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Th@ $D_{5h}(6)$ -C₈₀: highly symmetric fullerene cage stabilized by a single metal ion

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A novel endohedral metallofullerene (mono-EMF), Th@ D_{5h} (6)-C₈₀, has been successfully synthesized and fully characterized by mass spectrometry, single crystal X-ray diffraction, UV-vis-NIR, Raman spectroscopy and cyclic voltammetry. Single crystal XRD analysis unambiguously assigned the fullerene cage as the D_{5h} (6)-C₈₀, which is the first example that this highly symmetric cage is stabilized by a single metal ion. The combined experimental and theoretical studies further reveal that the D_{5h} (6)-C₈₀ cage, known only for its stabilization by 6 electron transfer, is stabilized by the 4-electron transfer from encapsulated Th ion for the first time.

Endohedral metallofullerenes (EMFs) are formed by encapsulating metal atoms or metallic clusters into the fullerene cages, which gives rise to complex host-guest interaction between them.¹⁻³ A simple ionic model of $M^{q+} @ C_{2n}^{q-}$ is commonly used to describe the electronic structure of EMFs. For mono-EMFs, it is a general understanding that the endohedral rare-earth metals can transfer either 2 or 3 electrons to the fullerene cages. Given the relatively simple ionic model, the molecular model of these EMFs has been well established after the contributions by both theoretical and experimental researchers. In general, the most stable isomer of a given mono-EMF can be well predicted and often agree with the experimental results.

However, recent studies on actinide mono-EMFs show formal transfers that can be up to four electrons $M^{q+}@C_{2n}{}^{q-}$ (q = 3 or 4) as observed in most of the isomeric structures characterized so far.⁴ For thorium, a series of theoretical and experimental studies have shown that it normally exhibited an oxidation state of +4 in mono-EMFs.⁵⁻⁹ For uranium, due to its unique flexibility on the oxidation states, which could range from +2 to +6, the possible isomeric structures appears to be far more complicated than previously learned from those lanthanide-based EMFs. Additionally, strong covalent interaction between the actinide metal ion and the parent cages was also revealed.⁵

Thus, actinide mono-EMFs display unique metal-cage interactions in comparison with lanthanide-based EMFs. It turned out that the selection pattern of Th or U has broken the commonly acknowledged rules derived from previous EMF studies. For instance, the intramolecular four electrons transferred pattern makes Th@ $C_{3\nu}(8)$ -C₈₂ the first example for which a single metal ion can be embedded in a $C_{3\nu}(8)$ - C_{82} cage, and the same phenomenon was also observed for Th@ T_d (19151)-C₇₆.^{6, 9} Further studies show that, the unique four-electron transfer and the resulting strong host-guest interactions contribute to the unexpected stabilization of nonisolated pentagon rule (non-IPR) fullerene cages such as U@C₁(17418)-C₇₆, U@C₁(28324)-C₈₀, Th@C₁(28324)-C₈₀ and novel chiral EMF Th@ $C_1(11)$ -C₈₆.^{5, 8} These results demonstrated that, compared to that of the conventional lanthanide EMFs, encapsulated actinide metal ions show distinctively different selection patterns for their parent fullerenes. Further studies of these novel EMFs are necessary to fully understand the interaction of actinide metal ion and nano carbon cage structures.

 $D_{5h}(6)$ -C₈₀ is one of the seven IPR-satisfying isomers for C₈₀ and was previously revealed to have exceptional stability as a 6fold charged cage isomer due to the favorable distribution of the pentagons on the cage and the resulting least steric strain.¹⁰ Indeed, it has so far been observed that $D_{5h}(6)$ -C₈₀ can only be stabilized by a six electron transfer from inner species experimentally in the form of M₂@ D_{5h} -C₈₀ (M = La, Ce)^{11, 12} and M₃N@ D_{5h} -C₈₀ (M = Sc, Y, Dy, Tm and Lu).¹³⁻¹⁸ Though recent computational predictions have also suggested that the tetraanionic $D_{5h}(6)$ -C₈₀⁴⁻ species could be selected as the candidate to encapsulate clusters (Sc₂O¹⁹ and Sc₂S²⁰) through a 4-electron transfer,²⁰ it has never been proved experimentally.

Herein, for the first time, we report that the highly symmetric $D_{5h}(6)$ -C₈₀ is stabilized by a single metal ion, in the form of Th@ $D_{5h}(6)$ -C₈₀. This novel actinide mono-EMF has been fully characterized by single-crystal X-ray diffraction, mass spectrometry, UV-vis-NIR spectroscopy, Raman spectroscopy

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and electrochemistry. Computations also confirmed the formal four electron transfer and the stability of $Th@D_{5h}(6)-C_{80}$ compared to other isomers.

Thorium-based endohedral metallofullerenes were synthesized by a modified Krätschmer-Huffman DC arc discharge method. Graphite rods packed with ThO2 and graphite powder (molar ratio of Th:C = 1:24) were vaporized in the arcing chamber under a 200 Torr He atmosphere. The resulting soot was then collected and extracted with CS_2 for 12 h. Multistage high-performance liquid chromatography (HPLC) separation processes were employed to isolate and purify Th@C₈₀. The purity of the isolated compound was confirmed by the observation of single peak by HPLC and positive-ion-mode matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF MS), as shown in Fig. 1. The mass spectrum of the purified Th@C₈₀ shows a single peak at 1192.162 m/z. In addition, the experimental isotopic distribution agrees well with theoretical prediction.

The molecular structure of Th@C₈₀ was unambiguously determined by single-crystal X-ray diffraction analysis. Th@C₈₀ was co-crystallized with [Ni^{II}(OEP)] (OEP = 2, 3, 7, 8, 12, 13, 17, 18-octaethylporphyrin dianion) by slow diffusion of the benzene solution of [Ni^{II}(OEP)] into the carbon disulfide solution of the purified compound. The structure of Th@D_{5h}(6)-C₈₀ was resolved and refined in the $P2_1/c$ (No. 14) space group. Fig. 2a shows the molecular structure of this endohedral metallofullerene and the relationship with the co-crystallized [Ni^{II}(OEP)] molecule.

The crystallographic data unambiguously identified the fullerene cage as the highly symmetric $D_{5h}(6)$ -C₈₀ cage isomer. The $D_{5h}(6)$ -C₈₀ cage is disordered over two orientations with occupancies of 0.609(5) (cage A) and 0.391(5) (cage B). Inside the fullerene cage, the major Th site (Th1) has the dominant occupancy of 0.421(5), with the occupancies of other eight minor sites ranging from 0.0170(7) to 0.196(3) (Fig. S2 and Table S1). To the best of our knowledge, this is the first case that a



Fig. 1 HPLC chromatogram of purified Th@C₈₀ on the Buckyprep column with toluene as the eluent. HPLC condition, λ = 310 nm; flow rate, 4 mL / min. The inset shows the positive-ion mode MALDI-TOF mass spectrum and expansion of the experimental and theoretical isotopic distribution of Th@C₈₀.



Fig. 2 Ortep drawing showing the relationship between the fullerene cage and porphyrin moiety for Th@ $D_{5h}(6)$ -C₈₀·[Ni^{III}(OEP)] with 30% thermal ellipsoids. The major Th site with a fractional occupancy of 0.421 and the major cage orientation of 0.609 are shown. For clarity, the solvent molecules and minor metal sites are omitted.

 $D_{5h}(6)$ -C₈₀ was stabilized by a single metal ion. Previously, $D_{5h}(6)$ -C₈₀ is best known for hosting a pair of metal ions or metallic cluster which transfer 6 electrons to the carbon cage.

As observed in other reported actinide mono-EMFs, all Th atoms sites in Th@ $D_{5h}(6)$ -C₈₀ are away from the cage center and are close to the carbon cage, due to the strong host-guest interactions.⁷ Th1 resides over a [6,6]-bond (C32A and C53A), with the identical Th-C distances 2.326 Å. Note that this C-C bond (C32A-C53A) acts as the junction of two pentagonal rings and a pair of adjacent hexagons as shown in Fig. 2b. Interestingly, such a coordination pattern between the Th⁴⁺ ion and the fullerene cage is remarkably different from previous reported Th-based mono-EMFs in which the tetravalent thorium atom mainly coordinates to three pentagonal rings, as proposed for Th@ $C_{3v}(8)$ -C₈₂, Th@ $T_d(19151)$ -C₇₆ and Th@ $C_1(28324)$ -C₈₀.^{5-7, 9} Moreover, the Th-C distance observed here is the shortest one in crystallographically characterized Th-based mono-EMFs as compared in Table S2.

In addition, the interaction between the metal ion and $D_{5h}(6)-C_{80}$ in Th@ $D_{5h}(6)-C_{80}$ is also notably different from those in the previously reported $D_{5h}(6)-C_{80}$ based EMFs. In Th@ $D_{5h}(6)-C_{80}$, Th1 locates over a C-C bond and deviates from the 5-fold axis as shown in Fig. S3a. But for Ce₂@ $D_{5h}(6)-C_{80}$, each primary cerium site lies over a hexagonal ring, while other Ce sites in Ce₂@ $D_{5h}(6)-C_{80}$ are circled around C_5 axis to form a two-dimensional circulation along the cage belt of ten contiguous hexagons.²¹ In Sc₃N@ $D_{5h}(6)$ -C₈₀, optimized positions of scandium ions are at the vicinity of two carbon atoms of the fullerene. Furthermore, from the top view, the three Sc atoms are distributed around the pentagons where the C_5 axis is located, as shown in Fig. S3c.²²

The unique coordination pattern, the shorter Th-C distance along with the special position of inner Th ion suggest that there may exist specially strong interaction between the inner actinide metal ion and the fullerene cage, which contributes to the exceptional stability of this cage isomer through a 4-electron transfer from the embedded Th⁴⁺ ion.

Fig. 3a presents the UV–vis–NIR absorption spectrum of Th@ $D_{5h}(6)$ -C₈₀. UV–vis–NIR absorption pattern of fullerene is highly sensitive to the isomeric structure and the charge state of the carbon cage. The spectrum of Th@ $D_{5h}(6)$ -C₈₀ exhibits three characteristic peaks at 448, 680 and 1433 nm. These features are strikingly

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different from those of the six-electron transferred $Ce_2@D_{5h}(6)-C_{80}$ or $Lu_3N@D_{5h}(6)-C_{80}$ which display only one broad absorption peak at 467 nm and 468 nm,^{12, 17} respectively, indicating that the charge transfer between the inner species and the outer fullerene cage of these two $D_{5h}(6)-C_{80}$ based EMFs is essentially different from Th@D_{5h}(6)-C_{80}. In addition, the absorption spectrum of Th@D_{5h}(6)-C_{80} is also notably different from that of the Th@C_1(28324)-C_{80}, which doesn't show obvious absorption,⁵ likely due to the difference in symmetry of the corresponding isomeric cage structures. Moreover, the absorption onset of Th@D_5h(6)-C_{80}, is located at around 1430 nm, which results in a small HOMO-LUMO gap of 0.84 eV.

Fig. 3b shows the low energy Raman spectroscopy of Th@ $D_{5h}(6)$ -C₈₀. The Raman spectrum of Th@ $D_{5h}(6)$ -C₈₀ consists of two regions: the radial modes of carbon cages (200-600 cm⁻¹) and the metal-to-cage vibrational modes (below 200 cm⁻¹).²³ In the carbon cage vibrational mode range, the vibration at 219 cm⁻¹ and 479 cm⁻¹ could be assigned to $H_g(1)$ -derived modes and the $A_g(1)$ modes of D_{5h} cage respectively, which agrees with the crystallographic results.²⁴ For a representation of the breathing mode of the cage at 219 cm⁻¹, see Fig. S6. In the metal-to-cage vibrational mode range, a sharp peak at 150 cm⁻¹ is observed. This frequency, which can be assigned to the Th-to-cage vibrational mode (see Fig. S6),³ is very close to those for Th@ $C_{3\nu}(8)$ -C₈₂ (148 cm⁻¹),⁹ Th@ $C_1(11)$ -C₈₆ (153 cm⁻¹),⁸ and Th@ $C_1(28324)$ -C₈₀ (155 cm⁻¹),⁵ indicating similar 4+ charge state of Th in the D_{5h} cage. These results, together with the crystallographic results, suggest the electronic state of Th@D_{5h}(6)-C₈₀ is Th⁴⁺@D_{5h}(6)-C₈₀⁴⁻.

Cyclic voltammetry (CV) has also been employed to investigate the redox properties of these mono-EMFs. The cyclic voltammetry of Th@ D_{5h} (6)-C₈₀ presents two oxidation peaks and three reduction peaks (Fig. 4). It is noteworthy that, the first reduction potential of Th@ D_{5h} (6)-C₈₀ (-0.63 V) is shifted positively by ca. 0.4-0.5 V compared with those of the other Th-based mono-EMFs listed in Table 1.^{5, 6, 8, 9}

This result suggests that Th@ $D_{5h}(6)$ -C₈₀ is a much better electron acceptor. The electrochemical gap of Th@ $D_{5h}(6)$ -C₈₀ (0.89 eV) is also notably smaller than that of the Th@ $C_1(28324)$ -C₈₀ (1.46 eV). This result correlates well with the small optical band gap (0.87 eV) of Th@ $D_{5h}(6)$ -C₈₀ compared to 1.24 eV of the Th@ $C_1(28324)$ -C₈₀.

Moreover, the overall redox pattern of Th@ $D_{5h}(6)$ -C₈₀ presents some resemblance to that of Ce₂@ $D_{5h}(6)$ -C₈₀, in which both of the EMFs have two oxidation steps and three reduction steps.¹² However, the first oxidation (+0.26 V) and reduction potentials (-0.63 V) of Th@ $D_{5h}(6)$ -C₈₀ are more positive and negative respectively than those of the Ce₂@ $D_{5h}(6)$ -C₈₀ resulting in a larger electrochemical gap



Fig. 3 (a) UV–vis-NIR absorption spectrum of Th@ $D_{5h}(6)$ -C₈₀. (b) Low-energy Raman spectrum of Th@ $D_{5h}(6)$ -C₈₀ at 785 nm excitation.



Fig. 4 Cyclic voltammograms of Th@ D_{5n} (6)-C₈₀ in *o*-dichlorobenzene (0.05 M (*n*-Bu)₄NPF₆ as the supporting electrolyte; scan rate 100 mV/s).

of Th@D_{5h}(6)-C₈₀. These differences suggest that the two D_{5h}(6)-C₈₀ based EMFs may still have different metal-to-cage charge transfer, which agrees with the abovementioned spectroscopic analysis.¹² It is noteworthy that, as summarized in Table S3, although the EC gap of Th@D_{5h}(6)-C₈₀ is larger than Ce₂@D_{5h}(6)-C₈₀, it is significantly smaller than the gap of Lu₃N@D_{5h}(6)-C₈₀ (1.78 eV), suggesting the latter cluster fullerene may still have higher stability.

Computational analysis at PBEO/TZP level (see Computational Details) confirms the formal four electron transfer from the Th atom to the $D_{5h}(6)$ -C₈₀ cage. All of the highest-occupied molecular orbitals of Th@D_{5h}(6)-C₈₀ are essentially based on the C₈₀ cage with null or minor contributions from Th atom (Fig. S4). Besides, all the valence orbitals of thorium (7s, 6d and 5f) are empty (see LUMOs in Fig. S4). Therefore, we can assume that thorium is formally Th⁴⁺. We have considered different positions of the Th atom inside the $D_{5h}(6)$ -C₈₀ cage (see Table S4). In the most-favoured position, the Th ion is also located over a pyracylenic [6,6]-bond with two identical Th-C distances of 2.419 Å, slightly larger than the crystallographic ones (2.326 Å). As shown in Table 1, Th@ $D_{5h}(6)$ - C_{80} is the lowest-energy isomer, with non-IPR Th@ $C_1(28324)$ - C_{80} , recently isolated and characterized,⁵ as almost degenerated, in good agreement with experiments. Other isomers are found at 2 kcal mol⁻¹ (IPR 5) or higher energies. The abundance of Th@ $D_{5h}(6)$ -C₈₀ is predicted to drop significantly with temperature (Fig. S5) due to the high symmetry of the $D_{5h}(6)$ cage, with non-IPR Th@ $C_1(28324)$ - C_{80} as the most abundant isomer for the whole range of temperatures.⁵ However, $Th@D_{5h}(6)-C_{80}$ is among the three most abundant isomers up to 1500 K, in accordance with experiments.

First reduction and oxidation potentials were predicted at -0.54 and +0.38 V, in rather good agreement with experiment (-0.63 and +0.26 V, respectively), albeit somewhat shifted to more positive values. The computed electrochemical gap, 0.92 V, almost matches the experimental one, 0.89 V. Both oxidation and reduction take place on the carbon cage. The significantly lower value of the first reduction potential for Th@ $D_{5h}(6)$ -C₈₀ (by 0.84 V, see Table S3) is due to

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the different formal charge transfer (4 vs 6) and the rather deep LUMO of $Th@D_{5h}(6)-C_{80}$.

Table 1.	Relative energies for	tive energies for different Th@C $_{80}$ isomers along with the symmetries of the					
empty ca	ages. ^{a)}						
	isomer ^{b)}	APP	Svm	Th@C ₈₀			

isomer ^{b)}	APP	Sym	Th@C ₈₀
31920	IPR 3	<i>C</i> _{2v}	5.6
31922	IPR 5	<i>C</i> ₂ <i>v</i>	2.1
31923	IPR 6	D_{5h}	0.0
31924	IPR 7	I _h	15.0
28319	APP1	<i>C</i> ₁	8.4
28324	APP1	<i>C</i> ₁	0.5
^{a)} Energies in kcal mol ⁻¹ . ^{b)} spiral algorithm.	somer number	following the	Fowler and Manolopo

In summary, a novel actinide mono-EMF, Th@ $D_{5h}(6)$ -C₈₀, has been fully characterized by single-crystal X-ray diffraction, various spectroscopies and electrochemistry. Crystallographic analysis revealed that, a single Th ion is encapsulated in a $D_{5h}(6)$ -C₈₀ cage. Combined UV-vis-NIR, Raman spectroscopy, electrochemical and computational results suggest that four electrons are transferred from Th ion to the outer cage in Th@ $D_{5h}(6)$ -C₈₀. To best of our knowledge, this is the first observation that a $D_{5h}(6)$ -C₈₀ cage isomer could be stabilized by a single metal ion as well as the four-electron charge transfer. The discovery and characterization of this novel actinide EMF shed light into unexplored metal-cage interaction of the interaction between the metal ion and the nano carbon cage is still needed in future studies.

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Conflicts of interest

There are no conflicts to declare.

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