Synthesis of New Fullerene Dimers and Open-Cage Fullerenes by Solid-State and Liquid-Phase Reactions of C_{60} with N-Containing Aromatics and with Organosilicon Compounds

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We recently developed a new method to functionalize C_{60} in the solid state, by the use of a mechanochemical technique of high-speed vibration milling. This method has been successfully applied to the first [2+2] dimerization of C_{60},[1] cross-dimerization of C_{60} and C_{70},[2] trimerization[3] and [4+2] cycloadditions of C_{60},[4] in addition to the complexation with water-soluble host molecules[5] and a nucleophilic addition to C_{60}.[6]

Particularly when the reaction was conducted with a nitrogen-containing (diaza) aromatic compound such as phthalazine, the [4+2] reaction took place, which was followed by extrusion of nitrogen and further addition or rearrangements to give novel C_{60} derivatives, a dimer connected by a bicyclic framework **1** (by a solid-state reaction) and a bonzo-derivative of an open-cage fullerene **2** with an eight-membered ring orifice (by a thermal liquid-phase reaction).[7]

Similarly, when a solid-state reaction of C_{60} was conducted with 3,6-di-2-pyridyl-1,2,4,5-tetrazine under high-speed vibration milling, the [4+2] addition/ nitrogen-extrusion product **3** was formed quantitatively. This can further react with C_{60} in solid state to give the dimer **4**. Both dimers **1** and **4** undergo the photochemical intramolecular [2+2] reaction between the two C_{60} cages.

On the other hand, a thermal liquid-phase reaction of C_{60} with 4,6-dimethyl-1,2,3-triazine at 180 °C afforded, after silica-gel chromatography, an open-cage fullerene derivative **5** with an eight-membered ring orifice in addition to an azacyclohexadiene fused C_{60} **6**. A photochemical reaction of the open-cage fullerenes **2** and **5** with singlet oxygen was found to give the fullerene derivatives with 12-membered ring orifice **7** and **8** respectively.

Furthermore, the solid-state reaction of C_{60} with dichlorodiphenylsilane and lithium metal afforded a new C_{60} dimer with the two C_{60} cages connected by a silicon arom and a single bond, **9**.

For the new fullerene dimers **1**, **4**, and **9**, the two C_{60} cages were found to be able to communicate with each other upon electrochemical reduction, and were reduced stepwise but not at the same time for each of the three-wave redox steps as observed by cyclic voltammetry.

References:

1. Wang, G-W.; Komatsu, K. et al. *Nature* **1997**, *387*, 583.
2. Komatsu, K. et al. *Chem. Commun*., **2000**, 1583.
3. Komatsu, K. et al. *Chem. Lett*., **2000**, 1016; Kunitake, M.; Komatsu, K. et al., *Angew. Chem. Int Ed*., in press.
4. Murata, Y.; Komatsu, K. et al. *J. Org. Chem*., **1999**, *64*, 3483.
5. Komatsu, K. et al. *J. Chem. Soc., Perkin 1*, **1999**, 2963.
6. Wang, G.-W.; Komatsu, K. et al. *Chem. Commun.* **1996**, 2059.
7. Murata, Y.; Komatsu, K. et al., *J. Org. Chem*., **2001**, *66*, 7235.