Poly(9-Vinylcarbazole)/Graphene Nanoheterostructure Interfaces: *Ab Initio* Dynamics Studies for Photovoltaic and Optoelectronic Applications

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**Abstract**: Polymer photovoltaics have great technological potential as an alternative source of electrical energy. The demand for inexpensive, renewable energy sources drives new approaches to produce low-cost polymer solar cells. In the last decade, the development of these solar cells has progressed rapidly. One of the limiting parameters of these polymer photovoltaics is the mismatch between their absorption spectrum and the terrestrial solar spectrum.

Using low-band-gap polymers is a viable method to expand the absorption spectrum of solar cells and increase their efficiency. We report first-principles calculations on the binding of Poly(9-vinylcarbazole), PVK, to graphene. Considering the different relative orientations of the subsystems, our calculations predict reasonable binding energies, demonstrating interactions between the polymer and graphene. The band gap value we have calculated in this work is low enough to make the nanoheterostructure exceedingly promising for photovoltaic applications.

**Keywords**: DFT; GGA-PBE; LDA-PZ; optoelectronics; PVK; nanoheterostructure; interfaces; organic photovoltaic.

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### 1. Introduction

Controlling the properties of crystalline graphene makes it one of the fascinating research topics in modern times. It has special electronic, mechanical, and thermal properties [1-7]. Its charge carriers behave like massless Dirac particles. Electronic band gap tuning of graphene has uses in nanoelectronics, opto- and acousto-electronics devices [1,8]. More recently, this subject has been studied in two-dimensional and nanoheterostructures [9]. Much work is also being done on graphene because of its novel properties. In references [10-15], band gap opening in graphene is a possibility using several ways; prominent among them are
hydrogenation, [10] interactions with substrates, [11,12] molecular adsorptions, [13] one other method would be deposited on a latticed-matched substrate. An example is SiO$_2$ or hexagonal boron nitride (h-BN) in Refs. [14,15]. Band gap engineering by doping was carried out in Refs. [16-18] successfully recently. Ref. [16,17] showed that by doping graphene nanoribbons by either N or B, n-type or p-type semiconducting graphene can be realized.

Graphene functionalization is a prominent source for novel technological applications, especially when we consider polymer nanocomposites [19,20]. Chemical modification of carbon nanomaterials with functional monomers, polymers, and the process of physical wrapping over this category of materials have become requisite practices for manufacturing nano-hybrid materials that have both predetermined tailored properties and high-tech functionalities [21-24].

Polymers are well known to interact with carbon nanomaterials like graphene by means of any of the following principles, viz. strong covalent [25] or electrostatic interactions, [26] π-stacking, [27, 28] hydrogen bonding, [29] or weak van der Waals intermolecular interactions [30, 31]. Functionalization using conjugated polymers by non-covalent means is mostly preferred because in attaching chemical groups, the carbon nanomaterials' bonding network is not interrupted [32, 33]. On the other hand, covalent functionalization is always accompanied by unwanted signals. These always adversely affect the already well-defined existing properties of the materials [34]. In references [35-37], it has been vividly demonstrated that peculiar desired novel mechanical, electrical, vibrational, and optical properties have been obtained when conjugated polymers are allowed to interact with carbon nanomaterials.

The purpose of functionalization is to optimize the bond strength in order to acquire a strong interfacial bonding in the composite. In recent times, both theoretical and experimental works attempted to resolve this contention by resorting to myriad quantum mechanical computational methods such as density functional theory (DFT) as well as molecular dynamics simulations [35,36,38-43]. Reference [39] shows that it is within the realms and confines of computational power to improve the polymer-carbon nanomaterial alignment by aptly tailoring the temperature, polymer density, and chain length using molecular dynamics simulations. The orientation of polymers on carbon nanostructures, in general, also depends on the flexibility of the polymer backbone [44]. In recent works [21-24], the electronic properties of functionalized nanocomposites are quite different from insulating bulks. DFT predicts [21-24], that the functionalized solids can be semiconducting.

Organic photovoltaic technologies have recently experienced remarkable development, achieving excellent power conversion efficiency in a single-junction cell [45]. This progress was largely enabled by creating new organic semiconductors comprising a meticulously designed π-conjugated backbone, as typified by recent non-fullerene n-type or acceptor semiconductors bearing a highly ring-fused core unit flanked by strongly electron-withdrawing end groups [46]. In general, active layers of organic photovoltaic devices are composed of p-type or donor and n-type semiconductors to form the p-n interface, i.e., the heterojunction. The photovoltaic process in organic photovoltaic devices starts with light absorption by either the p- or n-type material to form excitons, which then diffuse into the p-n interface and form a charge transfer state. The charge transfer state is generated by the electron or hole transfer process between the p- and n-type materials. In an ideal sequence, these charge transfer states dissociate into free electrons and holes to be transported toward and extracted at the respective electrodes. Thus, strong light absorption over a wide range of wavelengths and efficient generation of charge transfer states at the p-n interface, which can be achieved by tuning the
molecular orbital energy level, are the main concerns in designing semiconductors for organic photovoltaic devices. This molecular orbital tuning is mainly linked to the structure of π-backbones.

The bandgap of the semiconductor absorber defines a range where the material is efficient at converting the incident photons into charge carriers in the design process of photovoltaics. The Sun's emission spectrum is paramount in determining the range of semiconductor bandgap energies if a good conversion efficiency is expected. In homojunction devices, a 1.1 eV to 1.7 eV gap value is realized. A direct semiconductor with a high bandgap value is the preferred choice for photovoltaic energy conversion [47]. In order to increase microprocessors' computing power directly to increase photovoltaic conversion efficiency, there was the need to eliminate wafers' bulk defects [48]. A result of exposing silver and platinum electrodes to the sunlight [49] was when the photovoltaic effect was first observed. Photovoltaic technology has seen improvements since that time through many innovative techniques. Several generations of novel solar cells sprung into life with various categorizations [50,51]. This generational categorization comes as a result of production methods [52].

Moreover, discovering other phenomena from areas like electronics, photonics, and quantum mechanics enhances the capabilities of photovoltaic cells. We now have flexible solar cells and painted cells [53]. Above all, photovoltaic systems are seen as photovoltaic cells, to mention a few cables connecting these components [54]. Nowadays, photovoltaic technology has overcome all the desired expectations. As it stands, photovoltaic panels are manufactured for utilization everywhere. Their production processes are superior to that of fossil fuel sources. We can measure the ecological footprint by looking at the ratio of CO₂ produced in the process [55].

Similarly, recycling is very high on the agenda when considering building photovoltaic industries. Non-renewable sources still dominate energy production by far at the moment. The hope is that new energy sources will soon overtake fossil fuels for a better future. Because photovoltaic technology is cheap, it is the surest potential and is also handy to come by [56]. The increasing demand of our societies caused by the ever-growing of our population requires an enormous effort to shift from conventional energy production methods and turn to renewable energies [57]. In methods that are well-known for conventional energy production, the maximum capacity is known to be constant for life; however, for photovoltaics, the scenario is different because performance depends on cell age. Hence, taking into account the capacity of the installation lifetime is essential [58, 59]. One needs to take into account many factors to plant a photovoltaic system. For success, optimization tools are essentially an important approach to adopt [60]. We have experienced rapid development of organic photovoltaic devices in the past few years. The significant improvement in power conversion efficiency is because of the discovery of new π-conjugated frameworks and careful substituent engineering to achieve optimal morphology in bulk-heterojunction active layers [61]. It was observed that the important aspects of the light-to-electricity conversion in organic photovoltaic devices, such as light absorption, exciton diffusion, and charge-carrier transport, are influenced by the morphological characteristics of active layers [62]. The importance of active-layer morphology on the performance of organic photovoltaic devices has made interfacing engineering a prudent aspect of organic photovoltaic semiconductor design. Prominent non-covalent functionalization engineering focusing on flexible interfacing that regulates morphology and enhances the molecular electronic structure of organic semiconductors is indispensable. But what is lacking in these composites is the understanding of the relationship between the
electronic properties and the adsorption phenomenon at the interfaces. In this paper, we report the non-covalent functionalization of a graphene sheet by a conducting polymer, poly(9-vinylcarbazole), PVK, to produce an electroactive heterojunction nanocomposite with good electrochemical properties.

2. Materials and Methods

All the calculations are performed using (DFT) using the QUANTUM ESPRESSO code version 6.5.4 [63,64]. We used a supercell approach for infinite and continuity for PVK and graphene nanoheterojunction. The supercell is aligned along the x-axis. A 15 Å thick vacuum layer was allowed in y- and z-directions to avoid periodic image interactions of the supercell. The supercell has a lattice parameter of 6.902 Å. We have performed calculations using both the LDA in the Perdew-Zunger parametrization [65] and the GGA in the "Perdew-Burke-Ernzerhof parametrization [66]. We used the ultrasoft pseudopotentials [67] in describing the electrons-ions interactions. The plane wave basis sets method was utilized to describe the exchange-correlation effects through the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [68]. The van der Waals (vdW) interaction was included through Grimme's D3 correction term [69]. For treatment of carbon nanosystems Refs. [70-72] shows that this interaction is important to apply. In our work, the plane-wave kinetic energy cutoff was 30 Ryd, and the charge density cutoff was 180 Ryd. 0.002 Ryd was the energy convergence value. We fully relaxed all the configurations to forces on each atom less than 0.001 Ryd/Bohr. A Γ-centered 5x5x1 Monkhorst-Pack scheme [73] k-point grid was the method of sampling the Brillouin zone to obtain optimized geometry of the supercell. Fine 9x9x1 grids were computational tools used to realize non-self-consistent field calculations. From this, quantized energy levels were determined. We also determined Fermi energy for band structure calculations along the Γ-B-Z-Y-Γ direction. DOS and PDOS were then calculated. With the aid of the VESTA software [74], we generated all the optimized figures for each configuration. The modeled supercells were viewed with the help of Xcrysden software, version 1.5.60 [75].

3. Results and Discussion

3.1. Structure of PVK monomer.

A PVK monomer, N-vinylcarbazole structure is shown in Figure 1 above. Poly(9-vinylcarbazole) (PVK) is a conjugated polymer with hydrophobic properties. PVK films are mainly used as holes. PVK is a temperature-resistant [76] thermoplastic polymer produced by radical polymerization from the monomer, N-vinylcarbazole. It is photoconductive and, thus, the basis for photorefractive polymers and organic light-emitting diodes [77]. Conjugated polymers such as Poly(9-vinylcarbazole) in recent times have become the sources of efficient hole transport materials for the construction of p-i-n type, inverted planar heterojunction perovskite solar cells. Consequently, Poly(N-vinylcarbazole), a hole transport organic semiconducting polymer, found its use in applications of electronic and optical material devices [78]. The well-known titanium oxide (TiO₂) quantum dots fillers that find potential applications in polymeric solar cells as donor-acceptor layers [79] are mainly synthesized from PVK. The functionalization of carbon nanotubes (CNTs) to form conductive reinforcements on epoxy groups are realized through PVK applications [80]. PVK is employed in Iridium composites surface modifications to fabricate highly efficient organic light-emitting devices. The electrical
conductivity of PVK changes according to the intensity of illumination. As a consequence, PVK is sometimes classified as a semiconductor or photoconductor, the extreme brittleness of Poly(9-vinylcarbazole) can be reduced by copolymerization with a small amount of isoprene [81].

![Figure 1. PVK monomer unit cell, N-vinylcarbazole, structure used in this work.](image1)

3.2. Nanoheterostructure Structural Properties.

Various nanoheterostructure configurations studied in the current manuscript are shown in Figure 2. Figure 2(a) shows that the dimer backbone is aligned parallel to the graphene sheet. The dimer backbone is aligned perpendicular to the sheet, as shown in Figure 2(b). In the third configuration, the dimer chains point away from the graphene sheet, Figure 2(c). In Figure 2(d), the dimer chains point toward the graphene sheet.

![Figure 2. Configurations studied for the PVK dimer-graphene system. Stacking types in various forms of poly(9-vinylcarbazole)/graphene (PVK/GR) nanoheterostructure composite models studied in this paper. (a) the dimer backbone is aligned parallel to the graphene sheet, (b) the dimer backbone is aligned perpendicular to the graphene sheet, (c) the dimer chains point away from the graphene sheet and in (d) the dimer chains point towards the graphene sheet. A minimum separation distance, $d_{min} \approx 3.323$ Å was kept between the dimer and graphene sheet throughout in all the configurations. The polymer is represented by a monomer, as shown in Figure 1, which is justified by the fact that the electronic gaps of the monomer and the dimer are found in this study to deviate by only 0.11 eV.](image2)
The structural stability of the poly(9-vinylcarbazole)/graphene nanoheterostructures was evaluated by calculations. Using equation (1) [82], we computed the adsorption energies. With the help of equation (2) [82], the formation energy per atom was computed for the various configurations. These calculations enabled us to determine the most energetically favorable stacking structure.

In this work, the adsorption distance was found to be $d_{\text{min}} \approx 3.323$ Å. We therefore calculated the adsorption energies, $E_{\text{ad}}$, in relation to this measured value for poly(9-vinylcarbazole)/graphene nanoheterostructures at the LDA and GGA+vdW levels, as shown and recorded accordingly in Table 1.

$$E_{\text{ad}} = -(E_{\text{PVK/GR}} - E_{\text{PVK}} - E_{\text{GR}})$$

where $E_{\text{PVK/GR}}$, $E_{\text{PVK}}$, $E_{\text{GR}}$ represent the total ground-state energy of the poly(9-vinylcarbazole)/graphene composite, the total energy of PVK, the total energy of GR, respectively. These values are according to DFT predictions. From theory, when $E_{\text{ad}} > 0$, this means that the surface adsorption is thermodynamically feasible. Increasing values of $E_{\text{ad}}$ is indicative of the fact that the adsorbate molecule can strongly bind onto the surface of PVK/GR nanoheterostructure. Table 1 shows the patterns of preferences of PVK/GR(a), PVK/GR(b), PVK/GR(c), and PVK/GR(d) nanoheterostructure configurations to adsorb favorably on PVK/GR surface.

Among the four nanoheterojunctions studied, it is seen that interactions of PVK/GR(c) and PVK/GR(d) nanoheterostructure configurations are considerably weak compared to the other two (Table 1). Compared to the other configurations, the adsorption energies of PVK/GR(c) and PVK/GR(d) nanoheterostructures are generally found to be the weakest, i.e., $E_{\text{ad}} \approx 1.129$ and $1.123$ eV (Table 1). This phenomenon depicts physisorption activity towards these surfaces. For PVK/GR(a) and PVK/GR(b) configurations, the adsorption energies, $E_{\text{ad}} \approx 2.275$ and $1.485$ eV (Table 1), which are attributed to the orientation and proximity of the functional groups to the graphene sheet to chemisorb at the PVK/GR surface. For the PVK/GR(a) nanoheterostructure configuration, the strongest tendency to chemisorb on the PVK/GR surface is found, i.e., $E_{\text{ad}} \approx 2.275$ eV (Table 1), via strong $\pi-\pi$ interactions between the carbazole unit and the graphene.

In Table 2, we have the values of the computed formation energies via equation (2).

$$\Delta E = E_{\text{CHN}} - N_C E_C - N_H E_H - N_N E_N$$

Here, $E_{\text{CHN}}$ represents the total energy of the ground state of the nanoheterostructure. $E_C$, total energy of ground state of carbon (graphite), $N_C$, nanoheterostructure carbon atoms. $E_H$, total energy in the ground state of $H$, $N_H$, number of hydrogen atoms, $E_N$, total energy in the ground state of $N$ and $N_N$, nitrogen atoms number contained in the nanoheterostructure.

Table 2 shows the values of calculated formation energies per atom for the individual nanoheterostructures. The novel nanoheterostructures have negative formation energies per atom. With this trend, the new structures are thermodynamically stable. For a detailed study of the novel structures, the formation energy per atom for PVK and GR were individually determined as $-5.263$ eV and $-6.486$ eV, respectively. These values differ by far from formation energies per atom in Table 2. Hence, our novel nanoheterostructures display high
degree of stability and are thermodynamically favorable and have advantage over the individual molecules.

Table 1. Adsorption Energy Determined Using Equation 1.

<table>
<thead>
<tr>
<th>Model type (GGA+vdW)</th>
<th>Adsorption Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVK/GR(a)</td>
<td>2.275</td>
</tr>
<tr>
<td>PVK/GR(b)</td>
<td>1.485</td>
</tr>
<tr>
<td>PVK/GR(c)</td>
<td>1.137</td>
</tr>
<tr>
<td>PVK/GR(d)</td>
<td>1.123</td>
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<table>
<thead>
<tr>
<th>Model type (LDA)</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>PVK/GR(a)</td>
<td>2.223</td>
</tr>
<tr>
<td>PVK/GR(b)</td>
<td>1.435</td>
</tr>
<tr>
<td>PVK/GR(c)</td>
<td>1.129</td>
</tr>
<tr>
<td>PVK/GR(d)</td>
<td>1.134</td>
</tr>
</tbody>
</table>

It is observed after careful studies that the nanoheterostructure model in which the dimer backbone is aligned parallel to the graphene sheet, PVK/GR(a), is the most favored, most stable, in comparison with the three configurations; viz, one in which the dimer backbone is aligned perpendicular to the sheet, PVK/GR(b); where the dimer chains point away from the graphene sheet, PVK/GR(c); and where the dimer chains point towards the graphene sheet, PVK/GR(d). As a result of the stacking patterns in PVK/GR(a), PVK/GR(b), PVK/GR(c) and PVK/GR(d) configurations, the energy differences, $E_0$(eV), were observed to be steadily progressive in stability for our novel nanoheterostructures. For that matter, we have decided to focus our attention on the most stable nanoheterostructure, PVK/GR(a), for the present analysis.

Table 2. Formation Energy Per Atom Calculated Using Equation 2.

<table>
<thead>
<tr>
<th>Model type (GGA+vdW)</th>
<th>Formation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVK/GR(a)</td>
<td>-9.836</td>
</tr>
<tr>
<td>PVK/GR(b)</td>
<td>-9.692</td>
</tr>
<tr>
<td>PVK/GR(c)</td>
<td>-7.419</td>
</tr>
<tr>
<td>PVK/GR(d)</td>
<td>-7.227</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Model type (LDA)</th>
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</thead>
<tbody>
<tr>
<td>PVK/GR(a)</td>
<td>-9.891</td>
</tr>
<tr>
<td>PVK/GR(b)</td>
<td>-9.579</td>
</tr>
<tr>
<td>PVK/GR(c)</td>
<td>-7.341</td>
</tr>
<tr>
<td>PVK/GR(d)</td>
<td>-7.319</td>
</tr>
</tbody>
</table>

Table 3. Optimized Lattice Parameters a(Å), b(Å), c(Å), Energy gap Eg(eV) and Energy Difference $E_0$(eV) of PVK/GR(a), PVK/GR(b), PVK/GR(c) and PVK/GR(d) heterostructures.

<table>
<thead>
<tr>
<th>(GGA+vdW)</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>Eg(eV)</th>
<th>$E_0$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVK/GR(a)</td>
<td>11.741</td>
<td>8.598</td>
<td>8.651</td>
<td>1.687</td>
<td>39.987</td>
</tr>
<tr>
<td>PVK/GR(b)</td>
<td>8.523</td>
<td>9.871</td>
<td>9.117</td>
<td>0.317</td>
<td>8.284</td>
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<tr>
<td>PVK/GR(c)</td>
<td>6.533</td>
<td>10.573</td>
<td>6.657</td>
<td>0.121</td>
<td>0.000</td>
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<tr>
<td>PVK/GR(d)</td>
<td>7.856</td>
<td>6.867</td>
<td>7.774</td>
<td>0.113</td>
<td>9.191</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Model type (LDA)</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>Eg(eV)</th>
<th>$E_0$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVK/GR(a)</td>
<td>10.926</td>
<td>7.342</td>
<td>7.939</td>
<td>1.798</td>
<td>38.655</td>
</tr>
<tr>
<td>PVK/GR(b)</td>
<td>6.921</td>
<td>9.673</td>
<td>9.712</td>
<td>0.261</td>
<td>6.973</td>
</tr>
<tr>
<td>PVK/GR(c)</td>
<td>7.639</td>
<td>10.219</td>
<td>7.266</td>
<td>0.112</td>
<td>0.000</td>
</tr>
<tr>
<td>PVK/GR(d)</td>
<td>8.878</td>
<td>6.667</td>
<td>8.538</td>
<td>0.132</td>
<td>7.509</td>
</tr>
</tbody>
</table>
For the PVK/GR(a) configuration studied, the bond lengths in C−C and C−N exhibited slightly shorter bond lengths of 1.3931 Å and 1.4043 Å as compared to 1.4180 Å and 1.4853 Å respectively in pristine PVK (Table 5).

### Table 4. Studied Bond Lengths(Å), N−C, C−C & C−H in PVK/GR(a) Nanoheterostructure.

<table>
<thead>
<tr>
<th>Model type (GGA+vdW)</th>
<th>N−C</th>
<th>C−C</th>
<th>C−H</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVK/GR(a)</td>
<td>1.4043</td>
<td>1.3931</td>
<td>1.0767</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Model type (LDA)</th>
<th>N−C</th>
<th>C−C</th>
<th>C−H</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVK/GR(a)</td>
<td>1.4087</td>
<td>1.4173</td>
<td>1.0724</td>
</tr>
</tbody>
</table>

The novel nanoheterostructure configuration, PVK/GR(a), has stronger intra-chain interactions in comparison with the other ones. The stability of the nanoheterostructure stems from the shorter and stronger bond lengths. As a result, The C−N bonds in PVK/GR(a) nanoheterostructure are found stiffer compared to those in PVK structure. This gives rise to its stability and rigidity.

Variations arise in formation energy per atom calculated depending on the different choices made between the exchange-correlation functional. This trend is seen in Table 2. The values calculated with the LDA exchange-correlation functional are lower than those calculated with the GGA exchange-correlation functional.

### Table 5. Optimized C−N, C−C, C=C & C−H Bond Lengths(Å) of PVK before and after adsorption.

<table>
<thead>
<tr>
<th></th>
<th>C−N</th>
<th>C−C</th>
<th>C=C</th>
<th>C−H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>1.4853</td>
<td>1.4180</td>
<td>1.3593</td>
<td>1.0715</td>
</tr>
<tr>
<td>After</td>
<td>1.4141</td>
<td>1.3789</td>
<td>1.3276</td>
<td>1.0827</td>
</tr>
</tbody>
</table>

Table 3 shows the optimized lattice parameter values calculated for PVK/GR(a) nanoheterostructure. Both LDA and GGA correlation functionals were employed in the computations. It was observed that LDA gives smaller values of the lattice parameter compared with GGA. GGA calculations give a bandgap value of 1.687 eV as against the LDA calculation of 1.798 eV. Observations revealed that an identical trend can be mapped out in the calculated quantities for C−N, C−C & C−H bond lengths of the modeled nanoheterostructure, PVK/GR(a) in Table 4.

The C−N, C−C, C=C, and C−H bond lengths computed before and after the adsorption phenomenon in PVK are depicted in Table 5. There have been noticeable reductions in bond lengths of both neutral and adsorption states in C−N, C−C, and C=C. Considering C−H, bond lengths are longer than the neutral bond lengths. These changes are due to an adsorption energy of 2.275 eV relative to the adsorption distance, $d_{\text{min}} \sim 3.323 \text{ Å}$ computed. Shorter bond lengths in C−N, C−C and C=C for PVK imply strength in covalent character compared with those in PVK prior to the adsorption process. They, therefore, tend to possess higher binding energy leading to much stronger bonding in the PVK. Hence, in PVK, shorter bond lengths and, consequently stronger bonds are expected to arise for more stability, resulting in rigidity due to a strong covalent character. In contrast, the C−H bond lengths increase after adsorption. What it means is that the double bond character of PVK has been suppressed upon adsorption. The observed pattern falls in line with X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) experimental results for conjugated polymer interfaces.
3.3. Electronic properties of the nanoheterostructure.

The electronic band structure at high-symmetry k-points for PVK/GR(a) nanoheterostructure is depicted in Figure 3(a). The calculated band gaps for the PVK/GR(a) nanoheterostructure stacking, Figure 3(a), are 1.687 eV and 1.798 eV by GGA and LDA parameterizations, respectively. The nanoheterostructure configuration PVK/GR(a) is a p-type semiconductor with an energy gap value of 1.687 eV (1.798 eV), making it interesting for its applications in photovoltaic and optoelectronic devices. Coupled with the above attributes, PVK/GR(a) is a material that is preferred for fabrication applications in optoelectronic devices. The band gap of the novel PVK/GR(a) nanoheterostructure can be tuned desirably to find applications in a myriad of fields for photo-physical uses. Its properties show it is a promising candidate to facilitate the development of band gap engineering for applications in infrared optoelectronics, nanoelectronics, and nano-optics. When the band structure of PVK is compared with that of the newly modeled nanoheterostructure it can be seen that the new band is formed from the hybridization of valence states in the novel nanoheterostructure.

The band structures of the other configurations, viz PVK/GR(b), PVK/GR(c), and PVK/GR(d), show weak physical interactions between the constituents. The interactions in these configurations are rather found to be relatively weak, with electronic bandgaps of 0.317, 0.121, and 0.113 eV, respectively, according to DFT predictions. In these configurations, it is easy to trace back the pristine band features of PVK, which are only translated by approximately 0.4 eV in energy. The configuration in which the polymer backbone is oriented parallel to the graphene sheet resulted in an increase in band gap with approximately 0.130 eV. This increase can be a result of the disorder introduced into the nanoheterostructure by the presence of the carbazole functional group in the polymer backbone.

Configurations PVK/GR(a) and PVK/GR(b) show a higher band gap than configurations PVK/GR(c) and PVK/GR(d). This is so because the carbazole side chain acts as an electron-rich site. For that matter, the HOMO supersedes the LUMO in PVK/GR(c) and PVK/GR(d) and therefore lowers their band gaps.
3.4. Electronic Density of States Analysis.

The electronic DOS, total DOS (t-DOS), and partial DOS (p-DOS) of PVK/GR(a) nanoheterostructure have been plotted as shown in Figures 3(b, c & e), respectively. With the help of the above plots, we analyzed the nature of interactions and the origin of the energy gap in the nanoheterostructure. For comparison sake, the Fermi energy, $E_F$, is fixed as the reference of zero energy for bandgap, $E_g$, and the same for the DOS, which is shown in Figure 3. Figures 3(b, c, d & e) show only positive contributions to the total and partial density of states of electrons for the PVK/GR(a) nanoheterostructure stacking. We find many indications of hybridization between atoms of the polymer and the graphene because the corresponding densities of states show some common peaks. In Figure 2(a), when the polymer backbone comes close to the graphene sheet, a strong interaction arises between the two components because of the presence of the π-π sites in the conjugated polymer backbone and the graphene sheet. The densities of states in Figures 3(b) and 3(c) obtained for the nanoheterostructure in Figure 2(a) reveal that there is a significant hybridization in the electronic structure of the polymer/graphene nanoheterostructure, which is particularly observed around the Fermi energy when the polymer is added. For Figures 2(c) and 2(d), the polymer/graphene interaction is
rather a weak vdW type with only minor modifications in the physical, chemical, and electronic properties of the polymer/graphene nanoheterostructure. This is important for effective non-covalent functionalization. For these structures, a physisorption mechanism is confirmed by the calculated adsorption energies and also shown by the densities of states plots.

In the chemisorbed system, PVK/GR(a) nanoheterostructure configuration, DOS attributed to N atom contributions around the Fermi level is conspicuous and is well-aligned with the electronic DOS of C atom contributions at the highest occupied valence bands from the pristine adsorbate molecules. Despite pronounced differences in molecular configurations, interestingly, the electronic DOS of PVK/GR(a) showing chemisorption, Figure 3(c), is found to exhibit similar features as PVK/GR(b). Whereas for the physisorbed PVK/GR(c) and PVK/GR(d) molecules, the dominant electronic surface states which are close to the Fermi level with significant contributions are attributed to carbon atoms in the PVK/GR(c) and PVK/GR(d) molecules and are analogous to the pristine PVK electronic DOS.

On the whole, whether it be the physisorption or chemisorption process, we can evidently conclude that apart from some little differences in local electronic DOS, the fundamental trend of electronic DOS of our nanoheterojunction systems depends on the electronic DOS of adsorbate molecules is basically close to the Fermi level. Irrespective of being physisorption or chemisorption activity, the DOS pertaining to the adsorbates PVK/GR(a), PVK/GR(b), PVK/GR(c) and PVK/GR(d) configurations cannot be neglected and are taken to be the electronic states that are induced on the surfaces close to the Fermi level, \( E_F \). The surface-induced electronic states for which the electronic DOS of adsorbates contribute to adsorbates, synonymous features are also obtained by a peculiar electronic charge density distribution that is present in all the PVK/GR(a), PVK/GR(b), PVK/GR(c) and PVK/GR(d) nanoheterostructure configurations interfaces.

The atomic orbitals of PVK/GR(a) reveal that the DOS close to the energy gap is basically of \( p_z \) electronic character. They are the bonding and anti-bonding states of N atom. These atoms hybridize with those of \( p_z \) states of carbon atoms. The p-DOS in Figure 3(c) reveals that s- and p-orbitals of C atoms; p-orbitals of N atoms are the major contributors to the valence and conduction bands. It is noteworthy that both the top valence bands and the bottom of conduction bands are characterized by s- and p-orbital states of C and N atoms. Looking at the non-covalent \( \pi \)-stackings in PVK/GR(c) and PVK/GR(d) nanoheterostructure, the picture is different.

3.5. Charge transfer analysis.

The amount of charge transfer from PVK to the GR sheet was obtained when we projected the charge densities of the systems onto their atomic orbitals. The charge transfer was calculated by evaluating charge differences between Lowdin charges for pristine PVK and PVK/GR with the adsorbate molecules. We determined from this result whether the adsorbate molecule acts as an acceptor or a donor. The charge transfer from the polymer (PVK) to the graphene (GR) in the configurations of Figures 2(a) and 2(b) turns out to be 0.09 and 0.03 electrons, respectively, whereas for the configurations of Figures 2(c) and 2(d) we computed 0.02 and 0.01 electrons respectively in the opposite direction. Here we would like to point out that it is important to note that the size of the charge transfer slightly depends on the method chosen for calculations.
4. Conclusions

We have performed first-principles calculations using the pseudopotential plane wave method to study the interaction of a conjugated polymer, PVK, with graphene. A novel nanoheterostructure interface copolymer has been synthesized by DFT methods with low-bandgap characteristics. Using low-band-gap polymers is a viable method to expand the absorption spectrum of solar cells and increase their efficiency. This novel PVK/GR nanoheterostructure composite has a finite band gap and good stability, therefore promising applications for photovoltaic devices. We propose PVK/GR nanoheterostructure as a potential candidate for use in photovoltaics, optoelectronics, and nanoelectronics devices.

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Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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