# ADSORPTION OF VINAZENE MOLECULE ON GRAPHENE LAYER BY COMPUTATIONAL APPROACH

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To my beloved mother Jarina Abdullah who has given me the meaning of life.

For my family and friends thanks for the prayers and support

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# ABSTRACT

Graphene is a 2D nanomaterial sheet with considerably high charge carrier mobility and stable $sp^2$ hybrid structure but shows metallic behavior in pure form which limits its scope of advanced applications in semiconductor electronics industry. Adsorption is the process in which atoms, ions or molecules from a substance adhere to the surface of the adsorbent and is considered to be a potential approach to band gap opening. In this study, density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods are used to investigate the adsorption of 2-vinyl-4,5-dicyanoimidazole (vinazene) molecule to a graphene layer to show its potential for the organic photovoltaic applications. The objectives of this project are to determine the energy bandgap, the adsorption energy and the optical properties of the optimized structure of the vinazene-graphene system. The structural and electronic properties of vinazene molecule were first calculated using the Gaussian 09 program, a DFT-based software. For the combined system, the electronic and optical properties were calculated at several vinazene-graphene separation distances (1.0-12.0 Å) using the Dmol3 program, a software that incorporates both the DFT and TD-DFT methods at the level of generalized gradient approximation (GGA). The results showed that the adsorption of the vinazene molecule to graphene layer has opened up the energy bandgap with calculated values in the range of 0.12-0.19 eV. As for the adsorption energy the results showed that there are stronger intermolecular forces at shorter separation distance which significantly increase the adsorption values. The absorption spectra of the vinazene-graphene system which were calculated using TD-DFT method however showed only slight differences when compared to those from the previous studies. Thus, these results concerning the energy band gap, adsorption energy, and the optical properties highlight the potential of the vinazene-graphene system for the organic photovoltaic applications and point to new avenues for further research on graphene.

# ABSTRAK

Grafin ialah satu lembaran bahan nano 2D dengan kelincahan pembawa cas yang tinggi dan struktur hibrid $sp^2$ yang stabil tetapi menunjukkan sifat logam dalam bentuk tulen yang menghadkan skop aplikasi termaju dalam industri elektronik semikonduktor. Penjerapan ialah proses di mana atom, ion atau molekul daripada satu bahan yang tertarik pada permukaan penjerap dan dianggap sebagai satu pendekatan yang berpotensi untuk pembukaan jurang jalur. Dalam kajian ini, kaedah teori fungsian ketumpatan (DFT) dan teori fungsian ketumpatan bersandar masa (TD-DFT) digunakan untuk menyiasat penjerapan molekul 2-vinil-4,5-dicyanoimidazole (vinazene) ke satu lapisan grafin untuk menunjukkan potensinya dalam aplikasi fotovoltaik organik. Objektif projek ini adalah untuk menentukan jurang jalur tenaga, tenaga penjerapan dan sifat optik struktur teroptimum sistem vinazene-grafin. Sifat struktur dan elektronik molekul vinazene dikira terdahulu dengan menggunakan program Gaussian 09, sebuah perisian berasaskan DFT. Bagi sistem gabungan, sifat elektronik dan optik dikira pada beberapa jarak pemisahan vinazene-grafin (1.0-12.0 Å) menggunakan program Dmol3, sebuah perisian yang menggabungkan kedua-dua kaedah DFT dan TD-DFT pada tahap penganggaran kecerunan umum (GGA). Hasil menunjukkan bahawa penjerapan molekul vinazene ke lapisan grafin telah membuka jurang jalur tenaga dengan nilai yang dihitung dalam julat 0.12-0.19 eV. Bagi tenaga penjerapan, hasil menunjukkan bahawa terdapat daya antara molekul yang lebih kuat pada jarak pemisahan yang lebih pendek yang meningkatkan nilai penjerapan dengan ketara. Spektrum penyerapan sistem vinazene-grafin yang dikira dengan menggunakan kaedah TD-DFT bagaimanapun menunjukkan sedikit perbezaan sahaja berbanding dengan spektrum daripada kajian terdahulu. Oleh itu, hasil ini mengenai jurang jalur tenaga, tenaga penjerapan, dan sifat optik menyerlahkan potensi sistem vinazene-grafin untuk aplikasi fotovoltaik organik dan menunjukkan jalan baharu untuk penyelidikan lanjut mengenai grafin.

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# LIST OF SYMBOLS AND ABBREVIATIONS

| | |
|---|---|
| PV | Photovoltaics |
| OPV | Organic Photovoltaics |
| PCBM | $C_{61}$- butyric acid methyl ester |
| P3HT | Poly(3-hexylthiophene) |
| P3OT | Poly(3-octylthiophene) |
| 2D | 2-dimensional |
| $B_3N_3H_3$ | Borazine |
| $C_3N_3H_3$ | Triazene |
| $C_6H_6$ | Benzene |
| TCNE | Tetracyanoethylene |
| DFT | Density Functional Theory |
| Si | Silicon |
| CdTe | Cadmium Telluride |
| $CuInGaSe_2$ | Copper Indium Gallium Diselenide |
| *f*-Si | Polycrystalline Silicon |
| a-Si: H | Hydrogenated Amorphous Silicon |
| DSSC | Dye-Sensitized Nanostructured Solar Cells |
| vdW | Van der Waals |
| DAMN | Dicyanoimidazoles Compounds of Diaminomaleonitrile |
| EV-DPP | 4,7-bis(2-(1-(2-ethylhexyl)-4,5-dicyanoimidazol-2-yl)vinyl) Diketopyrrolopyrrole |
| DPP | Diketopyrrolophrrole |
| 3D | 3-dimensional |
| HF | Hartree-Fock |
| KS | Kohn Sham |

| | |
|---|---|
| XC | Exchange-Correlation |
| LDA | Local Density Approximation |
| LSDA | Local Spin Density Approximation |
| GGA | Generalized Gradient Approximation |
| B3LYP | Hybrid Functional |
| HOMO | Highest Occupied Molecular Orbital |
| LUMO | Lowest Unoccupied Molecular Orbital |
| TDDFT | Time-Dependent Density Functional |
| RG | Runge-Gross |
| ALDA | Adiabatic Approximations Functional |
| DNP | Double Numerical Polarized |
| PBE | Perdew-Burke-Ernzerhof |
| DOS | Density of States |
| Å | Angstrom |
| Ha | Hartree |
| InSb | Indium Antimonide |
| VB | Valence Band |
| CB | Conduction Band |
| $d$ | Distance |
| $Eg$ | Energy Gap |
| $E_{ads}$ | Energy Adsorption |
| nm | Nanometer |
| $\angle$ | Angles |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of Study

In the present era, electrical energy has become the vital need of life, as a lot of electrical appliances are used in our daily life. Besides this, in the present time, in this fast-paced world, our dependence on the novel energy resources for performing our daily life activities has been increased manifolds ever than before, particularly on the sustainable and renewable energy resources which can be converted into electrical energy directly and are green. The energy resources which are presently used are non-renewable such as fossil fuels, coal, and gas etc. By burning fossil resources for the generations of electricity, harmful gases such as carbon dioxide are also produced which are known as the main cause of the global warming and moreover they produce the environmental pollution as well. This in return can cause a more adverse impact on human health and comfort if the problem is not resolved timely and carefully (Ghommem et al., 2012).

To overcome the needs of electrical energy which are continuously increasing, there are few alternative energy sources discovered from nature that can be used instead of fossil fuels (Farret et al., 2006). The prime source of many energies to this earth is the sun, as the sun can cause rain, wind, waves and rivers etc, resulting in alternatives energy sources which are sustainable and green (Farret et al., 2006). For example, from the rain on mountains, correspondingly, rivers flow and then this water can be stored in

the dams to produce hydroelectric energy. It is because there is potential energy stored in the water which can drive the water turbines and generators to produce electric power. Similarly, the wind energy, in the area where the velocity of wind flow is very high, can be exploited for electricity generation. Additionally, the heat inside the earth, which is also called geothermal energy, can also be exploited to generate useful energy, because the hot rocks located in the core of the earth transfer their heat to water which is converted into high-pressure steam. This highly pressurized steam can be used to run steam turbines which in turn run generators to generate electricity (Farret et al., 2006).

Besides, the most promising alternative energy source is the solar energy received from the sun. This source of energy is directly converted into electricity via employing photovoltaics (PV) modules. These photovoltaic solar cells modules are frequently fabricated from thin films/wafers. The materials of these thin films or wafers usually are semiconductors materials capable of converting the incident solar photon energy into dc current. All these examples of alternatives sources of energy are absolutely renewable, free of cost, and causing no pollution to the earth (Farret et al., 2006).

From the photovoltaic solar cells, the organic photovoltaics (OPV) are also studied and have been introduced to be one of the alternatives ways of the electricity generation. OPV is one of the new technologies in producing electrical energy by converting the solar energy by the photovoltaic effect. This technology is used worldwide due to the lack/adverse effect of the fossil fuels nowadays. Since solar energy is an unlimited resource of energy, therefore, the study of OPV for utilizing this huge and free energy is very much in demand.

The organic materials are chosen in the photovoltaic technologies because of their stability, solubility and good efficiency. Besides good efficiencies, these are low-cost processing and tunable organic electron transport materials in OPV (Mcgehee, Sellinger, and Higgs 2011). In addition, graphene is one of the materials that are used in

utilizing photovoltaic cells besides silicon. Graphene is the two-dimensional carbon allotrope. Its amazing properties and potentials can be integrated into a huge number of the applications better than anything else. It is also used to improve the performance and efficiency of current materials and substances. Its properties show that it has high electron mobility and potential electronic structure for optoelectronics/photovoltaics particularly through engineering its electronic band-gap energy. However, graphene has a problem of the "lack of an energy gap" which can be tuned by organic materials (Chang et al. 2012; Lu, Chen, and Feng 2009; Neto 2009).

While keeping in view above mentioned features, here, an interfacing study between the 2-vinyl-4, 5-dicyanoimidazoles (vinazene) and graphene layer is carried out as the organic molecular adsorption on the graphene layer can lead to bandgap opening (Chang et al., 2012). These interfacing studies were theoretically studied using Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) to calculate the structural, electronic and optical properties. Therefore, this study could be, in turn, a potential and suitable source for the green energy production.

## 1.2 Problem Statement

The energy crises can be resolved by using the organic materials in the organic photovoltaics to convert solar energy into electrical energy (Covert, Greenstone, and Knittel 2016; Environ et al. 2011; Kippelen 2009). Recently, the phenyl $C_{61}$- butyric acid methyl ester (PCBM) as the electron acceptor while the poly(3-hexylthiophene) (P3HT) and poly(3-octylthiophene) (P3OT) as the donor has been studied for OPV applications. Although both donor and acceptor have shown the solubility and stability, PCBM has not revealed necessary and most favorable structure for the solution processed OPV devices. Moreover, the power efficiency of OPV devices, based on the above said organic materials and others which have been previously reported, are still lower compared to that of the conventional inorganic devices (Ma et al., 2008).

Recently, vinazene is reported a potential candidate for photovoltaic (PV) applications (Mohamad et al., 2015). Graphene, the most popular material, consisting of $sp^2$-hybridized 2-dimensional (2D) carbon structure, has shown striking electronic and mechanical properties. However, Graphene is a zero-gap semiconductor whereas in practical applications the energy gap is essential. In this regard, aromatic molecules of borazine ($B_3N_3H_3$), triazene ($C_3N_3H_3$) and benzene ($C_6H_6$) have been investigated to bandgap opening of the Graphene via adsorption using computational method implemented in the Vienna ab initio simulation package (VASP). Among these, triazene showed 0.06 eV while others molecule tetracyanoethylene (TCNE) gives 0.23 eV (Chang et al. 2012; Lu, Chen, and Feng 2009). Thus, in the present work, we will accomplish our project via computational approach to investigate the capability of the organic material, vinazene in exploiting and tuning the bandgap of graphene for enhancing its potential for OPV applications.

## 1.3 Objectives

The focus of this study is to investigate the potential of 2-vinyl-4, 5-dicyanoimidazole (vinazene) in tuning the bandgap of graphene for photovoltaic applications. Thus, the objectives of this research are outlined as follows:

1. To optimize the molecular structure of vinazene with different level of exchange-correlation functional (LSDA, GGA, B3LYP).

2. To determine the energy bandgap (electronic properties) of the optimized structure of the vinazene molecule and vinazene molecule interfaced with the graphene layer.

3. To calculate the adsorption energy of vinazene molecule interfaced with the graphene layer.

4. To determine the optical properties of vinazene molecule interfaced with the graphene layer.

## 1.4 Scope of Study

The present research work covers the study of vinazene and graphene structure and their interfacing study. Computations are performed through the density functional theory (DFT) and time-dependent DFT (TD-DFT) approach to study the structural, electronic and optical properties of the vinazene molecule and its interfacing with graphene. These two phases of the study are optimized using DFT approach with the different level of exchange-correlation functional (LSDA, GGA, B3LYP). Two different methods are used; Gaussian09 is used for vinazene molecular structure and Dmol3 for the interfacing study of the vinazene with the graphene layer.

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