

Synthesis and Characterization of Two Isomers of Th@C₈₂: Th@C_{2v}(9)-C₈₂ and Th@C₂(5)-C₈₂

Qingyu Meng,^{†,‡} Roser Morales-Martínez,^{‡,‡} Jiaxin Zhuang,^{†,‡} Yang-Rong Yao,[§] Yaofeng Wang,[†]

Lai Feng,^{*,‡} Josep M. Poblet,[‡] Antonio Rodríguez-Forteza,^{*,‡} and Ning Chen ^{*,‡}

[†] College of Chemistry, Chemical Engineering and Materials Science, and State Key Laboratory of Radiation Medicine and Protection, Soochow University, Suzhou, Jiangsu 215123, P. R.

China

[‡] Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, C/Marcel·lí Domingo 1, 43007 Tarragona, Spain

[§] Department of Chemistry, University of Texas at El Paso, 500 W University Avenue, El Paso, Texas 79968, United States

[‡] College of Energy, Soochow Institute for Energy and Materials Innovations & Key Laboratory of Advanced Carbon Materials and Wearable Energy Technologies of Jiangsu Province, Soochow University, Suzhou 215006, P.R. China

KEYWORDS: Endohedral metallofullerene, Actinide, Thorium, Density functional theory.

ABSTRACT: Actinide endohedral fullerenes have demonstrated remarkably different physicochemical properties compared to their lanthanide analogs. In this work, two novel isomers

of Th@C₈₂ were successfully synthesized, isolated, and fully characterized by mass spectrometry, X-ray single crystallography, UV-vis-NIR spectroscopy, Raman spectroscopy, and cyclic voltammetry. The molecular structures of the two isomers were determined unambiguously as Th@C_{2v}(9)-C₈₂ and Th@C₂(5)-C₈₂ by single crystal X-ray diffraction analyses. Raman and UV-vis-NIR spectroscopy further confirm the assignment of the cage isomers. Electrochemical gaps suggest that both Th@C_{2v}(9)-C₈₂ and Th@C₂(5)-C₈₂ possess stable closed-shell electronic structure. The computational results further confirm that Th@C_{2v}(9)-C₈₂ and Th@C₂(5)-C₈₂ exhibit a unique four-electron charge transfer from metal to carbon cage and are among the most abundant isomers of Th@C₈₂.

Introduction

Endohedral metallofullerenes (EMFs) feature unique electronic and physicochemical properties which are derived by the charge transfer from the embedded species to the carbon cage, shedding light on great potentials of applications in various fields such as biomedicine, organic photovoltaic devices, thermoelectric materials and molecular devices.¹⁻⁴ The earliest exploration of EMFs can date back to 1985 when Smalley *et al.* observed the signal of LaC₆₀⁺ in the gas phase.⁵ Since then, mono-metallofullerenes, mainly based on the rare-earth metals, have been the most widely studied fullerene species due to their relatively high yield. For conventional mono-EMFs, the endohedral rare-earth metals generally transfer either 2 or 3 electrons to the fullerene cages. Our recent studies revealed that actinide mono-EMFs display dramatically different structural and electronic features from those of the conventional lanthanide-based EMFs. In particular, the metal-to-cage four-electron-transfer makes Th@C_{3v}(8)-C₈₂ the first example for which a single metal ion can be encaged in a C_{3v}(8)-C₈₂ cage.⁶ Moreover, the encapsulated tetravalent metal ions and the resulting strong host-guest interactions contribute to the outstanding stabilization of novel chiral fullerene

cages in $\text{U}@C_1(17418)\text{-C}_{76}$, $\text{U}@C_1(28324)\text{-C}_{80}$, $\text{Th}@C_1(28324)\text{-C}_{80}$, $\text{Th}@C_1(11)\text{-C}_{86}$.^{7,9} It is conceivable that further exploration of actinide-based mono-EMFs may provide more insights into novel fullerene isomers as well as the unique interaction between actinide metal ion and the host fullerene cages.

Herein, we report the synthesis and characterization of two novel $\text{Th}@C_{82}$ isomers, $\text{Th}@C_{2i}(9)\text{-C}_{82}$ and $\text{Th}@C_{2i}(5)\text{-C}_{82}$. The two mono-EMFs were fully characterized by single-crystal X-ray diffraction, multiple spectroscopies and electrochemistry. Theoretical calculations were also utilized to analyze the electronic structures of the two molecules, suggesting that both cages are essentially stabilized by the unique four-electron-transfer from the endohedral Th ions.

Results and discussion

Synthesis, isolation and purification of $\text{Th}@C_{82}$. Thorium-based endohedral metallofullerenes were produced by a modified Krätschmer–Huffman DC arc discharge method. Graphite rods packed with ThO_2 and graphite powder (molar ratio of $\text{Th}:\text{C} = 1:24$), 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 $\text{Th}@C_{82}$ (Figure S1 and Figure S2). The purity of the sample was confirmed by the observation of single peaks by HPLC and positive-ion-mode matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF MS), as shown in Figure 1. The mass spectra of the purified two isomers of $\text{Th}@C_{82}$ show peaks at 1216.132 and 1216.223 m/z, respectively. In addition, the experimental isotopic distributions of the two samples agree well with theoretical predictions.

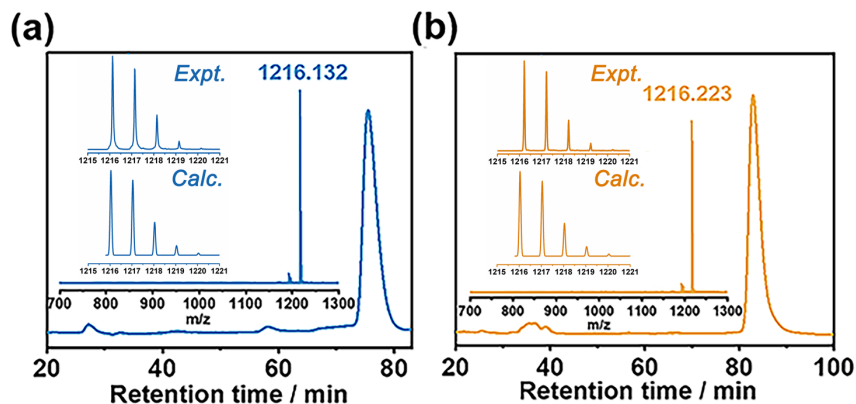


Figure 1. HPLC chromatograms of purified (a) Th@C₂(5)-C₈₂ and (b) Th@C₂(9)-C₈₂ on the Buckyprep column with toluene as the eluent. HPLC condition, $\lambda = 310$ nm; flow rate, 4 mL / min. The insets show the positive-ion mode MALDI-TOF mass spectra and expansions of the corresponding experimental isotopic distributions of the compounds in comparison with their calculated ones.

Molecular structures of Th@C₂(9)-C₈₂ and Th@C₂(5)-C₈₂. The molecular structures of Th@C₈₂ were unambiguously determined by single-crystal X-ray diffraction analyses. The two isomers were 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 compounds. The structure of Th@C₂(9)-C₈₂ was resolved and refined in the *P2₁/c* (No. 14) space group while the crystal of Th@C₂(5)-C₈₂ falls in the monoclinic *C2/m* (No. 12) space group. Figure 2 shows the molecular structures of these endohedral metallofullerenes and their relationship to the co-crystallized Ni^{II}(OEP) molecules.

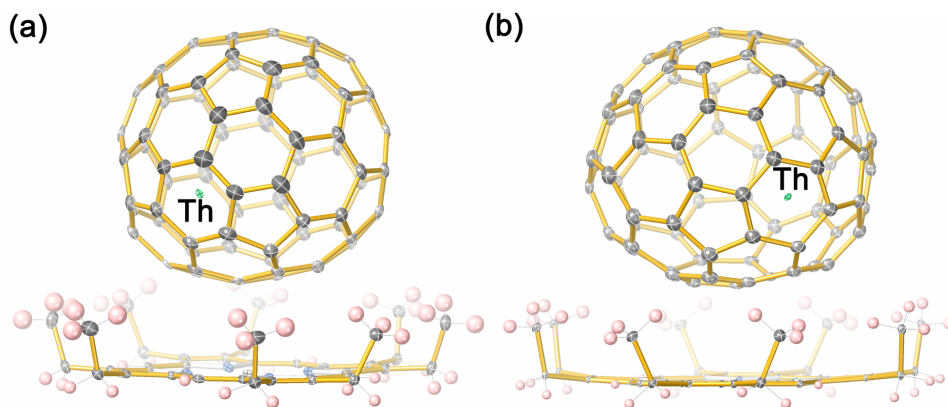


Figure 2. ORTEP drawings showing the relationship between the EMFs and porphyrin moieties for (a) $\text{Th}@C_{2v}(9)\text{-C}_{82}\cdot[\text{Ni}^{\text{II}}(\text{OEP})]$ and (b) $\text{Th}@C_2(5)\text{-C}_{82}\cdot[\text{Ni}^{\text{II}}(\text{OEP})]$ with 20% thermal ellipsoids. Only the major cage orientations and predominant thorium sites are shown. For clarity, the solvent molecules and minor metal sites are omitted.

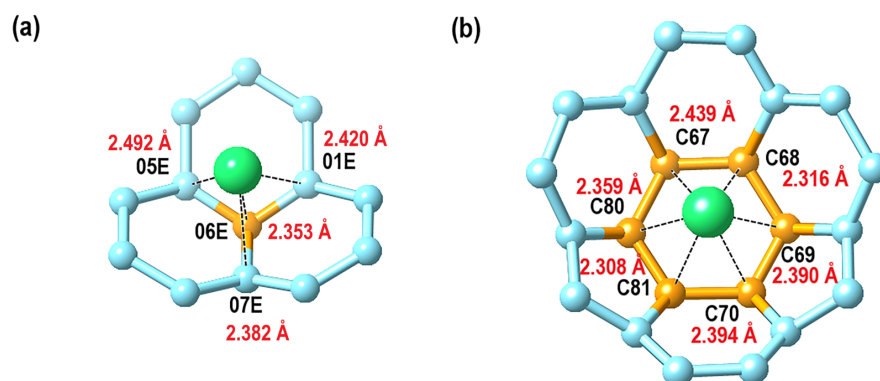


Figure 3. Perspective drawings showing the interaction of the major thorium site with the closest cage portion in (a) $\text{Th}@C_{2v}(9)\text{-C}_{82}$ and (b) $\text{Th}@C_2(5)\text{-C}_{82}$, respectively.

$\text{Th}@C_{2v}(9)\text{-C}_{82}$. As shown in Figure 2a, the $\text{Th}@C_{2v}(9)\text{-C}_{82}$ moiety is close to the adjacent $\text{Ni}^{\text{II}}(\text{OEP})$ with a short Ni-to-cage carbon distance (Ni1-C23E) of 2.804 Å. This value is similar to those reported for the co-crystals of $\text{U}@C_{2v}(9)\text{-C}_{82}\cdot[\text{Ni}^{\text{II}}(\text{OEP})]$ (2.787 Å) and $\text{Gd}@C_{2v}(9)\text{-C}_{82}\cdot[\text{Ni}^{\text{II}}(\text{OEP})]$ (2.787 Å).

$C_{82}[Ni^{II}(OEP)]$ (2.783 Å), indicating a typical π - π stacking interaction between the fullerene and porphyrin moiety.^{10,11} The fullerene cage can be clearly identified as $C_{2v}(9)-C_{82}$ over two disordered orientations with fractional occupancies of 0.637(3) and 0.363(3), respectively. The endohedral Th atom is slightly disordered over four sites (i.e., Th1, Th2, Th3 and Th4, see Figure S3a) with occupancies ranging from 0.4942(9) to 0.0502(11) (see Table S1). It is reasonable to assign the Th1 site to the major cage orientation. A closer look reveals that the major Th1 site is approaching a cage motif of phenalene that consists of three joint six-member rings with a short Th–C distance ranging from 2.353 to 2.492 Å (Table S3), as shown in Figure 3 a. The shortest Th–C distance of 2.353 Å is observed between Th1 and a cage carbon (i.e., C06E) at the intersection of three hexagons. Interestingly, such a metal-cage coordination model is very similar to that in previously reported $Th@C_{31}(8)-C_{82}$,⁶ indicating the favorable thorium position inside the fullerene cage. Note that it is unlike the majority of lanthanide EMFs (i.e., $M@C_{2v}(9)-C_{82}$, $M = La, Y, Gd, Sc$),¹¹⁻¹⁴ in which the endohedral metals tend to donate three electrons to the carbon cage and reside under a hexagon, indicating their significant differences in charge transfers as well as the metal-cage interactions.

$Th@C_2(5)-C_{82}$. For $Th@C_2(5)-C_{82}$, the fullerene cage has two orientations which are symmetrized by the crystallographic mirror plane. As a result, an intact cage can be obtained by one-half of the cage with the mirror image of the other, both having the occupancy of 0.5. Figure S4 presents two orientations of $C_2(5)-C_{82}$ carbon cage. Inside the cage, seven crystallographic sites for Th atoms can be identified with occupancies ranging from 0.274(2) to 0.0105(8) (Table S2). Since only Th2 resides at the symmetric plane, six additional positions (Th1A, Th3A, Th4A, Th5A, Th6A and Th7A) are generated via the mirror plane as shown in Figure S3b. Furthermore, the predominant Th site, Th1 (occupancy 0.274), is situated over a hexagon with the shortest Th–C distance in the range 2.308–2.439 Å (Table S4), as shown in Figure 3b. Theoretical calculations are also

employed to determine the optimized structure, which is in good agreement with the crystallographic result (see below).

Spectroscopic Characterizations.

Figure 4 and Figure S8 present the UV–vis–NIR absorption spectra of $\text{Th}@C_{2v}(9)\text{-C}_{82}$ and $\text{Th}@C_2(5)\text{-C}_{82}$. The spectrum of $\text{Th}@C_{2v}(9)\text{-C}_{82}$ exhibits characteristic peaks at 621, 799 and broad absorption at 1141 nm. As shown in Figure 4a, though this spectrum show resemblance to that of the $\text{U}@C_{2v}(9)\text{-C}_{82}$, notable differences can still be observed between them, suggesting differences between their electronic structures despite their almost identical molecular structures. More significant differences can be found between the absorption spectra of $\text{Th}@C_{2v}(9)\text{-C}_{82}$ and $\text{Sm}@C_{2v}(9)\text{-C}_{82}$, the later presenting four pronounced peaks at 451, 534, 740 and 961 nm.¹⁵ This can be rationalized by the fact that while $\text{Sm}@C_{2v}(9)\text{-C}_{82}$ features a two-electron charge transfer, the endohedral Th normally takes a formal +4 charge state. Likewise, the spectrum of $\text{Th}@C_2(5)\text{-C}_{82}$, presenting four pronounced peaks at 451, 534, 740 and 961 nm, shows significant differences from previously reported mono-metallofullerenes such as $\text{Sm}@C_2(5)\text{-C}_{82}$,¹⁶ due to the different charge transfer. On the other hand, though sharing the same isomeric cage structures and four electron charge transfer, the spectrum of $\text{Th}@C_{2v}(9)\text{-C}_{82}$ shows notable differences to those of the $\text{Er}_2C_2@C_{2v}(9)\text{-C}_{82}$,¹⁷ suggesting the major impact of the encapsulated species on the electronic structures of the corresponding EMFs.

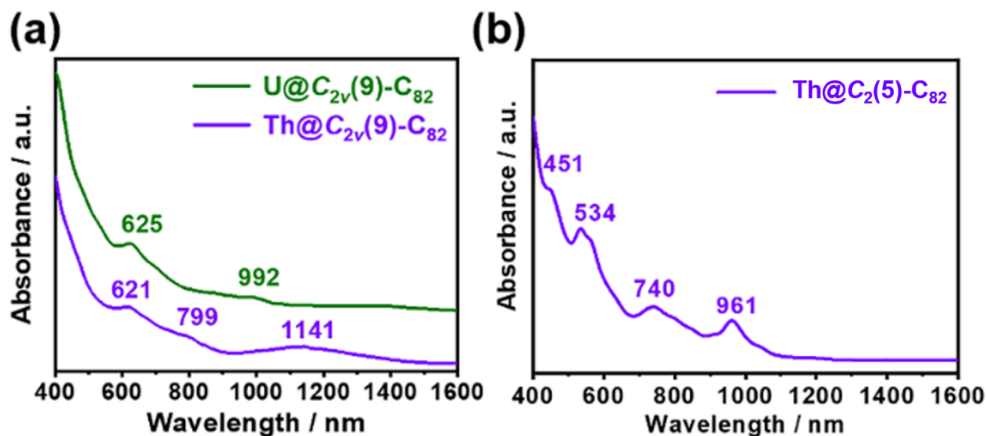


Figure 4. UV-vis-NIR absorption spectra of (a) $\text{Th}@C_{2v}(9)\text{-C}_{82}$ and $\text{U}@C_{2v}(9)\text{-C}_{82}$, and (b) $\text{Th}@C_2(5)\text{-C}_{82}$ in CS_2 .

$\text{Th}@C_{2v}(9)\text{-C}_{82}$ and $\text{Th}@C_2(5)\text{-C}_{82}$ were also characterized by low energy Raman spectroscopy, as shown in Figure 5. Sharp peaks at 151 and 152 cm^{-1} are observed for the Raman spectrum of $\text{Th}@C_{2v}(9)\text{-C}_{82}$ and $\text{Th}@C_2(5)\text{-C}_{82}$ respectively. These frequencies, which can be assigned to the metal-to-cage vibrational mode,¹⁸ are very close to those for $\text{Th}@C_{3v}(8)\text{-C}_{82}$ (148 cm^{-1}),⁶ $\text{Th}@C_1(11)\text{-C}_{86}$ (153 cm^{-1})⁸ and $\text{Th}@C_1(28324)\text{-C}_{80}$ (155 cm^{-1}),⁷ indicating similar strong metal-cage interaction in thorium-based endohedral mono-metallofullerenes. Indeed, the computed Raman spectra for $\text{Th}@C_{2v}(9)\text{-C}_{82}$ and $\text{Th}@C_2(5)\text{-C}_{82}$ confirm the metal-to-cage nature of these normal modes, whose predicted wavenumbers are 144 and 149 cm^{-1} , respectively (see SI for more details). It should be noted that, though the Vis-NIR absorption curve of $\text{Th}@C_{2v}(9)\text{-C}_{82}$ somewhat differs from that of $\text{U}@C_{2v}(9)\text{-C}_{82}$, the vibrational frequencies of $\text{Th}@C_{2v}(9)\text{-C}_{82}$ at 216 and 359 cm^{-1} , as shown in Figure 5a, show pronounced similarity to those of the $\text{U}@C_{2v}(9)\text{-C}_{82}$, further confirming that $\text{Th}@C_{2v}(9)\text{-C}_{82}$ and $\text{U}@C_{2v}(9)\text{-C}_{82}$ share the same cage isomer.¹⁰ In addition, the frequencies of the cage vibration modes observed in the range of 200-500 cm^{-1} for the spectrum of $\text{Th}@C_2(5)\text{-C}_{82}$ (215, 314 and 442 cm^{-1}) also show some resemblance compared to $\text{Eu}@C_2(5)\text{-C}_{82}$ ¹⁹ (frequencies at 215, 358 and 422 cm^{-1}).

cm^{-1}) and $\text{Th@C}_2(5)\text{-C}_{82}^{20}$ (frequencies at 222, 320 and 412 cm^{-1}), indicating the same cage symmetry.

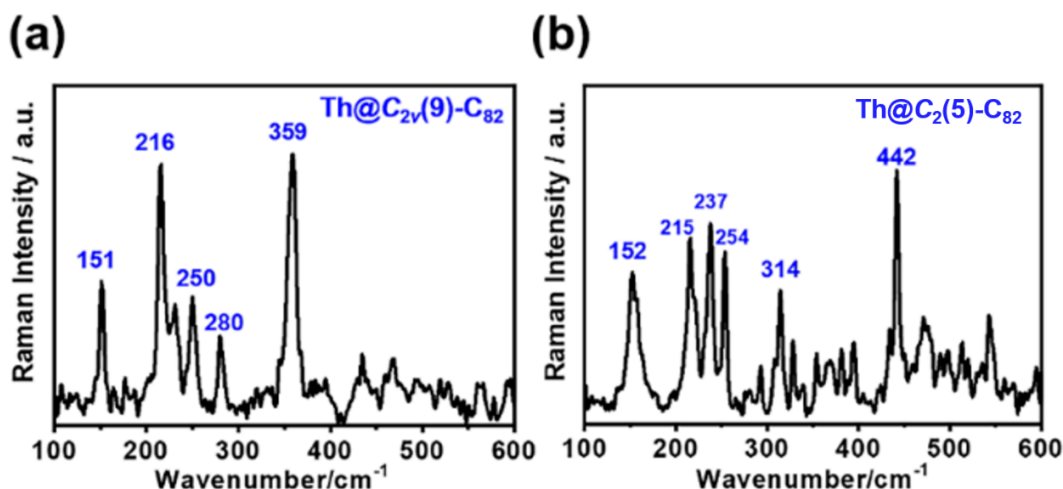


Figure 5. Low-energy Raman spectra of (a) $\text{Th@C}_{2v}(9)\text{-C}_{82}$ and (b) $\text{Th@C}_2(5)\text{-C}_{82}$ at 633 nm excitation.

Electrochemical Studies. Cyclic voltammetry (CV) was employed to investigate the redox properties of the two Th@C_{82} isomers. Table 1 summarized the redox potentials of $\text{Th@C}_{2v}(9)\text{-C}_{82}$ and $\text{Th@C}_2(5)\text{-C}_{82}$ as well as those of the structurally related compounds for comparison. As displayed in Figure 6, both $\text{Th@C}_{2v}(9)\text{-C}_{82}$ and $\text{Th@C}_2(5)\text{-C}_{82}$ present one reversible oxidation step (+0.20 and +0.26 V) and one irreversible oxidation step (+0.64 and +1.01 V). In addition, $\text{Th@C}_{2v}(9)\text{-C}_{82}$ shows three reduction steps at -1.05, -1.36 and -1.72 V and $\text{Th@C}_2(5)\text{-C}_{82}$ also presents three reduction potentials (-1.15, -1.65 and -2.16 V). As shown in Table 1, for the oxidation potential, compared to the first reported Th@C_{82} isomer of $\text{Th@C}_{3v}(8)\text{-C}_{82}$, $\text{Th@C}_{2v}(9)\text{-C}_{82}$ and $\text{Th@C}_2(5)\text{-C}_{82}$ show a generally negative shift. For reduction potentials, $\text{Th@C}_2(5)\text{-C}_{82}$ also shows significant negative shift compared to those of the $\text{Th@C}_{3v}(8)\text{-C}_{82}$, but $\text{Th@C}_{2v}(9)\text{-C}_{82}$ shows much more similarity to those of the $\text{Th@C}_{3v}(8)\text{-C}_{82}$.

Notably, the first reduction potential of $\text{Th}@C_{2v}(9)\text{-C}_{82}$ is much more negative with respect to $\text{U}@C_{2v}(9)\text{-C}_{82}$ (-1.05 vs -0.43 V).¹⁰ As a result, the electrochemical gap of $\text{Th}@C_{2v}(9)\text{-C}_{82}$, 1.25 V, is significantly larger than that of $\text{U}@C_{2v}(9)\text{-C}_{82}$ (0.53 V), in agreement with their different electronic structure. On the other hand, the obvious negative shifts of the redox potentials are also found for $\text{Th}@C_{2v}(9)\text{-C}_{82}$ compared with the four-electron-transferred $\text{Sc}_2\text{C}_2@C_{2v}(9)\text{-C}_{82}$,²¹ as listed in Table 1. Overall, relatively large electrochemical gaps for $\text{Th}@C_{2v}(9)\text{-C}_{82}$ (1.25 V) and $\text{Th}@C_2(5)\text{-C}_{82}$ (1.41 V) are correlated with the 4-electron thorium-cage charge transfer, i.e. formal Th^{4+} ($5f^6d^07s^0$), and confirm that both $\text{Th}@C_{2v}(9)\text{-C}_{82}$ and $\text{Th}@C_2(5)\text{-C}_{82}$ possess stable closed-shell electronic structure (vide infra), in contrast to $\text{U}@C_{2v}(9)\text{-C}_{82}$ and $\text{U}@C_2(5)\text{-C}_{82}$, with much smaller gaps (0.53 and 0.78 V, respectively) as a consequence of the unpaired electrons in the open 5f shell of U atom.¹⁰

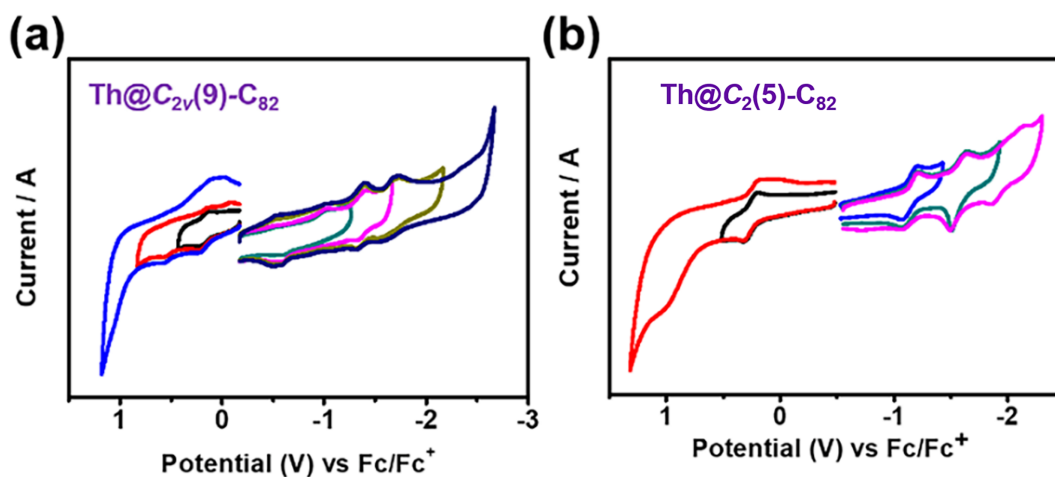


Figure 6. Cyclic voltammograms of (a) $\text{Th}@C_{2v}(9)\text{-C}_{82}$ and (b) $\text{Th}@C_2(5)\text{-C}_{82}$ in *o*-dichlorobenzene (0.05 M $(n\text{-Bu})_4\text{NPF}_6$ as the supporting electrolyte; scan rate 100 mV/s).

Table 1. Redox potentials (V vs. Fc/Fc^+) and electrochemical band gaps of $\text{Th}@C_{2v}(9)\text{-C}_{82}$, $\text{Th}@C_2(5)\text{-C}_{82}$ and the selected reference EMFs.

Compounds	$E^{2+/+}$	$E^{+/0}$	$E^{0/-}$	$E^{-2/-}$	$E^{2-/3-}$	$E_{\text{gap ec}}(\text{V})$	ref
-----------	------------	-----------	-----------	------------	-------------	-------------------------------	-----

Th@C _{2v} (9)-C ₈₂	+0.64 ^b	+0.20 ^a	-1.05 ^b	-1.36 ^a	-1.72 ^a	1.25	this work
Th@C ₂ (5)-C ₈₂	+1.01 ^b	+0.26 ^a	-1.15 ^a	-1.65 ^b	-2.16 ^b	1.41	this work
Th@C _{3v} (8)-C ₈₂		+0.46 ^a	-1.05 ^b	-1.54 ^b	-1.69 ^b	1.51	⁶
U@C _{2v} (9)-C ₈₂	+0.92 ^b	+0.10 ^b	-0.43 ^a	-1.42 ^a	-1.76 ^b	0.53	¹⁰
Sc ₂ C ₂ @C _{2v} (9)-C ₈₂	+0.67 ^a	+0.25 ^b	-0.74 ^a	-0.96 ^a		0.99	²¹

^aHalf-wave potential (reversible redox process). ^bPeak potential (irreversible redox process).

Computational analysis

To better understand the interaction between Th and the carbon cage as well as the formal charge transfer in these two new isomers of Th@C₈₂, we have analyzed their electronic structures at PBE/TZP level (see Computational Details). Both Th@C_{2v}(9)-C₈₂ and Th@C₂(5)-C₈₂ show occupied orbitals that are essentially delocalized on the carbon cage, with contributions of Th orbitals to HOMO smaller than 10% (see Figure 7). LUMO and higher-energy orbitals show much important contributions from Th. Therefore, we can confirm the formal transfer of four electrons from Th to the cage, even though the covalent interactions are not negligible and larger than for lanthanide EMFs, as found recently for other similar systems.⁷

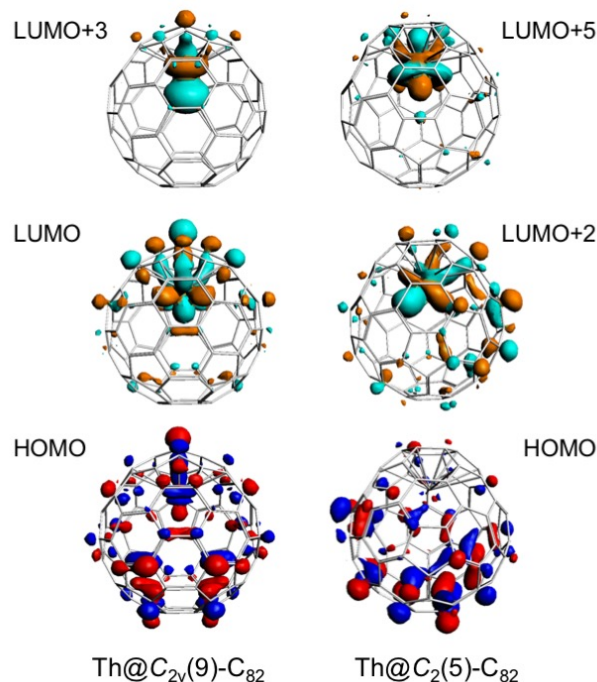


Figure 7. Frontier molecular orbitals of $\text{Th@C}_{2v}(9)\text{-C}_{82}$ and $\text{Th@C}_2(5)\text{-C}_{82}$. Occupied orbitals are essentially localized in the carbon cage (HOMO shows less than 10% contribution from Th orbitals).

For each of the isomers, we have confirmed, at the present methodology, that the most favored positions of the Th atom are in agreement with previous work.⁶ For $\text{Th@C}_{2v}(9)\text{-C}_{82}$, we have found that the Th atom is highly stabilized near triple-hexagon junctions surrounded by three pentagons, as observed in $\text{Th@C}_{3v}(8)\text{-C}_{82}$,⁶ and in line with the X-ray structure (see Figure 3a). The shortest Th...C distance is 2.386 Å, very similar to that found in the experiment (2.353 Å). Interestingly, the three nearest pentagons to the Th ion are among those with highest negative charges in the tetraanionic cage, as found for $\text{Th@C}_{3v}(8)\text{-C}_{82}$.⁶ Not only the site with the major occupancy in the experimental structure (Th1 49%) shows these characteristics, but also the second most-occupied site Th2 (40%). For $\text{Th@C}_2(5)\text{-C}_{82}$, Th is found to be very favored near a hexagon (see Figure 3b).

The closest Th-C distances range between 2.46 and 2.54 Å, with an average value of 2.500 Å, slightly larger than those found by X-ray crystallography (range 2.308-2.439 Å).

We have also checked that the thermodynamic abundances predicted for Th@C_{2v}(9)-C₈₂ and Th@C₂(5)-C₈₂ at the high temperatures of fullerenes formation are significantly enough to justify their formation. We have predicted, at PBE/TZP level, the molar fractions up to 4000 K within the FEM approximation^{22,23} for some of the IPR and non-IPR isomers with one adjacent pentagon pair (APP). Our selection of structures is based on a first screening based on the energies of the corresponding tetraanions (Table S6).⁶ Among the IPR structures, we have selected isomers 39714 (IPR 5), 39715 (IPR 6), 39717 (IPR 8) and 39718 (IPR 9), three of them corresponding to the so far isolated and characterized Th@C₈₂ isomers. From the 75 non-IPR structures with a single APP (APP1), we have selected those with the lowest energies as C₈₂⁴⁻ as well as some others which are intimately related by a single C₂ insertion to the most abundant Th@C₈₀ cages. This way we would be able to predict if there is a non-IPR APP1 cage that could encapsulate Th, as observed for Th@C₈₀.⁷

Table 2. Relative energies for tetraanions C₈₂⁴⁻ and Th@C₈₂ isomers (following the Fowler and Manolopoulos numbering) along with the symmetries of the empty cages.^{a,b)}

isomer	APP	Sym	C ₈₂ ⁴⁻	Th@C ₈₂
39717	IPR 8	C _{3v}	0.0	0.0
39718	IPR 9	C _{2v}	3.0	0.9
39714	IPR 5	C ₂	22.3	7.2
39715	IPR 6	C _s	8.4	7.6
37788	APP1	C ₁	41.2	15.0
39662	APP1	C _s	35.7	19.7

37897	APP1	C_1	41.4	20.9
39663	APP1	C_s	31.4	21.3
39656	APP1	C_1	31.3	21.4
38471	APP1	C_1	36.9	22.5
37359	APP1	C_1	37.9	26.3
39701	APP1	C_s	41.8	32.2
39686	APP1	C_1	31.2	33.2
39705	APP1	C_{2v}	19.5	37.1
39704	APP1	C_s	27.2	42.0
39706	APP1	C_1	50.4	49.3

^{a)}Energies in kcal mol⁻¹; ^{b)} Isomers 37788 and 39706 are obtained from a single C_2 insertion to $C_1(28324)-C_{80}$; Isomers 39662, 39656, 39686 and 39706 are obtained from a single C_2 insertion to $C_{2v}(5)-C_{80}$.

$Th@C_{2v}(9)-C_{82}$ is almost isoenergetic with $Th@C_{3v}(8)-C_{82}$, the lowest-energy isomer, as previously observed with similar computational settings. Isomer $Th@C_2(5)-C_{82}$ shows somewhat higher energy, at 7.2 kcal mol⁻¹, which is considerably lower than its relative energy as a tetraanion. This isomer is largely stabilized when containing the Th ion as a consequence of the favorable $Th\cdots C$ interactions. This significant change in the relative stability of $Th@C_{82}$ isomers as compared to that provided by the purely ionic model, i.e. computing the isomers as tetraanions, has been already observed in other monometallic actinidofullerenes⁷ and we are working to rationalize it. For non-IPR structures, significant stabilizations larger than 15 kcal mol⁻¹ are observed when inserting Th for isomers 37788, 39662 and 37897. On the opposite side, we find isomer 39705, obtained by direct C_2 insertion to $I_h(7)-C_{80}$ and which is the lowest-energy APP1 tetraanion, that is destabilized by the Th insertion more than 15 kcal mol⁻¹. From all the computed non-IPR APP1 $Th@C_{82}$ isomers, the only one that is competitive at high temperatures is $Th@C_1(37788)-C_{82}$ (Figure 8). $Th@C_{2v}(9)-C_{82}$ is predicted to be the most abundant isomer at 2000 K along with $Th@C_{3v}(8)-C_{82}$, in line with

experiments. Isomers $C_2(5)-C_{82}$ and $C_5(6)-C_{82}$ show similar abundances, which indicates that the latter could be also observed in future experiments. The tiny abundances of other APP1 structures compared to that of isomer $C_1(37788)-C_{82}$ are shown in the SI.

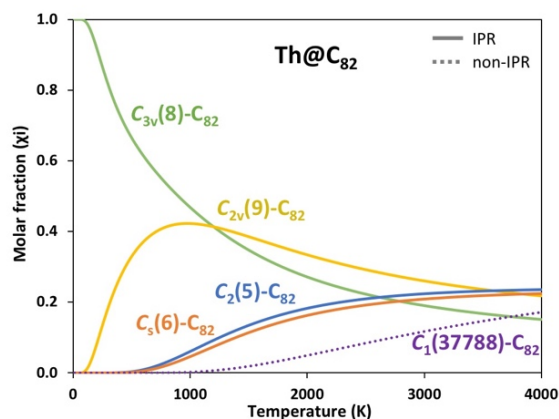


Figure 8. Molar fractions at different temperatures computed with the FEM approximation for some $\text{Th}@C_{82}$ isomers.

Conclusions

In conclusion, two novel isomers of $\text{Th}@C_{82}$ were successfully synthesized and isolated and fully characterized by mass spectrometry, X-ray crystallography, UV-vis-NIR spectroscopy, Raman spectroscopy, and cyclic voltammetry. The molecular structures of the two isomers were determined unambiguously as $\text{Th}@C_{2v}(9)-C_{82}$ and $\text{Th}@C_2(5)-C_{82}$ by single crystal X-ray diffraction analysis, respectively. The electrochemical studies, which show that the two isomers have large electrochemical gaps, confirm that both $\text{Th}@C_{2v}(9)-C_{82}$ and $\text{Th}@C_2(5)-C_{82}$ possess stable closed-shell electronic structure. Besides, UV-vis-NIR spectroscopic and computational analysis, corroborate that both $\text{Th}@C_{2v}(9)-C_{82}$ and $\text{Th}@C_2(5)-C_{82}$ exhibit four-electron charge transfer from metal to carbon cage. Finally, the structural and computational studies reveal that the Th atom is highly stabilized near a triple-hexagon junction in $\text{Th}@C_{2v}(9)-C_{82}$ and near a hexagon in $\text{Th}@C_2(5)-C_{82}$.

C₈₂. This study further confirms the unique electron transfer and interaction between actinide metal ion and the fullerene cage isomers.

Experimental Details

Synthesis and isolation of Th@C₈₂. The carbon soot containing thorium EMFs were synthesized by the direct-current arc discharge method. The graphite rods, packed with ThO₂ powders and graphite powders (1:24 molar ratio), were vaporized in the arcing chamber under a 200 Torr He atmosphere. The resulting soot was refluxed in CS₂ under an argon atmosphere for 12 h. The separation and purification of Th@C₈₂ were achieved by multi-stage HPLC procedures. Multiple HPLC columns, including Buckyprep-M column (25 × 250 mm, Cosmosil, Nacalai Tesque Inc.), Buckprep-D column (10 × 250 mm, Cosmosil, Nacalai Tesque, Japan), and Buckprep column (10 × 250 mm, Cosmosil, Nacalai Tesque, Japan), were utilized in the procedures. Further details are described in the Supporting Information.

Spectroscopic and Electrochemical Studies. The positive-ion mode matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) (Bruker, Germany) was employed for the mass characterization. The UV-vis-NIR spectra of the purified Th@C₈₂ were measured in CS₂ solution with a Cary 5000 UV-vis-NIR spectrophotometer (Agilent, USA). The Raman spectra were obtained using a Horiba Lab RAM HR Evolution Raman spectrometer using a laser at 633 nm. Cyclic voltammetry (CV) results were obtained in *o*-dichlorobenzene using a CHI-660E instrument. A conventional three-electrode cell consisting of a platinum counter-electrode, a glassy carbon working electrode, and a silver reference electrode was used for the measurements. (*n*-Bu)₄NPF₆ (0.05 M) was used as supporting electrolyte. The CV were measured at the scan rate of 100 mV/s.

X-ray Crystallographic Study. The black block crystals of Th@C₈₂ were obtained by slow diffusion of the CS₂ solution of the corresponding metallofullerene compounds into the benzene solution of [Ni^{II}(OEP)]. Single-crystal X-ray data of Th@C_{2v}(9)-C₈₂ and Th@C_{2v}(5)-C₈₂ were collected at 153 K and 100 K respectively, on a diffractometer (APEX II; Bruker Analytik GmbH) equipped with a CCD collector. The multiscan method was used for absorption correction. The structures were solved using direct methods²⁴ and refined on F² using full-matrix least-squares using the SHELXL2014 crystallographic software packages.²⁵ Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters.

Crystal data for Th@C_{2v}(9)-C₈₂·[Ni^{II}(OEP)]·1.5C₆H₆·CS₂: $M_r = 2001.61$, 0.12 mm × 0.08 mm × 0.05 mm, monoclinic, $P2_1/c$ (No. 14), $a = 17.660(4)$ Å, $b = 17.300(4)$ Å, $c = 26.630(5)$ Å, $\alpha = 90^\circ$, $\beta = 107.73(3)^\circ$, $\gamma = 90^\circ$, $V = 7750(3)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.716$ g cm⁻³, $\mu(\text{MoK}\alpha) = 2.282$ mm⁻¹, $\theta = 1.991\text{--}26.738$, $T = 153(2)$ K, $R_1 = 0.0911$, $wR_2 = 0.1555$ for all data; $R_1 = 0.0648$, $wR_2 = 0.1418$ for 12538 reflections ($I > 2.0\sigma(I)$) with 1995 parameters. Goodness-of-fit indicator 1.079. Maximum residual electron density 1.850 e Å⁻³.

Crystal data for Th@C_{2v}(5)-C₈₂·[Ni^{II}(OEP)]·C₆H₆: $M_r = 1870.76$, 0.1 mm × 0.08 mm × 0.06 mm, monoclinic, $C2/m$ (No. 12), $a = 25.000$ Å, $b = 15.304$ Å, $c = 19.938$ Å, $\alpha = 90^\circ$, $\beta = 94.11^\circ$, $\gamma = 90^\circ$, $V = 7608.6$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.647$ g cm⁻³, $\mu(\text{MoK}\alpha) = 2.266$ mm⁻¹, $\theta = 2.527\text{--}26.446$, $T = 100$ K, $R_1 = 0.1137$, $wR_2 = 0.2789$ for all data; $R_1 = 0.0941$, $wR_2 = 0.2604$ for 6463 reflections ($I > 2.0\sigma(I)$) with 1023 parameters. Goodness-of-fit indicator 1.036. Maximum residual electron density 1.916 e Å⁻³.

Computational Details. All the calculations were carried out using density functional theory (DFT) with the ADF 2017 package.²⁶ The PBE functional and Slater triple-zeta polarization basis sets (PBE-DG3/TZP) were used, including Grimme dispersion corrections.^{27, 28} Frozen cores

consisting of the 1s shell for C and the 1s to 5d shells for Th were described by means of single Slater functions. Scalar relativistic corrections were included by means of the ZORA formalism.

ASSOCIATED CONTENT

Supporting Information

HPLC profiles for the separation of Th@C₂₄(9)-C₈₂, Th@C₂(5)-C₈₂, experimental details and complementary computational results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Accession Codes

CCDC 2048051 and 2048069 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: chenning@suda.edu.cn

*E-mail: fenglai@suda.edu.cn

*E-mail: antonio.rodriquezf@urv.cat

Author Contributions

[‡]These authors contributed equally.

Funding Sources

National Science Foundation China (NSFC 91961109, 51302178, 51772195), Natural Science Foundation of Jiangsu Province (BK20200041), Spanish Ministry of Science (CTQ2017-87269-P)

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

N.C. thanks the National Science Foundation China (NSFC 91961109, 51302178), the Natural Science Foundation of Jiangsu Province (BK20200041), and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD). L.F. thanks the National Science Foundation China (NSFC 51772195). A.R.-F. and J.M.P. thank the Spanish Ministry of Science (CTQ2017-87269-P) for support. J.M.P. also thanks ICREA foundation for an ICREA ACADEMIA award.

REFERENCES

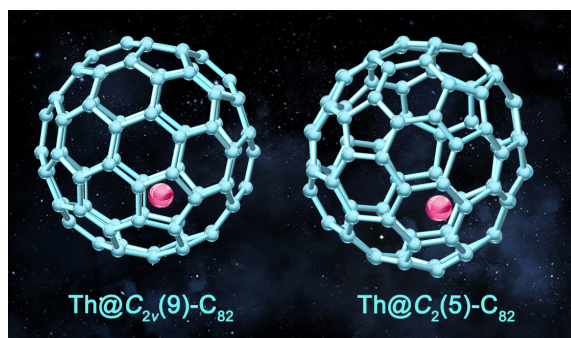
- (1) Qu, L.; Cao, W.; Xing, G.; Zhang, J.; Yuan, H.; Tang, J.; Cheng, Y.; Zhang, B.; Zhao, Y.; Lei, H. Study of rare earth encapsulated carbon nanomolecules for biomedical uses. *J. Alloys Compd.* **2006**, *408-412*, 400-404.
- (2) Ross, R. B.; Cardona, C. M.; Guldi, D. M.; Sankaranarayanan, S. G.; Reese, M. O.; Kopidakis, N.; Peet, J.; Walker, B.; Bazan, G. C.; Van Keuren, E.; Holloway, B. C.; Drees, M. Endohedral fullerenes for organic photovoltaic devices. *Nat. Mat.* **2009**, *8*, 208.

- (3) Rincon-Garcia, L.; Ismael, A. K.; Evangeli, C.; Grace, I.; Rubio-Bollinger, G.; Porfyrakis, K.; Agrait, N.; Lambert, C. J. Molecular design and control of fullerene-based bi-thermoelectric materials. *Nat. Mat.* **2016**, *15* (3), 289-93.
- (4) Wu, B.; Wang, T.; Feng, Y.; Zhang, Z.; Jiang, L.; Wang, C. Molecular magnetic switch for a metallofullerene. *Nat. Commun.* **2015**, *6*, 6468.
- (5) Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Tittel, F. K.; Smalley, R. E. Lanthanum complexes of spheroidal carbon shells. *J. Am. Chem. Soc.* **1985**, *107* (25), 7779-7780.
- (6) Wang, Y.; Morales-Martinez, R.; Zhang, X.; Yang, W.; Wang, Y.; Rodriguez-Forteza, A.; Poblet, J. M.; Feng, L.; Wang, S.; Chen, N. Unique Four-Electron Metal-to-Cage Charge Transfer of Th to a C₈₂ Fullerene Cage: Complete Structural Characterization of Th@C_{3v}(8)-C₈₂. *J. Am. Chem. Soc.* **2017**, *139* (14), 5110-5116.
- (7) Cai, W.; Abella, L.; Zhuang, J.; Zhang, X.; Feng, L.; Wang, Y.; Morales-Martinez, R.; Esper, R.; Boero, M.; Metta-Magana, A.; Rodriguez-Forteza, A.; Poblet, J. M.; Echegoyen, L.; Chen, N. Synthesis and Characterization of Non-Isolated-Pentagon-Rule Actinide Endohedral Metallofullerenes U@C₁(17418)-C₇₆, U@C₁(28324)-C₈₀, and Th@C₁(28324)-C₈₀: Low-Symmetry Cage Selection Directed by a Tetravalent Ion. *J. Am. Chem. Soc.* **2018**, *140* (51), 18039-18050.
- (8) Wang, Y.; Morales-Martinez, R.; Cai, W.; Zhuang, J.; Yang, W.; Echegoyen, L.; Poblet, J. M.; Rodriguez-Forteza, A.; Chen, N. Th@C₁(11)-C₈₆: an actinide encapsulated in an unexpected C₈₆ fullerene cage. *Chem. Commun.* **2019**, *55* (63), 9271-9274.

- (9) Jin, M.; Zhuang, J.; Wang, Y.; Yang, W.; Liu, X.; Chen, N. Th@ $T_d(19151)$ -C₇₆: A Highly Symmetric Fullerene Cage Stabilized by a Tetravalent Actinide Metal Ion. *Inorg. Chem.* **2019**, *58* (24), 16722-16726.
- (10) Cai, W.; Morales-Martinez, R.; Zhang, X.; Najera, D.; Romero, E. L.; Metta-Magana, A.; Rodriguez-Forteza, A.; Fortier, S.; Chen, N.; Poblet, J. M.; Echegoyen, L. Single crystal structures and theoretical calculations of uranium endohedral metallofullerenes (U@C_{2n}, 2n = 74, 82) show cage isomer dependent oxidation states for U. *Chem. Sci.* **2017**, *8* (8), 5282-5290.
- (11) Suzuki, M.; Lu, X.; Sato, S.; Nikawa, H.; Mizorogi, N.; Slanina, Z.; Tsuchiya, T.; Nagase, S.; Akasaka, T. Where does the metal cation stay in Gd@C_{2v}(9)-C₈₂? A single-crystal X-ray diffraction study. *Inorg. Chem.* **2012**, *51* (9), 5270-5273.
- (12) Sato, S.; Nikawa, H.; Seki, S.; Wang, L.; Luo, G.; Lu, J.; Haranaka, M.; Tsuchiya, T.; Nagase, S.; Akasaka, T. A co-crystal composed of the paramagnetic endohedral metallofullerene La@C₈₂ and a nickel porphyrin with high electron mobility. *Angew. Chem. Int. Ed. Engl.* **2012**, *51* (7), 1589-1591.
- (13) Hachiya, M.; Nikawa, H.; Mizorogi, N.; Tsuchiya, T.; Lu, X.; Akasaka, T. Exceptional chemical properties of Sc@C_{2v}(9)-C₈₂ probed with adamantylidene carbene. *J. Am. Chem. Soc.* **2012**, *134* (37), 15550-15555.
- (14) Lu, X.; Nikawa, H.; Feng, L.; Tsuchiya, T.; Maeda, Y.; Akasaka, T.; Mizorogi, N.; Slanina, Z.; Nagase, S. Location of the Yttrium Atom in Y@C₈₂ and Its Influence on the Reactivity of Cage Carbons. *J. Am. Chem. Soc.* **2009**, *131* (34), 12066-12067.

- (15) Okazaki, T.; Lian, Y.; Gu, Z.; Suenaga, K.; Hisanori, S. Isolation and spectroscopic characterization of Sm-containing metallofullerenes. *Chem. Phys. Lett.* **2000**, *320* (5), 435-440.
- (16) Yang, H.; Jin, H.; Wang, X.; Liu, Z.; Yu, M.; Zhao, F.; Mercado, B. Q.; Olmstead, M. M.; Balch, A. L. X-ray crystallographic characterization of new soluble endohedral fullerenes utilizing the popular C_{82} bucky cage. Isolation and structural characterization of $Sm@C_{3v}(7)-C_{82}$, $Sm@C_s(6)-C_{82}$, and $Sm@C_2(5)-C_{82}$. *J. Am. Chem. Soc.* **2012**, *134* (34), 14127-14136.
- (17) Ito, Y.; Okazaki, T.; Okubo, S.; Akachi, M.; Ohno, Y.; Mizutani, T.; Nakamura, T.; Kitaura, R.; Sugai, T.; Shinohara, H. Enhanced 1520 nm Photoluminescence from Er^{3+} Ions in Di-erbium-carbide Metallofullerenes (Er_2C_2)@ C_{82} (Isomers I, II, and III). *ACS Nano* **2007**, *1* (5), 456-462.
- (18) Popov, A. A.; Yang, S.; Dunsch, L. Endohedral fullerenes. *Chem. Rev.* **2013**, *113* (8), 5989-6113.
- (19) Hosokawa, T.; Fujiki, S.; Kuwahara, E.; Kubozono, Y.; Kitagawa, H.; Fujiwara, A.; Takenobu, T.; Iwasa, Y. Electronic properties for the C_{2v} and C_s isomers of $Pr@C_{82}$ studied by Raman, resistivity and scanning tunneling microscopy/spectroscopy. *Chem. Phys. Lett.* **2004**, *395* (1), 78-81.
- (20) Krause, M.; Kuran, P.; Kirbach, U.; Dunsch, L. Raman and infrared spectra of $Tm@C_{82}$ and $Gd@C_{82}$. *Carbon* **1999**, *37* (1), 113-115.
- (21) Lu, X.; Nakajima, K.; Iiduka, Y.; Nikawa, H.; Tsuchiya, T.; Mizorogi, N.; Slanina, Z.; Nagase, S.; Akasaka, T. The long-believed $Sc_2@C_{2v}(17)-C_{84}$ is actually $Sc_2C_2@C_{2v}(9)-C_{82}$: unambiguous structure assignment and chemical functionalization. *Angew. Chem. Int. Ed. Engl.* **2012**, *51* (24), 5889-5892.

- (22) Slanina, Z.; Lee, S.-L.; Uhlík, F.; Adamowicz, L.; Nagase, S. Computing relative stabilities of metallofullerenes by Gibbs energy treatments. *Theor. Chem. Acc.* **2007**, *117* (2), 315-322.
- (23) Slanina, Z.; Nagase, S. Sc₃N@C₈₀: Computations on the Two-Isomer Equilibrium at High Temperatures. *ChemPhysChem* **2005**, *6* (10), 2060-2063.
- (24) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42* (2), 339-341.
- (25) Sheldrick, G. Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71* (1), 3-8.
- (26) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. Chemistry with ADF. *J. Comput. Chem.* **2001**, *22* (9), 931-967.
- (27) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865-3868.
- (28) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, *32* (7), 1456-1465.



SYNOPSIS: For the first time, actinide metal Th atom inside C₂(5)-C₈₂ and C_{2v}(9)-C₈₂, Th@C₂(5)-C₈₂ and Th@C_{2v}(9)-C₈₂ have been synthesized and characterized. The electrochemical studies suggests that both Th@C_{2v}(9)-C₈₂ and Th@C₂(5)-C₈₂ possess stable closed-shell electronic structure. The theoretical investigations confirm that Th@C₂(5)-C₈₂ and Th@C_{2v}(9)-C₈₂ exhibit a unique four-electron charge transfer from metal to carbon cage and are among the most abundant isomers.