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Cu@C_{60} formation in rf-plasma and ring-current induced magnetism of C_{60}

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A new endofullerene, Cu@C_{60}, was synthesized and isolated. Ring-current induced diamagnetic interior and paramagnetic exterior of C_{60} have been quantitatively described using the Cu probe.

Endofullerenes are of great interest due to their doping-element dependent structural varieties. Applications, such as to field effect transistor (FET), MRI agent and quantum computer, have been proposed, based on different endofullerenes.[1–3] As for material research of endofullerenes, much progress has been made over the past decade. However, the elements that can be entrapped inside fullerenes are still only those within the groups of the left (Group 1–4) and the right (Groups 15 and 18) sides of the periodic table.[3–5] Whether or not other elements that occupy the majority and the middle portion of the periodic table can be encapsulated inside fullerenes and what kinds of electronic structures they may possess remains an unsolved mystery due partially to difficulties in their preparation. In this work, we report the first synthesis, isolation and characterization of an unconventional endofullerene, Cu@C_{60}. The endohedral nature and electronic structure of Cu have been clarified. In addition, ring-current induced magnetism for both interior and exterior of C_{60} cage has been obtained using the Cu probe.

The experimental setup for producing Cu@C_{60} was based on capacitor-type plasma that was similar to that used to produce fullerene polymers and N@C_{60}.[6–8] A sheet of copper foil was used to cover the cathode electrode, and subsequently copper ions were sputtered from the copper foil during plasma processing. C_{60} (100 mg, purity $>99.95\%$) was evaporated through resist heating, and collided with the copper ions in the plasma cathode-sheath region. High-purity nitrogen (99.99995%) was used as the buffer gas, and was kept at 10 Pa during plasma processing. The rf-plasma was operated at 13.56 MHz and 50 W. After evaporation of C_{60} in the rf-plasma, the deposit was collected and dissolved in CS_2 *via* ultrasonication. The soluble portion was filtered through a 0.2 μm PTFE syringe filter and used for analysis and isolation. ESR *g*-value measurements were taken using precision magnetic-field and frequency counters.

The ESR spectrum of the soluble portion was closely dependent on the ESR operation parameters. For example, at a very low microwave power (~ 10 μW) and very narrow modulation width (0.002 mT), only three sharp lines with a hyperfine constant of 0.567 mT could be observed, and they originated from N@C_{60}. When the microwave power was increased to 1.0 mW and the modulation width was set at 0.2 mT, besides the peaks from N@C_{60}, new ESR signals with four major peaks appeared, as is shown in Fig. 1. These ESR signals (without those from N@C_{60}) were also observed when Ar was used as the buffer gas, but not observed when aluminum foil (instead of copper foil) was used to cover the rf-plasma cathode. These additional ESR signals apparently originate from copper.

The origin of these ESR signals is further clarified by an analysis of the spectrum. First, the four major ESR peaks with equal integrated area correspond to the nuclear spin quantum number of Cu ($I = 3/2$). Second, when the integrated signal of the peak around 334 mT is deconvoluted into two components, the ratio of the two components is 2.246, which is in excellent agreement with the ratio of the natural abundance of ^{63}Cu and ^{65}Cu (2.247). Since Cu^{1+} ($3d^{10}$) is ESR silent while Cu^0 is unlikely due to its very different ESR saturation behavior from N@C_{60} as well as HPLC elution behavior that will be described below, Cu can only be in its oxidation state of 2+ ($3d^9$), after transferring two electrons to the C_{60} cage. Each ESR peak height and shape of Cu^{2+} is the combined result of the two Cu isotopes and the nuclear-spin quantum-number (m_I) -dependent line broadening.

Because the ESR spectrum was obtained from a solution sample at room temperature, anisotropic *g*-tensors of Cu ions that are usually observed in the solid phase are averaged out. After deconvoluting each ESR peak, we obtain isotropic hyperfine coupling (hfc) constants of 7.757 mT and 8.277 mT for ^{63}Cu and ^{65}Cu, respectively. The ratio of the two hfc constants (0.937) is in an excellent agreement with the ratio of theoretical gyromagnetic-ratio ($\gamma_n(^{63}\mathrm{Cu})/\gamma_n(^{65}\mathrm{Cu}) = 0.935$) of the two Cu^{2+} ions.[9]

Evidence for the endohedral nature of the copper ions is provided by both ESR and TOF-mass spectra. The ESR peaks from Cu^{2+} ions are much more clearly isolated from each other compared to the ESR peaks of Cu ions doped in other inorganic matrices or ligands.[10–11] We have also investigated various materials containing Cu^{2+}, such as Cu-doped zeolite and Cu amine complexes. The spectra of none of these materials show well-isolated quadruple peaks attributable to Cu ions because of the strong spin–dipolar interaction among Cu^{2+} ions. The Cu-ion signals reported here might be the first x-band cw-ESR spectrum with completely resolved hyperfine lines originating from m_I-dependent magnetic interaction. This improved resolution can only be explained by reduced spin–dipolar interaction among Cu^{2+} ions after being encaged inside C_{60} cages.

Evidence strongly indicating the endohedral nature of Cu^{2+} comes from the *g*-values of the Cu^{2+} ion signals when compared to those of other Cu^{2+} complexes and exohedral CuC_{60}.[12] The *g* values of ^{63}Cu and ^{65}Cu in Fig. 1 are 2.0483 and 2.0477, respectively. The *g*-values for other Cu^{2+} complexes in solution that possess no extra molecular magnetism, such as diethanoamine–Cu^{2+} (traced at 2.1210), are generally in range of 2.10–2.13.[13] The *g*-value shift becomes more evident when compared to that of the exohedral CuC_{60} complex. ESR spectrum of exohedral CuC_{60} shows a single broad peak centered at a *g*-value of 2.2016. These *g*-value data

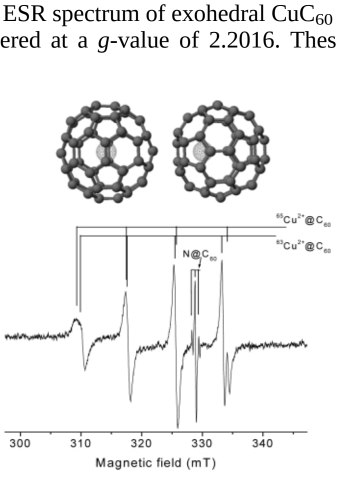

Fig. 1 ESR spectrum of vacuum-sealed Cu@C_{60} in CS_2. The quartet splittings of ^{63}Cu and ^{65}Cu are indexed. Over the ESR spectrum two views of Cu@C_{60} in B88-PW91 DFT geometry are shown.

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show that ESR for Cu@C_{60} is shifted upfield by ~3.5% and ~7% when compared to diethanoamine–$Cu^{2+}$and exohedral CuC_{60}, respectively. The upfield shift can be explained by considering the ring current effect of the fullerene cage in a magnetic field. Compared to diethanoamine–Cu^{2+} (without π conjugated electrons), Cu^{2+} inside C_{60} requires a higher magnetic field (+3.5%) for ESR due to the diamagnetic ring-current effect from C_{60}, while exohedral doping requires a lower magnetic field (−3.5%) due to the paramagnetic ring-current effect. These results imply that the local magnetic field induced by the ring-current effect is about 11.6 mT in a magnetic field of ~330 mT, a value that cannot be ignored when dealing with the magnetic properties of fullerenes and endofullerenes.

It is worthwhile noting that the extent of diamagnetic shielding of the fullerene cage observed in ESR is much larger (5470 times) than that observed in NMR for $^{3}He@C_{60}$, in which the resonance is shifted upfield only by 6.4 parts per million.[14] This difference is also in excellent agreement with the ratio (5509 times) between the Bohr magneton (μ_B) and the nuclear magneton of ^{3}He.

Pure Cu@C_{60} was obtained through HPLC, as is shown in Fig. 2. Appearing around 5.6 min is a mixture of pristine C_{60} and N@C_{60}. Cu@C_{60} elutes around 18 min., much later than C_{60}, indicating an enhanced interaction between Cu@C_{60} and the column fixed-phase material. The ratio of Cu@C_{60} to C_{60} is about 0.1%, estimated from ESR and HPLC results; ~20 μg of purified Cu@$C_{60}$was obtained from 100 mg initial C_{60}.

The TOF-mass spectrum of purified Cu@C_{60} is shown in Fig. 3. Besides the prominent peak (*m*/*z* 783) from Cu@C_{60}, peaks attributable to CuC_{58} (*m*/*z* 759) and $CuC_{60}O$ (*m*/*z* 799) can also be seen. The presence of the CuC_{58} peak and the absence of a C_{60} peak clearly confirm the endohedral nature of this metallofullerene, otherwise Cu instead of C_2 will be dissociated from its mother compound under laser irradiation.

In summary, Cu@C_{60}, a new endofullerene, has been generated in rf-plasma. The well-resolved ESR spectrum of Cu@C_{60} facilitated comparison with theoretical data on Cu^{2+} ions. Ring-current-induced diamagnetic interior and paramagnetic exterior of C_{60} have been quantitatively described using the Cu^{2+} probe. Purified Cu@C_{60} has been obtained, and further investigation of this novel metallofullerene is under way.

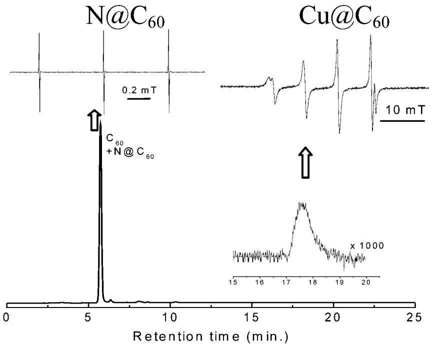

Fig. 2 HPLC trace of the soluble portion of the rf-plasma-treated C_{60} deposit. The sample was dissolved in toluene after replacing CS_2. HPLC conditions: semipreparative Buckyclutcher column, 3mL min^{-1} 7:3 toluene/hexane mobile phase. The peak around 5.6 min is due to a mixture of C_{60} and N@C_{60}, and the almost invisible peak around 18 min comes from Cu@C_{60}. Other small peaks following C_{60} are ESR silent and not yet clarified. ESR spectra of N@C_{60} and Cu@C_{60} are shown in the insets.

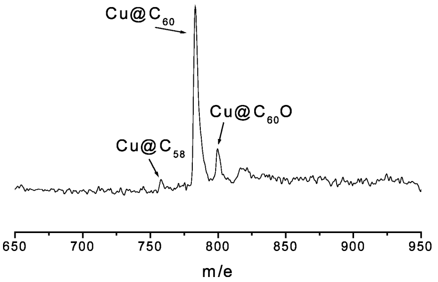

Fig. 3 TOF-MS spectrum of Cu@C_{60}.

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