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STRUCTURE OF IPR-VIOLATED FULLERENE, Sc₂@C₆₆

Isolated-pentagon rule (IPR) [1,2], stating that the most stable fullerenes are those in which all pentagons are surrounded by five hexagons, has been considered as the most important and essential rule in governing the geometry of fullerenes. In fact, all the fullerenes produced, isolated and structurally characterized to date have been known to satisfy IPR [3-5]. There are no IPR fullerenes possible between C_{60} and C_{70} , and so the observation of any fullerenes in that range means the violation of the IPR. Recently, Shinohara et al. have reported the first production, isolation of an IPR-violating metallofullerene, Sc₂@C₆₆ [6]. Immediately after the first production and isolation of Sc₂@C₆₆, the IPR-violated structure of the fullerene was determined for the first time [6] using synchrotron radiation powder data by the Maximum Entropy Method (MEM) combined with Rietveld analysis, MEM/Rietveld Method [5,7].

The purity (99.8%) of the material was confirmed by laser-desorption time-of-flight mass spectrometry.

Sc₂@C₆₆ powder sample grown from toluene solvent was sealed in a silica glass capillary (0.3 mm inside diameter). X-ray powder pattern with good counting statistics was measured by the synchrotron radiation (SR) X-ray powder experiment with imaging plate (IP) as detectors at beamline BL02B2 (Fig. 1). The exposure time on IP was 2 hours. The wavelength of incident X-rays was 0.75 Å. The X-ray powder pattern of Sc₂@C₆₆ was obtained with a 0.02° step up to 20.3° in 20, which corresponds to 2.0 Å resolution in d-spacing. By pre-Rietveld analysis of the MEM/Rietveld Method, the Sc₂@C₆₆ crystal structure is determined as that of space group Pmn2₁ (No.31); a=10.552(2) Å, b=14.198(2) Å, c=10.553(1) Å. The result of the pre-Rietveld fitting is shown in Fig. 2. The reliable factors of the pre-Rietveld fitting were $R_{wp} = 2.4\%$ and $R_l = 13.1\%$.

Although there are a number of ways to violate IPR, the most straightforward way being to generate the so-called "fused-pentagon" where



Fig. 1. The large Debye-Scherrer camera at BL02B2.



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Fig. 2. Fitting result of pre-Rietveld analysis for the $Sc_2@C_{66}$ *crystal.*

pentagons are adjacent with each other. For 66atom carbon cages with hexagonal and pentagonal faces, there are in total 4478 possible (non-IPR) structural isomers with $2 \times D_3$, $1 \times C_{3\nu}$, $18 \times C_{2\nu}$, $112 \times C_s$, $211 \times C_2$ and $4134 \times C_1$ symmetry [8]. Considering the observed 19-lines (5×2; 14×4) in the high resolution ¹³C NMR spectrum of Sc₂@C₆₆, only 8 structural isomers of C₆₆ with $C_{2\nu}$ symmetry are compatible with this ¹³C NMR pattern [6].

The MEM 3-D electron density distribution of $Sc_2@C_{66}$ is presented in Fig. 3(a) together with the $Sc_2@C_{66}$ geometry optimized by the non-local density function B3LYP/Basis set [Sc(LanL2DZ); C(3-21G)] calculations (Fig. 3(b)). The MEM charge densities, which has reliable factor of R_F=5.4%, clearly exhibit a pair of two-fold fused-pentagons on a C₆₆-C_{2v} cage that encapsulate a Sc₂ dimer. The present Sc₂@C₆₆ structure has the least number and degree of fused-pentagons out of the 4478 possible isomers.

Sc₂@C₆₆ shown in Fig. 3(b) contains two pairs of tow-fold fused pentagons to which the two Sc atoms are closely situated. The observed Sc-Sc distance is 2.87(9) Å, indicating the formation of a Sc₂ dimer in the C₆₆ cage. The intrafullerene electron transfers in endohedral metallofullerenes have been known to play crucial roles in stabilizing the metallofullerenes [3-5,9,10]. The number of electrons in the area corresponding to Sc₂ dimer from the MEM charge density is 40.0(2) e, which is very close to that of (Sc₂)²⁺ with 40 e. The ab initio calculation also indicates that the Sc₂ dimer donates two electrons to the C₆₆ cage providing a formal electronic state of (Sc₂)²⁺ @C₆₆²⁻. It is this charge-transfer interaction between the Sc₂ dimer and the fused pentagons that significantly decreases the strain energies caused by the pair of fused pentagons and thus stabilizes the fullerene cage. IPR is not necessarily a test for the stable geometry of endohedral metallofullerenes [6,9].

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Fig. 3. (a) The X-ray structure of the IPR-violating $Sc_2 @ C_{66}$ fullerene showing a top view along the C_2 axis and a side view. The equi-contour (1.4 e Å⁻³) surface of the final MEM electron charge density. The Sc_2 dimer is colored in red. The two pairs of fused-pentagons are clearly seen. (b) The calculated $Sc_2 @ C_{66}$ structures.

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