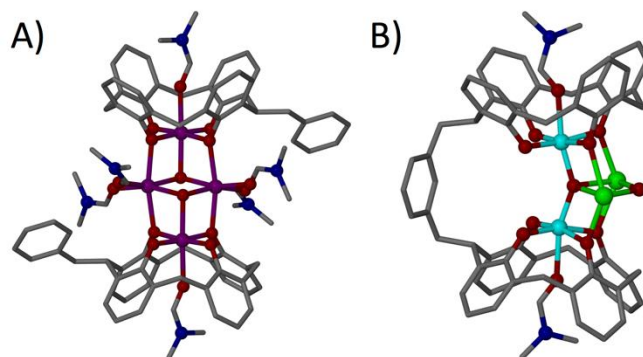


Figure 3. A) Structure of **4** showing *trans*-positioning of the benzyl groups at the C[4] methylene bridge. B) Structure of **5** showing the meta-tether at the methylene bridges and cluster core. Calix[4]arene ^tBu groups, ligated solvent molecules in **5**, H atoms, solvent of crystallisation and anion in **5** are omitted for clarity. Colour code: Mn – purple, Ln – green, Fe – pale blue, C – grey, N – royal blue, O – red. Figures not to scale.

Having established that cluster formation was tolerant towards benzyl substituents at the methylene bridge we synthesised compounds **1** – **3** using a slightly modified procedure to that reported for benzyl-C[4] (see Supp. Info.); this general synthetic route involves the use of the relevant α,α' -dibromoxylene in place of benzyl bromide. Reaction conditions used to form $[\text{Mn}^{\text{III}}\text{Mn}^{\text{II}}_2(\text{C}[4])_2]$, $[\text{Fe}^{\text{III}}\text{Ln}^{\text{III}}_2(\text{C}[4])_2]$ and $[\text{Mn}^{\text{III}}\text{Ln}^{\text{III}}_4(\text{C}[4])_4]$ clusters were employed with **1** – **3** in place of C[4] and single crystals were obtained in two instances. The first involved reaction of **2** with iron (II) nitrate nonahydrate and gadolinium(III) nitrate hexahydrate in a DMF/MeOH mixture and in the presence of Et_3N as a base. Single crystals of **5** were obtained by vapour diffusion of petroleum ether into the mother liquor and structure analysis (*P*-1) showed these to be $[\text{Fe}^{\text{III}}_2\text{Gd}^{\text{III}}_2(\mathbf{2}\text{-}8\text{H})(\mu_4\text{-O})(\mu\text{-OH})(\text{dmf})_7(\text{MeOH})(\text{H}_2\text{O})_2][\mathbf{2}\text{-H}]\cdot(\text{dmf})_{0.5}(\text{H}_2\text{O})_{1.5}$. The ASU comprises an octa-anionic **2** 'encapsulating' four metal ions in a distorted tetrahedron (Figure 3B), as well as bridging anions and terminal ligated solvent molecules in and around the cluster core. There are also co-crystallised solvent molecules and one half of a di-anionic **2** providing charge balance for the cationic cluster. From inspection of **5** and comparison with computational studies it is immediately obvious that compound **2** is indeed well suited to formation of the $[\text{Fe}^{\text{III}}_2\text{Ln}^{\text{III}}_2(\text{C}[4])_2]$ cluster type. In this regard, and although this is a known topology, this result suggests that rigid spacers can be further used to fine tune and or control cluster synthesis through the design of topologically directing C[4]-based ligands.

The second situation from which single crystals resulted involved the reaction of **3** with manganese (II) chloride tetrahydrate and dysprosium (III) chloride hexahydrate in a DMF/MeOH mixture and in the presence of Et_3N as a base. Single crystals of **6** were obtained upon diffusion of acetonitrile vapour into the reaction mixture. Structural analysis of the Dy(III) analogue (*C2/c*) showed these to be of formula $[\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}\text{Dy}_5(\mathbf{3}\text{-}8\text{H})_3(\mu_3\text{-OH})_8(\text{dmf})_8(\text{MeCN})_4(\text{H}_2\text{O})_9](\text{OH})_3(\text{H}_2\text{O})_{1.5}(\text{dmf})_{16}$ (Figure 4). The ASU is complex and comprises one half of this formula. There are three half molecules of **5**, all of which are tetra-anionic and house a Jahn-Teller distorted Mn^{III} ion (Mn1 – Mn3); these are arranged at the corners of a triangle (Figure 4A) with a total of twelve Mn-O(phenolate) distances in the range of 1.881(10) – 2.005(10) Å. Each Mn^{III} ion has a ligated solvent positioned along the JT axis such that it occupies an associated C[4] cavity from **5** (Mn1-N340(MeCN), Mn2-O30(dmf) and Mn3-N360(MeCN) distances in the range of 2.16(4) – 2.56(3) Å). The coordination spheres of Mn1 – Mn3 are completed by $\mu_3\text{-OH}$ anions that are positioned towards the centre of the triangle (Mn1-O13, Mn2-O14 and Mn3-O15 distances in the range of 2.073(12) – 2.135(11) Å). The O15 $\mu_3\text{-OH}$ bridges to two Dy^{III} ions (Dy1 and Dy3), both of which are octacoordinate and of square antiprismatic geometry. Dy1 has three terminal ligated solvent molecules with respective Dy1-O23(dmf), Dy1-O24(dmf) and Dy1-O25(H_2O) distances of 2.396(14), 2.396(13) and 2.358(14) Å. Dy3 also has three terminal ligated solvent molecules and these have respective Dy3-O20(H_2O), Dy3-O21(dmf) and Dy3-O22(H_2O) distances of 2.445(15), 2.464(15) and 2.331(13) Å. The O13 and O14 $\mu_3\text{-OH}$ anions bridge to Dy1 and Dy3 with O13-Dy1 and O14-Dy3 distances of 2.374(11) and 2.378(11) Å respectively. These also bridge to the final metal ion binding site that is occupied by disordered Mn^{II} / Dy^{III} ions, each present at 50% occupancy (respective O13-Mn4, O14-Mn, O13-Dy4A and O14-Dy4A distances of 2.003(13), 2.006(12), 2.553(12) and 2.511(11) Å). The Mn4 has distorted octahedral

geometry and has a ligated water molecule with an Mn4-O19 distance of 2.24(3) Å. Dy4A is heptacoordinate, has capped trigonal prismatic geometry and has ligated water and dmf molecules with Dy4A-O19A(H_2O) and Dy4A-O17(dmf) distances of 2.23(3) and 2.34(2) Å respectively. The central point of the triangle is occupied by a final $\mu_3\text{-OH}$ anion that bridges to all central metal ions in the triangle; this occurs with an O16-Mn4 distance of 2.241(13) Å and O16-Dy1, O16-Dy3 and O16-Dy4A distances in the range of 2.351(10) – 2.399(10) Å. Symmetry expansion of the ASU affords the trigonal antiprismatic assembly shown in Figure 4B in which the vertices are occupied by the expected $(\text{Mn}^{\text{III}}\text{-C}[4])^{\cdot-}$ moieties based on ligand composition. The antiprismatic nature of the assembly (Fig. S5) arises from the *p*-xylyl linkers that invoke a triply helical like arrangement. The cage carries an overall charge of 3+ and disordered hydroxide counterions are located at positions consistent with hydrogen binding interactions to both ligated waters and bridging $\mu_3\text{-OH}$ anions.

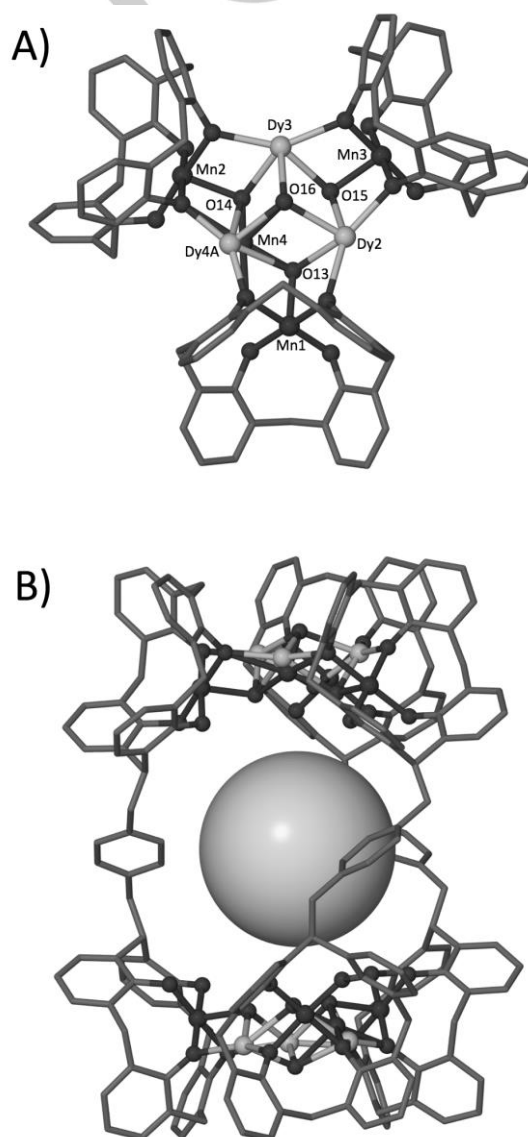


Figure 4. Structure of $[\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}\text{Dy}_5(\mathbf{3}\text{-}8\text{H})_3(\mu_3\text{-OH})_8(\text{dmf})_8(\text{MeCN})_4(\text{H}_2\text{O})_9](\text{OH})_3(\text{H}_2\text{O})_{1.5}(\text{dmf})_{16}$. **6.** A) Part of the asymmetric unit showing the triangular face and selected labels according to discussion. B) Symmetry expanded structure showing the trigonal antiprismatic cage with $(\text{Mn}^{\text{III}}\text{-C}[4])^{\cdot-}$ moieties at each vertex and a yellow sphere to emphasise the central cavity. Calix[4]arene^tBu groups, ligated solvent molecules, H atoms, solvent of crystallisation and anions omitted for clarity. Figures not to scale.

Diffuse electron density located in and around the central cavity is indicative of very badly disordered dmf of crystallization that could not be modeled. A search of the CSD for 3d-4f clusters with an O-bridged hemicubane core analogous to that in Figure 4A showed this to be relatively rare, returning only two general hits.^[16-17] The first is a Co^{III}₃Ln^{III}₃ cluster core supported by *N*-butyldiethanolamines, acetates and bridging hydroxides,^[16] differing to **6** in that one Co^{III} ion resides on the other side of the plane defined by the three central Ln^{III} ions; in **6** all three Mn^{III} ions are on the same side of the analogous plane. The second is a closely related series of phenolate, acetate and hydroxide-bridged Ni^{II}₃Ln^{III}₃ clusters, all of which possess three nickel ions residing on the same side of the plane as in **6**.^[17] The orientation of C[4]s in **6** is reminiscent of our triangular C[4]-supported enneanuclear Cu(II) clusters,^[18] supporting the concept that ligand design may be combined with large clusters to access a wide range of new assemblies.

Crystallographic disorder and the anisotropy of the Ln^{III} and Mn^{III} ions precludes quantitative interpretation of the magnetic behaviour of **6**, **6(MnGd)** and **6(MnTb)**, though susceptibility data reveals weak [ferrimagnetic] intramolecular exchange interactions in all three cases, as expected from cages containing just 3d-4f and 4f-4f interactions (Fig. S6). This is consistent with previously reported, structurally related calixarene-based complexes such as [Mn^{III}₂Mn^{II}₂(C[4])₂] and [Mn^{III}₂Ln^{III}₂(C[4])₂] in which the Mn^{III}-Mn^{II} and Mn^{III}-Gd^{III} interactions have been found to be weakly ferromagnetic and the Gd^{III}-Gd^{III} and Mn^{II}-Gd^{III} interactions weakly antiferromagnetic.^[9f] The presence of weak exchange is further corroborated by low temperature, high field magnetization data which tends toward saturation at S_{\max} in all cases (Fig. S7), VTVB data plotted against the reduced quantity $\mu_B B / kT$ (Fig. S8), show significant nesting of the VTVB data for **6** and **6(MnTb)**, with less nesting observed for **6(MnGd)**, a simple reflection of the larger anisotropy associated with the Ln ions in the former two cases. Ac susceptibility studies also reflect this, with the tails of frequency-dependent χ_M'' signals observed for both **6** and **6(MnTb)**, but not for **6(MnGd)**, indicative of the onset of slow magnetization relaxation and SMM behaviour in the former two (Fig. S9). Full details are given as SI.

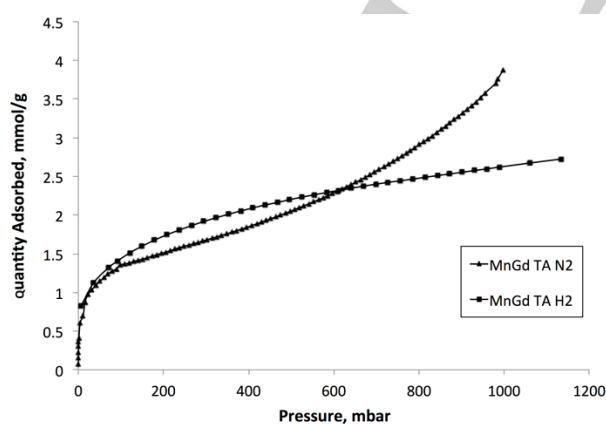


Figure 5. Nitrogen and hydrogen gas adsorption isotherms for desolvated **6**.

Given the cavity-containing nature of **6** we investigated desolvation and gas sorption properties of the gadolinium

analogue; **6(MnGd)** crystallises more rapidly than **6(MnDy)**, so was selected for scale-up. Mild heating under vacuum was performed prior to gas sorption studies and structural integrity was confirmed by PXRD (Fig. S10). The Nitrogen Adsorption Isotherm resembles a Type 2 Isotherm typically indicative of either a non-porous solid or solids with relatively large pores (Fig. 5). The time taken for each data point to reach equilibration and a BET Surface area of 125 m²/g suggest partial porosity to N₂. The H₂ uptake measurement by contrast was much quicker and shows a good uptake of 2.7 mmol/g, further indicating the pore accessibility for smaller probe gases.

To conclude, we have used computational chemistry to explore the possible conformations of three xylyl-tethered bis-C[4]s prior to synthesis and application in cluster forming chemistry. The *meta*-xylyl bis-C[4] formed a known cluster type in line with inspection of our structural library, presenting this as a potential method of controlling metal ion composition based on C[4] tethering. In a similar way, *para*-xylyl bis-C[4] is unable to form any of the known C[4]-supported cluster motifs due to ligand structure. Exploitation of this feature afforded a new trigonal antiprismatic metal-organic cage that displays thermal stability and uptake of both N₂ and H₂ gas. Future work will build on these results, focusing on the synthesis of a family of new nanoscale assemblies with targeted topologies through C[4]-tether design. These will be explored for utility as storage materials, host-guest sensors, platforms for postsynthetic modification and hosts for magnetically relevant guests.

Experimental Section

Benzyl-C[4] was synthesised according to literature procedure.^[15] The synthesis of **1** – **6** is included in the Supporting Information in addition to details relating to crystallographic, magnetic and gas sorption studies. Data for this paper are available via the following link: <http://dx.doi.org/10.7488/ds/1346>.

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Keywords: Calixarenes • Directed Assembly • Clusters • Metal-Organic Polyhedron • Gas Storage

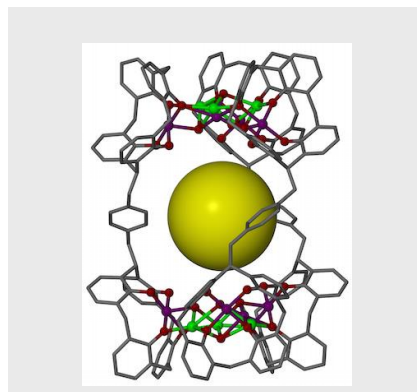
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COMMUNICATION

Synthetic modification at the calix[4]arene methylene bridge offers a unique opportunity to influence cluster-forming chemistry. The synthesis of xylyl-tethered bis-C[4]s and their use as directing species in cluster forming reactions is presented. These new ligands have been used to direct the assembly of a previously known $\text{Fe}^{\text{III}}_2\text{Ln}^{\text{III}}_2$ cluster, as well as a spectacular new metal-organic trigonal antiprism, that latter of which also displays thermal stability and uptake of N_2 or H_2 gas.



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