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Mapping the Molecular Electrostatic Potential of Fullerene

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FULLERENE (C_{60}) as well as fullerene based systems show unique properties dedicating them for many applications. Accordingly, the present work carried out to study the molecular electrostatic potential ESP of C_{60}. C_{60} and their decorated ZnO and OZn interacted with halides as XOZn where X is the halides F; Cl and Br respectively.

The studied structures calculated at density functional theory level at B3LYP/6-31g*. Electrostatic potential ESP is a perfect indication and identification for possible sites representing the electrophilic and/or nucleophilic attack. Throughout the ESP, it is easy to map then drive the ability of the studied fullerene for reactivity through the interaction with its surrounding structures by forming bonding and/or forming surface. The ESP in this work is utilized as a test for reactivity. The mapped contours of the studied C_{60} and its decorated structures show that, the distribution of charges and the electrostatic contour affected by decoration, which dedicated the decorated C_{60} for several applications.

Keywords: C_{60}, Decorated C_{60}, B3LYP/6-31g*, ESP.

Introduction

A fullerene is an allotrope of carbon in the form of a hollow sphere, it also known as Buckminsterfullerenes or buckyballs, symbolled as C_{60}. It first discovered early on 1985 then synthesized as bulk quantity five years later [1-3]. Many attempts carried out for the characterization of fullerene with different characterizing techniques to understand the vibrational characteristics; fine intermolecular vibrational modes; the surface morphology and optical absorption characteristics of fullerene in different forms[4-9]. Since the discovery of fullerene, it is a subject of intense research work, not only for its unique chemical properties but also for their emerging technological applications, in many

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fields such as materials science, electronics, and biology [10,11]. Fullerene early reported in sediment samples, which classified as geologic samples could be attributed to carbonaceous materials [12-14]. This findings pave the way toward isolation of fullerene from different environmental samples [15]. There are spectroscopic efforts for identification of fullerene in geological samples as well as environmental matrixes [16-18], beside of course the analytical efforts needed for the extraction of fullerene [19]. Based upon these considerations, this amazing molecule is not only carrying fantastic properties but it is also naturally occurre in the environment. More efforts are needed to understand the physical behaviors of fullerene. Better understanding of fullerene properties could be achieved with molecular modeling at different levels of theories [20-26], including semi-empirical quantum mechanical calculations, ab initio level of theory and finally calculations at density functional theory level.

This work is conducted to model the molecular electrostatic potential of fullerene C_{60}, decorated C_{60} with ZnO and OZn, and then decorated C_{60} with halides/metal oxides F-ZnO, Cl-ZnO and Br-ZnO respectively.

Calculations Details

In the present study, a model molecule built for C_{60} and decorated C_{60} with ZnO and OZnand then decorated C_{60} with halides F-ZnO, Cl-ZnO and Br-ZnO.

All the studied structures are subjected to calculations with GAUSSIAN09 [27] program at Spectroscopy Department, National Research Centre, Egypt. All model molecules C_{60}, decorated C_{60} with ZnO and OZn and decorated C_{60} with halides F-ZnO, Cl-ZnO and Br-ZnO are optimized at B3LYP/6-31g* [28-30]. Total dipole moment and HOMO/LUMO band gap energy are calculated at the same level of theory.

Results and Discussion

The contour of molecular ESP describing the surface of C_{60} as well as decorated C_{60} has been achieved through mapping the sites for the electrophilic as well as nucleophilic attacks [31]. This contour describes the charge distributions for the studied structure throughout colors. Mapping the colors indicates the site, each color represents certain charge so that, from negative to positive the colors are going to change from red to blue. The negativity is following color scheme according to the following color order

red > orange > yellow > green > blue which is mentioned earlier in the literature [32,33].

The B3LYP/6-31g* optimized structure for C_{60} is indicated in Fig. 1, the molecule is simply described as highly symmetric molecule. The molecular electrostatic potential ESP is calculated and mapped as shown in Fig. 2, which represents the ESP contour.

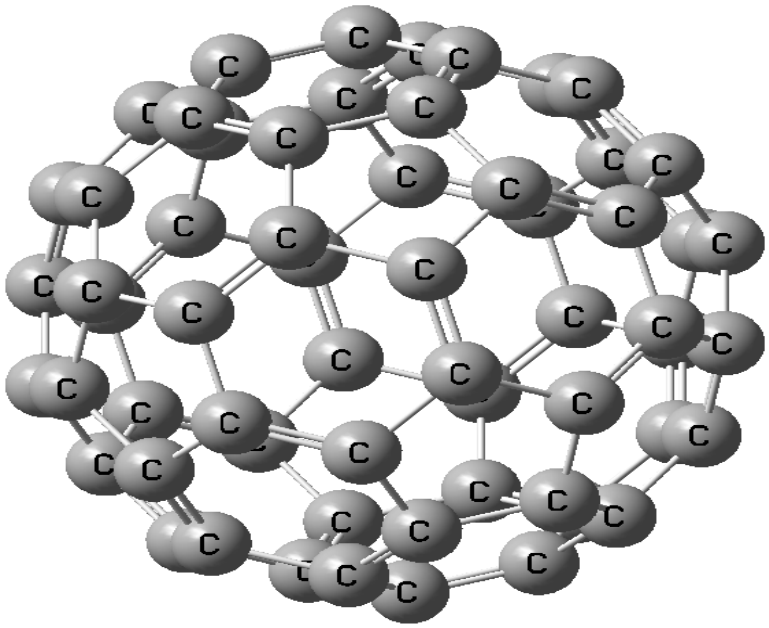


Fig. 1. B3LYP/6-31g* optimized structure for C_{60}.

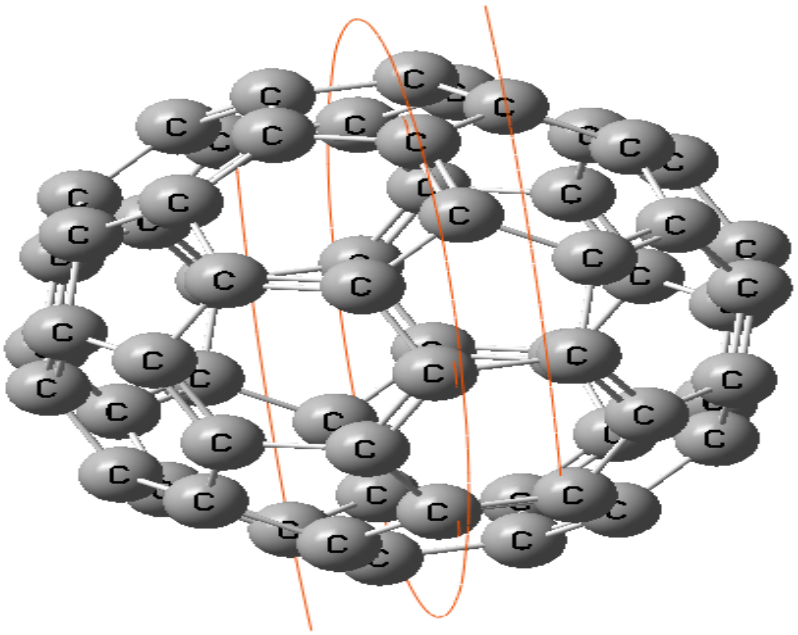


Fig. 2. Electrostatic potentials ESP of C_{60} molecular surface as contour.

The contour is uniformly distributed along the outer surface of fullerene. As indicated in Fig. 3 no surface is drawn for the C_{60}.

As shown in Fig. 4, C_{60} is decorated with ZnO to form C_{60}-ZnO. Zn of ZnO is interacted through physical interaction with C_{60} surface. Regarding the ESP of C_{60}-ZnO, the ESP contour is drawn in Fig. 5 which indicated that negative charge around oxygen indicated with red color, with an induction of another cavity of red color inside the C_{60}. Ongoing to the surface as indicated in Fig. 6 for the same structure, a surface localized covering the oxygen atom with another localized surface inside the C_{60} which confirming that indication of the contour in Fig. 4.

Figure 7 represents the B3LYP/6-31g* optimized structure for decorated C_{60}-OZn, in which the decoration took place as oxygen is interacted with the C_{60} surface. The ESP contour shows that red color, which is corresponding to negative charge, is surrounding oxygen as well as the surface of C_{60}, as compared with C_{60}-ZnO, the cavity of negative charge inside the C_{60} has increased (as shown in Fig. 8). As shown in Fig. 9 the surface is around oxygen and surrounding the C_{60}-ZnO. This surrounding surface is covering inside the C_{60}. ESP at a point is known as the energy needed to bring a positive charge from infinity to that point. For certain interaction, the charge is going to be redistributed which in turn maps the points constituting the surface of ESP of a given structure, which is C_{60} in our case. In this sense, the ESP contour is describing the molecular reactivity of C_{60} as well as its decorated compounds.

Decoration with metal oxides offers the possibility for the decorated C_{60} to interact with its surroundings and in terms of ESP is activating the surface of C_{60}.

In order to increase the activity of surface halides, it is supposed to interact with C_{60} throughout metal oxides. Accordingly, the decorated C_{60} has interacted with F, Cl, Br as indicated in Fig.10 to Fig. 18.

The B3LYP/6-31g* optimized structure for decorated C_{60}-F-ZnO is indicated in Fig. 10. As indicated in the contour of ESP in Fig. 11, the negative potential is located around both oxygen and fluorine atoms while no negative potential inside the C_{60} with less negativity is well distributed around the C_{60} surface. The surface as shown in Fig. 12 of the same structure show that, the surface is outside the C_{60} with two possible sites around oxygen and fluorine.

Figure 13 presents the optimized structure for C_{60}-Cl-ZnO. It is worth to mention that, Fig. 14 and 15 present the ESP contour and surface of C_{60}-Cl-ZnO. This structure is following the same behavior as that of C_{60}-F-ZnO.

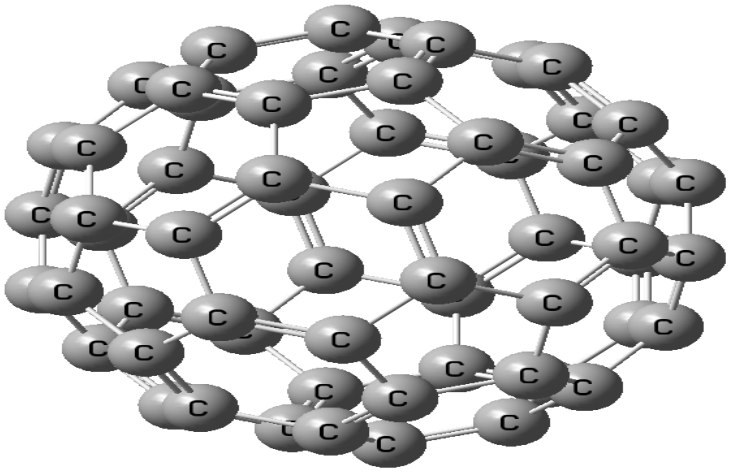
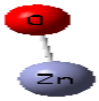


Fig. 3. Electrostatic potentials ESP of C_{60} molecular surface as total surface.



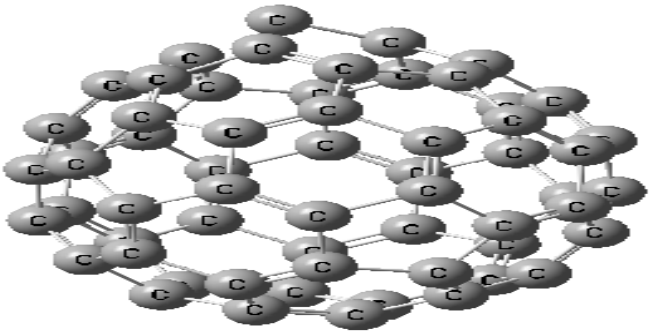


Fig. 4. B3LYP/6-31g* optimized structure for decorated C_{60}-ZnO.

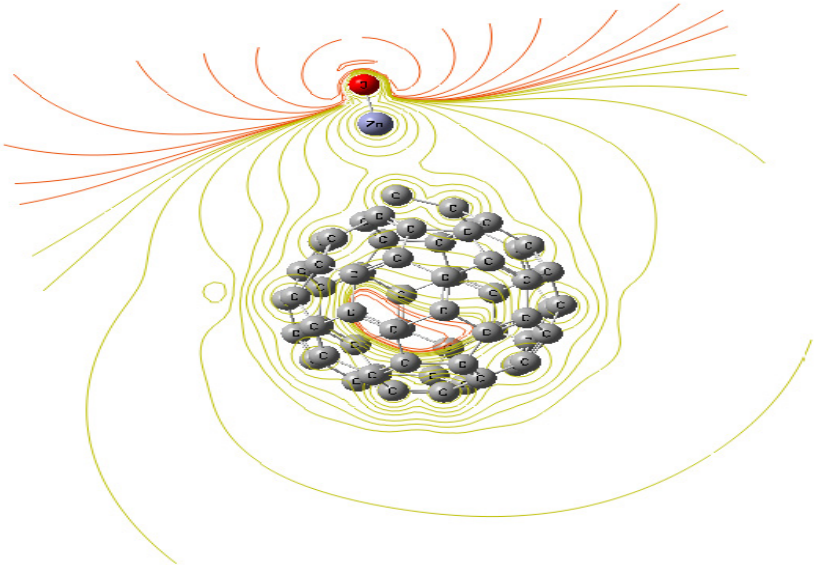


Fig. 5. Electrostatic potentials ESP of decorated C_{60}-ZnO molecular surface as contour.

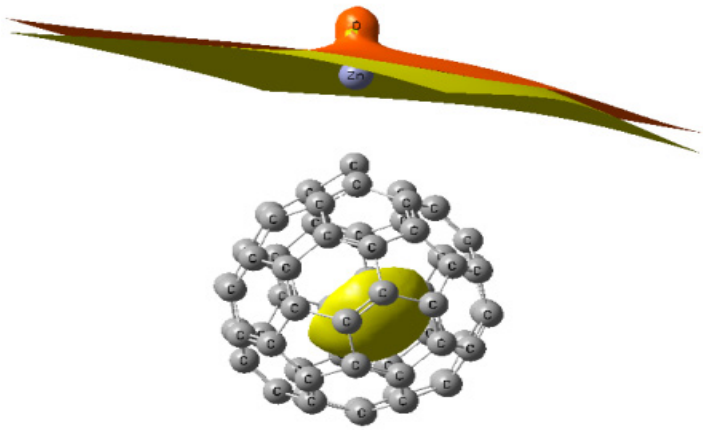


Fig. 6. Electrostatic potentials ESP of decorated C_{60}-ZnO molecular surface as total surface.

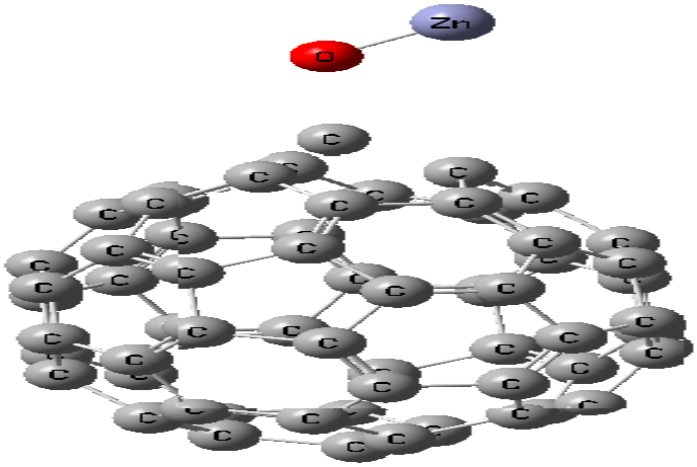


Fig. 7. B3LYP/6-31g* optimized structure for decorated C_{60}-OZn.

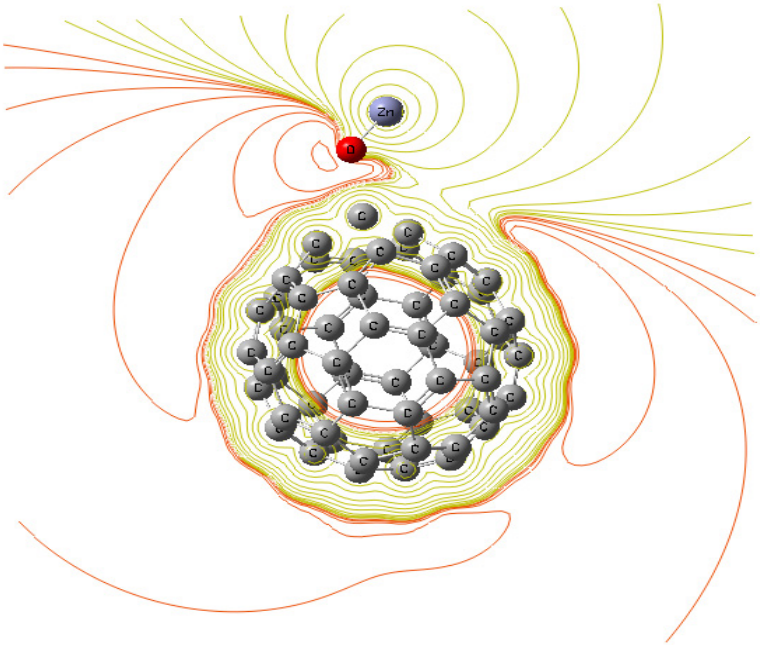


Fig. 8. Electrostatic potentials ESP of decorated C_{60}-OZn molecular surface as contour.

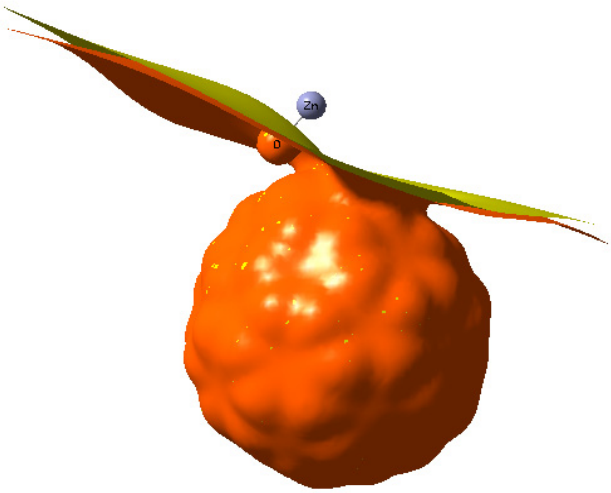


Fig. 9. Electrostatic potentials ESP of decorated C_{60}-OZn molecular surface as total surface.

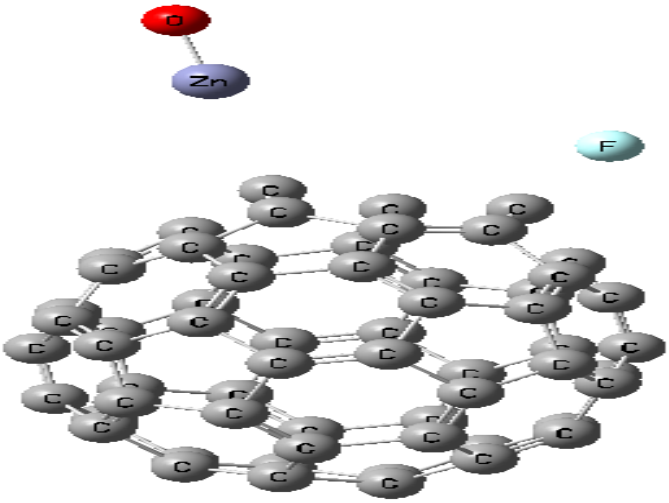


Fig. 10. B3LYP/6-31g* optimized structure for decorated C_{60}-F-ZnO.

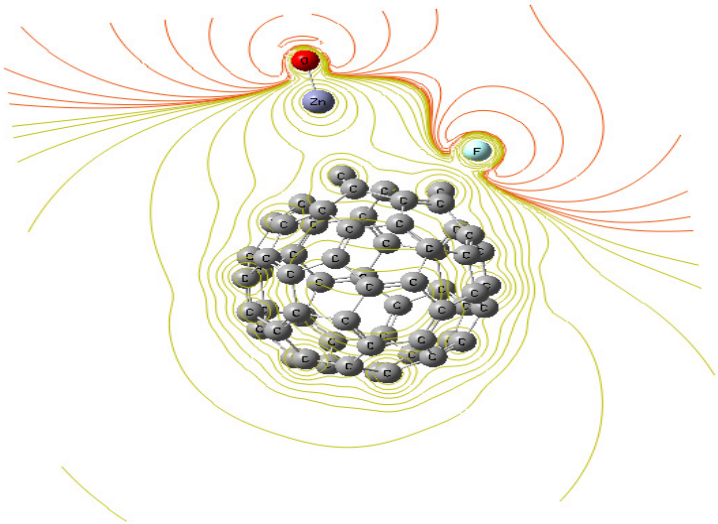


Fig. 11. Electrostatic potentials ESP of decorated C_{60}-F-ZnO molecular surface as contour.

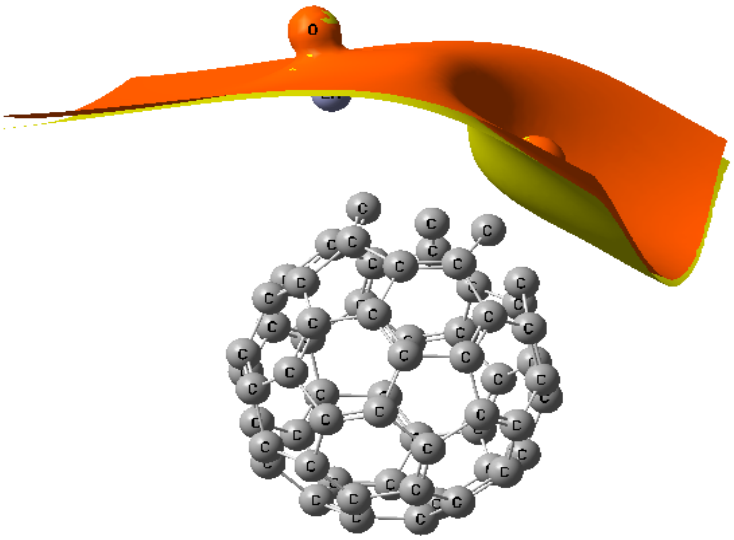


Fig. 12. Electrostatic potentials ESP of decorated C_{60}-F-ZnO molecular surface as total surface.

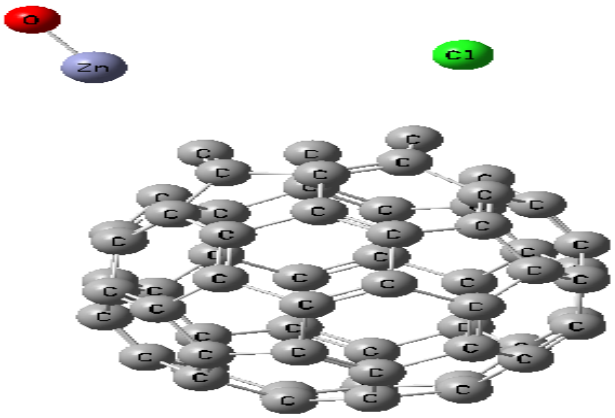


Fig. 13. B3LYP/6-31g* optimized structure for decorated C_{60}-Cl-ZnO.

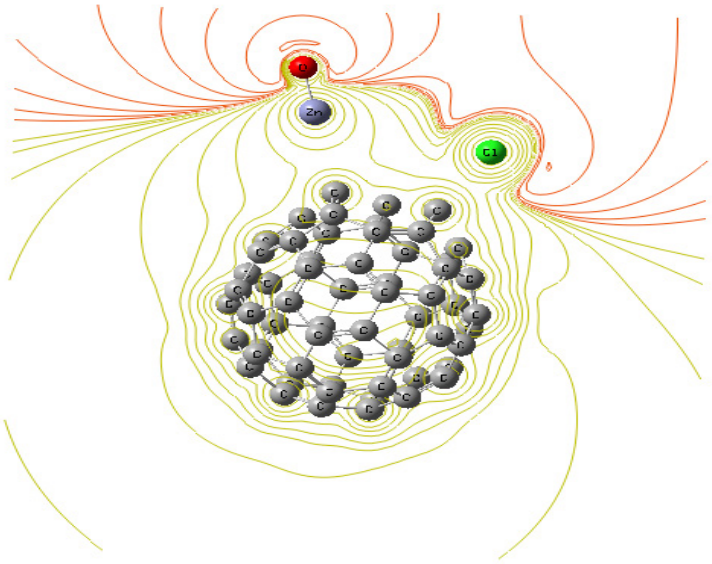


Fig. 14. Electrostatic potentials ESP of decorated C_{60}-Cl-ZnO molecular surface as contour.

Figure 16 presents B3LYP/6-31g* optimized structure for decorated C60-Br-ZnO. Figure 17 shows the contour of ESP which is following those of C_{60}-F-ZnO and C_{60}-Cl-ZnO. In addition, there is a negative potential inside the C_{60} as indicated in the case of decorated C_{60}. Again the surface which is in Fig. 18 is confirming the finding of ESP indicated in Fig. 17.

As stated above the ESP is mapping the active sites of a given chemical structure which could be a measure for reactivity for the studied structure. Mapping the ESP through colors facilitate the process of discussion of molecular modeling data.

Furthermore, the present work confirms the importance of computational methods in studying molecular systems [34,35].

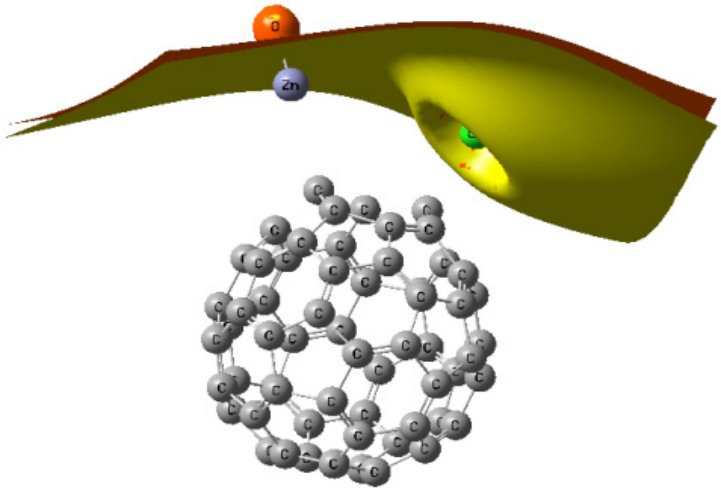


Fig. 15. Electrostatic potentials ESP of decorated C_{60}-Cl-ZnO molecular surface as total surface.

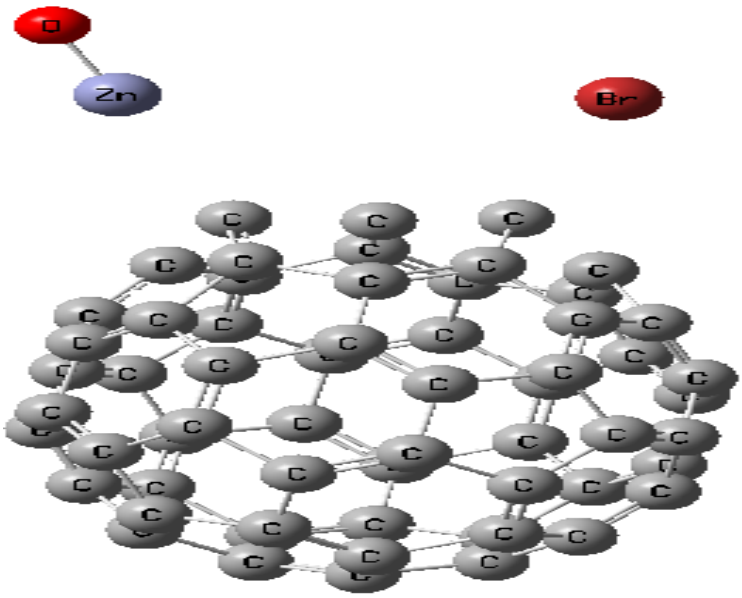


Fig. 16. B3LYP/6-31g* optimized structure for decorated C_{60}-Br-ZnO.

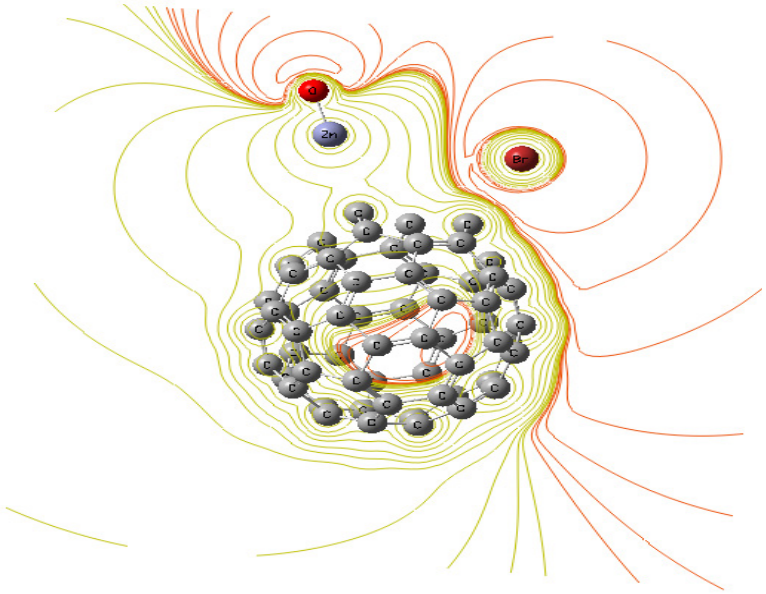


Fig. 17. Electrostatic potentials ESP of decorated C_{60}-Br-ZnO molecular surface as contour.

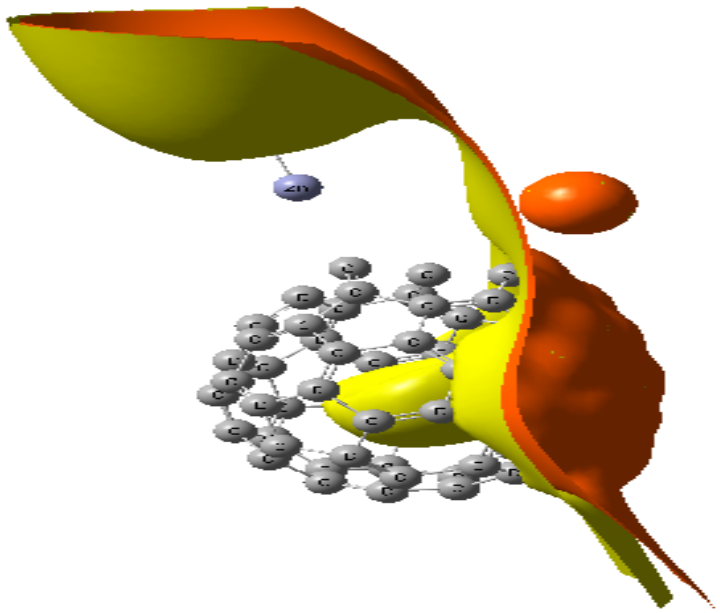


Fig. 18. Electrostatic potentials ESP of decorated C_{60}-Br-ZnO molecular surface as total surface.

Conclusion

Density functional theory at B3LYP/6-31g* is dedicated to study the ESP. For both C_{60} and its decorated structures, the distribution of charges affects ESP and then indicates the suitability of decorated C_{60} for interaction with surrounding gases. This computational study indicated that decorated C_{60} could act as gas sensor on one hand and also indicated that ESP is an important physical tool for judging the chemical reactivity of a given chemical structure on the other hand. This molecular modeling approach indicated the suitability of molecular modeling at different levels [36-38], for investigating different molecules and interactions in many areas of research.

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تعيين الجهد الكهروستاتيكي الجزيئي للفوليرين

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يعتبر مركب الفللورين ومشتقاته من المركبات ذات الخواص الكيميائية والفيزيقية المميزه التي تؤهلها للتطبيق في العديد من المجالات ولذلك نقوم في هذا البحث بدراسه سطح الجهد لهذا النوع من المركبات وهو مايعرف باسم molecular electrostatic potential ESP وتم ذلك لمركب الفلورين ثم يلي ذلك مركبات الفللورين التي يتم تحسين خواصها السطحية باضافة اكسيد الزنك ويتم الارتباط بطريقتين الاولي عن طريق الاكسجين والثانية عن طريق الزنك.كما تم دراسه ارتباط سطح الفلورين المحسن بالاكاسيد مع الهالوجينات وتم ذلك باستخدام نظرية كثافه الدوال المعروفة باسم density functional theory B3LYP/6-31g* وتعتبر دراسة سطح الجهد لهذا النوع من المركبات بمثابة اليه لمعرفة اماكن الارتباط التي يتم عن طريقها الارتباط بين الغازات علي سبيل المثال وبين سطح الفللورين او الفللورين المحسن وبالتالي يمكن تفسير الية الارتباط وكيفية تميز هذا النوع من المركبات من خلال خواصه السطحية التي تهيئه للعمل كمحسات للغاز بحساسية عالية خصوصا للغازات السامه وذلك جنبا الي جنب مع عدد اخر من التطبيقات المهمه.