ARE THE MOTION OF LA ATOMS INSIDE C_{80} CONTROLLABLE BY EXOHEDRAL ADDITION ?

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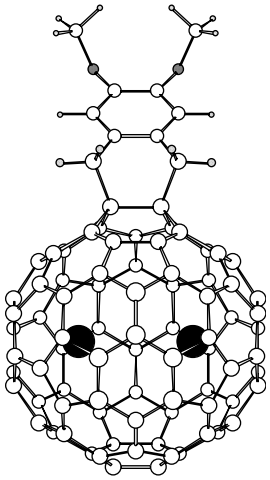
Among endohedral metallofullerenes whose structures have been determined, $La_2@C_{80}$ has been most extensively investigated since it has a unique I_h cage structure, as does C_{60}. From theoretical calculations [1] and NMR experiments [2], in 1996 we found that two La atoms can circulate inside C_{80} with small barriers. The time-averaged trajectory corresponding to the motion has been recently shown by the electron distribution determined by Maximum Entropy Method (MEM)/Rietvelt analysis of the synchrotron X-ray powder diffraction data [3]. It is of considerable interest how the dynamic properties of encapsulated metals are controllable, because molecular rotation within a cage is expected to be of great help in designing functional molecular devices. Thus, density functional calculations are carried out for exohedral cycloadducts of **1** [$La_2@C_{80}(C_8H_6(OCH_3)_2)$] and **2** [$La_2@C_{80}(Si_2Mes_4CH_2)$ (Mes = 2,4,6-$C_6H_2(CH_3)_3$)], as shown in Figure 1.

In adduct **1**, the two La atoms can freely circulate inside the C_{80} cage, as is so for $La_2@C_{80}$. In **2**, however, the in-plane motion is considerably hindered, while the barrier for the out-of-plane motion is still as small as that in $La_2@C_{80}$. Interestingly, even the barrier for the out-of-plane rotation is increased in a bis-adduct. Such restricted motion of two La atoms in **2** and the bis-adduct is due to the fact that the $Si_2Mes_4CH_2$ part can significantly donate electrons to the encapsulated La_2 as well as C_{80}. It is expected that combinations of exohedral and endohedral doping of fullerenes will extend and enrich the research area of metallofullerenes.

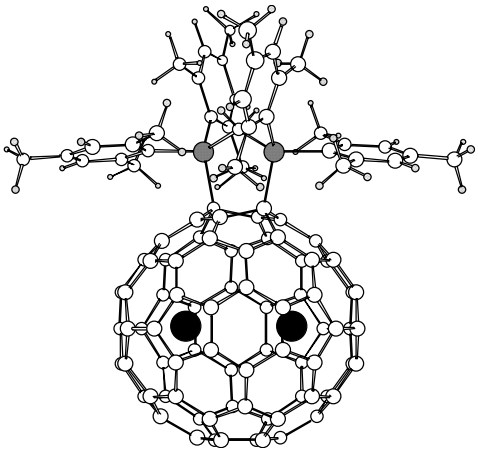
[1] K. Kobayashi, S. Nagase, T. Akasaka, *Chem. Phys. Lett.* **261** (1996) 501.

[2] T. Akasaka, S. Nagase, K. Kobayashi, M. Wälchli, K. Yamamoto, H. Funasaka, M. Kako, T. Hoshino, T. Erata, *Angew. Chem., Int. Ed. Engl.* **36** (1997) 1643.

[3] E. Nishibori, M. Takata, M. Sakata, A. Taninaka, H. Shinohara, *Angew. Chem. Int. Ed.* **40** (2001) 2998.



$La_2@C_{80}(C_8H_6(OCH_3)_2)$ (**1**)



$La_2@C_{80}(Si_2Mes_4CH_2)$ (**2**)

Figure 1*. The optimized structures of $La_2@C_{80}$ derivatives*