# Molecular and Electronic Structures of Di-erbium and Di-erbium-carbide Metallofullerenes $Er_2(C_2)@C_{82}$: Density Functional Theory Calculations

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Density functional theory geometry calculations have been performed to elucidate the molecular and electronic structures of di-erbium and di-erbium-carbide endohedral metallofullerenes $Er_2@C_{82}$ and $Er_2C_2@C_{82}$. $C_s(6)$ (I), $C_{2v}(9)$ (II), and $C_{3v}(8)$ (III) IPR isomers of C_{82} were considered. We have employed B3LYP using Ahlrich's SVP and TZVPP basis sets for carbon, and the Stuttgart-Dresden SRSC97-ECP effective core potential and basis sets both with explicit consideration of f electrons and without, assuming in the latter case a $6s^2 5d^1$ valence configuration to emulate the effects of strong electron correlation. The optimized structures are shown in Figure 1. We found that in each compound the erbium atom assume a trivalent state, where two electrons from each Er are transferred to the C_{82} cage (LUMO and LUMO+1 become doubly occupied, corresponding to the C_{82}^{4-} electronic state), and one is either transferred to C_2 (erbium carbide compounds) or engages in covalent Er-Er and Er-C bonding (erbium-only compounds). Such chemical bonding situation is comparable to that encountered in $Er_3N@$fullerene compounds, where the cages are found to be 6-fold negatively charged, and three covalent Er-N bonds exist. In particular, the C_2 unit engages in strong covalent binding to the Er atoms, which gives rise to the notion of only weak charge uptake as detected by MEM-Rietveld X-ray measurements. Since the Er 4f shell is occupied by only about eleven electrons according to Mulliken population analysis, Er^{3+}-like emission from $^4I_{13/2}$ to $^4I_{15/2}$ is consistent with the notion of only 2 electrons per Er fully transferred to the cage. The higher photoluminescent activity of isomer III compared to other isomers I and II stems from a sizable (LUMO+2)-(LUMO+1) gap in the $C_{3v}(8)$ cage. Our prediction for photoluminescence intensity for all three isomers is consistent with the experimental results by Shinohara and coworkers [1].

Figure 1: Optimized structures for $Er_2@C_{82}$ (I II III) and $Er_2C_2@C_{82}$ (I II III)

(I)	**(II-A)**	(II-B)	(II-C)	(III)

(I)	**(II-A)**	(II-B)	(II-C)	(III)
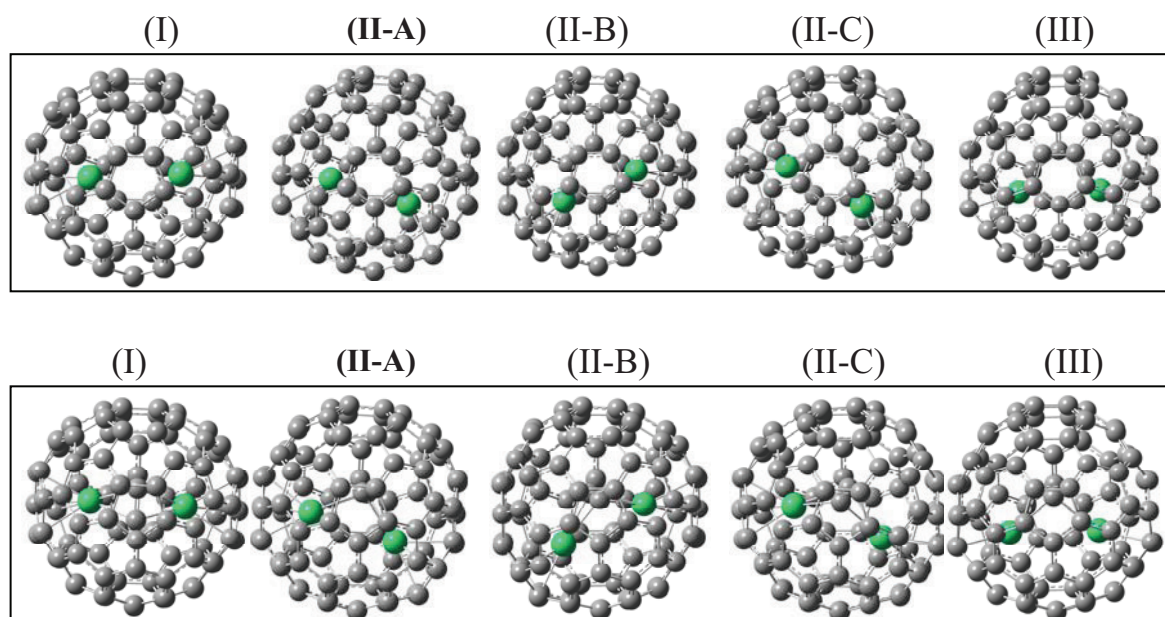
Reference

[1] Ito Y., Okazaki T., Okubo S., Akachi M., Ohno Y., Mizutani T., Nakamura T., Kitaura R., Sugai T., and Shinohara H. Enhanced 1520 Photoluminescence from Er3+ Ions in Di-Erbium-carbide Metallofullerenes $(Er_2C_2)@C_{82}$ (Isomers I, II, and III), ACS Nano, **1**(5), 456-462 (2007).