Chemical Modification of Tb@C_{82} by Copper(I)-Catalyzed Cycloadditions

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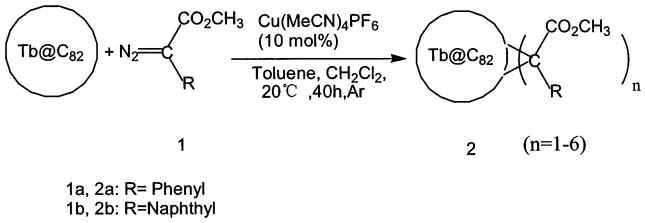
Endohedral metallofullerenes (EMF) have been expected to be a kind of new material for their novel electronic and physical properties.[1] Since chemical modification of EMF would trigger their applications as organic nanocomposites in many fields, much interest has focused on the synthesis of EMF derivatives. In recent years, with milligrams of EMF becoming available due to improved production and isolation procedures, some progress on the modification of EMF has been made,[2−8] and cycloadditions have been proved to be very efficient for EMF modifications. In 1995, Akasaka and co-workers first reported the chemical derivatization of La@C_{82}, Gd@C_{82}, and La_2@C_{80} by disilacyclopropane.[2−4] Additionally, Suzuki's group reported a thermal reaction between diphenyldiazomethane and La@C_{82}.[5] Both these studies raveled the unique chemical properties of EMF and provided the means of multiple functionalization for EMF. Herein, a copper(I) catalyst ($Cu(MeCN)_4PF_6$)[9] mediated reaction of Tb@C_{82} with α-diazocarbonyl compounds (**1** in Scheme 1) to produce multiadducts of Tb@C_{82} (**2** in Scheme 1) is first reported.

The synthesis of **2** is demonstrated with two different aryldiazoacetates, **1a** and **1b**, using the following procedure (Scheme 1). The Tb@C_{82} used in this investigation was produced by the improved arc method[10] and purified by single-step HPLC.[11] The purity was estimated to be higher than 95% based on HPLC and MS analysis. In a typical experiment, 37 mg of **1a** (in large excess) in CH_2Cl_2 was added dropwise to the toluene solution of 8 mg of Tb@C_{82} with copper(I) in the form of $Cu(MeCN)_4PF_6$ as a catalyst. The mixture was stirred at 20 °C for 40 h under an Ar atmosphere. The wine-red multiadducts were isolated from the unreacted material with column chromatography (silica, toluene: methanol = 93:7 v/v), but they could not be separated from each other.

Scheme 1



To convert all the available active sites on the Tb@C_{82} molecule, a large excess of **1** was used in these experiments. A matrix-assisted positive-ion MALID-TOF mass spectrum (Figure 1a) displayed a series of molecular ion peaks at m/z 1143 + $(148)_n$ (n = 1−6), indicating the presence of multiadducts (**2a**) with the loss of N_2. The observed isotope distributions also agreed well with the computer simulation for Tb@C_{82} $[CH_2(C_6H_5)CO_2CH_3]_n$ (Figure 2). However, in the negative-ion mass spectrum (Figure 1b), only three molecular ion peaks at m/z 1143 + $(148)_n$ (n = 1−3) could be identified, which suggests that introduction of the organic groups onto the fullerene cage would decrease the electron affinity of metallofullerene. So the positive-ion mode is found to be more suitable for displaying the degree of derivatization of the parent metallofullerene. In the case of **2b**, only mono- to tetra-adducts are observed due to the comparatively larger space hindrance caused by naphthyl groups.

Figure 3 shows the micro Fourier transform infrared spectrum of **2a**. A strong and sharp peak centered at 1739 cm^{-1} can be assigned to the C═O stretching vibration. Compared with the corresponding peak (1705 cm^{-1}) in a FT-IR spectrum of **1a**, the peak shifted to a higher frequency, indicating the loss of electron-withdrawing group N_2 on α-C. No peak at 2089 cm^{-1} corresponding to the C═N═N vibration was observed, which also confirmed the loss of N_2 during the reaction. Thus, these functionalized Tb@C_{82} compounds were identified, but their exact structures remain to be determined.

Since no change in physical appearance could be observed for the reaction mixture and no corresponding adducts could be detected by MS in the noncatalyzed reaction, it appears that copper(I) played a crucial role in the reaction. As **1a** and **1b** are more stable than diphenyldiazomethane, they almost did not react with Tb@C_{82} until the temperature was elevated to 60 °C, even though the reaction time was prolonged. Therefore, although metal carbenes generated from copper(I) and diazocompounds could not be directly detected during the reaction,[12] they are possibly involved as the reactive intermediates, as in the case of planar aromatic hydrocarbon.[13−15] To compare the chemical reactivity of Tb@C_{82} with those of empty fullerenes, C_{60} was used. Under the same conditions, C_{60} did not afford corre-

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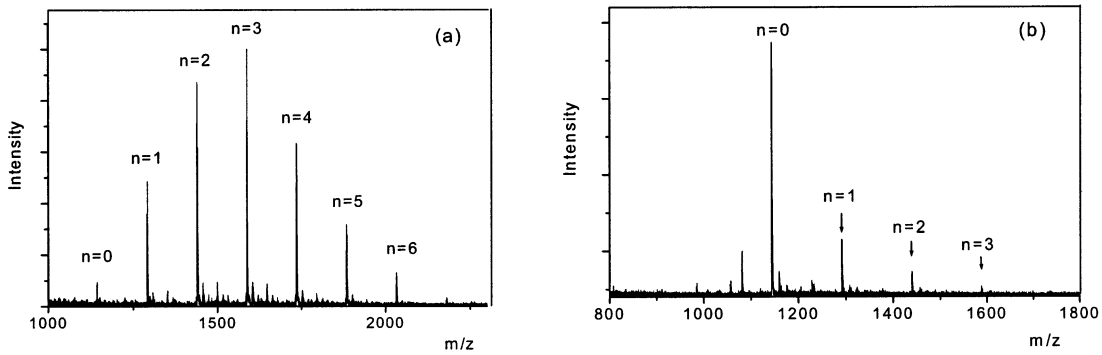

Figure 1. A matrix-assisted MALDI-TOF mass spectrum of multiadducts $Tb@C_{82}-(CphCO_2CH_3)_n$: (a) positive-ion mode (n = 0−6); (b) negative-ion mode (n = 0−3).

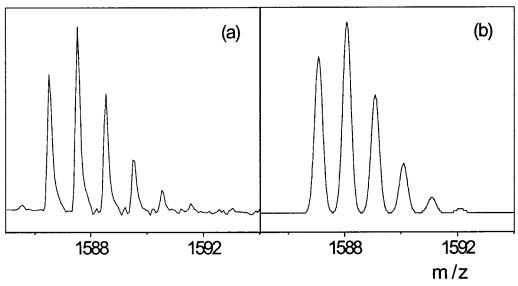

Figure 2. Mass spectra for the multiadducts $Tb@C_{82}[CH_2-(C_6H_5)COOCH_3]_n$ (n = 3): (a) observed isotope distributions; (b) its computer simulation.

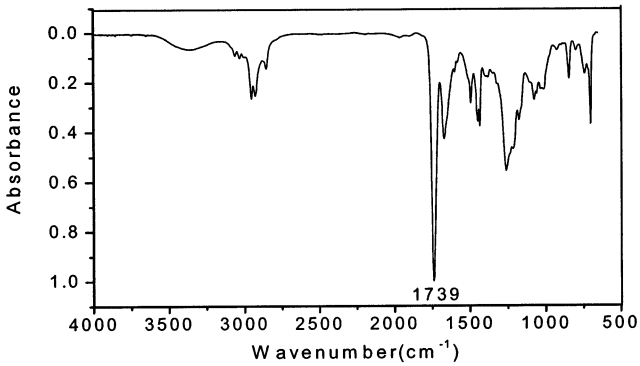

Figure 3. FT-IR spectrum of **2a**.

sponding multiadducts. The possible explanation is that C_{60} preferentially forms stable complexes with a wide variety of transition metals,[16] and therefore, the catalytic activity of copper(I) is suppressed.

To investigate the electronic structure of **2a**, further analysis based on XPS, UV/Vis/NIR, and fluorescence spectrum was carried out. In the XPS spectra of **2a** film, despite a relatively low signal-to-noise ratio, the peaks for Tb 4d and Tb $3d_{5/2}$ were observed. The binding energy of Tb 4d and Tb $3d_{5/2}$ are 153.2 and 1245.4 eV, respectively, which are close to the corresponding values (153.6 and 1244.8 eV) in the XPS spectra of $Tb@C_{82}$ film measured at the same time. It seems that the oxidation state of Tb in **2a** is 3+. In other words, the exohedral modification of $Tb@C_{82}$ has little effect on the valence of an endohedral metal atom, which is consistent with the EPR study of diphenylmethano-$La@C_{82}$.[5] The UV/Vis/NIR absorption spectrum of **2a** in toluene displayed no characteristic bands at 631, 990, and 1402 nm observed for $Tb@C_{82}$,[11] but exhibited a monotonically decreasing absorption coefficient with increasing wavelength in the range of 400−1500 nm, without characteristic features. This great difference may be attributed to the change in electronic structure of the fullerene cage for the introduction of organic groups.

The emission spectra of highly purified $Tb@C_{82}$ (1×10^{-5} M) obtained upon 340-nm excitation at room temperature showed a very weak fluorescence at 378 nm and no fluorescence at 554 nm observed for Tb^{3+}, which is more like the emission spectra of empty fullerenes.[17] Its derivatives (**2a**) diluted in toluene, having the same fluorescence intensity as $Tb@C_{82}$, showed a broader fluorescence band at 390 nm upon excitation at the same wavelength. The red shift can be attributed to the introduction of electron donors that stimulate electron transfer between the organic groups and the EMF in the excited states. The broader emission peak of **2a** is due to the existence of multiadducts series.

In conclusion, we have developed an efficient method of chemical modification for metallofullerenes via metal-catalyzed addition of diazocompounds. By this method, water-soluble EMF and a self-assembled monolayer based on EMF derivatives could be synthesized, which has potential use in biological and material sciences.

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