

Tunable Hybridization Between Electronic States of Graphene and Physisorbed Hexacene

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Non-covalent functionalization via physisorption of organic molecules provides a scalable approach for modifying the electronic structure of graphene while preserving its excellent carrier mobilities. Here we investigated the physisorption of long-chain acenes, namely, hexacene and its fluorinated derivative perfluorohexacene, on bilayer graphene for tunable graphene devices using first principles methods. We find that the adsorption of these molecules leads to the formation of localized states in the electronic structure of graphene close to its Fermi level, which could be readily tuned by an external electric field in the range of ± 3 eV/nm. The electric field not only creates a variable band gap as large as 250 meV in bilayer graphene, but also strongly influences the charge redistribution within the molecule-graphene system. This charge redistribution is found to be weak enough not to induce strong surface doping, but strong enough to help preserve the electronic states near the Dirac point of graphene. Our results further highlight graphene's potential for selective chemical sensing of physisorbed molecules under the external electric fields.

Introduction

Graphene—a planar layer of carbon atoms arranged in a hexagonal lattice—exhibits a linear electronic dispersion with the valence and conduction bands touching at the Dirac point.¹ As a result of this unique electronic structure, pristine graphene demonstrates an ultrahigh charge carrier mobility in excess of $200,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which can be exploited for novel, highly energy efficient electronic devices.^{2–4} However, the development of graphene-based electronic devices is primarily hindered by the absence of an intrinsic band gap in its electronic structure.⁵ Although various approaches for tailoring the electronic structure of graphene have been pursued in recent years,^{6–9} creating a significant band gap while maintaining large charge carrier mobilities in graphene remains a formidable challenge.

One strategy to modify the electronic structure of graphene is to utilize quantum confinement effects inherent in low dimensional structures such as quasi one-dimensional graphene nanoribbons.^{10,11} While this strategy can effectively induce the band gap, it also suffers from carrier scattering due to edge imperfections.¹² Another route is the chemical functionalization of graphene where the addition of covalent bonds to graphene (for example, via hydrogenation and fluorination) changes the hybridization of carbon atoms from sp^2 to sp^3 .¹³ While such covalent functionalization successfully alters the electronic properties of graphene, it also leads to a severe degradation of its transport properties.¹⁴ Recent demonstrations of heterostructures of graphene with other 2D materials (for example, boron nitride and transition metal dichalcogenides) also provide a possible option, but a consistent production of graphene heterostructure devices is difficult to control on large scale.^{15,16}

Among the various approaches being pursued to modify the electronic structure of graphene, non-covalent functionalization via physisorption of organic molecules offers an interesting pathway.^{9,17} This approach relies on conserving the integrity of the sp^2 -bonded carbon lattice and thus preserves the linear dispersion of electrons near the Dirac point.^{6,8} Moreover, the production of devices made of graphene with physisorbed molecules can be readily assisted by molecular self-assembly and can therefore be expected to be scalable.^{18,19} Recent studies have suggested that in

graphene physisorbed with small molecules such as NO₂ and NH₃, the application of a transverse external electric field can further enhance the tunability of the electronic structure of graphene by affecting the charge redistribution.^{20–25} Among the organic compounds that are amenable to physisorption on graphene, aromatic molecules are of particular interest.^{9,26} The face-centered parallel stacking of aromatic molecules on graphene surface can lead to a stable hybrid system via van der Waals (vdW) interactions,¹⁹ while the enhanced π - π electron interaction is expected to influence the electronic structure of graphene.⁹ Moreover, addition of functional groups with high electron or hole affinity to the aromatic molecules has been suggested as an effective approach to induce strong charge doping in graphene.^{22,27–30} This can allow a vertical integration of graphene with physisorbed organic molecules with tunable transport characteristics such as charge injection barriers.³¹ However, recent reports indicate that a strong surface charge doping of graphene by molecules or electric field can cause a significant shift of the Fermi level into the valence or conduction band, and often lead to a severe deformation of the π bands of graphene.^{21,32} As a result, the charge carrier mobility of graphene degrades, thus limiting the switching capability of graphene-based semiconducting devices.^{32,33} Therefore, identification of suitable organic molecules for non-covalent functionalization of graphene still remains an open challenge for controllable modification of its electronic properties.

Hexacene belongs to the group of acenes, the aromatic compounds formed by linear fusion of benzene rings (C_{4n+2}H_{2n+4}). Long-chain acenes possess low-lying molecular orbitals that are expected to hybridize with π electrons of graphene and thus influence its electronic structure.³⁴ Furthermore, it has been shown that the edges of hexacene can be readily functionalized with chemical groups with widely varying electron or hole affinity.³⁵ Recently, Watanabe *et al.* reported a successful way to synthesize hexacene that can remain stable up to 300 °C in dark conditions.³⁶ Moreover, organic field effect transistors (OFET) devices made of hexacene have demonstrated a highest charge carrier mobility ever reported for organic semiconductors.³⁶ These observations suggest that hexacene can be an attractive candidate for a stable physisorption on graphene. A good fundamental understanding of the electronic interactions between hexacene and graphene is

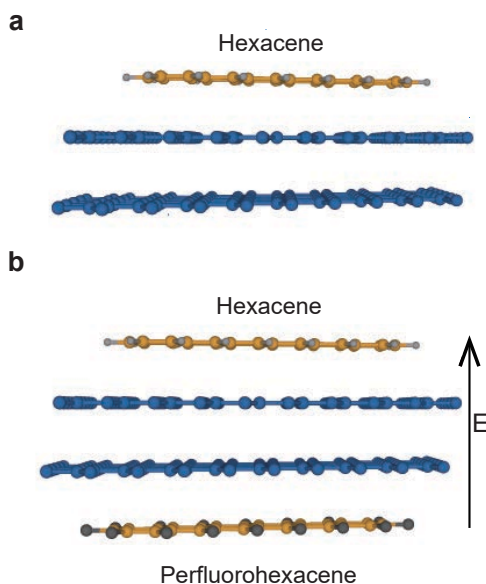


Figure 1: A schematic illustrating (a) single- and (b) dual-molecular adsorption of hexacene and perfluorohexacene on bilayer graphene. The arrow indicates the direction of an applied external electric field.

therefore essential.

Here we systematically investigate the effect of physisorbed hexacene and perfluorohexacene (fluorinated hexacene) on the electronic properties of bilayer graphene using first principles density functional theory simulations. We use perfluorohexacene as an effective tool to down-shift the molecular energy levels relative to hexacene, and induce significant π - π^* interactions and symmetry breaking in bilayer graphene. We examine how the functional groups and adsorption geometry of molecules influence the stability and the electronic structure of the bilayer graphene-molecule system. We show that the adsorption of hexacene and perfluorohexacene on bilayer graphene leads to a significant charge redistribution and the formation of localized states in graphene. By applying an external electric field to bilayer graphene adsorbed with hexacene and perfluorohexacene, we demonstrate that the induced localized states in graphene can be effectively controlled, potentially providing a new strategy for graphene-based sensors for a selective sensing of weakly adsorbed molecules.

Methods

To obtain optimized geometries and the electronic structures of all graphene-molecule systems considered in our study, we employed first principles density functional theory as implemented in Vienna *Ab Initio* Simulation Package.³⁷ We used the generalized gradient approximation of the Perdew-Burke-Ernzerhof form for the electron exchange-correlation functional.³⁸ The core and valence electrons were treated using projector augmented wave (PAW) scheme³⁹ with a kinetic energy cut-off of 600 eV for the plane-wave basis set. Since the generalized gradient approximation does not fully account for long-range dispersion interactions,⁴⁰ we used a Grimme's semi-empirical functional⁴¹ to account for these interactions in the weakly bound graphene-molecule system. To benchmark the accuracy of this functional, we obtained the equilibrium interlayer distance for pristine bilayer graphene to be 3.23 Å, which is in good agreement with the experimental values.⁴² We used a periodic 8×4 graphene supercell for investigating the adsorption of hexacene and perfluorohexacene on Bernal-stacked bilayer graphene. A single molecule in this supercell represents a nearly monolayer coverage for hexacene and perfluorohexacene on graphene with a molecular density of 9.846×10^{-11} mol/cm². This magnitude of molecular density is representative of the reported coverage of the aromatic molecules deposited on graphitic or graphene surfaces in various experimental studies.^{43–45} In each case, the periodic images were separated by a 30 Å vacuum, which was found to be large enough to avoid any spurious interactions between the periodic images. All structures were fully relaxed until the ionic forces were smaller than 0.01 eV/Å. Gaussian smearing was used for geometry relaxations, while Blöch tetrahedral smearing was employed for subsequent calculations of electronic structures.⁴⁶ Finally, for accurate calculations of the electronic structures, we used a fine $6 \times 12 \times 1$ Γ -centred grid for sampling the Brillouin zone.

First, we individually examined the adsorption of hexacene and perfluorohexacene on bilayer graphene using a single-molecular adsorption configuration as shown in Fig. 1(a). We considered two stacking sequences for this configuration, namely, *ABA* and *ABC*, using the same notation as in the case of few-layer graphene.⁴⁷ We also considered the simultaneous adsorption of hexacene

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