New Volleyballenes: Y$_{20}$C$_{60}$ and La$_{20}$C$_{60}$

Jing Wang$^1$ & Ying Liu$^{1,2}$

Two new stable Volleyballenes, the Y$_{20}$C$_{60}$ and La$_{20}$C$_{60}$ molecular clusters, are proposed on the basis of first-principles density functional theory. In conjunction with recent findings for the scandium system, these findings establish Volleyballene M$_{20}$C$_{60}$ molecules as a general class of stable molecules within the fullerene family. Both Y$_{20}$C$_{60}$ and La$_{20}$C$_{60}$ molecules have $T_h$ point group symmetries and relatively large HOMO-LUMO gaps.

Since the first observation of the C$_{60}$ fullerene molecule$^{1,2}$, much effort has been invested in the study of this novel molecular cluster. In the fullerenes, all the atoms are C atoms and they form a hollow sphere comprised of pentagonal and hexagonal rings. Very recently, on the basis of density functional theory (DFT) calculations, an exceptionally stable hollow cage, composed of 20 Sc atoms and 60 C atoms, the Volleyballene Sc$_{20}$C$_{60}$ was reported$^3$. This molecular cluster has a $T_h$ point group symmetry and a volleyball-like shape. This Volleyballene was the first buckyball to be spiked with metal atoms and is awaiting synthesis$^{4-8}$.

If the Volleyballene Sc$_{20}$C$_{60}$ does actually exist, it is expected that other early transition metals should be capable of forming molecules of a similar type, and might also display unusual stability. We have therefore extended our work to other transition metal systems, with particular attention to elements with a single d electron: yttrium (Y) and lanthanum (La). As in the case of Sc$_{20}$C$_{60}$, the M$_{20}$C$_{60}$ (M = Y and La) molecules also are found to display an enhanced stability with the volleyball-like shape. In the following, the stability and electronic properties of the Volleyballenes Y$_{20}$C$_{60}$ and La$_{20}$C$_{60}$ are investigated through their bonding characters and the vibrational frequencies, as well as through molecular dynamics simulations.

Figure 1 shows the configurations of the two new Volleyballenes M$_{20}$C$_{60}$ (M = Y and La), which both have $T_h$ point group symmetries within a tolerance of 0.1 Å. Similar to the case of Sc$_{20}$C$_{60}$, the new Volleyballenes are composed of six M$_{20}$C$_{10}$ subunits arranged in a crisscross pattern. In each M$_{20}$C$_{10}$ subunit, 10 carbon atoms form two head-to-head connected carbon pentagons (C-pentagon), and 8 transition-metal atoms form a single transition-metal octagon ($M$-octagon). The two connected C-pentagons are surrounded by the $M$-octagon, to give a structure that resembles the panels of a volleyball.

The 20 transition metal atoms link to form 12 suture lines with the average distances between transition-metal atoms being 3.411 Å for Y-Y and 3.617 Å for La-La. For the C-pentagons of the Y$_{20}$C$_{60}$ molecule, the lengths of the C-C bonds lie in the range 1.449–1.460 Å. Along with a 1.485 Å C-C bond connecting the two C-pentagons, the average C-C bond length is found to be 1.455 Å. The average Y-C bond length is 2.396 Å.

For La$_{20}$C$_{60}$, the C-C bond lengths are in the range 1.450–1.456 Å and the C-C bond connecting the two C-pentagons has a length of 1.490 Å, resulting in an average C-C bond length of 1.457 Å. The La-C bond length is 2.565 Å. Both the average C-C and M-C bond lengths, as well as the average M-M distance, in La$_{20}$C$_{60}$ are larger than the corresponding distances in Y$_{20}$C$_{60}$ indicating a larger-sized cage for La$_{20}$C$_{60}$. The reason may lie with the relatively larger atomic radius of La. All the calculated data including the binding energies per atom, are listed in Table 1. For the new Volleyballenes, the binding energies per atom are 6.622 and 6.565 eV, for Y$_{20}$C$_{60}$ and La$_{20}$C$_{60}$, respectively. For more details see Section I of the Supplementary Information.

The bonding characters of the Volleyballene M$_{20}$C$_{60}$ (M = Y and La) molecules were investigated by analyzing their deformation electron densities. The Volleyballenes Y$_{20}$C$_{60}$ and La$_{20}$C$_{60}$ have similar bonding characteristics, mainly due to their similar electron configurations, 4$d^55$s$^2$ for the Y atom and 5$d^6$6$s^2$ for the La atom. On the whole, there is electron transfer from the transition metal atoms to the C atoms. Mülliken population analysis showed an average charge transfer of 0.95e from each Y atom to the neighboring C atoms for Y$_{20}$C$_{60}$ while for La$_{20}$C$_{60}$, the average charge transfer is 0.69e. To better understand the chemical bonding, natural bonding orbital (NBO)$^9$ analysis was employed, and it was found that the results of the natural population analysis (NPA) are in accord with those of Mülliken population analysis (Table 1). The NPA showed an average charge transfer of 0.92e.

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1Department of Physics and Hebei Advanced Thin Film Laboratory, Hebei Normal University, Shijiazhuang 050024, China. 2National Key Laboratory for Materials Simulation and Design, Beijing 100083, China. Correspondence and requests for materials should be addressed to Y.L. (email: yliu@hebtu.edu.cn)
Figure 1. The configurations and deformation electron densities of Y$_{20}$C$_{60}$ and La$_{20}$C$_{60}$. The isosurface is taken to be 0.01 e/Å$^3$.

Figure 2. Simulated Raman spectrums for the Volleyballenes $M_{20}C_{60}$ ($M = Y$ and La) at a temperature of 300 K and using 488.0 nm incident light. The Lorentzian smearing was set to be 20.0 cm$^{-1}$. The labels show the frequencies corresponding to the peaks of the intensities.
from each Y to the neighboring C atoms in Y\(_{20}\)C\(_{60}\), while the charge transfer for La\(_{20}\)C\(_{60}\) was 0.78 \(e\). For the C atoms, there are obvious characteristics of \(sp^2\)-like hybridization, and each C atom has three \(\sigma\) bonds. As with the Sc atoms in the Volleyballene Sc\(_{20}\)C\(_{60}\), there are four lobes for each \(M\) atom in Volleyballene \(M\_20\)C\(_{60}\) \((M = Y\) and La\) molecules, pointing to the four neighboring C atoms. This strengthens the link between the \(M\_8\)C\(_{10}\) subunits.

The stability of the \(M\_20\)C\(_{60}\) molecules was further checked using ab initio molecular dynamics (MD) simulations with the constant-energy, constant-volume (NVE) ensemble. The simulation time step was set to be 1.0 fs with a total of 10000 dynamics steps. With initial temperatures of 2200 and 1800 K (~1100 and ~900 K effective temperatures) for Y\(_{20}\)C\(_{60}\) and La\(_{20}\)C\(_{60}\), respectively, the structures were not disrupted over the course of a 10.0 ps run.
HOMO-LUMO gaps, the two new Volleyballenes Y\textsubscript{20}C\textsubscript{60} and La\textsubscript{20}C\textsubscript{60} should be stable fullerene variants with atomic orbitals being much lower than those of the M\textsubscript{20}C\textsubscript{60} subunits. The large gaps are due mainly to the energies of the d\textsubscript{M} orbitals. Table 1. The HOMO-LUMO gaps are 1.395 eV for Y\textsubscript{20}C\textsubscript{60} and 1.254 eV for La\textsubscript{20}C\textsubscript{60}. The large gaps are due mainly to the energies of the d\textsubscript{M} orbitals. All these results are consistent in demonstrating that hybridization between the M d orbitals and C s-p orbitals is essential for stabilizing the cage structure of M\textsubscript{20}C\textsubscript{60} (M = Y and La).

For the Volleyballenes Y\textsubscript{20}C\textsubscript{60} and La\textsubscript{20}C\textsubscript{60}, relatively large HOMO-LUMO gaps were found, as listed in Table 1. The HOMO-LUMO gaps are 1.395 eV for Y\textsubscript{20}C\textsubscript{60} and 1.254 eV for La\textsubscript{20}C\textsubscript{60}. The large gaps are due mainly to the energies of the d\textsubscript{M} orbitals being much lower than those of the p orbitals. With relatively large HOMO-LUMO gaps, the two new Volleyballenes Y\textsubscript{20}C\textsubscript{60} and La\textsubscript{20}C\textsubscript{60} should be stable fullerene variants with moderately high chemical stability. In summary, first-principles studies have identified two new stable Volleyballenes, Y\textsubscript{20}C\textsubscript{60} and La\textsubscript{20}C\textsubscript{60}. In an initial report on the stability of Sc\textsubscript{20}C\textsubscript{60}, we speculated that Sc\textsubscript{20}C\textsubscript{60} might comprise one member of a Volleyballene family, and that other transition or rare-earth metals could also form stable M\textsubscript{20}C\textsubscript{60} molecular clusters. This speculation now appears to have been borne out.

Methods
The calculations were carried out with the exchange-correlation potential described by the Perdew-Burke-Ernzerhof (PBE) version of the general gradient approximation (GGA)\textsuperscript{10}. The double-numerical basis plus polarized functions (DNP)\textsuperscript{11} was chosen. For the transition metal atoms, relativistic effects in the core were included using the DNP method. All structures were fully relaxed, and geometric optimizations were performed with unrestricted spin and without any symmetry constraints as implemented in the DMol\textsuperscript{3} package\textsuperscript{13}.

| Sym.   | d\textsubscript{1} | d\textsubscript{2} | Q\textsubscript{C} | Q\textsubscript{M} | E\textsubscript{1} | E\textsubscript{2} |
|--------|----------------|----------------|----------------|----------------|---------------|---------------|
| Y\textsubscript{20}C\textsubscript{60} | 1.455 | 2.396 | 0.953 | 0.921 | 6.622 | 1.395 |
| La\textsubscript{20}C\textsubcript{60} | 1.457 | 2.565 | 0.693 | 0.797 | 6.565 | 1.254 |

Table 1. Summary of the calculated results for M\textsubscript{20}C\textsubscript{60} (M = Y and La). The data include the symmetry group (Sym.), the average C-C (d\textsubscript{1}) and M-C (d\textsubscript{2}) bond lengths, the average charge transfer from M to carbon atoms (Q\textsubscript{C} for Mülliken analysis and Q\textsubscript{M} for NBO analysis), the binding energy per atom (E\textsubscript{1}), and the HOMO-LUMO energy gap (E\textsubscript{2}) in units of Å for the lengths and eV for energy.

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**Author Contributions**
Y.L. designed the initial structures and performed the theoretical calculations J.W. and Y.L. analyzed the results and wrote the manuscript.

**Additional Information**

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