

Article

Synthesis and Characterization of a Novel Non-Isolated-Pentagon-Rule Isomer of Th@C₇₆:Th@C₁(17418)-C₇₆

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Abstract: A novel Non-Isolated-Pentagon-Rule (non-IPR) isomer of thorium-based endohedral mono-metallofullerenes (mono-EMFs), Th@C₁(17418)-C₇₆, was successfully synthesized and characterized using MALDI-TOF mass spectroscopy, single-crystal X-ray diffraction, UV-vis-NIR spectroscopy, and Raman spectroscopy. The molecular structure of this non-IPR isomer was determined unambiguously as Th@C₁(17418)-C₇₆ using a single-crystal X-ray diffraction analysis. The crystallographic results further revealed that the optimal Th site resided at the intersection of two adjacent pentagons, similar to that of U@C₁(17418)-C₇₆. Additionally, the UV-vis-NIR spectra of Th@C₁(17418)-C₇₆ exhibited distinct differences compared to the previously reported U@C₁(17418)-C₇₆, highlighting the distinctive electronic structure of actinium-based endohedral metallofullerenes (EMFs). The Raman spectrum of Th@C₁(17418)-C₇₆ exhibited similarities to that previously reported for thorium-based EMFs, indicating the analogous strong metal-cage interactions of thorium-based EMFs.

Keywords: endohedral metallofullerenes; mono-metallofullerenes; thorium; X-ray crystallography



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1. Introduction

Endohedral metallofullerenes (EMFs) are a specialized type of carbon nanomaterial featured by the encapsulation of metal atoms or metal clusters within the carbon cage of the fullerenes [1–3]. In 1991, Smalley et al. achieved the isolation of the first EMF, La@C₈₂, which initiated the exploration of the structure and properties of EMFs [4]. Subsequently, numerous types of mono-EMFs and endohedral clusterfullerenes have been synthesized and reported by researchers [5–8]. Depending on the differences between endohedral species, EMFs can be further classified as mono-metallofullerenes, di-metallofullerenes, tri-metallofullerenes, and clusterfullerenes [9–13]. The electron transfer and host–guest interactions between the endohedral metal units and fullerene carbon cages contribute to the intriguing electronic structures and physicochemical properties of these EMFs, thereby presenting immense potential in various cutting-edge fields, including biomedicine, organic photovoltaic devices, and single-molecule devices [14–17].

Mono-EMFs represent the most extensively studied type of EMF, with the majority of reported mono-EMFs being based on lanthanide metals. These metals are embedded within the carbon cage of the fullerene in the form of M@C_{2n} (M = Ce [18], Pr [19], Nd [20], Sm [21], Eu [22], Gd [23], Tb [24], Dy [25], Ho [26], Er [27], Yb [28], and Lu [29]). In recent years, research on actinium-based mono-EMFs has also been reported, primarily focused on uranium (U) and thorium (Th). Among them, the characterization of Th@C_{3v}(8)-C₈₂ [30] marked the beginning of the investigation into actinium-based mono-EMFs. In monometallic thorium-based EMFs, thorium usually exhibits an oxidation state of a +4 oxidation state. For example, Th@T_d(19151)-C₇₆ [31], Th@D_{5h}(6)-C₈₀ [32], Th@C_{2v}(9)-C₈₂,

Th@C₂(5)-C₈₂ [33], and Th@C₁(11)-C₈₆ [34] have been discovered in previous research. All of them demonstrate a four-electron charge transfer from the metal atom to the fullerene cage. Conversely, uranium's oxidation state displays a remarkable flexibility. In U@C_{2v}(9)-C₈₂, the endohedral uranium transfers three electrons to the C₈₂ carbon cage, while in U@C₂(5)-C₈₂, the endohedral uranium transfers four electrons to the C₈₂ fullerene cage [35]. Because of the contributions from f-orbital electrons, the unique characteristics and variability of oxidation states in actinide metals lead to more complex electron configurations in actinide-based EMFs compared to lanthanide-based EMFs. Actinide-based EMFs also exhibit stronger metal–cage interactions than those of lanthanide-based EMFs, and actinide metal ions have a more significant influence on the properties of actinide-based EMFs than previously observed for lanthanide-based EMFs. For example, previously reported mono-EMFs based on uranium, known as U@C₁(28324)-C₈₀, and mono-EMFs based on thorium, labeled as Th@C₁(28324)-C₈₀, possess the same fullerene carbon cage, and both of them undergo a four-electron charge transfer process. They demonstrate distinct electronic properties, as evidenced by significant differences in their UV-vis-NIR spectra [36].

Based on extensive research on actinium-based mono-EMFs, it is clear that the remarkable charge transfer and strong engagement between actinide metal ions and fullerene carbon cages are essential for stabilizing previously unstable fullerene cage structures. Thus, in addition to the experimentally verified isomers, there are numerous isomers that have only been predicted and researched theoretically in actinium-based mono-EMFs. Consequently, further experimental investigations are of paramount importance to exploring actinium-based mono-EMFs, as they will reveal the distinct electronic properties and carbon cage structures that differentiate them from traditional lanthanide-based mono-EMFs.

Recently, two independent computational studies proposed two possible isomeric structures of Th@C₇₆, one is referred to as Th@T_d(19151)-C₇₆, while the other is referred to as Th@C₁(17418)-C₇₆. [37,38]. Nevertheless, only the existence of Th@T_d(19151)-C₇₆ [31] has been experimentally confirmed. Further experimental investigation of Th@C₁(17418)-C₇₆ would contribute to a deeper understanding of the unique carbon cage structures, electronic properties, and host–guest interactions exhibited by actinide-based EMFs.

In this study, we present the synthesis and characterization of a novel non-IPR isomer of thorium-based mono-EMFs, Th@C₁(17418)-C₇₆. Th@C₁(17418)-C₇₆ was successfully synthesized by using a modified Krätschmer–Huffman direct-current DC arc-discharge method. It was thoroughly characterized through various techniques, including MALDI-TOF mass spectroscopy, single-crystal X-ray diffraction, UV-vis-NIR spectroscopy, and Raman spectroscopy. The crystallographic results revealed that the optimal Th site resided at the intersection of two adjacent pentagons, and the presence of a single Th ion played a crucial role in stabilizing the non-IPR C₇₆ fullerene cage.

2. Results and Discussion

2.1. Synthesis and Isolation of Th@C₇₆

Thorium-based EMFs were produced using a modified Krätschmer–Huffman direct-current DC arc-discharge method. Hollow graphite rods, packed with ThO₂ and graphite powder (molar ratio of Th: C = 1:24), were vaporized in an arcing reactor chamber under a 200 Torr helium atmosphere. The resulting soot was then collected and extracted with CS₂ for 12 h. Multistage high-performance liquid chromatography (HPLC) separation processes were employed to isolate and purify the Th@C₇₆ (Figure S1). The purity of the Th@C₇₆ was confirmed by the observation of single peaks with HPLC and positive-ion-mode matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry, as exhibited in Figure 1. The mass spectra of the isomer of Th@C₇₆ exhibited a peak at 1143.975 *m/z*, and the experimental isotopic distribution of the sample agrees well with the empirical projection.

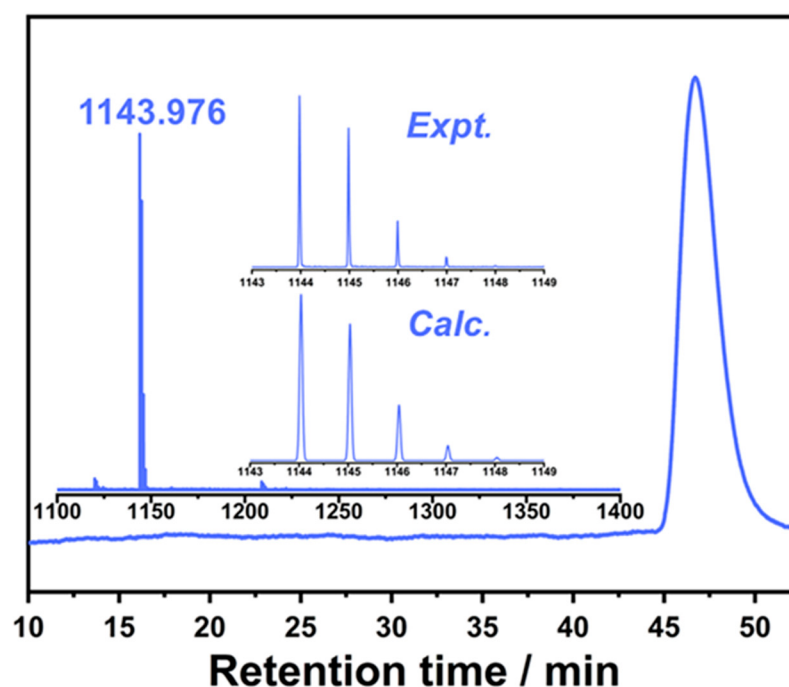


Figure 1. HPLC chromatogram of purified Th@C₇₆ on a Buckyprep column using toluene as the eluent, with a 4 mL/min flow rate. The mass spectra of Th@C₇₆ and associated empirical and hypothetical isotopic profiles of the sample are shown in the inset.

2.2. Molecular Structure of Th@C₁(17418)-C₇₆

The molecular configuration of Th@C₇₆ was unequivocally ascertained through single-crystal X-ray diffraction analyses. Th@C₇₆ and Ni^{II}-OEP (OEP = 2, 3, 7, 8, 12, 13, 17, 18-octaethylporphyrin dianion) were co-crystallized by slowly diffusing the benzene solution of Ni^{II}-OEP into the carbon disulfide solution of the purified compounds. The structure of Th@C₇₆ was resolved and refined in the C2/c (No. 15) space group. The experimental results clearly showed that this new isomer of Th@C₇₆ showed a different structure from the reported Th@T_d(19151)-C₇₆ [31]. It shares the same carbon cage structure with U@C₁(17418)-C₇₆, which possesses a low-symmetry C₁(17418)-C₇₆ cage and one adjacent pentagon pair [36]. Interestingly, crystallographic investigations of the C₁(17418)-C₇₆ carbon cage have primarily been limited to actinide metallofullerenes, and no previous studies have reported the observation of or noticed the same cage in lanthanide-based EMFs. This indicates that a stronger interaction between U or Th and fullerene cages may facilitate the stabilization of these unconventional fullerene cage isomers. On the other hand, Th@C₁(17418)-C₇₆ was also predicted to be the most advantageous product in experiments at elevated temperatures due to its dominant molar fraction [38]. This result verifies the theoretical predications.

Figure 2 shows the molecular structure of Th@C₁(17418)-C₇₆ and its relationship to the co-crystallized Ni^{II}(OEP) molecule. The Th@C₁(17418)-C₇₆ moiety is close to the adjacent Ni^{II}(OEP), with a short Ni-to-cage carbon distance (Ni1-C12) of 2.875 Å, demonstrating a characteristic interplay between the carbon cage and Ni^{II}(OEP). There are five crystallographic sites for the Th atoms with occupancies of 0.50 for Th1, 0.30 for Th2, 0.14 for Th3, 0.03 for Th4, and 0.025 for Th5 (see Figure S2). Th1 (occupancy 0.50) is situated at the intersection of two adjacent pentagons with the shortest Th–C distance in the range of 2.359–2.449 Å (Table S2), as shown in Figure 3. The shortest Th–C distances of the Th@C₁(17418)-C₇₆ are similar to those in Th@T_d(19151)-C₇₆, demonstrating similar interactions between the Th atom and the carbon cage [31]. In comparison to two examples of lanthanide-based non-IPR monometallic C₇₆ (M@C_{2v}(19138)-C₇₆, M = Eu [39], Sm [40]), although the major metal sites are all located at the intersection of two adjacent pentagons,

there are large differences in the shortest Th–cage distances. This discrepancy suggests that the interaction between the metal and cage in Th@C₇₆ could potentially possess a greater strength when compared to its lanthanide counterparts.

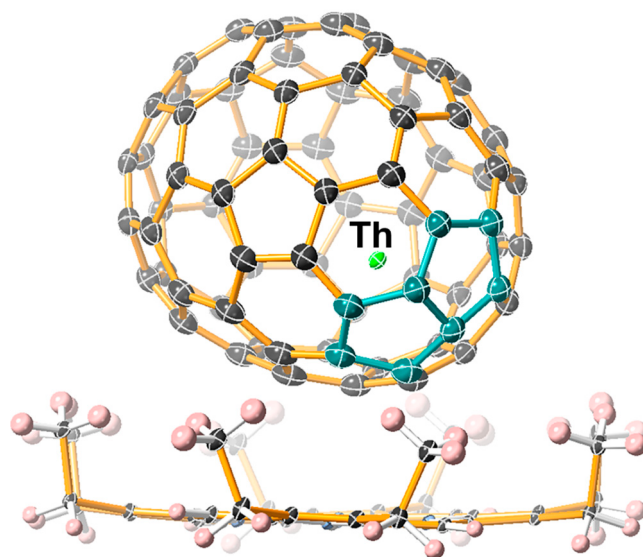


Figure 2. ORTEP drawings showing the relationship between the EMF and porphyrin moieties for Th@C₁(17418)-C₇₆·[Ni^{II}(OEP)] with 15% thermal ellipsoids. Only the major cage orientation and predominant thorium sites are shown.

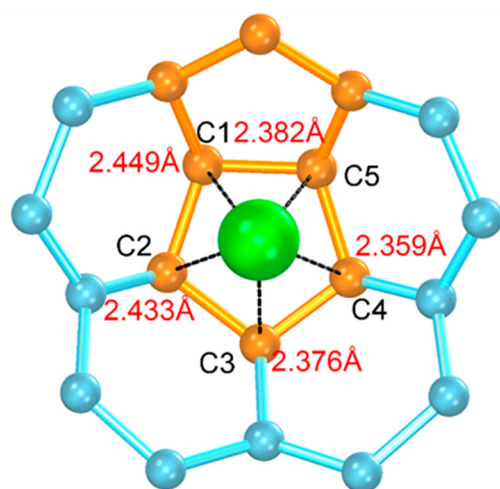


Figure 3. Perspective drawings showing the interaction of the major thorium closest cage portion in @C₁(17418)-C₇₆.

2.3. Spectroscopic Characterizations

UV-vis-NIR absorption is a useful technique that can help us to determine the electronic structures of EMFs. Normally, EMFs sharing the same cage and charge transfer exhibit almost identical absorption spectra [1]. The UV-vis-NIR absorption spectrum was utilized in this study to characterize the pure sample dissolved in a CS₂ solution, as depicted in Figure 4. This allowed for further analysis. Th@C₁(17418)-C₇₆ exhibits five characteristic peaks at 490, 602, 755, 930, and 1078 nm. The absorption onset occurs at approximately 1230 nm, indicating an optical band of 1.01 V. The absorption spectrum of U@C₁(17418)-C₇₆ [36], which shares the same cage isomer and charge transfer, though showing some similarity to that of the Th@C₁(17418)-C₇₆, only exhibits one absorption at 593 nm (Figure 4a). This result shows a notable influence of the actinide metal on the electronic structures of M@C₁(17418)-C₇₆ (M = U, Th). A similar phenomenon can also be

observed in $M@C_1(28324)-C_{80}$ [36] ($M = U, Th$), revealing that the endohedral metal itself also plays a significant role in the electronic structure of the EMFs. On the other hand, the spectrum of $Th@T_d(19151)-C_{76}$ [31] shows different characteristic peaks compared to those of the $Th@C_1(17418)-C_{76}$ (Figure 4b). This agrees with the crystallographic results that the $Th@C_{76}$ identified in this work is a novel isomer. To delve deeper into the electronic structure of $Th@C_1(17418)-C_{76}$, we conducted electrochemical tests on the compound. The cyclic voltammogram of $Th@C_1(17418)-C_{76}$ presents two oxidation peaks and three reduction peaks. However, the cyclic voltammogram of $U@C_1(17418)-C_{76}$ only presents one oxidation peak and three reduction peaks [36]. In addition, compared to the first oxidation potential of $U@C_1(17418)-C_{76}$ (0.14 V), the first oxidation potential of $Th@C_1(17418)-C_{76}$ (0.37 V) shows a significant positive shift. This result shows the notable influence of the actinide metal on the electronic structures of $M@C_1(17418)-C_{76}$ ($M = U, Th$).

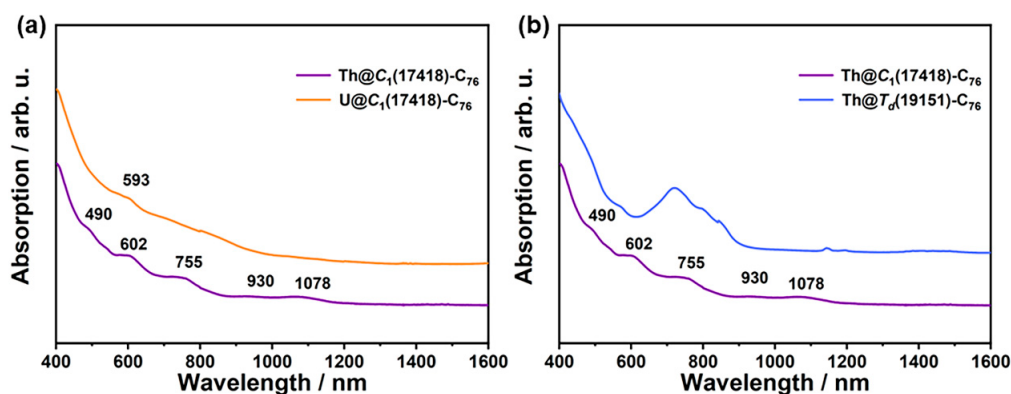


Figure 4. UV-vis-NIR absorption spectra of $Th@C_1(17418)-C_{76}$ and (a) $U@C_1(17418)-C_{76}$ and (b) $Th@T_d(19151)-C_{76}$ in CS_2 .

$Th@C_1(17418)-C_{76}$ was also characterized using low-energy Raman spectroscopy, as shown in Figure 5. Sharp peaks at 149, 218, and 479 cm^{-1} are observed for the Raman spectrum of $Th@C_1(17418)-C_{76}$. Similar frequencies also can be observed in $Th@D_{5h}(6)-C_{80}$ [32] (150 and 219 cm^{-1}), $Th@C_{2v}(9)-C_{82}$ (151 and 216 cm^{-1}), and $Th@C_2(5)-C_{82}$ [33] (152 and 215 cm^{-1}), indicating that thorium-based mono-EMFs have similar metal–cage interactions. Though the UV-vis-NIR absorption spectra of $Th@C_1(17418)-C_{76}$ differ from those of $U@C_1(17418)-C_{76}$, the vibrational frequencies on the Raman spectrum of $U@C_1(17418)-C_{76}$ are at 153, 219, and 359 cm^{-1} [36], showing notable similarities to those of the $Th@C_1(17418)-C_{76}$. This phenomenon can also be observed in $Th@C_1(28134)-C_{80}$ and $U@C_1(28134)-C_{80}$ [36], which also share the same carbon cage. This may indicate that the cage isomers play a major role on the metal–cage interaction of the corresponding EMFs.

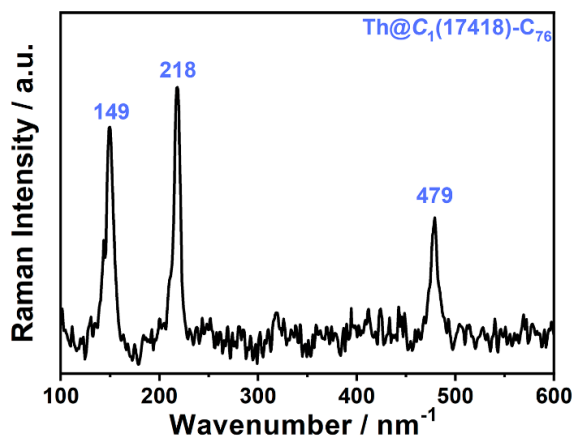


Figure 5. Low-energy Raman spectra of $Th@C_1(17418)-C_{76}$ at 633 nm excitation.

3. Materials and Methods

Materials. The chemicals employed in this research were Th₂O₃ (99.9%, School of Radiation Medicine and Protection of Soochow University, Suzhou, China), CS₂ (99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), toluene (99%, Sinopharm Chemical Reagent Co., Ltd.), hexane ethanol (99%, Sinopharm Chemical Reagent Co., Ltd.), hexane (99%, Sigma Aldrich Co., St. Louis, MO, USA), benzene (99%, Sigma Aldrich Co.), trichloromethane (99%, Sinopharm Chemical Reagent Co., Ltd.), ferrocene (99.8%, Beijing Bailing Wei Technology Co., Ltd., Beijing, China), Octaethylnickel porphyrin (99.8%, Beijing Bailing Wei Technology Co., Ltd.), tetrabutylammonium hexafluorophosphate (electrochemical-grade, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China), 1,2-dichlorobenzene (99%, Shanghai Aladdin Biochemical Technology Co., Ltd.), and graphite rods and graphite powder (Shanghai Fengyi Carbon Co., Shanghai, China).

Synthesis of Th@C₁(17418)-C₇₆. Th@C₁(17418)-C₇₆ was synthesized using the direct-current arc discharge method. ThO₂ powders and graphite powder were mixed in an atomic molar ratio of Th:C = 1:24 (equivalent to a mass ratio of ThO₂:C = 1:1.09). The resulting mixture was then uniformly filled into a hollow graphite rod and compacted to achieve dense packing. The filled graphite rod was placed into a tube furnace and subjected to a 12 h reduction process at 1000 °C under a nitrogen atmosphere, aiming to convert the metal oxide into a metal carbide.

After the reduction process, the compaction graphite rod containing the reduced material was utilized as the anode, while a solid graphite rod served as the cathode within a vacuum arc furnace. The furnace was evacuated to a pressure of 4 Pa and then filled with 200 Torr of helium gas. The distance between the electrodes was maintained at approximately 1 cm, and the current was set to 90 A using an electric welding machine. Plasma evaporation took place during the arc discharge process. The anode was manually rotated with the left hand to achieve the optimal evaporation positioning, while the cathode was rotated with the right hand to push the solid graphite rod towards the consumed mixture graphite rod. When the mixture rod was nearly depleted, the cathode was retracted rapidly to prevent any damage to the metallic target on the anode. Subsequently, the power supply of the electric welding machine was switched off. Once the furnace temperature cooled down to room temperature, air was introduced into the furnace to reach atmospheric pressure. The furnace cover was opened, and the carbon ash accumulated on the furnace wall was collected using tools like a test tube brush. The collected carbon ash was soaked in a solution of carbon disulfide and left to stand for 12 h. Once the first immersion was completed, the obtained carbon ash was immersed twice with the same operation, so that as much of the obtained fullerene sample as possible was extracted. The extraction of fullerene samples needs to be carried out in a glove box with specific filtration devices.

The carbon disulfide solution was separated from the solid carbon residues using a vacuum filtration device equipped with a 0.45 µm organic membrane, resulting in a carbon disulfide filtrate. The carbon disulfide solvent was then evaporated using rotary evaporation until no liquid remained, and an appropriate quantity of toluene solution was added to dissolve the residue. The resulting reddish brown solution underwent another round of filtration to eliminate the solid particles of fullerenes, resulting in a saturated crude extract solution of fullerenes, which could be further utilized for High-Performance Liquid Chromatography (HPLC) separation in subsequent steps.

Isolation of Th@C₁(17418)-C₇₆. The separation and purification of Th@C₁(17418)-C₇₆ was achieved using multi-stage HPLC procedures. The HPLC was performed with toluene as the mobile phase and a UV detector with a detection wavelength of 310 nm. A 10 mL chromatographic injector was used to inject samples of fullerenes dissolved in toluene into a preparative HPLC system for separation. Prior to injection, a disposable syringe filter was employed to filter the fullerene sample, mitigating the interference caused by solid particles during the chromatographic separation. Distinct chromatographic columns were employed for the separation at various stages of the process. Multiple HPLC columns, including a Buckyprep-M column (25 × 250 mm, Cosmosil, Nacalai Tesque Inc., Kyoto,

Japan), a Buckyprep column (10 × 250 mm, Cosmosil, Nacalai Tesque, Kyoto, Japan), and a 5PBB column (10 × 250 mm, Cosmosil, Nacalai Tesque, Kyoto, Japan), were utilized in the procedures. The purity of the target fractions was monitored by using MALDI-TOF during the separation process. In our mass spectrometry analysis, numerous signals corresponding to monometallic fullerenes based on thorium (Th), including Th@C₇₆, Th@C₈₀, Th@C₈₂, Th@C₈₄, Th@C₈₆, and Th@C₈₈, were observed. Among them, in particular, the isomer of Th@C₇₆ reported in this study has not been experimentally documented before. Therefore, in subsequent separation steps, our focus was solely on the purification and characterization of Th@C₇₆.

Th@C₁(17418)-C₇₆ was subjected to purification utilizing a four-stage high-performance liquid chromatography (HPLC) process, as shown in Figure S1. Initially, the compound was passed through a Buckyprep-Mcolumn (25 mm × 250 mm, Cosmosil, Nacalai Tesque) at a flow rate of 10 mL/min during the first stage of separation. Subsequently, the fraction eluted between 26 and 27.5 min (indicated by the color blue) was collected and reinjected into the Buckyprep column (10 mm × 250 mm, Cosmosil, Nacalai Tesque) for the second stage of separation, utilizing toluene as the eluent with a flow rate of 4 mL/min. The fraction containing Th@C₁(17418)-C₇₆ was obtained between 46 and 49.5 min (highlighted in red) and isolated accordingly. Moving on to the third stage of the separation, the 5PBB column (10 mm × 250 mm, Cosmosil, Nacalai Tesque) was employed, delivering a flow rate of 4 mL/min. The desired fraction, marked in orange, appeared within the 65 to 73 min range and specifically contained Th@C₁(17418)-C₇₆. Finally, the last stage involved passing the sample through the Buckyprep column (10 mm × 250 mm, Cosmosil, Nacalai Tesque) at a flow rate of 4 mL/min, bringing forth the achievement of pure Th@C₁(17418)-C₇₆. Notably, the confirmation of the extracted Th@C₁(17418)-C₇₆'s purity was impeccably established through the utilization of MALDI-TOF in positively charged mode, as visually exemplified in Figure 1.

Spectroscopic Studies of Th@C₁(17418)-C₇₆. The positive-ion mode matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) (Bruker, Karlsruhe, Germany) was employed for the mass characterization. A rotary evaporator was used to spin dry the fullerene sample under investigation. The substance was dissolved in carbon disulfide and the sample was transferred onto a mass spectrometry target using a pipette. A mass spectrometry analysis proceeded after the solvent evaporated. The purified Th@C₁(17418)-C₇₆ fullerene sample was dissolved in CS₂ and the carbon disulfide solution of the fullerene was transferred into a 2 mL quartz cuvette. A control experiment was prepared by adding blank carbon disulfide to another quartz cuvette. The Cary 5000 UV-vis-NIR spectrophotometer (Agilent, Santa Clara, CA, USA) was used to measure the ultraviolet-visible-near-infrared absorption wavelengths of the sample in the detection range of 400–1600 nm. After completing the measurements, the carbon disulfide solution was collected from the sample in a glass vial and the quartz cuvette was rinsed with clean carbon disulfide solution. The Raman spectra were obtained using a Horiba Lab RAM HR Evolution Raman spectrometer using a laser at 633 nm.

Electrochemical Studies of Th@C₁(17418)-C₇₆. The cyclic voltammetry was performed using a conventional three-electrode system consisting of a glassy carbon electrode as the working electrode, a silver wire as the reference electrode, and a platinum wire as the counter electrode. A 0.05 M (n-Bu)₄NPF₆ solution was prepared by adding ortho-dichlorobenzene to the electrolyte, which contained tetrabutylammonium hexafluorophosphate. Subsequently, the purified sample of monometallic fullerene was dissolved in the solution for a cyclic voltammetry analysis using a CHI-660E electrochemical workstation. The reference material used for calibration was ferrocene, and the scan rate was set at 100 mV/s.

X-ray Crystallographic Study. Single crystals of Th@C₇₆ were obtained, employing a solvent diffusion method characterized in a gradual process. A supersaturated solution of benzene (0.2 mL), encompassing Ni^{II}(OEP) (0.18 mg), was meticulously diffused into an impeccably concocted carbon disulfide solution (0.1 mL) of Th@C₁(17418)-C₇₆ (0.1 mg). Prior

to the crystal growth procedure, the fabricated fullerene sample underwent a comprehensive purification and cleaning step utilizing n-hexane. Filtering and cleaning devices were obtained by using a rubber-tipped dropper. The filter paper was folded to obtain a filter core approximately 1 cm in size, precisely filling the neck of the pipette. The fullerene sample requiring filtration and cleaning was dissolved in carbon disulfide, followed by drying with nitrogen gas. A small amount of hexane was added, and ultrasonication was applied to suspend the fullerene sample in the hexane solution. Using a pipette, the mixture of hexane and fullerene samples was transferred to a prepared filtration pipette, with the rate of filtration controlled at one drop per second. As fullerene samples are insoluble in hexane, they remained on the filter core. The filter core was then rinsed with carbon disulfide, and the cleaning solution was collected, resulting in a fully cleaned fullerene sample.

In explicit detail, the carbon disulfide solution of Th@C₁(17418)-C₇₆ and the benzene solution of Ni^{II}(OEP) were introduced into a precisely maintained 5 mm inner diameter nuclear magnetic resonance (NMR) tube, adhering to an exact volumetric ratio of 1:2. Prior to crystal growth, the NMR tube necessitated a series of sequential cleansing steps. The NMR tube was thoroughly filled with solutions of soap, ethanol, n-hexane, and carbon disulfide in a successive manner. The subsequent cleansing process involved subjecting the NMR tube to ultrasonic irradiation for a duration exceeding 30 min, with three cycles of ultrasonic treatment for each solution. To ensure a meticulously controlled and hermetically sealed environment, the aperture of the NMR tube was securely enclosed using a specialized sealing film. This meticulously prepared assembly was subsequently transferred to a refrigerated environment, maintaining a constant temperature of 4 °C, and left undisturbed, allowing for a designated duration of one month.

After the designated duration, we used an optical microscope to observe the NMR tubes, black prism-shaped crystals, exhibiting a remarkable specular gleam, precipitated within the NMR tube. The meticulous selection of appropriately sized and shaped black prism-shaped crystals was conducted to facilitate a subsequent single-crystal X-ray diffraction analysis. These selected crystals were subjected to thorough testing and characterization employing a cutting-edge single-crystal diffractometer; the model was the Bruker D8 Venture with metaljet. The single-crystal X-ray data of Th@C₁(17418)-C₇₆ were collected at 120 K, respectively, on a diffractometer (APEX II; Bruker Analytik GmbH, Karlsruhe, Germany) equipped with a CCD collector. The multiscan method was used for absorption correction. The structures were solved using direct methods and refined on F² using full-matrix least-squares using the SHELXL2014 crystallographic software packages. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters.

Crystal data for Th@C₁(17418)-C₇₆·[Ni^{II}(OEP)]·2C₆H₆: $M_r = 1892.47$, $0.1\text{ mm} \times 0.08\text{ mm} \times 0.06\text{ mm}$, monoclinic, $C2/c$ (No. 15), $a = 44.778(2)\text{ \AA}$, $b = 14.9844(11)\text{ \AA}$, $c = 25.431(22)\text{ \AA}$, $\alpha = 90^\circ$, $\beta = 121.405(3)^\circ$, $\gamma = 90^\circ$, $V = 14564(22)\text{ \AA}^3$, $Z = 8$, $\rho_{\text{calcd}} = 1.756\text{ g cm}^{-3}$, $\mu(\text{Ga K}\alpha) = 6.129\text{ mm}^{-1}$, $\theta = 2.756\text{--}58.099$, $T = 120.0\text{ K}$, $R_1 = 0.1339$, $wR_2 = 0.2547$ for all data; $R_1 = 0.0901$, $wR_2 = 0.2256$ for 10155 reflections ($I > 2.0\sigma(I)$) with 1220 parameters. Goodness-of-fit indicator 1.074. The Maximum residual electron density was $1.429\text{ e \AA}^{-3}$.

4. Conclusions

In conclusion, a novel non-IPR isomer of thorium-based mono-EMFs, the synthesis and characterization of Th@C₁(17418)-C₇₆ were accomplished through mass spectroscopy, single-crystal X-ray diffraction, Raman spectroscopy, and UV-vis-NIR spectroscopy. The crystallographic characterization unambiguously demonstrated that this isomer possesses a pair of adjacent pentagons, sharing the same carbon cage as the one previously reported for U@C₁(17418)-C₇₆. The major metal sites in U@C₁(17418)-C₇₆ and Th@C₁(17418)-C₇₆ are all situated at the intersection of two adjacent pentagons. Currently, the stabilization of the C₁(17418)-C₇₆ cage is only achieved by the encapsulation of U and Th, suggesting that the unique 5f electrons present in actinide metals enable them to stabilize uncommon carbon cage structures. In addition, despite similarity of their Raman vibrational spectra, the

UV-vis-NIR absorption spectra of $\text{U@C}_1(17418)\text{-C}_{76}$ and $\text{Th@C}_1(17418)\text{-C}_{76}$ exhibit notable differences. This work introduces a novel addition to the group of thorium-based mono-EMFs, enhancing the comprehension of the distinctive carbon cage structure, electronic properties, and interactions exhibited by actinium-based EMFs.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics11110422/s1>, Figure S1: HPLC isolation procedures of $\text{Th@C}_1(17418)\text{-C}_{76}$ and the pure sample's MALDI-TOF mass spectrum.; Figure S2: Ball and stick representation of disordered Th sites inside $\text{Th@C}_1(17418)\text{-C}_{76}$, five positions (Th1, Th2, Th3, Th4, and Th5) are observed.; Figure S3: Cyclic voltammograms of $\text{Th@C}_1(17418)\text{-C}_{76}$ in *o*-dichlorobenzene.; Table S1: Occupancies of disordered thorium sites in $\text{Th@C}_1(17418)\text{-C}_{76}$.; Table S2: Closest Th-Cage distances (Å) in $\text{Th@C}_1(17418)\text{-C}_{76}$.; Table S3: Crystallographic information of $\text{Th@C}_1(17418)\text{-C}_{76}$.

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Data Availability Statement: The crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre with the CCDC numbers 2295545 via www.ccdc.cam.ac.uk/data_request/cif (accessed on 18 September 2023). The other data are available upon reasonable request from the corresponding authors.

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