Trapping an unprecedented Ti$_3$C$_3$ unit inside the icosahedral C$_{80}$ fullerene: a crystallographic survey†

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The sub-nanometer cavity of fullerene cages is an ideal platform to accommodate otherwise unstable species for accurate structural characterization with, for example, rather accurate single crystal X-ray diffraction (XRD) crystallography. Herein, we report the successful entrapment of an isolated Ti$_3$C$_3$ moiety inside the icosahedral-C$_{80}$ cage to form Ti$_3$C$_3$@I$_{h}$-C$_{80}$ via an arc-evaporation process in the gas phase. The single crystal XRD crystallographic results unambiguously reveal that the C$_{36}$-unit adopts an unprecedented cyclopropane-like structure which coordinates with the three titanium atoms in an unexpected fashion where the triangular C$_3$-unit is nearly perpendicular to the Ti$_3$-plane. The intercalation of a cyclopropanated C$_3$-unit into the titanium layer is thus unambiguously confirmed. The theoretical results reveal that the Ti$_3$C$_3$ cluster transfers six electrons to the I$_h$-C$_{80}$ cage so that each titanium atom has a positive charge slightly above +2 and the C$_3$-unit is negatively charged with about −1. It is noteworthy that this is the first observation of the cyclopropane-coordination fashion in any reported organometallic complex, providing new insights into coordination chemistry.

Introduction

Fullerene cages serve as a protector to host a variety of isolated metal atom(s) or otherwise unstable metallic units to form so-called endohedral metallofullerenes (EMFs). By virtue of the solubility of EMFs, high-quality single crystals can be obtained and thus the interplay between the metallic species within the clusters, in addition to the metal–cage interactions, is possible to study by the sophisticated single crystal X-ray diffraction (XRD) approach. Up to now, a collection of EMFs containing one to three pure metal atoms, which are called mono-, di- and tri-EMFs, respectively, has been crystallographically confirmed.1–4 Interesting results such as direct bonding between the repulsive metal ions (e.g., Lu$^{2+}$–Lu$^{2+}$, U$^{3+}$–U$^{3+}$ or Y$^{2+}$–Y$^{2+}$) have been achieved taking advantage of the confinement effect of the fullerene cages.5–7

In addition, various metallic clusters, such as metal nitride, carbide, oxide, sulfide and even cyanide,11 have been successfully trapped inside fullerene cages. It is noteworthy that only with the protection of the fullerene cages are the metallic clusters able to exist and they transfer a certain number of electrons to the surrounding cages. As typical examples, an improbable monometallic cluster YCN$^{2+}$ was found in C$_6$(6)-C$_{82}$ featuring a two-electron-transfer configuration but the I$_h$-C$_{80}$ is able to host a variety of metallic species such as La$_2$,5 Sc$_3$N$^+$, Sc$_2$C$_2$,14 Sc$_4$C$_2$,15 TiSc$_2$C$_2$,16 TiDy$_2$C$_2$,17 Sc$_3$CH$^+$ and Sc$_2$C$_2$CN$^+$ which donate six electrons to the cage. It’s noted that encapsulation of a carbide cluster consisting of either an odd or an even number of carbon atoms is feasible. Impressively, Popov et al. theoretically revealed Sc$_4$C$_3$@C$_{80}$ encapsulating a triangular aromatic C$_3$ cluster with two pairs of Sc atoms coordinating with the C$_3$ moiety.20 Recently, Chen and coworkers$^{21}$ reported the structure of U$_2$C@C$_{80}$ where a non-bridged uranium-carbon double bond was identified. More interestingly, Popov and coworkers$^{22}$ reported that a titanium–carbon double bond (Ti═C) exists in TiLu$_2$C@I$_h$-C$_{80}$, representing the first example of EMFs with a multiple bond between the metal and the non-metal atom of the endohedral cluster. It is thus expected that novel and even unprecedented bonding features are possibly observed in EMFs containing different metallic clusters.

Herein, we report the preparation and systematic characterization of a brand-new titanium-containing EMF, namely Ti$_3$C$_3$@I$_h$-C$_{80}$, which is one of the rare examples of EMFs that do not contain group-III elements. X-ray crystallographic results reveal that the C$_{36}$-unit of the Ti$_3$C$_3$ cluster resembles cyclopropane with an average C–C distance of 1.380 Å, perpendicularly
coordinated with the Ti₃-moiety, exhibiting a totally unexpected coordination fashion in organometallic chemistry.

**Results and discussion**

Soot containing titanium-EMFs was synthesized by an arc discharge method using TiC as the precursor. SnCl₄ was first chosen to react with the extract for the enrichment of Ti-EMFs followed by multiple-stage HPLC separation to obtain a pure sample of Ti₃C₃@C₈₀ (Fig. S1 and S2†). Its MALDI-TOF mass spectrum shows a single peak at m/z 1139.8 (Fig. 1a) which is perfectly consistent with the calculated results of Ti₃C₈₃. Interestingly, the retention time of Ti₃C₃@I₈-C₈₀ in a Buckyprep column is much longer than that of Sc₃N@I₈-C₈₀ (Fig. S3†). Previous studies have suggested a correlation between the HPLC retention time and the molecular geometry of fullerenes. Generally, the retention mechanism is proportional to the cage polarizability and is dominated by π–π interactions with the stationary phase. This phenomenon may suggest a different electronic configuration of the title compound from that of Sc₃N@I₈-C₈₀. Consistently, the absorption spectrum of Ti₃C₃@I₈-C₈₀ (Fig. 1b) shows a small bandgap of 0.82 eV (onset at 1500 nm) in comparison with the large one of Sc₃N@I₈-C₈₀ (1.70 eV), suggesting a relatively low stability and unique electronic configuration of Ti₃C₃@I₈-C₈₀. In addition, no signal is observed in the EPR spectrum of Ti₃C₃@I₈-C₈₀ even at 100 K (Fig. S4†), indicative of its diamagnetic property with a closed-shell electronic configuration. Compared to the previously reported Ti-containing mixed-metal EMFs, such as TiSc₂N@I₈-C₈₀ (ref. 25) and TiY₂N@C₈₀, which feature obvious EPR signals at low temperatures, it can be concluded that our title compound has a different electronic structure, which is presumably attributed to the difference in the spin distribution of the embedded clusters.

The structure of Ti₃C₈₃ is unambiguously established as Ti₃C₃@I₈-C₈₀, instead of any other form such as Ti₃C@C₈₂, by a single crystal XRD study performed on a black crystal obtained by slow diffusion of a benzene solution of NiII(OEP) (OEP is the dianion of octaethyl porphyrin) into the CS₂ solution of the EMF. The Ti₃C₃@I₈-C₈₀·NiII(OEP)·2C₆H₆ cocystal falls into the monoclinic C2/m space group, where a half of NiII(OEP) and a half of Ti₃C₃@I₈-C₈₀ are included in its asymmetric unit cell. The crystallographic mirror plane coincides with one of the symmetric planes of the I₈-C₈₀ cage, resulting in a fully ordered I₈-C₈₀ cage by combining the existing half with its mirror image.

Inside the cage, disorder is observed for the Ti₃C₃ cluster (see ESI Fig. S5 and Table S1 for details†). Specifically, one carbon atom in the C₃-unit exhibits two disordered positions generated by the crystallographic mirror plane, whereas the other two located in the crystallographic mirror plane are fully ordered. Eleven Ti sites are distinguished for the three titanium atoms with occupancy values ranging from 0.127 to 0.506. In fact, three of the disordered sites apart from NiII(OEP) belong to one Ti atom, with Ti2 as the major one (occupancy = 0.505). Meanwhile, two major sites out of the remaining eight disordered Ti-positions close to NiII(OEP), namely Ti1 and Ti1A (occupancy = 0.506), can be assigned to the other two Ti atoms.

Fig. 2 displays the molecular structures of Ti₃C₃@I₈-C₈₀ showing only the major metal site together with the co-crystallized NiII(OEP) molecule. The porphyrin moiety nestles the
fullerene cage with the shortest Ni-cage–carbon distance of 2.950 Å, suggesting substantial π–π interactions. Interestingly, the three carbon atoms stay in the center of the cage to form cyclopropane with an average bond length of 1.380 Å. The Ti–Ti distances among the three titanium atoms are 2.976 Å for Ti1–Ti1A and 3.604 Å for Ti1–Ti2 and Ti1A–Ti2, respectively, which are comparable to the values observed in organotitanium complexes, indicating weak metal–metal interactions between the titanium atoms.27–29 From a geometric point of view, the three titanium atoms intercalate between the cage and the C3-unit, preventing the encapsulated carbon atoms from being merged with the cage framework.

Fig. 3 illustrates the configuration of the major Ti3C3 site showing its relationship to the adjacent cage frameworks. Each titanium atom is centered above a respective [5,6]-ring junction with average Ti–C (cage) distances of 2.12, 2.12, and 2.13 Å, respectively, which fall in the range of typical Ti–C single bond lengths in reported organotitanium compounds (usually 2.1 Å)30,31 suggestive of strong metal–cage interactions (see also Table S2, ESI†). In contrast, the Ti–C distances within the Ti3C3 cluster are spread in a wide range from 1.838 Å to 3.090 Å, indicative of a rather complicated coordination environment. Interestingly, the plane of the C3-unit is nearly perpendicular to that of the Ti3-moietie with a dihedral angle of 83.43°, presenting a unique coordination fashion between carbon and titanium. To the best of our knowledge, such an unusual coordination pattern for cyclopropane interacting with metal ions has never been reported in any organometallic complexes, despite the above-mentioned theoretical possibility of a triangular C3 unit inside the Sc4C3@C80.28

We have performed density functional theory (DFT) calculations at the B3LYP/3-21G~SDD level to understand the unique coordination environment in Ti3C3@Ih-C80. The calculated Wiberg indices for the bonds in the cyclopropane ring are 1.18, 0.80, and 0.75 while their calculated lengths are 1.39 Å, 1.58 Å, and 1.62 Å, respectively, a bit longer than the corresponding X-ray results. As for the Ti3-unit, there are six bond indices between the ring carbons and Ti atoms larger than 0.5, namely 0.88, 0.67, 0.64, 0.60, 0.59, and 0.58. There is one (weak) C–C double bond not bridged by Ti, one (weak) single bond bridged by one Ti, and one (still weaker) single bond bridged by two Ti atoms. In this simplified picture (Fig. 4a), each Ti atom is bonded to the ring via two Ti–C bonds, supporting the results of the geometry of the embedded Ti3C3 cluster (Fig. 4b) obtained by the single crystal X-ray method. Moreover, the electron distribution in Ti3C3@Ih-C80 is visualized in Fig. S6, ESI† for more graphical information about bonds between the carbons of the cage and also bonds in the encapsulate, showing a selected isosurface of electron density (i.e., every point of the surface has the same prescribed value of the electron density). At the selected constant electron density of 0.086 a.u., the bonds in the cage and especially in the Ti3C3 cluster are rather well visible, where the near-vertical coordination environment of the Ti3-unit and C3-unit was found. Such a clear picture further provides us with unique bonding information. The B3LYP/3-21G~SDD Mulliken charges in Ti3C3@Ih-C80 on Ti atoms are 2.77, 2.48, and 2.44 while on the ring carbons they are 0.41, 0.22. The Mulliken-charge choice is supported32 by the fact that it is in good agreement with the available observed charges33 for metallofullerenes. However, unless there are charges deduced from observations for a class of clusterfullerenes, it cannot really be decided which particular charge definition is the best34 for the class. Thus, the results for the isolated Ti3C3@Ih-C80 system demonstrate a charge transfer of about six electrons to the cage, matching the charge state of common (Ih-C80)6+ reflected by the Vis-NIR spectrum.

Theoretically, the Ti3C3 encapsulation is also favorable from the calculated energetics point of view.35 The B3LYP/6-31G~SDD encapsulation-energy gain per one encapsulated atom for Ti3C3@Ih-C80 is calculated to be about 18 kcal per mol per atom which is even larger than a relative energy gain computed for the recently isolated Y2C2@C1(1660)-C108.36 The
stability calculations indeed support the finding that a novel EMF containing a unique Ti3C3 cluster was experimentally obtained.

The electrochemical properties of Ti3C3@Ih-C80 were measured in o-dichlorobenzene (o-DCB) by cyclic voltammetry (CV) and the profile is shown in Fig. 5. In the anodic region, Ti3C3@Ih-C80 displays a reversible oxidation step at 0.30 V and an irreversible one at 0.77 V whereas in the cathodic region, three reversible reduction steps are observed at −0.62 V, −1.22 V and −2.31 V. The electrochemical gap is thus calculated to be 0.92 V which is quite smaller than those of the other Ih-C80 based Ti-containing EMFs, namely, TiLu2C@Ih-C80 (ref. 22), TiSc2C2@Ih-C80 and TiSc2C2@Ih-C80,16 suggesting a lower kinetic stability of Ti3C3@Ih-C80 which is also consistent with the Vis-NIR result. In addition, the irreversible oxidation process of Ti3C3@Ih-C80 has not been reported for the other Ti-based EMFs, followed by multi-stage HPLC separation conducted on an LC-908 machine (Japan Analytical Industry Co. Ltd.) sequentially employing a 5PBB column (20 × 250 mm) and a Buckyprep column (20 × 250 mm). More details about the SnCl4 treatment and HPLC separations are present in the ESI.†

**Table 1** Redox potentials of Ti3C3@Ih-C80 and typical Ti-based EMFs

| EMFs           | oxE1 | oxE2 | redE1 | redE2 | ΔEgap | Ref. |
|---------------|------|------|-------|-------|-------|------|
| Ti3C3@Ih-C80  | 0.77  | 0.30 | −0.62 | −1.22 | −2.31 | 0.92 | This work |
| TiLu2C@Ih-C80 | —    | 0.64 | −0.91 | —     | —     | 1.55 | 22 |
| TiSc2C2@Ih-C80| 0.66  | 0.66 | −0.67 | −1.51 | −1.66 | 1.33 | 16 |
| Sc2TiC2@Ih-C80| 0.53  | 0.53 | −0.76 | −1.01 | −1.96 | 1.26 | 16 |
| Dy2TiC2@Ih-C80| 0.61  | 0.61 | −0.97 | −1.62 | −1.87 | 1.58 | 17 |
| Dy2TiC2@Ih-C80| 0.47  | 0.47 | −1.14 | −1.58 | −2.21 | 1.61 | 17 |

*Half-cell values in V versus Fe(Cp)12+/0+ unless otherwise noted. b ΔEgap = oxE1 − redE1. c Irreversible peak value.

**Conclusions**

An unprecedented Ti3C3 cluster has been successfully entrapped inside the Ih-C80 cage to form a stable compound. X-ray results reveal a novel coordination fashion by which the cyclopropane-like C3-unit perpendicularly coordinates to the Ti3C3 moiety. The electronic configuration of (Ti3C3)6+@C80 was confirmed according to the Vis-NIR spectroscopic and electrochemical characterization in addition to DFT calculations. Successful entrapment of the Ti3C3 cluster inside fullerene cages and identification of the unprecedented cyclopropane-coordination fashion may stimulate intensive interest in creating new hybrid molecules with fullerenes as protectors and discovering new reactivities in coordination chemistry.

**Experimental**

**Synthesis and isolation of Ti3C3@Ih-C80**

Soot containing titanium-EMFs was produced by evaporating graphite rods packed with mixed TiC and graphite powder (mole ratio of Ti : C = 1 : 10) under a 400 mbar He atmosphere and 100 A current. The soot was extracted with CS2, and the filtered extract was treated with SnCl4 for the enrichment of Ti-EMFs, followed by multi-stage HPLC separation conducted on a PE Lambda 750S spectrophotometer in CS2. Cyclic voltammetry (CV) was performed in o-dichlorobenzene using a CHI-660E instrument with 0.05 M TBAPF6 as the electrolyte. The electron paramagnetic resonance (EPR) spectrum of Ti3C3@Ih-C80 was recorded with a Bruker A300 spectrometer in toluene.

**Crystallographic characterization**

Cocrystals of Ti3C3@Ih-C80 were obtained by slow diffusion of a benzene solution of NiII(OEP) into a Cs2 solution of the EMF in a glass tube at room temperature for one month. Single-crystal X-ray data were collected at 100 K using a radiation wavelength of 0.6525 Å with a MarCCD detector at beamline BL17B of the Shanghai Synchrotron Radiation Facility. A multi-scan method was used for absorption corrections. The structures were solved with direct methods and were refined with SHELXL-2014.†

**Crystal data of Ti3C3@Ih-C80-NiII(OEP)-2(C6H6)**

Black block, 0.31 × 0.24 × 0.20 mm, monoclinic, space group C2/m, a = 25.0964(9) Å, b = 15.1544(5) Å, c = 19.7269(7) Å, β = 95.3360(10)°, V = 7470.0(5) Å3, F000 = 1888.20, λ = 0.6525 Å, Z = 4, Dcalc = 1.679 Mg m−3, μ = 0.498 mm−1, T = 100 K, R1[I > 2σ(I)] = 0.049.
0.1079, \( \text{wR}_2 \) (all data) = 0.2972, GOF (on \( F^2 \)) = 1.068. The maximum residual electron density is 1.953 e Å\(^{-3}\). Crystallographic data have been deposited in the Cambridge Crystallographic Data Center (CCDC number: 1883920).†

**Computational study of Ti\(_3\)C\(_3@Ih\)-C\(_{80}\)**

The structure optimization started with a combined basis set, the standard 3-21G basis\(^*\) for C atoms and SDD basis\(^*\) with the SDD effective core potential for Ti atoms, applied within the density functional theory (DFT) approach, namely using Becke’s three parameter functional\(^*\) with the non-local Lee–Yang–Parr correlation functional\(^*\) (denoted as B3LYP/3-21G–SDD). Herein, analytical harmonic vibrational analysis is then carried out in order to confirm that the local-energy minimum was indeed localized. The B3LYP/3-21G–SDD optimized structure was further refined by performing re-optimizations with the standard 6-31+G* basis set\(^*\) for C atoms (B3LYP/6-31+G*–SDD). Moreover, in the latter structure the encapsulation energy\(^*\) (the energy gain upon encapsulation of three Ti and three C atoms into the C\(_{80}\) cage) was evaluated at the B3LYP/6-31G*–SDD level with inclusion of the basis set superposition error\(^*\) (BSSE/CP2) and the so-called steric correction that reflects the cage distortion upon encapsulation.\(^*\) All the computations were carried out with the Gaussian 09 program package.\(^*\)

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

Financial support from the NSFC (51672093, 51602112 and 51602097) is gratefully acknowledged. We thank the staff from the BL17B beamline of the National Center for Protein Science Shanghai at the Shanghai Synchrotron Radiation Facility for assistance during data collection and the Analytical and Testing Center in the Huazhong University of Science and Technology for all related measurements.

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