

The Electronic and Optical Properties of Pristine, Fluorinated and Chlorinated Pentacene Molecules: An ab-initio Study

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Abstract

In This research the effect of fluorine and chlorine substituents on the electronic and optical properties of pentacene molecule have been investigated based on density functional theory as implemented in SIESTA code. The results show that the full replacement of hydrogen atoms with fluorine and chlorine in pentacene molecule, leads to shrink the HOMO-LUMO gap by the value of 0.14 and 0.46 eV, respectively. Moreover, the cohesive energy of fluorinated (F-PENT) and chlorinated pentacene (Cl-PENT) follow F-PENT < PENT < Cl-PENT order with respect to the cohesive energy value of -7.54 eV corresponding to pristine pentacene. Therefore F- PENT shows better stability than others. The results of optical properties demonstrate that fluorinated and chlorinated pentacene have greater dielectric constant and refractive index with respect to pristine pentacene. The reflectivity feature along the long axis of pentacene molecule undergoes a red shift and accordingly the violet color of pentacene changes to blue and green by the influence of fluorination and chlorination, respectively. These results can be utilized to improve molecular electronic and optical devices.

Keywords: Pentacene Molecule; Optical Properties; HOMO-LUMO Gap; Halopentacene; Reflectivity; Dielectric Function.

1. INTRODUCTION

Organic molecular-based materials have received great attention due to the promising applications in optoelectronic devices. Although single - molecule electronics has been born more than forty years ago but during the past decade it has become an experimental reality [1-3] and recently various attempts has been devoted by scientists to reveal opportunities of molecular-scale electronics[4,5]. Among various organic materials, pentacene has been widely investigated to be used in electronic devices such as organic field effect transistors[6,7], light emitting diodes[8,9], photovoltaic cells[10] and organic spin valves[11] because of its high charge carrier mobility which is reported the value of $35 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ for pentacene single crystals[12]. Pentacene is a polycyclic aromatic hydrocarbon consisting of five linearly fused benzene rings as

shown in Figure. 1-(a). This is a compound of n-acene family ($\text{C}_{4n+2}\text{H}_{2n+4}$) with $n=5$ which acts as a p-type semiconductor. However these p-type materials have a small ambient stability. The other problem is in the production of pentacene based devices. Bulk pentacene is insoluble in common solvents so the costs of the device production increases. If we introduce polar substituents like fluorine and chlorine into pentacene, its solubility in organic solvents increases. Also scientists have verified that fluorinated and chlorinated pentacene behave as n-channel semiconductors [13, 14].

From experimental point of view some halopentacene thin films have been grown and characterized by different research groups [15-18]. Also to exhibit the ambipolar behavior of these compounds, a combination of PENT and halopentacene

are synthesized in the form of p-n junction for device purposes [14, 19].

Recently, the researches on single-layer graphene and graphene like nano-ribbons (GNRs) have received increasing attention [20, 21]. Interestingly, another way to interpret the pentacene and halopentacene molecules are to view them as a small hydrogen, fluorine and chlorine terminated graphene nano-ribbons (GNRs) namely H-GNRs, F-GNRs and Cl-GNRs respectively (see Figure. 1).

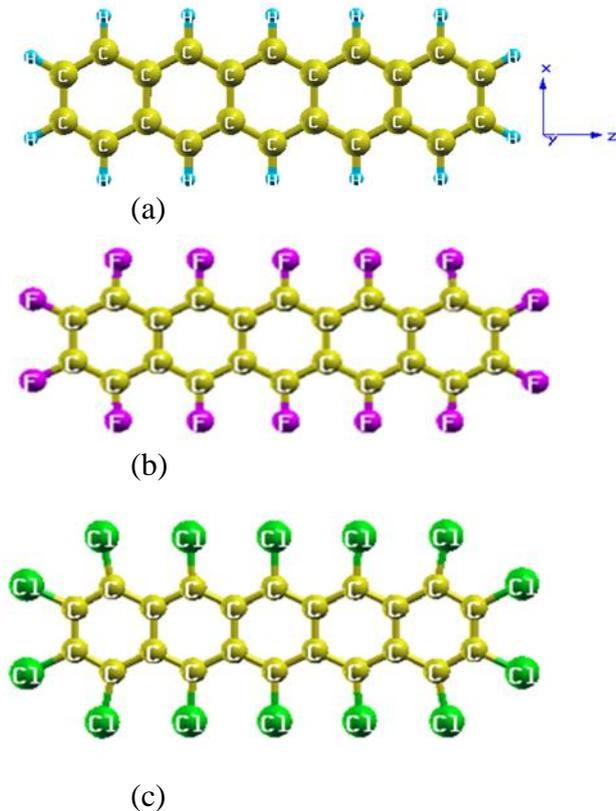


Figure 1. (a)pentacene molecule or hydrogen terminated graphene nano-ribbon (H-GNRs), (b)perfluoropentacene or fluorine terminated graphene nano-ribbon (F-GNRs), (c)chlorinated pentacene or chlorine terminated graphene nano-ribbon (Cl-GNRs).

Although some amount of works have been devoted to investigate the electronic properties of pentacene [22-24] but halopentacene (F-PENT and Cl-PENT) have been less studied [15, 25-27] especially the lack of theoretical works on

optical properties of these materials can be felt.

In this work, we theoretically analyze the structural, electronic and optical properties of two halopentacene molecules (F-PENT and Cl-PENT) in which all hydrogens in pentacene, are substituted with fluorine and chlorine. Since the interaction between the molecules in the molecular solids are weak van der Waals interactions, the optical properties of the individual molecules tend to be similar to the molecular solids [28].

Then we compare their various electronic and optical properties such as stability, HOMO-LUMO energy gap, dielectric constant, refractive index, absorption index and reflectivity with the ones for the pure pentacene molecule to see if the halopentacene can improve the efficiency of optoelectronic devices.

2. CALCULATIONS METHOD

The electronic and optical properties are calculated using density functional theory (DFT) implemented in SIESTA code [29]. Generalized gradient approximation (GGA) exchange correlation functional [30] is used throughout this work. In SIESTA code, core electrons which have not considerable effect in chemical and electronic properties are replaced by efficient Troullier-Martins pseudo potentials [31,32] and pseudo atomic orbitals (PAO's) basis set [33] have been used for the expansion of the wave functions of valence electrons. In this work double zeta polarized (DZP) sets are chosen to describe the valence electrons. We consider a super cell with dimensions of $20 \times 15 \times 30 \text{ \AA}^3$ to calculate the electronic structure, which is large enough to minimize the influence of the adjacent image molecules. For all molecules structural relaxation is performed by standard conjugate gradient for a force tolerance of 0.01 eV/\AA .

Optical calculations are sensitive to the dimensions of super cell, number of bands and number of k-points. Hence, we

increased the vacuum around the molecule until optical characteristics such as dielectric constant does not change considerably. The optimized super cell dimensions for pentacene, perfluoropentacene (F-PENT) and chlorinated pentacene (Cl-PENT) were obtained $50 \times 50 \times 50 \text{ \AA}^3$. The number of optical bands found to be 100,150 and 200 for pentacene (PENT), perfluoropentacene (F-PENT) and chlorinated pentacene (Cl-PENT) respectively which adding more bands doesn't cause any notable change in their resulted optical properties. Since we consider vacuum all around the molecules, only the Γ -point is enough to sampling the Brillouin zone. To examine optical properties in all three dimensions, the ribbons are exposed to the incident electric field parallel to x, y and z directions which are depicted in Figure. 1.

3. RESULTS

3.1. Stability

In order to investigate the chemical stability of the compounds, the cohesive energy and enthalpy of formation can be evaluated. The smaller the values, more stable is the compound. Cohesive energy is defined as the required energy to decompose the molecule to its constituent atoms. The enthalpy of formation is the change in enthalpy during the formation of a substance from its constituents in the standard state.

The cohesive energy E_{coh} and enthalpy of formation ΔH_f for C₂₂H₁₄, C₂₂F₁₄ and C₂₂Cl₁₄ molecules can be calculated according to the following relations:

$$E_{coh}(C_{22}X_{14}) = E_{tot}(C_{22}X_{14}) - 22E_{iso}(C) - 14E_{iso}(X) \quad (1)$$

$$\Delta H_f(C_{22}X_{14}) = E_{coh}(C_{22}X_{14}) - 22E_{coh}(graphite) - 7E_{coh}(X_2) \quad (2)$$

where X stands for H, F or Cl. $E_{tot}(C_{22}X_{14})$ is the total energy of the molecules, $E_{iso}(C)$ and $E_{iso}(X)$ are total

energies of the isolated C and X atoms, respectively.

In order to calculate the enthalpy of formation of the substituents, according to the second relation, the cohesive energy of carbon in the standard state i.e. graphite and H₂, F₂ and Cl₂ in the gas state are required.

The results of total and cohesive energy and enthalpy of formation for the studied molecules are represented in Table 1. The results show that fluorinated pentacene has the lower cohesive and formation energy than other two molecules, following the order of F-PENT < PENT < Cl-PENT.

Table 1. The values of total energy per atom, $E_{tot}(eV)/atom$, cohesive energy per atom, $E_{coh}(eV)/atom$, and enthalpy of formation $\Delta H_f(eV)$ of pentacene (PENT), perfluoropentacene (F-PENT) and chlorinated pentacene (Cl-PENT).

Molecule Name	$E_{tot}(eV)$ per atom	$E_{coh}(eV)$ per atom	$\Delta H_f(eV)$
PENT (C ₂₂ H ₁₄)	-118.41	-7.54	1.1
F-PENT (C ₂₂ F ₁₄)	-358.79	-7.72	-25.32
Cl-PENT (C ₂₂ Cl ₁₄)	-276.85	-6.94	2.14

3.2. Electronic Properties

In order to examine the electronic structure of the molecules, we start our discussion with the study of the electronic structure for intrinsic pentacene molecule. The calculated density of states (DOS) has been shown in Figure. 2. The energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) i.e. HOMO-LUMO energy gap is obtained 1.13 eV (Figure. 2-(a)) which is consistent with other theoretical calculations [11, 22], however it is underestimated with respect to the experimental value of 2.07eV extracted from UV-vis characterization's results [14]. The difference between the amounts of theoretical DFT calculations of HOMO-LUMO gap and the experimental

results are due to the limitations of the exchange-correlation functionals.

The examination of partial density of states (PDOS) of pentacene reveals that the main contribution in density of states around Fermi energy is related to C-2p orbital while s orbitals have trivial contribution (see Figure. 2-(b)).

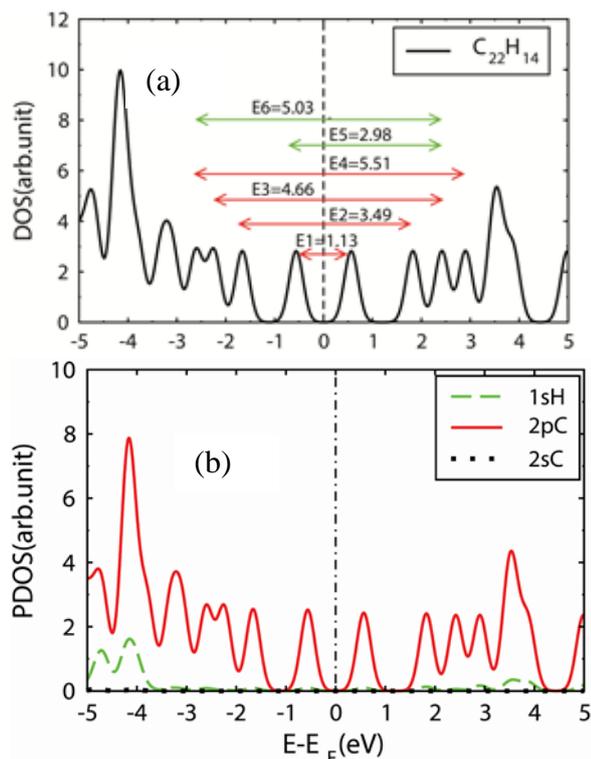


Figure 2. (a) Total and (b) Projected density of states of pentacene molecule.

Next, we replaced all hydrogen atoms with fluorine in pentacene which is known as perfluoropentacene (F-PENT). The calculated total and projected density of states of perfluoropentacene (F-PENT) are plotted in Figure. 3. The HOMO-LUMO gap of perfluoropentacene (F-PENT) is calculated to be about 0.99eV which is underestimated by the factor of $\frac{1}{2}$ with respect to the experimental UV-vis result of 1.95eV [14]. The difference between the calculated energy gaps of F-PENT and PENT is $\Delta E = 1.13 - 0.99 = 0.14$ eV in comparison to the corresponding experimental amount of $\Delta E_{UV-vis} = 2.07 - 1.95 = 0.12$ eV. The study of partial density of states of C and F atoms

shows that in the vicinity of Fermi energy, the main contribution in density of states is related to 2p-C and then 2p-F orbitals. The 2s orbitals of carbon and fluorine have minimal effect and can be neglected. (See Figure. 3 (b)).

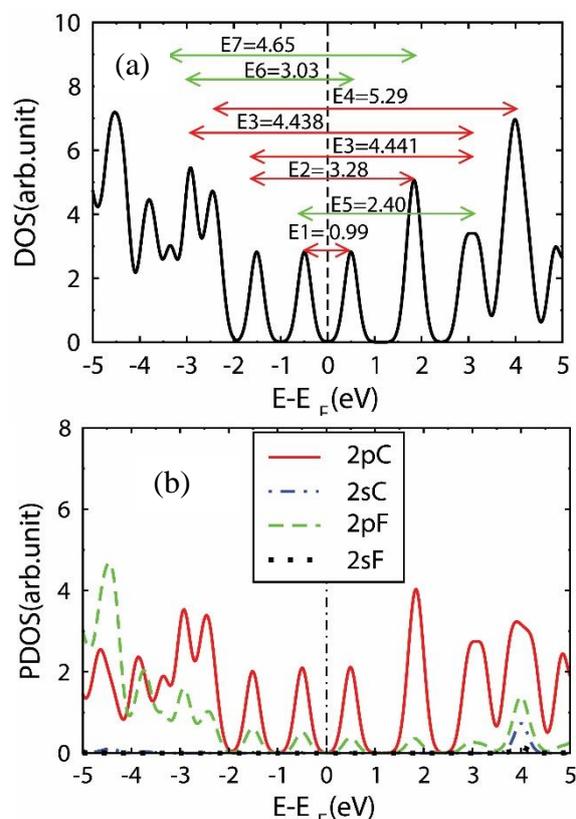


Figure 3. (a) Total DOS and (b) PDOS of perfluoropentacene molecule (F-PENT).

When all hydrogen in pentacene molecules is substituted by chlorine i.e. Cl-PENT the structural stability increased (see table. 1). The total and partial density of states (DOS) for chlorine substituted pentacene (Cl-PENT) has been shown in Figure. 4. The HOMO-LUMO energy gap decreases to the value of 0.67 eV which is smaller than both pentacene (PENT) and perfluoropentacene (F-PENT). Examination of partial density of states Figure. 4-(b) indicates that 2p-C has more contribution in HOMO and LUMO states than 3p-Cl whereas in lower energies 3p-Cl has more dominant role. In both cases as shown in Figure. 4-(b) the contributions of s orbitals can be ignored.

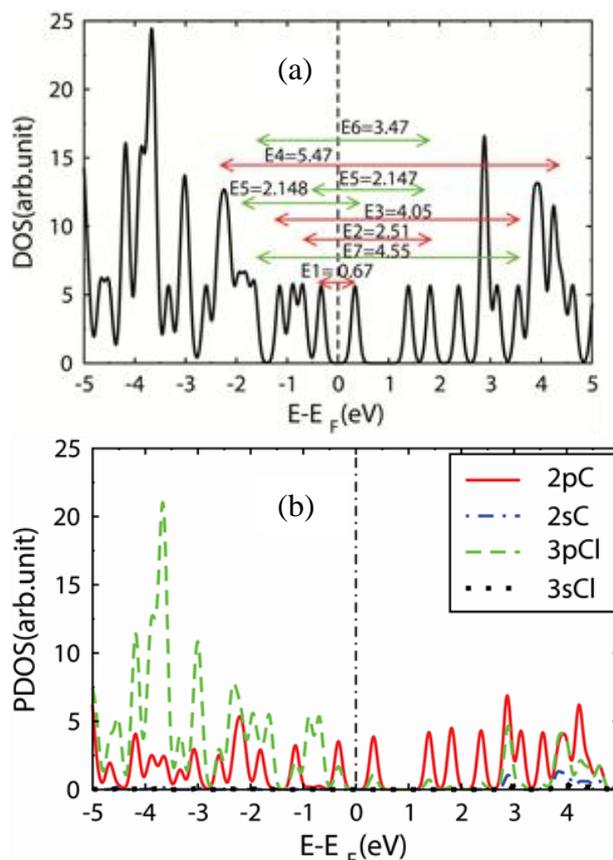


Figure 4. (a) Total DOS and (b) PDOS of chlorinated pentacene molecule (Cl-PENT).

3.3 Optical Properties

The dielectric function, the response of the material to the electromagnetic wave, is a complex function as follows:

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \quad (3)$$

where $\epsilon_1(\omega)$ is the real part and $\epsilon_2(\omega)$ is the imaginary part of the dielectric function. The imaginary part of the dielectric function is determined by the transitions rate between occupied and unoccupied molecular orbitals which will be calculated as follows:

$$Im[\epsilon_{ij}(\omega)] = \frac{4\pi e^2}{m^2 \omega^2} \sum_{U,O} \int dk \langle U | p^i | O \rangle \langle O | p^j | U \rangle \delta(\epsilon_U - \epsilon_O - \omega) \quad (4)$$

Where $|O\rangle$ and $|U\rangle$ are occupied molecular orbitals and unoccupied molecular orbitals, respectively.

After evaluation of imaginary part, the real part of dielectric function can be calculated from the imaginary part using Kramers–Kronig transformations [28, 34],

$$Re[\epsilon_{ij}(\omega)] = \delta_{ij} + \frac{2}{\pi} P \int_0^\infty \frac{\omega' Im[\epsilon_{ij}(\omega')]}{\omega'^2 - \omega^2} d\omega'$$

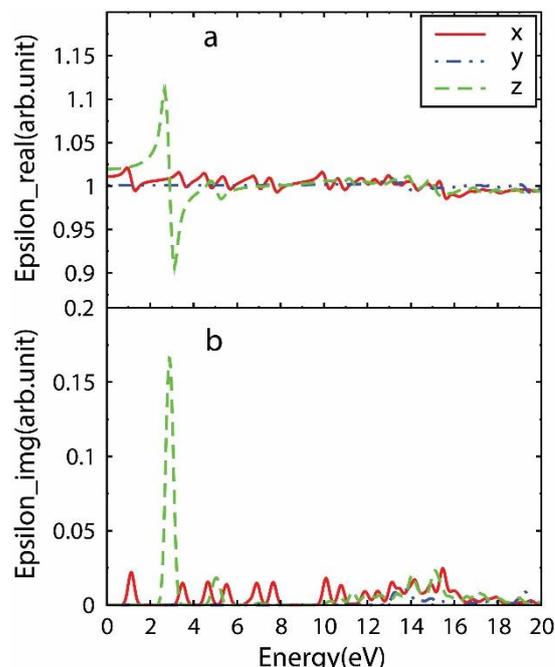


Figure 5. (a) The real and (b) imaginary parts of dielectric function of pentacene (PENT).

The real and imaginary parts of dielectric function for intrinsic (PENT), fluorinated (F-PENT) and chlorinated (Cl-PENT) pentacene molecules in different electric field polarizations have been shown in Figure. 5-7. obviously, optical anisotropy can be seen for all molecules due to its structural features. Fundamental resonance peaks located between 2-4 eV, are related to the polarization direction along the molecular axis ($E||z$). For $E||y$ which the electric field is perpendicular to the molecular plane, no main feature is specified. The main resonance peak for pentacene (PENT) is located about 3 eV whose location is in the same energy in both real and imaginary parts of dielectric function. For fluorinated (F-PENT) and chlorinated (Cl-PENT) pentacene this fundamental peak is split to two adjacent

peaks. The value of the real part of dielectric function at very low energies is called dielectric constant, which its maximum amount for pentacene molecule (PENT) is 1.019 for the incident electric field along z-axis. This amount increases to 1.028 for perfluoropentacene (F-PENT) and 1.040 for chlorinated pentacene (Cl-PENT). For other two directions x and y, the dielectric constants are summarized in Table 2. It is worth noting that the dielectric constant is a tensor of rank two and we expect nine components for it but since Cartesian coordinates correspond to the molecular axis, the non-diagonal elements are equal to zero [28].

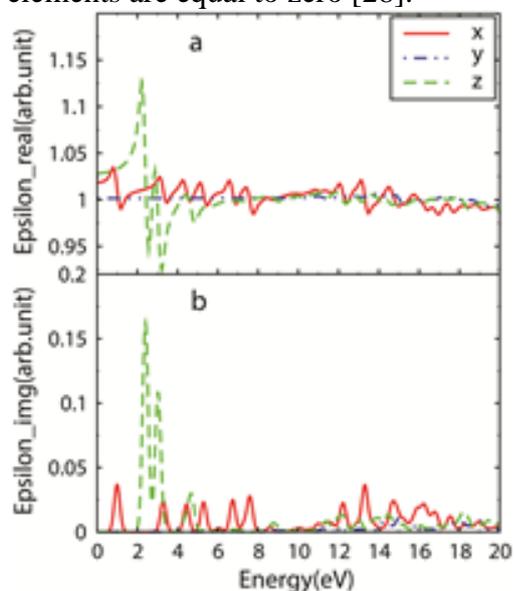


Figure 6. (a) The real and (b) imaginary parts of dielectric function of perfluoropentacene (F-PENT).

The absorption indices for the molecules for three different directions of incident electric field are depicted in Figure. 8. Prominent peaks of absorption index represent optical transmissions. For the sake of comparison, the allowed optical transitions between occupied valence levels to the unoccupied conduction levels corresponding to the first few optical absorption peaks, for PENT, F-PENT and Cl-PENT are shown in DOS diagrams in Figure. 2-(a), 3-(a) and 4-(a) respectively.

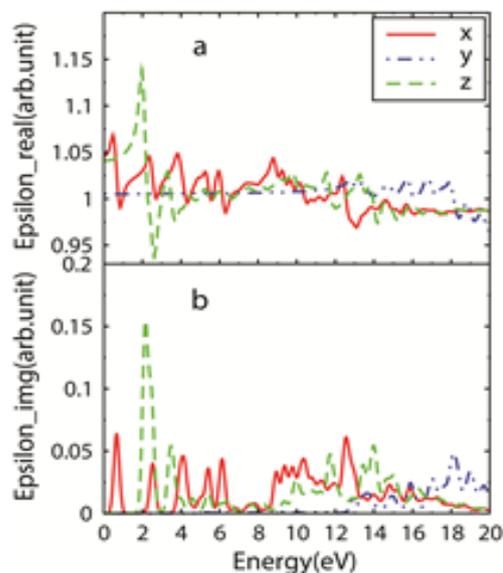


Figure 7. (a) The real and (b) imaginary parts of dielectric function of chlorinated pentacene (Cl-PENT).

Table 2. The values of the static dielectric constant for three x, y and z axis of electric field of pentacene (PENT), perfluoropentacene (F-PENT) and chlorinated pentacene (Cl-PENT).

Molecule Name	Static dielectric constant		
	ϵ_{xx}	ϵ_{yy}	ϵ_{zz}
PENT ($C_{22}H_{14}$)	1.019	1.000	1.011
F-PENT ($C_{22}F_{14}$)	1.028	1.001	1.018
Cl-PENT ($C_{22}Cl_{14}$)	1.040	1.005	1.046

In x-direction, the first absorption peak occurs in $E_1=1.13\text{eV}$ for pentacene (PENT) which is called optical gap. This amount for perfluoropentacene (F-PENT) and chlorinated pentacene (Cl-PENT) are 1.01 and 0.69 respectively, which are in agreement with our electronic calculations of HOMO-LUMO gap. So the absorption threshold is lower for halopentacene compared to pentacene. The main absorption peak in the range of visible light for pentacene (GNRs) is located at 2.98 eV which belongs to the electron transition from HOMO to LUMO+2. This is the optical gap of pentacene when E is along z direction.

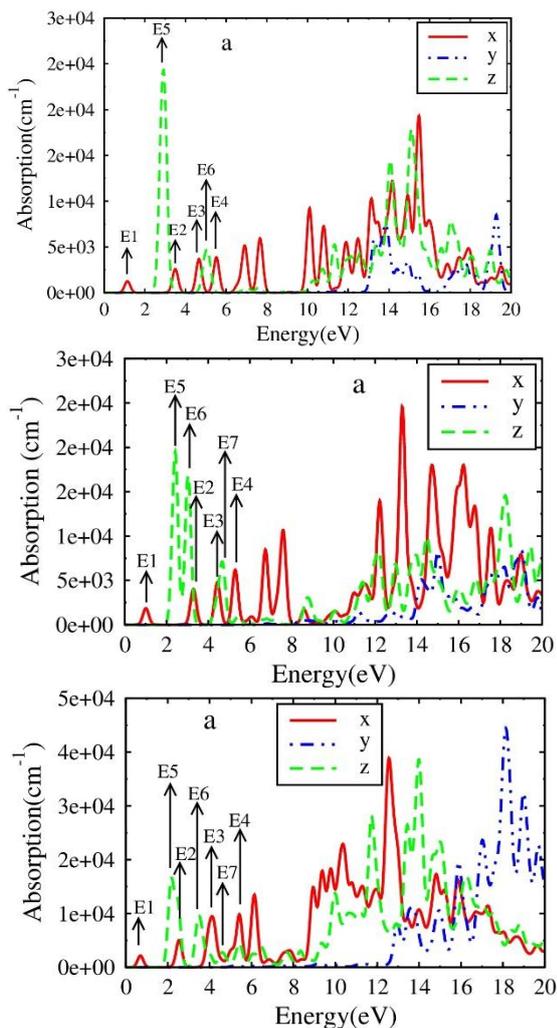


Figure 8. The absorption index of (a) pentacene (PENT) (b) perfluoropentacene (F-PENT) and (c) chlorinated pentacene (Cl-PENT). The arrows display the first few allowed optical transition.

From Figure. 8 the optical gap in z direction for perfluoropentacene (F-PENT) and chlorinated pentacene (Cl-PENT) are 2.4 and 2.15eV respectively. Also these peaks are related to the transition from HOMO to LUMO+2. When the electric field is perpendicular to the molecule plane no absorption can be seen until 13 eV. For higher energies 10-20 eV, a broad range of photon energy for all incident directions, will be absorbed.

The optical reflectivity indicates the fraction of the incident light which is reflected. The reflectivity of intrinsic

(PENT), fluorinated (F-PENT) and chlorinated pentacene (Cl-PENT) for the electric field parallel to the long axis of the molecule, in this case z axis, are depicted in Figure. 9.

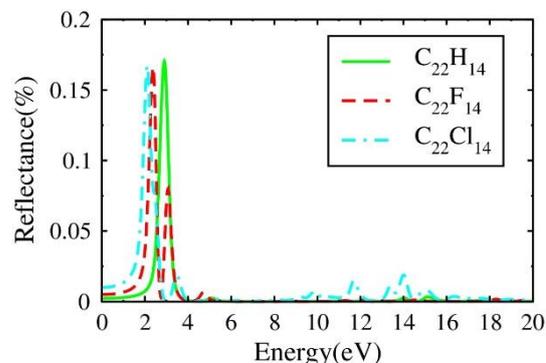


Figure 9. The reflectivity of pentacene (PENT), perfluoropentacene (F-PENT) and chlorinated pentacene (Cl-PENT).

Table 3. The values of the refractive index for three x,y and z directions of electric field for pentacene (PENT), perfluoropentacene (F-PENT) and chlorinated pentacene (Cl-PENT).

Molecule Name	Refractive index		
	X	y	z
PENT ($C_{22}H_{14}$)	1.005	1.000	1.009
F-PENT ($C_{22}F_{14}$)	1.009	1.000	1.014
Cl-PENT ($C_{22}Cl_{14}$)	1.020	1.002	1.022

Since other directions of the electric field does not propose any remarkable feature, we concentrate only on E||z direction. The unique feature for pentacene is located around 3 eV which is responsible for the violet color of the pentacene. Replacement of hydrogen in pentacene with fluorine and chlorine causes a red shift and creation of another peak in the vicinity of the first one. According to the dominant peak, we expect bluish color for fluorinated (F-PENT) pentacene and greenish color for chlorinated pentacene (Cl-PENT).

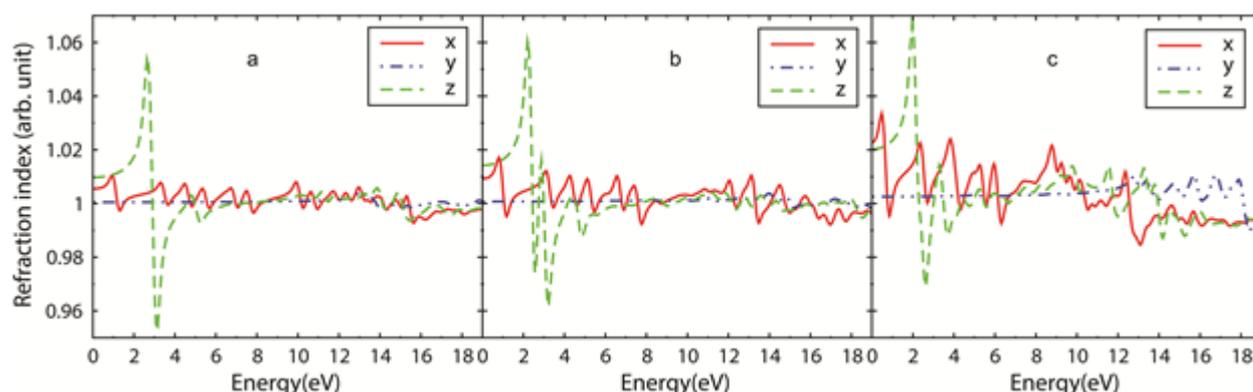


Figure 10. The refractive index of (a) pure pentacene (PENT) (b) perfluoropentacene (F-PENT) (c) chlorinated pentacene (Cl-PENT).

Figure. 9 reveals that for all molecules the value of reflectivity is less than 0.2% which is small amount.

This fact beside their low absorption, make these materials transparent. Finally to study another optical property of these materials, the refraction indices were calculated that have been shown in Figure. 10. The values of the refractive static index for x, y and z direction of the electric field, are listed in Table. 1. As represented in Figure.10, one can see that the refractive index for the z polarization axis has the highest value. The results show that for $E||x$ direction (perpendicular to plane of the molecules/ribbons), light passes through the molecule without deflection. The refractive static constants in the other two directions are almost the same for every molecule. Substitution chlorine and fluorine with hydrogen in pentacene molecule (PENT), increases the refractive static constant with respect to the pristine pentacene.

4. CONCLUSION

In this study, the electronic and optical properties of pentacene molecule (PENT) in the pure state and by full replacing hydrogen atoms with fluorine (F-PENT) and chlorine (Cl-PENT) were calculated using density functional theory. The results

of the electronic calculations show that fluorinated (F-PENT) and chlorinated pentacene (Cl-PENT), have smaller energy gap in comparison to the pristine pentacene (PENT). Also fluorine substitutions increase the stability of pentacene molecule where fluorinated pentacene has the maximum stability among the other two molecules. Optical calculation reveals that replacement of all hydrogens with fluorine and chlorine in pentacene molecule decreases the optical gap which is in agreement with the electronic gap trends. The violet color of pentacene changes to blue and green by introducing fluorine and chlorine respectively as reflectivity diagram expresses. We also demonstrate that the dielectric constant and refraction index increase such that chlorinated pentacene has the maximum values. Briefly, F-PENT and Cl-PENT are more stable with lower HOMO-LUMO gap, different color and greater dielectric constant and refractive index than PENT (pure pentacene), which is concluded that these GNRs can be used for developing molecular electronic and optical devices and also molecular gas sensors to recognize fluorine and chlorine.

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