Characterization of a strong covalent Th\(^{3+}\)-Th\(^{3+}\) bond inside an \(I_h(7)-C_{80}\) fullerene cage

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The nature of the actinide-actinide bonds is of fundamental importance to understand the electronic structure of the \(5f\) elements. It has attracted considerable theoretical attention, but little is known experimentally as the synthesis of these chemical bonds remains extremely challenging. Herein, we report a strong covalent Th-Th bond formed between two rarely accessible Th\(^{3+}\) ions, stabilized inside a fullerene cage nanocontainer as Th\(_2@I_h(7)-C_{80}\). This compound is synthesized using the arc-discharge method and fully characterized using several techniques. The single-crystal X-Ray diffraction analysis determines that the two Th atoms are separated by 3.816 Å. Both experimental and quantum-chemical results show that the two Th atoms have formal charges of +3 and confirm the presence of a strong covalent Th-Th bond inside \(I_h(7)-C_{80}\). Moreover, density functional theory and ab initio multireference calculations suggest that the overlap between the 7s/6d hybrid thorium orbitals is so large that the bond still exists at Th-Th separations larger than 6 Å. This work demonstrates the authenticity of covalent actinide metal-metal bonds in a stable compound and deepens our fundamental understanding of \(f\) element metal bonds.
Understanding the nature of chemical bonds is at the center of chemistry and is fundamental for the prediction of reactivity and consequent synthetic work. Many chemical compounds contain metal–metal bonds that are responsible for their structural and functional properties. Bonding between main group and d transition group elements have been intensively studied for many decades and significant advances have been achieved on the synthesis of f–d metal–metal bonds in recent studies1–3. In contrast, experimental studies of bonding between f-block metals is notably lagging behind4. Exploring the electronic structure of the 5f elements is crucial given their potential applications in different fields, such as in nuclear fuel recycling. Theory predicts that the U2 molecule should be stable in the gas phase5,6, and experimental evidence for its existence was reported in 1974 using mass spectrometry7. However, a long standing Holy Grail in inorganic chemistry is the synthesis and characterization of compounds that contain An–An bonds, and very little has been reported in this field. Most of the work concerning An–An bonds has been of a theoretical nature5,6,8–11. On the experimental side, Souter et al. reported the formation of U2H2 and U2H4 via laser ablation of U atoms in the presence of H2, stabilized in a solid argon matrix12. However, characterization was limited to infrared spectroscopy supplemented with Density Functional Theory (DFT) calculations. The authors stated in the article abstract that: ‘The molecules U(μ-H2)U and U2H4 represent the first examples of an actinide–actinide bond’. To our knowledge, there are only two other reports that claim the formation of An–An bonds, and very little has been extracted with CS2 for 12 h. A multistage HPLC procedure was employed to isolate and purify Th2@C80. After a four-stage HPLC separation protocol, the purified Th2@C80 was obtained (Supplementary Fig. 2). The purity of the isolated Th2@C80 was confirmed by the observation of a single peak by HPLC and by high-resolution matrix-assisted laser desorption-ionization time-of-flight positive-ion-mode mass spectrometry (MALDI-TOF/MS). The mass spectrum shows a prominent molecular ion peak with a mass-to-charge ratio of m/z = 1424.076 (Supplementary Fig. 1), corresponding to the empirical formula of [Th2C80]+ and the experimental isotopic distribution agrees well with the theoretical prediction.

Molecular structure of Th2@I6(7)-C80[NiII-OEP]. The molecular structure of Th2@C80 was determined by single-crystal X-ray diffraction analysis. Th2@C80 was co-crystallized with NiII-OEP (OEP = 2, 3, 7, 8, 12, 13, 17, 18-octaethylporphin diion) by slow diffusion of a benzene solution of NiII-OEP into a CS2 solution of Th2@C80. The structure was resolved and refined in the P21/c (No. 14) space group. Fig. 1a shows Th2@I6(7)-C80 and its relationship to the co-crystallized NiII(OEP) molecule. The crystallographic data indicate that the I6(7)-C80 cage is fully ordered. Inside the fullerene cage, two major Th positions (Th1 and Th2) are highly ordered and have dominant occupancies of 0.783(17) and 0.748(2), respectively, with the occupancies of minor sites...
ranging from 0.0028(7) to 0.1299(14) (Supplementary Table 1). Most of the reported lanthanide dimetallic endohedral fullerenes as well as the recently reported \( \text{U}_2@I_7\)–\(C_{80} \) commonly display severe disorder of the metals inside the highly symmetric \( I_7\)–\(C_{80} \).\(^{14,28}\) The highly ordered Th positions inside this cage are very unusual for pristine dimetallic endohedral fullerenes, suggesting a hindered metal motion, possibly caused by the bonding interactions between the Th ions and the fullerene cage as well as between the two Th ions. The ordered Th positions allow us to accurately determine the distance between major Th1 and Th2 as 3.816(6) Å. This distance is slightly longer than the U–U and La–La distances reported for \( \text{U}_2@I_7\)–\(C_{80} \)\(^{14} \) and \( \text{La}_2@I_8\)–\(C_{80}(\text{CH}_2\text{Ph})_2 \)\(^{22} \) but is comparable to the Ce–Ce bond distance in \( \text{Ce}_2@I_8\)–\(C_{80} \)\(^{28} \) and even shorter than the metal–metal bond distance observed in \( \text{La}_2@I_7\)–\(C_{80} \)\(^{19} \), Dy\(_2@I_8\)–\(C_{80}(\text{CH}_2\text{Ph})_2 \)\(^{21} \), and \( \text{Th}_2@C_{79}N \)\(^{20} \) (Supplementary Table 3). Th1 and Th2 reside under corresponding hexagons and the distances between the major thorium sites and the cage carbons all lie within the range of 2.483 (9)–2.559(9) Å, with Th1 and Th2 at distances to their corresponding hexagon centroids of 2.048 and 2.066 Å, respectively. (See Fig. 1b, Supplementary Table 2, and Supplementary Fig. 4). It is noteworthy that these Th–(ring centroid) distances are shorter than those for previously reported Th\(_2^+ \) complexes: 2.607, 2.52, 2.53, and 2.551 Å for \( \text{Ce}_2@I_8\)–\(C_{80} \)\(^{17} \), \( \text{C}_3\text{H}_3(\text{SiMe}_3)_2 \)–\(\text{Th} \)\(^{29} \), \( \text{C}_3\text{H}_3(\text{SiMe}_3^2\text{Bu})_2 \)–\(\text{Th} \)\(^{30} \), and \( \text{C}_3\text{Me}_6\)–\(\text{Th} \)\(^{31} \), respectively, indicating a strong interaction between the Th\(_2^+ \) cluster and the fullerene cage.

### Electronic structure and bonding in Th\(_2@I_7\)–\(C_{80} \)

DFT and ab initio calculations were performed to determine the electronic structure of the Th\(_2@I_7\)–\(C_{80} \) EMF and to characterize the nature of the Th–Th interaction. Since no more than 6e are transferred between the guest and the host\(^{32,33} \), the oxidation state of the Th atoms in Th\(_2@I_7\)–\(C_{80} \) should be +3, which is a rare situation given the tendency of Th atoms to formally transfer all four valence electrons to the groups with which they coordinate\(^{17,34–36} \). Accordingly, two electrons are available to form a Th–Th bond. At the DFT level, we have computed several structures corresponding to the electronic configurations \( \sigma^2, \sigma^1\pi^1, \) and \( \pi^2 \). When the two valence electrons are localized in the \( \sigma \) orbital, the Th–Th separation is computed to be 3.817 Å using the hybrid functional PBE0, a value that matches the experimental distance of 3.816 Å. The nature of the HOMO, a bonding \( \sigma \) Th–Th orbital (Fig. 2b), suggests that despite the long Th–Th distance, the two Th atoms are linked by a direct interaction. Although the LUMO is delocalized over the carbon cage, the lowest triplet corresponds to the promotion of one electron from the HOMO to a bonding orbital with a \( \pi (6d_{\sigma},6d_{\pi}) \) nature and, interestingly, the Th–Th distance shortens by 0.114 Å to 3.703 Å. If both the \( \sigma \) electrons are transferred to the \( \pi \) orbitals, the shortening is still larger, 0.309 Å. At the PBE0 level, the energy of the singlet (\( \sigma^2 \)) and triplet (\( \sigma^1\pi^1 \)) are almost degenerate with the triplet being about 1 kcal mol\(^{-1} \) lower in energy (Fig. 2a). Using the GGA PBE functional, the energy difference reaches 4 kcal mol\(^{-1} \) (Supplementary Table 5).

To properly characterize the nature of the ground state, we have performed CASPT2 calculations using the singlet DFT-optimized structure. As shown in Table 1, the ab initio ground state is a singlet with two electrons mainly localized in a \( \sigma \) (7s, 6d\(_\pi \)) orbital. The \( \pi_1 \) and \( \pi_2 \) bonding orbitals make a significant contribution (12%) to the wave function, whereas the antibonding \( \sigma^* \) orbital has an almost null contribution (Fig. 2c). Thus, the Th–Th bond can be seen as a \( \sigma \) bond with some contribution of bonding \( \pi \) orbitals to give an effective bond order of 0.99. When one electron is promoted from the \( \sigma \) orbital to one of the \( \pi \) orbitals the relative energy increases to 11.4 kcal mol\(^{-1} \) (9.5 kcal mol\(^{-1} \) with the triplet DFT structure). The discrepancy between DFT and CASPT2 results arises from the nature of the two electronic states. Whereas the triplet state is mono configurational, the singlet ground state has an important multiconfigurational nature that cannot be correctly described...
at the DFT level. In all DFT and CASPT2 calculations, only two electrons reside in molecular orbitals formed mainly by valence-shell Th orbitals, which confirms the oxidation state of +3 for the Th ions in the lowest energy states.

Both DFT and CASPT2 calculations suggest that the Th–Th interaction inside the icosahehdral C_{80} is covalent and clearly cannot be considered as a magnetic interaction. The covalent bond arises from the nature of the 7σ and 6d actinide orbitals that extend their overlap over very long distances, as shown in Supplementary Fig. 6. Because the overlap between Th orbitals can extend over distances larger than 6 Å, we have analyzed the thorium–thorium interaction inside cage D_{2}(821)-C_{104}, which can be visualized as two hemispheres of Ih actinides. A direct consequence is the presence of a relatively small energy gap between the σ(7s/6d_{z^2}) and σ*(7s/6d_{z^2}) orbitals. A partial population of the σ* orbital is observed in the CASSCF ground-state wave function, which leads to an effective bond order of 0.76 for the Th–Th bond, still very high considering the very long separation between the two Th atoms.

Finally, the Th–Th interaction was also characterized using Bader’s Quantum Theory of Atoms in Molecules (QTAIM). This theory uses several descriptors to characterize bonds through the topology of the electron density. Bader postulated that the presence of a bond critical point (bcp) between two atoms is a necessary and sufficient condition for the atoms to be bonded. Such a bcp was found that links the two Th atoms in Th_{2}@I_{6}(7)-C_{80}. A representation of the Laplacian of the electron density (\nabla^{2}\rho_{bcp}) distribution for the singlet ground state is given in Fig. 2d, which exhibits a non-negligible negative region in the internuclear Th–Th region. A direct consequence is that the value of the Laplacian of the charge density at the bcp is negative. These results are remarkable since metal–metal bonds typically exhibit depletion of the electron density in the internuclear region, that is, positive values in the Laplacian of \rho. The ELF plot also shows that the electron density is highly localized in the internuclear Th–Th bonding region. Indeed, when comparing the topological descriptors for Th_{2}, U_{2}, Lu_{2}, and La_{2} bonds inside C_{80} and C_{82} (Supplementary Table 6), we have found that the thorium–thorium bond exhibits the largest values even though its bond distance is the longest. Therefore, the thorium–thorium interaction is, up to now, the strongest one among the known actinide–actinide or lanthanide–lanthanide interactions.

As one cannot dissociate the Th_{2} unit inside the cage, it is not easy to give an accurate value for the Th–Th bond energy in Th_{2}@C_{80}. A rough estimate can be obtained from the relative energy of the triplet corresponding to the σ^{*}–σ^{1} configuration, as in this electronic configuration the Th–Th bond is effectively broken. However, the antibonding orbital is very high in energy and only the energies corresponding to the configurations σ^{1}σ^{1} and σ^{1}σ^{1}cage could be calculated. The latter triplet is about 2 eV higher in energy than the singlet ground state at CASPT2 level (Table 1). An alternative procedure is to compare the difference in the encapsulation energies of two La atoms and two Th atoms in C_{80}, which is 1.92 eV at the PBE0 level (1.7 eV at PBE). Assuming that the metal–cage interaction is approximately the same in both cases and that the bond is formed in the La_{2} case, the difference in encapsulation energy arises from the metal–metal bond in the dithorium EMF. Both procedures are rather approximate and have limitations, but it does not seem unreasonable to state that Th–Th bond energy is greater than 40 kcal mol^{-1}. It is worth mentioning that for cage D_{2}(821)-C_{104}, the difference in the encapsulation energies between dithorium and dilanthanum EMFs is still 0.45 eV at the PBE0 level and 0.25 eV at PBE (Supplementary Table 7). As already mentioned above, this strong metal–metal bond interaction is a result of a high overlap between 7s6d hybrid orbitals which extend over long distances (Supplementary Fig. 6). We are persuaded that this property could also be used in more traditional chemistry to obtain long-distance interactions between actinides, for example, through the design of appropriate ligands in organometallic chemistry. It is worth mentioning that uranium–uranium interactions are not that strong over long distances, as they occur through the more contracted 5f orbitals, their overlap decreasing much more rapidly with U–U separation. Actually, according to CASPT2 calculations, two U atoms within I_{6}C_{80} (d_{U1–U2} = 3.812 Å) show magnetic coupling with an effective bond order of 0.09. A detailed analysis of under what conditions two U atoms can exhibit a covalent interaction will be reported elsewhere.

### Table 1 CASPT2 energies and effective bond orders for Th_{2}@I_{6}(7)-C_{80} and Th_{2}@D_{2}(821)-C_{104} EMFs.

| Cage              | d_{Th–Th} | Config. | Spin | ΔE    | EBO   |
|-------------------|-----------|---------|------|------|-------|
| I_{6}(7)-C_{80}   | 3.817     | σ^{2}   | singlet | 0.0  | 0.99  |
|                   |           | σ^{1}   | triplet | 11.4 | 1.00  |
|                   |           | π^{2}   | triplet | 37.3 | 0.91  |
|                   |           | σ^{1}cage | triplet | 45.4 | 0.50  |
|                   |           | π^{1}   | triplet | 86.6 | 0.00  |
| D_{2}(821)-C_{104}| 3.702     | σ^{2}   | triplet  | 9.5  | 1.00  |
|                   |           | σ^{1}   | singlet  | 0.0  | 0.76  |
|                   |           | σ^{1}cage | singlet  | 13.4 | 0.50  |
|                   |           | π^{1}   | singlet  | 18.8 | 0.00  |
|                   |           | π^{1}cage | singlet  | 36.0 | 0.50  |

* CASSCF and CASPT2 calculations were performed at the ground state PBE0 geometries. All energies are given in kcal mol^{-1}.
* Effective Th–Th bond orders computed from CASSCF active MO occupations.
* σ Energy of the triplet computed using the DFT geometry of the triplet.
* MO occupations \(\sigma(1.73)\) \(\sigma(0.24)\).
* MO occupations \(\sigma(0.70)\) \(\sigma^{*}(0.30)\) \(\sigma^{*}(0.70)\).

**Spectroscopic properties of Th_{2}@C_{80}**

Purified Th_{2}@I_{6}(7)-C_{80} was characterized with UV–Vis–NIR and Raman spectroscopies as shown in Supplementary Fig. 5 and Fig. 3. The UV–Vis spectrum of Th_{2}@C_{80} shows three weak absorptions at 447, 488, and 683 nm, similar to typical I_{6}(7)-C_{80} cage based endofullerenes. Notably, a single vibration peak at 152 cm^{-1} can be observed in the low energy Raman spectrum and is assigned to a metal-to-cage vibration based on previous studies. This frequency is very close to 148 cm^{-1} for Th@C_{82}(8)-C_{82}, 153 cm^{-1} for Th@C_{71}(11)-C_{46}, and 155 cm^{-1} for Th@C_{72}(28324)-C_{40}, indicating similarly strong thorium–cage interactions. Moreover, the peaks at 220, 416 and 475 cm^{-1} also observed in the Raman spectra of U_{2}@I_{6}(7)-C_{80} and U_{2}@I_{7}(7)-C_{80}, can be assigned to the I_{6}(7)-C_{80} cage vibrational modes, consistent with the crystallographic analysis. The Raman peaks obtained at the DFT PBE level coincide well with the experimental ones (see Fig. 3). The computed frequencies for the optimized structure show six lower frequencies that correspond to the DFT level. In all DFT and CASPT2 calculations, only two electrons reside in molecular orbitals formed mainly by valence-shell Th orbitals, which confirms the oxidation state of +3 for the Th ions in the lowest energy states.
symmetric Th–Th stretching vibrations are found coupled with many other cage vibrations and appear at higher frequencies. The $^{13}$C NMR spectrum of Th$_2@I_h(7)$-C$_{80}$ characterized at 298 K show four signals in the range 125–145 ppm as shown in Supplementary Fig. 9. Though there are two signals identified as contamination caused by benzene impurities, signals at 144.05 and 129.27 ppm could be assigned to characteristic signals for a C$_{80}$ cage with $I_h$ symmetry. In particular, there is no paramagnetic broadening effect found in the $^{13}$C NMR spectrum of Th$_2@I_h(7)$-C$_{80}$ further proving that Th$_2@I_h(7)$-C$_{80}$ displays diamagnetic features and two electrons are available to form a Th–Th bond, agreeing well with the above computational results.

To determine the valence state of thorium inside the $I_h(7)$-C$_{80}$ cage, the X-ray absorption near edge structure (XANES) spectroscopy of Th$_2@I_h(7)$-C$_{80}$ was conducted along with the ThO$_2$ ($Th^{4+}$) as the reference species. The oxidation state of the metal in a statistical nature can be analyzed from the XANES region based on the edge position and the inflection point of the edge absorption. In terms of the edge position, the Th $L_3$-edge spectrum of Th$_2@C_{80}$ is shifted to lower energy side compared to that of the ThO$_2$ as shown in Fig. 4a. In addition, the maximum peak position in the first derivative of normalized $\mu(E)$ spectra is defined as $E_0$, namely the inflection point energies. In particular, the $E_0$ found for Th$_2@C_{80}$, 16306.7 eV, is shifted to lower energy by 4.7 eV compared with that of ThO$_2$, 16311.4 eV (see Fig. 4a inset and Supplementary Fig. 8), indicating that the two Th atoms encapsulated in the $I_h(7)$-C$_{80}$ cage have a lower charge state and agrees well with the theoretical predictions that the two Th ions exist in $+3$ oxidation state.

Moreover, the extended X-ray absorption fine structure (EXAFS) spectroscopy further provides information of the coordination environment of Th atoms. The radial distance space spectrum $\chi(R)$, obtained by the Fourier transform of the Th $L_1$-edge EXAFS oscillation, $\chi(k)$ of Th$_2@I_h(7)$-C$_{80}$ ($k$ range 2.54–10.42 Å$^{-1}$), is presented as the radial distribution function including the phase shift (+0.41 Å). This shift is determined by the difference between the first shell Th–C distance from single crystal structure (2.48 Å) and the first scattering path (2.07 Å).
shown in Fig. 4b, the predominant peak located around 2.47 Å can be assigned as the scattering path of Th–C interaction from the first coordination shell in Th2@Ih(7)-C80, which is consistent with the ferrocene like Th–C bonds observed in single crystal structure shown in Fig. 1b. Besides the relative strong first Th–C interactions, the observation of the second and third Th–C interaction suggests that Th ions may also have weaker but non-negligible interaction with carbon atoms in wider region. As shown in Supplementary Figs. 12 and 13, the Th–C distances of 2.90 Å and 3.35 Å (average values) can be found in the crystal structure of Th2@C80, which correspond to the second and third Th–C interaction peaks at 3.11 and 3.54 Å, respectively. Note that the differences between Th–C distances found in SCXRD and EXAFS might be ascribed to different methodologies as well as the different measure temperatures, as the single crystal X-ray data were collected at 113 K and the XAS experiment was carried out at room temperature (ca. 298 K).

Interestingly, the prominent peak located around 4.24 Å can be attributed to the scattering path of Th–Th bond in fourth coordination shell in Th2@Ih(7)-C80. Noteworthy that due to the obvious attenuation in higher χ(R), the strength of Th–Th bond with long distance in fourth coordination is not as strong as the typical metallic bond like Fe–Fe bond in first coordination of Fe foil. However, it still can be recognized since there is no scattering path signal of Th–C bond at this distance. Note that the scattering path of Th–Th interaction is a little longer than the bond distance (3.816 Å) observed from single crystal structure due to the phase shift.

Finally, quantitative χ(R) space spectra fitting with the k range from 0 to 11.06 Å−1 were also performed to validate local atomic structure and further obtain the bonding type and coordination numbers of Th in Th2@Ih(7)-C80 (Fig. 4c). The single crystal structure of Th2@Ih(7)-C80 shows that there is no bond existing under 2 Å, thus all the scattering path signals from 2 to 6 Å have been taken into the fitting consideration. The χ(R) space spectrum of Th2@Ih(7)-C80 displays Th–C bond with coordination number (CN) approaching 6.0 at 2.47 Å, 6.0 at 3.10 Å, and 8.0 at 3.563 Å, respectively (Supplementary Table 8), from first to third coordination shell which can be connected to Fig. 1b, Supplementary Figs. 12 and 13, respectively. Moreover, the obvious Th–Th metallic bond with coordination number (CN) approaching 1.0 at 4.24 Å from fourth coordination shell can be also observed. The good fitting results of y(k), χ(R), and real χ(R) space spectra, as shown in Fig. 4d, with reasonable R-factor (0.0218%, Supplementary Table 8) and the obtained fitting parameters quantitatively confirms the coexistence of Th–C and Th–Th bonds. Thus, the two Th3+ ions confined in C80 with Th–Th metallic bonding formation and the ferrocene like Th–C bonds can be confirmed by the combination of single crystal X-ray diffraction and XAFS characterization results, which agree well with the above discussed theoretical calculation results.

Discussion

In summary, we report the formation and characterization of a strong bond between actinides with low oxidation states inside a fullerene cage, namely, Th2@Ih(7)-C80. This compound was synthesized by the arc-discharge method. The single-crystal X-ray diffraction unambiguously determined that the two encapsulated Th atoms are separated by 3.816 Å inside an Ih(7)-C80. The overall agreement between the crystallographic, XAS, and quantum-computational results conclusively shows that the two encapsulated Th ions have formal charges of +3 and confirm the presence of a strong covalent Th–Th bond inside Ih(7)-C80, estimated to be ≥240 kcal mol−1. The computational studies reveal that the overlap between 7s5d hybrid thorium orbitals is so large that the bond still prevails at Th–Th separations larger than 6 Å, suggesting that this thorium–thorium bond is, up to now, the strongest one among the known actinide–actinide or lanthanide–lanthanide interactions.

This study presents an isolated compound with a strong covalent actinide metal-metal bond, paving the way for future experimental studies of these fundamentally important yet far from fully understood bonding motifs. Moreover, this study proves that the unique bonding environment inside fullerene cages make actinide endohedral fullerenes unique prototype molecules to study actinide–actinide bonding in detail. Because encapsulation always restricts the number of electrons that are transferred from the guest to the fullerene at ≤6, diactinide endohedral fullerences always have two or more electrons that are available to form single or multiple An–An bonds. Such bonds remain inaccessible by conventional synthetic procedures. These metal–metal bonds may help in the formation mechanisms of dimetallic endohedral fullerences and it is conceivable that stronger An–An bonds could be formed inside fullerene cages. Further studies are under way to better understand the multiple factors involved in the formation of encapsulated actinide–actinide clusters and the stabilization of the corresponding endohedral fullerences.

Methods

Synthesis, separation, and purification of Th2@C80. The carbon soot containing thorium EMFs was synthesized by the direct-current arc discharge method. The graphite rods, packed with ThO2 and graphite powder (molar ratio of Th/C = 1:24), were annealed in a tube furnace at 1000 °C for 20 h under an Ar atmosphere and then vaporized in the arcing chamber under 200 Torr He atmosphere. In total 1.2 kg of ThO2 and 1.73 kg of graphite powder were packed in each rod. The resulting soot was refluxed in Cs2, under an argon atmosphere for 12 h. On average ca. 210 mg of crude fullerene mixture per rod was obtained. In total, 100 carbon rods were vaporized in this work. The separation and purification of Th2@C80 was achieved by a multistage HPLC procedure (Supplementary Fig. 2). Multiple HPLC rods, including Buckyprep M (25 × 250 mm, Cosmosol, Nacalai Tesque Inc.), Buckyprep-D (10 × 250 mm, Cosmosol, Nacalai Tesque, Japan), and Buckyprep (10 × 250 mm, Cosmosol, Nacalai Tesque, Japan), were utilized in this procedure. Toluene was used as the mobile phase and the UV detector was adjusted to 310 nm for fullerene detection. The HPLC traces and corresponding MALDI-TOF spectra for the isolated fractions are shown in Supplementary Fig. 2. In total, ca. 1 mg of highly purified Th2@C80 was obtained for characterization.

X-ray crystallographic study. The black block crystals of Th2@Ih(7)-C80[NI1(NiOEP)] were obtained by slow diffusion of a carbon disulfide solution of Th2@C80 into a benzene solution of [NiII·(OEP)]. X-ray data were collected at 113 K using a diffractometer (Bruker D8 Venture) equipped with a CCD detector. The synchrotron X-ray measurement was conducted on a single crystal with dimensions ca. 0.2 mm for test. Presented data were produced as an average of three measurements. The carbon soot containing Th2@Ih(7)-C80·[NiII(OEP)]·1.5C6H6·CS2:M r=21/2(No. 14), α=90°, β=106.811°, γ=90°, V=77.376(10) Å3, Z=1, μ(Cu Kα)=1.897 g cm−3, ρ(Cu Ka)=13.585 mm−1, θ=3.12°–90°, θ′=22°. Presented data were collected at 113 K using a diffractometer (Bruker D8 Venture) equipped with a CCD detector. The synchrotron X-ray measurement was conducted on a single crystal with dimensions ca. 0.2 mm for test. Presented data were produced as an average of three measurements. The carbon soot containing Th2@Ih(7)-C80·[NiII(OEP)]·1.5C6H6·CS2:M r=21/2(No. 14), α=90°, β=106.811°, γ=90°, V=77.376(10) Å3, Z=1, μ(Cu Kα)=1.897 g cm−3, ρ(Cu Ka)=13.585 mm−1, θ=3.12°–90°, θ′=22°. Presented data were produced as an average of three measurements.

XAFS measurements. The X-ray absorption structure spectroscopy (Th L3, edge) were collected at BL11B in Shanghai Synchrotron Radiation Facility (SSRF). The samples were filled into the hole with 1.5 mm diameter on PTFE films (film thickness ca. 0.2 mm) for test. Presented data were produced as an average of three consecutives scans for Th2@C80 while two consecutives scans for ThO2.

Computational methods. DFT calculations for Th2@C80, EMFs were carried out with the ADF 2017 package56 using PBE and PBE0 exchange-correlation functional in combination with Slater TZP basis sets to describe the valence electrons of Th and C.59,60 Frozen cores were described by means of single Slater functions, consisting of the 1 s shell for C and the 1 s to 5 d shells for Th. Scalar relativistic corrections were included by means of the ZORA formalism. Dispersion corrections by Grimme were also included57. Relative energies were computed with GGA PBE and RPBE functionals reoptimizing the structures with each functional. CASPT2 calculations were performed with OpenMolcas. The active space contains six orbitals and two electrons in all cases. Test calculations with larger...
active spaces do not alter the results; Th-carbon bonding and anti-bonding orbitals enter the active space with occupation numbers close to 2 and 0, respectively. The computational costs were reduced by imposing the symmetry restrictions of the $D_{5h}$ group in the case of Th$_2@C_{80}$ and $D_3h$ for Th$_3@C_{84}$. Furthermore, we have used the Cholesky decomposition of the two-electron integrals with a $10^{-4}$ threshold. Scalar relativistic effects were taken into account with the Douglas–Kroll–Hess Hamiltonian. We have used the standard IPEA = 0.25 zeroth order Hamiltonian in the CASPT2 calculations and applied an imaginary level shift of 0.15 eV to avoid intruder states. CASPT2 calculations were performed using PBE0 geometries obtained under the symmetry constraints.

### Data availability

The X-ray crystallographic coordinates for the structure reported in this article are available in the Cambridge Crystallographic Data Centre (CCDC) under deposition number 1961861. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. A data set collection of computational results is available in the ioChem-BD repository and can be accessed via https://doi.org/10.19061/iochem-bd-2.455. All other data supporting the findings of this study are available from the corresponding authors on request.

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**Author contributions**

N.C. conceived and designed the experiments. Z.J.X. and W.Y.F. synthesized and isolated all the compounds. R.M.M., A.R.F., C.d.G., and J.M.P. performed the computations and theoretical analyses. Y.Y.R and Z.J.X. performed the crystallographic analysis. Z.J.X. and P.C.Y. performed the XAS measurements and Z.J.W. performed the XAS analyses. N.C., J.M.P., Z.J.X., C.d.G., Z.J.W., R.M.M., A.R.F., L.E., and W.S.A. co-wrote the manuscript.

**Competing interests**

The authors declare no competing interests.

**Additional information**

**Supplementary information**

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