

UN@C₂(13)-C₈₄: A Diatomic Cluster with a U≡N Triple Bond inside a C₈₄ Fullerene Cage

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A novel monometallic nitride clusterfullerene, UN@C₈₄, has been successfully synthesized and characterized. Single-crystal X-ray diffraction analysis reveals that a rare diatomic UN cluster, one of the smallest known encapsulated clusters, is encapsulated within a carbon cage of C₂(13)-C₈₄, featuring a U≡N triple bond with a very short bond length of 1.763(10) Å. This bond length remains nearly unchanged compared to previously reported UN@C₈₂ isomers, suggesting that the intrinsic nature of the encapsulated U≡N triple bond was not affected by cage size. Furthermore, combined with the previous studies about the metal position and the symmetry plane of the carbon cage, we find that in monometallic endohedral clusterfullerenes, the encapsulated metal atom preferentially aligns not only with the symmetry plane but also with the symmetry axis of the fullerene cage, namely the symmetry elements of the carbon cage, thereby preserving the overall molecular symmetry. These results deepen our understanding of positional preference for encapsulated metal atoms and provide valuable guidance for the crystallographic refinement of EMFs, offering new insights into the structural analysis, prediction, and further exploration of novel EMFs.

Introduction

The groundbreaking discovery of Sc₃N@C₈₀ in 1999 opened a new era in fullerene chemistry by revealing that the interiors of fullerene cages could capture and stabilize clusters composed of both metal and non-metal atoms, constructing clusterfullerenes as a booming type of fullerene.¹ Since then, various kinds of metallic clusters, including nitrides,¹⁻⁵ carbides,⁶⁻⁸ oxides,⁹⁻¹¹ sulfides,^{12, 13} cyanides,^{14, 15} hydrocarbons,^{16, 17} and carbonitrides,^{18, 19} have been successfully encapsulated into the fullerene cages. These fascinating metallic clusters endow endohedral metallofullerenes (EMFs) with variable potential applications in the field of biomedicines,²⁰ photovoltaics,²¹ single-molecule magnets,²² and single-molecule devices.^{23, 24}

The internal space of fullerenes is inherently limited, which restricts the size of clusters they can encapsulate. So far, the largest known clusters contain as many as seven atoms. In 2010, Stevenson and colleagues reported a new type of oxide cluster, which was composed of four scandium and three oxygen atoms, inside the popular I_h(7)-C₈₀ cage.²⁵ Other seven-atom clusters, such as Sc₄C₂H and Sc₄CNH, have similarly been stabilized within

the I_h(7)-C₈₀ cage.^{17, 26} In contrast, EMFs encapsulating small clusters, such as monometallic species, are relatively rare and have been identified in the recent decade. In 2013, Yang and colleagues reported a triatomic cyanide cluster encapsulated inside a C₈₂ cage, demonstrating that even one metal atom could form a viable cluster inside a fullerene cage.¹⁴ Theoretically, the smallest cluster would consist of just one metal and one non-metal atom. However, such clusters have been unexplored until very recently, when we reported the first diatomic clusterfullerenes, UN@C₂(5)-C₈₂ and UN@C₃(6)-C₈₂, which contain only one U and one N atoms with a rare U≡N triple bond.³ This result not only presents a new family of EMFs but also, more importantly, expands the cluster to the boundary of theoretically smallest clusters that can be encapsulated into the fullerene cages. Thus, it is highly desirable to explore more UN@C_{2n} family members to gain a deeper understanding of such new types of EMFs, providing new insights into the construction of novel EMFs.

Herein, we report the synthesis, isolation, and characterization of a new member of the UN@C_{2n} family, which is encapsulated inside a large C₈₄ cage. The molecular structure has been unambiguously determined by single-crystal X-ray diffraction, and the electronic properties were investigated using UV-visible-NIR spectroscopy and DFT calculations. Interestingly, the UN cluster is closely located on the two-fold axis of the carbon cage, revealing that the metal atom in monometallic EMFs preferentially aligns with the symmetry element of the carbon cage to keep the entire molecule symmetrical.

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Electronic supplementary information (ESI) available.

Results and discussion

Synthesis and isolation of UN@C₈₄.

The synthesis of carbon soot containing UN@C₈₄ was carried out using a modified Krätschmer-Huffman direct-current arc-discharge method.²⁷ Graphite rods were packed with a well-mixed powder of uranium oxide (U₃O₈) and graphite in a molar ratio of 1:30 (U:C). The packed rods were preheated under a N₂ atmosphere at 1000 °C before the arc-discharge process, performed in a vacuumed chamber maintained at 200 Torr He and 4 Torr N₂. Fullerenes were extracted with CS₂, and the targeted UN@C₈₄ was successfully isolated and purified through multiple high-performance liquid chromatography (HPLC) steps (Fig. S1). The sample purity was confirmed by the presence of a single chromatographic peak and further validated by mass spectrometry (Fig. 1). Additionally, the experimentally obtained isotopic distribution closely matched theoretical predictions, confirming the molecular composition of UN@C₈₄.

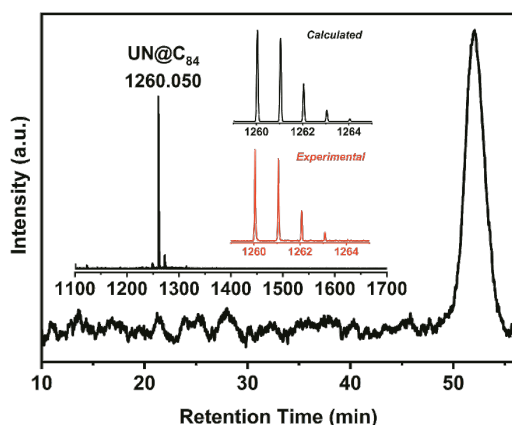


Fig. 1. HPLC profile of the purified UN@C₈₄ (10 mm × 250 mm Buckprep column; toluene as the eluent; flow rate: 4 mL/min). The inset shows the mass spectrum of UN@C₈₄. The experimental isotopic distribution is in good agreement with the calculated one.

Molecular structures of UN@C₂(13)-C₈₄.

To investigate the molecular structure of UN@C₈₄, Ni^{II}(OEP) (OEP = octaethylporphyrin dianion) was used as the crystalline mate because it can effectively hinder cage rotation and enhance crystalline quality.²⁸ A black block cocrystal of UN@C₈₄ with Ni^{II}(OEP) was obtained via the slow diffusion of a benzene solution of Ni^{II}(OEP) into a CS₂ solution of UN@C₈₄. Single-crystal X-ray diffraction (SC-XRD) analysis unambiguously identified the molecular structure of UN@C₈₄ as UN@C₂(13)-C₈₄, as shown in Fig. 2a. The shortest distance between the Ni atom and the cage carbon was measured at 2.839(14) Å, suggesting solid π - π interactions.

The SC-XRD further revealed that the cocrystal crystallizes in the C₂/m space group and exhibits two orientations with equal occupancy (0.50) with respect to the crystallographic mirror plane, which is commonly reported in analogous EMF/Ni^{II}(OEP) systems.²⁹ For the encapsulated UN cluster, the N is fully ordered, whereas the U atom displays thermal disorder, occupying two major sites, U1 (0.205/0.5) and U2 (0.191/0.5), along with three minor sites (Fig. S2). Due to the similar occupancies of U1 and U2 sites, density functional theory (DFT)

calculations were employed to determine the optimized position of the encapsulated U atom (see below). The theoretical results indicated that U1, located close to the C₂ axis of the C₂(13)-C₈₄ cage, is the most energetically favorable site (Fig. S3), figuring out the most stable configuration for UN@C₂(13)-C₈₄.

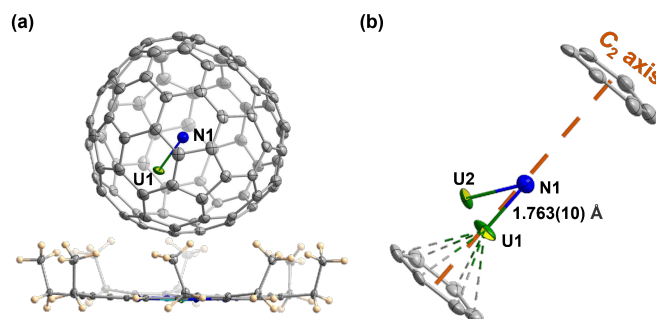


Fig. 2. (a) ORTEP drawing of UN@C₂(13)-C₈₄[Ni^{II}(OEP)] with 15% thermal ellipsoids. Only the major metal site is shown. For clarity, the solvent molecules and minor metal sites are omitted. (b) Positional relationship between the encapsulated UN cluster and the closest cage segments. The U1 and U2 sites are illustrated, and the orange dashed line represents the C₂ axis of the carbon cage.

As illustrated in Fig. 2b, U1 is located over a hexagon, with distances to the nearest cage carbons ranging from 2.411(22) to 2.745(20) Å (Table S1), comparable to those observed in UN@C₈₂ isomers. The bond length between U1 and the central nitrogen atom was measured at 1.763(10) Å. This value is significantly shorter than the U=N bond length reported for U₂N@I_h(7)-C₈₀ (1.934(3)/2.058(3) Å)² and aligns closely with the theoretical prediction (1.72 Å) for a U≡N triple bond,³⁰ confirming the presence of a terminal U≡N bond in UN@C₈₄. Moreover, this U≡N triple bond is shorter than those observed in organometallic compounds, such as (Cp^{iPr4})₂U(μ-N)B(C₆F₅)₃ (1.893(2) Å), [UN(Tren^{TIPS})] [Na(12C₄)₂] (1.825(15) Å) and [(NH₃)₈U(μ-N)Cl₂(NH₃)₃U(μ-N)U(NH₃)₈]Cl₆⁶⁺ (1.853/1.854 Å).³¹⁻³³ In addition, as a new member of the UN@C_{2n} family, the U≡N bond of UN@C₈₄ is compared to the previously reported UN@C₈₂ isomers (1.760(7) and 1.760(20) Å for UN@C_s(6)-C₈₂ and UN@C₂(5)-C₈₂, respectively).³ In addition, the lengths of the C₂(13)-C₈₄ and C₂(5)-C₈₂ cages along the C₂ axis are about 7.75 and 7.70 Å, suggesting that the nature of the encapsulated U≡N triple bond remains almost unchanged within the cages of C₈₂ and C₈₄.

As previously discussed, crystalline mates like Ni^{II}(OEP)²⁸ or decapyrrylcorannulene (DPC)³⁴ are effective in mitigating the rotational disorder of fullerene cages, thereby enhancing crystallographic quality. However, the positional disorder of encapsulated metal atoms remains an unresolved issue. This problem arises primarily from the relatively low energy barriers associated with metal-cage interactions, making it easier for the encapsulated metals to overcome these barriers and leading to difficulties in pinpointing the precise locations of the metals. For instance, in this study, resolving the major U1 and U2 sites required additional consistency between experimental crystallography and DFT calculations, highlighting the necessity of understanding the principles governing metal positions

within fullerene cages for efficiently constructing stable configurations of EMFs.

Recently, Echegoyen and colleagues proposed that encapsulated metal atoms tend to occupy symmetry planes of fullerene cages as long as these cages possess symmetry planes.³⁵ Unfortunately, this principle is inapplicable to $\text{UN@C}_2(13)\text{-C}_{84}$, as this structure features only a two-fold axis without symmetry planes. Nevertheless, our structural analyses reveal that the major U1 site is positioned close to this two-fold axis, while the U2 site deviates from it (Fig. 2b). This phenomenon appears to happen among other monometallic clusterfullerenes containing the $\text{C}_2(13)\text{-C}_{84}$ cage, such as $\text{YCN@C}_2(13)\text{-C}_{84}$ and $\text{DyCN@C}_2(13)\text{-C}_{84}$,³⁶ as shown in Fig. 3. A similar trend is observed in $\text{UN@C}_2(5)\text{-C}_{82}$ and other monometallic EMFs bearing the $\text{C}_2(5)\text{-C}_{82}$ cage like $\text{ThC}_2\text{@C}_2(5)\text{-C}_{82}$ and $\text{DyCN@C}_2(5)\text{-C}_{82}$,^{3, 37, 38} where the major metal site also closely aligns with the two-fold axis. Remarkably, for monometallic clusterfullerenes exhibiting both symmetry planes and axes (e.g., C_{2v} symmetry), the encapsulated metal atoms preferentially align not only with the symmetry plane but also with the symmetry axis of the fullerene cage (Fig. S4).^{36, 39-42} These results underscore a trend that, in monometallic EMFs, the encapsulated metal atom tends to align with the symmetry elements of the fullerene cage, maintaining the overall EMF molecule symmetrical. The favored position of the metal in these monometallic clusterfullerenes can be understood within an ionic model of interaction (see below).

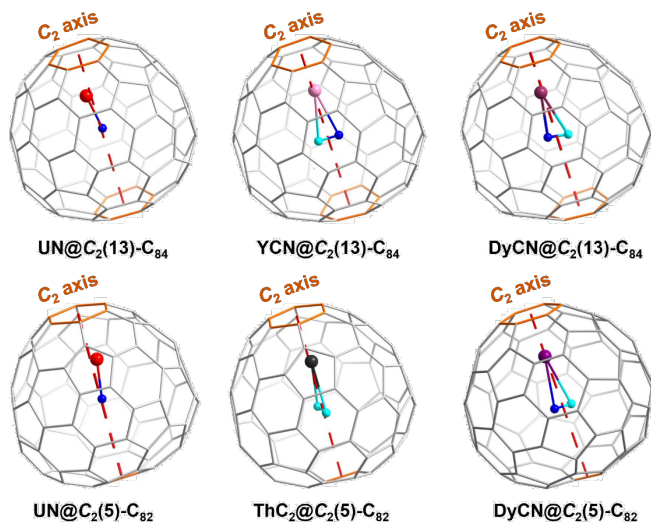


Fig. 3. Positional relationship between the encapsulated metal atom of mononuclear clusterfullerenes with the C_2 axis of the C_2 -symmetry carbon cages. Examples include $\text{UN@C}_2(13)\text{-C}_{84}$, $\text{YCN@C}_2(13)\text{-C}_{84}$, $\text{DyCN@C}_2(13)\text{-C}_{84}$, $\text{UN@C}_2(5)\text{-C}_{82}$, $\text{ThC}_2\text{@C}_2(5)\text{-C}_{82}$, and $\text{DyCN@C}_2(5)\text{-C}_{82}$. The orange dashed lines represent the C_2 axis of the carbon cages.

Spectroscopic characterization of $\text{UN@C}_2(13)\text{-C}_{84}$.

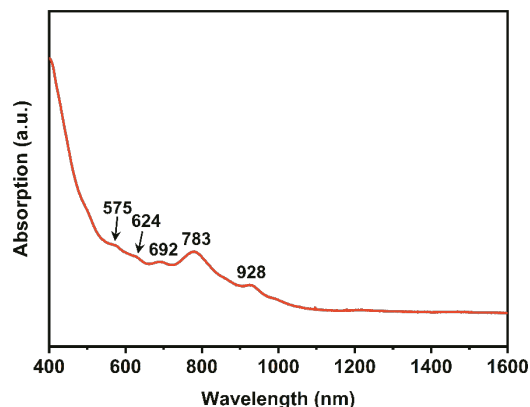


Fig. 4. The UV-vis-NIR absorption spectrum of $\text{UN@C}_2(13)\text{-C}_{84}$.

The UV-vis-NIR absorption spectrum of $\text{UN@C}_2(13)\text{-C}_{84}$, as shown in Fig. 4, displays three distinct peaks at 692, 783, and 928 nm, along with two shoulder peaks at 575 and 624 nm. These spectral features are strikingly similar to those observed in cyanide clusterfullerenes $\text{MCN@C}_2(13)\text{-C}_{84}$ ($\text{M} = \text{Y, Tb, Dy}$).³⁶ This observation is consistent with the crystallographic identification of the $\text{C}_2(13)\text{-C}_{84}$ cage, as the spectral profile is primarily dominated by the electronic structure of the carbon cage. In addition, the spectral resemblance suggests a two-electron transfer from the UN cluster to the carbon cage, consistent with the divalent nature of the cyanide clusterfullerenes. Previous studies have well identified the electronic configurations of UN@C_{82} isomers as $[\text{U}^{\text{VN}}]^{2+}\text{@C}_{82}$.³ Therefore, it is reasonable to propose that the UN@C_{2n} family features a two-electron transfer mechanism from the UN cluster to the carbon cage.

Computational analysis of $\text{UN@C}_2(13)\text{-C}_{84}$.

A study of all crystallographic positions was conducted using DFT geometry optimizations (PBE0/TZP level, see Computational Details). Position U1 has been verified as the energetically most favorable site. U1 is near an *s*-indacene motif (Fig. S5), and it is aligned with the C_2 axis. The optimizations of positions U2, U3, and U4 all converged to the same minimum as U1, displaying similar geometries and almost same energies. In contrast, position U5 adopts a pyracilene pattern offset from the C_2 axis and lies 12 kcal·mol⁻¹ above the U1 position.

For comparative purposes, additional positions, U_{SUM} , U_{THJ} , and U_{IND} , were analyzed, all of which represent local minima but are higher in energy than U1 (Fig. S5). While sumanene motifs typically serve as stable binding sites for actinides in mono-actinidofullerenes, the U_{SUM} position is merely a local minimum with an energy of 13.0 kcal·mol⁻¹ above U1, as shown in Table 1. The U_{THJ} position places the U atom in a triple-hexagon junction (THJ) pattern. Although this site is relatively close in energy (3.2 kcal·mol⁻¹) and location to U1, it represents a distinct binding environment, further offset from the C_2 axis. The U_{IND} position situates the U atom over an *s*-indacene pattern on the opposite side of the cage relative to U1. Despite sharing a similar local motif and C_2 axis, U_{IND} has a significantly higher energy at 33.3 kcal·mol⁻¹.

Table 1. Relative energies, distances, and U spin densities for the optimized structures of $\text{UN@C}_2(13)\text{-C}_{84}$.^a

	U1	U5	U _{SUM}	U _{THJ}	U _{IND}
ΔE	0.0	11.9	13.0	3.2	33.3
d(U–N)	1.765	1.742	1.744	1.740	1.738
d(U–C) ^b	2.513	2.412	2.488	2.411	2.501
d(N–C) ^b	3.881	3.745	3.585	3.848	3.791
$\rho_{\text{spin}}(\text{U})$	1.05	0.18	0.09	0.79	0.54

^a Relative energies in kcal mol⁻¹, distances in Å and Bader spin densities in e.

^b Shortest U–C and N–C distances.

From the molecular orbital analysis (Fig. S6), we confirm that the electronic structure of UN@C₂(13)-C₈₄ can be described as [U^{VI}N]²⁺@C₈₄²⁻, as found for UN@C₈₂.³ The unpaired electron is localized on U (f¹) and there is a triple U≡N bond. Interestingly, the higher-energy positions U5, U_{SUM}, and U_{IND} exhibit a different oxidation state for U. Instead of U^V as seen in position U1, the higher-energy sites U5 and U_{SUM} shift the spin density to the cage, resulting in a U^{VI} oxidation state, as in U@C₂₇B.⁴³ Site U_{IND} shows an intermediate behavior (spin density on U is 0.54).

To better understand why U is placed in the symmetry axis in these monometallic clusterfullerenes, we have examined the molecular electrostatic potential in the interior of the C₂(13)-C₈₄²⁻ and C₂(5)-C₈₄²⁻ dianionic cages (Fig. S7). We have found that the region with most negative values of the electrostatic potential (nucleophilic region) is indeed the position preferred by uranium, which lies along the symmetry axis of the cage, as found previously for monometallic M³⁺@C_{2v}(9)-C₈₂³⁻ by Kobayashi and Nagase.⁴⁴

Conclusions

In this work, we report a novel mononuclear clusterfullerene, UN@C₂(13)-C₈₄, and provide valuable insights into the structural and electronic properties of this unique EMF family. Single-crystal X-ray diffraction analysis identified the encapsulated diatomic UN cluster, one of the smallest known clusters, featuring a short U≡N triple bond with a measured length of 1.763(10) Å. Notably, this bond length remains nearly unchanged when compared to previously reported UN@C₈₂ isomers, highlighting the intrinsic nature of the encapsulated U≡N triple bond irrespective of cage size. UV-vis-NIR spectroscopy and analysis of the molecular orbitals revealed a two-electron transfer from the UN cluster to the carbon cage, confirming the electronic structure of UN@C₂(13)-C₈₄ as [UN]²⁺@[C₂(13)-C₈₄]²⁻. The crystallographic position with the highest occupation, U1, in the C₂ axis, is found as the lowest-energy position of U inside the cage. Moreover, combined with the previous studies, we found that in monometallic EMFs, the encapsulated metal atom preferentially aligns with the symmetry elements of the fullerene cage, including both symmetry planes and axes, thereby maintaining molecular symmetry. These findings not only enhance our understanding of the positional principles governing encapsulated metal atoms but also provide critical guidance for crystallographic refinement, structural prediction, and further exploration of novel EMFs.

Experimental

Spectroscopic Studies.

The positive-ion mode matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) (Bruker, Germany) was employed for the mass identification of UN@C₂(13)-C₈₄. The UV-vis-NIR spectrum of the purified UN@C₂(13)-C₈₄ was measured in CS₂ solution with a Cary 5000 UV-vis-NIR spectrophotometer (Agilent, USA).

X-ray Crystallographic Study.

The black block crystal of UN@C₂(13)-C₈₄ was obtained by slow diffusion of a CS₂ solution of UN@C₂(13)-C₈₄ into a benzene solution of [Ni^{II}(OEP)]. The crystallographic data of UN@C₂(13)-C₈₄ were collected at 120 K on a diffractometer (APEX II; Bruker D8 Venture) equipped with a CCD collector. The data were reduced with the program APEX 3. The structures were solved and refined using the Olex2 software⁴⁵ with SHELXT-2014 by the intrinsic phasing method and SHELXL-2018 by full-matrix least-squares based on F^2 .⁴⁶

Computational Details.

DFT calculations were carried out with the ADF 2019 package⁴⁷ using PBE0 exchange-correlation functional in combination with Slater TZP basis sets to describe the valence electrons of U, C, and N.⁴⁸ Frozen cores were described by means of single Slater functions, consisting of the 1s shell for C and N, 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.⁴⁹ Localized molecular orbitals were obtained with Pipek-Mezey method.⁵⁰ A data set collection of computational results is available in the ioChem-BD repository and can be accessed via <https://iochem-bd.urv.es/browse/edit-collection/100/2062/836e3b7f0fd78144af4f3d08>.⁵¹

Author contributions

Q.M., Y.R., and Y.S. contributed equally to this work. N.C., A.R.-F., and Y.-R.Y. handled the project administration; Q.M. and Y.S. performed the synthesis and isolation. Y.R., J.M.P., and A.R.-F. performed the DFT calculations; Y.-R.Y. grew the single crystals and solved the crystallographic data. Q.W., and Y.S. carried out the UV-vis-NIR characterization studies. Y.-R.Y. and Q.M. wrote the original draft; N.C., Y.-R.Y., J.M.P., and A.R.-F. reviewed the draft. All authors discussed the results.

Conflicts of interest

There are no conflicts to declare.

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