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Electron-spin excitation by implanting hydrogen to metallofullerene: the synthesis and spectroscopic characterizations of Sc₄C₂H@I₇₇-C₈₀

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A hydrogen-containing endohedral metallofullerene, Sc₄C₂H@I₇₇-C₈₀, was synthesized and its paramagnetism was measured by the low-temperature EPR spectrometry with a broad EPR signal. The electron-spin excitation by implanting H-atom would be a new method for preparation of stable paramagnetic metallofullerenes.

The paramagnetic metallofullerenes with unpaired spin(s) have potential applications in quantum information processing and electronic devices, etc. As many metallofullerenes are diamagnetic, the electron spin injection becomes an important way to produce spin-active species, e.g., the technique by electrochemical redox or chemical reduction with alkali-metals. However, this technique would produce either anion or cation radicals of the metallofullerenes, which are obviously not stable and apt to return to their diamagnetic states spontaneously. Therefore, it is necessary to investigate other method to excite paramagnetic property of metallofullerenes.

In 2007, Dunsch et al. reported an endohedral metallofullerene, Sc₃CH@C₈₀, in which the H forms covalent bonding with C and supplies an electron as revealed by theoretical calculations. Although the resulted Sc₃CH@C₈₀ is diamagnetic molecule, the existence of this stable metallofullerenes suggests the possibility to implant hydrogen into the metallofullerenes accompanied with an extra electron. Therefore, introducing H-atom to diamagnetic endohedral metallofullerenes could also realize electron spin excitation.

However, it requires a lot of energy to insert an atom into the metallofullerenene cage, so the H-containing paramagnetic metallofullerenes were synthesized by arc-discharging the metal-doped graphite with introducing a certain amount of hydrogen gas into the helium atmosphere. After deliberately comparing the metallofullerenene products before and after introducing the hydrogen gas in the arc-discharging process, a new species with 1165 molecular weight was discovered in the presence of hydrogen. Furthermore, along with the increasement of hydrogen ratio in the helium gas, the yield of this molecule increases simultaneously. Therefore, this molecule with 1165 molecular weight was supposed to be a H-containing endohedral metallofullerene. In addition, since the molecule with 1165 molecular weight has a nearly same retention time with the known Sc₄C₂@I₇₇-C₈₀ (1164 molecular weight) in the high performance liquid chromatography (HPLC) profile, so the relativity between these two species was proposed as well. Herein, we report the isolation, characterizations, and theoretical calculations of this new molecule of Sc₄C₂H@I₇₇-C₈₀. UV-vis, Raman, IR, and ESR spectroscopies as well as density functional theory (DFT) calculations were employed to disclose its structure and special electronic property. The structural and electronic properties of Sc₄C₂@I₇₇-C₈₀ were also analyzed for comparison.

![HPLC separation profile of Sc₄C₂H@C₈₀ and Sc₄C₂@C₈₀](image1)

Figure 1. (a) HPLC separation profile of Sc₄C₂H@C₈₀ and Sc₄C₂@C₈₀; (b) Observed mass spectrum of purified Sc₄C₂H@C₈₀; (c) Observed molecular ion peak of purified Sc₄C₂@C₈₀; (d) Simulated isotropic distributions of Sc₄C₂H@C₈₀; (e) Mass spectrum of a mixture of Sc₄C₂@C₈₀ and Sc₄C₂H@C₈₀.

Sc₄C₂H@I₇₇-C₈₀ was synthesized through arc-discharging method under a mixture atmosphere of 6 Torr H₂ and 194 Torr He. The...
produced fullerenes and metallofullerenes were isolated by multi-step HPLC, as shown in Figure 1a and S1. It can be seen that the Sc$_4$C$_2$H@I$_5$-C$_80$ has similar retention time with that of Sc$_4$C$_2@I_5$-C$_80$ on HPLC columns. In addition, the Sc$_4$C$_2$H@I$_5$C$_80$ and Sc$_4$C$_2@I_5$-C$_80$ have slightly shorter time than that of Sc$_4$N@I$_5$-C$_80$ revealing their similar molecular size and polarity. The MALDI-TOF mass spectra shown in Figure 1b exhibit mass-to-charge ratio (m/z) of 1165 for Sc$_4$C$_2$H@C$_80$, accounting for a chemical composition of Sc$_4$C$_2$H$_4$ whose simulated isotropic distributions are in good agreement with the experimental result. In order to obtain the accurate m/z of Sc$_4$C$_2$H$_4$, purified Sc$_4$C$_2@C$_80$ sample was added as internal standard. The main molecular ion peaks at 1164 and 1165 in Figure 1e are attributed to Sc$_4$C$_2@C$_80$ and Sc$_4$C$_2$H$_4$, respectively.

To elucidate the structure of Sc$_4$C$_2$H$_4$, spectroscopic characterizations were performed. It is generally acknowledged that the UV-Vis-NIR spectrum of metallofullerene is mainly related to the π-π* transitions, which are determined by the cage size and symmetry as well as the electronic structure.\(^1\)\(^,\)\(^2\)\(^,\)\(^3\)\(^,\)\(^4\)\(^,\)\(^5\) The onset wavelength of the Sc$_4$C$_2$H$_4$ is 933 nm (see Figure S4 in ESI), corresponding to an energy gap of 1.33 eV. Other absorption peaks present at 670, 416, and 335 nm. For comparison, the onset value of Sc$_4$C$_2@I_5$-C$_80$ was found at 969 nm and the optical band-gap was estimated to be 1.28 eV.\(^10\) Moreover, the resembling features of these two absorption spectra indicate that the Sc$_4$C$_2$H$_4$ has similar I$_5$-C$_80$ carbon cage.

Figure 2. (a) FTIR spectra and (b) low-energy Raman (laser wavelength 633 nm) spectra of Sc$_4$C$_2@C$_80$ and Sc$_4$C$_2$H@C$_80$. The asterisk refers to some impurity.

Figure 2 shows the IR and Raman spectra of Sc$_4$C$_2$H@C$_80$. For comparison, the vibration spectra of Sc$_4$C$_2@I_5$-C$_80$ were also exhibited. It is known that in IR spectrum the vibration frequencies between 1000 and 1600 cm\(^{-1}\) belong to the fingerprint peaks of cage-derived modes.\(^13\)\(^,\)\(^14\) Such characteristic tangential vibrations of Sc$_4$C$_2$H@C$_80$ were observed at 1460, 1380, 1356, and 1262 cm\(^{-1}\) as shown in Figure 2a. These tangential vibrations resembles to the corresponding modes in Sc$_4$C$_2@I_5$-C$_80$ as well as in other M$_2$N@I$_5$-C$_80$ (M = Sc, Y, Dy, Gd) with I$_5$-C$_80$ carbon cage.\(^13\)\(^,\)\(^14\) The asymmetrical Sc-C$_\text{carbide}$ vibrations appeared at 711 and 662 cm\(^{-1}\), which also resemble those of Sc$_4$C$_2@I_5$-C$_80$.\(^10\) Figure 2b shows the Raman spectra of Sc$_4$C$_2$H@C$_80$ and Sc$_4$C$_2@I_5$-C$_80$. Similar as their IR spectra, the Raman spectra of these two compounds exhibit analogous pattern, further confirming their similarity in cage symmetry and endohedral moiety. And the lines at about 407 and 233 cm\(^{-1}\) feature the I$_5$-C$_80$ modes as well as the endohedral Sc-C stretching modes.

![Figure 3. (a) DFT-optimized structure; (b) spin density distributions (blue parts); (c) SOMO; and (d) LUMO orbitals of Sc$_4$C$_2$H@C$_80$. (H: pink, Sc: green, C$_\text{carbide}$: yellow, C$_\text{cage}$: gray); (e) CV curves of Sc$_4$C$_2$H@C$_80$ (red) and Sc$_4$C$_2@C$_80$ (black) measured in o-dichlorobenzene with 0.05 M TBAPF$_6$ at a glassy carbon working electrode referring to saturated calomel electrode.](image-url)
As shown in Figure 3c and 3d, both of the singly occupied molecular orbitals (SOMOs) and the lowest unoccupied molecular orbitals (LUMOs) mainly reside on the endohedral Sc$_4$H cluster and partly on the cage. For reported Sc$_4$C$_2$H@I$_{80}$C$_{80}$ anion state, the added electron is mostly localized on the I$_8$C$_{80}$ cage. In Sc$_4$C$_2$H@I$_{80}$C$_{80}$, the H also supplies an electron; however, its unpaired spin mainly locates on the Sc$_4$ cluster. Therefore, it can be seen that the introduction of covalently bonding H not only influences the geometry of endohedral cluster but also greatly changes the molecular electronic structure.

The electrochemical property of Sc$_4$C$_2$H@I$_{80}$C$_{80}$ was then investigated, as shown in Figure 3e. For Sc$_4$C$_2$H@I$_{80}$C$_{80}$, its first oxidation potential appears at 0.20 V and three reduction peaks were observed at −0.87, −1.68, −1.95 V; whereas in Sc$_4$C$_2$@I$_{80}$C$_{80}$, the first oxidation potential appears at 0.01 V and two reduction peaks exhibit at −1.53 and −1.97 V, respectively.

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Notes and references

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A spin-active hydrogen-containing metallofullerene, Sc₄C₂H@C₈₀, with nested structure was synthesized and investigated.