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Probing the zero-field splitting in the ordered N@C_{60} in buckycatcher $C_{60}H_{28}$ studied by EPR spectroscopy

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ABSTRACT

The electronic structure of the endohedral fullerene ^{14}N@C_{60} spatially ordered in the crystal state by its supramolecular assembly with a buckycatcher $C_{60}H_{28}$ was investigated by X-band electron paramagnetic resonance (EPR) spectroscopy. The zero-field splitting (ZFS) found in the complex is significantly enhanced in comparison to the earlier reported data for the analogous systems. The large ZFS, presumably induced by the molecular order in the supramolecular complex makes it an attractive material for the future quantum control and coherence studies.

1. Introduction

Fullerenes and endohedral fullerenes are interesting new material for the applications not only in physics and chemistry but also in such interdisciplinary areas as quantum computation. The endohedral fullerene N@C_{60} has received significant attention because of its unique geometric and electronic structure. The chemically unbound open-shell nitrogen atom is located right in the center of the highly symmetric C_{60} cage, as a result, it exhibits the long coherence time associated with the unpaired electron spins [1,2]. Since the molecular carbon cage provides a handle for the fragile atomic spin system, endohedral fullerenes have been investigated as the promising materials for quantum-information processing (QIP) [2–5]. As an example, a linear chain of N@C_{60} or P@C_{60} has been proposed as a key element of a scalable architecture for spin quantum computing based on endohedral fullerenes [6–8]. Therefore, the design and preparation of molecular architectures with the aligned or ordered endohedral fullerenes is of premium importance for the future advancements in QIP.

Several strategies were proposed to obtain aligned or well-ordered endohedral fullerenes. For example, N@C_{60} is self-aligning in liquid crystals [9,10], confined in carbon nanotubes [11,12], or co-crystallized in an organic inclusion compound BrPOT [13]. In these complexes, the N atomic wavefunction was found to be sensitive to both the symmetry and the nuclear spin bath of the environment, despite of being well localized within the fullerene carbon cage. Obviously this type of ordered endohedral fullerenes enable the further in-depth studies of the second-rank tensor interactions, e.g., the dipolar coupling, nuclear quadruple interaction or fine-structure interaction, as well as the future applications of these materials in QIP. It is therefore crucial to prepare spatially ordered endohedral fullerenes separated by a well-defined distance. Herein, we use a newly developed molecular receptor, a 'buckycatcher' $C_{60}H_{28}$ [14], which forms a supramolecular assembly with N@C_{60} buckyball. The resulting N@C_{60}@$C_{60}H_{28}$ supramolecular complex crystallizes from toluene providing a solid material with the columnar alignment of the fullerene cages.

2. Materials and methods

Following the previously published procedure the endohedral fullerenes N@C_{60} was produced by ion implantation and purified by high performance liquid chromatography (HPLC) [10,15,16]. The final ratio of N@C_{60} to empty C_{60} used in the following experiments was 1.7×10^{-4} (170 ppm). $C_{60}H_{28}$ was synthesized as described earlier [14]. Co-crystallization was carried out by slow evaporation of toluene solution with a 1 : 1 ratio (mol : mol) between N@C_{60} (typically 1.5 g/L) and $C_{60}H_{28}$ at room temperature.

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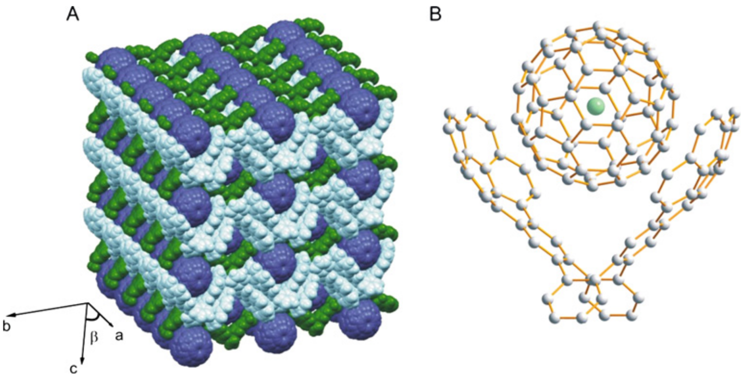

Fig. 1. (Color online.) (A) Columnar packing pattern of C_{60} fullerenes (blue) and solvating toluene molecules (green, disordered) in a $C_{60}H_{28}$ buckycatcher matrix (light blue) as obtained from X-ray diffraction (XRD) of a $C_{60}@C_{60}H_{28} \cdot 2PhMe$ single crystal (after Ref. [14]). Similar X-ray data (see text) were obtained on a crystal containing 170 ppm of $N@C_{60}$ in the fullerene fraction. The direction of a, b and c together with the angle β was shown at the left bottom. (B) Highlight of $N@C_{60}$ in a buckycatcher molecule (H atoms not shown). The N atom (green) is located exactly in the center of the C_{60} cage and forms no bonds to it.

After 2–3 days, the small dark single crystals were collected and transferred to an EPR tube. The sample layer of crystals collected in the 3.8 mm OD EPR tube is about 1 mm in height. The approximate spin density is 2.5×10^{17} cm^{-3} for the $N@C_{60}$ powder sample, which is about 2.8 times that in the final $N@C_{60}@C_{60}H_{28}$ complex crystals (average spin density 8.9×10^{16} cm^{-3}).

The X-band (9.7 GHz) continuous wave (cw) EPR experiments were performed with a Bruker Elexsys580 EPR spectrometer equipped with Oxford-900 liquid helium cryostats and ITC-503 temperature controller. The used EPR settings are shown in the Fig. 2 legend.

3. Results and discussion

The geometric structure of the $N@C_{60}@C_{60}H_{28}$ single crystal ($0.32 \times 0.25 \times 0.04$ mm^3) was explored by room temperature X-Ray Diffraction (XRD) yielding the following unit cell parameters: $a = 9.886(15)$ Å, $b = 22.64(8)$ Å, $c = 17.32(6)$ Å, $\beta = 97.5°$, and $V = 3843$ Å^3. These values are comparable to the earlier data from the $C_{60}@C_{60}H_{28}$ complex: [$a = 9.7730(15)$ Å, $b = 22.253(3)$ Å, $c = 17.334(3)$ Å, $\beta = 98.2°$, $V = 3731.2$ Å^3, at 100 K or $a = 9.8344(15)$ Å, $b = 22.500(4)$ Å, $c = 17.271(3)$ Å, $\beta = 97.7°$, and $V = 3788$ Å^3 at $T = 233$ K [14], showing that the partial implantation of $N@C_{60}$ molecules does not influence the structure of the inclusion complex. The small differences between our unit cell dimensions (room temperature) and the ones reported in Ref. [14] (low temperatures) can easily be explained by a thermal expansion of the crystals [17]. Also, inclusion of an atom of nitrogen to the fullerene cage is not expected to have any measurable effect on the size of the unit cell since only one of the every ca. 5900 fullerene molecules in the sample hosts the nitrogen guest.

As shown previously [14] the inclusion $C_{60}@C_{60}H_{28}$ complex co-crystallizes with two solvent molecules. Both the buckycatcher and the toluene molecules wrap around the “equatorial” region of the fullerene cages which are arranged in a columnar fashion along the crystallographic a axis with a close contact of the cages in their “polar” regions (Fig. 1A). Inspection of the X-ray crystal structure suggests that the inclusion complex $C_{60}@C_{60}H_{28}$ is bound by van deer Waals (dispersion) forces [14]. Subsequent theoretical studies also show that the fullerene-buckycatcher supramolecules are typical van deer Waals complexes with no specific electrostatic, orbital or charge transfer interactions [18].

The electronic structures of $N@C_{60}$ molecule and $N@C_{60}@C_{60}H_{28}$ complex are prone to the continuous wave (cw) EPR spectroscopy. The isolated ^{14}N atom has nuclear spin $I = 1$ and three unpaired electrons to form an effective spin $S = 3/2$. As has been reported previously [19], the spin wavefunction of $N@C_{60}$ diluted in an empty C_{60} crystal has cubic symmetry at room temperature with isotropic g-factor and isotropic hyperfine coupling constant (hfcc) A_{iso}. In high-spin systems with $S > 1/2$, field-independent dipole–dipole interaction between the constituting electron spins leads to a ‘zero-field splitting’ (ZFS), characterized by a tensor $\mathbf{D}$, which vanishes for cubic systems like $N@C_{60}$ in C_{60}. The ZFS for $N@C_{60}$ is not detected by EPR experiments at room temperature and is reported to be a small value of 0.52 MHz which is hardly resolved in the EPR spectrum recorded at 260 K [20,22].

For the high spin $S > 1/2$ systems with the cubic symmetry the EPR data can be described by the high-field approximate ($\omega_e \gg |a|, |D|, |E|$) spin Hamiltonian given in angular frequency units by equation,

$$H = \omega_e S_z - \omega_n I_z + A_{iso} S_z I_z + D\left(S_z^2 - \frac{15}{4}\right) + E\left(S_x^2 - S_y^2\right) \quad (1)$$

Here, $\omega_e = g\mu_B B_0/\hbar$ and $\omega_n = g_I \mu_n B_0/\hbar$ are the electron and nuclear Zeeman frequencies, g and g_I are the electron and nuclear g factors, μ_B and μ_n are the Bohr and nuclear magnetons, $\hbar$ is Planck’s constant and B_0 is the magnetic field applied along z axis in the laboratory frame. S_z and I_z indicate the z component of the Pauli matrix representing the quantized spin moment of electron spin and nuclear spin, respectively. The hyperfine constant A_{iso} describes the isotropic (Fermi contact) hyperfine coupling originating from the magnetic interaction between the unpaired electrons and the ^{14}N nuclei. In axial symmetry systems like $N@C_{60}@C_{60}H_{28}$, the zero-field splitting (ZFS) term can be written (as in Eq. (1)) with $D = \frac{3D_{ZZ}}{2}$ and $E = \frac{(D_{XX} - D_{YY})}{2}$, where $D_{XX,YY,ZZ}$ are the diagonal elements of the tensor $\mathbf{D}$ in its eigenframe [23].

Cw EPR spectra of $N@C_{60}$ powder and $N@C_{60}@C_{60}H_{28}$ crystals are shown in Fig. 2. Both spectra are centered on the isotropic electron g factor $g_{iso} \approx 2.002$ and comprise three main lines due to hyperfine coupling $A_{iso} = 15.89$ MHz. The observed peak-to-peak linewidth is 1.1 Gauss for $N@C_{60}@C_{60}H_{28}$ crystals which is about seven times that for $N@C_{60}$ powder (0.15 Gauss). The red and blue spectra in Fig. 2 display five feature absorption peaks in the new ordered material $N@C_{60}@C_{60}H_{28}$ complex crystals when measured respectively at room (290 K) or liquid helium (80 K) temperatures. It is clear that the molecular interaction between $N@C_{60}$ and $C_{60}H_{28}$ does not influence the g-value or the A_{iso}, which can also be confirmed by the identical linewidths of the three dominant peaks in the central of red spectrum in Fig. 2 which corresponding to $M_I = 0$ and $+/-1$.

The two new features appearing in the low (3438.3 Gauss) and high (3459.8 Gauss, not highlighted in Fig. 2) field of the $N@C_{60}@C_{60}H_{28}$ crystals spectrum (centered at $g \approx 2.002$) are assigned to be the accessible non-zero D. Undoubtedly the molec-