Molecularly Pillared Graphene with Dithiolene and Diamine Linking Groups

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Molecularly pillared graphene (MPG) is a class of 3D layered materials composed by graphene layers and interconnected via organic molecules (called molecular pillars) through covalent bonding. The combination of different molecular pillars with various chemical composition, size and rigidity, together with different pillar densities and functional groups leads to great prospects in controlling their electromechanical properties for specific applications [1-5]. The aim of this computational study is the investigation of the diversity of the structural and electromechanical properties of MPGs when different functional groups are incorporated to create the covalent bonding with the graphene layers. The study has been performed employing periodic boundary conditions within the frameworks of density functional (DFT) and tight binding (TB) levels of theory. Two MPG models have been designed with amine and thiol crosslinking functionalities and we compare the effect of this chemical modification on their structural and electronic properties. The computations were performed for unit cells of bilayer graphene with 72 carbon atoms per layer interconnected with 1,4-benzenediamine and 1,4-benzenedithiol, respectively (1 linker per layer), as shown in Fig. 1. Initially, we optimized the structures of molecular linkers linked to circumcoronene using the PBE functional [6] with the Gaussian package [7]. Subsequently, we performed geometry and cell optimizations simultaneously, by employing different computational methods in order to compare the obtained results: initial optimization was performed with the GFN1-xTB [8,9] method using the CP2K code [10]. The resulting structures were re-optimized within the gradient corrected (GGA) functional PBE using the Quantum Espresso package [11]. Then, the computations were repeated by including Grimme's dispersion correction D3. The Density of states (DOS) of the final optimized geometries were examined in all cases. All DOS computations were performed with the Quantum Espresso package. Our study shows that these structures present different structural characteristics, provided in Table 1. The DOS diagrams reveal that MPG with 1,4-benzenediamine exhibits a larger band gap than the MPG with 1,4-benzenedithiol (shown in Fig. 2). Therefore, by using different functional groups we can achieve different electronic properties for the MPGs.
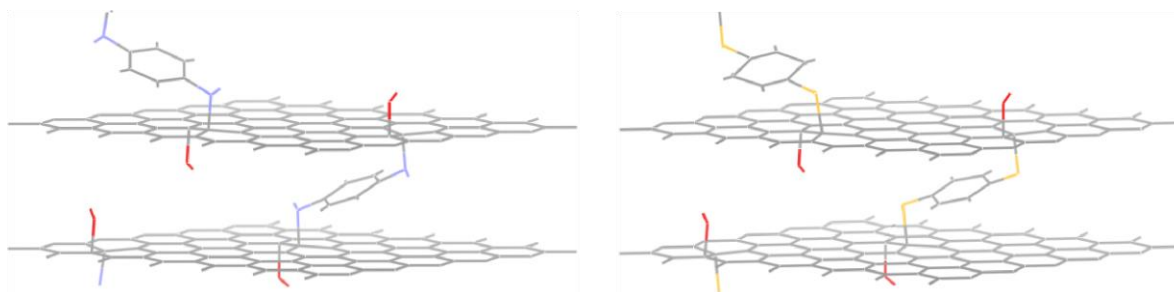

Figure 1. Unit cells of MPGs: (left) cell with 1,4-benzenediamine as a linker and (right) cell with 1,4-benzenedithiol.

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Table 1. Structural characteristics of optimized MPG unit cells. Torsion is calculated between the plane of linker and the estimated plane of (wrinkled) graphene layer.

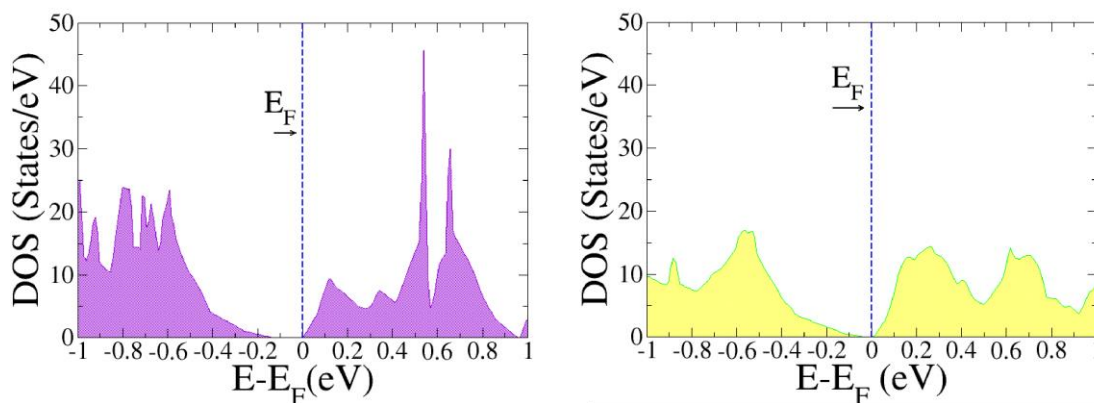| Linker	Unit cell volume ($Å^3$)	Torsion (∘)	d-spacing (Å)
1,4-benzenediamine	1931.00	21.317	5.27($\pm$0.06)
1,4-benzenedithiol	1952.02	17.524	5.25($\pm$0.06)

Figure 2. Density of states diagrams: DOS for MPG with 1,4-benzenediamine (left) and DOS for MPG with 1,4-benzenedithiol (right). Fermi energy was shifted to zero

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