Tuning of band gap due to fluorination of graphyne and graphdiyne

B Bhattacharya, N B Singh, and U Sarkar*
Department of Physics, Assam University, Silchar-788011, INDIA
E-mail: utpalchemiitkgp@yahoo.com (U. Sarkar).

Abstract. The electronic properties of graphyne and graphdiyne consisting of \( sp \) and \( sp^2 \) hybridized carbon atom have been investigated within the density functional theory (DFT) method. The corresponding changes in the electronic properties due to systematic functionalization by fluorine at different possible sites are reported. Our band structure calculations clearly infer that all fluorographyne are wide band gap semiconductor and the band gap can be tuned by fluorination and the possibility of modulating the band gap provides flexibility for its use in nanoelectronic devices. Projected density of state (PDOS) analysis provides the clear idea about the bonding nature of these novel materials in details and Crystal Orbital Hamilton Population (-COHP) analysis shed insight on the orbital participating in bonding and antibonding.

1. Introduction
Graphene [1] has received a great deal of attention due to its potential application in nanoelectronics. Its importance is attributed to its high mechanical strength, unique electronic properties like high electron mobility and having Dirac cone structure [2, 3]. Opening of band-gap is essential for the successful application of graphene in nano-electronics [4]. Experiments have verified that hydrogenation and fluorination of graphene leads to opening of the band gap [5, 6]. Unfortunately, the H and F atoms on graphene show tendency to aggregate with each other, which makes tuning the band gap extremely difficult [7]. Graphyne, a new layered carbon allotrope consisting of hexagonal rings joined together by acetylenic linkages is also been reported to have Dirac cones [8]. In comparison to graphene, the presence of acetylenic linkages in graphyne provides more flexibility for modulating the band gap. Graphdiyne, another allotrope of carbon, can be considered as an expanded form of graphyne having two acetylenic linkages. Considerable effort has been devoted to the experimental synthesis of graphyne [9] and graphdiyne [10].

In one of our previous studies [11], we have studied the pristine and BN-doped graphyne and other members of graphyne family and proposed a systematic way for widening their band gap. In this study, we investigate the possibility of widening and also tuning the band gap of graphyne and graphdiyne by fluorination based on first-principle calculations.
2. Computational details

We performed our first-principle calculations using the density functional theory (DFT) method [12] as implemented in the siesta package [13]. The GGA in Perdew-Burke-Ernzerhof (PBE) scheme are chosen to describe the exchange correlation part of density functional. The DZP basis set has been employed and the norm conserving Troullier-Martins pseudopotentials [14] are used to describe the interaction between cores and valence electron. Relaxation was done until the magnitudes of the forces acting on all atoms are less or equal to 0.040 eV/Å. Brillouin zone was sampled by 11×11×1 k-points with cut off 300 Rydberg. The vacuum space of 15 Å has been used along the z direction in order to avoid the interaction between two images. To study the stability of these systems, the cohesive energy is calculated as

\[
\text{Cohesive Energy} = \frac{E(\text{System}) - [nE(C) + mE(F)]}{n + m}
\]

where \(E(\text{System})\), \(E(C)\) and \(E(F)\) are energies of the whole system, carbon and fluorine atoms, and \(n\), \(m\) are the number of carbon and fluorine atoms present in the system respectively.

3. Results and discussions

The optimized geometries are presented in figure 1. The figure 1 (c-e) represents the graphyne with F atoms at linear chain, at ring and at both chain and ring respectively. The F atoms are arranged themselves in alternative carbon atom in such a manner that the structure attains chair like conformation.

![Figure 1. Optimize geometries with unit cell of: (a) graphyne; (b) graphdiyne; (c) graphyne with F at chain; (d) graphyne with F at ring; (e) graphyne with F at both chain and ring.](image)

Lattice length of all the considered systems are presented in table S1. It is observed that cell length increases when F atoms are introduced at different site and attains its maximum value when F atoms are introduced in the hexagonal ring site. The possible reason for the observed behaviour is the formation of different types of bonds at different sites.

3.1 Band structure

The calculated band-structure of pristine graphyne with other fluoro-graphynes is plotted in the figure 2 and the band-structure of graphdiyne with other fluoro-graphdiyne is given in supplementary material figure S1. The band gaps of the graphyne and graphdiyne along with their fluorine derivatives are tabulated in table S2 and figure S2 (a) [see in supplementary material].

From the table S2, it is clear that all the fluoro-graphynes are wide band gap semiconductor whose band gaps are found to be in the range of 1.647 to 3.750 eV and band gap depend on the functionalization site. We observed that the valence-band maximum (VBM) and conduction-band minimum (CBM) of graphyne (presented in figure 2a) are located at the same (M) point in the hexagonal Brillouin zone for graphyne and at gamma point for graphdiyne, which is a common feature of direct band gap semiconductor and consistent with our previous result [11]. Next, we calculate the band-structure by introducing fluorine atoms at the linear chain positions, at the hexagonal positions and at linear chain as well as in hexagonal positions and are presented in figure 2b, 2c and 2d respectively. The band-structure of graphyne with F atoms at linear chain site (figure 2b) indicates that both VBM and CBM remain at the M point and the band gap is 1.647 eV, which is much greater than that of graphyne. The presence of F atoms at the hexagons of...
graphyne increased the band gap to 3.750 eV, and the VBM and CBM are now shifted at K point, as shown in figure 2c. However the band-structure for graphyne with F atoms at chain as well as ring given in figure 2d, reveals that VBM (K-point) and CBM (Γ point) are now located at different points of the Brillouin zone with a wide band gap of 3.318 eV, that clearly shows its indirect band gap nature.

Figure 2. Bandstructure of structures: (a)graphyne, (b) graphyne with fluorine at chain (c) graphyne with fluorine at ring (d) graphyne with fluorine at both chain and ring.

We see that graphdiyne has a higher band gap compare to graphyne. Again, when we introduce F atoms at chain or ring site of graphdiyne, the system remains direct band gap semiconductor with VBM and CBM located at Γ point of the Brillouin zone. But whole fluorination of graphdiyne makes the structure an indirect band gap semiconductor.

3.2 Cohesive energy
The more negative cohesive energy signifies the greater stability of the system; it is clear from figure S2b that the pristine systems are more stable than other fluorine functionalized system. For graphyne, the stability on placing F atoms are in the order of pristine > F at chain > F at ring > F at chain and ring; while in graphdiyne, its order becomes pristine > F at ring > F at chain > F at chain and ring. It is also clear that for both the systems, the stability becomes less due to whole fluorination.

3.3 Density of states
The Density of states for pristine graphyne and graphidyne are presented in supplementary material S3. We have found that the first state near the Fermi level is mainly contributed by \( p_z \) orbitals of carbon atom which is consistent with our previous study [11].

Figure 3. Total and partial DOS of structures: (a)graphyne; (b) graphyne with fluorine at chain; (c) graphyne with fluorine at ring; (d) graphyne with fluorine at both chain and ring.

In figures 3a, 3b and 3c, we plotted the total and partial density of states when graphyne is functionalized by F atoms at the linear chain site, at the hexagonal position and throughout the system respectively. The contribution of carbon and F atom is presented in figures 3a (ii) and 3a (iii). From figure 3a (ii), it is clear that for carbon atom all the \( p \) orbitals is contributing in the valance band as well as in the conduction band. In case of fluorine atom, all the \( p \) orbitals are basically contributing (figure 3a (iii)) in the valence band only. For carbon atom, the \( p_z \) orbital first start to contribute to the energy levels in the conduction band compare to other orbital whereas all the \( p \) orbitals starts to contributing in the valence band near the Fermi level.

Figures 3b (i), 3b (ii), and 3b (iii) show the total DOS and the contribution of individual atoms to the density of states when F atoms are placed in the hexagonal positions of graphyne. We observed that the carbon atom contributes in the conduction band as well as in the valence band, but the fluorine atom only contributes in the valence band. It is clear from figure 3b (ii) that all the \( p \)
orbitals of C atoms (figure 3b (ii)) contribute both in the valance and conduction bands. We see that the energy level near the Fermi energy is mainly contributed by $p_z$ orbital of carbon atom in the conduction band while in the valence band the $p_x$ and $p_y$ orbital contribute first near the Fermi level. This feature was not seen when F atoms are situated at linear chain site of graphyne, in which all three $p$ orbitals of C atoms contribute near the Fermi level in the valence band. The F atoms contribution is mainly coming from $p_x$ and $p_y$ orbitals in the valence band as can be seen from figure 3b (iii).

For graphyne with F at chain and ring (3c (i), 3c (ii) and 3c (iii)), the energy levels near the Fermi level of valence band and conduction band come from the $p_x$ and $p_y$ orbital of the carbon atoms which is not seen in case of graphyne with F atom at chain and graphyne with F atom at ring. In this case due to whole fluorination the energy states contributed by $p_z$ orbital of carbon atoms are shifted towards high energy both in valence and conduction bands. Major contribution in the valence region comes from F atoms, but for conduction region, major contribution comes from C atoms. The same situation in the PDOS curve is observed for graphdiyne with F at chain, graphdiyne with F at ring and graphdiyne with F at chain and ring [see in supplementary material S3].

3.4 -COHP analysis

The -COHP analysis for pristine graphyne, graphdiyne, are demonstrated in figures S4a, and S4b respectively [in supplementary material]. It is clearly visible that, in pristine case only C-C interaction exists and it contributes bonding state near the Fermi level.

![Figure 4. -COHP analysis of: (a) C-C interaction in graphyne with F at chain; (b) C-F interaction in graphyne with F at chain.](image)

Then we report -COHP analysis by putting F atoms at chain (figure 4) and observed two considerable interaction, carbon-carbon (C-C) and carbon-fluorine (C-F). In C-C interaction (figure 4 (a)) of graphyne, contributed the bonding states near the Fermi level and all the bonding states are mainly contributed by $p-p$ orbital pair. In the valence and conduction region near the Fermi level all the three $p$ orbitals contribute. The C-F interaction (figure 4 (b)) mainly contributes antibonding state near the Fermi level the contribution arises mainly from $p-p$ orbital pair.

![Figure 5. -COHP analysis of: (a) C-C interaction in graphyne with F at chain and ring; (b) C-F interaction in graphyne with F at chain and ring.](image)

The -COHP analysis of graphyne family with F at ring (see in supplementary material S5) has a remarkable feature that, the presence of F at ring shifts the bonding and antibonding states away from the Fermi level (in both conduction band and valence band) than graphyne with F at chain site and thus increase the band gap. The C-C interaction contribute bonding state near the Fermi level both
in valence and conduction region while C-F bond contribute antibonding state arises from \(p-p\), and \(s-p\) orbital pair of carbon and fluorine atom.

Next we consider the –COHP analysis of graphyne with F atom at both chain and ring. In C-C interaction (figure 5 (a)) the bonding states near the Fermi level in the valence band mainly contributed by \(p_x-p_x\) and \(p_y-p_y\) pair of carbon atom and in CB all the three \(p\) orbitals contributes equally. The C-F interaction (figure 5 (b)) contributed antibonding state mainly dominated by \(p-p\) orbital pair of neighbouring carbon and fluorine atom. From the above analysis, it is clear that the functionalization by fluorine activate the participation of \(p_x-p_x\), \(p_y-p_y\), \(s-p\) and \(s-s\) orbital pair of neighbouring carbon atom near the Fermi level.

4. Conclusion
In summary, we have carried out density functional theory calculation of pristine and fluorinated graphyne and graphdiyne to investigate its electronic properties. It has been found that fluorination widens the band gap of graphyne and graphdiyne depending on its functionalization site showing the trend pristine < system with F at chain < systems with F at chain and ring < system with F at ring. The fluorination either at chain or at ring site remains these systems as direct band gap semiconductor, but due to full fluorination, these systems become an indirect semiconductor. Again the fluorination decrease the stability of these system and the whole fluorinated system shows less stability compare to other fluorinated system (system with F at chain or system with F at ring). The fluorine atom mainly contributed in the valence band and the fluorination at different sites of these fundamental structures activates the \(p_x\), \(p_y\), and \(s\) orbitals near the Fermi level. Our results show that, the C-C interaction of neighboring carbon basically contributes bonding state while the C-F interaction always contributes antibonding state near the Fermi level.

Acknowledgement
Dr U Sarkar would like to thank SHARCNET Canada for providing computational facilities for this research work and International Centre for Theoretical Physics (ICTP), Trieste, Italy for hosting him as a regular associate.

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