

Synthesis of Symmetrical and Unsymmetrical Ferrocenyl Substituted Diketopyrrolopyrroles

M.Sc. Thesis

By

Charu Popli



**DISCIPLINE OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY INDORE
JUNE-2017**

Synthesis of Symmetrical and Unsymmetrical Ferrocenyl Substituted Diketopyrrolopyrroles

A THESIS

Submitted in partial

fulfillment of the requirements for the award of the degree

of

Master of Science

by

Charu Popli



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INDIAN INSTITUTE OF TECHNOLOGY INDORE
JUNE-2017



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Synthesis of Symmetrical and Unsymmetrical Ferrocenyl Substituted Diketopyrrolopyrroles** in the partial fulfillment of the requirements for the award of the degree of **Master of Science** and submitted in the **Discipline of Chemistry, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2015 to June 2017 under the supervision of Dr. Rajneesh Misra, Associate Professor, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Charu Popli

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

Dr. Rajneesh Misra

Charu Popli has successfully given his/her M.Sc. Oral Examination held on.....

Signature of Supervisor of MSc thesis

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Date:/....../....

Date:/....../....

Signature of PSPC Member #1

Signature of PSPC Member #2

Date:/....../....

Date:/....../....

Dedicated to my Parents.....

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ABSTRACT

Ferrocenyl-substituted diketopyrrolopyrroles (DPPs) with the symmetrical π -bridged donor–acceptor (D– π –A) frameworks D'– π –D–A–D– π –D' as well as unsymmetrical D–A–D– π –D' frameworks were designed and synthesized by a Pd-catalyzed Sonogashira cross-coupling reaction. The photophysical, computational, and electrochemical properties were also investigated and show substantial donor–acceptor interactions between the ferrocene and DPP moieties. DFT studies reveal that HOMO-LUMO gap decreases on incorporation of ferrocenyl unit to DPP. The symmetrical ferrocenyl-DPPs have more thermal stability than the unsymmetrical derivatives.

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ACRONYMS

OLEDs	Organic light emitting diodes
OPVs	Organic photovoltaics
OFETs	Organic field-effect transistors
D-π-A	π - bridged donor acceptor
DPP	Diketopyrrolopyrrole
DMSO	Dimethyl sulfoxide
D-A	Donor-Acceptor
DMF	<i>N, N</i> -Dimethyl formamide
LR	Lawesson reagent
TMS	Tetramethylsilane
NMR	Nuclear magnetic resonance
SCE	Saturated calomel electrode
PdCl₂(PPh₃)₂	Dichlorobis(triphenylphosphine) palladium(II)
PPh₃	Tri-phenylphosphine
TCNE	Tetracyanoethylene
DCM	Dichloromethane
NBS	<i>N</i> -Bromosuccinimide
DFT	Density functional theory
TDDFT	Time-dependent density functional theory
HRMS	High Resolution Mass Spectroscopy
CDCl₃	Chloroform-d
CuI	Copper Iodide
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular orbital

NOMENCLATURE

π	pi
λ	Wavelength
δ	Chemical shift
nm	Nanometre
$^{\circ}\text{C}$	Degree Celsius
mmol	Millimole
mL	Millilitre
RT	Room temperature
eV	Electron Volt
V	Volt

CHAPTER ONE

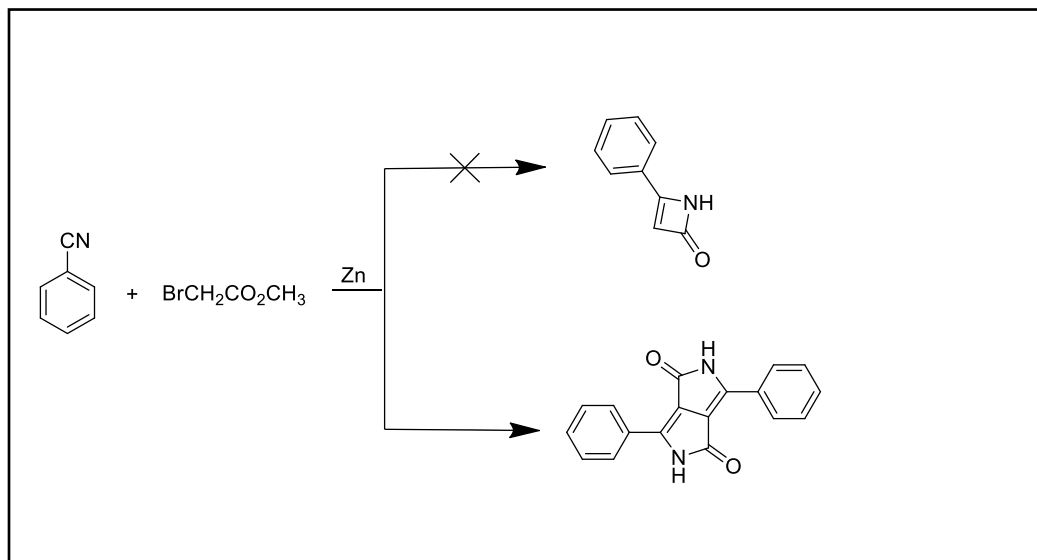
1. INTRODUCTION

1.1. General Introduction

The growing energy demand throughout the world has given great attention towards exploring the clean and renewable energy sources. Production of energy from sunlight using photovoltaic technology is one of the most important long-term solution. Donor–acceptor molecular architectures with extended π -conjugation are of significant interest due to their wide variety of applications as organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), two photon absorption and organic field-effect transistors (OFETs) [1]. The broad absorption bands in the visible region and low HOMO-LUMO gap values in small organic molecules make them potential candidate for optoelectronics [2].

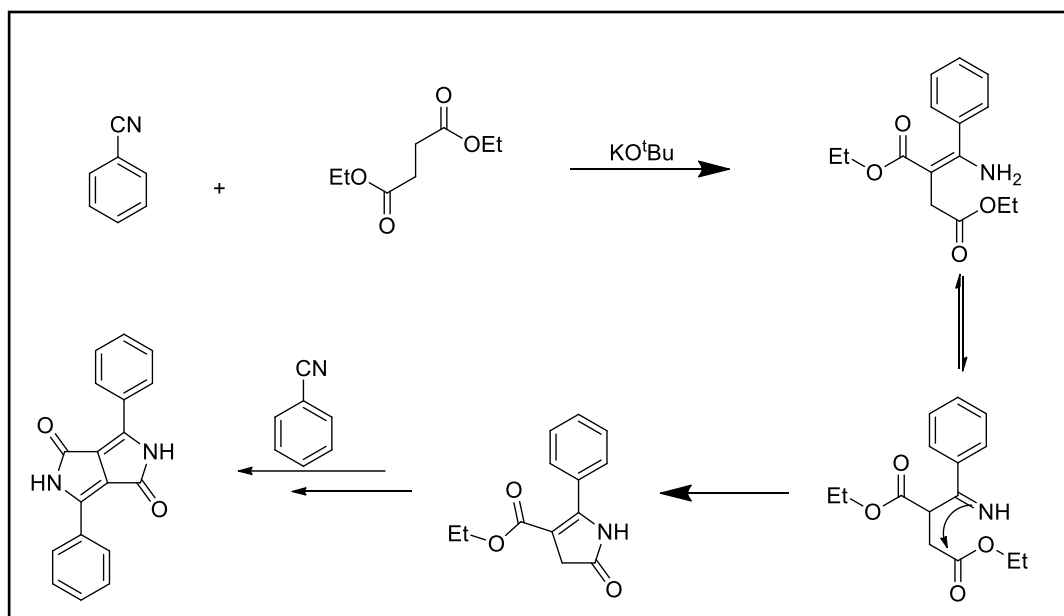
Our group is involved in the development of donor–acceptor molecules for optoelectronic applications. The diketopyrrolopyrrole (DPP) is a widely recognized as an acceptor due to its strong electron-withdrawing nature [3].

Farnum, *et al.* in 1974, for the first time reported the synthesis of DPP (Scheme 1). The desired reaction was failed and accidentally the diphenyl DPP was formed in low yield (5-20%) [4].



Scheme 1. Preparation of **DPP** (Farnum, et al. 1974).

The first DPP pigment has been developed in 1986 and came to market for applications like paints, plastics, fibers and inks. After Farnum's synthesis there are several other reports for the synthesis of DPP came [5-7]. Succinic ester route is regarded as the best one from all the routes [5,6]. In this succinic ester is condensed by pseudo-Stobbe condensation reaction with an aromatic nitrile in the presence of strong base to get desired the DPP in a yield over 60% (Scheme 2). The formation of pyrrolinone esters from the initially formed enaminoesters is the key step of this mechanism, further it reacts with another benzonitrile under basic conditions and subsequent ring closure gives the desired product.



Scheme 2. Preparation of **DPP** via the succinic ester route.

There are number of publications found in literature on the synthesis of DPP from Morton and Riggs [8-10]. The synthesis of unsymmetrical DPP was also reported more recently [11,12]. Methods such as the microwave have also been reported for the synthesis of DPP [13].

The DPP is a bicyclic 8 π electron system contains two lactam units. Typical diphenyl-DPPs have melting points over 350 °C and low solubility in most of the organic solvents. They show an absorption in the visible region [5,14,15] and strong fluorescence between 500 and 600 nm [16].

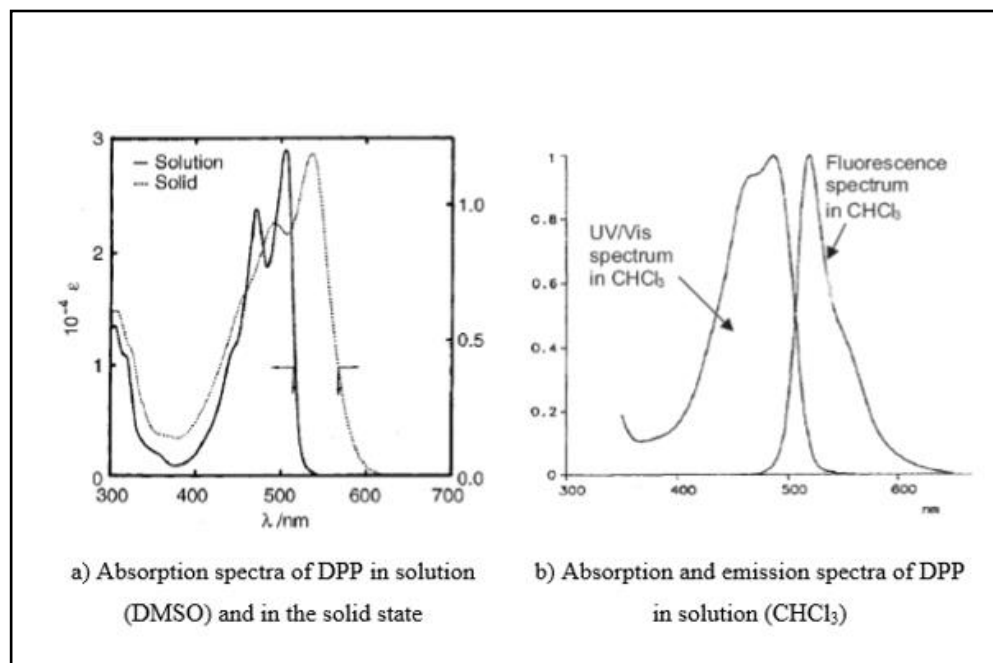


Figure 1. UV/vis absorption and photoluminescence spectra of diphenyl DPP.

The X-ray of diphenyl-DPP shows that the whole molecule is almost in one plane [15, 17-22]. The phenyl rings of DPP are twisted out of the plane by 7°. The intermolecular hydrogen bonding between neighboring lactam NH and carbonyl units dominates the structure of DPP in the solid state which determines the molecular packing. The π - π interaction between the layers of DPPs is then understandable. The optimum interlayer distance between the planes is 3.36 Å and the distance between phenyl ring planes is 3.54 Å is short enough for the significant π - π interaction.

DPP has unique structure because of its aromatic conjugated structure enhances the π - π stacking and improves charge transport abilities. The substitution of fused aromatic DPP with appropriate electron donor in the conjugated backbone gives strong interaction in the solid through D-A and π - π interactions result in highly ordered structure. The energy levels of conjugated DPP adjusted to produce p-type, n-type, or ambipolar organic semiconductors depends on the type of moieties incorporated. DPP exhibit high thermal stability which is required for fabricating stable electronic devices. The DPP based small molecules have been widely used for organic

photovoltaics because of their excellent light absorbing and charge transporting ability.

There are many reports found in literature on the applications of DPP-based materials for example OLEDs, chemical sensors and memory devices.

The thiophene flanked DPP derivatives have been widely used due to their easy synthesis, high performance, and better D-A interactions. The furan based DPPs have emerged as versatile semiconducting materials with numerous applications in various polymer optoelectronics devices.

1.2. Polymers and semiconducting materials based on DPP

The generic use of DPP polymers as organic semiconductors was first patented by Turbiez *et al.* in 2008 [23] and high mobility organic field effect transistors have been published in the same year [24]. Also, the first use of PDPPs in solar cells was demonstrated in 2008 by Wienk *et al* [25].

Beyond PDPPs, also defined low molecular weight compounds based on DPP, hereafter referred to as small molecules, were used as organic semiconductors, first reported in 2008 by the group of Thuc-Quyen Nguyen [26] and at the same time applied as donor materials in solar cells [27]. In 2009 this group demonstrated DPP based small molecule solar cells with nanoscale phase separation and high photovoltaic efficiencies with a report counting more than 500 citations, being the most cited DPP paper upto date [28].

DPPs have gained enormous interest in the design of semiconducting organic materials due to their extended absorption range [29], the excellent stability, their remarkable aggregation behavior, [30] their superior performance in transistors [31-33], integrated circuits [34] and solar cells [35]. Over the past few years the performance boundaries of organic semiconductors were pushed over several orders of magnitude, not without

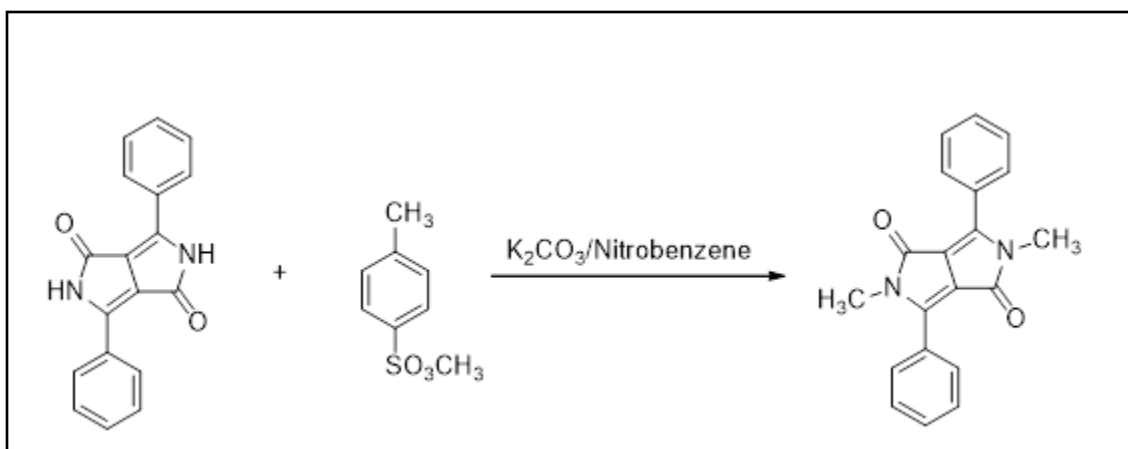
the aid of DPPs. Charge carrier mobilities in organic field effect transistors for example have improved from about $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in 2008 [36] to 12-18 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for hole transport [37,38] and over 6 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for electron transport [39].

Likewise, organic solar cell efficiencies have improved greatly over the last years and low molecular weight DPP compounds as well as DPP polymers have contributed significantly to this success [40,41]. The careful optimization of the catalytic system for the polycondensations allowed to obtain polymers with very high molecular weights that exhibited improved power conversion efficiency up to 8% in organic solar cells [42]. Furthermore, side chains were optimized on different DPP systems in order to tailor material properties towards high performance in organic electronics [43,44].

1.3. *N*-Alkylation of DPP

The following Scheme 3 is the example of *N*-methylation of diphenyl-DPP [45].

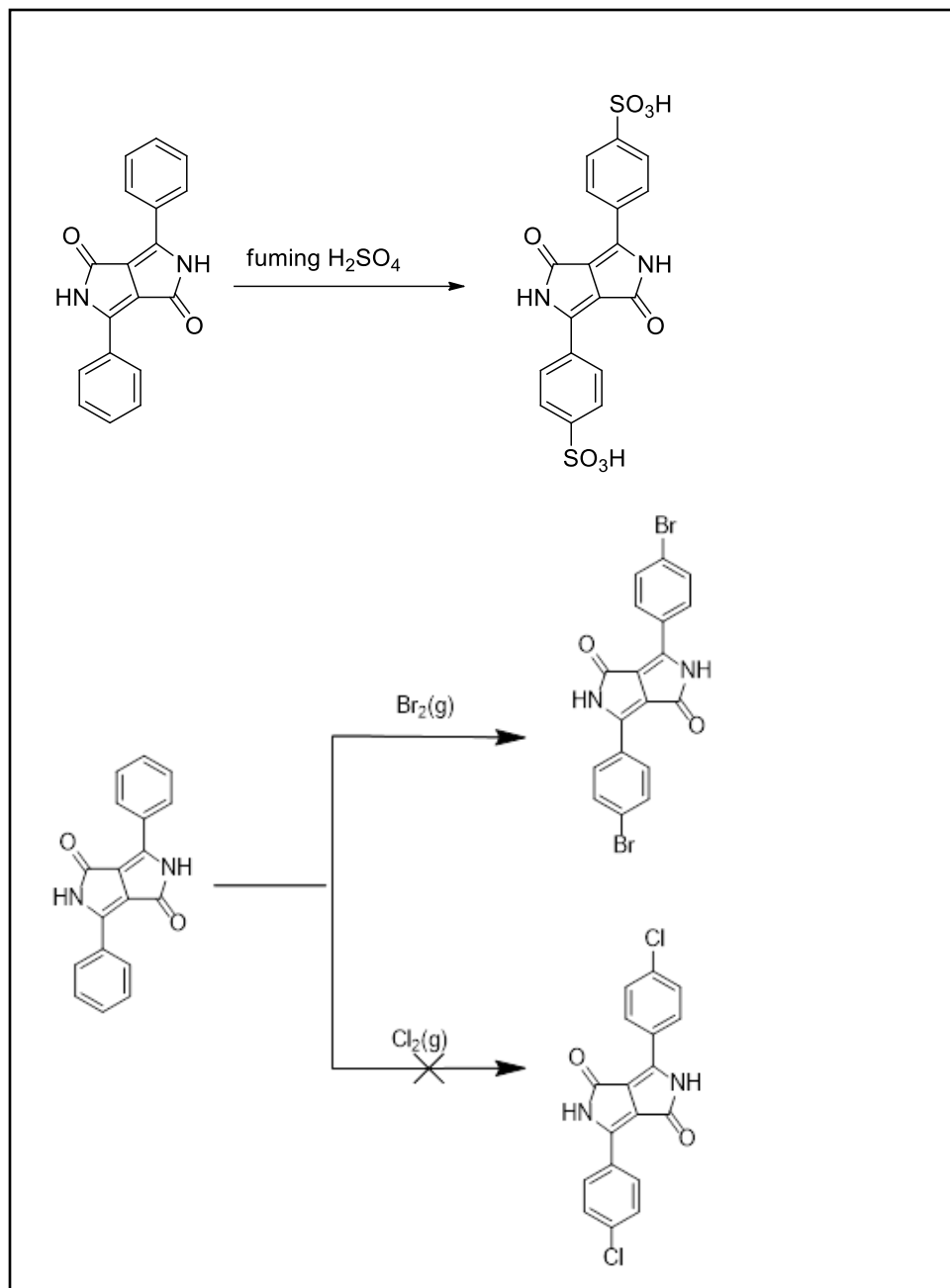
The *N*-alkylation of DPP results in the loss of intermolecular hydrogen bonding and solubilities are drastically raised. The *N*-substituted DPP based chromophores exhibit fluorescence in solution with a quantum yield up to 95%.



Scheme 3. The *N*-methylation of **DPP**.

1.4. Electrophilic aromatic substitution

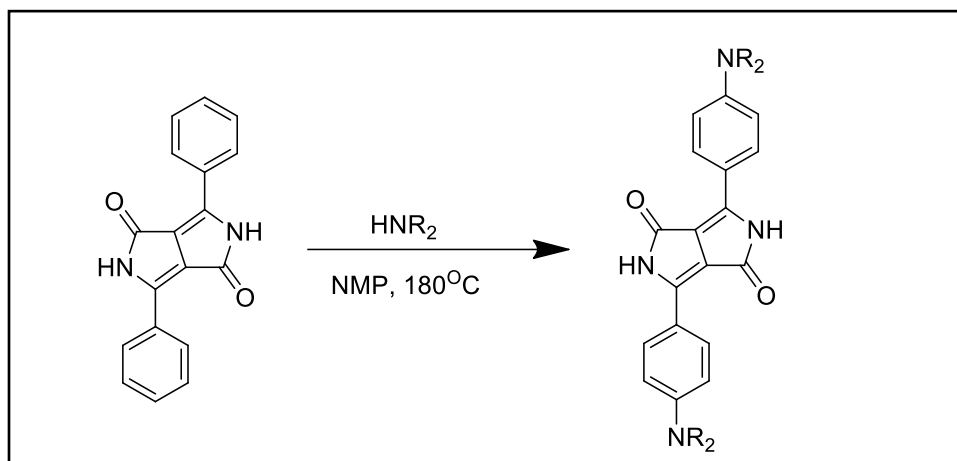
DPP shows ESR and get sulfonated by oleum to form the disulfonic acid and the salts of the disulfonic acid. The sulfonation gives rise to water soluble DPP. The 4,4'-dibromophenyl DPP can be synthesized from the reaction of diphenyl DPP with Br₂ gas but the chlorination does not happen which may be due to the reason that bromine is a better leaving group and nucleophile compared to chlorine [5].



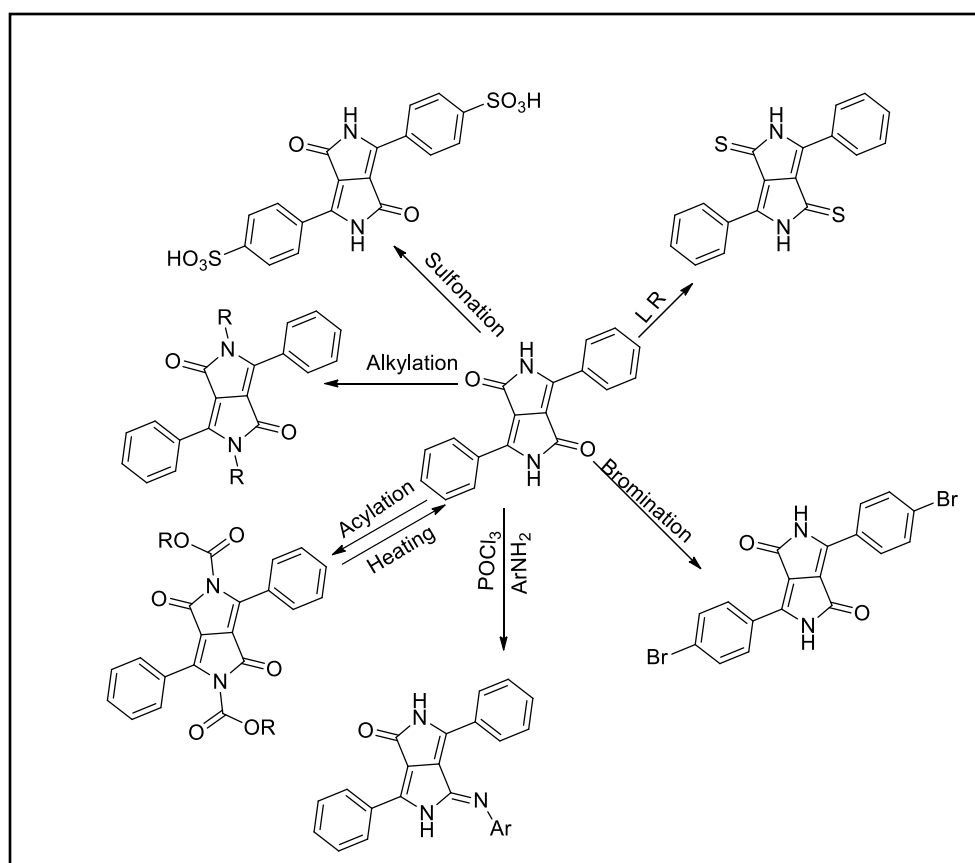
Scheme 4. Electrophilic aromatic substitution.

1.5. Nucleophilic aromatic substitution

At high temperature, nucleophilic aromatic substitution has been reported in literature (Scheme 5).



Scheme 5. Nucleophilic aromatic substitution.



Scheme 6. Reactions of **DPP**.

1.6. Aim of the Project

The substitution of the DPP with a donor will result in a strong D-A molecular system. The ferrocene group is a widely studied donor for various applications and its derivatives are thermally and photochemically stable. Ferrocene exhibit highly reversible redox active center with strong nonlinear optical (NLO) response.

Herein, we have synthesized symmetrical and unsymmetrical DPP systems of $D'-\pi-D-A-D-\pi-D'$ and $D-A-D-\pi-D'$ type in which the ferrocene and thiophene moieties act as donors and the DPP unit act as acceptor. The *N*-alkylated derivatives of DPP were used to improve the solubility in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran, and toluene. Here, our aim is to study the effect of ferrocene on the photophysical and electrochemical properties of DPP. The structural, optical and electrochemical properties of these DPP derivatives were explored.

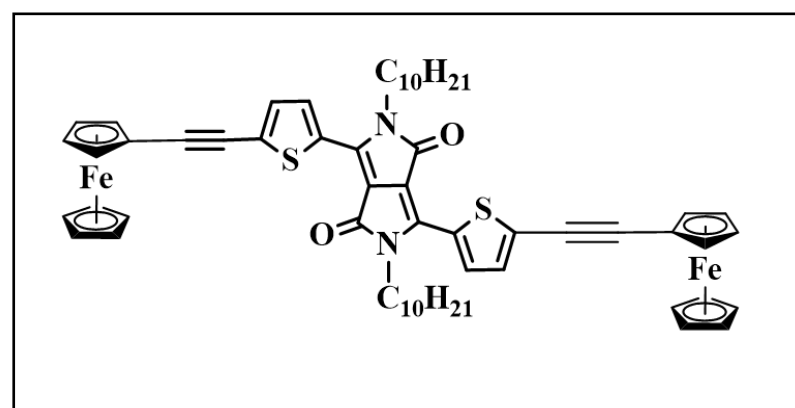
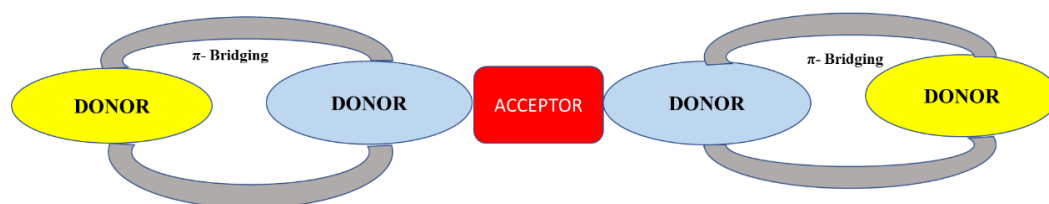
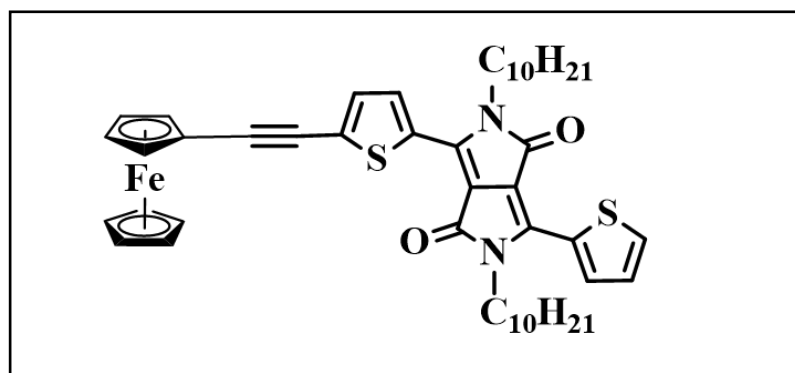
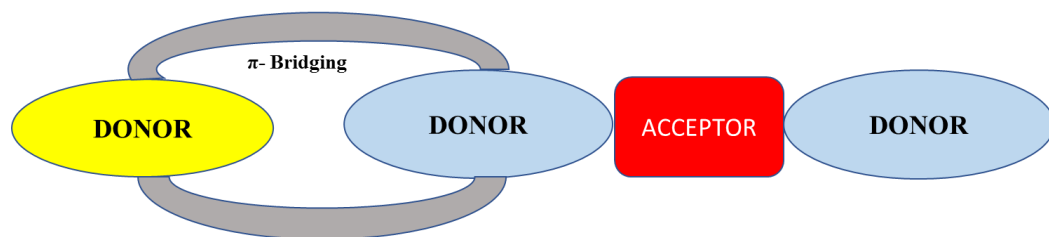


Figure 2. Bonding in DPP 5 and DPP 6.

CHAPTER TWO

2. EXPERIMENTAL SECTION

2.1. Materials and methods

Chemicals were used as received unless otherwise indicated. All the oxygen or moisture sensitive reactions were carried out under argon atmosphere. ^1H NMR spectra were recorded using a Brukar AV 400 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using residual protonated solvent as an internal standard $\{\text{CDCl}_3, 7.26 \text{ ppm}\}$. ^{13}C NMR spectra were recorded using a 100 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using the solvent as internal standard $\{\text{CDCl}_3, 77.0 \text{ ppm}\}$. The ^1H NMR splitting patterns have been described as “s, singlet; d, doublet; t, triplet and m, multiplet.” The HRMS spectra of the compounds were recorded by using Bruker Daltonics MicroTOF-Q II mass spectrometer using chloroform as solvent. UV-visible absorption spectra of all compounds were recorded on Parkin Almer UV/Vis spectrophotometer lambda 35 in chloroform solution. Cyclic voltamograms and differential pulse voltamograms were recorded on CH1620D electrochemical analyzer using Glassy carbon as working electrode, Pt wire as the counter electrode, and Saturated Calomel Electrode (SCE) as the reference electrode. The scan rate was 100mVs^{-1} for cyclic voltammetry. A solution of tetrabutylammonium hexafluorophosphate (TBAPF_6) in CHCl_3 (0.1M) was used as supporting electrolyte.

2.2. General procedure for synthesis of precursors

2.2.1. Synthesis of DPP 1

DPP 1 was prepared with 65% yield by using procedure which involves the reaction of 2-thiophenecarbonitrile with half equivalent of dimethyl succinate in presence of strong base sodium tert-butoxide in tert-butanol at 120 °C for 12 hours under argon atmosphere and worked up by methanol-hydrochloric acid (300mL methanol:15mL concentrated HCl), filtered on Buchner funnel and finally washed with methanol yielded maroon solid as shown in scheme 7.

2.2.2. Synthesis of DPP 2

To make soluble **DPP 1** it was reacted with excess amount of 1-bromodecane in presence of base K_2CO_3 in *N,N*-dimethylformamide (DMF) at 145 °C for 12 hours under argon atmosphere. The reaction contents were cooled to room temperature and solvent was removed under vacuo. The crude compound was purified by silica column chromatography (eluted with 50% dichloromethane in hexane) yielded 23% shiny crystalline solid (**DPP 2**) as shown in scheme 7. 1H NMR (400 MHz, $CDCl_3$): δ = 8.92 (m, 2 H), 7.62 (m, 2 H), 7.27 (d, 2 H), 4.06 (m, 4 H), 1.73 (m, 4 H), 1.30 (s, 24 H), 0.88 (m, 6 H) ppm. HRMS (ESI): calcd. for $C_{34}H_{48}N_2O_2S_2$ $[M]^+$ 581.3220; found 581.3343. UV/Vis (CH_2Cl_2): λ_{max} (ϵ , $M^{-1} cm^{-1}$) = 551 nm (4.6×10^4).

2.2.3. Synthesis of DPP 3 and DPP 4

DPP 2 was brominated with one equivalent and two equivalents of *N*-Bromosuccinimide to give monobrominated **DPP 3** and dibrominated **DPP 4** respectively. Bromination reaction was carried out at room temperature in dry chloroform and compounds were purified by the use of silica-column chromatography, eluted with 30–80% of dichloromethane in hexane yielded 90% of pure compounds as shown in scheme 8.

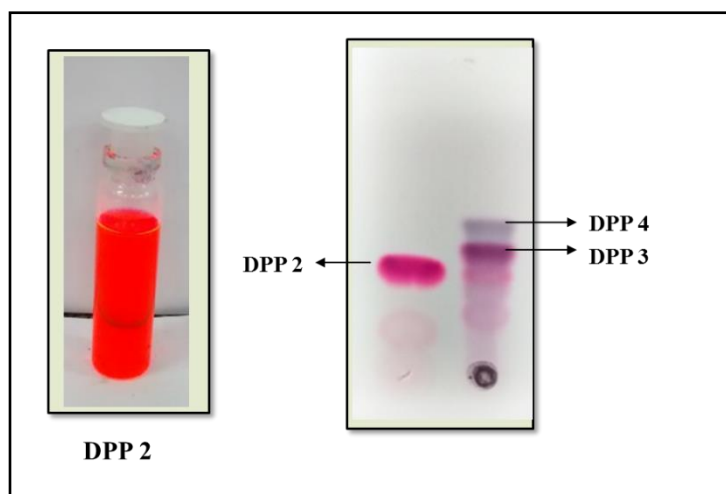


Figure 3. Photograph of **DPP 2** in DCM in day light and TLC showing separation between **DPPs 2, 3 and 4**.

2.2.4. Synthesis of DPP 5

In a 100mL round-bottom flask monobromo-substituted **DPP 3** (0.200 g, 0.30 mmol) and ethynylferrocene (0.064 g, 0.30 mmol) were dissolved in dry toluene (10 mL) and triethylamine (6 mL). The reaction mixture was degassed with argon for 10 min, and then $\text{PdCl}_2(\text{PPh}_3)_2$ (0.028 g, 0.030 mmol), PPh_3 (0.014 g, 0.060 mmol), and CuI (0.006 g, 0.030 mmol) were added (Scheme 9). The reaction mixture was stirred at 80 °C overnight. After completion of reaction, the mixture was cooled to room temperature. The solvents were removed in vacuo, and the product was purified by repeated chromatography on a silica column (hexane/dichloromethane, 3:1) to yield **DPP 5**. (0.191 g, 80 % yield); m.p. 92 °C. ^1H NMR (400 MHz,

CDCl₃): δ = 8.94 (d, J = 4 Hz, 1 H), 8.89 (d, J = 4 Hz, 1 H), 7.65 (d, 1 H), 7.32 (d, 1 H), 7.29 (m, 1 H), 4.56 (s, 2 H), 4.33 (s, 2 H), 4.28 (s, 4 H), 4.07 (m, 4 H), 1.75 (s, 4 H), 1.42 (s, 4 H), 1.26 (s, 24 H), 0.87 (m, 6 H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 161.4, 161.3, 139.9, 139.3, 135.5, 135.4, 132.3, 130.8, 129.9, 129.7, 129.5, 128.7, 108.2, 107.9, 98.2, 78.8, 71.7, 70.2, 69.6, 63.9, 53.5, 42.3, 31.9, 30.1, 30.0, 29.8, 29.6, 29.4, 29.3, 22.7, 14.2 ppm; HRMS (ESI): calcd. for C₄₆H₅₆N₂FeO₂S₂ [M]⁺ 788.3128; found 788.3122; UV/Vis (CH₂Cl₂): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 584 nm (4.6×10^4).

2.2.5. Synthesis of DPP 6

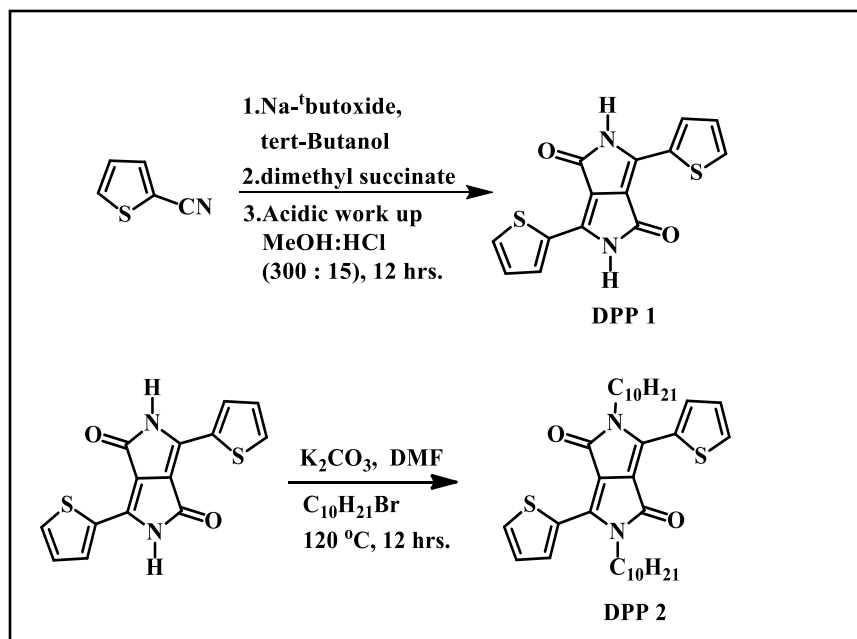
In a 100mL round-bottom flask dibromo-substituted **DPP 4** (0.200 g, 0.28 mmol) and ethynylferrocene (0.116 g, 0.56 mmol) dissolved in dry toluene (10 mL) and triethylamine (6 mL). The reaction mixture was degassed with argon for 10 min, and then PdCl₂(PPh₃)₂ (0.020 g, 0.028 mmol), PPh₃ (0.014 g, 0.056 mmol), and CuI (0.006 g, 0.028 mmol) were added (Scheme 9). The reaction mixture was stirred at 80 °C overnight. After completion of the reaction, the mixture was cooled to room temperature. The solvents were removed in vacuo, and the blue product was purified by chromatography on a silica column (hexane/dichloromethane, 3:1) to yield **DPP 6**. (0.230 g, 85 % yield); m.p. 130 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.90 (d, 2 H), 7.32 (d, 2 H), 4.55 (s, 4 H), 4.32 (d, 4 H), 4.28 (d, 4 H), 4.07 (m, 4 H), 1.75 (s, 4 H), 1.42 (s, 6 H), 1.25 (s, 22 H), 0.86 (m, 6 H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 163.1, 139.0, 135.5, 132.3, 129.8, 129.6, 108.5, 78.8, 71.7, 70.2, 69.6, 63.9, 53.5, 42.4, 31.9, 30.1, 29.8, 29.6, 29.3, 27.0, 22.7, 14.2 ppm; HRMS (ESI): calcd. for C₅₈H₆₄N₂Fe₂O₂S₂ [M]⁺ 996.3106; found 996.3019; UV/Vis (CH₂Cl₂): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 624 nm (4.4×10^4).

CHAPTER THREE

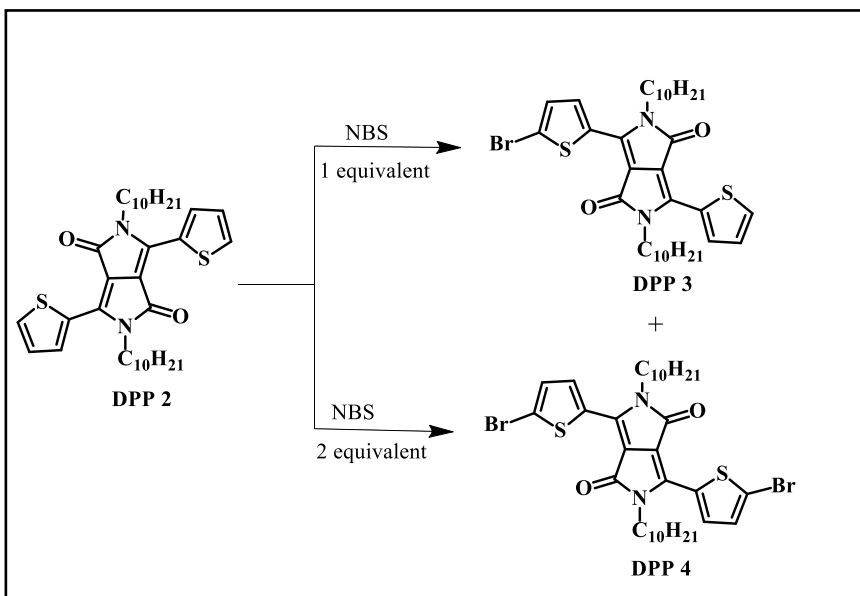
3. Results and Discussion

3.1. Synthesis and characterization

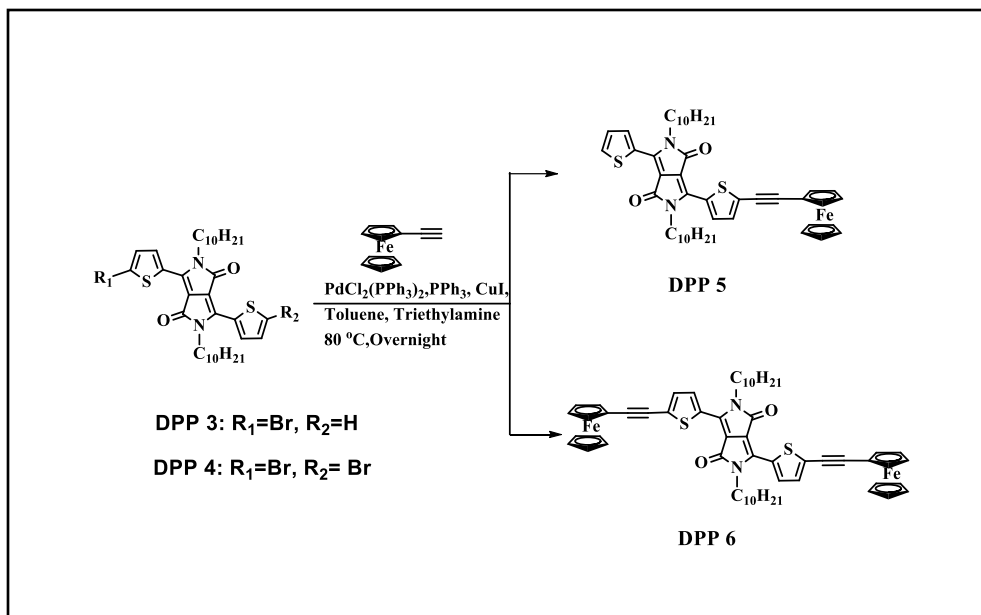
DPP 2 (23% yield) was synthesized by reacting **DPP 1** with excess amount of 1-bromodecane in presence of base K_2CO_3 in *N, N*-dimethylformamide (DMF) (scheme 7). Ferrocenyl-**DPPs 5** and **6** were synthesized by a Pd-catalyzed Sonogashira cross-coupling reaction. Monobromo and dibromo-substituted **DPPs 3** and **4** were synthesized according to reported procedures (Scheme 8). The Sonogashira cross coupling reactions of mono- and dibrominated **DPPs 3** and **4** were carried out with 1 and 2 equiv. of ethynylferrocene to give unsymmetrical ferrocenyl-**DPP 5** and symmetrical ferrocenyl-**DPP 6** in 80 and 85 % yield, respectively (Scheme 9). The ferrocenyl-DPPs were purified by column chromatography over silica gel and recrystallization techniques. 1H NMR of **DPP 2** shows peaks between $\delta=0.8$ to 4.0 ppm for aliphatic alkyl chains protons and $\delta=7.2$ to 9.0 ppm for thiophene protons. 1H NMR of **DPP 5** shows peaks between $\delta=0.8$ to 4.0 ppm for aliphatic alkyl chains protons and $\delta=4.2$ to 4.6 ppm for ferrocenyl protons and $\delta=7.2$ to 9.0 ppm for thiophene protons which include a peak at $\delta=9.0$ ppm which is absent in **DPP 6** as it contains two ferrocenyl units attached to two thiophene units of DPP. 1H NMR of **DPP 6** shows peaks between $\delta=0.8$ to 4.0 ppm for aliphatic alkyl chains protons and $\delta=4.2$ to 4.8 ppm for ferrocenyl protons and $\delta=7.0$ to 8.8 ppm for thiophene protons.



Scheme 7. Synthesis of **DPP 1** and **DPP 2**.



Scheme 8. Synthesis of **DPP 3** and **DPP 4**.



Scheme 9. Synthesis of Ferrocenyl substituted **DPP 5** and **DPP 6**.

3.2. Photophysical Properties

The electronic absorption spectra of **DPP 2** and ferrocenyl **DPPs 5** and **6** in dichloromethane exhibit broad bands that cover the entire UV/Vis region. The strong absorption bands at longer wavelengths correspond to π - π^* transition. The symmetrical **DPPs 6** shows red shifted absorption bands as compared to **DPP 2** and **DPP 5**, due to extended conjugation. A photograph of ferrocenyl-**DPPs 5** and **6** in dichloromethane in daylight is shown in Figure 4.

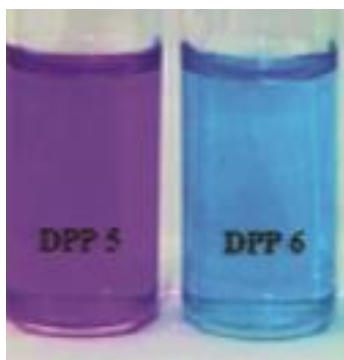
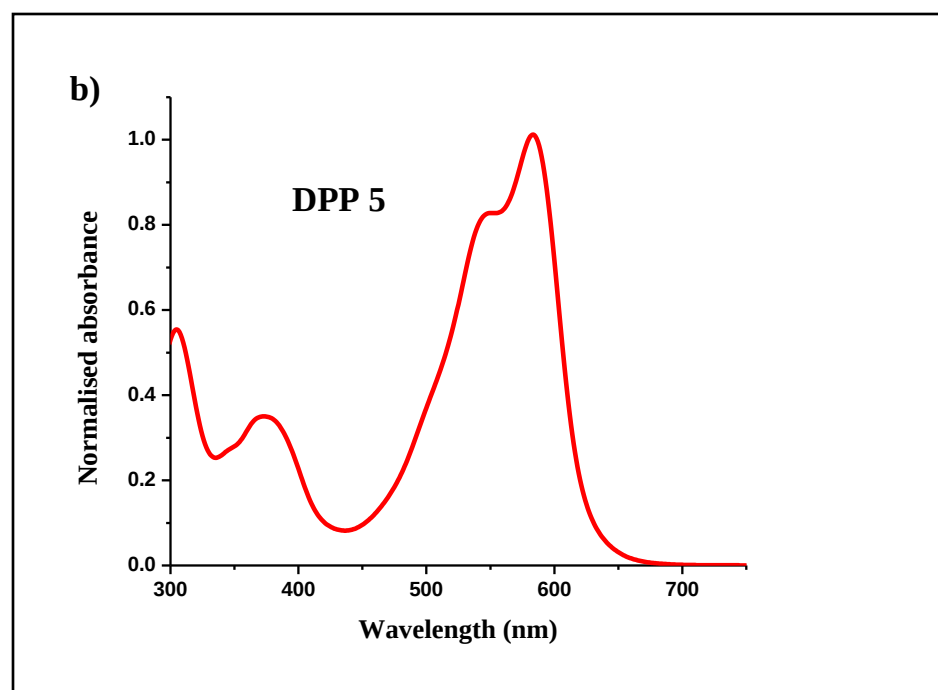
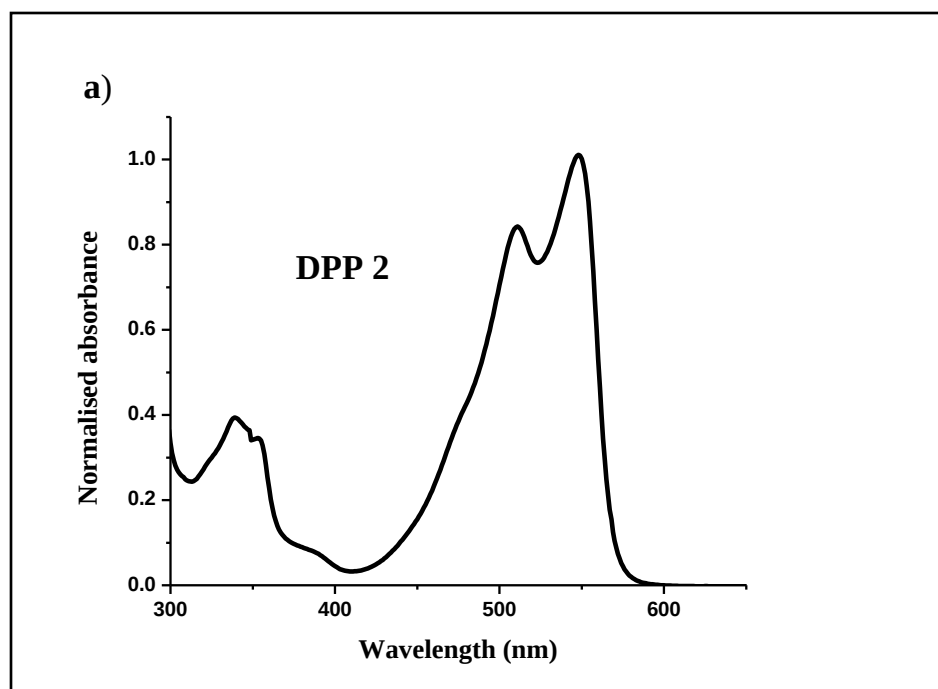


Figure 4. Ferrocenyl-**DPPs 5** and **6** in dichloromethane in daylight.



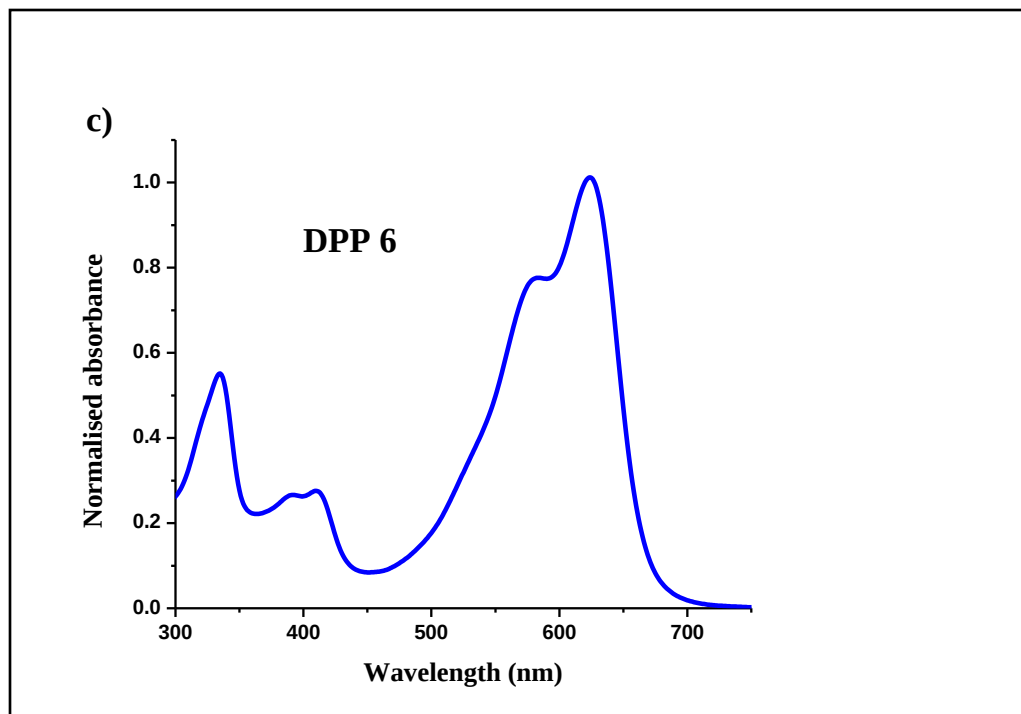
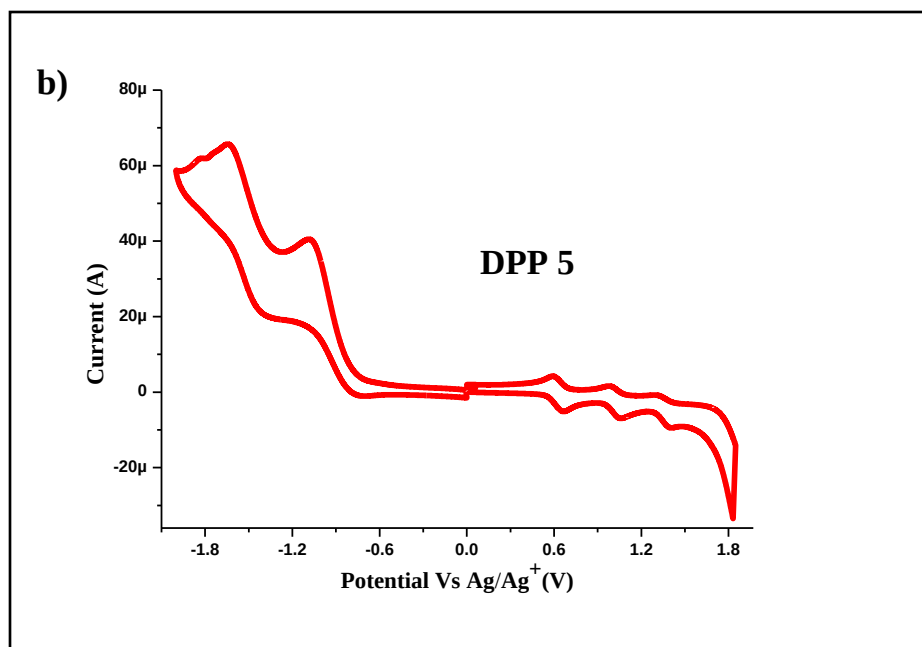
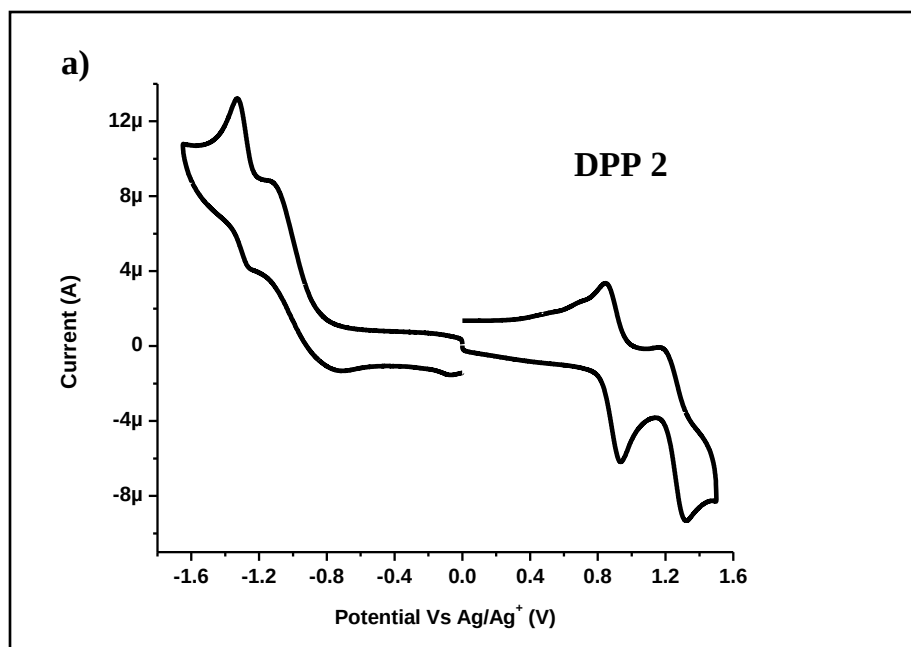


Figure 5. UV-Visible spectra of (a) **DPP 2**, (b) **DPP 5**, (c) **DPP 6** in dichloromethane.

3.3. Electrochemical Properties

The electrochemical behavior of **DPP 2**, **5**, **6** were studied by the cyclic voltammetric (CV) analysis in dichloromethane solution using tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as supporting electrolyte. The electrochemical data are listed in Table 2 and representative cyclic voltammograms of **DPP 2**, **5** and **6** are shown in Figure 6. The plot for **DPP 2** show two oxidation waves for two unsymmetrical thiophene moieties at 0.87 eV and 1.26 eV, whereas two reduction waves due to the formation of mono and di anion of DPP at -1.04 eV and -1.26 eV respectively were observed. The plot for **DPP 5** shows three oxidation waves, one for ferrocenyl moiety and other two for the two thiophene moieties (i.e., the terminal and the adjacent thiophene to the ferrocene). The plot for **DPP 6** exhibit only two oxidation waves, one is related to the thiophene and the other to the ferrocene unit. The DPP moiety shows two

reduction waves in ferrocenyl-DPPs corresponds to mono and dianion formation.



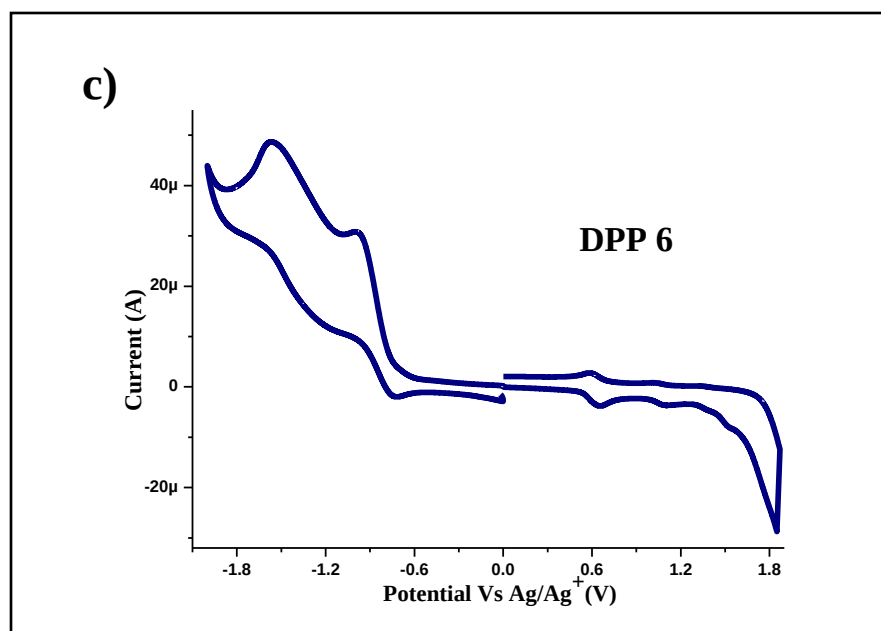


Figure 6. CV plots of: (a) **DPP 2**, (b) **DPP 5**, (c) **DPP 6**.

3.4. Thermogravimetric Analysis

The thermal properties of the **DPP 2**, **5** and **6** were investigated by the thermogravimetric analysis (TGA) under nitrogen atmosphere and their thermograms are shown in Figure 7. The **DPPs 5** and **6** exhibit good thermal stability upto 376 °C at 10% weight loss under nitrogen atmosphere. The decomposition temperatures for 10% weight loss in **DPPs 2**, **5**, **6** were found to be 355 °C, 377 °C, 387 °C respectively. The trend in thermal stability follows the order **6** > **5** > **2**. This trend in thermal stability reveals that symmetrical ferrocenyl **DPP 6** is thermally more stable as compared to unsymmetrical ferrocenyl **DPP 5**.

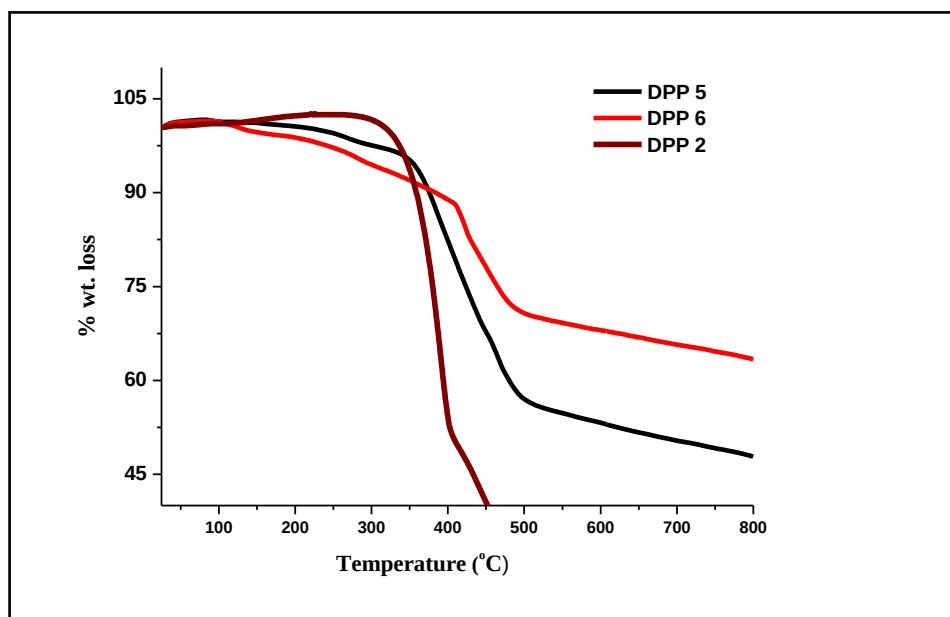


Figure 7. Thermogravimetric analysis of **DPPs 2**, **5** and **6** measured at a heating rate of 10 °C / min under nitrogen atmosphere.

Table 1. Photophysical and thermal properties of **DPPs 2, 5 and 6**.

Compound	λ_{abs} (nm)	$\epsilon/10^4$ ($\text{M}^{-1}\text{cm}^{-1}$) ^a	T_d ($^{\circ}\text{C}$) ^b
DPP 2	551	4.6	355
DPP 5	584	4.6	377
DPP 6	624	4.4	387

^aAbsorbance measured in dichloromethane at 1×10^{-4} M concentration, ϵ : extinction coefficient; ^bDecomposition temperatures for 10% weight loss at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$, under a nitrogen atmosphere.

Table 2. Electrochemical properties of **DPPs 2, 5 and 6**^a.

Compound	$E^3(\text{Oxid})$ (eV)	$E^2(\text{Oxid})$ (eV)	$E^1(\text{Oxid})$ (eV)	$E^1(\text{Red})$ (eV)	$E^2(\text{Red})$ (eV)
DPP 2	-	1.26	0.87	-1.04	-1.26
DPP 5	1.33	1.00	0.60	-0.97	-1.49
DPP 6	-	1.06	0.61	-0.87	-1.43

^aThe electrochemical analysis was performed in a 0.1 M solution of Bu_4NPF_6 in dichloromethane at 100 mVs^{-1} scan rate, versus Ag/Ag^+ at $25\text{ }^{\circ}\text{C}$.

3.5. Theoretical Calculations

Density functional theory (DFT) calculations were then performed by using the Gaussian09W program to understand the geometry and electronic structure of **DPPs 2, 5 and 6**. The geometry optimizations were carried out in the gas phase, and the DFT calculations were performed at B3LYP/6-31+G**. The optimized structures of **DPPs 2, 5 and 6** exhibit a planar geometry. Frontier molecular orbitals (FMO) of **DPPs 2, 5 and 6** is shown

in Table 3. The HOMO of **DPPs 2, 5** and **6** is distributed throughout the entire molecule. The LUMO of **DPPs 2, 5** and **6** is localized on DPP and thiophene units. The theoretical values obtained by DFT calculations were in good agreement with the optical band gaps calculated from the UV/Vis absorption and the electrochemical band gaps calculated from CV analysis (Table 4). The trend in the theoretical HOMO–LUMO values follow the order of **2**>**5** >**6**. This shows that the HOMO–LUMO value decreases with an increase in the number of ferrocene units.

Table 3. HOMO and LUMO orbitals of **DPPs 2, 5** and **6** at the B3LYP/6-31G** level.

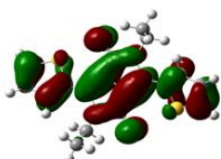
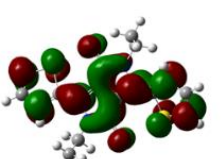
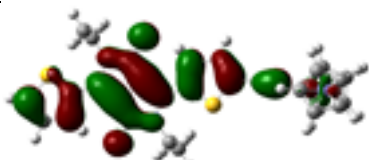
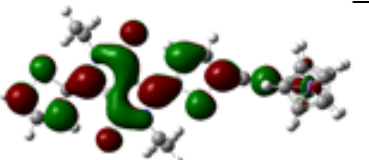
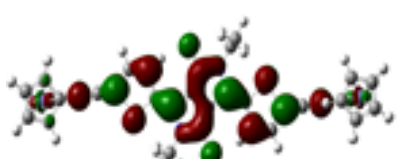
Compound	HOMO (eV)	LUMO (eV)
DPP 2	 -4.98	 -2.44
DPP 5	 -4.82	 -2.57
DPP 6	 -4.72	 -2.63

Table 4. Comparison of band gaps in **DPPs 2, 5 and 6**.

Compound	Theoretical band gap (eV)	Optical band gap (eV)	Electrochemical band gap (eV)
DPP 2	2.54	2.12	1.49
DPP 5	2.25	1.91	1.17
DPP 6	2.09	1.77	1.12

All the major transitions were calculated from TD-DFT and shown in Table 5 for **DPP 2, DPP 5, DPP 6** which are due to π - π^* transitions.

Table 5. Calculated electronic transitions for **DPPs 2, 5 and 6** in the gas phase.

Compound	Wavelength (nm)	Composition	f^a
DPP 2	503	HOMO→LUMO (0.70)	0.43
	322	HOMO-7→LUMO (0.14)	0.30
DPP 5	562	HOMO→LUMO (0.66)	0.83
	609	HOMO-2→LUMO+3 (0.36)	0.18
DPP 6	636	HOMO→LUMO (0.59)	1.23
	589	HOMO→LUMO (0.38)	0.39

f^a = Oscillation strength

CHAPTER FOUR

4. Conclusions

In summary, we have synthesized symmetrical and unsymmetrical ferrocenyl-DPPs **5** and **6** by employing a Sonogashira cross-coupling reaction. There is a systematic redshift in the absorption bands from **DPP 2** to **DPP 5** and then to **DPP 6**. These derivatives also demonstrated enhanced thermal stability. Photophysical, electrochemical, and computational studies show absorption in visible region with low HOMO-LUMO gap values. The high thermal stability and low HOMO–LUMO gap values of **DPPs 2, 5** and **6** make them potential candidates for organic photovoltaics. Currently, we are synthesizing new donor-substituted DPPs for optoelectronic and photovoltaics applications.

APPENDIX A.

^1H NMR, ^{13}C NMR and HRMS spectrum of compounds.

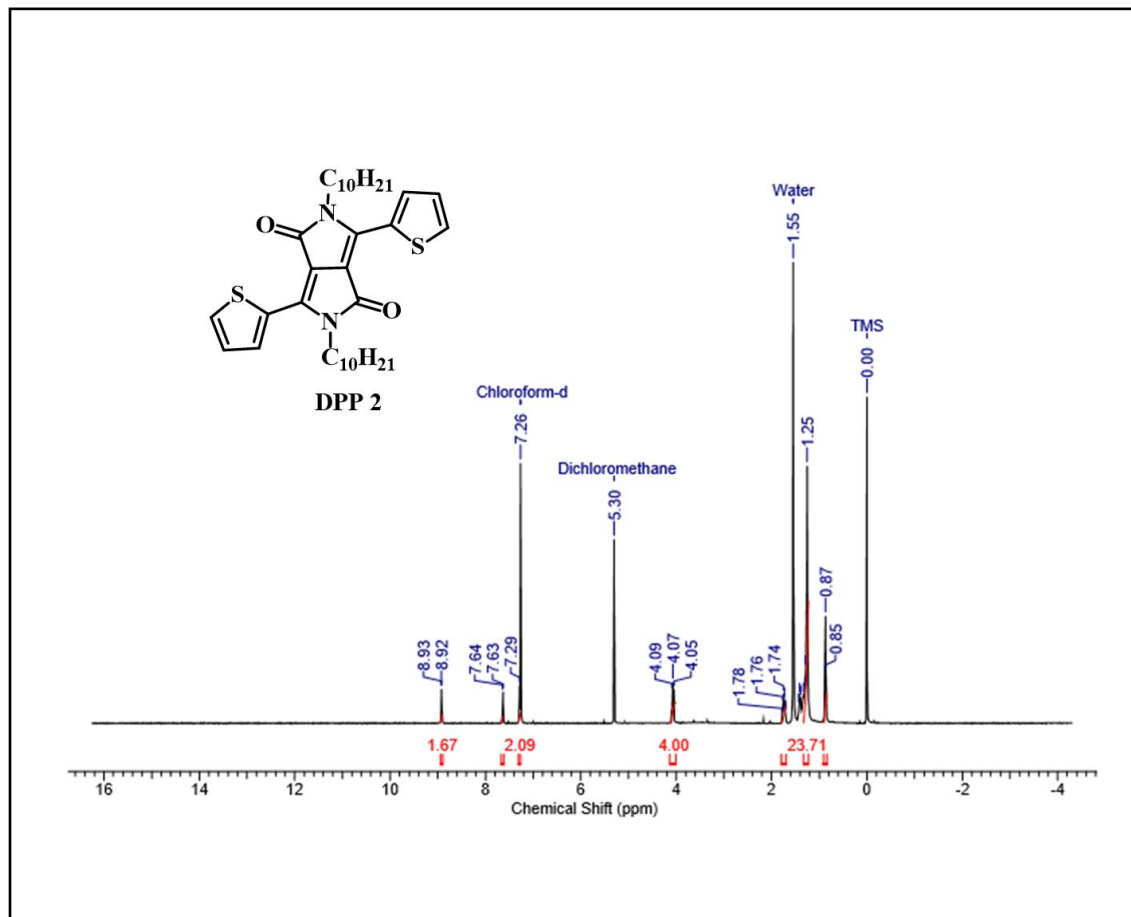


Figure 8. 400 MHz ^1H NMR spectrum of **DPP 2** in CDCl_3 .

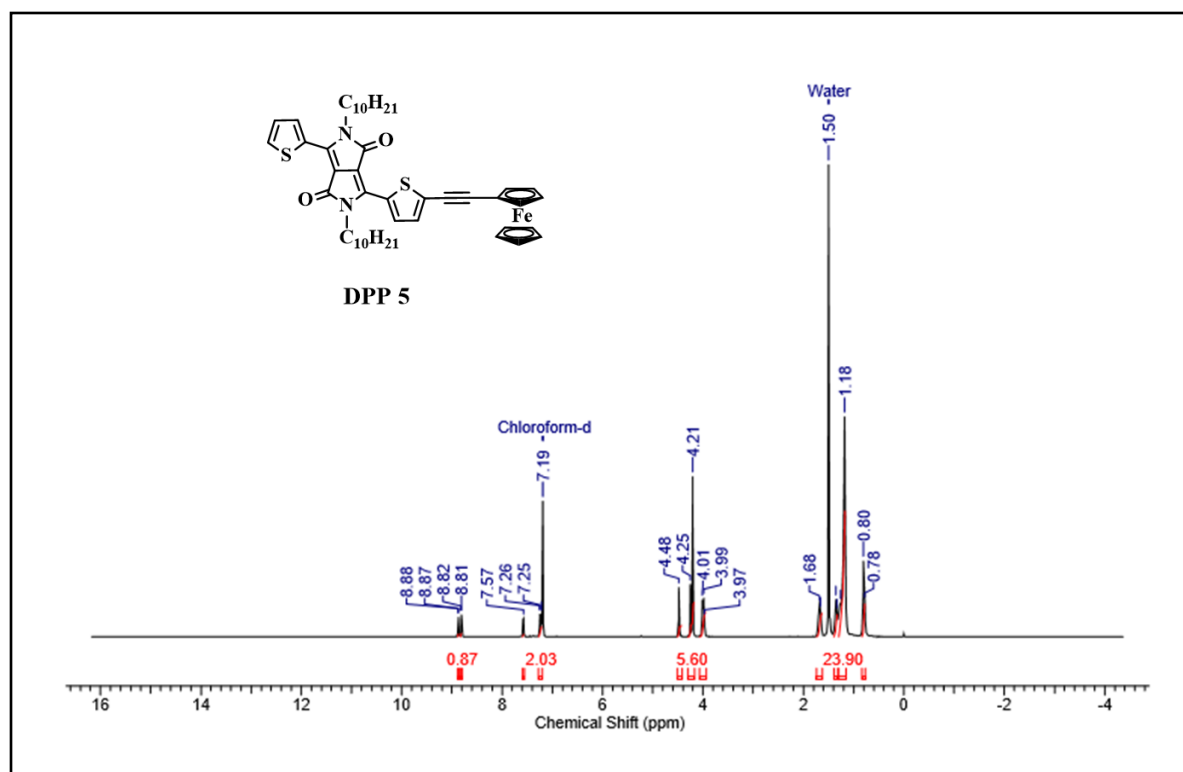


Figure 9. 400 MHz ^1H NMR spectrum of **DPP 5** in CDCl_3 .

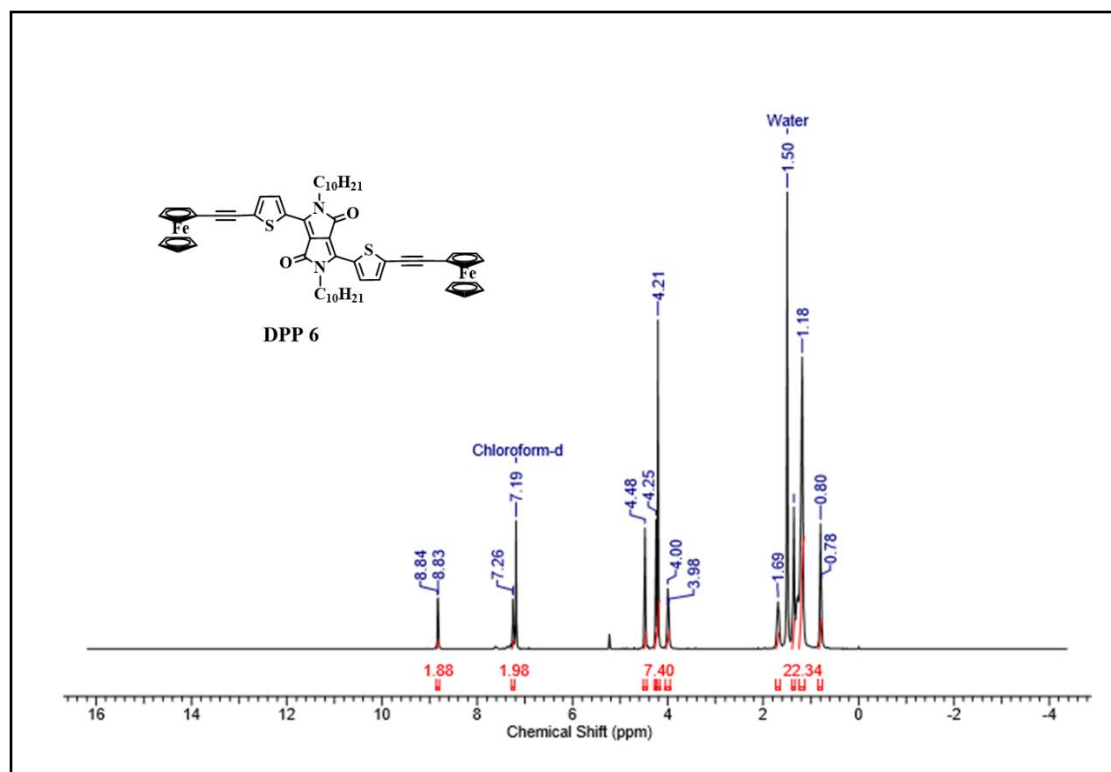


Figure 10. 400 MHz 1H NMR spectrum of **DPP 6** in $CDCl_3$.

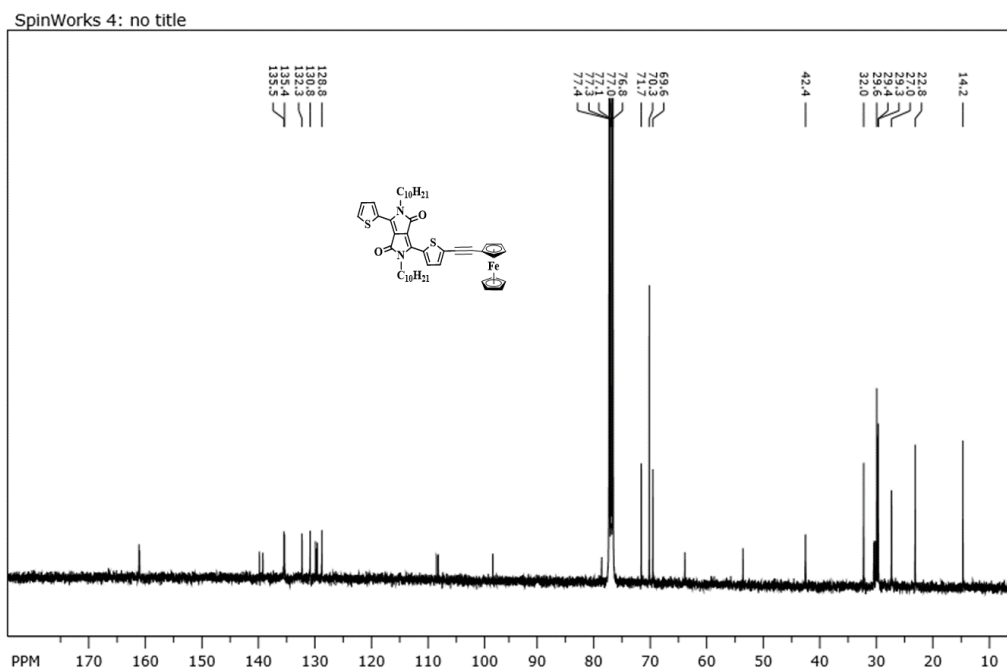
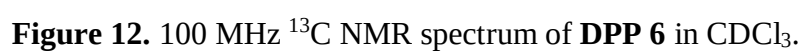


Figure 11. 100 MHz ^{13}C NMR spectrum of **DPP 5** in CDCl_3 .



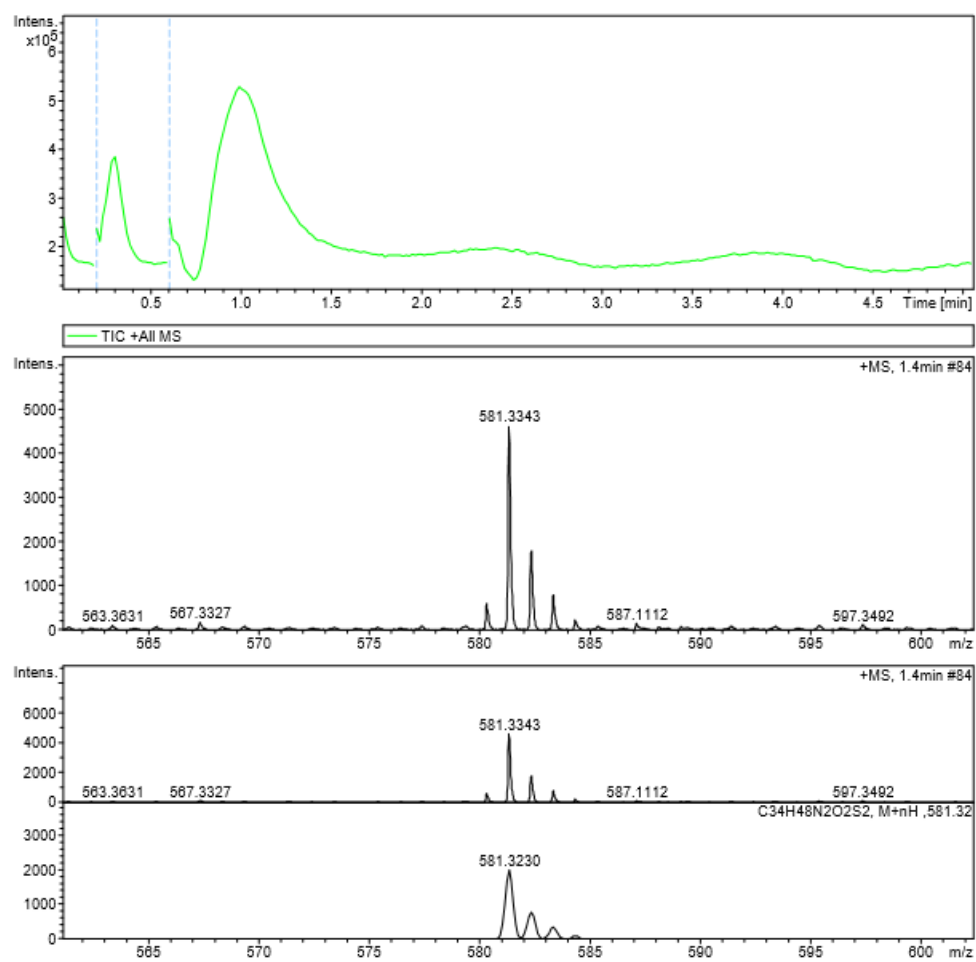


Figure 13. HRMS of DPP 2.

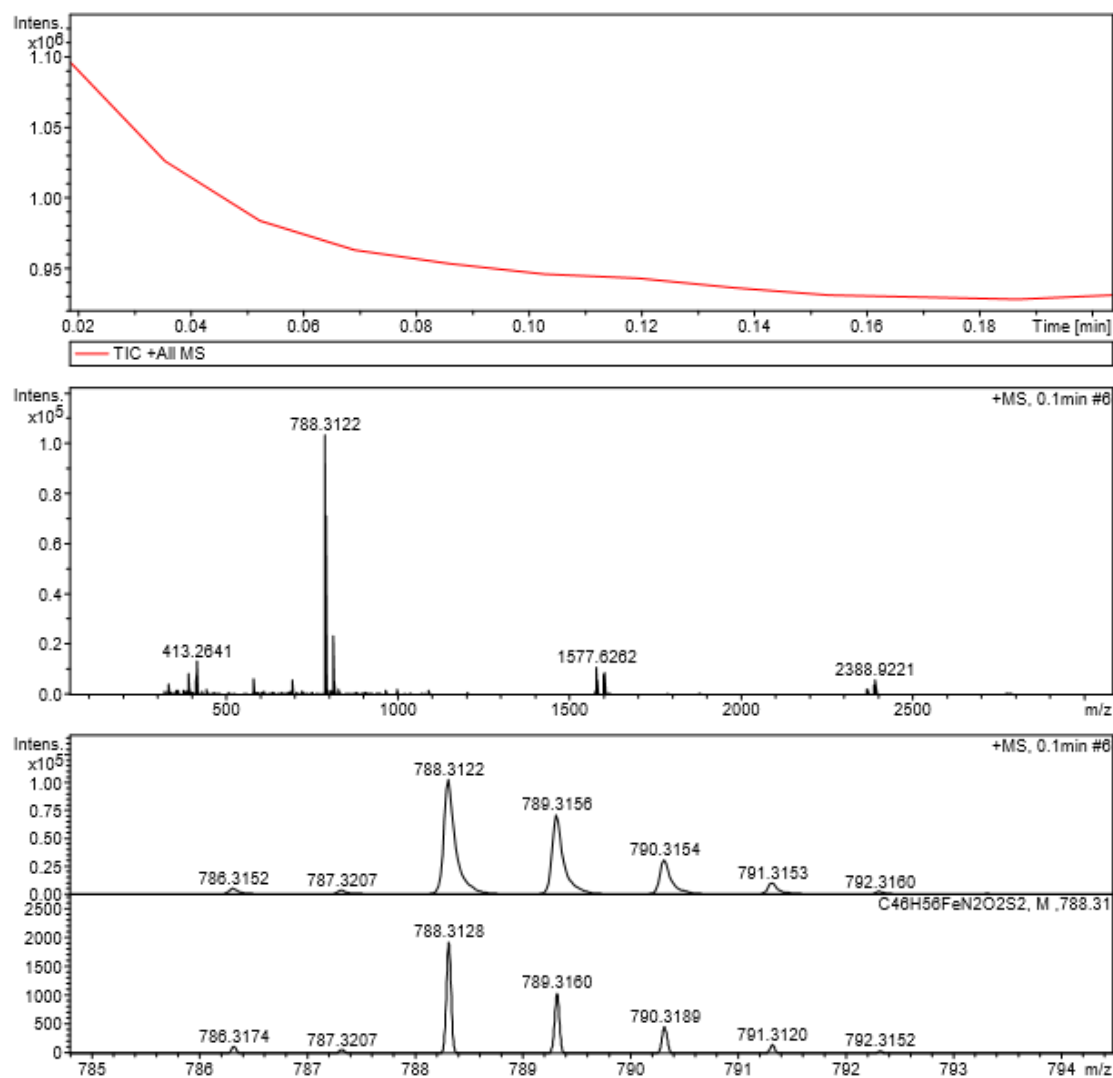


Figure 14. HRMS of DPP 5.

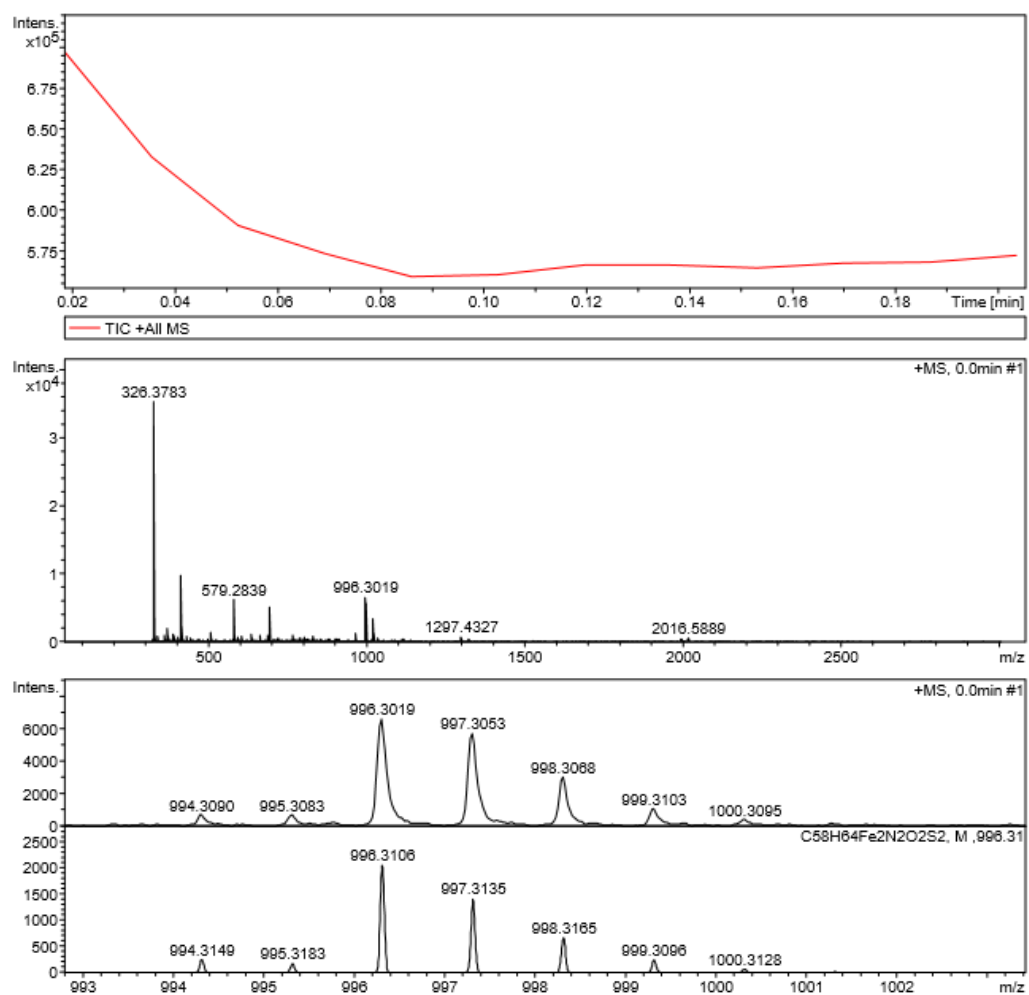


Figure 15. HRMS of DPP 6.

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