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An *Improbable* Monometallic Cluster Entrapped in a Popular Fullerene Cage: YCN@C_s(6)-C_{82}

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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@C_s(6)-C_{82}. X-ray crystallography and ^{13}C NMR characterization unambiguously determine the cage symmetry and the endohedal cyanide structure, unexpectedly revealing that the entrapped YCN cluster is triangular. The unprecedented monometallic clusterfullerene structure unveiled by YCN@C_s(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[1,2]. Endohedral metallofullerenes (EMFs) thus formed have now been revealed to host a variety of species inside the carbon cage, including atoms, ions, or clusters[2–8]. 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[2–8]. As the first and representative conventional EMFs, monometallofullerenes (mono-EMFs) had 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 monometallofullerenes isolated by Smalley et al in 1991[2], featuring a three-electron transfer from La to the C_{82} cage[1–3]. Later on, a wealth of other mono-EMFs M@C_{2n} (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[8–11]. With the isolation and identification of $Sc_3N@C_{80}$ 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[8], including metal carbide clusterfullerenes ($M_xC_2@C_{2n}$)[12,13], metal hydrocarbon clusterfullerenes ($Sc_3CH@C_{80}$)[14], metal oxide clusterfullerenes (e.g., $Sc_4O_2@C_{80}$)[15], metal sulfide clusterfullerenes (e.g., $Sc_2S@C_{82}$)[16] and metal carbonitride clusterfullerene ($Sc_3NC@C_{80}$)[17]. Interestingly, upon extending the number of entrapped metal ions within endohedral fullerenes, usually the supposed multimetallofullerenes ($M_x@C_{2n+2}$) turn out to be metal carbide clusterfullerenes ($M_xC_2@C_{2n}$) instead[12,13]. 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_{82} cage – YCN@C_s(6)-C_{82}. The synthesis, isolation and unambiguous structural determination by single crystal X-ray crystallography and ^{13}C NMR characterization of YCN@C_s(6)-C_{82} are elaborately presented. The electronic structures of YCN@C_s(6)-C_{82} 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_{82}. Soot containing YCN@C_{82} was synthesized by the modified Krätschmer-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_{82}. Isolation of YCN@C_{82} (~10 mg) was accomplished by five-step HPLC, and the high purity of the isolated YCN@C_{82} (≧99.5%) 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_s(6)-C_{82} is unambiguously determined by single crystal X-ray diffraction crystallography performed on a high-quality cocrystal of YCN@C_{82} with Ni^{II}(OEP) (OEP = octaethylporphyrin), which was obtained by diffusing a benzene solution of YCN@C_{82} into a chloroform solution of Ni^{II}(OEP)[1–9,21]. The asymmetric unit cell of the cocrystal YCN@C_{82}·Ni^{II}(OEP)·$1.73C_6H_6$·$1.27CHCl_3$ contains an entire molecule of both YCN@C_{82} and Ni^{II}(OEP), while the cavities are filled with disordered solvent molecules. Although Ni^{II}(OEP) is fully ordered, two disordered cage orientations with respective occupancies of 0.55 and 0.45 are present and as many as five metal positions are distinguishable (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 located near the center of the fullerene cage (Supplementary Information S3). Fig. 1 shows the X-ray structure of YCN@C_{82}·Ni^{II}(OEP)·$1.73C_6H_6$·$1.27CHCl_3$ involving only the major cage (0.55 occupancy), the major yttrium (0.50 occupancy) and the CN unit (1.0 occupancy) and its relation to the Ni^{II}(OEP) molecule, and all solven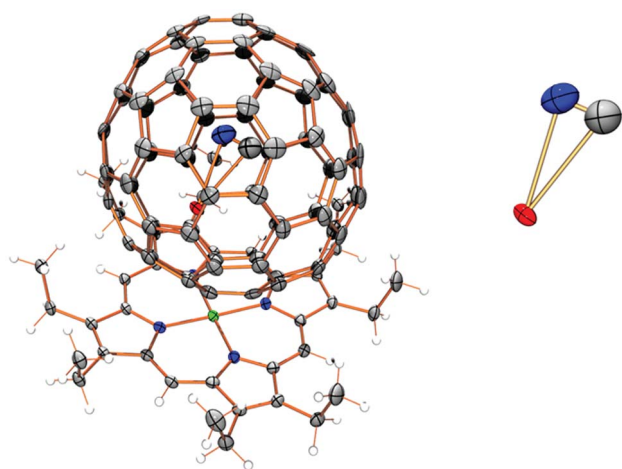t molecules were omitted for clarity. It clearly reveals the presence of an 82-atom carbon cage with C_s(6) symmetry instead of an 84-atom cage, thus ruling out the possibility of the endohedral azafullerene structure Y@$C_{83}N$.

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)[17] 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 $[Au(CN)_2]^-$)[22] and nitrile compounds (e.g. 1.157 Å for CH_3CN)[23]. 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 $Gd_2C_2@D_3(85)$-C_{92}, $Sc_2C_2@C_{3v}(8)$-C_{82}(Ad), and $Sc_3C_2@I_h$-C_{80}, in which the X-ray crystallographically determined C-C bond lengths (1.04, 1.107, 1.11 Å respectively[13,24,25]) are shorter than those predicted by theoretical computations and the C-C triplet bonds in alkyne compounds (1.21 Å). The stronger bonding between Y and C/N 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[22,23]. Recently, Dorn et al. revealed that the Y_2C_2 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[26]. However, in our present case of YCN@C_s(6)-C_{82}, 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_s(6)-C_{82} 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_s-symmetric C_{82} cage instead of any C_{84}-isomer or the isomeric carbide cluster azafullerene structure $YC_2@C_{81}N$ (Supplementary Information S4)[27]. 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 the 6 cage carbon atoms on the mirror plane. This value is obviously downfield shifted as compared with those of the analogues carbide clusterfullerenes with the same cage (e.g. 244.4 ppm for $Sc_2C_2@C_s$(6)-C_{82}[28], 256.2 ppm for $Y_2C_2@C_s$(6)-C_{82})[26]. Besides, compared to the entrapped NC moiety of the reported metal carbonitride clusterfullerenes $Sc_3NC@C_{80}$, for which the experimental ^{13}C NMR signal was unknown[17] while the simulated chemical shift is 306.6 ppm[18], the chemical shift of the internal CN-unit of YCN@C_s(6)-C_{82} might be different since the formal charge state of the internal CN-unit of YCN@C_s(6)-C_{82} is different to that of the entrapped NC moiety of $Sc_3NC@C_{80}$ as discussed below.

A more detailed analysis of the ^{13}C NMR results of YCN@C_{82} can further exclude the possibility of the isomeric carbide cluster structure with an azafullerene cage, namely $YC_2@C_{81}N$, for which two substitution sites of nitrogen atom in the C_{82} cage are possible: 1) if
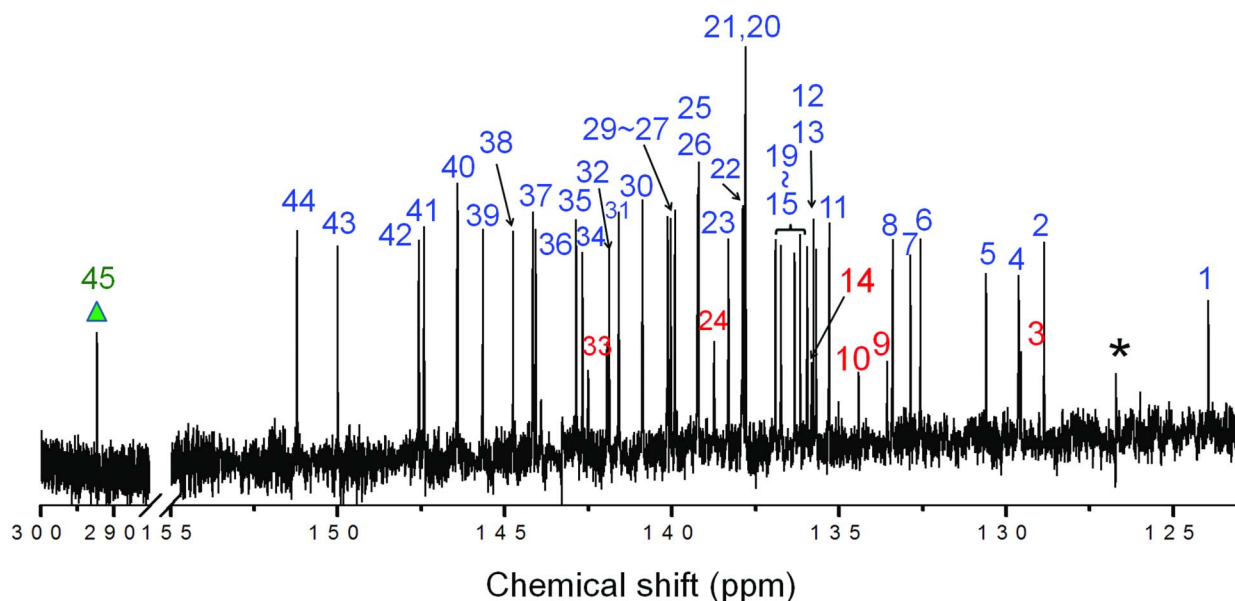

Figure 1 | Drawing of the crystallographically determined structure of YCN@C_s(6)-C_{82} with the major C_{82} cage (0.55 occupancy) and the most abundant yttrium location (0.50 occupancy), and its relation to the Ni^{II}(OEP) molecule. Thermal ellipsoids are set at 30% probability level. Solvent molecules, 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.

Figure 2 | ^{13}C NMR (125 MHz) spectrum of YCN@C_{82} showing a 38 × 2C (labeled by blue numbers), 6 × 1C (labeled by red numbers) pattern for the sp^2 carbon atoms of the cage. The filled triangle marks the ^{13}C nuclei signal of the internal YCN cluster, and the asterisk labels an unidentified impurity.

the nitrogen atom substitutes any of the 6 carbon atoms on the mirror plane, 43 lines for the sp^2 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 C_2 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 ^{13}C NMR spectrum of our new endohedral compound rules out the possible structure of YC$_2$@C_{81}N. In addition, according to our DFT computations, the alternative most stable structure of YC$_2$@C_{81}N is remarkably energy-unfavorable. Among all the considered YC$_2$@C_{81}N isomers, those with the nitrogen atom substituting any of the 6 carbon atoms on the mirror plane of the C_s-C_{82} cage (i.e., the C_{81}N cages remain the C_s symmetry) are ~80 kcal/mol higher in energy than the lowest-energy YCN@C_{82} structure, while others are at least 20.2 kcal/mol higher in energy.

Electronic structure of YCN@C_{82}. The electronic structure of YCN@C_{82} 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@C_{82} (Supplementary Information S6). Room-temperature ESR spectroscopic measurement reveals that YCN@C_{82} is ESR-silent. This is dramatically different to the analogous C_{82}-based mono-EMFs entrapping a trivalent Group-III metal M@C_{82} (M = Sc, Y, La etc.), which are typically ESR-active due to their open-shell electronic structures[3–7]. Instead, divalent metal-based C_{82} mono-EMFs, such as Yb@C_{82}, Ca@C_{82}, and Sm@C_{82}, are usually ESR-silent owing to their closed-shell structures[5,27]. The similarity of the ESR behaviour of YCN@C_{82} to those of divalent metal-based C_{82} mono-EMFs suggests a similar two-electron transfer. Thus, an electronic configuration of $[Y^{3+}(CN)^-]^{2+}@[C_{82}]^{2-}$ can be proposed, for which the $(CN)^-$ moiety typically existing in the traditional metal cyanide inorganic compounds[22] is obviously different to the $[NC]^{3-}$ unit within the reported $[Sc^{3+}]_3[NC]^{3-}@[C_{80}]^{6-}$ (refs. 17, 18). Indeed, the proposed electronic configuration of $[Y^{3+}(CN)^-]^{2+}@[C_{82}]^{2-}$ is confirmed by the cyclic voltammetric study. YCN@C_{82} 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@C_{82} highly resembles that of the reported Yb@C_s(6)-C_{82}, 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[27]. Again, such a high resemblance of the reduction behaviour of YCN@C_s(6)-C_{82} to that of Yb^{2+}@$[C_s(6)$-$C_{82}]^{2-}$ confirms the proposed electronic configuration of $[Y^{3+}(CN)^-]^{2+}@[C_{82}]^{2-}$ featuring a formal two-electron transfer from the entrapped YCN moiety to C_{82} cage.
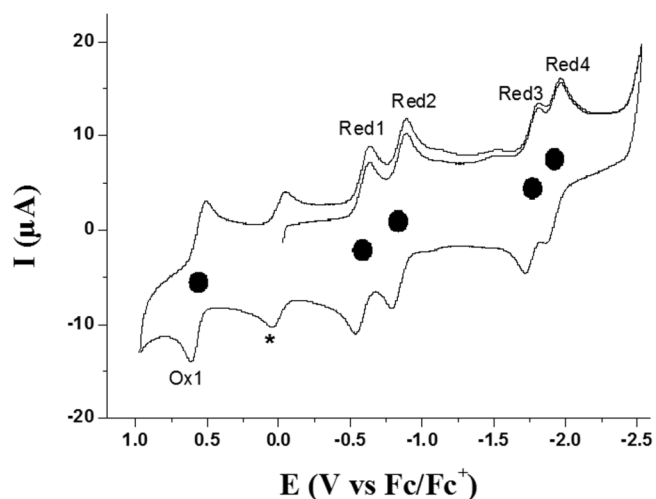

Figure 3 | Cyclic voltammogram of YCN@C_{82} in o-dichlorobenzene (o-DCB) solution with ferrocene (Fc) as the internal standard and tetrabutylamonium hexafluorophosphate (TBAPF$_6$) as supporting electrolyte. Scan rate: 100 mV/s. Each redox step is marked with a number and a solid dot to aid comparison. 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 monometallic clusterfullerene entrapping an improbable yttrium cyanide cluster — $YCN@C_s(6)$-C_{82}. X-ray crystallography and ^{13}C NMR spectroscopic study assure the elucidation of its cage isomeric structure of $C_s(6)$-C_{82}, which entraps an unprecedented triangular YCN cluster. A closed-shell electronic configuration of $[Y^{3+}(CN)^-]^{2+}@[C_{82}]^{2-}$ is established on the basis of XPS, ESR and cyclic voltammetric studies. The existence of such an improbable monometallic cyanide clusterfullerene portends the possibility of creating novel EMFs entrapping other types of clusters. Our successful synthesis and structural elucidation of the first monometallic 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 Krätschmer-Huffman generator by vaporizing composite graphite rods ($\Phi 8 \times 150$ mm) containing a mixture of Y_2O_3 (99.99%), TiO_2 (99.99%) and graphite powder with a molar ratio of $1:1:15$ (Y : Ti : C) with the addition of 10 mbar N_2 into 400 mbar He as described previously[19,20]. For comparison, a reference synthesis by using a mixture of Y_2O_3 and graphite powder ($1:15$, without involvement of TiO_2) was also carried out. The as-produced soot was Soxhlet-extracted by CS_2 for 24 h, and the resulting brown-yellow solution was distilled to remove CS_2 and then immediately redissolved in toluene ($\sim$200 ml) and subsequently passed through a 0.2 μm Telflon 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 in both positive and negative ion modes (Biflex 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 ultrahigh vacuum conditions into an ESCALAB 250 spectrometer (Thermo-VG Scientific, England) where they were studied using monochromatic Al K_α radiation (1486.6 eV) with an energy resolution of 0.6 eV. ESR spectrum of $YCN@C_{82}$ was measured in toluene solution using a JES-FA200 FT-EPR X-band spectrometer (JEOL, Japan). The ^{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_6-acetone 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 tetrabutylamonium hexafluorophosphate ($TBAPF_6$, 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 voltammogram 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^+ couple.

X-ray crystallographic study. Crystal growth for $YCN@C_{82} \cdot Ni^{II}(OEP) \cdot 1.73C_6H_6 \cdot 1.27CHCl_3$ was accomplished by layering a solution of ca. 1.0 mg $YCN@C_{82}$ in 1 ml benzene over a solution of 3.0 mg $Ni^{II}(OEP)$ in 3 ml chloroform. After the two solutions diffused together over a period of 7 days, small black crystals suitable for X-ray crystallographic study formed upon a slow evaporation of benzene. X-ray data collection for the crystal of $YCN@C_{82} \cdot Ni^{II}(OEP) \cdot 1.73C_6H_6 \cdot 1.27CHCl_3$ ($0.37 \times 0.30 \times 0.30$ mm³) was carried out at 107 K on a Gemini S Ultra diffractometer (Oxford diffraction Ltd., UK) with a 92 mm Sapphire CCD image plate detector. $YCN@C_{82} \cdot Ni^{II}(OEP) \cdot 1.73C_6H_6 \cdot 1.27CHCl_3$ crystallizes in the monoclinic space group $P2_1/c$; $a = 17.685(5)$ Å, $b = 16.933(5)$ Å, $c = 27.340(5)$ Å, $V = 7795(3)$ Å³, $Z = 4$. A numerical absorption correction utilizing equivalents was employed. The structure was solved by direct methods and refined using all data (based on F^2). Hydrogen atoms were located in a difference map, added geometrically, and refined with a riding model. Refinement of 13450 reflections, 1765 parameters, and 1922 restraints yielded $wR_2 = 0.2246$ for all data and a conventional R_1 of 0.0806 based on 10964 reflections with $I > 2\sigma(I)$. CCDC 886828 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge on application to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Acknowledgments

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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