Monash University

Ph.D. Thesis

Tailoring the Electronic Structure of Graphene via Molecular Adsorption

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A thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy in the
Department of Materials Science and Engineering

February 2016
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Graphene demonstrates many exceptional properties that makes it a promising candidate in various applications, such as electronics, energy-related and biomedical. However, there are still many challenges remaining to realize graphene’s fullest extent possible. In recent years, graphene functionalization has become the primary driving force for enhancing the performance of graphene-based devices. Among the various approaches of graphene functionalization, molecular adsorption has received growing attention due to its low cost, flexibility and effectiveness in controlling the properties of graphene. Here, density functional calculations are employed to investigate three specific graphene-molecule systems used for electronic, catalytic and sensing applications, focusing on the interplay between graphene and adsorbed molecules. Major challenges facing functionalized graphene are thoroughly examined and discussed, such as identifying novel adsorbates, refining surface conditions, and strengthening electronic signals arising from graphene-molecule interactions. The work presented in this thesis aims to provide critical theoretical insights into the electronic structure of graphene modified by molecular adsorption, and help the design and development of future graphene-based devices.
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Contents

Abstract iii
Acknowledgements iv
Contents vi
List of Figures ix
List of Tables xi

1 Introduction 1
  1.1 Nanotechnology and Nanomaterials in a Changing World ............... 1
  1.2 Roadmap for Graphene ........................................... 2
  1.3 Graphene Functionalization: Basic Principles and Challenges .......... 4
  1.4 Research Aims ................................................... 8
  1.5 Thesis Outline .................................................. 8

2 Literature Review 10
  2.1 Fundamental Electronic Properties of Graphene ......................... 10
      2.1.1 Massless Dirac Fermions ................................... 10
      2.1.2 Graphene Stacks .............................................. 13
  2.2 Manipulation of Electronic Properties of Graphene via Molecular Adsorption .......................................................... 15
  2.3 Progress on Physisorption of Aromatic Molecules on Graphene .......... 19
      2.3.1 Theoretical Results ........................................... 19
      2.3.2 Experimental Results ......................................... 23
  2.4 Progress on Functionalized Graphene as Catalytic Support for Fuel Cells 26
  2.5 Progress on Graphene for DNA Sequencing and Biosensing ............ 31
  2.6 Summary and Conclusions .......................................... 33

3 Methodology 34
  3.1 Introduction to Density Functional Theory ............................ 34
      3.1.1 Theoretical Background ....................................... 34

vi
3.1.2 Key Elements in DFT Calculations .......................... 37
   3.1.2.1 Periodic Boundary Condition and Supercell ............ 37
   3.1.2.2 Reciprocal Space, $k$ points and Brillouin Zone ....... 38
   3.1.2.3 Energy Cutoffs .................................. 39
3.1.3 Dissection of Practical DFT Calculation Processes .......... 39
3.2 Characterization and Data Analysis ............................ 41
   3.2.1 Structural and Energetic Parameters ....................... 41
      3.2.1.1 Model Construction .......................... 41
      3.2.1.2 Adsorption and Formation Energy .................. 41
   3.2.2 Electronic Analysis .................................. 42
      3.2.2.1 Density of States and Band Structure Diagrams ....... 42
      3.2.2.2 Bader Charge Analysis .......................... 43
      3.2.2.3 Charge Density Difference ....................... 43
      3.2.2.4 Work Function and Dipole moments ................ 44
3.3 Computational Resources .................................... 44
4 Tunable Hybridization Between Electronic States of Graphene and
   Physisorbed Hexacene ............................................. 46
4.1 Foreward .................................................... 46
4.2 Introduction ............................................... 48
4.3 Computational Details ........................................ 51
4.4 Results and Discussions ..................................... 53
   4.4.1 Electronic Structure of Hexacene and Perfluorohexacene .. 53
   4.4.2 Electronic Structure of Bilayer Graphene upon Adsorption . 56
   4.4.3 Effect of the Applied External Electric Field .............. 61
4.5 Conclusions .................................................. 68
5 Graphene-Platinum Nanocomposites for Electrocatalysis .......... 69
5.1 Introduction ............................................... 69
5.2 Computational Details ........................................ 72
5.3 Results and Discussions ..................................... 74
   5.3.1 Adsorption of Pt Monomer and Pt Dimer ................ 74
   5.3.2 Adsorption of Pt-13 Clusters .......................... 77
   5.3.3 Electronic Structures of Adsorbed Pt$_{13}$ Clusters ....... 79
5.4 Conclusions .................................................. 85
6 Interaction of DNA Nucleobase With Graphene: the Role of Inter-
   molecular Interactions .............................................. 86
6.1 Introduction ............................................... 86
6.2 Computational Details ........................................ 88
6.3 Results and Discussions ..................................... 90
   6.3.1 Coverage Dependence of Adsorption Geometries of Nucleobases
         on Graphene ............................................. 90
   6.3.2 Electronic Structure Modifications ...................... 96
   6.3.3 Effects of Molecular Dipole Moments on the Work Function .. 100
## Contents

6.3.4 Comparison of Computational and Experimental Results . . . . 104
6.4 Conclusions . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 105

7 Conclusions and Future Work 106

7.1 Concluding Remarks . . . . . . . . . . . . . . . . . . . . . . . . . . . 106
7.2 Future Work . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 109
  7.2.1 Identification of DNA Methylation . . . . . . . . . . . . . . . . 109
  7.2.2 Electrical Detection of Nitric Oxide Using Fe Porphyrin Sup-
 ported on Graphene . . . . . . . . . . . . . . . . . . . . . . . . . 111

A Publication: Tunable Hybridization Between Electronic States of Graphene
and Physisorbed Hexacene 113

Bibliography 123
# List of Figures

1.1 Roadmap for graphene: timeline of graphene applications ................................ 3
1.2 Origin of chemical reactivity of graphene. ..................................................... 5
1.3 Effect of molecular adsorption/addition on the electronic properties of graphene ................................................................. 7
2.1 The structure of graphene. ..................................... 12
2.2 $\pi$ bands of graphene. ........................................ 13
2.3 Electronic properties of bilayer graphene. .................................................. 14
2.4 Stacking configurations of graphene multilayers. ...................................... 15
2.5 Doping of graphene ........................................... 17
2.6 Built-in electric field upon molecular adsorption ..................................... 18
2.7 Adsorption configurations in a graphene-aromatic molecule system ............ 21
2.8 Electronic structure modification by adsorption of aromatic molecules ....... 22
2.9 Dual molecular adsorption on bilayer graphene ....................................... 23
2.10 Experimental characterization of adsorption of aromatic molecules on graphene ................................................................. 24
2.11 Graphene-based field effect transistor (FET) based on the adsorption of aromatic molecules ......................................................... 26
2.12 Theoretical investigations of noble metal nanoparticles on pristine graphene and GO sheets .................................................... 28
2.13 Experimental characterization of noble metal nanoparticles / functionalized graphene sheet .................................................... 30
2.14 Fast DNA sequencing using a graphene-based device .................................. 32
2.15 Coverage-dependence of electronic modifications by adsorbed nucleobase on graphene ................................................................. 33
3.1 Practical DFT calculation processes ......................................................... 40
4.1 Simulation setup for adsorption of hexacene and perfluorohexacene on graphene ................................................................. 52
4.2 Electronic structure of hexacene and perfluorohexacene .......................... 54
4.3 Density of states of graphene upon adsorption of hexacene and perfluorohexacene ................................................................. 58
4.4 Charge redistribution at the interface ....................................................... 59
4.5 Planar-averaged charge density difference analysis ................................... 60
4.6 Electronic structure of graphene upon adsorption of hexacene at high molecular density ................................................................. 62
### List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.7</td>
<td>Effect of external electric field on the electronic structure of bilayer graphene in dual-molecular adsorption of hexacene and perfluorohexacene at monolayer coverage</td>
</tr>
<tr>
<td>4.8</td>
<td>Band structure diagrams of bilayer graphene upon dual-molecular adsorption under external electric field</td>
</tr>
<tr>
<td>4.9</td>
<td>Band structure diagrams of monolayer graphene upon dual-molecular adsorption under external electric field</td>
</tr>
<tr>
<td>5.1</td>
<td>Structure of Pt nanoparticles and functionalized graphene sheet</td>
</tr>
<tr>
<td>5.2</td>
<td>Adsorption of a Pt monomer on the functionalized graphene</td>
</tr>
<tr>
<td>5.3</td>
<td>Adsorption of a Pt dimer on the functionalized graphene</td>
</tr>
<tr>
<td>5.4</td>
<td>Adsorption of a Pt\textsubscript{13} cluster on the functionalized graphene</td>
</tr>
<tr>
<td>5.5</td>
<td>Changes to electronic states of Pt-graphene nanocomposites</td>
</tr>
<tr>
<td>5.6</td>
<td>Charge redistribution at the Pt-functional graphene interface</td>
</tr>
<tr>
<td>6.1</td>
<td>Structural changes of nucleobases upon adsorption on graphene</td>
</tr>
<tr>
<td>6.2</td>
<td>Hydrogen bonding between nucleobases</td>
</tr>
<tr>
<td>6.3</td>
<td>Evolution of energetic properties of the graphene-base system as a function of molecule coverage</td>
</tr>
<tr>
<td>6.4</td>
<td>Tilt of nucleobases at high molecular coverages</td>
</tr>
<tr>
<td>6.5</td>
<td>Electronic structure of DNA/RNA nucleobases on graphene</td>
</tr>
<tr>
<td>6.6</td>
<td>Charge redistribution in the graphene-base system</td>
</tr>
<tr>
<td>7.1</td>
<td>The cytosine methylation</td>
</tr>
<tr>
<td>7.2</td>
<td>NO detection using Fe porphyrin supported on graphene</td>
</tr>
</tbody>
</table>
List of Tables

3.1 Computational cost of DFT calculations ............................................ 45

4.1 Adsorption energy and adsorption distance of hexacene and perfluoro-
hexacene ................................................................. 55

5.1 Energetic and structural changes upon adsorption of a Pt monomer and
Pt dimer on the functionalized graphene sheet .................................... 75

5.2 Energetic and structural changes upon adsorption of a Pt_{13} cluster on
the functionalized graphene sheet .............................................. 78

5.3 Charge transfer at the Pt-functionalized graphene interface .................. 83

5.4 d-band center changes upon adsorption of a Pt_{13} cluster ................. 84

6.1 Unit cell for full molecular coverage of DNA/RNA nucleobase on graphite 89

6.2 Tilt angles of nucleobases .................................................. 92

6.3 Molecular dipole moments and work function changes ....................... 101
To my father and mother, to my grandparents, and to all the people I love and care.

To those who want to make a difference in their lives and those who help others achieve success.

Everyone is born different. We all deserve a chance to shine.
PART A: General Declaration

Monash University

Declaration for thesis based or partially based on conjointly published or unpublished work

General Declaration

In accordance with Monash University Doctorate Regulation 17.2 Doctor of Philosophy and Research Master’s regulations the following declarations are made:

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes one original papers published in peer reviewed journals and two unpublished publications. The core theme of the thesis is Tailoring the Electronic Structure of Graphene via Molecular Adsorption. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the candidate, working within the Department of Materials Science and Engineering under the supervision of Dr. Nikhil V. Medhekar.

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research.

In the case of Chapter 4 my contribution to the work involved the following:

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Signed: .........................................................

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Chapter 1

Introduction

1.1 Nanotechnology and Nanomaterials in a Changing World

Nanotechnology has infiltrated into our everyday life in a very subtle and pervasive fashion. We are currently experiencing the benefits of nanotechnology over a wide range of applications including transportation, electronics, and medicals [1–3]. The 21st century is deemed to be the century of nanotechnology, with the world calling on nanotechnology for a sustainable solution to issues such as overpopulation, increasing energy demand and environmental pollution. Allocation of R&D investments towards nanotechnology and production of new nanomaterials is expected to increase to approximately 1.5 trillion U.S. dollars globally by the end of 2015[2, 4]. Today, nano-related research has become the primary driving force of innovation, and some of those prototypes existing only in the laboratory today may revolutionize our tomorrow [1].

The dimension of nanomaterials spans from the subnanometer scale to several hundred nanometers. These small structures exhibit significantly distinct physical,
chemical and biological properties compared to their bulk form. Study on nanomateri-
als requires multidisciplinary effort throughout the design, fabrication and application
process [1, 5, 6]. Computational approaches (e.g., modeling and simulation) have be-
come crucial links in studies on materials at the nanoscale over recent years [7–9].
These computational methods and theories have not just helped understanding the
behavior of materials observed in experiments, but also provide direction and guidance
for future experimental characterizations [7, 10, 11]. The merging of computational
modeling and experimental techniques will inevitably become the standard for future
nanoscale research.

Nanotechnology is now in a golden era. A number of nanotechnololgy opportunities
lie in fields including health, efficient energy, food security and marine research [12–
16]. The novel properties of nanomaterials have been promising, yet commercialization
of these materials remains a grand challenge and requires extensive investigations.
The work presented in this thesis uses computational approaches to investigate the
electronic structure of one of the most promising nanomaterials to date – graphene[17].
It is hoped that the outcome of this research could help the future development of
graphene-based devices, and thereby contribute to the future nanotechnology markets.

1.2 Roadmap for Graphene

Graphene is a single layer of carbon atoms arranged in a hexagonal lattice [18, 19].
Graphene was presumed not to exist in the free state, until in 2004 when Novoselov et
al. successfully isolated stable graphene films from highly oriented pyrolytic graphite
by means of mechanical exfoliation[20]. This discovery marked the beginning of a large
number of investigations on graphene, which remains an area of intense research in
the physics, chemistry and material science community today [21–29]. Graphene possesses many fascinating properties that enable its implementation in a wide range of applications, particularly electronic [30–34]. Graphene has a unique gapless electronic structure. It exhibits the highest carrier mobility measured for any material and has the ability to sustain ultrahigh current density [32, 33, 35–37]. The charge carrier concentration of graphene can be controlled by an applied electric field and gate tunable [38–41]. Graphene-based electronic devices (e.g., field-effect transistors (FET), touch screens and electrochemical sensors) made in the laboratories have shown many potential advantages that can lead to improved performance and new applications [31, 42, 43].

Fig. 1.1. Roadmap for graphene: timeline for graphene applications. — A possible timeline for graphene applications in (a) electronics and (b) photonics with the advance of graphene technologies. The time indicates the availability of a functional device prototype. These applications are also ranked in terms of the quality of graphene. Adapted with permission from Ref. [17]. © 2012 Nature Publishing Group.

Graphene is a promising material, yet also controversial. The media has described
graphene as "the miracle material" that can replace many current technologies [17]. However, there are many obstacles ahead for graphene to be incorporated into practical applications. In the field of electronics, the superior electronic properties of graphene are expected to reshape the current semiconducting industry dominated by silicon-based devices [44–46]. Although graphene is unlikely to meet the industrial requirements and replace silicon completely in the next 20 – 30 years, it can become a complementary technology in conventional devices to boost their performance[46]. Moreover, there are many fundamental aspects of graphene that have yet to be clearly explained [3, 17]. Figure 1.1 gives an indication of a possible timeline for electronic and photonic applications of graphene [17]. The structure of graphene for specific applications can be controlled and modified by choosing an appropriate synthesis method [47–49]. The modification of the graphene structure is vital for graphene’s future role in technological applications [3, 50, 51]. There are many strategies available to modify the graphene structure to reach its full potential. This will be briefly discussed in Section 1.3.

1.3 Graphene Functionalization: Basic Principles and Challenges

The structural, chemical and electronic properties of graphene need to be modified in various applications like semiconductors, sensors, supercapacitors and energy storage devices [17, 25, 50, 52, 53]. Over the last decade, extensive studies have been devoted to study modifications on graphene for a wide range of applications [25, 26, 54–56]. Various experimental and theoretical approaches have been utilized to explore effective and precise ways to functionalize graphene, and thereby develop advanced devices [50, 51, 57].
Fig. 1.2. **Origin of chemical reactivity of graphene.** — (a) Graphene functionalization can either occur on the basal plane or edges. Edges, structural defects (e.g., vacancies) and curved surfaces (marked in black, red and purple) provide high chemical reactivity for functionalization. Pristine hexagonal structure (marked in blue) can also be functionalized with strong dopants or weak adsorbates. The underlying pictures show the local structure of (b) pristine hexagonal lattice, (c) zigzag and armchair edges, (d) monovacancy and (e) a curved graphene sheet. Adapted with permission from Ref. [50]. © 2012 The Royal Society of Chemistry.

Pristine graphene consists of a chemically unsaturated surface made up of sp²-hybridized carbon atoms (highlighted in blue in Figure 1.2 (a)). The π orbitals of graphene are coupled and form a stable conjugated π-bond network (Figure 1.2 (b)). The chemically inert graphene surface can be functionalized by covalent addition, leading to conversion of sp² to sp³ hybridization [57, 58]. Graphene can also react with metals and organic molecules via metal-π, π-π and π-π* interactions to form a relatively weak bonding system [59–62]. On the other hand, practically synthesized graphene always contains some structural defects such as edges, vacancies, dislocations, and corrugated surfaces (highlighted in Figure 1.2 (a)). These structural impurities alter the local electronic structure of graphene (Figure 1.2 (c-e)) and possess higher chemical
reactivity than a pristine surface. The carbon atoms at these defective sites are much easier to reconfigure and/or be covalently functionalized\cite{63, 64}. Graphene functionalization is based on these different types of reactivity.

Graphene functionalization by covalent addition / noncovalent interaction have different impacts on electronic attributes of graphene, as displayed in Figure 1.3 \cite{50, 57, 59, 60}. Covalent functionalization destroys the honeycomb structure of graphene and induces strong lattice scattering. This approach can increase the solubility and chemical reactivity of graphene at a low cost, thus finding its applications such as printable graphene electronics, hydrogen storage and electrocatalysis\cite{29, 42, 65}. However, the distorted graphene lattice leads to a drastic reduction in graphene’s carrier mobility, making it unsuitable for electronic applications\cite{59}. Typical covalent functionalization methods include cutting graphene into graphene nanoribbons\cite{66, 67} or graphene nanomeshes\cite{68, 69}, introducing defects\cite{70} and chemical functionalisation by covalent bonding or substituting of atoms or molecules\cite{71, 72}. Alternatively, the noncovalent functionalization route preserves the structural integrity of graphene via weak van der Waals interactions. This approach can achieve desired electronic structure modifications without disrupting the basic electronic properties of graphene. It also enables precise and flexible control of the charge carrier type (p-type/n-type) and density\cite{60, 73}. Noncovalent functionalization is favorable in applications such as logic transistors and sensors. Typical noncovalent functionalization methods include graphene-substrate interaction\cite{74}, physisorption of molecules on graphene\cite{75} and application of strains\cite{76}, external electrical fields\cite{41, 77} or magnetic fields\cite{78}.

There are still many challenges remaining to achieve rational and cost-effective graphene functionalization. Firstly, graphene functionalization often occurs randomly, which is a critical issue for applications such as integrated circuits and sensors. The
Chapter 1: Introduction

Fig. 1.3. Effect of molecular adsorption/addition on electronic properties of graphene. — Schematic showing the effect of covalent/noncovalent molecular functionalization on the electronic properties of graphene. Adapted with permission from Ref. [59]. © 2013 Wiley.

grain size, doping level and/or number of stacking layers of graphene need to be precisely controlled to ensure functionalization occurs on selected regions [50, 57]. This requires a significant improvement to current graphene production techniques. Secondly, current graphene functionalization can not achieve structural uniformity, which limits its use in practical devices [50, 51]. This requires refinement and standardization of functionalization methods. Finally, the performance of functionalized graphene-based devices still needs to be enhanced. Functionalized graphene must prove its superior selectivity, catalytic activity, and/or bio/environmental compatibility over conventional materials [17]. This requires a comprehensive research into the mechanisms behind graphene functionalization, as well as the interaction between graphene and other materials. The development of new experimental and computational tools will allow exploration of these challenges and new capabilities of functionalized graphene.
1.4 Research Aims

This thesis aims to investigate three specific cases closely related with graphene functionalization. Although the details of these cases are different, they all linked with a common broad aim: to improve the efficiency of current graphene-based devices by modifying the electronic structure of graphene using adsorption of molecules. The specific aims of the work presented in this thesis are summarized as follows:

1. The interaction of bilayer graphene with physisorbed long-chain acenes, namely, hexacene. The work aims to provide a tunable and scalable approach for opening a band gap in graphene while preserving many of its excellent properties for electronic and sensing applications.

2. The Pt-graphene nanocomposites. The work aims to present an effective approach to control the catalytic activity of graphene for energy storage applications.

3. The interaction between graphene and DNA/RNA nucleobases. The work aims to address the capability of graphene in DNA/RNA sequencing and biosensing, as well provide theoretical insight into the graphene-organic molecule system.

1.5 Thesis Outline

The structure of this thesis is organised as follows. Chapter 2 discusses the fundamental electronic properties of graphene and the latest development on graphene functionalization. The progress review will be focused on functionalization of graphene for electronic, catalytic and biosensing applications. Chapter 3 briefly introduces the computational methods and tools used in The work presented in this thesis. Chapter 4-6 covers the three specific cases as mentioned in Section 1.4. Chapter 7 highlights the
key findings and concluding remarks obtained from this thesis, followed by a discussion of possible future work.
Chapter 2

Literature Review

This chapter is structured as follows: the first part will review the fundamental electronic properties of graphene, then it will introduce the theoretical background of graphene functionalization by molecular adsorption. The remaining parts will focus on recent progress on specific topics concerned in the main chapters (Chapter 4-6).

2.1 Fundamental Electronic Properties of Graphene

2.1.1 Massless Dirac Fermions

Graphene is arranged in a hexagonal structure consisting of two interpenetrating triangular sublattices as displayed in Figure 2.1 (a). Each carbon atom forms three $\sigma$-bonds with its nearest three neighbours as a result of $sp^2$ hybridization of $2s$, $2p_x$ and $2p_y$ orbitals. The three $\sigma$-bonds lie in the same plane with an angle of 120°. The $2p_z$ orbital, perpendicular to the lattice plane, overlaps with $2p_z$ orbitals of other atoms to form a weak $\pi$ bond. The electronic properties of graphene are determined by these delocalized $\pi$ electrons [23, 52].
Chapter 2: Literature Review

The real space lattice vectors of graphene are written as:

\[ a_1 = \frac{a}{2}(3, \sqrt{3}), a_2 = \frac{a}{2}(3, -\sqrt{3}), \]  

(2.1)

where \( a \approx 1.42 \) Å is the carbon-carbon bond length. The lattice constant is 2.46 Å. The corresponding lattice vectors in the reciprocal space (Fig. 2.1 (b)) are expressed as:

\[ b_1 = \frac{2\pi}{3a}(1, \sqrt{3}), b_2 = \frac{2\pi}{3a}(1, -\sqrt{3}). \]  

(2.2)

The lattice constant in the reciprocal space is \( 4\pi/\sqrt{3}a \). The first Brillouin zone is a hexagon (Figure 2.1 (b)). The six corners of the first Brillouin zone are of particular importance for the electronic properties of graphene and are named the K points.

The electronic band structure of graphene was first calculated by Wallace in 1947 [79] and then by others in the 1950s [80, 81]. Using the tight-binding approximation (TBA), the electronic dispersion relationship \((E(k))\) for \( \pi \) electrons is derived as [32, 33]:

\[ E_{\pm}(k) = \pm \sqrt{3 + f(k) - t'f(k)}, \]  

(2.3)

\[ f(k) = 2 \cos(\sqrt{3}k_ya) + 4 \cos(\frac{\sqrt{3}}{2}k_ya) \cos(\frac{3}{2}k_xa), \]  

(2.4)

where \( f(k) \) describes the nearest-neighbour hopping, \( t \) and \( t' \) are the nearest-neighbour and second nearest-neighbour hopping coefficient respectively, \( k_x \) and \( k_y \) are lattice vectors in the reciprocal space, as shown in Figure 2.2. The upper half is the \( \pi^* \) anti-bonding band and the bottom half is the \( \pi \) bonding band. The two \( \pi \) electrons in the unit cell of graphene completely occupy the bonding band, leaving the anti-bonding band unfilled. The two bands degenerate and touch at the K points (also known as the Dirac points), which correspond to the Fermi level \((E_F)\) of graphene. Graphene is therefore viewed as a gapless semimetal material.
Fig. 2.1. The structure of graphene. — (a) The honeycomb lattice of graphene. $\mathbf{a}_1$ and $\mathbf{a}_2$ are two primitive lattice vectors. The two interpenetrating triangular sublattices are denoted as A and B. (b) The reciprocal lattice of graphene and its first Brillouin zone. $\mathbf{b}_1$ and $\mathbf{b}_2$ are two primitive lattice vectors in the reciprocal space. $\Gamma$, K and M are high symmetry points in the first Brillouin zone.

The energy dispersion around the K points yields a linear behavior expressed as:

$$E_k = \pm \nu_F \hbar k.$$

The linear dispersion near the K points is the most interesting aspect of the electronic properties of graphene. Electrons near the K points behave like massless Dirac fermions, which are relativistic particles with zero effective mass travelling at a speed comparable to that of light ($\nu_F$, the Fermi velocity, is approximately $10^6$ m/s for pristine graphene. [32]) This unique character leads to many novel phenomena such as the anomalous quantum Hall effect, the Klein’s paradox and edge effects [35, 82, 83].
Fig. 2.2. π bands of graphene. — The π band and π* band of graphene calculated using tight binding approximation (TBA). The dispersion relationship is plotted along high symmetry points ΓMKΓ. The Fermi level is adjusted to 0. The parameters used for the graph are based on Ref. [32].

2.1.2 Graphene Stacks

Bilayer graphene is made up of two coupled graphene monolayers, typically arranged in a Bernal (AB-stacked) configuration shown in Figure 2.3(a). The electronic structure of bilayer graphene was first studied in 2006 under the TBA scheme [84–87]. The band structure of an AB-stacked bilayer graphene (Figure 2.3(b)). There are two π bands and two π* bands in the diagram by taking into account the 2p_z orbital of each of the four atoms (i.e., A1, A2, B1 and B2) in the unit cell. The two bands touch at the K points and the other two split away from the Fermi level. The touching bands are attributed to the hopping between A1 and B2, and the separated bands are a result of strong coupling between A2 and B1. The degeneration of π bands becomes parabolic near the K points in contrast to the linear shape in monolayer graphene. Intrinsic bilayer graphene remains a gapless semimetal. Bilayer graphene can be engineered to open a band gap by breaking the interlayer symmetry. This can be achieved by
applying a bias gate voltage, a magnetic field, external doping or a mechanical strain [38, 41, 88–91].

![Fig. 2.3. Electronic properties of bilayer graphene. — Schematics showing (a) the crystal structure of AB-stacked graphene. Atoms A1 and B1 are on the bottom layer and atoms A2, B2 are on the top layer. (b) The $\pi$ and $\pi^*$ bands of bilayer AB-stacked graphene. The band structure diagram is drawn along K$_\Gamma$K$_+$+. (K$_+$ and K are corresponding to K and K’ as mentioned in Section 2.1.1. The inset shows an enlarged picture of energy states near Dirac point K$_+$. Adapted with permission from Ref. [87]. © 2013 IOP Publishing.](image)

Multilayer graphene stacks have also attracted significant attentions in recent years. These stacks can occur in three inequivalent orientations in graphene (Figure 2.4). The stacking of the multilayer structure can follow ABABAB... (Bernal), ABCABC... (rhombohedral) or an arbitrary stacking order. The stacking orders have significant effects on the electronic band structure near the Dirac points. [32] The interlayer coupling can be easily tuned via changing the stacking order and/or the interlayer spacing, implying that opening a band gap could be more readily achieved. [92, 93] Multilayer graphene provides more flexibility with regard to band gap engineering [94, 95]. However, the physical properties of these multilayer structures can be more difficult to control compared to monolayer and bilayer graphene [30].
2.2 Manipulation of Electronic Properties of Graphene via Molecular Adsorption

In Section 2.1, it was established that the unique electronic properties of graphene are determined by the sublattice symmetry of the hexagonal structure. Despite fascinating properties such as massless dispersion and ultrahigh carrier mobility, the chemical inertness and gapless band structure of pristine graphene make it difficult to find direct applications in various fields, particularly for making advanced semiconducting devices [3, 46, 96]. The importance of graphene functionalization for realizing graphene’s general applicability was briefly addressed in Section 1.3. In this section, the theoretical background and progress of graphene functionalization by molecular adsorption will be reviewed.

Composed of chemically unsaturated sp$^2$ carbon atoms, graphene is a good candidate for surface engineering. The first documentation on interactions between graphene and adsorbed molecules appeared in 2003, which reported the induction of magnetism...
on graphene by C adatoms [97]. Since then, a large number of studies have been devoted to the topic, exploring interactions between graphene and metal adatoms, gas molecules or organic molecules [98–106]. These interactions between graphene and molecules are generally classified into two categories: substitutional addition and charge transfer adsorption [50]. The former refers to incorporation of foreign atoms in the honeycomb lattice of graphene via covalent bonds (i.e., graphene carbon atoms are converted from $sp^2$ to $sp^3$), while the latter achieves functionalization through charge transfer between graphene and adsorbates and usually does not disrupt the $sp^2$ hybridization of graphene carbon atoms [50, 59]. This review will focus on the details of charge transfer adsorption.

Charge transfer adsorption is also known as surface transfer doping. Doping occurs as a consequence of charge transfer between graphene and the adsorbate. The charge transfer is closely related with the energy level alignment between graphene and the adsorbate [102, 103, 107, 108]. If the highest occupied molecular orbital (HOMO) of the adsorbate is higher than the Fermi level of graphene, charge will transfer from the adsorbate to graphene. If the lowest unoccupied molecular orbital (LUMO) of the adsorbate is lower than the Fermi level of graphene, charge will transfer from graphene to the adsorbate. If the Fermi level of graphene is between the HOMO and LUMO of the adsorbate, the trend of charge transfer can be either way, depending on the molecular structure. Generally, molecules with strong electron withdrawing groups lead to p-type doping of graphene and molecules with strong electron donating groups lead to n-type doping. The p-type doping shifts the Fermi level to the valence band, while the n-type doping shifts the Fermi level to the conduction band (Figure 2.5) [75, 109–116]. In some cases, there is no direct charge transfer between graphene and the adsorbate, thereby the doping effect does not occur. Significant charge redistribution and rehybridization between orbitals of graphene and the adsorbate can still be observed. This kind of
molecule is suitable for non-destructive, reversible and tunable control of electronic structure of graphene [117–119].

![Schematic showing band structures of (a) pristine, (b) p-doped and (c) n-doped graphene. The position of the Fermi level (EF) is indicated.](image)

**Fig. 2.5. Doping of graphene.** — Schematic showing band structures of (a) pristine, (b) p-doped and (c) n-doped graphene. The position of the Fermi level ($E_F$) is indicated.

Charge redistribution is not necessarily accompanied by a band gap opening. The band gap can only be opened if the degree of charge redistribution is enough to make the underlying two sublattice points of graphene inequivalent [30, 50, 120]. The $\pi$ electrons of graphene may redistribute to other regions in or above the lattice, or directly transfer to adsorbed molecules. In both cases a band gap is opened if the local sublattice symmetry is broken [30, 57]. This is very difficult to achieve on monolayer graphene by weak physisorbed molecules. An alternative is to sandwich the monolayer graphene with molecules. This approach can successfully open a band gap but the magnitude is limited to under 50 meV [120, 121]. On the other hand, bilayer graphene is very effective in band gap opening upon molecular adsorption. The mechanism can be interpreted as the formation of a built-in electric field (Figure 2.6) [104, 122]. A strong built-in electric field will cause asymmetry between the two graphene layers that leads to a band gap opening. The interlayer symmetry of bilayer graphene is
much easier to break and tune than the intralayer symmetry of monolayer graphene [123].

Fig. 2.6. **Built-in electric field upon molecular adsorption.** — The charge redistribution resembles a built-in electric field as presented in (a) monolayer graphene and (b) bilayer graphene. The arrows indicate the direction of the built-in electric field.

The electronic properties of graphene can be further modified with a vertical external electric field. The external electric field can enhance or reduce the effect of the built-in electric field generated by the adsorbed molecules, depending on the direction of the applied field [104, 124–126]. Therefore the external electric field is a very useful tool for creating a sizeable and tunable band gap in graphene-based electronic devices [127].

Using graphene as an effective sensing tool is another motivation for studying the graphene-molecule system [57, 128]. Interactions between graphene and adsorbed molecules leave molecule-specific electronic fingerprints on the electronic structure of graphene, as well as the adsorbate. These features can be used to identify and select specific molecules [129–131]. A typical example is to apply graphene in biosensing and DNA sequencing [132–134]. Graphene offers relatively low cost, high surface area, multi-functionality compared to conventional materials [57]. In addition, graphene-molecule interactions can also be used to tune the catalytic activity in energy-related applications [135, 136].

In summary, graphene functionalization by molecular adsorption is a promising method for modifying the electronic properties of graphene. Interactions between
Chapter 2: Literature Review

graphene and adsorbed molecules can be utilized to tune the band structure of graphene for advanced electronic applications, as well as to affect the behavior of the adsorbate for potential sensing and energy storage applications. Designing and synthesizing molecules that can effectively tailor and tune the electronic properties of graphene will be a critical task in the near future.

2.3 Progress on Physisorption of Aromatic Molecules on Graphene

Physisorption of aromatic molecules on graphene is of particular interest in graphene functionalization. The aromatic rings of these organic molecules interact with the underlying graphene surface by means of π-π interactions. The cofacial π-π stacking between graphene and the aromatic molecules can effectively tailor the electronic structure of graphene via interfacial charge redistribution, while preserving many of graphene’s superior properties [57]. Extensive studies have been focused on interactions between graphene and various aromatic compounds, from both experimental and theoretical perspectives [57, 60, 137]. The recent progress on this topic is reviewed in this section.

2.3.1 Theoretical Results

Theoretical investigations, especially \textit{ab initio} calculations, have proven useful in providing an atomic-level understanding of the interactions in the graphene-molecule system, particularly the π-π interactions [60, 138–141]. Even so, the π-π interactions are still not well understood today. The π-π interactions are described as a kind of van der
Waals force that arises from the contact between $\pi$ electron clouds of two aromatic rings \[142, 143\]. The $\pi-\pi$ interactions lead to mainly attractive forces between aromatic rings and stabilize the molecular system \[60, 144\]. There could exist many high-symmetry adsorption configurations of aromatic molecules on graphene (an example for 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) is shown in Figure 2.7 (a)) \[104, 145\]. The planar contact between aromatic molecules and graphene is usually more stable than the edge-face contact (i.e., perpendicular contact) \[104, 146\]. This can be explained by the theory that the face-centered coupling is favored when the electron-rich aromatic ring and the electron-deficient aromatic ring are in contact. The electron-withdrawing or electron-donating functional groups in aromatic molecules tend to polarize the $\pi$ electron density away from or towards the aromatic ring, thereby leaving a relatively electron-deficient or electron-rich aromatic ring \[142\]. The strength of $\pi-\pi$ interactions can be controlled by replacing functional groups in the aromatic molecule, and/or tuning the molecular concentration \[107, 147–149\]. The molecular concentration is a critical factor when investigating the molecular self-assembly process on graphene. The structure of the graphene-molecule system is determined by the interplay of graphene-molecule interactions and molecule-molecule interactions (Figure 2.7 (b)) \[104, 109, 139, 150\].

The electronic structure of the graphene-molecule system is modified via orbital hybridization between graphene and adsorbed molecules \[57, 151\]. The adsorption of aromatic molecules leaves significant electronic fingerprints on the electronic states of graphene, as shown in Figure 2.8 \[152\]. The molecular electronic states appear in the density of states (DOS) of graphene as localized peaks (Figure 2.8 (a-b)). The molecular states in the vicinity of the Fermi level of graphene can significantly affect the linear dispersion relationship near the Dirac point. Therefore the energy level
alignment at the graphene-molecule interface is a critical factor for choosing appropriate molecules for functionalization [152–154]. The amount of charge redistribution at the interface is usually determined by the number of functional groups in aromatic molecules. Aromatic molecules with numerous strong electron-withdrawing or electron-donating functional groups can induce large amount of charge transfer (Figure 2.8 (c)) [119, 145, 148, 152, 153, 155–160]. Some aromatic molecules with strong graphene-molecule interactions can shift the Fermi level of graphene to the conduction or valence band, resulting in n-type doping or p-type doping of graphene [114, 116, 124, 161–163]. The adsorption of aromatic molecules can also modify the energy level of the vacuum, and thereby alter the work function of the system (Figure 2.8 (d)) [106, 164–167]. In terms of band gap opening, the intralayer symmetry of monolayer graphene is hard to break by weak $\pi$-$\pi$ interactions [120, 123]. Bilayer graphene is a better choice for band gap engineering by the adsorption of aromatic molecules. Significant charge redistribution upon adsorption of aromatic molecules can break the interlayer symmetry
between two graphene layers, thus opening a band gap \[123, 124, 149, 168, 169\].

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**Fig. 2.8.** **Electronic structure modification by adsorption of aromatic molecules.** — (a-d) show the electronic properties of graphene-hexaazatriphenylene–hexacarbonitrile (HATCN) system. (a) density of states (DOS) of the graphene-HATCN system, projected density of states (PDOS) of graphene and HATCN, and the local density of states (LDOS) of the localized peak near the Fermi level of graphene (LUPS). (b) DOS of a single HATCN molecule showing HOMO and LUMO. (c) Planar-averaged charge density difference \(\Delta \rho\) and amount of charge transfer \(\Delta Q\), and top view of charge density difference at 0.001 e\(\cdot\)Å\(^{-3}\). (d) electrostatic potential \(E(z)\). Adapted with permission from Ref. [152]. © 2013 American Chemical Society.

Theoretical calculations are also powerful tools to explore new functionalization strategies and assist in the design of experiments. Over the years, theoretical reports have proposed many novel strategies to achieve effective graphene functionalization and many of these strategies have been realized in experiments [124, 170–172]. These approaches include dual molecular doping combined with an external electric field.
(Figure 2.9), which introduces the possibility of achieving tunable hybridization in bilayer graphene while preserving properties of graphene via the molecular screening effect [124].

Fig. 2.9. **Dual molecular adsorption on bilayer graphene.** — Schematic model showing dual adsorption of bis(trifluoromethanesulfonyl)imide (TFSI) and benzyl viologen (BV) on opposite sides of bilayer graphene. Adapted with permission from Ref. [124]. © 2012 American Physical Society.

### 2.3.2 Experimental Results

Aromatic molecules can be deposited onto graphene by either the physical vapor deposition (PVD) in an ultrahigh vacuum (UHV) chamber, solution processing, or sublimating at high temperature in a protective atmosphere [115, 173–176]. The $\pi-\pi$ stacking between graphene and aromatic molecules makes the system stable against other chemical modifications. Intermolecular interactions play an important role in controlling the molecular configuration on the graphene surface. During the molecular assembly process, various molecular and environmental factors need to be precisely controlled to obtain a clean molecular layer on the graphene surface. These factors include temperature, molecular pressure and concentration, deposition rate and surface
Fig. 2.10. Experimental characterization of adsorption of aromatic molecules on graphene. — Adsorption of PTCDA on graphene. STM images of (a) PTCDA monolayer on the graphene surface and (b) molecular-resolution of PTCDA on graphene with the unit cell of PTCDA highlighted. A graphical presentation is given in Figure 2.7. Adapted with permission from Ref. [115]. © 2009 Nature Publishing Group.

defects on graphene [60, 177, 178]. The molecular adsorption geometry can be observed by advanced characterization techniques such as atomic force microscopy (AFM), scanning tunnelling microscopy (STM), Kelvin probe force microscopy (KPFM) and high-resolution transmission electron microscopy (HR-TEM) [60, 115, 123, 170, 179–181]. Figure 2.10 shows STM images of adsorption of PTCDA on graphene [115]. As can be seen in the figure, the herringbone unit cell of the self-assembled PTCDA layer is visible under high-resolution conditions at a temperature close to the ambient environment. This pilot study provided a general idea for deposition and growth of aromatic molecules. Subsequently, many other aromatic molecules are identified to form stable well-ordered structure at laboratory ambient conditions, which opens a promising route towards using graphene in organic semiconducting devices [75, 172, 182–185].

Graphene adsorbed by aromatic molecules has been used to fabricate prototypical electronic and sensing devices [55, 186–188]. Many previous studies were focused on studying the role of graphene in development of field effect transistors (FET), a
basic unit in integrated circuits [26, 31]. In recent years, using physisorbed aromatic molecules on graphene has become a common approach to modify the properties of graphene-based FETs [106, 189, 190]. Figure 2.11 (a) shows a schematic view of a graphene-based FET with adsorbed aromatic molecules on the graphene surface [106]. The performance of graphene-based FETs is greatly improved after the strong surface doping of aromatic molecules leads to a band gap opening. The doping effect of adsorbed molecules is measured as the shift of the charge neutrality point (the minimum in $I_{sd}$, representing the Dirac point in the graphene band structure) in the conductivity spectrum (Figure 2.11 (c)). The shift is sensitive to the molecular concentration, thereby revealing the potential of using graphene-based FETs as chemical sensors to detect small concentration of chemical compounds [191, 192].

In conclusion, the physisorption of aromatic molecules on graphene is a promising approach to tune the electronic properties of graphene, but there remain some challenges that need to be overcome. Firstly, the physical origin of graphene-molecule interactions is still not well understood, and this problem is critical for designing suitable aromatic molecules for functionalization. Moreover, current processing methods of depositing aromatic molecules on graphene can not be used for the large-scale production [60]. The current techniques need to be refined to achieve precise control of the molecular concentration and the adsorption pattern. With these issues resolved, the use of graphene functionalized with aromatic molecule will accelerate the development of next-generation electronic and sensing devices.
Fig. 2.11. **Graphene-based field effect transistor (FET) based on the adsorption of aromatic molecules.** — (a) schematic showing the cross-section through a graphene FET with adsorbed molecules on the graphene surface. (b) an optical profiler map of the top surface of a graphene channel and Ti / Au electrodes in FET devices. (c) gate voltage dependent source-drain current spectra of a graphene FET at constant source voltage as a function of melamine coverage. The inset figure shows the evolution of the conductivity minimum (the Dirac point) upon the adsorption of melamine. Adapted with permission from Ref. [106]. © 2015 The Royal Society of Chemistry.

### 2.4 Progress on Functionalized Graphene as Catalytic Support for Fuel Cells

The high-energy demands that will arise in the future calls for the development of sustainable energy technologies as an alternative of fossil fuels [193, 194]. Fuel cells are one of those approaches that convert the chemical energy of gaseous redox reactions into electric energy with low environmental impacts [195–199]. Noble metal particles (e.g., Pt, Pd and Ru) are widely used as catalysts for electrochemical reactions in the
Designing an optimal catalyst structure is important for improving the performance of fuel cells. The catalyst support is a critical component in the catalyst structure because it significantly affects the stability and lifetime of catalysts [205]. The support material should be able to stabilize the catalysts and prevent aggregation of metal particles. Moreover, it needs to be chemically inert and durable in the oxidative environment [206–209]. Carbon materials (e.g., carbon black and carbon nanotubes) are good candidates as they have a large specific surface area and excellent electrical conductivity to form strong bonding with metal particles, as well as good resistance to corrosion and degradation [210–216]. In recent years, graphene-based catalytic support has received considerable attentions as graphene-supported catalysts show better catalytic activity and stability over other carbon materials [205, 217–219]. In particular, graphene-supported catalysts have better tolerance to CO poisoning [217, 219–221]. CO poisoning is a critical issue in the operation of fuel cells. Even a trace amount of CO can significantly contaminate the noble metal particles and decrease the lifespan of catalysts. [222, 223]. Strong interactions between graphene and metal particles can effectively reduce the binding strength of gaseous molecules on the noble metal catalysts, thus making the catalysts less susceptible to CO poisoning [224–226].

The catalytic activity of noble metal particles is sensitive to surface conditions [226–230]. Graphene oxides (GO) and reduced graphene oxides (rGO) are more suitable choices than pristine graphene as catalytic support materials. The surface defects and attached functional groups on GO (e.g., epoxy, hydroxyl and carbonyl) act as anchor points to enhance the adsorption of noble metal catalysts on the surface [224, 225]. Previous theoretical calculations have shown that on pristine graphene, the aggregation of noble metal nanoparticles is much more energetically favorable than a uniform dispersion (Figure 2.12 (a)). The induced surface defects and functional groups can
Fig. 2.12. Theoretical investigations of noble metal nanoparticles on pristine graphene and GO sheets. — schematics showing adsorption of a Pt$_{13}$ cluster on (a) pristine graphene, (b) GO sheets at a small oxygen coverage (i.e., an epoxy group attached on the graphene surface) and (c) GO sheets at high oxygen coverages (only epoxy groups are considered in these coverages). Adapted with permission from Ref. [227]. © 2014 American Chemical Society.

significantly increase the diffusion barrier of noble metal nanoparticles and anchor the nanoparticles near the defective sites (Figure 2.12 (b) and (c)). The anchoring effects can be explained as a consequence of the hybridization between d orbitals of the noble metal and orbitals of graphene, and can be enhanced by tuning the concentration or configuration of defects [227, 231–237].

In practice, the graphene-supported noble metal catalysts are synthesized by means of solution processing, hydrothermal evaporation or electrodeposition [53, 205, 238].
The production process based on GO is more cost effective than using other carbon nanomaterials. Many previous experimental investigations reported that these noble metal catalysts dispersed on rGO can achieve uniform distribution on the substrate and the average diameter of the nanoparticles can reach around 2 nm (Figure 2.13) [217]. As a result, the catalytic activity of these uniform distributed nanoparticles are significantly improved [217, 219, 239–242]. However, precise control over the morphology of the functionalized graphene sheet is still not available for large-scale production. In addition, there still lacks knowledge of the mechanisms behind the interactions between functionalized graphene and noble metal particles [205, 238]. These challenges need to be resolved before graphene-based catalytic support materials find a competitive place in the commercial market.
Fig. 2.13. Experimental characterization of noble metal nanoparticles / functionalized graphene sheet. — (a) TEM image of functionalized graphene sheets. (b) High energy resolution photoemission spectra of the C 1s region in functionalized graphene sheets. (c) TEM images of Pt-functionalized graphene sheet. (d) Pt nanoparticle size distribution of Pt-functionalized graphene sheet. Adapted with permission from Ref. [217]. © 2009 Elsevier.
2.5 Progress on Graphene for DNA Sequencing and Biosensing

Biological science and engineering have always been at the center stage of scientific research. Future biomedical studies will require advanced tools for imaging, detection, diagnosis and drug delivery purposes. The unique properties of graphene have shown vast potentials in these applications [3, 17]. In the field of DNA sequencing and biosensing, graphene-based nanodevices offer great advantages over conventional methods in terms of sensitivity, selectivity, speed and cost [54, 243]. Graphene functionalization plays a critical role in designing novel devices for biomolecule detection. rGO, graphene nanoribbons and graphene nanopores have been used in these devices to achieve fast and reliable biomolecule differentiation [133, 134, 244–251]. Figure 2.14 shows an example of using a graphene nanoribbon as a nanofluidic channel to detect single stranded DNA (ssDNA) [134]. This device measures the conductance changes of a graphene nanoribbon that arise from the $\pi-\pi$ interaction between the nucleobase and the surface (highlighted in Figure 2.14 (b)). Each nucleobase leaves distinct electronic fingerprints on graphene and the single-base resolution required for nucleobase sequencing can therefore be achieved.

There have been numerous studies on interactions between graphene and double stranded DNA (dsDNA), single stranded DNA (ssDNA), nucleotides and nucleobases [159, 164, 252–261]. Interactions between graphene and nucleobases are of particular importance for a good understanding of the base-specific information obtained from sensing devices. Recently, Dotschuk et al. demonstrated a systematic experimental study on the coverage-dependence behavior of interactions between DNA nucleobases and graphene [164]. The measurement of electric transport properties (Figure 2.15) showed distinct electronic signals from each DNA nucleobase and significant different
Fig. 2.14. Fast DNA sequencing using a graphene-based device. — Schematics showing (a) nanodevices with an armchair graphene nanoribbon (AGNR) used for ssDNA sequencing (b) a snapshot highlighting the contact between individual nucleobases and a graphene nanoribbon (d, stacking distance, \( \theta \), tilt angle). Adapted with permission from Ref. [134]. © 2011 Nature Publishing Group.

trends as the molecular coverage increases. Local changes in the adsorption geometry due to the interplay between graphene-base interaction and intermolecular interaction can effectively affect the accuracy of molecular detection. This work enables a new direction for designing future DNA sequencing and sensing devices. These future devices need to carefully optimize the contact between biomolecules and graphene for improving sensitivity and selectivity. Furthermore, this work sets out the motivation of an in-depth view from the theoretical perspective to examine the interactions between
nucleobases and graphene tuned by the molecular coverage.

![Fig. 2.15. Coverage-dependence of electronic modifications by adsorbed nucleobase on graphene.](image)

Fig. 2.15. **Coverage-dependence of electronic modifications by adsorbed nucleobase on graphene.** — Schematic showing charge carrier density changes ($\Delta n$) of graphene induced by the adsorption of DNA nucleobases as a function of molecular coverage. Adapted with permission from Ref. [164]. © 2015 Nature Publishing Group.

### 2.6 Summary and Conclusions

It has only been a decade since the discovery of graphene and since then graphene-based nanotechnology has dominated the direction of materials research. It is evident from this brief literature review that properties of graphene can surpass those of many conventional materials, therefore making graphene a promising candidate in a variety of applications, such as electronic, catalytic and biosensing. Graphene functionalization is an effective approach to improve the performance of graphene-based devices. This literature review presents two research directions that can be investigated using theoretical calculations: searching for optimal adsorbates for graphene functionalization, and finding a novel setup for graphene functionalization by molecular adsorption. These two directions provide the motivation for the work presented in this thesis.
Chapter 3

Methodology

This chapter presents a general introduction to computational methods and analytical tools used throughout this thesis. It will focus on the theoretical background of density functional theory (DFT), as well as DFT calculation processes. In addition, details of electronic analysis will also be discussed. Finally, details of computational resources will be briefly described.

3.1 Introduction to Density Functional Theory

3.1.1 Theoretical Background

The advance of physical sciences and engineering requires a good understanding of the properties of materials at the atomic level [8, 262, 263]. DFT is a quantum mechanical approach for solving the Schrödinger equation and determining the electronic properties of materials. DFT expresses the complex many-body Schrödinger equation in terms of the electron probability density [264–266]. Although this restricts the scope...
of DFT to only the ground state, DFT has proven its computational effectiveness and high accuracy in describing the electronic structure of materials in many fields and has been the dominant method for quantum mechanical simulations for the past three decades [267–271]. The following will briefly describe the basic theory behind the establishment of DFT.

DFT is a practical response to a fundamental problem in physics and chemistry: how to describe the electronic state of a many-particle system. This problem can be described using the Schrödinger equation. The time variant form of the Schrödinger equation is written as: \( \mathcal{H}\Psi = E\Psi \), where \( \mathcal{H} \) is the Hamiltonian operator, \( \Psi \) is the wave function of the many-particle system (also known as the eigenfunction) and \( E \) is the eigenvalue representing the total energy of the system [272, 273]. For a many-particle system, the wave function should be expanded to include the kinetic energy (both the nuclear and electron kinetic energy), as well as the interaction between them (electron-electron, nuclear-nuclear and electron-nuclear). However, the nuclear-related terms can be neglected under the Born-Oppenheimer approximation, which assumes that electrons move in a field of static nuclei because the mass of nuclei is much larger than that of electrons [274]. The many-body Schrödinger equation is then rewritten in terms of an N-electron wave function. The Hartree method further simplifies the problem by converting the equation to be expressed as products of one-electron wave functions [266, 275]. However, even if we use the wave function of an individual electron, the problem remains complicated because of an insufficient description of electron-electron interactions.

An alternative to solve the problem is to relate the wave function to a similar property: the density of electrons at a particular position in space (electron density). This brings out the theoretical foundation of DFT [264]. Kohn and Hohenberg first
proposed the DFT theorems and the derivation of a set of suitable DFT equations was obtained by Kohn and Sham in the 1960s [276]. The DFT theorems point out that the ground-state Schrödinger equation can be expressed as a functional of the electron charge density. This reduced the number of dimensions involved in finding the solution of the Schrödinger equation from 3N to 3, because the electron density at a certain point \( \rho(\mathbf{r}) \) only involves three spatial variables. The DFT formalism is completed by the derivation of the Kohn-Sham equation, which uses the Hartree form of the Schrödinger equation for many-body system and incorporates electron density functionals, expressed as [264]:

\[
\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \Psi_i(\mathbf{r}) = \epsilon_i \Psi_i(\mathbf{r}) \quad (3.1)
\]

where the first three terms cover all contributions to the electron wave function from electron kinetic energy, Coulomb interactions resulting from interaction between pairs of electrons as well as between the electron and nucleus. The term \( V_{XC}(\mathbf{r}) \) is called the exchange-correlation potential and includes contributions from all other quantum mechanical interactions.

The definition of the exchange-correlation functional is a critical issue in DFT. One approach is based on the local electronic density, called the local density approximation (LDA) [277]. The LDA is quite useful in constructing the exchange-correlation functional for bulk solids, but it is not as good for molecules and atoms, where the electron density is usually not sufficiently uniform in molecules and atoms. Another common approach is the generalized gradient approximation (GGA) [278], which considers both local electron density and the gradient of electron density. The GGA should be more accurate than the LDA as it includes more physical information, but there are some exceptions. GGA can be further enhanced by containing more physical information,
which known as meta-GGA and hyper-GGA [279, 280].

Dispersion interactions (van der Waals (vdW) interactions) play an important role in weakly bonded systems [264, 281]. Conventional DFT methods (e.g., LDA and GGA) are not reliable in describing long-range electron correlations [282, 283]. To overcome this, many correction schemes have been proposed. A semi-empirical model developed by Grimme (DFT-D2) is used throughout this thesis to account for these interactions [284–286]. This model adds a semi-empirical potential to the conventional DFT. The DFT-D2 has been shown to fit experimental observations much better than conventional DFT methods [253, 254].

3.1.2 Key Elements in DFT Calculations

3.1.2.1 Periodic Boundary Condition and Supercell

The DFT calculation is a useful tool to predict the crystal structure of materials. Crystals are presented in the DFT calculations by applying a periodic condition on the edges of the simulation box, known as the periodic boundary condition [262, 287]. The simulation box is called the supercell. The supercell is surrounded by its duplicated images, forming a system with an infinite domain size. Particles in the supercell act with each other as well as with particles in adjacent images. The position of a particle in a supercell is defined by lattice translation vectors:

\[ \mathbf{r} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \]

(3.2)

where \( \mathbf{a}_1, \mathbf{a}_2, \) and \( \mathbf{a}_3 \) are three lattice translation vectors. The potential of electrons in crystals can also be expressed by a periodic function, i.e \( V(\mathbf{r}) = V(\mathbf{r} + \mathbf{T}) \), where \( \mathbf{T} = \mathbf{r} \) when \( n_1, n_2 \) and \( n_3 \) are any integers. Bloch derived that the solution to the
Schrödinger equation for electrons with periodic potential has the form:

$$\Psi_k(r) = u_k(r) \exp(i \mathbf{k} \cdot \mathbf{r}),$$ (3.3)

which is known as Bloch’s theorem [288]. Bloch’s theorem implies that the electron wave function of a crystal can be solved in a supercell. Bloch’s theorem is the theoretical foundation of applying DFT to calculate the electronic structure of materials.

### 3.1.2.2 Reciprocal Space, \( k \) points and Brillouin Zone

As described in Section 3.1.2.1, Bloch’s theorem paves the way for DFT to express the electronic structure of a crystal using a supercell. Note that the expression of Bloch’s theorem presents the plane wave as a Fourier expansion \( \exp(i \mathbf{k} \cdot \mathbf{r}) \). The \( \mathbf{k} \) vector can be conveniently described using a reciprocal space, or \( \mathbf{k} \) space. The calculation of the electron wave function can be significantly affected by how we map the reciprocal space. Reciprocal lattice vectors are defined as:

$$b_1 = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}, \quad b_2 = \frac{\mathbf{a}_1 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}, \quad b_3 = \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3},$$ (3.4)

where \( \mathbf{a}_1 \), \( \mathbf{a}_2 \) and \( \mathbf{a}_3 \) are lattice vectors in the real space.

In practical DFT calculations, handling the integrals in the reciprocal space is critical to achieve a convergent result. A convergent result means the result has reliable physical information and is comparable to experimental observations. Integrals in the reciprocal space are obtained by sampling \( \mathbf{k} \) points in the Brillouin zone, which is defined as the Wigner-Seitz unit cell in the reciprocal space [281].

The number of sampled \( \mathbf{k} \) points should be sufficient to obtain the rational electronic structure of materials. The most common sampling method used was developed
Chapter 3: Methodology

3.1.2.3 Energy Cutoffs

The cutoff energy for plane waves ($E_{\text{cut}}$) is another critical parameter in DFT calculations. The Fourier expansion of the plane wave $\exp(ik \cdot r)$ is an infinite sum and in practice is truncated below a specific kinetic energy [264]. The cutoff energy also needs to be appropriately chosen to achieve a balance between convergence and computational efficiency.

3.1.3 Dissection of Practical DFT Calculation Processes

Figure 3.1 presents a simplified view of the practical DFT calculation processes. Initially, the molecular geometry must be carefully prepared. Convergence tests for the k-point grid and the cutoff energy need to be done beforehand. Convergence tests examine the energy of a system as a function of the k-point density or the cutoff energy. An appropriate k-point grid or cutoff energy should be selected above which the energy of the molecular system converges. After initial steps, further calculations are made on the molecular structure to check if the electron density and total energy converges, and that forces acting on atoms and axial stresses reach certain criteria. If not, the structure is slightly altered and resent for another iteration. This process is called the structural relaxation. After the relaxation is finished, the structure is sent for a self-consistent loop to obtain accurate electron density and other related data. The DFT
Set up initial parameters (geometries, potentials of each element and calculation algorithms).

Solve the Kohn-Sham equation.

Calculate the electron density and total energy of the system, and check if the electron density and total energy converges.

Check if the geometry is stable (forces act on atoms and axial stresses are minimum)

Run a self-consistent loop to obtain accurate electron density of the system and other properties.

Output

Set up new structural parameters.

Fig. 3.1. Practical DFT calculation processes. — Schematic showing a flow chart of how to obtain electronic structure of materials using DFT.

methods as implemented in Vienna Ab Initio Simulation Package (VASP) are used in the work presented in this thesis [291].
3.2 Characterization and Data Analysis

DFT calculations can yield many useful results including structural, energetic, electrochemical and mechanical properties of materials. In the following how the molecular structure is prepared and how the properties of materials are analyzed in DFT calculations will be briefly introduced.

3.2.1 Structural and Energetic Parameters

3.2.1.1 Model Construction

The graphene-molecule system is constructed based on small programs written in MATLAB programing language. These initial structures must be carefully examined using visualization tools such as VESTA before performing the structural relaxation [292], otherwise the relaxed structure may be trapped in a local energy minima (i.e., not fully energetically optimized). This issue is critical when the different adsorption configurations of molecules on graphene are considered.

3.2.1.2 Adsorption and Formation Energy

Molecules attached to the surface via van der Waals interactions (i.e., physisorption) or forming covalent bonds (i.e., chemisorption). The adsorption energy ($E_{ad}$) is defined to quantify how strong the adsorbed molecule prefers to bond with the surface:

$$E_{ad} = E_{surf+mol} - E_{surf} - E_{mol},$$

(3.5)
where $E_{\text{surf+mol}}$, $E_{\text{surf}}$ and $E_{\text{mol}}$ are referred to as the energy of the surface-adsorbate system, the relaxed isolated surface and the relaxed isolated adsorbed molecule contained in the surface environment, respectively. A negative value of $E_{\text{ads}}$ means the adsorption process is exothermic. The chemisorption usually leads to larger negative adsorption energy values compared with the physisorption [265].

The formation energy ($E_{\text{form}}$) is used to characterize how strong the surface-adsorbate system can occur starting from the isolated molecules/surface in their standard state. The definition of the formation energy is:

$$E_{\text{form}} = E_{\text{surf+mol}} - E_{\text{surf,s}} - E_{\text{mol,s}},$$

(3.6)

where $E_{\text{surf+mol}}$, $E_{\text{surf,s}}$ and $E_{\text{mol,s}}$ are referred as the energy of the surface-adsorbate system, the isolated surface in the vacuum and the isolated molecule in the vacuum (neglecting any intermolecular interactions), respectively. A negative value of $E_{\text{form}}$ signifies the thermodynamic stability of the surface-adsorbate system with respect to its individual constituents.

### 3.2.2 Electronic Analysis

#### 3.2.2.1 Density of States and Band Structure Diagrams

The electron density of states (DOS) is defined as the concentration of available electronic states per energy interval. The DOS information is obtained via the self-consistent calculation as mentioned in Section 3.1.3. To obtain this information for the relevant range in VASP, the energy range and interval can be specified using NEDOS, EMIN and EMAX tag. The number of sampled energy points (NEDOS) then needs to
be sufficient to resolve localized peaks properly. In practice, the energy range (EMIN and EMAX) is usually modified to focus on the DOS near the Fermi level [293].

The DOS is calculated on all \( \mathbf{k} \) points in the reciprocal space. A more detailed view of the electronic structure can be observed by examining the band structure diagram. The band structure diagram is defined as the energetic dispersion of the extended wave functions (known as energy bands) along specific \( \mathbf{k} \) points. These specific \( \mathbf{k} \) points are usually selected around the high symmetry points in the Brillouin zone. In practice, the band structure diagram is plotted along a series of lines forming a loop starting and ending at the same point.

### 3.2.2.2 Bader Charge Analysis

Bader charge analysis is used to quantify the charge redistribution in the substrate-adsorbate system. A code developed by Henkelman et al. is used to calculate the Bader decomposition of charge density [294]. The Bader algorithm decomposes the electron charge density into atomic regions separated by surfaces where the gradient of charge density is minimum [295].

### 3.2.2.3 Charge Density Difference

Charge density difference calculations are used to visualize and analyze the charge redistribution in the surface-adsorbate system. It is defined as:

\[
\Delta \rho = \rho_{\text{surf}+\text{mol}} - \rho_{\text{surf}} - \rho_{\text{mol}},
\]

where \( \rho_{\text{surf}+\text{mol}} \), \( \rho_{\text{surf}} \) and \( \rho_{\text{mol}} \) are the electron charge density of the surface-adsorbate system, isolated surface and isolated adsorbate, respectively. Note that the isolated
structures need to remain in their adsorbed state (i.e., no additional structural relaxation is needed.) The output from charge density difference calculations can be visualized to display regions with significant charge accumulation/depletion upon adsorption of molecules on the surface.

3.2.2.4 Work Function and Dipole moments

The work function \((W)\) is the minimum energy required to move an electron from the solid to a point in the vacuum. It is obtained by calculating the local electrostatic potential. The output of this calculation gives the energy of vacuum, and the work function is calculated as:

\[
W = E_{\text{vac}} - E_F,
\]

where \(E_{\text{vac}}\) and \(E_F\) are the energy of the vacuum and the Fermi level, respectively. The work function change of the substrate upon adsorption is often correlated with the dipole moment of adsorbed molecules [296]. The molecular dipole moment is derived based on partial charges obtained from Bader charge analysis.

3.3 Computational Resources

DFT calculations consume significant computational resources, as shown in Table 3.1. These calculations are usually performed at high performance computational facilities. Throughout this Ph.D., the following computational facilities were used:

- Monash Sun Grid (MSG), Monash University, Clayton, Victoria, Australia.
- National Computational Infrastructure (NCI), Canberra, Australian Capital Territory, Australia.
Table 3.1. **Computational cost of DFT calculations.** — The case of adsorption of hexacene and perfluorohexacene on graphene is used as an example to show the consumption of resources in a computational project.

<table>
<thead>
<tr>
<th>Hexacene adsorption project</th>
<th>Structural relaxation</th>
<th>Single-point self-consistent calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of CPU cores</td>
<td>64</td>
<td>256</td>
</tr>
<tr>
<td>Requested memory (GB)</td>
<td>128</td>
<td>512</td>
</tr>
<tr>
<td>Typical running time for a convergent calculation (hour)</td>
<td>20</td>
<td>8</td>
</tr>
<tr>
<td>Estimated total committed CPU hours (hour)</td>
<td>30000</td>
<td>300000</td>
</tr>
<tr>
<td>Estimated total disk occupied (GB)</td>
<td>40</td>
<td>3000</td>
</tr>
</tbody>
</table>

- Multi-modal Australian ScienceS Imaging and Visualisation Environment (MAS-SIVE), Clayton, Victoria, Australia.
- Pawsey Super Computing Centre, Perth, Western Australia, Australia.
- High Performance Computing Facility, Xi’an Jiaotong University, Xi’an, China.

Overall, this computational project requires a fundamental understanding of physics and chemistry behind these computational methods. These results will present a clear picture of the properties of materials at the atomic level.
Chapter 4

Tunable Hybridization Between Electronic States of Graphene and Physisorbed Hexacene

4.1 Foreward

The research presented in this chapter is published as:


The copy of the published paper is attached in appendix A.
PART B: Suggested Declaration for Thesis Chapter

[This declaration to be completed for each conjointly authored publication and to be placed at the start of the thesis chapter in which the publication appears.]

Monash University

Declaration for Thesis Chapter [Chapter 4]

Declaration by candidate

In the case of Chapter [insert chapter number], the nature and extent of my contribution to the work was the following:

<table>
<thead>
<tr>
<th>Nature of contribution</th>
<th>Extent of contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I am the first author for this published work. Carried out all the research activities and wrote the manuscript.</td>
<td>100</td>
</tr>
</tbody>
</table>

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

<table>
<thead>
<tr>
<th>Name</th>
<th>Nature of contribution</th>
<th>Extent of contribution (%) for student co-authors only</th>
</tr>
</thead>
<tbody>
<tr>
<td>J. Cervenka</td>
<td>General advice, discussion and editing the manuscript</td>
<td>Not a student</td>
</tr>
<tr>
<td>N. V. Medhekar</td>
<td>Conceptualization of the idea, editing the manuscript, overseeing all aspects of this research</td>
<td>Not a student</td>
</tr>
</tbody>
</table>

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate’s and co-authors’ contributions to this work*.

<table>
<thead>
<tr>
<th>Candidate’s Signature</th>
<th>Date</th>
<th>Main Supervisor’s Signature</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Note: Where the responsible author is not the candidate’s main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.
Chapter 4: Adsorption of Hexacene on Bilayer Graphene

4.2 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 [20]. 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 [25, 26, 297]. However, the development of graphene-based electronic devices is primarily hindered by the absence of an intrinsic band gap in its electronic structure [17]. Although various approaches for tailoring the electronic structure of graphene have been pursued in recent years [50, 51, 60, 298], 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 [66, 299]. While this strategy can effectively induce the band gap, it also suffers from carrier scattering due to edge imperfections [300]. 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 $sp^3$ [30]. While such covalent functionalization successfully alters the electronic properties of graphene, it also leads to a severe degradation of its transport properties [59]. 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 [96, 301].

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 [60, 302]. 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 [50, 51]. 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. [151? ] Recent studies have suggested that in graphene physisorbed with small molecules such as NO$_2$ and NH$_3$, the application of a transverse external electric field can further enhance the tunability of the electronic structure of graphene by affecting the charge redistribution. [41, 104, 123, 170, 303, 304] Among the organic compounds that are amenable to physisorption on graphene, aromatic molecules are of particular interest [60, 120]. The face-centered parallel stacking of aromatic molecules on graphene surface can lead to a stable hybrid system via van der Waals (vdW) interactions [?], while the enhanced π-π electron interaction is expected to influence the electronic structure of graphene [60]. 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. [75, 123, 149, 157, 305]. This can allow a vertical integration of graphene with physisorbed organic molecules with tunable transport characteristics such as charge injection barriers [108]. 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 [104, 124]. As a result, the charge carrier mobility of graphene degrades, thus limiting the switching capability of graphene-based semiconducting devices [124, 152]. Therefore, identification of suitable organic molecules for non-covalent functionalization of graphene still remains an open challenge for controllable modification of its electronic properties.
Chapter 4: Adsorption of Hexacene on Bilayer Graphene

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 \(\pi\) electrons of graphene and thus influence its electronic structure. \([306]\). Furthermore, it has been shown that the edges of hexacene can be readily functionalized with chemical groups with widely varying electron or hole affinity. \([307]\). Recently, Watanabe et al. reported a successful way to synthesize hexacene that can remain stable up to 300 °C in dark conditions \([308]\). Moreover, organic field effect transistors (OFET) devices made of hexacene have demonstrated a highest charge carrier mobility ever reported for organic semiconductors \([308]\). 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 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 \(\pi-\pi^*\) 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.
4.3 Computational Details

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 \textit{Ab Initio} Simulation Package [291]. We used the generalized gradient approximation of the Perdew-Burke-Ernzerhof form for the electron exchange-correlation functional [278]. The core and valence electrons were treated using projector augmented wave (PAW) scheme [309] 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 [282], we used a Grimme’s semi-empirical functional [286] 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 [310]. We used a periodic $8 \times 4$ 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 $9.846 \times 10^{-11}$ mol/cm$^2$. 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 [177, 311, 312]. 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 [313]. Finally, for accurate calculations of the electronic structures, we used a fine $6 \times 12 \times 1$ \Gamma-centred grid for sampling the
First, we individually examined the adsorption of hexacene and perfluorohexacene on bilayer graphene using a single-molecular adsorption configuration as shown in Fig. 4.1(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 [77]. We also considered the simultaneous adsorption of hexacene and perfluorohexacene in a dual-molecular configuration shown in Fig. 4.1(b). Finally, the influence of external electric fields normal to the plane of graphene was investigated by introducing dipolar sheets at the center of supercells [314].

Fig. 4.1. Simulation setup for adsorption of hexacene and perfluorohexacene on graphene. — 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.
4.4 Results and Discussions

4.4.1 Electronic Structure of Hexacene and Perfluorohexacene

We first obtained the optimized geometries of hexacene and perfluorohexacene molecules and calculated their electronic structure. The relaxed geometries of hexacene and perfluorohexacene are shown in Fig. 4.2(a). The average C-H bond length for hexacene and the average C-F bond length for perfluorohexacene were calculated to be 1.09 Å and 1.35 Å respectively. These bond lengths are in close agreement with previous structural calculations reported by Kadantsev et al. [306]. Figure 4.2(b) depicts an energy level diagram showing the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of hexacene and perfluorohexacene with respect to the position of the Fermi level of graphene. The HOMO-LUMO band gaps of hexacene and perfluorohexacene are narrow, namely, 0.80 eV and 0.59 eV, respectively. The calculated electronic band gap of these molecules is smaller than the experimentally determined band gaps by 0.5 eV – 0.6 eV due to a systematic underestimation of band gap values of semiconducting materials obtained by DFT calculations employing the generalized gradient approximation [308, 315, 316].

Next we obtained optimized ground state configurations of hexacene and perfluorohexacene adsorbed on bilayer graphene in single as well as dual-molecular configurations shown in Fig.4.1. In each case, the adsorption energy is calculated as $\Delta E = E_{\text{graphene/molecule}} - E_{\text{graphene}} - E_{\text{molecule}}$, where $E_{\text{graphene/molecule}}$ is the total energy of the fully-relaxed graphene-molecule supercell, while $E_{\text{graphene}}$ and $E_{\text{molecule}}$ is the energy of bilayer graphene and isolated molecules in the same supercell, respectively. A negative value of the adsorption energy indicates an exothermic, thermodynamically
Fig. 4.2. **Electronic structure of hexacene and perfluorohexacene.** — (a) Relaxed geometries of hexacene and perfluorohexacene. The C-C, C-H and C-F bond lengths (in Å) are indicated. (b) The energy level diagram of the band alignment between the Fermi level of bilayer graphene, and the HOMO and LUMO of hexacene and perfluorohexacene (in eV). The energy of vacuum is regarded as zero.

Favorable adsorption. The values for adsorption energy and the average adsorption distance from the nearest graphene layer for each configuration are summarized in Table 4.1. We find that the adsorption of both hexacene and perfluorohexacene on bilayer graphene is thermodynamically favorable in all configurations considered. The resulting adsorption distance of the molecules from graphene is close to the interlayer distance between graphene layers (~3.23 Å), indicating that graphene and the molecules are bound by weak van der Waals dispersion interactions. The adsorption distance and the adsorption energies are also nearly unaffected by the change of stacking sequence from ABC to ABA, also suggesting that the molecule-bilayer graphene interactions are
largely confined between the molecule and the adjacent graphene layer.

Table 4.1. **Adsorption energy and adsorption distance of hexacene and perfluorohexacene.** — Adsorption energy and the average adsorption distance for monolayer coverage of hexacene and perfluorohexacene on bilayer graphene in single- and dual-molecular adsorption configurations.

<table>
<thead>
<tr>
<th>Stacking sequence</th>
<th>Adsorption energy (eV)</th>
<th>Average adsorption distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexacene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ABA</td>
<td>-1.756</td>
<td>3.19</td>
</tr>
<tr>
<td>ABC</td>
<td>-1.751</td>
<td>3.19</td>
</tr>
<tr>
<td>Perfluorohexacene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ABA</td>
<td>-2.246</td>
<td>3.16</td>
</tr>
<tr>
<td>ABC</td>
<td>-2.239</td>
<td>3.16</td>
</tr>
<tr>
<td>Dual-molecular adsorption (hexacene+perfluoroxacene)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ABAB</td>
<td>-4.015</td>
<td>3.20 (hexacene)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.17 (perfluorohexacene)</td>
</tr>
<tr>
<td>ABCA</td>
<td>-4.005</td>
<td>3.19 (hexacene)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.16 (perfluorohexacene)</td>
</tr>
</tbody>
</table>

Our results show that perfluorohexacene binds more strongly to bilayer graphene than hexacene (adsorption energy of -2.25 eV vs. -1.76 eV) in a single-molecular adsorption configuration. The stronger binding of perfluorohexacene correlates with a higher electron affinity and chemical reactivity of perfluorohexacene relative to hexacene. Finally, in the case of simultaneous, dual-molecular adsorption of hexacene and perfluorohexacene on bilayer graphene, the adsorption energy of the total hexacene and perfluorohexacene complex is nearly equal to the sum of the adsorption energies of individual molecules in single-molecular adsorption. This observation suggests that the adsorption system can be relatively easily adjusted from a single-molecular configuration to a dual-molecular configuration, or vice versa, at a very low energy cost. The adsorption distances of hexacene and perfluorohexacene in dual-molecular adsorption are found to be slightly larger than for the single-molecular adsorption cases.
Chapter 4: Adsorption of Hexacene on Bilayer Graphene

4.4.2 Electronic Structure of Bilayer Graphene upon Adsorption

Following the structural optimisation, we next investigate the electronic properties of bilayer graphene upon molecular adsorption. Our results show that the molecular stacking sequence did not have any effect on the density of states curves. Consequently, Fig. 4.3 presents the partial density of states (PDOS) for bilayer graphene with single-molecular adsorption with ABA stacking and for dual-molecular adsorption with ABCA stacking sequence. We find that the physisorbed hexacene and perfluorohexacene has a negligible effect on the $\pi$ states of bilayer graphene in the vicinity of the Dirac point. No shift in the Fermi level of bilayer graphene was observed upon adsorption of hexacene or perfluorohexacene. The magnitude of the band gap induced in bilayer graphene upon adsorption of these molecules is also negligible (3 meV and 5 meV for hexacene and perfluorohexacene, respectively). These observations point to a weak interaction between graphene and the molecules. Nevertheless, the low lying highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of adsorbed molecules hybridize with $\pi/\pi^*$ states of graphene, giving rise to two localized states near the Fermi level of bilayer graphene (see Fig. 4.3(a-d)). These states were found in PDOS of bilayer graphene at -0.18 eV and 0.61 eV after the adsorption of hexacene and at -0.43 eV and 0.18 eV after the adsorption of perfluorohexacene. The position of HOMO and LUMO of hexacene and perfluorohexacene states is slightly altered in comparison to that of isolated molecules (refer Fig. 4.3 (b)). To gain further insight into the localized states in graphene, we also plotted the corresponding partial charge densities by integrating the charge density in an energy range $\pm0.02$ eV around the localized peaks. The partial charge density plots (Fig. 4.3(e,f)) show the shape of HOMO/LUMO of hexacene/perfluorohexacene, and present the signature of hybridization between graphene
Chapter 4: Adsorption of Hexacene on Bilayer Graphene

and the adsorbed molecules. It is evident that the induced localized states in graphene are located on the nearest carbon atoms of the top graphene layer. The presence of these hybridized states near the Dirac point of graphene implies that both electrons and holes can be injected from graphene to molecules at a relative low energy cost. In dual-molecular adsorption configuration (Fig. 4.3 (d)), the PDOS can be regarded as a superposition of the energy states from the single-molecular adsorption on graphene. Moreover, we observe that a 8 meV band gap is opened, equal to the sum of the band gap values of individual molecules. This indicates that the interaction between bilayer graphene and acene molecules in dual-molecular configuration is essentially governed by the interaction of a single graphene layer with the adjacent adsorbed molecule.

In order to further assess the influence of molecular adsorption on the electronic properties of graphene, we calculated the charge density difference as defined by $\Delta \rho = \rho_{\text{graphene/molecule}} - \rho_{\text{graphene}} - \rho_{\text{molecule}}$, where $\rho_{\text{graphene/molecule}}$, $\rho_{\text{graphene}}$ and $\rho_{\text{molecule}}$ are the electronic charge densities of the adsorbed system, isolated graphene and the molecule, respectively. With this definition, a positive value of $\Delta \rho$ indicates an accumulation of electronic charge and a negative value indicates a charge depletion. The distribution of the charge density difference for single-molecular adsorption of hexacene and perfluorohexacene is shown in Fig. 4.4. In the case of adsorption of hexacene on bilayer graphene (Fig. 4.4 (a)), the charges are depleted from the region 0.6 Å–1.0 Å above the top graphene layer and accumulated close to hexacene in the region 2.6 Å–2.8 Å above the graphene layer. This charge redistribution primarily arises from the electrostatic interaction between the aromatic rings of hexacene and graphene—the interaction between hydrogen atoms of hexacene and carbon atoms of graphene or hexacene is found to be negligible [317]. Overall, the interaction between hexacene and bilayer graphene is not strong enough to lead to a significant direct charge transfer between graphene and hexacene, but only to a charge redistribution on carbon atoms of the molecule and
Fig. 4.3. **Density of states of graphene upon adsorption of hexacene and perfluorohexacene.** — (a) Total density of states of a pristine bilayer graphene. (b-d) Partial densities of states (PDOS) of bilayer graphene upon single-molecular adsorption of hexacene (b), single-molecular adsorption of perfluorohexacene (c), and dual-molecular adsorption of hexacene and perfluorohexacene (d). In all cases, the molecular concentration is $9.85 \times 10^{-11}$ mol/cm$^2$ and represents monolayer coverage. $(\text{Hex})_H$, $(\text{Hex})_L$, and $(\text{P-Hex})_H$, $(\text{P-Hex})_L$, denote the localized states induced by hybridization with HOMO and LUMO of hexacene, and HOMO and LUMO of perfluorohexacene, respectively. The Fermi level is set to zero in each case. (e-f) Partial charge density plots for the localized states in PDOS of bilayer graphene upon single-molecular adsorption of hexacene (e) and single-molecular adsorption of perfluorohexacene (f). The isosurface level is set to 0.0003 e/Å$^3$.

the nearest graphene layer. In contrast to hexacene, the charge redistribution is significantly different for perfluorohexacene physisorbed on bilayer graphene as shown in Fig. 4.4 (b). Since fluorine atoms are strong electron-attracting groups, the $\pi$ electrons are polarized away from the aromatic rings leading to a relatively electron-deficient aromatic core of perfluorohexacene. Similarly, a strong interaction between fluorine and graphene gives rise to a significant charge depletion from the carbon atoms in graphene close to fluorine atoms in perfluorohexacene, indicating a net charge transfer
from graphene to perfluorohexacene. By comparing the charge distribution of hexacene and perfluorohexacene on bilayer graphene, it is evident that interaction between graphene and perfluorohexacene is largely controlled by the presence of fluorine functional groups.

![Hexacene and Perfluorohexacene](image)

Fig. 4.4. **Charge redistribution at the interface.** — The distribution of charge density difference for single-molecular adsorption of (a) hexacene and (b) perfluorohexacene on bilayer graphene at monolayer coverage. Red and green isorufaces indicate the accumulation and depletion of electrons at a level of 0.0003 e/Å³, respectively.

To quantify the charge transferred from graphene to adsorbed molecules, we plotted the variation of the planar-averaged and the integrated planar-averaged charge density difference as a function of the distance from the basal plane of graphene as shown in Fig. 4.5. The planar-averaged charge density difference $\Delta \rho_{\text{avg}}(z)$ along a plane parallel to the basal plane of graphene is obtained by integrating the charge density difference across the plane, whereas the integrated charge density difference $\Delta \rho(z)$ is simply calculated by integrating $\Delta \rho_{\text{avg}}(z)$ curve from the boundary of the periodic box to the position of the plane. The extremum in the integrated charge density difference curve in the region between graphene and the adsorbed molecule (indicated by red lines in Fig. 4.5) denotes the neutral plane and the magnitude of the net charge transfer. According to this analysis, graphene donates 0.035 $e^-$ per molecule to hexacene and a larger fraction 0.050 $e^-$ per molecule to perfluorohexacene. The magnitude of net charge transfer obtained here is qualitatively consistent with
Bader charge population analysis [294], which yields a net charge transfer of 0.02 $e^-$ and 0.18 $e^-$ per molecule from graphene to hexacene and perfluorohexacene, respectively. The differences in the magnitudes of the net charge transfer obtained by these two methods can be attributed to the different ways of calculating the net charges on each ion. Bader charge analysis takes into account both core charges and valence charges, while the charge density difference calculation is more suitable for interpreting the charge redistribution close to the Fermi level [? ]. Nevertheless, the small magnitude of charge transfer for both molecules is indicative of a weak interaction between the molecules and bilayer graphene.

Fig. 4.5. Planar-averaged charge density difference analysis. — The planar-averaged ($\Delta \rho_{\text{avg}}(z)$) and integrated planar-averaged ($\overline{\Delta \rho}(z)$) charge density difference curves for single-molecular adsorption of (a) hexacene and (b) perfluorohexacene on bilayer graphene at monolayer coverage. The positions of the top graphene layer (TG) and the molecule are marked by green and yellow dashed lines, respectively. Blue solid lines denote the neutral plane.
Finally, few recent experimental studies have reported that as the density of the adsorbed acene molecules is increased beyond the near-monolayer coverage considered here, the molecules tend to tilt rather than maintain a planar orientation on graphene [312, 318]. In order to confirm this observation, we have also studied the adorption of hexacene on bilayer graphene at a nominal molecular concentration of $1.31 \times 10^{10}$ mol/cm$^2$ using a $8 \times 3$ graphene supercell. Figure 4.6 shows the adsorption geometry as well as the electronic interaction between hexacene and bilayer graphene at this coverage. We find that hexacene shows a remarkable $11^\circ$ tilt with respect to the basal plane of graphene, in qualitative agreement with the experimental observations [312, 318]. This tilt arises due to a stronger repulsive intermolecular interaction between neighbouring hexacene molecules at high coverage. The cofacial $\pi-\pi$ interactions that contribute to the stability of hexacene adsorption at lower concentrations are disrupted, causing the adsorption at high coverage to be less energetically favorable (adsorption energy $-1.534$ eV per molecule). Moreover, the electronic interactions between graphene and hexacene also vary spatially, leading to an asymmetric charge redistribution pattern as shown in Figure 4.6. Compared to the corresponding patterns at low coverages, a significantly larger charge rearrangement is observed in the region of the molecule where hexacene is closer to the graphene than in the region where hexacene is away from the graphene. This imbalance in the charge redistribution breaks the local symmetry of bilayer graphene, inducing a 54 meV band gap.

4.4.3 Effect of the Applied External Electric Field

The results presented in earlier sections show that in general, the adsorbed aromatic acene molecules interact weakly with bilayer graphene, leading to the formation of localized states and a weak p-type doping of graphene. Since external electric fields
can enhance the interactions between adsorbate and substrate [124, 303, 304], next we investigate whether the external electric field could be effectively utilized to tune the electronic structure and molecule-specific localized states in bilayer graphene. Specifically, we studied the effect of the electric field in the range of -3 to 3 eV/nm, applied perpendicular to the basal plane of bilayer graphene in the dual-molecular hexacene/-bilayer graphene/perfluorohexacene adsorption configuration at a monolayer coverage as shown in Fig. 4.6(b). In our notation, a positive electric field is oriented towards hexacene from perfluorohexacene. Figure 4.7(a) presents PDOS of bilayer graphene as a function of the strength of the field. The application of the electric field leads to the opening of a considerable band gap in bilayer graphene, as well as to the shift in

Fig. 4.6. Electronic structure of graphene upon adsorption of hexacene at high molecular density. — (a) Adsorption geometry with 11° tilt angle. (b) PDOS of bilayer graphene. The grey region indicates a 54 meV band gap, the Fermi level is set to zero. (c) Charge density difference along a plane parallel to the basal plane of graphene. The position of the cutplane is 0.62 Å above the top graphene layer. The color bar indicates the level of isosurface (unit in 10⁻⁴ e/Å³).
the energy levels of the localized states arising due to the hybridization with HOMO
and LUMO states of the molecules. The external electric field causes an accumula-
tion of electrons in one layer and a depletion of electrons in the other layer of bilayer
graphene, thus breaking the interlayer symmetry [41]. The band gap generated in
bilayer graphene is thus a result of the interplay between the field-induced interlayer
symmetry breaking and the asymmetric charge transfer between graphene and the ad-
sorbed hexacene and perfluorohexacene molecules. In several cases, the magnitude of
band gap is difficult to determine from the PDOS of bilayer graphene alone as the gap
region is occupied by the localized states. In order to correctly identify the band gaps,
we have calculated the electronic band structure for each case as shown in Fig. 4.8.
The localized states can then be readily identified from these band structure diagrams
as the flat bands between the $\pi$ and $\pi^*$ bands of bilayer graphene.

It is evident that both the shape of the PDOS as well as the magnitude of the
band gap in bilayer PDOS shows a strong dependence on the strength and the direction
of the external electric field. For example, the band gap increases linearly with the
electric field till a maximum of $\sim 250$ meV when the field is oriented from hexacene
towards perfluorohexacene (that is, a negative electric field). For a positive field, the
band gap reaches $\sim 200$ meV for the field magnitude of 1 eV/nm, then reduces to
$\sim 115$ meV for the field of 2 eV/nm or greater. This observed contrast in the trend
between negative and positive fields can be attributed to the distinct charge transfer
behavior of the adsorbed hexacene and perfluorohexacene molecules as shown in Fig.
4.7 (b). For instance, for fields $E \geq 2$ eV/nm, the HOMO of perfluorohexacene and the
LUMO of hexacene are pinned in the vicinity of the Fermi level. The pinning of these
localized states near the Fermi level enhances the driving force for transferring charge
from hexacene to perfluorohexacene, which is favored by the application of a positive
electric field. Therefore the charge transfer between hexacene and perfluorohexacene is
Fig. 4.7. Effect of external electric field on the electronic structure of bilayer graphene in dual-molecular adsorption of hexacene and perfluorohexacene at monolayer coverage. — (a) PDOS of bilayer graphene as a function of external electrical field (in eV/nm). The peaks induced by hybridization with HOMO and LUMO states of hexacene and perfluorohexacene are denoted. The grey region indicates the band gap induced in bilayer graphene. The Fermi level is set to zero. (b) Positions of the localized states in bilayer graphene induced by the hybridization with HOMO and LUMO states of hexacene and perfluorohexacene. (c) Induced charges in hexacene (Hex), perfluorohexacene (P-Hex), and top and bottom graphene layers (TG, BG), calculated by Bader charge population analysis.

maximized as shown in Fig. 4.7 (c). The charge inequivalence between two graphene layers is reduced for positive electric fields greater than 1 eV/nm, leading to a saturation of the band gap. For negative fields on the other hand, the charge transfer trend is reversed. The energy difference between the HOMO of perfluorohexacene and the LUMO of hexacene increases with the strength of the negative electric field. Therefore the charge transfer between the two graphene layers is less affected and the magnitude of band gap increases rapidly with the magnitude of the field.

Figure 4.8(a) also shows a comparison between the electronic band structure diagrams of bilayer graphene adsorbed with hexacene and perfluorohexacene to those with
Fig. 4.8. **Band structure diagrams of bilayer graphene upon dual-molecular adsorption under external electric field.** — (a) Electronic band structure diagrams for dual-molecular adsorption of hexacene and perfluorohexacene with monolayer coverage on bilayer graphene as a function of the strength of the electric field (in eV/nm). The corresponding diagrams for pristine bilayer graphene are also shown for comparison. The $\pi$ and $\pi^*$ bands of bilayer graphene are labeled in red color. The inset shows the first Brillouin zone of the supercell compared against that of the unit cell of graphene. (b) The variation of the band gap at K ($E_K$, blue) and the true band gap along $\Gamma X$ line in the Brillouin zone ($E_T$, yellow) with the strength of the electric field.
Chapter 4: Adsorption of Hexacene on Bilayer Graphene

the pristine bilayer graphene. Our obtained band structures for pristine graphene are in good agreement with previous works [319]. It is evident that due to the deformation of $\pi$ and $\pi^*$ bands, the field-induced band gap in pristine bilayer graphene is no longer located at the K point, but instead along $\Gamma$-X line of the Brillouin zone. However, the $\pi$ and $\pi^*$ bands of bilayer graphene with dual-molecular adsorption are less deformed close to the Fermi level due to the screening by molecules, indicating that the energy dispersion relationship in the vicinity of the K point is relatively well preserved. This can be clearly seen by comparing the magnitude of band gap at K ($E_K$) and the true band gap along $\Gamma$-X line ($E_T$) presented in Fig. 4.8(b). It can be seen that in general, the range of band gaps that can be induced in bilayer graphene with molecular adsorption (100 meV – 250 meV) is comparable to the pristine bilayer graphene (200 meV – 300 meV). Overall, the band structures follow a similar trend as the DOS plots of dual molecular adsorption on bilayer graphene shown in Fig. 4.7 (a), where graphene $\pi$ and $\pi^*$ states hybridize with the localized HOMO and LUMO bands of the molecules, forming new localized bands with a flat dispersion. These results show that the energy of these localized states can be varied as a function of the strength and polarity of the applied electric field, thereby modifying the electronic structure of bilayer graphene. Finally, for completeness, we briefly compare the electronic structure of bilayer graphene with dual-molecular adsorption under the electric field to that of monolayer graphene. Figure 4.9 shows band structure diagrams for dual-molecular adsorption of hexacene and perfluorohexacene on monolayer graphene as a function of the strength of the electric field. We find that the electronic structure of monolayer graphene with dual-molecular adsorption is significantly different from the bilayer graphene for negative electric fields. The localized states induced in monolayer graphene due to hybridization with the HOMO/LUMO states of the adsorbed molecules are relatively further away from the Fermi level of graphene. Moreover, negative electric fields lead to much lower band gaps in
monolayer graphene (less than 50 meV). For positive electric fields, both monolayer and bilayer graphene show a similar magnitude of the band gaps (~120 meV). When compared with Fig. 4.8, these observations highlight the interplay between the charge transfer and the breaking of the symmetry between the top and bottom layer in bilayer graphene. In general, these results suggest that by the application of external electric field to bilayer graphene with dual molecular gating, the electronic structure can be more flexibly controlled, leading to opening of considerable band gaps.

Fig. 4.9. Band structure diagrams of monolayer graphene upon dual-molecular adsorption under external electric field. — Electronic band structure diagrams for dual-molecular adsorption of hexacene and perfluorohexacene with monolayer coverage on monolayer graphene as a function of the strength of the electric field (in eV/nm). The $\pi$ and $\pi^*$ bands of bilayer graphene are labelled in red color.
4.5 Conclusions

Here we have used self-consistent density functional theory calculations to study the effect of physisorption of hexacene and its fluorine derivative, perfluorohexacene, on the electronic structure of bilayer graphene. We find that although the overall interaction between graphene and molecules is weak, the adsorption of these molecules results in a significant charge redistribution. This charge redistribution gives rise to the hybridization of HOMO/LUMO energy levels of the molecules with the $\pi$ electrons of graphene, leading to the formation of localized states in bilayer graphene. We have shown that the external electric fields can be used to tune the electronic properties of graphene-molecule system, effectively opening large band gaps of the order of 250 meV in bilayer graphene. Furthermore, external electric fields can also influence the energies of the localized states in graphene, an effect that can be utilized in organic field effect transistor (OFET) devices by aligning the electronic states of acene channels with that of graphene electrodes. This effect can also be potentially useful in the sensing of different organic molecules on the surface of graphene transistors. Graphene transistors have proven to be extremely sensitive sensors [101], but their selectivity remains a major problem for their practical use. In summary, we have shown that hexacene, a stable and high mobility organic electronic material, and its derivatives, are promising candidates for surface electronic structure modification of graphene for potential applications in organic electronics and sensing.
Chapter 5

Graphene-Platinum

Nanocomposites for Electrocatalysis

5.1 Introduction

Noble metal (e.g. Pt, Ru and their alloys) particles confined in nanometer length scale have proven to be ideal catalysts for electrochemical applications such as proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs). [193, 194, 320], but in practice the catalytic efficiency can be seriously hindered by the aggregation of nanoparticles and susceptibility to CO poisoning [206–208]. In recent years, graphene has shown its potential as the next-generation catalytic support material, owing to its excellent properties such as high specific surface area, superior electrical conductivity and structural durability [205, 217–219, 321]. Moreover, it exhibits enhanced tolerance to CO poisoning compared with other competing materials such as carbon black and carbon nanotubes [217, 219–221]. Despite these exciting discoveries,
Chapter 5: *Graphene-Platinum Nanocomposites for Electrocatalysis*  

graphene-based catalyst structure still needs to be refined to meet requirements in real applications.

The chemically inert surface of pristine graphene is not suitable for supporting metal nanoparticles, because the weakly adsorbed metal nanoparticles can readily self-assemble into large clusters on the planar surface. This sintering effect significantly reduces the surface area of catalysts, thereby decreasing the catalytic activity [211, 322, 323]. The presence of structural defects on the as-synthesized graphene surface offers a promising direction to solve this problem. The defective sites on graphene (e.g. vacancies, edges and adatoms) bind more strongly with metal nanoparticles compared to pristine graphene, which is attributed to their higher chemical reactivity [224, 227, 228]. This effect is highlighted in several experimental studies in which the Pt-graphene nanocomposites are synthesized through solution processing of graphene oxides (GO) [211, 324, 325]. These studies show that the oxygen-containing functional groups spread on the surface of GO are strong trapping sites for metal nanoparticles and strongly enhance the catalytic activity [326, 327]. In addition, using GO offers the advantage of producing graphene-based materials at low manufacturing cost and large scale [21]. These exciting results lead to a growing interest in investigating the interactions between metal nanoparticles and defective sites for improving the performance of these nanocomposite structures in energy-related applications.

Most previous theoretical investigations have been focused on interactions between structural defects on graphene and noble metal nanoparticles [211, 224–226, 231, 232, 236, 328, 329]. There is therefore a lack of knowledge on how functional groups attached on the surface of GO affect the binding of noble metal nanoparticles. A recent study has shown that high concentration of doped oxygen atoms on graphene sheets can effectively stabilize the adsorption of Pt clusters and thereby enhance their dispersion
The energy barrier of adsorption of CO on the Pt cluster increased after the strong interactions between the functionalized graphene sheet and the Pt cluster modify the electronic structure of the Pt cluster \[227\]. However, the study only concerned the effect of epoxy group. Previous experimental and theoretical observations have suggested that other functional groups on GO sheets such as hydroxyl and carbonyl can also significantly affect the binding of metal nanoparticles with the substrate \[330, 331\]. Therefore, it is necessary to examine how an individual functional group on GO interacts with metal nanoparticles.

Here we conduct a systematic study to investigate the feasibility of using graphene decorated with oxygen-containing functional groups as a support for Pt nanocatalysts using self-consistent density functional theory (DFT) calculations. We simulate the effect of three different functional groups (epoxy, hydroxyl and carbonyl) on the adsorption of Pt monomer, dimer and Pt\(_{13}\) clusters. The three functional groups are abundant on GO. We examine how the functional groups affect the stability of the substrate-adsorbate system and their influence on the morphology of Pt clusters. We show that functional groups act as anchoring sites that tend to stabilize the Pt clusters on the graphene sheet. Specifically for Pt\(_{13}\) clusters, we are interested in the effect of adsorption of low-symmetry Pt\(_{13}\) clusters on the electronic structure of the Pt-graphene system. We show that the type of the functional group present on the surface of GO plays a critical role in anchoring the adsorption of Pt nanoparticles, which suggests a new direction for designing next-generation support materials in fuel cells.
5.2 Computational Details

All calculations were performed using the plane-wave DFT method as implemented in the Vienna ab initio simulation package (VASP) [291]. The projector augment wave (PAW) methods were used to describe the core and valence electrons [309]. The Perdew-Burke-Ernzerhof (PBE) form of the generalised gradient approximation (GGA) was employed to describe electron exchange and correlation [315]. Since GGA is known to underestimate the long-range interactions such as van der Waals interactions [282], we applied a semiempirical functional developed by Grimme (DFT-D2) to account for these forces [286]. All calculations were performed on a periodic 6×6 graphene supercell. Vertical periodic images were separated by 18 Å of vacuum space to avoid interactions between them. For all structural optimization and electronic structure calculations, the kinetic cut-off energy for the plane-wave basis set was 400 eV. The Brillouin zone was sampled using a 9×9×1 Γ-centered k-point mesh. Bader charge analysis was used to quantify the charge transfer between graphene and platinum particles [294].

We investigated the adsorption of platinum monomer, dimer and Pt_{13} cluster (Figure 5.1 (a)). The Pt_{13} cluster represents the smallest magic cluster according to the geometric shell model [332, 333]. The computational cost spent on finding the optimum configuration of Pt_{13} clusters was expected to be expensive, therefore we only considered the distorted cuboctahedron shape (Figure 5.1 (a)) because previous theoretical studies have suggested that the distorted cuboctahedron configuration is much more energetically stable (by nearly 1 eV) when adsorbed on graphene than high-symmetry configurations (e.g. icosahedron and standard cuboctahedron) [224, 227, 228]. These low-symmetry configurations were obtained with the help of ab initio molecular dynamics (MD). The Pt_{13} cluster on graphene was first thermalized at 500 K for 10 fs, and then cooled to 1 K over 2.5 fs. This thermal treatment procedure was repeated 7 times.
to generate reasonable statistics. The lowest-energy structure was selected for further structural relaxation. In terms of the substrate, we used graphene decorated with three different oxygen-containing functional groups (epoxy, hydroxyl and carbonyl) (Figure 5.1 (b)) as well as pristine graphene for reference. For epoxy and hydroxyl group, the adsorption process was studied using two different setups: one had the Pt cluster and the functional group on the same side of graphene, while in the other case the Pt cluster and the functional group were on different sides of the substrate. The effect of the concentration of functional groups was not considered in this study, as we focused on the interactions between Pt nanoparticles and various individual functional groups.

Fig. 5.1. **Structure of Pt nanoparticles and functionalized graphene sheet.** — Schematics showing optimized geometries in vacuum for (a) a Pt monomer, a Pt dimer and a Pt\textsubscript{13} cluster; and (b) functionalized graphene sheets (epoxy, hydroxyl and carbonyl pair). The blue, orange, yellow and fray spheres represent C, Pt, O and H atoms, respectively.
5.3 Results and Discussions

5.3.1 Adsorption of Pt Monomer and Pt Dimer

First, we obtain the lowest-energy configurations of the adsorption for a Pt monomer on pristine and functionalized graphene sheets as shown in Figure 5.2. We briefly report the adsorption energy for the lowest-energy configuration in each case in Table 5.1. The adsorption energy ($E_{ad}$) is calculated as:

$$E_{ad} = E_{\text{graphene}+Pt_n} - E_{\text{graphene}} - E_{Pt_n},$$

where $E_{\text{graphene}+Pt_n}$ is the energy of fully relaxed Pt-graphene system, and $E_{\text{graphene}}$ and $E_{Pt_n}$ are energies of isolated graphene and molecules in the same supercell, respectively. On pristine graphene, the platinum monomer is adsorbed most strongly on the bridge site, which is in good agreement with previous studies [224, 231, 334, 335]. For graphene decorated with functional groups (Figure 5.2), the platinum monomer is adsorbed on the second or third nearest bridge site to the location of the functional group. The adsorption energy (Table 5.1) shows that the platinum monomer binds more strongly near functional groups by 0.1 – 0.6 eV compared to adsorption on pristine graphene. The adsorption strength follow the order: carbonyl > hydroxyl > epoxy. The opposite-side adsorption of a Pt monomer on epoxy and hydroxyl graphene is more energetically favorable than the same-side adsorption, because the Pt-O interaction occurring in the same-side adsorption plays an important role in the stability of the Pt-graphene system. It has been reported that if Pt atoms are in close contact with the oxygen-containing group, the Pt atoms tend to extract oxygen atoms from the substrate, thereby the adsorption of Pt atoms on graphene is weakened [227]. The interactions between the Pt monomer and graphene also lead to a small structural distortion of the substrate.
Table 5.1. **Energetic and structural changes upon adsorption of a Pt monomer and Pt dimer on the functionalized graphene sheet.** — Adsorption energy \( (E_{\text{ad}}) \), Pt-C bond length \( (d_{\text{Pt-C}}) \) for adsorption of Pt monomers, and Pt-Pt bond length \( (d_{\text{Pt-Pt}}) \) for adsorption of a Pt dimer on the pristine and functionalized graphene.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Pt monomer</th>
<th>Pt dimer</th>
<th>Pt dimer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( E_{\text{ad}} ) (eV)</td>
<td>( d_{\text{Pt-C}} ) (Å)</td>
<td>( E_{\text{ad}} ) (eV)</td>
</tr>
<tr>
<td>pristine</td>
<td>-1.94</td>
<td>2.10</td>
<td>-1.40</td>
</tr>
<tr>
<td>epoxy same side</td>
<td>-2.05</td>
<td>2.06</td>
<td>-1.51</td>
</tr>
<tr>
<td>epoxy opposite side</td>
<td>-2.36</td>
<td>2.06</td>
<td>-1.73</td>
</tr>
<tr>
<td>hydroxyl same side</td>
<td>-2.22</td>
<td>2.07</td>
<td>-1.89</td>
</tr>
<tr>
<td>hydroxyl opposite side</td>
<td>-2.55</td>
<td>2.03</td>
<td>-2.27</td>
</tr>
<tr>
<td>carbonyl</td>
<td>-2.58</td>
<td>2.05</td>
<td>-2.54</td>
</tr>
</tbody>
</table>

The formation of Pt-C bond upon adsorption is accompanied by 0.2 – 0.5 Å out-of-plane displacement of the underlying graphene carbon atoms relative to the graphene surface. The Pt-C bond length decreases with increasing adsorption strength as shown in Table 5.1.

Next, we examine the adsorption of a Pt dimer on pristine and functionalized...
graphene. The lowest-energy structures are shown in Figure 5.3. We find a near-vertically oriented dimer adsorbed on pristine graphene, with one platinum atom adsorbed 2.25 Å above the pristine, while the other is not in touch with the surface. When functional groups are present, similarly to the adsorption of a Pt monomer, the Pt dimer prefers to adsorb near the second-nearest or third-nearest site of the functional group as shown on Figure 5.3. The vertically oriented adsorption configuration is also found for these adsorption cases except for the same-side adsorption on epoxy graphene and adsorption on carbonyl graphene. In the latter two cases, the platinum dimer is rotated 60° with respect to the vertical position, making the configuration more planar. The difference in the adsorption geometry can be explained by the difference in the strength of Pt-O interaction. The Pt-O lengths for epoxy and carbonyl graphene are 2.43 Å and 2.07 Å, while 3.10 Å for hydroxyl graphene. It can be seen that stronger Pt-O interaction leads to a more planar adsorption configuration. The adsorption of Pt dimer on functionalized graphene is energetically more favorable than on pristine graphene by 0.1 – 1.1 eV (Table 5.1). The order of adsorption energy of a Pt dimer on functionalized graphene follows the same order as the adsorption of a Pt monomer. In addition, as before, the adsorption of Pt dimer leads to a small structural deformation of both the Pt dimer and the substrate. The Pt-Pt bond lengths are elongated by 0.01 – 0.05 Å upon adsorption compared with the gas-phase bond length of 2.33 Å (Table 5.1). The C-C bond lengths below the Pt dimer are also elongated by 0.02 – 0.05 Å compared with those at the isolated state.

In summary, the adsorption of a Pt monomer and dimer is strongly anchored by the presence of oxygen-containing functional groups. Interactions between Pt atoms and the functional group have significant influences on the binding strength of Pt atoms on graphene, as well as the geometries of the Pt atoms and the substrate. Carbonyl and hydroxyl group have shown stronger interactions with the Pt atoms than epoxy.
5.3.2 Adsorption of Pt-13 Clusters

Finally we consider the adsorption of a Pt$_{13}$ cluster. We place a Pt$_{13}$ cluster in different positions near the functional group and then select the lowest-energy configuration after structural relaxation for each case. As shown in Figure 5.4, the Pt$_{13}$ clusters are adsorbed about 2.2 Å above the first-nearest or second-nearest site of the functional group. The lowest-energy Pt$_{13}$ cluster configurations exist in low-symmetry forms, which is consistent with previous calculations on adsorption of Pt clusters on defective graphene/hexagonal boron nitride (h-BN) [224, 228]. The adsorption energy for the lowest-energy configurations is shown in Table 5.2. It can be seen that the adsorption of a Pt$_{13}$ cluster on functionalized graphene is much more energetically favorable than adsorption on pristine graphene. Pt$_{13}$ clusters bind most strongly with the carbonyl graphene, followed by hydroxyl and epoxy. The opposite-side adsorption
Table 5.2. **Energetic and structural changes upon adsorption of a Pt\textsubscript{13} cluster on the functionalized graphene sheet.** — Adsorption energy, Pt-C and averaged Pt-Pt bond length for adsorption of Pt\textsubscript{13} clusters on graphene

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Adsorption energy (eV)</th>
<th>d\textsubscript{Pt-C} (Å)</th>
<th>d\textsubscript{Pt-Pt} (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine</td>
<td>-2.70</td>
<td>2.21</td>
<td>2.61</td>
</tr>
<tr>
<td>epoxy same side</td>
<td>-3.07</td>
<td>2.21</td>
<td>2.60</td>
</tr>
<tr>
<td>epoxy opposite side</td>
<td>-3.48</td>
<td>2.23</td>
<td>2.59</td>
</tr>
<tr>
<td>hydroxyl same side</td>
<td>-2.99</td>
<td>2.18</td>
<td>2.61</td>
</tr>
<tr>
<td>hydroxyl opposite side</td>
<td>-3.15</td>
<td>2.20</td>
<td>2.59</td>
</tr>
<tr>
<td>carbonyl</td>
<td>-3.97</td>
<td>2.22</td>
<td>2.60</td>
</tr>
</tbody>
</table>

is 0.3 eV more favorable than the same-side adsorption. The trend is consistent with the adsorption of a Pt monomer and Pt dimer and can be attributed to the Pt-O interaction.

The presence of functional groups on graphene can induce significant structural distortions in Pt\textsubscript{13} clusters, as seen in Figure 5.4. The averaged Pt-Pt bond length is used to quantify the morphological changes of Pt\textsubscript{13} clusters (see Table 5.2). The averaged Pt-Pt bond lengths of Pt\textsubscript{13} clusters upon adsorption on functionalized graphene are slightly larger (up to 0.02 Å) than that upon adsorption on pristine graphene. These bond lengths are larger than the relaxed unsupported Pt cluster (2.58 Å). This agrees well with the trend observed in Pt\textsubscript{13} clusters anchored by vacancies on graphene [224, 226].

Bottom Pt atoms in the Pt\textsubscript{13} cluster form bonds with underlying carbon atoms of graphene, leaving the rest of the cluster with a large number of undercoordinated Pt atoms. As seen from Figure 5.4, three Pt atoms are bound with the basal carbon atoms of graphene upon adsorption on pristine graphene and same-side adsorption on hydroxyl graphene, while two Pt atoms form bonds with carbon atoms of graphene in other cases. The undercoordinated metal atoms possess strong chemical reactivity,
implying that the extent of undercoordination in the Pt cluster can directly affect the catalytic activity [336]. To lower the susceptibility to CO poisoning, the extent of undercoordination in the Pt cluster needs to be reduced in order to decrease the adsorption energy of CO on the Pt cluster [225]. The functional groups on graphene can tune the extent of undercoordination in the Pt cluster via formation of strong Pt-C bonds between basal Pt and C atoms. It can be seen that the presence of a single functional group does not effectively reduce the extent of undercoordination. However, this still shows consistency with previous studies that the extent of undercoordination in the Pt cluster is significantly affected by the presence of surface defects [226, 227].

5.3.3 Electronic Structures of Adsorbed Pt$_{13}$ Clusters

Next, we examine the electronic structure of adsorbed Pt atoms on pristine and functionalized graphene. The electronic structure of adsorbed Pt monomers and dimers has been examined in detail in previous reports [337, 338] and will not be discussed. The electronic structure of Pt$_{13}$ clusters adsorbed on functionalized graphene will be focused in the following. As the size of Pt$_{13}$ clusters (around 0.7 nm) is closer to that obtained in experimental studies [217, 219, 339], The results here can provide a explanation to a recent experimental investigation on Pt nanoparticles adsorbed on partially decorated reduced graphene oxides (PRGO) [338].

The total density of states (DOS) of the Pt-graphene nanocomposite are projected on to the p orbitals of the substrate atoms and d orbitals of the Pt atoms at the interfacial region, which are involved in the formation of Pt-C bonds. The p and d DOSs of these atoms in the isolated graphene and Pt$_{13}$ cluster are also plotted to show how the electronic states are affected upon adsorption. Compared with the DOS of pristine graphene, sharp peaks appear in the vicinity of the Fermi level in
Fig. 5.4. Adsorption of a Pt$_{13}$ cluster on the functionalized graphene. — Schematics showing low-energy configurations for adsorption of a Pt$_{13}$ cluster on the pristine and functionalized graphene.
Fig. 5.5. Changes to electronic states of Pt-graphene nanocomposites. — Spin-polarized projected density of states (PDOS) plots for adsorption of Pt$_{13}$ clusters on pristine and functionalized graphene: p band of (a) graphene upon adsorption (the PDOS upon the same-side adsorption of Pt$_{13}$ clusters is labeled blue, while the PDOS for the opposite side adsorption is labeled red.) (b) free graphene, d band of (c) Pt$_{13}$ cluster upon adsorption and (d) free Pt$_{13}$ cluster.

the DOS of functionalized graphene (Figure 5.5 (b)). It is evident that the covalent addition of oxygen atoms contributes to these localized electronic states around the Fermi level. These localized states make the graphene surface highly reactive. These sharp peaks diminish after the adsorption of the Pt$_{13}$ cluster and a slight broadening of the electronic states (Figure 5.5 (a)) is observed. Meanwhile, the d DOSs of Pt$_{13}$ clusters upon adsorption show significant broadening (Figure 5.5 (c)). The overall electronic states become smooth and continuous, compared to DOSs of isolated clusters (Figure 5.5 (d)). These observations provide strong evidence of hybridization between
the electronic states of graphene and Pt$_{13}$ clusters. The effect of the Pt-O interaction is obvious by comparing the PDOS of the substrate upon same-side and opposite-side adsorption of the Pt cluster on epoxy and hydroxyl graphene (Figure 5.5 (a)). It can be seen that for epoxy graphene, the difference in surface contact has limited impact on the electronic states of the substrate upon adsorption, while for hydroxyl graphene the same-side adsorption leads to smoother electronic states compared with the opposite side adsorption.

The Bader charge analysis is used to quantify the amount of charge redistribution between Pt cluster and the substrate. We divide the Pt$_{13}$ cluster into three regions (bottom, middle and top) and sum the partial charges accumulated in each region (Figure 5.6 (a)). The results are presented in Table 5.3. The bottom region includes
all interfacial Pt atoms, while small gas molecules (e.g. CO and O\textsubscript{2}) are usually adsorbed near top Pt atoms during electrocatalysis. In all cases the graphene surface receives charges transferred from the Pt cluster. The amount of redistributed charges is proportional to the binding strength between graphene and the Pt\textsubscript{13} cluster. Carbonyl graphene receives the most charges from the Pt cluster (1 electron) and has the strongest Pt-graphene binding. We found that the presence of functional groups significantly affects the charge redistribution in the Pt cluster. Pt atoms in the top region are slightly negatively charged on a functionalized graphene sheet, while positively charged on pristine graphene. As interfacial interactions increases, redistributed charges are more concentrated in the bottom region. This effect is expected to reduce the adsorption strength of gas molecules on the top region, as previous reports have indicated that top Pt atoms at highly charged state is vulnerable to CO adsorption \cite{225, 226}. The charge density difference plots are obtained to further support our findings. As shown in Figure 5.6 (b), the charge redistribution mainly occurs in there
Table 5.4. **d-band center changes upon adsorption of a Pt$_{13}$ cluster.** — Averaged d-band center ($\epsilon_d$) of Pt$_{13}$ cluster upon adsorption on pristine and functionalized graphene.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>d-band center ($\epsilon_d$) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>bottom</td>
</tr>
<tr>
<td>pristine</td>
<td>-1.94</td>
</tr>
<tr>
<td>epoxy same side</td>
<td>-2.12</td>
</tr>
<tr>
<td>epoxy opposite side</td>
<td>-2.21</td>
</tr>
<tr>
<td>hydroxyl same side</td>
<td>-2.19</td>
</tr>
<tr>
<td>hydroxyl opposite side</td>
<td>-2.20</td>
</tr>
<tr>
<td>carbonyl</td>
<td>-2.28</td>
</tr>
</tbody>
</table>

Interfacial region between the substrate and the Pt$_{13}$ cluster. Significant charge depletion is observed around Pt atoms near the substrate and accompanied by charge accumulation in the vicinity of the substrate. It is obvious that the amount of redistributed charges becomes more concentrated in the interfacial area as the binding between functionalized graphene and the Pt cluster increases.

Nørskov’s d-band theory has been widely used to explain bond formation and reactivity mechanisms in various transition metal systems [340, 341]. The averaged d-band center ($\epsilon_d$) of Pt$_{13}$ clusters is upon adsorbed on graphene and at the isolated state is calculated (see Table 5.4). The averaged d-band center of Pt$_{13}$ clusters adsorbed on functionalized graphene undergoes substantial downshift compared with pristine graphene. The downshift of the d-band center is positively correlated with the binding strength between graphene and the Pt$_{13}$ cluster. The interfacial Pt atoms have the largest downshift and the the downshift slightly reduces in middle and top Pt atoms. According to d-band theory, the downshift of the d-band center is expected to reduce the adsorption energy of CO on the Pt cluster, thus lowering the possibility of CO poisoning. In summary, we have clearly demonstrated other common groups on GO (hydroxyl and carbonyl) are more effective in anchoring the Pt cluster and mitigate CO poisoning. The actual calculation of adsorption of CO on the Pt cluster will be
conducted in the future.

5.4 Conclusions

In this work, we have used self-consistent density functional theory calculations to study the binding of Pt atoms and clusters on graphene decorated with epoxy, hydroxyl and carbonyl groups. We find that the adsorption of Pt atoms and clusters on functionalized graphene is more energetically favorable than on pristine graphene. Moreover, the presence of functional groups also induces significant morphological changes in the catalyst structure. Furthermore, it has been shown that the functional groups have a significant impact on the electronic structure of the Pt-graphene nanocomposites. Strong binding between functionalized graphene and the Pt$_{13}$ cluster leads to larger amount of charge transfer from the Pt$_{13}$ cluster to graphene, as well as downshifting the d-band center of the Pt$_{13}$ cluster. These results clearly demonstrate that functionalized graphene can significantly enhance the catalytic activity of the Pt catalyst and its tolerance to CO poisoning. We have highlighted that the carbonyl and hydroxyl group attached to the graphene surface are more effective in anchoring the Pt nanoparticles than the epoxy group. These results will provide critical knowledge for the design and development of future graphene-based catalyst support via controlling the composition of functional groups on the surface of GO.
Chapter 6

Interaction of DNA Nucleobase With Graphene: the Role of Intermolecular Interactions

6.1 Introduction

Interaction between DNA nucleobases and graphene has received intensive attention due to its fundamental importance in various potential applications, such as biosensing, DNA sequencing, drug delivery and diagnostics [134, 244–247, 250, 342–345]. Graphene, owing to its two-dimensional structure and unique electronic properties [17, 20, 21, 32, 36], has great advantages over conventional materials and other carbon nanostructures as the host material for realization of next-generation DNA sequencing and sensing schemes and construction of supramolecular structures using nucleobase binding [346–351]. Previous studies have shown that DNA nucleobases are bound to graphene by non-covalent interactions in a π-π stacking geometry [159, 253, 254]. The
π-stacking between graphene and DNA nucleobases is strong enough to stabilize the adsorbate-substrate system but weak enough to be broken by external forces to allow applications in DNA sensing and sequencing [134, 260, 352].

Interaction between DNA nucleobases and graphene has received intensive attention due to its fundamental importance in various potential applications, such as biosensing, DNA sequencing, drug delivery and diagnostics. Graphene, owing to its two-dimensional structure and unique electronic properties, has great advantages over conventional materials and other carbon nanostructures as the host material for realization of next-generation DNA sequencing and sensing schemes and construction of supramolecular structures using nucleobase binding. Previous studies have shown that DNA nucleobases are bound to graphene by non-covalent interactions in a π-π stacking geometry. The π-stacking between graphene and DNA nucleobases is strong enough to stabilize the adsorbate-substrate system but weak enough to be broken by external forces to allow applications in DNA sensing and sequencing.

While most of previous theoretical studies focused on studying base-specific interactions of DNA and RNA nucleobases with graphene [159, 164, 252–259, 261, 353], the role of intermolecular interactions in the nucleobase-graphene system has remained unexplored. A recent experimental study of adsorption of layers of individual DNA nucleobases on graphene field-effect transistors has, however, demonstrated that the intermolecular interaction have a strong impact on the electronic structure of graphene [164]. The electronic transport in graphene have shown a distinct coverage-dependent doping behavior for each of the nucleobases, providing a new pathway for their discrimination. In contrast to DFT calculations, which have predicted p-type doping of graphene by DNA unclebases at a low coverage regime [159, 253, 254], the experiment
has measured n-type doping for cytosine and thymine, varying n-type to p-type doping for guanine and p-type doping for adenine in a submonolayer to over a monolayer coverage [164]. As the main differences between these studies can be attributed to a difference in the molecular adsorption geometry, flat vs. tilt (30-45°), and density of adsorbed nucleobases on graphene, it is important to investigate these effects in more detail. Understanding interplay between base-base and substrate-base interactions will be also important for graphene-based sensing and nanopore sequencing of DNA strands, in which the nucleobases are closely spaced, typically within 7.5 Å [244].

Here we use first principle electronic structure calculations to study the adsorption of single-nucleobase layers on graphene as a function of increasing molecular density and investigate the role of intermolecular base-base interactions on the adsorption geometry and electronic structure. We demonstrate that the intermolecular interactions have a profound impact on the electronic structure of graphene and the adsorption geometry of nucleobases, particularly at high molecular coverages. Based on the thorough analysis of the adsorption energetics, molecular dipole moment, induced charge transfer and work function changes in graphene as a function of the molecular coverage, we have identified the conditions for transition between p-type and n-type doping of graphene by DNA/RNA nucleobases, providing possible explanations of the recently reported experimental findings [164].

6.2 Computational Details

All calculations were performed with the Vienna ab initio simulation package (VASP) [291] using the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA) [278] to describe electron exchange and correlation. A
semiempirical functional developed by Grimme (DFT-D2) [286] is applied to describe dispersion forces [261]. For all electronic structure calculations, the kinetic cut-off energy for the plane-wave basis set was set to 600 eV. All structures were relaxed until the atomic forces on all atoms were less than 0.01 eV/Å. The vertical periodic images are separated by 30 Å of vacuum space to avoid interactions between them. Different molecular coverage of cytosine on graphene was obtained by placing a single nucleobase molecule on differently sized graphene supercells. The molecular coverage standard of nucleobase monolayer (ML) on graphene is defined in Table 6.1. This monolayer coverage represents the experimentally observed self-assembled nucleobase layers on graphite using scanning tunnelling microscopy [354]. Hence 5×5, 5×4, 4×4, 3×4, 3×3 and 3×2 graphene supercells are equal to 0.32, 0.40, 0.50, 0.67, 0.89 and 1.35 ML, respectively. The sampling for the Brillouin zone included 12×12×1, 15×15×1, 20×15×1, 20×20×1 and 20×30×1 Γ-centered grids for 5×5, 4×4, 3×4, 3×3 and 3×2 graphene supercells accordingly.

Table 6.1. **Unit cell for full molecular coverage of DNA/RNA nucleobase on graphite.** — Unit cell size for full molecular coverage (1 ML) of self-assembled DNA/RNA nucleobase layer on graphite. These values are used for calculating the molecular coverage in our calculations.

<table>
<thead>
<tr>
<th>DNA/RNA nucleobase</th>
<th>unit cell size (Å²)</th>
<th>nitrogen atoms per unit cell</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>guanine</td>
<td>47</td>
<td>5</td>
<td>[355]</td>
</tr>
<tr>
<td>cytosine</td>
<td>42.4</td>
<td>3</td>
<td>[355]</td>
</tr>
<tr>
<td>adenine</td>
<td>187</td>
<td>20</td>
<td>[356]</td>
</tr>
<tr>
<td>thymine</td>
<td>89</td>
<td>4</td>
<td>[357]</td>
</tr>
<tr>
<td>uracil</td>
<td>146.3</td>
<td>8</td>
<td>[354]</td>
</tr>
</tbody>
</table>
6.3 Results and Discussions

6.3.1 Coverage Dependence of Adsorption Geometries of Nucleobases on Graphene

The structural changes of DNA/RNA nucleobases (Figure 6.1 (a)) upon adsorption on graphene are characterized by calculating rotation angles of the nucleobases. The rotation angles are defined as angles between the adsorbed geometry and the ideal planar geometry around three perpendicular axes, namely $\alpha$, $\beta$ and $\gamma$, as shown in Figure 6.1 (b). Table 6.1 summarizes the rotation angles of nucleobases on graphene at different molecular coverages. At low molecular coverages (0.3 – 0.7 ML), the adsorption geometry of nucleobases resembles AB stacking of graphite. The adsorption geometry starts to deviate from the AB stacking as the molecular coverage increases, and at 1.4 ML it is obvious that the nucleobase layer has a highly tilted adsorption geometry. The tilt of the molecular plane is accompanied by an increase of the averaged vertical distance between nucleobases and graphene, which changes from around 3.2 Å at around 0.3 ML to 4 – 4.5 Å at about 1.4 ML (Figure 6.1 (c)). This indicates the influence of graphene-base interaction considerably diminishes at high molecular coverages.

The intermolecular interactions play a critical role at high molecular coverages. A clear evidence is the formation of hydrogen bonding (e.g., N-H...O and C-H...N) between neighboring molecules (Figure 6.1 (a)). The hydrogen bonding between nucleobase pairs has been identified as a key factor in determining the DNA structure and stabilizing the self-assembled nucleobase layers on graphite and the metal surface [358, 359]. We observe a transition from the planar hydrogen bonding to the non-planar
hydrogen bonding as the molecular coverage rises from 0.7 ML to 1.4 ML. The head-to-tail hydrogen bonding between nucleobase pairs is distorted after the molecular plane of nucleobases becomes highly tilted (Figure 6.2 (b)). This has been the case for every nucleobase except for guanine, where a tail-to-tail N-H...O hydrogen bonding parallel to the graphene surface is found at 1.49 ML (Figure 6.2 (c)). It has been reported that the planar homopairing between nucleobases leads to stronger intermolecular binding strength than the non-planar homopairing [360]. Hence, guanine is expected to have
### Table 6.2. Tilt angles of nucleobases.

<table>
<thead>
<tr>
<th>DNA/RNA Nucleobase</th>
<th>Coverage (ML)</th>
<th>α</th>
<th>β</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>guanine</td>
<td>0.35</td>
<td>1.00</td>
<td>0.38</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>0.55</td>
<td>2.64</td>
<td>0.2</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>0.74</td>
<td>2.62</td>
<td>0.27</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>0.99</td>
<td>14.55</td>
<td>0.89</td>
<td>11.72</td>
</tr>
<tr>
<td></td>
<td>1.49</td>
<td>45.87</td>
<td>0.97</td>
<td>3.66</td>
</tr>
<tr>
<td>cytosine</td>
<td>0.32</td>
<td>0.83</td>
<td>1.24</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.66</td>
<td>1.28</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>0.67</td>
<td>1.04</td>
<td>0.85</td>
<td>3.73</td>
</tr>
<tr>
<td></td>
<td>0.89</td>
<td>0.38</td>
<td>1.62</td>
<td>4.09</td>
</tr>
<tr>
<td></td>
<td>1.35</td>
<td>28.76</td>
<td>14.63</td>
<td>13.22</td>
</tr>
<tr>
<td>adenine</td>
<td>0.35</td>
<td>0.52</td>
<td>1.65</td>
<td>3.78</td>
</tr>
<tr>
<td></td>
<td>0.55</td>
<td>0.84</td>
<td>2.46</td>
<td>3.25</td>
</tr>
<tr>
<td></td>
<td>0.74</td>
<td>0.32</td>
<td>1.14</td>
<td>20.33</td>
</tr>
<tr>
<td></td>
<td>0.99</td>
<td>1.36</td>
<td>2.91</td>
<td>21.95</td>
</tr>
<tr>
<td></td>
<td>1.49</td>
<td>66.84</td>
<td>9.67</td>
<td>23.87</td>
</tr>
<tr>
<td>thymine</td>
<td>0.34</td>
<td>3.26</td>
<td>0.69</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>0.53</td>
<td>2.87</td>
<td>0.58</td>
<td>3.86</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>1.16</td>
<td>1.16</td>
<td>20.62</td>
</tr>
<tr>
<td></td>
<td>0.94</td>
<td>0.49</td>
<td>0.60</td>
<td>24.98</td>
</tr>
<tr>
<td></td>
<td>1.42</td>
<td>45.17</td>
<td>2.41</td>
<td>4.33</td>
</tr>
<tr>
<td>uracil</td>
<td>0.30</td>
<td>2.35</td>
<td>0.04</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>0.46</td>
<td>2.00</td>
<td>0.10</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>0.62</td>
<td>0.31</td>
<td>0.47</td>
<td>21.75</td>
</tr>
<tr>
<td></td>
<td>0.82</td>
<td>0.49</td>
<td>0.60</td>
<td>24.98</td>
</tr>
<tr>
<td></td>
<td>1.27</td>
<td>37.69</td>
<td>3.42</td>
<td>2.07</td>
</tr>
</tbody>
</table>

the strongest intermolecular interaction among all nucleobases.

We verify these findings from structural characterizations by calculating the adsorption energy of nucleobases on graphene per molecule, defined as $E_{ad} = E_{gra-base} - E_{gra} - E_{base}$, where $E_{gra-base}$ is the total energy of relaxed graphene-base system, $E_{gra}$ and $E_{base}$ are energies of the free-standing graphene and the nucleobase layer. The adsorption energy gradually increases as the molecular coverage rises (Figure 6.3 (a)).
suggesting the binding between graphene and the nucleobase layer weakens. This coincides with the trend observed in the averaged distance between graphene and nucleobases as a function of the molecular coverage (Figure 6.1 (c)). We also calculate the formation energy ($E_{\text{form}}$) to quantify the thermodynamic stability of the graphene-base system with respect to the isolated state of its individual constituents, written as $E_{\text{form}} = E_{\text{gra-base}} - E_{\text{gra}} - E_{\text{iso-base}}$. The energy of the isolated nucleobase ($E_{\text{iso-base}}$) is defined as the energy of a nucleobase molecule contained in the vacuum and excluding intermolecular interactions (in this work, we place the isolated nucleobase in a vacuum space equal to the area of a $10 \times 10$ graphene supercell). The formation energy
decreases as the molecular coverage increases from 0.3 to 1.0 ML, and increases at 1.4 ML ((Figure 6.3 (b)). The formation energy at 1.4 ML is the highest among all cases, signifying the formation of a high density nucleobase layer on graphene is energetically favorable.

The intermolecular binding energy is defined as the difference between the adsorption energy and the formation energy. The intermolecular binding energy increases up to 1.0 ML and slightly reduces at 1.4 ML (Figure 6.3 (c)). The evolution of the intermolecular binding energy at high molecular coverages reflects the transition from the planar hydrogen bonding to the non-planar hydrogen bonding. The non-planar hydrogen bonding tends to reduce the intermolecular binding energy. To summarize the observed trend of intermolecular interactions of DNA/RNA nucleobases on graphene it can be concluded that (i) the competition between graphene-base interaction and base-base interaction grows as the molecular coverage rises and is profoundly affected by the geometrical changes of nucleobases, in particular the highly tilted geometry, and (ii) the base-base interaction prevails over the graphene-base interaction at molecular coverage above 1.0 ML, i.e., the crossover point between graphene-base and base-base interaction.

To further examine the effect of the tilted molecular geometry on the electronic structure of the graphene-nucleobase system, we examine two different rotation modes at the highest molecular coverage investigated as defined in Figure 6.4 (a). Mode I has the same tilted adsorption geometry as that at low molecular coverages, except for the high tilt angles. Mode II changes the side of the molecule close to the graphene surface (e.g., for thymine, the side with the methyl group is far from the surface in Mode I, while in Mode II the methyl group is close to the surface). Figure 6.4 (b) shows the adsorption energy of these two modes for various nucleobases. Mode II configurations are 0.09 –
Fig. 6.3. Evolution of energetic properties of the graphene-base system as a function of molecule coverage — (a) adsorption energy, (b) formation energy and (c) intermolecular binding energy of DNA/RNA nucleobases on graphene as the molecular coverage increases.
0.16 eV less energetically favorite than Mode I. Although Mode II configurations do not present the minimal energy configuration, they provide possible explanations for a recent experimental report on using a graphene-based field transistor as a base-specific probe and their importance will be addressed in the following sections [164].

Fig. 6.4. **Tilt of nucleobases at high molecular coverages.** — (a) the left images schematically shows the side-view of adsorption of thymine at 0.34 ML. The molecular plane (black line) has a small deviation from the planar position (red dash line). The right shows the side-views of adsorption of thymine at 1.42 ML. Two different rotation modes are presented. (b) Schematic showing how nucleobases contact with the graphene surface in Mode I and Mode II configurations as a result of high tilt at high molecular coverages. The central dashed line separates the nucleobases into two parts. In Mode I, the bottom part is close to the surface, while in Mode II the top part is close to the surface. The adsorption energy ($E_{ad}$) for the two rotation modes is labeled.

### 6.3.2 Electronic Structure Modifications

The adsorption of DNA/RNA nucleobases has no significant influence on the electronic states of graphene in the vicinity of the Fermi level, because their molecular
Fig. 6.5. **Electronic structure of DNA/RNA nucleobases on graphene.** — (a) Electronic structure of graphene upon adsorption of cytosine at 0.89 ML. (Left) the band structure diagram of graphene upon adsorption cytosine (red) and pristine graphene (black). (Right) the projected density of states (PDOS) of graphene (black) and cytosine (blue) upon adsorption. (b) The position of localized peaks in the PDOS of graphene near the Fermi level (i.e., the HOMO/LUMO level of nucleobases) as a function of molecular coverage. (c) The HOMO-LUMO gap of DNA/RNA nucleobases upon adsorption on graphene as a function of molecular coverage.

levels, namely the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), are far from the Dirac point (Figure 6.5 (a)), in accordance with previous calculations [254, 361]. Increasing molecular coverage tends to shift the energy of HOMO and LUMO of nucleobases (Figure 6.5 (b)), and alters the HOMO-LUMO band gap (Figure 6.5 (c)). These features in the electronic states of graphene upon adsorption of nucleobases are strongly dependent on the molecular
coverage and orientation. It is evident from Figure 6.5 (c) that the HOMO-LUMO gap of nucleobases undergoes a sharp change at high molecular coverages. These results can be explained by a complex change of electronic coupling in the system as the molecular density increases and will be discussed in detail below.

The Bader charge analysis is used to quantify the amount of electrons transferred from graphene to nucleobases \( q \) as shown in Figure 6.6 (a). For adenine, thymine and uracil, the amount of charge transferred to cytosine per molecule decreases with increasing coverage. For guanine and cytosine, the amount of redistributed charges reaches a local minimum near 0.9 ML and shows a small uprise at high molecular coverages. We relate this with experimental measurements by calculating the induced charge carrier density on nucleobases \( \Delta n = q/A \), where \( A \) is the surface area of the substrate per one adsorbed molecule), as shown in Figure 6.6 (b). It can be seen that the induced charge carrier density on nucleobases increases steadily as the molecular coverages rises. The uprise of the amount of redistributed charges at high molecular coverages for guanine and cytosine leads to a significant increase of the induced charge carrier density on nucleobases. This is in line with observed trends in previous coverage dependent experiments [106, 164].

We further examine the charge redistribution by calculating the charge density difference in the interfacial region between nucleobases and graphene. Figure 6.6 (c-f) shows the charge density difference \( \Delta \rho \) at the interfacial region for four different molecular coverages (0.35, 0.79, 0.99 and 1.49 ML). At low coverages (0.35 and 0.79 ML), there is charge depletion near the graphene surface and charge accumulation on cytosine. The degree of charge redistribution gradually decreases as the coverage increases. At high coverages (0.99 and 1.49 ML), most of charge redistribution concentrates along the edges of the adsorbed molecules. It is obvious at high molecular...
coverages the graphene-base interaction is not mainly contributed by $\pi$-$\pi$ interaction between aromatic cores, but significantly affected by the contact between side functional groups and graphene due to the tilted geometry.

Fig. 6.6. Charge redistribution in the graphene-base system. — (a) Charge transfer from graphene to nucleobases ($q$) per molecule and (b) induced charge carrier density on nucleobases ($\Delta n$) as a function of molecular coverage. (c-f) Side views of distribution of charge density difference ($\Delta \rho$) for adsorption of guanine on graphene at (c) 0.35, (d) 0.79, (e) 0.99 and (f) 1.49 molecular coverage. The yellow isosurfaces denote the charge accumulation, and cyan denote the charge depletion. The isosurface levels are $\pm 0.0004$ e/Å$^3$. 
6.3.3 Effects of Molecular Dipole Moments on the Work Function

The molecular dipole moments play a crucial role in tuning the energy level alignment in the substrate-adsorbate system. The component of the molecular dipole moment normal to the surface (in the graphene-nucleobase system, the $z$-component) is of particular importance because the local electric field generated by this dipole upon adsorption can significantly affect the work function of the substrate-adsorbate system. We calculate the $z$-component of the dipole moment of nucleobases ($\mu_z$) via the Bader charge analysis as shown in Table 6.3. A positive value of $\mu_z$ refers to the induced dipole moment directed from the nucleobase to the graphene surface. The molecular dipole moment can be strongly influenced by structural alterations and intermolecular forces as molecular coverage increases, especially when nucleobases are in a highly tilted configuration at high molecular coverages. It is evident from Table 6.3 that the direction of the molecular dipole moment of Mode II is opposite to that of Mode I and low molecular coverage configurations. The reversed molecular dipole moment of Mode II configurations can significantly affect the interfacial energy level alignment and the charge rearrangement across the interface.

Previous experiments have shown that can considerably tune the work function of graphene, leading to the Dirac point shift up to 0.3 eV [362, 363]. We examine the work function shift of the graphene-nucleobase system by calculating the difference between the electrostatic potential of the vacuum region ($E_{\text{vac}}$) and the Fermi level ($E_F$), in respect to the work function of pristine graphene (4.25 eV), as shown in Table 6.3. The work function changes at 1.4 ML undertake a large shift compared to that at low molecular coverages. For uracil and thymine, the work function changes reach to about
Table 6.3. **Molecular dipole moments and work function changes.** — The z-component of dipole moments of nucleobases ($\mu_z$), work function change compared to pristine graphene ($\Delta W$), and effective molecular dipole moments estimated from the Helmholtz equation ($\mu_{\text{eff}}$) as a function of molecular coverage.

<table>
<thead>
<tr>
<th>DNA/RNA Nucleobase</th>
<th>Coverage (ML)</th>
<th>$\mu_z$ (e( \cdot )Å)</th>
<th>$\Delta W$ (eV)</th>
<th>$\mu_{\text{eff}}$ (e( \cdot )Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>guanine</td>
<td>0.35</td>
<td>0.26</td>
<td>0.21</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>0.55</td>
<td>0.22</td>
<td>0.29</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>0.74</td>
<td>0.11</td>
<td>0.18</td>
<td>0.06</td>
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1 eV upshift for Mode I configurations and 0.4 eV downshift for Mode II configurations. These values are much larger than previous experiments on the work function engineering of graphene via physical/chemical treatments [364, 365]. In addition, for adenine and guanine, the stable adsorption configuration at 1.4 ML (Mode I) results in
a negative work function change, opposite to that at low molecular coverages. This can provide an alternative to differentiate nucleobases in applications like DNA sequencing by applying appropriate contact between nucleobases and graphene.

Next, we will examine the origin of these work function shifts induced by the adsorption of nucleobases. There are mainly two contributions to the work function shift ($\Delta W$) in a substrate-adsorbate system: (i) interfacial charge rearrangement due to the substrate-adsorbate interaction and (ii) the change of the molecular geometry upon adsorption. The contribution from the change of the molecular geometry is expected to dominate at high molecular coverages, as the tilt of nucleobases leads to large molecular dipole moments. We investigate the correlation between the molecular dipole and the work function change by calculating the effective molecular dipole moment with a simple Helmholtz equation: $\mu_{\text{eff}} = \Delta W \epsilon A/e$. The Helmholtz equation has been commonly used for describing work function modifications of metals by atoms and molecules in the literature [366–368]. However, this model does not well account for work function changes caused by varying the geometry of adsorbed molecules and intermolecular interactions in the physisorption system. Therefore we can see a large misfit to the Helmholtz equation by comparing $\mu_z$ and $\mu_{\text{eff}}$ in Table 6.3, particularly at high molecular coverages. At low molecular coverages (0.30 – 0.90 ML), $\mu_z$ roughly fits the trend calculated by the Helmholtz equation ($\mu_{\text{eff}}$), the small intrinsic molecular dipole is mainly tuned by the weak interactions between graphene and nucleobases. The small local structural changes of nucleobases (e.g., the pyramidalization of the amino group (-NH$_2$) [369]) arising from graphene-base interactions mainly contribute to induced molecular dipole moments. At nearly 1 ML molecular coverage, contributions from these small structural changes become negligible as graphene-base interactions are surpassed by the base-base interactions. As the molecular coverage rises to 1.4 ML, the strong base-base interaction leads to a significant tilt of the molecular plane
and large molecular dipole moments up to $0.48 \text{ e} \cdot \text{Å}$ (guanine and uracil). These large molecular dipole moments are accompanied by significant work function changes for all nucleobases except guanine. The adsorption of guanine at high molecular coverages leads to a similar level of work function shift compared with low molecular coverages. These results prove the complexity of the correlation between the molecular dipole and the work function change at high molecular coverages when significant adsorption geometry changes and strong intermolecular interactions are dominating in the graphene-nucleobase system.

We find that the extent of work function changes upon adsorption of nucleobases is roughly inversely proportional with the sequence of the intermolecular binding energy. As shown in Figure 6.3, the sequence of the intermolecular binding energy follows as $G > C > A > T > U$ at 1.4 ML. Guanine has the strongest intermolecular binding energy and also the strongest binding with graphene among all nucleobases at 1.4 ML. The effect of strong molecular dipole moments is suppressed by a combined influence of graphene-nucleobase interactions and base-base interactions. A strong depolarization effect can occur to cancel the effect of an individual molecular dipole. Hence the work function shift is small. Conversely, uracil has the lowest intermolecular binding energy (0.24 eV vs. 0.75 eV for guanine), and the work function changes can reach 1.04 eV. These results indicate that the intermolecular interactions and molecular screening effects (e.g. depolarization effect) can significantly lower the effective electric field originated from molecular dipole moments, particularly at high molecular coverage. We conclude that the final magnitude of the work function change of graphene at high coverage is determined by subtle interplay between base-base and graphene-base interactions, screening effects and geometry changes of adsorbed molecules and graphene.
6.3.4 Comparison of Computational and Experimental Results

We note that our computed graphene work function changes caused by adsorption of nucleobases is partly contrary to recent experiments reported by Dontschuk et al. [164], where graphene work function changes were observed upon adsorption of nucleobases on graphene using graphene field-effect transistor and X-ray photoelectron spectroscopy measurements. To check if this difference can be explained by different structures in our calculations and the experiments, we first compare our relaxed structures with the experimentally determined the nucleobase geometry on graphene by angular dependent near edge X-ray adsorption fine structure (NEXAFS). NEXAFS found that all DNA nucleobases adsorbed on graphene with high tilt angle $\alpha = 30 - 45^\circ$ [164], which is very close to the geometry we obtained at 1.4 ML. However, the calculated work function change of graphene upon adsorption of nucleobases at high molecular coverages is very different from that in the experiments (0.08 – 0.12 eV) [164].

The difference between theoretical investigations and experimental results can be attributed to a variety of factors. In the experiments, graphene was synthesized using the chemical vapor deposition (CVD) and transferred to SiO$_2$ substrates, followed by additional annealing process at 250 °C. The DNA nucleobases were deposited on the graphene surface at 138 – 235 °C under ultra high vacuum (UHV) conditions [164]. While in our DFT calculations, the graphene-nucleobases system is placed under the ground state and we do not concern the effect of the substrate, surface defects, temperature and the external environmental conditions. Previous studies has suggested that the surface defects, the substrate for graphene, and external conditions can result in different electronic responses from nucleobases compared to theoretical predictions.
[258, 361]. Despite this differences, our results still show the importance of the knowledge of adsorption geometry and orientation of the interface dipole moments of nucleobases on the electronic structure of graphene, which will be in particular important for graphene-based sensing [370]. The Mode I and Mode II calculations at high molecular coverages can be used to explain the experimental observations and help to identify the direction of molecular dipole moments on graphene. Furthermore, the results show that graphene’s electronic structure can be effectively tuned between n-type and p-type doping by changing the geometry of adsorbed molecules, which provides a new strategy for nanoscale p-n junctions in graphene.

6.4 Conclusions

In conclusion, we demonstrated that intermolecular interaction have an important role on the adsorption behaviour of DNA/RNA nucleobases on graphene as a function of molecular coverage. As the coverage increases, the dominant interaction in the graphene-base system gradually changes from graphene-base to base-base interactions. Nucleobases at low molecular coverage exhibit a nearly planar adsorption configuration, while at high molecular coverage they tends to rotate and form stronger intermolecular bonding. The geometric changes of adsorbed molecules have large impact on the electronic structure of the system, particularly on the work function that can be tuned by -0.43 eV to 1.04 eV by controlling the orientation of the adsorbed molecules. The results present a new perspective on the interaction in a $\pi-\pi$ stacking system, providing better understanding of adsorption of the complexity of organic compounds on graphene and understanding the electronic finger prints of DNA bases on graphene in DNA sequencing and sensing.
Chapter 7

Conclusions and Future Work

7.1 Concluding Remarks

The work presented in this thesis uses computational approaches to highlight the potential of using molecular adsorption for improving the performance of graphene-based devices. The identification and development of new materials and strategies for modifying the electronic properties of graphene is critical to secure the role of graphene in next-generation novel devices. We have attempted to use the adsorption of long-chain acenes, Pt nanoparticles, and DNA/RNA nucleobases on graphene and examined their influences on the electronic properties of graphene, as well as having assessed the capability of graphene in electronic, catalytic and sensing applications. Furthermore, we have explored the underlying mechanisms behind interactions between graphene and physisorbed molecules, which will help solve some challenges facing graphene-based devices and guide the design of future experiments. In the following we will provide a brief review of the work undertaken in this thesis, accompanied by conclusions and possible future investigations.
First, we have conducted a systematic study of using physisorbed hexacene and perfluorohexacene to control the electronic structure of bilayer graphene. We note that several approaches are being attempted to tailor the electronic properties of graphene, such as using graphene nanoribbons and introduction of covalent bonding. These methods open a sizable band gap, but at the expense of degraded carrier transport properties. In this study, we use noncovalent functionalization of graphene with organic molecules to achieve a fine tuning of the electronic structure of graphene without disturbing the integrity of the lattice, thereby largely preserving graphene’s excellent properties. We have identified that hexacene and perfluorohexacene are promising candidates for offering a controllable modification of the electronic properties of graphene. Moreover, we have used a novel setup by applying an external electric field to a dual molecular adsorption system to enhance the scalability and tunability of the graphene-molecule system. The results obtained from this study will hopefully inspire experimentalists to improve the performance of organic field effect transistor (OFET) devices with graphene electrodes.

Next, we have investigated the electronic structure of the Pt-graphene nanocomposites (i.e., interactions between Pt nanoparticles and functionalized graphene). We note that functionalized graphene sheets, such as GO and rGO, offer a great potential as support materials for noble metal catalysts for fuel cells. Interactions between platinum atoms and graphene need to be well understood to improve the design of the catalyst structure. However, most previous theoretical studies have focused on interactions between graphene and structural defects (e.g., vacancies), and little is known on interactions between graphene and individual oxygen-containing functional groups (e.g., epoxy, hydroxyl and carbonyl). In this study, we have shown that those functional groups have strong anchoring effects on the adsorption of Pt nanoparticles. We find
that the hydroxyl and carbonyl group are much more effective in enhancing the adsorption of Pt nanoparticles, thus improving the catalytic activity of these nanoparticles. We anticipate that results from this study will benefit experimentalists in optimizing the morphology of functionalized graphene sheets for improving the performance of noble metal catalysts in energy-related applications.

Finally, we have systematically studied interactions between graphene and DNA/RNA nucleobases (i.e., adenine, guanine, thymine, cytosine and uracil). Interactions between graphene and individual nucleobases leave distinct base-specific information in the electronic states of graphene. We present a new perspective on this graphene-nucleobase system by examining the influence of molecular concentration. We show that the coupling between graphene and nucleobases at high molecular coverages becomes very complicated considering the interplay between the graphene-base interaction and the base-base interaction. We conclude that the conventional model for explaining the relation between molecular dipoles and the energy level alignment of the graphene-molecule system (i.e., the Helmholtz equation) is not applicable when the molecular geometry is significantly affected by intermolecular interactions. The results of this study will provide useful information for future experiments to improve the efficiency of the graphene-based DNA/RNA sequencing and sensing devices. In addition, this study highlights the importance of being able to tune the electronic structure of graphene using different molecular coverages in a physisorbed system.

In conclusion, we provide a comprehensive view of modifying the electronic properties of graphene via molecular adsorption from the atomistic level. We have successfully shown the vast potential of functionalized graphene in electronic, catalytic and sensing applications. We have also identified that there are still many challenges ahead for functionalized graphene to be used in practical applications, including its production,
control of defects and reactivity. Results from our computational work are expected to assist future experimental design and control, and eventually realize the potential of graphene in the commercial market. Beyond the work presented in this thesis, we have proposed several future projects that could expand our understanding of the modifications on the electronic structure of graphene. The next section will cover these proposals via brief introductions and preliminary results.

7.2 Future Work

7.2.1 Identification of DNA Methylation

DNA methylation is described as the process of adding methyl groups (-CH$_3$) to DNA [371]. DNA methylation is an important epigenetic process that significantly affects the expression of genes. For mammals, the methylation process is observed only in CpG dinucleotides, where the C5 position of cytosine is methylated (i.e. cytosine is methylated into 5-methylcytosine.) [371–373]. This cytosine methylation process does not alter the DNA sequence, but has a significant great impact on cell development and division. In recent years, the cytosine methylation process has received extensive attention because it has been found that an aberrant methylation process occurs during the development of many diseases, and nearly all types of cancer [374, 375]. Fast and accurate detection of DNA methylation is therefore critical for the disease diagnosis. Graphene has shown its potential in differentiating methylated regions and non-methylated regions in DNA [251, 376]. However, interactions between graphene and methylated nucleobases still remains unexplored, which can provide important knowledge for further optimization of the experimental setup to achieve good selectivity and efficiency.
This future work is inspired by our results in Chapter 6, which will focus on using graphene for detecting the cytosine methylation (Figure 7.1 (a)). The effect of adsorption of cytosine and 5-methylcytosine on graphene at a low molecular coverage (0.32 ML) have been calculated. As seen from the Figure 7.1 (b), the methylated cytosine leaves slightly different electronic fingerprints on the electronic states of graphene compared to cytosine. Investigation could be pursued further to magnify the difference between cytosine and methylated cytosine by changing the adsorption geometry of the molecules.

Fig. 7.1. The cytosine methylation. — (a) relaxed grometies of cytosine (left) and 5-methylcytosine (right). (b) Partial density of states (PDOS) of graphene upon adsorption of cytosine and 5-methylcytosine. The localized states arising from the HOMO (black dash line) and LUMO (black line) of the adsorbed molecule are labeled.
7.2.2 Electrical Detection of Nitric Oxide Using Fe Porphyrin Supported on Graphene

Nitric oxide (NO) is a signaling molecule that plays an important role in many biological processes such as neurotransmission and immune response. The detection of NO is therefore essential for biomedical studies and diagnosis \[377–379\]. However, a sensitive and accurate detection of NO is hard to realize as normally NO has a short half-life (5-50 seconds) and a very low concentration (nanomolar scale) \[377, 380\]. Graphene-based sensing devices have been developed in recent years to achieve direct detection of NO in real time. Although these devices have shown a rapid response and good selectivity towards NO, their practical functionality still needs to be optimized to meet the requirement in real biological systems \[130, 381, 382\]. Hence, a good understanding of sensing mechanisms in these graphene-based devices is important.
A recent study has demonstrated that graphene-based FET noncovalently functionalized with hemin chloride (a type of Fe porphyrin) can achieve accurate NO detection in real time [381]. This motivates us to investigate the physical origin of the high sensitivity and selectivity resulting from this system. Currently, a model resembling the experimental scenario has been constructed as shown in Figure 7.2 [381]. This future work is expected to conduct a systematic study on the binding between NO and the underlying Fe porphyrin complex under the influence of the $\pi-\pi$ interactions between graphene and Fe porphyrin. New setups and alter external conditions will be attempted to enhance the NO sensitivity of the system.
Appendix A

Publication: Tunable Hybridization Between Electronic States of Graphene and Physisorbed Hexacene
Tunable Hybridization Between Electronic States of Graphene and Physisorbed Hexacene

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ABSTRACT: Noncovalent 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 field.

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. As a result of this unique electronic structure, pristine graphene demonstrates an ultrahigh charge carrier mobility in excess of 200 000 cm² V⁻¹ s⁻¹, which can be exploited for novel, highly energy efficient electronic devices.1,2 However, the development of graphene-based electronic devices is primarily hindered by the absence of an intrinsic band gap in its electronic structure.3 Although various approaches for tailoring the electronic structure of graphene have been pursued in recent years,6,10−15 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.6,7 While this strategy can effectively induce the band gap, it also suffers from carrier scattering due to edge imperfections.11,12 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 sp² to sp³.13 While such covalent functionalization successfully alters the electronic properties of graphene, it also leads to a severe degradation of its transport properties.13 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 the large scale.13,16

Among the various approaches being pursued to modify the electronic structure of graphene, noncovalent functionalization via physisorption of organic molecules offers an interesting pathway.17−19 This approach relies on conserving the integrity of the sp²-bonded carbon lattice and thus preserves the linear dispersion of electrons near the Dirac point.5,6 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.20−22 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.21−23 Among the organic compounds that are amenable to physisorption on graphene, aromatic molecules are of particular interest.24−26 The face-centered parallel stacking of aromatic molecules on graphene surface can lead to a stable hybrid system via van der Waals (vdW) dispersion.
interactions,19 while the enhanced \( \pi - \pi \) electron interaction is expected to influence the electronic structure of graphene.13 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.13,15 This can allow a vertical integration of graphene with physisorbed organic molecules with tunable transport characteristics such as charge injection barriers.13 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 leads to a severe deformation of the \( \pi \) bands of graphene.7,12 As a result, the charge carrier mobility of graphene degrades, thus limiting the switching capability of graphene-based semiconducting devices.13,15 Therefore, identification of suitable organic molecules for noncovalent 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 union of benzene rings (\( \text{C}_\text{n} \text{H}_{2n} \)). Long-chain acenes possess low-lying molecular orbitals that are expected to hybridize with \( \pi \) electrons of graphene and thus influence its electronic structure.25 Furthermore, it has been shown that the edges of hexacene can be readily functionalized with chemical groups with widely varying electron or hole affinity.7 Recently, Watanabe et al. reported a successful way to synthesize hexacene that can remain stable up to 300 °C in dark conditions.25 Moreover, organic field-effect transistor (OFET) devices made of hexacene have demonstrated the highest charge carrier mobility ever reported for organic semiconductors.26 These observations suggest that hexacene can be an attractive candidate for stable physisorption on graphene. A good fundamental understanding of the electronic interactions between hexacene and graphene is 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 \( \pi - \pi \) 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.27 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) scheme29 with a kinetic energy cutoff of 600 eV for the plane-wave basis set. Since the generalized gradient approximation does not fully account for long-range dispersion interactions,30 we used a Grimme’s semiempirical functional31 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.32 We used a periodic \( 8 \times 4 \) 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 \( 9.846 \times 10^{-11} \text{mol/cm}^2 \). 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.33,34 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 Blöchl tetrahedral smearing was employed for subsequent calculations of electronic structures.35 Finally, for accurate calculations of the electronic structures, we used a fine \( 6 \times 12 \times 1 \) centered 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 Figure 1a. We considered two stacking sequences for this configuration, namely, ABA and ABC, using the same notation as in the case of few-layer graphene.36 We also considered the simultaneous adsorption of hexacene and perfluorohexacene in a dual-molecular configuration shown in Figure 1b. Finally, the influence of external electric fields normal to the plane of graphene was investigated by introducing dipolar sheets at the center of supercells.36

![Figure 1. 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.](image-url)
RESULTS AND DISCUSSION

Electronic Structure of Hexacene and Perfluorohexacene. We first obtained the optimized geometries of hexacene and perfluorohexacene molecules and calculated their electronic structure. The relaxed geometries of hexacene and perfluorohexacene are shown in Figure 2a. The average C–H bond length for hexacene and the average C–F bond length for perfluorohexacene were calculated to be 1.09 and 1.35 Å, respectively. These bond lengths are in close agreement with previous structural calculations reported by Kadantsev et al. Figure 2b depicts an energy level diagram showing the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of hexacene and perfluorohexacene with respect to the Fermi level of graphene. The HOMO–LUMO band gaps of hexacene and perfluorohexacene are narrow, namely, 0.80 and 0.59 eV, respectively. The calculated electronic band gap of these molecules is smaller than the experimentally determined band gaps by 0.5 eV due to a systematic underestimation of band gaps by 0.5–0.6 eV due to a systematic underestimation of band gap values of semiconducting materials obtained by DFT calculations employing the generalized gradient approximation.

Single- and Dual-Molecular Adsorption on Bilayer Graphene. Next we obtained optimized ground state configurations of hexacene and perfluorohexacene adsorbed on bilayer graphene in single as well as dual-molecular configurations shown in Figure 1. In each case, the adsorption energy is calculated as \( \Delta E = E_{\text{graphene/molecule}} - E_{\text{graphene}} \), where \( E_{\text{graphene/molecule}} \) is the total energy of the fully relaxed graphene-molecule supercell, while \( E_{\text{graphene}} \) and \( E_{\text{graphene/molecule}} \) are the energy of bilayer graphene and isolated molecules in the same supercell, respectively. A negative value of the adsorption energy indicates an exothermic, thermodynamically favorable adsorption. The values for adsorption energy and the average adsorption distance from the nearest graphene layer for each configuration are summarized in Table 1. We find that the adsorption of both hexacene and perfluorohexacene on bilayer graphene is thermodynamically favorable in all configurations considered. The resulting adsorption distance of the molecules from graphene is close to the interlayer distance between graphene layers (~3.23 Å), indicating that graphene and the molecules are bound by weak van der Waals dispersion interactions. The adsorption distance and the adsorption energies are also nearly unaffected by the change of stacking sequence from ABC to ABA, also suggesting that the molecule–bilayer graphene interactions are largely confined between the molecule and the adjacent graphene layer.

Our results show that perfluorohexacene binds more strongly to bilayer graphene than hexacene (adsorption energy of \(-2.25\) eV vs \(-1.76\) eV) in a single-molecular adsorption configuration. The stronger binding of perfluorohexacene correlates with a higher electron affinity and chemical reactivity of perfluorohexacene relative to hexacene. Finally, in the case of simultaneous, dual-molecular adsorption of hexacene and perfluorohexacene on bilayer graphene, the adsorption energy of the total hexacene and perfluorohexacene complex is nearly equal to the sum of the adsorption energies of individual molecules in single-molecular adsorption. This observation suggests that the adsorption system can be relatively easily adjusted from a single-molecular configuration to a dual-molecular configuration, or vice versa, at a very low energy cost. The adsorption distances of hexacene and perfluorohexacene in dual-molecular adsorption are found to be slightly larger than for the single-molecular adsorption cases.

Electronic Structure of Bilayer Graphene upon Adsorption. Following the structural optimization, we next investigate the electronic properties of bilayer graphene upon molecular adsorption. Our results show that the molecular stacking sequence did not have any effect on the density of states curves. Consequently, Figure 3 presents the partial density of states (PDOS) for bilayer graphene with single-molecular adsorption with ABA stacking and for dual-molecular adsorption with ABCA stacking sequence. We find that the physisorbed hexacene and perfluorohexacene has a negligible effect on the \( \pi \) states of bilayer graphene in the vicinity of the

Table 1. Adsorption Energy and the Average Adsorption Distance for Monolayer Coverage of Hexacene and Perfluorohexacene on Bilayer Graphene in Single- and Dual-Molecular Adsorption Configurations

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Stacking Sequence</th>
<th>Adsorption Energy (eV)</th>
<th>Average Adsorption Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexacene</td>
<td>ABC</td>
<td>-1.756</td>
<td>3.19</td>
</tr>
<tr>
<td></td>
<td>ABA</td>
<td>-2.246</td>
<td>3.16</td>
</tr>
<tr>
<td>Perfluorohexacene</td>
<td>ABC</td>
<td>-2.239</td>
<td>3.16</td>
</tr>
<tr>
<td></td>
<td>ABAB</td>
<td>-4.015</td>
<td>3.20</td>
</tr>
<tr>
<td>Dual-molecular</td>
<td>ABAB</td>
<td>-3.17</td>
<td>(perfluorohexacene)</td>
</tr>
<tr>
<td>Adsorption</td>
<td>ABCA</td>
<td>-4.055</td>
<td>3.19</td>
</tr>
<tr>
<td>(hexacene)</td>
<td></td>
<td>-3.16</td>
<td>(perfluorohexacene)</td>
</tr>
</tbody>
</table>

This table presents the partial density of states at the Fermi level for bilayer graphene upon single- and dual-molecular adsorption of hexacene and perfluorohexacene. The ABA stacking sequence is preferred due to its lower adsorption energy compared to the ABC sequence, indicating a stronger binding of perfluorohexacene to bilayer graphene.
that the interaction between bilayer graphene and acene molecules in dual-molecular configuration is essentially governed by the interaction of a single graphene layer with the adjacent adsorbed molecule.

In order to further assess the influence of molecular adsorption on the electronic properties of graphene, we calculated the charge density difference as defined by

$$\Delta \rho = \rho_{\text{graphene/molecule}} - \rho_{\text{graphene}} - \rho_{\text{molecule}},$$

where \(\rho_{\text{graphene/molecule}}\) and \(\rho_{\text{graphene}}\) are the electronic charge densities of the adsorbed system, isolated graphene, and the molecule, respectively. With this definition, a positive value of \(\Delta \rho\) indicates an accumulation of electronic charge and a negative value indicates a charge depletion. The distribution of the charge density difference for single-molecular adsorption of hexacene and perfluorohexacene is shown in Figure 4. In the case of adsorption of hexacene on bilayer graphene (Figure 4a), the charges are depleted from the region 0.6–1.0 Å above the top graphene layer and accumulated close to hexacene in the region 2.6–2.8 Å above the graphene layer. This charge redistribution primarily arises from the electrostatic interaction between the aromatic rings of hexacene and graphene—the interaction between hydrogen atoms of hexacene and carbon atoms of graphene or hexacene is found to be negligible. Overall, the interaction between hexacene and bilayer graphene is not strong enough to lead to a significant direct charge transfer between graphene and hexacene, but only to a charge redistribution on carbon atoms of the molecule and the nearest graphene layer. In contrast to hexacene, the charge redistribution is significantly different for perfluorohexacene physisorbed on bilayer graphene as shown in Figure 4b. Since fluorne atoms are strong electron-attracting groups, the \(\pi\) electrons are polarized away from the aromatic rings leading to a relatively electron-deficient aromatic core of perfluorohexacene. Similarly, a strong interaction between fluorne and graphene gives rise to a significant charge depletion from the carbon atoms in graphene close to fluorne atoms in perfluorohexacene, indicating a net charge transfer from graphene to perfluorohexacene. By comparing the charge distribution of hexacene and perfluorohexacene on bilayer graphene, it is evident that interaction between graphene and perfluorohexacene is largely controlled by the presence of fluorne functional groups.

To quantify the charge transferred from graphene to adsorbed molecules, we plotted the variation of the planar-averaged and the integrated planar-averaged charge density difference as a function of the distance from the basal plane of graphene as shown in Figure 5. The planar-averaged charge density difference for the adsorbed molecule is defined as

$$\Delta \rho_{\text{planar}} = \langle \Delta \rho \rangle_{\text{planar}},$$

where the average is taken over the basal plane of graphene. The magnitude of the band gap induced in bilayer graphene upon adsorption of these molecules is also negligible (3 and 5 meV for hexacene and perfluorohexacene, respectively). These observations point to a weak interaction between graphene and the molecules. Nevertheless, the low-lying highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of adsorbed molecules hybridize with \(\pi\) and \(\pi^*\) states of graphene, giving rise to two localized states near the Dirac point of graphene (see Figure 3a–d). These states were found in PDOS of bilayer graphene at \(-0.18\) and 0.61 eV after the adsorption of hexacene and at \(-0.43\) and 0.18 eV after the adsorption of perfluorohexacene. The position of HOMO and LUMO of hexacene and perfluorohexacene states is slightly altered in comparison to that of isolated molecules (refer Figure 2b). To gain further insight into the localized states in graphene, we also plotted the corresponding partial charge densities by integrating the charge density in an energy range \(\pm 0.02\) eV around the localized peaks. The partial charge density plots (Figure 3e,f) show the shape of HOMO/LUMO of hexacene/perfluorohexacene, and present the signature of hybridization between graphene and the adsorbed molecules. It is evident that the induced localized states in graphene are located on the nearest carbon atoms of the top graphene layer. The presence of these hybridized states near the Dirac point of graphene implies that both electrons and holes can be injected from graphene to molecules at a relative low energy cost. In dual-molecular adsorption configuration (Figure 3d), the PDOS can be regarded as a superposition of the energy states from the single-molecular adsorption on graphene. Moreover, we observe a 8 meV band gap is opened, equal to the sum of the band gap values of individual molecules. This indicates

Figure 3. (a) Total density of states of a pristine bilayer graphene. (b–d) Partial densities of states (PDOS) of bilayer graphene upon single-molecular adsorption of hexacene (b), single-molecular adsorption of perfluorohexacene (c), and dual-molecular adsorption of hexacene and perfluorohexacene (d). In all cases, the molecular concentration is 9.85 \(\times 10^{-11}\) mol/cm\(^2\) and represents monolayer coverage. (Hex)\(_h\), (Hex)\(_l\), and (P-Hex)\(_h\), (P-Hex)\(_l\), denote the localized states induced by hybridization with HOMO and LUMO of hexacene, and HOMO and LUMO of perfluorohexacene, respectively. The Fermi level is set to zero in each case. (e,f) Partial charge density plots for the localized states in PDOS of bilayer graphene upon single-molecular adsorption of hexacene (e) and single-molecular adsorption of perfluorohexacene (f). The isosurface level is set to 0.0003 e/Å\(^3\).

Figure 4. Distribution of charge density difference for single-molecular adsorption of (a) hexacene and (b) perfluorohexacene on bilayer graphene at monolayer coverage. Red and green isosurfaces indicate the accumulation and depletion of electrons at a level of 0.0003 e/Å\(^3\), respectively.
density difference $\Delta \rho_{avg}(z)$ along a plane parallel to the basal plane of graphene is obtained by integrating the charge density difference across the plane, whereas the integrated charge density difference $\Delta \rho(z)$ is simply calculated by integrating the $\Delta \rho_{avg}(z)$ curve from the boundary of the periodic box to the position of the plane. The extremum in the integrated charge density difference curve in the region between graphene and the adsorbed molecule (indicated by red lines in Figure 5) denotes the neutral plane and the magnitude of the net charge transfer. According to this analysis, graphene donates 0.035 $e^-$ per molecule to hexacene and a larger fraction 0.050 $e^-$ per molecule to perfluorohexacene. The magnitude of net charge transfer obtained here is qualitatively consistent with Bader charge population analysis,\textsuperscript{52} which yields a net charge transfer of 0.02 $e^-$ and 0.18 $e^-$ per molecule from graphene to hexacene and perfluorohexacene, respectively. The differences in the magnitudes of the net charge transfer obtained by these two methods can be attributed to the different ways of calculating the net charges on each ion. Bader charge analysis takes into account both core charges and valence charges, while the charge density difference calculation is more suitable for interpreting the charge redistribution close to the Fermi level.\textsuperscript{53} Nevertheless, the small magnitude of charge transfer for both molecules is indicative of a weak interaction between the molecules and the bilayer graphene. Finally, few recent experimental studies have reported that as the density of the adsorbed acene molecules is increased beyond the near-monolayer coverage considered here, the molecules tend to tilt rather than maintain a planar orientation on graphene.\textsuperscript{45,54} In order to confirm this observation, we have also studied the adsorption of hexacene on bilayer graphene at a nominal molecular concentration of $1.31 \times 10^{-10}$ mol/cm$^2$ using a 8 x 3 graphene supercell. Figure S1 in the Supporting Information shows the adsorption geometry as well as the electronic

Figure 5. Planar-averaged ($\Delta \rho_{avg}(z)$) and integrated planar-averaged ($\Delta \rho(z)$) charge density difference curves for single-molecular adsorption of (a) hexacene and (b) perfluorohexacene on bilayer graphene at monolayer coverage. The positions of the top graphene layer (TG) and the molecule are marked by green and yellow dashed lines, respectively. Blue solid lines denote the neutral plane.

Figure 6. Effect of external electric field on the electronic structure of bilayer graphene in dual-molecular adsorption of hexacene and perfluorohexacene at monolayer coverage. (a) PDOS of bilayer graphene as a function of external electrical field (in eV/nm). The peaks induced by hybridization with HOMO and LUMO states of hexacene and perfluorohexacene are denoted. The gray region indicates the band gap induced in bilayer graphene. The Fermi level is set to zero. (b) Positions of the localized states in bilayer graphene induced by the hybridization with HOMO and LUMO states of hexacene and perfluorohexacene. (c) Induced charges in hexacene (Hex), perfluorohexacene (P-Hex), and top and bottom graphene layers (TG, BG), calculated by Bader charge population analysis.
interaction between hexacene and bilayer graphene at this coverage. We find that hexacene shows a remarkable $11^\circ$ tilt with respect to the basal plane of graphene, in qualitative agreement with the experimental observations.\textsuperscript{45,54} This tilt arises due to a stronger repulsive intermolecular interaction between neighboring hexacene molecules at high coverage. The cofacial $\pi-\pi$ interactions that contribute to the stability of hexacene adsorption at lower concentrations are disrupted, causing the adsorption at high coverage to be less energetically favorable (adsorption energy $-1.534 \text{ eV per molecule}$). Moreover, the electronic interactions between graphene and hexacene also vary spatially, leading to an asymmetric charge redistribution pattern as shown in Figure S1. Compared to the corresponding patterns at low coverages, a significantly larger charge rearrangement is observed in the region of the molecule where hexacene is closer to the graphene than in the region where hexacene is away from the graphene. This imbalance in the charge redistribution breaks the local symmetry of bilayer graphene, inducing a $54 \text{ meV}$ band gap.

**Effect of the Applied External Electric Field.** The results presented in earlier sections show that, in general, the adsorbed aromatic acene molecules interact weakly with bilayer graphene, leading to the formation of localized states and a weak p-type doping of graphene. Since external electric fields can enhance the interactions between adsorbate and substrate,\textsuperscript{32,34,52} we next investigate whether the external electric field could be effectively utilized to tune the electronic structure and molecule-specific localized states in bilayer graphene. Specifically, we studied the effect of the electric field in the range of $-3$ to $3 \text{ eV/nm}$, applied perpendicular to the basal plane of bilayer graphene in the dual-molecular hexacene/bilayer graphene/perfluorohexacene adsorption configuration at a monolayer coverage as shown in Figure 1b. In our notation, a positive electric field is oriented toward hexacene from perfluorohexacene. Figure 6a presents PDOS of bilayer graphene as a function of the strength of the electric field. The application of the electric field leads to the opening of a considerable band gap in bilayer graphene, as well as to the shift in the energy levels of the localized states arising due to the hybridization with HOMO and LUMO states of the molecules. The external electric field causes an accumulation of electrons in one layer and a depletion of electrons in the other layer of bilayer graphene, thus breaking the interlayer symmetry.\textsuperscript{20} The band gap generated in bilayer graphene is thus a result of the interplay between the field-induced interlayer symmetry breaking and the asymmetric charge transfer between graphene and the adsorbed hexacene and perfluorohexacene molecules. In several cases, the magnitude of band gap is difficult to
It is evident that both the shape of the PDOS as well as the magnitude of the band gap in bilayer PDOS shows a strong dependence on the strength and the direction of the external electric field. For example, the band gap increases linearly with the electric field until a maximum of ~250 meV when the field is oriented from hexacene toward perfluorohexacene (that is, a negative electric field). For a positive field, the band gap reaches ~200 meV for the field magnitude of 1 eV/nm, then reduces to ~115 meV for the field of 2 eV/nm or greater. This observed contrast in the trend between negative and positive fields can be attributed to the distinct charge transfer behavior of the adsorbed hexacene and perfluorohexacene molecules as shown in Figure 6b. For instance, for fields $E \geq 2$ eV/nm, the HOMO of perfluorohexacene and the LUMO of hexacene are pinned in the vicinity of the Fermi level. The pinning of these localized states near the Fermi level enhances the driving force for transferring charge from hexacene to perfluorohexacene, which is favored by the application of a positive electric field. Therefore, the charge transfer between hexacene and perfluorohexacene is maximized as shown in Figure 6c. The charge inequivalence between two graphene layers is reduced for positive electric fields greater than 1 eV/nm, leading to a saturation of the band gap. For negative fields, on the other hand, the charge transfer trend is reversed. The energy difference between the HOMO of perfluorohexacene and the LUMO of hexacene increases with the strength of the negative electric field. Therefore, the charge transfer between the two graphene layers is less affected and the magnitude of band gap increases rapidly with the magnitude of the field.

Figure 7a also shows a comparison between the electronic band structure diagrams of bilayer graphene adsorbed with hexacene and perfluorohexacene to those with the pristine bilayer graphene. Our obtained band structures for pristine graphene are in good agreement with previous work. It is evident that, due to the deformation of the π and π* bands, the field-induced band gap in pristine bilayer graphene is no longer located at the K point, but instead along $Γ−X$ line of the Brillouin zone. However, the π and π* bands of bilayer graphene with dual-molecular adsorption are less deformed close to the Fermi level due to the screening by molecules, indicating that the energy dispersion relationship in the vicinity of the K point is relatively well preserved. This can be clearly seen by comparing the magnitude of band gap at K ($E_1$) and the true band gap along $Γ−X$ line ($E_1$) presented in Figure 7b.

It can be seen that, in general, the range of band gaps that can be induced in bilayer graphene with molecular adsorption (100–250 meV) is comparable to the pristine bilayer graphene (200–300 meV). Overall, the band structures follow a similar trend as the DOS plots of dual molecular adsorption on bilayer graphene shown in Figure 6a, where graphene π and π* states hybridize with the localized HOMO and LUMO bands of the molecules, forming new localized bands with a flat dispersion. These results show that the energy of these localized states can be varied as a function of the strength and polarity of the applied electric field, thereby modifying the electronic structure of bilayer graphene. Finally, for completeness, we briefly compare the electronic structure of bilayer graphene with dual-molecular adsorption under the electric field to that of monolayer graphene. Figure 5 in the Supporting Information shows band structure diagrams for dual-molecular adsorption of hexacene and perfluorohexacene on monolayer graphene as a function of the strength of the electric field. We find that the electronic structure of monolayer graphene with molecular adsorption is significantly different from the bilayer graphene for negative electric fields. The localized states induced in monolayer graphene due to hybridization with the HOMO/LUMO states of the adsorbed molecules are relatively further away from the Fermi level of graphene. Moreover, negative electric fields lead to much lower band gaps in monolayer graphene (less than 30 meV). For positive electric fields, both monolayer and bilayer graphene show a similar magnitude of the band gaps (~120 meV). When compared with Figure 7, these observations highlight the interplay between the charge transfer and the breaking of the symmetry between the top and bottom structure in bilayer graphene. In general, these results suggest that by the application of external electric field to bilayer graphene with dual molecular gating, the electronic structure can be more flexibly controlled, leading to opening of considerable band gaps.

■ CONCLUSIONS

Here we have used self-consistent density functional theory calculations to study the effect of physisorption of hexacene and its fluorine derivative, perfluorohexacene, on the electronic structure of bilayer graphene. We find that, although the overall interaction between graphene and molecules is weak, the adsorption of these molecules results in a significant charge redistribution. This charge redistribution gives rise to the hybridization of HOMO/LUMO energy levels of the molecules with the π electrons of graphene, leading to the formation of localized states in bilayer graphene. We have shown that the external electric fields can be used to tune the electronic properties of the graphene-molecule system, effectively opening large band gaps on the order of 250 meV in bilayer graphene. Furthermore, external electric fields can also influence the energies of the localized states in graphene, an effect that can be utilized in organic field effect transistor (OFET) devices by aligning the electronic states of acene channels with that of graphene electrodes. This effect can also be potentially useful in the sensing of different organic molecules on the surface of graphene transistors. Graphene transistors have proven to be extremely sensitive sensors, but their selectivity remains a major problem for their practical use. In summary, we have shown that hexacene, a stable and high mobility organic electronic material, and its derivatives, are promising candidates for surface electronic structure modification of graphene for potential applications in organic electronics and sensing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b05428.

Additional figure for the adsorption of hexacene on bilayer graphene in the $8 \times 3$ graphene supercell and band structure diagrams for dual-molecular adsorption of hexacene and perfluorohexacene on monolayer graphene (PDF)

19532

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