Theoretical Studies of Photoluminescence Properties of Endohedral Metallofullerenes

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Density functional theory geometry calculations have been performed to elucidate the molecular and electronic structures of di-thulium and di-thulium-carbide endohedral metallofullerenes $Tm_2@C_{82}$ and $Tm_2C_2@C_{82}$. 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 Ahlrichs 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. The optimized structures in the quintet electronic ground states are shown in Figure 1.

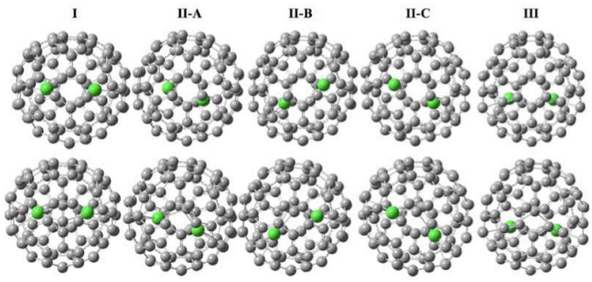

Figure 1. Optimized B3LYP/SRSC97+SVP geometries for $Tm_2@C_{82}$ (I II III) (top) and $Tm_2C_2@C_{82}$ (I II III) (bottom) in the quintet electronic states.

In the case of the $Tm_2C_2@C_{82}$ systems, in analogy to the corresponding $Er_2C_2@C_{82}$ and $Sc_2C_2@C_{82}$ [1] systems, we found that the thulium atoms assume a trivalent state, where two electrons are transferred to the C_{82} cage (LUMO and LUMO+1 become doubly occupied, corresponding to the C_{82}^{4-} electronic state), and one electron is transferred to the C_2 unit, such that the formal charge distribution can be described as $(Tm_2)^{6+}(C_2)^{2-}@(C_{82})^{4-}$. In this case, the *f*-shell is occupied by only 12 electrons, which makes it possible for the di-thulium-carbide compounds to emit at 1,800 nm, characteristic for the $Tm^{3+}\ ^3F_4 \rightarrow {}^3H_6$ transition. The electronic ground state of this system is well described as a quintet.

In the case of the $Tm_2@C_{82}$ systems, we find that thulium atoms typically assume an exotic divalent state, where only 1 ½ electrons are transferred to the C_{82} cage (LUMO becomes doubly occupied, LUMO+1 becomes singly occupied), and ½ electron is occupying a Tm-Tm bond. The formal charge distribution in this system can be described as $(Tm_2)^{3+}@(C_{82})^{3-}$. The thulium atoms in this case assume a *divalent* state, and the ground state of the system can also be described by a quintet, although the triplet state with no Tm-Tm bond, better described as $(Tm_2)^{4+}@(C_{82})^{4-}$, is nearby and in some isomers lower in energy than the quintet by 1-2 kcal/mol. In both triplet and quintet states, the *f*-shell is occupied by 13 electrons, which makes it possible for the di-thulium-carbide compounds to emit at 1,200 nm, characteristic for the $Tm^{2+}\ ^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition. This situation is very different from the analogous erbium compounds, which exhibit at the same level of theory a robust, doubly occupied Er-Er bond, with Er atoms being trivalent and emitting at the same wavelengths as the di-erbium-carbide metallofullerenes [2]. The difference between $Tm_2@C_{82}$ and $Er_2@C_{82}$ compounds can be seen in the slightly higher electronegativity of Tm, in comparison to Er.

The number of transferred electrons is increased to about four in $Tm_2@C_{80}$-I_h compounds. Consistent with this observation, we show that for hypothetical $Tm_2C_2@C_{80}$ compounds the cage can only attain four negative charges, even though the C_{80}-I_h cage has a strong affinity for six negative charges. On the other hand, our calculations predict that for tri-thulium nitride metallofullerenes Tm can exist in the trivalent form as $(Tm_3)^{9+}N^{3-}@C_{2n}^{6-}$ (2*n*=80 and 82).

[1] R. Valencia, T. Rodriguez-Fortea, J. M. Poblet, *J. Phys. Chem. C,* **112**, 4550-4555 (2008).
[2] Y. Ito, T. Okazaki, S. Okubo, M. Akachi, Y. Ohno, T. Mizutani, T. Nakamura, R. Kitaura, T. Sugai, and H. Shinohara H. *ACS Nano,* **1**(5), 456-462 (2007).