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## Addition of Benzyne to Gd@C$_{82}$

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Endohedral metallofullerenes (EMFs) have attracted broad attention because of their novel properties and potential applications.[1] Since organic functionalization of EMFs would bring them many new applications, much interest has been focused on this subject.[2] In 1995, the first exohedral adduct of EMFs was synthesized by the cycloaddition of disilirane to La@C$_{82}$.[3] Then nucleophilic reactions of diazolcarbonyl compounds or bromomalate with EMFs were also investigated, and multiple adducts with cyclopropane rings were obtained.[4–6] Recently, the Diels–Alder reaction of Sc$_3$N@C$_{80}$ with *o*-quinomethane afforded a novel monoadduct with a planar symmetry.[7] These achievements show that cycloaddition is an efficient method for exohedral functionalization of EMFs. Although [1+2], [3+2], and [4+2] cycloadditions of metallofullerenes have been reported, [2+2] cycloaddition of EMFs has not been investigated

yet. Moreover, investigations on the properties of metallofullerene derivatives have rarely been reported.[7] In this paper, we present the first synthesis, isolation, and characterization of the [2+2] cycloadducts of EMFs.
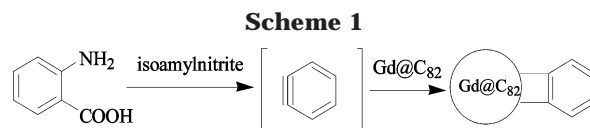
Scheme 1

In a typical synthesis (Scheme 1), 20 mL of toluene solution containing both ~2 mg of Gd@C$_{82}$ (purity >98%) and 0.5 mL of isoamyl nitrite was bubbled with argon for 10 min, and then 50 mg of anthranilic acid was added. After being stirred under argon for 5 h at room temperature, the mixture was washed with saturated aqueous NaHCO$_3$ and water.[8] The organic layer was concentrated and filtered for HPLC separation using a Buckyprep column (Nacalai Tesque Co.) with toluene as the eluent.

The HPLC chromatogram of the crude mixture is shown in Figure 1a. The small peaks during 6 and 15 min contain several multiple adducts. The two peaks at 17.6 and 19.3 min are assigned to the two isomers of monoadduct Gd@C$_{82}$(C$_6$H$_4$). They are marked as **Monoadduct I** and **Monoadduct II**, respectively, for clarity. Unreacted Gd@C$_{82}$ appears at 35.2 min. There are no discernible peaks behind Gd@C$_{82}$. It is evident that monoadducts dominate the reaction. Assuming that the products have similar absorption coefficients with Gd@C$_{82}$ at 400 nm, the yields for **Monoadduct I** and **Monoadduct II** are estimated to be ~40% and ~5%, respectively, from their HPLC peak areas. Because the two peaks at 17.6 and 19.3 min are overlapped with each

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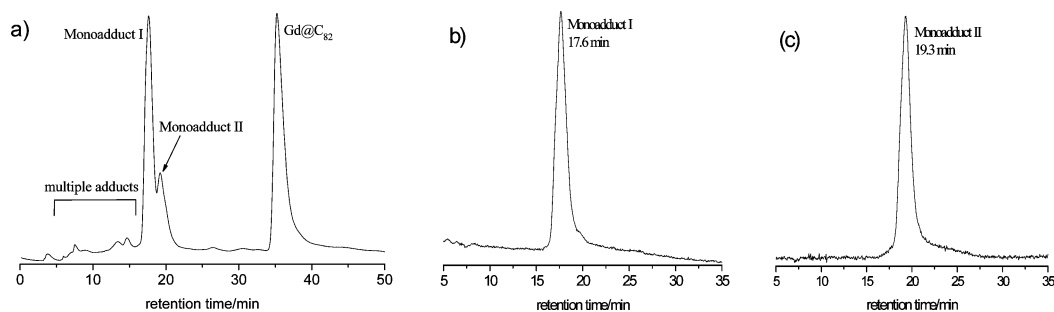
Figure 1. HPLC chromatogram of the crude reaction mixture after being stirred for 5 h (a) and HPLC traces of purified **Monoadduct I** (b) and **Monoadduct II** (c).
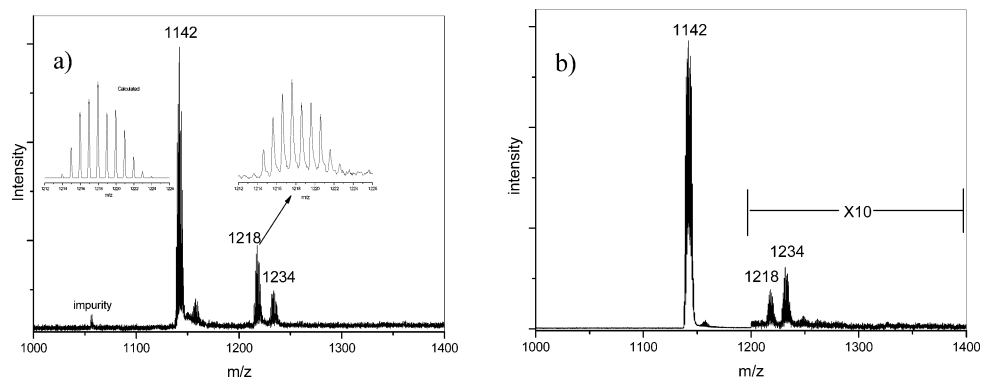

Figure 2. MALDI TOF mass spectra of **Monoadduct I** (a) and **Monoadduct II** (b) using anthracene as the matrix. The insets in (a) are the computer simulation results of $Gd@C_{82}(C_6H_4)$ and the observed isotope distributions of **Monoadduct I**.

other, further separation was carried out using the same column. The HPLC traces of finally purified **Monoadduct I** and **Monoadduct II** are displayed in Figure 1b and 1c, respectively.

Formation of the 1:1 adducts were verified by matrix-assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI TOF) using anthracene as the matrix. Figure 2a and 2b are the mass spectra for **Monoadduct I** and **Monoadduct II**, respectively, which are similar to each other. In both spectra, four peaks are discernible. The peak at m/z 1218 is undoubtedly ascribable to the 1:1 adduct, and its isotope distributions agree well with the computer simulation results of $Gd@C_{82}(C_6H_4)$ (insets in Figure 2a). While the peak at m/z 1234 should be assigned to $Gd@C_{82}(C_6H_4)O$, which was obviously generated during the mass spectral sampling process since almost all manipulations before mass analysis were conducted under an argon atmosphere. The same phenomenon could also be seen for C_{60} analogues.[8] The base peak at m/z 1142 is ascribed to the parent metallofullerene $(Gd@C_{82})$, which was derived from the monoadducts during the laser desorption process by cleaving the outside addend.[3,6,7] The following peak at m/z 1158 should be assigned to $Gd@C_{82}O$, which must be originated from $Gd@C_{82}$-$(C_6H_4)O$. Mass spectral peaks ascribable to multiple adducts are not found within the spectra. In addition, the intensity of the peak at m/z 1234 is higher than that of the peak at m/z 1218 in Figure 2b while it is on the contrary in Figure 2a. Since they were synthesized and characterized under identical conditions, this result may indicate that **Monoadduct II** is more sensitive to oxygen than **Monoadduct I**.

The vis-NIR absorbance spectra of **Monoadduct I**, **Monoadduct II**, and the parent $Gd@C_{82}$ are shown in
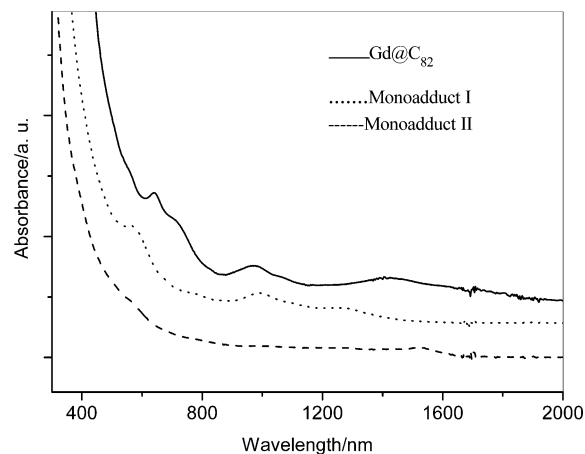

Figure 3. Vis-NIR spectra of $Gd@C_{82}$ (solid line), **Monoadduct I** (dotted line), and **Monoadduct II** (dashed line) in toluene.

Figure 3 and they are shifted from each other for clarity. The spectrum of $Gd@C_{82}$ shows three salient absorbance bands at 640, 980, and 1410 nm, which resemble that of the C_{2v}-symmetric $La@C_{82}$.[9] So the molecular symmetry of the $Gd@C_{82}$ used here should also be C_{2v}. **Monoadduct I** shows three characteristic bands at 560, 990, and 1280 nm with an onset at 1500 nm. However, **Monoadduct II** shows no absorbance band over the vis-NIR region but the onset is discernible at ~1600 nm. Although the reason the absorbance spectra of the two

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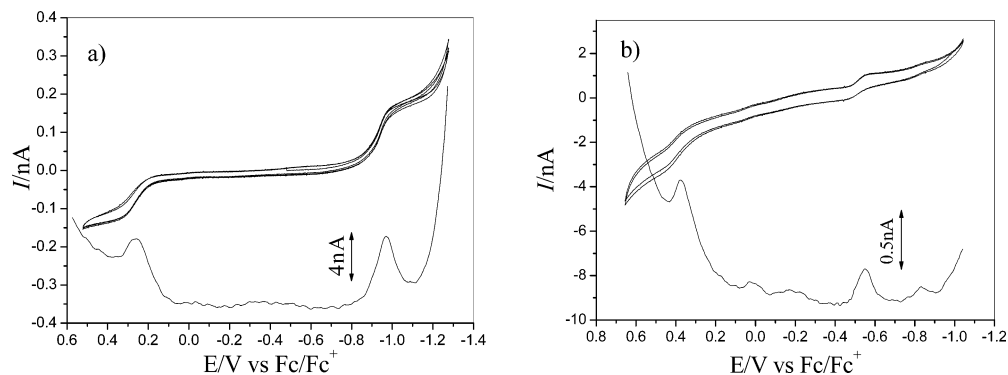
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Figure 4. CV (20 mV/s scan rate) and DPV (50 mV pulse height, 60 ms pulse width, 4 mV/s scan rate) of **Monoadduct I** (a) and **Monoadduct II** (b) in acetonitrile/toluene (1:4 v/v) containing 0.1 M (n-Bu)$_4$NPF$_6$ at -10 °C.

monoadducts are widely different is not clear now, a conclusion can be drawn that the electronic structure of Gd@C$_{82}$ has been altered by the exohedral addition.

The cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of **Monoadduct I** and **Monoadduct II** are shown in Figure 4a and 4b, respectively. For **Monoadduct I**, one reversible oxidation at 0.26 V and one reversible reduction at -0.97 V are observed, which is significantly different from the redox potentials of Gd@C$_{82}$, which have one reversible oxidation at 0.20 V and two reversible reductions at -0.25 and -1.25 V in the potential range of -1.5 and 0.8 V.[10] In general terms, the reduction potentials of C$_{60}$ are cathodically shifted 0.1–0.4 V when it is functionalized.[11] However, this is the first observation for the cathodic shift of metallofullerene derivatives. Moreover, because Gd@C$_{82}$ ($E^{red}_1 = -0.25$ V) is much easier to be reduced than C$_{60}$ ($E^{red}_1 = -0.85$ V[11]), the cathodic shift (0.71 V) is relatively large. As for **Monoadduct II**, one reversible oxidation (at 0.38 V) and one reversible reduction (at -0.55 V) are very evident and three peaks at 0.02, -0.18, and -0.83 V are relatively small in the DPV curve. This result may due to the partial oxidation of **Monoadduct II** during the experimental procedure. Because of the insufficiency of the sample, it is not

possible to elucidate the electronic structures clearly at present. Nevertheless, the CV and DPV results provide a fact that the electronic structure of Gd@C$_{82}$ has indeed been modified by exohedral modification. Moreover, the novel electochemical behavior of **Monoadduct I** brings a possible application as an electronic switch because it has no response to the potential between -0.97 and $+0.26$ V but gives a strong current when the two critical potentials are exceeded.

In summary, we have successfully synthesized the first [2+2] cycloadducts of metallofullerenes. Our data show that monoadducts dominate the reaction, and the exohedral addend has strong reductive effect on the metallofullerene. These derivatives may have potential use in material science. However, it is still very difficult to determine the structures of these adducts because of their paramagnetic nature and the difficulty in preparing single crystals.

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