MODELLING AND SIMULATION OF STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF ORGANIC SEMICONDUCTING MATERIALS

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To my beloved family; mother and father,
sister, husband, who have been with me
throughout my studies.

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ABSTRACT

Organic semiconductor materials (OSMs) involving thiophene, vinazene, di-indenoperylene (DIP) and copper phthalocyanine (CuPc) are computationally explored at both the isolated molecule and the molecular crystal levels, to expose their potential in optoelectronics. The calculations are performed within the first-principles pseudo-potential quantum mechanical approaches designed within density functional theory at the level of different flavors of exchange-correlation energy/potential functional. All the studied molecules exhibit π-orbital and free electron pairs. The study revealed that the total energy values of isolated molecules of thiophene, vinazene, di-indenoperylene (DIP) and CuPc are 552.7140Ha, 487.7079Ha, 1227.9865Ha and 1887.9308Ha respectively, and those for the corresponding molecular crystals are 5337.5117Ha, 3901.8748Ha, 2455.2992Ha and 3775.2523Ha respectively. In the electronic structure investigations, it is found that the delocalization of electrons from the π-conjugation characteristics of the OSMs, has resulted in the electronic hybridization in their electronic structures, and consequently, increased the charge population in the highest occupied molecular orbitals. The obtained energy-gap values for CuPc, DIP, vinazene and thiophene molecules are 0.847eV, 1.490eV, 3.300eV and 4.723eV respectively. In investigations of the optical properties, substantially high values of absorption observed particularly in molecular crystals, accompanied with low values of resistivity, have resulted in the significant lowering of the loss function. The moderate charge carrier mobility in OSMs is also reflected from the obtained dielectric function and conductivity spectra. Besides, on the application part, the graphene zero energy-gap is resolved via the study of thiophene molecule as the adsorbate and graphene surface as the substrate by employing the interfacial approach. To validate the OSM findings for organic photovoltaic (OPV) applications, performance calculations of a simulated vinazene-based device have been executed. From the obtained results that show peak shifting in transmission spectra, gradual increasing of current in current-voltage (I-V) characteristic curve and conductance spectra that exhibit a sinusoidal pattern, it is believed that vinazene molecule can be recognized as good OPV active material.

ABSTRAK

Bahan semikonduktor organik (OSMs) yang melibatkan tiofena, vinazena, di-indenoperilena (DIP) dan kuprum ftalosianina (CuPc) telah diteroka secara pengkomputeran pada kedua-dua tahap molekul terpencil dan hablur molekul, untuk mendedahkan potensi mereka di dalam optoelektronik. Pengiraan telah dilakukan menggunakan pendekatan kuantum mekanik berpseudo-keupayaan berasas prinsip-pertama direka dalam teori fungsian ketumpatan pada pelbagai peringkat fungsian tenaga/keupayaan pertukaran-kolerasi. Semua molekul yang dikaji mempamerkan orbital-π dan pasangan elektron bebas. Kajian ini mendedahkan nilai tenaga keseluruhan molekul terpencil bagi tiofena, vinazena, di-indenoperilena (DIP) dan CuPc masing-masing ialah 552.7140Ha, 487.7079Ha, 1227.9865Ha dan 1887.9308Ha, dan bagi hablur molekul yang sepadan masing-masing ialah 5337.5117Ha, 3901.8748Ha, 2455.2992Ha dan 3775.2523Ha. Dalam kajian struktur elektron, didapati bahawa pentaksetempatan elektron daripada OSMs bercirikan konjugat-π, telah menghasilkan penghibridan elektron didalam struktur elektron, dan seterusnya, meningkatkan populasi cas di dalam orbital molekul terisi tertinggi. Jurang-tenaga yang diperolehi bagi molekul CuPc, DIP, vinazena dan tiofena masing-masing ialah 0.847eV, 1.490eV, 3.300eV dan 4.723eV. Dalam kajian sifat optik, nilai penyerapan yang cukup tinggi terlihat terutamanya dalam hablur molekul, disertai dengan nilai kerintangan yang rendah, telah menghasilkan penurunan ketara dalam nilai fungsi kehilangan. Kelincahan pembawa cas yang sederhana dalam OSMs juga tertunjuk daripada spektrum fungsi dieletrik dan kekonduksian yang diperolehi. Disamping itu, pada bahagian aplikasi, jurang-tenaga sifar grafin telah dirungkai melalui kajian dengan molekul tiofena sebagai bahan terjerap dan permukaan grafin sebagai substrat melalui pendekatan antara muka. Untuk mengesahkan hasil kajian OSM bagi aplikasi fotovolta organik (OPV), pengiraan prestasi peranti berasas-vinazena yang bersimulasi telah dilakukan. Daripada keputusan yang diperolehi yang menunjukkan peralihan puncak pada spektrum penghantaran, peningkatan beransur-ansur arus pada lengkung ciri arus-voltan (I-V) dan spektrum konduksian yang mempamerkan pola sinusoid, adalah dipercayai bahawa molekul vinazena boleh diakui sebagai bahan aktif OPV yang baik.

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LIST OF ABBREVIATIONS

PV	-	Photovoltaics
SM	-	Semiconductor material
OSM	-	Organic semiconductor material
ISM	-	Inorganic semiconductor material
OPV	-	Organic photovoltaics
DSSC	-	Dye-sensitized solar cells
DFT	-	Density Functional Theory
CuPc	-	Cu-Phthalocyanine
LDA	-	Local Density Approximation
GGA	-	Generalized Gradient Approximation
BLYP	-	Becke-Lee-Yang-Parr
Vinazene	-	2-vinyl-4,5-dicyanoimidazoles
HOMO	-	Highest occupied molecular orbital
LUMO	-	Lowest unoccupied molecular orbital
DIP	-	Di-indeno perylene
HF	-	Hatree-Fock
KS	-	Kohn-Sham
PBE	-	Perdew-Burke-Ernzerhof
PW91	-	Perdew-Wang 1991
DOS	-	Density of states
NEGF	-	non-equilibrium Green's Function

LIST OF SYMBOLS

$\hat{H}_T$	-	Hamiltonian of the total system
$\hat{H}$		Hamiltonian for many body system of electron
M_i	-	Mass of nucleus at position R_i
m_e	-	Mass of electrons at position r_i
ρ	-	Ground state density
V_{ext}	-	External potential
O	-	Any observable
F_{HK}	-	Hohenberg-Kohn density functional
E_0	-	Exact ground-state electronic energy
Ψ_0	-	Trial wave function yielding the ground state electron density
ρ_0	-	Ground-state electron density
v_{KS}	-	Kohn-Sham single-particle potential
ψ_i	-	Wave function of the N single particle orbital
μ	-	Exact chemical potential of the system
T_{KS}	-	Kinetic energy of Kohn-Sham N non-interacting system
E_H	-	Energy from the Hatree contribution
E_{XC}	-	Exchange-correlation energy
ε_{XC}^{Hom}	-	Exchange correlation energy density of an interacting homogeneous electron gas
$\nabla\rho$	-	Gradient of electron density
x_μ	-	Atomic basis functions
$C_{i\mu}$	-	Molecular orbital expansion coefficient
Y_{lm}	-	Spherical harmonic

$\mathbf{G}$	-	Reciprocal lattice vector
E_{cut}	-	Cutoff energy
P	-	The spin-polarization
E_g	-	Energy gap

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CHAPTER 1

INTRODUCTION

1.1   Background of study

Industrialization, a drastic rise in the population and globalization, has increased the demand for sustainable and clean energy sources manifold ever than before. Moreover, conventional energy resources are rapidly depleting and concurrently creating problems such as global warming/environment pollution etc. In order to cope with these issues, clean and economical energy sources are in great demand as an alternative to oil and fossil fuels. Hence, researchers have shown considerable interests in exploring alternative energy resources. As a matter of fact, the sun is the source that provides an abundance of renewable solar energy and is a viable source to realize the dream of cheaper and green energy. Apparently, the sunlight supplies approximately 10^4 times larger energy than our present needs. However, the biggest challenge is the conversion of solar energy into electrical energy in addressing the issue of world energy demands over a longer period of time through cheaper and environment-friendly technologies.

In resolving the issue, photovoltaic (PV) technology is the most practical and attractive approach to exploit the sustainable energy source at all level as well as to overcome future energy crisis. The demands on PV technology are rapidly increasing with time [1]. The key to exploiting PV technology is majorly relying on the

semiconductor materials (SMs) since solar energy is converted into electricity directly [2-3] by manipulating the potential of SM materials. Day by day, this technology is attracting more and more attention of the researchers towards exploring, tailoring and investigating the new and better SMs, which can realize the dream of green/sustainable energy. Although some SMs are already exploited in the technology, most of the modules are based on inorganic semiconductor materials (ISMs). Recently, researchers have diverted their interests in the organic SMs (OSMs) as well. It is due to the fact that the PV modules that are based on the conventional ISMs are very expensive if compared to the OSMs. Moreover, the optoelectronic device manufacturing based on the OSMs is easier than the ISMs. Regardless of the advantages, OSMs -based device efficiency is rather low [4-5]. Hence, the study of OSMs generally seeks opportunities to dominate in PV technology with enhanced performance over the current market of conventional crystalline silicon and other ISMs.

The OSM-based device of organic photovoltaics (OPV) is thin, light and flexible. The versatility of OPV as the future energy efficient technology is paving towards replacing the utilization of conventional silicon in the mass production. Some examples of OPV technology that have been introduced these days are OPV polymers, OPV DSSC (dye-sensitized solar cells) and OPV oligomers. OPV devices consist of one or several photoactive OSMs overlaid between two electrodes of cathode and anode [5] Photoactive OSMs play a key role in the performance of optoelectronic/photovoltaic devices. Therefore, in order to determine suitable and efficient photoactive OSMs and attain their respective properties, comprehensive investigations on their electronic structure and optoelectronic properties are necessary. In this regard, the use of ab initio quantum mechanical computational techniques in performing virtual experiment may lead to a cheaper experiment and shorter developmental cycle.

Computational ab initio methodologies based on Density Functional Theory (DFT) are intensely used by the theoretical researchers to solve the complex problems. It was found to be more reliable and provides better results concerning the electronic structure calculations in designing and modeling new materials and tuning

their properties without prior experimental knowledge. This feature of DFT has brought a new insight into the investigation and education field.

1.2   Problem statement

Organic materials are relatively at an early stage of development if compared to the inorganic materials. Thus, further research on novel OSMs for their applications in advance technologies is essential. Despite progress in the exploration of better performance OPV technology, application dilemma is certainly resolved with a better understanding of the OSMs electronic structure and corresponding optoelectronic properties which can unveil the novel features and functionalities of a material [6-7]. Furthermore, with the knowledge of electronic structure and properties, one can successfully tune material properties for the application in a device for stable and good performance [8-9]. Though numbers of study are found pertaining to OSMs comprehending their potential for OPV technology, rarely are focused on atomic level physical properties of the OSMs which show a correlation between the structures of the molecule and molecular crystal. Moreover, the available research reports on the materials under investigation, are giving piecemeal information about the pertinent properties which predict for their implementation within a particular device [5, 10]. Hence, a comprehensive study on the reported OSMs optoelectronic properties and the implementation of the studied OSMs to be adopted in OPV technology seems vague.

OSMs based on small molecules have also attracted a lot of interest recently [11]. Particularly, OSMs small molecule of thiophene, vinazene, perylene, and Cu-phthalocyanine (CuPc) containing π-conjugation has opened a new door for the optoelectronics by showing intense electrons population [12]. In-depth knowledge of these π-conjugated molecules involving the geometrical influences, optoelectronic properties and fundamental understanding of the concerned phenomena at atomic scale level is mandatory. However, those studies that are accompanied by optical characteristics are still scarce. Evidently, numbers of experimental and theoretical work involving structural and electronic properties on thiophene, perylene, and Cu-phthalocyanine (CuPc) have been proposed [8, 13-15], while optical properties

investigation based on theoretical works are scarcely done [16], compared to experimental work [17-18]. Differently in vinazene, where both electronic and optical properties study based on theoretical work remains elusive [19-21].

As the π-conjugated molecule study is on demand, the theoretical studies on the molecular crystal of thiophene, vinazene, perylene, and Cu-phthalocyanine (CuPc) for OPV purposes are also scarce [22-23] especially involving optical properties study [24]. Besides, investigation on electronic properties, optical properties and the ideal packing of the molecular crystals' structural arrangement resulted from the transition from molecule to molecular crystal is remained elusive as well. This has stirred up our interest to further expose the potential of molecular crystal while the molecule being the key building blocks for the OSMs of thiophene, vinazene, perylene, and Cu-phthalocyanine (CuPc) [25-26]. All of these dilemmas need to be clarified in order to further enhance OPV performance through OSMs potential in realizing the dream of providing a base of alternate cheaper sustainable energy sources for future's green energy technologies.

1.3   Objectives

The aim of this research is to study the physical properties of a class of organic semiconductor materials in the form of isolated molecules and molecular crystals for organic photovoltaic applications using the theoretical approach of Density Functional Theory (DFT).

In order to achieve the aim, the following objectives are performed:

i) To optimize the geometrical structure of organic materials (thiophene, vinazene, perylene, and Cu-phthalocyanine (CuPc))
ii) To investigate the electronic properties of the organic materials in isolated molecule and molecular crystal
iii) To investigate the optical properties of the organic materials in isolated molecule and molecular crystal
iv) To simulate OPV device and investigate its efficiency

1.4   Scope of study

This research is covered by performing theoretical investigations relating to OSMs isolated molecule and molecular crystal of thiophene, vinazene, perylene, and Cu-phthalocyanine. A thorough study is performed using a quantum mechanical ab initio approach called as Density Functional Theory (DFT). The calculations are carried out on the basic and established laws of nature without involving any additional assumption or models. To perform DFT calculations, computational codes (DMol3 [25, 27], CASTEP [28] and VASP [29]), framed within the DFT, are utilized to model, design and simulates the chosen OSMs in order to achieve the objectives. Each code is providing different approaches, basis, potential, exchange-correlation energy parameterizations, advantages, and disadvantages. However, in general, all the codes are designed within DFT.

Planar structure OSMs are chosen for OPV technology. Optimization of geometrical structures of the chosen OSMs is performed at the isolated molecule level at first in order to contribute as the backbone of molecular crystal simulation later. Packing arrangements of the molecules are being focused in designing the molecular crystal structure. In isolated molecules, influences of the heteroatom, functional groups, carbon-only based structure, and the presence of metal element are being highlighted through the variety of chosen OSMs. Whereas intermolecular forces attributed from the packing arrangements and the delocalization and localization of π-conjugated system are discussed for molecular crystal structure.

To provide an extensive study as well as for future reference, electronic properties are executed (based on pseudopotential approach) with several exchange-correlation functional such as Local Density Approximation (LDA) [30], Generalized Gradient Approximation (GGA) [31] and hybrid functional of Becke-Lee-Yang-Parr (B3LYP) [32-33] with different parameterizations. On the other hand, in optical properties, the spectra of absorption, reflectivity, loss function, real and imaginary of conductivity and dielectric function are investigated at PBE-GGA functional level.

In order to emphasize the potential of OSMs in OPV applications through the study of electro-optical properties, this research has been extended through the simulations of interfacial study and substitution of OSM in device applications as well. Some OSMs are selected to perform the respective study. The properties of OSMs are engineered solely with energy efficient technologies particularly OPV applications in order to provide an overview and predictions about the OSMs behaviors and properties before turning the respective OSMs into practical use. These approximations and methods are complementary for this research on optoelectronic properties for OPV applications.

1.5 Significance of study

This research offers comprehensive study on optoelectronic properties of various OSMs that covered from molecule to crystal level and depicts the OSMs potential in OPV applications through computational approaches. The chosen OSMs are studied with regard to active OPV components either donor or acceptor materials (n-type or p-type materials) to be employed in OPV. In order to spawn a new generation of solar-powered products which give benefits in several aspects of cost/money, sustainability, lifetime and friendly to environments, the research was conducted through the state of the art ab initio methods based on DFT. Moreover, prediction of properties, that have not been explored experimentally yet, are determined within a short time and low cost. This research will assist to solve the problems which constantly arise as stated in sub-chapter 1.2 and difficult to decipher experimentally. The computed optical and electronic properties highlight the promising future of OSMs in OPV technology. In addition, this research may provide promising characteristics of OPV materials that could be a strong footing to the experimentalist, academicians, and industrial scientists to fabricate optoelectronic devices based on the chosen OSMs that are beneficial to the country, community and future generation of green energy technology.

1.6   Structure of thesis

In this thesis, several OSMs covered in two phases of the isolated molecule and molecular crystal level based on the framework of DFT. The DFT based calculations have been rationalized mostly within the computational codes of DMol3, CASTEP, and VASP. In Chapter 1, general and background of the research have been provided. The objectives of this study are highlighted as well in this chapter corresponding to the defined problem statements. Plus, to allow one to understand the direction of this study, the scope and significance of study are also elaborated within this chapter.

In Chapter 2, an overview of the previous works done on the selected OSMs of thiophene, vinazene, perylene, and CuPc are presented. Most of the existing theoretical or experimental studies related to the OSMs have been reported either using the same methodologies or otherwise. In addition to that, the development of the theoretical works from the scratch and the DFT-based framework is described too, to give an exclusive understanding of the present study. In Chapter 3, the methodologies used throughout this study are presented. The employed computational codes according to a different level of study are explained and the computational details including the necessary procedures to be done appropriately have been included as well.

Chapter 4 presents the investigation of structural properties of both isolated molecule and molecular crystal of thiophene, vinazene, perylene, and CuPc. Optimization of the structures that lead in obtaining structure stability, lattice parameters, arrangements of molecules, brief structural strengths and advantages in response to different influences of the heteroatom, functional groups, carbon-only based structure, and the presence of metal elements is being discussed in this chapter.

Chapter 5 contains the investigation results on the electronic properties of the optimized structures. This chapter is compromised with the energetic difference on each molecule structures which is obtained via the energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital

(LUMO), whereas for crystal structures via the formation of bandstructure. Various exchange-correlation potentials have been executed for the calculations of the energy gap in this chapter. In addition, the total and partial density of states in relations with the obtained PBE-GGA energy gap has been discussed within this chapter too.

Chapter 6 contains the investigated results on the optical properties of the optimized structures. Reflectivity, refractive index, absorption, together with real and imaginary parts of the frequency-dependent dielectric and conductivity function are part of the properties that have been discussed by relying on the practical characteristics that may serve as good optoelectronic system and devices, especially in the organic photovoltaic field. Calculations in this chapter have been conducted through PBE-GGA parameterizations.

In Chapter 7, discussions on the simulations of interfacial study and the substitution of OSM in device applications have been highlighted. In the interface study, thiophene and graphene have been chosen as the adsorbate and substrate materials. The separation distance between thiophene and graphene was varied from 1.00Å to 3.00Å to tune the energy gap produced. The adsorption and binding energy curve are depicted in this chapter and based on the discussion, the appearance of physisorption characteristics has been distinguished. To further the investigation, simulation on device applications is performed and discussed in this chapter too. Instead of thiophene, vinazene is chosen since the same work on thiophene has been previously done by others. The density of states of the vinazene molecule, the device only and the system have been elaborated in brief. The transmission spectrum, I-V characteristics curve and conductance curve in respect to zero and applied bias have been discussed in details where broadening in the bias windows are clearly observed.

Last but not least, Chapter 8 provides the conclusions drawn from this research and recommendations for future work as well.

REFERENCES

1. Hernandez, R., S. Easter, M. Murphy-Mariscal, F. Maestre, M. Tavassoli, E. Allen, C. Barrows, J. Belnap, R. Ochoa-Hueso, and S. Ravi, *Environmental impacts of utility-scale solar energy.* Renewable and Sustainable Energy Reviews, 2014. **29**: p. 766-779.

2. Brabec, C.J., *Organic photovoltaics: technology and market.* Solar Energy Materials and Solar Cells, 2004. **83**(2): p. 273-292.

3. Benanti, T.L. and D. Venkataraman, *Organic solar cells: An overview focusing on active layer morphology.* Photosynthesis Research, 2006. **87**(1): p. 73-81.

4. Williams, A. *Organic PV: can UK start-ups carve out a niche?* 2012; Available from: http://optics.org/indepth/3/6/2

5. Nunzi, J.-M., *Organic photovoltaic materials and devices.* C. R. Physique, 2002. **3**(4): p. 523–542.

6. Wang, H., Z. Xie, Y. Ma, and J. Shen, *Progress on the optoelectronic functional organic crystals.* Science in China Series B: Chemistry, 2007. **50**(4): p. 433-452.

7. Martin, R.M., *Electronic structure: basic theory and practical methods*. 2004: Cambridge university press.

8. Refaely-Abramson, S., R. Baer, and L. Kronik, *Fundamental and excitation gaps in molecules of relevance for organic photovoltaics from an optimally tuned range-separated hybrid functional.* Physical Review B, 2011. **84**(7): p. 075144.

9. Lu, Y.H., W. Chen, Y.P. Feng, and P.M. He, *Tuning the Electronic Structure of Graphene by an Organic Molecule.* The Journal of Physical Chemistry B, 2008. **113**(1): p. 2-5.

10. Li, Y., *Molecular design of photovoltaic materials for polymer solar cells: toward suitable electronic energy levels and broad absorption.* Accounts of Chemical Research, 2012. **45**(5): p. 723-733.

11.   Rojas-Ruiz, F.A., L.Y. Vargas-Méndez, and V.V. Kouznetsov, *Challenges and Perspectives of Chemical Biology, a Successful Multidisciplinary Field of Natural Sciences.* Molecules, 2011. **16**(3): p. 2672.

12.   Lozzi, L., S. Santucci, S. La Rosa, B. Delley, and S. Picozzi, *Electronic structure of crystalline copper phthalocyanine.* The Journal of chemical physics, 2004. **121**(4): p. 1883-1889.

13.   de Oteyza, D.G., E. Barrena, M. Ruiz-Osés, I. Silanes, B.P. Doyle, J.E. Ortega, A. Arnau, H. Dosch, and Y. Wakayama, *Crystallographic and electronic structure of self-assembled DIP monolayers on Au (111) substrates.* The Journal of Physical Chemistry C, 2008. **112**(18): p. 7168-7172.

14.   Downes, J.E., C. McGuinness, P.-A. Glans, T. Learmonth, D. Fu, P. Sheridan, and K.E. Smith, *Electronic structure near the Fermi level of the organic semiconductor copper phthalocyanine.* Chemical physics letters, 2004. **390**(1): p. 203-207.

15.   Marom, N., O. Hod, G.E. Scuseria, and L. Kronik, *Electronic structure of copper phthalocyanine: A comparative density functional theory study.* The Journal of chemical physics, 2008. **128**(16): p. 164107.

16.   Ramaniah, L.M. and M. Boero, *Structural, electronic, and optical properties of the diindenoperylene molecule from first-principles density-functional theory.* Physical Review A, 2006. **74**(4): p. 042505.

17.   El-Nahass, M., F. Bahabri, A. Ghamdi, and S. Al-Harbi, *Structural and transport properties of copper phthalocyanine (CuPc) thin films.* Egypt J Sol, 2002. **25**(2): p. 307.

18.   Wróbel, D. and A. Dudkowiak, *Porphyrins and phthalocyanines–functional molecular materials for optoelectronics and medicine.* Molecular Crystals and Liquid Crystals, 2006. **448**(1): p. 15/[617]-38/[640].

19.   Nepraš, M., N. Almonasy, F. Bureš, J. Kulhánek, M. Dvořák, and M. Michl, *Fluorescence and photophysical properties of D-π-A push-pull systems featuring a 4, 5-dicyanoimidazole unit.* Dyes and Pigments, 2011. **91**(3): p. 466-473.

20.   Bloking, J.T., X. Han, A.T. Higgs, J.P. Kastrop, L. Pandey, J.E. Norton, C. Risko, C.E. Chen, J.L. Breedas, M.D. McGehee, and A.Sellinger., *Solution-Processed Organic Solar Cells with Power Conversion Efficiencies of 2.5%*

using Benzothiadiazole/Imide-Based Acceptors. Chem. Mater, 2011. **23**(24): p. 5484−5490.

21. Kulhánek, J., F. Bures, A. Wojciechowski, M. Makowska-Janusik, E. Gondek, and I. Kityk, *Optical operation by chromophores featuring 4, 5-dicyanoimidazole embedded within poly (methyl methacrylate) matrices.* The Journal of Physical Chemistry A, 2010. **114**(35): p. 9440-9446.

22. Facchetti, A., M.-H. Yoon, C.L. Stern, G.R. Hutchison, M.A. Ratner, and T.J. Marks, *Building blocks for n-type molecular and polymeric electronics. Perfluoroalkyl-versus alkyl-functionalized oligothiophenes (nTs; n= 2-6). Systematic synthesis, spectroscopy, electrochemistry, and solid-state organization.* Journal of the American Chemical Society, 2004. **126**(41): p. 13480-13501.

23. Fedorov, I., Y. Zhuravlev, and V. Berveno, *Structural and electronic properties of perylene from first principles calculations.* The Journal of chemical physics, 2013. **138**(9): p. 094509.

24. Fuke, K., K. Kaya, T. Kajiwara, and S. Nagakura, *The polarized reflection and absorption spectra of perylene crystals in monomeric and dimeric forms.* Journal of Molecular Spectroscopy, 1976. **63**(1): p. 98-107.

25. Delley, B., *From molecules to solids with the DMol3 approach.* The Journal of Chemical Physics, 2000. **113**(18): p. 7756-7764.

26. Zang, L., Y. Che, and J.S. Moore, *One-dimensional self-assembly of planar π-conjugated molecules: adaptable building blocks for organic nanodevices.* Accounts of Chemical Research, 2008. **41**(12): p. 1596-1608.

27. Delley, B., *An all-electron numerical method for solving the local density functional for polyatomic molecules.* The Journal of Chemical Physics, 1990. **92**(1): p. 508-517.

28. Clark, S.J., M.D. Segall, C.J. Pickard, P.J. Hasnip, M.I.J. Probert, K. Refson, and M.C. Payne, *First principles methods using CASTEP.* Zeitschrift für Kristallographie, 2005. **220**(5/6): p. 567–570.

29. Kresse, G. and J. Furthmuller, *Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set.* Phys. Rev. B, 1996. **54**(16): p. 11169-11186.

30.	Perdew, J.P. and Y. Wang, *Accurate and simple analytic representation of the electron-gas correlation energy.* Physical review B, 1992. **45**(23): p. 13244-13249.

31.	Perdew, J.P., K. Burke, and M. Ernzerhof, *Generalized gradient approximation made simple.* Physical review letters, 1996. **77**(18): p. 3865.

32.	Lee, C., W. Yang, and R.G. Parr, *Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density.* Physical review B, 1988. **37**(2): p. 785.

33.	Becke, A.D., *Density-functional thermochemistry. III. The role of exact exchange.* The Journal of chemical physics, 1993. **98**(7): p. 5648-5652.

34.	Chapin, D.M., C.S. Fuller, and G.L. Pearson, *A New Silicon p-n Junction Photocell for Converting Solar Radiation into Electrical Power.* Journal of Applied Physics, 1954. **25**(5): p. 676-677.

35.	Kippelen, B. and J.-L. Brédas, *Organic photovoltaics.* Energy & Environmental Science, 2009. **2**(3): p. 251-261.

36.	Bharam, V. and D. Day, *Advantages and challenges of silicon in the photovoltaic cells.* 2012.

37.	Tang, C.W., *Twolayer organic photovoltaic cell.* Appl. Phys. Lett. 48, 1986. **183**.

38.	Hiramoto, M., H. Fujiwara, and M. Yokoyama, *Three-layered organic solar cell with a photoactive interlayer of codeposited pigments.* Applied Physics Letters, 1991. **58**(10): p. 1062-1064.

39.	Zhang, W., S.C. Tse, J. Lu, Y. Tao, and M.S. Wong, *Solution processable donor-acceptor oligothiophenes for bulk-heterojunction solar cells.* Journal of Materials Chemistry, 2010. **20**(11): p. 2182-2189.

40.	Ooi, Z.E., T.L. Tam, R.Y.C. Shin, Z.K. Chen, T. Kietzke, A. Sellinger, M. Baumgarten, K. Mullen, and J.C. deMello, *Solution processable bulk-heterojunction solar cells using a small molecule acceptor.* Journal of Materials Chemistry, 2008. **18**(39): p. 4619-4622.

41.	Lin, Y., Y. Li, and X. Zhan, *Small molecule semiconductors for high-efficiency organic photovoltaics.* Chemical Society Reviews, 2012. **41**(11): p. 4245-4272.

42. Tsumura, A., H. Koezuka, and T. Ando, *Macromolecular electronic device: Field-effect transistor with a polythiophene thin film.* Applied Physics Letters, 1986. **49**(18): p. 1210-1212.

43. Li, G., R. Zhu, and Y. Yang, *Polymer solar cells.* Nature Photonics, 2012. **6**(3): p. 153-161.

44. Huynh, W.U., J.J. Dittmer, and A.P. Alivisatos, *Hybrid nanorod-polymer solar cells.* science, 2002. **295**(5564): p. 2425-2427.

45. Harsányi, G., *Polymer films in sensor applications: a review of present uses and future possibilities.* Sensor Review, 2000. **20**(2): p. 98-105.

46. Beaujuge, P.M. and J.M. Fréchet, *Molecular design and ordering effects in π-functional materials for transistor and solar cell applications.* Journal of the American Chemical Society, 2011. **133**(50): p. 20009-20029.

47. Gao, Y., H. Ding, H. Wang, and D. Yan, *Electronic structure of interfaces between copper-hexadecafluoro-phthalocyanine and 2,5-bis(4-biphenylyl) bithiophene.* Applied Physics Letters, 2007. **91**(14): p. 142112.

48. Kulkarni, A.P., C.J. Tonzola, A. Babel, and S.A. Jenekhe, *Electron transport materials for organic light-emitting diodes.* Chemistry of materials, 2004. **16**(23): p. 4556-4573.

49. Burroughes, J., D. Bradley, A. Brown, R. Marks, K. Mackay, R. Friend, P. Burns, and A. Holmes, *Light-emitting diodes based on conjugated polymers.* nature, 1990. **347**(6293): p. 539-541.

50. Yin, C., *The Interplay of Nanostructure and Efficiency of Polymer Solar Cells*, in *Institut für Physik und Astronomie*. 2008, University of Potsdam.

51. Spanggaard, H. and F.C. Krebs, *A brief history of the development of organic and polymeric photovoltaics.* Solar Energy Materials and Solar Cells, 2004. **83**(2): p. 125-146.

52. Mishra, A. and P. Bäuerle, *Small molecule organic semiconductors on the move: promises for future solar energy technology.* Angewandte Chemie International Edition, 2012. **51**(9): p. 2020-2067.

53. Lai, Y., H. Li, J. Pan, J. Guo, L. Kang, and Z. Cao, *Synthesis of Ultrathin Nanosheets of Perylene.* Crystal Growth & Design, 2015. **15**(3): p. 1011-1016.

54. Zhang, X., X. Zhang, K. Zou, C.-S. Lee, and S.-T. Lee, *Single-crystal nanoribbons, nanotubes, and nanowires from intramolecular charge-transfer organic molecules.* Journal of the American Chemical Society, 2007. **129**(12): p. 3527-3532.

55. Heeger, A.J., A.G. MacDiarmid, and H. Shirakawa, *The Nobel Prize in Chemistry.* The Royal Swedish Academy of Sciences, 2000.

56. Carlé, J.E., M. Jørgensen, M. Manceau, M. Helgesen, O. Hagemann, R. Søndergaard, and F.C. Krebs, *Fused thiophene/quinoxaline low band gap polymers for photovoltaic's with increased photochemical stability.* Solar Energy Materials and Solar Cells, 2011. **95**(12): p. 3222-3226.

57. Valentine, A.J.S. and D.A. Mazziotti, *Theoretical Prediction of the Structures and Energies of Olympicene and its Isomers.* The Journal of Physical Chemistry A, 2013. **117**(39): p. 9746–9752.

58. M. Contakes, S., S. T. Beatty, K. K. Dailey, T. B. Rauchfuss, and D. Fenske, *pi-Complexes of Phthalocyanines and Metallophthalocyanines.* Organometallics, 2000. **19**: p. 4767-4774.

59. Wonneberger, C.L.a.H., *Perylene Imides for Organic Photovoltaics: Yesterday, Today, and Tomorrow.* Advanced Materials, 2012. **24**: p. 613–636.

60. Nakamura, J.-i., C. Yokoe, K. Murata, and K. Takahashi, *Efficient organic solar cells by penetration of conjugated polymers into perylene pigments.* Journal of Applied Physics, 2004. **96**(11): p. 6878-6883.

61. López-Martínez, E.I., L.M. Rodríguez-Valdez, N. Flores-Holguín, A. Márquez-Lucero, and D. Glossman-Mitnik, *Theoretical study of electronic properties of organic photovoltaic materials.* Journal of Computational Chemistry, 2009. **30**(7): p. 1027-1037.

62. McGehee, M.D. and A.J. Heeger, *Semiconducting (conjugated) polymers as materials for solid-state lasers.* Advanced Materials, 2000. **12**(22): p. 1655-1668.

63. Meijer, H.E. and L.E. Govaert, *Mechanical performance of polymer systems: the relation between structure and properties.* Progress in Polymer Science, 2005. **30**(8): p. 915-938.

64. Chan, H.S.O. and S.C. Ng, *Synthesis, characterization and applications of thiophene-based functional polymers.* Progress in Polymer Science, 1998. **23**(7): p. 1167-1231.

65. Fischerh, I. and M. Sundbom, *Semi-Empirical Parameters In Pi-Electron Systems. 3. Heteroatomic Molecules Containing Nitrogen.* Acta Chemica Scandinavica, 1968. **22**(2): p. 607-&.

66. Duro, J.A., G. de la Torre, J. Barberá, J.L. Serrano, and T. Torres, *Synthesis and liquid-crystal behavior of metal-free and metal-containing phthalocyanines substituted with long-chain amide groups.* Chemistry of materials, 1996. **8**(5): p. 1061-1066.

67. Lu, X. and Z. Chen, *Curved Pi-conjugation, aromaticity, and the related chemistry of small fullerenes.* Chemical Reviews, 2005. **105**(10): p. 3643-3696.

68. Cameron, M.D., *Victor Meyer and the thiophene compounds.* Journal of Chemical Education, 1949. **26**(10): p. 521.

69. Cordell, F.R. and J.E. Boggs, *Structure and degree of aromatic character in furan, pyrrole, and thiophene.* Journal of Molecular Structure: THEOCHEM, 1981. **85**(1-2): p. 163-178.

70. Mishra, R., K. Jha, S. Kumar, and I. Tomer, *Synthesis, properties and biological activity of thiophene: A review.* Der Pharma Chemica, 2011. **3**(4): p. 38-54.

71. Rittmeyer, S.P. and A. Groß, *Structural and electronic properties of oligo- and polythiophenes modified by substituents.* Beilstein journal of nanotechnology, 2012. **3**(1): p. 909-919.

72. Pham-Tran, N.-N. and M.T. Nguyen, *Electronic structure and properties of some oligomers based on fluorinated 1H-phospholes: n-versus p-type materials.* Comptes Rendus Chimie, 2010. **13**(8): p. 912-922.

73. Kupka, T., R. Wrzalik, G. Pasterna, and K. Pasterny, *Theoretical DFT and experimental Raman and NMR studies on thiophene, 3-methylthiophene and selenophene.* Journal of molecular structure, 2002. **616**(1): p. 17-32.

74. Yang, X., L. Wang, C. Wang, W. Long, and Z. Shuai, *Influences of crystal structures and molecular sizes on the charge mobility of organic semiconductors: oligothiophenes.* Chemistry of materials, 2008. **20**(9): p. 3205-3211.

75. Pillai, M., G. Samuel, S. Banerjee, B. Mathew, H. Sarma, and S. Jurisson, *Technetium-99m complexes of polydentate amine-pyrrole and amine-thiophene ligands.* Nuclear medicine and biology, 1999. **26**(1): p. 69-77.

76. Luschtinetz, R. and G. Seifert, *Theoretical studies on the structural and electronic properties of π-stacked cyano-thiophene-based molecules.* Computational and Theoretical Chemistry, 2013. **1023**: p. 65-73.

77. Shin, R.Y.C., P. Sonar, P.S. Siew, Z.-K. Chen, and A. Sellinger, *Electron-Accepting Conjugated Materials Based on 2-Vinyl-4,5-dicyanoimidazoles for Application in Organic Electronics.* The Journal of Organic Chemistry, 2009. **74**(9): p. 3293-3298.

78. Lim, E., S. Lee, and K.K. Lee, *Small-Molecule Vinazene Acceptors for Bulk Heterojunction Organic Photovoltaics.* Molecular Crystals and Liquid Crystals, 2012. **565**(1): p. 98-105.

79. Inal, S., M. Schubert, A. Sellinger, and D. Neher, *The relationship between the electric field-induced dissociation of charge transfer excitons and the photocurrent in small molecular/polymeric solar cells.* The Journal of Physical Chemistry Letters, 2010. **1**(6): p. 982-986.

80. Akinpelu, A., B. Merzougui, S. Bukola, A.-M. Azad, R.A. Basheer, G.M. Swain, Q. Chang, and M. Shao, *A Pt-free electrocatalyst based on pyrolized vinazene-carbon composite for oxygen reduction reaction.* Electrochimica Acta, 2015. **161**: p. 305-311.

81. Woo, C.H., T.W. Holcombe, D.A. Unruh, A. Sellinger, and J.M. Fréchet, *Phenyl vs alkyl polythiophene: a solar cell comparison using a vinazene derivative as acceptor.* Chemistry of Materials, 2010. **22**(5): p. 1673-1679.

82. Schubert, M., C. Yin, M. Castellani, S. Bange, T.L. Tam, A. Sellinger, H.-H. Hörhold, T. Kietzke, and D. Neher, *Heterojunction topology versus fill factor correlations in novel hybrid small-molecular/polymeric solar cells.* The Journal of Chemical Physics, 2009. **130**(9): p. 094703.

83. Donaldson, D., J. Robertson, and J. White. *The crystal and molecular structure of perylene.* in *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences.* 1953: The Royal Society.

84. Camerman, A.t. and J. Trotter. *The crystal and molecular structure of perylene.* in *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences.* 1964: The Royal Society.

85.   Sugiyasu, K., N. Fujita, and S. Shinkai, *Visible-light-harvesting organogel composed of cholesterol-based perylene derivatives.* Angewandte Chemie, 2004. **116**(10): p. 1249-1253.

86.   Lane, P., J. Rostalski, C. Giebeler, S. Martin, D. Bradley, and D. Meissner, *Electroabsorption studies of phthalocyanine/perylene solar cells.* Solar Energy Materials and Solar Cells, 2000. **63**(1): p. 3-13.

87.   Heinrich, M.A., J. Pflaum, A.K. Tripathi, W. Frey, M.L. Steigerwald, and T. Siegrist, *Enantiotropic polymorphism in di-indenoperylene.* The Journal of Physical Chemistry C, 2007. **111**(51): p. 18878-18881.

88.   Liao, Q., H. Zhang, W. Zhu, K. Hu, and H. Fu, *Perylene crystals: tuning optoelectronic properties by dimensional-controlled synthesis.* Journal of Materials Chemistry C, 2014. **2**(45): p. 9695-9700.

89.   Moser, F.H. and A.L. Thomas, *Phthalocyanine compounds.* Journal of Chemical Education, 1964. **41**(5): p. 245.

90.   Guillaud, G., J. Simon, and J. Germain, *Metallophthalocyanines: Gas sensors, resistors and field effect transistors1In memory of Christine Maleysson. 1.* Coordination Chemistry Reviews, 1998. **178**: p. 1433-1484.

91.   F. Barbe, D. and C. R. Westgate, *Electron Trapping and Bulk Conduction in b—Form Metal—Free Phthalocyanine Single Crystals in Vacuum.* Solid State Communications, 1969. **7**(7): p. 563—566.

92.   Bała, W., M. Wojdyła, M. Rębarz, M. Szybowic, M. Drozdowski, A. Grodzicki, and P. Piszczek, *Influence of central metal atom in MPc (M= Cu, Zn, Mg, Co) on Raman, FT-IR, absorbance, reflectance, and photoluminescence spectra.* Journal of Optoelectronics and Advanced Materials, 2009. **11**(3): p. 264-269.

93.   Zhu, F., M. Grobosch, U. Treske, M. Knupfer, L. Huang, S. Ji, and D. Yan, *Interfacial energy level bending in a crystalline p/p-type organic heterostructure.* Applied Physics Letters, 2011. **98**(20): p. 203303.

94.   Shirota, Y., *Organic materials for electronic and optoelectronic devices. Basis of a presentation given at Materials Chemistry Discussion No. 2, 13–15 September 1999, University of Nottingham, UK.* Journal of Materials Chemistry, 2000. **10**(1): p. 1-25.

95.   Chizhov, I., G. Scoles, and A. Kahn, *The Influence of Steps on the Orientation of Copper Phthalocyanine Monolayers on Au(111).* Langmuir, 2000. **16**(9): p. 4358-4361.

96.   Gutiérrez-Pérez, R.-M., N. Flores-Holguín, D. Glossmann-Mitnik, and L.-M. Rodriguez-Valdez, *Electronic structure study using density functional theory in organic dendrimers.* Journal of molecular modeling, 2011. **17**(8): p. 1963-1972.

97.   Blase, X., C. Attaccalite, and V. Olevano, *First-principles GW calculations for fullerenes, porphyrins, phtalocyanine, and other molecules of interest for organic photovoltaic applications.* Physical Review B, 2011. **83**(11): p. 115103.

98.   Palandage, K. and G.W. Fernando, *Role of point defects on conductivity, magnetism and optical properties in In2O3.* Physics Letters A, 2010. **374**(28): p. 2879-2885.

99.   Williamson, A.J., *Quantum Monte Carlo calculations of electronic excitations.* 1996, Robinson College.

100.   Parr, R.G., *Density functional theory of atoms and molecules.* 1980: Springer.

101.   Buimaga-Iarinca, L. and C. Morari, *Adsorption of small aromatic molecules on gold: a DFT localized basis set study including van der Waals effects.* Theoretical Chemistry Accounts, 2014. **133**(7): p. 1-11.

102.   Camacho-Mendoza, R., E. Aquino-Torres, J. Cruz-Borbolla, J. Alvarado-Rodríguez, O. Olvera-Neria, J. Narayanan, and T. Pandiyan, *DFT analysis: Fe4 cluster and Fe(110) surface interaction studies with pyrrole, furan, thiophene, and selenophene molecules.* Structural Chemistry, 2014. **25**(1): p. 115-126.

103.   Dreizler, R.M. and E.K. Gross, *Density functional theory: an approach to the quantum many-body problem.* 2012: Springer Science & Business Media.

104.   Hohenberg, P. and W. Kohn, *Inhomogeneous electron gas.* Physical review, 1964. **136**(3B): p. B864.

105.   Haynes, P., *Linear-scaling methods in ab initio quantum-mechanical calculations. Cambridge, 1998*, Dissertation for the degree of Doctor of Philosophy. University of Cambridge-UK.

106.   Levy, M., *Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v-*

representability problem. Proceedings of the National Academy of Sciences, 1979. **76**(12): p. 6062-6065.

107.   Levy, M. and J.P. Perdew, *The constrained search formulation of density functional theory*, in *Density functional methods in physics*. 1985, Springer. p. 11-30.

108.   Kohn, W. and L.J. Sham, *Self-consistent equations including exchange and correlation effects.* Physical review, 1965. **140**(4A): p. A1133.

109.   Rushton, P.P., *Towards a non-local density functiona description of exchange and correlation*. 2002, Durham University.

110.   Čertík, O. *Density Functional Theory (DFT)*. Quantum Field Theory and Quantum Mechanics 2009; Available from: http://www.theoretical-physics.net/dev/quantum/dft.html#equation-noninteract.

111.   Kent, P.R.C., *Techniques and applications of quantum Monte Carlo*. 1999, University of Cambridge.

112.   Vosko, S.H., L. Wilk, and M. Nusair, *Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis.* Canadian Journal of physics, 1980. **58**(8): p. 1200-1211.

113.   Langreth, D.C. and M. Mehl, *Beyond the local-density approximation in calculations of ground-state electronic properties.* Physical review B, 1983. **28**(4): p. 1809.

114.   Perdew, J.P., J. Chevary, S. Vosko, K.A. Jackson, M.R. Pederson, D. Singh, and C. Fiolhais, *Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation.* Physical review B, 1992. **46**(11): p. 6671.

115.   Hammer, B., L.B. Hansen, and J.K. Norskov, *Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals.* Phys. Rev. B, 1999. **59**(11): p. 7413-7421.

116.   Becke, A.D., *Density-functional exchange-energy approximation with correct asymptotic behavior.* Physical Review A, 1988. **38**(6): p. 3098.

117.   Perdew, J.P., *Density-functional approximation for the correlation energy of the inhomogeneous electron gas.* Physical review B, 1986. **33**(12): p. 8822.

118.   Boese, A.D. and N.C. Handy, *A new parametrization of exchange–correlation generalized gradient approximation functionals.* The Journal of Chemical Physics, 2001. **114**(13): p. 5497-5503.

119.   Hamprecht, F.A., A.J. Cohen, D.J. Tozer, and N.C. Handy, *Development and assessment of new exchange-correlation functionals.* The Journal of Chemical Physics, 1998. **109**(15): p. 6264-6271.

120.   Tsuneda, T., T. Suzumura, and K. Hirao, *A new one-parameter progressive Colle–Salvetti-type correlation functional.* The Journal of Chemical Physics, 1999. **110**(22): p. 10664-10678.

121.   Haid, S., M. Marszalek, A. Mishra, M. Wielopolski, J. Teuscher, J.E. Moser, R. Humphry-Baker, S.M. Zakeeruddin, M. Grätzel, and P. Bäuerle, *Significant Improvement of Dye-Sensitized Solar Cell Performance by Small Structural Modification in π-Conjugated Donor–Acceptor Dyes.* Advanced Functional Materials, 2012. **22**(6): p. 1291-1302.

122.   Fournier, R., J. Andzelm, and D. Salahub, *Analytical gradient of the linear combination of Gaussian-type orbitals—local spin density energy.* The Journal of Chemical Physics, 1989. **90**(11): p. 6371-6377.

123.   Clark, S., *Complex structures in tetrahedrally bonded semiconductors.* 1994, University of Edinburgh.

124.   *CASTEP background theory.* 2014; Available from: http://www.tcm.phy.cam.ac.uk/castep/documentation/WebHelp/content/modules/castep/thcastepplanebasis.htm.

125.   Pickett, W.E., *Pseudopotential methods in condensed matter applications.* Computer Physics Reports, 1989. **9**(3): p. 115-197.

126.   Toll, J.S., *Causality and the dispersion relation: logical foundations.* Physical review, 1956. **104**(6): p. 1760.

127.   Dresselhaus, M., *Solid State Physics Part II Optical Properties of Solids.* 2001.

128.   Tan, G., L. DeNoyer, R. French, M. Guittet, and M. Gautier-Soyer, *Kramers–Kronig transform for the surface energy loss function.* Journal of electron spectroscopy and related phenomena, 2005. **142**(2): p. 97-103.

129.   Zahid, F., M. Paulsson, and S. Datta, *Electrical conduction through molecules.* Advanced Semiconductors and Organic Nano-Techniques, 2003. **3**.

130.   Balzer, K. and M. Bonitz, *Nonequilibrium Green's Functions*, in *Nonequilibrium Green's Functions Approach to Inhomogeneous Systems*. 2013, Springer Berlin Heidelberg: Berlin, Heidelberg. p. 15-38.

131.   Rozhkov, A., G. Giavaras, Y.P. Bliokh, V. Freilikher, and F. Nori, *Electronic properties of mesoscopic graphene structures: charge confinement and control of spin and charge transport.* Physics Reports, 2011. **503**(2): p. 77-114.

132.   Harrison, N., *An introduction to density functional theory.* NATO SCIENCE SERIES SUB SERIES III COMPUTER AND SYSTEMS SCIENCES, 2003. **187**: p. 45-70.

133.   Mohamad, M., R. Ahmed, A. Shaari, and S. Goumri-Said, *First principles investigations of vinazene molecule and molecular crystal: a prospective candidate for organic photovoltaic applications.* Journal of molecular modeling, 2015. **21**(2): p. 1-7.

134.   Goumri-Said, S., M. Benali Kanoun, A. Manchon, and U. Schwingenschlögl, *Spin-polarization reversal at the interface between benzene and Fe(100).* Journal of Applied Physics, 2013. **113**(1): p. 013905.

135.   Bak, B., D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *The structure of thiophene.* Journal of Molecular Spectroscopy, 1961. **7**(1–6): p. 58-63.

136.   Nardelli, M., G. Fava, and G. Giraldi, *The crystal and molecular structure of α-thiophene-and α-selenophene-carboxylic acids.* Acta Crystallographica, 1962. **15**(8): p. 737-746.

137.   Yoon, M.-H., A. Facchetti, C.E. Stern, and T.J. Marks, *Fluorocarbon-modified organic semiconductors: molecular architecture, electronic, and crystal structure tuning of arene-versus fluoroarene-thiophene oligomer thin-film properties.* Journal of the American Chemical Society, 2006. **128**(17): p. 5792-5801.

138.   Paul G. Rasmussen, Sarah E. Reybuck, David M. Johnson, and R.G. Lawton, *Cylic imidazole compounds having relatively low hydrogen content and relatively high nitrogen content and polymers formed therefrom*, in *United States Patent-US006096899A*. 2000.

139.   Kadish, K., K. Smith, and R. Guilard, *The Porphyrin Handbook: Synthesis and Organic Chemistry, Vol. 1*. 2000, Academic Press, San Diego.

140. Johnson, D.M. and P.G. Rasmussen, *An improved synthesis of 2-vinyl-4, 5-dicyanoimidazole and characterization of its polymers.* Macromolecules, 2000. **33**(23): p. 8597-8603.

141. Goodwin, T.H., *943. Calculated bond lengths in some cyclic compounds. Part VII. The series naphthalene, perylene, terrylene, quaterrylene, and the lengths of low-order bonds.* Journal of the Chemical Society (Resumed), 1960: p. 4851-4856.

142. Liao, M.-S. and S. Scheiner, *Electronic structure and bonding in metal phthalocyanines, metal= Fe, Co, Ni, Cu, Zn, Mg.* The Journal of Chemical Physics, 2001. **114**(22): p. 9780-9791.

143. Brown, C., *Crystal structure of β-copper phthalocyanine.* Journal of the Chemical Society A: Inorganic, Physical, Theoretical, 1968: p. 2488-2493.

144. Shin, R.Y.C., T. Kietzke, S. Sudhakar, A. Dodabalapur, Z.-K. Chen, and A. Sellinger, *N-type conjugated materials based on 2-vinyl-4, 5-dicyanoimidazoles and their use in solar cells.* Chemistry of materials, 2007. **19**(8): p. 1892-1894.

145. Rasmussen, P., S. Reybuck, D. Johnson, and R. Lawton, *Imidazole containing compounds having relatively low hydrogen content and relatively high nitrogen content and polymers and copolymers formed therefrom.* 2001, Google Patents.

146. Rasmussen, P.G., S.E. Reybuck, D.M. Johnson, and R.G. Lawton, *Compounds and polymers formed from imidazoles.* 1999, Google Patents.

147. Fukui, K., T. Yonezawa, and H. Shingu, *A molecular orbital theory of reactivity in aromatic hydrocarbons.* The Journal of Chemical Physics, 1952. **20**(4): p. 722-725.

148. Sargent, A.L. and E.P. Titus, *C−S and C−H Bond Activation of Thiophene by Cp*Rh(PMe3): A DFT Theoretical Investigation.* Organometallics, 1998. **17**(1): p. 65-77.

149. Hochgesang, F.P., *Molecular structure and spectroscopy of thiophene and its derivatives.* Chemistry of Heterocyclic Compounds: Thiophene and its Derivatives, 1952. **3**: p. 81-142.

150. Galano, A., *Influence of Silicon Defects on the Adsorption of Thiophene-like Compounds on Polycyclic Aromatic Hydrocarbons: A Theoretical Study*

Using Thiophene + Coronene as the Simplest Model. The Journal of Physical Chemistry A, 2007. **111**(9): p. 1677-1682.

151. Alguno, A.C., W.C. Chunga, R.V. Bantaculob, R.M. Vequizob, H. Miyatac, E.W. Ignacio, and A.M. Bacala, *Ab initio and density functional studies of polythiophene energy band gap.* NECTEC Technical Journal, 2001. **2**(9): p. 215-218.

152. Diaz, A., J. Crowley, J. Bargon, G. Gardini, and J. Torrance, *Electrooxidation of aromatic oligomers and conducting polymers.* Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 1981. **121**: p. 355-361.

153. Perger, W., *Calculation of band gaps in molecular crystals using hybrid functional theory.* Chemical physics letters, 2003. **368**(3): p. 319-323.

154. Chaudhry, A.R., R. Ahmed, A. Irfan, S. Muhammad, A. Shaari, and A.G. Al-Sehemi, *Effect of heteroatoms substitution on electronic, photophysical and charge transfer properties of naphtha [2, 1-b: 6, 5-b'] difuran analogues by density functional theory.* Computational and Theoretical Chemistry, 2014. **1045**: p. 123-134.

155. Bhatnagar, A., P. Sharma, and N. Kumar, *A review on "Imidazoles": their chemistry and pharmacological potentials.* Int J PharmTech Res, 2011. **3**(1): p. 268-282.

156. Perdew, J.P. and Y. Wang, *Accurate and simple analytic representation of the electron-gas correlation energy.* Physical Review B, 1991. **45**(23): p. 13244.

157. Walker, B., X. Han, C. Kim, A. Sellinger, and T.-Q. Nguyen, *Solution-processed organic solar cells from dye molecules: An investigation of diketopyrrolopyrrole: vinazene heterojunctions.* ACS applied materials & interfaces, 2012. **4**(1): p. 244-250.

158. Rappoport, D., N.R. Crawford, F. Furche, and K. Burke, *Which functional should I choose?* Computational Inorganic and Bioinorganic Chemistry, 2008.

159. Halasinski, T.M., J.L. Weisman, R. Ruiterkamp, T.J. Lee, F. Salama, and M. Head-Gordon, *Electronic absorption spectra of neutral perylene (C20H12), terrylene (C30H16), and quaterrylene (C40H20) and their positive and negative ions: Ne matrix-isolation spectroscopy and time-dependent density*

functional theory calculations. The Journal of Physical Chemistry A, 2003. **107**(19): p. 3660-3669.

160. Ferraris, J., D. Cowan, V.t. Walatka, and J. Perlstein, *Electron transfer in a new highly conducting donor-acceptor complex.* Journal of the American Chemical Society, 1973. **95**(3): p. 948-949.

161. Kimball, D., R. Munns, S.P. Fisher, M. Bartolo, J. Valdez, S.J. Teat, S. Tsui, and E.W. Reinheimer, *Utilizing Perylene in New Organic Donor–Acceptor Materials: Highlighting the Synthesis, Structure and Physical Properties of Perylene-pDNB and Perylene-TCNP.* Journal of Chemical Crystallography, 2015. **45**(4): p. 169-177.

162. Evangelista, F., V. Carravetta, G. Stefani, B. Jansik, M. Alagia, S. Stranges, and A. Ruocco, *Electronic structure of copper phthalocyanine: An experimental and theoretical study of occupied and unoccupied levels.* The Journal of Chemical Physics, 2007. **126**(12): p. 124709.

163. Rosa, A. and E.J. Baerends, *Origin and Relevance of the Staggering in One-Dimensional "Molecular Metals". A Density Functional Study of Metallophthalocyanine Model Dimers.* Inorganic Chemistry, 1992. **31**(23): p. 4717-4726.

164. Koole, R., E. Groeneveld, D. Vanmaekelbergh, A. Meijerink, and C. de Mello Donegá, *Size effects on semiconductor nanoparticles*, in *Nanoparticles*. 2014, Springer. p. 13-51.

165. Van Veen, E., *Triplet $\pi \to \pi^*$ transitions in thiophene, furan and pyrrole by low-energy electron-impact spectroscopy.* Chemical physics letters, 1976. **41**(3): p. 535-539.

166. Flicker, W.M., O.A. Mosher, and A. Kuppermann, *Electron impact investigation of electronic excitations in furan, thiophene, and pyrrole.* The Journal of Chemical Physics, 1976. **64**(4): p. 1315-1321.

167. Lui, C., A. Frenzel, D. Pilon, Y.-H. Lee, X. Ling, G. Akselrod, J. Kong, and N. Gedik, *Trion-induced negative photoconductivity in monolayer MoS 2.* Physical review letters, 2014. **113**(16): p. 166801.

168. DiCésare, N., M. Belletête, C. Marrano, M. Leclerc, and G. Durocher, *Conformational analysis (ab initio HF/3-21G*) and optical properties of symmetrically disubstituted terthiophenes.* The Journal of Physical Chemistry A, 1998. **102**(26): p. 5142-5149.

169. Nithya, N., R. Mahalakshmi, and S. Sagadevan, *Growth, optical, thermal and electrical properties of nonlinear optical□-glycine single crystal.* Scientific Research and Essays, 2015. **10**(13): p. 421-429.

170. Kang, T.-T., M. Yamamoto, M. Tanaka, A. Hashimoto, A. Yamamoto, R. Sudo, A. Noda, D. Liu, and K. Yamamoto, *Terahertz characterization of semiconductor alloy AlInN: negative imaginary conductivity and its meaning.* Optics letters, 2009. **34**(16): p. 2507-2509.

171. Smith, N., *Drude theory and the optical properties of liquid mercury.* Physics Letters A, 1968. **26**(3): p. 126-127.

172. Yang, L.-M. and R. Pushpa, *Tuning electronic and optical properties of a new class of covalent organic frameworks.* Journal of Materials Chemistry C, 2014. **2**(13): p. 2404-2416.

173. Fu, H.-B. and J.-N. Yao, *Size effects on the optical properties of organic nanoparticles.* Journal of the American Chemical Society, 2001. **123**(7): p. 1434-1439.

174. Kawada, A., A. McGhie, and M. Labes, *Protonic conductivity in imidazole single crystal.* The Journal of Chemical Physics, 1970. **52**(6): p. 3121-3125.

175. Singer, K.D., J.E. Sohn, L. King, H. Gordon, H. Katz, and C. Dirk, *Second-order nonlinear-optical properties of donor-and acceptor-substituted aromatic compounds.* JOSA B, 1989. **6**(7): p. 1339-1350.

176. Cho, B.R., S.B. Park, S.J. Lee, K.H. Son, S.H. Lee, M.-J. Lee, J. Yoo, Y.K. Lee, G.J. Lee, and T.I. Kang, *1, 3, 5-tricyano-2, 4, 6-tris (vinyl) benzene derivatives with large second-order nonlinear optical properties.* JOURNAL-AMERICAN CHEMICAL SOCIETY, 2001. **123**(26): p. 6421-6422.

177. Samyn, C., T. Verbiest, and A. Persoons, *Second-order non-linear optical polymers.* Macromolecular rapid communications, 2000. **21**(1): p. 1-15.

178. Liu, W., A. Tkatchenko, and M. Scheffler, *Modeling adsorption and reactions of organic molecules at metal surfaces.* Accounts of Chemical Research, 2014. **47**(11): p. 3369-3377.

179. Zhang, X., Z. Lu, L. Ye, C. Zhan, J. Hou, S. Zhang, B. Jiang, Y. Zhao, J. Huang, and S. Zhang, *A Potential Perylene Diimide Dimer-Based Acceptor Material for Highly Efficient Solution-Processed Non-Fullerene Organic*

Solar Cells with 4.03% Efficiency. Advanced Materials, 2013. **25**(40): p. 5791-5797.

180. Usanmaz, A., *The effect of monomer crystal structure on the solid-state polymerization of N-vinylcarbazole.* Macromolecular Chemistry and Physics, 1981. **182**(8): p. 2351-2357.

181. Nalwa, H.S. and S. Miyata, *Nonlinear optics of organic molecules and polymers.* 1996: CRC press.

182. Ehrenreich, H. and H. Philipp, *Optical properties of Ag and Cu.* Physical review, 1962. **128**(4): p. 1622.

183. Barbarella, G., M. Melucci, and G. Sotgiu, *The Versatile Thiophene: An Overview of Recent Research on Thiophene-Based Materials.* Advanced Materials, 2005. **17**(13): p. 1581-1593.

184. Francis Garnier, A.Y., Ryad Hajlaoui, Gilles Horowitz, Francoise Deloffre, Bernard Servet, Simone Ries, and Patrick Alnot, *Molecular engineering of organic semiconductors: design of self-assembly properties in conjugated thiophene oligomers.* Journal of the American Chemical Society, 1993. **115**(19): p. 8716-8721.

185. Johansson, E. and S. Larsson, *Electronic structure and mechanism for conductivity in thiophene oligomers and regioregular polymer.* Synthetic Metals, 2004. **144**(2): p. 183-191.

186. Denis, P.A. and F. Iribarne, *Thiophene adsorption on Single Wall Carbon Nanotubes and graphene.* Journal of Molecular Structure: THEOCHEM, 2010. **957**(1–3): p. 114-119.

187. Margine, E.R., M.L. Bocquet, and X. Blase, *Thermal Stability of Graphene and Nanotube Covalent Functionalization.* Nano Letters, 2008. **8**(10): p. 3315-3319.

188. Baei, M., *Covalent Functionalization of Zn12O12 Nanocluster with Thiophene.* Journal of Cluster Science, 2013. **24**(3): p. 749-756.

189. Nogueira, A.F., B.S. Lomba, M.A. Soto-Oviedo, C.R.D. Correia, P. Corio, C.A. Furtado, and I.A. Hümmelgen, *Polymer Solar Cells Using Single-Wall Carbon Nanotubes Modified with Thiophene Pedant Groups.* The Journal of Physical Chemistry C, 2007. **111**(49): p. 18431-18438.

190.   Fuchs, J.-N. and M.O. Goerbig, *Introduction to the physical properties of graphene.* Lecture Notes, 2008.

191.   Lazar, P., F.e. Karlický, P. Jurečka, M.s. Kocman, E. Otyepková, K.r. Šafářová, and M. Otyepka, *Adsorption of small organic molecules on graphene.* Journal of the American Chemical Society, 2013. **135**(16): p. 6372-6377.

192.   Zheng, X., S.-H. Ke, and W. Yang, *Conductive junctions with parallel graphene sheets.* The Journal of Chemical Physics, 2010. **132**(11): p. 114703.

193.   Boukhvalov, D., *Tuneable molecular doping of corrugated graphene.* Surface Science, 2010. **604**(23): p. 2190-2193.

194.   Georgakilas, V., M. Otyepka, A.B. Bourlinos, V. Chandra, N. Kim, K.C. Kemp, P. Hobza, R. Zboril, and K.S. Kim, *Functionalization of graphene: covalent and non-covalent approaches, derivatives and applications.* Chemical reviews, 2012. **112**(11): p. 6156-6214.

195.   Loh, K.P., Q. Bao, P.K. Ang, and J. Yang, *The chemistry of graphene.* Journal of Materials Chemistry, 2010. **20**(12): p. 2277-2289.

196.   Chen, F. and N. Tao, *Electron transport in single molecules: from benzene to graphene.* Accounts of Chemical Research, 2009. **42**(3): p. 429-438.

197.   Boukhvalov, D. and M. Katsnelson, *A new route towards uniformly functionalized single-layer graphene.* Journal of Physics D: Applied Physics, 2010. **43**(17): p. 175302.

198.   Bedolla, P.O., G. Feldbauer, M. Wolloch, S.J. Eder, N. Dörr, P. Mohn, J. Redinger, and A.s. Vernes, *Effects of van der Waals Interactions in the Adsorption of Isooctane and Ethanol on Fe (100) Surfaces.* The Journal of Physical Chemistry C, 2014. **118**(31): p. 17608-17615.

199.   Martinez, C.R. and B.L. Iverson, *Rethinking the term "pi-stacking".* Chemical Science, 2012. **3**(7): p. 2191-2201.

200.   Mao, H.Y., Y.H. Lu, J.D. Lin, S. Zhong, A.T.S. Wee, and W. Chen, *Manipulating the electronic and chemical properties of graphene via molecular functionalization.* Progress in Surface Science, 2013. **88**(2): p. 132-159.

201.   Hippel, A.R.v., *The Molecular Designing of Materials and Devices*. 1965, MIT Press, Cambridge, Mass.

202. Hippel, F.N.v., *Arthur von Hippel: The Scientist and the Man.* MRS Bulletin, 2005. **30**.

203. Aviram, A. and M. Ratner, *Molecular rectifiers.* ChemicalPhysicsLetters, 1974. **29**(2).

204. Fan, Z.-Q., Z.-H. Zhang, M. Qiu, X.-Q. Deng, and G.-P. Tang, *The site effects of B or N doping on I-V characteristics of a single pyrene molecular device.* Applied Physics Letters, 2012. **101**(7).

205. Matsuura, Y., *Current rectification in nickelocenylferrocene sandwiched between two gold electrodes.* Journal of Chemical Physics, 2013. **138**(1).

206. Tsutsui, M. and M. Taniguchi, *Single Molecule Electronics and Devices.* Sensors, 2012. **12**: p. 7259-7298.

207. Lin, L., J. Jiang, and Y. Luo, *Elastic and inelastic electron transport in metal-molecule(s)-metal junctions.* Physica E, 2013. **47**: p. 167-187.

208. Boyen, H.-G., P. Ziemann, U. Wiedwald, V. Ivanova, D.M. Kolb, S. Sakong, A. Gross, A. Romanyuk, M. Büttner, and P. Oelhafen, *Local density of states effects at the metal-molecule interfaces in a molecular device.* Nature Materials, 2006. **5**(5).

209. Y.L.Liu, X.Q.Deng, and X.C.Duan, *The electronic transport properties for a single-wall ZnO nanotube with different coupling interfaces.* Physica E, 2013. **52**: p. 21-26.

210. Paulsson, M., F. Zahid, and S. Datta, *Resistance of a molecule.* arXiv preprint cond-mat/0208183, 2002.

211. Matsuura, Y., *Current rectification in nickelocenylferrocene sandwiched between two gold electrodes.* Journal of Chemical Physics, 2013. **138**.

212. Li, M.-J., M.-Q. Long, K.-Q. Chen, and H. Xu, *Fluorination effects on the electronic transport properties of dithiophene-tetrathiafulvalene (DT-TTF) molecular junctions.* Solid State Communications, 2013. **157**: p. 62-67.

213. Cui, B., Y. Xu, G. Ji, H. Wang, W. Zhao, Y. Zhai, D. Li, and D. Liu, *A single-molecule diode with significant rectification and negative differential resistance behavior.* Organic Electronics, 2014. **15**(2): p. 484-490.

214. Deng, X., Z. Zhang, G. Tang, Z. Fan, M. Qiu, and C. Guo, *Rectifying behaviors induced by BN-doping in trigonal graphene with zigzag edges.* Applied Physics Letters, 2012. **100**(6): p. 063107.

215. Obodo, J., K. Gkionis, I. Rungger, S. Sanvito, and U. Schwingenschlögl, *Hydrogen bonding as the origin of the switching behavior in dithiolated phenylene-vinylene oligomers.* Physical review B, 2013. **88**(8): p. 085438.

216. Zheng, X., Z. Dai, X. Shi, and Z. Zeng. *The role of the electrodes in a molecular conductor: an eigenchannel analysis.* in *Journal of Physics: Conference Series.* 2006: IOP Publishing.

217. Troisi, A. and M.A. Ratner, *Conformational molecular rectifiers.* Nano Letters, 2004. **4**(4): p. 591-595.