SYNTHESIS, CHARACTERIZATION AND THEORETICAL STUDIES OF CHALCONE AND ETHYNYLATED SCHIFF-BASE DERIVATIVES FOR POTENTIAL LIGHT EMITTING APPLICATIONS

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SYNTHESIS, CHARACTERIZATION AND THEORETICAL STUDIES OF CHALCONE AND ETHYNYLATED SCHIFF-BASE DERIVATIVES FOR POTENTIAL LIGHT EMITTING APPLICATIONS

by

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LIST OF ABBREVIATIONS

A	Acceptor
Anth	Anthracene
ATR	Attenuated Total Reflectance
AFM	Atomic Force Microscopy
B3LYP	Becke-style 3-Parameter Density Functional Theory (using the Lee-Yang-Parr correlation functional)
CIF	Crystallographic Information File
CuI	Copper Iodide
D	Donor
DFT	Density Functional Theory
DMSO	Dimethyl Sulfoxide
FMOs	Frontier Molecular Orbitals
FESEM	Field Emission Scanning Electron Microscopy
GIAO	Gauge-Invariant Atomic Orbital
HOMO	Highest Occupied Molecular Orbital
ICT	Intermolecular Charge Transfer
I-V	Current-Voltage
LUMO	Lowest Unoccupied Molecular Orbital
MeOH	Methanol
NaOH	Sodium Hydroxide
NMR	Nuclear Magnetic Resonance
NOR Lab	Nano-Optoelectronics Research & Technology Laboratory

ORTEP	Oak Ridge Thermal Ellipsoid Plot
OLED	Organic Light Emitting Diode
ppm	Parts per million
SADABS	Siemens Area Detector Absorption Correction
SAINT	SAX Area-detector Integration (SAX-Siemens Analytical X-ray)
SMART	Siemens Moecular Analysis Research Tools
TD-DFT	Time Dependent Density Functional Theory
TMS	Tetramethylsilane
THF	Tetrahydrofuran
USM	Universiti Sains Malaysia
UV	Ultraviolet
UV-Vis	Ultraviolet Visible
*w*R	Weighted Reliability Index

SINTESIS, PENCIRIAN DAN KAJIAN TEORI TERBITAN KALKON DAN TERETILINASI BES-SCHIFF UNTUK POTENSI APLIKASI PEMANCAR CAHAYA

ABSTRAK

Ciri fotofizikal dan elektrokimia bahan organik sedang dikaji secara aktif untuk meningkatkan pengangkutan cas bagi OLED berprestasi tinggi. Diinspirasikan oleh bahan organik berkonjugasi tinggi π, dua siri sebatian baharu yang menampilkan konfigurasi penderma-pi-penerima (D-π-A) iaitu terbitan kalkon (**1-6**) dan terbitan teretilinasi bes-Schiff (**7-12**) telah berjaya direka dan disintesis menggunakan kaedah pemeluwapan Claisen-Schmidt dan kaedah pemeluwapan bes-Schiff. Struktur hablur semua sebatian telah diselesaikan dan dimurnikan menggunakan analisis pembelauan sinar-X hablur-tunggal. Pengiraan Teori Fungsian Ketumpatan (DFT) mengesahkan geometri molekul yang dioptimumkan adalah setanding dengan keputusan eksperimen. Gambar rajah padatan hablur semua sebatian mendedahkan interaksi antara molekul termasuk interaksi C—H···O, N—H···N, C—H···π dan π···π, yang menyumbang kepada pemindahan cas dan kestabilan struktur. Kumpulan berfungsi dan struktur kimia molekul semua sebatian telah dikenal pasti secara kuantitatif oleh analisis spektroskopi Fourier Transform Inframerah (FTIR) dan ^{1}H dan ^{13}C Resonans Magnet Nuklear (NMR). Spektrum UV-Vis mendedahkan bahawa semua sebatian mempamerkan panjang gelombang penyerapan maksimum dalam julat semikonduktor dengan nilai antara 2.52 dan 2.94 eV untuk sebatian (**1-6**) dan 2.73 hingga 2.85 eV untuk sebatian (**7-12**). Jurang tenaga HOMO-LUMO yang dikira untuk sebatian kalkon berada dalam julat 2.33 eV hingga 3.32 eV manakala teretilinasi bes-Schiff adalah 2.31 hingga 3.06 eV, yang

kedua-dua sebatian berada dalam julat semikonduktor. Tambahan pula, analisis FESEM mendedahkan filem nipis (**2**, **3**, **5**, **6**, **9**, **10**, **11**, **12**) mempunyai permukaan homogen tanpa lubang jarum dan mempamerkan struktur bentuk zarah hablur terkumpul. Mikroskopi AFM mengesahkan filem (**1**, **2**, **5**, **8**, **9**, **10**) mempunyai permukaan yang licin bagi menghalang berlakunya litar pintas elektrik. Selain itu, terbitan teretilinasi bes-Schiff (**7-12**) menunjukkan voltan operasi yang lebih rendah iaitu 6.1 hingga 10.7 V berbanding terbitan kalkon (**1-6**) dengan 9.0 hingga 15.4 V. Oleh itu, semua sebatian menawarkan potensi dalam aplikasi pemancar cahaya.

SYNTHESIS, CHARACTERIZATION AND THEORETICAL STUDIES OF CHALCONE AND ETHYNYLATED SCHIFF-BASE DERIVATIVES FOR POTENTIAL LIGHT EMITTING APPLICATIONS

ABSTRACT

The photophysical and electrochemical characteristics of organic materials are being studied actively to enhance charge transport for high-performance OLEDs. Inspired by highly π-conjugated organic materials, two series of new compounds featuring of donor-pi-acceptor (D-π-A) configuration namely chalcone derivatives (**1**-**6**) and ethynylated Schiff-base derivatives (**7**-**12**) compounds were succesfully designed and synthesized using Claisen-Schmidt condensation and Schiff-base condensation methods, respectively. The crystal structures of all compounds were solved and refined using single-crystal X-ray diffraction analysis. Density Functional Theory (DFT) calculations confirmed the optimized molecular geometries are comparable to the experimental results. The crystal packing diagrams of all compounds revealed intermolecular interactions including C—H···O, N—H···N, C—H···π and π···π interactions, which contribute to charge transfer and structural stability. The functional groups and molecule's chemical structure of all compounds were quantitatively identified by Fourier Transform Infrared (FTIR) and ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy analyses, respectively. The UV-Vis spectra revealed that all compounds exhibit maximum absorption wavelengths within the semiconductor range, with values between 2.52 and 2.94 eV for compounds (**1**-**6**) and 2.73 to 2.85 eV for compounds (**7**-**12**). The calculated HOMO-LUMO energy gaps for chalcone compounds in range of 2.33 eV to 3.32 eV meanwhile ethynylated Schiff-base is 2.31 to 3.06 eV, which both compounds fall

within the semiconductor range. Furthermore, FESEM analysis revealed the thin films (**2**, **3**, **5**, **6**, **9**, **10**, **11**, **12**) have a homogeneous surface without pinholes and exhibit an agglomerated crystal particle-shape structure. AFM microscopy confirmed the smooth surface of films (**1**, **2**, **5**, **8**, **9**, **10**) preventing electrical short circuits. Ethynylated Schiff-base derivatives (**7-12**) demonstrated lower operating voltages values of 6.1 to 10.7 V as compared to chalcone derivatives (**1-6**) of 9.0 to 15.4 V. Therefore, all compounds offers great potential in light-emitting applications.

CHAPTER 1

INTRODUCTION

1.1 Overview of Organic Light Emitting Diodes (OLEDs)

The generation of electronic displays has evolved from the first generation of cathode-ray tubes (CRT) to the second generation of liquid crystal display (LCD) and plasma display panels (PDP). Nowadays, organic light emitting diodes (OLEDs) are emerging as the next generation and are becoming one of the latest devices in the lighting industry. Active research and production of organic light emitting diodes (OLEDs) began in 1987, when Eastman Kodak's Tang and VanSlyke demonstrated that bright luminance was achieved >1000 cd/m^2 and efficiency of 1.5 lm/W at a driving voltage of ~10V from bilayer OLED system using a small molecule of aluminium tris(8-hydroxyquinoline) (Alq$_3$) sandwiched between anode and cathode (Tang & VanSlyke, 1987). Since their report, much effort has been made to develop practical OLEDs technology in flat-panel display and lighting applications for achieving highly efficient luminance, long-lasting and low-cost device. For instance, Burroughes and his group from Cambridge University successfully developed the conjugated polymer OLEDs based on poly(p-phenylene vinylene) (PPV) that provide an opportunity to explore the wet-processing method (Burroughes *et al.*, 1990). Four years later, Kido *et al*. (1994) continued the development of OLED studies on white OLEDs at Yamagata University. In 1998, phosphorescent OLEDs were invented by Baldo *et al*. (1998) to enhance the performance of OLEDs. Afterwards, the multi-photon OLEDs (Koden, 2016) and thermally activated delayed fluorescence (TADF) OLEDs (Endo *et al.*, 2011, Youn Lee *et al.*, 2012, Wu *et al.*, 2014) were invented for performances improvement. Since 2012, research on commercially flexible OLED technologies has been actively developed for future OLED business with a number of private companies.

The typical OLED structure is composed of a substrate, a conductive layer, an emissive layer and both anode and cathode terminals which are approximately 100 to 500 nanometres thick. Heterojunctions or known as multi-layer OLEDs constituted a stack of organic layers which widely employed in fabrication to increase the device efficiency and to overcome the accumulation of excess electrons and holes (Ugale *et al.*, 2018). The multi-layer OLED architecture usually includes different functional layers such as hole injection layer (HIL) and electron injection layer (EIL), hole transporting layer (HTL), electron transporting layer (ETL) and emissive layer (EL), shown in Figure 1.1. These layers are sandwiched between two electrodes where the emissive layer acts as recombination site region of holes and electrons, producing a light photon. Traditionally, the OLEDs are fabricated in a vacuum deposition system under a high vacuum environment at $10^{-4} \sim 10^{-5}$ Pa. A single-layer OLED has gained popularity since the fabrication is quite simple yet less expensive. In the year 2000, the single-layer OLED with Al cathode, obtained by spin coating has been successfully performed and achieved high external quantum efficiency of 2.0 % and a current efficiency of 8.5 cd/A at 22 V by Y.D. Jin *et al.* and cowerkers (Jin *et al.*, 2000). In their studies, the active layer consists of a blend of Alq_3/rubrene/polystyrene (PS) with weight ratios y: x:100.

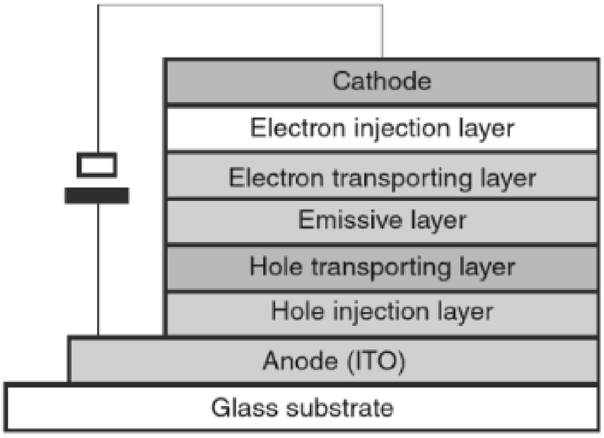

Figure 1.1 Typical structure of multilayer OLEDs (Lee *et al.*, 2017)

The OLEDs are based on certain organic small molecules which behave as diode semiconductors when the external current is applied. Organic materials can be considered as candidates for practical light emitting devices if they exhibit high fluorescent quantum efficiency in the visible spectrum. Thus, this research focus on the to study of potential of organic chalcone and Schiff-base materials on single layer OLED by adopting the different donor and acceptor substituents and different conjugated π-bond molecular structures, respectively.

1.2 Organic π-Conjugated Materials

The selection of materials in organic electronics is of great importance for optoelectronic applications. This is to ensure the organic materials must having a good ability to transport and behave similar to conductors or semiconductors. The synthesis of novel π-conjugated organic materials is essential for discovering basic structure-property connections. The conjugation effect occurs when the molecules consisting alternating single or double bonds which contributes to π-π conjugation as illustrated in Figure 1.2. Many of the organic molecules that emit light are often π-conjugated compounds, in which the p_z and p_y orbitals of nearby C-atoms overlap to produce π-orbitals and π-bonds. Electrons in π-orbitals are delocalized along the bond axis connecting the two C-atoms as a result of the overlap (Bassani *et al.*, 2005). The delocalized π-electron cloud in organic polymers such as polyaromatic hydrocarbons (PAHs) extends along the entire length of the chain as depicted in Figure 1.3. This delocalization could reduce the energy gap of the organic molecules, promoting efficient charge transfer. Thus, polyaromatic hydrocarbons (PAHs) such as napthalene, anthracene and pyrene are excellent in π-electron delocalization and charge transfer since PAHs materials possess a rigid and planar π-conjugated skeleton (Li *et al.*, 2020). Furthermore, PAHs materials also have outstanding properties since they are mostly bulky and stable moiety.

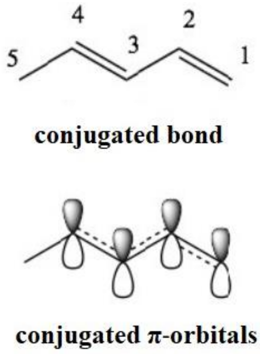

Figure 1.2 Conjugated bond and π-orbitals in alternating single or double bonds (Hissler *et al.*, 2003)

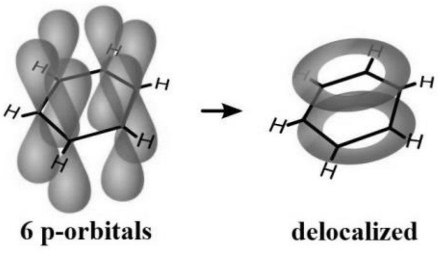

Figure 1.3 The delocalized electrons from the p-orbitals form rings in benzene (Alevel Chemistry, n.d.)

1.3 Problem Statements

In the last decade, light emitting diode (LED) based on inorganic materials have become fascinating candidates in solid-state lighting applications due to long-life and good compatibility with integrated circuits for large area display panels such as computer monitors, television screens and instrument displays. Inorganic LEDs are light emitting diodes made of a crystalline semiconductor. Although the inorganic LED can operate at low operating voltage and serves a flexible size for display screen size, however its efficiency is comparatively lower than the organic LED. For instance, white light emitting diodes (WLED) practicably use inorganic material such as lead halide perovskite $CsPbX_3$ (X = Cl, Br, I) nanocrystals encounter a drawback in which the device is unstable to work at a high operation current caused by the deep traps occurred at the quantum dots surface (Zhang *et al.*, 2018). In addition, inorganic LEDs suffer from high cost production due to expensive deposition techniques (Sessolo & Bolink, 2011, Haque *et al.*, 2017). Apart from that, the inorganic materials usually lack extended π-electron delocalization and high cost maintainances of synthesis.

Due to that, many scientists have put a great effort to discover new materials to enhance LED performances in terms of quantum efficiency, lifetime and low production cost. In order for the compounds to exhibit a good fluorescence, the molecules should have suitable selected π-conjugated core, linking groups, terminal functionality and fine control of their self-assembly (Manohara *et al.*, 2019). These organic compounds are practically constructed based on push-pull systems where the electron-donating group (D) is linked to an electron-withdrawing group (A) through a π-conjugated spacer. In most situations, the intensity of the push-pull effects determines how chromophores behave on a molecular level.

Two organic materials having a π-conjugated system which act as a bridge are the main interest in this research to investigate their photophysical and electrochemical properties with a wide range of substitutions at both end-capped. Therefore, this thesis will discuss further on the role of bulky substituents attached to the design fragments of two classes of organic compound series which lead to high optical properties.

1.4 Objectives

Based on the research problem, there are several objectives have been identified and need to be achieved during this research study. The objectives of this study are as listed below.

1. To design, synthesize and characterize two distinct classes of organic compounds featuring mixed moieties of chalcone and ethynylated Schiff-base derivatives using crystallographic and spectroscopic analytical methods to elucidate their structural, chemical and optical properties.
2. To fabricate the single-layer OLED thin films of these derivatives using a solution process of spin-coating technique.
3. To study the microstructural and electrical properties of OLED thin films using Field Emission Scanning Electron Microscopy (FESEM), Atomic Force Microscopy (AFM) and current-voltage characterization.

CHAPTER 2

LITERATURE REVIEW

2.1 Molecular Organic Architecture

Recent studies have highlighted the potential of OLEDs in displays, lighting, and automotive sectors. For instance, OLED displays have gained significant attention in smartphones, televisions and wearable devices due to their superior image quality, wider viewing angles and thinner form factors (Zou *et al.*, 2020). In the lighting industry, OLEDs offer a more energy-efficient and customizable alternative to traditional lighting sources (Pode, 2020). Moreover, OLEDs are being integrated into automotive applications such as dashboards and head-up displays to enhance driver experience and safety (Blankenbach, 2018). As research continues to advance, OLED technology is expected to play a pivotal role in shaping future technological advancements. Due to that many scientists are working on designing the molecular organic system which determine the final device performance. The development of the OLEDs nowadays not depends in the processing technology but also based on in-depth understanding of synthesis of new organic materials and structure-property relationship for OLEDs behaviour (Dechun, 2013).

Several approaches must be addressed in order to develop and synthesize a range of conjugated organic materials with varied structures and functional moieties to suit the needs of these organic devices. Firstly, the arrangement of the organic molecules system that must equipped with strong configuration push-pull system. The D-A arrangement also referred to as "push-pull" systems, confirms effective intermolecular charge transfer (ICT) from the electron-donating group to the electron-accepting group via π-bond conjugation and generates the donor-acceptor system (Khan *et al.*, 2021). Many chemical compounds with extended π-bond conjugated arrangements that contain donor groups (N-CH_3, O-CH_3, -OH) and acceptor groups (CN, NO_2, CF_2) have been studied, primarily correspond to donor-π-acceptor (D-π-A) chromophores as shown in Figure 2.1. However, conjugated organic material carrying D-π-A system experiencing effect of aggregation caused quenching (ACQ) in solid state and it is an obstacle for the development of solid-state optoelectronic devices like OLEDs (Karuppusamy *et al.*, 2017, Rajeswara Rao *et al.*, 2013). To overcome this drawbacks, the introduction of aggregation induced enhanced emission (AIEE) is employed to organic the materials in enhancing the fluorescence in both liquid and solid state (Luo *et al.*, 2001). One method of doing this is by incorporating bulky substituents to the bulky group and alkyl chain in the luminophore moiety. These are intended to reduce H-aggregation (head to head) molecular arrangement and π-π stacking intermolecular interaction (An *et al.*, 2002). The molecular organic D-π-A with AIEE characteristics must be designed to obtaining the J-aggregation (head to tail) molecular arrangement for potential light emitting diodes.

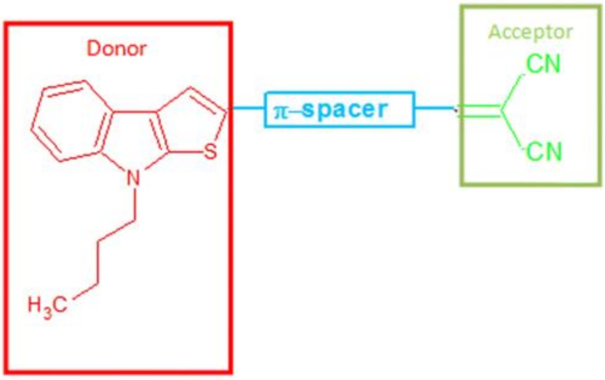

Figure 2.1 Molecular structure of studied D–π–A compounds based on indole (El Mouhi *et al.*, 2019)

Secondly, the selection of donor materials are crucial for the property of optoelectronic device. Polyaromatic materials such as pyrene and anthracene are an electron rich moiety which can donate the electron and form an effective D-π-A system when it is combined with an electron acceptor moiety. The π-electrons could enhance the intramolecular charge transfer (ICT) and hence increase the conjugation efficiency of polyaromatic based material (Puranik *et al.*, 2021). Latest research reported that strong electron-donating groups (EDGs) at the *para*-position of 4’-methoxychalcone derivatives and good molecular planarity were beneficial to their solid-state fluorescent quantum yields (Lin *et al.*, 2022). Therefore, in an attempt to investigate this property, two set of compounds were selected for realizing this organic materials such as chalcone and Schiff-base compounds featuring D-π-A system.

Intermolecular charge transfer (ICT) plays a crucial role in Organic Light-Emitting Diodes (OLEDs) because it directly influences the efficiency of light emission. ICT facilitates the formation of excitons, bound electron-hole pairs responsible for luminescence (Sarma & Wong, 2018). Moreover, ICT enables efficient energy transfer between molecules within the OLED material, thereby minimizing non-radiative energy loss (Wang *et al.*, 2020).

2.2 Synthesis of Chalcone

Chalcone are widely distributed in plants and are considered to be a precursor of flavonoids and isoflavonoids. The standard chalcone consists of two aromatic rings connected with the π-bridge also known as enone moiety bridge. There are many methods to synthesize chalcones which includes Claisen-Schmidt condensation (Winter *et al.*, 2016), Sizuki-Miyaura Coupling reaction (Tang *et al.*, 2010), Sonogashira Isomerization Coupling reaction (Cho, 2005) and Carbonyative Heck Coupling reaction (Lian *et al.*, 2016). For this research, Claisen-Schmidt condensation was employed due to its simplicity in procedure, short reaction time, more environmentally friendly and without further required for column chromatography (Kumar *et al.*, 2010).

Over the past six years, there are six significant reported studies that used Claisen-Schmidt condensation method to synthesize chalcones compounds (Baggio *et al.*, 2016, Karuppusamy *et al.*, 2017, Zaini *et al.*, 2019, Anizaim *et al.*, 2019, Zainuri *et al.*, 2021, Alsaee, Bakar, *et al.*, 2022). The reaction is prepared by dissolving of appropriate ketone and aldehye moieties in methanol solvent with the presence of sodium hydroxide NaOH base as catalyst. The synthesized compound is filtered, washed successively and purified by recrystallization. The synthetic scheme for the reported chalcone synthesized by this approach is shown in the Figure 2.2.

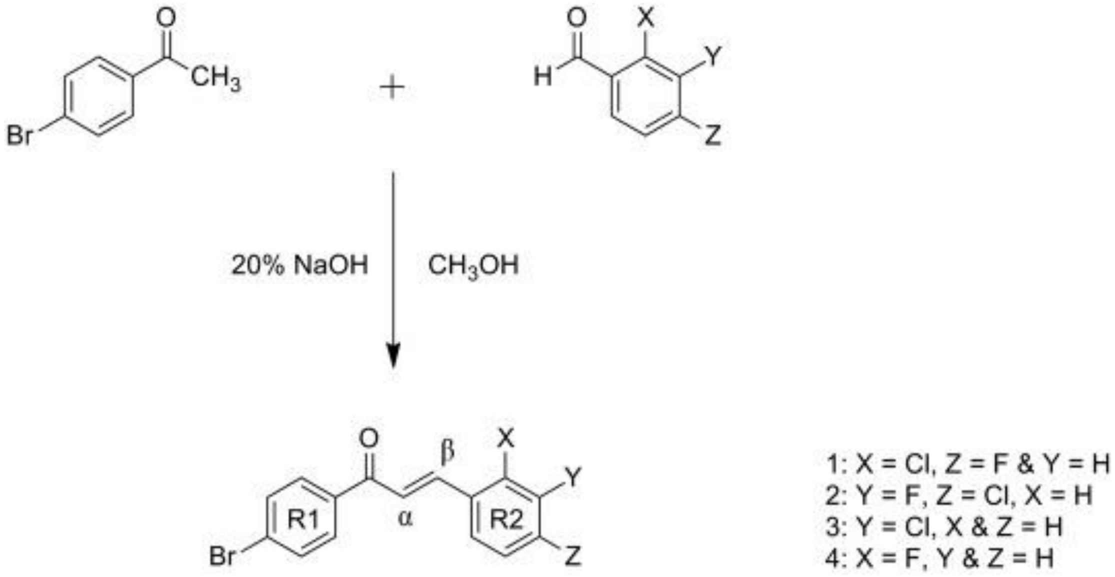

Figure 2.2 Synthesis scheme of halogenated chalcone derivatives at *ortho-*, *meta-* and *para-* position of aromatic ring R2 (Zaini *et al.*, 2019)

Ahmad *et al.* (2016) also synthesized novel chalcone derivatives by conventional and microwave irradiation methods. Both of these methods used potassium hydroxide (KOH) solution as base catalysts. For microwave irradiation methods, the final mixture was placed under microwave irradiated for about 2-6 minutes at 180 watts. The synthetic scheme is shown in Figure 2.3. Chalcone fragment is one of the example that contains π-conjugated skeleton at the enone bridge and their both end-capped which can be further tuning with donor and acceptor groups for D-π-A chalcone configuration system.

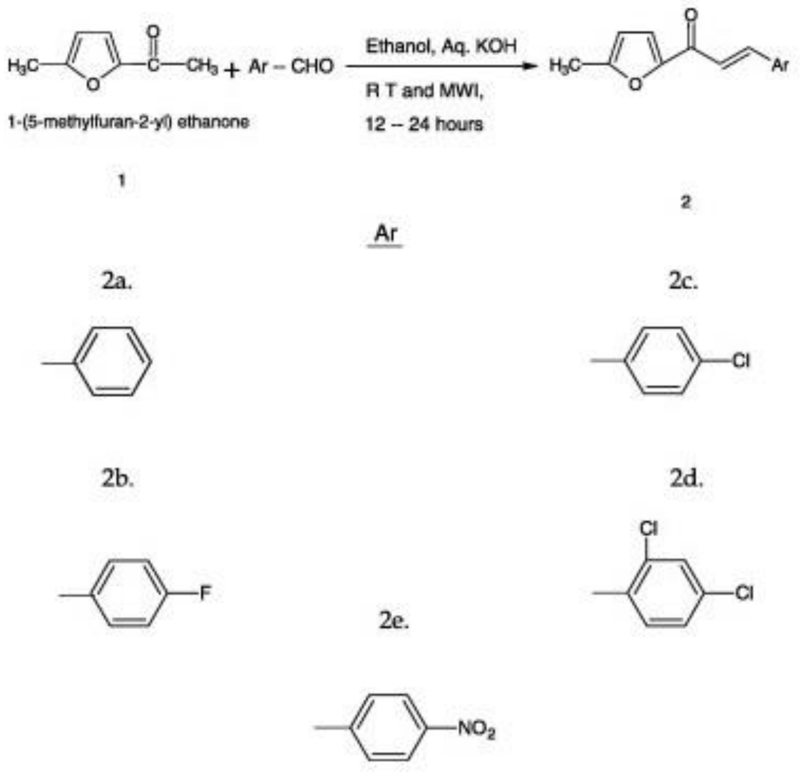

Figure 2.3 Synthetic scheme of chalcone derivatives using conventional and microwave irradiation methods (Ahmad *et al.*, 2016)

2.3 Synthesis of Sonogashira Cross-Coupling

Sonogashira cross-coupling reactions involve reacting terminal acetylenes and aryl or alkenyl halides in the presence of palladium (Pd) and copper(I) catalysts with base under 24 hours reflux condition (Perez, 2021). The final mixture is filtered and proceed for column chromatography to obtain the purity of the product. In this research, the final product was used as precursor materials to react with aldehyde in the Schiff-base reaction to obtain the final product. There are several reported studies were prepared using Sonogashira cross-coupling reaction with different moieties and solvents (Maragani *et al.*, 2012, Daud *et al.*, 2014, Khairul *et al.*, 2017, Lim *et al.*, 2018, Zaini, Khairul, *et al.*, 2020b, Mohammed, Khairul, Rahamathullah, Razak, *et al.*, 2022, Daud *et al.*, 2022) as presented in Figure 2.4, 2.5, 2.6 and 2.7. Nevertheless, several recent research have reported on copper-free Sonogashira cross-coupling reactions which provide advantages in adopting green chemistry principles and making the reactions more economically feasible (Gazvoda *et al.*, 2018, Kanwal *et al.*, 2020, Mohajer *et al.*, 2021).

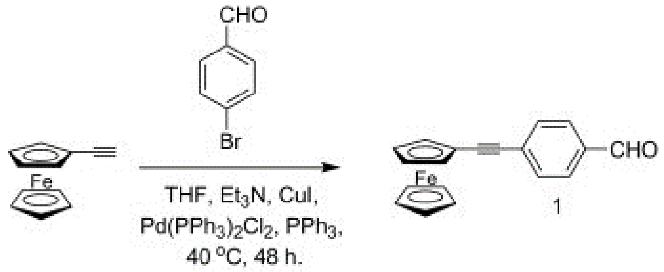

Figure 2.4 Synthesis of 4-(2-ferrocenyl-ethynyl)-benzaldehyde (Maragani *et al.*, 2012)

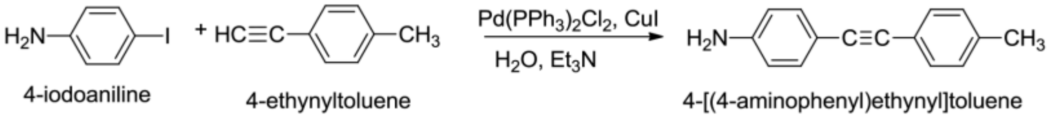

Figure 2.5 Synthesis of 4-[(4-aminophenyl)ethynyl]toluene using triethylamine solvent (Daud *et al.*, 2014)

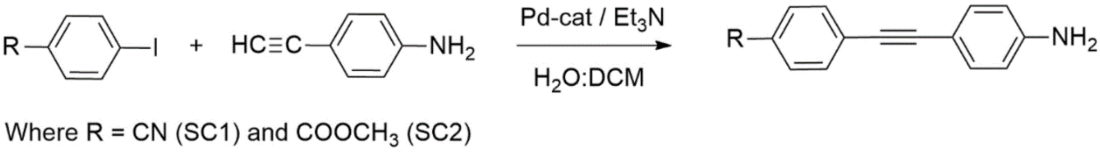

Figure 2.6 Synthesis of 4-[(4-aminophenyl)ethynyl derivatives using dichloromethane solvent (Daud *et al.,* 2022)

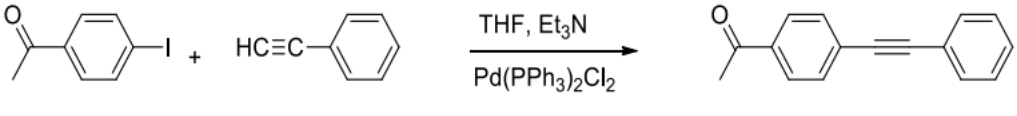

Figure 2.7 Synthesis of 4-[(4-aminophenyl)ethynyl derivatives using tetrahydrofuran and triethylamine solvents (Mohammed, Khairul, Rahamathullah, Razak, *et al.*, 2022)

2.4 Synthesis of Schiff-Base

Another type of organic compounds that posesses a π-conjugated motifs materials is Schiff-base compounds. The Schiff-base was first discovered by Hugo Schiff in 1864 and considered as a subclass of imines which consisting of functional group carbon-nitrogen double bond (C=N) in the structure (Fabbrizzi, 2020). Normally, the reaction involved approximately 24 hours condensation of an aldehyde or ketone with a primary amine in ethanol solvent as shown in Figure 2.8. The synthesis of Schiff-base compounds consist of various methods such as eco-friendly conventional and microwave irradiation methods (Yang & Sun, 2006, Mishra & Jain, 2014, Ali *et al.*, 2020, Mermer & Boulebd, 2023).

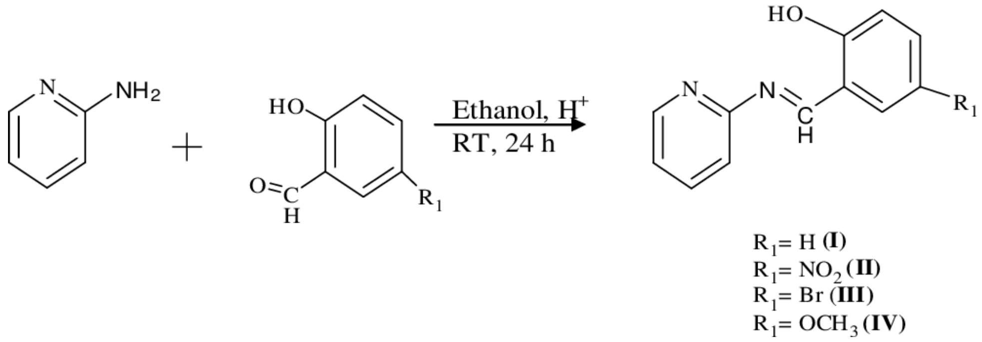

Figure 2.8 General scheme for formation of Schiff-base derivatives (Dueke-Eze *et al.*, 2011)

The reported studies by Lim *et al*. prevail that the Schiff-base compounds were successfully synthesized by condensation reaction to form a tail-free nematogen of ethynylated Schiff-base (ESB-NO_2) and possesses excellent photophysical properties for solution-processable OLED (Lim *et al.*, 2018). Figure 2.9 shows the synthetic pathway mechanism of the formation of ethynylated Schiff-base (ESB-NO_2).

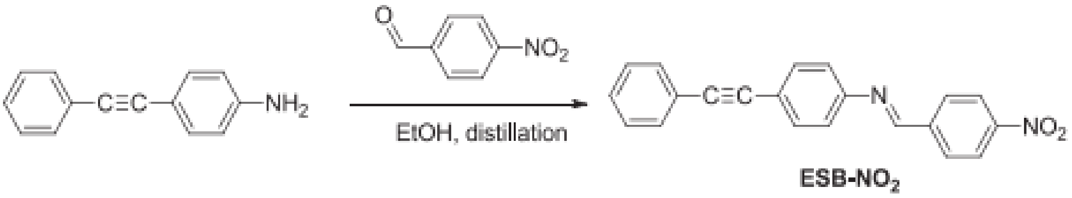

Figure 2.9 Mechanism formation of ethynylated Schiff-base (ESB-NO_2) (Lim *et al.*, 2018)

2.5 Single Crystal X-Ray Diffraction Studies

X-ray diffraction studies is one of important analysis to investigate the structure-property of the molecule as potential use of organic light emitting materials. In this study, chalcone and Schiff-base were chosen as two promising compound due to their distinctive features of π-conjugation system. Each compound has a specific molecular structure and configuration. The chalcone molecular structures exist as either *trans* (*E*) or *cis* (*Z*) isomers having two aromatic rings connected by a three-carbon α,β-unsaturated carbonyl system as shown in Figure 2.10. In most cases, the configuration of chalcone with *E* isomer is more stable than *Z* isomer. The unstable of *Z* isomer is due to the existence of strong steric effect occurred between carbonyl group and the aromatic ring B (Aksöz & Ertan, 2011).

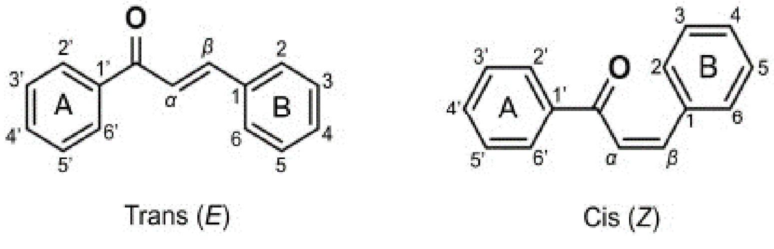

Figure 2.10 Chalcone scaffold structural and numerical representations (Gomes *et al.*, 2017)

Meanwhile, the carbonyl bond (C=O) adopts *s-cis* or *s-trans* conformation with respect to the vinylenic double bond due to free rotation along the single bond between C-carbonylic and C-α (Nowakowska, 2005). Typically, the conformer *s-cis* chalcone giving almost a fully planar rather than *s-trans* chalcone, which provides increased in conjugation, fluorescent and high intramolecular charge transfer (ICT) to the entire molecule. One related reported studies by (Yu *et al.*, 2017) were found that most of the synthesized chalcones containing pyrene and anthracene substituted donor groups formed different types of *s-cis* configurations (Figure 2.11). Additionally, the anthracenyl chalcones which originated from the anthracenyl-ketone moiety exhibit *s-trans* (*E*) configuration in their molecular structure (Figure 2.12). However, fewer studies reported on *s-trans* (*Z*) for bulky subsituents chalcone. Furthermore, the existence of intermolecular hydrogen bond C—H···F in the molecular structure of (*E*)-1-(anthracen-9-yl)-3-(2-chloro-6-fluorophenyl)-prop-2-en-1-one (Abdullah *et al.*, 2016) locked the enone moiety in *s-trans* (*E*) configuration thus generating an *S*(6) ring motif (Figure 2.13).

The Schiff-base molecular structure comprises of a double bond linking carbon and nitrogen atoms (C=N). Chemically, this compound is known as imines or azomethine functional group. Three of the reported studies about Schiff-base compounds (Khalaji *et al.*, 2015, Cinar *et al.*, 2020b, Dege *et al.*, 2021) exhibited the intramolecular interactions O—H···N where all of the structures forming a *S*(6) ring motif between the *ortho*-position of hydroxy group substituent to the imine group of Schiff-base (Figure 2.14). Schiff-base ligands are now actively being researched due to their ease of synthesis by condensation of designated aldehydes and imines. Previous study carried out by (Lin *et al.*, 2014a) has successfuly formed a crystal structure of novel ferrocenyl Schiff-bases with phenylethynyl moiety (Figure 2.15).

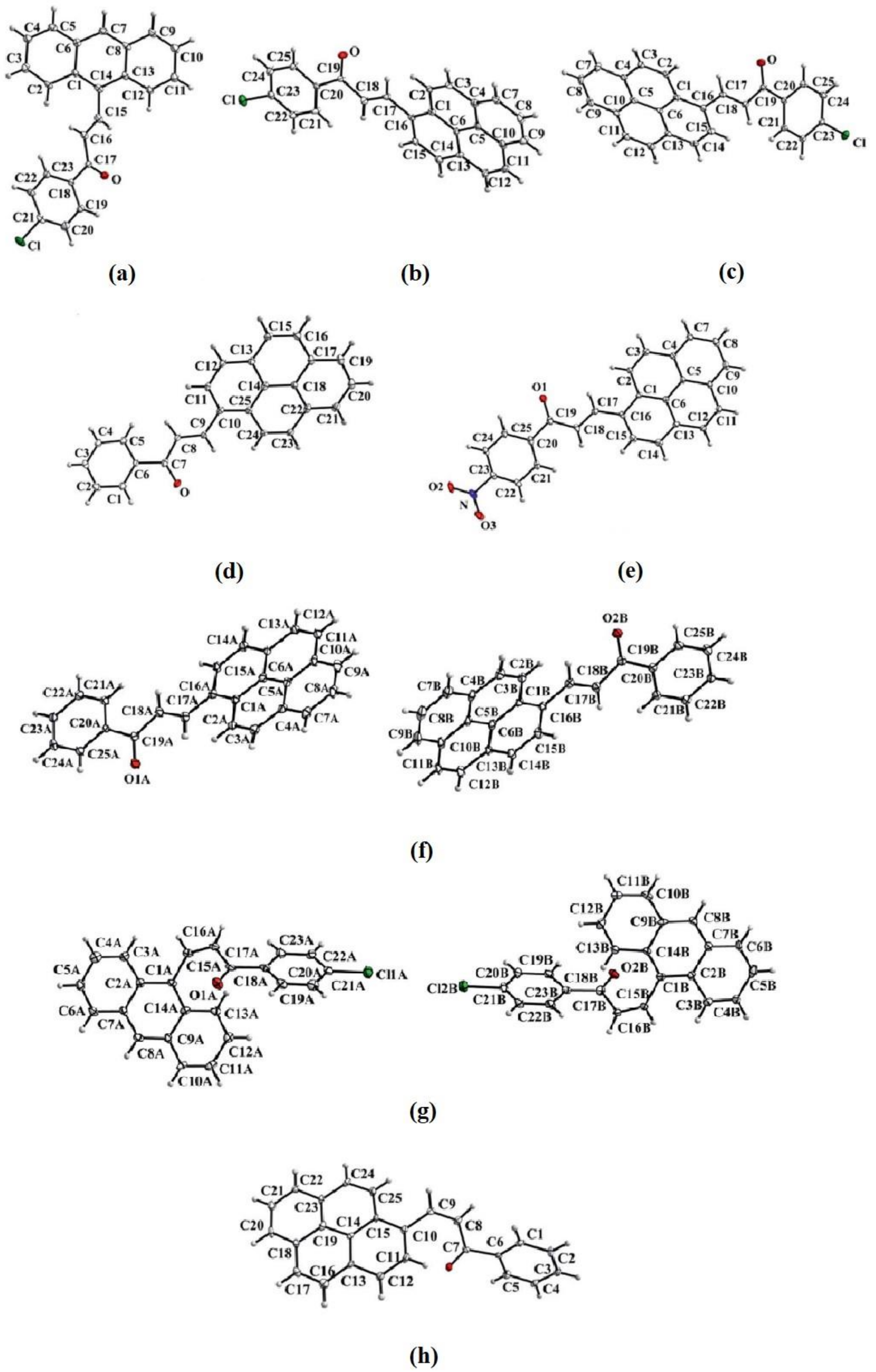

Figure 2.11 Chalcone structures of (a), (b), (c), (d), (e) and (f) featuring *s-cis* (*E*) whereas (g) and (h) featuring *s-cis* (*Z*) configurations (Yu *et al.*, 2017)

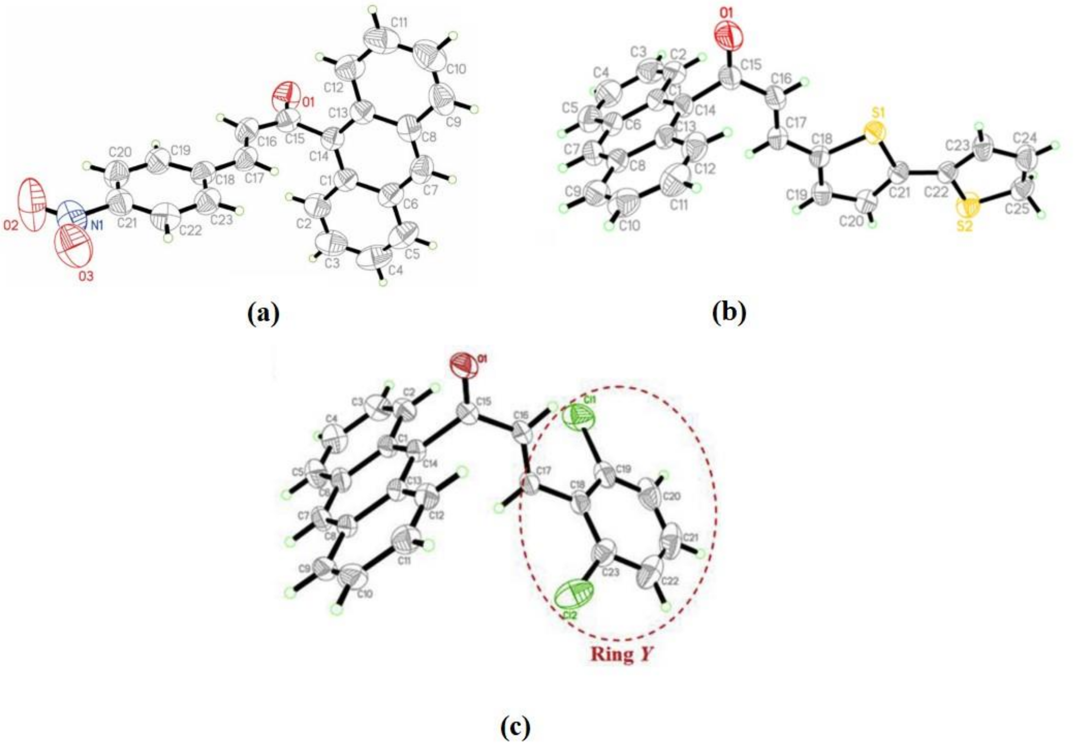

Figure 2.12 Chalcone structures of (a) (Patil *et al.*, 2019), (b) (Zainuri *et al.*, 2021) and (c) (Zainuri, Razak, *et al.*, 2018a) adopt *s-trans* (*E*) configurations

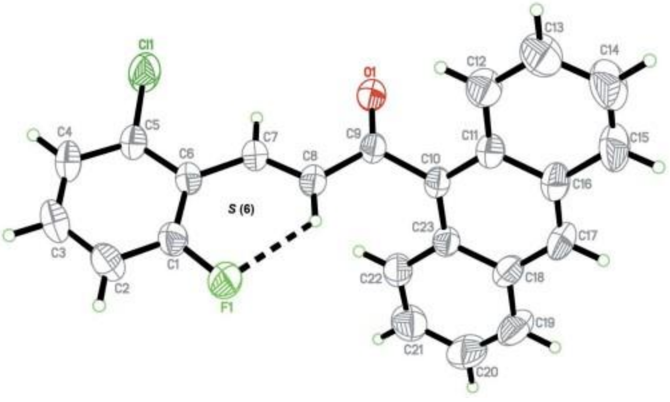

Figure 2.13 Structure of (*E*)-1-(anthracen-9-yl)-3-(2-chloro-6-fluorophenyl)-prop-2-en-1-one (Abdullah *et al.*, 2016)

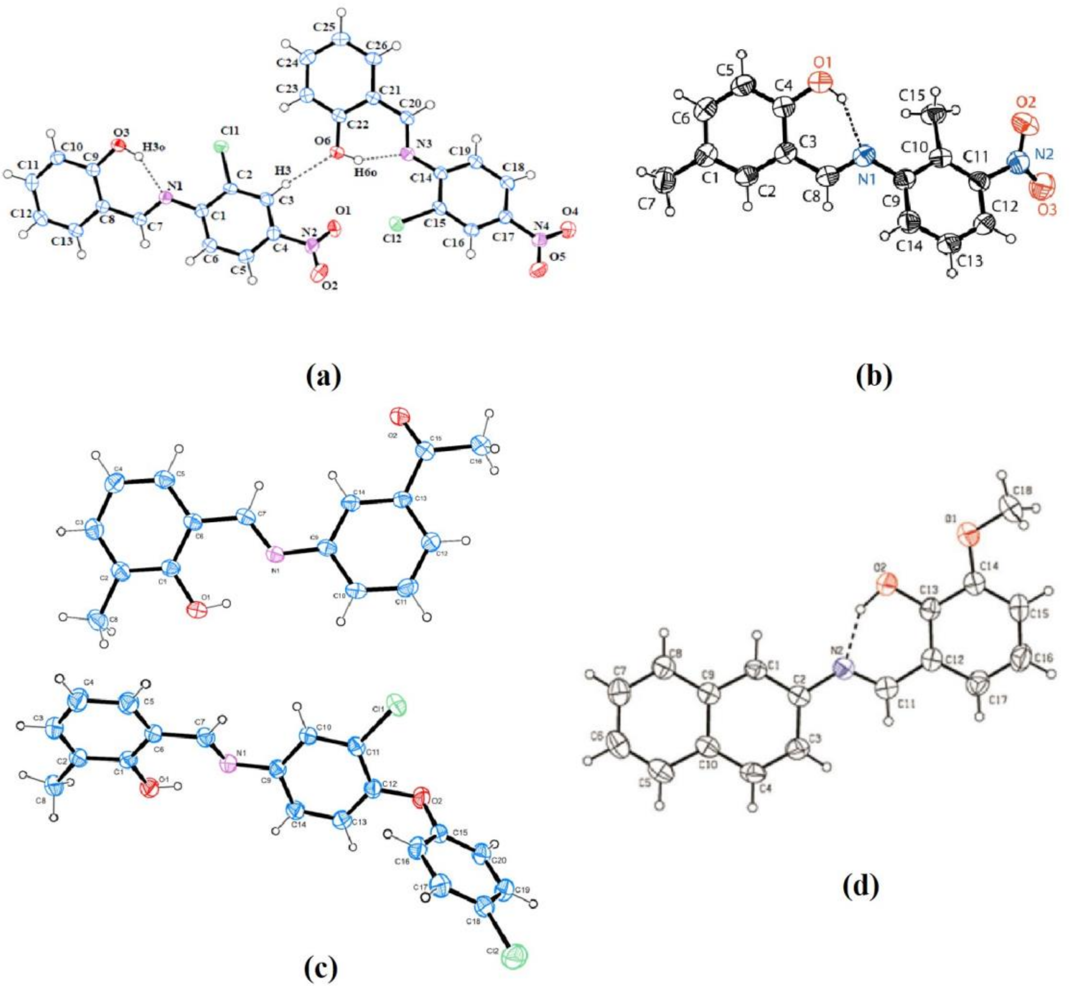

Figure 2.14 The molecular structure of Schiff-base derivatives forming *S*(6) six-membered ring *via* intramolecular O—H⋯N interactions observed in related imine-phenol Schiff-bases (a) (Khalaji *et al.*, 2015), (b) (Cinar *et al.*, 2020b), (c) (Dege *et al.*, 2021) and (d) (Karthikeyan *et al.*, 2020)

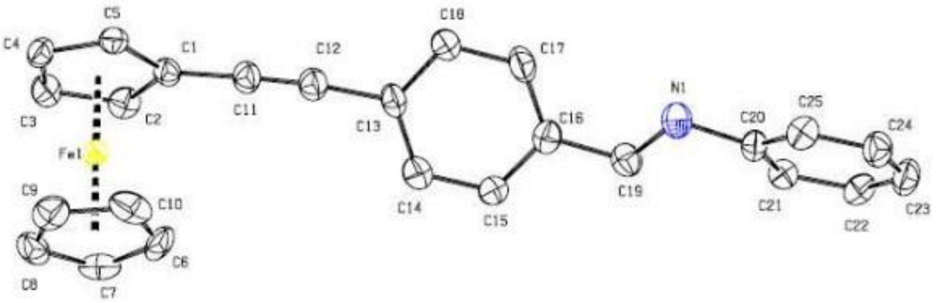

Figure 2.15 The structure of ferrocenyl Schiff-base (Lin *et al.*, 2014b)

The different types of crystal packing bring a significant impact on the fluorescence behaviour of the molecules which primarily caused by intermolecular interactions and molecular orientation. The existence of hydrogen bonds, halogen bonds and π-π interactions can help stabilizes the crystal structure, facilitate an efficient intermolecular charge transfer between the molecules thus offering a small HOMO LUMO energy gap (Ashfaq *et al.*, 2022, Gilday *et al.*, 2015). Moreover, the head-to-tail molecular structure orientation due to intermolecular interaction and face-to-face stacking confirmation as a result of π-π interaction lead to a faster charge transfer (Figure 2.16) (Alsaee *et al.*, 2023). Another study published by (D'Aléo *et al.*, 2015) found that the compound comprising pyrene with a methoxy group on the napthalene-group assembled to a face-to-face molecular arrangement, resulting in an increase in emission efficiency in the condensed phase. Meanwhile, the edge-to-face orientation of the crystal structure indicates the presence of H-like aggregates which quenches the photoluminescence properties (Figure 2.17). In addition, the crystals with the smallest dihedral angles and the least torsion extent possess the longest emission peak wavelengths, which correlate to red fluorescence (Yu *et al.*, 2017).

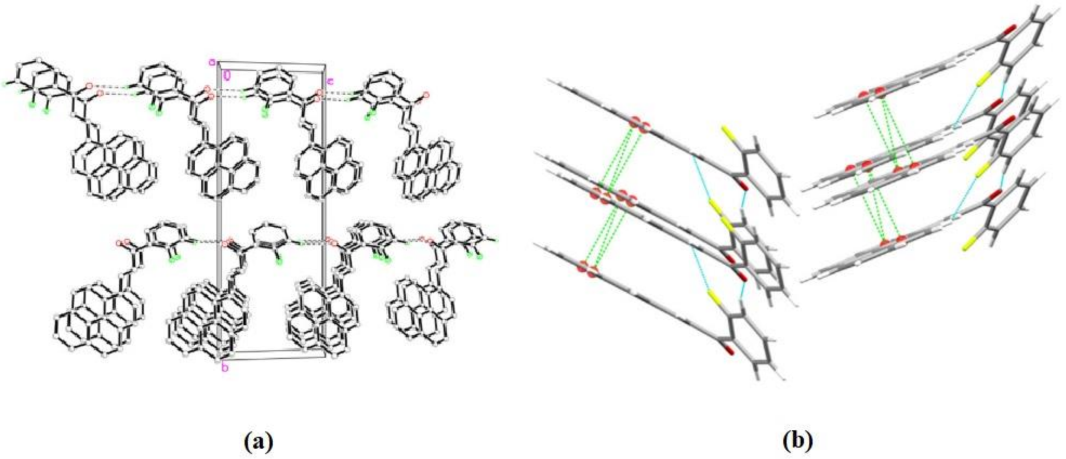

Figure 2.16 The conjugated pyrene donor and halogen acceptor substituent are connected through (a) head-to-tail intermolecular C—H···O and C—H···F bonds, (b) π-π stacking interactions (Alsaee *et al.*, 2023)

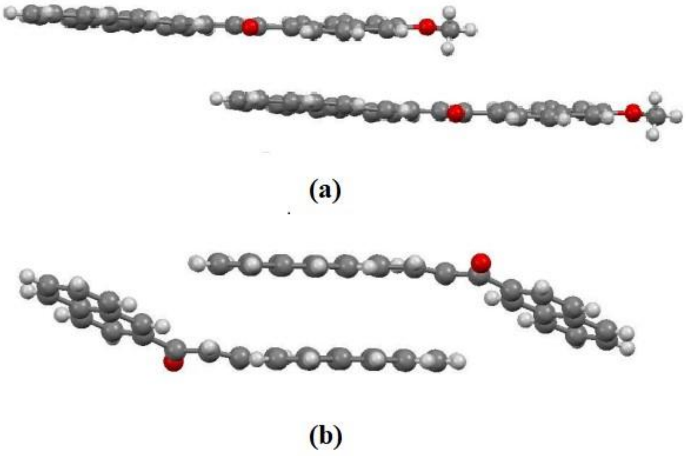

Figure 2.17 Crystal packing diagram depicted π-π stacking interactions assembled in (a) head-to-head (b) edge-to-face orientation (D'Aléo *et al.*, 2015)

2.6 Fourier Transform Infrared (FTIR) Studies

FTIR is a method that is very helpful for confirming the presence of functional groups in a compound. Due to its wide spectrum of functional groups, FTIR is primarily effective for identifying organic molecular functional groups (Aksöz & Ertan, 2012). The frequency ranges are measured as wavenumbers typically over the range 4000 – 400 cm^{-1}. In the FTIR spectrum, three typical significant functional groups of interest for chalcone derivatives were identified as stretching vibrations: *v*(C−H), *v*(C=O), and *v*(C=C) shown in Figure 2.18.

Band assignment	Experimental vibrational wavenumber (cm^{-1})	Literature report
ν(C−H)	3051, 3049	(Zainuri *et al.*, 2021)
	3038	(Alsaee, Bakar, *et al.*, 2022)
	2985.60	(Prabhu *et al.*, 2020a)
	3261, 3102	(Patil *et al.*, 2019)
	3110.2, 3071.7	(Parol *et al.*, 2020a)
	3100 – 2991	(Alsaee *et al.*, 2023)
	3092, 3054	(Zainuri, Abdullah, *et al.*, 2018)
ν(C=O)	1655, 1625	(Zainuri *et al.*, 2021)
	1670	(Alsaee, Bakar, *et al.*, 2022)
	1670	(Yu *et al.*, 2017)
	1658.67	(Prabhu *et al.*, 2020a)
	1642	(Patil *et al.*, 2019)
	1661.9	(Parol *et al.*, 2020a)
	1678 – 1576	(Alsaee *et al.*, 2023)
	1638, 1652	(Zainuri, Abdullah, *et al.*, 2018)
ν(C=C) (aromatic)	1572, 1592	(Zainuri *et al.*, 2021)
	1584, 1490	(Alsaee, Bakar, *et al.*, 2022)
	1593	(Patil *et al.*, 2019)
	1531.6, 1422.3	(Parol *et al.*, 2020a)
ν(C=C) (α, β-unsaturated ketone)	1584	(Alsaee, Bakar, *et al.*, 2022)
	1520	(Yu *et al.*, 2017)
	1577.66	(Prabhu *et al.*, 2020a)
	1801	(Patil *et al.*, 2019)
	1597.9	(Parol *et al.*, 2020a)
	1599	(Alsaee *et al.*, 2023)
	1616, 1629	(Zainuri, Abdullah, *et al.*, 2018)

Table 2.1 The band assignments with their several vibrational wavenumbers for chalcone compounds

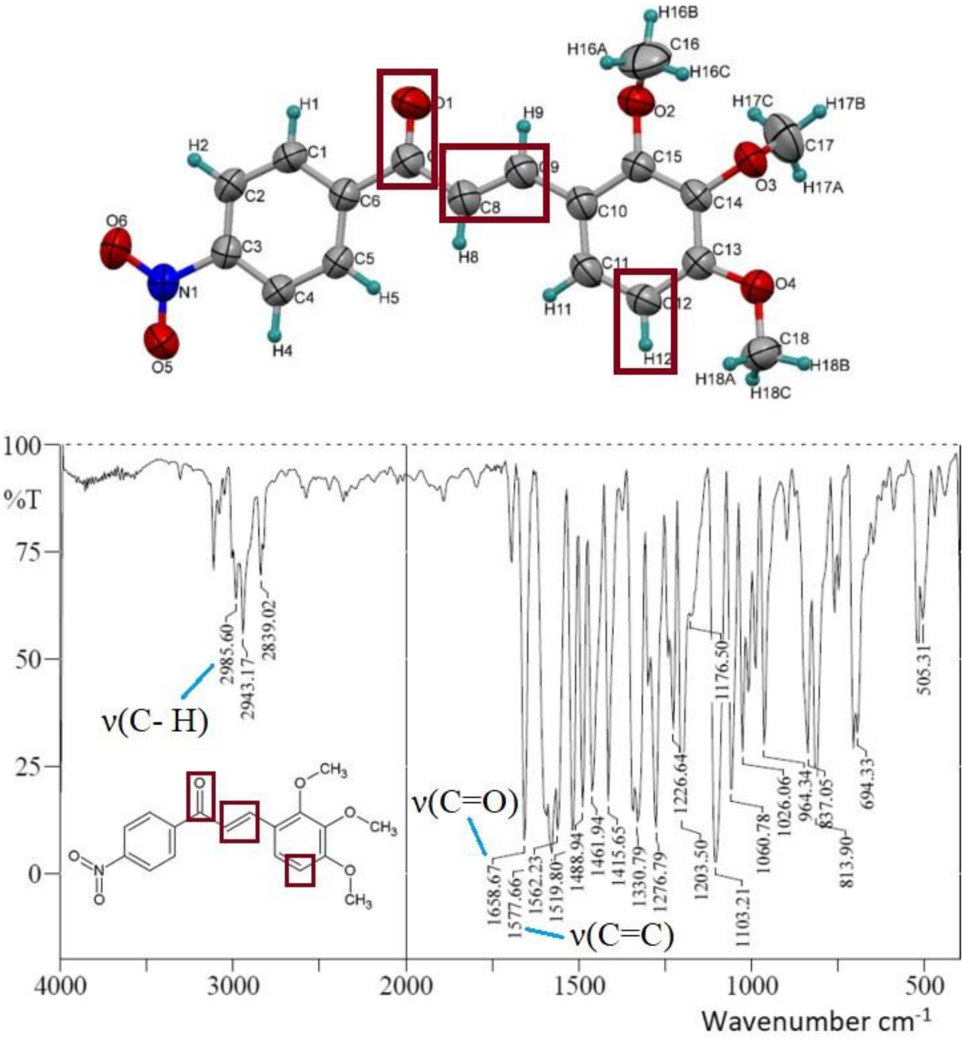

Figure 2.18 The scaffold chalcone compound of (2*E*)-1-(4-nitrophenyl)-3-(2,3,4-trimethoxyphenyl)prop-2-en-1-one (NPTMP) featuring three distinct functional groups with its spectrum (Prabhu *et al.*, 2020a)

The C−H stretching mode is occured above 3000 cm^{-1} which exhibited as a multiplicity of weak to moderate bands compared to the aliphatic C−H stretch (Coates, 2000). From the previous reported C–H stretching frequencies, the wavenumber appears to be in the range of 2986 – 3261 cm^{-1} as shown in Table 2.1. The C–H in-plane bending vibrations usually occur in the region of 1300 – 1000 cm^{-1} while the C–H out-of-plane bending modes generally occur in the region of 1000 – 710 cm^{-1} (Varsányi, 2012).

The wavenumber of the C=O stretch attributed to a carbonyl group is primarily affected by the bond strength, which is determined by inductive, conjugative, steric, and lone pair of electron on oxygen (Panicker *et al.*, 2015). The carbonyl stretching C=O vibration was identified by strong band due to the considerable dipole moment caused by the large partial positive and negative charge of the carbonyl carbon and oxygen, respectively (Zainuri *et al.*, 2021). Most of the reported studies found that the wavenumber of C=O stretching vibrations were observed at range of 1600 cm^{-1} when they conjugate with the carbonyl group since it is highly polar due to the double bond (Table 2.1). The position of the C=O vibration is extremely sensitive to several factors such as physical state, electronic effects by substituents and ring strains.

Generally, the C=C stretching mode is expected in the region of 1667 – 1640 m^{-1} (Silverstein & Bassler, 1962). This C=C mode can be observed by strong doublet band in FT-IR spectrum owing to the amount of charge transfer between the donor and acceptor groups (Ravindra *et al.*, 2008). Study showed by (Parol *et al.*, 2020a), the peak appeared at 1597.9 cm^{-1} demonstrates C=C is conjugated with the C=O group. Likewise (Socrates, 1995) also reported that the C=C stretching mode is expected around 1600 cm^{-1} when conjugated with C=O carbonyl.

Meanwhile, the ethynylated Schiff-base compound comprises of several significant functional groups of interest in the molecular structure backbone. They include *v*(C−H), *v*(C=N), and *v*(C≡C) stretching bands as shown in Figure 2.19. Table 2.2 shows the vibrational wavenumbers of each bands for several reported studies.