# Manganese Doping Effect on the Sensing and Electronic Properties of Selected Carbon Fullerenes: a DFT Study

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*Abstract* — **In this study, the electronic properties of the different types of undoped Carbon Fullerenes (Cn) and Mn atom doped fullerene (MnCn-1) nanostructures have been investigated by density functional theory (DFT). The carbon fullerene isomers between C20 and C40 were selected. The sensing and electronic properties of selected fullerene structures were calculated based on the highest occupied molecular orbital energy (EHOMO) and the lowest unoccupied molecular orbital energy (ELUMO), energy gap (Eg) and work function (Φ) values. The density of states (DOS) were generated for frontier molecular orbital (FMO) analysis. The sensing mechanism of carbon fullerenes has been determined by calculating the band gap and work function variation, %ΔEg and %ΔΦ, during the Mn atom dopping. This study will give an idea about these materials for drug delivery and sensing applications.**

*Keywords* — **Carbon Fullerene, Mn doped carbon fullerene, DFT.**

## I. INTRODUCTION

Fullerenes are a class of polyhedral molecules composed of carbon atoms. The main properties of fullerenes are as follows. It is a spherical system rich in π-electrons. There is an internal cavity that is readily filled by guest atoms and molecules. Fullerenes have dimensions of the order of $10^{-9}$ m, which is the lower limit of nanoparticle dimensions.

Fullerenes were first discovered experimentally in September 1985. Buckminsterfullerene, named after American architect Buckminster Fuller, was observed by a group of scientists including Richard Smalley, Robert Curl, and Harry Kroto of Rice University, whose geodesic dome was formed. They shared the Nobel Prize in 1996 for this new discovery. Shortly afterwards, other fullerenes were discovered with more and fewer carbon atoms. There are structures that can range from 18 atoms to hundreds of atoms. The Buckyball, which contains 60 carbon atoms, is the most popular [1,2]. Fullerenes are closed-frame carbon structures consisting of 12 pentagons and a certain number of hexagons. The structure consisting of 12 pentagons without hexagons is the smallest possible fullerene [3].

Theoretically, the smallest possible fullerene is $C_{20}$. This structure is considered the smallest fullerene with a dodecahedral cage structure. Under normal conditions, the most thermodynamically stable form of carbon is graphite, which is a stack of loosely bound graphene sheets and flat atomic honeycomb lattices. Each atom is connected to three neighbors, forming a fourth valence electron system, meaning that carbon atoms are sp2-hybridized. Geometrical imperfections in graphene sheets can result in a closed 3D structure. Thus, the smallest possible fullerene, $C_{20}$, is called a dodecahedron [4]. The rigid geometry regularity of this structure consists only of hexagons and pentagons. They are generally high point symmetry groups of molecules up to Icosahedral symmetry (Ih) for $C_{60}$, the most famous representative of fullerenes [5].

Due to their very practical properties, Fullerenes have an important place in nanotechnology and industrial research today. As more applications of Fullerenes become available, the demand for these molecules will increase. Therefore, it is expected that Fullerene studies will continue more intensively [6].

## II. MATERIAL AND METHOD

In this study, the following Carbon-Fullerenes and Mn-doped Carbon-Fullerenes were used.

**Carbon-Fullerenes**

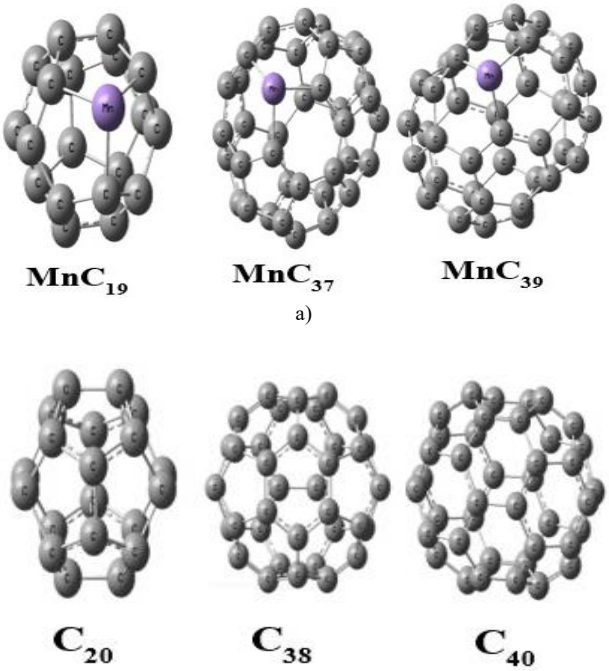


Fig. 1 Carbon-Fullerenes Mn doped Carbon-Fullerenes a), Mn doped Carbon-Fullerenes b)

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*A. Density functional theory (DFT)*

Density functional theory (DFT) is a theory used to describe the behavior of electrons in atoms and molecules using the principles of quantum mechanics and statistical mechanics. DFT is based on the electron density rather than the wave functions of electrons. The electron density is a measure of the probability of finding electrons at each point in a system. DFT differs from previous approaches in theory because of the difficulty of analytically solving the behavior of electrons.DFT therefore relies on mathematical and computational methods to predict various properties such as energy, structure, reactivity, and spectral properties by optimizing variables such as minimizing or maximizing a functional of the electron density. DFT is a successful approach that considers electron-electron interactions as interactions between electron and electronic density, and accepts and uses electron density as the fundamental variable, to determine the ground state properties of many-electron systems. Its foundations were laid in 1927 by Thomas (Thomas, L. H., 1927) and Fermi (Fermi, E., 1928.), who worked in the same period as Hartree (Hartree, D. R., 1928)[7,8].

The time-dependent Schrödinger equation,

$$i\hbar\, \partial\, \psi/\, \partial t = \mathbf{H} \tag{1}$$

**H** is the Hamiltonian operator, $\psi$ is the wave function and $i\hbar\ \partial/\partial t$ is the energy operator. For a single particle in potential V,

$$i\hbar\, \partial\, \psi/\, \partial t = -\hbar^{2}/2\ \ \nabla^{2}_{i}\, \psi + V(r_i)\psi \tag{2}$$

In this equation, m is the mass of the electron. The first term on the right-hand side of the equation is the kinetic energy of the system, and the second term is the potential energy. This equation can be solved for a hydrogen atom. However, an analytical solution is not possible for more complex systems.

*B. DFT calculations using Gaussian*

Gaussian approximates orbital shapes and orbital energies of a given molecular geometry using a model chemistry. It consists of two parts:

- Calculation using large basis sets are more accurate because they are less restrictive on the location of the electrons.
- Such calculations are also more expensive because they require computing more integrals.

*C. Methods*

- These differ mainly according to how, or if, "electron correlation" is treated.
- Electron correlation is the tendency of electrons to avoid each orher, even within the same orbital.

Structure optimisations, all energy calculations, charge analysis, frontier molecular orbital calculations were performed using **Gaussian 09 program package** at the level of density functional theory **(DFT) method** in combination with Beck's three-parameter (**M06-2X/6-311G(d)**) hybrid exchange functioning with the correlation functional of **B3LYP/6-311G(d,p)** is used for small clusters. All the optimization calculations converged to an optimized geometry, which corresponds to a true energy minimum. The optimized molecular structures deduced from vibrational frequency calculations are visualized by Gauss View program.

*D. Frontier molecular orbital (FMO) analysis and electronic properties*

The electronic and sensing properties of Mn doped fullerens have been computed based on the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy values by frontier molecular orbitals (MO) analysis. The LUMO-HOMO energy gap ($E_g$) was calculated as:

$$E_g = E_{LUMO} - E_{HOMO} \tag{3}$$

where $E_{LUMO}$ and $E_{HOMO}$ are LUMO and HOMO energies, respectively.

In order to evaluate the sensing properties, the work function is defined as $\Phi = -E_F$ with the Fermi level energy, $E_F$, the percentage change values of work function, Φ and energy gap Eg of nanomaterial after drug adsorption, as $\%\Delta\Phi$ and $\%\ \Delta\ E_g$ respectively were also determined. The Fermi level energy $E_F$ and quantum molecular descriptors based on HOMO and LUMO energies, such as chemical potential, hardness, electrophilicity index were calculated using the following equations.

$$E_F = E_{HOMO} + \frac{(E_{LUMO} - E_{HOMO})}{2} \tag{4}$$

To obtain the sensing mechanism of the nanotubes, the variation in the Eg bandgap by the functionalization process is taken into account by:

$$\%\Delta Eg = \left(\frac{Eg2 - Eg1}{Eg1}\right) x100 \tag{5}$$

where the $E_g$ values of pristine and f-SWCNTs are $E_{g1}$ and $E_{g2}$, respectively. Another key parameter in determining the sensing ability of the nanotubes is work function (Φ). The Φ-type sensors detect the adsorbed molecule by changing the gate voltage and producing an electrical signal. The Φ value can be defined by the Fermi energy level of $E_F$ as follows

$$\Phi = V_{el(+\infty)} - E_F \tag{7}$$

where $V_{el(+\infty)}$ is the electronic electrostatic potential energy far from the nanotubes surface, estimated to be zero, The Φ value is due to the minimum energy needed to induce electron emission from the $E_F$ energy level. Both $\%\Delta E_g$ and $\%\Delta\Phi$ values represent the percentage of band gap and work function of the fullerences to the pristine ones, respectively[9].

## III. RESULTS AND DISCUSSION

In this study, the electronic properties of the different types of undoped Carbon Fullerenes (Cn) and Mn atom doped fullerene ($MnC_{n-1}$) nanostructures have been investigated by density functional theory (DFT). These calculations were made using B3LYP and M062X methods and LANL2DZ basis set in Gaussian 9 and Gauss View6 (https://gaussian.com/) package programs. The sensing and

electronic properties of selected fullerene structures were calculated based on the highest occupied molecular orbital energy ($E_{HOMO}$) and the lowest unoccupied molecular orbital energy ($E_{LUMO}$), Fermi energy($E_F$),energy gap ($E_g$) and work function (Φ) values. The sensing mechanism of carbon fullerenes has been determined by calculating the band gap and work function variation, $\%\Delta E_g$ and $\%\Delta\Phi$, during the Mn atom dopping. The density of states (DOS) were generated for frontier molecular orbital (FMO) analysis.

Firstly, calculations were made HOMO_LOMO energies, fermi energy, forbidden band energy and work function C20, C38 and C40. Firstly, HOMO_LOMO energies, fermi energy, gap energy and work function calculations were made for the selected fullerene structures. All calculated values are listed in Table 1.

TABLE 1
EHOMO, ELUMO, EF , EG AND Φ VALUES OF CN (ALL ENERGIES ARE IN EV).

| Fullerenes | $E_{HOMO}$ | $E_{LUMO}$ | $E_F$ | $E_g$ | Φ |
|---|---|---|---|---|---|
| $C_{20}$ | -5,059 | -3,107 | -4,083 | 1,952 | 4,083 |
| $C_{38}$ | -5,649 | -4,362 | -5,006 | 1,287 | 5,006 |
| $C_{40}$ | -5,712 | -4,465 | -5,089 | 1,248 | 5,089 |

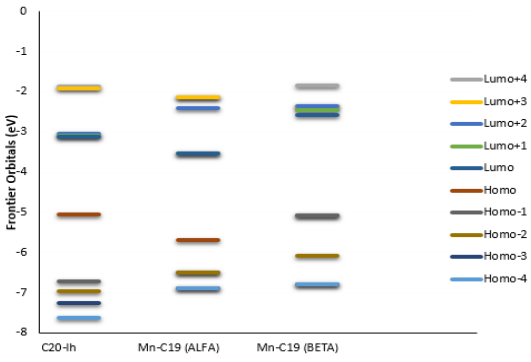
As can be seen from the table , as the number of carbon atoms increases, the negativity of homo-lomo and fermi energies increases. Except for C20, the gap energies and work functions also increase depending on the number of carbon atoms.

Secondly, electronic properties were calculated for selected Mn doped fullerenes. The obtained values are given in Table 2.

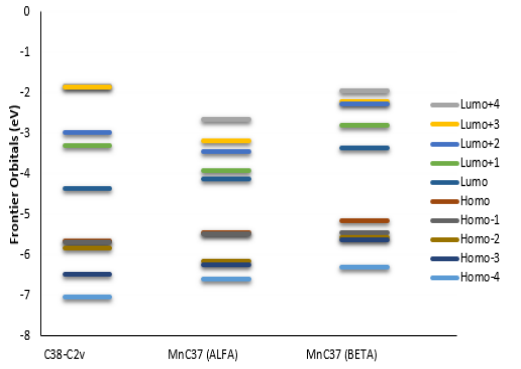
TABLE 2
EHOMO, ELUMO, EF , EG , %ΔEG , Φ AND ΔΦ VALUES OF THE DOPED MN (ALL ENERGIES ARE IN EV)

| Fullerenes | $E_{HOMO}$ | $E_{LUMO}$ | $E_F$ | $E_g$ | $\%\Delta E_g$ | Φ | ΔΦ |
|---|---|---|---|---|---|---|---|
| $MnC_{19}$ (spin up) | -5,679 | -3,526 | 4,602 | 2,153 | 10,289 | 4,602 | 9,633 |
| $MnC_{19}$ (spin down) | -5.085 | -2,571 | 3,828 | 2,514 | 28,816 | 3,828 | -8,818 |
| $MnC_{37}$ (spin up) | -5,435 | -4,108 | 4,771 | 1,329 | 3,277 | 4,771 | -4,694 |
| $MnC_{37}$ (spin down) | -5.145 | -3,366 | 4,255 | 1,779 | 33,859 | 4,225 | -10,803 |
| $MnC_{39}$ (spin up) | -5,393 | -4,044 | 4,720 | 1,351 | 8,242 | 4,720 | 14,809 |
| $MnC_{39}$ (spin down) | -5,295 | -3,288 | 4,291 | 2,006 | 60,722 | 4,291 | 4,387 |

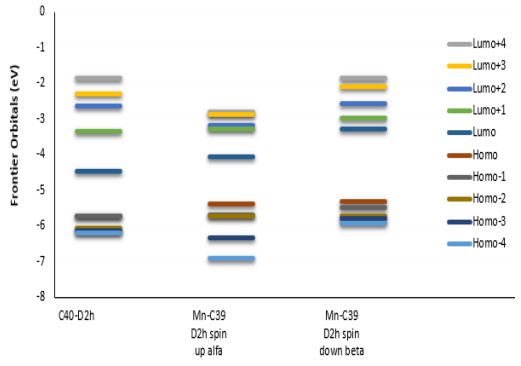
As seen in Table 1, two types of calculations were made for a fullerene group. These are spin up and spin down states. There is a slight difference in the energy calculations for these two states. On the other hand, the gap energy and work function variations reach very different values. These values, shown in bold in the table, are much larger than 10. Thus, these materials can be used as sensors. This situation shows an important feature of the selected fullerenes. A clear insight of electronic properties for pristine and Mn-Cn, the variation of electron affinity EA(=-$E_{LUMO}$) and ionization potential IP(=-$E_{HOMO}$) with fullerene diameter, and metal doping are detected. EA increases with fullerene diameter for pristine fullerens, whereas IP decreases[9].
For the frontier molecular orbital analysis, the density of states was calculated. Figure 2a,2b and 2c were drawn from the calculations obtained.




a)




b)




c)

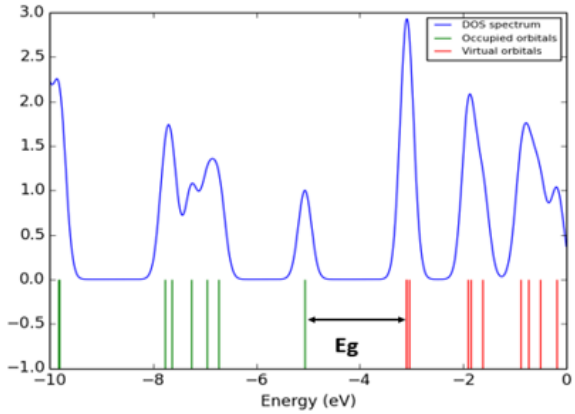
Fig. 2. The density of states generated for frontier molecular orbital analysis.

As can be seen from the figures, $\%\Delta E_g$ values are quite large in the selected Mn doped fullerenes. Especially, it reached the highest value in the $MnC_{39}$ (spin down) case.

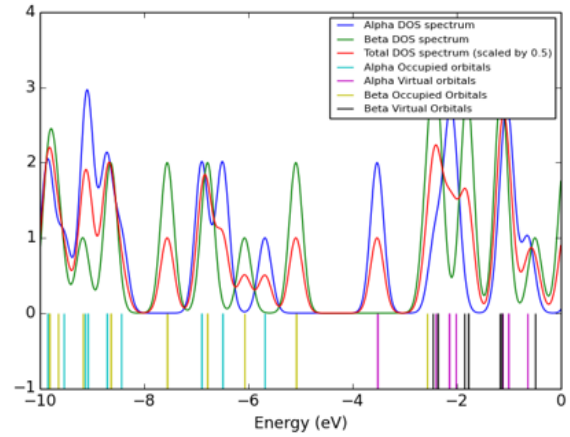
Thus, $MnC_{39}$ fullerene can be a functional sensor candidate for drug delivery applications.

The energy gap, an important element in the determination of chemical reactivity and charge transfer, was determined to monitor the stability of the Mn doped fullerences. The HOMO-LUMO energy bandgap gives information about a system's decrease or increase in chemical reactivity and chemical stability. Chemical reactivity decreases when the energy gap Eg increases.

In addition, DOS graphs for $C_{20}$ and $MnC_{19}$ fullerenes are given separately in Figure 3a and Figure 3b. When the figures are examined carefully, the importance of the Mn contribution is clearly revealed.




a)




b)

Fig. 3 DOS for C20 a), DOS for MnC19 b)

## IV. CONCLUSION

In this study, the electronic properties of Mn doped fullerenes were investigated by applying DFT calculations. Based on quantum chemical calculations, it was found that $MnC_{n-1}$ fullerenes exhibited a semiconductor character as indicated in some previous calculations. Two types of calculations were made for Mn doped fullerene (spin up and spin down states). There is a slight difference in the energy calculations for these two states. The gap energy and work function variations reach very different values. These values are much larger than 10. These materials can be used as sensors. This situation shows an important feature of the selected fullerenes. Based on the percentage change of band gap and work function results, doped fullerenes were improved by optimization. Thus, it shows that these materials can be used as a sensor for detection and recognition. If the obtained results are compared with previous calculations, fullerenes with a quantum confinement effect can be used in drug delivery studies.

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