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Location of the Yttrium Atom in Y@C$_{82}$ and Its Influence on the Reactivity of Cage Carbons

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Endohedral metallofullerenes (EMFs) are generated by encapsulation of metal atom(s) or metallic clusters inside the hollow cavities of fullerenes. Because of the electron transfer from the encaged metallic species to the carbon cage, this new class of hybrid molecules has shown unique structures, novel properties, and promising applications in biology, medicine, and electronics.[1] Although the cavities of fullerenes can contain as many as six atoms, monometallofullerenes—EMFs with only one metal atom inside—are viewed to be the simplest examples for unraveling the structures and properties of EMFs.[1]

Ever since the first extraction of La@C$_{82}$ in 1991,[2] the structure of the fullerene cage and location of the encapsulated metal atom have been of intensive interest to aid in understanding the properties of EMFs and the formation mechanisms as well.[1] It was once assumed that the La atom was trapped inside the most stable C_2 isomer of C$_{82}$.[3] However, theoretical[4] and experimental[5] studies showed that encapsulation of the La atom inside a considerably less stable C_{2v} isomer of C$_{82}$ is the most suitable for La@C$_{82}$ because three electrons are donated from the La atom.[4] More interestingly, it was disclosed that the La atom in La@C_{2v}-C$_{82}$ is not located in the center of the C$_{82}$ cage but sits closely to a hexagonal ring along the C_2 axis.[5,6] That off-center location of La brings the adjacent carbons both high π-orbital axis-vector (POAV)[7] values and high negative charge densities. Consequently, one carbon is most reactive toward the electrophile diazirine adamantylidene (AdN$_2$, **1**), affording only two monoadduct isomers.[8] Single-crystal XRD results of La@C$_{82}$(Ad) unambiguously confirmed the position of the encaged La atom because it was only slightly changed by the addition of Ad. Thus, it presents an efficient way to clarify the location of the metal atom in monometallofullerenes by determining the addition patterns of **1** to EMFs. A recently revealed case is Gd@C_{2v}-C$_{82}$, in which the Gd atom was previously proposed to sit on a [6,6]-bond opposite the hexagonal ring where La sits in La@C_{2v}-C$_{82}$.[9] However, the addition position of **1** in Gd@C$_{82}$[10] is identical to that in La@C$_{82}$,[8] which confirms that the Gd atom in Gd@C_{2v}-C$_{82}$ is also located under a hexagonal ring along the C_2 axis[11] so that it makes the adjacent carbons highly reactive toward **1**.

Actually, a milestone was set for Y@C$_{82}$ when the first structural model of the endohedral nature of EMFs was obtained on it in 1995,[12] which clarified the long debate on whether the metal atom of EMFs is really inside. However, that report showed neither the cage structure nor the correct location of the Y atom.[12] In 2005, ^{13}C NMR results of the anion of Y@C$_{82}$ revealed a C_{2v} cage structure.[13] As NMR does not give information about the location of the Y atom inside Y@C$_{82}$, X-ray structural analysis is highly desirable.[14,15] However, because of the difficulties in preparation of single crystals of pristine metallofullerenes, derivatives of EMFs are often chosen for determination of the parent EMF's structures by a single crystallographic XRD method. Furthermore, as little was known about the chemical properties of Y@C$_{82}$,[16,17] it is therefore meaningful to investigate its chemical behaviors.

Herein, we report the synthesis, isolation, and characterization of the two carbene derivatives of Y@C$_{82}$. The first single crystallographic data unambiguously show that the Y atom is located under a hexagonal ring along the C_2 axis, which accounts for the high selectivity of Y@C$_{82}$ toward the electrophile **1**.

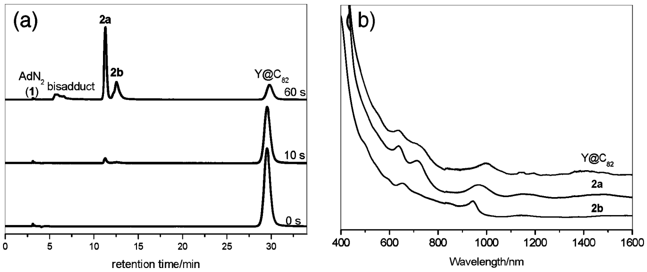

Figure 1. (a) HPLC profiles of the reaction mixture of Y@C$_{82}$ and **1**. (b) vis−NIR spectra of Y@C$_{82}$, **2a**, and **2b**.

The reaction between Y@C$_{82}$ and **1** was triggered by light and monitored using high performance liquid chromatography (HPLC). Figure 1a, which depicts the HPLC profiles, shows that the two starting materials of **1** and Y@C$_{82}$ appeared at 3 and 30 min, respectively. After irradiation for 10 s, new peaks appeared between 11 and 13 min, which are monoadduct isomers as confirmed by mass spectrometry. To obtain monoadducts only, the reaction was terminated after the mixture was irradiated for 60 s, when a small amount of bisadducts appeared. Subsequent separation with preparative HPLC gave the two isomers **2a** (major) and **2b** (minor).

As presented in Figure 1b, the vis−NIR spectrum of **2a** resembles that of pristine Y@C$_{82}$, indicating that the π-system of Y@C$_{82}$ is retained in **2a**. The spectrum of **2b** is a bit different, which means that the electronic structure is slightly changed by the addition of **1** in **2b**. These results imply that addition of the same group to different positions of the carbon cage can have a different effect on the electronic structures of EMFs.

The molecular structure of **2a** was established unambiguously by single-crystal XRD measurements, as shown in Figure 2. The Ad group adds to one of the [6,6]-bond consisting of the hexagonal ring closest to the metal atom. An open structure is concluded from the distance between C1 and C2 (2.107 Å). The structure of **2a** is almost identical to those of M@C$_{82}$(Ad) (M = La, Gd).[8,10] Such a

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similarity proves that the Y atom in pristine Y@C_{82} is also located under the hexagonal ring along the C_2 axis. Y−C1 and Y−C2 distances are 2.475 and 2.466 Å, respectively, which are shorter than the corresponding metal−carbon distances in M@C_{82}(Ad) (M = La, Gd) because of the smaller radius of Y^{3+}.

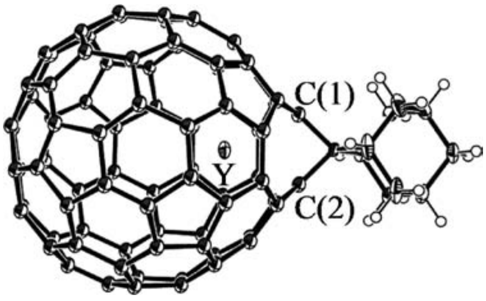

Figure 2. ORTEP drawing of one enantiomeric isomer of **2a** showing thermal ellipsoids at the 50% probability level. The CS_2 molecules are omitted for clarity.

Theoretical calculations were conducted to further understand the addition pattern of Ad to Y@C_{82}. Figure 3 shows the POAV values and charge densities for selected carbons of Y@C_{82} calculated at the B3LYP/3-21G∼dz level (3-21G at C atoms and dz basis with ECP at Y).[18] It is evident that the carbons on the hexagonal ring closest to the Y atom have both higher POAV values and charge densities than others. In fact, C1 has the highest negative charge density though a second highest value of POAV. As we have demonstrated that charge density is more effective than the POAV value when determining the reactivity of cage carbons toward **1**,[19,20] C1 is certainly more reactive than other cage carbons. After linking with C1, the Ad group makes a second bond with adjacent carbons. Because the formation of **2a** involves opening of the C1−C2 bond, **2b** must be generated by the addition of **1** to C1 and C3. It is noteworthy that only C1 is sufficiently reactive toward the carbene reagent Ad, although 24 kinds of nonequivalent carbons of Y@C_{82} exist. This high selectivity originates from the strong interactions between the encapsulated Y atom and the cage.

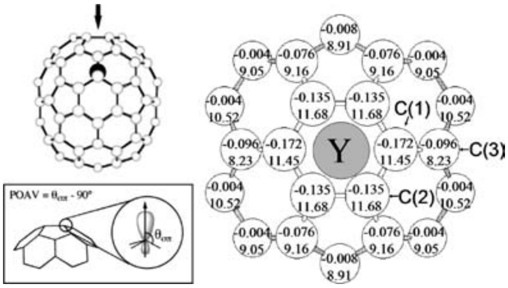

Figure 3. Charge density (upper) and POAV (lower) values of selected carbons of Y@C_{82}.

Electrochemical behaviors of **2a** and **2b** resemble those of the pristine Y@C_{82} (Figure S2), but the redox potentials of **2a** and **2b** are shifted cathodically (Table 1), proving that Ad has an electron-donating ability to Y@C_{82}. Moreover, the redox potentials of **2a** are more negative than the corresponding values of **2b**, which suggests that addition of the Ad group to different cage sites has a different effect on the intrinsic properties of EMFs.

Table 1. Redox Potentials (V) of Y@C_{82}, **2a**, and **2b**[a]

compound	$^{ox}E_1$	$^{red}E_1$	$^{red}E_2$	$^{red}E_3$
Y@C_{82}[b]	+0.10	−0.34	−1.33	
2a	−0.02	−0.54	−1.51	−1.84[c]
2b	+0.05	−0.43	−1.37	−1.70

[a] Half-cell potentials unless otherwise noted. Values are relative to ferrocene/ferrocenium couple. In 1,2-dichlorobenzene with 0.1 M (*n*-Bu)$_4$-NPF_6 at a Pt working electrode. [b] Reference 16. [c] Irreversible. DPV peak value.

In conclusion, we have presented the first single crystallographic results of the crucial metallofullerene Y@C_{82} by measuring its carbene derivative. Single-crystal X-ray results unambiguously confirm that the Y atom in Y@C_{82} is located under a hexagonal ring along the C_2 axis, which makes only one of the cage carbons sufficiently reactive toward the electrophile Ad (**1**). Furthermore, the electron-donating ability of the Ad group to EMFs was also confirmed, which is expected to be useful in future works dealing with the design and synthesis of applicable materials based on EMFs.

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Supporting Information Available: Complete refs 5, 8, 10, and 18, HPLC profiles, CV/DPV curves and ESR, NMR spectra of Y@C_{82}Ad. This material is available free of charge via the Internet at http://pubs.acs.org.

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