Isolation and Characterization of a U≡C Triple Bond in Isolable Fullerene Compounds

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Abstract

Despite decades of efforts, the actinide-carbon triple bond has remained an elusive target, defying isolation in any compound. Herein, we report the successful stabilization of uranium-carbon triple bonds in carbide-bridged bimetallic [U≡C–Ce] units encapsulated inside fullerene cages of C_{72} and C_{78}. The molecular structures of UCe@C_{2n} and the nature of the U≡C triple bond were characterized through X-ray crystallography and various spectroscopic analyses, revealing very short uranium-carbon bonds of 1.921(6) and 1.930(6) Å, with the metals existing in their highest oxidation states of +6 and +4 for uranium and cerium, respectively. Quantum-chemical studies further demonstrate that the C_{2n} cages are crucial for stabilizing the [U^{VI}≡C–Ce^{IV}] units through covalent and coordinative interactions. This work offers a new fundamental understanding of the elusive uranium-carbon triple bond and informs the design of complexes with similar bonding motifs, opening up new possibilities for creating distinctive molecular compounds and materials.

Introduction

The actinides are technologically important elements, where the understanding of their fundamental chemical properties and roles in the nuclear fuel cycle is critical for advancing nuclear technology\(^1\), which is important for building a diverse portfolio of carbon-free energy sources. Yet, despite this, the chemistry of the actinide series remains underdeveloped in comparison to transition metals and main group elements. Major in-roads into the understanding of the electronic properties and chemistry of the transition metals have been accomplished over the decades through the synthesis of molecular compounds possessing metal-ligand multiple bonds\(^2\), where critical understanding of d-orbital participation in bonding motifs and reactivity has been elucidated. While extensive study of the uranyl cation, [O≡U≡O]\(^{2+}\), has shown the 5f-orbitals to play a critical role in the formation of the formal uranium-oxygen triple bonds\(^3\)-\(^5\), 5f-orbital participation in other U≡E and U≡E bonding remains less clear and an intensive area of study\(^6\)-\(^9\). Indeed, efforts into the synthesis of uranium and actinide metal-ligand multiple bonds have intensified over the past two decades, with significant advances achieved in the synthesis of a variety of carbeno\(^10\)-\(^13\), imido\(^14\)-\(^17\), nitrido\(^18\),\(^19\), heavier-pnictogenido\(^20\)-\(^22\), oxo\(^23\)-\(^26\), and chalcogenido complexes\(^27\)-\(^29\).

Notable is the progress that has been made in developing methods for the synthesis of new actinide-ligand multiple bonds. Yet, a significant gap exists in the domain of molecular actinide complexes possessing so-called “true” alkylidene and alkylidyne bonds that are not stabilized through possible heteroatom resonance contributions\(^30\). Pioneering matrix-isolation experiments identified transient uranium methylidyne molecules X\(_3\)U≡CH (X = F, Cl, Br)\(^31\) and uranium carbides such as U≡C and C≡U≡C\(^32\). However, these molecules have only been observed through spectroscopic methods at low temperatures in noble-gas matrices and studied theoretically. A recent report shows that the use of a novel alkylidene transfer reagent leads to the isolation of the actinide allenylidenes possessing small but significant An=C=C=CPH\(_2\) (An = Th, U) resonance contributions\(^31\), which is highly promising as it shows that actinide-carbon multiple
bonds may potentially be synthetically accessible under less specialized laboratory conditions. The difficulty in isolating actinide-carbon multiple bonds is thought to arise from high bond polarization and orbital energy mismatch that leads to poor An–C π-overlap.\textsuperscript{34}

In an effort to counter the high reactivity of actinide fragments possessing unusual bonding motifs, we have successfully employed the capture and stabilization of such moieties within fullerene cages.\textsuperscript{35-42} The hollow cavity encloses the fragments preventing further reactivity, while the cage carbon atoms provide additional coordinative support to the metal center. In 2018, we reported the unprecedented isolation of the uranium endohedral metallofullerene \textit{U@C@C}$_{80}$ that contains a remarkable U=C=U unit.\textsuperscript{35} Characterization of its molecular structure through X-ray crystallography revealed short U=C bonds (2.03 Å) with an unusual U=C=U bend angle of 142.8(3)°, where poor π-overlap leads to significant charge accumulation on the carbide atom with a partial donation of the density into a U 5f/6d-hybrid orbital. Utilizing fullerene capture, we recently reported the synthesis and characterization of USc$_2$C@C$_{80}$ and USc$_2$NC@C$_{80}$, where electronic analysis indicates C=U=C and C=U=N bonding motifs possessing triple bond resonance contributions.\textsuperscript{41}

In this report, we describe the synthesis and characterization of endohedral metallofullerenes (EMFs) \textit{UCCe@C$_{2n}$} ($2n = 72$ and $78$) containing the first structurally characterized uranium-carbon triple bonds (U≡C) in a stable and isolable form. The mixed, bimetallic [U=C–Ce] carbide cluster contains uranium and cerium in their highest oxidation states of +6 and +4, respectively. Through X-ray crystallographic analyses, the structural characterization unveils the shortest uranium-carbon bonds ever recorded to date, measuring 1.921(6) and 1.930(6) Å, encapsulated within the C$_{72}$ and C$_{78}$ cages, respectively. The nature of the U≡C triple bond is investigated by ultraviolet-visible, infrared, and X-ray absorption spectroscopy as well as by quantum-theoretical analyses.

**Synthesis and molecular structures of \textit{UCCe@C$_{2n}$}**

\textit{UCCe@C$_{72}$} and \textit{UCCe@C$_{78}$} were synthesized by a modified Krätschmer-Huffman direct-current arc-discharge method. A drilled graphite rod, packed with a mixture of U$_3$O$_8$, graphite powder, and CeO$_2$ (in molar ratios of U : C : Ce = 1 : 24 : 1) was installed in an arcing reactor as the anode under a 200 Torr He atmosphere, and then arced with a graphite cathode at 100 A direct current, yielding the products in the carbon soot. The two targeted U-based metallofullerenes were extracted from the carbon soot by CS$_2$ solvent for 24 hours and then isolated by multi-step high-performance liquid chromatography (HPLC). The high purity of the two metallofullerenes was confirmed by chromatograms and mass spectra (Extended Data Fig. 1). Importantly, the experimental isotopic distributions of the two metallofullerenes all agree well with the theoretical simulation, providing strong confirmation of their elemental composition.

The molecular structures of the two EMFs (Fig. 1) were unambiguously determined as \textit{UCCe@D$_{24}(10611)$-C$_{72}$} and \textit{UCCe@D$_{36}(5)$-C$_{78}$} by co-crystallization with Ni$^{II}$(OEP) (OEP = 2, 3, 7, 8, 12, 13, 17, 18-octa-ethyl-porphyrin dianion, a crystallization promoter to improve the crystallization of the EMFs and hinder the

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rotation of the fullerene cages) via solid π-π interactions. $D_2$ and $D_{3h}$ represent the symmetry of the isolated fullerene cages, and the numbers in parentheses are their isomeric codes$^{44}$. Both co-crystals crystallized in the monoclinic space group $P2_1/c$ with one EMF&Ni$^{II}$(OEP) adduct in the asymmetric unit. Relative to the Ni$^{II}$(OEP) molecule, the EMFs comprise two symmetrical orientations with similar occupancies, suggesting that two EMF&Ni$^{II}$(OEP) conformations coexist in the co-crystals with very small energy differences.

Crystalllographic disorder within EMF cages and clusters is commonplace, but in the cases of UCCe@C$_{72}$ and UCCe@C$_{78}$, the central carbide atom, C$_{co}$, is fully ordered and provides a clear anchoring point. In UCCe@C$_{72}$, the cluster exhibits a nearly fully ordered arrangement of uranium and cerium atoms, for which the major metal sites refine well to 86% occupancy with very good refinement parameters of the crystallographic model. Conversely, while disorder within the cluster is more apparent in UCCe@C$_{78}$, it still exhibits a significant component with 58% site occupancy for the uranium and cerium atoms.

In UCCe@C$_{72}$, the U and Ce atoms each possess $\eta^8$-coordination to pentalene fragments of the cage, forming metal-carbon bond distances of 2.4-2.6 Å, with cerium exhibiting slightly longer Ce–C bonds within this range. On the other hand, the metal atoms in UCCe@C$_{78}$ are each $\eta^6$-coordinated to the C$_6$-rings of the C$_{78}$ cage. The U$_{co}$Ce clusters are nearly linear with measured U–Ce–C angles of 178.4(3)$^\circ$ and 174.5(3)$^\circ$ situated on the long two-fold axis of $D_2$-C$_{72}$, and on the three-fold axis of $D_{3h}$-C$_{78}$, respectively. Furthermore, the interatomic distances and angles, including the bond lengths of C$_{Cage}$–U, Ce–C$_{Cage}$, C$_{co}$–Ce, and the U–C$_{co}$–Ce angles in the theoretically optimized spin-singlet UCCe@C$_{2n}$ molecules (vide infra), all fit well with the experimental values (Extended Data Table 1). For example, the C$_{co}$–Ce distances in C$_{72}$ and C$_{78}$ are measured as 2.183(6) and 2.143(6) Å, in good agreement with the calculated values (2.20 and 2.17 Å) but shorter than the sum of the single bond covalent radii of Ce and C (2.38 Å)$^{45}$.

The most salient feature of the two EMFs is the very short U–C$_{co}$ bond lengths, measured as 1.921(6) and 1.930(6) Å inside C$_{72}$ and C$_{78}$, respectively, which is well below the sum of the covalent U=C double bond radii (2.01 Å)$^{45}$. This is far shorter than the U=C distance in the methanide coordinated U(VI) oxo carbene complex ([$\{O=U=CR_2\}Cl_2$] (2.184(3) Å)$^{11}$, which exhibits double bond character enhanced through the inverse trans influence contributions with the oxo atom$^{11}$. As would be expected with a higher U=C bond order, the U–C$_{co}$ bonds in UCCe@C$_{72}$ and UCCe@C$_{78}$ are significantly shorter than the U=C=U bonds in U$_2$C@C$_{80}$ (2.028(5) and 2.033(5) Å)$^{35}$, and also shorter than the U=C bond lengths of 2.060(1) to 2.163(4) Å in USc$_2$C$_2$@C$_{80}$ that results from the multiple and pronounced multicentric bonding character of its cluster$^{41}$. Furthermore, the U–C$_{co}$ bond distances of the U$_{co}$Ce moieties are comparable to the computed distances of X$_3$U≡CH molecules (1.90-1.94 Å; $X = H$ or halogen)$^{31}$ and only slightly longer than those computed for the matrix isolated species U≡C and C≡U≡C (1.86 Å and 1.83 Å)$^{32}$. On top of this, the experimentally determined distances agree well with the U–C$_{co}$ bond lengths calculated for UCCe@C$_{72}$ and UCCe@C$_{78}$ (Extended Data Table 1). Altogether, these results provide strong and compelling evidence for the presence of a genuine U≡C bond, the first of its kind in an isolable molecular system.

**Spectroscopic properties of UCCe@C$_{2n}$**
To support the unique structural parameters of UCe@C_{2n} and investigate the bonding nature of the encapsulated UCe units, spectroscopic studies, including Fourier Transform InfraRed (FTIR) absorption spectroscopy, Visible-Near-InfraRed (Vis-NIR) absorption spectroscopy, and X-ray Absorption Spectroscopy (XAS), were performed. As shown in Fig. 2A-B, the experimental FTIR absorption spectra of UCe@C_{2n} are in good agreement with the corresponding calculated ones. These spectra exhibit two bands of fullerene vibrations, with one ranging from 1600 to 1000 cm\(^{-1}\) and the other below 900 cm\(^{-1}\), separated by a gap of approximately 100 cm\(^{-1}\) in between, which is consistent with previous studies\(^{46}\). In addition, the endohedral triatomic U=O=O-C unit contributes 9 modes, 8 of which are very weak due to the heavy metal atoms and are located between approximately 50 and 200 cm\(^{-1}\). These modes include 3 translational rocking modes, 2 torsional wagging modes, 2 bending modes, and one symmetrical stretching mode, all with low IR intensity. The more intense ‘asymmetric stretching’ of C\(_n\) between the two heavy metal atoms is near 800 cm\(^{-1}\), coupling with near-degenerate fullerene vibration modes and resulting in split bands. Calculations reveal that for UCe@C_{72}, there is one stronger (770 cm\(^{-1}\)) and one weaker (780 cm\(^{-1}\)) feature with asymmetric C\(_n\) stretching admixture, while for UCe@C_{78}, there is one stronger feature (781 cm\(^{-1}\)) and one weak peak nearby (846 cm\(^{-1}\)).

Vis-NIR absorption spectra of EMFs are known to be dominated by the \(\pi \rightarrow \pi^*\) transitions of the carbon cages and are sensitive to the cage isomerism, degree of charge transfer, and covalent-overlap interactions between the fullerene cage and the endo-units\(^{47}\). As shown in Fig. 2C, UCe@D\(_2\)-C\(_{72}\) presents an overall similar absorption profile as Ce\(_2\)-D\(_2\)-C\(_{72}\)\(^{48}\). The absorption spectrum of UCe@D\(_{3h}\)-C\(_{78}\) features a strong peak at 583 nm and two broad shoulders on both sides at 458 and 738 nm, which bears an overall resemblance to that of U\(_2\)C\(_2\)-D\(_{3h}\)-C\(_{78}\) (Fig. 2D)\(^{36}\). The Ce\(_2\) and U\(_2\)C\(_2\) endo-units populate the lowest three adjacent virtual orbitals of D\(_2\)(10611)-C\(_{72}\)\(^{46}\) and D\(_{3h}\)(5)-C\(_{78}\)\(^{36}\). Accordingly, it appears reasonable to assume that the electronic configurations of UCe@C\(_{72}\) and UCe@C\(_{78}\) are formally [UCe][Ce\(^{6+}\)][C\(_{2n}\)]\(^{6-}\), with the metal atoms in their highest formal oxidation states, U\(^{6+}\) and Ce\(^{4+}\), brought together by a bridging C atom using four bonding electron pairs (formally C\(^{4-}\)).

To further corroborate the oxidation state assignments of the encapsulated metal elements for a full representation of the electronic structure and chemical bonding inside the fullerene cages, the Ce-2p\(_{3/2}\) and U-2p\(_{3/2}\) X-ray absorption spectra of UCe@C\(_{78}\) and several reference compounds were recorded in Fig. 2E-F. A dominant shift to higher edge energies occurs from ligation by soft organic \(\pi\)-systems to oxo and chloro anions with more polar bonds. The \(\pi\)-pair donation significantly reduces the effective positive charge on the metal cations. Within each group of ligand environments, the edge energy increases by \(\sim 1\) eV per formal oxidation number, as indicated by the black arrows. Hence, the observed spectra suggest a formal charge assignment of U\(^{6+}\) and Ce\(^{4+}\) for UCe@C\(_{78}\), which is in line with the common electronegativities of the elements (U/Ce \(\approx 1.2\))\(^{49}\) as well as with the calculated effective averaged atomic charge distribution of UCe@C\(_{2n}\) (Extended Data Table 2).

**Computational studies of molecular structure and bonding in UCe@C\(_{2n}\)**

To elucidate the chemical bonding and electronic structure of UCe@C\(_{2n}\) and to explore the role of the fullerene cages for EMF formation, quantum chemical studies were conducted for UCe@C\(_{2n}\) and for model complexes LUCeC\(_{3}\) (L = C\(_{3}\)H\(_7\) and H\(_3\)). Theoretical calculations using density functional theory (DFT) were used to derive...
the canonical molecular orbitals (MOs), electron density distributions, effective charges, interaction energies, localized bonding, and bond multiplicities.

Insight into the bonding of endohedral bimetallic carbide UC\(_2\)Ce clusters is provided by Natural Localized Molecular Orbitals (NLMOs). The four electron pairs on the carbon of the UC\(_3\)Ce unit form four optimally localized MOs, two \(\sigma\)-pairs and two \(\pi\) pairs (with UC\(_3\)Ce along the \(z\)-axis). The atomic orbital (AO) contributions of the NLMOs for UC\(_n\)Ce\(_{2n}\) (\(2n = 72\) and 78) are displayed in Fig. 3 and Extended Data Table 3. For UC\(_n\)Ce\(_{2n}\) (Fig. 3A), one \(\sigma\) pair forms a 2-center U–C\(_\text{c}\) covalent bond with U(5f6d) and C\(_\text{c}\)(2p) hybrids in almost equal proportions. The two U–C\(_\text{o}\) \(\pi\_{x,y}\) pairs with 53% C\(_\sigma\)2p AOs mixed with 38% U AOs extend a bit into Ce (8%), showing some 3-center character. The other localized \(\sigma\) pair also displays a 3-center character with a dominant density (66%) on the central C\(_\text{O}\) atom and smaller contributions on Ce (23%) and U (9%). The summed-up bond order indices indicate a triple U≡C bond (one \(\sigma\) and two \(\pi\)) and a single bond for the comparatively short C\(_\text{O}\)–Ce distance due to the slight 3-center character\(^{50}\).

UC\(_n\)Ce\(_{2n}\) shows a similar bonding pattern for U≡C\(_\text{O}\) as in UC\(_n\)Ce\(_{2n}\) (Fig. 3B), which are both further supported by Principal Interacting Orbital (PIO) analysis and Adaptive Natural Density Portioning (AdNDP) analysis. PIO analysis using U and C\(_\text{e}\) as fragments reveals that there is a U≡C triple bond consisting of one \(\sigma\) and two \(\pi\) bonds, each accounting for \(\sim 30\%\). The U–C \(\pi\) bond is slightly more polar than the U–C \(\sigma\) bond. Furthermore, AdNDP analysis also exhibits a similar 2-center U–C \(\sigma\) bond and two 3-center U–C(\(\rightarrow\)Ce) \(\pi\) and \(\pi\) bonds. The calculated bond indices (Extended Data Table 3) suggest a bond order of nearly three for U≡C\(_\text{O}\) and of slightly more than one for C\(_\text{O}\)–Ce, consistent with the experimental distances.

Based on DFT calculations, the MO energy level schemes for UC\(_n\)Ce\(_{2n}\) are shown in Fig. 4. Briefly, the central C\(_\text{O}\) atom in the endohedral cluster can form four electron-pair bonds to its two adjacent metal atoms, U and Ce, leaving six electrons with U/\C\(_\text{e}\) (the left panel of Fig. 4). Upon encapsulating UC\(_n\)Ce into \(D_2\)-\(C_{72}\) or \(D_{3h}\)-\(C_{78}\) cages, the corresponding three lowest unoccupied MOs of the \(C_{2n}\) cage accept six electrons from U/\C\(_\text{e}\), yielding \([U/C_{\text{e}}\text{Ce}]^{6+}\) inside \([C_{2n}]^{6-}\) and formal oxidation numbers as shown in \([U^{\text{VI}}/\text{Ce}^{\text{IV}}]^{6+}\@C_{2n}^{6-}\). In addition, the EMF MOs have significant metal contributions (Extended Data Fig. 2), suggesting orbital interactions between U/\C\(_\text{e}\) and C\(_\text{e}\), which is also confirmed by PIO analysis and the contour line diagrams of NLMOs.

Our theoretical analyses indicate that the hexavalent C\(_{2n}\) fullerene cages help to stabilize \([U=\text{Co–Ce}]\) species with U(VI) and Ce(IV) inside the cages based on four factors: the effective coordinative interactions, charge transfer, appropriate fullerene size, as well as the matrix-like cage environment that protect the U≡C\(_\text{O}\)–Ce species against redox lability\(^{35}\). The unique fullerene cages serve as a protective ligand to stabilize elusive actinide multiple bonding.

**Conclusion**

In summary, we present the isolation and characterization of two systems possessing uranium-carbon triple bonds found in the cerium-capped clusters of the EMFs of UC\(_n\)Ce\(_{2n}\) (\(2n = 72\) and 78). Solid-state molecular characterization by X-ray crystallographic analysis reveals the shortest uranium-carbon bonds reported to date in an isolable molecular complex. Indeed, the U=C bonds (1.921(6) and 1.930(6) Å) are significantly shorter than those reported for the carbeno methanide complex (\([\text{O}=\text{U}=@\text{C}_\text{R}_2]2\text{Cl}_2\) (2.184(3) Å)\(^{41}\), and shorter than the U=C bonds (2.028(5) and 2.033(5) Å) in U\(_2\)C\(_6\). The computational model agrees well with the empirical data,
further confirming the uranium-carbon triple bonds. The joint experimental and theo-
retical investigation shows that the endohedral [U≡C0Ce] unit and the [C2n] fullerene cages synergistically combine to fit each other geometrically without appreciable strain. The stabilities of the triatomic U≡C0Ce unit are enhanced by charge transfer and coordinative donation of fullerene π-pairs to the metal atoms, leading to formal charges C2n6− and corresponding U6+ and Ce4+ oxidation states. Notably, we have preliminary evidence for the formation of UCSc@C82 (Extended Data Fig. 3), which suggests the possibility of synthesizing a range of endohedral actinide (An)/lanthanide (Ln) compounds featuring AnCLn clusters with An≡C bonding, protected by C2n fullerene cages. Our success in the isolation of UCCE@C2n (2n = 72 and 78) further establishes the feasibility of using fullerene cages for trapping and accessing molecular complexes featuring elusive and reactive actinide-ligand multiple bonds. This method opens up opportunities to create model compounds for further studies in this field that may provide critical insight into the synthetic design and electronic properties of non-fullerene compounds with similar bonding motifs. Enhancing our fundamental understanding of the chemical properties of the actinide elements is crucial for improving the nuclear fuel cycle, necessary for advancing carbon-free energy technologies, and also for developing improved methods for the environmental remediation of these elements.

References


Here, we stress the conceptual difference between multiple bond order and multiple bond character. The “U-C triple bond character” mentioned in Ref. (41) means that three (more or less) polycentric LMOs (localized molecular orbitals) interact, forming a bond with a significant admixture of multiple bond character.

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orbitals) each contribute significantly to the U-C interaction, summing up to a bond strength of double order in chemical terms. In contrast, the present “U-C triple bond order” indicates a respectively shorter bond length, larger bond-energy increment, and larger local force constant, caused by four LMOs.

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63 Gaussian 16 Rev. A.03 (Wallingford, CT, 2016).


Methods

Materials

Reagents used for synthesis were: U$_3$O$_8$ (99.9%, China Isotope & Radiation Corporation); CeO$_2$ (99.9%, Aladdin); Graphite rod (99.9%, Huixian Yintai Machinery Manufacturing Corporation); Graphite powder (99.9%, Huixian Yintai Machinery Manufacturing Corporation); Carbon disulfide (HPLC ≥99.9%, Aladdin); Acetone (AR, Chinasun Specialty Products Co., Ltd.); Toluene (AR, Chinasun Specialty Products Co., Ltd.); n-Hexane (HPLC ≥99.9%, Rhawn); Methanol (HPLC ≥99.9%, Meryer); 1,2-dichlorobenzene (99%, Sigma-Aldrich); Benzene (99.8%, Sigma-Aldrich); He (99.999%, purchased from Jinhong Gas).

Synthesis and Isolation

UCCe@C$_{2n}$ ($2n = 72$ and 78) were synthesized by a modified Krätschmer-Huffman direct-current arc-discharge method. Briefly, a drilled graphite rod, fully packed with a mixture containing graphite powder, U$_3$O$_8$, and CeO$_2$ (molar ratio of C : U: Ce = 24 : 1: 1), was installed in a VDK250 arcing reactor (Beijing Technol Science Co., Ltd., China) as the anode under a 200 Torr atmosphere, then arced with a graphite cathode under a 100 A direct current, yielding the products of carbon soot. UCSc@C$_{82}$ was also produced using the same method with raw materials of graphite powder, U$_3$O$_8$, and Sc$_2$O$_3$. The targeted U-based metallofullerenes were extracted from the carbon soot by CS$_2$ for 24 hours, then isolated using an LC-9204 recycling preparative HPLC machine.

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Five types of Cosmosil columns (Nacalai Tesque Inc., Japan), including a preparative Buckyprep-M (20 × 250 mm), a semi-preparative Buckyprep-M (10 × 250 mm), a semi-preparative Buckprep (10 × 250 mm), a semi-preparative 5PYE (10 × 250 mm), and a semi-preparative 5PBB (10 × 250 mm), were utilized in the HPLC procedures.

**Mass spectroscopy**
Mass spectra were recorded on a Microflex LRF matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF, Bruker Daltonics Inc., U.S.) spectrometer using positive-ion mode.

**Visible-near-infrared (Vis-NIR) absorption spectroscopy**
The Vis-NIR spectra of the purified UCe@C\textsubscript{2n} molecules dissolved in toluene were recorded on a Cary5000 spectrometer (Agilent Technologies Co. Ltd., U.S.) in the range of 400-1600 nm.

**Fourier transform infrared (FTIR) absorption spectroscopy**
The FTIR spectra of the purified UCe@C\textsubscript{2n} solids were recorded on a Vertex 70 spectrometer (Bruker Daltonics Inc., U.S.) at room temperature with a resolution of 2 cm\(^{-1}\).

**X-ray absorption near edge spectroscopy (XANES)**
The XANES spectra of the purified UCe@C\textsubscript{78} and other reference compounds were performed at the BL14W1 XAS beamline of the Shanghai Synchrotron Radiation Facility (SSRF). The samples were prepared into a hole of a perforated PTFE film (film thickness: ca. 0.3 mm, hole diameter: ca. 1 mm).

**Single-crystal X-ray diffraction (SC-XRD)**
Black block crystals of UCe@C\textsubscript{2n} were obtained by a slow diffusion co-crystallization method. The CS\textsubscript{2} solution of the samples was slowly diffused into a benzene solution of Ni\textsuperscript{II}(OEP)\textsuperscript{51} (OEP = 2, 3, 7, 8, 12, 13, 17, 18-octaethylporphyrin dianion), yielding black block co-crystals suitable for SC-XRD studies after ca. three weeks. The crystallographic data were recorded on a Bruker D8 Venture single-crystal X-ray diffractometer (Bruker Daltonics Inc., U.S.) equipped with Mo K\(\alpha\) radiation (0.71073 Å) at 100 K. The refinement of the crystallographic structures was performed in the Olex2 software\textsuperscript{52} packed with SHELXL-2018\textsuperscript{53} by the full-matrix least-squares method.

**Quantum Computational Methods**
The geometries and vibrational frequencies (starting with the XRD geometric structures) were calculated for different spin states of the UCe@C\textsubscript{2n} molecules. The generalized gradient approximation (GGA), meta-GGA, and hybrid-GGA Kohn-Sham density-functional (DF) approximations were applied, using the PBE\textsuperscript{54,55} with or without the dispersion-correction of the Becke-Johnson damping scheme (D3BJ)\textsuperscript{56,57}, the MN15L\textsuperscript{58} and B3LYP\textsuperscript{59}, and the PBE0\textsuperscript{60} functionals. The ADF-2019\textsuperscript{61,62} and the Gaussian-16\textsuperscript{63} program packages were applied.

With ADF-2019, the scalar relativistic effects were simulated with the zero-order regular approximation (ZORA)\textsuperscript{64-66}. Slater-type orbital (STO) basis sets of triple-\(\zeta\) plus two polarization functions (TZ2P) quality\textsuperscript{67} were employed for the endohedral atoms. Double zeta polarized (DZP) basis sets were used for the cage carbon atoms. With
Gaussian-16, the Stuttgart-Dresden-Cologne quasi-relativistic effective core potentials, including ECP60MWB\textsuperscript{60} for U and ECP28MWB\textsuperscript{69} for Ce, with the adapted basis sets, were used. The double-\(\zeta\) 6-31G\(^*\) basis set for all C atoms\textsuperscript{70,71} was applied. The vibrational frequencies in terms of IR wavenumbers were computed in the harmonic approximation, with the MN15L functional, and then scaled by a factor of 0.96, which was reproduced from the experimental frequency of free C=O molecule (2143 cm\(^{-1}\)). For the FTIR absorption curves, the Lorentzian line shape function with 4 cm\(^{-1}\) full width at half-maximum was applied to all lines.

With ADF-2019, bond order analyses, including the Mayer bond order\textsuperscript{72}, the Gopinathan-Jug bond order\textsuperscript{73}, and the Nalewajski-Mrozek bond order No. 3\textsuperscript{74}, and an effective charge analysis were obtained. Natural localized molecular orbitals (NLMO) and the Wiberg bond index (WBI)\textsuperscript{75} were obtained from the NBO-6.0 program\textsuperscript{76}. Adaptive natural density portioning (AdNDP)\textsuperscript{77}, Pipek’s delocalized index (DI), and ‘quantum theory of atoms in molecules’ (QATAM)\textsuperscript{78} analyses were obtained from the Multiwfn program\textsuperscript{79}, throughout using the results from the B3LYP density functional.

**Data availability**

The crystallographic data of UCCe@C\(_{2n}\) (2\(n\) = 72 and 78) can be obtained free of charge from the Cambridge Crystallographic Data Centre with CCDC numbers 2239921 and 2239922, respectively, via https://www.ccdc.cam.ac.uk/data_request/cif. The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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**Author contributions**

N.C. and J.L. administrated the project; N.C., J.L., and W.H.E.S. supervised the project; Y.-R.Y. and Q.M. performed the synthesis and isolation. J.Z. performed the DFT calculations; Y.-R.Y. grew the single crystals and solved the crystallographic data. M.G. and Y.Y. carried out the Vis-IR and IR characterizations. Y.-R.Y. and J.X.Z carried out the XAS characterization. Y.-R.Y., J.Z., and W.H.E.S. wrote the original draft; N.C., J.L., H.-S.H, S.Y., S.F., L.E., and W.H.E.S. reviewed the draft. All authors discussed the results and commented on the manuscript.

**Competing interests**

The authors declare that they have no competing interests.
Fig. 1. Oak Ridge thermal ellipsoid plots (ORTEP) of the predominant crystal conformations, drawn at 20% ellipsoids. Left: (A and C): UCCE@D2-C72. Right: (B and D): UCCE@D3h-C78. Top (A and B): triatomic unit inside the fullerene cage above the co-crystallized NiII(OEP) molecule; all solvent molecules and hydrogen atoms are omitted. Bottom (C and D): the endohedral unit with the sandwiching parts of the cage, interatomic distances in Å, and central bond angle in °.
Fig. 2. IR, Vis-NIR, and XAS results of UC\text{Ce@C}_{2n}. Top: experimental and simulated FTIR spectra of (A) UC\text{Ce@C}_{72} and (B) UC\text{Ce@C}_{78}. Middle: Comparison of Vis-NIR absorption spectra (C) of UC\text{Ce@D}_{2}-\text{C}_{72} with Ce\text{e@D}_{2}-\text{C}_{72} and (D) of UC\text{Ce@D}_{3h}-\text{C}_{78} with U\text{e@D}_{3h}-\text{C}_{78}. Bottom: Comparison of L3-edge XAS of UC\text{Ce@C}_{78} (E) for Ce-2p\text{3/2} with Ce\text{IV}O_{2}, Ce\text{III}_{2}-\text{C}_{72} and Ce\text{III}Cl_{3}, and (F) for U-2p\text{3/2} with uranyl(U\text{VI})-dinitrate, U\text{IV}_{2}\text{C@C}_{80}, U\text{IV@C}_{2}-\text{C}_{82} and uranium(U\text{IV}) di-sulfate; inserts: derivative spectra highlighting the ‘edge energies’ of the first peaks by vertical lines.
Fig. 3. The four natural localized molecular orbitals (NLMOs) on the endohedral UC\textsubscript{Ce} unit for (A) UC\textsubscript{Ce}@C\textsubscript{72} and (B) UC\textsubscript{Ce}@C\textsubscript{78}. The value of isosurfaces is ±0.05 a.u. at B3LYP level.
Fig. 4. Molecular orbital energy level scheme for UCCe@C_{2n}. **Left:** the (endohedral) atomic valence orbital energy levels C-2s/2p, Ce-4f/5d/6s, and U-5f/6d/7s. **Middle-Left:** the \( \equiv \) unit. **Right:** the \( C_{2n} \) fullerenes (\( D_2(10611) \)-C_{72} or \( D_{3h}(5) \)-C_{78}). **Middle-Right:** the compound UC\(_a\)Ce@C\(_{2n}\) molecules. Occupied orbital energy ranges are hatched. Orbital levels dominated by the endohedral U/C\(_a\)/Ce atoms are shown in red, dominated by the fullerene C-atoms in black.
Extended Data

Extended Data Fig. 1. HPLC chromatograms and mass spectra of purified UCnC2n. (A-B) HPLC chromatograms of purified UCnC272 and UCnC278 on a 10×250 mm semi-preparative Buckyprep column with a 4 mL/min flow rate using toluene as the eluent. (C-D) Positive-ion mode MALDI-TOF mass spectra of purified UCnC272 and UCnC278. The inserts show the corresponding experimental and theoretical isotopic distributions, both in good agreement.
Extended Data Fig. 2. Isosurfaces (±0.05 a.u.) of canonical frontier MOs of (A) UCCE@C$_{72}$ and (B) UCCE@C$_{78}$ at Kohn-Sham PBE level. The occupied MOs and the virtual unoccupied MOs with opposite phases are shown in red/blue and green/orange, respectively. Canonical MOs with significant UCCE and cage contributions are labeled in red and black, respectively. The MOs, such as HOMO, HOMO-6, and HOMO-11 of UCCE@C$_{72}$ or HOMO, HOMO-2, and HOMO-5 of UCCE@C$_{78}$, show significant orbital interactions between the metal atoms and the carbon cage.
Extended Data Fig. 3. HPLC isolation process and mass spectrum of UCSc@C$_{82}$.

(A) The first-step HPLC chromatogram of extracted fullerene mixture containing UCSc@C$_{82}$ (condition: 20×250 mm preparative Buckyprep-M column; flow rate 13.0 mL/min; toluene as eluent); (B) The second-step HPLC chromatogram of the collected fraction (29.5-33.2 min, highlighted as red) from the first step (condition: 10×250 mm semi-preparative Buckyprep column; flow rate 4.0 mL/min; toluene as eluent); (C) The third-step HPLC chromatogram of the collected fraction (72.2-75.2 min, highlighted as red) from the second step (condition: 10×250 mm semi-preparative 5PBB column; flow rate 4.0 mL/min; toluene as eluent); (D) The final-step HPLC chromatogram of the collected fraction (95.9-105.9 min, highlighted as red) from the third step (condition: 10×250 mm semi-preparative Bucky-M column; flow rate 4.0 mL/min; toluene as eluent). The highlighted fraction (31.5-33.4 min) containing isolated UCSc@C$_{82}$ was collected. (E) The HPLC chromatogram of purified UCSc@C$_{82}$ on a 10×250 mm semi-preparative Buckyprep column with a 4 mL/min flow rate using toluene as the eluent. (F) Positive-ion mode MALDI-TOF mass spectrum of purified UCSc@C$_{82}$. The insert shows the corresponding experimental and theoretical isotopic distributions, which are in good agreement.
Extended Data Table 1. Geometric parameters of UCCE in C\(_{2n}\) (2\(n\) = 72 and 78) and between two C\(_7\)H\(_7\). Bond lengths (in Å, average values are italic) and bond angles (in \(^\circ\)) are from X-ray diffraction of UCCE@C\(_{2n}\)·[Ni-OEP] co-crystals and from PBE/TZ2P calculation (in parentheses) of UCCE@C\(_{2n}\) and C\(_7\)H\(_7\)>UCCE<C\(_7\)H\(_7\).

<table>
<thead>
<tr>
<th>Species</th>
<th>Bond lengths</th>
<th>Bond angles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L*–U</td>
<td>U≡C(_o)</td>
</tr>
<tr>
<td>UCCE@C(_{72})</td>
<td>2.49 (2.51)</td>
<td>1.92 (1.91)</td>
</tr>
<tr>
<td>UCCE@C(_{78})</td>
<td>2.43 (2.48)</td>
<td>1.93 (1.90)</td>
</tr>
<tr>
<td>H(_2)&gt;UCCE&lt;H(_3)</td>
<td>(1.99)</td>
<td>(1.88)</td>
</tr>
<tr>
<td>C(_7)H(_7)&gt;UCCE&lt;C(_7)H(_7)</td>
<td>(2.55)</td>
<td>(1.89)</td>
</tr>
</tbody>
</table>

*L for UCCE@C\(_{72}\) is the pentalene portions, for UCCE@C\(_{78}\) is the benzene portions, for H\(_2\)>UCCE<H\(_3\) is the H\(_3\), for C\(_7\)H\(_7\)>UCCE<C\(_7\)H\(_7\) is the carbon rings.
## Extended Data Table 2. Different charge analyses of UC\textsubscript{o}Ce@C\textsubscript{2n} at the PBE/TZ2P level.

Charge analyses include Hirshfeld charges, Voronoi deformation density (VDD) charges, and multipole-derived charges reconstructed up to quadrupoles (MDC-q).

<table>
<thead>
<tr>
<th>Atom</th>
<th>UC\textsubscript{o}Ce@C\textsubscript{72}</th>
<th>UC\textsubscript{o}Ce@C\textsubscript{78}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hirshfeld</td>
<td>VDD</td>
</tr>
<tr>
<td>U</td>
<td>0.595</td>
<td>0.493</td>
</tr>
<tr>
<td>C\textsubscript{o}</td>
<td>-0.433</td>
<td>-0.514</td>
</tr>
<tr>
<td>Ce</td>
<td>0.465</td>
<td>0.282</td>
</tr>
<tr>
<td>UC\textsubscript{o}Ce</td>
<td>+0.63</td>
<td>+0.26</td>
</tr>
<tr>
<td>C1</td>
<td>-0.023</td>
<td>-0.019</td>
</tr>
<tr>
<td>C2</td>
<td>-0.016</td>
<td>-0.017</td>
</tr>
<tr>
<td>C3</td>
<td>-0.019</td>
<td>-0.021</td>
</tr>
<tr>
<td>C4</td>
<td>-0.017</td>
<td>-0.022</td>
</tr>
<tr>
<td>C5</td>
<td>-0.023</td>
<td>-0.019</td>
</tr>
<tr>
<td>C6</td>
<td>-0.016</td>
<td>-0.016</td>
</tr>
<tr>
<td>C7</td>
<td>-0.019</td>
<td>-0.022</td>
</tr>
<tr>
<td>C8</td>
<td>-0.018</td>
<td>-0.023</td>
</tr>
<tr>
<td>C64</td>
<td>-0.013</td>
<td>-0.011</td>
</tr>
<tr>
<td>C65</td>
<td>-0.018</td>
<td>-0.018</td>
</tr>
<tr>
<td>C66</td>
<td>-0.012</td>
<td>-0.010</td>
</tr>
<tr>
<td>C67</td>
<td>-0.025</td>
<td>-0.019</td>
</tr>
<tr>
<td>C68</td>
<td>-0.013</td>
<td>-0.012</td>
</tr>
<tr>
<td>C70</td>
<td>-0.018</td>
<td>-0.019</td>
</tr>
<tr>
<td>C71</td>
<td>-0.012</td>
<td>-0.011</td>
</tr>
<tr>
<td>C72</td>
<td>-0.025</td>
<td>-0.019</td>
</tr>
<tr>
<td>C\textsubscript{56} remainder</td>
<td>-0.34</td>
<td>+0.02</td>
</tr>
</tbody>
</table>

**Note:** The endohedral UC\textsubscript{o}Ce units show similar charge distributions in the C\textsubscript{72} and C\textsubscript{78} cages. Formal U\textsuperscript{VI} is effectively more positively charged than formal Ce\textsuperscript{IV}. The formal 6-electron charge transfer from UC\textsubscript{o}Ce to the C\textsubscript{2n} cages is primarily compensated by C\textsubscript{2p}-\pi\textsuperscript{2}-pair back donation, resulting in a slight negative charge on the two \pi\textsuperscript{2}-coordinated pentalene portions of C\textsubscript{72} and the two \pi\textsuperscript{2}-coordinated benzene portions of C\textsubscript{78}, which are even less negatively charged than the rest of the cage carbons.
Extended Data Table 3. The AO compositions of NLMOs and bond order indices of UC\textsubscript{6}Ce species.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Bond type</th>
<th>Atomic % contributions to localized MOs</th>
<th>Bond order indices*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>U 5f/6d/7s</td>
<td>C\textsubscript{o} 2s/2p</td>
</tr>
<tr>
<td>UC\textsubscript{6}Ce@C\textsubscript{72}</td>
<td>U=C\textsubscript{o} 2\pi</td>
<td>46 82/16/2</td>
<td>50 51/49</td>
</tr>
<tr>
<td></td>
<td>C\textsubscript{o}–Ce  $\sigma$</td>
<td>38 78/22/0</td>
<td>53 0/100</td>
</tr>
<tr>
<td>UC\textsubscript{6}Ce@C\textsubscript{78}</td>
<td>U=C\textsubscript{o} 2\pi</td>
<td>9 35/40/25</td>
<td>66 64/36</td>
</tr>
<tr>
<td></td>
<td>C\textsubscript{o}–Ce  $\sigma$</td>
<td>50 84/14/2</td>
<td>47 44/55</td>
</tr>
</tbody>
</table>

*G-J = Gopinathan-Jug bond order; N-M = Nalewajski-Mrozek #3bond order; WBI = Wiberg bond index; DI = Pipek delocalization index.