

Fullerene-like Polyoxotitanium Cage with High Solution Stability

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S Supporting Information

ABSTRACT: We present the formation of the largest titanium–oxo cluster, $[\text{Ti}_{42}(\mu_3\text{-O})_{60}(\text{OiPr})_{42}(\text{OH})_{12}]^{6-}$, with the first fullerene-like Ti–O shell structure. The $\{\text{Ti}_{42}\text{O}_{60}\}$ core of this compound exemplifies the same icosahedral (I_h) symmetry as C_{60} , the highest possible symmetry for molecules. According to the coordination environments, the Ti centers in this cluster can be arranged into a Platonic $\{\text{Ti}_{12}\}$ icosahedron and an Archimedean $\{\text{Ti}_{30}\}$ icosidodecahedron. The solution stability of this cluster was confirmed by electrospray ionization mass spectrometry. The spherical body of the $\{\text{Ti}_{42}\text{O}_{60}\}$ core has an inside diameter of 1.05 nm and an outside diameter of 1.53 nm, which could be directly visualized by high-resolution transmission electron microscopy. Our results demonstrate that titanium oxide can also form fullerene-like shell structures.

The discovery of fullerenes in 1985 opened an entirely new branch of chemistry.^{1,2} After that, the synthesis of highly connected and symmetric spherical clusters and cages has made up a challenging field for chemists and material scientists.^{3–6} The ordered arrangement of atoms in these giant molecules presents aesthetically pleasing structures and intriguing physical properties.^{7–9} Although the synthesis of inorganic fullerene-like structures has attracted much interest, the known examples of such regular polyhedral clusters are quite few, with representative examples like $\{\text{As}_{20}\}$ reported by Eichhorn,¹⁰ $[\{\text{Cp}^*\text{Fe}(\eta^5\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-P}_5)\}_{12}\{\text{CuCl}\}_{10}\{\text{Cu}_2\text{Cl}_3\}_5\{\text{Cu}(\text{CH}_3\text{CN})_2\}_5]$ reported by Scheer,¹¹ and $\{\text{Mo}_{132}\text{O}_{372}\}$ reported by Müller.¹² It still remains a great challenge to explore the fullerene-like clusters of other molecular systems.

Polyoxotitanate nanoparticles are technologically important materials with wide applications in photovoltaic cells, solar energy conversion, and degradation of environmental pollutants.^{13–17} As the structure and reactivity model compounds of polyoxotitanate nanoparticles, molecular titanium–oxo clusters have recently attracted increasing research interest, and their precise structures have allowed theoretical studies of electronic and catalytic properties.^{18–21} Although many polyoxotitanium cages with different structural types have been prepared, the point-group symmetries of these molecules are usually very low.^{22–24} On the other hand, the nuclearities of polyoxotitanium clusters might have a significant size effect on their physical characteristics.^{20,25} Before this work, the largest polyoxotitanate cluster reported contained 34 titanium atoms.¹⁹ Here we report the preparation and characterization of the first fullerene-like titanium oxide spherical molecule,

$\text{H}_6[\text{Ti}_{42}(\mu_3\text{-O})_{60}(\text{OiPr})_{42}(\text{OH})_{12}]$ (**TOF-1**, where TOF = titanium oxide fullerene), which is also the largest titanium–oxo cluster characterized to date.

Electrospray ionization mass spectrometry (ESI-MS) analysis indicated that the cluster core of **TOF-1** is stable in solution. In addition, dispersing the clusters into the cavities of a thin film of HKUST-1 (or $\text{Cu}_3(\text{BTC})_2$, BTC = 1,3,5-benzenetricarboxylate) allowed the cores of **TOF-1** to be clearly visualized by high-resolution transmission electron microscopy (TEM). The phase purity, band-gap structure, and thermal stability of **TOF-1** were also investigated.

Through the solvothermal reaction of $\text{Ti}(\text{OiPr})_4$ in the presence of formic acid, colorless crystals of **TOF-1** were obtained in high yield. Single-crystal X-ray diffraction analysis revealed that **TOF-1** crystallizes in a highly symmetric cubic crystal system with space group $Fm\bar{3}$. The cluster core of **TOF-1** contains 42 Ti atoms bridged by 60 $\mu_3\text{-O}^{2-}$ ions to give a spherical structure built up from 12 pentagonal $\{(\text{Ti})\text{Ti}_5\}$ fragments (Figure 1). The outer face of the **TOF-1** cluster is functionalized with 42 isopropoxide molecules as terminal ligands, with Ti–O_{term} bond lengths in the range between 1.70 and 1.80 Å. The spherical body of **TOF-1** has an inside diameter of 1.05 nm (taking off the ionic radius of two Ti^{4+} ions) and an outside diameter of 1.53 nm (not including carbon and hydrogen atoms). According to the coordination environments, the 42 Ti atoms in **TOF-1** can be divided into two different kinds: 12 seven-coordinate Ti (Ti1) and 30 five-coordinate Ti (Ti2 and Ti3) (Figure S1). The pentagonal-bipyramidal geometry around Ti1 is further completed by a terminal hydroxyl ligand located inside the cluster shell of **TOF-1**. Remarkable is the observation that the central $\{\text{TiO}_7\}$ unit is connected to five $\{\text{TiO}_5\}$ units through sharing of edges, while each $\{\text{TiO}_5\}$ unit is further linked to four adjacent ones by sharing of corners. The packing of **TOF-1** clusters in the crystal structure gives a highly ordered cubic arrangement (Figure S2).

The spherical structure of **TOF-1** is full of symmetry beauty, which can be emphasized in Figure 2. First, the 12 seven-coordinate Ti atoms are arranged into a Platonic icosahedron, endowing the **TOF-1** cluster with icosahedral (I_h) symmetry, which is the highest possible molecular symmetry²⁶ and can be compared to that of the C_{60} structure. Second, the remaining 30 five-coordinate Ti atoms form an icosidodecahedron, which is an Archimedean solid with 12 pentagonal $\{\text{Ti}_5\}$ faces and 20 triangular $\{\text{Ti}_3\}$ faces. The $\{\text{Ti}_{12}\}$ icosahedron is encapsulated

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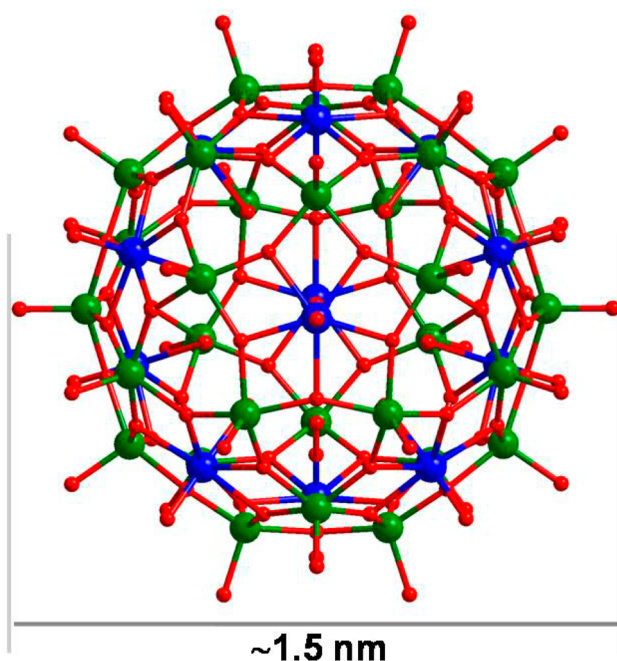


Figure 1. Molecular structure of cluster **TOF-1**. The seven-coordinate Ti1 atoms, five-coordinate Ti2 and Ti3 atoms, and O atoms are presented in blue, green, and red, respectively. H and C atoms have been omitted for clarity.

by the $\{Ti_{30}\}$ icosidodecahedron through location of its 12 vertices at the centers of the 12 pentagonal $\{Ti_5\}$ faces.

Considering the I_h symmetry of **TOF-1** and the 60 oxygen atoms in its shell inspired us to conjecture that an O_{60} fullerene might exist in this structure. Indeed, as shown in Figure 2e, each seven-coordinate Ti1 atom stabilizes a pentagonal $\{O_5\}$ ring, which is the necessary building unit of fullerene topologies, and the 12 Ti1 atoms in **TOF-1** give rise to the formation of 12 $\{O_5\}$ pentagons, which also agrees with the 12 $\{C_5\}$ pentagons in C_{60} . Around each $\{O_5\}$ pentagon, five distorted $\{O_6\}$ rings can be identified (Figure S3). Four of the

six oxygen atoms in each of these $\{O_6\}$ rings are from the coordination geometry of Ti2 or Ti3, while the other two oxygen atoms are coordination atoms of Ti1. The distortion of the $\{O_6\}$ ring from the standard hexagon should be attributed to the five-coordinate tetragonal-pyramidal geometry of Ti2/Ti3, which results in a $\{O_4\}$ square. Compared with the 120° angles in a hexagon, such 90° angles are compressed and give rise to distortions. Similar to C_{60} , each $\{O_6\}$ ring is also alternately surrounded by three $\{O_5\}$ pentagons and another three $\{O_6\}$ rings. Therefore, here we first obtained a fullerene arrangement of O_{60} that is stabilized by titanium atoms (Figure 2f).

From the above structural analysis, we can conclude that **TOF-1** is a highly symmetrical structure consisting of several regular polyhedra. The presences of the $\{Ti_{12}\}$ icosahedron, the $\{Ti_{30}\}$ icosidodecahedron, and the O_{60} fullerene cage confirm that **TOF-1** is a fullerene-type titanium oxide structure. Moreover, if we remove the seven-coordinate Ti1 atoms and also the terminal ligands, a $\{Ti_{30}O_{60}\}$ sphere is obtained, giving rise to a fullerene-type TiO_2 nanoball structure (Figure S4).

The phase purity of the crystalline samples of **TOF-1** was proved by powder X-ray diffraction (PXRD) analysis (Figure S5). The solid-state UV absorption spectrum of **TOF-1** indicates that it is transparent in the range of 400–800 nm (Figure 3a). The optical band gap of **TOF-1** was estimated to be 3.62 eV according to the Kubelka–Munk function.²⁷ To study the thermal stability of **TOF-1**, thermogravimetric analysis (TGA) was performed on polycrystalline samples under a N_2 atmosphere at a heating rate of $10^\circ C/min$ from 30 to $800^\circ C$ (Figure S7). The shell structure of **TOF-1** is retained up to $280^\circ C$. The weight loss between 30 and $300^\circ C$ can be attributed to the decomposition of the 42 isopropoxide ligands. The calculated weight loss is 43.83%, and the observed loss was 42.60%.

Despite the ever-increasing research interest in the synthesis of polyoxotitanium clusters, their solution behavior is often poorly understood. Samples of **TOF-1** could be readily dissolved in toluene (~ 1.8 g/L). We then used ESI-MS to

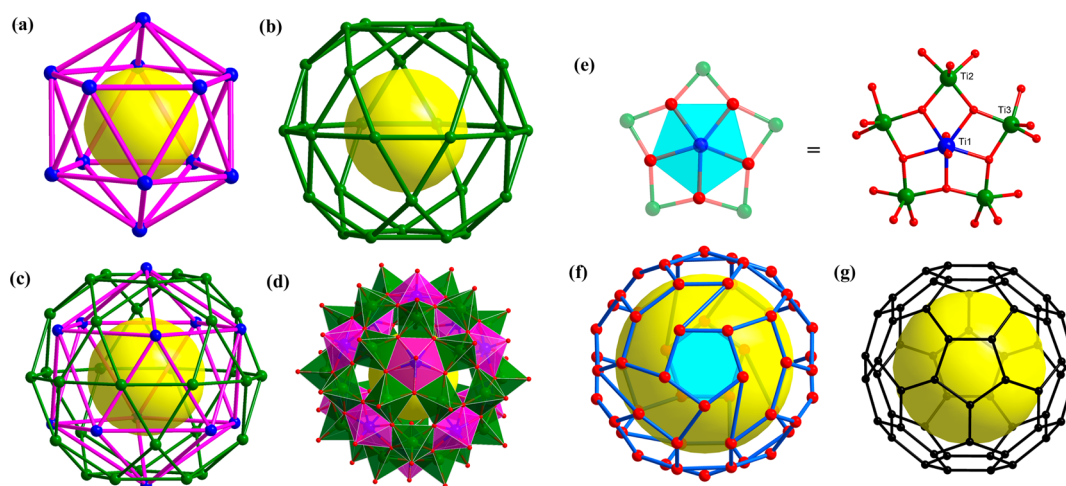


Figure 2. Topological drawings of the polyhedra in **TOF-1**. (a) The Platonic icosahedral arrangement of the 12 seven-coordinate Ti atoms. (b) The Archimedean icosidodecahedral arrangement of the 30 five-coordinate Ti atoms. (c) Interpenetrating display of the $\{Ti_{12}\}$ icosahedron@ $\{Ti_{30}\}$ icosidodecahedron. (d) Polyhedral presentation of the molecular structure of **TOF-1**, with the 12 $\{TiO_7\}$ and 30 $\{TiO_5\}$ units highlighted in purple and green, respectively. (e) Evolution of the $\{O_5\}$ pentagon from the pentagonal-bipyramidal coordination geometry of Ti1 atoms (blue), which is further stabilized by the surrounding Ti2 and Ti3 atoms (green). (f, g) Spherical structures of O_{60} in **TOF-1** and C_{60} . The spherical hollow characteristics of the above polyhedra are indicated by semitransparent yellow balls.

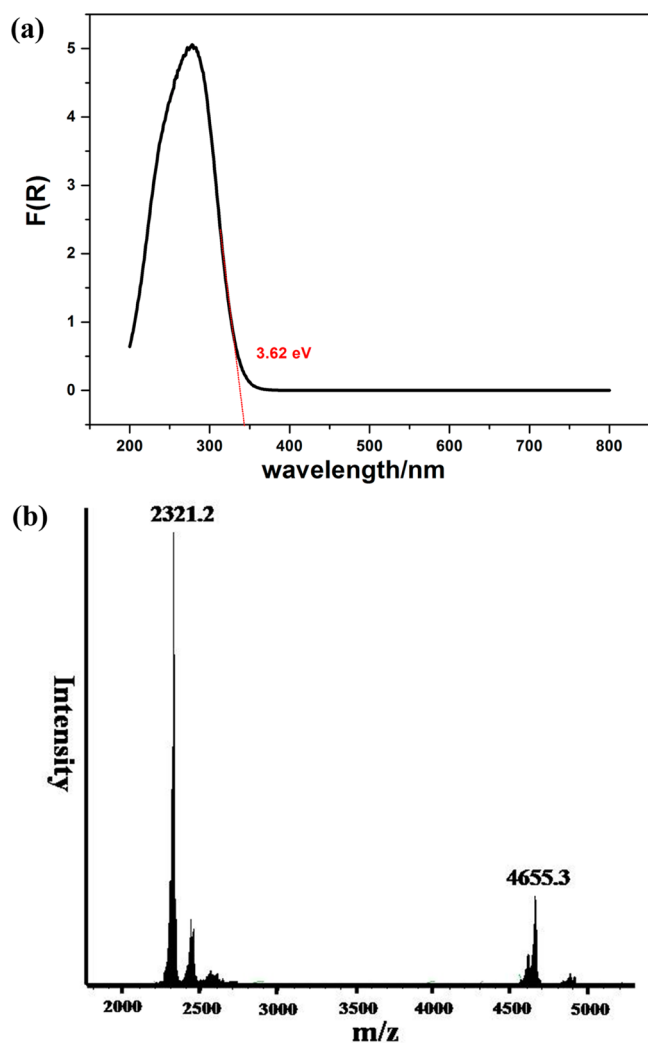


Figure 3. (a) Solid-state UV absorption spectrum of TOF-1. (b) Negative-mode ESI-MS spectrum of TOF-1 in toluene/methanol solution.

investigate the solution stability of TOF-1 in mixed toluene/methanol solvents. As shown in Figure 3b, the signals centered at m/z 2321.2 and 4655.3 can be attributed to the species $\{H_{12}Ti_{42}(O)_{60}(CH_3O)_{42}(CH_3OH)_{10}(H_2O)_2\}^{2-}$ and $\{H_7Ti_{42}(O)_{60}(CH_3O)_{42}(CH_3OH)_{10}(H_2O)_3\}^-$, respectively, in which the terminal isopropoxide ligands have been completely exchanged with methoxide ligands. Moreover, solution electronic absorption spectra of TOF-1 in toluene remained unchanged for several days (Figure S10). These studies confirm the high solution stability of the $\{Ti_{42}O_{60}\}$ cluster core of TOF-1.

From the view of size, the diameter of the cluster core of TOF-1 is 1.53 nm, making it comparable to that of nanosized TiO_2 particles. Therefore, it might be possible to directly observe individual TOF-1 clusters by TEM analysis, as has been done for those nanoparticles in materials research. To carry out such single-cluster inspection, the molecules of TOF-1 should be isolated from each other. Taking advantage of the high solution stability of TOF-1, we decided to use the recently developed liquid-phase epitaxy (LPE) layer-by-layer approach to disperse TOF-1 clusters into the cavities of a thin film of HKUST-1 (Figure S11).²⁸ The spray version of the LPE process was applied in a sequential fashion with $Cu(OAc)_2$,

H_3BTC , and TOF-1 (Figure S12). Between successive steps, the substrate was rinsed with pure ethanol. After 60 LPE cycles, a thin film of TOF-1@HKUST-1 was obtained. The compact and homogeneous distribution of TOF-1 in the film was confirmed by TEM images and electron mapping records (Figure 4). In addition, individual TOF-1 cores could be clearly

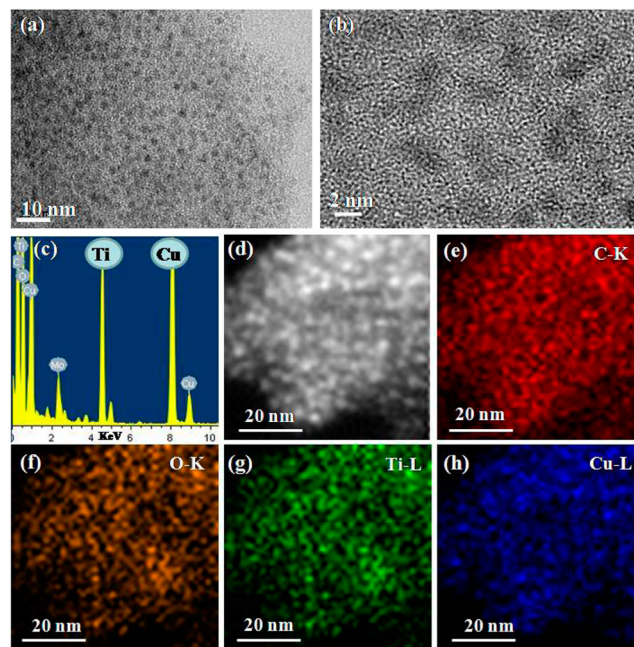


Figure 4. Characterization of the TOF-1@HKUST-1 thin film obtained via the in situ layer-by-layer LPE approach: (a, b) TEM images; (c) TEM-EDS data; (d–h) element mapping.

observed by high-resolution TEM. The size of the identifiable dark dots compares well with the diameter of the TOF-1 cluster as determined by X-ray crystallography. This is the first time that a single polyoxotitanate cluster has been directly imaged by microscopy.

In summary, the first fullerene-like titanium oxide molecule has been synthesized and characterized, confirming that highly symmetrical, full-shell, spherical Ti–O structural motifs can be achieved through the proper arrangement of $\{TiO_x\}$ coordination polyhedra. The high solution stability of the TOF-1 clusters allows them to be dispersed into HKUST-1 thin films. Moreover, TOF-1 represents a large cluster core with diameter above 1.5 nm, which can be directly visualized by high-resolution TEM. We expect that this finding can open a direction for the preparation of highly symmetric titanium–oxo clusters, which will not only enrich the inorganic fullerene family but also benefit the discovery of novel titanium oxide materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b00613.

Experimental and characterization details; additional figures and images; PXRD pattern; IR, 1H NMR, ESI-MS spectra; and TGA analysis (PDF)

Crystallographic data for TOF-1 (CIF)

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Notes

The authors declare no competing financial interest.

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