JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

Cite This: J. Am. Chem. Soc. 2019, 141, 20249−20260

pubs.acs.org/JACS

Diuranium(IV) Carbide Cluster U_2C_2 Stabilized Inside Fullerene Cages

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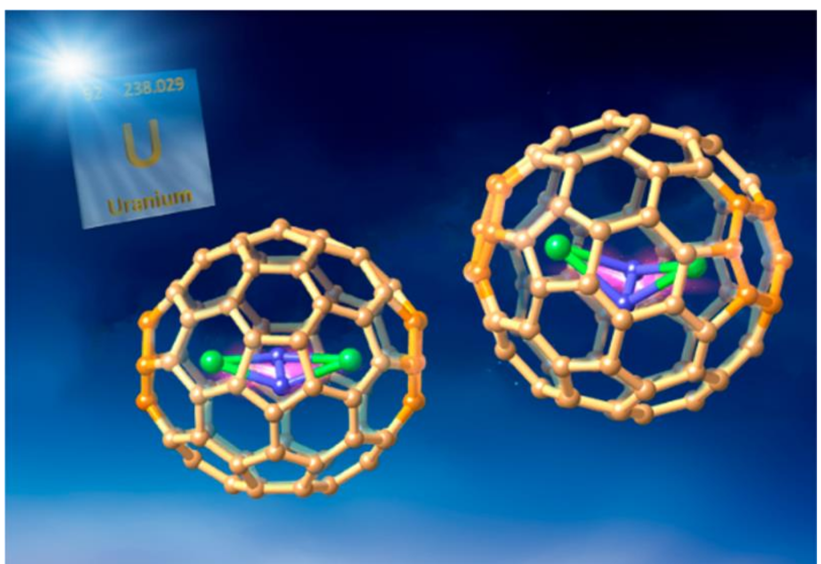
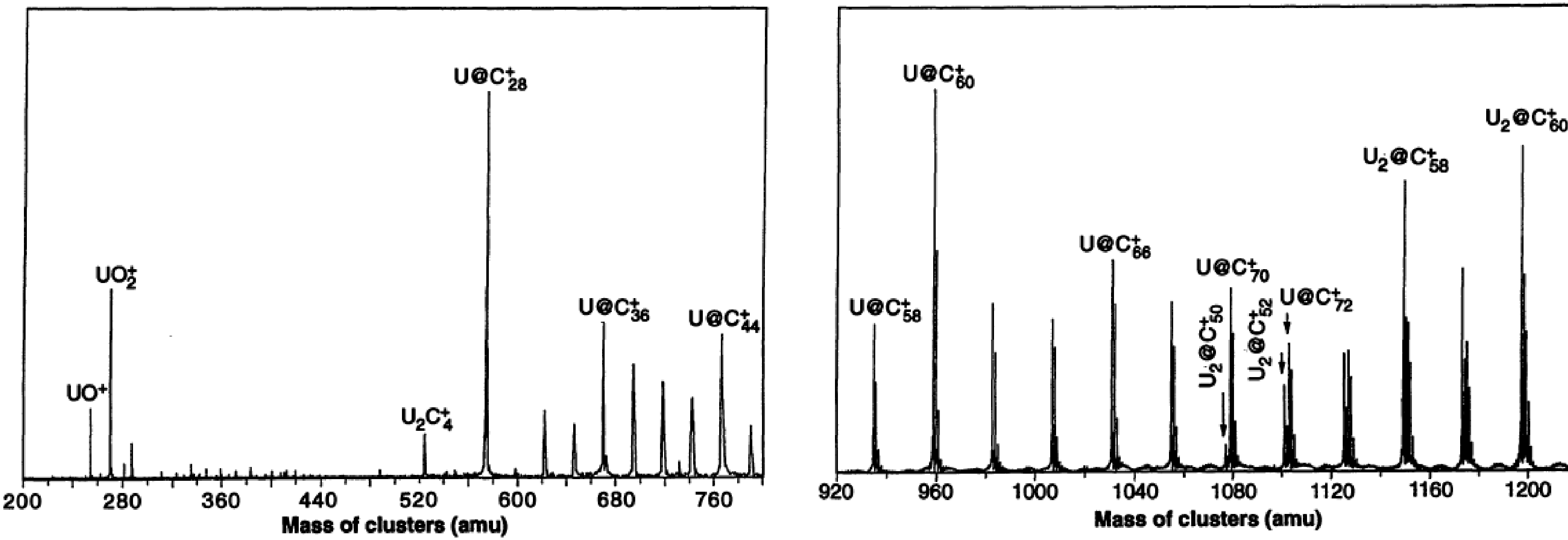


Published : December 3, 2019

Jayoti Roy
22/02/2020

Uranium Stabilization of C_{28}: A Tetravalent Fullerene

Ting Guo, M. D. Diener, Yan Chai, M. J. Alford, R. E. Haufler, S. M. McClure, T. Ohno, J. H. Weaver, G. E. Scuseria,* R. E. Smalley*



Fourier transform-ion cyclotron resonance (FT-ICR) mass spectrum of positive carbon-uranium cluster ions produced by laser vaporization of a graphite-UO_2 composite disk.

SCIENCE VOL. 257 18 SEPTEMBER 1992

nature COMMUNICATIONS

ARTICLE

DOI: 10.1038/s41467-018-05210-8 OPEN

A diuranium carbide cluster stabilized inside a C_{80} fullerene cage

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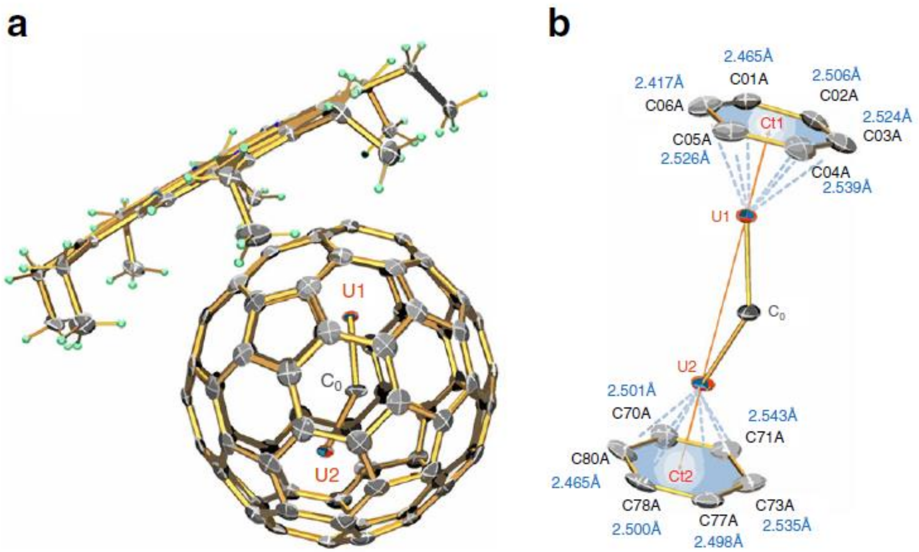


(a) UCU@I_h(7)-C_{80}·[Ni^{II}-OEP] structure showing the relationship between the fullerene cage and the [Ni^{II}-OEP] ligands.
(b) Fragment view showing the interaction of the major U1–C0–U2 cluster with the closest aromatic ring fragments of the cage with centers Ct1 and Ct2.
The orange line connects Ct1–U1–U2–Ct2

Introduction

- Actinide endohedral metallofullerenes (EMFs) are novel fullerenes that encapsulate actinide atoms and clusters.

- This study demonstrates that it is feasible to observe novel endohedral structures with new actinide clusters and bonding motifs.

- This uranium carbides act as refractory ceramic materials and fuel for nuclear reactors. Such fuel is intended for nuclear-powered rockets due to its better power density, and uranium carbides are desirable candidates for new generations of nuclear reactors at very high temperatures.

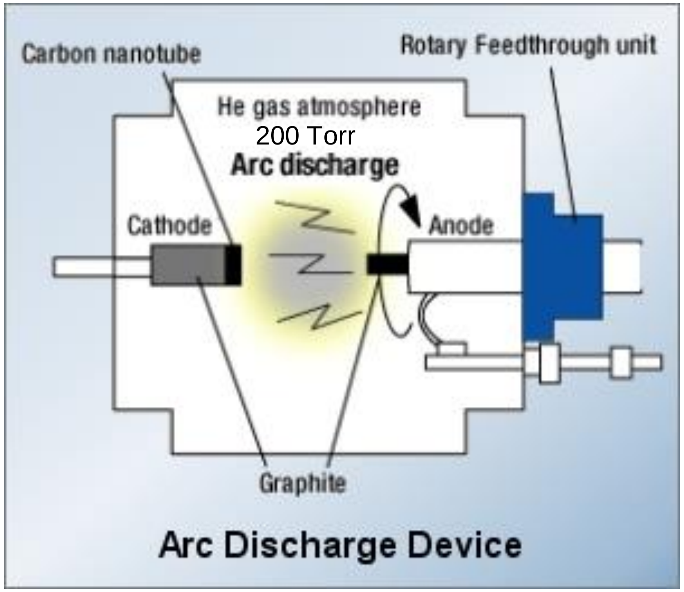
- Synthesis of two novel uranium carbide cluster EMFs, $U_2C_2@I_h(7)\text{-}C_{80}$ and $U_2C_2@D_{3h}(5)\text{-}C_{78}$, both of which were characterized by mass spectrometry, single-crystal X-ray crystallography, nuclear magnetic resonance spectroscopy (NMR), X-ray absorption spectroscopy (XAS), UV−vis−NIR, Raman spectroscopy, as well as density functional theory (DFT) calculations.

- $U_2C_2@I_h(7)\text{-}C_{80}$ and $U_2C_2@D_{3h}(5)\text{-}C_{78}$ are the first examples of structurally characterized uranium(IV) carbides (U_2C_2 motif), forming a butterfly shape in which the two bridged C atoms are linked by a C≡C triple bond. In particular, $U_2C_2@I_h(7)\text{-}C_{80}$ represents the first example of hexavalent M_2C_2 cluster that can be embedded in an $I_h(7)\text{-}C_{80}$ fullerene cage.

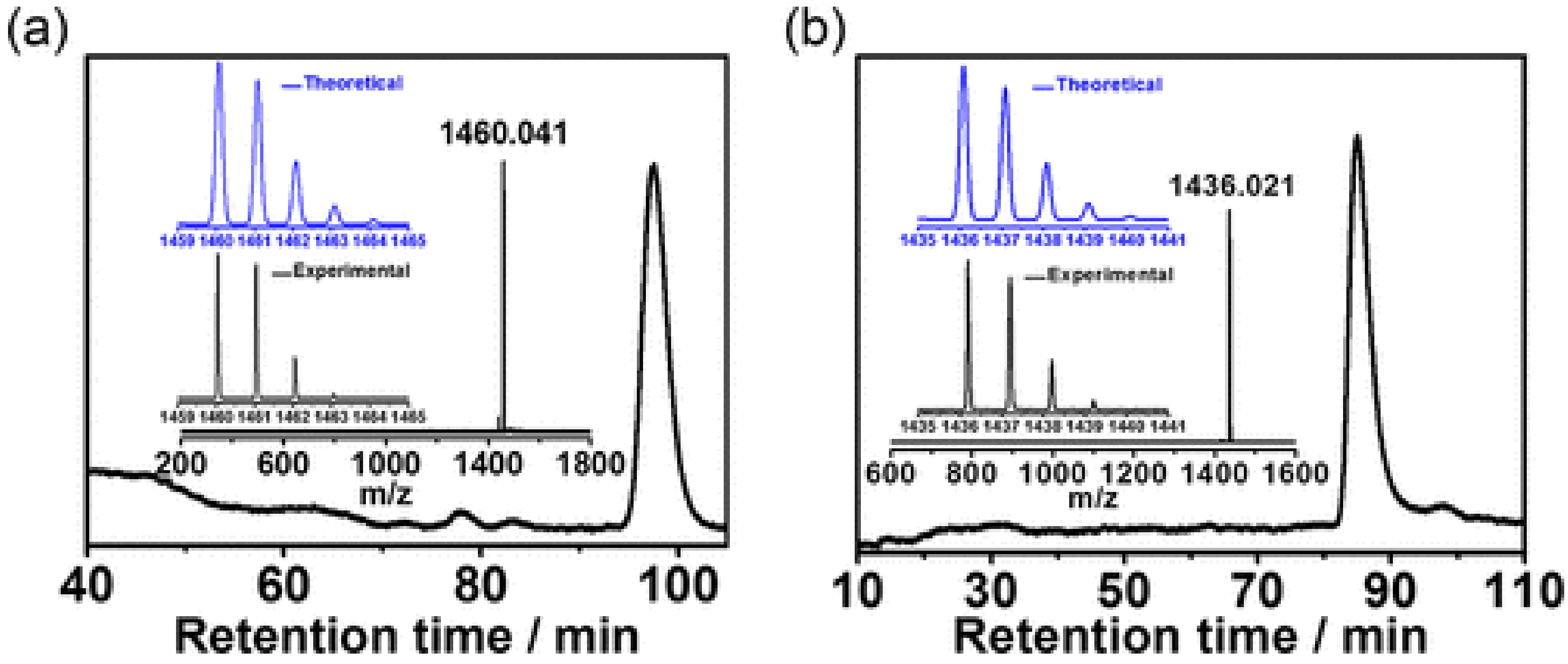
Result and discussion

Synthesis and isolation

- Graphite rods, packed with U_3O_8 and graphite powder (U/C = 1:30) was vaporized in the arcing chamber under 200 Torr He atmosphere.
- The resulting soot was then collected and extracted with CS_2 for 12 h.
- Multistage HPLC procedures were employed to isolate and purify $U_2C_2@C_{2n}$ (2n = 78, 80).
- The positive-ion mode MALDI-TOF mass spectra of purified $U_2C_2@C_{80}$ and $U_2C_2@C_{78}$ show peaks at m/z 1460.04 and 1436.02

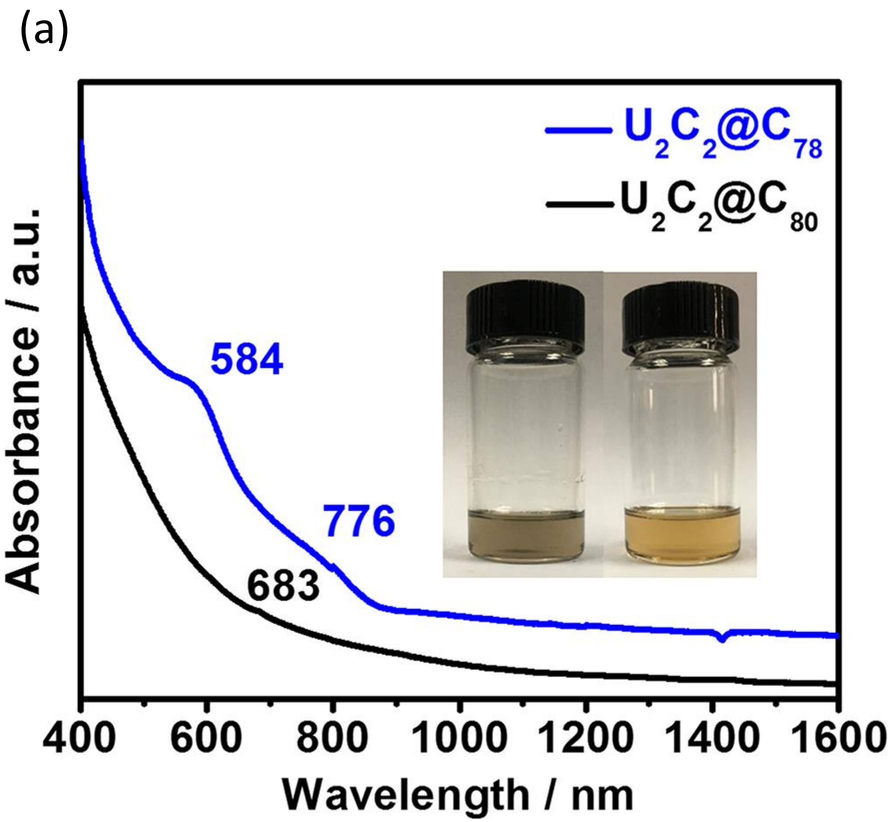


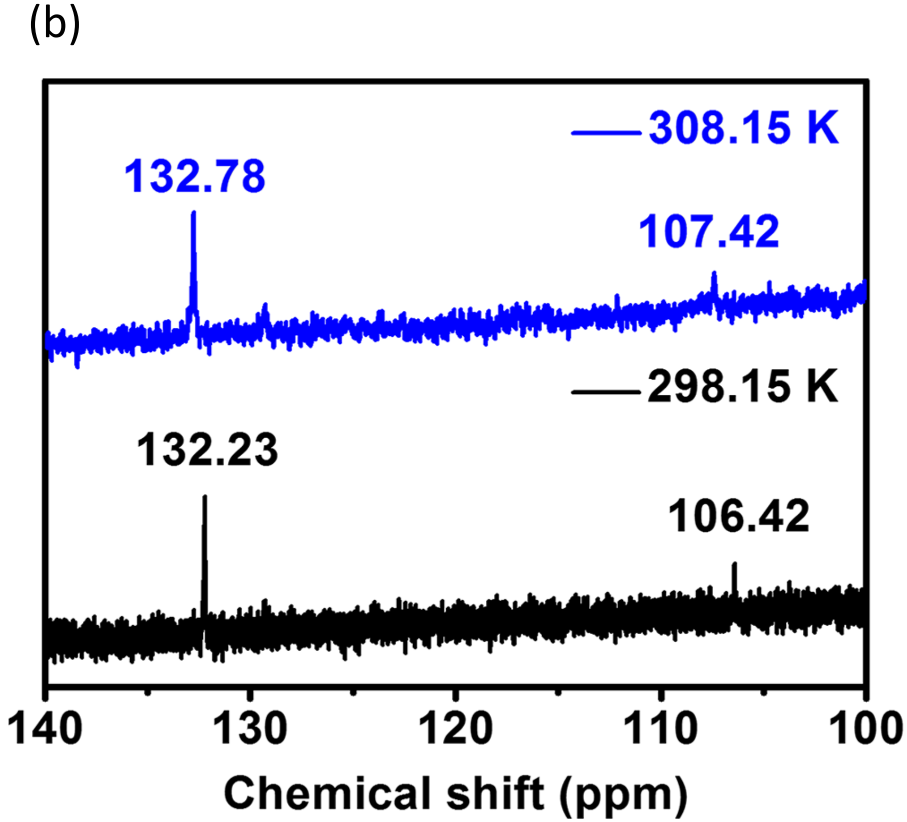
Isolation of $U_2C_2@C_{2n}$



HPLC chromatogram of purified $U_2C_2@C_{80}$ (a) and $U_2C_2@C_{78}$ (b) with toluene as the eluent. The insets show the positive-ion mode MALDI-TOF mass spectra and expansions of the corresponding experimental isotopic distributions of $U_2C_2@C_{80}$ and $U_2C_2@C_{78}$ in comparison with the theoretical ones.

Spectroscopic studies

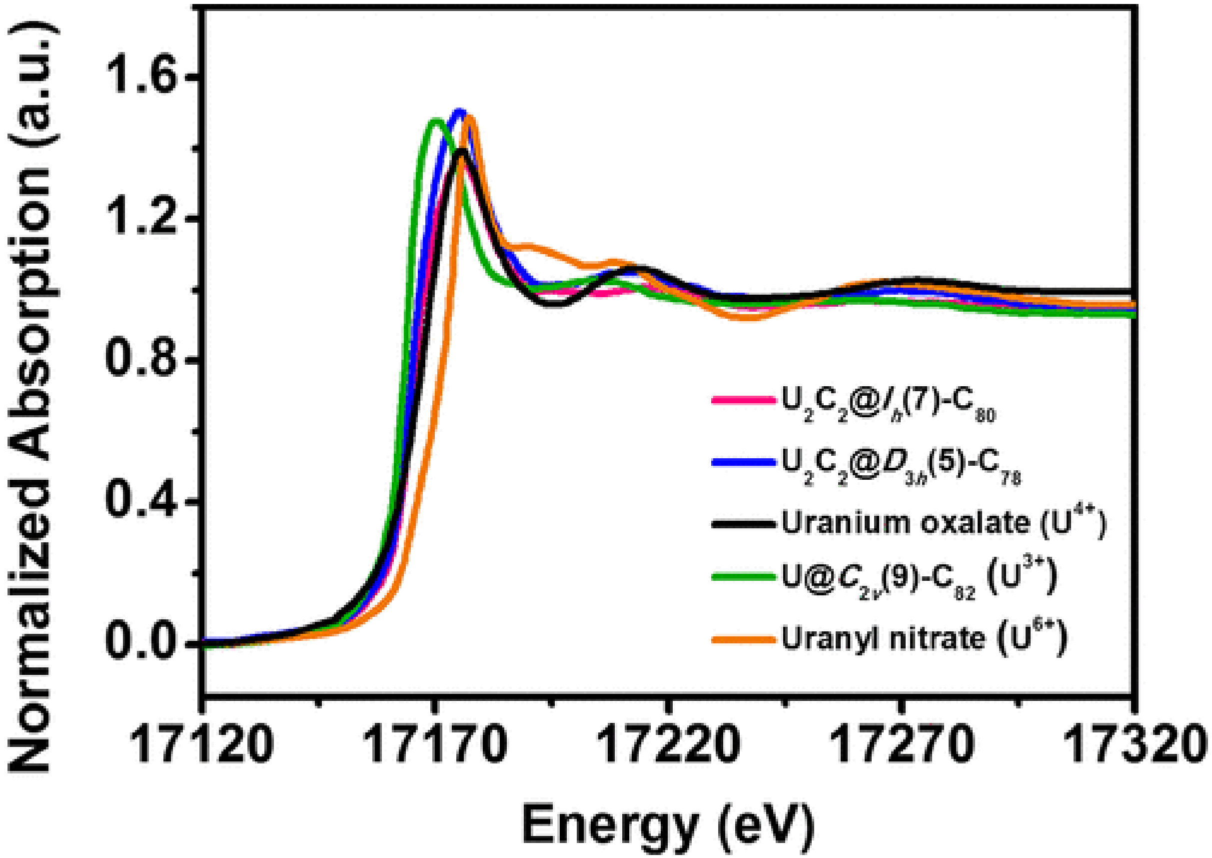




(a) UV−vis−NIR spectra of $U_2C_2@I_h(7)$-C_{80} (black) and $U_2C_2@D_{3h}(5)$-C_{78} (blue) in CS_2. The insets show the photographs of 0.3 mg of $U_2C_2@D_{3h}(5)$-C_{78} (left) and 0.3 mg of $U_2C_2@I_h(7)$-C_{80}(right) dissolved in 3 mL of CS_2 solution, respectively.

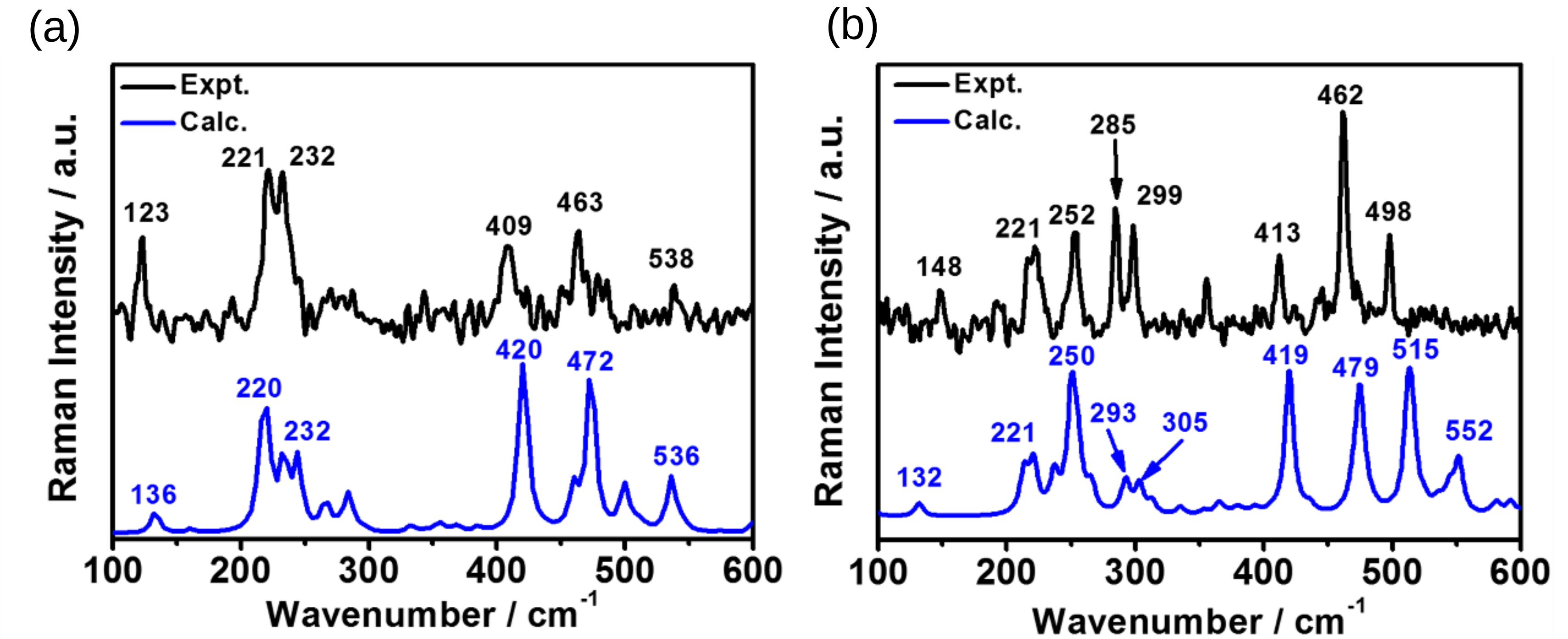
(b) ^{13}C NMR (600 MHz) spectra of $U_2C_2@I_h(7)$-C_{80} (CS_2, 298 and 308 K).

XAS spectroscopic studies



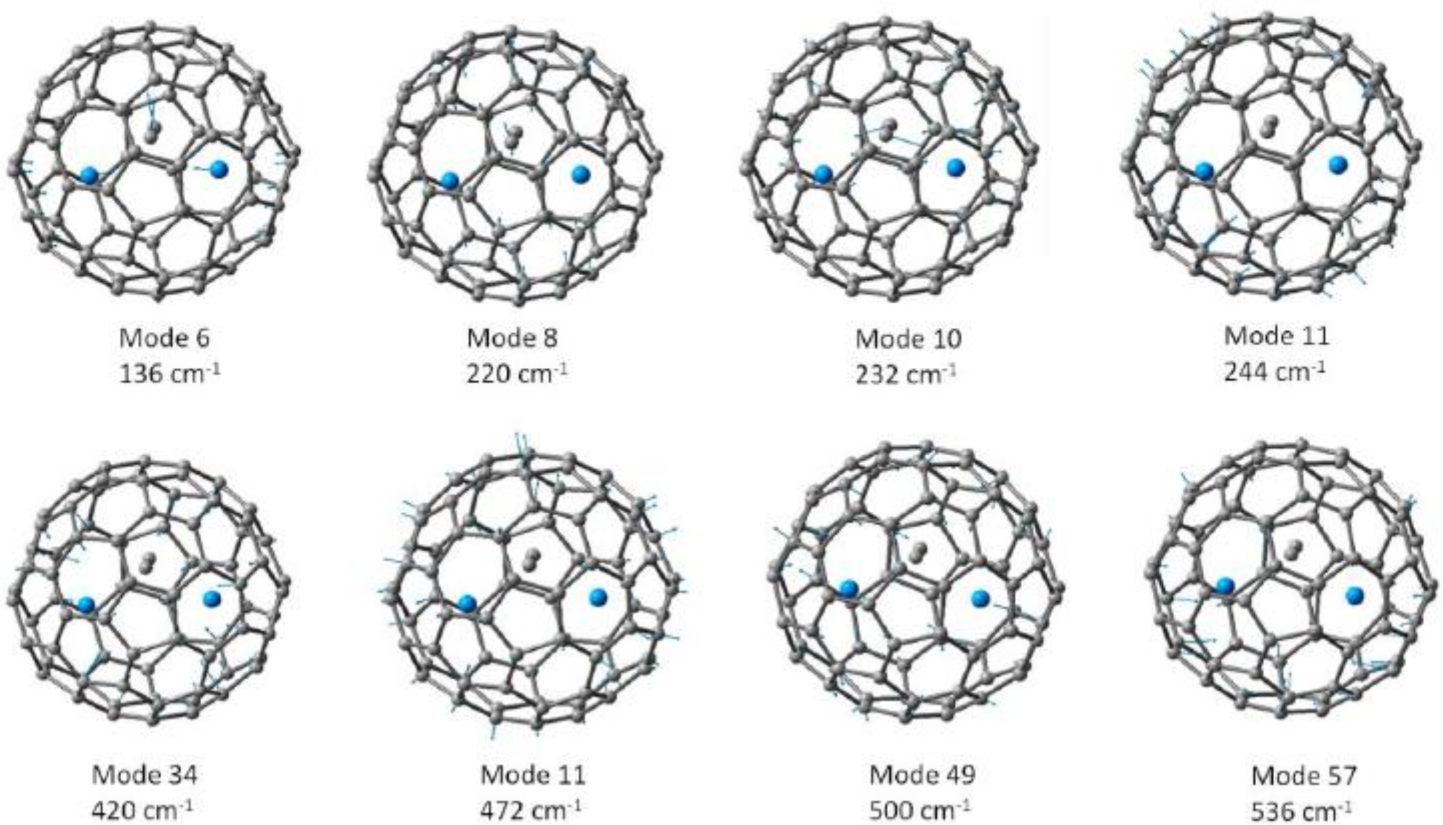
U L_3-edge XAS spectra of $U_2C_2@I_h(7)\text{-}C_{80}$ and $U_2C_2@D_{3h}(5)\text{-}C_{78}$, as compared to those of $U@C_{2v}(9)\text{-}C_{82}$ (U^{3+}), uranium-oxalate (U^{4+}), and uranyl-nitrate (U^{6+}).

Raman spectroscopic studies



Experimental and computational Raman spectra of (a) U_2C_2@I_h(7)-C_{80} (b)U_2C_2@D_{3h}(5)-C_{78}.

Raman spectroscopic studies



Vibrational modes assigned to the major peaks of the Raman spectrum of $U_2C_2@I_h(7)\text{-}C_{80}$.

Molecular structures

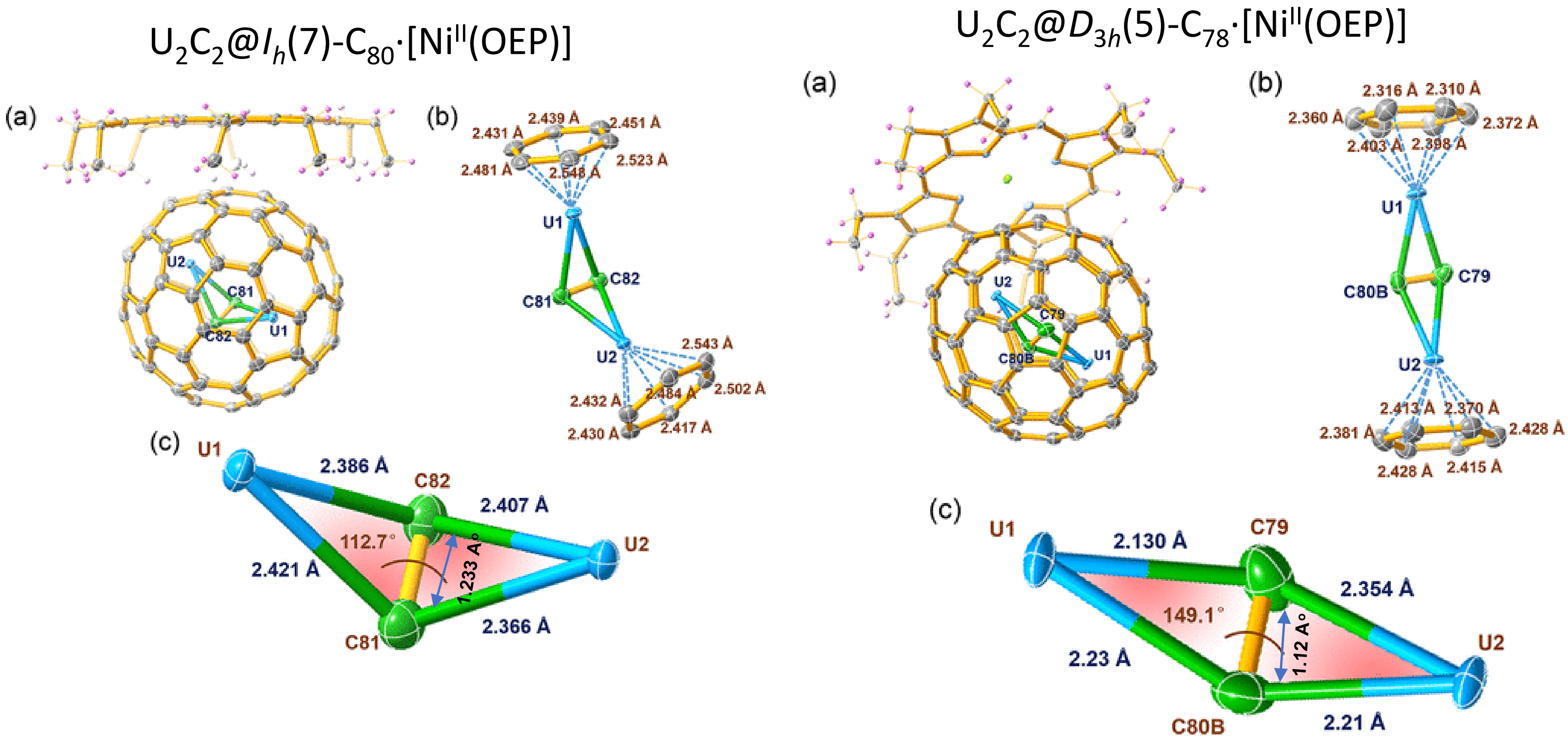
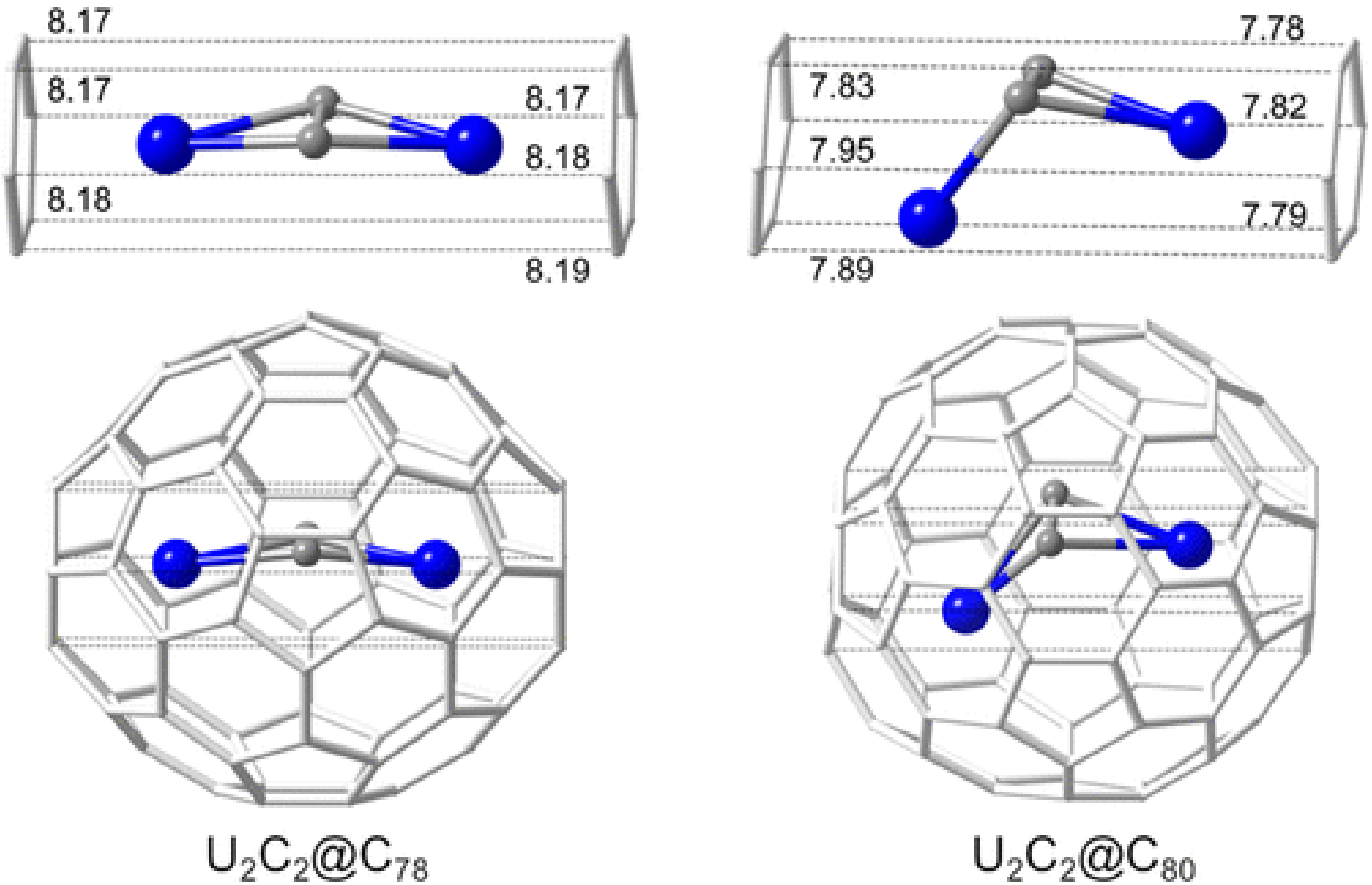


Figure 2. (a) ORTEP drawing of $U_2C_2@I_h(7)\text{-}C_{80}\cdot[Ni^{II}(OEP)]$ (OEP = 2, 3, 7, 8, 12, 13, 17, 18-octaethylporphyrin dianion) and $U_2C_2@D_{3h}(5)\text{-}C_{78}\cdot[Ni^{II}(OEP)]$ with 20% thermal ellipsoids. (b) View showing the relationship of the major U_2C_2 cluster with the closest cage portions. (c) Configuration of the endohedral U1−C_2−U2 fragment.

Geometric Parameters of U_2C_2 Unit

	$U_2C_2@I_h(7)$-C_{80}	**$U_2C_2@D_{3h}(5)$-C_{78}**
C–C/Å	1.233	1.127
M–M/Å	3.855	4.164
M–C/Å	2.421/2.386/ 2.366/2.407	2.130/2.23/ 2.354/2.21
dihedral angle/deg	112.7	149.1
ring centroid distance/Å	7.86	8.01

Comparison of the bonding in $U_2C_2@D_{3h}(5)\text{-}C_{78}$ and $U_2C_2@I_h(7)\text{-}C_{80}$



Comparison between the depth of $D_{3h}(5)\text{-}C_{78}$ and $I_h(7)\text{-}C_{80}$ cages.

Conclusions

❖ Actinide cluster fullerenes, $U_2C_2@I_h(7)$-C_{80} and $U_2C_2@D_{3h}(5)$-C_{78}, have been successfully synthesized and characterized.

❖ Crystallographic analyses unambiguously show that a novel uranium carbide cluster, U2C2, was encapsulated inside both Ih(7)-C80 and D3h(5)-C78 cages. The U2C2 cluster in U2C2@C80 adopts a butterfly-shaped geometry with a U−C2−U dihedral angle of 112.7° and a U−U distance of 3.855 Å, the U−U distance in U2C2@C78 is 4.164 Å and the U−C2−U dihedral angle increases to 149.1°.

❖ The combined experimental and quantum-chemical results suggest that the formal U oxidation state is +4 in the U_2C_2 cluster.