Republic of Iraq
Ministry of Higher Education and Scientific Research
University of Babylon
College of Education for Pure Sciences
Department of Physics

Electronic Properties of Organic Molecule as Laser Active Meduims

Research

Submitted to the council of the College of Education for Pure Sciences University of Babylon Partial Fulfillment of the Requirements for the Degree of Higher Diploma Education / Physics of Materials and it`s Applications

By

Saba Mahdi Abdulkadhim Abed

Supervised by

Asst. Prof .Dr. Saba Razaq Salman Fahad

2023 A.D. ***1445 A.H***

﴿ قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا
عَلَّمْتَنَا إِنَّكَ أَنْتَ الْعَلِيمُ الْحَكِيمُ ﴾

صَدَقَ اللهُ العَلِيُّ العَظِيمُ

سورة البقرة :الآية ٣٢

Dedication

To the greatest man of the universe, the Holly Prophet Mohammad and The Prophet's family (Peace and Praises Be upon them)

To my Father Prof. Dr. Mahdi Abdulkadhim Abed

To my Dear Mother

To my husband and my partner Ehab and my children

Ali and Yaman With my love ....

To my Dear brother and sister

With my love

To anyone who helped me and saw I deserved it

Dedicate this effort.....

Saba

Acknowledgements

In the name of God the most gracious and the most merciful. I praise Allah, the lord of earth and heaven for completing my research. I would like to extend my thanks and gratitude to my Supervisors (Assistant Prof. Dr. Saba Razzaq Salman Fahd) for having suggested this topic for me and for their extinguished efforts and sound advice and directions that have helped in smoothing out every difficulty encountered during my work.

Thanks to the Deanery of the College of Education for the Pure Sciences/ University of Babylon and the Department of Physics for offering me the opportunity to complete my research. I also would like to express my grateful thanks to my professors and fellow postgraduate students.

Many thanks go to those who supported me and alleviated difficulties that. I have faced during my work and to everyone who helped me in a way or another.

Finally, I can only thank everyone who extended a helping hand to accomplish this modest work.

God grants success

Saba ✍

Supervisor Certification

I certify that the preparation of this research, entitled **"Electronic Properties of Organic Molecule as Laser Active Meduims"** was made under my supervision by **Saba Mahdi Abdulkadhim Abed** at physics department the college of education for pure sciences university of Babylon in partial fulfillment of the requirements .

Signature:

(Supervisor)

Name: **Dr. Saba Razzaq Salman Fahd**

Title: Asst.Prof

Address: College of Education for Pure Sciences/ University of Babylon

Date: 10 /9/ 2023

In view of the available recommendation, I forward this thesis for debate by the examination committee.

Signature:

Name: ~~Khalid~~ Hanen Abass

Title : Prof

(Head of Physics Department)

Date / / 2023

Examining Committee Certification

We certify that we have read this thesis entitled entitled **"Electronic Properties of Organic Molecule as Laser Active Meduims"** and as committee, examined the student **(Saba Mahdi Abdulkadhim Abed)** its contents and that in our opinion it meets the standards of a research for the Degree of Higher Diploma Education / Physics of Materials and its applications.

Signature:

Name: Dr.Shurooq Sabah Abedul Abbas

Title: Professor

Address: University of Babylon

Date: 10/ 9 /2023

Signature:

Name: Dr.Salar Hussein Ibrahem

Title: Assistant Professor

Address: University of Babylon

Date:10/ 9/2023

Signature:

Name: Dr.Saba Razaq Salman Fahad

Title: Assistant Professor

Address: University of Babylon

Date:10 / 9 2023

Approved by the Council of the college of Education for pure Sciences.

Signature:

Name: Bahaa Hussien Salih Rabee

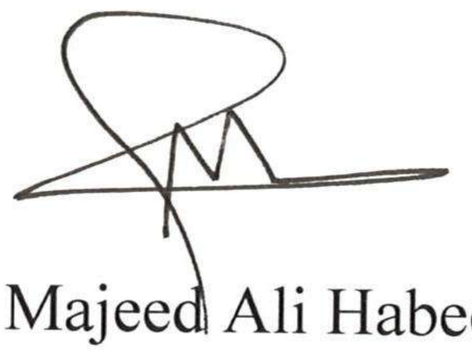
Title: Professor

Address: Dean of the college of pure Sciences, University of Babylon

Date: / / 2023

Scientific Supervisor Certification

This is to certify that I have read this thesis, entitled **"Electronic properties of organic molecule as laser Active Meduims"** and I found that this thesis is qualified for debate.

Signature: 

Name: Dr. Majeed Ali Habeeb

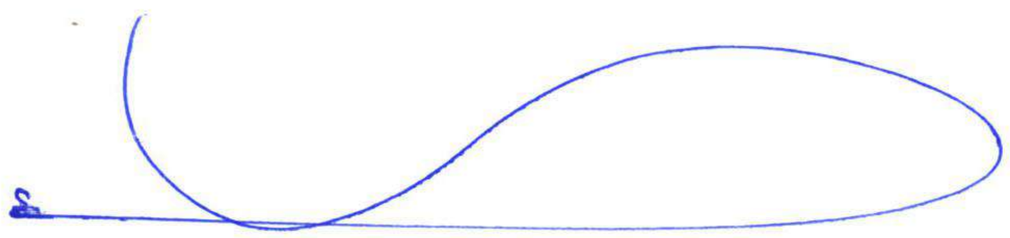
Title: Professor

Address: University of Babylon College of Education for Pure Science, Department of Physics

Date: 10/9/2023

Linguistic Supervisor Certification

This is to certify that I have read this thesis, entitled **"Electronic properties of organic molecule as laser Active Meduims"** And I found that this research is qualified for debate.

Signature: 

Name: Dr. Sameer Hassan Hadi

Title: Professor

Address: University of Babylon College of Education for Pure Science, Department of Physics

Date: 10/9/ 2023

Abstract

This research includes a study of the optical properties of molecules of demonstrates thiophene/phenylene co-oligomers (TPCOs) because of their special importance and use their electronic and structural advantages, which is considered as a suitable candidate for optical and thermoelectric applications.The researcher used the density functional theory (DFT) according to the electric and optical characteristics of molecules of thiophene/phenylene with different partial length . The researcher noticed that the increase in the units of thiophene/phenylene from leads to an increase in the emission oscillator from (3.14 – 3.80). It has been also noticed that the longest wavelength (λ_{max}) of the molecules is within the visible region, as it oscillates from 617 nm for T2P to 659 nm for T3P. Based on these results, we can conclude that changing the molecular length does not affects only the absorption intensity, but also leads to a displacement in the wavelengths within the visible rang . this all helps. In devising promising filters for the

designing of thermoelectric devices in addition to being suitable as effective laser media.

Concerning the electric characteristics such as the distribution of molecular orbitals distribution, HOMO-LUMO gaps. The results indicated that the lowest unoccupied molecular orbitals LUMO are localized on the (C–C) bonds and shown more contribution than that of the highest occupied molecular orbitals HOMO, which are concentrated on the (C=C) bonds. In addition, the electronic calculations proved that the transport mechanism of the charge carriers in this kind of molecules is the LUMO-dominate transport mechanism.

List of Contents

Chapter 1 : Introduction

Chapter 2 : Density Functional Theory

Chapter 3 : Single Molecule Transport Theory

List of Abbreviations

Abbreviation	Physical meaning
OLEDs	Organic Light Emitting Diodes
OSSL	Organic Solid-State Lasers
ASE	Amplified Spontaneous Emission
DFT	Density Functional Theory
TD-DFT	Time-Dependent Density Functional Theory
UV	Ultra-violet
NIR	Near-infrared
LCAO	**L**inear **C**ombination of **A**tomic **O**rbital
R-G	Runge-Gross theorem

HF	Hartree-Fock
TPCOs	Thiophene/phenylene co-oligomers
B3LYP	Becke 3 (Lee-Yang-Parr**)**
HOMOs	High Occupied Molecular Orbitals
LUMOs	Lowest Unoccupied Molecular Orbitals
PDOS	Partial Density of States
TDOS	Total Density of States

List of Figures

List of Tables

List of Symbols

Symbol	Physical Meaning
m_n	Mass
Z_m	Atomic number
R_n	Position
T_e	Kinetic energy for the electron
T_n	Kinetic energy for the nuclei
U_{ee}	Interaction energy between all electrons
f_{em}	Emission oscillator strength
Ψ	Wave function
h	Planck's constant
$\hat{H}$	Hamiltonian operator
M	Nuclei number

N	Electrons number
$\vec{r}_i$	Position of the *i-th* electron
R_I	Position of the I-th nucleus
E_i	Numerical value of the energy of the i^{th} state
U_{nn}	Interaction energy terms between the nuclei
U_{en}	Interaction between electrons and nuclei
m_e	Mass of the electron
m_n	Mass of the nucleus
e	Electron charge
Z_n	Nuclear charge
K	chemical potential
n_f	Refractive index
∇_i^2	Laplacian operator
$V_{ext}(\vec{r})$	External potential
T	Energy of the electrons and nuclei
EΦ	The trial function
$\hat{J}_i$	Exchange operator
β	For N-electrons system slater determinant
α	Spin down
$\hat{F}$	Fock operator
E_0	Denotes the energy of the ground state
R	Outside of the core radius

ε_o	on-site energies
k	Wavenumber
δV	Voltage associated with the chemical potential mismatch
σ_{em}	Cross-sectional area
ΔV	Potential drop
$\hbar$	Planck's reduced constant
K_B	Boltzmann constant
C_o	Light in vacuum
E	Emission intensity

Chapter One

Introduction

1.1. Introduction

In the mid-1960s, Gordon Moore observed that the number of transistors per unit area on a chip was doubling approximately once. every two years. He modestly speculated that this trend could continue for a further ten years, but nearly half a century later, the exponential growth continues. However, if Moore's law is to continue, the transistors will have to shrink to atomic scale within twenty years and enter the field of nanoelectronics [1].

Recently, new insights in the field of nanoscience have been obtained from the application of fundamental modeling techniques such as density functional theory (DFT), and molecular dynamics. Advances in computer technology have led to an increase in computational capability which has made possible the modeling and simulation of complex systems with millions of degrees of freedom. However, the full potential of novel theoretical and modeling tools has not been reached yet [2].

1.2. Organic Molecules

Organic molecules are chemical compounds with complicated structures. Composed of many atoms, apart from electronic properties they also exhibit special physicochemical features [3]. When organic molecules create molecular solid-state devices with crystal or amorphous structures, the properties of these devices follow from organic molecule interactions. Therefore in molecular solid-state structures, the energy levels of

individual molecules form continuous bands of energy. Due to the weak interactions between the molecules, molecular solid-state structures exhibit the properties of the individual molecules to a greater degree than the properties characteristic for solid-state materials [4]. A special feature of the molecular solid state is the fact that singlet and triplet states are excited due to light interaction being able to move across the material. These mobile quasi-particles are called excitons. Furthermore, excitons can be generated not only by light but also from the recombination process of charge carriers with opposite signs, electrons and holes injected into the system [5]. This has important implications and enables the application of organic materials to light-emitting devices able to produce any colour. Owing to the excitation of the organic material by electromagnetic waves with energy, carriers are generated. Taking into account these features of organic materials, it could be conclude that they have significant potential in many fields of science and technology. Therefore an understanding of their properties is salient, and our current knowledge remains insufficient [6].

1.3. Electrical Pumping of Organic Laser Active Medium

Organic solid-state lasers (OSSL) have received a lot of attention in recent years due to their ease of manufacture and ability to cover a broad range of lasing wavelengths from near infrared to ultraviolet. Optically

pumped OSSL have progressed to the point that they can reach impressively low thresholds for laser and/or amplified spontaneous emission (ASE), as well as operation that is almost constant. However, the ultimate aim in the field of OSSL is to achieve electrically pumped lasing, which will allow for the development of low-cost, portable, and flexible solid OSSL devices [7,8].

Because of the following considerations, electrically pumped OSSL lasing is far more difficult than optically pumped OSSL lasing. First, according to spin statistics, three-quarters of excitons generated during current injection are triplets, which have a lengthy decay period [9].

Second, polarons, excitons, and other species that are not engaged in optical pumping will cause repeated annihilation and absorption losses when electrical pumping is used. The recent advances have reported promising signs of current injection OSSL, which has opened up the possibility of developing small and low-cost electrically powered organic laser systems [10]. Regardless of these organic laser gain medium, electrical pumping was used to investigate light amplification. As a result, it's crucial to conduct theoretical analysis and forecast potentially good electrical pumping options, which must have a large stimulated emission cross section, low annihilation or absorption losses, and a short lifetime, ideally with high mobility [8]. In this context, the purpose of this communication is to offer an universal computational approach for

systematically screening out electrically pumped lasing molecules over a broad spectrum of organic solid-state luminous materials using efficient electronic structure computations based on density functional theory (DFT) and time-dependent DFT (TD-DFT) [10,11].

Organic dyes absorb light in the ultraviolet (UV) to near-infrared (NIR) spectral range. Multiple conjugated double bonds are present in all of these compounds, limiting their spectral characteristics and chemical reactivities. The large range of chemical configurations that may operate as laser dyes is one of the major reasons for dye lasers' surge in popularity. Laser dyes emit light over the whole visible spectrum, as well as the NUV and IR spectral regions. more than 500 distinct dyes with varying absorption and emission bands may be discovered. Laser dyes are typically classified according to their chemical structures [11].

1.4. Literature Review

Oday A. Al-Owaedi *et al* in 2016 [12], introduced a theoretical and experimental studies of trans-Ru complexes. They interpreted the electronic properties of such molecules in terms of the transport mechanisms (LUMO-dominated conductance). These results have significant implications for the future design of organometallic complexes for studies in molecular junctions.

Oday A. Al-Owaedi *et al* in 2017 [13], have highlighted research on the critical role of metal complexes in preventing orthogonal contacts, which helped to explain why some organometallic compounds had very high conductance values.

Mohsin K. Al-Khaykanee *et al* in 2018 [14], have work that comprised a study of the charge transport of 4,4-bipyridine molecules with a variety of sterically-induced twist angles between the two pyridyl rings, which was done using density functional theory DFT and Green's function formalism. Different molecular orientations within the junctions were shown to be the cause of high and low conductance peaks, according to one experiment. The conductances of both geometries were proportional to twisted angle demonstrating that the electrical current travels through the C-C bond joining the pi systems of the two rings.

Guang-Ping Zhang *et al* in 2019 [15], optimizing the conductance switching performance in photo switchable dimethyldihydropyrene/cyclophanediene single-molecule junctions. Designing molecular switches with high stability and performance is still a great challenge in the field of molecular electronics. For this aim, key factors influencing the charge transport properties of molecular devices require to be carefully addressed.

Masoud Baghernejad *et al* in 2020 [16], have mentioned that the influence of heteroatoms on electron transport via asymmetric and

symmetric alkyne-terminated benzodichalcogenophene compounds has been investigated using a combination of experimental and theoretical methods. Experiments, DFT-based theory, and a simple tight binding model were all in excellent agreement. The decreased conductance of the asymmetric molecule is caused by the asymmetry created by differing bond lengths in the two 5-membered rings of the molecule, as demonstrated by the tight-binding modeling of heteroatom replacement in these non-bipartite cores. In addition, they discover that the differing overlap integrals of the CO and C-S bonds must be taken into consideration in the tight binding model.

Yi Jiang *et al* in 2020 [17], have studied a variety of gain materials including organic dyes, fluorescent semiconductor emitters, triplet gain media, and biological materials, covering a wide spectrum from UV to NIR. Some gain media are already commercial available, including some laser dyes, i.e. TDAF-1 (79), PFO (203), F8BT (225) and bis-styrylbenzene), introducing branched flexible chains, constructing triplet gain media and triplet harvesters, may be beneficial to the development of robust organic gain media for OSLDs. They hope that in the future, intense efforts will be paid to explore various successful ways to realize electrically pumped organic lasers and promote their practical application, inspired by the recent advancements.

1.5. The Aims of the Study

The primary aim of this research is to fully understand, by density function theory, the electronic and optical properties properties of organic molecule. and conducting analysis of work results and providing forecasts for the use of these nanostructures in the field of optoelectronics applications.

Chapter Two

Theoretical Part

2.1 Introduction

Theoretical computations in physics and chemistry are generally used when the mathematical method is adequately industrialized and can be automatic for application on a computer[18,19]. In theoretical physics and chemistry, the important laws of the physics are combined with mathematical methods to study developments of chemical relevance. Computational chemistry, also called molecular modeling, is important and basic that is applied in the molecular science research[20]. The molecular modeling methods in physics are now pervasive used to examine computationally many properties such as energies of molecules, molecular geometries, electronic structure, electron and charge distributions, infrared (IR), ultra-violet (UV), nuclear magnetic resonance (NMR) spectra, and the physical properties of the biological, inorganic, organometallic, polymeric, catalysis drug and other molecular systems[21-23]. The computational physics and chemistry can employ four main methods: they are included the molecular mechanic methods, Semiempirical methods (SE), ab-initio methods and the density functional theory methods. The key to theoretical physics is the molecular quantum mechanics[24-26]. Over the past 30 years the DFT has proved to be a principally effective tool for discovering organometallic rations and yields dependable structures and energies at reasonable computational cost. It has consequently become the method of

choice in most theoretical searches and studies of most molecular systems[21,26].

2.2 Schrödinger Equation

The Schrödinger equation, which was called after Erwin Schrödinger who exposed it in 1926, is supposed to be the significant equation to label the motions of atomic and subatomic systems, electrons and nucleus, even macroscopic systems as large as the universe. The time dependent form of Schrödinger equation is as the following equation [22]:

$$i\hbar \frac{\partial}{\partial t}\Psi(\vec{r},t) = -\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t) + V(\vec{r},t)\Psi(\vec{r},t) = H(\vec{r},t)\Psi(\vec{r},t) \quad \ldots(2.1)$$

In simple form:

$$\widehat{H}\Psi(\vec{r},t) = E\Psi(\vec{r},t) \quad \ldots(2.2)$$

Where $\Psi(\vec{r}, t)$ is the wave function, $\widehat{H}$ is the Hamiltonian operator, and E is the total energy of the system. The Hamiltonian operator consists of two terms, the kinetic energy of the electrons and the nuclei ($\hat{T}$) and potential energy components ($\hat{V}$):

$$\widehat{H} = \hat{T} + \hat{V} \quad \ldots(2.3)$$

The total Hamiltonian of the molecular system $\widehat{H}$ covering M centers and N electrons in atomic units as follows [25,26]:

$$\widehat{H}_{total} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{A=1}^{M}\frac{1}{2m_A}A_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{r_{AB}} \quad \ldots(2.4)$$

$$\widehat{H}_{total} = \hat{T}e + \hat{T}n + \hat{V}ne + \hat{V}_{ee} + \hat{V}nn \quad \ldots(2.5)$$

In equations (2.4) and (2.5), the total kinetic energy is the sum of the electronic ($\hat{T}_e$) and nuclear ($\hat{T}_n$) kinetic energies, the total potential energy are the sum of three components: the nuclei-electrons interactions ($\hat{V}_{ne}$), theelectron-electron interactions ($\hat{V}_{ee}$) and the interactions between the nuclei ($\hat{V}_{nn}$), $Z_{A,,B}$ are the nuclei charge of atoms A and B, m_A is the mass of atom A, r_{AB} is the distance between nuclei A and B, r_{iA} is the distance between nucleus A and electron i, and $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the distance between electrons i and j.

2.3 Hartree-Fock Approximation

The interpretation of the quantum mechanical behavior for all electrons in the systems is required to compute the many-electron wave functions for the system using the time-independent Schrödinger equation. The solution needs many of (around 10^{23}) simultaneous differential equations, such a calculation is very difficult and needs to reducing the methods and the problem itself [25,26]. Hartree in 1928 simplifies the problem by approaching an idea about the form of the many-electron wave

functions from the product of a set of single-electron wave functions [19]. Taking this idea, it was possible to proceed using the variational principle [20]. From the variational principle, the lowest energy eigenvalue $E_{\emptyset}$ of the trial function Φ can be expressed as in the form [20,26]

$$E_{\Phi} = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \geq E_O \qquad \ldots (2.6)$$

In Eq. (2.6), E_o denotes the energy of the ground state. Using this theorem, the exact ground-state wave function is approached from the trial function that gives the lowest energy. Hartree look at the Hamiltonian equation of the many-electron system in which it was possible to treat each electron separately as a single-particle.

In Hartree-Fock (HF) approximation, the wave function Ψ can be written in a determinant called the "Slater determinant". This determinant reflects the spin of all the electrons and the Pauli exclusive principle. The electrons can have a spin up (α) or a spin down (β). For N-electrons system, Slater determinant takes the following form [20,27-28]:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(1)\alpha(1) & \Psi_1(1)\beta(1) & \Psi_2(1)\alpha(1) & \Psi_2(1)\beta(1) \ldots & \Psi_N(1)\alpha(1) & \Psi_N(1)\beta(1) \\ \Psi_1(2)\alpha(2) & \Psi_1(2)\beta(2) & \Psi_2(2)\alpha(2) & \Psi_2(2)\beta(2) \ldots & \Psi_N(2)\alpha(2) & \Psi_N(2)\beta(2) \\ \vdots & & \vdots & & \vdots & \\ \Psi_1(N)\alpha(N) & \Psi_1(N)\beta(N) & \Psi_2(N)\alpha(N) & \Psi_2(N)\beta(N) \ldots & \Psi_N(N)\alpha(N) & \Psi_N(N)\beta(N) \end{vmatrix}$$

$\ldots .(2.7)$

Where $\Psi = \frac{1}{\sqrt{N!}}$ represents a normalization factor.

The main step in HF methods is to introduce the molecular orbital growth, determining the corresponding coefficients based on the variation principle [19]. The molecular orbitals $\Psi_i(r)$ solves the HF equation using the iterative process of the self-consistent-field (SCF) to yield the HF equation as in the form [20,24]:

$$\hat{F}\,\Psi_i\,(\vec{r}) = \varepsilon_i \Psi_i(\vec{r}) \qquad \ldots . (2.8)$$

$\hat{F}$ is the Fock operator, ε_i is the energy of ith spin orbital Ψ_i. For closed shell systems, Fock operator for the i-the electron in the system takes the form [29]:

$$\hat{F}(i) = \hat{h}(i) + \sum_{I=1}^{n/2}[2\hat{J}_j(i) - \hat{K}_j(i)] \qquad \ldots (2.9)$$

Where $\hat{h}(i)$ called the Hamiltonian of a single electron, it is the core Hamiltonian, which includes the Coulomb operator ($\hat{J}_j(i)$) and exchange operator($\hat{K}j(i)$) [27]:

$$\hat{J}_\iota\Psi(\vec{r}) = \int \frac{\Psi_i^*(\vec{r})\Psi_\iota(\vec{r})}{|\vec{r}-\vec{r}\,'|}\, dV'\, \Psi(\vec{r}) \qquad \ldots(2.10)$$

$$\hat{K}_\iota\,\Psi\,(\vec{r}) = \int \frac{\Psi_i^*(\vec{r})\Psi_j(\overrightarrow{r'})}{|\vec{r}-\vec{r}\,'|}\, dV'\, \Psi(\vec{r}) \qquad \ldots (2.11)$$

Another alteration involves growing the molecular orbital (MO) in terms of the Linear Combination of Atomic Orbital (LCAO) [26,27]. Thus, an discrete molecular orbital T_i is defined as:

$$\Psi_i = \sum_{\mu=1}^{N} C_{\mu i}\Phi_\mu \qquad \ldots(2.12)$$

The coefficients $C_{\mu i}$ indicate that the molecular orbital expansion constants. For orbital expansion, an appropriate set of basic functions has to be selected, with that the constants $C_{\mu i}$ may then be adjusted to minimize the total electronic energy calculated from the many-electron wave function. The resulting value of the energy will then be as close as possible to the exact ground state energy E_o of the system [27,30]:

$$E\ (\Phi_1, \Phi_2, \ \ldots \ldots, \Phi_N) \geq E_o \qquad \ldots (2.13)$$

2.4 Density Functional Theory (DFT)

The density functional theory (DFT) describes a wide applications in physics and chemistry due to investigate the electronic structure and properties of many-electron systems. DFT shows the properties of a many-electron system can be determined from information of the electron density distribution by using functional [30]. DFT is the most popular and versatile method available in computational physics and chemistry. Moreover, DFT proved to be very successful for computing the ground state properties of materials [19,20].The opening point of density theory was made by Thomas and Fermi model established in 1927. Thomas-Fermi model calculated the energy of an atom by the half of the kinetic energy of the atom as a function of electron density [27,31,32]. DFT method computes properties of a many particle system as a functional of electron density or probability density

$P(\vec{r})$. $P(\vec{r})$ that meansthe probability of electrons in volume element $d\vec{r}$ with any spin for a given state. It is dependent on only three coordinates self-sufficiently of the number of electrons of the system [33,34]:

$$N = \int \rho(\vec{r}) d\vec{r} \quad \dots (2.14)$$

The main concepts of DFT depend on the ground state energy and all other ground state electronic properties that are uniquely determined by the electron density. Hohenberg and Kohn (HK) in 1964, proved two important theorems to establish the principles of DFT as a quantum mechanical method [38]. They proved that the ground state of a many electron system can be determined by the ground state electron density $\rho(\vec{r})$[35,36]. According to these theorems, the ground state energy functional $E_V[p]$ can be labeled as in the following [32,37]:

$$E_V[\rho] = \int \rho(\vec{r}) V_{ext}(\vec{r}) d\vec{r} + F_{HK}[\rho] \quad \dots (2.15)$$

$F_{HK}[\rho]$ represents a functional of $\rho(\vec{r})$ to be determined which contains kinetic energy and all the electron-electron connections. $F_{HK}[\rho]$ is the HK functional of density independent of the external potential $V_{ext.}(\vec{r})$. Considering of the particle preservation, the difference of ground state energy satisfies to the following principle [32,37,38]:

$$\delta\{E_V[\rho] - k[\int \rho(\vec{r}) d\vec{r} - N]\} = 0 \quad \dots (2.16)$$

which gives:

$$K = \frac{\delta E_V[\rho]}{\delta \rho(\vec{r})} = V_{ext.}(\vec{r}) + \frac{\delta F_{HK}[\rho]}{\delta \rho(\vec{r})} \quad \ldots (2.17)$$

Where K indicates the chemical potential. From Eq. (.216) and Eq. (2.17), the ground state electron properties of a many-electron system can be calculated exactly. HK theorems did not give the real expression of energy functional $F_{HK}[\rho]$, in which kinetic functional and exchange-correlation functional were not known [20,38 ,39].

2.5 Time-Dependent Density Functional Theory (TD-DFT)

The time-dependent density functional theory (TD-DFT) spreads the important idea of the ground-state DFT which can be used to examine the excited-state properties of a system in the presence of time-dependent potentials, such as electric or magnetic fields. The influence of fields on molecules can be studied with TD-DFT as an application for representative excitation energies, oscillator strength, wavelength, molecular orbital character and electronic transitions of the molecules [40-42]. The theoretical of TD-DFT based on the Runge-Gross theorem (R-G theorem) in 1984. The R-G theorem explained the association between the time-dependent external potential $\hat{V}_{ext.}(\vec{r}, t)$ and $\rho(\vec{r}, t)$ of the system. R-G.theorem designated that when two external $\hat{V}_{ext.}(\vec{r}, t)$ potentials and $\hat{V}_{ext.}(\vec{r}, t)$ have an alteration of more than a time-dependent function, their own electron densities $\rho(\vec{r}, t)$ and $p'(\vec{r}, t)$ are also dissimilar [43-45].Runge and Gross discussed how

excited states are obtained using TD-DFT. The starting point of studying time-dependent systems is the time-dependent Schrodinger equation. The TD-DFT is straight related to the Schrodinger equation [$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t)=\hat{H}\Psi(\vec{r},t)$] where the Hamiltonian is known to be [41,43,44]:

$$\hat{H}=\hat{T}+\hat{V}_{\text{elec. elec.}}+\hat{V}_{ext.}(\vec{r},t) \quad \ldots (2.18)$$

Here, $\hat{H}$ consists of the kinetic energy operator $\hat{T}$,lectron-electron repulsion $\hat{V}_{\text{elec. elec.}}$ (Coulomb operator) and the external potential $\hat{V}_{ext.}.(\vec{r})$. Where $\hat{V}_{ext.}.(\vec{r})$ is given in the following operators:

$$\hat{V}_{ext.}.(\vec{r})=\sum_{i=1}^{N}V_{ext.}(\vec{r})_i t) \quad \ldots (2.19)$$

The densities of the system rise from a fixed first state $\Psi(t_0)=\Psi(0)$. The first state, $\Psi(0)$, is arbitrary, it must not be the ground-state or some other eigen state of the first potential $\hat{V}_{ext.}.(\vec{r},t_0)=\hat{V}_0(\vec{r})$. The R-G theorem indicates that there exists an one-to-one correspondence between the time-dependent external potential $\hat{V}_{ext.}(\vec{r},t)$, and the time-dependen electron density $\rho(\vec{r},t)$, for systems developing from a fixed first many- body state. Translation to it, the density determines the external potential, and next helps in obtaining the time-dependent many-body wave functions [41,45]. As this wave-function controls all observables of the system as an important, the saying point is that all observables are functionals of $\rho(\vec{r},t)$. The statement of the theorem is the "densities $\rho(\vec{r},t)$ and $\rho'(\vec{r},t)$ evolving from the same

initial state $\Psi(0)$ under the effect of two potentials $\hat{V}_{ext.}(\vec{r},t)$ and $\hat{V}'(\vec{r},t)$ are always different provided that the potentials differ by additional than a chastely time-dependent function [41,43,46]:

$$\hat{V}_{ext.}(\vec{r}) = \hat{V}'_{ext.}(\vec{r},t) + C(t) \quad \ldots (2.20)$$

Where the $C(t)$ allows increase to wave functions that are different only bya phase factor $\exp(-iC(t))$, therefore, the same electronic density is stable. R-G theorem states that the density is a functional of the external potential and of the first wave function on the space of potentials differing by more than the addition of $C(t)$.

2.6 The Software

All calculations in this study have been performed by using the Gaussian 09 package of Programs, Gauss View 5.0.8, Gauss Sum 3.0 and other assistant programs. These programs are described as below:

2.6.1 Gaussian 09 (G09) Program

The Gaussian program is a computational software package initially published by John Pople in 1970. Gaussian program is a very high-end quantum mechanical software package. The "09" mentions to the year 2009 in which the software was published [47].Gaussian is capable of running all of the major methods in molecularmodeling, including molecular mechanics, ab-initio, semi-empirical, HF and DFT. Moreover, excited state computes

can be done by different methods in this program [49].The name originates Gaussian comes from the use of the Gaussian Type Orbitals that Gaussian's originator, John Pople, used to try to overcome the computational difficulties that get up from the use of Slater Type Orbitals. A number of researchers, such as S.F. Boys and Isaiah Shavitt, Pople, quite brilliantly, recognized that the (relatively) simple, substitution of a series of Gaussian functions for the Slater function, would greatly simplify the rest of the calculation of the Schrödinger equation. Pople (1998) was awarded the Nobel Prize in chemistry (along with Walter Kohn) for this work [47,49].

2.6.2 Gauss View Program

Gauss View was designed to import the input files for the Gaussian program and also used to prove the output files for Gaussian program in the dimensional photo, Gaussian view which not used as calculation program, but it is simplicity the work on Gaussian program and supply the users three major advantages. First: enable the user to draw the molecules including the big one, also enable the rotation, transferring and changing it size easily and the mouse. Second: Gaussian view permits to achieve many of the Gaussian calculation, making the complex input preparation for the routine work and the advanced method. Third: Gaussian view permits the inspection of Gaussian calculations results using variety of geometrical techniques and

this involved the balanced molecular patterns electronic density surfaces [47,49].

2.6.3 Gauss Sum 3.0

The Gauss Sum 3.0 is a software application recorded by Noel O'Boyle. Gauss Sum 3.0 uses the plotting program (Gnuplot17) for picture graphs. The Gauss Sum is that can examines the output of widely computational physics and chemistry program (such as Gaussian 09 Program) [47,50].Gauss Sum can get ready more information such as a geometry optimization, plot the density of states (DOS) spectrum, source information on the UV-Vis. Transition states, scheme the UV-Vis spectrum and the circular dichroism spectrum, abstract data on IR and Raman vibrations and plotting the IR and Raman spectra, which may be scaled using general or individual scaling factors [48]. Throughout the computational studies carried out in this study, Gauss Sum 3.0 has been used in the ground state calculation of DFT to plotting the IR, Raman and DOS spectra. Also for the excitation state calculation of TD-DFT it is used to plotting the UV-Vis spectrum and it is showed the excitation energies, electronic transition configurations and oscillator strengths for the optical transitions for the studied compounds.

Chapter Three

Results and Discussion

3.1. Introduction

Over the years, great efforts have been devoted to the development of organic solid-state lasers (OSSL) due to the easy and economic fabrication, covering a wide-range lasing wavelength from near infrared to ultraviolet [51-54]. To date, optically pumped OSSL have been maturely developed, with the achievement of remarkably low laser and/or amplified spontaneous emission (ASE) thresholds and quasi-continuous wave operation [55,56]. The ultimate goal in the field of OSSL is, however, to realize electrically pumped lasing so as to truly enable the creation of low-cost, portable, and flexible solid OSSL devices. Compared to optically pumped OSSL, lasing under electrical pumping is much more challenging because of the following factors. First, triplet exciton tends to accumulate under electrical pumping based on spin statistics [57], that is, three quarters of excitons formed under current injection are triplets, which usually have a long decay time [53]. Second, under electrical pumping, multiple annihilation and absorption losses will be induced by polarons, excitons, and other species that are not involved in optical pumping [53,54]. Recently, there are encouraging progresses reporting promising indications of current injection OSSL [58], which opened up the opportunities in realizing compact and low-cost electrically driven organic laser devices. Notwithstanding the advancements achieved in previous studies [58], obstacles still remain for organic laser gain media to observe light

amplification under electrical pumping. Therefore, it is of significant importance to carry out theoretical evaluation and predict potentially good electrical pumping candidates, which require a large stimulated emission cross section [53,54].

With that in mind, the goal of this study is to propose a general computational protocol to systematically screen out electrically pumped lasing molecules over a range of organic solid-state fluorescent materials, with the assistance of efficient electronic structure calculations based on density functional theory (DFT) and time-dependent DFT (TD-DFT). The ability of realizing general lasing behavior will be evaluated from one perspective that is closely related to the stimulated emission cross section.(see Figure 3.1)

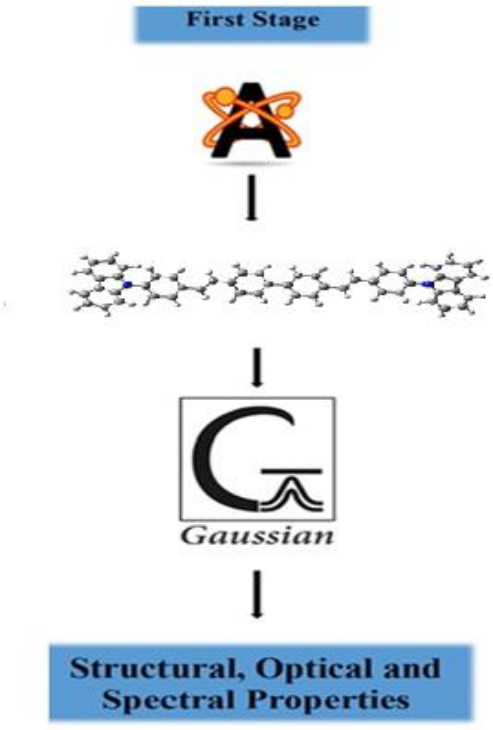
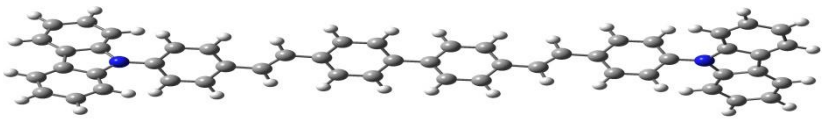


Figure 3.1. Steps of transport calculations.

3.2. Structural Properties of Molecules

The thiophene/phenylene co-oligomers (TPCOs) are ranked as a newly occurring class of organic semiconductors. The materials are characterized by that thiophenes and phenylenes are hybridised at the molecular level with their various mutual arrangements. These molecular arrangements produce peculiar morphological features in the solid state and excellent electronic and optical properties. In this study, those characteristics have been outline in light of the structure/property relationship with central emphasis upon the crystal structure and its relevance to the leading-edge optoelectronic functionalities. These topics are most suitably approached by device studies including field-effect transistors and light-emitting devices. The device characteristics in close connection with current-injected lasers will be described as shown in Figure 3.2 and Table 3.1.



T2P

T3P

Figure3.2. The optimized single molecules.

The crystal structure of the thiophene/phenylene co-oligomers (TPCOs) is characterized by the molecular layered structure, this structure being very often observed for crystals of ‘‘direction-defined’’ long molecules with a large aspect ratio [52]. As far as the straight-chain molecules like oligophenylenes are concerned, the layered structure can be seen for the compounds of two aromatic rings or more . In their crystals, the molecules tend to be disposed with the molecular long axes tilting with respect to the bottom crystal plane [52,59,60]. The tilting can be measured by an angle between the molecular long axis and the normal to the bottom crystal plane [61,62]. In the case of the straight-chain molecules the said angle is around 10–20° [52]. The tilting angles, however, are generally small with the non-straight molecules typified by the TPCOs [61-63]. Here the molecular long axis is defined as a line connecting the terminal carbon atoms of the molecule. In the case of phenyl (thiophene) terminals, the relevant carbon atoms are located at the p-position on phenyls (α-position of thiophenes) [61-63]. Figure 3.1 shows optimized molecules under study in this research. The structural aspects of these molecules are distinguished by various molecular lengths, since the shortest molecule (T2P) has a molecule length of 3.202 nm, while the longest one (T3P) posses 3.695 nm. All structural aspects are shown in Table 3.1.

Table 3.1. The structural aspect of all molecules. L (H…H), is the molecule length. C–C is the carbon-carbon single bond. C=C is the carbon-carbon double bond. C–N is the carbon-nitrogen single bond.

Molecule	L (nm)	C–C (nm)	C=C (nm)	C–N (nm)
T2P	3.202	0.149	0.139	0.145
T3P	3.695	0.149	0.139	0.145

3.3. Molecular Orbitals Distribution

Before calculating the spectral properties, this molecule have been optimized using the standard Gaussian 09 software package. The B3LYP level of theory with basis set 6-311G, are used to calculate the geometry and orbital energy levels.

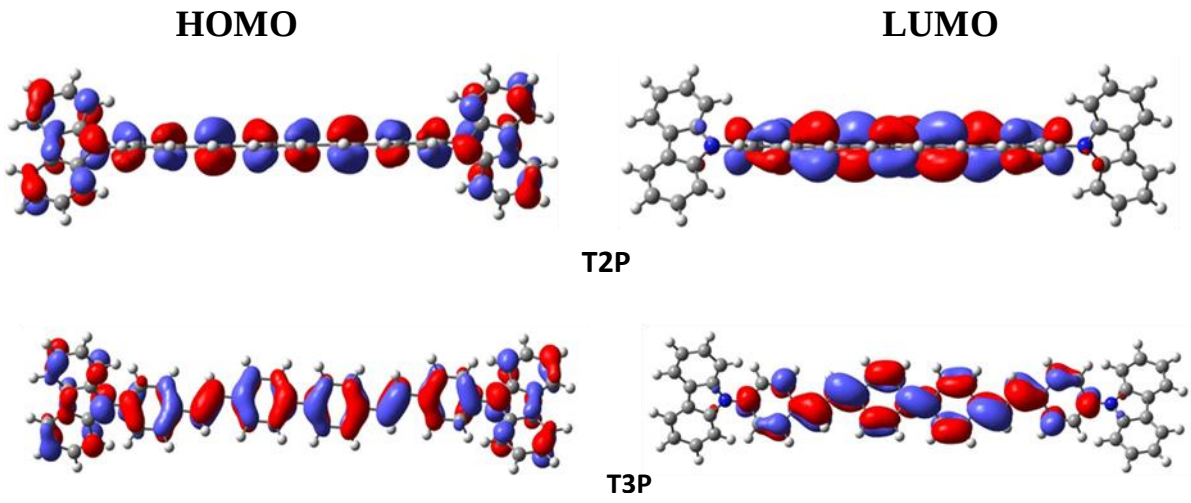


Figure 3.3. Iso-surfaces (±0.02 (e/bohr^3)$^{1/2}$) of the HOMOs and LUMOs.

The studies of the scattering patterns of the frontier molecular orbital (FMO) is very important to depicted the optoelectronic properties of the designed molecules because these are related to the excitation properties of

the molecules. The plots of FMO's of the designed molecules including highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) at the ground states (S_0) are shown in the Figure 3.3 Furthermore, we have investigated distribution patterns for each molecule in terms of partial density of states (PDOS) and the total density of states (TDOS) based on Mullikan population analysis. These orbitals are real functions and have either a positive or negative sign [68,69]. Crucially, the sign of the HOMOs on the left side of the backbone of molecule are of opposite to the sign on the right side, whereas the LUMOs have the same sign on the left and right the backbone. As discussed in a previous study [68], this means that for each molecule, the HOMO orbital product is negative and the LUMO orbital product is positive. Therefore, their inter-orbital quantum interference is constructive within the HOMO-LUMO gap. In addition, Figure 3.3 shows that the HOMOs of molecule are extended over the backbone. So HOMOs and LUMOs energies is (1.2,0.9)ev for T2P, (1.13,0.8)ev for T3P respectively.

These results could be interpreted in terms of a high electronegativity of the carbon atoms in the backbone of the molecule, so it enhance the delocalization of pi-electrons by pulling the electron density from the side groups, and therefore an decrease in HOMO and LUMO energy is observed. Depending on this, the difference in the HOMO-LUMO gap value of these molecules may be ascribed to the Nitrogen atoms, which

may led to a difference in the value of the electronegativity.

3.4. Emission Oscillator Strength (f_{em})

In particular, the emission characteristics are deeply connected with the molecular symmetry and alignment. As already stated previously, the emission oscillator strength value can be subtly and precisely tuned by choosing the TPCO materials and a desired mutual arrangement of thiophenes and phenylenes within the molecule. Because of the nearly upright molecular alignment the emission dominates from crystal edges.

Figure 3.4 represents this feature with several molecule length. These results reflect the superior ability of the optical confinement is one of the attractive characteristics of the TPCOs and makes their crystals an excellent candidate for laser media. In relation to the light amplification such emission behaviour is advantageous for causing spectrally narrowed emissions including the laser oscillation.

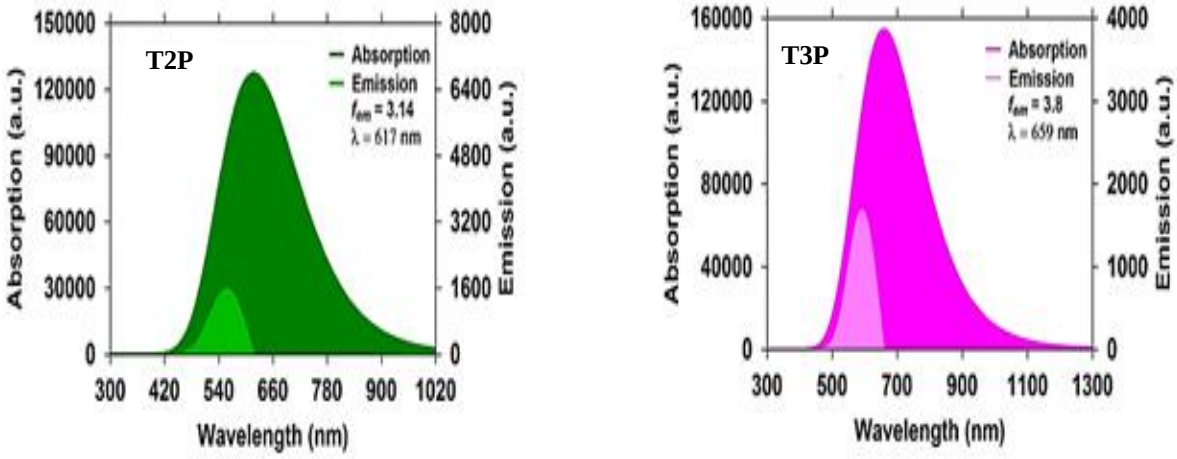


Figure 3.4. Represents the absorption, emission and emission oscillator strength of molecules.

Figure 3.4 presents the absorption and emission results for all molecules under study in this research. Initially, it can be noticed that the absorption intensity of molecules have increased with increasing of the molecule length from 120000 (a.u.) to 140000 (a.u.). In fact, Figure 3.4. illustrates that T2P molecule has the smallest emission oscillator strength (f_{em}) (3.14), while, the highest value of f_{em} is introduced via T3P molecule, It is well known that the light amplification from these structures at room temperature will be difficult, which consistent with previous studies [64]. Since, the calculated emission cross section σ_{em} of a laser transition is consider an important parameter in a laser gain medium. It can affect laser performance in terms of threshold energy, output energy, maximum gain, etc.

Under conventional lasing mechanism, a large σ_{em} is a prerequisite of a good laser gain medium [65]. Theoretically, for a given photoluminescence (PL) material, σ_{em} is directly proportional to the emission oscillator strength f_{em} via [65]:

$$\sigma_{em}(v) = \frac{e^2}{4\varepsilon_0 m_e c_0 n_F} g(v) f_{em} \quad (3.1)$$

where e is the electron charge, ε_0 is the vacuum permittivity, m_e is the mass of electron, c_0 is the speed of light, n_F is the refractive index of the gain material, ν is the frequency of the corresponding emission, and $g(v)$ is the normalized line shape function with $\int g(v)\, dv = 1$. According to the aforementioned facts, all molecules have a high value of f_{em}, which directly leads to high σ_{em}, and therefore any of these materials is possible to be a good optical gain medium in practice. In addition, these results predicate a fact that the molecules with long molecule length properties (see Figure 3.4), possess a high fluorescence, and hence they are suitable for laser gain media, which is consistent with references [66-67].

On the other hand, molecules with a long molecule length have a good emission oscillator strength (f_{em}), since they owned $f_{em} > 2$, and that means those structures are promising candidates for laser gain medium.

Furthermore, most of molecules have produced the maximum emission at wavelengths ranging from 617 to 659 nm, which is in the visible region.

These results bring us to an important outcome that those molecules could be powerful for the optoelectronic applications such as light emitting diodes.

Chapter Four

Conclusions and Future Works

4.1. Conclusions

In conclusion, we described various features of the thiophene/phenylene (TP) materials. It includes the characteristics of the TP structures and their relevance to the structure/property relationship.

1- In relation to the important future application, we dealt with several features associated with the laser oscillation from the organic semiconductors, such as the emission oscillator strength, charges distribution and orbitals, Since, the increasing of molecule length enhances noticeably some of spectral, optical properties,

2- The TP materials are expected to become important to a solar cell development. The TPCOs may play a pivotal role in the field of organic semiconductor materials and their optoelectronic device applications.

3- Finally, this thesis introduces a successful and powerful strategies to develope the organic light-emitting diodes (OLEDs) in a single molecule technology, which can greatly simplify the display fabrication process and lead to new applications in electrically pumped organic lasers, and smart displays

4.2. Future Works

Molecular Nanotechnology is a field that can be consider a source of scientific and cognitive inspiration and innovation, so I suggest some of ideas for the future work as follows:

1- Study the phonon transport properties of of the thiophene/phenylene (TP) structures, and their applications.

2- Investigation the electronic and thermoelectric properties of TP molecules with different electrodes (carbon nanotubes and graphene).

3- Study the optoelectronics properties of TP molecules under magnetic field effects.

REFERENCE

References

[1] R. Martel, T. Schmidt, H. R. Shea, T. Hertel, and Ph. Avouris., Single- and Multiwall Carbon Nanotube Field-Effect Transistors. App. Phys. Lett., 1998. p. 2447–2449.

[2] A. Kolmakov and M. Moskovits. , Chemical Sensing and Catalysis by One- Dimensional Metal-Oxide Nanostructures. Annu. Rev. Mater. Res., 2004. p.151–180.

[3] C. Wang, Y. Hu,C.Lieber and S.Sun Ultrathin Au nanowires and their transport properties. J Am Chem Soc, 2008. 130(28): p. 8902.

[4] M. Tsutsui, and M. Taniguchi, Single Molecule Electronics and Devices. Sensors (Basel, Switzerland), 2012. 12(6): p. 7259-7298.

[5] R. Waser, and M. Aono, Nanoionics-based resistive switching memories. Nature Materials, 2007. 6 (3): p. 833.

[6] P**.** Franzon, D.Nackashi,C.Amsinck,N.Dispigna and S.Sonkusale"Molecular Electronics – Devices and Circuits Technology", in Vlsi-Soc: From Systems To Silicon: Proceedings of IFIP TC 10, WG 10.5, Thirteenth International Conference on Very Large Scale Integration of System on Chip (VLSI-SoC 2005), October.

References

[7] D. Fichou, S. Delysse, and Nunzi, J.-M., First evidence of stimulated emission from a monolithic organic single crystal: α-Octithiophene. Adv. Mater. 1997. p. 1178–1181.

[8] S. Chénais, and S. Forget, Recent advances in solid-state organic lasers. Polym.Int. 2012. p. 390–406.

[**9]** M.C. Petty, S. Kasap and P. Capper, Molecular Electronics, in Springer Handbook of Electronic and Photonic Materials, Editors. 2017, Springer International Publishing: Cham. p. 1-1.

[10] J. Gierschner, Varghese, S. and Park, S. Y., Organic single crystal lasers.: a materials view. Adv. Opt. Mater. 2016. 4: p. 348–364

[11] C. Robert Neuman, Jr., Organic Molecules and Chemical Bonding. G. Somasundaram and A. Ramalingam, Chem. Phys. Lett.,2000, 324: p. 25–30.

[12] Oday A. Al-Owaedi, David C. Milan, Marie-Christine Oerthel, Sören Bock, Dmitry S. Yufit, Judith A. K. Howard, Simon J. Higgins, Richard J. Nichols, Colin J. Lambert, Martin R. Bryce, Paul J. Low. Experimental and Computational Studies of the Single-Molecule Conductance of Ru(II) and Pt(II) trans-Bis(acetylide) Complexes. Organometallics. 2016. 35: p. 2944−2954.

References

[13] Oday A. Al-Owaedi, Sören Bock, David C. Milan, Marie-Christine Oerthel, Michael S. Inkpen, Dmitry S. Yufit, Alexandre N. Sobolev, Nicholas J. Long, Tim Albrecht, Simon J. Higgins, Martin R. Bryce, Richard J. Nichols, Colin J. Lambert, Paul J. Low., Insulated molecular wires: inhibiting orthogonal contacts in metal complex based molecular junctions. Nanoscale. 2017. 9: p. 9902–9912.

[14] Mohsin Kadhim Abed Al-Khaykanee., Quantum Theory of Electronic and Thermal Transport through Nano-scale and Single-Molecule Devices. Department of Physics, Lancaster University, UK Ph.D. Thesis 2018

[15] P. Guang- Zhanga, Yan-Qi Mua, Jin-M. Zhaoa and Hui Huang. ,Optimizing the conductance switching performance in photo switchable dimethyldihydropyrene/cyclophanediene single-molecule junctions. Physica E: Low-dimensional Systems and Nanostructures. 2019.

[16] Masoud Baghernejad, Yang Yang and Oday A. Al-Owaedi. ,Constructive Quantum Interference in Single-Molecule Benzodichalcogenophene Junctions. Chemistry - A European Journal • February 2020.

References

[17] Yi Jiang, Yuan-Y. Liu, Xu Liu, He Lin and Kun Gao., Organic solid-state lasers: a materials view and future development. Chem Soc RevDOI: 2020.10: p. 1039/d0cs00037j.

[18] F. Jensen, "Introduction to Computational Chemistry", Second Edition, New York, John Wiley and Sons Ltd, 2007.

[19] C. J. Cramer, "Essentials of Computational Chemistry: Theories and Models", Second Edition, John Wiley and Sons Ltd., The Atrium, Southern Gate, Chichester, England, 2004.

[20] D. C. Young, "Computational Chemistry: A Practical Guide for Applying Techniques to Real-World Problems", NY: John Wiley andSons, Inc., New York, 2001.

[21] Y. Wang, "Theoretical Studies on Water Splitting Using Transition Metal Complexes", Ph.D. Thesis, Royal Institute of TechnologyStockholm, Sweden, 2014.

[22] D. D. Fitts, "Principles of Quantum Mechanics as Applied to Chemistry and Chemical Physics", Published by Cambridge UniversityPress, New York, 2002.

[23] A. Hamid, "The Approximation Treatment of Dicyclopentdienyl Vanadium, cyclopentadienyl niobium and cyclopentadienyl tantalum dichloride as a model for Ziegler-Natta Catalyses", Ph.D. Thesis, Basrah University, Iraq, 2004.

[24] M. Mueller, "Fundamentals of Quantum Chemistry: Molecular Spectroscopy and Modern Electronic Structure Computations", Kluwer Academic/Plenum Publishers, New York, 2001.

[25] P. A. Cox, "Introduction to Quantum Theory and Atomic Structure", Oxford University Press Inc., New York, 1996.

[26] D. W. Rogers, "Computational Chemistry Using the PC", Third

Edition, John Wiley and Sons, Inc., Hoboken, New Jersey, 2003.

[27] B. K. Lipkowitz, R. Larter, R. T. Cundari and D. B. Boyd, "Reviews in computational chemistry", John Wiley and Sons,Inc., Hoboken, New Jersey, 21, 2005.

[28] M. Fayngold and V. Fayngold, "Quantum Mechanics and Quantum Information", Published by Wiley-VCH Verlag GmbH and Co. KGaA,Weinheim, Germany, 2013.

[29] A. Szabo and S. N. Ostlund, "Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory", Macmillan Publishing Co., Inc., Mineola, New York, 1989.

[30] R. J. Reimers, "Computational Methods for Large Systems: Electronic Structure Approaches for Biotechnology and Nanotechnology", Published by John Wiley and Sons, Inc., Hoboken, New Jersey, 2011.

[31] R. O. Jones, "Density functional theory: Its origins, rise to prominence,and future", Reviews of Modern Physics, 87, 897-923, 2015.

[32] W. Koch and M. C. Holthausen,"A Chemist's Guide to Density Functional Theory", Second Edition, Wiley-VCH Verlag GmbH, Weinheim, 2001.

[33] W. J. Hehre, "A Guide to Molecular Mechanics and Quantum Chemical Calculations", Wave function, Inc., Printed in the UnitedStates of America, 2003.

[34] P. Piecuch, J. Maruani, G. Delgado-Barrio and S. Wilson, "Advances in the Theory of Atomic and Molecular Systems, Conceptual and Computational Advances in Quantum Chemistry", Springer Dordrecht Heidelberg London New York, 2009.

[35] A. Gonis, "The Pursuit of Fallacy in Density Functional. Theory: The Quest for Exchange and Correlation, the Rigorous Treatment of Exchange in the Kohn-Sham Formalism and the Continuing Search

for Correlation", World Journal of Condensed Matter Physics, 4, 200- 225, 2014.

[36] A. F. Oliveira, G. Seifert,T. Heinec and H. A. Duarte, "Density-Functional Based Tight-Binding: an Approximate DFT Method", Journal Braz. Chem. Soc., 20, 7, 1193-1205, 2009.

[37] J. Kohanof, "Elements of first-principles electronic structure calculations: Theory and Computational Methods",Cambridge University Press, 2006.

[38] J. P. Perdew, A. Ruzsinszky, L. A. Constantin, J. Sun,and G. I. Csonka, "Some Fundamental Issues in Ground-State Density Functional Theory: A Guide for the Perplexed", Journal Chemical Theory Computation., 5, 4, 902-908, 2009.

[39] K. Capelle, "A Bird's-Eye View of Density-Functional Theory", Brazilian Journal of Physics, 36, 4A, 1318-1343, 2006.

[40] K. M. Bichinho, G. P. Pires, J. H. Santos, M. M. C. Forte and C. R. Wolf, "Determination of Mg, Ti and Cl in Ziegler-Natta catalysts by WDXRF", Journal Analytica Chimica Acta, 512, 359-367, 2004.

[41] S. Botti, "Applications of Time-Dependent Density Functional Theory", Physica Scripta, T109, 54-60, 2004.

[42] M. Petersilka, U. J. Gossmann, and E. K. U. Gross, "Excitation Energies from Time-Dependent Density-Functional Theory", Physical Review Letters, 76, 8, 1212-1215, 1996.

[43] C. Fiolhais, F. Nogueira and M. Marques, "A Primer in Density Functional Theory", Springer-Verlag Berlin Heidelberg New York, 2003.

[44] P. Samal, "Studies in Excited-State Density-Functional Theory", Ph.D. Thesis, Indian Institute of Technology, India, 2006.

[45] A. L. M. Marques, C. A. Ullrich, F. Nogueira, A. Rubio and K. B. K. U. Eberhard, "Time-Dependent Density Functional Theory",

Springer, Berlin Heidelberg, 2006.

[46] Y. Li and C. A. Ullrich,"Time-dependent V-representability on lattice systems", The Journal of Chemical Physics, 129, 1-9, 2008.

[47] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M.Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishid, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavacharii, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma,V.G. Zakrzewski, G.A.Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, "Gaussian 09, revision A. 02 Gaussian, Inc", Wallingford CT., 2009.

[48] T.Williams and C. Kelley"Gnuplot-An interactive plotting program, Version 3.7.3", http://www.gnuplot.info. and http://gausssum.sourceforge.net.

[49] A. B. Pacheco, "Electronic Structure Calculations in Quantum Chemistry", HPC Training Louisiana State University, 2011.

[50] W. M. Kinney, "Python for Data Analysis", O'Reilly Media, Inc. United States of America, 2013.

References

[51] D. Fichou, S. Delysse, and Nunzi, J.-M. First evidence of stimulated emission from a monolithic organic single crystal: α-Octithiophene. Adv. Mater. 9, 1997 . p. 1178–1181

[52] S. Chénais, and S. Forget, Recent advances in solid-state organic lasers. Polym. Int. 61, 2012. p . 390–406.

[53] A. J. C. Kuehne, and Gather, M. C. Organic lasers: recent developments onmaterials, device geometries, and fabrication techniques. Chem. Rev. 116, 2016. p .12823–12864.

[54] J. Gierschner, S. Varghese, and Park, S. Y. Organic single crystal lasers: amaterials view. Adv. Opt. Mater. 4, 2016. p.348–364.

[55] H. Nakanotani, et al. Extremely low-threshold amplified spontaneous emission of 9,9′-spirobifluorene derivatives and electroluminescence from field-effect transistor structure. Adv. Funct. Mater. 17. 2007. p. 2328–2335 .

[56] A. S. D. Sandanayaka, et al. Quasi-continuous-wave organic thin-film distributed feedback laser. Adv. Opt. Mater. 4, 2016. p. 834–839 .

[57] Baldo, M. A., O'Brien, D. F., Thompson, M. E. and Forrest, S. R. Excitonic singlet-triplet ratio in a semiconducting organic thin film. Phys. Rev. B 60, 1999. p. 14422–14428 .

References

[58] A. S. D. Sandanayaka, et al. Indication of current-injection lasing from an organic semiconductor. Appl. Phys. Express 12, 2019. p. 061010 .

[59] K. N. Baker, A. V. Fratini, T. Resch, H. C. Knachel, W. W. Adams, E. P. Socci and B. L. Farmer, Polymer, 1993, 34, 1571–1587.

[60] S. Hotta and K. Waragai, J. Mater. Chem., 1991. 1: p. 835–842.

[61] S. Hotta and K. Waragai, Adv. Mater., 1993. 5: p. 896–908.

[62] S. Hotta and M. Goto, Adv. Mater., 2002.14: p. 498–501.

[63] T. Yamao, Y. Taniguchi, K. Yamamoto, T. Miki, S. Ota, S. Hotta, M. Goto and R. Azumi, Jpn. J. Appl. Phys., 2007.46: p. 7478–7482.

[64] T. Yamao, Y. Nishimoto, K. Terasaki, H. Akagami, T. Katagiri, S. Hotta, M. Goto, R. Azumi, M. Inoue, M. Ichikawa and Y. Taniguchi, Jpn. J. Appl. Phys., 2010. 49: p. 04DK20.

[65] Ou, Q., Peng, Q., and Shuai, Z. .Computational screen-out strategy for electrically pumped organic laser materials. Nature communications, 2020. 11 (1) :p. 1-10 .

[66] H. Nakanotani, Furukawa, T., Hosokai, T., Hatakeyama, T., and Adachi, C. . Light amplification in molecules exhibiting thermally activated delayed fluorescence. Advanced Optical Materials, 2017. 5 (12).

[67] Ye, H., Kim, D. H., Chen, X., Sandanayaka, A. S., Kim, J. U., Zaborova, E. and Adachi, C. .Near-infrared electroluminescence and

low threshold amplified spontaneous emission above 800 nm from a thermally activated delayed fluorescent emitter. Chemistry of Materials, 30 (19): p. 6702-6710, 2018.

[68] C. J. Lambert, Liu, S.-X. Chem. Eur. J. 2018, 24, 4193-4201;K.Yoshizawa, T. Tada, and A. Staykov, J. Am. Chem. Soc. 2008. 130: p.9406

[69] R. Stadler, Jacobsen, K. W. Phys. Rev. B 2006. 74: p.161405.

الخلاصه :

يتضمن هذا البحث دراسه خصائص جزيبات للثيوفين /فنيلين المشترك (TPCOs) لما لها اهميه خاصه بسبب مميزاتها الإلكترونية والتركيبية ، والتي تقدم كمرشح مناسب للتطبيقات البصرية والكهروحراريه . تم استخدام نظريه كثافه الحالات لحساب الخصائص البصرية والإلكترونية لجزئيات الثيوفين /فنيلين المشترك (TPCOs) باطوال جزيئيه مختلفة حيث ان زياده وحدات الثيوفين /فنيلين المشترك(TPCOs) من (T2P-T3P) ينتج عنها زياده في قوة مذبذب الانبعاث من (3.80 – 3.14) . لاحظنا ايضا أن اطول طول موجي (λ_{max}) للجزيئات يكون ضمن المنطقة المرئية ، حيث يتذبذب من 617 نانومتر لـ T2P إلى659 نانومتر لـT3P . بناءً على هذه النتائج ، تم الاستنتاج أن تغيير طول الجزيئي لا يؤثر فقط على قوه مذبذب الانبعاث و شدة الامتصاص ، بل يؤدي أيضًا إلى إزاحة في الأطوال الموجية ضمن المدى المرئي ، هذا كله يساعد في ابتكار مرشحات واعده لتصميم اجهزه كهروحراريه بالإضافة الى كونها تصلح كأوساط ليزر فعاله .اما بالنسبة للخصائص الإلكترونية مثل توزيع المدارات الجزيئية ، وفجوات HOMO-LUMO. أظهرت النتائج أن أقل المدارات الجزيئية غير المشغولة LUMO موضعية على روابط (C-C) وأظهرت مساهمة اقل من تلك الموجودة في أعلى المدارات الجزيئية المشغولة HOMO ، والتي تتركز على روابط (C=C). بالإضافة إلى ذلك ، أثبتت الحسابات الإلكترونية أن آلية نقل حاملات الشحنة في هذا النوع من الجزيئات هي آلية النقل التي يهيمن عليها LUMO.

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة بابل / كلية التربية للعلوم الصرفة
قسم الفيزياء

الخواص الالكترونية لجزيئات عضوية كأوساط ليزرية فعاله

بحث مقدم
الى مجلس كلية التربية للعلوم الصرفة في جامعة بابل وهو جزء
من متطلبات نيل درجة الدبلوم العالي تربية /
فيزياء المواد وتطبيقاتها

من قبل

صبا مهدي عبد الكاظم عبد

بإشراف

أ.م.د. صبا رزاق سلمان فهد

١٤٤٥هـ ٢٠٢٣ م