An Improbable Monometallic Cluster Entrapped in a Popular Fullerene Cage: YCN@Cs(6)-C$_{82}$

Shangfeng Yang$^{1}$, Chuanbao Chen$^{1}$, Fupin Liu$^{1}$, Yunpeng Xie$^{2}$, Fengyu Li$^{3}$, Mingzhi Jiao$^{1}$, Mitsuaki Suzuki$^{4}$, Tao Wei$^{1}$, Song Wang$^{1}$, Zhongfang Chen$^{3}$, Xing Lu$^{2,4}$ & Takeshi Akasaka$^{4}$

$^{1}$Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Materials for Energy Conversion & Department of Materials Science and Engineering, University of Science and Technology of China (USTC), Hefei 230026, China, $^{2}$State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, China, $^{3}$Department of Chemistry, Institute for Functional Nanomaterials, University of Puerto Rico, San Juan, Puerto Rico 00931, USA, $^{4}$Life Science Center of Tsukuba Advanced Research Alliance, University of Tsukuba, Ibaraki 305-8577, Japan.

Since the first proposal that fullerenes are capable of hosting atoms, ions, or clusters by the late Smalley in 1985, tremendous examples of endohedral metallofullerenes (EMFs) have been reported. Breaking the dogma that monometallofullerenes (mono-EMFs) always exist in the form of M@C$_{2n}$ while clusterfullerenes always require multiple (two to four) metal cations to stabilize a cluster that is unstable as a single moiety, here we show an unprecedented monometallic endohedral clusterfullerene entrapping an yttrium cyanide cluster inside a popular C$_{82}$ cage—YCN@Cs(6)-C$_{82}$. X-ray crystallography and $^{13}$C NMR characterization unambiguously determine the cage symmetry and the endohedral cyanide structure, unexpectedly revealing that the entrapped YCN cluster is triangular. The unprecedented monometallic clusterfullerene structure unveiled by YCN@Cs(6)-C$_{82}$ opens up a new avenue for stabilizing a cluster by a single metal cation within a carbon cage, and will surely stimulate further studies on the stability and formation mechanism of EMFs.

The spherical empty interior of fullerene triggers intuitively the idea of entrapping atoms into the cage so as to modulate the molecular and electronic properties of fullerenes$^{1-3}$. Endohedral metallofullerenes (EMFs) thus formed have now been revealed to host a variety of species inside the carbon cage, including atoms, ions, or clusters$^{2-4}$. EMFs exhibit unique electronic properties as a consequence of charge transfer and electrostatic interactions between the entrapped species and the carbon cage, enabling their potential applications in electronics and biomedicine and so on$^{2-3}$. As the first and representative conventional EMFs, monometallofullerenes (mono-EMFs) have been extensively investigated in the early study of EMFs, and nowadays it has been commonly accepted that mono-EMFs always exist in the form of M@C$_{2n}$,$^{1-5}$ Among them, La@C$_{82}$ is the first stable monometallofullerene isolated by Smalley et al. in 1991$^{12}$, featuring a three-electron transfer from La to the C$_{82}$ cage$^{1-9}$. Later on, a wealth of other mono-EMFs M@C$_{82}$ (M = Sc, Y, La, Lu, Ca, Mg) have been successfully isolated, featuring the transfer of two or three electrons from the entrapped metal ion to the carbon cage, which is sufficient for the mutual stabilization of the entrapped metal cation and carbon cage that are not even available in their empty form$^{1-6}$. Thus, it seems improbable to entrap a single metal cation in the form other than M@C$_{2n}$.

During the past decade the family of EMFs was significantly enlarged by the clusterfullerenes especially metal nitride clusterfullerenes$^{6-11}$. With the isolation and identification of Sc$_{2}$N@C$_{80}$ as the first metal nitride clusterfullerene in 1999 (ref. 9), the concept of stabilizing multiple metal ions by cluster formation with nonmetal atoms has brought about the consequent discovery of other five types of clusterfullerenes, including metal carbide clusterfullerenes (M$_{3}$C@C$_{82}$)$^{12-14}$, metal hydrocarbon clusterfullerenes (Sc$_{6}$CH@C$_{80}$)$^{14}$, metal oxide clusterfullerenes (e.g., Sc$_{2}$O$_{2}$@C$_{80}$)$^{15}$, metal sulfide clusterfullerenes (e.g., Sc$_{4}$S@C$_{80}$)$^{16}$ and metal carbonitride clusterfullerene (Sc$_{4}$NC@C$_{80}$)$^{17}$. Interestingly, upon extending the number of entrapped metal ions within endohedral fullerenes, usually the supposed multimetallofullerenes (M$_{n}$@C$_{2n}$ + 2) turn out to be metal carbide clusterfullerenes (M$_{3}$C@C$_{82}$) instead$^{12-14}$. Noteworthy, for all the reported six types of clusterfullerenes, multiple (two to four) metal cations are always required for the metal clusters, which are highly charged and thus unstable as a single molecule. As a consequence, an intriguing question is whether a single metal cation is able to stabilize a cluster in the carbon cage or not.
Herein, we report the discovery of an unprecedented stable monometallic clusterfullerene entrapping an yttrium cyanide cluster inside a popular C_{62} cage – YCN@C_{6(6)}-C_{62}. The synthesis, isolation and unambiguous structural determination by single crystal X-ray crystallography and $^{13}$C NMR characterization of YCN@C_{6(6)}-C_{62} are elaborately presented. The electronic structures of YCN@C_{6(6)}-C_{62} have been systematically studied by various spectroscopies, revealing the intriguing feature of this brand-new entrant of EMF family.

**Results**

**Synthesis, isolation and structural elucidation of YCN@C_{62}**. Soot containing YCN@C_{62} was synthesized by the modified Kratschmer-Huffman DC-arc discharging method using a 1:1 mixture of Y_2O_3 and TiO_2 as the raw material under 400 mbar He and 10 mbar N_2 (refs. 19,20), and the introduction of TiO_2 in the raw mixture is found to be essential for the formation of YCN@C_{62}. Isolation of YCN@C_{62} (~10 mg) was accomplished by five-step HPLC, and the high purity of the isolated YCN@C_{62} (~99.3%) is assured by both the recycling HPLC and laser desorption time-of-flight (LD-TOF) mass spectroscopic (MS) analysis (Supplementary Information S1–S2).

The molecular structure of YCN@C_{6(6)}-C_{62} is unambiguously determined by single crystal X-ray diffraction crystallography performed on a high-quality single crystal of YCN@C_{62} with Ni(OEP) (OEP = octaethylporphyrin), which was obtained by diffusing a benzene solution of YCN@C_{62} into a chloroform solution of Ni(OEP)Cl (occupancy: 0.50, 0.25, 0.19, 0.03, and 0.03 for Y1, Y2, Y3, Y4, and Y5, respectively). In contrast, the CN unit is fully ordered which is found to be essential for the formation of YCN@C_{62}. Isolation of YCN@C_{62} (~10 mg) was accomplished by five-step HPLC, and the high purity of the isolated YCN@C_{62} (~99.3%) is assured by both the recycling HPLC and laser desorption time-of-flight (LD-TOF) mass spectroscopic (MS) analysis (Supplementary Information S1–S2).

![Figure 1](drawing.png)

**Figure 1** Drawing of the crystallographically determined structure of YCN@C_{6(6)}-C_{62} with the major C_{62} cage (0.55 occupancy) and the most abundant yttrium location (0.50 occupancy), and its relation to the Ni(OEP) molecule. Thermal ellipsoids are set at 30% probability level. Solvent molecules, the minor cage and minor metal positions are omitted for clarity. Inset shows the triangular configuration of the internal YCN cluster to ensure a clear visualization. Red: Y; Blue: N; Grey: C.

The electronic structures of YCN@C_{6(6)}-C_{62} have been systematically studied by various spectroscopies, revealing the intriguing feature of this brand-new entrant of EMF family.

For the endohedral YCN moiety, both N and C atoms are located near the cage center, whereas the metal is located between the CN unit and one side of the cage. As a result, the entrapped YCN cluster is triangular, but not linear (see inset of Fig. 1). For the major yttrium atom site with a 0.50 occupancy (Y1), the Y1-N and Y1-C bond distances are 2.383 Å and 2.484 Å, respectively. The shorter bond distance of Y1-N compared to Y1-C suggests a relatively stronger covalent bond between Y and N atoms, which is due to the larger electronegativity of N atom compared to C atom. Note that the determined N-C bond length, 0.935 Å, is smaller than that reported for Sc_3NC@C_{80} (1.193 Å) and those of the C-N triplet bonds in traditional inorganic metal cyanide compounds or cyano coordination complexes (e.g. 1.14 – 1.17 Å for AuCN and [Au(CN)_2]) and nitride compounds (e.g. 1.157 Å for CH_3CN). The unusually short N–C bond indicates an extraordinary bonding nature in the YCN cluster upon entrapped in carbon cage. Interestingly, the shrinking of the C–N bond found in the present study is similar to that found for the C–C bond in the metal carbide clusterfullerenes such as Gd_2C_2@D_3h(85)-C_{62}, Sc_2C_2@C_{8(6)}(8)-C_{62}(Ad), and Sc_2C_2@H_2-C_{60}, in which the X-ray crystallographically determined C–C bond lengths (1.04, 1.107, 1.11 Å respectively) are shorter than those predicted by theoretical computations and the C–C triple bonds in alkyne compounds (1.21 Å). The stronger bonding between Y and CN atoms due to the space confinement of the interior of the carbon cage might be responsible for such a shrinking phenomenon. Besides, the triangular structure of YCN cluster is rather intriguing since it is different from the linear structures commonly found in traditional metal cyanide complexes. Recently, Dorn et al. revealed that the YsC2 cluster tends to adopt a linear structure if the interior of the fullerene cage is sufficiently spacious whereas a constrained “butterfly” structure is adopted upon decreasing the size of a fullerene cage. However, in our present case of YCN@C_{6(6)}-C_{62}, a linear structure is less favoured than the triangular conformation although the space is obviously enough for both, and this is presumably due to the conjunct effects of the strong coordination ability of the yttrium metal and the confining effect of the cage. Such an unprecedented triangular cyanide cluster configuration provides a new concept into modern coordination chemistry, specifically with the charged monometallic complexes inside a confined nanospace.

$^{13}$C NMR spectroscopy further corroborates the determined cyanide cluster structure and the cage symmetry of YCN@C_{6(6)}-C_{62} as well (Fig. 2). The apparent 44 signals in the aromatic region (120–155 ppm), in which 38 lines are in full intensity and 6 lines are in half intensity, point to either a C_C symmetric C_{62} cage instead of any C_{64} isomer or the isomeric carbide cluster azafullerene structure YC_2@C_{48}N (Supplementary Information S4). More convincingly, the $^{13}$C NMR signal of the internal CN unit is observed at δ = 292.37 ppm with the intensity being comparable to those of 6 cage carbon atoms on the mirror plane. This value is obviously downfield shifted as compared with those of the analogous carbide clusterfullerenes with the same cage (e.g. 244.4 ppm for Sc_2C_2@C_{6(6)}-C_{62}, 256.2 ppm for Y_2C_2@C_{6(6)}-C_{62}). Besides, compared to the entrapped NC moiety of the reported metal carbonitrile clusterfullerenes Sc_3NC@C_{60} for which the experimental $^{13}$C NMR signal was unknown, the simulated chemical shift is 306.6 ppm, the chemical shift of the internal CN-units of YCN@C_{6(6)}-C_{62} might be different since the formal charge state of the internal CN-units of YCN@C_{6(6)}-C_{62} is different to that of the entrapped NC moiety of Sc_3NC@C_{60} as discussed below.

A more detailed analysis of the $^{13}$C NMR results of YCN@C_{62} can further exclude the possibility of the isomeric carbide cluster structure with an azafullerene cage, namely YC_2@C_{48}N, for which two substitution sites of nitrogen atom in the C_{62} cage are possible: 1) if
the nitrogen atom substitutes any of the 6 carbon atoms on the mirror plane, 43 lines for the sp² carbon atoms (38 lines with full intensity + 5 lines with 1/2 intensity) plus 1 or 2 line(s) in the much lower field contributed from the encaged C₂ moiety would be observed; 2) if the nitrogen atom substitutes any of the 76 carbon atoms apart from the mirror plane, the whole molecule would exhibit as many as 81 lines of the carbon cage because of the lowered symmetry. Therefore, the observed ¹³C NMR spectrum of our new endohedral compound rules out the possible structure of YC₂@C₈₁N. In addition, according to our DFT computations, the alternative most stable structure of YC₂@C₈₁N is remarkably energy-unfavorable. Among all the considered YC₂@C₈₁N isomers, those with the nitrogen atom substituting any of the 6 carbon atoms on the mirror plane of the C₂-C₈₂ cage (i.e., the C₈₁N cages remain the C₃₅ symmetry) are

80 kcal/mol higher in energy than the lowest-energy YCN@C₈₂ structure, while others are at least 20.2 kcal/mol higher in energy.

Electronic structure of YCN@C₈₂. The electronic structure of YCN@C₈₂ was studied by UV-vis-NIR, X-ray photoemission spectroscopy (XPS), electron spin resonance (ESR) spectroscopy and electrochemistry (Supplementary Information S5-S7). The XPS result shows that the Y atom takes a valency of +3 in YCN@C₈₂ (Supplementary Information S6). Room-temperature ESR spectroscopic measurement reveals that YCN@C₈₂ is ESR-silent. This is dramatically different to the analogous C₈₂-based mono-EMFs entrapping a trivalent Group-III metal M@C₈₂ (M = Sc, Y, La etc.), which are typically ESR-active due to their open-shell electronic structures. Instead, divalent metal-based C₈₂ mono-EMFs, such as Yb@C₈₂, Ca@C₈₂ and Sm@C₈₂, are usually ESR-silent owing to their closed-shell structures. The similarity of the ESR behaviour of YCN@C₈₂ to those of divalent metal-based C₈₂ mono-EMFs suggests a similar two-electron transfer. Thus, an electronic configuration of [Y⁺⁺(CN)⁻]⁺@[C₈₂]⁻⁻ can be proposed, for which the (CN)⁻ moiety typically existing in the traditional metal cyanide inorganic compounds is obviously different to the [NC]⁻⁻ unit within the reported [Sc⁺⁺]⁺[NC]⁻⁻@[C₈₀]⁻⁻ (refs. 17, 18). Indeed, the proposed electronic configuration of [Y⁺⁺(CN)⁻]⁺@[C₈₂]⁻⁻ is confirmed by the cyclic voltammetric study. YCN@C₈₂ exhibits one reversible oxidation step at +0.56 V and four reversible reduction steps at −0.59, −0.84, −1.76, and −1.92 V versus Fc/Fc⁺, respectively (Fig. 3). Interestingly, the first two reduction steps as well as the last two reduction steps are mutually close, whereas there is an abrupt large separation (0.92 V) between the second and third reduction steps (see also Supplementary Information S8). Such a reduction behaviour of YCN@C₈₂ highly resembles that of the reported Yb@C₆₋₆-C₈₂, for which one (quasi-) reversible oxidation step and four reversible reduction steps specifically with a comparable large separation (0.89 V) between the second and third reduction steps were observed. Again, such a high resemblance of the reduction behaviour of YCN@C₆₋₆-C₈₂ to that of Yb⁺⁺@[C₆₋₆-C₈₂]⁻⁻ confirms the proposed electronic configuration of [Y⁺⁺(CN)⁻]⁺@[C₈₂]⁻⁻ featuring a formal two-electron transfer from the entrapped YCN moiety to C₈₂ cage.

Figure 2 | ¹³C NMR (125 MHz) spectrum of YCN@C₈₂ showing a 38 × 2C (labeled by blue numbers), 6 × 1C (labeled by red numbers) pattern for the sp² carbon atoms of the cage. The filled triangle marks the ¹³C nuclei signal of the internal YCN cluster, and the asterisk labels an unidentified impurity.

Figure 3 | Cyclic voltammogram of YCN@C₈₂ in o-dichlorobenzene (o-DCB) solution with ferrocene (Fc) as the internal standard and tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. Scan rate: 100 mV/s. Each redox step is marked with a number and a solid dot to aid comparison. The small peak at around −1.50 V is due to an unknown impurity. The asterisk labels the oxidation peak of ferrocene.
Discussion

It has been commonly believed that monometallofullerenes (mono-EMFs) always exist as a simple form of M@C_{2n} and clusterfullerenes always require multiple (two to four) metal cations to stabilize a cluster that is unstable as a single moiety. Now we break these dogmas by presenting the first example of monometallomeric clusterfullerene entrapping an improbable yttrium cyanide cluster — YCN@C_{82}. X-ray crystallography and \textsuperscript{13}C NMR spectroscopic study assure the elucidation of its cage isomeric structure of C_{6}(C_{6})_{28}, which entraps an unprecedented triangular YCN cluster. A closed-shell electronic configuration of [Y\textsuperscript{3+}(CN)\textsuperscript{-}]\textsuperscript{2-}@C_{82} is established on the basis of XPS, ESR and cyclic voltammetric studies. The existence of such an improbable monometallomeric cyanide clusterfullerene portends the possibility of creating novel EMFs entrapping other types of clusters. Our successful synthesis and structural elucidation of the first monometallomeric clusterfullerene mark a breakthrough for fullerene research and will stimulate further studies on the stability and formation mechanism of EMFs, both theoretically and experimentally.

Methods

Synthesis and isolation. YCN@C_{82} was synthesized in a modified Kratschmer-Huffman generator by vaporizing composite graphite rods (Ø = 150 mm, containing a mixture of C\textsubscript{60} (99.999%), TiO\textsubscript{2} (99.999%) and graphite powder with a molar ratio of 1 : 1.15 (Y : Ti : C) with the addition of 10 mbar N\textsubscript{2} into 400 mbar He as described previously\textsuperscript{44}. For comparison, a reference synthesis by using a mixture of Y_{2}O\textsubscript{3} and graphite powder (1 : 1.5, without involvement of TiO\textsubscript{2}) was also carried out. The as-produced soot was Soxhlet-extracted by CS\textsubscript{2} for 24 h, and the resulting brown-yellow solution was distilled to remove CS\textsubscript{2} and then immediately redissolved in toluene (200 ml) and subsequently passed through a 0.2 mm Teflon filter (Sartorius AG, Germany) for HPLC separation. The isolation of YCN@C_{82} was performed by five-step HPLC as described in details in Supplemental Information S1. The purity of the isolated YCN@C_{82} was further checked by both the recycling HPLC and laser desorption time-of-flight (LD-TOF) mass spectroscopic (MS) analysis running both in positive and negative ion modes (Bilieux III, Bruker Daltonics Inc., Germany).

Spectroscopic characterizations. UV-vis-NIR spectrum of YCN@C_{82} dissolved in toluene was recorded on a UV-vis-NIR 3600 spectrometer (Shimadzu, Japan) using a quartz cell of 1 mm layer thickness and 1 nm resolution. For XPS measurements, thin films of YCN@C_{82}, drop-coated onto KBr single crystal disks were transferred under a pressure at 340 K for 24 h and stored in glove box films of YCN@C_{82} drop-coated onto KBr single crystal disks were transferred under a pressure at 340 K for 24 h and stored in glove box.

Electrochemical study. Electrochemical study of YCN@C_{82} was performed in a dichlorobenzene (o-DCB, anhydrous, 99%, Aldrich). The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBP\textsubscript{6}, puriss. electrochemical grade, Fluka) which was dried under a pressure at 340 K for 24 h and stored in glove box prior to use. Cyclic voltammmogram experiments were performed with a CHI 660 potentiostat (CHI Instrument, USA) at room temperature in a glove box. A standard three-electrode arrangement of a platinum (Pt) wire as working electrode, a platinum coil as counter electrode, and a silver wire as a pseudo-reference electrode was used. In a comparison experiment, ferrocene (Fc) was added as the internal standard and all potentials are referred to the Fc/Fc\textsuperscript{+} couple.

X-ray crystallographic study. Crystal growth for YCN@C_{82} was carried out at 107 K on a Gemini S Ultra (Oxford Diffraction Ltd., UK) using a 92 mm Sapphire CCD image plate diffractometer (Oxford diffraction Ltd., UK) with a 92 mm Sapphire CCD image plate. YCN@C_{82} was synthesized by the reaction of a Rb salt of the cyanide (prepared from Na\textsubscript{2}CN) and a mixture of C\textsubscript{60} and TiO\textsubscript{2} (in a 1 : 1.15 molar ratio of Y : Ti : C) and redissolving the as-produced soot in toluene (200 ml) and passing through a 0.2 mm Teflon filter (Sartorius AG, Germany) for HPLC separation. The isolated YCN@C_{82} was performed by five-step HPLC as described in details in Supplemental Information S1. The purity of the isolated YCN@C_{82} was further checked by both the recycling HPLC and laser desorption time-of-flight (LD-TOF) mass spectroscopic (MS) analysis running both in positive and negative ion modes (Bilieux III, Bruker Daltonics Inc., Germany). The \textsuperscript{13}C NMR spectroscopic study was performed at 125 MHz in an Advance 500 spectrometer (Bruker, Germany) at room temperature in carbon disulfide with d\textsubscript{6}-dichloroethane as an external lock.

Electrochemical study. Electrochemical study of YCN@C_{82} was performed in o-dichlorobenzene (o-DCB, anhydrous, 99%, Aldrich). The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBP\textsubscript{6}, puriss. electrochemical grade, Fluka) which was dried under a pressure at 340 K for 24 h and stored in glove box prior to use. Cyclic voltammmogram experiments were performed with a CHI 660 potentiostat (CHI Instrument, USA) at room temperature in a glove box. A standard three-electrode arrangement of a platinum (Pt) wire as working electrode, a platinum coil as counter electrode, and a silver wire as a pseudo-reference electrode was used. In a comparison experiment, ferrocene (Fc) was added as the internal standard and all potentials are referred to the Fc/Fc\textsuperscript{+} couple.

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Author contributions
S.F.Y., X. L. and Z. F. C. conceived and designed the experiments, S.F.Y., X. L., Z. F. C. and T. A. co-wrote the paper, C. B. C. and M. Z. J. conducted the synthesis, F. P. L. accomplished the crystal growth and diffraction data collection, X. L. carried out the NMR measurement and analyzed the data, T. W. performed the isolation, C. B. C. and F. P. L. made the spectroscopic measurements, S. W. carried out the electrochemical study, F. Y. L. and Z. F. C. performed the computational work, Y. P. X., M. S., X. L. and T. A. participated in the X-ray structure analysis. All authors discussed the results and commented on the manuscript.

Additional information
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Competing financial interests: The authors declare no competing financial interests.

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