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Endohedral Fullerenes

A Co-Crystal Composed of the Paramagnetic Endohedral Metallofullerene La@C_{82} and a Nickel Porphyrin with High Electron Mobility**

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Endohedral metallofullerenes containing one or more atoms inside a hollow fullerene cage have attracted much attention because of their novel properties, which are attributable to intramolecular interactions between the metal atom and the fullerene cage.[1] Recent isolation and purification of various endohedral metallofullerenes has encouraged the investigation of their physical and chemical properties. La@C_{82} (Figure 1 a) is an abundantly produced endohedral metallofullerene. It has been of particular interest to determine the fullerene cage structure and metal positions because this information is necessary to explain the properties and reactivities of endohedral metallofullerenes. In this context, NMR spectroscopy,[2] 2D EPR spectral analysis,[3] X-ray powder diffraction analysis,[4] chemical functionalization,[5] and theoretical calculation[6] were conducted, yielding results clarifying that the La atom is mostly encapsulated inside the C_{2v} cage of C_{82}, and demonstrating that the La atom is not located in the center of the C_{82} cage but instead sits closely to a hexagonal ring along the C_2 axis. Furthermore, according to molecular orbital calculations, three electrons are transferred from the La atom to the C_{82} cage forming the open-shell electronic structure described as $La^{3+}C_{82}{}^{3-}$.[6] Although La@C_{82} has interesting electronic properties, such as low reduction and oxidation potentials,[1] for the development of functional materials, neither its single-crystal form nor the solid-state transport properties have been reported. A few reports have studied the charge-carrier mobility of M@C_{82}-(C_{2v}) (M = Ce, Pr, Dy atom),[7] however, these μ values were much smaller, by four orders of magnitude, than that of fabricated C_{60} thin films.[8] Herein, we have successfully synthesized single-crystal of La@C_{82} with [Ni^{II}(OEP)] (OEP = octaethylporphyrin) as a co-crystal and observed anisotropic and high electron mobility up to 0.9 $cm^2\,V^{-1}\,s^{-1}$ using flash-photolysis time-resolved microwave conductivity (TRMC) measurements.[9]

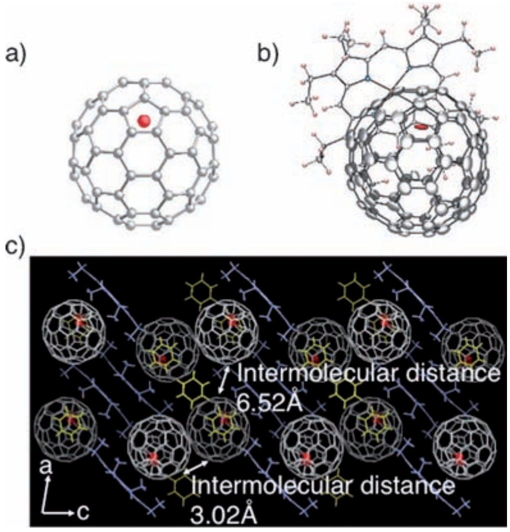

Figure 1. a) La@C_{82}(C_{2v}), b) ORTEP drawing of **1** showing thermal ellipsoids set at 50% probability level. Solvent molecules of benzene are omitted for clarity. c) Packing structure of **1**·1.5 benzene. Porphyrin molecules are shown as purple and benzene molecules are shown as yellow for clarity.

Black crystals of La@C_{82}·[Ni^{II}(OEP)] (**1**) were obtained by diffusion of a benzene solution of the La@C_{82} into a CH_3Cl solution of [Ni^{II}(OEP)]. The structure of **1** was confirmed using single-crystal X-ray structure analysis.[10] Figure 1 b shows a drawing of the La@C_{82} molecule and its orientation

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relative to the [Ni^{II}(OEP)] molecule. Details of the structure of **1** are as follows. Two equal orientations of La@C_{82} are related using a crystallographic mirror plane. The La atom was observed to be disordered at an off-center position near a hexagonal ring of the C_{82}(C_{2v}) cage, indicating oscillation of the encapsulated La atom. As usual with structures of this type,[11] the eight ethyl groups of the porphyrin surround the La@C_{82}. The molecular packing of **1**·1.5 benzene is shown in Figure 1 c. The π–π interaction might play an important role in the interaction between La@C_{82} and [Ni^{II}(OEP)]. Some intermolecular distances (3.02 and 3.23 Å; Figure 1 c) between La@C_{82} units are shorter than the sum of van der Waals radii of the carbon atom (3.35 Å), thereby suggesting that porphyrin molecules form an ordered molecular arrangement that controls the intermolecular distance.

To investigate the charge transport properties, TRMC measurements were performed on **1**. The TRMC measurements serve as an electrode-less measurement tool for the determination of the intrinsic charge-carrier mobility in organic materials. Figure 2 presents the conductivity transient ($\phi\Sigma\mu$) observed for the co-crystal of **1**, where ϕ and $\Sigma\mu$, respectively, denote the photo-carrier generation yield and the sum of mobilities for the positive and negative charge carriers. The single crystal was set in a microwave cavity to investigate the anisotropic conductivity transients by rotating the sample stage relative to the direction of the microwave electric field in the resonant cavity (Supporting Information, Figure S1). The highest value of $\phi\Sigma\mu$ is 3.0×10^{-3} $cm^2V^{-1}s^{-1}$ and occurs when the *c* axis of the crystal is parallel to the electronic field. (The highest values in the other directions are: along the *a* axis, 1.0×10^{-3} $cm^2V^{-1}s^{-1}$; 30° gradient, 4.0×10^{-4} $cm^2V^{-1}s^{-1}$; 45° gradient, 5.0×10^{-4} $cm^2V^{-1}s^{-1}$.) As described above, the shortest intermolecular distance between the La@C_{82} units is 3.02 Å. The anisotropic conductivity presumably occurs because of the presence of close-packed [Ni^{II}(OEP)] and benzene molecules (Figure 1 c). For example, there are benzene molecules between the La@C_{82} molecules in the *b* axis direction. These benzene molecules are expected to block the charge-carrier transport by acting as an insulator between the La@C_{82} molecules.

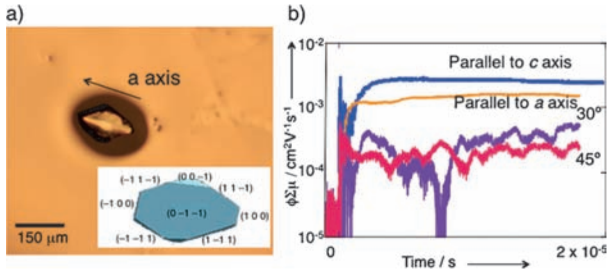

Figure 2. a) Photograph of co-crystal **1**. Inset: crystal shape with indices. b) Conductivity transients observed for a co-crystal of **1**. The blue and orange lines show transients observed along the direction parallel to the stacking axis (blue: *c* axis; orange: *a* axis) of the crystal. Violet and red lines are along the direction rotated 30° and 45° to the *a* axis. The transients were recorded under excitation at 532 nm with 1.5×10^{16} photons cm^{-2}.

To confirm the charge-carrier species, the conductivity transients were measured for co-crystals of **1** in polycrystalline forms under Ar and SF_6 atmospheres (Figure 3). Compared with the value of $\phi\Sigma\mu$ under Ar atmosphere ($\phi\Sigma\mu$: 1.0×10^{-3} $cm^2V^{-1}s^{-1}$), markedly the faster decay rate (a pseudo first order decay rate: $k\approx8\times10^4$ s^{-1}) and the lower transient conductivity ($\phi\Sigma\mu$: 1.5×10^{-4} $cm^2V^{-1}s^{-1}$) were observed under SF_6 atmosphere, which is a strong electron scavenger. Consequently, the major charge carriers were derived from electrons on La@C_{82}. The effects from [Ni^{II}(OEP)] were also confirmed by tracing the conductivity transients in the identical polycrystalline forms after exposing benzene vapor for 2 h at 353 K, leading to disordering of La@C_{82}. The conductivity transient showed remarkable drops (Figure 3), even lower than that observed under SF_6, and this is also suggestive that the aligned La@C_{82} molecules is responsible for providing highly conductive pathways for electrons.

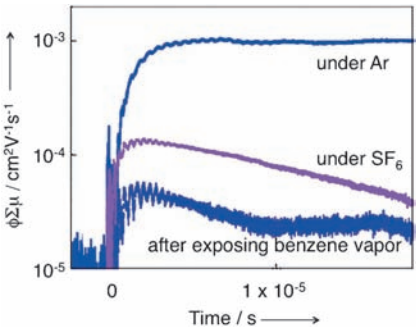

Figure 3. The transient was observed for the identical polycrystalline **1** under Ar (blue), SF_6 (pink) atmospheres, and after exposing to benzene vapor for 2 h at 353 K (purple). The excitation was carried out at 355 nm, 1.5×10^{16} photons cm^{-2}.

To determine the charge-carrier generation yield, photocurrent integration measurements were taken of a microcrystal of **1** placed onto an Au interdigitated electrode. The transient photocurrent was observed mainly under the applied bias (0–20 V). Using the maximum yield of $\phi\approx4.0\times10^{-3}$ determined by integration of the transient photocurrent in the co-crystal of **1** the minimum estimate of the intracolumnar electron mobility along the *c* axis is calculated as 0.9 $cm^2V^{-1}s^{-1}$. The minimum estimates of the electron mobility along the *a* axis, 30°, and 45° gradients are, respectively, 0.3, 0.1, and 0.1 $cm^2V^{-1}s^{-1}$. This electron mobility of **1** is higher than that of single-crystal [Ni^{II}(OEP)] ($\mu=0.07$ $cm^2V^{-1}s^{-1}$).[12] Thus the observed high electron mobility of **1** arises from the La@C_{82} units. It is the thoroughly ordered molecular arrangement in an organic crystal with La@C_{82} that enables a high electron transport.

To provide a theoretical insight into single-crystals of **1** as a π-conjugated organic material, geometry optimization and electronic property calculations were performed using $DMol^3$ code[13] within the framework of density functional theory. Generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE)[14] form was used for the exchange-correlation functional. Double numerical atomic orbital basis set was adopted. No significant deformation was found between the optimized structure and the experimental one. The band structure calculated for the optimized **1** crystal (Figure 4 and Figure S8), indicates some bands cross the Fermi level. Clearly, this crystal possesses a metallic character and thus good electrical conduction.

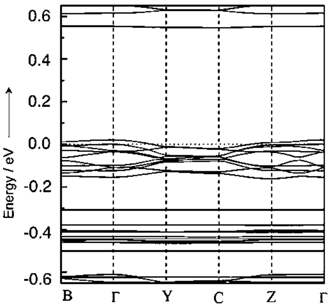

Figure 4. Band structure of **1**.

In conclusion, we prepared the paramagnetic endohedral metallofullerene co-crystal of La@C_{82}·[Ni^{II}(OEP)]. Its structure has been determined, making for the first time that La@C_{82} has been characterized by single-crystal X-ray crystallographic analysis without chemical modification. The X-ray structure of the La@C_{82} component is confirmed as being coincident with that suggested before based on the results of other analytical methods. Furthermore, for the co-crystal **1**, TRMC revealed high electron mobility with large anisotropy. The observed values for **1** in the single-crystal state are much higher than those of M@C_{82}(C_{2v}) in the film state. Therefore, to obtain a high electronic mobility it is important to produce an aligned crystal of endohedral metallofullerenes. These findings encourage our great expectations of realizing endohedral metallofullerene materials.

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Keywords: charge transport · fullerenes · lanthanum · porphyrins · structure elucidation

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[10] Crystal data of La@C_{82}·Ni^{II}(OEP): $C_{130}H_{56}N_4NiLa$, FW = 1871.4, monoclinic, space group $C2$m, $a = 25.385(3)$, $b = 15.1638(16)$, $c = 19.777(2)$ Å, $\beta = 94.9300(10)°$, $V = 7584.8(14)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.639$ g cm^{-3}, μ($Mo_{K\alpha}$) = 0.874 mm^{-1}, $T = 90$ K, crystal size 0.12 × 0.10 × 0.09 mm^3. $\theta = 1.57–25.03°$, 16455 refractions collected (6920 independent $R_{int} = 0.0590$), $R_1 = 0.1286$, $wR_2 = 0.3140$ for all data, $R_1 = 0.1214$, $wR_2 = 0.3091$ for 6145 reflections ($I > 2.0\sigma(I)$) and 969 parameters, GOF on $F^2 = 1.102$. The respective maximum and minimum residual electron densities are 1.824 and −1.160 e Å^{-3}. CCDC 845762 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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