

Elucidation of the Molecular Structures of Novel Metallofullerene Derivatives

Using synchrotron X-rays, the molecular structures of a chemically modified non-isolated-pentagon rule (non-IPR) endohedral metallofullerene $\text{La}_2@C_{72}$ and a radical adduct of $\text{La}@C_{82}$ have been unambiguously determined. The results for the $\text{La}_2@C_{72}$ derivative confirm that the two La metals coordinate strongly with the [5,5]-junction carbons, so these carbons are no longer as reactive as those in empty non-IPR fullerenes. On the other hand, the characteristic C-C single bond of the radical adduct of $\text{La}@C_{82}$ was observed using X-ray crystallographic analysis.

Endohedral metallofullerenes (EMFs) are cage-like carbon molecules with metals trapped inside the hollow cavities [1]. Due to the presence of metallic species and electron transfer from metal atoms to cage, EMFs have attracted much attention from the whole scientific community. Chemical functionalization and structural elucidation of EMFs are very important for creating functional materials for electronic, molecular and biomedicine applications. Currently, the structural determination of EMFs mainly relies on the nuclear magnetic resonance technique, but this does not provide enough information on the dynamic behavior of the internal metals. Accordingly, single crystal X-ray diffraction (SCXRD) is the ultimate solution for the structural elucidation of EMFs. To solve the problem of severe disorders existing in the crystal lattice which are caused by free rotation of the spherical molecules, pristine EMFs should be substituted by adding one (or more) addend to the cage; the resulting derivatives show remarkable order of the crystal state and are particularly suitable for SCXRD analysis.

It has been established as the isolated-pentagon

rule (IPR) that all pentagons are isolated in the most stable fullerene [2]. Since it was first proposed by Kroto in 1987 [3,4], the IPR has proved particularly valuable in unraveling the cage structures of higher fullerenes and metallofullerenes. In this study, the derivatives of $\text{La}_2@C_{72}$, which has a cage structure violating the well-known IPR, were synthesized and structurally determined using synchrotron X-rays, including three mono-adduct isomers and one bis-adduct, for the first time [5]. It was thus unambiguously confirmed that $\text{La}_2@C_{72}$ has a cage corresponding to the isomer coded #10611 [2]. Furthermore, it was found that the encapsulated metals do not rotate inside the cage, but coordinate strongly with the fused-pentagon carbons. Thus, it was experimentally proved that the stabilization of the highly reactive fused-pentagon carbons by the internal metals is the main reason for the isolation of such non-IPR species. However, the X-ray structure of a bis-adduct shows that the fused pentagon regions are still more reactive than other parts of the cage as a result of high surface curvature, thus forming a candy-like fullerene derivative (see Fig. 1).

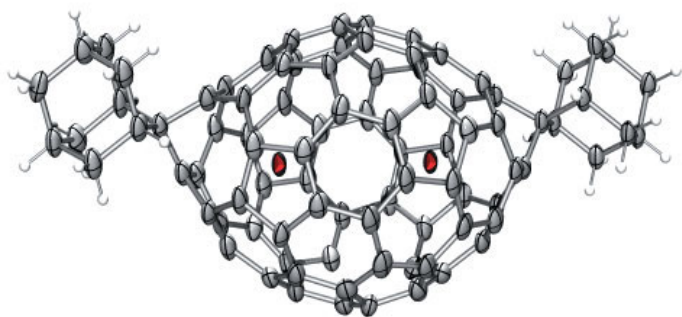


Figure 1
ORTEP drawing of a $\text{La}_2@C_{72}$ derivative with 50% probability ellipsoids. Carbon, hydrogen and lanthanum atoms are colored gray, white and red, respectively.

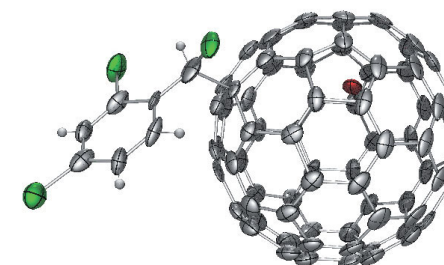


Figure 2
ORTEP drawing of $\text{La}@C_{82}\text{CHClC}_6\text{H}_4\text{Cl}_2$ with 50% probability ellipsoids. Carbon, hydrogen, chlorine and lanthanum atoms are colored gray, white, green and red, respectively.

Meanwhile, on the basis of the unique radical character of $\text{La}@C_{82}$, it was chemically modified using radical coupling reaction [6]. X-ray crystallographic analysis revealed the molecular structure of one of the adducts ($\text{La}@C_{82}\text{CHClC}_6\text{H}_4\text{Cl}_2$). As shown in Fig. 2, the trichlorobenzyl group is linked to the fullerene cage by forming one carbon-carbon single bond. The addition site is near the equator of $\text{La}@C_{82}$, which is very distinct from those of the monoaddition derivatives of $\text{M}@C_{82}$ reported previously. To the best of our knowledge, this is the first report showing an $\text{M}@C_{82}$ derivative in which the addition site of the addend is near the equator of $\text{M}@C_{82}$.

REFERENCES

- [1] (a) T. Akasaka, W. Fred and S. Nagase, Eds. *Chemistry of Nanocarbons*, (Wiley; London, 2010); (b) M. Yamada, T. Akasaka and S. Nagase, *Acc. Chem. Res.* **43** (2010) 92.
- [2] P.W. Fowler and D.E. Manolopoulos, *An Atlas of Fullerenes* (Clarendon: Oxford, 1995) 254.
- [3] H.W. Kroto, *Nature* **329** (1987) 529.
- [4] T.G. Schmalz, W.A. Seitz, D.J. Klein and G.E. Hite, *J. Am. Chem. Soc.* **110** (1988) 1113.
- [5] X. Lu, H. Nikawa, T. Tsuchiya, Y. Maeda, M.O. Ishitsuka, T. Akasaka, M. Toki, H. Sawa, Z. Slanina, N. Mizorogi and S. Nagase, *Angew. Chem. Int. Ed.* **47** (2008) 8642.
- [6] Y. Takano, A. Yomogida, H. Nikawa, M. Yamada, T. Wakahara, T. Tsuchiya, M.O. Ishitsuka, Y. Maeda, T. Akasaka, T. Kato, Z. Slanina, N. Mizorogi and S. Nagase, *J. Am. Chem. Soc.* **130** (2008) 16224.

BEAMLINE

1B (shutdown in FY2008)

Y. Takano, X. Lu and T. Akasaka (Univ. of Tsukuba)