

# Band gap opening in bilayer graphene by the simultaneous adsorption of electron donating and electron acceptor molecules



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## ABSTRACT

We have employed dispersion corrected density functional theory to study the adsorption of strong electron acceptor and electron donating molecules onto bilayer graphene. Radical 4-(1,3-dimethyl-2,3-dihydro-1H-benzimidazol-2-yl)phenyl)dimethylamine (N-DMBI) was selected as n-type dopant while 2,3,5,6-tetrafluoro-7,7,8,8-tetra-cyanoquinodimethane (F4-TCNQ) played the role of p-type dopant. When one of these molecules is adsorbed onto bilayer graphene the adsorption energies are 0.14 eV larger than those computed for monolayer graphene. However, when they are concomitantly adsorbed on opposite sides of bilayer graphene the adsorption energy is larger than the sum of the individual interaction energies due to a synergic effect obtained from the combination of electron donor and acceptor molecules. Although radical N-DMBI and F4-TCNQ shift the position of the Fermi level and induce p-type and n-type character on bilayer graphene, respectively, when they are co-adsorbed a different behavior is seen since a charge imbalance is induced. As a consequence, a gap of 0.21 eV is opened and Mexican hat-like energy bands were observed. This finding may pave the way towards the development of new graphene based field effect transistors.

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## 1. Introduction

The chemical functionalization of graphene and the heteroatom doping are useful methods to open a band gap in graphene. However, these methods alter the mobility of carriers making very difficult the development of a graphene based electronic devices that can replace the silicon era. In this sense, the use of molecules to interact with graphene via non bonded interactions is a very appealing method because the conjugated  $sp^2$  framework of graphene is prone to interact via pi stacking, CH- $\pi$  interactions, to mention just the most popular weak interactions that can exist between adsorbates and substrates. 2,3,5,6-tetrafluoro-7,7,8,8-tetra-cyanoquinodimethane (F4-TCNQ) and its cousin TCNE, are perhaps the most studied molecules that have been used to alter the properties of pristine graphene [1–6], doped graphene [7] and defective graphene [8]. In particular we have shown that F4-TCNQ molecule increases the chemical reactivity of graphene [9]. It is well established that adsorbed molecules like TCNE can fine tune the carrier concentration and the electronic properties [5]. In the same way that electron acceptors alter the electronic properties of graphene, donors proved to be equally useful. For example, among them, we can highlight tetrathiafulvalene (TTF)

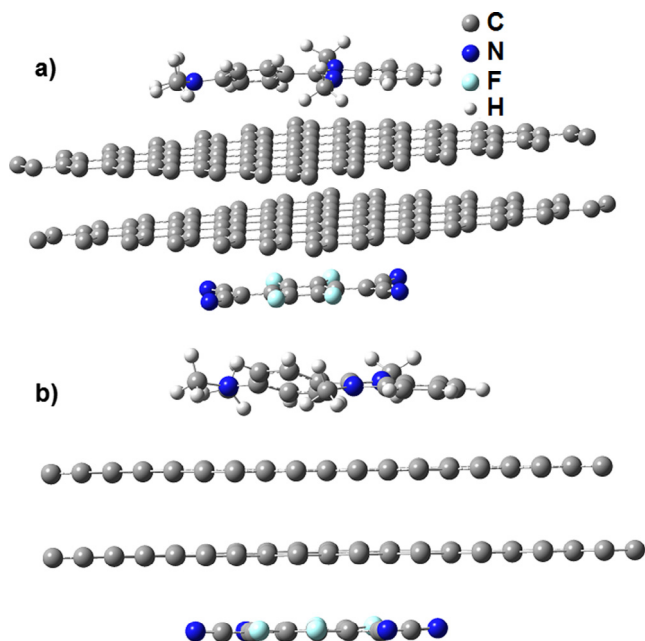
[10,11], and perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) [12], are adsorbed onto graphene via  $\pi$  stacking, opening sizable gaps [13,14]. The interaction between graphene and the adsorbed molecules was explained by Chen et al. [15] showing the importance of the alignment of the energy levels and the modifications of the work function.

As early as 2012, Park et al. [16] used the dual doping of bilayer graphene to break the degeneracy of the  $\pi$  and  $\pi^*$  bands at the k-point opening a band gap as high as 200 meV. This was achieved by placing bilayer graphene between F4-TCNQ and a  $NH_2$ -functionalized monolayer. In the same vein, Wang et al. [17,18] used amorphous  $SiO_2$ , decamethylcobaltocene and TCNE to open gaps from 98 to 211 meV. In a recent work we studied the adsorption of the electron donor molecule radical 4-(1,3-dimethyl-2,3-dihydro-1H-benzimidazol-2-yl)phenyl)dimethylamine (N-DMBI) onto graphene [19,20]. We found that this molecule increases the chemical reactivity of graphene and induces a metallic character because the Fermi level is shifted upwards as the conduction band becomes populated by the electrons donated by radical N-DMBI [20]. In an attempt to open a gap, we simultaneously adsorbed the latter molecule and the electron acceptor F4-TCNQ on opposite sides of monolayer graphene. Interestingly, the electrons donated by radical N-DMBI were completely transferred to F4-TCNQ and graphene almost completely

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**Table 1**Adsorption energies (eV) onto  $7 \times 7$  monolayer and bilayer graphene determined at the VDW-DF/DZP level.

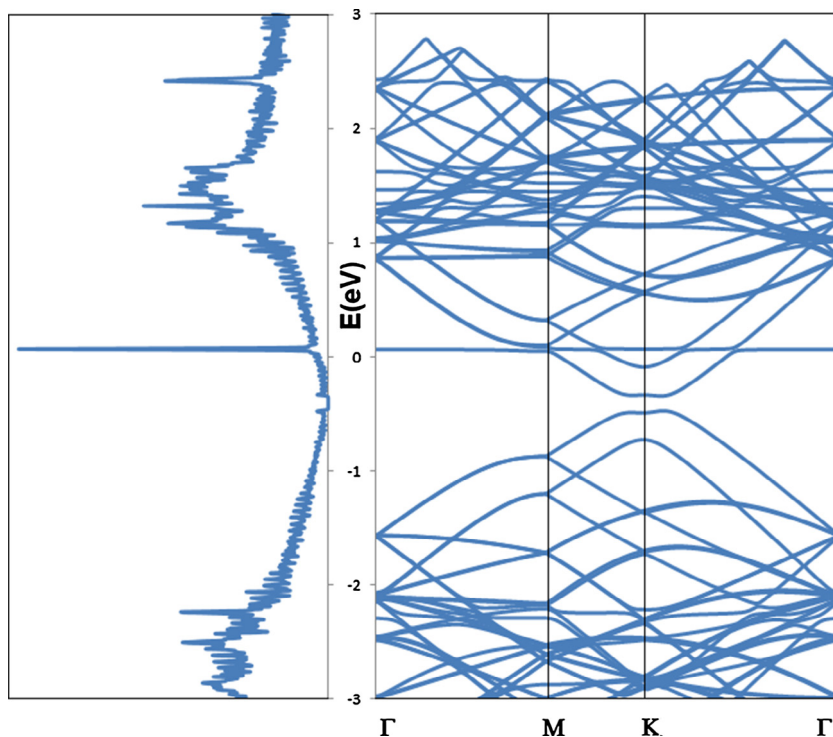
	$E_{\text{ads}}$ (BSSE uncorrected)	$E_{\text{ads}}$ (BSSE corrected)	$E_{\text{def}}$ BG <sub>77</sub>	$E_{\text{def}}$ R-N-DMBI	$E_{\text{def}}$ F4-TCNQ
BG <sub>77</sub> /R-N-DMBI	3.38	2.05	0.0036	0.2457	
BG <sub>77</sub> /F4-TCNQ	2.93	1.54	0.020		0.0202
R-N-DMBI/BG <sub>77</sub> /F4-TCNQ	6.55	4.02	0.038	0.2468	0.0678
G <sub>77</sub> /R-N-DMBI	3.19	1.91	0.0030	0.239	
G <sub>77</sub> /F4-TCNQ	2.76	1.41	0.017		0.0214
R-N-DMBI/G <sub>77</sub> /F4-TCNQ	6.60	4.00	0.031	0.2617	0.0817

**Fig. 1.** Optimized structure determined for  $7 \times 7$  bilayer graphene AB stacked with one R-N-DMBI molecule adsorbed on top and one F4-TCNQ molecule adsorbed on the other layer, at the VDW-DF/DZP level of theory.

recovered its semimetallic character. Inspired by the good results obtained for dual doped bilayer graphene [16–18], we decided to study the changes observed in the electronic structure of bilayer graphene when a strong electron donating molecule like radical N-DMBI is adsorbed onto bilayer graphene at the same time that a strong electron acceptor as F4-TCNQ is adsorbed on the opposite layer. Our results indicated that a charge imbalance can be induced in bilayer graphene and thus a sizable gap can be opened with a Mexican hat-like energy bands that are useful to construct graphene based field effect transistors.

## 2. Methods

We investigated the adsorption of electron donating and electron acceptor molecules onto bilayer graphene, by means of spin polarized VDW-DF [21] density functional theory (DFT) calculations as implemented in SIESTA [22,23]. We selected the double-zeta basis set with polarization functions and fixed the orbital confining cut-off to 0.01 Ry. The split norm used was the default value of 0.15. The DFT implementation in SIESTA is affected by a significant basis set superposition error (BSSE), even with relatively low degree of radial confinement [24]. In order to circumvent this inconvenience, we used the counterpoise correction suggested by Boys and Bernardi [25]. We employed relaxed structures to estimate the BSSE corrected binding energies and took monomer

**Fig. 2.** Density of states and band structure determined for  $7 \times 7$  bilayer graphene with one molecule of radical N-DMBI adsorbed, at the VDW-DF/DZP level. Only the spin up is shown because the spin down is identical.

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