Synthesis and Characterization of Non-Isolated-Pentagon-Rule Actinide Endohedral Metallofullerenes $\text{U}@[\text{C}_1(17418)\text{-C}_{76}]$, $\text{U}@[\text{C}_1(28324)\text{-C}_{80}]$, and $\text{Th}@[\text{C}_1(28324)\text{-C}_{80}]$: Low-Symmetry Cage Selection Directed by a Tetravalent Ion

Wenting Cai, Laura Abella, Xingxing Zhang, Lai Feng, Yaofeng Wang, Roser Morales-Martínez, Ronda Esper, Mauro Boero, Alejandro Metta-Magaña, Antonio Rodríguez-Fortea, Josep M. Poblet, Luis Echegoyen, and Ning Chen

1. INTRODUCTION

Fullerenes are all-carbon molecules consisting of 12 pentagonal carbon rings and a variable number of hexagons. So far, most experimental results showed that the pentagons on pristine empty fullerenes are surrounded by five hexagons, thus obeying the isolated pentagon rule (IPR). However, the numbers of IPR cage isomers are very limited, whereas non-IPR fullerenes containing fused pentagons (pentacene units) are common and numerous. In contrast to IPR fullerenes, the non-IPR isomers...
are strongly destabilized due to the enhanced local steric strain on the fused pentagons caused by enforced bond angles accompanied by higher pyramidalization of the carbon atoms.\textsuperscript{1,15} Two strategies have shown practical effectiveness in generating non-IPR fullerene cages. One is exohedral halogenation so as to release the high bond strain of the fused pentagons.\textsuperscript{6–11} For instance, some non-IPR fullerenes can be obtained as their chlorinated derivatives or perfluoroalkylated fullerenes.\textsuperscript{9,12} However, the functionalized cages are severely distorted by the added groups, and some structures undergo skeletal transformations.

Endohedral metal doping is another practical way for the stabilization of non-IPR fullerene cages without changing the cage framework. In these structures, substantial electron densities transferred from the encapsulated metallic species to the cages are significantly localized on the fused pentagons, and stabilization results from coordination of metal ions with the cage interactions. Due to the very long-established principles based on the knowledge of the fullerene cage interactions and stabilization from the encapsulated metallic species, the very recent discovery of U\textsubscript{2}C\textsubscript{2}@C\textsubscript{80} even showed that U can take a formal 5+ charge state in the encapsulated cluster.\textsuperscript{39} In contrast to the corelike 4f orbitals of the lanthanides, the 5f orbitals of the actinides are chemically effective in stabilizing cages.\textsuperscript{40,41} In particular, different from the common Ln\textsuperscript{3+} charge state, actinides were found to adopt variable charge states depending on the cluster and the cage structures. For instance, four electrons of the Th atom are formally transferred to the C\textsubscript{76}(8)-C\textsubscript{76} cage in Th@C\textsubscript{76}(8)-C\textsubscript{76}.\textsuperscript{38} The oxidation state of U in U@D\textsubscript{18}(1)-C\textsubscript{74} and two U@C\textsubscript{72} isomers, U@C\textsubscript{72}(5)-C\textsubscript{72} and U@C\textsubscript{72}(9)-C\textsubscript{72}, can be 3+ or 4+, depending on the isomeric cage structure.\textsuperscript{36} The very recent discovery of U@C\textsubscript{76} even showed that U can take a formal 5+ charge state in the encapsulated cluster.\textsuperscript{39} Hence, we report the synthesis, isolation and systematic characterization of three new non-IPR actinide EMFs, U@C\textsubscript{71}(17418)-C\textsubscript{76}, U@C\textsubscript{71}(28324)-C\textsubscript{80} and Th@C\textsubscript{71}(18748)-C\textsubscript{80}. It is rather surprising to observe that two unanticipated non-IPR cage isomers C\textsubscript{71}(17418)-C\textsubscript{76} and C\textsubscript{71}(28324)-C\textsubscript{80} which have never been observed before, were stabilized as actinide EMFs with a relatively high product yield. Combined experimental and computational studies have been performed to rationalize these unexpected results, which provide deeper understanding and new insights into the metal–cage interactions and stabilization of EMFs.

2. RESULTS AND DISCUSSION

2.1. Preparation, Purification, and Spectroscopic Characterizations of U and Th EMFs. Th@C\textsubscript{80}, U@C\textsubscript{80}, and U@C\textsubscript{76} were synthesized by a modified direct current arc-discharge method.\textsuperscript{34} The graphite rods packed with U\textsubscript{3}O\textsubscript{8} graphite powder and ThO\textsubscript{2} graphite powder (molar ratio of M/C = 1:24) were annealed and then vaporized in the arcing chamber under a 200 Torr helium atmosphere. The collected raw soot was refluxed in CS\textsubscript{2} under an argon atmosphere for 12 h. Multistage HPLC separation procedures were employed to isolate and purify Th@C\textsubscript{80}, U@C\textsubscript{80} and U@C\textsubscript{76} (see Figures S1–S3). The purity of the isolated Th@C\textsubscript{80}, U@C\textsubscript{80}, and U@C\textsubscript{76} were confirmed by the observation of single peaks by HPLC (Figure 1a–c). The positive-ion mode MALDI-TOF mass spectra of the purified Th@C\textsubscript{80}, U@C\textsubscript{80}, and U@C\textsubscript{76} show
single peaks at 1192.077, 1198.083, and 1150.120 m/z, respectively.

To obtain additional structural information for these new compounds, both vis–NIR and Raman spectroscopies were performed (see Figures S4 and S5). The vis–NIR absorption spectrum of U@C_{80} exhibits a distinct absorption at 593 nm, which differs from those reported for Sm@C_{80}(19138)-C_{76}. In addition, U@C_{80} exhibits only one broad absorption at 575 nm, while no obvious absorption was observed for Th@C_{80}. However, the low-energy Raman spectroscopic results show that the features of U@C_{80} around the cage vibration range are similar to those of Th@C_{80}, indicating that the cage isomer for U@C_{80} and Th@C_{80} is likely to be the same.

2.2. Crystallographic Identifications of U and Th based on Non-IPR EMFs. The three compounds under study were cocry stallized with Ni^{II}(OEP) (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin dianion) to obtain good crystals suitable for X-ray measurements. Their molecular structures were determined with single crystal X-ray diffraction (XRD) crystallography. Notably, the fullerene cages for Th@C_{80}, U@C_{80}, and U@C_{76} are not the same isomers found for the previously reported U_{2}@C_{1}(7)-C_{80}, U_{2}@C_{1}(7)-C_{80}, and Sm@C_{2}(19138)-C_{76}. In brief, both U@C_{80} and Th@C_{80} possess the same carbon cage with C_{1h} symmetry and one pair of fused pentagons, namely, the C_{1}(28324)-C_{80} cage. Similarly, U@C_{76} possesses the C_{1}(17418)-C_{76} cage with low symmetry and a fused pentagon pair as well. Interestingly, this cage was also predicted to be the most thermodynamically favorable candidate for a single Th atom at elevated temperatures. Figure 2a–c show the molecular structures of these EMFs showing the major components together with the co crystallized Ni^{II}(OEP) molecule. For all three compounds, the fused pentagons on the cages are close to the adjacent Ni^{II}(OEP) moieties. Interestingly, the porphyrin molecule faces a different side of the C_{1}(28324)-C_{80} cage when different metal atoms (U, Th) are encapsulated. The shortest distances between Ni and a cage carbon range from 2.954 to 3.024 Å, suggesting substantial π–π interactions between the fullerene cages and Ni^{II}(OEP).

2.2.1. Th@C_{1}(28324)-C_{80}. As shown in Figure 3a,b, a fully ordered non-IPR cage of C_{1}(28324)-C_{80} was clearly identified in the case of Th@C_{1}(28324)-C_{80}. Inside the fullerene cage, the thorium ion is slightly disordered over four positions (i.e., Th1, Th2, Th3, and Th4), which are short distances (0.9–3.4 Å) apart. The major Th site with 0.47 occupancy is residing very close to the edge of the fused pentagon pair with the distances ranging from 2.366 to 2.544 Å (see Figure S6 and Table S1), which are almost comparable to the shortest Th–C distances (i.e., 2.340(14)–2.494(10) Å) previously reported for Th@C_{3}(8)-C_{82}.38

2.2.2. U@C_{1}(28324)-C_{80}. This crystal falls in the monoclinic C2/m space group, as commonly encountered for many analogous EMF/Ni(OEP) systems, which contains two halves of the fullerene cage and a symmetry-related Ni(OEP) molecule. Accordingly, an intact cage is obtainable by combining one-half of the cage with the mirror image of the other, both having an occupancy value of 0.50. Because the C_{1}(28324)-C_{80} cage is chiral, the two cage orientations are actually enantiomers. Figure S7 presents these two enantiomers (cages 1 and 1A), with the internal metal atom omitted for clarity. Inside the cage, the disorder of the U atom is different from that of the Th atom. There are four crystallographic sites for the uranium ion with occupancies of 0.32 for U1, 0.08 for U2, 0.08 for U3, and 0.02 for U4. Moreover, because only U2 resides at the symmetric plane, three additional metal sites (U1A, U3A, U4A) are generated via the crystallographic mirror plane (as shown in Figure 3c). Figure 3d shows the major site of the U atom (U1) in cage 1. Crystallographically, it is impossible to determine whether either or both of U1 and its mirror-related site U1A are occupied (see Figure S8). However, our calculations confirm that the U1 configuration is the most stable structure, while the U1A site does not lie at an energy minimum. Similar to the major Th site in Th@C_{1}(28324)-C_{80}, U1 is also located under the fused pentagons in the framework of C_{1}(28324)-C_{80}. However, the closest U–Cage contacts for U1 were determined to be in the range of 2.267–2.640 Å, which are
slightly shorter than the closest Th−cage contacts (see Figure S9 and Table S2).

2.2.3. $U@C_{1}(17418)$−$C_{76}$. This chiral fullerene cage is disordered with two enantiomers possessing nearly equal occupancy (cage 1/cage 2 = 0.58:0.42, as shown in Figure 4a). Within the cage, five U sites with fractional occupancies ranging from 0.04 to 0.33 were identified. Figure 4b shows cage 1 with all the metal sites. A closer look reveals that both U1 and U2 sites are very close to the fused pentagons of this cage (as shown in Figure 4b). The shortest U−cage distances for U1 were determined to be in the range of 2.290−2.517 Å (see Figure S10 and Table S3).

It is worth noting that another $C_{76}$ cage isomer, namely, $C_{1}(17894)$−$C_{76}$, was also considered at the very beginning. Topologically, the $C_{1}(17894)$−$C_{76}$ cage can be obtained after only one Stone−Wales (SW) transformation step from the $C_{1}(17418)$−$C_{76}$ cage (Figure 5). Crystallographic results revealed that $C_{1}(17894)$−$C_{76}$ exhibits very similar $R_{t}$ values to those of $C_{1}(17418)$−$C_{76}$ ($R_{t}(U@C_{1}(17894)-C_{76}) = 0.1283$; $R_{t}(U@C_{1}(17418)-C_{76}) = 0.1236$). Consequently, it is difficult, if not impossible, to unambiguously assign which cage isomer we have based exclusively on the crystallographic analysis alone. Fortunately, in combination with the corresponding electrochemical and theoretical studies, the $C_{1}(17418)$−$C_{76}$ cage was unambiguously assigned (see sections 2.4 and 2.5). This may be a rare case, but it raises a cautionary note for future structural analysis of fullerene cages, as it demonstrates that the SW related structures could be easily erroneously assigned by conventional crystallographic analyses alone. Thus, a combination of single-crystal X-ray characterization, theoretical calculations, and further structural characterizations is highly recommended to determine the final structural assignment.

2.2.4. Topological Connection between $U@C_{1}(17418)$−$C_{76}$ and $U@C_{1}(28324)$−$C_{80}$. Interestingly, the U atom selects two non-IPR chiral carbon cages, $C_{1}(17418)$−$C_{76}$ and $C_{1}(28324)$−$C_{80}$, that are intimately related. The two enantiomers of $C_{1}(17418)$−$C_{76}$, arbitrarily named $e_{1}$ and $e_{2}$, share significant portions of their cage structures with the two enantiomers of $C_{1}(28324)$−$C_{80}$ (Figure 6). In fact, enantiomer $e_{1}$ of $C_{1}(28324)$−$C_{80}$ can be obtained after a Stone−Wales (SW) transformation on $C_{1}(17418)$−$C_{76}$ ($e_{1}$), followed by two consecutive $C_{2}$ insertions. A completely energetically equivalent chiral path exists that connects the other two enantiomers ($e_{2}$). Remarkably, enantiomer $e_{1}$ ($e_{2}$) of $C_{1}(17894)$−$C_{76}$ and enantiomer $e_{2}$ ($e_{1}$) of $U@C_{1}(28324)$−$C_{80}$ are topologically connected by only two $C_{2}$ insertions with no further rearrangements; these paths would be less energetically demanding than those that preserve the same chirality (Figures 6 and S11 for more details). Therefore, these connections are enantiomerically dependent.

2.3. Electronic Structures and Isomer Abundances for $Th@C_{80}$ and $U@C_{80}$. A detailed study was carried out to analyze the electronic structure of $Th@C_{80}$ and $U@C_{80}$ and to understand the key factors that govern the encapsulation of these two actinides. As observed in the X-ray structure, the optimal location of Th in $Th@C_{80}$ is near the pentalene motif. This site maximizes the number of contacts between the metal ion and the neighboring carbon atoms, as shown in Figure 7b. The shortest computed values range between 2.50 and 2.69 Å, which are on average slightly longer than the experimental ones (Figure S6 and Table S2). Molecular orbital (MO) analysis confirmed the formal transfer of four electrons from the guest to the host upon encapsulation (Figure 8).

Thus, the four valence electrons of the Th atom are transferred to the lower-lying unoccupied cage orbitals, which
are mainly localized on the C₈₀ framework. Several locations of Th within the fullerene were computed, and we found that the relative energies can vary significantly with the position of metal ion. It is evident from the values in Figure 7d that for an atom that behaves as a tetravalent cation the position closest to the pentalene is much more favorable than any other position. In particular, it is significantly lower in energy than those locations near the sumanene motifs (A and B in Figure 7d), which were recently found to show comparable energies to those near the pentalenens for a non-IPR C₇₄ cage with one adjacent pentagon pair.37

For tetraniionic C₈₀⁴⁻ species, the highly symmetrical IPR I₈ and D₅h are the carbon cages with the lowest energies. The most stable non-IPR tetraniions with one pentalene appear at relative energies between 30.9 and 36.1 kcal·mol⁻¹ with respect to isomer I₈ (Table 1). For anionic non-IPR cages, the pentalene motif concentrates a significant amount of the negative charge, as shown in the molecular electrostatic potential distribution and atomic charges computed for C₇₃(28324)-C₈₀⁴⁻ (Figure 7c and S12). This electronic charge polarization is not a direct result of adding four electrons to molecular orbitals strongly localized on the pentalene. There is always a repolarization of the electronic density that results in a partial concentration of the negative charge on the pentalene due to its higher pyramidalization.49 After the formal encapsulation of a tetravalent Th ion near the pentalene motif, all the non-IPR cages are significantly stabilized (Table 1). Compared to the other APP1 cages, this stabilization has a much more important impact on the observed C₇₃(28324) cage, which can be attributed to the higher negative charge on the pentalene and to the larger number of Th–cage contacts (Table S1 and Figure S6). Thus, the observed C₇₃(28324) non-IPR isomer and the IPR C₇₃(31922) and D₅h(31923) cages were found within a range of energy less than 2 kcal·mol⁻¹ (Table 1). Other GGA and hybrid density functionals were used to verify this result. Even though none of the tested functionals predicted the synthesized isomer Th@C₇₃(28324) as the lowest in energy, we found it to be among those with the lowest energies (Tables S4–S6).

In a Krätschmer–Huffman reactor, the fullerenes are formed at very high temperatures (1500–3000 K).44 Therefore, in addition to the potential energy differences, we have analyzed the relative stability of the most favorable EMFs in terms of their relative free energies, in order to incorporate thermal and entropic effects. The prediction of relative isomer concentrations requires determining the partition functions. The rotational–vibrational partition functions were constructed

Table 1. Relative Energies, Number of Adjacent Pentagon Pairs, Cage Symmetries, and Spin Densities for Selected Empty and Endohedral Metallofullerenes

<table>
<thead>
<tr>
<th>isomer</th>
<th>APP</th>
<th>sym</th>
<th>C₈₀</th>
<th>δE</th>
<th>C₈₀⁻⁺</th>
<th>δE</th>
<th>C₈₀⁻⁻</th>
<th>δE</th>
<th>La@C₈₀</th>
<th>δE</th>
<th>U@C₈₀ (Q)</th>
<th>δE</th>
<th>SD (fi)</th>
<th>U@C₈₀ (T)</th>
<th>δE</th>
<th>SD (fi)</th>
<th>Sc₂O@C₈₀</th>
<th>δE</th>
</tr>
</thead>
<tbody>
<tr>
<td>31920</td>
<td>0</td>
<td>C₁</td>
<td>0</td>
<td>16.7</td>
<td>32.7</td>
<td>6.4</td>
<td>5.5</td>
<td>0</td>
<td>9.0</td>
<td>2.55</td>
<td>4.8</td>
<td>2.17</td>
<td>31.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31922</td>
<td>0</td>
<td>C₂</td>
<td>2.9</td>
<td>3.0</td>
<td>9.9</td>
<td>0.0</td>
<td>0.0</td>
<td>0</td>
<td>12.6</td>
<td>2.66</td>
<td>7.6</td>
<td>2.42</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31923</td>
<td>0</td>
<td>D₅h</td>
<td>5.1</td>
<td>0.0</td>
<td>3.8</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>17.1</td>
<td>2.50</td>
<td>17.3</td>
<td>2.21</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31924</td>
<td>0</td>
<td>I₈</td>
<td>16.2</td>
<td>4.2</td>
<td>0.0</td>
<td>13.0</td>
<td>11.6</td>
<td>11.6</td>
<td>11.5</td>
<td>2.66</td>
<td>5.1</td>
<td>2.21</td>
<td>/</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28119</td>
<td>1</td>
<td>C₇</td>
<td>14.9</td>
<td>27.5</td>
<td>36.1</td>
<td>13.0</td>
<td>8.1</td>
<td>8.1</td>
<td>13.2</td>
<td>2.74</td>
<td>14.8</td>
<td>2.45</td>
<td>11.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28124</td>
<td>1</td>
<td>C₇</td>
<td>21.5</td>
<td>28.0</td>
<td>31.4</td>
<td>13.7</td>
<td>1.4</td>
<td>1.4</td>
<td>13.5</td>
<td>2.66</td>
<td>0.5</td>
<td>2.21</td>
<td>16.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31876</td>
<td>1</td>
<td>C₁</td>
<td>15.3</td>
<td>24.0</td>
<td>31.8</td>
<td>14.1</td>
<td>18.6</td>
<td>18.6</td>
<td>13.2</td>
<td>2.74</td>
<td>14.8</td>
<td>2.45</td>
<td>11.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31891</td>
<td>1</td>
<td>C₁</td>
<td>19.1</td>
<td>25.7</td>
<td>30.9</td>
<td>21.0</td>
<td>23.2</td>
<td>23.2</td>
<td>20.7</td>
<td>2.35</td>
<td>27.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Energies are in kcal·mol⁻¹. †Isomer number according to the spiral algorithm by Fowler and Manolopoulos.51 *Number of adjacent pentagon pairs (APP). ‡Mulliken spin density populations for U atoms in triplet and quintet states. Values taken from ref 52.
using the rigid rotor and harmonic oscillator (RRHO) approximation and the related free-encapsulated model (FEM) as proposed by Slanina.\(^{48,49}\) The contribution due to chirality was also considered.\(^{50}\) Both approximations predict the IPR \(\text{Th}@C_{28}(31922)-C_{80}\) as the most abundant isomer up to around 1100 K. The experimentally observed structure, \(\text{Th}@C_{2}(28324)-C_{80}\) was found to be the most abundant isomer above 1100 K within the FEM model (Figure 9), and the most

abundant APP1 isomer in the whole range of temperatures in both approximations. The molar fractions of EMFs with highly symmetric cages (i.e., \(\text{Th}@D_{3h}(31923)-C_{80}\) and \(\text{Th}@I_{d}(31924)-C_{80}\)) are almost negligible in the whole range of temperatures.

Similar analysis was performed for the \(\text{U}@C_{80}\) family. Given that \(\text{U}\) retains two or three electrons in its valence shell, the ground state is not a singlet. We have optimized all eight isomers in Table 1 in triplet and quintet states. In the triplet state, the formal electron transfer between host and guest can be four or three electrons, while in the quintet state it must be three (see Scheme 1). Accordingly, the atomic spin densities (SD) computed for \(\text{U}\) range between 2.50 and 2.74 e for the triplet (\(F\)) and between 2.17 and 2.45 e for the triplet (\(F\)). We have not estimated the energies of triplet states with \(F\) configuration for \(\text{U}\), but we presume them to be similar to those for the quintet states, since the only difference among them is the magnetic interaction between a local magnetic moment of \(S = 3/2\) in the \(U\) atom (\(F\)) and an unpaired electron on the cage, which can be coupled in either ferromagnetic (parallel) or antiferromagnetic (antiparallel) manner.

Like in the \(\text{Th}@C_{80}\) family, non-IPR \(\text{U}@C_{2}(28324)-C_{80}\) and IPR \(\text{U}@C_{3}(31922)-C_{80}\) were found to be the lowest in energy, differing by only 0.5 kcal-mol\(^{-1}\). Although at very low temperatures the IPR isomer is the dominant species, above 500 K the experimentally determined cage \(C_{2}(28324)-C_{80}\) is predicted to be the most abundant (Figure 9). In the two EMFs, the ground state corresponds to a triplet state, in which the metal is formally \(U^{4+}\); the quintet states were computed between 9 and 13 kcal-mol\(^{-1}\) higher in energy than the corresponding triplet states. In fact, in six of the eight computed structures, the triplet state was easier to converge or lower in energy than the quintet. Only in one IPR and one non-IPR cage the triplet and quintet states were found to have similar energies. For \(\text{U}@C_{2}(31920)-C_{80}\) and \(\text{U}@C_{3}(31891)-C_{80}\), we were unable to converge a quintet state. These results suggest that \(U\) prefers to be in an oxidation state 4+ instead of 3+, even though for some carbon cages, it has been reported that the oxidation state 3+ is also an option for \(U\).\(^{36}\)

2.4. Computational analysis for \(\text{U}@C_{76}\). After an initial screening of the lowest-energy tetraanions, we analyzed in detail the structure and relative energies of six isomers for \(\text{U}@C_{76}\) the IPR isomer of \(T_{d}\) symmetry, and five non-IPR fullerenes with one adjacent pentagon pair (APP1). Among the tetraanions, the IPR cage is much lower in energy than the non-IPR ones (Table 2). However, as in \(C_{80}\), the encapsulation of \(U\) alters significantly the relative stabilities of the five non-IPR isomers. Although the IPR EMF is still the lowest in energy, there are five isomers in a range of only 6 kcal-mol\(^{-1}\). In Figure 10, we can observe that at very low temperatures the IPR isomer is the dominant species, but its concentration rapidly decreases when \(T\) increases. Contrariwise, the abundance of the isolated and characterized \(\text{U}@C_{1}(17418)-C_{76}\) increases rapidly to a maximum at 500 K becoming the most abundant isomer up to 1000 K and the second most abundant isomer at higher temperatures. In contrast, the abundance of \(\text{U}@C_{1}(17894)-C_{76}\) another possible isomer based exclusively on the crystallographic analysis, remains low below 1000 K but increases to a comparable level to that of the \(\text{U}@C_{1}(17418)-C_{76}\) at higher temperature. The ground state for \(\text{U}@C_{1}(17418)-C_{76}\) is a triplet with the two unpaired electrons localized on uranium. The theoretically predicted shortest \(U-C\) bond distances range between 2.41 and 2.52 Å, which agrees well with experimental results. A triplet state with formally three unpaired electrons on \(U\) and the fourth electron delocalized on the fullerene was found at +6.8 kcal-mol\(^{-1}\). Electron spin density distributions (Figure S13) for the triplet and quintet states show the different nature of the two electronic states, which can be formally associated with oxidation states for \(U\) of 4+ and 3+, respectively. Despite this different nature, the uranium–carbon bond lengths are very similar for the two states, as shown in Table S7. To confirm these results, which show that there are several \(U@C_{76}\) isomers within a quite narrow energy range, we have explored other density functionals as well as introduced spin–orbit corrections (see last

![Figure 9. Computed molar fraction as a function of the temperature (K) using the free-encapsulating model (FEM) for the lowest-energy isomers of \(\text{Th}@C_{80}\) (top) and \(\text{U}@C_{80}\) (bottom). Dashed and continuous lines are used for IPR and non-IPR isomers, respectively.](image-url)

![Scheme 1. Schematic Representation of the Electronic Structure for \(U^{3+}@C_{2n}^{3-}\) (Quintet or Triplet) and \(U^{4+}@C_{2n}^{4-}\) (Triplet)](image-url)
For a gap of 1.46 V, compared to 0.85 V for U@C80. This large difference is somewhat unexpected since Th@C80 and U@C80 are irreversible. The observed and computed redox potentials of U@C76 are comparable to those of the cage orbitals (Figure S15).

Analysis of Redox Potentials for U and Th Non-IPR EMFs. The electrochemical properties of Th@C17894-C80, U@C17894-C80, and U@C17418-C76 were investigated by means of cyclic voltammetry (CV) using a glassy carbon electrode with ortho-dichlorobenzene and tetra(n-butyl)-ammonium hexafluoro-phosphate (o-DCB/n-Bu4NPF6) as solvent/electrolyte (see Figure S14). Three reversible reductive steps and one reversible oxidative step were observed for U@C17418-C76. However, for the other two compounds with the C80 cage, the electrochemical behavior is very different. Only the first redox process of U@C17894-C80 is electrochemically reversible, whereas all of the redox processes of Th@C17894-C80 are irreversible. The observed and computed redox potentials of U@C17418-C76 and Th@C17894-C80 are summarized in Table 3 (see Table S9 for more details). The first oxidation potential of Th@C17894-C80 is at ~1.22 V, which is far more negative than that of U@C17894-C80, resulting in a large electrochemical gap of 1.46 V, compared to 0.85 V for U@C80. This large difference is somewhat unexpected since Th@C80 and U@C80 have the same cage structure and four electron charge transfer. Computed redox potential calculations in combination with MO analysis allow us to rationalize this significant difference. For Th@C17894-C80, the Th 5f empty orbitals are quite high in energy, and the LUMO is localized on the carbon cage (Figure 8), but for U@C17894-C80 the energies of the U 5f orbitals are comparable to those of the cage orbitals (Figure S15).

Consequently, reduction processes are totally different, with reduction of the cage for Th@C17418-C76 at ~1.22 V (computed ~1.28 V) and reduction of the metal at a much lower potential of ~0.57 V (computed ~0.83 V) for U@C17894-C80. A simple inspection of the occupied frontier orbitals for these two EMFs leads to the conclusion that Th and U endohedral fullerenes should also display a quite different anodic peak, since for Th the oxidation should occur on the cage orbitals, whereas for U the oxidation should take place at the actinide. Nevertheless, to create an U5+ ion is very difficult, and all attempts to oxidize the U ion have failed, the result being that the first oxidation potential strongly depends on the carbon cage. Hence, whereas the first oxidation potential for U@C17418-C76 is estimated from DFT calculations to be +0.12 V (computed +0.14 V) and reduction of the metal at a much lower potential of ~0.57 V (computed ~0.83 V) for U@C17894-C80, the Th 5f empty orbitals are quite high in energy, and the LUMO is localized on the carbon cage (Figure 8), but for U@C17894-C80 the energies of the U 5f orbitals are comparable to those of the cage orbitals (Figure S15).

Table 3. Comparison of Observed and Computed Redox Potentials

<table>
<thead>
<tr>
<th>species</th>
<th>isomer</th>
<th>mE1</th>
<th>mE2</th>
<th>ΔE, exp.</th>
<th>ΔE, DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>U@C76</td>
<td>17418</td>
<td>0.12</td>
<td>−0.85</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17894</td>
<td>−0.22</td>
<td>−0.87</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>U@C80</td>
<td>28324</td>
<td>0.24</td>
<td>−1.22</td>
<td>1.46</td>
<td></td>
</tr>
<tr>
<td></td>
<td>28324</td>
<td>0.22</td>
<td>−1.28</td>
<td>1.51</td>
<td></td>
</tr>
</tbody>
</table>

*All values are given in V referred to Fe/Fc*. The computed values of the first oxidation potentials for Th@C17418-C76 and Th@C17894-C80 are +0.06 and ~0.24 V, respectively.

Table 2. Relative Energies and Atomic Spin Density Populations for Several EMFs with 76 Carbon Atoms

<table>
<thead>
<tr>
<th>cage</th>
<th>sym</th>
<th>C76−</th>
<th>ΔE</th>
<th>Th@C76</th>
<th>ΔE</th>
<th>SDa</th>
</tr>
</thead>
<tbody>
<tr>
<td>19151</td>
<td>T2</td>
<td>0.00</td>
<td>0.0</td>
<td></td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>17418</td>
<td>C1</td>
<td>30.9</td>
<td>7.3</td>
<td></td>
<td>9.2</td>
<td>2.67</td>
</tr>
<tr>
<td>17459</td>
<td>C1</td>
<td>24.5</td>
<td>14.6</td>
<td></td>
<td>4.5</td>
<td>2.60</td>
</tr>
<tr>
<td>17750</td>
<td>C1</td>
<td>31.8</td>
<td>13.3</td>
<td></td>
<td>10.8</td>
<td>2.67</td>
</tr>
<tr>
<td>17894</td>
<td>C1</td>
<td>31.2</td>
<td>14.0</td>
<td></td>
<td>7.8</td>
<td>2.64</td>
</tr>
<tr>
<td>19138</td>
<td>C2</td>
<td>15.5</td>
<td>10.5</td>
<td></td>
<td>4.1</td>
<td>2.58</td>
</tr>
<tr>
<td>19142</td>
<td>C1</td>
<td>29.5</td>
<td>31.2</td>
<td></td>
<td>23.6</td>
<td>2.73</td>
</tr>
</tbody>
</table>

“Energies are in kcal-mol−1. All isomers are non-IPR (APP1) except the first one. Mulliken atomic spin density population. X-ray crystal structure for U@C76 and isomer proposed for Th@C76 by Zhao and co-workers. Non-IPR cage that also fits acceptably the X-ray diffraction data.

Figure 10. Computed molar fraction as a function of the temperature (K) using the free-encapsulating model (FEM) for the lowest-energy isomers of U@C76.
simplicity, we have represented the MO energies for the Th derivatives since their ground states are always singlet states. The HOMO is about 300 mV lower in energy for U@C(17418)-C_{76}. In summary, combining all experimental and computational data, we conclude that the most likely isomer of the experimentally isolated U@C_{76} corresponds to U@C_{76}(17418).

2.6. Why Are C_{6}(17418)-C_{76} and C_{6}(28324)-C_{80} Formed? Importance of Thermal Effects and Molecular Symmetry in Cage Selection. Soon after the discovery of Sc_{6}N@C_{40}^{53}, many theoretical studies highlighted the relevance of topology and the high symmetry of theicosahedral C_{60} cage when it encapsulates a guest that transfers six electrons to the carbon cage, as for example M_{6}N (M = Sc, Y, Lu, and other trivalent lanthanides with minor abundances).^{54-57} La_{2}, or U_{2}^{40,58,59}. For EMFs that show a 4-electron transfer, there is lower isomer selectivity and no prevalent cage exists in this case.

Since Th and U behave, in general, as tetravalent ions, in monoacontidine EMFs there are important charge concentrations that induce strong interactions between the fullerene and the actinide. A direct consequence is that many non-IPR forms gain significant relative stability when the actinide is encapsulated. Nevertheless, this is not enough to completely reverse the relative energies of IPR and non-IPR EMFs, as shown in Tables 1 and 2. A key point is that the formation of fullerenes occurs at very high temperatures, and several other factors are also relevant at thermodynamic equilibrium. First, if the internal guest has mobility inside the fullerene, as assumed by the FEM model, then the symmetry of the fullerene cage is very relevant. For instance, fullerenes with I_{h} and D_{sh}^{58} symmetry contribute to the rotational partition function q_{rot} with values of the symmetry index σ equal to 60 and 10, respectively, whereas for a fullerene with C_{6} symmetry the corresponding value is 1. Car-Parrinello molecular dynamics simulations carried out for U@C_{80} have shown that U has rather limited mobility at 300 K, but much higher mobility at temperatures of fullerene formation (Figure 12). This fact justifies the use of the FEM model in our isomer abundance analysis.

A second factor to be accounted for in cage selection at high temperatures is that nonsymmetric cages are chiral. However, we recently reported the IPR U^{4+}@D_{3h}-C_{74}.^{36,53} With 74 atoms, there is only one IPR isomer and three isomers containing a pentalene (APP1). The IPR cage is between 15 and 34 kcal mol^{-1} lower in energy than the APP1 isomers (Table S10). The capture of isomer D_{3h} occurs because it does not lose too much stability with respect to the non-IPR EMFs once U is encapsulated. This happens because it has a particular structure that results in a short uranium-fullerene bond distance, 2.35 Å (DFT), the shortest among all the uranofullerenes analyzed so far. Consequently, the thermal and entropic effects cannot counterbalance the energy differences; hence, the IPR form is the dominant one up to 2800 K (Figure S16). Similar results were found for Th@C_{74}.^{37} Therefore, highly symmetric EMFs are only formed during the arc-discharging process preferentially when their relative energies with respect to the less symmetric EMFs are large enough. The prototypical example is I_{h}-C_{60}, which is able to encapsulate many different guests that can exhibit a six-electron transfer. Among them, Sc_{6}N@C_{40} is the most relevant, since it is the third most abundant fullerene after C_{60} and C_{70}. In other words, temperature works against symmetry, but it does not always win.

2.7. Covalency of Actinide–Fullerene Interactions.

The existence of formal Th^{4+} or U^{4+} ions interacting with C_{2n}^{4−} cages and the fact that the computed encapsulation energies correlate with the amount of charge transferred (Tables S11 and S12) lead us to assume that the metal–cage interaction can be described as essentially ionic, as found for other families of cluster fullerenes. It is remarkable that covalent contributions to metal–cage interactions were found to be non-negligible.^{60,61} Recently, the Th–cage interaction was analyzed for several Th@C_{2n} systems, and in addition to the strong metal–cage electrostatic attraction, significant covalent Th–cage interactions were found, which were larger than those for lanthanide EMFs.^{34,37} From a comparison between Th@C_{60} and U@C_{60}, we have found some evidence that the U–cage interactions show a higher degree of covalency than for Th–cage ones, in line with the smaller electronegativity difference, 0.85 vs 1.25 units in the Pauling scale for U–C and Th–C, respectively. Appreciably higher mixing and overlapping of the 5f orbitals of the actinide with the cage was observed for U@C_{60} compared to Th@C_{60} (see Figures 7 and S15). Additionally, focusing on the topology of the molecular electron density (QTAIM),^{52} we found that the descriptors at the actinide–cage bond critical points (BCP), as for example the density, kinetic or potential (or total) energy densities, and Mayer bond order (MBO), indicate somewhat larger covalency (largest values) for the U–C interaction, in line with the shorter U–C distances; see Table 4. In agreement with the higher ionicity for Th endohedral fullerenes, the computed Bader atomic charge is more positive when the encapsulated metal is Th (+2.12 e) than when it is U (+1.70 e). Therefore, this
isomeric cage structures can be observed, the use of other observed in future work with endohedral fullerenes, where many Th@C80, and U@C76, have been successfully synthesized and competitive in some circumstances, like in the formation of U@C80 and U@C76. The actinide EMFs present with trivalent metals, such as, Sc2O3, Sc2C2, and so on.

The actinide ion displays high mobility within the fullerene; the stabilization of some non-IPR fullerenes originates from strong host–guest interactions. This is particularly true in the encapsulation of tetravalent cations, where the interactions between the cation and the pentalene motif for the non-IPR fullerene are much stronger than for fullerenes that host clusters between the cation and the pentalene motif for the non-IPR encapsulation of tetravalent cations, where the interactions

4. EXPERIMENTAL SECTION

4.1. Synthesis and Isolation of Th@C80, U@C80, and U@C76. The carbon soots containing actinide EMFs were synthesized by the direct-current arc discharge method. The graphite rods, packed with ThO2/graphite powder and UO2/graphite powder (molar ratio of M/C = 1:24), were vaporized in the arcing chamber under 200 Torr He atmosphere. The resulting soot was refluxed in CS2 under an argon atmosphere for 12 h. The separation and purification of Th@C80, U@C80, and U@C76 were achieved by multistage HPLC procedures. Multiple HPLC columns, including Buckyprep-M column (25 × 250 mm, Cosmosil, Nacalai Tesque Inc.), Buckyprep-D column (10 × 250 mm, Cosmosil, Nacalai Tesque, Japan), and Buckyprep column (10 × 250 mm, Cosmosil, Nacalai Tesque, Japan), were utilized in this procedure. Further details are described in the Supporting Information.

4.2. Spectroscopic Studies. The positive-ion mode matrix-assisted laser desorption/ionization time-of-flight (MALDI) was used for mass characterizations. The U@C80, U@C76, and U@U70 in CS2 solution were measured with a Cary 5000 UV–vis–NIR spectrophotometer (Agilent, USA). Raman spectra were obtained on a Horiba Lab RAM HR Evolution Raman spectrometer using a laser at 633 nm.

4.3. Electrochemical Studies. CV results were obtained in dichlorobenzene using a CHI-660E instrument. A conventional three-electrode cell consisting of a platinum counterelectrode, a glassy carbon working electrode, and a silver reference electrode was used for all measurements. (nBu)4NPF6 (0.05 M) was used as the supporting electrolyte. The CVs were measured at a scan rate of 100 mV/s.

4.4. Single-crystal X-ray diffraction. Crystalline blocks of U@C80 (2n = 76, 80) and Th@C80 were obtained by layering a benzene or chloroform solution of NiII(OEP) over a nearly saturated solution of the respective endohedral in CS2 in a glass tube. Over a 20 day period, the two solutions diffused into each other, and black crystals formed. XRD measurements were performed at 150 K on a Bruker P4 machine equipped with a graphite monochromator. The multiscan method was used for absorption corrections. The CVs were measured at a scan rate of 100 mV/s.

4.5. Computational Details. The PBE functional and Slater TZP basis sets (PBE/TZP level) were used for all calculations. The final wR2 was 0.3750 (all data) and R1 (6682 with I > 2σ(I)) = 0.1236. CCDC 1835947 contains the crystallographic data.
valence electrons and the ionic cores was treated through the pseudopotential (PP) approximation (Martins–Troullier type for C and Goedecker–Teter–Hutter type for U). The PBE functional was selected. The simulations were carried out in a cubic cell with a side length of 14 Å, a fictitious electron mass of 3100 a.u. and a time step of 0.121 fs.

Bond critical point (BCP) descriptors for Th@C_{128}(28324)-C_{80} and U@C_{128}(28324)-C_{80} were obtained using the Multiwfn program. Wave functions used for the analysis were from Gaussian 16. Geometry optimizations were performed at the DFT level using the PBE functional. A double-$\zeta$ 6-31G(d,p) basis set was used for C atoms and Stuttgart–Dresden basis sets with effective core potential (SDD) for Th and U atoms. A data set collection of computational results is available in the ioChem-BD repository\(^7\) and can be accessed via https://doi.org/10.19061/iochem-bd-2-31.

## ASSOCIATED CONTENT

### 1 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b10435.

HPLC profiles for the separation of Th@C_{128}(28324)-C_{80}, U@C_{128}(28324)-C_{80} and U@C_{128}(17418)-C_{76}. UV–vis–NIR absorption spectra and low energy Raman spectra of Th@C_{128}(28324)-C_{80}, U@C_{128}(28324)-C_{80} and U@C_{128}(17418)-C_{76}. Cyclic voltammetry of Th@C_{128}(28324)-C_{80}, U@C_{128}(28324)-C_{80} and U@C_{128}(17418)-C_{76} in o-dichlorobenzene containing 0.05 M n-BuNPF_6. Additional results from computations on Th@C_{128}(28324)-C_{80}, U@C_{128}(28324)-C_{80} and U@C_{128}(17418)-C_{76} and related systems (relative energies with different functionals, M–C distances, spin densities, MO diagrams, etc.) (PDF)

Crystallographic information files for U@C_{128}(17418)-C_{76}, Ni^{II}(OEP)·(CHCl_3), Th@C_{128}(28324)-C_{80}Ni^{II}(OEP)·2·(C_6H_6), and U@C_{128}(28324)-C_{80}Ni^{II}(OEP)·2(CHCl_3) (CIF, CIF, CIF)

## AUTHOR INFORMATION

### Corresponding Authors

*E-mail: chennng@suda.edu.cn.
*E-mail: echegoyen@utep.edu.
*E-mail: josepmaria.poblet@urv.cat.

### ORCID

Lai Feng: 0000-0003-0278-5502
Muaro Boero: 0000-0002-5052-2849
Antonio Rodríguez-Fortea: 0000-0001-5864-5629
Josep M. Poblet: 0000-0002-4533-0623
Luís Echegoyen: 0000-0003-1107-9423
Ning Chen: 0000-0002-9405-6229

### Author Contributions

†W.-C., L.A., and J.Z. contributed equally to this work.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We acknowledge Prof. Shuao Wang (Soochow University) and Prof. Marilyn M. Olmstead (University of California, Davis) for kind technique support and insightful discussions. C.N. thanks the National Science Foundation China (NSFC 51302178) the NSF of Jiangsu Province (BK20171211), Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), and the project of scientific and technologic infra-

structure of Suzhou (SZS201708). L.E. thanks the US National Science Foundation (NSF) for generous support of this work under the NSF-PREM program (DMR 1205302) and CHE-1801317. The Robert A. Welch Foundation is also gratefully acknowledged for an endowed chair to L.E. (grant AH-0033).

J.M.P. and A.R-F thank the Spanish Ministry of Science (CTQ2017-87269-P) and the Generalitat de Catalunya (2017SGR629 and XRQTC) for support. J.M.P. also thanks ICREA foundation for an ICREA ACADEMIA award. R.M.-M. thanks Spanish Ministry of Science for a PhD fellowship. M.B. thanks HPC - Equipex Equip@Mes/CPER Alsacalcul at the University of Strasbourg, and Grand Equipement National de Calcul Intensif (GENCI) under allocation DARI-A2 A0040906092. Research reported in this article was also partially supported by the National Institute of General Medical Sciences of the National Institutes of Health under linked Award Numbers R15 GM118969, TL4GM118971, and UL1GM118970.

## REFERENCES


(5) Kroto, H. W. The stability of the fullerences C_{24}, C_{28}, C_{32}, C_{36}, C_{50}, C_{60} and C_{70}. Nature 1987, 329, 529–531.


(9) Troshin, P. A.; Avent, A. G.; Darwish, A. D.; Martinsinovich, N.; Abdulsala, A. K.; Street, J. M.; Taylor, R. Isolation of Two Seven-Membered Ring C_{58} Fullerene Derivatives: C_{58}F_{2}Cl_{4} and C_{58}F_{4}Cl_{4}. Science 2005, 309, 278–281.


(14) Chen, D.-L.; Tian, W. Q.; Feng, J.-K.; Sun, C.-C. Structures and Electronic Properties of \( C_{60}Cl_{32} \) and \( C_{60}Cl_{64} \) Fullerene Compounds. ChemPhysChem 2007, 8, 2386–2390.

(15) Chen, N.; Mulet-Gas, M.; Li, Y. Y.; Stene, R. E.; Atherton, C. W.; Rodriguez-Forte, A.; Poblet, J. M.; Echegoyen, L. \( \text{Sc}_2\text{S}_8@C_{78}(8792)\)-\( C_{90} \): a metallic sulfide cluster inside a non-IPR \( C_{90} \) cage. Chem. Sci. 2013, 4, 180–186.


(19) Yang, S. F.; Popov, A. A.; Dunsch, L. Violating the Isolated Pentagon Rule (IPR): The endohedral Non-IPR cage of \( \text{Sc}_2\text{N}_8@C_{78} \). Angew. Chem., Int. Ed. 2007, 46, 1256–1259.

(20) Zhang, M.; Hao, Y.; Li, X.; Feng, L.; Yang, T.; Wan, Y.; Chen, N.; Slanina, Z. K.; Uhlík, F.; Cong, H. Facile Synthesis of an Extensive Family of \( \text{Sc}_2\text{O}_6@C_{72} \) \((n=35–47) \) and Chemical Insight into the Smallest Member of \( \text{Sc}_2\text{O}_6@C_{72}(8792)–C_{90} \). J. Phys. Chem. C 2014, 118, 28883–28889.


(23) Kato, H.; Taninaka, A.; Sugai, T.; Shinohara, H. Structure of a Missing-Caged Metallofullerene: \( \text{La}_2\text{S}_8@C_{72} \). J. Am. Chem. Soc. 2003, 125, 7782–7783.


(26) Yang, S. F.; Dunsch, L. A large family of dysprosium-based trimetallic nitride endofullerenes: \( \text{Dy}_2\text{N}_8@C_{76} \) \((39 \leq n \leq 44) \). J. Phys. Chem. B 2005, 109, 12320–12328.

(27) Fu, W.; Xu, L.; Azumendi, H.; Ge, J.; Fuhrer, T.; Zuo, T.; Reid, J.; Shu, C.; Harich, K.; Dorn, H. C. \( ^{115}\text{In} \) and \( ^{117}\text{In} \) NMR Cluster and Carbon Cage Studies of an Yttrium Metallofullerene Family, \( Y\text{N}_8@C_{72} \) \((n=40–43) \). J. Am. Chem. Soc. 2009, 131, 11762–11769.

(28) Alegret, N.; Chaur, M. N.; Santos, E.; Rodríguez-Forte, A.; Echegoyen, L.; Poblet, J. M. Bingle-Hirsch Reactions on Non-IPR \( \text{Gd}_2\text{N}_8@C_{76} \) \((2n=82 and 84) \). J. Org. Chem. 2010, 75, 8299–8302.


(64) Baerends, E. J., E.; D. E.; Ros, P. *ADF, 2013.01; SCM: Amsterdam, 2013.*


(66) *CPMD 4.1; IBM Corp.: Armonk, NY, 2015.*


