Al-imam Muhammad ibn Saud Islamic University
College of Science
Department of Chemistry

A-π-D-π-A based small molecules as organic semiconductors

A graduation research project
submitted to the Department of Chemistry in partial fulfillment of the requirements for the completion of the degree of Bachelor of Science in Chemistry

By

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List of Abbreviation:

FT-IR	Fourier transformer infrared
UV-vis	Ultraviolet-visible
GAA	Glacial acetic acid
EtOH	Ethanol
Mp	Melting point
OPDs	Organic photodetectors
OPVs	Organic photovoltaic cells
OLEDs	Organic light- emitting diodes
OFETs	Organic field- effect transistors
DSSCs	Dye-sensitized solar cells
OPVs	Organic photovolatic cells
SMOs	Small molecule organic semiconductor
HOMO	High occupied molecular orbitals
LUMO	Lowest unoccupied molecular orbitals
OSCs	Organic semiconductors
OSCMs	Organic semiconductive materials
ICT	Intramuscular charge transfer
D	Donor
A	Acceptor
DFT	Density functional theory

List of symbols:

λ_{onset}	Lambda Onset
λ_{max}	Lambda Max
E_{opt}	Energy Optical
E_g	Energy Gap
ε	Molar Coefficient
eV	Electron volt
°C	Celsius degree

Acknowledgment

At the end of our graduation project, we would like to extend our sincere gratitude to everyone who contributed to the success of this work and supported us throughout our academic journey. Our sincere appreciation goes to our respected supervisor, Dr. Sondos Al Mahmoud, whose consistent guidance and dedication have been invaluable throughout the research process. . We deeply appreciate the valuable opportunity to visit the central laboratory at Imam Muhammad bin Saud University under your supervision. This experience allowed us to gain practical knowledge and hands-on expertise in using FT-IR and UV-Vis techniques, which significantly enriched our research experience. We also wish to express our heartfelt thanks to our parents for their constant support and encouragement, serving as a true source of strength in achieving this accomplishment.

Abstract

Small-molecule organic semiconductors (SMOS) are a promising alternative to inorganic semiconductors due to their flexibility, ease of fabrication, and low cost. Their primary advantage lies in their precisely defined molecular architecture and high charge transfer efficiency, enabling precise control over their electronic and optical properties for use in a variety of applications. In this research, by using the Schiff base reaction, two compounds were synthesized with different positions of the acceptor group—ortho and para—revealing variations in their energy levels, Highest occupied molaecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), as well as optical and physical properties. Regarding electron transport energy (band gap energy, E_g), the **Ortho-C** showed E_g of 3.13 eV, while the **Para-C** showed 2.989 eV. In terms of optical properties, it was found that the **Ortho-C** has a higher absorption capacity compared to the **Para-C**. Moreover, the **Ortho-C** exhibited a melting point in the range of 218-220°C, whereas the **Para-C** displayed a higher melting point of 254-256°C. This difference in melting points, along with the variations in band gap energy, can be attributed to the influence of the three-dimensional shape (molecular geometry) of both compounds.

الملخص

تعد أشباه الموصلات العضوية ذات الجزيئات الصغيرة (SMOS) بديلاً واعدًا لأشباه الموصلات غير العضوية نظرًا لمرونتها وسهولة تصنيعها وتكلفتها المنخفضة. تكمن ميزتها الأساسية في بنيتها الجزيئية المحددة بدقة وكفاءة نقل الشحنة العالية، مما يتيح التحكم الدقيق في خصائصها الإلكترونية والبصرية لاستخدامها في مجموعة متنوعة من التطبيقات. في هذا البحث، باستخدام تفاعل قاعدة شيف، تم تصنيع مركبين بمواضع مختلفة لمجموعة المستقبلة للالكترونات - أورثو وبارا - مما يكشف عن اختلافات في مستويات الطاقة (HOMO-LUMO)، بالإضافة إلى الخصائص البصرية والفيزيائية. فيما يتعلق بطاقة نقل الإلكترون (الفجوة الطاقية)، سجل مركب أورثو ٣,١٣ إلكترون فولت، بينما سجل مركب بارا ٢,٩٨٩ إلكترون فولت. من حيث الخصائص البصرية، وجد أن مركب أورثو يتمتع بسعة امتصاص أعلى مقارنة بمركب بارا. علاوة على ذلك، أظهر مركب أورثو نقطة انصهار في نطاق ٢١٨-٢٢٠ درجة مئوية، في حين أظهر مركب بارا نقطة انصهار أعلى من ٢٥٤-٢٥٦ درجة مئوية. يمكن أن يعزى هذا الاختلاف في نقاط الانصهار، إلى جانب الاختلافات في طاقة الفجوة النطاقية، إلى تأثير الشكل ثلاثي الأبعاد (الهندسة الجزيئية) لكلا المركبين.

1. Introduction

1.1. Overview of Organic semiconductors

The interest in organic semiconductors (OSCs) arises from their unique properties and their chemical and mechanical advantages in conducting electricity and generating light.

The concept of (OSCs) refers to organic compounds that contain carbon and hydrogen atoms, and sometimes heteroatoms, bonded through covalent bonds. These compounds exhibit a combination of mechanical and chemical properties.

In 1906, it was observed that some organic compounds, such as solid anthracene, exhibited photoconductivity. However, this was not considered significant due to their weak light conductivity. Then, 35 years later in 1941, the concept of electron transport was proposed, which has led to the foundation for electrical conductivity,[1] with its full potential being realized in the 1980s. Later, in 1946 the existence of electron transport in organic compounds was proven. This discovery marked the beginning of the competition between organic and inorganic semiconductors.[2]

An organic semiconductor compound is identified by possessing specific characteristics such as resonance, bandgap (E_g), high occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs), as well as aromatic compound properties like π-conjugation. Additionally, they feature electron-donating and electron-withdrawing groups that can control the E_g.[3] **fig.(1).** [11]

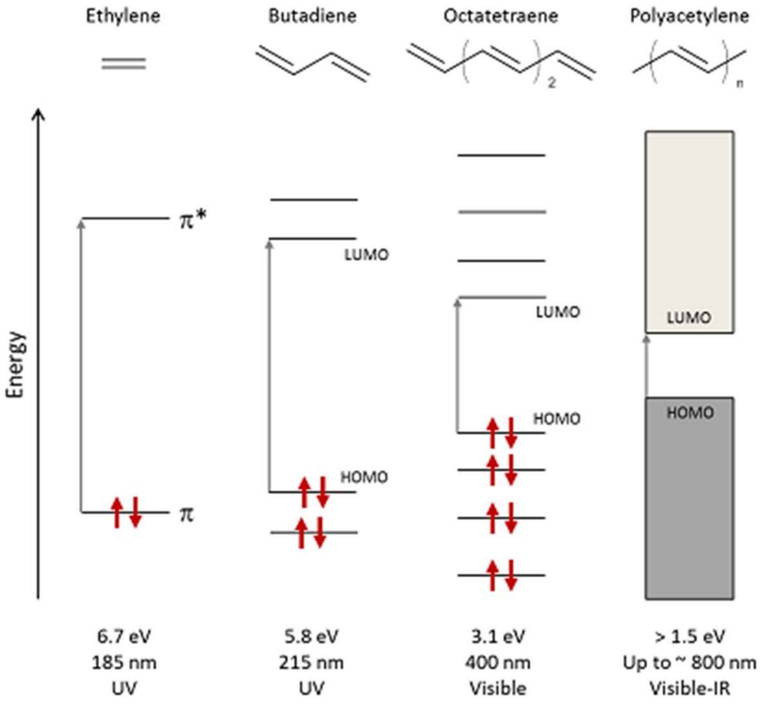


Fig 1. Relationship between conjugation and energy levels HOMO and LUMO

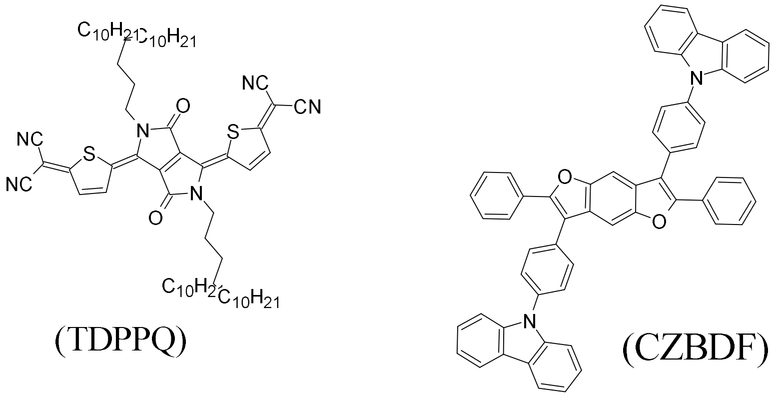
1.1.1.Type of Organic semiconductors (n-type and p-type)

Based on the nature of charge transport in organic semiconductors, charge carriers are classified into three types:

i) n-type: These are carriers of negative charge (electrons) or compounds with electron-withdrawing groups. A compound is identified as n-type if it gains electrons and has its LUMO at a lower energy level, [3] such as thiophene-diketo-pyrrolopyrrole-based quinoidal (TDPPQ) **Fig.(2)** .[4]

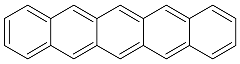
ii)p-type: These are carriers of positive charge (holes) or compounds with electron-donating groups. A compound is identified as p-type if it creates a hole upon losing an electron,[3] such as Pentacene **Fig.(2)** .[5]

iii) Ambipolar organic semiconductors: These compounds exhibit both n-type and p-type characteristics, meaning they can transport both electrons and holes, [3] such as 9,9'-[(2,6-Diphenylfuro[2,3-f][1]benzofuran-3,7-diyl)di-4,1-phenylene]bis(9H-carbazole) (CZBDF) **Fig.(2)** .[6]



(TDPPQ)

(CZBDF)



(Pentacene)

Fig 2. Examples of different types of organic semiconductors.

1.1.2. Advantage of Organic semiconductors over their inorganic counterparts

The search for new materials has expanded into organic semiconductors, which offer tunable properties such as optical, electrochemical, and electrical characteristics. Organic semiconductors (OSCs) are efficiently manufactured with low environmental impact and are compatible with flexible substrates, making them ideal for low-cost domestic applications. They enable lightweight, flexible electronics and efficient light emission with simplified manufacturing processes that reduce costs.

While microelectronics relies on inorganic semiconductors like silicon, organic semiconductors have emerged as promising alternatives, especially in applications like organic field-effect transistors (OFETs). Organic semiconductive materials (OSCMs) have been widely studied for use in optoelectronic devices, offering advantages such as flat, flexible electronics.[7,8]

1.2. Organic semiconductors categories

Organic semiconductors are divided into small molecules like anthracene and polymers like polyacetylene. The main distinction between small molecules and polymers is that polymers consist of long chains, unlike the simpler structures of small molecules. In device fabrication, small molecules are processed via chemical solutions or vacuum deposition, whereas polymers are typically limited to solution processing.

Small molecules are ideal for applications that require precise structural order, such as transistors with high switching speeds, as they can be annealed at low temperatures to form well-defined films. Polymers, with their smooth, uniform films, offer advantages in processability and film morphology but may face challenges in achieving high device performance due to issues such as alignment and charge transfer between chains. In conclusion, small molecules are suitable for highly ordered applications. **Fig.(3)** shows examples of both categories. [9-12]

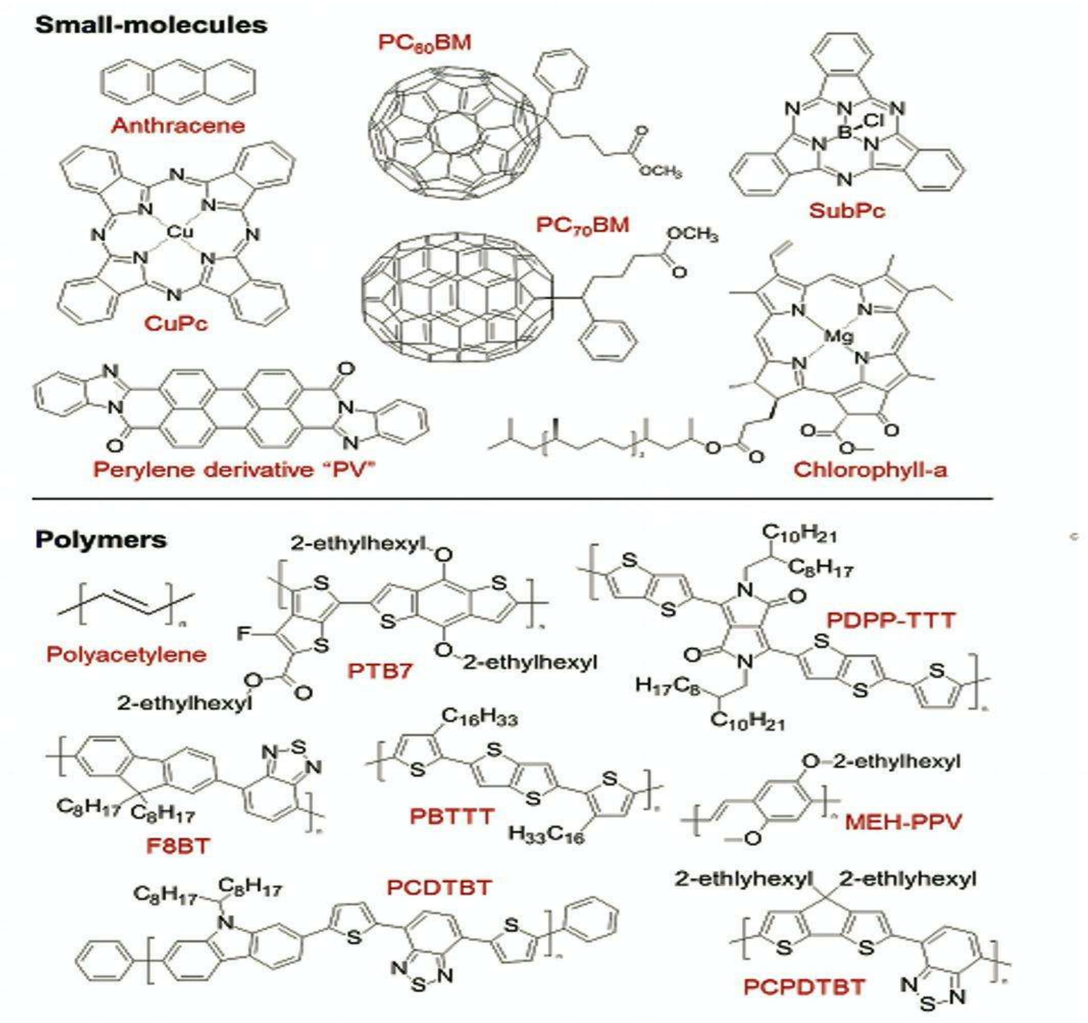


Fig 3. Chemical structures of various and widely used small-molecule and polymer semiconductors.[11]

1.3. A-π-D-π-A structure of small molecules in organic semiconductors

In recent years, small organic semiconductor molecules were designed to have an architecture known as push-pull system , which refers to a molecular design that contains an electron donor (push), an electron acceptor (pull), and a delocalized π system of electrons as shown in **Fig.(4)**.[13] This contributes to enhancing the intramolecular charge transfer (ICT) and controlling the properties. The advantages of the push-pull system are that most of its molecules are generally colored which gives them the ability to absorb sunlight. Moreover, it is possible to change the arrangement of the donor (D) and acceptor(A) units and increase the alternating of π bonds within the molecule to modify and improve the optical and electronic properties so that the compound can achieve the desired goal.[14-16]

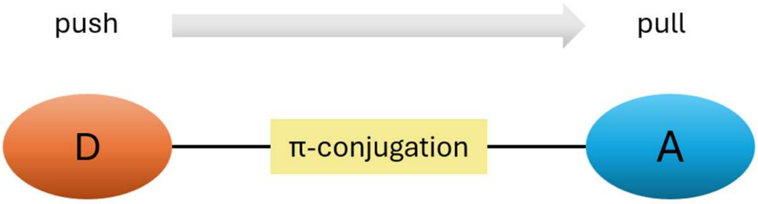


Fig 4. An illustration of Push-Pull system.

Small molecules of organic semiconductors of the type (A-π-D-π-A) have been used in organic solar cell applications and other applications. It is a molecular architecture with a specific arrangement of groups within the molecule, in which two electron-deficient acceptor units (A) are linked to an electron-rich donor central unit (D) by two π-conjugated bridges,[17,18] as shown in the **Fig.(5)**.[19] There are many other systems such as (D-A-D,[20] D-D-A,[21] D-A-A,[22] π-conjugated systems), and all of them have the property of ICT, but the efficiency of this property varies from one molecular structure to another. ICT depends on the choice of groups within the molecule so that there are (Acceptor-Donor) groups, and the presence of a (π-conjugation) system between the donor and the acceptor helps in the movement of electrons and reduce the energy gap (E_g) between the (HOMO, LUMO). ICT is related to the optical properties that is needed to study the efficiency of the compound in applications for small molecules organic semiconductor, in order to be used in various applications.[23,24] The molecular architecture of small molecule organic semiconductors are modified by introducing different acceptor (A) and donor (D) groups to adjust the electronic and optical properties.

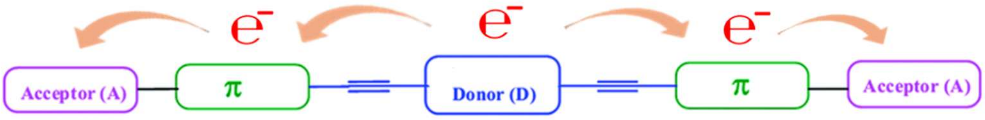


Fig 5. A-π-D-π-A molecular architecture and ICT.

In this research the (A-π-D-π-A) molecular architecture was chosen because when compared with other molecular architecture, it is found that it has distinguishable features and characteristics from other structures in more than one application. When compared with the (D-π-A-π-D) molecular architecture in the application of organic solar cells (OSCs) as shown in **Fig.(6)**, it was found that both molecular structures have the same absorption spectrum but differ in the possibility of ICT. Therefore, optical property calculations and density functional theory (DFT) were performed to verify the efficiency of the two molecular architecture, and it was concluded that (A-π-D-π-A) has a stronger ICT property compared to (D-π-A-π-D), which is required to generate photocurrent in organic solar cells, and this is attributed to the presence of a higher electron density at the ends in the (A-π-D-π-A) structure compared to the (D-π-A-π-D) structure.[24]

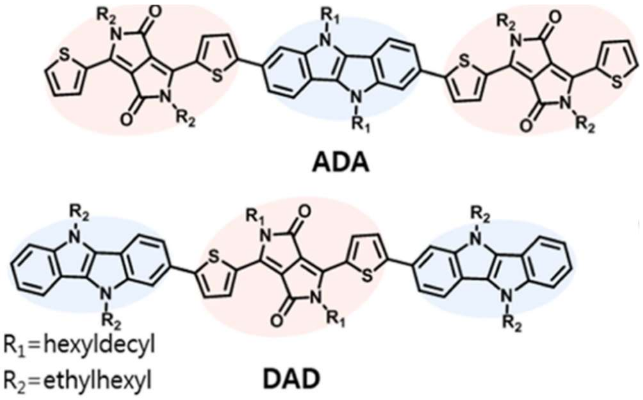
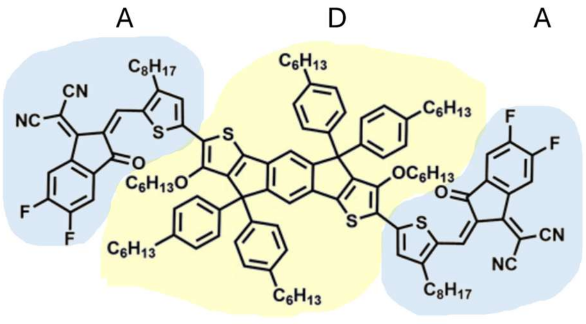


Fig 6. A-D-A vs D-A-D systems.

Among the previous compounds that were synthesized by previous researchers and have the same molecular architecture (A-π-D-π-A) is a compound named IDIOT-4F as shown in **Fig.(7)**, which was used in an optoelectronic device, because its molecular structure can be easily modified. It also has charge transfer property, good optical response and has a wide absorption spectra ranging from the visible region to the infrared region, these features support the use of this structure in their application.[17] Also, some other researchers synthesized three compounds with the same molecular architecture (A-π-D-π-A), they used STF as a central donor group (D) and used three different acceptor groups (A) as shown in **Fig.(7)**. They concluded that the STFYT compound had a better property over STFRDN and STFRCN compounds, that made it more effective in organic solar cells.[18] This indicates that the choice of acceptor groups and donor groups is important because it has an effect on the properties of the compound.



IDTOT-4F

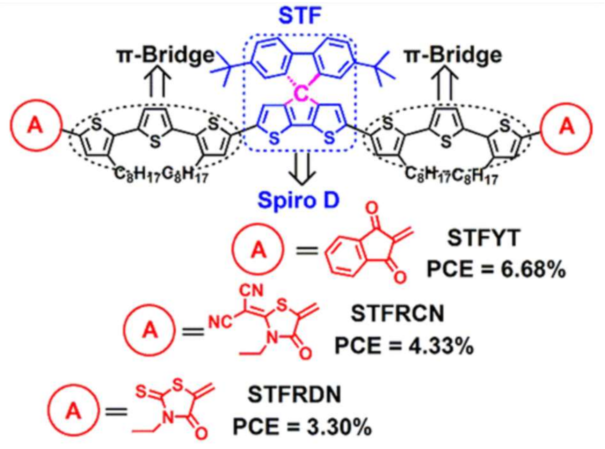
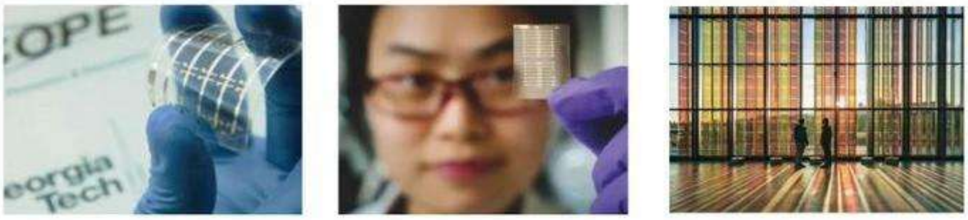


Fig 7. IDTOT-4F and STF compounds with A-π-D-π-A molecular architecture

1.4. Applications of organic semiconductors.

Organic semiconductors are widely utilized in various applications due to their unique properties, such as high chemical tolerance, flexibility, lightweight nature, and low production costs. These materials, which consist of carbon-based molecules, offer significant advantages over traditional counterparts (inorganic semiconductora).[25] For example, organic photovoltaic cells (OPVs) are lightweight and environmentally friendly, making them ideal for portable applications and a viable alternative to silicon-based solar cells.[26] Similarly, organic light-emitting diodes (OLEDs) are used in high-efficiency, high-brightness, thin-film displays,[27] while thin-film organic transistors (OFETs) find applications in access cards and sensors.[28] Additionally, dye-sensitized solar cells (DSSCs) stand out due to their semi-transparent and colorful appearance,[29] and organic photodetectors (OPDs),[30] and sensors further expand the scope of organic semiconductor technology.[25] These versatile applications highlight the growing importance of organic semiconductors in modern technology. Different applications are shown in **Fig.(8)**.



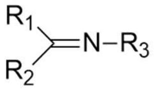
a. OFETs b. Sensor. c. DSSCs

d. OLEDS. e. OPVs. f. OPDs.

Fig 8. Examples of different applications of organic semiconductors. a,[31] b,[32] c,[33] d,[34] e,[35] f,[36]

1.5. Schiff base-based materials.

“Schiff bases “refer to a class of organic compounds named after the German chemist Hugo Schiff, who first described their structure in 1864. These compounds are formed by the nucleophilic addition reaction between aldehydes or ketones and primary amines under suitable conditions and are characterized by the presence of a carbon-nitrogen double bond (C=N-) in their structure. The carbon-nitrogen double bond is known as an azomethine or imine. The general structure of these compounds is shown in **Fig. (9)**.[37]



R1,R2,R3 = Alkyl or Aryl

Fig 9. General structure of Schiff base compounds.

1.5.1. Schiff Base-Based Materials in Organic Semiconductors: Examples and Applications.

Schiff base compounds play a pivotal role in various applications, particularly in the development of organic semiconductors. For example, as shown in **Fig. (10)**, N-(pyren-1-ylmethylene)-9H-fluoren-2-amine (PyFA) has been extensively employed in OLED applications.[38] Additionally, salicylaldehyde-based Schiff bases have demonstrated potential as green-emitting materials for OLED fabrication.[39] Dimedone-derived Schiff bases are considered promising materials for organic optoelectronic devices due to their favorable properties.[40] Copper(II) complexes, such as Cu-Sal derivatives, have been effectively utilized as sensitizers in dye-sensitized solar cells (DSSCs).[29] Furthermore, conjugated small-molecule azomethines, including structures like TPA-Th-TPA, have been synthesized via Schiff base condensation for photovoltaic applications.[41]

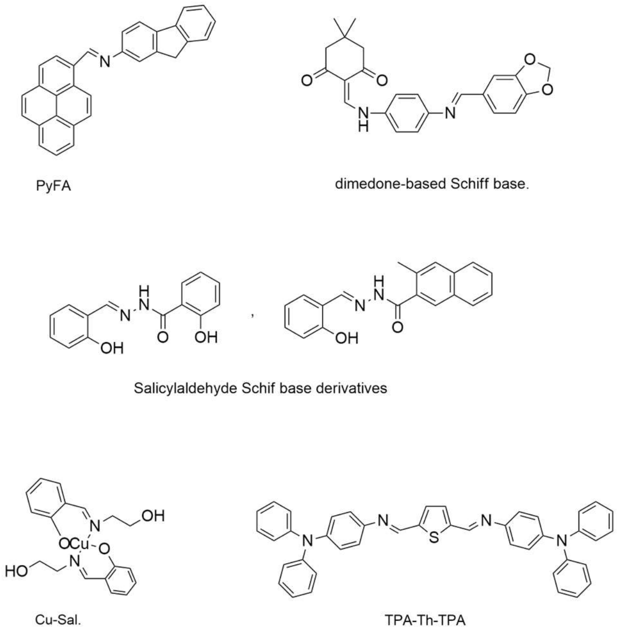


Fig 10. Examples of Schiff base organic semiconductors.

1.5.2. The importance of Schiff base reaction.

Researchers are increasingly focusing on reducing chemical waste, minimizing the use of toxic and hazardous chemicals, and shortening reaction times.[42] Schiff bases have attracted the attention of chemists due to their ease of preparation and formation. They are synthesized through a simple reaction between compounds containing an amine group ($-NH_2$) and aldehydes or ketones, with water produced as a by-product. see **Fig. (11)**.[37]

Water is a by-product in Schiff reactions, resulting in a special advantage in terms of green chemistry, as it is non-toxic and environmentally friendly. Additionally, conjugated Schiff bases possess distinctive properties such as high thermal stability, broad spectral absorption, small band gap, and high electrical conductivity. Therefore, the use of Schiff bases in organic semiconductors is an attractive option due to their chemical efficiency, unique electronic properties, Schiff base compounds exhibit intramolecular proton transfer and integrate donor and acceptor functions, with electronic transitions controlled by the donor-π-bridge-acceptor structure. Furthermore, the C=N bonds enhance electronic conductivity due to π-electron delocalization, in addition to their ease of synthesis, which aligns with the principles of green chemistry.[43]

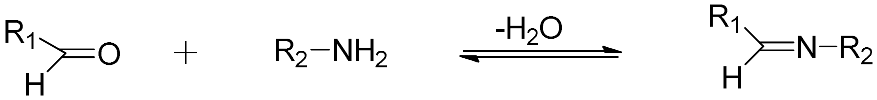


Fig 11. Schiff base formation reaction.

2. Experimental.

2.1.General experiment

Reagents were purchased from several companies: Fischer Scientific, MERCK , Riedel-deHaën, and LOBA Chemie. Uv-Vis measurements were carried out using SHIMADZU UV-2600i and FTIR measurements were performed using AGILENT 630. Density Functional Theory (DFT) calculations were conducted using Orca version 5.0.3 quantum chemistry program package and the input files were generated with the Avogadro 1.2.0 visualization software. Melting point (MP) was recorded using a SMP10 Stuart Scientific melting point machine. Chemical structure was drawn using ChemDraw Pro 12.0.2 , UV-Vis and FTIR spectra were plotted using Excel.

2.2. Synthesis

Ortho-C:

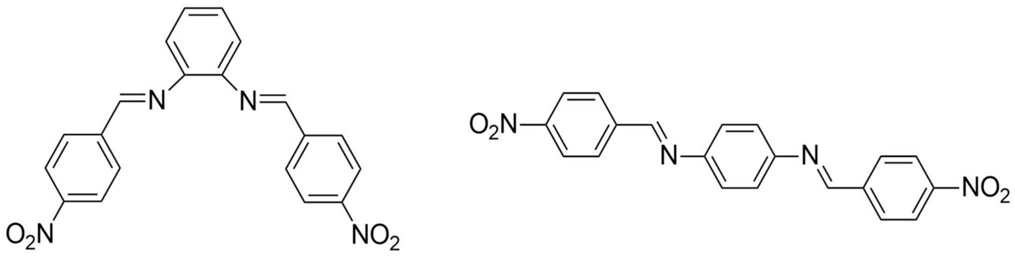
4-Nitrobenzaldehyde (0.27 g, 1.85 mmol) and 1,2-Phenylenediamine (0.1 g, 0.925 mmol) were dissolved in ethanol (20 mL). Then, 3 drops of glacial acetic acid (GAA) were added, causing the color to change from orange to red. The reaction mixture was stirred under reflux for about 4 hours. Afterward, the mixture was cooled to room temperature then in an ice bath, and the yellow precipitate formed was filtered and washed with cold ethanol to remove impurities, yielding a yellow solid (0.095 g, 2.7%). Mp (218-220 ° C). FT-IR (ν, cm^{-1}); 954 (Csp^2-H), 1509 (C=C), 1600 (C=N), 1444 (N=O), 1341 (N-O).

Para-C:

4-Nitrobenzaldehyde (0.56 g, 3.7 mmol) and 1,4-Phenylendiamine (0.2 g, 1.85 mmol) were dissolved in 20 mL of ethanol, and then three drops of glacial acetic acid (GAA) were added to the mixture, causing the color to change from yellow to orange. The mixture was stirred under reflux for 3.5 hours. After the reaction is complete, the mixture was cooled to room temperature then in an ice bath, and a yellow precipitate formed, which was filtered and washed with cold ethanol to remove impurities. A yellow solid was obtained (0.347 g, 50.14% yield). Mp (254-256 °C). FT-IR (ν, cm^{-1}); 965 (Csp^2-H), 1520 (C=C), 1595 (C=N), 1341 (N=O), 1310 (N-O).

3. Aim

The aim of this research is to synthesize two A-π-D-π-A based compounds using the Schiff base reaction, with different acceptor group positions (ortho and para), to investigate the effect of this positional variation on electronic properties (energy levels HOMO and LUMO) and optical properties of the target compounds. In this design, the nitro group ($-NO_2$) attached to the phenyl ring acts as a strong electron-withdrawing group due to its resonance effect **Fig.(12)**. Additionally, the imine group (-CH=N), with its conjugated double bond, partially donates electrons to the aromatic system.



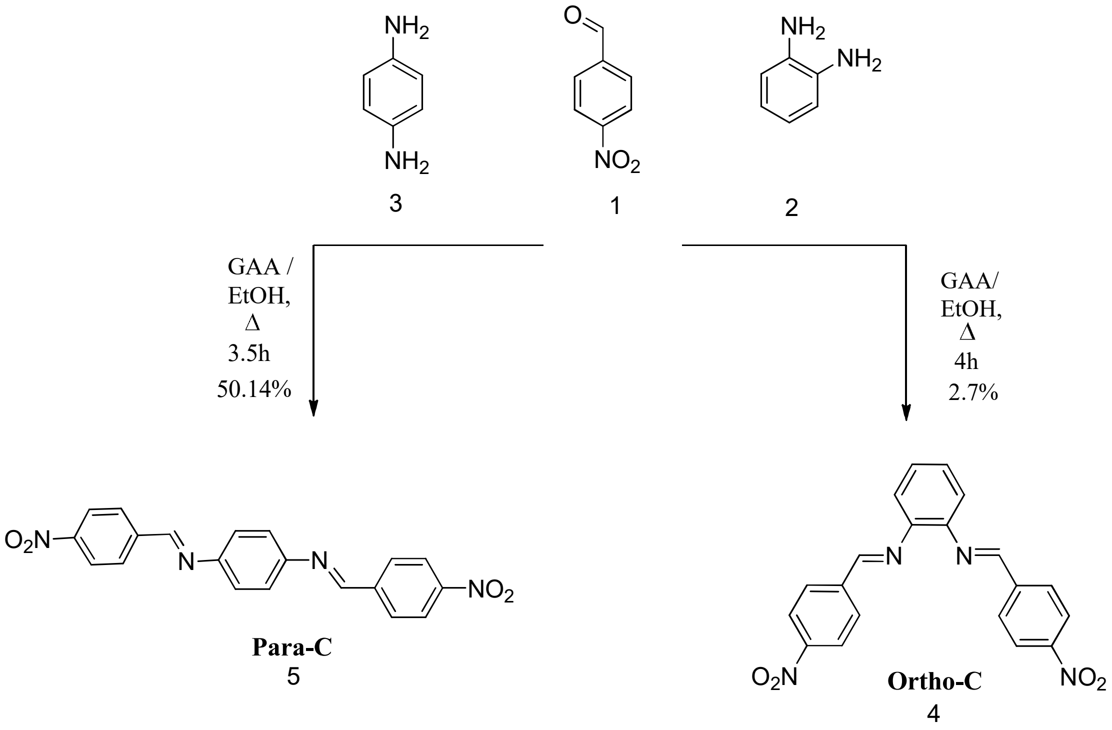
Ortho-C **Para-C**

Fig 12.Chemical structure of the target compounds.

4. Result and discussion.

4.1. Synthesis

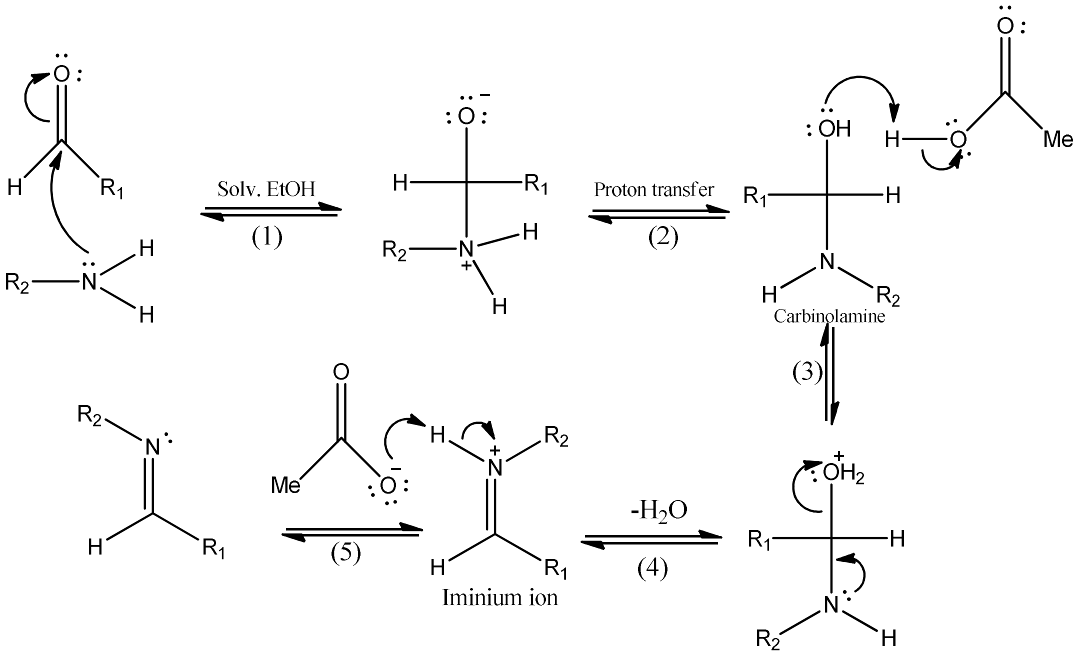
In scheme1: The reaction of 4-nitrobenzaldehyde (1) with para-phenylenediamine (2) and separately with ortho-phenylenediamine (3) resulted in the production of two types of products: an **Ortho-C** (4) with a yield of 2.7% and a **Para-C** (5) with a yield of 50.14%. This was achieved using the Schiff base in the presence of glacial acetic acid (GAA) as a catalyst.



*scheme 1: Preparation of **Ortho-C** and **Para-C** using Schiff base reaction.*[45]

Schiff bases are compounds formed by a nucleophilic addition reaction between aldehydes or ketones and primary amines, characterized by a carbon-nitrogen double bond (C=N-).[37]

The reaction mechanism occurs when a ketone or aldehyde reacts with an amine, the lone-pair of electrons on the nitrogen initiate a nucleophilic attack, forming a dipolar tetrahedral intermediate Scheme 2. This is followed by the transfer of a proton from nitrogen to oxygen, producing a neutral carbinolamine. An acid catalyst then protonates the hydroxyl oxygen, facilitating the elimination of water by the lone-pair electrons on nitrogen, which leads to the formation of an iminium ion. Finally, the deprotonation ($-H^+$) of nitrogen results in the formation of the neutral imine product.[44]



scheme 2: The reaction mechanism for the production of imine via Schiff base.[44]

The synthesized compounds were characterized using FT-IR spectroscopy as well as UV-Vis spectroscopy. FT-IR analysis was performed to all starting materials and target compounds to detect the consumption of the starting materials and the formation of the target compounds. The FT-IR results of the starting materials (1) and (2) revealed the presence of carbonyl (C=O) (for compound 1) peak at approximately 1701 cm^{-1} **Fig.(13)**, and two peaks for the primary amine (for compound 2) appear at 3367-3384 cm^{-1} **Fig.(14)**. However, the results do not show the presence of either the carbonyl or the amine in the product (Ortho-C), indicating that the starting materials have fully reacted **Fig.(15).** This was associated with the presence of the imine (-C=N) band at ~1600 cm^{-1}, indicating the formation of the target compound. A similar behavior was observed for compound Para-C **Fig.(17**) when compared to the starting materials (1) and (3), **Fig.(13)** and **Fig.(16)** .[45]

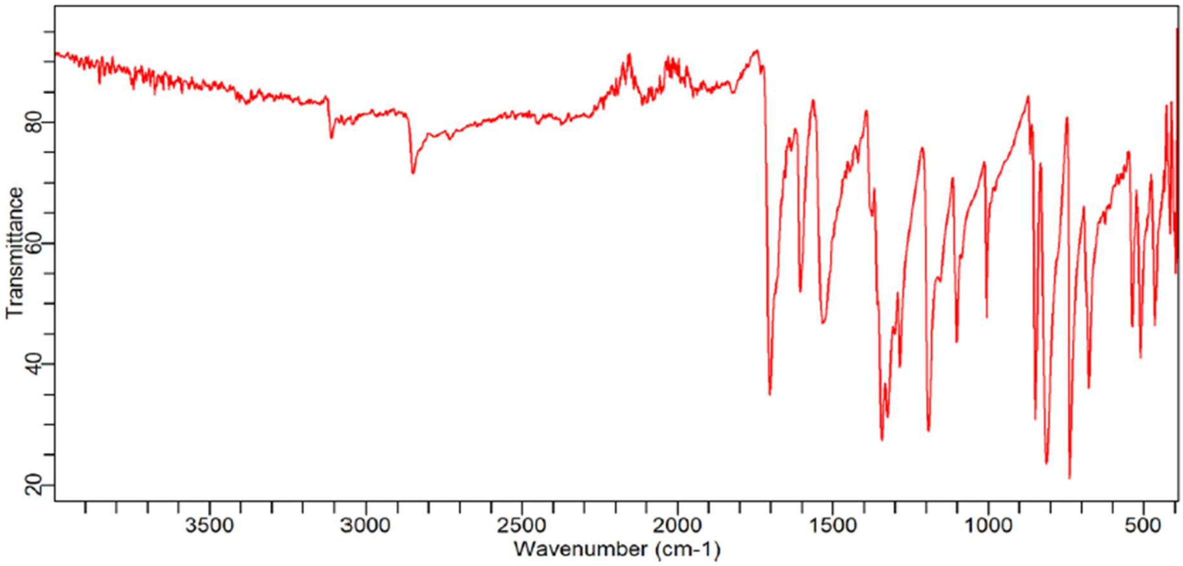


Fig 13. FTIR spectra of 4-nitrobenzaldehyde (1).

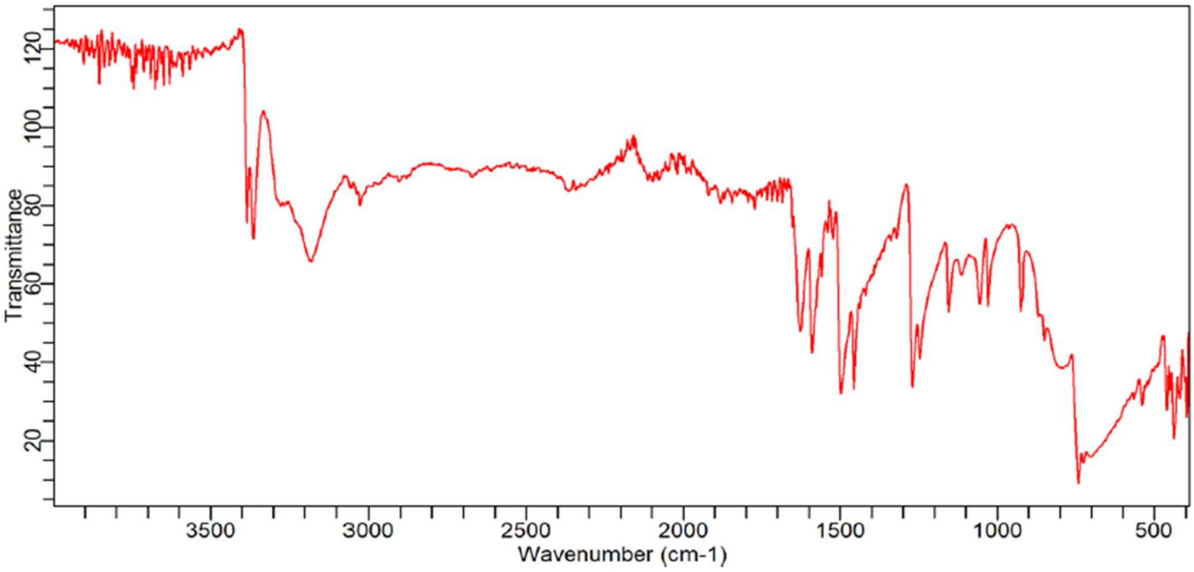


Fig 14. FTIR spectra of o-Phenylenediamine (2).

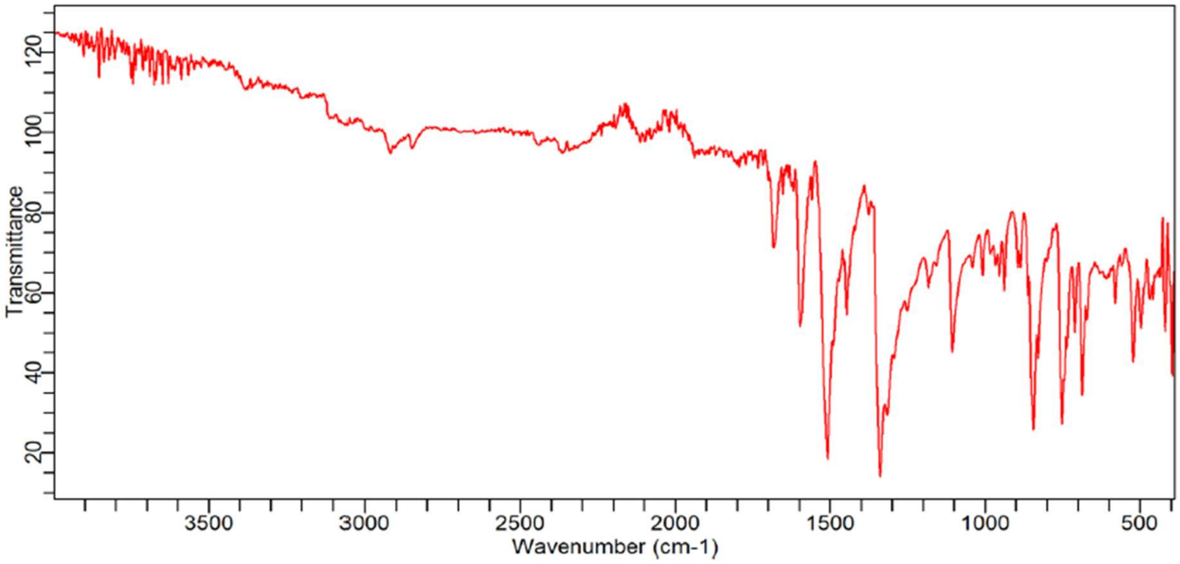


Fig 15. FTIR spectra of ***Ortho-C*** *(4).*

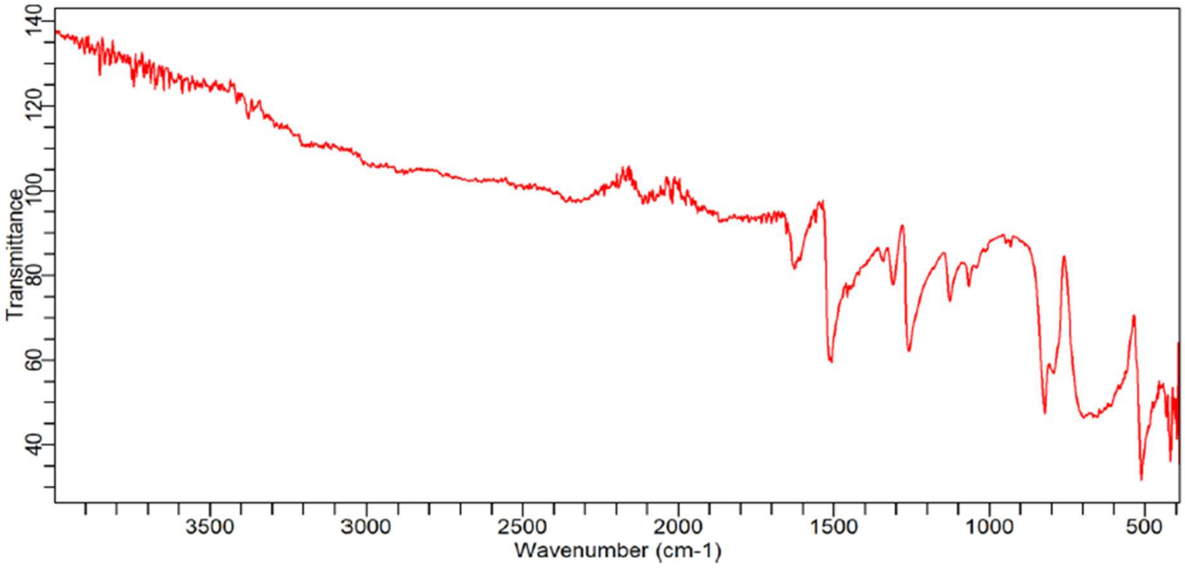


Fig 16. FTIR spectra of p-Phenylenediamine (3).

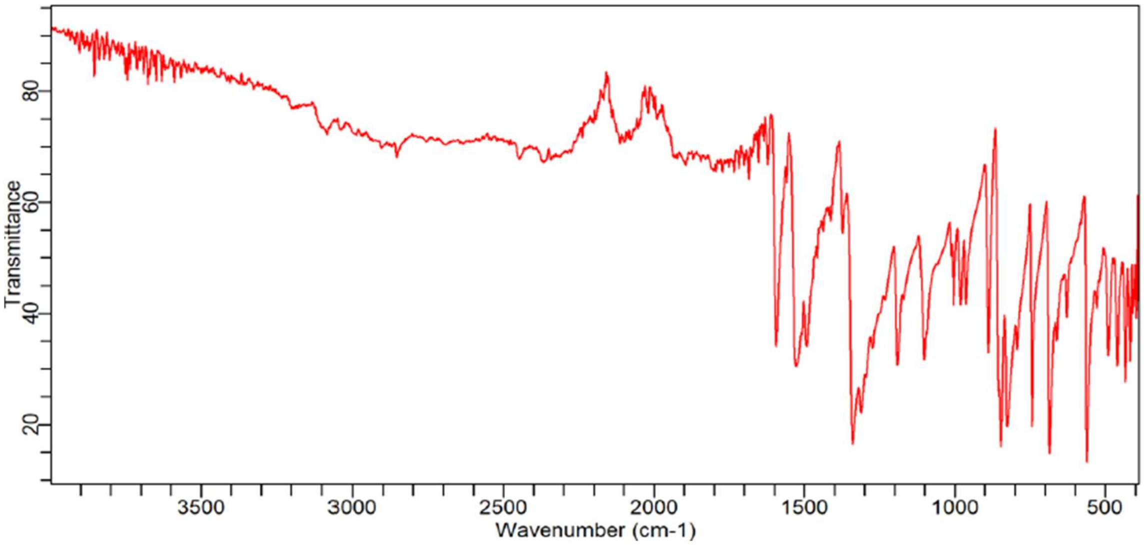


Fig 17. FTIR spectra of ***Para-C*** *(5).*

4.2. Theoretical study

To study the electronic properties of the target compounds and the energy gap (E_g) between the energy levels HOMO (ground state) and LUMO (excited state) for both compounds, density functional theory (DFT) was performed using the Orca and Avogadro software. As shown in **Fig.(18)**, there is a difference between the two compounds in the E_g as the **Para-C** has a smaller E_g than the **Ortho-C** by 0.141ev. At **Para-C** the HOMO energy level of **Para-C** the electron density is distributed throughout the entire compound, but it is mainly localized in the core of the compound, while at the LUMO energy level is distributed throughout the compound with high localization on the terminal groups. On the other hand, in the HOMO energy level of **Ortho-C** ,electron density is distributed throughout the compound and is localized on the core of the compound, while at the LUMO energy level is localized on the terminal groups and in the core of the compound the electron density is very low.

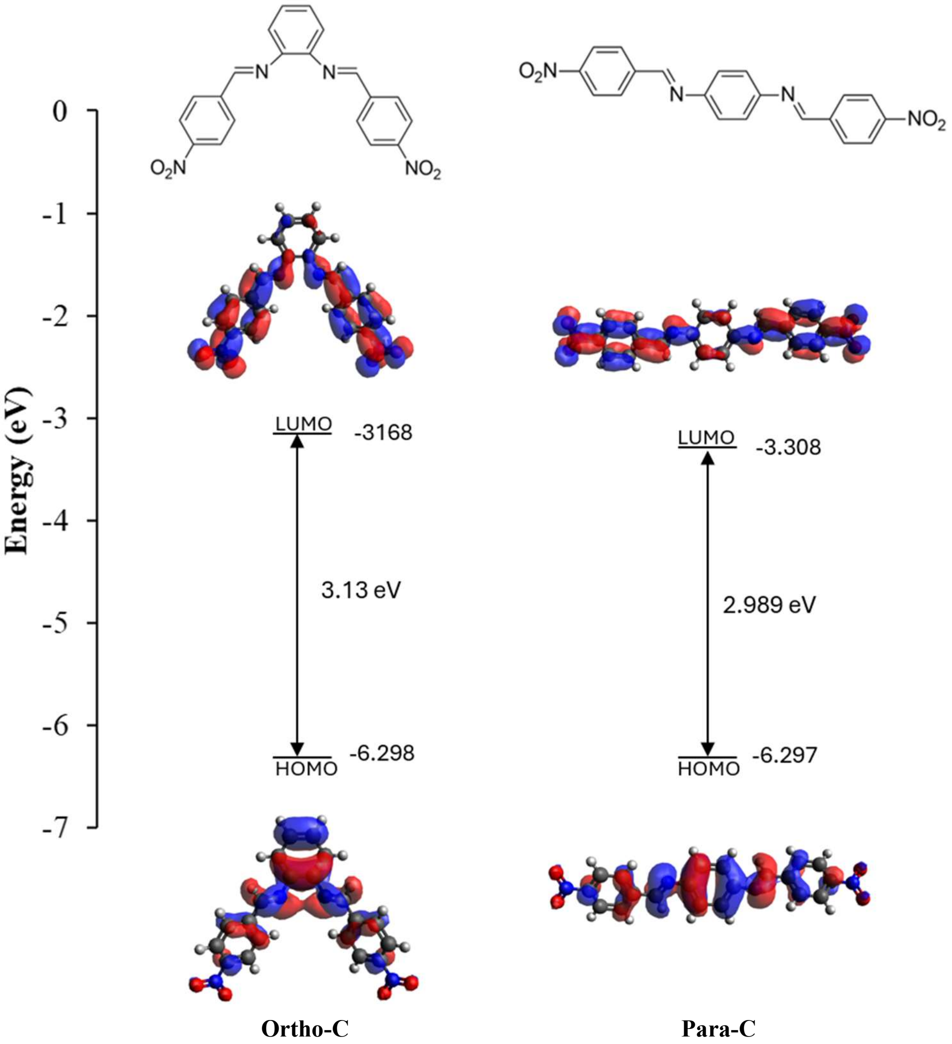


Fig 18. Energy levels HOMO, LUMO and energy band gap E_g.

The molecular geometry of both **Ortho-C** and **Para-C** are twisted. However, in the side view, **Ortho-C** has greater twist, as shown in the **Fig.(19)** , due to the steric hindrance that makes the benzene rings take certain angles in order to maintain stability and this affects the conjugation negatively. As a result, the **Para-C** has more conjugation than the **Ortho-C**, which makes it have a lower E_g. This can also affect the physical properties of the compounds such as melting point. For example, **Para-C** was found to have a higher melting point (Mp) (254-256 ℃) than that of **Ortho-C** (218-220 ℃). This can indicate that **Para-C** is planar which increases the π-π stacking interaction that plays an important role in increasing Mp, as opposed **Ortho-C**.

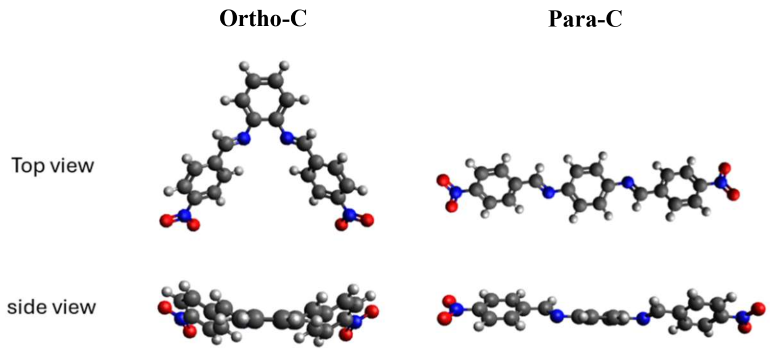


*Fig 19. Molecular geometry for **Ortho-C** and **Para-C** in two side*

4.3. Optical properties

In this study, two compounds, were analyzed in their liquid state using UV spectroscopy after dissolving in EtOH (10^{-5}M) . The absorption spectra of both **Ortho-C and Para-C** are shown in the **fig(20)**, which highlights the differences in their absorption properties. Additionally, **Table (1**) presents the optical properties of the compound.

For **Para-C**, the experimental results show that , λ_{onset} is at 460.7 nm, corresponding to an experimentally calculated optical band gap (E_{opt}) of 2.69 eV. Additionally, the compound showed three λ_{max} bands t observed at 207.5, 279.5, and 388.5 nm, with ε of 81900, 26500, and 22700 L/mol·cm, respectively. From a theoretical perspective, the calculated E_g was found 2.989 eV, showing significant agreement with the experimental value.

For **Ortho-C**, the experimental results show that the λ_{onset} is at 456.5 nm, with an experimentally calculated E_{opt} of 2.71 eV. The λ_{max} were abtained at 208, 259, and 331.5 nm, with ε of 138500, 90100, and 55000 L/mol·cm, respectively. The theoretical results indicate a calculated of E_g of 3.13 eV.

When comparing the two compounds, **Para-C** exhibits a smaller E_{opt} of both experimentally and theoretically compared to **Ortho-C** , indicating a higher efficiency in intramolecular charge transfer due to its more uniform electronic distribution at the LUMO level and greater stability.

In terms of absorption, **Ortho-C** shows a significantly higher molar absorption coefficient ε=138500 L/mol.cm compared to **Para-C** ε=81900 L/mol.cm, highlighting its stronger absorption capability at specific wavelength. **Table (1)**.

Compound	λ_{onset} (nm)	E_{opt} (eV)	λ_{max} (nm)	ε (L/mol.cm)
Para-C	460.7	2.69	207.5	81900
			297.5	26500
			388.5	22700
Ortho-C	456.5	2.71	208	138500
			259	90100
			331.5	55000

*Table 1. Optical properties of **Para-C** and **Ortho-C**.*

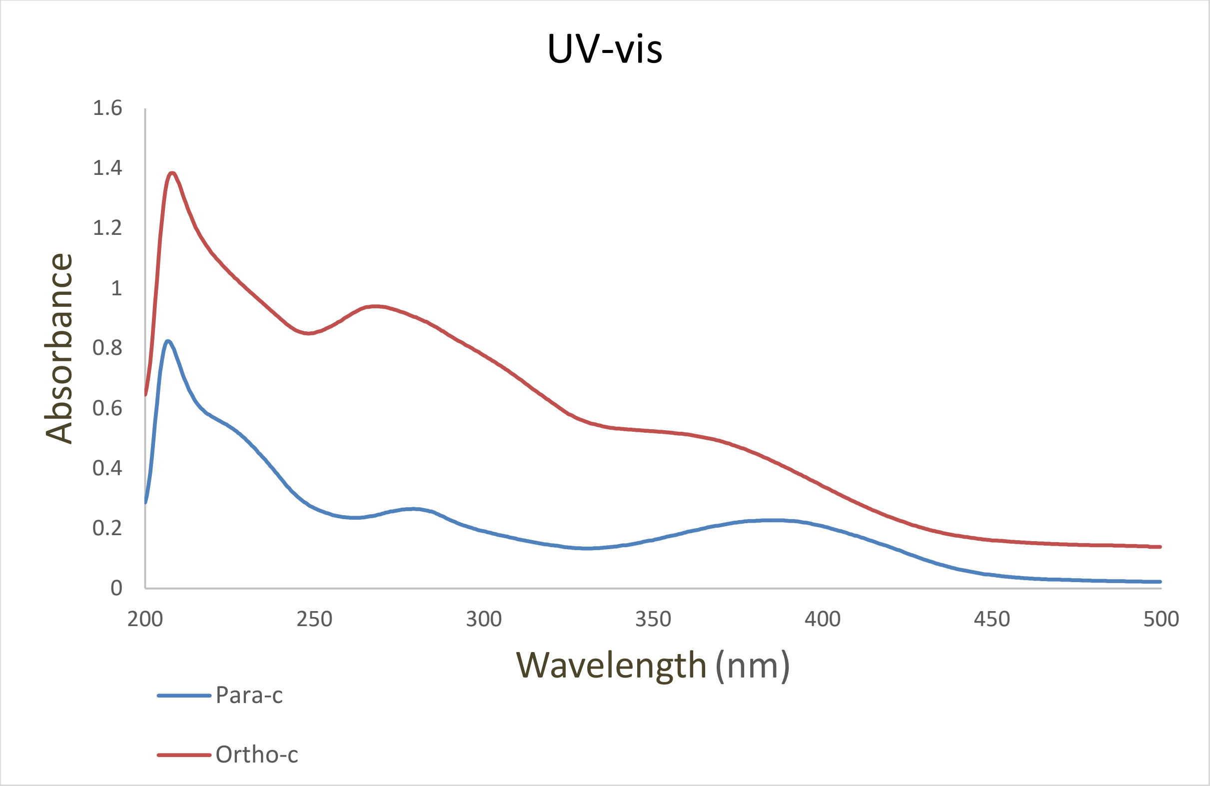


*Fig 20. UV-Vis absorption spectra of **Para-C** and **Ortho-C** in EtOH (10^{-5} M).*

5. Conclusion

In this study, two small-molecular organic semiconductors of based on A-π-D-π-A system were synthesized using the Schiff base reaction. The compound **Para-C** exhibits a lower energy gap E_g of 2.69 eV compared to **Ortho-C**, which has an E_g of 2.71 eV. This indicates that **Para-C** requires less energy for electron transfer between the HOMO and LUMO energy levels, suggesting higher charge transfer efficiency.

In terms of absorptivity, the results showed that **Ortho-C** has a higher molar absorption coefficient of 138,500 $M^{-1}\cdot cm^{-1}$ compared to **Para-C**, which has a coefficient of 81,900 $M^{-1}\cdot cm^{-1}$, reflecting its superior light absorption ability. This contrast between the two compounds highlights the impact of the electron-acceptor group's position on the electronic and optical properties. While **Para-C** demonstrates a higher potential for charge transfer efficiency, **Ortho-C** stand out in light absorption.

6. Recommendation

To enhance the efficiency of producing the two compounds (**Para-C** and **Ortho-C**), it is recommended to optimize the reaction conditions such as using a different solvents, such as dry ethanol, adjusting the temperature, and increasing the reaction time to ensure higher yield and reproducibility in future reactions. Additionally, expanding the application of A-π-D-π-A type compounds in organic solar cells, organic light-emitting diodes (OLEDs), and dye-sensitized solar cells (DSSCs) is essential to evaluate their efficiency in practical applications.

Advanced theoretical studies are also recommended to analyze electron density distribution and predict the performance of these compounds under various conditions to improve their design for specific applications. To ensure sustainability, eco-friendly chemical methods can be adopted by using non-toxic solvents and catalysts and minimizing waste in alignment with green chemistry practices. Furthermore, material stability tests under diverse environmental conditions, such as temperature and humidity, should be conducted to ensure their long-term stability.

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