Communication

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Highly Selective and Simple Synthesis of $C_{2m}-X-C_{2n}$ Fullerene Dimers

Yuliang Zhao,*,† Zhenling Chen,† Hui Yuan,† Xingfa Gao,† Li Qu,† Zhifang Chai,*,† Gengmei Xing,†
Soichiro Yoshimoto,‡ Eishi Tsutsumi,‡ and Kingo Itaya‡

Institute of High Energy Physics, Chinese Academy of Science, Beijing 100039, China, and Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba-yama 04, Sendai 980-8579, Japan

Received March 28, 2004; E-mail: zhaoyuliang@ihep.ac.cn; Chaizf@ihep.ac.cn

In a gas-phase experiment, Shvartsburg et al. recently revealed the presence of several ball-and-chain fullerene dimers (e.g., $C_{60}-C_{n-60}$) in which fullerenes are linked by carbon atoms.[1] When fullerene cages are linked by a bridge atom, they form $C_{2m}-X-C_{2n}$ type dimers. In particular, the all-carbon ($C_{2m}-C-C_{2n}$ type) fullerene dimers are of considerable interest for their unique properties and as model compounds in nanomaterials research and in polymer and supramolecular sciences.[2-5] Dragoe et al.[6] synthesized the first $C_{2m}-C-C_{2n}$ type dimer C_{121}[7] (following a suggestion of Osterodt and Vogtle) in a thermolysis reaction of $C_{60}CBr_2$ with C_{60} at the high temperature of 723 K. So far, no other $C_{2m}-C-C_{2n}$ type dimers have been reported. In this study, we employed energetic radiation to induce fullerene dimerization reactions. This is a new and highly selective method for the synthesis of $C_{2m}-X-C_{2n}$ ($m = n$ or $m \neq n$) products without $C_{2m}-C_{2n}$ formations.

The synthesis method is simple, as described in Scheme 1. Three samples, C_{70} (30 g), [$C_{60} + C_{70}$] (30 g mixture, wt/wt = 1:1), and C_{60} (30 g), were separately wrapped in high-purity aluminum foils, radiated by reactor neutron beams for 2 h, and then dissolved in toluene under ambient conditions. Each sample was separated by HPLC (Waters 600E) with Cosmosil 5PBB and Buckyprep columns (Nacalai Tesque) using toluene as a mobile phase. The chromatographic results with the 5PBB column (see Figure S-1a in Supporting Information) show intensive peaks at $t_R = 84.1$ (**1**–I), 94.0 (**1**–II), 104.0 (**1**–III), 201.7 (**2**), and 231.0 (**3**) min in addition to the unchanged reactants C_{60} (17.0 min) or C_{70} (30.2 min). The fractions obtained with the 5PBB column were further separated using Buckyprep columns (see Figure S1b,c in Supporting Information). The HPLC fractions were analyzed by MALDI-TOF-MS (AutoFlex, Bruker Co.). The results (Figure 1) indicate that fractions **1**–I, **1**–II, and **1**–III are three isomers of C_{121} ($m/z = 1453.2$). This is consistent with the theoretical prediction of three isomers for C_{121}.[8] The fraction **2**–I (106.2 min, $m/z = 1693.7$) is a new molecule C_{141}, whose mass and characteristic isotopic pattern are also in complete agreement with the theoretical prediction. Fractions **2**–II (121.0 min), **3**–II (112.9 min), and **3**–III (118.4 min) have the same mass, $m/z = 1573.4$, and are three isomers of another new molecule C_{131}. A small fraction **3**–I at $t_R = 106.6$ min has a mass of C_{141}. It was assigned to be the same isomer as the fraction **2**–I because of the same chromatographic retention time. Here, in addition to the formation of new molecules, of particular interest is the fact that no even-numbered fullerene dimers such as C_{120}, C_{130}, or C_{140} were observed, though according to the known processes for dimer formations they should have been more probable.

Dragoe et al. studied the structure of C_{121} in detail.[3,8] C_{131} and C_{141} must have the same structure, as supported by results from
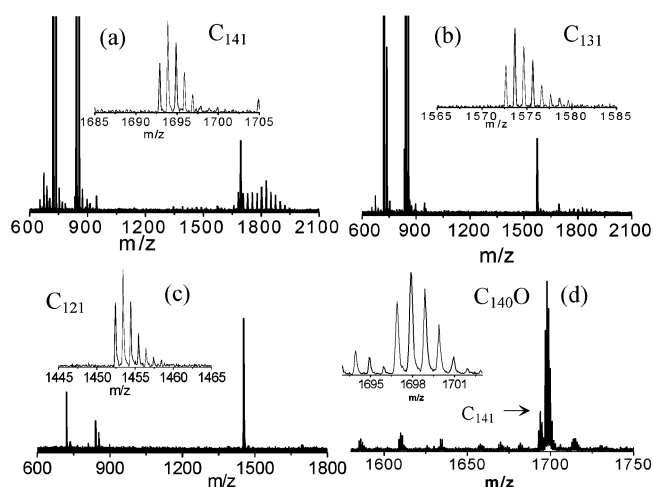
Figure 1. MALDI-TOF MS of C_{141} (a), C_{131} (b), C_{121} (c), and $C_{140}O$ (d). The inset is the observed isotopic pattern (negative ionization, reflection mode, and 9-nitroanthracene as a matrix). For HPLC analyses of these products of three irradiated samples, see Figures S1–6 in Supporting Information.

Scheme 1
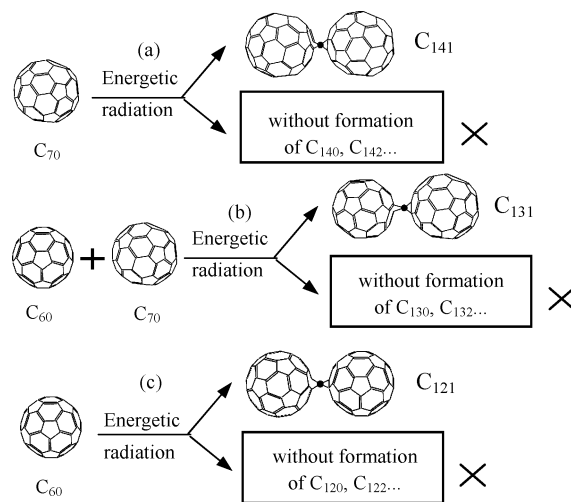
the STM, FT-IR, UV–vis, and ^{13}C NMR measurements. We measured C_{141} and C_{131} by using high-resolution in situ scanning tunneling microscopy (STM, Digital Instruments Nanoscope E). The adlayer of C_{141} or C_{131} was formed on coronene-modified Au-(111). High-resolution STM images were taken in an aqueous HClO$_4$ solution with the constant-current mode. The potential of the tip and the tunneling current were 0.35 V and 1.0 nA, respectively. The entire molecule of C_{141} (Figure 2a) or C_{131} (Figure 2b) was clearly recognized as a pair of round bright spots in contact with each other, suggesting that the molecule is not a single big

† Chinese Academy of Science.
‡ Tohoku University.
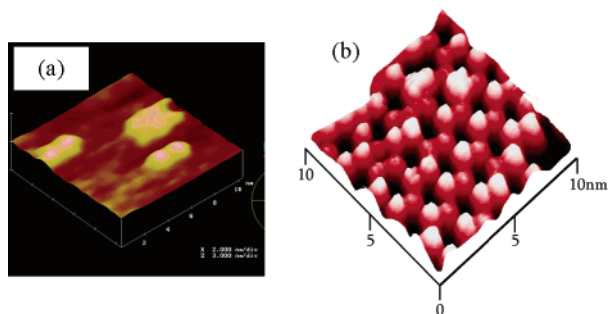
Figure 2. High-resolution in situ STM images of C_{141} (a) and C_{131} (b). Difference in size between C_{60} and C_{70} units and the bridge space between side-cage units are clearly recognized.

cage but consists of two cage units. Thus, C_{131} and C_{141} must have the structures of $C_{60}-C-C_{70}$ and $C_{70}-C-C_{70}$, similar to that of C_{121} ($C_{60}-C-C_{60}$).[3,8] Here the linear depiction is not meant to signify a linearity of the molecule.

The measurements of FT-IR spectra of C_{131} and C_{141} verified the presence of C_{60} and/or C_{70} monomers in C_{131} or C_{141} molecules. Moreover, peaks for a cyclopropane skeletal stretch[2] in spectra of C_{131} (1025.8 cm^{-1}) and C_{141} (1026.9 cm^{-1}) were also observed (see Figure S7a–c in Supporting Information). ^{13}C NMR of C_{131} were measured in a solvent of 1-chloronaphthalene with Cr(acac)$_3$ as a relaxant and benzene-d_6 for the internal lock. Resonances from sp^2 carbons were theoretically expected in the range from 113 to 141 ppm, which were completely covered by strong signals (in the region from 117 to 140 ppm) of the solvent. Resonances at 64.49, 63.44, 62.02, 61.57, and 59.78 ppm in the sp^3 region were observed. The first four signals were assigned to the bridgehead carbons, and the last one was assigned to the intermediate bridge carbon atom.

Results of UV–vis absorption measurement of C_{141} and C_{131} (see Figure S8 in Supporting Information) revealed that the energy required for $\pi-\pi^*$ transition in C_{131} or C_{141} is similar to that in the C_{60} or C_{70} monomer. The absorption bands of C_{131} (324 nm) and C_{141} (323 nm) are very close to those of C_{60} (335 nm) and C_{70} (334 nm). This suggests the existence of C_{60} and/or C_{70} cage units in C_{131} and/or C_{141}. Visible absorptions of C_{131} and C_{141} were largely diminished in comparison with those of C_{70}. This also supports the structures of $C_{60}-C-C_{70}$ and $C_{70}-C-C_{70}$, because the bridged structure largely restrains the C_{70} vibration. The $\pi-\pi^*$ absorption bands in C_{131} or C_{141} showed a blue shift of about 10 nm from those in C_{60} or C_{70}. This is consistent with the prediction of Hückel molecular orbit theory that the energy required for transition of π-electron decreases with increasing the number of conjugated double bonds in a molecule.

To understand the observation that only C_{121}, C_{131}, and C_{141} products were formed without C_{120}, C_{130}, and C_{140}, we performed further experiments by introducing other atoms into the reaction system of pure fullerenes. Prior to radiation, C_{70} was chemically modified using ozone for 4 h to form $C_{70}O$, which was then neutron-radiated under the same conditions as those stated before. The obtained products were only $C_{140}O$ and C_{141} (Figure 1d). An oxobridge and a carbon bridge were alternatively inserted between two fullerene cages to form only $C_{2m}-X-C_{2n}$ products, without direct dimerization to form C_{140}. This is different from any of the known reactions for the fullerene dimer formation. [2,9] Theoretical calculations for all possible isomers of C_{141} and C_{131} using PM3, B3LYP/3-21G, and B3LYP/6-31G(d) indicated that, unlike the structure of C_{140}, the C_{141} isomer of the lowest total energy had a

new structure: both of the two side cages open [6.6] rings located at the equator (instead of cap) region of C_{70} cage to create new chemical bonds for the spiro-carbon of bridge atom. This new structure makes C_{141} less polar than C_{131} and provides satisfactory explanation to the fact that t_R of C_{131} is longer than C_{141} in accordance with the correlation between the polar nature and the chromatographic retention time.[10]

In conclusion, we present here the first highly selective reaction that produces only $C_{2m}-X-C_{2n}$ ($m = n$ or $m \neq n$) without $C_{2m}-C_{2n}$ type fullerene dimers. Utilizing the new method, we have synthesized C_{141}, C_{131}, C_{121}, and $C_{140}O$, of which C_{141} and C_{131} were prepared and characterized for the first time. The C_{121}-like structures of C_{131} and C_{141} were supported by STM, FT-IR, UV–vis, and ^{13}C NMR results. The method is capable of producing new $C_{2m}-X-C_{2n}$ molecules by chemical modification of precursors to introduce different X-atoms into the reaction system prior to radiation. The energetic neutron radiation could create reactive sites for covalently bonded bridges between fullerene molecules originally only weakly bound by van der Waals force. This may open a new subject and provide a practical approach for polymer sciences of fullerenes and fullerene derivatives.

Supporting Information Available: Data of HPLC separations, isolations of products from three different starting materials, and FT-IR spectra and UV–vis absorption spectra for new molecules C_{141} and C_{131}. This material is available free of charge via the Internet at http://pubs.acs.org.

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