

ELECTRONIC STRUCTURES OF DIRECT-STACKED BIPHENYLENE NETWORK: A DFT STUDY

¹Art Anthony Z. Munio, ²Alvanh Alem G. Pido, ³Kenneth Ian M. Balili

College of Arts and Sciences, Jose Rizal Memorial State University – Tampilisan Campus
7116 Tampilisan, Philippines¹, Department of Physics, Mindanao State University – Main Campus, 9700
Marawi City, Philippines², Department of Physics, Mindanao State University – Iligan Institute of Technology,
9200 Iligan City, Philippines³

artanthonymunio@jrmsu.edu.ph¹, alvanhalem.pido@msumain.edu.ph²,
kennethian.balili@g.msuiit.edu.ph³

ABSTRACT

We provide a theoretical report on the electronic structures of direct-stacked Biphenylene networks using density functional theory. The calculations reveal that direct-stacking of Biphenylene networks leads to splitting and shifting of the electronic bands, which leads to the slight deviation of the electronic density of states of the direct-stacked Biphenylene network compared to the monolayer Biphenylene network. However, in general, the band structure and density states of the direct-stacked systems resemble that of the monolayer Biphenylene network. The calculations on the charge density difference show a very small charge redistribution in the direct-stacked systems. These findings provide preliminary understanding of the properties of Biphenylene network in its stacked form.

Keywords: Electronic structures, biphenylene, density functional theory, electronic bands, density of states charge density difference

INTRODUCTION

Nanomaterials in general are promising for a wide range of technological applications [1,2, 5]. Owing to their nanoscale size, these materials have unique properties due to the quantum mechanical effects and how their atoms bonded with one another [15, 18]. Carbon-based nanomaterials such as graphene and carbon nanotubes (CNTs) are widely studied due to their superior properties compared to traditional materials [3, 14, 18]. Although, the properties of nanomaterials highly depend on their chemical surroundings [4, 14]. For instance, graphene and few-layered graphene shows a distinct electronic structure and the photoluminescence property of the CNTs cannot be demonstrated in the bulk form [13, 19]. Thus, it is important to examine the property of isolated nanomaterial and its bulk form to evaluate the desirable properties for a certain application. One of the most reliable methods to investigate the properties of solids is via first-principles calculation as we have demonstrated from our previous report and other first-principles studies [13, 16, 17, 20-23].

A newly synthesized carbon-based nanomaterial (Biphenylene network) consisting of eight-, six-, and four- carbon rings, was successfully synthesized via on-surface inter-polymer hydrogen fluoride (HF)-zipping reaction [6]. This is similar to graphene and carbon nanotubes which are composed of carbon atoms bonded in sp^2 hybridization and stable in high temperatures [3, 18]. This material has attracted attention due to its impressive properties which are promising for conductive composites, energy storage, and an efficient catalyst for oxygen reduction reaction [12]. However, we anticipate that this material may have a problem in the dispersion due to the strong van der Waals interactions between networks as we have demonstrated in our recent report [17]. Stacked 2D nanomaterials show interesting properties owing to the quantum mechanical effects [15]. For example, stacked graphene shows different electronic structures compared to monolayer graphene [18, 19]. Therefore, it is important to examine the electronic structures of the newly synthesized Biphenylene

network. Here, we provide a short theoretical study on the electronic structures of direct-stacked Biphenylene networks using density functional theory (DFT).

COMPUTATIONAL DETAILS

All calculations are conducted using DFT-PBE level theory with Grimme-D3 dispersion corrections using plane-wave basis set and ultrasoft pseudopotential [7-11]. The monolayer, bilayer, and trilayer direct-stacked Biphenylene networks are optimized using the following convergence criteria: 0.0001 Ry/Bohr and 0.05 Pa for the force and stress threshold, respectively. The cutoff-energy and cutoff-charge density are set to 50 Ry and 250 Ry, respectively. The k-points sampling is set to $11 \times 11 \times 1$ using Monkhorst-pack grids. Figure 1 shows the optimized structures [17] used in this work.

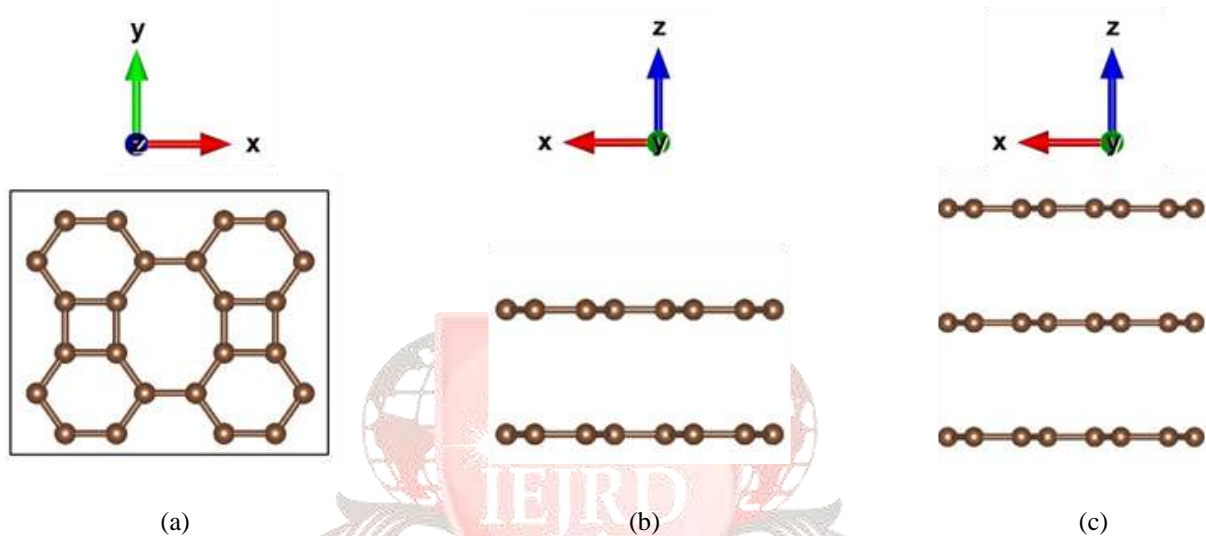


Figure 1. (a) 2×2 supercell of Biphenylene network and side views of (b) bilayer and (c) trilayer direct-stacked Biphenylene network. From [17]

In the electronic structure calculations, the eigenstates are calculated using the following k-path: Γ -X-M-Y- Γ -M, with 30 k-points considered between high symmetry points. The electronic density of states of the monolayer, bilayer, and trilayer direct-stacked Biphenylene networks are calculated using the tetrahedra method. To further evaluate the redistribution of the electronic charge density, we calculated the charge density difference (CDD) of the stacked systems.

RESULTS AND DISCUSSION

The electronic band structures of the monolayer, bilayer and trilayer Biphenylene networks are displayed in Figure 2. In Figure 2a, the band structure of the monolayer Biphenylene network shows a tilted Dirac cone located just above the Fermi energy at ~ 0.23 eV near the Γ high symmetry point. This is consistent with the recent first-principles report [16]. In Figure 2b, the Dirac cone of the bilayer Biphenylene is shifted to the higher energy level. This shifting of electronic bands may be due to the suppression of the p_z orbitals due to the van der Waals interaction between the layers. Similar trends are observed in the trilayer network as shown in Figure 2c. The electronic bands of the direct-stacked Biphenylene networks are split. This is attributed to the direct-stacking of the layers of the Biphenylene network in which van der Waals interactions caused a shifting in the energy levels of the stacked systems.

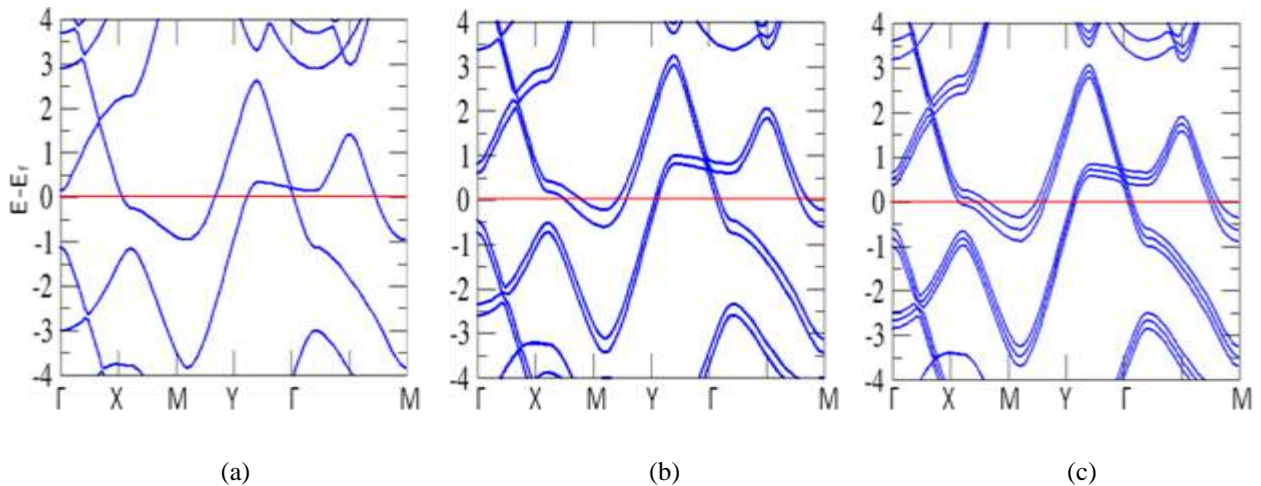


Figure 2. Electronic band structure of (a) monolayer (b) bilayer and (c) trilayer Biphennylene network.

Figure 3 shows the density of states (DOS) of the network. The shifting of the electronic DOS is also observed where the bilayer Biphennylene network has much-displaced energy levels relative to the trilayer. In all cases, the stacked Biphennylene networks remain metallic as depicted by the nonzero DOS at the Fermi energy, and the main feature of the band structure and density of states of the monolayer is reproduced.

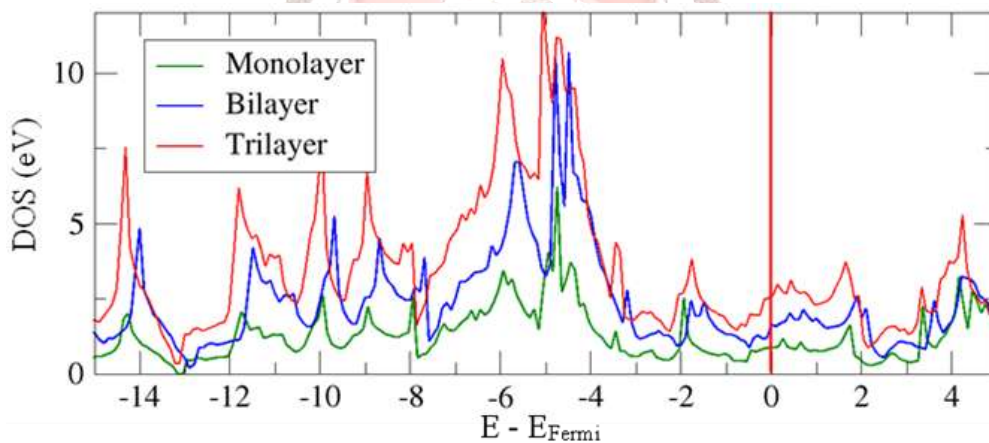
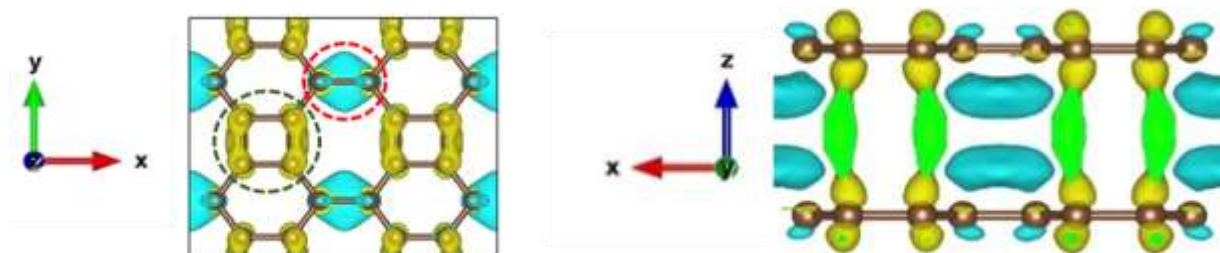


Figure 3. Density of states of monolayer, bilayer, and trilayer Biphennylene network.

The charge redistributions of the bilayer and trilayer are displayed in Figure 4. In both direct-stacked systems, the accumulation of electronic charge is between the four carbon rings highlighted by the green dashed line and the depletion region is mainly on the red dashed line. Despite the small charge redistribution, this still leads to the shifts and splitting of the electronic bands as shown in Figure 2.



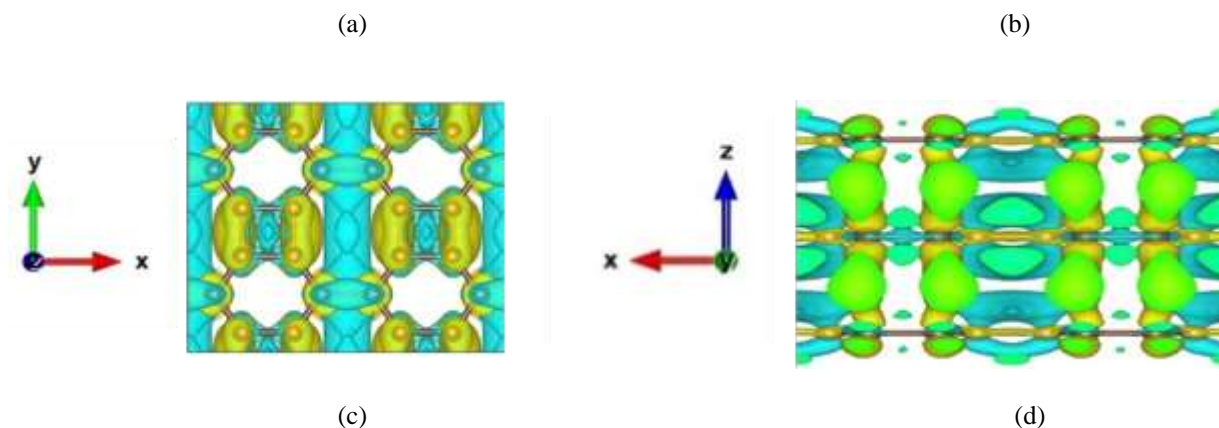


Figure 4. CDD isosurface of (a,b) bilayer and (c,d) trilayer direct-stacked Biphenylene network. The yellow and cyan isosurfaces denote the accumulation and depletion region of the electronic charge.

CONCLUSION

A short DFT calculation was conducted to examine the electronic structures and electronic charge density difference of the direct-stacked Biphenylene network. According to the electronic structure calculations, splitting and shifting of electronic bands are observed in the direct-stacked bilayer and trilayer systems. Nevertheless, the electronic structures of the direct-stacked system resemble that of the monolayer. In all cases, the Biphenylene networks remain metallic.

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