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Investigations into cluster formation with alkyl-tethered bis-calix[4]arenes

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Abstract: Calix[4]arenes are versatile ligands capable of forming a wide range of cluster motifs when reacted with 3*d*, 4*f* or 3*d*/4*f* metal ions. Synthetic modification at the calix[4]arene methylene bridge offers a unique opportunity to explore cluster formation with these alternative building blocks. Here we present the synthesis of a range of bis-calix[4]arenes that are tethered by alkyl chains, as well as exploratory structural studies into cluster-forming reactions. Single crystals were formed in four cases, and from the *X*-ray structures elucidated it is possible to conclude that sufficiently long alkyl tethers allow for the formation of established cluster topologies without disruption to the core coordination chemistry.

Keywords: calixarenes; coordination chemistry; clusters; transition metals; lanthanide metals

Introduction

Methylene-bridged calix[4]arenes (C[4]s, Fig. 1A) are cyclic polyphenols that have found widespread use in the synthesis of a variety of non-covalent or metal-directed structures (1-6). Their versatility in this regard relates to the fact that both the upper- and lower-rims can be modified with relative ease, thereby allowing the chemist to introduce a range of directing functionalities at either position (7). We, amongst others (8-20), recently ‘mapped out’ the transition, lanthanide metal and 3*d*-4*f* cluster-forming chemistry of methylene-bridged C[4]s. In doing so we have reported a wide range of new polymetallic clusters that include a) $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{TBC}[4])_2]$ Single-Molecule Magnets (SMMs, Fig. 1B) (9,10), b) $[\text{Mn}^{\text{III}}_4\text{Ln}^{\text{III}}_4(\text{C}[4])_4]$ clusters (Fig. 1C) that are magnetic refrigerants or SMMs depending on the lanthanide employed (13,14) and c) $[\text{Cu}^{\text{II}}_9(\text{TBC}[4])_3]$ clusters (11) that are versatile anion binding materials. More recently we found that it is also

possible to sequentially interchange Ln^{III} for Mn^{II} ions in the aforementioned $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{TBC}[4])_2]$ SMMs to afford new $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}\text{Ln}^{\text{III}}(\text{TBC}[4])_2]$ and $[\text{Mn}^{\text{III}}_2\text{Ln}^{\text{III}}_2(\text{TBC}[4])_2]$ species (20). Preferred metal ion binding is observed in a number of different scenarios, an example being the persistent incorporation of the $[\text{Mn}^{\text{III}}(\text{TBC}[4])]$ moiety within all $3d$ and $3d-4f$ clusters of manganese. These empirical metal ion ‘binding rules’ therefore offer a route to control the incorporation of a minimum number of specific paramagnetic ions in a resulting cluster through a) choice of $\text{C}[n]$ employed and b) the metal ions used in cluster synthesis. It is noteworthy to mention that the thia-, sulfinyl- and sulfonyl-bridged $\text{C}[4]$ s (21-31) have also been utilised in the construction of polymetallic clusters, and more recently in the programmed formation of nanometer scale metal-organic assemblies. Their utility stems from the fact that the S, SO or SO_2 bridging groups influence the resulting coordination chemistry (Fig. 1D), binding four metal ions rather than one (as is the case for methylene-bridged analogues). Both systems therefore have different merits when considering the construction of polymetallic clusters, but standard $\text{C}[4]$ s can also be modified at the methylene bridge. Synthetic alteration, in addition to the use of bridge-modified $\text{C}[4]$ s for the construction of new / related clusters, is an area we are currently investigating and is the focus of this contribution.

FIGURE 1 – PLEASE SEE END OF MANUSCRIPT

Synthetic access to $\text{C}[4]$ s that deviate from classical methylene bridge composition (i.e. those that contain ≥ 1 different bridge) has been known for some time (32-37). Elegant work by the Böhmer and Biali groups (amongst others) detailed the synthesis of such species through the use of stepwise and fragment condensation methods. Later efforts,

chiefly by Biali, focused on functionalisation at multiple C[4] bridge positions, but in this case utilising the pre-formed calixarene framework as a synthetic platform (38-42). Fantini has demonstrated the ability to undertake synthetic modification at one C[4] methylene bridge to a) introduce a number of different substituents and b) directly link C[4]s together at the bridge position (43-46). To us, expansion of this direct C[4]-C[4] link presented an opportunity to systematically influence (and thus potentially control) C[4]-supported cluster-formation through the introduction of different organic spacers. Here we report the synthesis of a series of alkyl-tethered bis-C[4]s and exploratory studies into cluster formation with these new ligands.

Results and Discussion

Synthesis of alkyl-tethered bis-C[4]s

As reported, TBC[4] lower-rim protection (with resulting OMe groups) allows for mono-lithiation at one methylene bridge via reaction with n BuLi as shown in Figure 2A. Reaction of mono-lithiated MeO-TBC[4] (**1**) with chosen dibromoalkanes afforded a series of bis-MeO-TBC[4]s with the calixarenes tethered by propyl, butyl and hexyl to decyl chains (47,48). Subsequent lower-rim deprotection afforded the series of target bis-C[4]s in moderate yields, with all TBC[4] sub-units adopting cone conformations due to typical stabilising H-bonding interactions. With an interest in examining the structures of compounds **9** – **15** in the absence of metal ions / prior to cluster formation, we attempted crystallisation from a range of solvents including toluene, ethyl acetate and acetonitrile. Single crystals suitable for *X*-ray diffraction studies were isolated in just one case, that being the acetonitrile solvate of TBC[4]-(CH₂)₃-TBC[4] (**9**). Crystals of **9**·4MeCN were found to be in a monoclinic space group and structure analysis was carried out in the space group *P*2₁/*c*. The asymmetric unit contains one molecule of **9** and four co-

crystallised MeCN (Figure 2B), two of which reside in the TBC[4] cavities; in this arrangement they form CH... π interactions that are consistent with those found in the MeCN solvate of TBC[4] (49). From inspection it is clear that the TBC[4] cavity is unperturbed by bridge modification and is thus open for occupation by metal ions as anticipated.

FIGURE 2 – PLEASE SEE END OF MANUSCRIPT

Cluster synthesis and structural investigations

With compounds **9** – **15** isolated, we began investigations into cluster synthesis with these new ligands by targeting reaction conditions known to afford the $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{TBC}[4])_2]$ (9,10), $[\text{Mn}^{\text{III}}_4\text{Ln}^{\text{III}}_4(\text{C}[4])_4]$ (13,14) and series of $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{TBC}[4])_2]$ / $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}\text{Ln}^{\text{III}}(\text{TBC}[4])_2]$ / $[\text{Mn}^{\text{III}}_2\text{Ln}^{\text{III}}_2(\text{TBC}[4])_2]$ species discussed in the introductory section (20). All reactions produced purple solutions but we were only able to grow single crystals suitable for diffraction studies in four cases. Structural analysis (below) revealed that three of these (**16** – **18**) were isostructural, with the main difference being the length of alkyl tether present between the TBC[4] sub-units; these were formed with **13** – **15**, octyl-, nonyl- and decyl-tethered bis-TBC[4]s respectively. In all three cases the cluster core was analogous to the ‘butterfly’ topology found in $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{TBC}[4])_2]$ (9,10). The fourth case in which single crystals were isolated also involved compound **14**, and the components were found to assemble into a new cluster (**19**) that is very closely related to $[\text{Mn}^{\text{III}}_4\text{Ln}^{\text{III}}_4(\text{C}[4])_4]$ (13,14); the only significant difference in this new cluster is that there are changes to the anions incorporated within the core. In the interest of brevity we have limited discussion here to the structures of **16** and **19**, with comparisons made between the former and **17-18**.

Reaction of **13** with manganese(II) dichloride tetrahydrate in a DMF/MeOH mixture, and in the presence of Et₃N as a base, afforded single crystals of [Mn^{III}₂Mn^{II}₂(**13**-8H)(μ₃-OH)₂(DMF)_{5.5}(MeOH)_{0.5}](H₂O)_{1.5} (**16**) upon slow evaporation of the mother liquor. The crystals were found to be in a monoclinic cell and structure solution was performed in the space group *P2₁/c*. The asymmetric unit (ASU) contains the entire cluster shown in Figure 3A in addition to co-crystallised solvent molecules. Comparison of Figures 1B and 3A shows the clear structural relation between these two clusters, with the major difference being the presence of an octyl tether between the TBC[4] sub-units in **16**. Within the cluster, Mn1 is bound in the tetraphenolic TBC[4] pocket formed by oxygens O1 – O4 (Mn1-O range of 1.919(9)-1.974(9) Å) and it is in the third oxidation state with Jahn-Teller distorted octahedral geometry. Its coordination sphere is completed by a ligated dmf residing in the TBC[4] cavity (Mn1-O15, 2.297(11) Å) and a μ₃-hydroxide (Mn1-O9, 2.141(9) Å), which is also bonded to Mn3 and Mn4 (2.184(9) and 2.183(9) Å respectively), both in the second oxidation state and possessing distorted octahedral geometry. In addition, Mn3 coordination is completed by two dmf molecules (Mn3-O11 Mn3-O12 with respective distances of 2.138(10) and 2.124(11) Å), two μ-phenoxide oxygens (Mn3-O4 and Mn3-O8 with respective distances of 2.237(8) and 2.237(9) Å) and a μ₃-hydroxide (Mn3-O10, 2.155(9) Å), bridging Mn3 with Mn4 and Mn2, both of which have similar coordination environments to those described for Mn1 and Mn3; there are negligible differences in bond lengths observed. Analogous reactions with either **14** or **15** in place of **13** in the synthesis of **16** above afforded single crystals of [Mn^{III}₂Mn^{II}₂(**14**-8H)(μ₃-OH)₂(MeOH)(dmf)₅](MeOH)(dmf)(H₂O) (**17**) and [Mn^{III}₂Mn^{II}₂(**15**-8H)(μ₃-OH)₂(dmf)₆](dmf)_{1.5}(MeOH)_{0.5}(H₂O)_{1.5} (**18**) respectively, both of which are shown in Figure 3B and 3C for comparison. Although there are slight changes in the composition of peripheral ligated solvent, as well as solvent of

crystallisation upon moving from **16** to **18**, the clusters and overall assemblies are near identical. It is therefore clear that the formation of the general ‘butterfly’ $\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2$ cluster motif is favourable with alkyl tethers greater or equal to octyl in length.

FIGURE 3 – PLEASE SEE END OF MANUSCRIPT

Reaction of **14** with manganese (II) chloride tetrahydrate and gadolinium (III) chloride hexahydrate in a DMF/MeOH mixture, and in the presence of Et_3N as a base, afforded single crystals of $[\text{Mn}^{\text{III}}_4\text{Gd}^{\text{III}}_4(\mathbf{14}\text{-8H})(\mu_3\text{-CO}_3)_2(\mu_3\text{-OH})_4(\text{H}_2\text{O})_6(\text{dmf})_6](\text{dmf})_6(\text{MeOH})_4$ (**19**) after slow evaporation of the mother liquor. The crystals were found to be in a triclinic cell and structure solution was performed in the space group $P\bar{1}$. The ASU comprises one half of the assembly (Figure 4A), related to its symmetry equivalent through an inversion centre. The two Mn^{III} ions in the ASU are bound in the TBC[4] phenolic pockets with Mn1-O and Mn2-O distances in the ranges of 1.900(7) – 1.988(6) and 1.913(6) – 1.986(6) Å respectively. Their Jahn Teller distorted octahedral coordination spheres are completed by ligated dmf molecules residing in the TBC[4] cavities (Mn1-O9 and Mn2-O10 distances of 2.263(6) and 2.262(7) Å respectively), and μ_3 -hydroxides (Mn1-O12 and Mn2-O13 distances of 2.245(5) and 2.233(6) Å respectively). The latter bridge to octacoordinate, square antiprismatic Gd^{III} ions within the cluster core, with respective Gd1-O12, Gd1-O13, Gd2-O12 and Gd2-O13 distances of 2.419(5), 2.427(6), 2.379(6) and 2.390(6) Å. Gd1 is also bound to two μ -phenoxides (Gd1-O3 and Gd1-O7 distances of 2.375(6) and 2.393(6) Å respectively) belonging to TBC[4]s, two ligated water molecules (Gd1-O14 and Gd1-O15 distances of 2.410(7) and 2.428(6) Å respectively) and two μ -carbonates (Gd1-O16 and Gd1-O18 distances of 2.397(6) and 2.394(6) Å respectively). These carbonates are the bridging

units between Gd1, Gd2 and their symmetry equivalents, with Gd2 coordination being essentially identical to that of Gd1; the only difference is the presence of a ligated dmf rather than a water molecule, occurring with a Gd2 – O11 distance of 2.305(7) Å. Symmetry expansion of the ASU around the inversion centre affords the assembly shown in Figure 4B. Comparison with Figure 1C shows that these square within square (or Mn^{III} tetra-capped Ln^{III} square) topologies are very closely related, the main difference being the incorporation of μ_3 -carbonates in **19** rather than nitrates in our previously reported example (13,14). Charge balance in the previously reported μ -nitrate cluster is provided by hydroxide counterions that are proximal to the cluster core; this is not seen in **19** due to the incorporation of μ_3 -CO₃²⁻ anions (50). Further examination of Figure 4B shows that the bis-TBC[4]s are just of an appropriate tether length to allow for formation of this cluster type, suggesting that slightly shorter chains (e.g. hexyl / heptyl) would not be suitable for synthesis of this structural arrangement; significantly shorter chains such as propyl or butyl would clearly not be suitable.

FIGURE 4 – PLEASE SEE END OF MANUSCRIPT

Conclusions

We have expanded upon the synthetic chemistry associated with bis-TBC[4]s and report a range of new molecular building blocks possessing alkyl tethers of varied chain length. These molecules may find utility in the field of supramolecular chemistry as a whole, but in this contribution we have begun to investigate their potential as platforms for cluster synthesis. Attempts to isolate single crystals of clusters with tether chain lengths shorter than octyl have yet to be successful, but this will be the focus of future work. Although this is the case, we have established information relating to the possible minimum chain

length required in order to form some known cluster motifs, and by this rationale one can expect the formation of markedly different assemblies when shorter tethers are employed. Results from this continuing study will be communicated in due course.

Experimental

All reagents were purchased from Sigma-Aldrich and used as supplied without further purification.

General procedure for the synthesis of bis-tetramethoxycalix[4]arenes 2 – 8: *n*-BuLi (2.5 M in hexane, 1.5 eq.) was added to a stirred solution of tetramethoxycalix[4]arene (1 eq.) in dry THF (40 mL) under an N₂ atmosphere, causing a rapid colour change from pale yellow to blood red. After ten minutes of stirring the chosen dibromoalkane (1.15 eq.), as a solution in 20 mL of dry THF, was added dropwise over 40 minutes, with concomitant change in colour from blood red to yellow. Following addition the reaction mixture was stirred for a further 12 hours before being quenched by addition of H₂O. Volatiles were removed and the resulting solid was dried under vacuum. The crude material was then dissolved in CH₂Cl₂ (300 ml) and washed with brine (3 × 100 ml). The organic layer was separated, dried over MgSO₄, and the solvent was removed under reduced pressure to afford a gummy yellow solid that was dried under vacuum. The resulting yellow solid was recrystallised from hot CHCl₃/MeOH to afford a white powder of the pure target bis-MeO-C[4]. In all cases ¹H NMR spectra of the products are very difficult to interpret due to fluxionality caused by the lower-rim methoxy groups. Although this is the case it was possible to gauge reaction completion for these synthetic intermediates by the disappearance of characteristic OH groups for the C[4] lower-rim. Compounds 2 – 8 were therefore used in the deprotection step below to afford the target lower-rim hydroxy C[4]s 9 – 15.

Synthesis of 2,2'-(Propane-1,3-diyl)bis(5,11,17,23-tetra-*p*-tert-butyl-25,26,27,28-tetra-methoxycalix[4]arene, 2: Reagents used in the general synthesis were 2.50 g (3.55 mmol) tetramethoxycalix[4]arene in 40 mL dry THF, 2.1 mL (5.32 mmol) *n*-BuLi (2.5 M in hexane) and 358 mg (1.77 mmol) 1,3-dibromopropane in 20 mL of dry THF. Yield: 1.44 g (56 %).

Synthesis of 2,2'-(Butane-1,4-diyl)bis(5,11,17,23-tetra-*p*-tert-butyl-25,26,27,28-tetra-methoxycalix[4]arene, 3: Reagents used in the general synthesis were 2.50 g (3.55

mmol) tetramethoxycalix[4]arene in 40 mL dry THF, 2.1 mL (5.32 mmol) *n*-BuLi (2.5 M in hexane) and 383 mg (1.77 mmol) 1,4-dibromobutane in 20 mL of dry THF. Yield: 1.30 g (50 %).

Synthesis of 2,2'-(Hexane-1,6-diyl)bis(5,11,17,23-tetra-*p*-tert-butyl-25,26,27,28-tetra-methoxycalix[4]arene, 4: Reagents used in the general synthesis were 2.83 g (4.02 mmol) tetramethoxycalix[4]arene in 40 mL dry THF, 2.4 mL (6.36 mmol) *n*-BuLi (2.5 M in hexane) and 564 mg (2.31 mmol) 1,6-dibromohexane in 20 mL of dry THF. Yield: 1.40 g (24 %).

Synthesis of 2,2'-(Heptane-1,7-diyl)bis(5,11,17,23-tetra-*p*-tert-butyl-25,26,27,28-tetra-methoxycalix[4]arene, 5: Reagents used in the general synthesis were 3 g (4.26 mmol) tetramethoxycalix[4]arene in 40 mL dry THF, 2.55 mL (6.38 mmol) *n*-BuLi (2.5 M in hexane) and 650 mg (2.52 mmol) 1,7-dibromoheptane (97%) in 20 mL of dry THF. Yield: 2.14 g (33 %).

Synthesis of 2,2'-(Octane-1,8-diyl)bis(5,11,17,23-tetra-*p*-tert-butyl-25,26,27,28-tetra-methoxycalix[4]arene, 6: Reagents used in the general synthesis were 3g (4.26 mmol) tetramethoxycalix[4]arene in 40 mL dry THF, 2.55 mL (6.38 mmol) *n*-BuLi (2.5 M in hexane) and 670 mg (2.45 mmol) 1,8-dibromooctane in 20 mL dry THF. Yield: 2.83 g (44 %)

Synthesis of 2,2'-(Nonane-1,9-diyl)bis(5,11,17,23-tetra-*p*-tert-butyl-25,26,27,28-tetra-methoxycalix[4]arene, 7: Reagents used in the general synthesis were 3 g (4.26 mmol) tetramethoxycalix[4]arene in 40 mL dry THF, 2.55 mL (6.38 mmol) *n*-BuLi (2.5 M in hexane) and 720 mg (2.53 mmol) 1,9-dibromononane (97%) in 20 mL dry THF. Yield: 2.08 g (32 %).

Synthesis of 2,2'-(Decane-1,10-diyl)bis(5,11,17,23-tetra-*p*-tert-butyl-25,26,27,28-tetra-methoxycalix[4]arene, 8: Reagents used in the general synthesis were 3 g (4.26 mmol) tetramethoxycalix[4]arene in 40 mL dry THF, 2.55 mL (6.38 mmol) *n*-BuLi (2.5 M in hexane) and 760 mg (2.52 mmol) 1,10-dibromodecane (97%) in 20 mL dry THF. Yield: 2.29 g (35 %).

General procedure for the synthesis of bis-tetrahydroxycalix[4]arenes 9 – 15: Cyclohexyl iodide (90 eq.) was added to a DMF (30 ml) solution of the chosen bis-MeO-C[4] and the resulting mixture was heated at reflux for 48h with a concomitant change in colour from pale yellow to dark orange. The solution was poured into H₂O (250 ml), causing the precipitation of an orange solid. The orange precipitate was collected, was

washed several times with water, and stirred in MeOH for 15 minutes to afford a white solid. The white solid was filtered, washed several times with MeOH, collected under reduced pressure and dried under vacuum. **Alternative workup procedure for bis-tetramethoxycalix[4]arenes:** Occasionally the workup procedure above leads to very low yields (particularly for longer alkyl chains). On occasions that a solid did not crash out of solution upon addition of water the product was extracted with CHCl₃, washing the water phase until the orange colour disappeared. The organic layer was collected, dried over MgSO₄ and filtered. The solvent was removed under reduced pressure and the resulting crude solid was recrystallised from hot CHCl₃/MeOH. In all cases the target bis-C[4]s were checked for purity by TLC (CHCl₃/Hex 1:1) and purified by column chromatography (CHCl₃/Hex 1:1 → EtOAc) to remove C[4] impurities.

Synthesis of 2,2'-(Propane-1,6-diyl)bis(5,11,17,23-tetra-*p*-tert-butyl-tetrahydroxycalix[4]arene, 9: Reagents used in the general synthesis were 0.880 g (0.61 mmol) of **2**, 11.6 g (54.9 mmol) of cyclohexyl iodide in 30 mL DMF. Purification by chromatography column (CHCl₃/Hex 1:1 → EtOAc) afforded 556 mg of pure product (Yield: 68 %). ¹H NMR (CDCl₃): 10.27 (s, 8H, -OH), 7.00 (m, 16H, ArH), 4.40 (t, 2H, ³J_{HH} = 7.9 Hz, Ar-CH-CH₂-), 4.17 (m, 6H, Ar-CH₂-Ar), 3.41 (m, 6H, Ar-CH₂-Ar), 2.18 (m, 4H, Ar-CH-CH₂), 1.31 (m, 2H, CH₂-CH₂-CH₂), 1.13 (m, 72H, C(CH₃)₃). ¹³C NMR (CDCl₃): 146.85, 146.64, 144.38, 144.25, 131.20, 127.82, 127.70, 127.51, 127.21, 125.95, 125.91, 125.22, 121.77, 104.99, 34.17, 34.03, 32.76, 32.62, 31.43; MS calculated for C₉₁H₁₁₆O₈ (1336.87); found 1354.91 (M+NH₄)⁺. **Crystal data for 9·4MeCN (CCDC ?????????):** C₉₉H₁₂₈N₄O₈, *M* = 1502.05, Colourless Block, 0.35 x 0.30 x 0.18 mm³, monoclinic, space group *P*2₁/*c* (No. 14), *a* = 19.3316(19), *b* = 25.164(2), *c* = 19.117(2) Å, *b* = 105.346(6)°, *V* = 8968.1(16) Å³, *Z* = 4, Bruker X8 Apex II CCD Diffractometer, MoKα radiation (λ = 0.71073 Å), *T* = 100(2)K, 2θ_{max} = 46.6°, 58266 reflections collected, 12880 unique (R_{int} = 0.1318). Final *Goof* = 1.211, *RI* = 0.0979, *wR2* = 0.2272, *R* indices based on 5751 reflections with *I* > 2σ(*I*) (refinement on *F*²).

Synthesis of 2,2'-(Butane-1,6-diyl)bis(5,11,17,23-tetra-*p*-tert-butyl-tetrahydroxycalix[4]arene, 10: Reagents used in the general synthesis were 2.42 g (1.65 mmol) of **3**, 31.3 g (0.150 mol) of cyclohexyl iodide in 40 mL DMF. Purification by chromatography column (CHCl₃/Hex 1:1 → EtOAc) afforded 1.462 g of pure product (Yield: 65 %). ¹H NMR (CDCl₃): 10.27 (s, 8H, ArOH), 7.00-6.91 (M, 16H, ArH), 4.40 (t, 2H, ³J_{HH} = 7.8 Hz, Ar-CH-CH₂-), 4.18 (m, 6H, Ar-CH₂-Ar), 3.42 (m, 6H, Ar-CH₂-Ar), 2.11 (m, 4H,

Ar-CH-CH₂), 1.32 (m, 4H, CH₂-CH₂-CH₂), 1.13 (m, 72H, C(CH₃)₃). ¹³C NMR (CDCl₃): 146.83, 146.69, 144.38, 144.28, 131.10, 127.80, 127.70, 127.55, 127.24, 125.94, 125.14, 121.77, 34.18, 34.03, 32.78, 32.64, 32.47, 31.43, 28.43; MS calculated for C₉₂H₁₁₈O₈ 1350.88, found 1369.92 (M+NH₄)⁺.

Synthesis of 2,2'-(Hexane-1,6-diyl)bis(5,11,17,23-tetra-*p*-tert-butyl-tetrahydroxycalix[4]arene, 11: Reagents used in the general synthesis were 1.40 g (0.95 mmol) of **4**, 18 g (85.5 mmol) of cyclohexyl iodide in 30 mL DMF. Purification by chromatography column (CHCl₃/Hex 1:1 → EtOAc) afforded 333 mg of pure product (Yield: 25 %). ¹H NMR (CDCl₃): 10.29 (s, 8H, -OH), 7.09-6.97 (m, 16H, ArH), 4.46 (t, 2H, ³J_{HH} = 7.8 Hz, Ar-CH-CH₂-), 4.27-4.22 (m, 12H Ar-CH₂-Ar), 3.48 (d, 4H, ²J_{HH} = 13.6 Hz, Ar-CH-CH₂), 2.16 (s, 8H, -CH₂-), 1.2 (s, 72H, C(CH₃)₃). ¹³C NMR (CDCl₃): 146.8, 144.3, 131.2, 127.7, 126.0, 34.2, 34.0, 32.8, 31.4, 29.0, 27.5. MS calcd. for C₉₄H₁₂₂O₈ (1379.90); found: 1397.9 (M+NH₄)⁺.

Synthesis of 2,2'-(Heptane-1,7-diyl)bis(5,11,17,23-tetra-*p*-tert-butyl-tetrahydroxycalix[4]arene, 12: Reagents used in the general synthesis were 2.04 g (1.35 mmol) of **5**, 25.6 g (121.9 mmol) of cyclohexyl iodide in 30 mL DMF. Purification by chromatography column (CHCl₃/Hex 1:1 → EtOAc) afforded 1.123 g of pure product (Yield: 60 %). ¹H NMR (CDCl₃): 10.28 (s, 8H, -OH), 7.09-6.96 (m, 16H, ArH), 4.46 (t, 2H, ³J_{HH} = 7.6 Hz, Ar-CH-CH₂-), 4.27-4.22 (m, 6H Ar-CH₂-Ar), 3.48 (d, 4H, ²J_{HH} = 14.0 Hz, Ar-CH-CH₂), 2.16 (s, 10H, -CH₂-), 1.2 (s, 72H, C(CH₃)₃). ¹³C NMR (CDCl₃): 146.8, 144.3, 131.2, 127.8, 125.97, 125.11, 121.11, 121.9, 34.2, 34.03, 32.8, 31.4, 29.5. MS calcd. for C₉₅H₁₂₄O₈ (1393.1); found: 1411.9 (M+NH₄)⁺.

Synthesis of 2,2'-(Octane-1,8-diyl)bis(5,11,17,23-tetra-*p*-tert-butyl-tetrahydroxycalix[4]arene, 13: Reagents used in the general synthesis were 2.83 g (1.86 mmol) of **6**, 35 g (167.4 mmol) of cyclohexyl iodide in 30 mL DMF. NMR and TLC (CHCl₃/Hex 1:1) showed that the compound was pure enough and did not need any further purification. ¹H NMR (CDCl₃): 10.28 (s, 8H, -OH), 7.09-6.97 (m, 16H, ArH), 4.42 (t, 2H, ³J_{HH} = 8 Hz, Ar-CH-CH₂-), 4.28-4.23 (m, 6H Ar-CH₂-Ar), 3.48 (d, 4H, ²J_{HH} = XX Hz, Ar-CH-CH₂), 2.16 (s, 12H, -CH₂-), 1.2 (s, 72H, C(CH₃)₃). ¹³C NMR (CDCl₃): 146.8, 144.3, 131.3, 127.7, 125.94, 36.5, 34.2, 34.02, 32.8, 31.4, 30.9, 29.5, 29.4. MS calcd. for C₉₆H₁₂₆O₈ (1407.01); found: 1425.9 (M+NH₄)⁺.

Synthesis of 2,2'-(Nonane-1,9-diyl)bis(5,11,17,23-tetra-*p*-tert-butyl-tetrahydroxycalix[4]arene, 14: Reagents used in the general synthesis were 1.935 g (1.26 mmol) of **7**, 23.8 g (113.5 mmol) of cyclohexyl iodide in 30 mL DMF. Purification by

chromatography column (CHCl₃/Hex 1:1 → EtOAc) afforded 0.55 g of pure product (Yield: 31 %). ¹H NMR (CDCl₃): 10.29 (s, 8H, -OH), 7.1-6.98 (m, 16H, ArH), 4.47 (t, 2H, ³J_{HH} = 7.7 Hz, Ar-CH-CH₂-), 4.27-4.22 (m, 6H Ar-CH₂-Ar), 3.49 (d, 4H, ²J_{HH} = 14.05 Hz, Ar-CH-CH₂), 2.16 (s, 14H, -CH₂-), 1.2 (s, 72H, C(CH₃)₃). ¹³C NMR (CDCl₃): 146.8, 144.3, 131.2, 127.8, 127.55, 127.20, 125.96, 125.11, 121.9, 35.6, 34.2, 34.05, 32.8, 31.4, 30.98, 29.6, 29.5. MS calcd. for C₉₇H₁₂₈O₈ (1421.1); found: 1439.9 (M+NH₄)⁺.

Synthesis of 2,2'-(Decane-1,10-diyl)bis(5,11,17,23-tetra-*p*-tert-butyl-tetrahydroxycalix[4]arene, 15: Reagents used in the general synthesis were 2.29 g (1.48 mmol) of **8**, 28 g (133 mmol) of cyclohexyl iodide in 30 mL DMF. Purification by chromatography column (CHCl₃/Hex 1:1 → EtOAc) afforded 0.455 g of pure product (Yield: 21 %). ¹H NMR (CDCl₃): 10.28 (s, 8H, -OH), 7.1-6.97 (m, 16H, ArH), 4.47 (t, 2H, ³J_{HH} = 7.8 Hz, Ar-CH-CH₂-), 4.27-4.22 (m, 6H Ar-CH₂-Ar), 3.48 (d, 4H, ²J_{HH} = 13.6 Hz, Ar-CH-CH₂), 2.16 (s, 16H, -CH₂-), 1.2 (s, 72H, C(CH₃)₃). ¹³C NMR (CDCl₃): 146.8, 144.3, 131.2, 127.8, 125.95, 35.6, 34.2, 34.02, 31.4, 29.6, 29.5. MS calcd. for C₉₈H₁₃₀O₈ (1436.02); found: 1454.01 (M+NH₄)⁺.

Synthesis of [Mn^{III}₂Mn^{II}₂(13-8H)(μ₃-OH)₂(DMF)_{5.5}(MeOH)_{0.5}](H₂O)_{1.5}, 16: MnCl₂·4H₂O (2 eq., 14.1 mg, 0.071 mmol) and **13** (1 eq., 50 mg, 0.0355 mmol) were dissolved in a 1:1 DMF/MeOH mixture (20 mL). After 10 minutes of stirring Et₃N (0.05 mL) was added and the resulting deep purple solution stirred for 2 hrs. The reaction mixture was filtered to leave a deep purple solution. Purple crystals suitable for diffraction studies were obtained upon slow evaporation of the mother liquor. **Crystal data for 16 (CCDC ?????????):** C₁₁₃H_{165.5}N_{5.5}O_{18.5}Mn₄, *M* = 2116.76, Purple Block, 0.02 x 0.02 x 0.09 mm³, monoclinic, space group *P*2₁/*c*, *a* = 25.1565(8), *b* = 20.0930(6), *c* = 22.7572(7) Å, β = 97.681(2)°, *V* = 11399.9(6) Å³, *Z* = 4, Bruker D8 with PHOTON 100 detector, synchrotron radiation (λ = 0.77490 Å), *T* = 100(2)K, 2θ_{max} = 41.5°, 65220 reflections collected, 8958 unique (*R*_{int} = 0.1114). Final *Goof* = 1.102, *R* = 0.1210, *wR* = 0.2991.

Synthesis of [Mn^{III}₂Mn^{II}₂(14-8H)(μ₃-OH)₂(MeOH)(dmf)₅](MeOH)(dmf)(H₂O), 17: MnCl₂·4H₂O (4 eq., 27.8 mg, 0.14 mmol) and **14** (1 eq., 50 mg, 0.035 mmol) were dissolved in a 1:1 DMF/MeOH mixture (20 mL). After 10 minutes of stirring Et₃N (0.05 mL) was added and the resulting deep purple solution stirred for 2 hrs. The reaction mixture was filtered to leave a deep purple solution. Purple crystals suitable for diffraction studies were obtained upon slow evaporation of the mother liquor. **Crystal data for 17 (CCDC ?????????):** C₁₁₇H₁₇₆N₆O₂₀Mn₄, *M* = 2206.39, Purple Block, 0.3 x 0.3 x 0.4 mm³, triclinic, space group *P*-1, *a* = 12.375(3), *b* = 18.727(4), *c* = 25.238(5) Å, α =

84.03(3), $\beta = 88.68(3)$, $\gamma = 89.00(3)^\circ$, $V = 5815(2) \text{ \AA}^3$, $Z = 2$, Bruker Apex-II diffractometer, Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), $T = 100(2)\text{K}$, $2\theta_{\text{max}} = 41.1^\circ$, 42921 reflections collected, 11547 unique ($R_{\text{int}} = 0.1056$). Final $Goof = 1.077$, $RI = 0.0963$, $wR2 = 0.2652$.

Synthesis of $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(15\text{-}8\text{H})(\mu_3\text{-OH})_2(\text{dmf})_6](\text{dmf})_{1.5}(\text{MeOH})_{0.5}(\text{H}_2\text{O})_{1.5}$, **18:** $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (1 eq., 6.9 mg, 0.0348 mmol) and **15** (1 eq., 50 mg, 0.0348 mmol) were dissolved in a 1:1 DMF/MeOH mixture (20 mL). After 10 minutes of stirring Et_3N (0.05 mL) was added and the resulting deep purple solution stirred for 2 hrs. The reaction mixture was filtered to leave a deep purple solution. Purple crystals suitable for diffraction studies were obtained upon slow evaporation of the mother liquor. **Crystal data for 18 (CCDC ?????????):** $\text{C}_{121}\text{H}_{181.5}\text{N}_{7.5}\text{O}_{19.5}\text{Mn}_4$, $M = 2272.99$, Purple Block, $0.1 \times 0.15 \times 0.04 \text{ mm}^3$, triclinic, space group $P-1$, $a = 12.7808(5)$, $b = 19.2134(8)$, $c = 27.4523(12) \text{ \AA}$, $\alpha = 74.294(2)$, $\beta = 82.588(3)$, $\gamma = 85.413(2)^\circ$, $V = 6428.2(5) \text{ \AA}^3$, $Z = 2$, Bruker D8 with PHOTON 100 detector, synchrotron radiation ($\lambda = 0.77490 \text{ \AA}$), $T = 100(2)\text{K}$, $2\theta_{\text{max}} = 62.4^\circ$, 98239 reflections collected, 31909 unique ($R_{\text{int}} = 0.0399$). Final $Goof = 1.024$, $RI = 0.0914$, $wR2 = 0.2740$.

Synthesis of $[\text{Mn}^{\text{III}}_4\text{Gd}^{\text{III}}_4(14\text{-}8\text{H})(\mu_3\text{-CO}_3)_2(\mu_3\text{-OH})_4(\text{H}_2\text{O})_6(\text{dmf})_6](\text{dmf})_6(\text{MeOH})_4$, **19:** $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (2 eq., 13.9 mg, 0.071 mmol), $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (1 eq., 9.3 mg, 0.035 mmol) and **14** (1 eq., 50 mg, 0.035 mmol) were dissolved in a 1:1 DMF/MeOH mixture (20 mL). After 10 minutes of stirring Et_3N (0.05 mL) was added and the resulting deep purple solution stirred for 2 hrs. The reaction mixture was filtered to leave a deep purple solution. Purple crystals suitable for diffraction studies were obtained upon slow evaporation of the mother liquor. **Crystal data for 19 (CCDC ?????????):** $\text{C}_{236}\text{H}_{356}\text{N}_{12}\text{O}_{48}\text{Mn}_4\text{Gd}_4$, $M = 4978.07$, Purple Block, $0.2 \times 0.35 \times 0.4 \text{ mm}^3$, triclinic, space group $P-1$, $a = 14.9707(7)$, $b = 21.9372(6)$, $c = 22.0011(6) \text{ \AA}$, $\alpha = 113.205(3)$, $\beta = 93.322(3)$, $\gamma = 107.520(3)^\circ$, $V = 6203.1(4) \text{ \AA}^3$, $Z = 1$, Bruker APEX-II diffractometer, Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$), $T = 153(2)\text{K}$, $2\theta_{\text{max}} = 153.6^\circ$, 121039 reflections collected, 25512 unique ($R_{\text{int}} = 0.1112$). Final $Goof = 1.039$, $RI = 0.0855$, $wR2 = 0.2296$.

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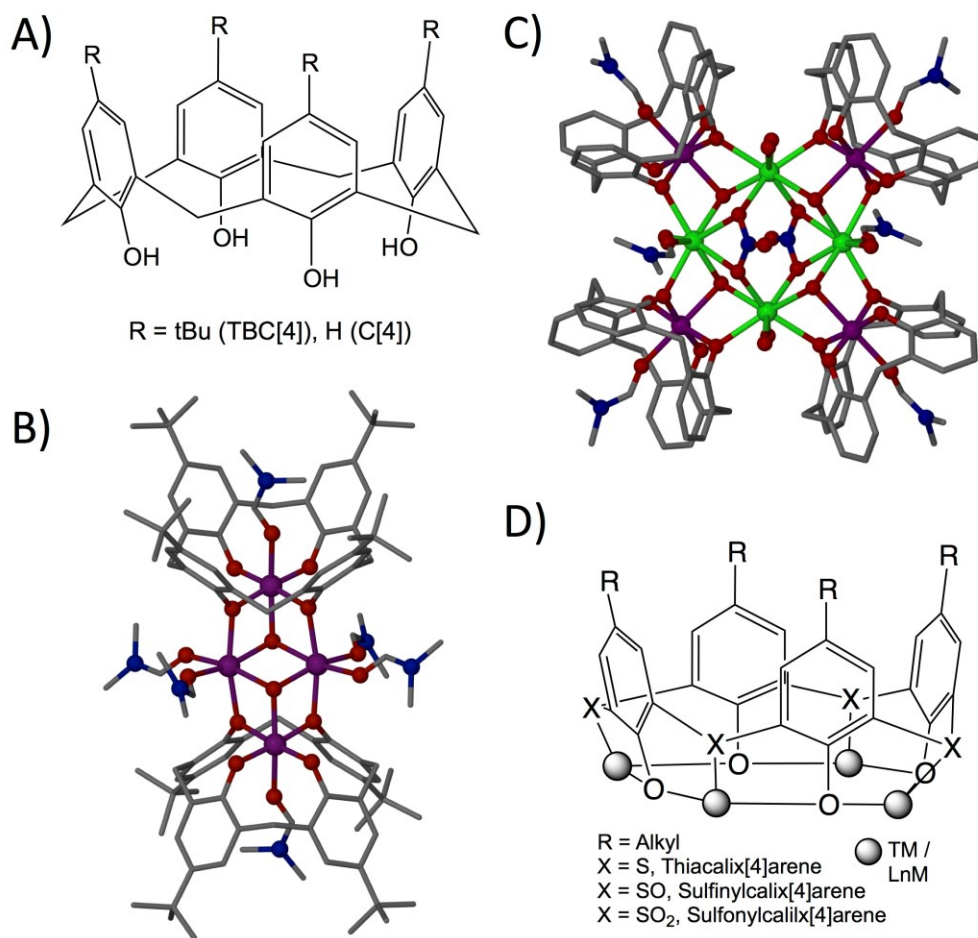


Figure 1. Schematic of the general C[4] framework. B) Structure of a $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{TBC}[4])_2]$ Single-Molecule Magnet (SMM) (9,10). C) Structure of a $[\text{Mn}^{\text{III}}_4\text{Ln}^{\text{III}}_4(\text{C}[4])_4]$ cluster (13,14). D) Schematic of metal ion binding typically found for thia-, sulfinyl- and sulfonyl-bridged C[4]s (21-31).

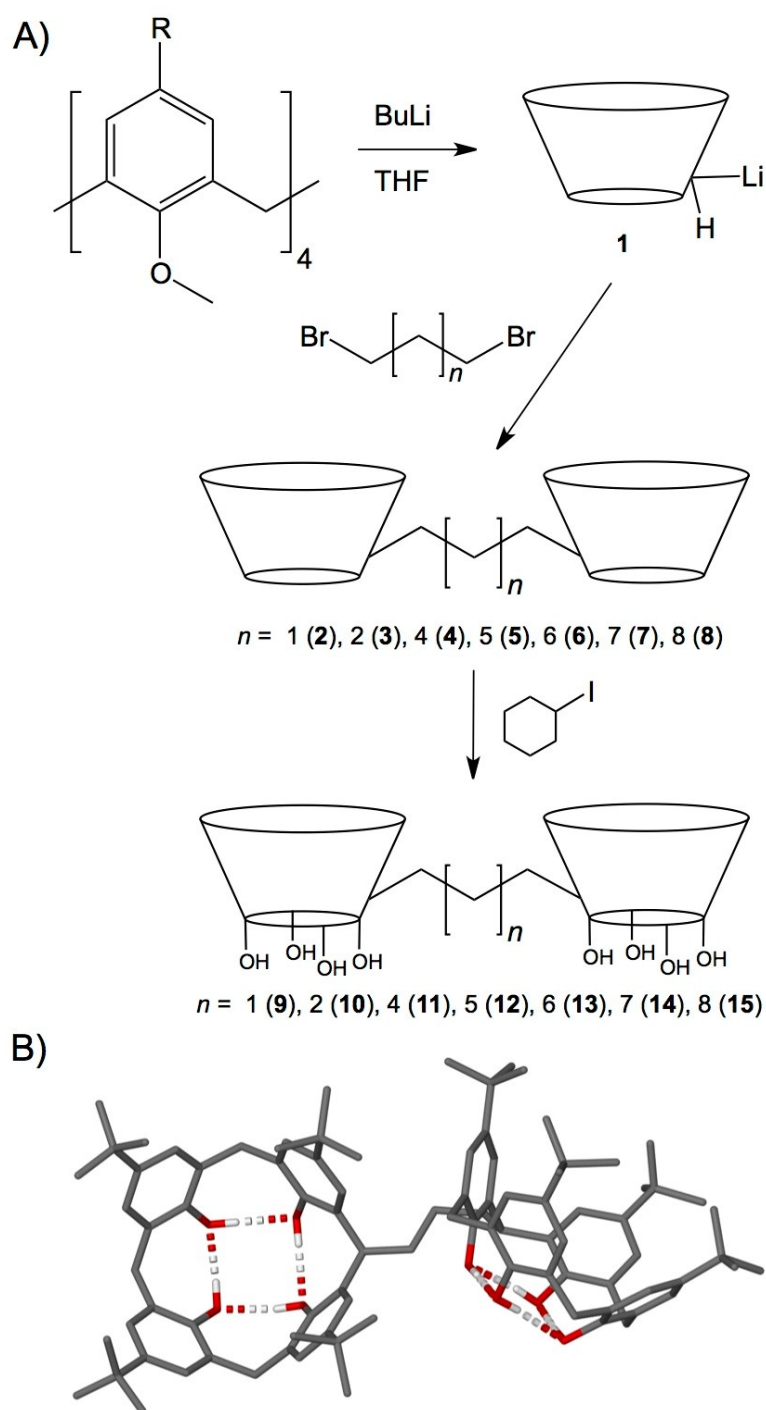


Figure 2. A) Synthetic scheme for the series of bis-TBC[4]s tethered by propyl, butyl and hexyl – decyl chains (compounds **9** – **15** respectively) (47). B) Part of the single crystal X-ray crystal structure of **9**·4MeCN showing the TBC[4] cavities stabilised by H-bonding interactions. H atoms (other than those involved in cavity stabilisation) and MeCN of crystallisation are omitted for clarity.

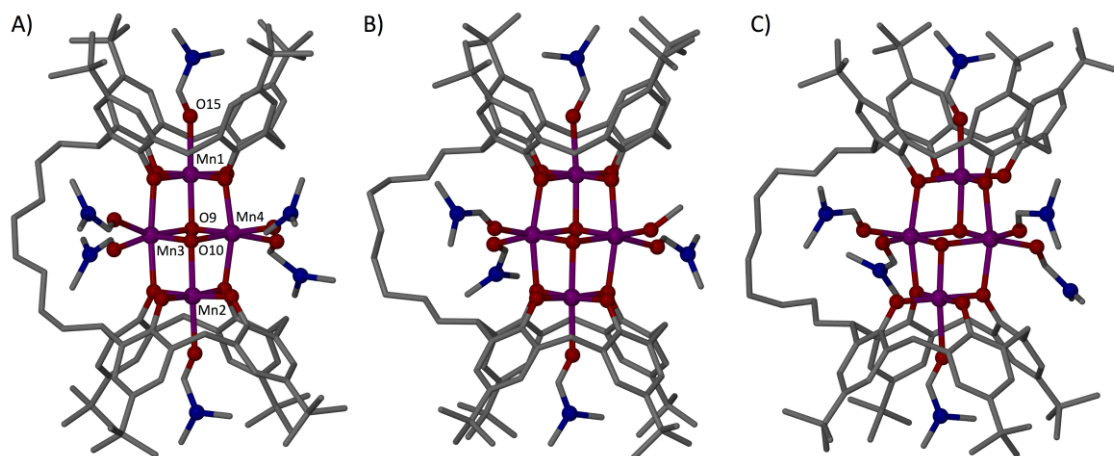


Figure 3. Partial single crystal X-ray structures of the new Mn^{III}₂Mn^{II}₂ clusters (**16** – **18**, A – C respectively) formed with **13** – **15**. Selective labels in (A) relate to discussion of compound **16**. H atoms and solvent of crystallisation have been omitted for clarity. Figures not to scale.

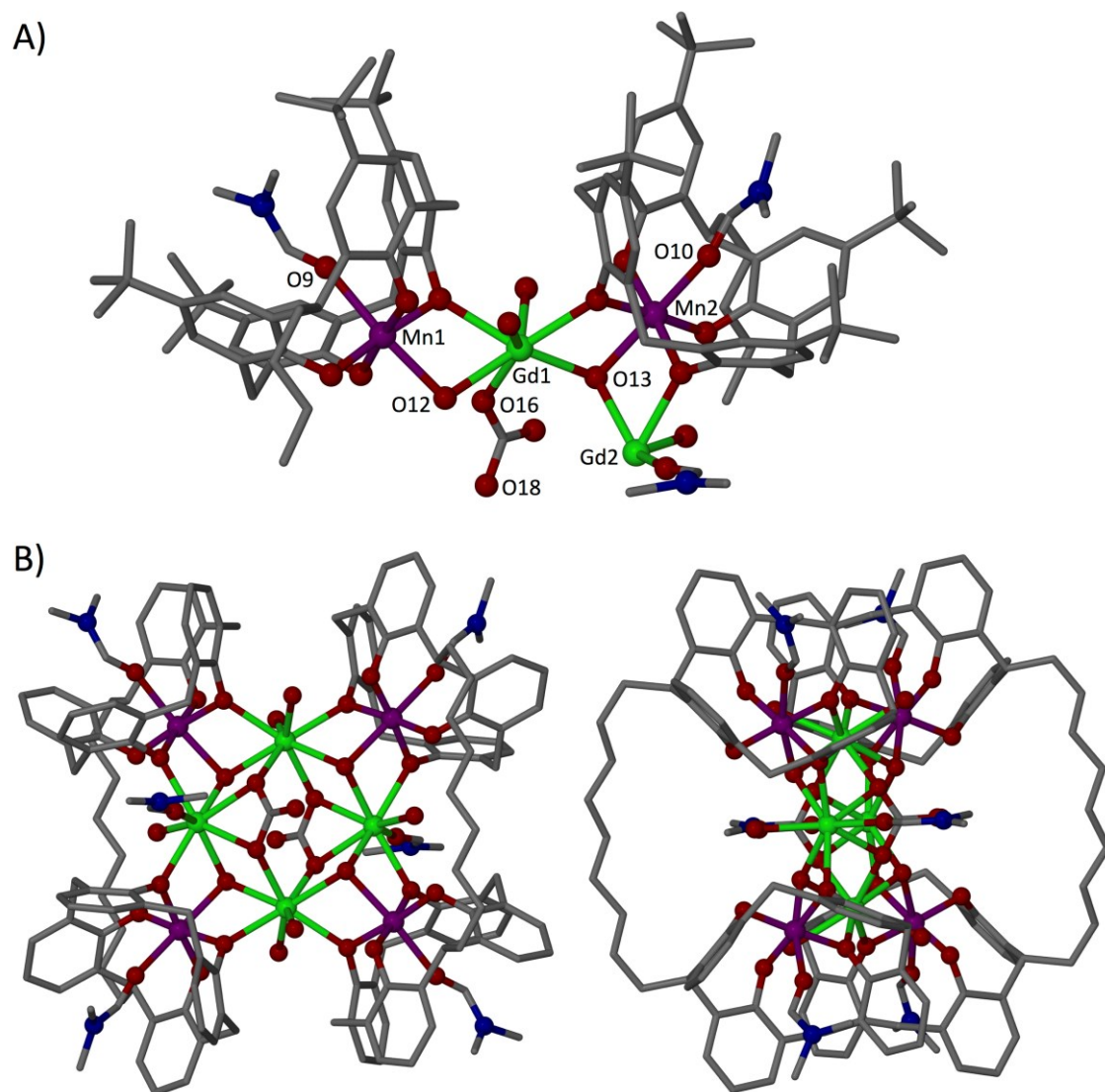


Figure 4. A) Selectively labelled partial single crystal X-ray structure of the new $\text{Mn}^{\text{III}}_4\text{Gd}^{\text{III}}_4$ cluster (**19**) formed with **14**. H atoms and solvent of crystallisation have been omitted for clarity in (A) and (B). TBC[4] upper-rim ^tBu groups are omitted in B such that the two views emphasise the nonyl tether between the TBC[4] sub-units. Figures not to scale.