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Mn$_4$-hinged bithiacalix[4]arenes accommodating fullerenes†

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The calixarene-Mn$_4$-calixarene dumbbell-like unit can accommodate different fullerenes with its changeable curved surfaces and the addition of fullerenes completely remodels the packing of the dumbbell units.

Due to their unique photoacceptance properties, fullerenes have drawn much attention in plastic solar cells. To construct self-organized electroactive nanostructures with fullerenes, the formation of stable associates is a pre-requisite. Up to now, a variety of noncovalent associates with different receptors such as cyclodextrins,[1] cyclotriveratrylene[2] and porphyrins[3] have been reported. Besides supramolecular interactions, like $\pi \cdots \pi$ interactions, hydrogen bonds, C–H$\cdots \pi$ interactions and Van der Waals forces,[4] the concave-convex complementary interactions were also found to play a distinct role in the stabilization of the associates.[5] Especially, there were several works on the metal–organic receptors with curved surfaces for the accommodation of fullerenes.[6]

As the third generation of host compounds, calixarene and its derivatives exhibited a special ability for the fullerene encapsulations. Several solid state associates with fullerenes have also been prepared and characterized.[7] However, the solid state associates with a metal-bonded calixarene as the receptor were rarely described. Herein, we present the syntheses and structures of a dumbbell-like metal-calixarene unit with concave surfaces and its three associates with fullerenes, following our successful syntheses of a series of polynuclear compounds with thiacalix[4]arene (H$_4$TC4A) or phenyl-thiacalix[4]arene (H$_4$PTC4A).[8] Single-crystal X-ray diffraction data was used to determine the structures for all the compounds.‡ It is found that the proper concave surfaces of the dumbbell unit are crucial for the molecular recognition of the fullerenes. The receptor compound can be formulized as Mn$_4$(PTC4A)$_2\cdot$2CHCl$_3$ (named as

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1) and three noncovalent associates as [Mn$_4$(PTC4A)$_2$]$_2\cdot$C$_{60}$ (**2a**), [Mn$_4$(PTC4A)$_2$]$_2\cdot$C$_{70}$ (**2b**) and [Mn$_4$(PTC4A)$_2$]$\cdot$2C$_{60}$ (**3**).

Colourless crystal blocks of compound **1**, accompanied by a few orange sheets of compound Mn$_4$(PTC4A)$_2$ (**1′**), were obtained by the solvothermal reaction of Mn(CH$_3$COO)$_2\cdot$4H$_2$O and H$_4$PTC4A in a 1 : 1(v/v) CH$_3$OH–CHCl$_3$ mixed solvent (total 10 mL) with several drops of water at 130 °C. Compounds **2a**, **2b** and **3** can be easily obtained by diffusing the toluene solution of fullerenes into that of **1** or by just mixing them. The crystal structure determinations reveal that all the fullerenes are located at the concave surfaces of the Mn$_4$(PTC4A)$_2$ units and the concave surfaces were adjusted to accommodate either different fullerenes or more fullerene molecules.

The structure of compound **1** consists of dumbbell-like units, which are composed of two PTC4A ligands and an in-between planar Mn$^{II}_4$ core (Fig. 1). The single-crystal X-ray diffraction determination reveals that there is one crystallographically independent PTC4A ligand and that there are two crystallographic sites for the metal atoms (Mn1 and Mn2), adopting a Mn1–Mn2–Mn1A–Mn2A quadrilateral mode. Both the Mn1 and Mn2 atoms are six-coordinated by four phenoxo oxygen atoms and two sulfur atoms. The dumbbell-like unit has a small waist and
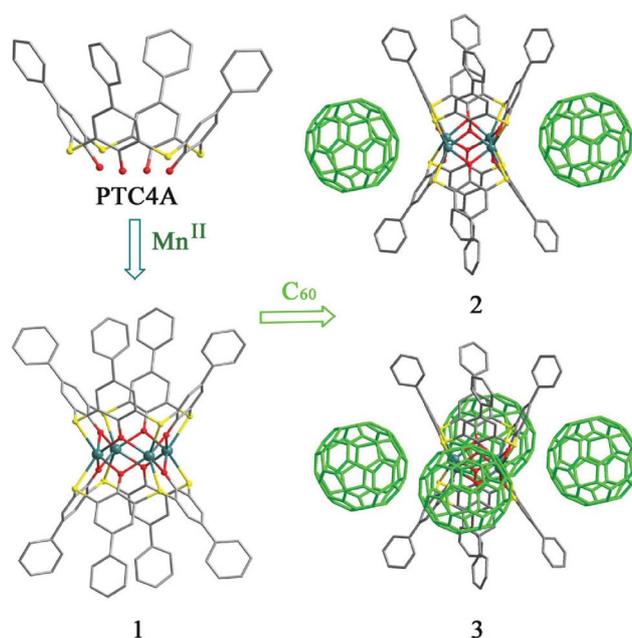

Fig. 1 Scheme for the formation of compounds **1**–**3**.

four curved surfaces with the dihedral angles being 109.9° (for curved surface 1A, measured with the plates through two opposite phenolic aromatic rings from the upper and bottom calixarenes), 139.8° (1B), 109.9° (1C) and 139.8° (1D). The PTC4A ligands adopt a cone conformation and are arranged in an up-down mode. In the extended structure, one phenyl group from one dumbbell-like unit is protruded into the cavity of an opposite PTC4A from an adjacent dumbbell, to form a dimeric 'hand-shake' motif with C–H···π interactions (3.4 Å). The 'hand-shake' motifs are interconnected head-to-tail with each other to form chains (Fig. S1†), which are quite similar to those in the reported PTC4A compounds.[8] That is, the hand-shake motifs appear to be a stable assembly of the PTC4A ligands. The extended structure of compound **1'** is similar to that of **1** and is also formed by dumbbell-like $Mn_4(PTC4A)_2$ units, which also exhibit a 'hand-shake' mode and form chains. Differently, there are no chloroform solvent molecules in the lattice. Furthermore, there are four different crystallographic sites for the Mn atoms and two crystallographically independent PTC4A ligands in an asymmetric unit, which indicates the absence of an inversion centre in the dumbbell-like unit. The dihedral angles for the four curved surfaces are 120.5° (1A), 131.6° (1B), 104.1° (1C) and 118.2°(1D), respectively.

Compounds **2a**, **2b** and **3** are constructed from the isolated dumbbell-like units and fullerenes and the toluene solvent molecules filled in the interstices, whose contribution was subtracted in the structure refinement. However, the ratios of the dumbbell unit to the fullerenes are different for the different complexes, 2 : 1 for **2a** and **2b**, which are isomorphous and 1 : 2 for **3**. The successful assembly of the fullerenes and the dumbbell-like $Mn_4(PTC4A)_2$ units awarded us the opportunity to investigate the interactions between the metal-PTC4A units and the incorporated fullerenes and the transformation of the metal-PTC4A array. It is found that the 'hand-shake' mode of the dumbbell units in **1** was destroyed when the fullerenes were introduced in **2** and **3**(Fig. 2).
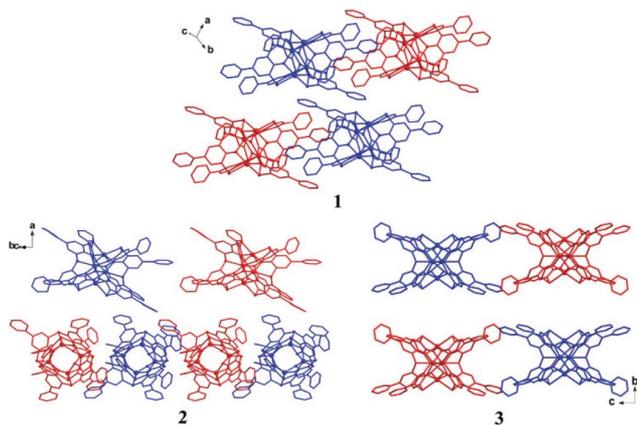

Fig. 2 The arrays of the dumbbell-like units in compounds **1–3**.

In compounds **2** and **3**, the shape of the $Mn_4(PTC4A)_2$ dumbbell-like unit and the coordination environment of the metal ions are similar to those in **1**, except for minor differences in the bond distances and bond angles (Table S2†). The dihedral angles for the four curved surfaces of a $Mn_4(PTC4A)_2$ unit are 122.7° (2A), 114.1° (2B), 130.2° (2C) and 105.1° (2D) in **2a** and 120.1° (3A/3B/3C/3D) in **3**, respectively. These values deviate from

those in **1**, three of the angles become smaller while the fourth turns bigger in **2** and two of the angles become smaller while the other two get bigger in **3**. The supramolecular interactions between the $Mn_4(PTC4A)_2$ units and the fullerenes are mainly $\pi···\pi$ interactions, as indicated by structure analysis (Fig. S2†).[9] The dihedral angle of the aromatic rings in C_{60} that contact with the curved surfaces of each dumbbell units is *ca.* 109°. Theoretically, compound **2/3** can accommodate three/four C_{60} molecules, as there are three/four curved surfaces with angles larger than 109°. With a close examination and comparison of the curved surface angles however, one finds that only the curved surfaces with an angle larger than *ca.* 120° are capable of incorporating C_{60} molecules. The same results can also be gained for compound **2b** (123.4 and 128.4°). The PTC4A ligands in compounds **2a**, **2b** and **3** also adopt a cone conformation and the cavity size formed by the ligands in one dumbbell unit (by measuring the distance between the nearest carbon atoms of two opposite phenyl groups) are 8.0 × 9.5 and 7.6 × 12.6 Å^2 in **2a**, 8.5 × 9.6 and 7.6 × 12.6 Å^2 in **2b** and 8.4 × 9.9 and 8.4 × 9.9 Å^2 in **3**, all of which are larger than the size of C_{60} (7.10 × 7.10 Å^2). However, all the phenyl groups can rotate along the single bonds between the phenyl groups and the phenolic aromatic rings to some extent and some small dihedral angles between two opposite phenyl groups form, which is unfavourable for the formation of the $\pi···\pi$ interactions between the encapsulated spherical fullerene molecules and the PTC4A ligands. That might be the reason why no fullerenes are encapsulated in the cavities of the calixarenes. On the other hand, according to the structural analyses of **2–3**, the curved surface with a dihedral angle larger than 120° might be a recognition site for fullerene molecules.

In the structure of **2**, one dumbbell unit is bound to two fullerenes simultaneously. Each fullerene molecule is clamped by four different $Mn_4(PTC4A)_2$ dumbbell units, with their curved surfaces, to form a crystal nucleus and then the opposite curved surfaces of these four dumbbells are bound to four other fullerene molecules, simultaneously. This results in a '2-4' connection topology of **2**, by repeating the processes (Fig. 3-upper and Fig. S3†). In compound **3**, one $Mn_4(PTC4A)_2$ unit captures four C_{60} molecules, one in each of its four curved surfaces (3A–3D), through $\pi···\pi$ interactions (face to face distance: 3.5–3.6 Å) to form one dimensional chains, which are interconnected into layers by the $\pi···\pi$ interactions (3.8 Å) between the C_{60} molecules. The layers are then interconnected with each other by C–H···π interactions between the phenyl groups from different layers to achieve a three-dimensional '4-6' topology (Fig. 3-bottom and Fig. S4–6†). In addition, all the C_{60} molecules in **3** are interconnected into zigzag fullerene chains (Fig. S5†) in which the two nearest C_{60} molecules are separated by 10.0 Å (consistent with the distance observed in a face-centred cubic lattice of the pure C_{60} crystals[10]). The two closest adjacent $Mn_4(PTC4A)_2$ units are separated by 10.7 Å (centre-to-centre) in **2a**, 10.8 Å in **2b** and 14.4 Å in **3** by C_{60} molecules, all of which are shorter than the distance found in compound **1** (14.8 Å). The $Mn_4(PTC4A)_2$ dumbbell unit can capture different or different amounts of fullerenes with its changeable curved surfaces and the addition of fullerenes completely remodelled the stable packing diagrams of **1**, leading to the formation of the different associates. Taking the preparation of compounds **2** and **3** into account, one can find that the formation of the compounds is governed by the fullerene concentration,
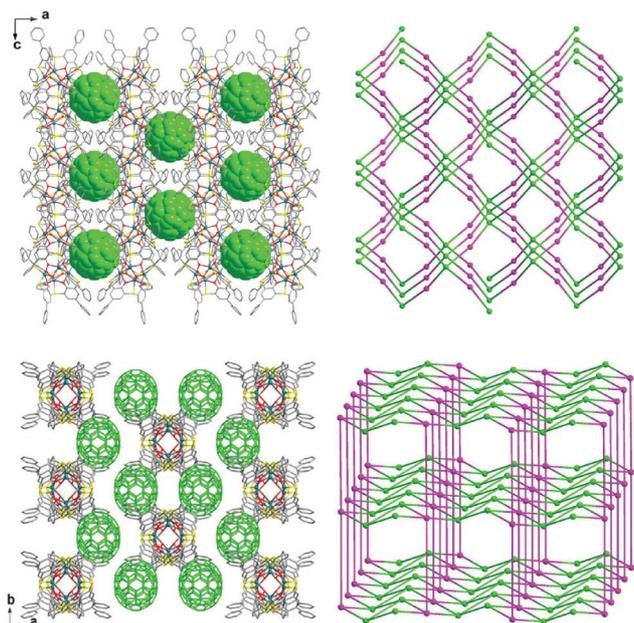
Fig. 3 Packing diagrams (left) and topologies (right) for compounds **2** (upper) and **3** (bottom). Purple ball: $Mn_4(PTC4A)_2$, Green ball: fullerene.

but not the type of fullerenes, that is, when the concentration of fullerenes is not high (or when the fullerene solution diffuses into the solution of **1**), the compounds with a lower fullerene/dumbbell ratio (1 : 2) formed, no matter whether the fullerene was C_{60} or C_{70}, otherwise, the compound with a higher fullerene/dumbbell ratio (2 : 1) formed.

In summary, dumbbell-like $Mn_4(PTC4A)_2$ units and their assemblies with fullerenes were obtained and structurally determined. It is the first time that the metal-hinged thiacalix[4]arene-fullerene compounds have been gained to date. It was found that the curved surfaces of the dumbbell with a dihedral angle larger than 120° are recognition sites for the fullerenes. This work could promote the design and synthesis of metal-calixarene-fullerene complexes for use as functional materials.

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