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Self-Assembly of Nanoscale, Porous *T*-Symmetric Molecular Adamantanoids

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Treatments of lanthanide nitrate or perchlorate and C_2-symmetric 2,2′-hydroxy-1,1′-binaphthalene-6,6′-dicarboxylic acid (6,6′-H_2BDA) led to diastereoselective self-assembly of nanoscale, porous molecular adamantanoids $[Ln_4(BDA)_6(H_2O)_{12}]\cdot 12DMF$ (Ln = Gd, La, **1a**,**b**). These adamantanoid clusters possess perfect *T* symmetry as a result of the C_2-symmetric nature of BDA bridging ligands and C_3-symmetric nature of lanthanide ions. Face-to-face intercluster hydrogen bonds formed between 2,2′-dihydroxyl groups of BDA ligands and carboxylate oxygen atoms direct the assembly of 3D polycages based on chiral molecular adamantanoid building blocks which possess two different types of open channels.

Well-defined supramolecular architectures with inner cavities such as molecular cages, capsules, tubes, and cylinders have received intense attention owing to their implications in host−guest chemistry,[1] as models of biological systems,[2] and in catalysis and molecular machines.[3] In particular, metallosupramolecular systems can be readily assembled from well-chosen metal centers and rigid bridging ligands by taking advantage of many factors including favorable symmetry and entropy effects, preprogrammability of the building blocks, and sometimes the reversibility of metal−ligand ligation.[4] For example, Fujita et al. and Stang et al. have synthesized a series of nanosized molecular cages, bowls, tubules, and capsules using square-planar Pt(II) or Pd(II) metallocorners and C_2- or C_3-symmetric pyridine-based bridging ligands.[5,6] Raymond et al. and Saalfrank et al. described a variety of highly symmetrical M_xL_y clusters derived from octahedronal metal centers and C_2- or C_3-symmetric bis- and tris-bidentate catecholamide ligands.[7,8] Recently, Yaghi et al. and Zaworotko et al. independently reported the synthesis of nanometer-sized polygons based on 1,3-benzenedicarboxylic acid.[9,10] Recent results also indicated that rigid metallosupramolecular architectures can maintain their structures in the absence of guests and thus pointed to the possibility of reversible access to their void spaces. However, chemical functionalization of or direct incorporation of exploitable functional groups into such metallosupramolecular architectures, which is critical to the development of functional supramolecular systems, remains essentially unexplored.

Our recent investigations of metallosupramolecular architectures built from bridging ligands containing exploitable functional groups have led to new materials that are capable of bulk enantioselective separations and chiral sensing.[11] We report here diastereoselective self-assembly of nanoscale, porous *T*-symmetric molecular adamantanoids starting from simple lanthanide(III) salts and C_2-symmetric 2,2′-hydroxy-1,1′-binaphthalene-6,6′-dicarboxylic acid (6,6′-H_2BDA). We envisioned that the combination of C_2-symmetric bridging (ditopic) ligands with potentially C_3-symmetric (tritopic)

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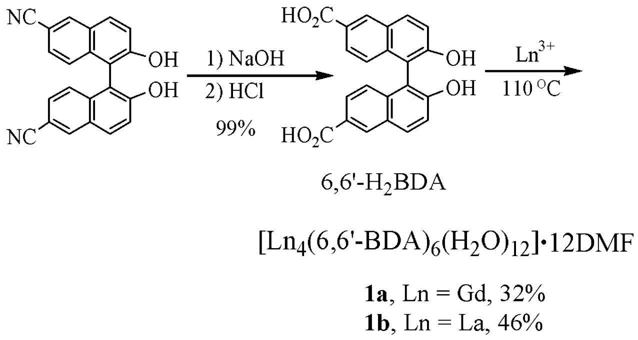
Scheme 1



metal ions could lead to supramolecular polyhedra with *T* symmetry. Of particular interest to us is the introduction of the 2,2′-dihydroxyl groups in the 6,6-H$_2$BDA ligand, which can be utilized by the resulting polyhedra to form ordered higher-dimensional networks through intermolecular hydrogen bonds and, more importantly, are potentially exploitable for enantioselective processes. Strong intermolecular hydrogen-bonding interactions indeed led to 3D polycages based on chiral *T*-symmetric Ln$_4$(BDA)$_6$ (Ln = Gd, La) molecular adamantanoid building blocks.

As illustrated in Scheme 1, 6,6′-H$_2$BDA was prepared in excellent yield from 6,6′-dicyano-2,2′-dihydroxy-1,1′-binaphthalene, which can be readily synthesized from racemic 1,1′-bi-2-naphthol (BINOL).[12] The clusters with the general formula of [Ln$_4$(6,6′-BDA)$_6$(H$_2$O)$_{12}$]·12DMF (Ln = Gd, **1a**, La, **1b**; DMF = *N,N*′-dimethylformamide) were synthesized in moderate yields (32% for **1a** and 46% for **1b**) from hydrated lanthanide nitrate or perchlorate and 6,6′-H$_2$BDA in DMF at 110 °C for 15 days. The crystal formulations were based on elemental microanalysis results and thermogravimetric analyses.[13] Both materials are stable in air and insoluble in water and common organic solvents such as CH$_3$CN, EtOH, MeOH, DMF, and DMSO. The IR spectra of **1a** and **1b** exhibited bands characteristic of carboxylate groups at 1650−1320 cm^{-1}. The very broad peaks around 3414 cm^{-1} suggested the formation of hydrogen bonds in the solid state.

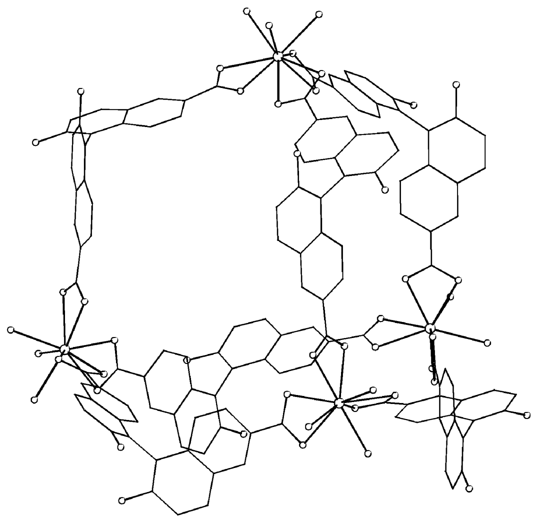


Figure 1. A view of the molecular adamantanoid of **1a**. The circles with increasing sizes represent C, O, and Gd, respectively.

A single-crystal X-ray diffraction study performed on **1a** reveals a nanosized chiral porous cluster with *T* symmetry constructed from C_3-symmetric lanthanide centers and C_2-symmetric 6,6′-BDA groups (Figure 1).[14] The asymmetric unit consists of one-third of a Gd ion, a half 6,6′-BDA group, one coordinated water molecule, and one disordered DMF guest molecule. Within each adamantanoid, the Gd atoms reside on crystallographic 3-fold axes and adopt a nearly idealized tricapped trigonal prismatic geometry by coordinating to three chelating carboxylate groups from three different 6,6′-BDA ligands and three water molecules, with Gd−O bond distances of 2.414(7)−2.519(5) Å. Each of the six BDA groups lies on a crystallographic 2-fold axis and coordinates to two gadolinium atoms through its two chelating carboxylate groups with a Gd−Gd separation of 15.657(1) Å. This arrangement of metal ions and coordination ligands thus leads to a molecular adamantanoid with the vertices occupied by the lanthanide ions and the centers of the 6,6′-BDA ligands. The two naphthalene rings of the BDA ligand are twisted along the pivotal C−C bond at the 1,1′-positions with a dihedral angle of 101.8°; the bulk of the naphthol moieties are pointing away from the cavity of the molecular adamantanoid to give rise to a porous cluster. With four crystallographic C_3 axes running through the metal vertices and three crystallographic C_2 axes bisecting three pairs of opposite BDA edges, each [Ln$_4$(6,6′-BDA)$_6$(H$_2$O)$_{12}$] adamantanoid of **1a** possesses perfect *T* point group symmetry. Metal−ligand ligation has thus induced self-resolution (self-recognition) of the BDA ligands, and all the BDA ligands on each adamantanoid possess the same handedness of chirality.

A space-filling representation of **1a** clearly indicates the formation of a porous, nanosized cage with wide apertures (Figure 2). The overall size of the cluster is ~23 Å, while the aperture on each face has diagonal distances of ~15 × 15 Å. Each adamantanoid cage of **1a** has an open cavity of ~1700 Å^3, which is occupied by six DMF guest molecules. The porous adamantanoid cluster reported here is quite different from previously reported M$_4$L$_4$ polyhedra which are ionic and tightly closed boxes with little or no aperture through the faces of the polyhedra.[7,8] Moreover, to our knowledge, cluster **1** represents the largest molecular adamantanoids that have been crystallographically characterized and is a rare example of chiral molecular polyhedrons.

The packing of admantanoid clusters of **1a** is also noteworthy. Each conformationally rigid adamantanoid cluster of **1a** has 12 hydroxyl groups (O3) and 12 carboxylate

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(13) TGA shows that **1a** and **1b** experience 21.8% and 22.0% weight losses by 330 °C, corresponding to the loss of 12 DMF molecules (22.2% and 22.9% expected for **1a** and **1b**, respectively). Anal. Calcd (found) for C$_{168}$H$_{180}$Gd$_4$N$_{12}$O$_{60}$, **1a**: C, 51.00 (51.78); H, 4.59 (4.28); N, 4.25 (4.13). Anal. Calcd (found) for C$_{168}$H$_{180}$La$_4$N$_{12}$O$_{60}$, **1b**: C, 51.97 (52.01); H, 4.67 (4.32); N, 4.33 (4.71).

(14) X-ray single-crystal diffraction data for **1a** were collected on a Siemens SMART CCD diffractometer. Crystal data for **1a**: cubic, space group $Fd\bar{3}$ (No. 203), $a = 36.392(4)$ Å, $V = 48196(10)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.109$ g·cm^{-3}, μ(Mo Kα) = 1.152 mm^{-1}. Least-squares refinement based on 3525 reflections with $I > 2\sigma(I)$ and 183 parameters led to convergence, with a final R1 = 0.070, wR2 = 0.177, and GOF = 1.09.

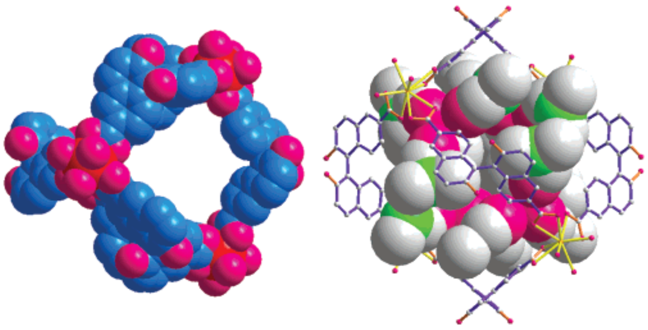

Figure 2. Left: A space-filling model of the adamantanoid cage of **1a** as viewed down the [011] direction. Right: A view showing the inclusion of DMF molecules inside an adamantanoid cage of **1a**.

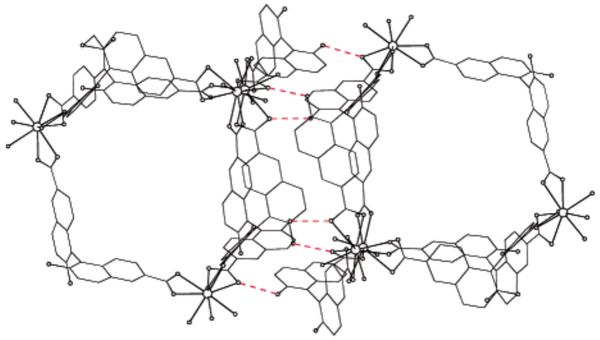

Figure 3. A view of six hydrogen bonds between the faces of adjacent adamantanoid clusters of **1a**. The O2−O3 distance is 2.71(1) Å, while the O2−H3b−O3 angle is 176.5(1)°.

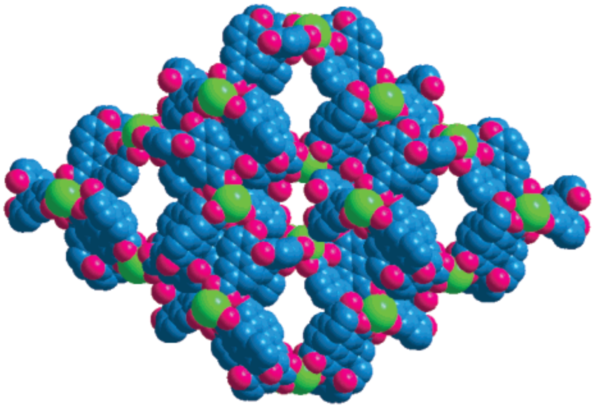

Figure 4. A space-filling model of **1a** as viewed down the [011] direction. Two types of rhombus-shaped open channels are clearly visible.

oxygen (O2) atoms engaged in 24 intercluster hydrogen-bonding interactions with four adjacent adamantanoid clusters. The two faces of the adjacent adamantanoid clusters are related by a $\bar{3}$ axis and thus are ideally positioned to form six pairs of hydrogen bonds between the hydroxyl groups and carboxylate oxygen atoms (Figure 3). As a result of these hydrogen-bonding interactions, each adamantanoid cluster of **1a** is surrounded by four adjacent clusters of opposite handedness, and compound **1a** crystallizes in the centrosymmetric space group $Fd\bar{3}$.[15]

Face-to-face intercluster hydrogen bonds in **1a** thus lead to a neutral 3D polycage with T_h symmetry, as shown in Figure 4. Rhombus-shaped zigzag channels with dimensions of ~11 × 15 Å have resulted and are formed by stacking of adamantanoid clusters of opposite chirality along the [011] directions. Furthermore, smaller rhombus-shaped channels with dimensions of ~6 × 8 Å have formed via the arrangement of four adjacent adamantanoid clusters of opposite chirality in the (011) planes; the void space is filled by six other DMF molecules. Calculations using PLATON indicate that **1a** has 59% of total volume occupied by solvent molecules.[16] Highly directional hydrogen bonding in **1a** has clearly steered the packing of adamantanoid clusters into a porous 3D polycage. The present results exemplify hierarchical control in the self-assembly of supramolecular systems with interactions of varying strength.

We have also prepared the lanthanum analogue **1b** in a procedure similar to that used for the preparation of **1a**. Cell parameter determination,[17] powder X-ray diffraction, IR, and microanalysis results indicated that **1b** is isostructural to **1a**. The insolubility of **1a** and **1b**, presumably due to extensive intercluster hydrogen bonds, has precluded further investigations of their solution properties. Nevertheless, the ability to exchange the included DMF molecules has been demonstrated; the ^{1}H NMR spectrum indicated that ~40% of the included DMF molecules in **1b** have been exchanged upon soaking a solid sample of **1b** in DMSO-d_6 overnight. The powder X-ray diffraction pattern of a DMSO-exchanged sample of **1b** was similar to that of a pristine solid of **1b**.

In conclusion, we have synthesized novel nanosized chiral porous molecular adamantanoids with T symmetry based on C_2-symmetric binaphthyldicarboxylate ligands and C_3-symmetric lanthanide(III) ions. Metal−ligand coordination has directed the self-resolution of racemic BDA ligands to form chiral molecular adamantanoids of $[Ln_4(6,6'\text{-BDA})_6(H_2O)_{12}]$, while hydroxyl groups on the peripheries of BDA ligands allow for the molecular adamantanoids to self-assemble into a unique T_h-symmetric polycage through preordered hydrogen bonds. This work thus illustrates the hierarchical control in the formation of supramolecular assemblies via a combination of metal−ligand ligation and hydrogen-bonding interactions. Ongoing work is aimed at enlarging the open channels of the polycages through structural modifications of dicarboxylic acid bridging ligands and exploiting these novel supramolecular assemblies for potential applications in adsorption, ion exchange, size-selective catalysis.

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Supporting Information Available: Experimental procedures, one table, two figures, and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Attempts to synthesize homochiral solids based on molecular adamantanoids have failed. Enantiopure 6,6′-H_2BDA epimerizes even at 110 °C to give bulk racemic samples of **1a** in the presence of $Gd(NO_3)_3$.

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(17) Unit cell parameters for **1b**: cubic, $a = 36.573(6)$ Å, $V = 48920(16)$ Å^3.