U$_2@I_h(7)$-C$_{80}$: Crystallographic Characterization of a Long-Sought Dimetallic Actinide Endohedral Fullerene

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$^\S$Supporting Information

ABSTRACT: The nature of actinide–actinide bonds has attracted considerable attention for a long time, especially since recent theoretical studies suggest that triple and up to quintuple bonds should be possible, but little is known experimentally. Actinide–actinide bonds inside fullerene cages have also been proposed, but their existence has been debated intensively by theoreticians. Despite all the theoretical arguments, critical experimental data for a dimetallic actinide endohedral fullerene have never been obtained. Herein, we report the synthesis and isolation of a dimetallic actinide endohedral metallofullerene (EMF), U$_2@C_{80}$. This compound was fully characterized by mass spectrometry, single crystal X-ray crystallography, UV–vis–NIR spectroscopy, Raman spectroscopy, cyclic voltammetry, and X-ray absorption spectroscopy (XAS). The single crystal X-ray crystallographic analysis unambiguously assigned the molecular structure to U$_2@I_h(7)$-C$_{80}$. In particular, the crystallographic data revealed that the U–U distance is within the range of 3.46–3.79 Å, which is shorter than the 3.9 Å previously predicted for an elongated weak U–U bond inside the C$_{80}$ cage. The XAS results reveal that the formal charge of the U atoms trapped inside the fullerene cage is +3, which agrees with the computational and crystallographic studies that assign a hexaanionic carbon cage, (I$_h$-C$_{80}$)$^6^-$. Theoretical studies confirm the presence of a U–U bonding interaction and suggest that the weak U–U bond in U$_2@I_h(7)$-C$_{80}$ is strengthened upon reduction and weakened upon oxidation. The comprehensive characterization of U$_2@I_h(7)$-C$_{80}$ and the overall agreement between the experimental data and theoretical investigations provide experimental proof and deeper understanding for actinide metal–metal bonding interactions inside a fullerene cage.

1. INTRODUCTION

Understanding chemical bonding is at the very heart of chemistry. The nature of actinide–actinide bonds has attracted considerable attention for a long time, especially since recent theoretical studies suggest that triple and up to quintuple bonds should be possible.$^1$–$^3$ However, although metal–metal bonds for d-block elements have been intensively studied for transition metal compounds, not much is known experimentally for the chemical bond between actinide atoms.$^4$ To date, experimental evidence for diactinides are limited to mass spectroscopic observation of U$_2$ and Th$_2$ in the gas phase.$^1$

Although possible U–U interactions have been discussed for binuclear uranium compound, there is still no conclusive evidence of its existence and it remains as one of the holy grails of inorganic chemistry.$^7$ Difficulty with synthesis and characterization has largely hindered the exploration of actinide metal–metal bonds using conventional actinide chemistry. Matrix isolation methods were used to prepare U(μ-$\mu$-H$_2$)U and U$_2$H$_4$, characterized using infrared and DFT calculations, and these
Endohedral metallofullerenes (EMFs) are known as ideal hosts for clusters that contain multiple metal ions. It has been shown in numerous cases that clusters with unique electronic structures, which would not be stable independently, can be stabilized by charge transfer from the encapsulated ions or clusters to the cages. Some of these encapsulated metal ions do not exhibit their highest oxidation states and result in covalent metal–metal bonds. Lanthanide–lanthanide bonding inside fullerene cages has been intensively studied and the existence of La–La, Sc–Sc, Y–Y, and Tb–Tb single bonds have been experimentally established. A very recent example is Lu, reported by Lu et al., in which two Lu ions in a +2 oxidation state form a Lu–Lu single bond. Popov et al. also reported that in the benzyl monoadducts of Dy, a single-electron metal–metal bond was formed inside the C80 cage, resulting in remarkable single-molecule magnetism with a record high blocking temperature.

Dimetallic uranium EMFs were originally experimentally observed by mass spectrometry by Smalley et al. On the basis of their observations, it is reasonable to assume that actinide–actinide bonds, which are extremely difficult to prepare by conventional actinide chemistry, may be formed inside fullerene cages as stabilizing nanocontainers. This topic has been intensively debated by theoreticians in recent years. Lu et al. suggested that a 6-fold U bond could exist inside a C60 cage. A subsequent report by Gagliardi et al. argued that this bond may be an artifact due to the small and constrictive size of the C60 cage. They also predicted that inside larger cages, C70–C80, the two U atoms prefer to bond to the internal walls of the fullerene cages rather than forming a U–U bond. Very recently, theoretical studies by Straka et al. also predicted the existence of a cage-imposed U–U bond inside a C80 cage. Their study predicted a stable EMF, U2@I7-C80, which has double ferromagnetic U–U bonds with a bond distance of 3.9 Å, although in the title of the article they call it “an unwilling U–U bonding.” Despite all the arguments from theoretical studies, critical experimental data for a dimetallic actinide EMF have never been obtained, leaving the possibility of forming actinide–actinide bonds inside fullerenes as an open question up to now. Herein, following the successful synthesis and characterization of Th@C82 and U@C82, we present the synthesis, isolation, and full characterization of a dimetallic actinide EMF, U2@I7-C80. Critical crystallographic data were obtained in this study. These results reveal the crystal structure of U2@I7-C80 and show that, though the U positions are disordered inside the fullerene cage, the U–U bond distance is within the range of 3.46–3.79 Å. The systematic characterization of U2@I7-C80 which agreed with theoretical studies, shows evidence of a weak U–U bonding interaction inside the C80 fullerene cage.

2. RESULTS AND DISCUSSION

U2@I7-C80 was synthesized by a modified arc discharge method. Graphite rods, packed with U3O8 and graphite powder, were vaporized in the arcing chamber under a He atmosphere. The resulting soot was then extracted with chlorobenzene. The mass spectrum of an as-extracted solution of the fullerene mixture (Figure S1) shows that a large family of U-based metallofullerenes with multiple cages was generated during the arcing process, along with empty fullerenes C80 (n = 42–66). The mass spectrum shows that the majority of the fullerenes generated during this process are mono-EMF (U@C80) and empty fullerenes. U2@C80 was generated as a minor product during this process, along with the other dimetallic U-based fullerenes U2@C78 and U2@C82. However, the previously reported and theoretically studied U2@C80 was not detected using these conditions. A multistage HPLC procedure was employed to isolate and purify U2@C80 (Figure S2). After a three-stage HPLC separation protocol, the purified U2@C80 was obtained. The purity of the isolated U2@C80 was confirmed as a single peak by HPLC (Figure 1b). The positive-ion mode MALDI-TOF mass spectrum of purified U2@C80 (Figure 1a) shows a peak at m/z = 1436.100, and the experimental isotopic distribution agrees well with the theoretical prediction.

The structure of U2@C80 was characterized by means of single crystal X-ray diffraction (XRD). The molecular structure was resolved and refined in the C2/m space group. Figure 2 shows the X-ray structure of U2@I7-C80 together with a cocrystallized NiII-octaethyl porphyrin [NiII(OEP)] moiety. The typical host–guest interaction can be observed between the U2@I7-C80 and the [NiII(OEP)] with 20% thermal ellipsoids. Only the major U sites (U1 and U2 with a common occupancy of 0.195(2)) are shown. For clarity, the solvent molecules and minor metal sites are omitted. (b) View showing the interaction of the major U2 cluster with the closest cage portion.
U4/U6/U8/U10, each with the distribution over a belt-region near or opposite to the Ni6(OEP) moiety (Figure 3). Among the multiple U sites, the U sites with similar occupancies were paired into sets during refinement, giving rise to five sets of U2 with occupancies ranging from 0.195(2) to 0.0427(19). (See Figure 3 for disordered positions of U atoms). Only the U1 cluster (i.e., U1 and U2) with major occupancy is shown in Figure 2. Nevertheless, because of the fact that crystallographic mirror plane mismatches the molecular symmetry and some of the U sites (i.e., U1−6, U8) are residing off the mirror plane, these U sites cannot be solely determined due to the presence of C2/m positional disorder (see Table S1). If only the major U sites (i.e., U1 and U2) are considered, then there are four X-ray models of the I6(7)-C80 cage (i.e., S1, S2, S3, and S5, see Figure S3). In these models, metal positions are not very different from each other. In general, U1 and U2 are residing under hexagons, being close to or slightly off a C2 axis of the I6-C80 cage. The U−U distance is found to be 3.723(6) Å in models S1 and S5, while the U−U distance is 3.751(6) Å for S2 and S3 models. Similarly, the U−U distance obtained from other U sites ranges from 3.793(7) to 3.46(2) Å (for details see Table S1). All these U−U distances are shorter than that reported for the U−U bond distance in the lowest energy minimum isomer U2@I6(7)-C80 calculated at the DFT/BP86/SVP/SDD computational level (3.894 Å).24 As summarized in Table 1, compared with the metal−metal bond distances reported for Ce6@I6−C80 and La6@I6−C80 (Ce−Ce: 3.767−3.833 Å and La−La: 3.840 Å), the U1−U2 distance is also slightly shorter.28 Considering their similar ionic radii (1.01 Å for Ce6, 1.025 Å for U6 and 1.032 Å for La6), the shorter U−U distance might indicate a stronger metal−metal bonding interaction. Moreover, as shown in Table 1, these U−U distances are even comparable to the recently reported La−La bond distance in La6@I6−C80(C6H6).

Table 1. Metal−Metal Distance [Å] of Dimetallic Endohedral Fullerenes with C80 Cage

<table>
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<tr>
<th>Compound</th>
<th>M−M distance [Å]</th>
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<tr>
<td>U2@I6(7)-C80</td>
<td>3.793−3.460</td>
<td>this work</td>
</tr>
<tr>
<td>Ce6@I6-C80</td>
<td>3.833−3.767</td>
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</tr>
<tr>
<td>La6@I6-C80</td>
<td>3.840</td>
<td>29</td>
</tr>
<tr>
<td>La6@I6-C80(C6H6)</td>
<td>3.779−3.676</td>
<td>19</td>
</tr>
<tr>
<td>Dy6@I6-C80(CH2Ph)</td>
<td>3.893/3.896</td>
<td>17</td>
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</table>

Figure 3. View showing the molecule in the same orientation as in Figure 2a and with all U positions (orange).

Figure 4. UV−vis−NIR absorption spectrum of U2@I6(7)-C80 in CS2.

and slightly shorter than the Dy−Dy distance in Dy6@I6−C80(CH2Ph).17,19 In the above mentioned cases, relatively strong single electron metal−metal bonds were recorded. Thus, the crystallographic data for the U−U distance, though somewhat uncertain because of the disordered U positions, show evidence that the two U atoms are weakly bonded inside the fullerene cage. Nevertheless, this U−U distance is evidently longer than twice the empirical single bond radius of uranium (2 × 1.7 Å = 3.4 Å),30 suggesting that the U−U bond order is lower than one, which agrees with the previous theoretical prediction of an elongated weak bond. The closest U−C contacts are in a range of 2.377−2.578 Å (see Figure 3 and Table S1). Such U−C contacts agree well with the previously reported calculation results and are comparable to those found in the smallest EMF of U2@C80, where the U−C closest contacts are within 2.44−2.51 Å.31 In comparison, in models Sii, Siii, and Siv the closest U−C contacts are distributed over a wider range of 2.24−2.82, 2.24−2.69, and 2.264−2.82 Å, respectively (see Figure 3 and Tables S2−S5). Nevertheless, it is noteworthy that even the longest U−C distance (2.82 Å) is still very close to that reported for the U−Cmethanide bond (i.e., 2.779 Å),32 indicating strong bonding-interactions between the U2 cluster and the I6(7)-C80 cage.

Figure 5. Absorbance of the U2@I6(7)-C80 in CS2 solution.

with the metal−metal bond distances reported for Ce6@I6−C80 and La6@I6−C80 (Ce−Ce: 3.767−3.833 Å and La−La: 3.840 Å), the U1−U2 distance is also slightly shorter.28 Considering their similar ionic radii (1.01 Å for Ce6, 1.025 Å for U6 and 1.032 Å for La6), the shorter U−U distance might indicate a stronger metal−metal bonding interaction. Moreover, as shown in Table 1, these U−U distances are even comparable to the recently reported La−La bond distance in La6@I6−C80(C6H6) absorption peaks at 556 and 680 nm. Though featureless absorption spectra are typical for endohedral fullerenes with an I6−C80 cage,26 the absorption spectrum notably shows even less features than the representative I6−C80 cage based endohedral fullerenes, such as Sc6N@I6−C80 and La6@I6−C80. The absorption onset is ca. 1100 nm, which corresponds to a band gap of 1.13 eV.

The photoluminescence (PL) spectrum of the U2@I6(7)-C80 is shown in Figure S5. It shows broad emissions lines at 420, 450, and 476 nm. This emission pattern is similar to those typically observed for uranyl compounds, but the emission peaks are shifted substantially.33 Very recently, we have reported that Th@C60(8)-C80 displays a strong PL emission in both solution and solid states, an unprecedented feature for fullerene compounds.25 The observation of PL emission for U2@I6(7)-C80 suggests that compared to lanthanide EMFs, the transitions based on the endohedral actinide ions seem to be exceptionally strong and the expected self-absorption effect from the fullerene cage observed for most of the fullerenes studied so far is unable to quench the U or Th based PL emission. It
shows that the charge transfer based photoluminescence is much brighter for actinide EMFs. Thus, the interaction between the actinide ions and the fullerene cages is likely to be substantially different from those for the lanthanide EMFs.

The features of the low-energy Raman spectrum of U2@[Ih(7)-C80] (Figure 6) show similarities to those of La2@[Ih(7)-C80] and Ce2@[Ih(7)-C80] as well as to those of other cluster-fullerenes with Ih-C80 cages.8

One major peak is observed at 122 cm⁻¹. This metal-to-cage vibration has similar but slightly lower wavenumber as compared to that of the U@[Ih(7)-C80]. 0.84 eV, is still very close to those of La2@[Ih(7)-C80] and Ce2@[Ih(7)-C80].

In the 17–18 keV X-ray region, U-2p½ core electrons can be excited into unoccupied valence orbitals with a U-6d-7s admixture. The XAS spectra for U2@[Ih(7)-C80] and U@C2s(9)-C82, along with those for the reference compounds, uranium sulfate (U³⁺), uranium oxalate (U⁴⁺), and uranium nitrate (U⁵⁺) at U L₃-edge are shown in Figure 8. The white line peak of U2@[Ih(7)-C80] shows an energy very close to that of U³⁺, as well as to that of the U@C2s(9)-C82, which contains a U³⁺ ion inside the fullerene cage.26 This suggests that U2@[Ih(7)-C80] has a formal charge state described by (U³⁺)₂@[C80]⁶⁻, which is in perfect agreement with our structural assignment and further confirms our theoretical predictions.24

To obtain a better understanding of the experimental results we have made use of computational methods based on density functional theory (see Experimental Details). We have first studied the different possible positions of the two U atoms inside the Ih(7)-C80 cage according to the occupancies found by the XRD analysis, in particular, those derived from the U(1) and U(2) positions, S₁–Sₕ models (see Figure 9). The optimized structures are essentially the same as the experimental ones, showing only small deviations of the positions of the U atoms. We have computed the highest spin state of the molecule (septet), considering within the ionic model that (i) electrons in the carbon cage are paired and (ii) there are two U³⁺ ions combined ferromagnetically. The septet was shown to be the lowest energy spin state for U2@[Ih(7)-C80] and for other diuranium EMFs.24 The relative energies between these four structures are very similar, within only 1.6 kcal mol⁻¹ (see Figure 9 and Table S6), in good agreement with the disorder shown by the U atoms in the crystallographic structure.

The structures with the lowest energies are S₁₀ and S₁₁, which are symmetry-equivalent, along with S₅. The computed U–U distances for S₁₀ and S₁₁, 3.74 Å, and for S₅, 3.79 Å (see Table S6), are somewhat longer than the experimental one (3.72 Å) but smaller than those computed previously for the same system.25 Interestingly, the S₁₀ structure, with the U₁ unit slightly displaced from the C₆ symmetry axis of Ih(7)-C80, shows a more compressed U–U distance (3.72 Å), which matches the experimental one. The U–C distances are also rather well-reproduced. For the four structures, the computed spin densities on the U ions are around 3.2 electrons each, in
Table 2. Redox Potentials (V vs Fc/Fc⁺) of the U₂@C₈₀ and M₂@I₆-C₈₀ Dimetallofullerenes (M = La and Ce)ᵃᵇ

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<th>compound</th>
<th>E²⁺/⁺</th>
<th>E⁺/⁰</th>
<th>E⁰/⁻</th>
<th>E⁻/⁻</th>
<th>E²⁻/⁻</th>
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<th>E₄⁻/⁻</th>
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<td>U₂@C₈₀⁻²⁻⁻⁻⁻</td>
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<td>+0.40</td>
<td>−0.44</td>
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<td>[0.40]</td>
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<td>[−1.47]</td>
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<td>−1.71</td>
<td>−2.13</td>
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<td>0.87</td>
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<tr>
<td>La₂@C₈₀⁻¹⁻⁻⁻⁻</td>
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“Computed oxidation and reduction potentials and electrochemical gaps (in V) along with the experimental values obtained by CV.ᵇ The computed values are anodically shifted by 150 mV.ᵇ Peak potential (irreversible redox process).ᵇ Half-wave potential (reversible redox process).ᵇ Computed values in square brackets.

Figure 8. U L₁-edge XAS spectra of of U₂@I₆(7)-C₈₀ compared to those of U@C₈₆(9)-C₈₂ (blue), NaU²⁺-sulfate (black), U⁴⁺-oxo-hydroxo-formate (red) and uranyl(U⁶⁺)-nitrate (green).

Figure 9. Representations of the optimized structures (S₁–S₆) of U₂@I₆(7)-C₈₀ and their relative energies in kcal mol⁻¹. Second row, a view from the top, shows the position of the U with respect to the nearest hexagon of the cage. Structures S₅ and S₆ would be symmetry-equivalent.

Figure 10. Representation of the occupied and virtual molecular alpha orbitals and their energies for oxidized, neutral and reduced systems U₂@I₆(7)-C₈₀ (q = +1, 0, −1).

descriptors to analyze bonds via 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 criterion for the atoms to be bonded. More recently, it has been shown that the delocalization index δ(A, B) provides a quantitative measure of the degree of electron sharing between two atoms. For the U–U interaction, we located a bond critical point in the middle of the two U ions and found a δ(U, U) equal to 0.80, which is larger than the corresponding value (0.37) reported for the La–La bond in La₂@C₈₀. In this dimetallofullerene, the La–La bond of 3.764 Å is mainly formed via the overlap between s and d orbitals. In addition, we obtained a Mayer bond order for the U–U bond interaction of 0.34 (Table 3). All these descriptors clearly suggest the presence of a U–U bonding interaction. In order to confirm the existence of this interaction, we have also performed CASSCF calculations for U₂@I₆(7)-C₈₀ at the computed DFT geometry (see Computational Methods). The ground state was found to be a singlet with an effective bond order of 0.1. Because CASSCF calculations do not include dynamic electron correlation, electrons tend to be overlocalized; thus, the presence of a still perceptible interaction is clearly indicative of U–U coupling. In contrast, the same type of calculations performed on the U₂⁺⁺⁺ unit at the same metal–metal separation
of the U–U distance and, therefore, a weakening of the U–U bond is observed upon oxidation, even though some of the bond indicators do not appreciably change when compared to the neutral state (see Table 3 and Figure S6). Because the involved uranium orbitals in the redox processes have a low bonding nature (Figure 10), the changes in the U–U bond distances can be also attributed to a change in the formal oxidation state from +3 to +2.5 upon reduction and to +3.5 upon oxidation, which in turn decreases (or increases) the metal–metal repulsion. Thus, the electron accumulation (or depletion) in the intermetal region, and decrease (or increase) of the metal–metal repulsion are interconnected. Foroutan-Nejad et al. already pointed out that the formation of the weak U–U bond inside a fullerene is a consequence of the confinement and not due to the strong orbital overlaps among f orbitals.24

Finally, we assigned the peaks observed in the low-energy Raman spectrum of U2@Ih(7)-C80 focusing mainly on the region between 100 and 250 cm−1. Our computations are able to reproduce the most important features of the experimental spectrum in that range. Structures S1 and Siii show a low-frequency peak at around 120 cm−1, corresponding to the longitudinal metal-to-cage mode of the U2 unit inside the Ih(7)-C80 cage coupled with the symmetric U–U stretching (see Figure S7). No peak appears for the metal-to-cage vibration based on the longitudinal motion of the U2 unit as if it were a rigid unit (i.e., with almost no change in the U–U distance; see the Supporting Information). The peaks at 207 and 211 cm−1 can be assigned to breathing modes of the cage with no involvement of the U ions. All these peaks appear to be shifted by around 10–20 cm−1 to lower frequencies when compared to those obtained experimentally (see Figure 6).

3. CONCLUSIONS

In this work, we report the synthesis and the isolation of a dimetallic actinide EMF, U2@C80. U2@C80 has been fully characterized by mass spectrometry, single crystal X-ray crystallography, UV–vis–NIR, cyclic voltammetry, Raman spectroscopy, PL spectroscopy and XAS. Crystallographic analysis unambiguously assigned the molecular structure to U2@Ih(7)-C80 and revealed that the U–U bond distance ranges between 3.46 and 3.79 Å, which is shorter than the 3.9 Å previously predicted for an elongated weak U–U bond inside the C80 cage. The XAS results further confirmed that the formal charge state of U inside the fullerene cage is +3, which agrees with previous computational studies and with our crystallographic assignment of an (Ih-C80)− cage. Theoretical studies suggest that the different structures derived from the U occupations obtained from the X-ray structure show low relative energies, in good agreement with the disorder of U atoms observed crystallographically. Furthermore, the theoretical studies confirm the presence of a U–U bonding interaction and find that the singular U–U bond in U2@Ih(7)-C80 was slightly strengthened upon reduction and weakened upon oxidation, essentially due to the decrease (increase) in the U–U repulsion when reducing (oxidizing) the system. The comprehensive characterization of U2@Ih(7)-C80 and the overall agreement between the experimental data and theoretical investigations provide experimental evidence and deeper understanding of actinide–actinide interactions inside a fullerene cage.

Table 3. Spin Multiplicities of the Computed States, U–U Distances, Spin Densities and Selected Bonding Parameters for U2@Ih(7)-C80 (q = +1, 0, and −1)

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<tr>
<th>State</th>
<th>q = +1</th>
<th>q = 0</th>
<th>q = −1</th>
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<td>2S+1</td>
<td>S</td>
<td>6</td>
<td>7</td>
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<td>d1/u</td>
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<td>spin</td>
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<td>ρ(bcp)</td>
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EXPERIMENTAL DETAILS

Synthesis and Isolation of U2@I2(7)-C80. The carbon soot containing uranium EMFs were synthesized by the direct-current arc discharge method. The graphite rods, packed with U3O8 powders and graphite powders (1:24 molar ratio), were vaporized in the arcing chamber under 200 Torr He atmosphere. The resulting soot was refluxed in chlorobenzene under an argon atmosphere for 12 h. The separation and purification of U2@I2(7)-C80 was achieved by a multistage HPLC procedure. 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.

Spectroscopic and Electrochemical Studies. The positive-ion mode matrix-assisted laser desorption/ionization time-of-flight (Bruker, German) was employed for the mass characterization. The UV−vis−NIR spectrum of the purified U2@I2(7)-C80 was measured in CS2 solution with a Cary 5000 UV−vis−NIR spectrophotometer (Agilent, USA). The Raman spectrum was obtained using a Horiba Lab RAM HR Evolution Raman spectrometer using a laser at 633 nm. Steady-state photoluminescence (PL) spectra were recorded using an FL5980 (Edinburgh Instrument, UK) with excitation at 406 nm at room temperature.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) results were obtained in o-dichlorobenzene using a CHI-660E instrument. A conventional three-electrode cell consisting of a platinum counter-electrode, a glassy carbon working electrode, and a silver reference electrode was used for both measurements. (n-Bu)4NPF6 (0.05 M) was used as supporting electrolyte. The CV and DPV were measured at the scan rate of 100 mV/s and 20 mV/s, respectively.

X-ray absorption spectroscopy (XAS) experiments were performed at the Beijing Synchrotron Radiation Facility (BSRF, beamline 1W1B).

X-ray Crystallographic Study. The black block crystals of U2@I2C80([NiII(OEP)]-[NiII(OEP)]) were obtained by slow diffusion of a benzene solution of U2@I2C80 into a CHCl3 solution of [NiII(OEP)]. X-ray data were collected at 173 K using a diffractometer (APEX II; Bruker Analytik GmbH) equipped with a CCD detector. The multiscan technique was used for absorption correction. The structure was solved using direct methods (SIR2004) and refined on F2 using full-matrix least-squares using SHELXL2014-within the WinGX package.

Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters.

Crystal data for U2@I2C80([NiII(OEP)]-CHCl3; M; = 2223.27, 0.22 mm × 0.15 mm × 0.11 mm, monochlinc, C2/m (No. 12), a = 25.1208(9) Å, b = 15.5044(6) Å, c = 19.5147(6) Å, α = 90°, β = 95.4922(2)°, γ = 90°, V = 7865.8 (5) Å3, Z = 4, μ(Cu Kα) = 1.952 g cm−3, μ(Cu Kα) = 14.136 mm−1, θ = 3.354°-74.641°, T = 173(2) K, R1 = 0.1253, wR2 = 0.3706 for all data; R1 = 0.1136, wR2 = 0.3419 for 8027 reflections (I > 2σ(I)) with 1032 parameters. Goodness-of-fit indicator 1.576. Maximum residual electron density 1.653 e Å−3.

Computational Methods. Optimisations without symmetry restrictions of U2@I2(7)-C80 S-Si2Si isomers were carried out with the ADF 2017 package using density functional theory (DFT). The exchange-correlation functionals of Becke and Perdew (BP86) were used. Slater triple-ζ polarization (TZP) basis sets were used to describe the valence electrons of U and C. Frozen cores were described by means of single Slater functions, consisting of the 1s shell for C and the 1s to 5d shells for U. Scalar relativistic corrections were included by means of the ZORA formalism. Dispersion corrections by Grimme were also included. Electrochemistry calculations were performed at the same level of theory BP86/TZP, with dichlorobenzene as solvent (COSMO). Raman spectra were computed using the Gaussian 09 package, since ADF 2017 does not allow Raman intensity calculations for spin unrestricted systems. These calculations were also performed at the DFT level using the BP86 exchange-correlation functional. A double-ζ 6-31G(d,p) basis set was used for carbon atoms and Stuttgart–Dresden basis sets with effective core potential (SDD) for uranium atoms. Optimisation followed by frequency and Raman intensity calculation were computed for the S-Si2Si isomers.

The plots of the electron localization function (ELF) and delocalization indexes of the neutral, reduced and oxidized species of U2@I2(7)-C80 S8 were obtained using the Multiwfn program. Wave functions used for the analysis were obtained by Gaussian 09 single point calculations of the optimized structures obtained with ADF 2017.

CASSCF calculations were performed with Molcas 8. The active space contains 6 electrons distributed in all possible ways over 6 uranium orbitals. Test calculations with larger active spaces do not alter the results; tiny bonding contributions were observed from the U-7s orbitals. The one-electron basis set for uranium has been taken from the study of the neutral U-dimer by Gagliardi and Roos and contains (1s, 10p, 10d, 6f, 3g, 1h) ANO-RCC functions. The same basis set type was used for carbon with {3s, 2p, 1d} functions for each atom of the C80 cage. Scalar relativistic effects were included through the Douglas-Kroll-Hess Hamiltonian.

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-2-20.51

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b10865.

HPLC profiles for the separation of U2@I2C80 and computational details (PDF)

Additional crystal data for U2@I2C80[NiII(OEP)].CHCl3 (CIF)

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Notes

The authors declare no competing financial interest.

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