Electronic Supplementary Material (ESI) for Nanoscale.

Self-Assembly of Endohedral Metallofullerenes: A Decisive Role of Cooling Gas and Metal-Carbon Bonding

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Supplementary information

Metal-metal and metal-carbon ring interactions (M=Sc, Ti, Fe)

To compare metal-metal and metal-carbon interactions in the conditions of the fullerene self-assembly, we used a model system, a C_{12} ring with the metal atoms placed in the center and then optimized it at the DFT-B3LYP level (in the optimized structures, metal atoms shifted from the center, and the ring has elongated shape). This way, coordination of a metal atoms to a multiple carbon coordination sites is described. The binding energy for the M-C_{12} system, as well as binding energies of metal dimers (Sc, Ti, Fe) computed with two variants of DFTB approach are listed in the Table S1.

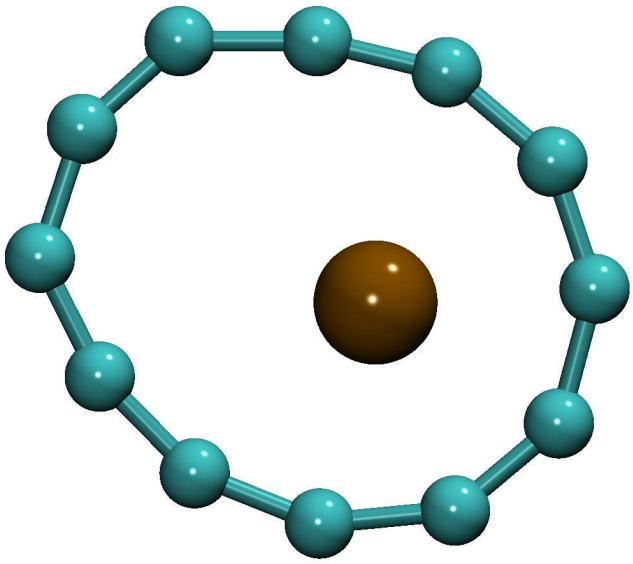

Figure S1. Monocyclic C_{12} (cyan) coordinating single metal atom (brown) in the center.

Table S1. Metal-metal and metal-ring binding energies (eV)

E_b(eV)	Sc-Sc	Ti-Ti	Fe-Fe	Sc-C_{12}	Ti-C_{12}	Fe-C_{12}
Standard DFTB	-4.23	-7.57	-4.86	-3.81	-7.77	-2.29
SCC-DFTB	-4.23	-7.57	-4.86	-3.03	-7.68	-1.36

Binding energies are defined as

$E_b = E_{M2} - 2E_M$ for metal dimers and

$E_b = E_{C12-M} - E_{C12} - E_M$ for M-C_{12} system (M=Sc, Ti, Fe)

Traditional DFTB *versus ab initio* molecular dynamics for annealing process of Sc containing cage

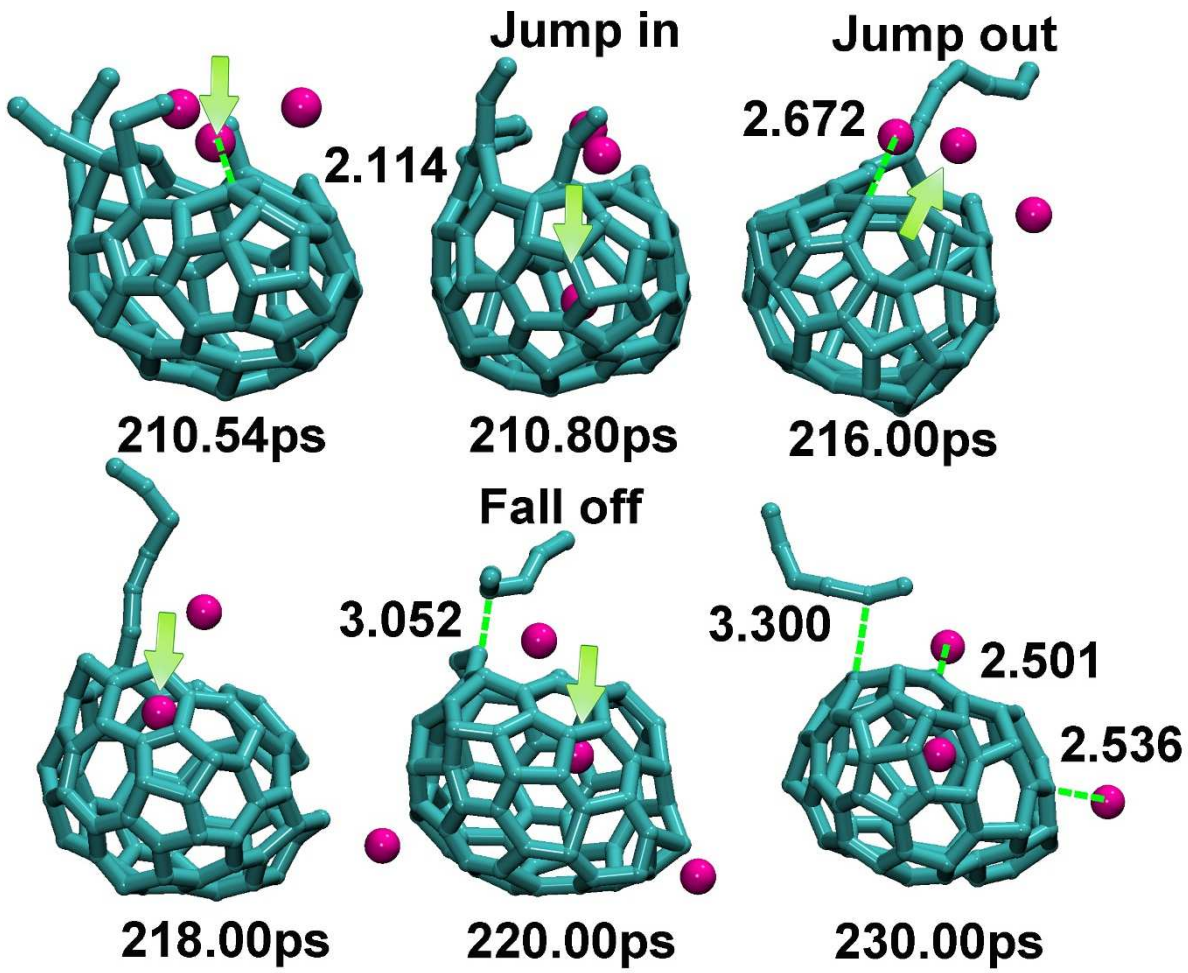

Figure S2. **Annealing process of Sc containing cage by DFTB molecular dynamics** Key event snapshots of a typical trajectory during the fullerene formation (Sc@C_{70}- Traj(0)-8a) at 210 ps as computed at the DFTB level . Carbon and Sc atoms are cyan and pink respectively.

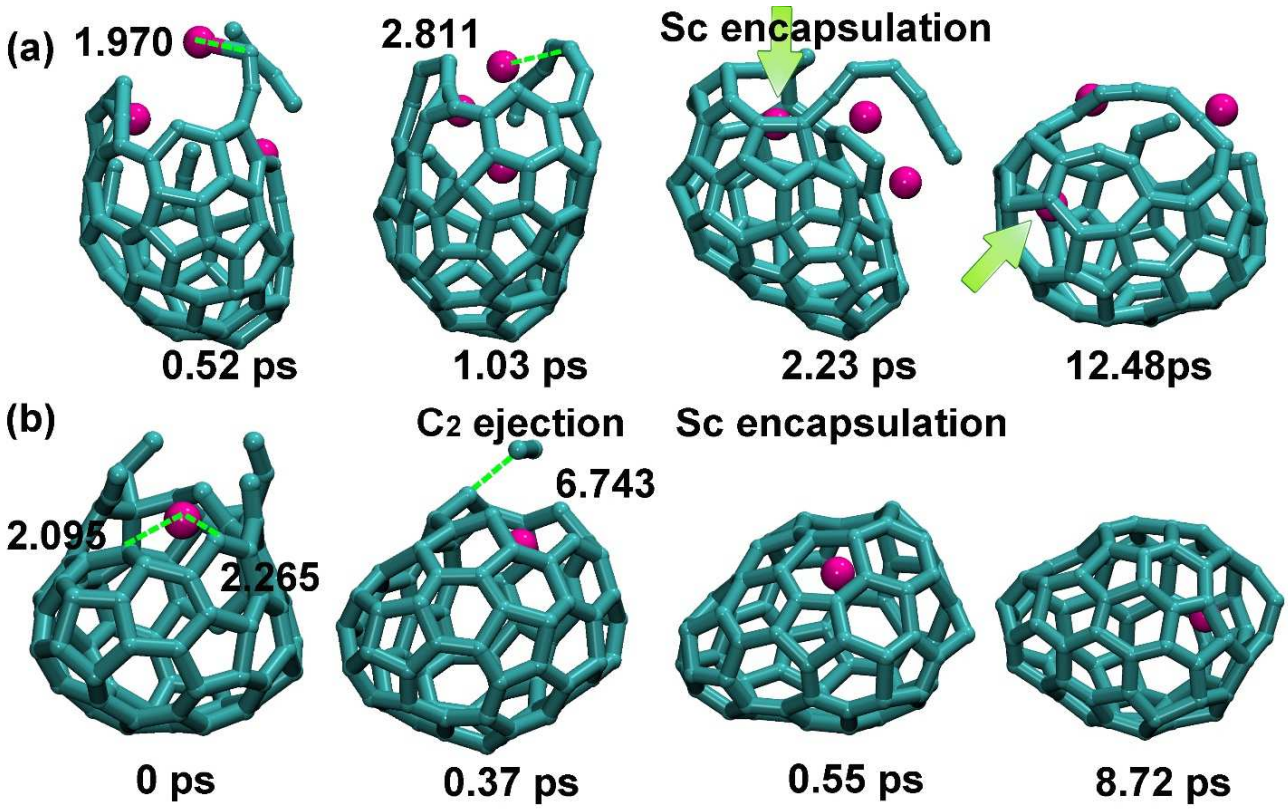

Figure S3. **Annealing process of Sc containing cage by *ab initio* molecular dynamics.** The initial steps of (a) and (b) are extracted single frames from trajectories of Sc@C_{70}-Traj(0)-8a at 210 ps and Traj(0)-3a at 210.34 ps, respectively. Carbon and Sc atoms are cyan and pink.

Sc forms Sc-C σ bonds into the cage wall at stage of cage formation as shown as in figure S2. At 210.80 ps, one Sc jumps into the cage very fast, and then jumps out and reform Sc-C σ bond due to the presence of defects which is in good agreement of TEM experiment.[1] Another Sc starts to go inside at 218 ps. The metal atoms jump in/out dynamically until the cage closes. We also observed "fall off" process that antenna drops off from the cage which is also consistent with formal theoretical work although different models applied.[2]

We further employ *ab initio* molecular dynamics method to compare with above result. Two key event structures extracted from the trajectories of normal DFTB are performed for annealing process as shown as in figure S3. From both trajectories, one Sc could directly go into the cage whining 2ps with the defects nearby self-healing, which is in good agreement with normal DFTB's results.

Typical examples of an attempted Sc-EMF formation by SCC-DFTB

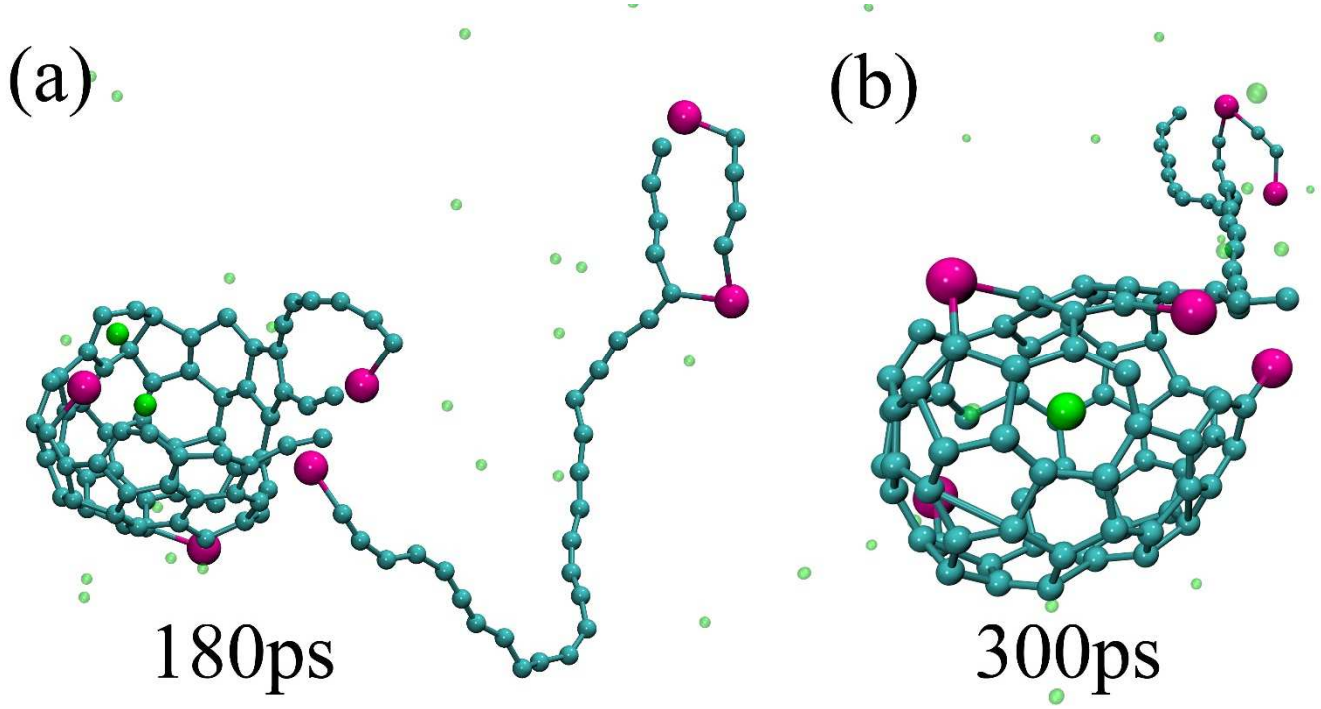

Figure S4. (a) and (b) are the key frames from trajectories by SCC-DFTB approach. Carbon, Sc, and He atoms are cyan, pink and green.

In figure S4, we can find a half cage is already formed terminated Sc atoms at the edge. One He atom goes into the carbon cup and stay a long time until the cage fully close. The distance of C and He can as short as 2.5-2.7 Å with long life time (longer than 100ps) resulting He being encapsulated. Note that a very long carbon chain also can been found by SCC-DFTB with He which is quite different from the result by traditional DFTB method.

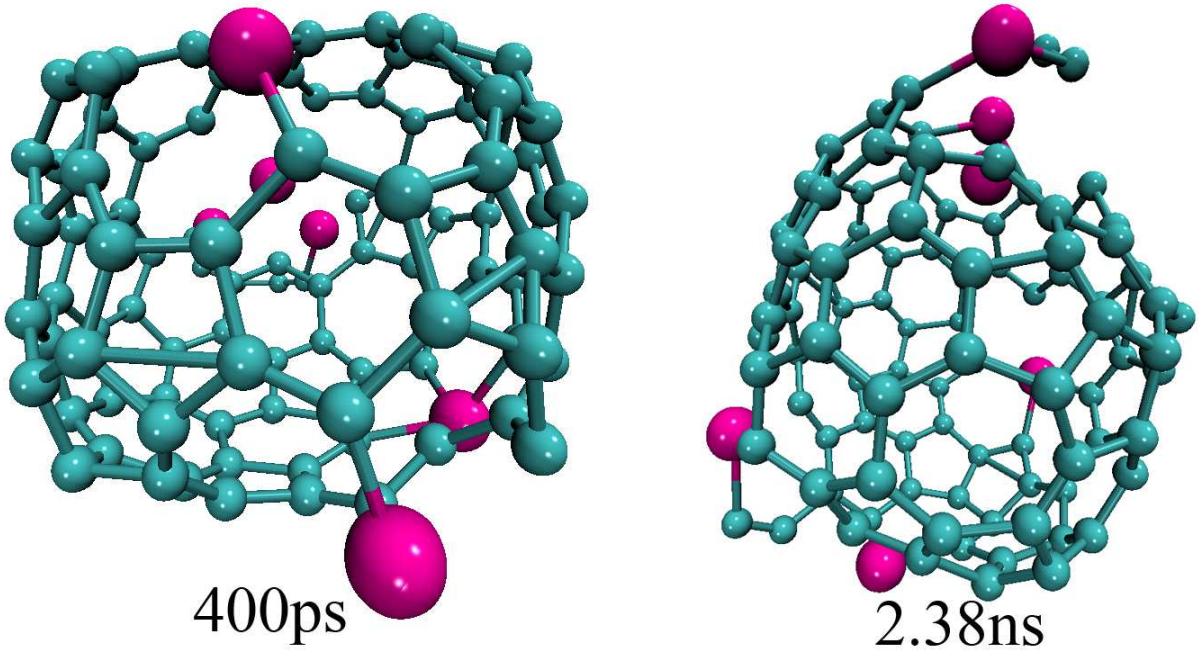

Figure S5. A typical example of the Sc-fullerene annealing at the SCC-DFTB level. Sc atoms remain bonded to the edges w/o endohedral fullerene formation.

MD simulations in the system with large Ti:C ratio (100:100)

Figure below shows examples of the titan-carbon cluster formed in the simulations with large amount of Ti in the system.

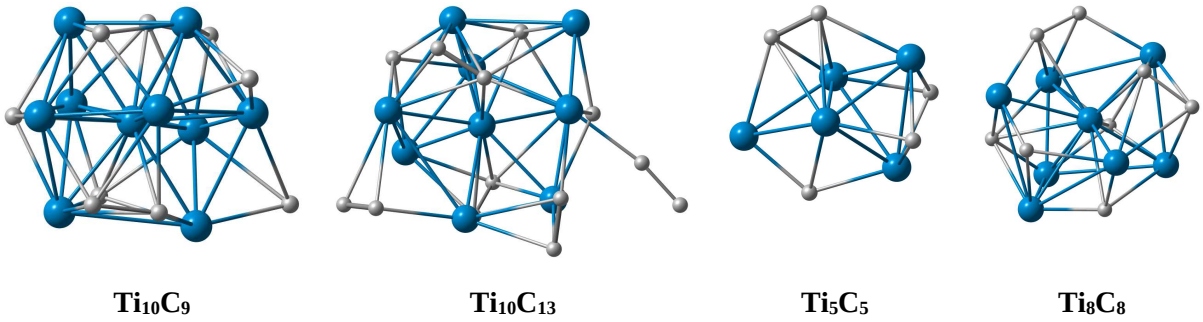

Figure S6. Titanium-carbon cluster formed in MD simulations in the 100C:100Ti system.

Atomic charges of metal atoms during EMF formation

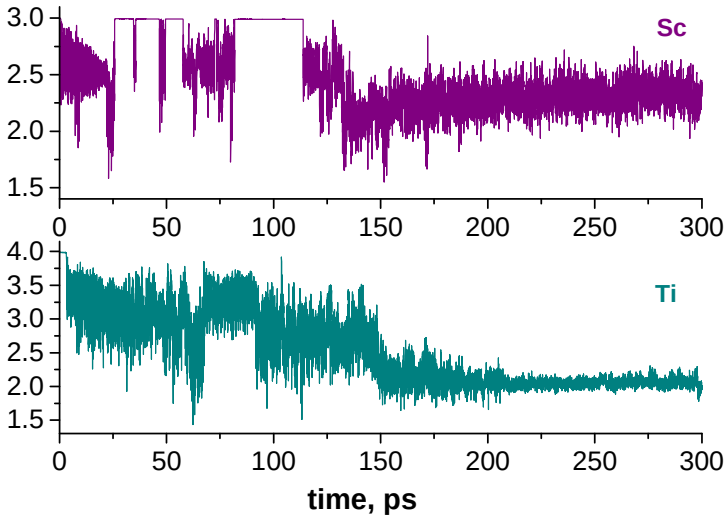

Figure S7. Evolution of Mulliken atomic charges of metal atoms during the EMF formation.

References

(1) Sato, Y.; Yumura, T.; Suenaga, K.; Urita, K.; Kataura, H.; Kodama, T.; Shinohara, H.; Iijima, S. *Physical Review B* **2006**, *73*.

(2) Irle, S.; Zheng, G. S.; Wang, Z.; Morokuma, K. *Journal of Physical Chemistry B* **2006**, *110*, 14531.