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Research Article

Ultra Small Fluorine Carbon Nanoclusters by Density Functional Theory

Yelda Kadioglu[1,2]

[1] *Department of Physics, Faculty of Science, Aydın Adnan Menderes University, Aydın, Turkey*
[2] *Department of Physics, Faculty of Natural and Mathematical Sciences, University of Maryland Baltimore Country, Baltimore, USA*

Abstract

Density functional theory (DFT) calculations were performed in order to provide theoretical knowledge about fluorine-carbon alloy nanoclusters in this study. While fluorine atoms do not show a stable nanocluster formalism, carbon atom addition initiates the formation of FxCy nanoclusters by a strong F-C bonding mechanism. Single fluorine systems were the most favorable nanoclusters in FxCy alloys. FC2, FC3, FC4 nanoclusters were found to be minimum energy structures for three, four and five atoms respectively. The cohesive energy values of nanoclusters increase with the increasing number of carbon atoms in nanoclusters. Shape dependent magnetic moment was found in particular nanoclusters. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy gap (HLG) values of each stable cluster were also presented which provide information about chemical reactivity. The findings of this study can be a basis for fluorine-carbon alloy applications in nanotechnology.

Keywords: Nanocluster, Fluorine-carbon alloy, Density functional theory.

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*Corresponding author: Yelda Kadioglu
E-mail: yeldaakadioglu@gmail.com

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1. Introduction

Nanoclusters are of significant interest in recent years due to being an intermediate model between atoms and bulk structures. Their formation process helps us to understand the physics under the nature of crystallization and transition from nanocluster to bulk state. They also play a role especially in the design and production of new materials in nanotechnology. Therefore, investigations on nanoclusters are important in a wide range of areas for next-generation technology.

Nanoclusters can be composed of a few to a hundred atoms and possess different behaviours from their bulk counterparts due to quantum confinement effects. For example, gold has been known as one of the least reactive metals in the bulk form, however, it shows catalytic properties in nanosized [1].

It is known that the chemical, optical, magnetic etc. properties of nanoclusters can be controlled by their geometric structure sensitively [2]. The size, shape and compositions of nanoclusters are crucial for understanding the mechanism of the relationship between their geometric structure and electronic properties especially.

Carbon-bound fluorine atoms are unique in organic chemistry. Because of the high industrial demand for carbon and fluorine contained organic molecules, C-F bond formation has become active research field [3]. Due to the major successes of fluorinated compounds in medicinal chemistry [4], they are more attractive recently. Similarly, fluorinated compounds are also frequently synthesized in modern medicinal chemistry and have led to a large number of highly effective drugs [5].

Graphite fluoride composed of carbon and fluorine atoms is a well-known covalent derivative of graphite with interesting electrochemical and electronic properties and potential applications in hydrogen storage. It has been synthesized [6,7] and can be used as a wide bandgap two-dimensional (2D) material in electro-optical applications [8].

The F-F bond is known as one of the weakest of all covalent bonds [9]. However, F-C is one of the strongest bonds in organic chemistry and this makes carbon substitution attractive to obtain stable nanoclusters for fluorine. The main purpose of this study is to obtain strongly bonded nanoclusters by adding C atoms to weakly bonded fluorine nanoclusters. Therefore the nanoclusters of fluorine and carbon (F_xC_y) were investigated in this study systematically to make stronger clusters. There is no study about small fluorine-carbon nanoclusters so far. By this motivation, the structural characterizations of fluorine-carbon nanoclusters were investigated in this study. While pure fluorine clusters do not show nanocluster formalism, carbon atom addition to these systems systematically, increase cohesive energy values and initiates the formation of nanoclusters. The results of this study can be useful for the design and functionalization of fluorine-carbon alloys in nanotechnology.

2. Materials and Methods

All DFT calculations were carried out by using the SIESTA package which uses a numerical atomic orbital basis set [10]. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functionals were used within generalized gradient approximation (GGA) [11]. The calculations have been performed at Gamma point. Mesh cut off has been taken as 300 Ry. The tolerance value in the maximum difference between input and output density matrix has been used of 10-5. Spin polarization was taken into account in all calculations.

Cohesive energy (Ecoh) of the clusters wers calculated by the formula below [12].

$$E_{coh} = \frac{(x \times E_F) + (y \times E_C) - E_{cluster}}{x + y}$$

where Ecluster is the total energy of isolated nanocluster, EF and EC are the energy of free fluorine and free carbon atoms respectively. The parameters x and y are the numbers of F and C atoms in the cell.

3. Results and Discussion

The possible shape and compositions of fluorine-carbon nanoclusters (FxCy, x+y=5) up to five atoms are shown in Figure 1, Figure 2 and Figure 3. The geometric structures of clusters were obtained after the optimization process and the most stable (minimum energy) structures of each cluster system are shown in yellow shaded areas. Each red letter on the top side of figures corresponds to the different cluster shapes below and each number denotes a compound containing a different number of F or C atoms and permutations of one F or C atom. Therefore each cluster name is symbolized by three-component. The first number is the number of atoms in nanocluster, the subsequent letter is the shape of nanocluster and the last number is composition of the nanocluster. For example, 3a1 is the nanocluster in the first row in the leftmost column in Figure 1.

Cohesive energy (Ecoh) is a quantity of the energy required to separate constituent atoms apart from each other and shows how these atoms bond together strongly. Hence the calculated Ecoh values per atom were written on the figures for each nanocluster system.

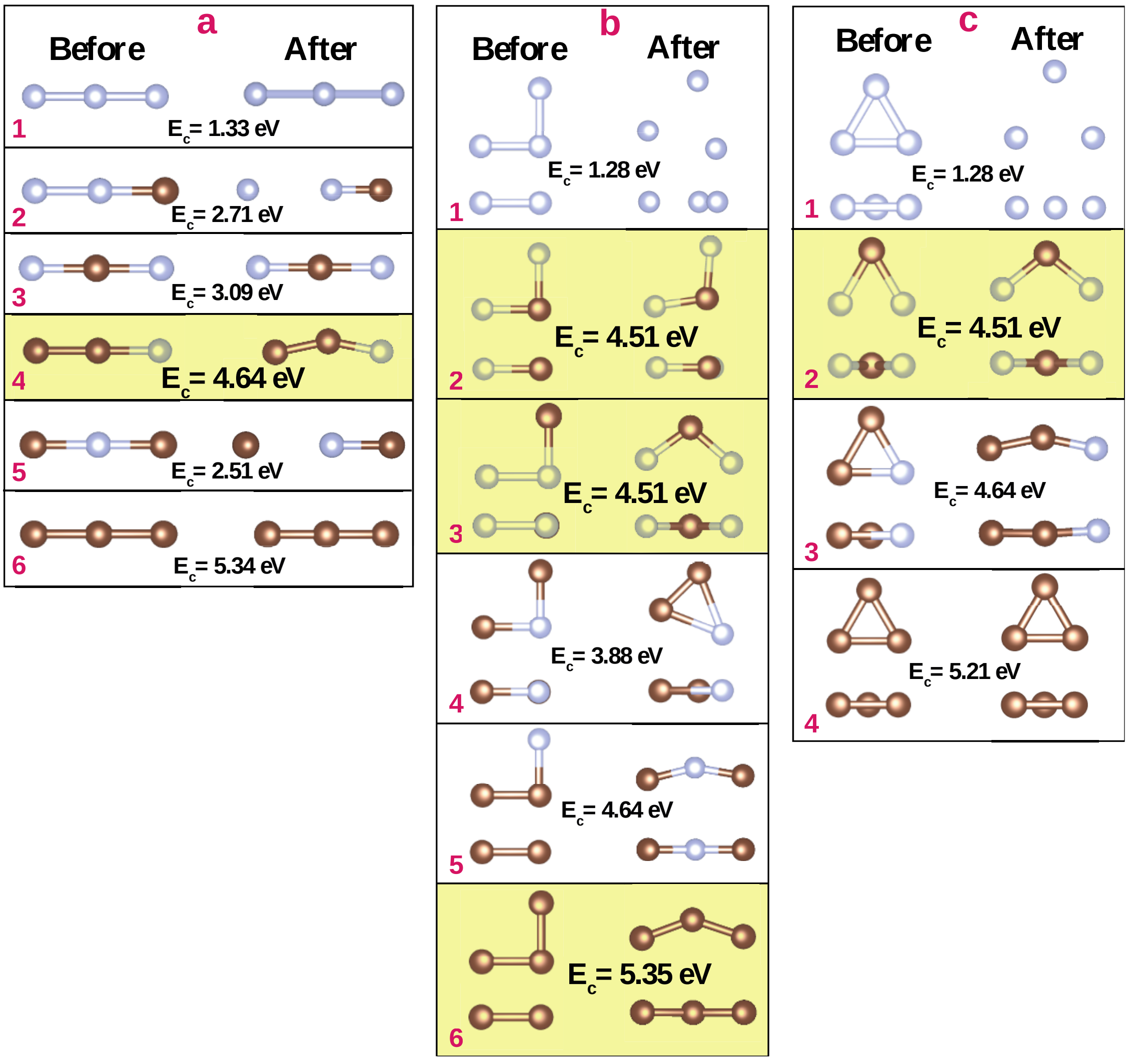

Figure 1. The optimized structures of three atom nanoclusters before and after relaxation process. The grey and brown coloured atoms represent fluorine and carbon atoms respectively. Each column shows different cluster shapes. Both of top and view side of each cluster were shown. Cohesive energy values were also presented. The most stable nanoclusters with the highest cohesive energy values in each number of carbon atoms were shown in yellow shaded areas.

Fluorine nanoclusters are shown in the first rows of figures. The F-F bond length for dimer was found as 1.41 Å which is an excellent consistency with the literature [9]. However, fluorine atoms do not exhibit a stable clustering as can be seen from the figures. F-F bond length was calculated as 1.63 Å in 3a1 nanoclusters (Figure 1). Except for this three atom clustering, other forms of fluorine atoms show either dimer forms such as F_2 molecule or aggeration of unconnected atoms. However, it can be seen that clustering process starts with the C atom addition to the system. As a result of this situation, E_{coh} values of systems increase significantly when the C atoms add into the system. The F-F distance on triangle clusters is 1.87 Å because of the repulsive interaction inherent in the so-called lone-pair bond weakening effect [13,14,15]. Adding carbon atoms increases the cohesive energy to more than three times for 3b and 3c systems. The minimum energy cluster for one carbon and two fluorine atoms system is L-shaped (3b2,3b3 and 3c2). The cohesive energy for them is 4.51 eV/atom and the bond length of F-C atoms on these nonmagnetic clusters is 1.33 Å. Two carbon and one fluorine system cluster (3a4) shape is the most stable one among three atom clusters of F_xC_y system with 4.64 eV/atom E_{coh} value. It has a 175° angle with 1.28 Å of both C-C and C-F bond lengths. The magnetic moment value of this cluster is 1.0 μ_B. Nonmagnetic three atom bare carbon cluster is shown as 3b6 cluster and it has a 141° angle with a 1.31 Å bond length between C atoms.

Four atom F_xC_y clusters are presented in Figure 2. The F clusters given in linear (4a1) and rectangular (4b1) form initially have transformed into F_2 molecules. 4c1 and 4d1 tetragonal forms have an F-F distance of about 1.86-1.89 Å, showing no chemical bond between them. The addition of one C atom to the linear system shows the formation of F-C dimer and F_2 molecules separately in the 4a2 system. In 4b2 and 4c2 systems, we can see a CF_2 nanocluster and one free F atom as a final position. One C atom in 4d2 system shows a stable nanocluster with a high E_{coh} value in three dimensions. The 1.33 Å bond length of F-C atoms and 1.0 μ_B magnetic moment value in this cluster have also been calculated. The most stable nanocluster among F_2C_2 systems is a 4d3 structure in linear form with a 5.13 eV/atom E_{coh} value. It is a nonmagnetic cluster with 1.29 Å F-C and 1.21 Å C-C bond lengths. 4d4 and 4d5 structures have the same final configuration therefore they have same E_{coh} value of 5.43 eV/atom. The magnetic moment value of this cluster is 1.0 μ_B. C-C bonds are about 1.38-1.41 Å and F-C bond length is 1.29 Å. The four atom C cluster (4a7) is the most stable structure among rectangular and three-dimensional shapes. It has a linear form and 2.0 μ_B magnetic moment value. Its E_{coh} value is 5.64 eV/atom and C-C bond lengths are between 1.31-1.33 Å.

There are many compositions of five atoms F_xC_y clusters as can be seen in Figure 3. Carbon clusters prefer linear shape for five atoms with an E_{coh} value of 6.17 eV/atom. It is the highest E_{coh} value among the systems considered in this study and show zero magnetization. The fully bonded state of the atoms in linear shape has not been formed except for the 5a16 composition. Carbon clusters with one carbon four fluorines atoms are the most stable in the shape of 5e2 structure which is called carbon tetrafluoride or tetrafluoromethane molecule in literature and it is nonmagnetic. The most stable two carbons three fluorines systems are seen as 5b7 and 5b8 clusters which are in the same shape with 1.0 μ_B magnetic moment value. 5e8 is the most stable shape for three carbons two fluorines systems and it is nonmagnetic. 5b13 result in linear shape and it is the most stable structure for four carbons and one fluorine atom with a 1.0 μ_B magnetic moment value.

Among the alloy nanoclusters, those with minimum energy were obtained as FC_2 for three atoms, FC_3 for four atoms and FC_4 for five atoms. It is obvious that single fluorine systems are the most favorable nanoclusters for F_xC_y alloys.

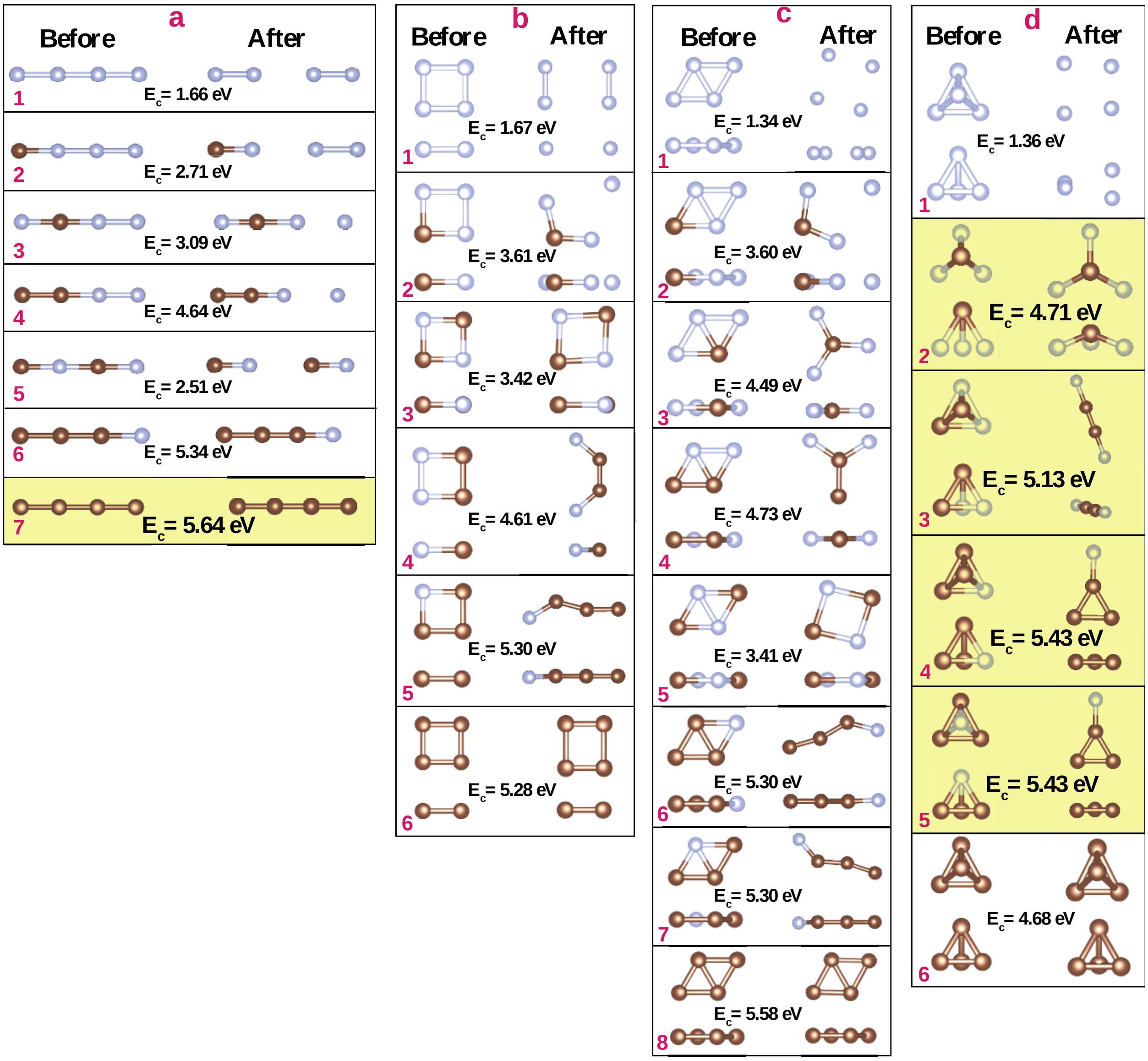

Figure 2. The optimized structures of four atom nanoclusters before and after the relaxation process. The grey and brown coloured atoms represent fluorine and carbon atoms respectively. Each column shows different cluster shapes. Both of top and view side of each cluster were shown. Cohesive energy values were also presented. The most stable nanoclusters with the highest cohesive energy values in each number of carbon atoms were shown in yellow shaded areas.

It is interesting to found nanoclusters in same compositions which have different magnetic moment value. 3a3 and 3b2 structures have one C and two F atoms and 3c2 as well. But 3a3 structure has a 2 μ_B magnetic moment value while 3b2 and 3c2 are nonmagnetic. Here the orientation of the F atoms is the determining factor. Similarly, 4c4 and 4d3 structures are nonmagnetic while the other same composition clusters have 2 μ_B magnetic moments. Shape dependent magnetic moment has been found in F_xC_y clusters but further step on this subject is beyond the scope of this study.

The difference between of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is known as the HOMO-LUMO gap (HLG). High HLG is an indicator of high chemical stability. In other words, high HLG is an unfavorable energetic process in terms of electrons due to action from lower HOMO to higher LUMO, therefore high HLG represents low chemical reactivity.

HLG values of the most stable clusters are shown in Figure 4. Since 3b2, 3b3 and 3c2 clusters have the same structure after the optimization process, only the HLG value of the 3b2 cluster representing them was calculated. This also applies to 4d4 and 4d5 structures and similarly to 5b7 and 5b8 structures. 3a4 structure shows a minimum HLG value among the three atoms clusters, while the highest HLG value belongs to the 3b2 structure with the value of 3.29 eV. Three atoms carbon clusters show a relatively high HLG value of 2.48 eV. 4d3 nanocluster has the highest HLG value among the alloy clusters. The minimum HLG value among all stable nanoclusters in this study was calculated for 5b13 nanocluster with the value of 0.49 eV. However, the most chemically stable nanocluster with the highest HLG value is the F_4C (5e2) structure (tetrafluoromethane). It is known as an extremely stable gas [16] and this is consistent with having the highest HLG value of 13.34 eV in this study.

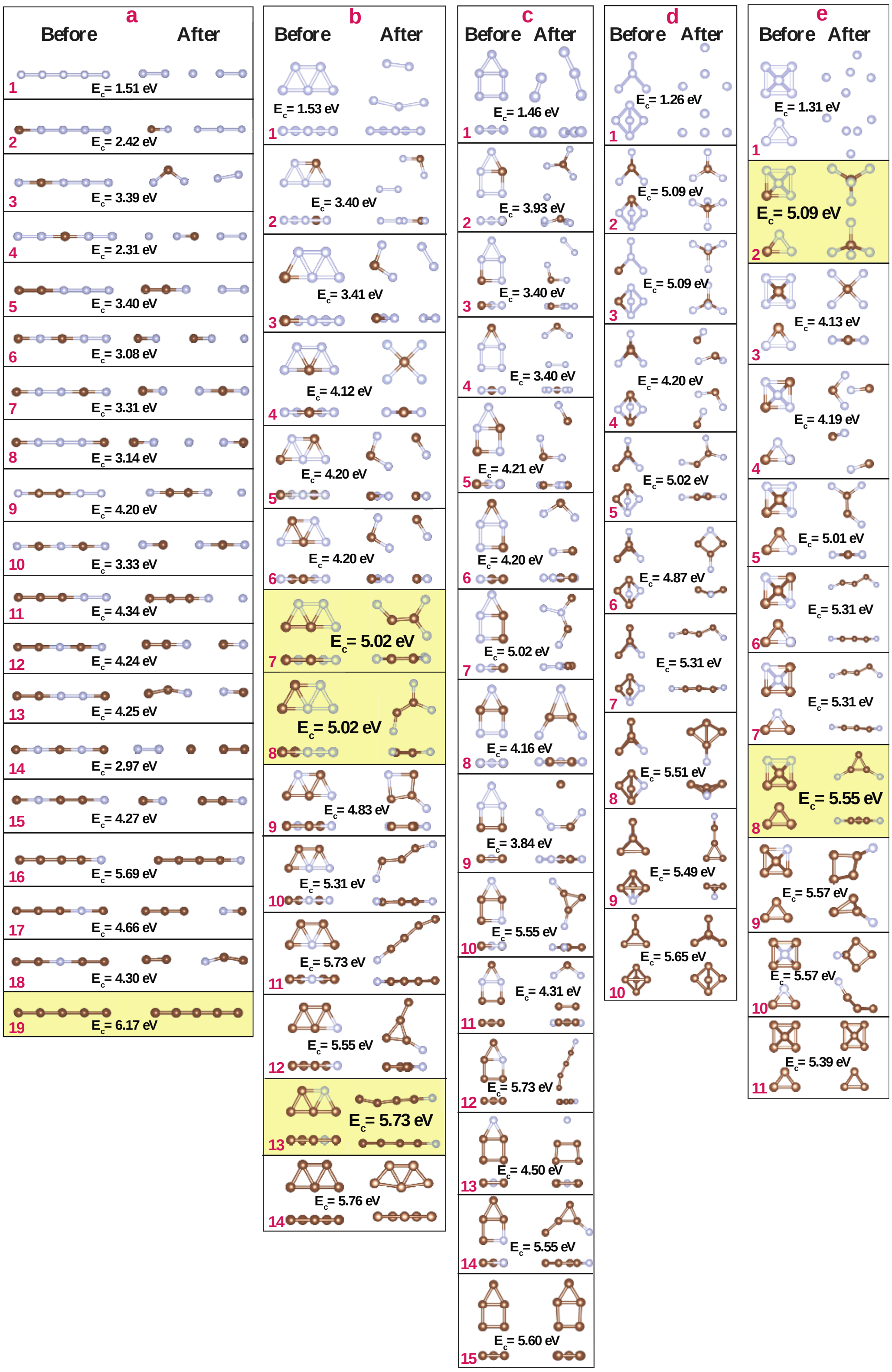

Figure 3. The optimized structures of five atom nanoclusters before and after the relaxation process. The grey and brown coloured atoms represent fluorine and carbon atoms respectively. Each column shows different cluster shapes. Both of top and view side of each cluster were shown. Cohesive energy values were also presented. The most stable nanoclusters with the highest cohesive energy values in each number of carbon atoms were shown in yellow shaded areas.

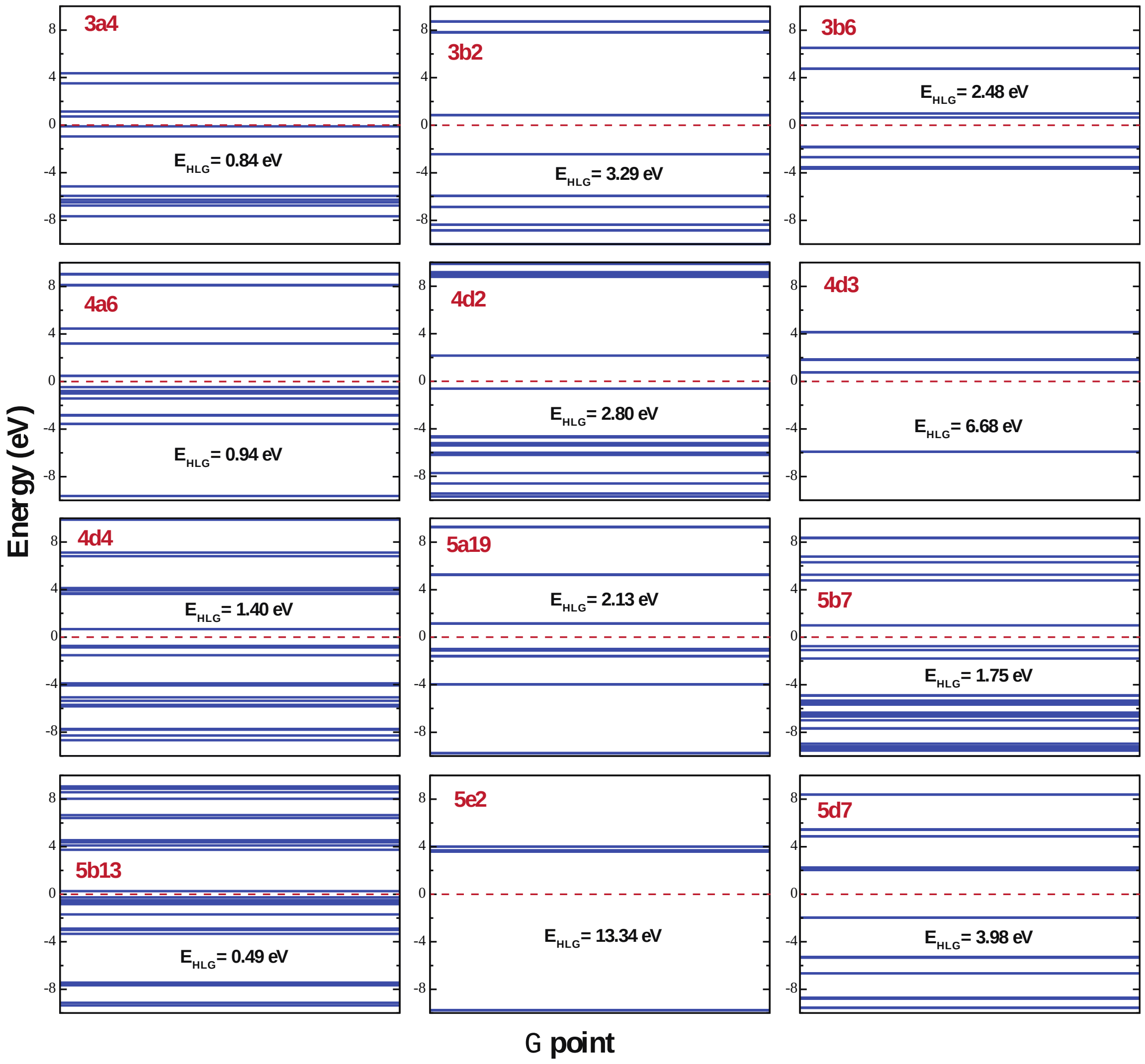

Figure 4. HOMO LUMO energy gap (E_{HLG}) graphs of each stable nanocluster. Fermi level was set to zero levels and shown by the red dashed line.

4. Conclusion

In conclusion, the structural formalism of fluorine-carbon alloy nanoclusters was investigated in this study. Fluorine atoms did not show a stable nanocluster configuration. However, carbon atoms affected the formation of fluorine-carbon nanoclusters by strong F-C bonding and formed stable and strongly bonded F_xC_y clusters. The cohesive energy values of nanoclusters increased with an increasing number of carbon atoms. The minimum energy compositions were obtained for FC_2 (3 atoms), FC_3 (4 atoms), FC_4 (5 atoms) clusters except for carbon clusters. Hence single fluorine systems were the most favorable nanoclusters for F_xC_y alloys. There were the same composition nanoclusters which had different magnetic moment values leading shape-dependent magnetic moment. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy gap (HLG) values were also presented. According to these values, the F_4C molecule which is called tetrafluoromethane showed the highest HLG value indicating lowest chemical activity among the nanoclusters in this study. These results can provide an insight into applications on nanotechnology and the studies on organic chemistry.

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