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

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Supporting information

S1: The HPLC separation and isolation of the C_{2n} -C- C_{2m} products from neutron-irradiated $[C_{60}+C_{70}]$ mixture.

Fig. S-1. HPLC separation of C_{2n} -C- C_{2m} products from starting materials with 5PBB columns (a), and isolation of isomers with Buckyprep columns, (b) and (c).

The sample was dissolved in toluene under air atmosphere and separated by the HPLC (Waters 600E, USA) coupling with Cosmosil 5PBB and Buckyprep columns (Nacalai Tesque, Japan) using toluene as a mobile phase. In chromatographic results of 5PBB column (Fig. S1(a)), new intensive fraction peaks emerging at $T_R=84.1$ (**1-I**), 94.0 (**1-II**), 104.0 (**1-III**), 201.7 (**2**) and 231.0 (**3**) min are observed in addition to peaks of the unchanged C_{60} ($T_R=17.0$) or C_{70} ($T_R=30.2$) reactants. 5PBB fractions **2** and **3** were further separated using Buckyprep columns (Figs. S1(b) and S1(c)), respectively. These HPLC fractions were analyzed by a matrix assisted laser desorption time-of-flight mass spectrometer (AutoFlex, Bruker Co., Germany). The results indicate that fractions **1-I**, **1-II** and **1-III** are three isomers of C_{121} , ($m/z=1453.2$). The fraction **2-I** ($T_R=106.2$ min) gave $m/z=1693.7$, it was assigned to a new molecule C_{141} because both the mass and characteristic isotopic pattern were in agreement with theoretical predictions. Fractions **2-II** ($T_R=121.0$ min), **3-II** ($T_R=112.9$ min) and **3-III** ($T_R=118.4$ min) had the same mass of $m/z=1573.4$, they were three isomers of a new molecule

C_{131} . A small fraction 3-I ($T_R=106.6$ min) in Fig. S1(c) gave the mass of C_{141} . It is considered to be the same isomer with fraction 2-I of Fig. S1(b), because their chromatographic retention times were almost the same. They can be mixed in samples 2 and 3 during manipulation of collection of 5PBB fractions. C_{60} irradiation

S2: The HPLC analysis of the C_{121} products from the neutron-irradiated C_{60} .

Fig. S-2. HPLC analyses of C_{121} products from starting materials C_{60} with 5PBB columns (a), and isolation of isomers with Buckyprep columns, (b), (c) and (d). 5PBB: 20×250 mm with guard column, using toluene as the mobile phase, 9.9 mL/min, HPLC, LC908-C60, Japan Analytical Industry Co; Buckyprep: 10×250 mm with guard column, using toluene as the mobile phase, 1.6 mL/min, HPLC, Waters 600E)

S3: The HPLC analysis of the C_{141} from the neutron-irradiated C_{70} .

Fig. S-3. HPLC analyses of C_{141} from starting materials C_{70} with 5PBB columns (10×250 mm with guard column, using toluene as the mobile phase, 3.2 mL/min, HPLC, Waters 600E) .

S4: The HPLC analysis of the $C_{140}O$ from the neutron-irradiated epoxide $C_{70}O$.

Fig. S-4. HPLC analyses of $C_{140}O$ from starting materials $C_{70}O$ with 5PBB columns (10×250 mm plus guard column, using toluene as the mobile phase, 1.6 mL/min, HPLC, Waters 600E) .

S5: Full scale of Fig. S-1(b)

Fig. S-5. Analyses of C_{2n} -C- C_{2m} products with Buckyprep columns (for the detail, see Fig. S-1(b)).

S6: Full scale of Fig. S-1(c)

Fig. S-6. Analyses of C_{2n} -C- C_{2m} products with Buckyprep columns (for the detail, see Fig. S-1(c)).

S7: FT-IR spectra of C_{141} , C_{131} , C_{121} , C_{70} and C_{60} .

Figure S-7, FT-IR spectra of C_{141} (a), C_{131} (b), C_{121} (c), C_{70} (d) and C_{60} (e).

FT-IR spectra for C_{131} and C_{141} were measured. The characteristic peaks for C_{60} are at 1429 and 1182 cm^{-1} , for C_{70} at 1431 and 1132 cm^{-1} . While C_{131} -I gives main absorption at wavenumbers of 1737, 1650, 1556, 1463, **1430**, 1360, 1270, **1182**, **1130**, 1072, 1026 cm^{-1} , C_{141} at 1730, 1650, 1531, **1430**, 1276, **1130**, 1073 and 1027 cm^{-1} . The expected peak for a cyclopropane skeletal stretch was also observed in spectra of C_{131} (1025.8 cm^{-1}) and C_{141} (1026.9 cm^{-1}). Accordingly, these results revealed the coexistence of cyclopropane structures, C_{60} and C_{70} cage units in C_{131} , and cyclopropane structures and the C_{70} cage unit in C_{141} molecule.

The FT-IR spectra were measured with the liquid film of the sample in toluene solution. The observed C-H stretching frequencies are from the solvent of toluene. One sees that the relative intensity of the C-H absorption shows an increasing tendency from C_{60} and C_{70} to C_{121} , C_{131} , and C_{141} , this is because the corresponding solubility of the sample in toluene is decreased in the same sequence.

S8: UV-vis absorption spectra of C_{141} , C_{131} , C_{70} and C_{60}

Figure S-8, UV-vis absorption spectra of C_{141} , C_{131} , C_{70} and C_{60}