

Electronic Properties of $M_2(C_2)@C_{82}$ ($M=Sc, Ti, Fe$) Endohedral Metallofullerenes

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The electronic structures of di-scandium, di-titanium and di-iron (carbide) endohedral metallofullerenes (EMFs), $M_2(C_2)@C_{82}$ ($M=Sc, Ti, Fe$) (Figure 1), were investigated using density functional theory (DFT) and the self-consistent charge density functional tight-binding (SCC-DFTB, in the following abbreviated “DFTB”) method. The latter method is computationally considerably more economical than first principles DFT, yet shows comparable accuracy.

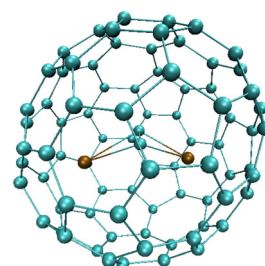


Figure 1 Sc2C2@C82

Before we perform calculations for metal containing fullerenes, we first checked the optimized parameters of the selected empty cage isomer: the $C_{82}-C_{3v}$ (8) fullerene cage. This fullerene cage is known as the cage isomer with the largest (LUMO+2) – (LUMO+1) gap and thus is found as the most abundant metal carbide EMFs [1]. Its large (LUMO+2) – (LUMO+1) gap, more than 1 eV, is well reproduced by DFTB.

First, for di-scandium and di-titanium (carbide) EMFs, we performed geometry optimizations for the six isomers proposed by Valencia *et al.* [1] using the DFTB and DFT (B3LYP/def-SV(P) [2] level of theory) methods and we found in the results that DFTB calculations could reproduce the tendency of the relative isomer energies predicted by the DFT method. Reproduction is not perfect, however, if we consider that the DFTB methods take us much cheaper computational cost, these results are not unacceptable. Actually, we chose relatively smaller basis set for our DFT calculations, nevertheless geometry optimizations using DFT calculations needed about one month. On the other hand, using DFTB method, geometry optimizations finished within two hours, that is, in this case the economical DFTB method is about 360 times faster than the DFT method. Optimized geometries of clusters in some isomers are different from the bent model which was thought to be the most stable, and these distorted clusters are more stable than the proper cluster (Figure 2).

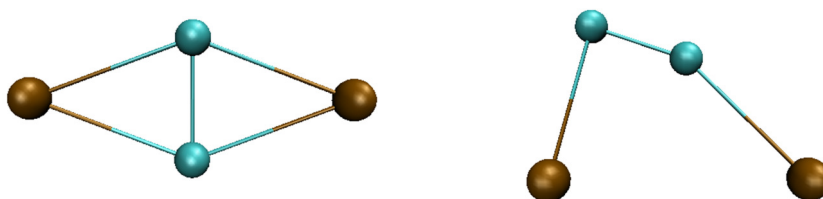


Figure 2 proper (left) and distorted (right) Sc2C2 inner cluster

With these results, we then analyzed the molecular orbital (MO) diagrams of the most stable isomer of di-scandium and di-titanium (carbide) EMFs. The di-scandium (carbide) EMFs were confirmed that they were formally seen as $(\text{Sc}_2)^{4+}@\text{(C}_{82})^{4-}$ and $(\text{Sc}_2\text{C}_2)^{4+}@\text{(C}_{82})^{4-}$ by DFT calculations[1, 3], therefore the MO diagram of di-scandium (carbide) EMFs were drawn based on our DFTB results here and they showed the same formal charges as DFT calculations. For di-titanium (carbide) EMFs, because we could not find any theoretical data about them, we draw two MO diagrams with our DFT (B3LYP/def-SV(P)) and DFTB results. From the DFT results, di-titanium (carbide) EMFs are seen as $(\text{Ti}_2)^{4+}@\text{(C}_{82})^{4-}$ and $(\text{Ti}_2\text{C}_2)^{4+}@\text{(C}_{82})^{4-}$, on the other hand DFTB results indicate the different formal charge state: $(\text{Ti}_2)^{6+}@\text{(C}_{82})^{6-}$ and $(\text{Ti}_2\text{C}_2)^{6+}@\text{(C}_{82})^{6-}$ (Figure 3).

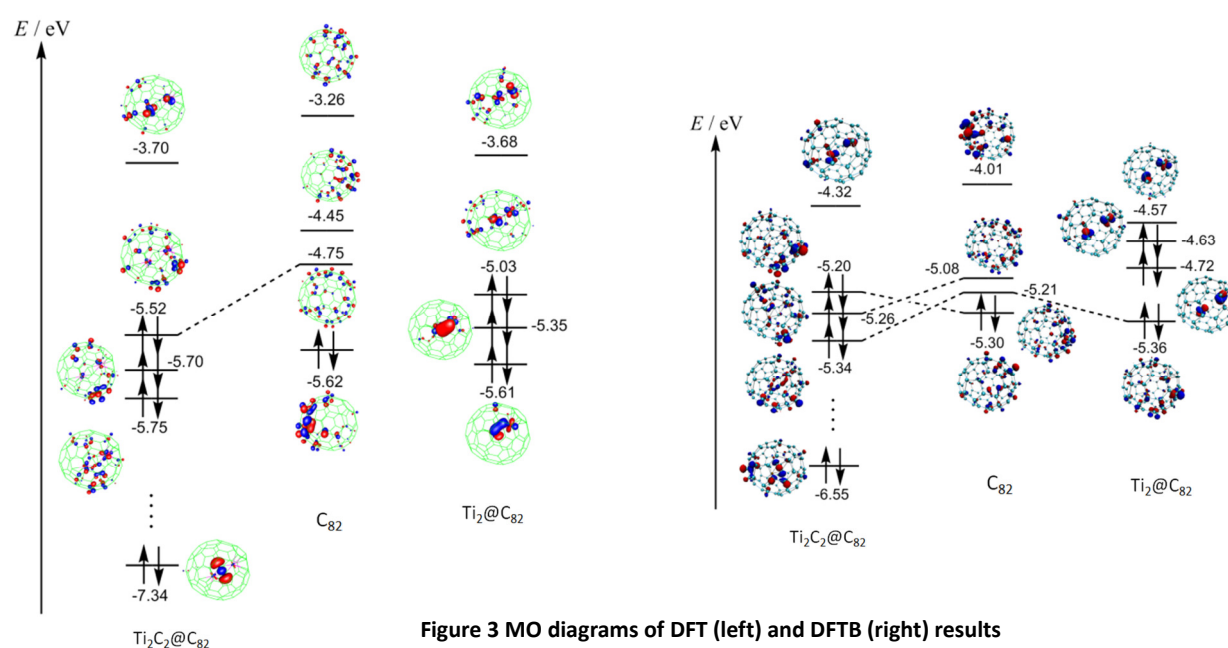


Figure 3 MO diagrams of DFT (left) and DFTB (right) results

Finally, we investigated di-iron (carbide) EMFs, which has not been synthesized yet, likely because iron tends to form larger clusters before individual atoms can be encapsulated in fullerene cages. We considered all possible spin states (from singlet to undectet); in general, binding energies of iron inside the EMFs are much smaller compared to the more electropositive Sc and Ti metals. Details will be discussed in the poster session on the designated day.

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