#### DESIGN AND SYNTHESIS OF PUSH-PULL CHROMOPHORES BASED ON DIKETOPYRROLOPYRROLE

Ph.D. Thesis

By CHARU POPLI



#### DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2024

#### DESIGN AND SYNTHESIS OF PUSH-PULL CHROMOPHORES BASED ON DIKETOPYRROLOPYRROLE

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Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

> by CHARU POPLI



#### DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2024



#### INDIAN INSTITUTE OF TECHNOLOGY INDORE

I hereby certify that the work which is being presented in the thesis entitled **Design** And Synthesis Of Push-Pull Chromophores Based On Diketopyrrolopyrrole in the partial fulfillment of the requirements for the award of the degree of Doctor Of Philosophy 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 January 2018 to July 2024 under the supervision of Dr. Rajneesh Misra, Professor, Indian Institute of Technology 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.

chare Pokle 17/1/2025

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

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#### CHARU POPLI

#### **SYNOPSIS**

Diketopyrrolopyrrole (DPP) pigment was first developed and synthesized by Farnum *et al.* featuring two phenyl units. This  $8-\pi$ electron fused ring known as pentalene, displayed remarkable insolubility in typical organic solvents and bright red colouration. Later, Iqbal and co-workers improved the synthetic process using succinic method. Subsequently, a wide range of DPP derivatives, displaying colours from red to blue, have been designed which include DPP pigments flanked by phenyl, pyridyl, thienyl, furayl, and seleneyl groups. These substituents can influence the planarity of the DPP pigment, its energy levels, and the distance between  $\pi$ - $\pi$  stacked molecules. DPP pigments contain two amine and carbonyl units in their structure (Figure 1), capable to form strong hydrogen bonds, which leads to less solubility in common organic solvents. However, alkylation can disrupt these hydrogen bonds, significantly and improves the solubility. To synthesize DPP-based small organic molecules (SOMs)/polymers, reactions such as Stille, Suzuki coupling, electrochemical polymerization, and Buchwald coupling were used. Strong electron deficiency, outstanding planarity of the DPP unit, a broad  $\pi$ -conjugation system, and exceptional aggregation qualities are the favourable features of DPP-based small organic molecules (SOMs). Diketopyrrolopyrrole (DPP) derivatives have good thermal stability and broad optical absorbance, which makes them ideal for a wide range of applications. In solar cells, DPP derivatives are used for their improved photovoltaic properties, for enhancing the efficiency and performance of these devices. DPP based derivatives contribute to aggregation-induced emission in the field of organic electronics, thus increasing the efficiency of light emission and are also crucial in photodynamic therapy to produce reactive oxygen species in response to light stimulation for cancer treatment. These compounds are utilized in bioimaging due to their fluorescent characteristics, which enable accurate visualization of biological processes and tissues. The DPP based derivatives are used for the development of laser dyes as well as used for the fabrication of photoconductive materials for improving the efficiency of various electronics and optoelectronic devices. They are also used in making fluorescent sensors due to their high sensitivity and specificity. The extensive utility of DPP derivatives across these diverse applications highlights their significance in both industrial and therapeutic contexts.



Figure 1. The molecular structure of Diketopyrrolopyrrole (DPP).

Different chemically active functional groups are present in the structure of DPP such as the double bonds in the DPP, the aromatic rings at positions 3 and 6, and the oxygen and nitrogen atoms in the amide moiety. Nucleophilic attacks can occur at the carbonyl carbon atom and the  $\alpha$ ,  $\beta$ -unsaturated system within the bicyclic DPP unit, particularly at the 3 and 6 positions. Donor–Acceptor architectures featuring strong absorption in the visible to near-infrared (NIR) range and a reduced HOMO–LUMO gap hold considerable promise for organic photovoltaic applications. Our research has explored various donor (e.g., carbazole, triphenylamine, ferrocene) and acceptor (TCBD) functionalized DPPbased D–A systems. The comprehensive investigation of their photophysical, electrochemical, and computational characteristics indicates their potential applications in the field of organic electronics.

#### The main objectives of this study are:

- To investigate the impact of substituting various donor and acceptor units on the diketopyrrolopyrrole core and to explore the donor-acceptor interactions in molecular system by tuning the HOMO-LUMO gap.
- To improve the photonic properties of diketopyrrolopyrrole chromophores by modifying the donor strength at the terminal positions and incorporating cyano-based acceptors between the diketopyrrolopyrrole core and its substituents.
- To study the effect of extended conjugation on the photophysical and electrochemical properties of DPP based chromophores.
- To study the electronic structure, electron density distribution across the HOMO and LUMO energy levels, and the photophysical properties of donor-acceptor functionalized diketopyrrolopyrrole through density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations.



**Figure 2**. General representation of donor-acceptor functionalized diketopyrrolopyrroles in this work.

#### **Chapter 1: Introduction**

This Chapter elucidates the methodologies employed for synthesizing and functionalizing DPP derivatives, as well as their diverse applications in the field of organic photovoltaics and bioimaging.

#### **Chapter 2: Materials and experimental techniques**

This Chapter provides a comprehensive overview of the general experimental procedures, characterization techniques, and specific instruments utilized for analysis and characterization. Each method and tool are described in detail to ensure clarity and reproducibility.

#### Chapter 3: Design and Synthesis of *N*-phenyl carbazole Substituted Diketopyrrolopyrrole Based Monomers and Dimers: A Comparative Study

In an effort to see the effect of conjugation length and substitution at different positions of N-phenyl carbazole, we designed and synthesized symmetrical and unsymmetrical acetylene bridged N-phenyl carbazole based diketopyrrolopyrroles (DPPs 5–9) by the Pd-catalyzed Sonogashira cross-coupling and Stille coupling reactions. A comparative study of isomeric N-phenyl carbazole (meta- and paraisomers), attached to the DPP were performed. The N-phenyl carbazole based DPP monomers (5–7, 10 and 11) exhibit absorption in the visible region whereas the corresponding dimers (8 and 9) show broad absorption towards near-infrared (NIR) region with lowering of HOMO-LUMO gap. The *para-N*-phenyl carbazole based DPPs (8, 10 and 11) show red shifted absorption compared to their meta-substituted analogues (9, 5 and 6). The emission spectra reveal that DPP monomers (5–7) are fluorescent in nature whereas quenching of fluorescence was observed in DPP dimers (8 and 9). The thermogravimetric analysis shows higher thermal stability for *meta-N*-phenyl carbazole based DPPs as compared to their para-based analogues. Monomers of carbazole based DPPs are thermally more stable as compared to their dimers. The electrochemical study reveals multiple oxidation waves related to donor moieties (such as thiophene and carbazole) and one reduction wave corresponding to DPP unit.



**Figure 3.** Chemical structure of *N*-phenyl carbazole functionalized DPPs **5** –**11**.

# Chapter 4: Symmetrical and Unsymmetrical N, N-<br/>dimethylaniline/TriphenylamineFunctionalizedDiketopyrrolopyrrolesFunctionalized

In order to investigate the effect of using different donors and variable length, symmetrical and unsymmetrical *N*, *N*-dimethylaniline and Triphenylamine (TPA) functionalized DPPs (**NDPPs 1–8**) were designed and synthesized by the Sonogashira cross-coupling reaction followed by click type [2+2] cycloaddition retro-electrocyclization reaction. The photophysical and electrochemical properties were systematically studied. The incorporation of TCBD in **NDPPs 1**, **3** and **6** red shifted the absorption spectra towards NIR region and lowers the HOMO–LUMO gap due to increase in donor-acceptor interactions. The absorption spectra of DPP based derivatives **NDPPs 1–6** exhibit a strong electronic absorption band in the visible region corresponding to  $\pi$ - $\pi$ \* transition. The TCBD bridged DPP derivatives exhibit an additional band at longer wavelength corresponding to intramolecular charge transfer (ICT) band. The attack of tetracyanoethylene (TCNE) on the side of *N*, *N*- dimethylaminophenyl group in **NDPP 6** indicates the strong donor strength of it as compared to triphenylamine thus exclusively an asymmetric product **NDPP 7** was obtained. The broad absorption in visible region extended upto NIR region, multiple redox potentials and low HOMO–LUMO gap indicates that these molecules are potential candidate for optoelectronic and photovoltaic applications.



**Figure 4.** Normalized electronic absorption spectra of **NDPP 1**–**NDPP 8** in dichloromethane at  $1.0 \times 10^{-5}$  M concentration (solid line) and as thin film (dashed lines).

#### Chapter 5: Impact of Donor Strength on [2+2] Cycloaddition Retroelectro-cyclization in Tetracyanobutadiene-Functionalized Diketopyrrolopyrrole Derivatives

In this Chapter various unsymmetrical ferrocene functionalized DPPs (**FcDPPs 1–8**) were designed and synthesized by Sonogashira crosscoupling reaction followed by click type [2+2] cycloaddition retroelectrocyclization reaction. Mono-TCBD functionalization took place on acetylene bridge linked to *N*, *N*-dimethyl amino phenyl side (**FcDPP 6**) indicating strong donor strength of *N*, *N*-dimethylamino phenyl unit in comparison to the ferrocene where as in **FcDPP 1** and **FcDPP 2**, the attack of first TCNE took place at acetylene bridge linked to ferrocene side indicating strong donor strength of ferrocene relative to triphenylamine and *N*-phenyl carbazole unit. An additional band at longer wavelength corresponding to ICT was observed in the TCBD bridged derivatives (**FcDPPs 2**, **4**, **5**, **7** and **8**), while only  $\pi$ - $\pi$ \* transition band was observed in acetylene bridged derivatives (**FcDPPs 1**, **3** and **6**). The electrochemical studies on **FcDPPs 1–8** explained that presence of powerful acceptor Diketopyrrolopyrrole unit and additional cyano based acceptors TCBD tune the HOMO-LUMO energy levels significantly.



Figure 5. Normalized electronic absorption spectra of FcDPPs 3–8 in dichloromethane at  $1.0 \times 10^{-5}$  M concentration (solid line) and as thin film (dashed line).

#### Chapter 6: Phenothiazine Based Diketopyrrolopyrrole Derivatives Functionalized with Different Donors.

A series of phenothiazine based DPP derivatives P-1-P-6 were designed and synthesized by the Pd-catalyzed Sonogashira crosscoupling reaction followed by click type [2+2] cycloaddition retro-electrocyclization reaction in which Diketopyrrlopyrrole (DPP) unit was used as an electron withdrawing unit and phenothiazine (PZ), triphenylamine (TPA), N, N-dimethylamino phenyl (NDI), N-phenyl carbazole (NPC) moieties were used as an electron donating units. In these chromophores variation of donor unit and  $\pi$ -linker units are the key factors in tuning the photophysical and electronic properties, which was systematically investigated by the photophysical, electrochemical and computational studies. The di-substituted phenothiazine-based derivatives P-4–P-6 exhibit broader absorption spectra relative to mono-substituted derivatives P-1-P-3 within the range of 300-800 nm due to extended  $\pi$ -conjugation. The cyclic voltammograms of phenothiazine-based derivatives P-1-P-6 explained that the presence of diketopyrrolopyrrole entity as powerful acceptor in the molecular system enhanced the  $\pi$ conjugation and tuned the HOMO-LUMO energy levels. The computational studies revealed that there was a good agreement with experimental data.



**Figure 6.** Cyclic voltammograms of **P-1–P-3** in DCM using TBAF as electrolyte.

#### Chapter 7: Diketopyrrolopyrroles Functionalized Mono-, Di- and Tri- Substituted Triphenylamine Derivatives: A Comparative Study

In this Chapter we have investigated the effect of number of diketopyrrolopyrrole (DPP) and ferrocenyl–diketopyrrolopyrrole units on the photophysical and electrochemical properties. We have designed and synthesized DPP and ferrocenyl-DPP based mono–, di– and tri–substituted derivatives with triphenylamine (TPA) as a central core **TPA–DPPs 1–6** by the Pd-catalyzed Sonogashira cross–coupling reactions. The photophysical and electrochemical properties of DPP and ferrocenyl-DPP based derivatives were studied and compared. The electronic absorption spectra show that the ferrocenyl-DPP based derivatives **TPA–DPPs 1–6** exhibit the red shifted absorption compared to DPP based derivatives **TPA–DPPs 1–3**. The di- and tri- substituted DPP (**TPA–DPPs 2** and 3) and ferrocenyl-DPP based TPA (**TPA–DPPs 5** and 6) show slight red shifted absorption compared to monomer analogues (**TPA–DPPs 1** and 4). The electrochemical investigation exhibits additional low voltage oxidation peak in ferrocenyl-DPP based

derivatives due to oxidation of ferrocenyl unit. The **TPA–DPPs 1–6** exhibit good thermal stability. The effect of additional end capping ferrocene has also been investigated which exhibit red shift of absorption, additional low oxidation potential and lowers the HOMO-LUMO gap.



**Figure 7.** Structure of DPP based chromophores **TPA-DPP 1–TPA-DPP-6**.

#### **Chapter 8: Conclusion and Future Prospects**

This Chapter highlights the key achievements of the research and discusses future directions for developing new materials for optoelectronic applications. It outlines the significant findings and suggests potential advancements and innovations in the field.

#### LIST OF PUBLICATIONS

- Popli, C.<sup>\$</sup>, Jang, Y. <sup>\$</sup>, Patil, Y., Misra, R.\* (2020), Formation of Highly Efficient, Long-Lived Charge Separated States in Star-Shaped Ferrocene-Diketopyrrolopyrrole-Triphenylamine Donor–Acceptor– Donor Conjugates, *Chem. Eur. J.*, 26, 15109–15115 (DOI: doi.org/10.1002/chem.202002851)<sup>†</sup>
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#### **TABLE OF CONTENTS**

LIST OF	FIGURESxxii
LIST OF	SCHEMESxxvi
LIST OF	TABLESxxix
NOMEN	CLATURExxxi
ACRON	YMSxxxii
Chapter	01: Introduction
1.1	Background 1
1.2	Diketopyrrolopyrrole (DPP) 3
1.2.	Synthesis of Diketopyrrolopyrrole
1.3.	Preparation of DPP through the Peformatsky approach
1.3.1	Succinic method
133	Condensation approach and related methods 7
134	Synthesis of DPPs using 2.5-Dihydrofuro[4.3-c]furan-1.4-
dione	es (DFFs) as precursors
1.3.5	. Additional alternative techniques for synthesizing DPPs9
1.4.	Reactive functionalization sites of DPP/ Reactions of DPP 10
1.4.1	. Reactive amide group of DPP10
1.4.2	. Reactions of carbonyl group of DPP13
1.4.3	. Reactions at 3 and 6 positions of DPP16
1.5.	Applications of Diketopyrrolopyrroles17
1.5.1	. Organic solar cells17
1.5	5.1.1. Bulk heterojunction organic solar cells
1.5	5.1.2. Dye sensitized solar cells (DSSC)
1.5	5.1.3. Perovskite solar cells (PSCs)
1.5.2	. Photothermal cancer therapy
1.5.3	. Fluorescent Probes
1.5.4	. Electrochromic applications
1.5.5	. Two photon absorption (TPA)26
1.5.6	. Aggregation-I nduced Emission (AIE)
1.5.7	. OFETs
1.6.	Current Work

1.7.	Organization of thesis	.34
1.8.	References	.36

Chapter 02: Materials and Experimental Techniques	53
2.1. Introduction	53
2.2. Chemicals for synthesis	53
2.3. Spectroscopic measurements	54
2.3.1. Mass spectrometry	54
2.3.2. NMR spectroscopy	54
2.3.3. UV-Vis spectroscopy	54
2.3.4. Fluorescence spectroscopy	54
2.4. Electrochemical studies	55
2.5. Computational Calculations	55
2.6. References	56

#### Chapter 03: Design and synthesis of *N*-phenyl carbazole

#### substituted diketopyrrolopyrrole based monomers and

dimers: A comparative study	57
3.1. Introduction	57
3.2. Results and Discussion	58
3.3. Photophysical and Thermal properties	60
3.4. Electrochemical properties	64
3.5. Theoretical calculations	67
3.6. Experimental Section	70
3.7. Conclusions	74
3.8. References	75

#### Chapter 04: Symmetrical and Unsymmetrical N, N-

#### dimethylaniline/Triphenylamine Functionalized

Diketopyrrolopyrroles	
4.1. Introduction	84
4.2. Results and Discussion	85
4.3. Photophysical properties	

4.4. Electrochemical properties	92
4.5. Theoretical calculations	95
4.6. Experimental Section	99
4.7. Conclusions	
4.8. References	

# Chapter 05: Impact of Donor Strength on [2+2]Cycloaddition-Retroelectrocyclization inTetracyanobutadiene-Functionalized DiketopyrrolopyrroleDerivatives.1145.1. Introduction1145.2. Result and Discussions1165.3. Photophysical Properties1205.4. Electrochemical Properties1235.5. Theoretical Calculations1275.6. Experimental Section:1305.7. Conclusions1365. 8. References137

#### Chapter 06: Phenothiazine Based Diketopyrrolopyrrole

D	erivatives Functionalized with Different Donors	.142
	6.1. Introduction	.142
	6.2. Result and Discussions	.144
	6.3. Photophysical Properties	.146
	6.4. Redox Properties	.149
	6.5. Theoretical calculations	.151
	6.6. Experimental section:	.155
	6.7. Conclusions	.161
	6.8. References	.161

Chapter 07: Ferrocenyl-diketopyrrolopyrroles functionalized	
mono-, di- and tri- substituted triphenylamine deriv	vatives: A
comparative study	
7.1. Introduction	166
7.2. Results and discussion	168
7.3. Photophysical properties	169
7.4. Thermogravimetric analysis	173
7.5. Lifetime measurements	174
7.6. Electrochemical properties	175
7.7. Theoretical calculations	178
7.8. Experimental Section:	
7.9. Conclusions	187
7.10. References	

# Chapter 08: Conclusions and Future Scope 195 8.1. Conclusions 195 8.2. Future scope 199 8.3. References 200

#### **LIST OF FIGURES**

#### **Chapter: 01: Introduction**

Figure 1. 1. Schematic representation of frontier molecular
orbitals of push-pull chromophore2
Figure 1. 2. Structure of DPP flanked with different aromatic
groups4
Figure 1. 3. Functionalization sites of Diketopyrrolopyrrole10
Figure 1. 4. DPP based chromophores for BHJ organic solar
cells19
Figure 1. 5. DPP based chromophore for dye sensitized solar
cells21
Figure 1. 6. DPP based chromophore for PSCs22
Figure 1. 7. DPP based nanoparticles for Photothermal cancer
therapy
Figure 1. 8. DPP based chromophores as fluorescent probes. 25
Figure 1. 9. DPP based chromophore for electrochromic
applications
Figure 1. 10. DPP based chromophore for TPA based
applications
Figure 1. 11. DPP based chromophore showing AIE effect30
Figure 1. 12. DPP based chromophore for OFETs

Chapter 03: Design and synthesis of *N*-phenyl carbazole substituted diketopyrrolopyrrole based monomers and dimers: A comparative study.

# Chapter 04:Symmetrical and Unsymmetrical N, N-dimethylaniline/TriphenylamineFunctionalizedDiketopyrrolopyrrolesFunctionalized

Chapter 05: Impact of Donor Strength on [2+2] Cycloaddition-Retroelectrocyclization in Tetracyanobutadiene-Functionalized Diketopyrrolopyrrole Derivatives.

Figure 5. 1. Structures of ferrocenyl substituted DPF	's FcDPPs
1–8	116

Figure 5. 2. Normalized electronic absorption spectra of
<b>FcDPPs 1-8</b> in $10^{-5}$ M DCM (solid lines) and in thin films (dash
lines)120
Figure 5. 3. Normalized UV-vis absorption spectra of FcDPPs
<b>5</b> and <b>7</b> in different solvents122
Figure 5. 4. Cyclic voltammograms of FcDPPs 1–8 in
dichloromethane solvent using 0.1 M tetrabutylammonium
hexafluorophosphate ( $Bu_4NPF_6$ ) as supporting electrolyte126
Figure 5. 5. The electron density distribution and the HOMO-
LUMO gap in <b>FcDPPs 3–8</b> 127
Figure 5. 6. HOMO-LUMO gap calculations of FcDPP 1, 2 and
TCNE

#### **Chapter 06: Phenothiazine Based Diketopyrrolopyrrole Derivatives Functionalized with Different Donors**

Figure 6. 1. Structure of phenothiazine functionalized
diketopyrrolopyrrole P-1–P-6144
<b>Figure 6. 2.</b> Electronic absorption spectra of <b>P-1–P-6</b> in $10^{-5}$ M
DCM
Figure 6. 3. Normalized UV-vis absorption spectra of P-1 and
<b>P-4</b> in different solvents148
Figure 6. 4. Cyclic voltammograms of P-1–P-6 in
dichloromethane solvent using 0.1 M tetrabutylammonium
hexafluorophosphate (Bu <sub>4</sub> NPF <sub>6</sub> ) as supporting electrolyte150
Figure 6. 5. Frontier molecular orbitals of phenothiazine based
DPPs <b>P-1–P-8</b> calculated by DFT using B3LYP/6-31G (d, p) for
C, H, N, S, O152
Figure 6. 6. HOMO-LUMO gap of P-1–P-6 calculated by DFT
using B3LYP/6-31+G (d, p) for C, H, O, N and S153
Figure 6. 7. Theoretical absorption spectra of P-1 and P-2155

Chapter 07: Ferrocenyl-diketopyrrolopyrroles functionalized mono-, di- and tri- substituted triphenylamine derivatives: A comparative study

> Figure 7. 1. Chemical structures of DPP and ferrocenyl-DPP based derivatives **TPA-DPPs 1-6**.....168 Figure 7. 2. Normalized UV-vis absorption spectra of DPP and ferrocenyl-DPP based derivatives with TPA as central core Figure 7. 3. Emission spectra of DPP based derivatives TPA-**DPP 2–6** in DCM......173 Figure 7. 4. Thermogravimetric analysis of TPA-DPPs 1-6 under a nitrogen atmosphere.....174 Figure 7. 5. Time resolved decay curves of TPA–DPPs 1–3 at Figure 7. 6. CV (black line) and DPV (red line) curves of TPA-Figure 7. 7. The FMOs of DPP and ferrocenyl-DPP based derivatives **TPA–DPPs 1** and **4** estimated by DFT calculations. Figure 7. 8. The FMOs of DPP and ferrocenyl-DPP based derivatives TPA-DPPs 2 and 5 estimated by DFT calculations. Figure 7. 9. The FMOs of DPP and ferrocenyl-DPP based trimers TPA-DPPs 3 and 6 estimated by DFT calculations. 180

#### **LIST OF SCHEMES**

#### **Chapter 01: Introduction**

Scheme 1. 1. Proposed reaction mechanism for the synthesis of
DPP by Farnum
Scheme 1. 2. Updated reaction mechanism suggested for the
synthesis of DPP by Ciba-Geigy5
<b>Scheme 1. 3.</b> Retrosynthetic analysis of DPP6
Scheme 1. 4. Synthesis of DPP by succinic method
Scheme 1. 5. Synthesis of multiple DPPs during mixed
condensation reaction7
Scheme 1. 6. Synthesis of DPP from 8 or 97
<b>Scheme 1. 7.</b> Synthesis of DFF ( <b>13</b> )
<b>Scheme 1. 8.</b> Synthesis of DPP <b>16</b> from DFF ( <b>13</b> )9
Scheme 1. 9. Synthesis of DPP by succinic amide9
Scheme 1. 10. Different Mesomeric structures of anions
formed by deprotonation of DPP11
Scheme 1.11. Alkylation of DPPs using CsCO <sub>3</sub> and
acetonitrile
Scheme 1.12. Synthesis of water soluble DPP 32 by Gryko and
coworkers
Scheme 1. 13. Synthesis of <i>N</i> -arylated DPP13
Scheme 1. 14. Various reactions of carbonyl group of DPP 2.
Scheme 1. 15. Synthesis of expanded DPP 4815
Scheme 1. 16. Halogenation of DPP 2
Scheme 1. 17. Coupling Reactions of Dibromo DPPs

#### 

### Chapter 04: Symmetrical and Unsymmetrical *N*, *N*-dimethylaniline/Triphenylamine Functionalized

#### **Diketopyrrolopyrrole**s

#### Chapter 05: Impact of Donor Strength on [2+2] Cycloaddition-Retroelectrocyclization in Tetracyanobutadiene-Functionalized Diketopyrrolopyrrole Derivatives.

Scheme 5. 1. Synthetic scheme of ferrocene based DPPs	
FcDPPs 1, 3 and 6	.117
Scheme 5. 2. Synthetic scheme of ferrocene based DPP	
derivatives FcDPPs 2, 4, 5, 7, 8 and 9	.119

#### Chapter 06: Phenothiazine Based Diketopyrrolopyrrole

#### **Derivatives Functionalized with Different Donors**

Scheme 6. 1. Synthesis of Diketopyrrolopyrrole based
intermediates <b>2–4</b> 145
Scheme 6. 2. Synthesis of phenothiazine functionalized DPPs
<b>P-1–P-3</b>
Scheme 6. 3. Synthesis of phenothiazine functionalized DPPs
<b>P_4_P_6</b> 146

Chapter 07: Ferrocenyl-diketopyrrolopyrroles functionalized mono-, di- and tri- substituted triphenylamine derivatives: A comparative study

#### **LIST OF TABLES**

Chapter 03: Design and synthesis of *N*-phenyl carbazole substituted diketopyrrolopyrrole based monomers and dimers: A comparative study

# Chapter04:SymmetricalandUnsymmetricalN.dimethylaniline/TriphenylamineFunctionalizedDiketopyrrolopyrroles

 Table 4. 1. The optical and theoretical/computational properties

 of NDPPs 1–8.
 .90

 Table 4. 2. The redox properties<sup>a</sup> of symmetrical and

 unsymmetrical DPP based derivatives NDPPs 1–8.

 .95

 Table 4. 3. Major electronic transitions of NDPPs 1-8 calculated

 by TD-DFT.

 .97

Chapter 05: Impact of Donor Strength on [2+2] Cycloaddition-Retroelectrocyclization in Tetracyanobutadiene-Functionalized Diketopyrrolopyrrole Derivatives.

<b>Table 5. 1.</b> The optical and theoretical/computational properties
of <b>FcDPPs 1-8</b> 123
Table 5. 2. The electrochemical properties <sup>a</sup> of ferrocene-based
derivatives FcDPP 1–FcDPP 8124
Table 5. 3. Major electronic transitions of FcDPPs 1–8
calculated by TD-DFT

#### **Chapter 06: Phenothiazine Based Diketopyrrolopyrrole Derivatives Functionalized with Different Donors**

Table 6. 1. The optical and theoretical/computation	ional properties
of <b>P-1–P-6</b>	149
Table 6. 2. The electrochemical properties <sup>a</sup> of	phenothiazine
based DPPs P-1–P-6.	151
Table 6. 3. Major electronic transitions of P-1–P-	<b>6</b> calculated by
TD-DFT	154

Chapter 07: Ferrocenyl-diketopyrrolopyrroles functionalized mono-, di- and tri- substituted triphenylamine derivatives: A comparative study

Table 7. 1. The optical properties of DPP and ferrocenyl–DPP
based derivatives with TPA as central core TPA-DPPs 1-6.
Table 7. 2. The electrochemical properties of DPP and
ferrocenyl-DPP based derivatives with TPA as central core
<b>TPA–DPPs 1–6</b>
Table 7. 3. Major electronic transitions of TPA-DPPs 1-6
calculated by TD-DFT181
# NOMENCLATURE

λ	Wavelength
3	Extinction coefficient
α	Alfa
β	Beta
γ	Gamma
π	Pi
φ	Fluorescence
	quantum yield
σ	Sigma
Å	Angstrom
nm	Nanometer
cm	Centimeter
0	Degree
°C	Degree Centigrade
mmol	Millimol
mL	Milliliter
μL	Microliter
a. u.	Arbitrary Unit

# ACRONYMS

D-A	Donor-acceptor
NMR	Nuclear Magnetic Resonance
PPh <sub>3</sub>	Triphenylphosphin
DMF	Dimethylformamide
DCM	Dichloromethane
Ph	phenyl
IR	Infrared
UV-Vis	UV-Visible Spectroscopy
Calcd.	Calculated
CDCl <sub>3</sub>	Chloroform-d
ESI-MS	Electrospray Ionization- Mass
	Spectrometry
EtOH	Ethanol
MeOH	Methanol
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TEA	Triethylamine
EAA	Ethylacetate
Tol	Toluene

# **Chapter 01: Introduction**

## 1.1.Background

Push-pull chromophores with extended  $\pi$ -conjugation have attracted significant interest within the scientific community. This is primarily attributed to their broad utility across various domains such as optoelectronics, data storage, OLEDs, and biological research.<sup>[1]</sup> These molecules are characterized by a conjugated core with an electrondonating (push) group and an electron-withdrawing (pull) group at opposing ends. The asymmetric distribution of electron density within the molecule creates a dipole moment, resulting in unique electronic properties that make push-pull chromophores highly versatile. The photonic and electronic properties of the push-pull systems can be easily tuned by altering the strength of push and pull units in the  $\pi$ -conjugated systems.<sup>[2]</sup> The combination of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of push and pull units in the push-pull systems result in a set of new HOMO and LUMO energy levels as shown in Figure 1.1, which is more tuned compared to individual HOMO and LUMO energy levels of push and pull units and also exhibited narrow energy gap. Thus, the HOMO-LUMO energy gap of organic chromophores can be effectively perturbed by altering the donor and acceptor units in the push-pull systems.<sup>[3]</sup>



Figure 1. 1. Schematic representation of frontier molecular orbitals of push-pull chromophore.

Emerging Applications of Push-Pull Chromophores:

- 1. In the field of optoelectronics, push-pull chromophores play a crucial function in shaping emission wavelengths and promoting effective charge transfer. This amplifies sensitivity in photodetectors and empowers the fine-tuning of light emission in OLEDs, thus propelling advancements in optoelectronic technologies.<sup>[4]</sup>
- 2. Push-pull chromophores are crucial in nonlinear optics, particularly in photonic devices like modulators and switches, due to their strong nonlinear optical responses.<sup>[5]</sup> These devices are essential for signal processing and telecommunications, utilizing the light manipulation capabilities of push-pull chromophores to enhance nonlinear functionalities.
- 3. In photovoltaics, especially in organic solar cells <sup>[6]</sup>, push-pull chromophores utilize efficient light absorption, adjustable energy levels, and charge mobility to enhance power conversion efficiency.
- 4. Across various sensing technologies, push-pull chromophores play a vital role in chemical sensors <sup>[7]</sup> and imaging probes <sup>[8]</sup> via

enhancing sensitivity and selectivity in chemical detection. Through their functionalization, they facilitate accurate detection and imaging across a spectrum of biological and medical applications.

#### **1.2. Diketopyrrolopyrrole (DPP)**

The distinctive feature of DPP pigment lies in its fundamental structure comprising two amine units and carbonyl groups forming a bicyclic structure. This particular arrangement imparts strong electron deficient character to DPP pigments, rendering them suitable for designing donor-acceptor (D-A) conjugated materials. The initial design and synthesis of DPP pigments by Farnum and co-workers in 1974 involved incorporating two phenyl units, resulted in a low yield of the compound *i.e.* a fused ring hydrocarbon called pentalene with eight  $\pi$  electrons, exhibited high insolubility in organic solvents and displayed a deep red colour. <sup>[9]</sup> Later, Iqbal and co-workers adapted the synthesis technique involving just one reaction step employing an aromatic nitrile and dialkyl succinate.<sup>[10]</sup> This alteration paved the way for producing various DPP derivatives spanning a range of colours. These derivatives include isomeric DPP as well as DPP variants flanked by phenyl, pyridyl, thienyl, furanyl, or seleneyl groups as shown in Figure 1.2. Incorporation of these diverse groups altered the planarity of the DPP pigment, its energy levels, and the distance between  $\pi$ - $\pi$  stacking. DPP pigments exhibit low solubility because of the hydrogen bonding established by the core carbonyl and amine units in their solid state. However, introducing alkyl chains can disrupt this hydrogen bonding, resulting in improved solubility. DPP chromophores and their derivatives are essential in designing high-performance materials for electronic devices, including sensors and solar cells. Numerous articles have been published highlighting the applications of DPP chromophores in organic field-effect transistors (OFETs)<sup>[11]</sup>, sensors<sup>[12]</sup>, and solar cells<sup>[13]</sup>, emphasizing the effect of structural modifications and band gap engineering on the device properties. Researchers are particularly interested in exploring structural modifications and optimizing energy level alignment and morphology/crystallinity to achieve high performance in organic photovoltaic (OPV) devices.



Figure 1. 2. Structure of DPP flanked with different aromatic groups.

#### **1.3. Synthesis of Diketopyrrolopyrrole**

#### **1.3.1.** Preparation of DPP through the Reformatsky approach.

During the early 1970s, Donald Farnum and his research group endeavored to produce  $\beta$ -lactam **1** by reacting ethyl bromoacetate with benzonitrile in the presence of zinc using the Reformatsky method. Instead of the desired product, they unexpectedly isolated a previously unknown product **2** as shown in Scheme 1.1, possessing unique properties such as bright red colour and low solubility.<sup>[9]</sup> Farnum proposed a reaction mechanism which was later found to be incorrect. In the 1980's, Scientists of Ciba-Geigy revisited Farnum's work, revealing a true mechanism involving the Reformatsky reaction involving ethyl bromoacetate and benzonitrile.<sup>[10],[14]</sup> Subsequent alkylation and cyclization steps led to the formation of DPP **2** as shown in Scheme 1.2. In 2005, Shaabani *et al.* improved the yield by using a modified Reformatsky reaction upto 70%.<sup>[15]</sup>



**Scheme 1. 1.** Proposed reaction mechanism for the synthesis of DPP by Farnum.



**Scheme 1. 2.** Updated reaction mechanism suggested for the synthesis of DPP by Ciba-Geigy.

#### **1.3.2.** Succinic method

A retrosynthetic approach (Scheme 1.3) proposed by the scientists of Ciba-Geigy indicated that starting with benzonitrile and a succinic acid ester would be favoured. In fact, benzonitrile reacts with dialkyl succinate when alkali metal alkoxides are present, efficiently producing **DPP 2**. This reaction under the Reformatsky conditions, results in the direct formation of diester **4** from succinate and nitrile (Scheme 1.2.). Fine-tuning of conditions revealed optimal results using specific parameters, rendering the succinic method a proficient approach for DPP synthesis, particularly from unhindered aromatic nitriles. Despite limitations associated with nitriles that are either rich in electrons or impeded by large groups, Ciba-Geigy's base-promoted condensation of nitriles with succinic acid esters (Scheme 1.4.) remains a widely employed and practical method, offering simplicity, a wide range of usable nitriles, and high yields.<sup>[10], [14], [16]</sup>



Scheme 1. 3. Retrosynthetic analysis of DPP.



Scheme 1. 4. Synthesis of DPP by succinic method.

#### **1.3.3.** Condensation approach and related methods

The following synthetic method addresses the challenge of obtaining asymmetrical DPPs exclusively, overcoming limitations observed in the succinic method. While the succinic method is effective for symmetric DPPs, it faces difficulties in the synthesis of asymmetrical pigments due to the formation of various DPP derivatives as shown in Scheme 1.5., making separation challenging.<sup>[10],[14]</sup> In order to tackle this issue, chemists at Ciba-Geigy developed a method based on the reaction of nitriles with aminoester 8 or lactam 9 under basic conditions. Aminoester 8 can be obtained by reacting a nitrile with the dianion 7 produced from succinic ester. Upon exposure to acidic conditions, compound 8 cyclizes to form 3-alkyloxycarbonyl-2-pyrrolin-5-one (9). Both aminoester 8 and lactam 9 undergoes a reaction with nitriles in the presence of alkoxides, resulting in the formation of DPP. (Scheme 1.6). This approach enables the precise synthesis of both symmetric and asymmetric DPP pigments with excellent efficiency.<sup>[17]</sup>



Scheme 1. 5. Synthesis of multiple DPPs during mixed condensation reaction.



Scheme 1. 6. Synthesis of DPP from 8 or 9.

# **1.3.4.** Synthesis of DPPs using 2,5-Dihydrofuro[4,3-c]furan-1,4diones (DFFs) as precursors.

The following method involves converting unstable bisdiazotetraketones 12 into 13 diketofurofurans (DFFs) by heating, with milder conditions achieved through refluxing the suspension in toluene as shown in Scheme 1.7. <sup>[18]</sup> This provides an alternative route for the DFF synthesis via the thermolysis of diacylsuccinates. DFFs derivatives lack intermolecular hydrogen bonding as seen in corresponding DPP pigments. The process of synthesis of *N*, *N*-diaryl DPP **16** from DFF, involves interactions with aromatic amines using DCC and a catalytic amount of TFA as shown in Scheme 1.8. This convenient method, demonstrated by Langhals and co-workers, involves nucleophilic attack, ringopening elimination, and cyclization, enabling controlled and efficient DFF to DPP transformation.<sup>[19]</sup> This method broadens the availability of symmetrical tetraaryl DPPs, thus acting as reactants in the synthesis of various functional dyes.



Scheme 1. 7. Synthesis of DFF (13).



Scheme 1. 8. Synthesis of DPP 16 from DFF (13).

# 1.3.5. Additional alternative techniques for synthesizing DPPs

Gompper *et al.* introduced a different method for synthesizing DPP, using succinic acid diamide and *N*, *N*-dimethylbenzamide diethyl acetal (**19**), resulting in the formation of DPP **2** in 30% yield, along with compound **21**. Conversion of **21** to DPP **2** using potassium tert-butoxide results in an overall DPP yield of around 60%. The reaction of succinic amide with tetramethylurea acetal (**20**) forms non-conjugated tautomer **22** which undergoes *N*-methylation to produce yellow DPP derivative **23** with trimethyloxonium salt (Scheme 1.9.). Despite lower synthetic importance, these methods provide diverse pathways for obtaining different DPP derivatives.<sup>[20]</sup>



Scheme 1. 9. Synthesis of DPP by succinic amide.

#### 1.4. Reactive functionalization sites of DPP/ Reactions of DPP

The structure of DPP incorporates various chemically active functional groups. These groups exhibit distinct reactivity characteristics. Notably, certain units within the structure are susceptible to electrophilic attack such as the oxygen and nitrogen atoms within the amide moiety, the double bonds within the DPP, and the aromatic rings situated at the 3 and 6 positions. Conversely, nucleophilic attacks are also plausible, involving the carbonyl carbon atom and the  $\alpha$ ,  $\beta$ -unsaturated system within the bicyclic DPP unit. Such nucleophilic additions occur at the 3 and 6 positions. In specific instances, nucleophilic reactions may extend to the aromatic substituents.



Figure 1. 3. Functionalization sites of Diketopyrrolopyrrole.

# 1.4.1. Reactive amide group of DPP

In alkaline conditions, diketopyrrolopyrrole (DPP) undergoes deprotonation, forming ambidentate anions, where the negative charge is dispersed between the oxygen and nitrogen atoms of the amide group. (**24** and **25**, Scheme 1.10.). The charge can alternatively shift to the other oxygen atom, creating a mesomeric structure (**26**). This stabilization contributes to DPP's relatively high acidity.<sup>[21]</sup> Despite this, DPP pigments exhibit low solubility due to strong intermolecular hydrogen bonding, necessitating the use of solvents with partial dissolution capabilities.



**Scheme 1. 10.** Different Mesomeric structures of anions formed by deprotonation of DPP.

The enhancement of solubility in standard organic solvents is achieved by alkylation of the DPP molecule using alkyl halides or alkyl sulfonates in the presence of potassium carbonate. Typically, alkylations are carried out in dimethylformamide (DMF) at temperatures exceeding 100 °C. [22],[23] The reactivity towards alkylation is influenced by the aromatic substituents at 3 and 6 positions of the DPP, affecting the solubility and acidity thus, aprotic and polar solvents, notably DMF, are commonly employed in such reactions. Similarly, Amabilino and co-workers employed acetonitrile (MeCN) as alternative solvent for DPP alkylation in place of most commonly used solvent DMF, where they utilized Cesium carbonate as a catalyst, as demonstrated in Scheme 1.11.<sup>[24]</sup> Recent advancements have focused on synthesizing water-soluble Diketopyrrolopyrrole 32 by coupling 31 with Nalkyl substituents containing quaternary ammonium moieties. Gryko and coworkers conducted this reaction in dimethylformamide (DMF) at 40 °C for 1 hour, employing sodium hydride (NaH) and subsequently replacing the bromide counterion with a chloride anion using sodium chloride (NaCl) in water (Scheme 1.12).<sup>[25]</sup>



Scheme 1.11. Alkylation of DPPs using CsCO<sub>3</sub> and acetonitrile.



Scheme 1.12. Synthesis of water soluble DPP 32 by Gryko and coworkers.

Riggs *et al.* conducted one side *N*-arylation of DPP by reacting ester **33** with *N*-arylbenzimidoyl chloride **34**, resulting in the formation of mono-*N*-arylated DPP **35** in 63% yield and enamine **36** (Scheme 1.13).<sup>[26]</sup> Subsequent reactions of **35** with methyl-*p*toluenesulfonate and potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) in dimethylformamide (DMF) yielded unsymmetrical DPP **37** in 56– 89% yield, while the treatment of **35** with benzyl bromide produced the *N*-benzyl DPP derivative **38** in 63–95% yield. Furthermore, the reaction of DPP **35** with 1-fluoro-2,4dinitrobenzene resulted in the formation of DPP **39** in 80–82% yield (Scheme 1.13). <sup>[26]</sup>



Scheme 1. 13. Synthesis of *N*-arylated DPP.

#### 1.4.2. Reactions of carbonyl group of DPP

The carbonyl groups in DPP, act as electrophilic center and can undergo various transformations. When treated with  $P_4S_{10}/LR$ (Lawesson's reagent), DPPs yield dithioketo-pyrrolopyrroles (**40**) in good yields (Scheme 1.14).<sup>[20], [27]</sup> By this method, DPP **2** was converted to dithiolactam **40**, a compound existing in several polymorphic crystalline forms. The resulting compounds were studied for their photophysical and electronic properties, mainly by Mizuguchi and co-workers.<sup>[28]</sup> Compound (**40**) reacts with alkyl halides to primarily yield *S*, *S*-dialkylated compound **41**.<sup>[20], [29], [30]</sup> This discrepancy is attributed to the superior nucleophilicity of sulfur atoms compared to nitrogen or oxygen atoms. The alkylthiol groups in diazapentalenes (**41**) are very reactive and undergo nucleophilic substitution reactions as their interaction with malononitrile sodium salt leads to the production of the dicyanomethylene derivative **42**. <sup>[20]</sup> The direct substitution of carbonyl oxygen atoms in DPP with nucleophiles poses a challenge; however, activation of the carbonyl group can be achieved by employing phosphoryl chloride. Chemists from Ciba-Geigy developed a method to activate carbonyl groups in DPP using POCl<sub>3</sub> where DPP 2 is heated with an excess of POCl<sub>3</sub> and catalytic DMF, it results in the production of phosphorylated salt 43 as shown in Scheme 1.14. [31] which is more reactive toward nucleophiles than the starting DPP and undergoes reactions with sodium sulfide and aromatic amines, leading to monothiocarbonyl DPP derivative **44** and dye **45**, respectively.<sup>[31]</sup> Würthner *et al.* introduced a novel approach for expanding the DPP chromophore, which involves combining the aromatic nucleophilic substitution reaction of DPP with the substitution of carbonyl oxygen atoms using aromatic amines.<sup>[32]</sup> Initially, arylation of DPP with 1fluoro-2-nitro-4-(trifluoromethyl)benzene results in the formation of N, N-diaryl derivatives with moderate yields (50-57%). The subsequent reduction of nitro groups to amino groups followed by reaction with TiCl<sub>4</sub> and DABCO in mesitylene at elevated temperatures leads to the generation of fully conjugated polycyclic compounds of type 48.<sup>[32]</sup> These compounds feature a rare 6-5-5-5–5–6 fused ring system as shown in Scheme 1.15.



Scheme 1. 14. Various reactions of carbonyl group of DPP 2.

The reactions and transformations described above showcase the versatility of DPP structures and their potential applications in various fields, including materials science and organic electronics.



Scheme 1. 15. Synthesis of expanded DPP 48

#### 1.4.3. Reactions at 3 and 6 positions of DPP

Various Diketopyrrolopyrrole (DPP) derivatives with aromatic substituents at positions 3 and 6 are explored in the literature. <sup>[33-36]</sup> These aryl groups are integral constituents of dyes and pigments derived from the DPP framework, participating in characteristic reactions typical of aromatic compounds, particularly electrophilic aromatic substitution. DPP **2** also reacts differently with bromine and chlorine, leading to *para*-dibrominated DPP **49** and a chlorine addition product **50**, respectively (Scheme 1.16.).<sup>[10]</sup>



Scheme 1. 16. Halogenation of DPP 2.

Bromination of *N*, *N*-disubstituted DPPs with heteroaromatic substituents (thiophene, furan, and selenophene) is highly efficient. These DPP derivatives serve as starting materials in Pd-catalyzed cross-coupling reactions, including the Suzuki<sup>[33]</sup>, Stille<sup>[34]</sup>, Heck<sup>[33]</sup>, Sonogashira<sup>[35]</sup>, and Buchwald–Hartwig<sup>[36]</sup> reactions (Scheme 1.17). These reactions proceed in high yields, expands the DPP chromophore and shifts the absorption maxima, making them useful for applications in semiconducting devices like organic field-effect transistors (OFETs) and organic photovoltaics (OPVs).



Scheme 1. 17. Coupling Reactions of Dibromo DPPs.

#### 1.5. Applications of Diketopyrrolopyrroles

The donor-acceptor functionalized DPP based chromophores have garnered considerable interest across diverse applications, encompassing organic light-emitting diodes (OLEDs), photovoltaic devices and bioimaging. The following segment explores important applications of DPP based derivatives.

#### 1.5.1. Organic solar cells

As global warming escalates, the need for eco-friendly and non-CO<sub>2</sub> emitting electricity production is in demand. To harness photovoltaic cells as a clean energy source and reducing the cost of solar energy production is crucial.<sup>[37]</sup> The primary hurdle lies in the high cost of crystalline silicon.<sup>[38]</sup> A promising alternative is thin films of organic small molecules/polymers, offering easy application over diverse substrates using wet-processing techniques. Organic solar cells (OSCs), particularly smallmolecule and polymer-based type derivatives, attract attention for their simple structure, ease of fabrication, and low production costs. Achieving a precise balance in device fabrication, morphology, molecular design, and interfacial layers is key for maximizing Power Conversion Efficiencies (PCEs). Smallmolecule OSCs employ highly conjugated systems, while polymer-based OSCs use long-chained molecular systems. These solar cells can be further classified into three types based on production methods: organic bulk heterojunction thin-film solar cells, organic tandem solar cells, and organic dye-sensitized solar cells.

#### 1.5.1.1. Bulk heterojunction organic solar cells

Bulk Heterojunction (BHJ) solar cells employ a single layer with donor and acceptor materials to convert solar energy into electricity. The basic structure of device includes a glass substrate, a transparent metal electrode, a hole contact layer, BHJ active layer, and an electron contact.<sup>[39]</sup> The simplified working principle involves photon absorption, exciton formation, exciton diffusion and splitting, charge transportation, and charge collection. <sup>[39]</sup> The donor material, usually a conjugated polymer, absorbs light, generate excitons with an electron-hole pair. The BHJ interface facilitates exciton splitting, ensuring electron and hole carriers to reach their respective electrodes without recombination. The active layer should possess wide absorption, nanoscale phase separation, suitable HOMO/LUMO alignment, and high charge mobility. BHJ solar cells, introduced in 1995, offer advantages like low cost, light weight, and easy fabrication compared to traditional photovoltaic devices.<sup>[40]</sup>

Chen and co-workers synthesized star-shaped donor-acceptor (D-A) small molecules, denoted as **51**, **52**, and **53**, *via* Suzuki cross-coupling reaction (Figure 1.4).<sup>[41]</sup> These compounds displayed narrow optical band gaps (1.68–1.72 eV) and low-energy highest occupied molecular orbital (HOMO) levels ( $-5.09 \sim -5.13$  eV), indicating their promising suitability as electron donors in organic solar cells (OSCs). Subsequently, the photovoltaic characteristics of these small molecules when blended with [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) as the electron acceptor were examined. Among them, the OSC incorporating the **51**:PC<sub>61</sub>BM blend demonstrated the highest power conversion efficiency (PCE) of 2.98%, exhibiting an open-circuit

voltage (V<sub>oc</sub>) of 0.72 V, a short-circuit current density (J<sub>sc</sub>) of 7.94 mA/cm<sup>2</sup>, and a fill factor (FF) of 52.2%. This superior performance is attributed to the highest hole mobility of molecule **51** compared to **52** and **53**, which yielded PCE of 1.63% and 1.98%, respectively.<sup>[41]</sup>



Figure 1. 4. DPP based chromophores for BHJ organic solar cells.

#### 1.5.1.2. Dye sensitized solar cells (DSSC)

Dye-sensitized solar cells (DSSCs) are a hybrid organic-inorganic system that uses small-molecule absorber dyes adsorbed onto electron-accepting materials such as titanium dioxide. These cells, introduced in 1991, have gained attention for their lightweight, colorful, and flexible characteristics, making them an alternative to conventional silicon-based solar cells due to their low cost and simple fabrication.<sup>[42]</sup>DSSCs consist of a mesoporous metal oxide semiconductor sensitized with an organic dye as the working electrode, supported by a transparent electrode and counter electrode with an electrolytic solution between them. The four major steps in DSSC operation include photon absorption, electron ejection, carrier transportation, and dye regeneration. The cell's efficiency is determined by factors like photocurrent density,

open circuit voltage, and fill factor.<sup>[43]</sup> The sensitizer, a crucial component, influences light harvesting and charge separation, with various donor-acceptor groups and metal-free organic dyes being explored for enhanced performance.

Yemene *et al.* synthesized five DPP chromophores, designated as **54–58**, utilizing direct C-H arylation with a 3,6-dithienyl backbone (Figure 1.5).<sup>[44]</sup> These chromophores exhibited broad absorption spanning 350–800 nm with high molar extinction coefficients. In terms of power conversion efficiency (PCE) for dye-sensitized solar cells (DSSCs), the performance of all five dyes was relatively similar, ranging from 2.83% – 3.35%. Dyes incorporating phenothiazine as a linker (**54**, **55**, and **58**) demonstrated higher open-circuit voltage (V<sub>oc</sub>) compared to those with phenyl linkers. Notably, dye **57**, featuring phenothiazine as the donor and phenyl as the spacer, exhibited the highest short-circuit voltage (J<sub>sc</sub>). When combined with Chenodeoxycholic acid (CDCA), dye **57** showed an increased PCE of 3.41%. Enhancing the performance of these dyes could be achieved through device engineering strategies.<sup>[44]</sup>



Figure 1. 5. DPP based chromophore for dye sensitized solar cells.

### 1.5.1.3. Perovskite solar cells (PSCs)

Perovskite solar cells (PSCs) are a type of solar cell that utilizes perovskite-structured materials as the light-harvesting active layer. The perovskite structure typically involves a metal cation (such as lead or tin), an organic cation (such as methylammonium or formamidinium), and a halide anion (such as iodide or bromide). The unique crystalline structure of perovskite materials allows for efficient absorption of sunlight and the generation of electric charge carriers. PSCs have garnered significant attention in recent years due to their rapid progress in efficiency and the ease of fabrication. They offer advantages such as low-cost production, simple processing methods (including solution-based processes), and the potential for flexibility in design and application. [45] However, challenges remain, including stability

issues, toxicity concerns associated with lead-based perovskites, and scalability hurdles. Researchers continue to explore and develop new perovskite formulations, encapsulation techniques, and device architectures to address these challenges and unlock the full potential of perovskite solar cells for large-scale, efficient, and sustainable solar energy harvesting.

Kini and co-workers designed and synthesized two Hole transporting materials (HTMs) based on DPP via a straightforward approach (Figure 1.6).<sup>[46]</sup> These molecular engineering compounds displayed intense absorption within the wavelength range of 500 to 750 nm. The photovoltaic device utilizing HTM 59, doped with lithium bis(trifluoromethanesulfonyl)imide, achieved a maximum power conversion efficiency (PCE) of 15.57%. This remarkable efficiency was attributed to excellent energy level alignment, optimal balance between aggregation and processability, facilitating effective passivation of the perovskite layer through enhanced surface coverage and suppression of charge recombination. Conversely, HTM 60 exhibited a slightly lower PCE of 14.49%, primarily due to its poor film quality stemming from its propensity for high aggregation.<sup>[46]</sup>



Figure 1. 6. DPP based chromophore for PSCs.

#### 1.5.2. Photothermal cancer therapy

Photothermal therapy (PTT) has emerged as a promising approach for cancer treatment due to its high selectivity towards tumor cells and minimal side effects, addressing limitations of traditional methods like chemotherapy and surgery.<sup>[47]</sup> PTT involves using light-absorbing agents to convert near-infrared (NIR) light into heat energy, destroying tumor cells. Accurate tumor localization and sizing are crucial, leading to the integration of non-invasive imaging techniques. Photoacoustic (PA) imaging, with its spectral selectivity and ability to reconstruct optical absorption distribution, serves as an effective tool.<sup>[48]</sup> Various photothermal transducers, including organic agents, have been developed to enhance PTT efficacy. PTT, through NIR laser-induced tumor cell ablation, is gaining attention for its high selectivity and noninvasiveness in cancer treatment.

In the pursuit of synergistic cancer therapy, there exists a compelling imperative to devise a singular, versatile compound proficient in amalgamating photodynamic therapy (PDT), photothermal therapy (PTT), and chemotherapy modalities. The desired compound should additionally demonstrate solubility, responsiveness to minimal irradiation levels, and exceptional tumor-targeting efficacy. To achieve this objective, Dong et al. have conjugated the chemotherapy drugs chlorambucil and alltrans retinoic acid onto a small dye molecule diketopyrrolopyrrole (designated as **61** and **62**) as shown in Figure 1.7.<sup>[49]</sup> The resultant soluble nanoparticles (NPs) of 61 and 62, formed via reprecipitation, exhibit selective accumulation in tumors, release chemotherapy drugs under acidic conditions, and demonstrate efficient generation of reactive oxygen species (ROS) and photothermal conversion under low-power xenon lamp irradiation (40 mW/cm<sup>2</sup>). Both NP formulations effectively eradicate cancer cells and suppress cancer growth at a low dosage (0.4 mg/kg).<sup>[49]</sup>



Figure 1. 7. DPP based nanoparticles for Photothermal cancer therapy.

#### 1.5.3. Fluorescent Probes

Fluorescent probes are invaluable tools for analyte detection due to their simplicity, selectivity, sensitivity, rapid response, and interference resistance and play critical roles across various fields including life sciences, environmental monitoring, human health, and industries such as food and pharmaceuticals. Diketopyrrolopyrrole (DPP) dyes, encompassing small molecules, polymers, and organic nanoparticles and act as promising fluorescent probes owing to their advantageous properties including high photostability, fluorescence quantum yields, and thermal stability.

Probe **63**, featuring  $\alpha$ ,  $\beta$ -unsaturated ketone and DPP components, was tailored for the selective and sensitive detection of CN<sup>-</sup> ions. Its reaction with CN<sup>-</sup> ions resulted in a distinctive blue shift in the UV-vis spectrum, accompanied by a colour change in solution. Furthermore, the fluorescence of probe **63** was completely quenched upon interaction with CN<sup>-</sup> ions, demonstrating a remarkably low detection limit. Additionally, test strips based on probe **63** proved effective in detecting CN<sup>-</sup> ions in solutions.<sup>1501</sup> On the other hand, probe **64**, a versatile and highly selective probe, was developed for the detection of Al<sup>3+</sup> and Fe<sup>3+</sup> ions, each eliciting distinct

fluorescence signals. The addition of  $Al^{3+}$  ions led to significant changes in the absorption spectrum, while Fe<sup>3+</sup> induced a different absorption response along with alterations in fluorescence emission characteristics. These findings underscore the potential of probes **63** and **64** as valuable tools for analytical and diagnostic applications in various domains (Figure 1.8).<sup>[50]</sup>



Figure 1.8. DPP based chromophores as fluorescent probes.

### **1.5.4.** Electrochromic applications

Electrochromism is a phenomenon where the absorption and emission spectra of certain dyes can shift significantly under a strong electric field. It involves reversible colour changes in response to electrochemical reactions, typically transitioning between transparent and coloured states or between different coloured states.<sup>[51]</sup> Electrochromic materials may exhibit multiple colours if more than two redox states are available, termed polyelectrochromic or multicolour electrochromism. This optical change is induced by a small electric current at low voltages. Electrochromic devices function like rechargeable batteries, with an electrochromic electrode separated from a counter electrode by an electrolyte, undergoing colour changes through charging and discharging the electrochemical cell.

Lim and co-workers developed and created a small molecular electrochromic material utilizing a DPP framework along with substantial side chains. This material, identified as **65**, consisted of a core composed of dithiophene-phenylene, a  $\pi$ -linker of DPP, and an end unit of rhodanine (Figure 1.9.). The electrochromic

behavior of molecule **65** led to a blue colouration with rapid switching occurring in just 0.4 seconds and a coloration efficiency exceeding  $300 \text{ cm}^2/\text{C}$ . <sup>[52]</sup>



Figure 1. 9. DPP based chromophore for electrochromic applications.

#### 1.5.5. Two photon absorption (TPA)

Two-photon absorption (TPA) is a nonlinear optical phenomenon where two photons, collectively possessing sufficient energy, are simultaneously absorbed by a molecule or material, causing an electronic excitation. This process occurs when the energy of individual photons is insufficient for electron transition, but when combined, they meet the required energy threshold.<sup>[53]</sup> TPA is more likely in materials with high nonlinear susceptibilities, characterized by large transition dipole moments and electronic resonances. TPA finds applications in various fields:

1. **Multiphoton Microscopy:** TPA is extensively used in techniques like two-photon fluorescence microscopy and second harmonic generation microscopy, offering reduced photodamage and increased penetration depth compared to onephoton excitation methods.<sup>[54]</sup>

- 2. **Optical Data Storage:** TPA is explored for highdensity optical data storage systems, enabling subdiffraction-limited spatial resolution and encoding information in precise three-dimensional structures.<sup>[55]</sup>
- 3. **Photodynamic Therapy (PDT):** TPA is utilized in targeted cancer treatment, activating photosensitizing agents selectively in tumor tissues with near-infrared light, inducing localized cytotoxicity and tumor cell death.<sup>[56]</sup>
- 4. Advanced Optical Devices and Sensors: Materials exhibiting strong TPA characteristics are studied for all-optical switches, modulators, and sensors, offering nonlinear optical response and potential performance enhancements.<sup>[57]</sup>

Overall, TPA presents unique advantages in various scientific and technological domains, driving ongoing research and technological advancements.

Grzybowski and co-workers devised and synthesized novel  $\pi$ -expanded diketopyrrolopyrroles (**66–69**) as shown in Figure 1.10.<sup>[58]</sup> Through strategic positioning of a fluorene framework at the edges of diketopyrrolopyrrole *via* tandem Friedel–Crafts-dehydration reactions, they produced dyes with exceptional solubility. Photophysical analyses of these innovative dyes revealed superior properties compared to expanded DPPs, particularly in terms of two-photon absorption cross-section. By introducing two amine groups at the peripheral positions of resulting dyes (**68** and **69**), two-photon absorption cross-section values reaching around 2000 GM at approximately 1000 nm were attained. Coupled with high fluorescence quantum yields (0.84–0.96), these dyes exhibited a two-photon brightness of roughly 1600 GM. With strong red emission (665 nm), these newly developed  $\pi$ -expanded diketopyrrolopyrroles show significant potential as two-photon dyes for bioimaging applications.<sup>[58]</sup>



Figure 1. 10. DPP based chromophore for TPA based applications.

## 1.5.6. Aggregation-Induced Emission (AIE)

The phenomenon of AIE was first observed by Scheibe and Jelley in 1936, and the term "aggregation-induced emission" was officially coined by Tang and his coworkers in the early 2000s, where emission occurs when molecules are in an aggregated state.<sup>[59]</sup> AIE was observed in the  $\pi$ conjugated fluorescent organic materials containing functional groups capable of free rotation, such as triphenylamine or tetraphenylethene. However, understanding the AIE mechanism poses challenges as it contradicts classical photophysics concepts. Multiple mechanisms have been proposed to explain Aggregation-Induced Emission (AIE), including the restriction of intramolecular rotation (RIR), the suppression of intramolecular transfer (ICT), twisted charge intramolecular charge transfer (TICT), and the generation of J-aggregates.<sup>[60]</sup> Despite ongoing efforts, a universal theory to explain AIE remains evasive, but significant research is underway to identify AIE systems and develop industrial applications.

Diketopyrrolopyrrole (DPP) is a well-known  $\pi$ -conjugated fluorescent organic dye appreciated for its outstanding fluorescence characteristics. Due to its electron-deficient nature, DPP serves as an electron acceptor when coupled with electron donor such electron-rich an as triphenylamine moieties. Hwang and co-workers synthesized a range of diketopyrrolopyrrole compounds integrating three distinct triphenylamine moieties (70–72) depicted in Figure 1.11.<sup>[61]</sup> These compounds displayed unique red emissions indicative of aggregation-induced emission. Disparities in luminescence properties among the synthesized diketopyrrolopyrrole compounds were attributed to the diverse functional groups attached to the triphenylamine moieties. Fluorescence quantum yields of solid thin films for diketopyrrolopyrrole-based chromophores 70, 71 and 72 were determined to be 31%, 26% and 9%, respectively. Consequently, diketopyrrolopyrrole compounds featuring optimized triphenylamine moieties exhibit promising potential as superior solid-state emissive materials through aggregation-induced emission.<sup>[61]</sup>



Figure 1. 11. DPP based chromophore showing AIE effect.

# 1.5.7. OFETs

Organic Field-Effect Transistors (OFETs) are electronic devices that employ organic semiconductors as their active components. They function by regulating the movement of charge carriers (electrons or holes) within the semiconductor layer *via* an external electric field. Typically, an OFET comprises three primary elements: 1. Substrate: Generally crafted from glass or silicon, it provides the structural support for the transistor. 2. Gate electrode: Positioned on the substrate, it governs the flow of charge carriers within the semiconductor layer by applying voltage. 3. Organic semiconductor layer: Positioned between the gate electrode and the source/drain

electrodes, this layer facilitates the transportation of charge carriers.<sup>[62]</sup> OFETs offer numerous advantages over conventional silicon-based transistors, such as flexibility, cost-effectiveness in manufacturing, and compatibility with large-area, solution-based processing methods. These characteristics make OFETs appealing for a range of uses, such as flexible displays, electronic paper, and sensor technology. <sup>[63]</sup>

The synthesis of donor-acceptor (D-A)-type diketopyrrolopyrrole (DPP)-based small molecules (73 and 74) was conducted for their application as the active solution-processable organic field-effect layer in transistors (OFETs) by Lim et al.<sup>[64]</sup> Both molecules, 73 and 74 (Figure 1.12) incorporate silaindacenodithiophene as electron donor units along with DPP serving as an electron-accepting linker and octylrhodanine as the electron-accepting end group. Variations in side chains were introduced to investigate their impact on OFET performance. Compound 73 features a simple branched alkyl side chain, while 74 is characterized by a bulky siloxane-terminated hybrid alkyl chain. The enhanced crystallinity observed in 74, attributed to its siloxane side chains, results in notably high field-effect mobility (up to  $3.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ). Notably, **74** exhibits excellent solubility and maintains its high mobility even when processed in the environmentally friendly solvent 2-methyltetrahydrofuran with low-temperature annealing at 100 °C, owing to the presence of bulky siloxane-terminated alkyl side chains.<sup>[64]</sup>



Figure 1. 12. DPP based chromophore for OFETs.

## 1.6. Current Work

Donor-acceptor (D–A) architectures play a crucial role in organic photovoltaics, particularly those exhibiting strong absorption in the visible to near-infrared (NIR) region and a narrow HOMO– LUMO gap. To enhance absorption in the NIR region and reduce the HOMO–LUMO gap, researchers have explored various modifications of the diketopyrrolopyrrole (DPP) unit through symmetrical and unsymmetrical functionalization with different donors, acceptors, and linkers. The substitution of different donor and acceptor units has been studied extensively to understand their impact on the photonic, thermal, and electrochemical properties of these DPP-based D–A systems. By adjusting the strength of the donor or acceptor units, researchers can fine-tune the photophysical, electrochemical properties, and HOMO–LUMO gap of these systems. Various donor units such as carbazole, triphenylamine, ferrocene, phenothiazine and acceptor unit TCBD and DPP have been integrated to obtain various D–A systems. Investigation of their photophysical, thermal and electrochemical properties help in explaining their potential applications in diverse fields. These findings suggest the versatility and suitability of these tailored DPP-based D–A systems for a range of practical applications.

## Main objectives of the current work

- Development and synthesis of donor-acceptor (D–A) functionalized diketopyrrolopyrrole (DPP) based chromophores tailored for optoelectronic applications and ultrafast investigations.
- 2. Synthesis of both symmetrical and unsymmetrical DPPbased chromophores by modifying the donor/acceptor unit at the 3- and 6- positions.
- **3.** Examination of the impact of various donor/acceptor functionalization on the photophysical and redox characteristics of DPP.
- Alteration of the HOMO-LUMO gap through modifications in conjugation length and the introduction of acceptors such as TCBD into the D-A system.
- 5. Exploration of the electronic structure, electron density distribution across HOMO and LUMO energy levels, and photophysical attributes of DPP chromophores utilizing density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations.

#### **1.7. Organization of thesis**

**Chapter 1** of the thesis provides in-depth overview of the historical evolution of different synthetic approaches, functionalization methods, reactivity, and applications of DPPs across various domains. It outlines recent advancements in functionalization strategies, which are subsequently investigated in D-A systems in later Chapters.

**Chapter 2** of the thesis provides a concise overview of the equipment and standard procedures employed in the current research.

**Chapter 3** of the thesis explores the effects of conjugation length and positional substitution on *N*-phenyl carbazole in both symmetrical and unsymmetrical acetylene-bridged *N*-phenyl carbazole-based diketopyrrolopyrroles. It also investigates their photophysical and redox properties.

**Chapter 4** outlines a sequence of investigations involving the synthesis of symmetrical and unsymmetrical Diketopyrrolopyrrole derivatives functionalized with *N*, *N*-dimethylaniline/Triphenylamine moieties, alongside an examination of the impact of varied donor and acceptor groups on their optoelectronic characteristics.

**Chapter 5** of the thesis presents an array of unsymmetrical Diketopyrrolopyrrole derivatives functionalized with ferrocene groups, alongside an investigation into the influence of donor strength on [2+2] cycloaddition-retroelectrocyclization within tetracyanobutadiene-functionalized diketopyrrolopyrrole derivatives.

**Chapter 6** of the thesis presents the development and synthesis of a range of symmetric and asymmetric chromophores based on
Diketopyrrolopyrrole, featuring phenothiazine functionalization and incorporating diverse donors such as triphenylamine, *N*phenyl carbazole, and *N*, *N*-dimethylamine. Additionally, the Chapter delves into the examination of their photophysical, redox, and computational properties.

Chapter 7 of the thesis introduces a collection of Diketopyrrolopyrrole (DPP) and ferrocenyl-DPP derivatives, mono-, di-, and tri-substituted, featuring triphenylamine as a central core, synthesized via Pd-catalyzed Sonogashira crosscoupling reactions. The Chapter involves the examination and comparison of the photophysical and electrochemical characteristics of these DPP and ferrocenyl-DPP based derivatives.

**Chapter 8** of the thesis outlines the key aspects of the research and discusses potential future directions.

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# Chapter 02: Materials and Experimental Techniques

### **2.1. Introduction**

This Chapter outlines the materials used, the overall synthetic methods, the techniques for characterization, and the instrumentation utilized in this thesis.

### 2.2. Chemicals for synthesis

Standard purification procedures were applied to common solvents used in synthesis. <sup>[1]</sup> 2-thiophene carbonitrile, sodium *tert*-butoxide, dimethyl succinate, concentrated hydrochloric acid, and 1-bromodecane were sourced from Spectrochem India. Triethylamine was obtained from S. D. Fine Chem. *Ltd.*, while CuI, Pd(PPh<sub>3</sub>)<sub>4</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, ferrocene, and tetrabutylammonium hexafluorophosphate (TBAF<sub>6</sub>), Ethynyl ferrocene were procured from Aldrich Chemicals USA. Silica gel (100 – 200 mesh and 230 – 400 mesh) was purchased from Rankem Chemicals, India, and TLC pre-coated silica gel plates (Kieselgel 60F254, Merck) were obtained from Merck, India.

Dry solvents including dichloromethane, chloroform, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), *tert*-butanol, and methanol were sourced from Spectrochem and S. D. Fine Chem. *Ltd*. Oxygen or moisture-sensitive reactions were conducted under a nitrogen/argon atmosphere using the standard Schlenk method. Unless specified, solvents and reagents were used as received. *N*-Bromosuccinimide was recrystallized from hot water before use. Photophysical and electrochemical studies utilized spectroscopic grade solvents.

### 2.3. Spectroscopic measurements

### 2.3.1. Mass spectrometry

High resolution mass spectra (HRMS) were recorded on Brucker-Daltonics, micrOTOF-Q II mass spectrometer using positive and negative mode electrospray ionizations.

## 2.3.2. NMR spectroscopy

<sup>1</sup>H NMR (400/500 MHz), and <sup>13</sup>C NMR (100 MHz) spectra were recorded on the Bruker Avance (III) 400 MHz, using CDCl<sub>3</sub> and acetone-d<sub>6</sub> as solvent. Chemical shifts in <sup>1</sup>H, and <sup>13</sup>C NMR spectra were reported in parts per million (ppm). In <sup>1</sup>H NMR chemical shifts are reported relative to the residual solvent peak (CDCl<sub>3</sub>, 7.26 ppm). Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), and the coupling constants *J*, are given in Hz. <sup>13</sup>C NMR chemical shifts are reported relative to the solvent residual peak (CDCl<sub>3</sub>, 77.16 ppm).

# 2.3.3. UV-Vis spectroscopy

UV-Vis absorption spectra were recorded using a Varian Cary100 Bio UV-Vis and PerkinElmer LAMBDA 35 UV/Vis spectrophotometer.

### 2.3.4. Fluorescence spectroscopy

Fluorescence emission spectra were recorded upon specific excitation wavelength on a Horiba Scientific Fluoromax-4 spectrophotometer. The slit width for the excitation and emission was set at 2 nm.

### The fluorescence quantum yields ( $\phi_F$ )

The fluorescence quantum yields ( $\phi_F$ ) of compounds were calculated by the steady-state comparative method using following equation,  $\phi_F = \phi_{st} \times S_u/S_{st} \times A_{st} / A_u \times n_2 D_u/n_2 D_{st} \dots (Eq. 1)$ Where  $\phi_F$  is the emission quantum yield of the sample,  $\phi_{st}$  is the emission quantum yield of the standard,  $A_{st}$  and  $A_u$  represent the absorbance of the standard and sample at the excitation wavelength, respectively, while  $S_{st}$  and  $S_u$  are the integrated emission band areas of the standard and sample, respectively, and  $nD_{st}$  and  $nD_u$  the solvent refractive index of the standard and sample, u and st refer to the unknown and standard, respectively.

### 2.4. Electrochemical studies

Cyclic Voltamograms (CVs) were recorded on CHI620D electrochemical analyzer using Glassy carbon as working electrode, Pt wire as the counter electrode, and Ag/Ag<sup>+</sup>/SCE as the reference electrode. The scan rate was 100 mVs<sup>-1</sup>. A solution of tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in CH<sub>2</sub>Cl<sub>2</sub> (0.1 M) was employed as the supporting electrolyte.

# **2.5.** Computational Calculations

The density functional theory (DFT) calculations were carried out at the B3LYP/6-31G\*\* level for C, N, O, H, S and Lanl2DZ level for Fe in the Gaussian 09 program.<sup>[2]</sup>

### 2.6. References

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# Chapter 03: Design and synthesis of *N*-phenyl carbazole substituted Diketopyrrolopyrrole based monomers and dimers:A comparative study

### **3.1. Introduction**

The development of clean and renewable energy sources has become one of the most important goal undertaken by modern science.<sup>[1]</sup> Organic small molecules based on donor-acceptor (D-A) design have been investigated for their use in organic light emitting diodes (OLEDs), organic photovoltaics (OPVs), nonlinear optical (NLO) switches and data storage devices.<sup>[2]</sup> The optoelectronic properties of D–A molecular framework with extensive  $\pi$ -conjugation can be easily perturbed by varying the donor and acceptor unit.<sup>[2],[3]</sup>

Diketopyrrolopyrrole (DPP) has recently captured the attention of many researchers in building efficient D-A architecture due to its planarity, well conjugated structure, broad absorption in visible region and high photochemical stability.<sup>[4],[5]</sup> The DPP derivatives have been widely used for various optoelectronic applications due to their high optical densities and exceptional stabilities with high tendency to form semi crystalline structure.<sup>[6]</sup> Various D-A functionalized DPPs have been reported for application in OLEDs, organic field-effect transistors (OFETs), OSCs and photothermal cancer therapy.<sup>[11-13]</sup> Introduction of long alkyl chain at *N*- atom of DPP unit enhances the solubility in organic solvents.<sup>[7],[8]</sup>

Triphenylamine, carbazole and ferrocene are widely used donors in organic electronics. The planar heteroarenes (like thiophene, carbazole) have been introduced in organic small molecular backbone in order to introduce desirable characteristics like high charge mobility and broader absorption.<sup>[9],[10]</sup> Carbazole is an aromatic heterocyclic compound possesses good electron donating and charge transport property.<sup>[14]</sup> Carbazole is commonly used donor for the synthesis of molecular architectures for organic electronics and photonic applications. The

small molecules and polymers based on carbazole functionalized DPP have reported in literature for efficient OPV applications.<sup>[17],[18]</sup>



Figure 3. 1. Chemical structures of *meta-* and *para N-*phenyl carbazole based DPPs.

Recently Our group have reported the *para-N*-phenyl carbazole functionalized DPPs (**10** and **11**) for BHJ OSCs.<sup>[15],[16]</sup> In continuation of this work, we were further interested to see positional effect of *N*-phenyl carbazole on photophysical and electrochemical properties of DPP. In this regard we have synthesized *meta-N*-phenyl carbazole functionalized DPPs (**5**–**7**) and dimers (**8** and **9**) of *meta-* and *para-N*-phenyl carbazole functionalized DPP. The effect of number of donor as well as acceptor units on photophysical and electrochemical properties of DPP was also investigated. The unsymmetrical DPP derivative containing *meta-* and *para-N*-phenyl carbazole (**7**) was also synthesized for comparison.

### **3.2. Results and Discussion**

The *meta N*-phenyl carbazole-substituted DPPs **5** and **6** were synthesized by the Pd-catalyzed Sonogashira cross-coupling reaction of **1** and **2** with 1.1 and 2.2 equivalents of *N*-(3-Ethynylphenyl) carbazole in 60% and 65% yield respectively (Scheme 3.1.).



Scheme 3. 1. Scheme for synthesis of DPP based derivatives 5–7.

The Pd-catalyzed Sonogashira cross-coupling reaction of dibromo **2** with one equivalent of *N*-(4-ethynylphenyl) carbazole forms **3**, which on subsequent Pd-catalyzed Sonogashira cross-coupling reaction with 1.1 equivalents of *N*-(3-ethynylphenyl) carbazole gives **7** in 45% yield (Scheme 3.1). We have recently reported the synthesis and photophysical properties of *para*-substituted DPPs **10** and **11** which we have taken here for the sake of comparison. The Pd-catalyzed Stille cross–coupling reaction of **3** and **4** with 0.4 equivalents of bis(tributylstannyl)acetylene resulted in 55% and 53% yield of **8** and **9** respectively (Scheme 3.2).



Scheme 3. 2. Synthesis of *meta* and *para N*-phenyl carbazole based DPP dimers 8 and 9.

The carbazole substituted DPPs **5–9** were purified by repeated silica gel column chromatography and recrystallization techniques. The DPPs **5– 9** are readily soluble in common organic solvents and were fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, (5–7) HRMS, (8 and 9) MALDI techniques.

### 3.3. Photophysical and Thermal properties

The electronic absorption spectra of DPPs **5–9** in  $2 \times 10^{-4}$  M concentration were recorded in dichloromethane at room temperature [Figure 3.2. (a) and (b)] and data are listed in Table 3.1.

The carbazole based DPP monomers (5–7) and dimers (8 and 9) show absorption in visible to near-infrared (NIR) region. The *para-N*-phenyl carbazole based DPPs (10 and 11) showed red shifted absorption compared to their *meta*-substituted analogues (5–7).

The DPPs **5–9** exhibit absorption maxima at 578 nm, 612 nm, 613 nm, 621 nm, and 628 nm respectively which are due to  $\pi$ - $\pi$ \* transitions. The lower wavelength absorption maxima for **5–7** were observed at 541 nm, 568 nm and 570 nm respectively. The di-*N*-phenyl carbazole based DPPs (**6** and **11**) exhibited red shifted absorption compared to mono-*N*-phenyl carbazole based DPPs (**5** and **10**) respectively due to extension of conjugation. The absorption bands of *para- N*-phenyl carbazole substituted DPPs (**8**, **10** and **11**) show red shifted absorption compared to their *meta*-substituted analogues (**9**, **5** and **6**) respectively which may be due to better electronic communication.



Figure 3. 2. (a) Normalized electronic absorption spectra of DPPs 5–7 and 10–11 in dichloromethane, (b) Normalized electronic absorption spectra of 5 and DPPs 8–10 in dichloromethane.

The absorption maximum of asymmetric *N*-phenyl carbazole substituted DPP **7** lies in between **6** and **11**. The ethyne bridged *meta*and *para*-*N*-phenyl carbazole based DPP dimers **8** and **9** exhibit broad absorption bands and absorption maxima at 628 nm and 621 nm respectively. Red shift of 9 nm and 12 nm were observed for dimers **9** and **8** compared to their monomer analogues **5** and **10** respectively. The optical band gap of **5**–**9** are 1.99 eV, 1.81 eV, 1.82 eV, 1.58 eV and 1.39 eV respectively. The optical band gap follows the order **5** > **10** > **6** > **7** > **11** > **9** > **8**, which indicates that increase in conjugation length results in red shift of absorption maxima with lowering of optical gap. The Figure 3.2.(b) and Table 3.1. show that the dimerization of carbazole based DPP results in the red shifted broad absorption with lowering of optical gap. The colored photograph of *N*-phenyl carbazole based DPPs **5–9** is shown in Figure 3.3.



Figure 3. 3. Photograph of DPPs 5–9 in DCM taken in day light.

The emission spectra of **5–9** were recorded in dichloromethane at room temperature (Figure 3.4). The *N*-phenyl carbazole based DPP derivatives **5–7** are highly emissive in nature and show emission bands at 602 nm, 634 nm and 634 nm respectively. Fluorescence quantum yield for **5–9** are 0.64, 0.65, 0.79, 0.03 and 0.22 respectively using Rhodamine 6G in ethanol as standard which shows quenching of fluorescence takes place in dimers **8** and **9**.



Figure 3. 4. Emission spectra of 5–9 in dichloromethane.



**Figure 3. 5.** Thermogravimetric analysis of DPPs **5–9** under a nitrogen atmosphere.

The thermal properties of DPPs **5–9** were investigated by thermogravimetric analysis (TGA) under nitrogen atmosphere and their thermograms are shown in Figure 3.5. The DPPs **5–9** exhibit good thermal stability. The decomposition temperatures at 5% weight loss were found to be 402 °C, 426 °C, 414 °C, 279 °C, 297 °C 333 °C and 398 °C for **5–11** respectively. The thermal stability follows the order **6** > **7** > **5** > **11** > **10** > **9** > **8** indicating that *meta*-substituted *N*-phenyl carbazole based DPPs exhibit higher thermal stability compared to that of *para*-substituted DPPs.<sup>[14]</sup> The carbazole based monomers are comparatively more stable than their dimer analogues.

DPP	$\lambda_{abs}(nm)$	Е	T <sup>b</sup>	E <sup>c</sup>	E <sup>d</sup>
		$(\times 10^4 \text{ M}^{-1} \text{ cm}^{-1})^{a}$	(°C)	(eV)	(eV)
5	578	2.7	402	1.99	2.22
	541	2.4			
6	612	1.9	426	1.89	2.06
	568	1.6			
7	613	3.8	414	1.88	2.04
	570	3.4			
8	628	2.9	279	1.39	1.56
9	621	6.2	297	1.58	1.58
10	580	3.8	333	1.93	2.21
	543	3.5			
11	616	6.3	398	1.73	2.03
	571	5.5			

**Table 3. 1.** The photophysical, thermal and computational properties of DPPs **5–11**.

<sup>a</sup>Absorbance measured in  $CH_2Cl_2$  solution;  $\epsilon$ : extinction coefficient; <sup>b</sup>Decomposition temperatures at 5% weight loss at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere; °Optical band gap; <sup>d</sup>Theoretical HOMO-LUMO gap.

### **3.4. Electrochemical properties**

The electrochemical properties of carbazole based DPPs **5–9** were explored by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques in dichloromethane using 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) as supporting electrolyte. The CV and DPV plots are shown in Figure 3.6. The corresponding electrochemical data are listed in Table 3.2.<sup>[14]</sup>

DPPs **5–9** show two oxidation peaks, first corresponds to the oxidation of thiophene moiety and second related to oxidation of carbazole moiety respectively (Table 3.2). The DPPs **5–9** show one reduction peak corresponding to reduction of DPP moiety at -0.96 V, -0.96 V, -0.97 V, -0.97 V and -1.34 V respectively. The reduction potential of DPPs **5–11** follow the trend **9** > **10=11** >**7=8** >**5=6** which indicate that *para*-

substituted monomer (**10** and **11**) are difficult to reduce as compared to their *meta*-substituted monomer (**5** and **6**).





Figure 3. 6. CV (black line) and DPV plots (red line) of 5–9 in DCM.

The first oxidation potential of DPPs **5–11** follow the trend **8** >**6**=**7** >**5**=**9** >**10** >**11** which indicate that *meta* substituted monomer **5**–**7** are difficult to oxidize as compared to *para* substituted monomer **10** and **11** while it is difficult to oxidize *para* substituted dimer **8** as compared to its meta analogue **9**. The electrochemical data (Table 3.2) shows that the dimerization of *meta N*-phenyl carbazole based DPP makes reduction harder in **9** as compared to its monomer **5** whereas oxidation of *para-N*-phenyl carbazole based DPP **8** is harder after dimerization.

DPP	$E^{1}$	$E^{1}$	$E^2$
	Red (V)	Oxid (V)	Oxid (V)
5	-0.96	0.95	1.39
6	-0.96	0.96	1.38
7	-0.97	0.96	1.40
8	-0.97	1.00	1.42
9	-1.34	0.95	1.49
10	-1.03	0.93	1.60
11	-1.03	0.92	1.20

Table 3. 2. Electrochemical properties<sup>a</sup> of DPPs 5–11.

<sup>a</sup>The electrochemical analysis was performed in a 0.1 M solution of  $Bu_4NPF_6$ in dichloromethane at 100 mVs<sup>-1</sup> scan rate, versus Ag/Ag<sup>+</sup> at 25 °C.

### **3.5.** Theoretical calculations

### **Density Functional Theory Calculations**

To get deeper insights into the structures and geometry of DPPs **5–9**, density functional theory (DFT) calculations were carried out using the Gaussian 09W program.<sup>[19]</sup> The long alkyl chains on lactam ring was replaced by ethyl group to reduce the computation time. The DFT calculations were performed at the B3LYP/6-31+G\*\* for C, H, O, N and S level of theory.



**Figure 3. 7.** Frontier molecular orbitals (FMOs) of **6**, **7** and **11** estimated from DFT calculations.

The electron density distribution of HOMO and LUMO in **6**, **7** and **11** shown in Figure 3.7. The FMOs of carbazole based dimers **8** and **9** are shown in Figure 3.8. The *N*-phenyl carbazole based DPPs show planar geometry and the HOMO and LUMO electron density is distributed on DPP unit. The electron density in HOMO and LUMO of dimers **8** and **9** are located on both the DPP units. The calculated HOMO energy levels for **5**–**11** are -4.96, -4.97, -4.93, -4.82, -4.86, -4.93 and -4.90 eV and the corresponding LUMO levels are -2.74, -2.91, -2.89, -3.11, -3.13, -2.72 and -2.87 eV respectively.



**Figure 3. 8.** FMOs of **8** and **9** estimated by DFT calculations at B3LYP level.

# **Time Dependent Density Functional Theory (TD-DFT) Calculation**

To get an idea about the various electronic transitions, the time dependent density functional theory (TD-DFT) calculation was performed. The results of TD-DFT indicates that **5** and DPPs **8–11** show two main electronic transitions in the Vis-NIR region whereas **6** and **7** shows only one electronic transition in visible region. The major

electronic transitions of carbazole based DPPs with compositions, oscillator strengths and assignments are shown in Table 3.3. The transitions that occur from HOMO to LUMO in longer wavelength are due to  $\pi$ - $\pi$ \* transitions of DPP moiety. The other transitions in short wavelength region for 5, 10 and 11 are due to charge transfer transitions. The main charge transfer transition in 5, 10 and 11 occur from HOMO-3 to LUMO, HOMO-3 to LUMO and HOMO-5 to LUMO respectively while the other short wavelength transitions in 8 and 9 from HOMO-1 to LUMO+1 corresponds to  $\pi$ - $\pi$ \* transitions of DPP moiety.

Compound	Wavelength	Composition	$f^{a}$
	(nm)		
5	573	HOMO→LUMO (0.71)	1.06
	381	HOMO-3→LUMO (0.48)	0.51
6	629	HOMO $\rightarrow$ LUMO (0.71)	1.77
7	640	HOMO→LUMO (0.70)	1.99
8	798	HOMO→LUMO (0.71)	3.54
	552	HOMO-1→LUMO+1	0.50
		(0.67)	
9	785	HOMO $\rightarrow$ LUMO (0.71)	3.25
	545	HOMO-1→LUMO+1	0.39
		(0.69)	
10	575	HOMO→LUMO (0.71)	0.75
	388	HOMO-3→LUMO (0.37)	0.20
11	578	HOMO $\rightarrow$ LUMO (0.71)	1.39
	366	HOMO-5→LUMO (0.54)	0.25

**Table 3. 3.** Major electronic transitions of DPPs **5–11** calculated by TD-DFT.

*f*<sup>a</sup>=oscillation strength

The DFT and TD-DFT calculations results show that, as the number of *N*-phenyl carbazole and DPP unit increases, it enhances the conjugation with the red shift in absorption that lowers the HOMO–LUMO gap.

### 3.6. Experimental Section

### **General Methods**

Chemicals were used as received unless otherwise indicated. All moisture-sensitive reactions were performed under an argon atmosphere using the standard Schlenk method. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded by using CDCl<sub>3</sub> as the solvent. The <sup>1</sup>H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl<sub>3</sub>, 7.26 ppm). The multiplicities are given as s (singlet), d (doublet), t (triplet), or m (multiplet), and the coupling constants, J are expressed in Hz. The <sup>13</sup>C NMR chemical shifts are reported relative to the solvent residual peak (CDCl<sub>3</sub>,77.02 ppm). HRMS and MALDI were recorded on an ESI-TOF and MALDI-TOF spectrometer. The UV/vis absorption spectra of DPPs were recorded on UV/vis spectrophotometer in CH<sub>2</sub>Cl<sub>2</sub>. The TGA analysis were performed on a thermal analysis system at the heating rate of 10°C/min under a nitrogen atmosphere. Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) were recorded on an electrochemical analyzer using a glassy carbon working electrode, a Pt wire counter electrode, and a saturated  $Ag/Ag^+$  reference electrode.

# Synthesis of 5

In a 100 mL round-bottom flask, **1** (0.250 g, 0.37 mmol) and *N*-(3ethynylphenyl) carbazole (0.111 g, 0.41 mmol) were dissolved in anhydrous tetrahydrofuran (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 15 min and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.017 g, 0.015 mmol), and CuI (0.006 g, 0.030 mmol) were then added. The reaction mixture was stirred overnight at 70°C. After completion of the reaction, the reaction mixture was allowed to cool down to room temperature. The solvent was removed under vacuum and the crude
product was purified by repeated silica gel column chromatography with hexane/DCM (3:1) as an eluent to get **5** in 60% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.91 (2H, d, J = 4 Hz), 8.16 (2H, d, J = 8 Hz), 7.77 (1H, s), 7.62 (4H, m), 7.43 (5H, m), 7.29 (3H, m), 4.08 (4H, m), 1.75 (4H, m), 1.42 (4H, m), 1.33 (24H, m), 0.85 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 161.4, 140.7, 140.5, 138.8, 138.2, 135.7, 135.2, 133.5, 131.1, 131.0, 130.4, 130.2, 130.0, 129.7, 128.7, 127.9,127.8, 126.1, 124.3, 123.6, 120.4, 120.3, 109.7, 108.7, 107.9, 96.4, 83.5, 42.4, 31.92, 31.91, 30.1, 30.0, 29.7, 29.6, 29.5,29.3, 26.9, 22.7, 14.2, 14.1; HRMS (ESI) *m*/*z* calcd for C<sub>54</sub>H<sub>59</sub>N<sub>3</sub>S<sub>2</sub>O<sub>2</sub> + Na: 868.3941 [M + Na<sup>+</sup>], found 868.3948; UV/vis (Dichloromethane)  $\lambda_{max}$  578 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (2.7×10<sup>4</sup>).

# Synthesis of 6

In 100 mL round-bottom flask, **2** (0.250 g, 0.34 mmol) and *N*-(3ethynylphenyl) carbazole (0.199 g, 0.75 mmol) were dissolved in anhydrous tetrahydrofuran (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 15 min and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.017 g, 0.015 mmol) and CuI (0.005 g, 0.027 mmol) were then added. The reaction mixture was stirred overnight at 70°C. After completion, the reaction mixture was allowed to cool to room temperature. The solvent was removed under vacuum and the crude was purified by silica gel column chromatography with hexane/CH<sub>2</sub>Cl<sub>2</sub> (3:1) as an eluent to get **6** in 65 % yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.94 (2H, d, J = 4 Hz), 8.16 (4H, d, J = 8 Hz), 7.62 (8H, m), 7.32 (14H, m), 4.06 (4H, s), 1.75 (4H, m), 1.43 (6H, m), 1.25 (22H, m), 0.84 (6H, m) ); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ in ppm): 160.9, 140.4, 138.9, 137.9, 135.3, 133.3, 130.6, 130.2, 130.0, 129.9, 129.7, 127.9, 127.7, 127.6, 125.9, 123.9, 123.3, 120.3, 120.2, 120.1, 120.0, 109.6, 109.54, 109.52, 109.51, 109.4, 108.6, 83.2, 53.51, 53.50, 53.44, 53.41, 53.2, 42.2, 31.74, 31.71, 31.70, 31.68, 31.60, 30.0, 29.9, 29.8, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 26.73, 26.71, 26.6, 22.4, 13.92, 13.90; HRMS (ESI) m/z calcd for

 $C_{74}H_{70}N_4O_2S_2 + Na: 1133.4832 [M + Na^+], \text{ found } 1133.4927; UV/Vis$ (Dichloromethane)  $\lambda_{max} 612 \text{ nm}, \epsilon [M^{-1}\text{cm}^{-1}] (1.9 \times 10^4).$ 

# Synthesis of 7

In a 250 mL round-bottom flask, 2 (0.500 g, 0.68 mmol) and N-(4ethynylphenyl) carbazole (0.182 g, 0.68 mmol) were dissolved in anhydrous tetrahydrofuran (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 15 min and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.039 g, 0.034 mmol), and CuI (0.006 g, 0.030 mmol) were then added. The reaction mixture was stirred overnight at 65°C. After completion, the reaction mixture was allowed to cool to room temperature. The solvent was removed under vacuum and the crude was purified by silica gel column chromatography with hexane/CH<sub>2</sub>Cl<sub>2</sub> (3:1) as an eluent to get 3 in 40% yield and then in a 100 mL round-bottom flask, 3 (0.200 g, 0.21 mmol) and N-(3-ethynylphenyl) carbazole (0.067, 0.25 mmol) were dissolved in anhydrous tetrahydrofuran (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 15 min and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.017 g, 0.015 mmol), and CuI (0.006 g, 0.030 mmol) were then added. The reaction mixture was stirred overnight at 65°C. After completion, the reaction mixture was allowed to cool to room temperature. The solvent was removed under vacuum and the crude was purified by silica gel column chromatography with hexane/CH<sub>2</sub>Cl<sub>2</sub> (3:1) as an eluent to get 7 in 45% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.96 (2H, s), 8.15 (4H, m), 7.80 (2H, d, *J*= 8 Hz), 7.63 (5H, m), 7.45 (9H, m), 7.33 (6H, m), 4.10 (4H, d, *J* = 8 Hz), 1.76 (4H, m), 1.44 (4H, m), 1.34 (24H, m), 0.86 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 161.2, 140.7, 140.4, 139.2, 139.1, 138.2, 135.6, 135.5, 133.5, 133.4, 133.1, 130.9, 130.7, 130.4, 130.2, 130.0, 128.8, 128.1, 127.9, 126.9, 126.1, 124.2, 123.7, 123.5, 121.0, 120.4, 120.3, 109.7, 108.9, 108.8, 96.6, 83.5, 83.2, 42.4, 31.9, 30.1, 29.5, 29.4, 29.3, 29.2, 26.9, 22.7, 14.1; HRMS (ESI) m/z calcd for C<sub>74</sub>H<sub>70</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub> + Na: 1133.4832 [M + Na<sup>+</sup>], found 1133.4870; UV/Vis (Dichloromethane)  $\lambda_{max}$  613 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (3.8×10<sup>4</sup>).

## Synthesis of 8

In a 250 mL round-bottom flask, 2 (0.500 g, 0.68 mmol) and N-(4ethynylphenyl) carbazole (0.182 g, 0.68 mmol) were dissolved in anhydrous tetrahydrofuran (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 15 min and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.039 g, 0.034 mmol), and CuI (0.006 g, 0.030 mmol) were then added. The reaction mixture was stirred overnight at 65°C. After completion, the reaction mixture was allowed to cool to room temperature. The solvent was removed under vacuum and the crude was purified by silica gel column chromatography with hexane/CH<sub>2</sub>Cl<sub>2</sub> (3:1) as an eluent to get **3** in 35% yield and then in a 100 mL round-bottom flask, **3** (0.200 g, 0.21 mmol) were dissolved in 20 mL toluene. The reaction mixture was degassed with argon for 15 min and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.039 g, 0.034 mmol) and Bis(tributylstannyl)acetylene (0.065 g, 0.11 mmol) were then added. The reaction mixture was stirred overnight at 85 °C. After completion, the reaction mixture was allowed to cool to room temperature. The solvent was removed under vacuum and the crude was purified by silica gel column chromatography with hexane/DCM (1:1) as an eluent to get 8 in 55% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ in ppm): 8.97 (2H, s), 8.14 (4H, s), 7.61(26H, m), 4.08 (8H, s), 1.76 (8H, m), 1.42 (58H, m), 0.93 (14H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ in ppm): 140.7, 134.6, 130.5, 130.3, 128.2, 126.2, 123.6, 120.5, 120.3, 109.8, 109.7, 42.5, 32.0, 30.2, 29.8, 29.7, 29.6, 29.5, 29.4, 27.0 22.8, 14.2; MALDI m/z calcd for C<sub>110</sub>H<sub>116</sub>N<sub>6</sub>O<sub>4</sub>S<sub>4</sub>: 1713.7974 [M<sup>+</sup>], found 1713.979; UV/Vis (Dichloromethane)  $\lambda_{max}$  628 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (2.9×10<sup>4</sup>).

## Synthesis of 9

In a 250 mL round-bottom flask, **2** (0.500 g, 0.68 mmol) and *N*-(3ethynylphenyl) carbazole (0.182 g, 0.68 mmol) were dissolved in anhydrous tetrahydrofuran (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 15 min and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.039 g, 0.034 mmol), and CuI (0.006 g, 0.030 mmol) were then added. The reaction mixture was stirred overnight at 65°C. After completion, the reaction mixture was allowed to cool to room temperature. The solvent was removed under vacuum and the crude was purified by silica gel column chromatography with hexane/CH<sub>2</sub>Cl<sub>2</sub> (3:1) as an eluent to get **4** in 35% yield and then in a 100 mL round-bottom flask **4** (0.200 g, 0.21 mmol) were dissolved in 20 mL toluene. The reaction mixture was degassed with argon for 15 min and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.039 g, 0.034 mmol) and Bis(tributylstannyl)acetylene (0.065 g, 0.11 mmol) were then added. The reaction mixture was stirred overnight at 85 °C. After completion, the reaction mixture was allowed to cool to room temperature. The solvent was removed under vacuum and the crude was purified by silica gel column chromatography with hexane/DCM (1:1) as an eluent to get **9** in 53% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.94 (2H, s), 8.13 (4H, s), 7.50 (10H, m), 7.35 (10H, m), 7.25 (6H, m), 4.04 (8H, m), 1.73 (8H, m), 1.41 (54H, m), 0.84 (14 H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 140.7, 134.6, 130.5, 130.3, 128.2, 126.2, 123.6, 120.5, 120.3, 109.8, 109.7, 42.5, 32.0, 30.23, 30.21, 30.1, 29.82, 29.80, 29.8, 29.7, 29.6, 29.5, 29.4, 27.0, 26.98, 22.82, 22.80, 14.2; MALDI m/z calcd for C<sub>110</sub>H<sub>116</sub>N<sub>6</sub>O<sub>4</sub>S<sub>4</sub>: 1713.7974 [M<sup>+</sup>], found 1713.945; UV/Vis (Dichloromethane)  $\lambda_{max}$  621 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (6.2×10<sup>4</sup>).

# **3.7.** Conclusions

We have designed and synthesized *meta-* and *para-substituted* symmetrical as well as unsymmetrical *N*-phenyl carbazole based DPP derivatives **5–9** in order to see the effect of number of donor and acceptor unit on photophysical and electrochemical properties of DPP. The *N*-phenyl carbazole based DPP derivatives exhibit broad absorption in visible to NIR region. The *para* substituted DPPs show red shifted absorption compared to their *meta-substituted* analogues. The dimerization of *N*-phenyl carbazole based DPP results in the red shifted broad absorption with lowering of HOMO-LUMO gap. The quenching of fluorescence was observed in emission spectra of dimers **8** and **9**. The electrochemical investigation showed multiple oxidation waves due to thiophene and carbazole donors whereas only one reduction wave was

observed which is related to reduction of DPP unit. The broad absorption in Vis-NIR region, low HOMO-LUMO gap and good thermal stability make these derivatives potential candidates for optoelectronic applications.

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# Chapter 04: Symmetrical and Unsymmetrical N, N-dimethylaniline/Triphenylamine Functionalized Diketopyrrolopyrroles

## 4.1. Introduction

The use of solar energy for the production of clean and renewable fuels is required for fulfilling the future energy demands. In this direction, the field of organic electronics has drawn great deal of attention of scientific community.<sup>[1-11]</sup> Organic small molecules with extensive  $\pi$ -conjugation based on donor-acceptor (D-A) framework have been studied for their wide range of optoelectronic applications such as OSCs, nonlinear optical (NLO) switches, sensors, fluorescent near-infrared (NIR) probes and data storage devices.<sup>[12-27]</sup> The optoelectronic properties of D-A framework can be tuned by designing D– $\pi$ –A– $\pi$ –D, A– $\pi$ –D– $\pi$ –A, D– $\pi$ – A type of molecular systems.<sup>[28-37]</sup> Diketopyrrolopyrrole (DPP) is  $\pi$ conjugated bicyclic di-lactam moiety and is one of the widely used organic dyes due to its simple synthesis and excellent thermal stability.<sup>[28-40]</sup> DPP derivatives exhibit poor solubility in organic solvents due to strong  $\pi$ - $\pi$  interactions and Hydrogen bonding interactions but the N-alkylation enhances its solubility in common organic solvents.<sup>[41-48]</sup> DPP possesses features like strong electron accepting property, planarity and high fluorescence quantum yield.<sup>[49-55]</sup> The combination of donor thiophene with acceptor DPP (*i.e.* dithienyl DPP) led to small organic molecule with absorption in visible region. The literature reveals that DPP coupled with a variety of donors are explored as small organic molecules for BHJ solar cells. A variety of linear and star shaped DPP derivatives have been reported for optoelectronic applications. The nature of donor used for the design of efficient small organic molecules significantly influences the D-A interaction.<sup>[54,55]</sup> N, N-dimethylaminophenyl and Triphenylamine (TPA) are widely used donor unit for the synthesis of various organic molecules based on D-A framework. 1,1,4,4-Tetracyanobutadiene (TCBD) is a strong electron-withdrawing group that can be incorporated into electron-rich alkynes by [2+2] cycloaddition– retroelectrocyclization reaction. The motivation of choosing this work is to compare the changes observed in the photophysical and electrochemical properties on substituting two sides of acceptor (DPP) with different donors (*N*, *N*-dimethylaniline and TPA) and to study further the effect of incorporation of TCBD moiety. Herein We designed and synthesized symmetrical and unsymmetrical DPP based derivatives **NDPPs 1–8** by the Sonogashira cross-coupling reaction and followed by [2+2] cycloaddition–retroelectrocyclization reaction.



**Figure 4. 1.** Chemical structure of symmetrical and unsymmetrical DPP based derivatives **NDPPs 1–8** 

## 4.2. Results and Discussion

The N. Nsymmetrical and unsymmetrical dimethylaminophenyl/Triphenylamine functionalized DPP derivatives (NDPPs 1-8) were synthesized using a Pd-catalyzed Sonogashira crosscoupling reaction followed by [2+2]cycloadditionretroelectrocyclization reactions with tetracyanoethylene (TCNE) as shown in Figure 4.1. The Sonogashira cross-coupling reaction of **DPP** 1 with an equivalent of 4-ethynyl-N, N-dimethylaniline in toluene as solvent and triethylamine as a base at 80°C for 12 h gives NDPP 1 in 60% yield. Similarly, the reaction of **DPP 2** with two equivalents of 4ethynyl-N, N-dimethylaniline at 80°C for 12 h yielded NDPP 3 in 70% yield and synthesized here for the sake of comparison as shown in Scheme 4.1.



Scheme 4. 1. Synthesis of *N*, *N*-Dimethylaminophenyl functionalized DPP based derivatives NDPPs 1–5.

Further, **DPP 3** underwent a Sonogashira cross-coupling reaction with an equivalent of Triphenylamine at 80°C for 12 h in toluene as solvent and triethylamine as solvent gives **NDPP 6** in 75% yield. The [2+2] cycloaddition-electrocyclization reaction of **NDPP 1** with an equivalent of TCNE in dichloromethane as solvent at room temperature for 1 h yielded **NDPP 2** in 85% yield, while **NDPP 3** reacted with 1.0 and 2.0 equivalents of TCNE in DCM solvent at room temperature to give **NDPP 4** and **NDPP 5** in 75% and 90% yields, respectively. The reaction of the unsymmetrical DPP-based derivative **NDPP 6** with 1.0 and 2.0 equivalents of TCNE in DCM at room temperature produced **NDPP 7** 



and **NDPP 8** in yields of 80% and 85%, respectively, as shown in Scheme 4.2.

Scheme 4. 2. Synthesis of *N*, *N*-Dimethylaminophenyl and triphenylamine functionalized DPP based derivatives NDPPs 6–8.

All *N*-dimethylaniline/Triphenylamine the synthesized Ν, functionalized DPPs NDPPs 1-8 were purified by repeated silica gel column chromatography and recrystallization techniques and are readily soluble in common organic solvents such as dichloromethane, chloroform, toluene, tetrahydrofuran, ethyl acetate and dimethylsulfoxide.and were fully characterized by common spectroscopic techniques (<sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS). The <sup>1</sup>H NMR spectra of NDPP 6 exhibit a singlet for the six methyl protons of the N, N-dimethylaminophenyl group at 3.0 ppm, and the four phenyl protons of the same group appear in the region of 6.5–7.5 ppm. After incorporating a tetracyanobutadiene group (NDPP 7), the singlet for the six methyl protons shifts to 3.12 ppm, and the peaks for the four phenyl protons shift beyond 7.5 ppm. This shift indicates that the TCNE attack initially occurs at the more electron-rich acetylene bridge linked to the N, N-dimethylaminophenyl group, resulting in the synthesis of **NDPP 7**. This suggests the strong donor strength of the N, N-dimethylaminophenyl group relative to the triphenylamine group.

## 4.3. Photophysical properties

The electronic absorption spectra of symmetrical and unsymmetrical DPP based derivatives **NDPPs 1–8** were recorded in DCM solution at  $1.0 \times 10^{-5}$  M and as film at room temperature (Figure 4.2.) and the corresponding data are listed in Table 4.1.

The acetylene bridged derivatives NDPP 1, NDPP 3 and NDPP 6 exhibits a broad absorption band in the region of 400-700 nm corresponding to  $\pi$ - $\pi$ \* transition. A red shifted absorption band was observed for disubstituted DPP based derivatives (NDPP 3 and NDPP 6) relative to mono-substituted DPP based derivative (NDPP 1) due to extended conjugation. In the TCBD bridged derivatives (NDPP 2, NDPP 4, NDPP 5, NDPP 7 and NDPP 8) red shift in absorption band were observed relative to the corresponding acetylene bridged derivatives (NDPP 1, NDPP 3 and NDPP 6) due to increase in donoracceptor interactions as well as two absorption bands were observed, one at the shorter wavelength corresponding to  $\pi$ - $\pi$ \* transition and other at longer wavelength corresponding to Intramolecular charge transfer (ICT) from donor to acceptor unit. Substitution of one N, Ndimethylaniline group of NDPP 3 with TPA as a donor yields unsymmetrical derivative NDPP 6. The blue shifted absorption maxima of triphenylamine linked DPP derivatives NDPP 6 (629 nm) and NDPP 7 (722 nm) relative to N, N-dimethylaminophenyl linked DPP derivatives NDPP 3 (632 nm) and NDPP 4 (732 nm) indicate strong donor-acceptor interactions in N, N-dimethylaminophenyl linked DPP derivatives.



**Figure 4. 2.** Normalized electronic absorption spectra of **NDPPs 1–8** in dichloromethane at  $1.0 \times 10^{-5}$  M concentration (solid line) and as thin film (dashed lines).

The optical band gap and theoretical HOMO-LUMO gap of **NDPPs 1– 8** were calculated from onset absorption and time dependent density functional theory (TD-DFT) calculations respectively and the data are listed in Table 4.1. implies that the incorporation of TCBD unit significantly lowers the HOMO–LUMO gap.

NDPP	$\lambda_{abs}(nm)^a$	$\lambda_{abs}(nm)^b$	3	E <sup>c</sup> (eV)	E <sup>d</sup> (eV)
			(×10 <sup>4</sup> M <sup>-</sup>		
			<sup>1</sup> cm <sup>-1</sup> ) <sup>a</sup>		
NDPP 1	585	605	1.48	1.89	2.17
	558	538	1.32		
NDPP 2	678	783	1.11	1.54	1.92
	467	496	1.41		
NDPP 3	632	711	4.72	1.75	1.99
	598	597	1.41		
NDPP 4	732	776	0.61	1.40	1.67
	467	478	0.58		
NDPP 5	734	765	1.72	1.48	1.75
	682	702	1.43		
	471	488	3.06		
NDPP 6	629	650	0.97	1.76	2.07
	594	607	0.83		
NDPP 7	722	737	1.02	1.40	1.68
	467	477	0.92		
NDPP 8	738	768	0.70	1.48	1.74
	683	700	0.57		
	473	485	1.11		

**Table 4. 1.** The optical and theoretical/computational properties of **NDPPs 1–8**.

<sup>a</sup> Absorbance measured in DCM solution; *ε*: extinction coefficient; <sup>b</sup>absorbance measured in film; <sup>c</sup>Optical band gap; <sup>d</sup>Theoretical band gap.

The computational calculations showed good agreement with experimental absorption spectra. The absorption band get broadened up to 1000 nm in thin film compared to in solution due to aggregation in solid state. The solvent dependent absorption spectra of **NDPPs 1–8** were recorded in toluene, dichloromethane (DCM), tetrahydrofuran (THF), ethylacetate (EAA) and *N*, *N*-dimethylformamide (DMF) solvents at concentration of  $1.0 \times 10^{-5}$  M. In the acetylene bridged derivatives (**NDPP 1, NDPP 3** and **NDPP 6**), no significant changes

were observed in the absorption spectra with the increase in polarity of solvent while in TCBD bridged derivatives (**NDPP 2**, **NDPP 4**, **NDPP 5**, **NDPP 7** and **NDPP 8**) blue shifts in the absorption band at longer wavelength was observed while no significant change were observed in the absorption band at shorter wavelength with the increase in polarity of solvent as shown in Figure 4.3.



Figure 4. 3. Normalized absorption spectra of NDPP 1 and NDPP 4 in different solvents at  $1.0 \times 10^{-5}$  M concentration.

## 4.4. Electrochemical properties

The electrochemical properties of the symmetrical and unsymmetrical N, N-dimethylaniline/TPA functionalized DPP derivatives NDPPs 1-8 voltammetry were explored by cyclic (CV) technique in dichloromethane solvent using 0.1M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) as a supporting electrolyte. The cyclic voltammograms of NDPPs 1-8 are shown in Figure 4.4. and the corresponding redox data are listed in Table 4.2.

The acetylene bridged derivatives **NDPPs 1**, **3** and **6** exhibit one reduction waves corresponding to reduction of DPP unit. The TCBD bridged **NDPPs 2**, **4**, **5**, **7** and **8** exhibit three reduction waves in which first two waves correspond to the reduction of TCBD moiety into monoand di- anion formation and the remaining wave corresponds to the reduction of DPP moiety. The derivatives **NDPPs 1–8** exhibit multiple oxidation waves corresponding to oxidation of various donors such as *N*, *N*-dimethylaminophenyl, Triphenylamine and thiophene attached to DPP unit.

The first oxidation potential of **NDPPs 1–8** follow the trend **NDPP 5**>**NDPP 8**>**NDPP 2**>**NDPP 7**> **NDPP 6**> **NDPP 4**>**NDPP 1**> **NDPP 3**. The redox properties revealed that it was difficult to oxidize the TCBD incorporated derivatives (**NDPPs 2, 4, 5, 7** and **8**) relative to their corresponding acetylene bridged derivatives (**NDPPs 1, 3** and **6**) however reduction becomes easier in the former ones due to presence of strong acceptor (Tetracyanobutadiene).





Figure 4. 4. Cyclic voltammograms of NDPPs 1–8 in DCM using TBAF as electrolyte.

The electrochemical data (Table 4.2.) shows that the substitution of triphenylamine on side of DPP makes reduction easier in **NDPP 6** as compared to its symmetrical *N*, *N*-dimethylaminophenyl functionalized derivative **NDPP 3** whereas oxidation becomes difficult due to the presence of relatively weak donor triphenylamine.

**Table 4. 2.** The redox properties<sup>a</sup> of symmetrical and unsymmetrical DPP based derivatives **NDPPs 1–8**.

	<i>E</i> <sup>3</sup>	$E^2$	$E^1$	$E^1$	$E^2$	<i>E</i> <sup>3</sup>
NDPP	Red	Red	Red	Oxid	Oxid	Oxid
	( <b>V</b> )	( <b>V</b> )	( <b>V</b> )	(V)	( <b>V</b> )	(V)
NDPP 1	-	-	-1.23	0.81	1.03	1.19
NDPP 2	-1.49	-0.65	-0.43	1.17	1.44	-
NDPP 3	-	-	-1.18	0.77	1.20	1.53
NDPP 4	-1.43	-0.66	-0.45	0.88	1.15	-
NDPP 5	-1.65	-0.84	-0.39	1.47	-	-
NDPP 6	-	-	-1.66	0.91	1.23	1.56
NDPP 7	-1.57	-0.65	-0.46	1.00	1.18	1.42
NDPP 8	-1.61	-0.77	-0.35	1.35	-	-

<sup>a</sup>The electrochemical analysis was performed in a 0.1 M solution of  $Bu_4NPF_6$ in dichloromethane at 100 mVs<sup>-1</sup> scan rate, versus SCE at 25 °C.

# **4.5.** Theoretical calculations

## **Density Functional Theory Calculations**

The density functional theory (DFT) calculations were carried out to understand the geometry, and the electronic structure of the symmetrical and unsymmetrical *N*, *N*-dimethylaminophenyl/Triphenylamine functionalized derivatives **NDPPs 1–8** using the Gaussian09W program.<sup>[56]</sup> The long alkyl chains on lactam ring were replaced by ethyl group to reduce the computation time. The DFT calculations were performed at the B3LYP/6-31+G\*\* for C, H, O, N and S level of theory. The frontier molecular orbitals (FMOs) of **NDPPs 2-8** are shown in Figure 4.5.



**Figure 4. 5.** HOMO-LUMO gap of **NDPPs 3-8** calculated *via* B3LYP/6-31+G\*\* for C, H, O, N and S level of theory.

The electron density at highest occupied molecular orbitals (HOMOs) of NDPPs **1**, **3** and **6** are distributed over the whole molecule whereas the electron density in their lowest unoccupied molecular orbitals (LUMOs) are localized mainly on the DPP core as shown in Figure 4.5. The D–A interaction has been observed in TCBD bridged **NDPPs 2**, **4**, **5**, **7** and **8** from donors (*N*, *N*-dimethylaminophenyl/TPA to acceptors (DPP and TCBD moieties) which is reflected from FMOs. The calculated HOMO energy levels for **NDPPs 1–8** are -4.62, -5.40, -4.40, -5.00, -5.73, -4.52, -5.07, -5.73 eV and the corresponding LUMO levels are -2.45, -3.48, -2.41, -3.33, -2.45, -3.39 and -3.99 eV respectively. The theoretically calculated HOMO-LUMO gap follow the trend **NDPP 1>NDPP 6>NDPP 3>NDPP 2>NDPP 5>NDPP 8>NDPP 7>NDPP 4**.

Time Dependent Density Functional Theory (TD-DFT) Calculation To get an idea about the various electronic transitions, the time dependent density functional theory (TD-DFT) calculation was performed. The major electronic transitions in NDPPs 1–8 calculated from TD–DFT with composition and oscillator strengths are shown in Table 4.3. The transitions that occur from HOMO–LUMO in longer wavelength are due to intramolecular charge transfer while the other transitions in shorter wavelength region for **NDPPs 1**, **3** and **6** are due to  $\pi$ - $\pi$ \* transitions of DPP moiety. The ICT band in TCBD incorporated DPP based derivatives **NDPPs 2**, **4**, **5**, **7** and **8** arises from the transitions HOMO-1 $\rightarrow$ LUMO+1, HOMO $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO respectively while the other major transitions correspond to  $\pi$ - $\pi$ \* transition. The HOMO–LUMO gap values obtained from DFT calculations shows that the incorporation of TCBD unit lowers the HOMO-LUMO gap in **NDPPs 1**, **3** and **6** which found to be in good agreement with the optical band gap values from the onset absorption.

NDPP	Wavelength	Composition	Oscillation
	( <b>nm</b> )		strength
			$(f^{a})$
NDPP 1	555.34	HOMO→LUMO	0.92
	419.01	(0.71)	0.13
	376.62	HOMO-1→LUMO	0.12
		(0.63)	
		HOMO→LUMO+1	
		(0.50)	
NDPP 2	674.16	HOMO→LUMO	0.73
	455.28	(0.70)	0.14
	430.00	HOMO→LUMO+2	0.12
		(0.63)	
		НОМО-	
		1→LUMO+1 (0.69)	
NDPP 3	575.17	HOMO→LUMO	1.27
	396.03	(0.71)	0.16

**Table 4. 3.** Major electronic transitions of NDPPs 1-8 calculated byTD-DFT.

		HOMO→LUMO+1	
		(0.43)	
NDPP 4	695.36	HOMO→LUMO	1.02
	470.82	(0.70)	0.15
	423.23	HOMO→LUMO+2	0.13
		(0.64)	
		НОМО-	
		2→LUMO+1 (0.63)	
NDPP 5	738.78	HOMO→LUMO	1.19
	537.74	(0.71)	0.05
	457.62	HOMO→LUMO+2	0.01
		(0.70)	
		НОМО-	
		1→LUMO+1 (0.68)	
NDPP 6	676.37	HOMO→LUMO	0.36
	445.24	(0.70)	0.34
	380.39	HOMO-1→LUMO	0.09
		(0.66)	
		HOMO-5→LUMO	
		(0.50)	
NDPP 7	691.48	HOMO→LUMO	1.01
	465.85	(0.70)	0.16
	429.93	HOMO→LUMO+2	0.14
		(0.63)	
		НОМО-	
		2→LUMO+1 (0.69)	
NDPP 8	584.24	HOMO→LUMO	0.99
	459.46	(0.70)	0.10
		НОМО-	
		1→LUMO+1 (0.63)	

 $f^{a}$ =oscillation strength

# 4.6. Experimental Section

## **General methods**

The chemicals were used as received unless otherwise indicated. All the moisture sensitive reactions were performed under argon atmosphere using the standard Schlenk method. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded by using CDCl<sub>3</sub> as the solvent. The <sup>1</sup>H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl<sub>3</sub>, 7.26 ppm). The multiplicities are given as: s (singlet), d (doublet), m (multiplet), and the coupling constants, *J*, are given in Hz. The <sup>13</sup>C NMR chemical shifts are reported with relative to the solvent residual peak (CDCl<sub>3</sub>, 77.02 ppm). HRMS were recorded on a mass spectrometer (ESI-TOF). The absorption spectra of DPPs were recorded on UV-visible Spectrophotometer in dichloromethane. Cyclic voltammograms (CVs) were recorded on an electrochemical analyzer using glassy carbon as working electrode, Pt wire as the counter electrode, and saturated calomel electrode as the reference electrode.

## Synthesis of NDPP 1

**DPP 1** (0.250 g, 0.37 mmol) and 4-ethynyl-*N*, *N*-dimethylaniline (0.080 g, 0.55 mmol) were dissolved in a 100 mL round bottom flask containing anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 min followed by addition of  $Pd(PPh_3)_4$  (0.017 g, 0.015 mmol), and CuI (0.006 g, 0.030 mmol). The reaction mixture was stirred overnight at 80°C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (3:2) as an eluent to get **NDPP 1** in 60% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 8.93 (2H, m), 8.66 (1H, m), 7.62 (1H, d), 7.39 (2H, m), 7.31 (1H, m), 6.66 (1H, m), 6.56 (1H, m), 4.02 (4H, m), 2.88 (6H, m), 1.73 (4H, m), 1.33 (28H, m), 0.86 (6H, m) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 161.4, 161.2, 150.6, 139.6, 139.5, 135.8, 135.2, 133.1,132.9, 131.9, 130.6, 130.2, 129.9, 129.3, 128.6,

112.0, 111.7, 108.6, 108.0, 107.9, 80.8, 42.3, 40.1, 31.9, 30.1, 30.0, 29.5, 29.3, 29.2, 26.9, 22.7, 14.1; HRMS m/z calcd for  $C_{44}H_{57}N_3O_2S_2$ : 746.3784 [M+Na<sup>+</sup>], found 746.3282; UV/vis (Dichloromethane)  $\lambda_{max}$  585 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (1.48×10<sup>4</sup>).

## Synthesis of NDPP 2

**NDPP 1** (0.100 g, 0.138 mmol) and tetracyanoethylene (0.026 g, 0.207 mmol) were dissolved in 50 mL round bottom flask containing anhydrous dichloromethane under argon atmosphere. The reaction mixture was allowed to stirred for 15 minutes at room temperature. The solvent was removed under vaccum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (1:4) as an eluent to get **NDPP 2** in 85% yield.<sup>[58]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.96 (2H, s), 7.41 (4H, d), 7.31 (2H, s), 6.65 (4H, m), 4.09 (4H, s), 3.02 (12H,s), 1.76 (4H, s), 1.35 (28H, m), 0.87 (6H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 161.2, 150.6, 139.0, 135.7, 132.9, 131.9, 130.1, 129.4, 111.7, 108.7, 108.3, 100.0, 80.9, 42.4, 40.1, 31.9, 30.1, 29.6, 29.3, 26.9, 22.7, 14.1; HRMS m/z calcd for C<sub>54</sub>H<sub>66</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: 889.4519 [M+Na<sup>+</sup>], found 889.4521; UV/vis (Dichloromethane)  $\lambda_{max}$  632 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (4.72×10<sup>4</sup>).

## Synthesis of NDPP 3

**DPP 2** (0.250 g, 0.34 mmol) and 4-ethynyl-*N*, *N*-dimethylaniline (0.122 g, 0.84 mmol) were dissolved in a 100 mL round bottom flask containing anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 min followed by addition of  $Pd(PPh_3)_4$  (0.017 g, 0.015 mmol), and CuI (0.006 g, 0.030 mmol). The reaction mixture was stirred overnight at 80°C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (3:2) as an eluent to get **NDPP 3** in 70% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 9.16 (1H, d), 9.02 (1H, d), 7.78 (4H, m), 7.34 (1H, s), 6.71 (2H, d), 4.07 (4H, s), 3.17 (6H, s), 1.72 (4H,

m), 1.41 (28H, m), 0.87 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 162.0, 161.4, 160.6, 157.9, 154.6, 143.9, 139.9, 137.9, 137.3, 135.6, 135.1, 133.3, 132.5, 129.2, 117.7, 114.2, 113.3, 113.1, 112.7, 112.3, 111.9, 108.4, 80.1, 42.7, 42.5, 40.2, 31.9, 30.4, 29.8, 29.5, 29.3, 29.2, 26.8, 22.7, 14.2, 14.1; HRMS m/z calcd for C<sub>50</sub>H<sub>57</sub>N<sub>7</sub>O<sub>2</sub>S<sub>2</sub>: 874.3907 [M+Na<sup>+</sup>], found 874.3336; UV/vis (Dichloromethane)  $\lambda_{max}$  678 nm,  $\epsilon$ [M<sup>-1</sup>cm<sup>-1</sup>] (1.11×10<sup>4</sup>).

# Synthesis of NDPP 4

**NDPP 3** (0.100 g, 0.11 mmol) and tetracyanoethylene (0.018 g, 0.14 mmol) were dissolved in 50 mL round bottom flask containing anhydrous dichloromethane under argon atmosphere. The reaction mixture was allowed to stirred for 10 minutes at room temperature. The solvent was removed under vaccum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (1:4) as an eluent to get **NDPP 4** in 75% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 9.20 (1H, d), 9.03 (1H, d), 7.78 (3H, m), 7.42 (2H, m), 7.35 (1H, m), 6.68 (4H, m), 4.07 (4H, d), 3.17 (3H, s), 3.07 (3H, s), 1.75 (4H, s), 1.33 (28H, m), 0.86 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 162.0, 161.4, 160.3, 157.6, 154.5, 150.8, 143.1, 140.1, 138.7, 138.6, 137.9, 137.0, 135.07, 135.02, 134.8, 133.5, 133.4, 133.2, 133.0, 132.7, 132.6, 128.4, 117.8, 114.2, 113.3, 113.2, 113.1, 113.0, 112.4, 112.2, 112.0, 111.9, 111.8, 111.7, 108.7, 108.0, 102.6, 42.8, 42.7, 42.6, 42.5, 40.4, 40.3, 40.2, 40.0, 32.1, 32.0, 31.9, 30.5, 30.4, 30.3, 30.2, 30.1, 30.0, 29.9, 29.8, 29.7, 29.5, 29.3, 29.2, 27.0, 26.9, 26.8, 22.9, 22.8, 22.7, 14.3, 14.1; HRMS m/z calcd for  $C_{60}H_{66}N_8O_2S_2$ : 994.4745  $[M^+],$ found 994.4227; UV/vis (Dichloromethane)  $\lambda_{max}$  731 nm,  $\in [M^{-1}cm^{-1}]$  (0.61×10<sup>4</sup>).

## **Synthesis of NDPP 5**

**NDPP 3** (0.100 g, 0.11 mmol) and tetracyanoethylene (0.035 g, 0.27 mmol) were dissolved in 50 mL round bottom flask containing anhydrous dichloromethane under argon atmosphere. The reaction mixture was allowed to stirred for 15 minutes at room temperature. The

solvent was removed under vaccum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (1:9) as an eluent to get **NDPP 5** in 90% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ in ppm): 9.14 (2H, d), 7.78 (6H, m), 6.72 (4H, m), 4.06 (4H, m), 3.18 (12H, s), 1.71 (4H, m), 1.25 (28H, m), 0.87 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ in ppm): 161.5, 160.6, 158.0, 154.6, 139.4, 139.1, 138.5, 136.8, 132.5, 117.6, 114.1, 113.3, 112.8, 112.7, 112.4, 111.5, 81.8, 42.9, 40.3, 31.9, 30.3, 29.5, 29.3, 29.2, 26.8, 22.7, 14.1; HRMS m/z calcd for C<sub>66</sub>H<sub>66</sub>N<sub>12</sub>O<sub>2</sub>S<sub>2</sub>: 1145.4765 [M+Na<sup>+</sup>], found 1145.4892; UV/vis (Dichloromethane)  $\lambda_{max}$  735 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (1.72×10<sup>4</sup>).

# Synthesis of NDPP 6

**DPP 2** (0.250 g, 0.34 mmol) and 4-ethynyl-N, N-diphenylaniline (0.082 g, 0.30 mmol) were dissolved in a 100 mL round bottom flask containing anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 min followed by addition of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.017 g, 0.015 mmol), and CuI (0.006 g, 0.030 mmol). The reaction mixture was stirred overnight at 60°C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (3:2) as an eluent to get DPP 3 in 55% yield. DPP 3 (0.150 g, 0.16 mmol) and 4-ethynyl-*N*, *N*-dimethylaniline (0.035 g, 0.24 mmol) were dissolved in a 100 mL round bottom flask containing anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 min followed by addition of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.017 g, 0.015 mmol), and CuI (0.006 g, 0.030 mmol). The reaction mixture was stirred overnight at 80°C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (1:1) as an eluent to get NDPP 6 in 75% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.93 (2H, m), 7.35 (9H, m), 7.12 (5H, m), 7.01 (2H, m), 6.65 (2H, m), 4.07 (4H, m), 3.02 (6H, s), 1.74 (4H, m), 1.35 (28H, m), 0.86 (6H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 146.9, 132.9, 132.6, 132.0, 129.5, 125.3, 124.0, 121.7, 111.8, 42.4, 40.1, 31.9, 30.1, 29.6, 26.9, 22.7,14.1; HRMS m/z calcd for C<sub>64</sub>H<sub>70</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: 1013.4832 [M+Na<sup>+</sup>], found 1013.4985; UV/vis (Dichloromethane)  $\lambda_{max}$  629 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (0.97×10<sup>4</sup>).

# **Synthesis of NDPP 7**

**NDPP 6** (0.100g, 0.10 mmol) and tetracyanoethylene (0.015g, 0.12 mmol) were dissolved in 50 mL round bottom flask containing anhydrous dichloromethane under argon atmosphere. The reaction mixture was allowed to stirred for 15 minutes at room temperature. The solvent was removed under vaccum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (1:4) as an eluent to get **NDPP 7** in 80% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 9.16 (1H, d), 9.03 (1H, d), 7.78 (3H, m), 7.38 (2H, m), 7.30 (4H, m), 7.12 (5H, m), 7.01 (2H, m), 6.73 (2H, m), 4.06 (4H, m), 1.72 (4H, m), 1.41 (28 H, m), 0.88 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 162.0, 161.4, 160.5, 157.7, 154.5, 149.0, 146.8, 142.9, 139.9, 138.3, 137.9, 137.2, 135.3, 135.2, 132.8, 132.7, 132.5, 132.3, 129.5, 129.1, 125.5, 124.2, 121.4, 117.8, 114.2. 113.9, 113.8, 109.0, 100.7, 81.8, 79.9, 42.5, 40.2, 31.9, 31.8, 30.4, 29.9, 29.7, 29.5, 29.3, 29.2, 26.8, 22.7, 14.1; HRMS m/z calcd for  $C_{70}H_{70}N_8O_2S_2$ : 1141.4955 [M+Na<sup>+</sup>], found 1141.5012; UV/vis (Dichloromethane)  $\lambda_{max}$  722 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (1.02×10<sup>4</sup>).

## Synthesis of NDPP 8

**NDPP 6** (0.100 g, 0.10 mmol) and tetracyanoethylene (0.032 g, 0.25 mmol) were dissolved in 50 mL round bottom flask containing anhydrous dichloromethane under argon atmosphere. The reaction mixture was allowed to stirred for 5 h at room temperature. The solvent was removed under vaccum and the crude product was purified by

repeated silica gel column chromatography with hexane/DCM (1:9) as an eluent to get **NDPP 8** in 85% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 9.15 (2H, d), 7.66 (6H, m), 7.39 (4H, m), 7.28 (1H, m), 7.22 (3H, m), 6.91 (2H, d), 6.72 (2H, d), 4.07 (4H, s), 3.18 (6H, s), 1.58 (4H, s), 1.41 (28H, m), 0.88 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 161.9, 161.5, 160.6, 158.0, 157.4, 154.6, 154.1, 144.3, 139.6, 139.3, 139.1, 138.6, 138.4, 136.9, 136.7, 132.5, 131.8, 130.2, 126.8, 120.7, 118.1, 117.6, 114.1, 113.4, 113.3, 112.8, 112.6, 112.4, 111.5, 81.8, 81.6, 42.9, 40.2, 31.9, 30.3, 29.7, 29.5, 29.4, 29.3, 29.2, 26.7, 22.7, 14.1; ; HRMS m/z calcd for C<sub>76</sub>H<sub>70</sub>N<sub>12</sub>O<sub>2</sub>S<sub>2</sub>: 1269.5078 [M+Na<sup>+</sup>], found 1269.5268; UV/vis (Dichloromethane)  $\lambda_{max}$  738 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (0.70×10<sup>4</sup>).

## 4.7. Conclusions

In conclusion, symmetrical and unsymmetrical N, N-dimethylaniline and TPA-functionalized DPPs (NDPPs 1-8) were designed and synthesized using Pd-catalyzed Sonogashira cross-coupling reactions, followed by a click-type [2+2] cycloaddition-electrocyclization ringopening reaction. In NDPP 6, TCNE attacks initially targeted the more electron-rich acetylene bridge linked to the N, N-dimethylaminophenyl group, resulting in the formation of NDPP 7. This observation underscores the strong electron-donating nature of the N, Ndimethylaminophenyl group compared to the triphenylamine group. The photophysical and electrochemical properties of NDPPs 1-8 were extensively studied. Incorporation of the TCBD unit led to a red shift in absorption spectra, additional low reduction potentials, and a reduced HOMO-LUMO gap. Moreover, NDPPs 1-8 demonstrated good solubility in common organic solvents. Electrochemical analysis revealed two additional low-voltage reduction waves in TCBD-based derivatives, attributed to oxidation of the TCBD unit. The broad absorption in the visible region, multiple redox potentials, and low HOMO-LUMO gap collectively indicate the potential of these molecules for optoelectronic applications.

## 4.8. References

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# Chapter 05: Impact of Donor Strength on [2+2] Cycloaddition-Retroelectrocyclization in Tetracyanobutadiene-Functionalized Diketopyrrolopyrrole Derivatives.

# 5.1. Introduction

Organic semiconductors have gained significant attention in recent years due to their potential applications in electronic and optoelectronic devices such as organic photovoltaics <sup>[1-4]</sup>, organic field-effect transistors<sup>[5]</sup>, and organic light-emitting diodes<sup>[6]</sup>. The design and</sup> synthesis of novel small molecules with tailored electronic properties is crucial for achieving improved device performance and efficiency. Diketopyrrolopyrrole (DPP) is a  $\pi$ -conjugated bicyclic di-lactam moiety and is one of the widely used organic dyes.<sup>[7-10]</sup> DPP derivatives exhibit poor solubility in organic solvents due to strong  $\pi$ - $\pi$  interactions and H-bonding interactions but the N-alkylation enhances its solubility in common organic solvents. DPP derivatives have emerged as promising acceptor units in these materials due to their strong electronaccepting nature, good thermal stability, and high charge mobility.<sup>[11]</sup> These properties make them suitable candidates for use in organic photovoltaic devices and other optoelectronic applications.<sup>[12-15]</sup> To modulate the electronic properties of DPP-based molecules and enhance their charge transport abilities, the incorporation of electron-donating moieties is a common strategy.<sup>[16-17]</sup> In this regard, ferrocene, triphenylamine, and N, N-dimethylamine have gained attention as effective donor units. These donor units not only introduce a push-pull effect within the molecules but also enable tuning of the energy levels, charge carrier mobility, and photophysical properties of the resulting materials. The synthesis of these complex molecular architectures often requires efficient coupling methodologies that ensure regioselectivity and high yields. The Sonogashira cross-coupling reaction has proven to be a valuable tool for constructing carbon-carbon bonds under mild

conditions.<sup>[18-19, 23]</sup> This method allows for the incorporation of various functional groups and substituents with high precision, enabling the design of tailored molecular structures. Additionally, the [2+2] cycloaddition-retroelectrocyclization reaction, often referred to as a "click-type" reaction, has emerged as a powerful tool for the construction of conjugated systems.<sup>[20-22]</sup> This reaction involves the formation of a cyclobutane ring followed by its electrocyclic ringopening, resulting in the generation of a conjugated  $\pi$ -system. The clicktype reaction offers advantages such as high atom economy, regioselectivity, and compatibility with a wide range of functional groups, making it an attractive method for the construction of complex organic frameworks. In this study, we aim to design and synthesize a series of small organic molecules (FcDPP 1-FcDPP 8) by incorporating DPP as an acceptor unit and ferrocene, triphenylamine, and N, Ndimethylamine as donor units as shown in Figure 5.1. We employed the Sonogashira cross-coupling reaction to achieve efficient coupling of these units and subsequently explore the [2+2] cycloadditionretroelectrocyclization reaction to access  $\pi$ -conjugated systems with tunable electronic properties. By systematically varying the donor strength and position, we anticipate gaining insights into the impact of these modifications on the optoelectronic properties of the resulting materials. This research not only contributes to the fundamental understanding of structure-property relationships in organic semiconductors but also opens doors for the development of highperformance materials for various electronic and optoelectronic applications.



Figure 5. 1. Structures of ferrocenyl substituted DPPs FcDPPs 1-8.

#### 5.2. Result and Discussions

The ferrocene-based DPP derivative 1 was synthesized through the Sonogashira cross-coupling reaction involving dibromo DPP and ethynyl ferrocene, following a procedure documented in the literature.<sup>[23]</sup> Subsequent transformations of derivative 1 were achieved by subjecting it to Sonogashira cross-coupling reactions with various aryl alkynes, including 9-(4-ethynylphenyl)-9H-carbazole (a), 4ethynyl-N, N-dimethylaniline (b), and 4-ethynyl-N, N-diphenylaniline (c). The reactions were carried out using  $Pd(PPh_3)_4$  as a catalyst, CuI as a co-catalyst, toluene as a solvent, and triethylamine as base, at a temperature of 90 °C for 12 h. This methodology yielded FcDPP 1, FcDPP 6 and FcDPP 3 in yields ranging from 60% to 65%.as shown in Scheme 5.1. FcDPP 1 was subjected to a reaction with 1 equiv. of TCNE at room temperature for 24 hours, leading to the exclusive formation of the mono-TCBD bridged derivative, FcDPP 2, in 80% yield. Despite efforts to produce the di-TCBD bridged derivative (FcDPP 9) by employing harsher reaction conditions, such as elevating the temperature to 40 °C using DCM as the solvent, or to 80 °C using DCE as the solvent, were unsuccessful. The reaction of FcDPP 3 with 1 equiv. of TCNE in DCM at room temperature for 3 hours resulted in the formation of mono- and di-TCBD functionalized derivatives, FcDPP 4 and FcDPP 5, in 62% and 20% yields respectively. Moreover, the reaction of FcDPP 3 with 2 equiv. of TCNE at room temperature for 6 hours yielded FcDPP 5 in 85% yield. Upon reaction of FcDPP 6 with 1

equiv. of TCNE at room temperature for 15 minutes, **FcDPP 7** and **FcDPP 8** were generated in 68% and 20% yields respecticely. When **FcDPP 6** was reacted with 2 equiv. of TCNE at room temperature for 1 hour, **FcDPP 8** was synthesized in 90% yield as shown in Scheme 5.2. These results suggested that the attack of TCNE occurs primarily on the electron-rich triple bond, and the rate of the cycloaddition reaction with TCNE depends on the donor strength linked to it. Specifically, the reaction proceeds rapidly when employing a strong donor, such as *N*, *N*-dimethylaniline, taking only a few minutes to complete. However, with decreasing donor strength (as observed with TPA and *N*-phenyl carbazole), the reaction extends to several hours before reaching completion.



Scheme 5. 1. Synthetic scheme of ferrocene based DPPs FcDPPs 1, 3 and 6.

The ferrocene based DPP derivatives (**FcDPPs 1–8**) were purified by repeated silica gel column chromatography and recrystallization techniques. **FcDPPs 1–8** are readily soluble in common organic solvents and were fully characterized by common spectroscopic techniques (<sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS). The <sup>1</sup>H NMR spectra of **FcDPP 1** and **FcDPP 3** exhibit signals for protons of the ferrocene group in the region

of 4.0–4.5 ppm. After incorporating a tetracyanobutadiene group (**FcDPP 2** and **FcDPP 4**), the signals for ferrocene protons shifts in the region of 4.0–5.5 ppm, this shift indicates that the TCNE attack initially occurs at the more electron-rich acetylene bridge linked to the ferrocene group, resulting in the synthesis of **FcDPP 2** and **FcDPP 4**. This suggests the strong donor strength of the Ferrocene group relative to the *N*-phenyl carbazole and triphenylamine group. The <sup>1</sup>H NMR spectra of **FcDPP 6** exhibit a singlet for the six methyl protons of the *N*, *N*-dimethylaminophenyl group at 3.0 ppm but after incorporating a tetracyanobutadiene group (**FcDPP 7**), the singlet for the six methyl protons shifts to 3.17 ppm. This shift indicates that the TCNE attack initially occurs at the more electron-rich acetylene bridge linked to the *N*, *N*-dimethylaminophenyl group, resulting in the synthesis of **FcDPP 7**. This suggests the strong donor strength of the ferrocene bridge linked to the *N*, *N*-dimethylaminophenyl group, resulting in the synthesis of **FcDPP 7**. This suggests the strong donor strength of the ferrocene bridge linked to the *N*, *N*-dimethylaminophenyl group, resulting in the synthesis of **FcDPP 7**.



Scheme 5. 2. Synthetic scheme of ferrocene based DPP derivatives FcDPPs 2, 4, 5, 7, 8 and 9.

# **5.3.** Photophysical Properties

The electronic absorption spectra ferrocene based DPP derivatives **FcDPPs 1–8** were recorded in  $10^{-5}$  M DCM solution and as film at room temperature (Figure 5.2.) and the corresponding data are listed in Table 5.1.



**Figure 5. 2.** Normalized electronic absorption spectra of **FcDPPs 1-8** in  $10^{-5}$  M DCM (solid lines) and in thin films (dash lines).

The absorption spectra of FcDPP 1-8 exhibit broad absorption bands covering visible-NIR region from 400-900 nm in DCM solution and from 400–1100 nm in film prepared using spin coater. The absorption bands for TCBD bridged derivatives (FcDPPs 5, 7 and 8) at shorter wavelength region and longer wavelength region correspond to the  $\pi$ - $\pi^*$  transition and intramolecular charge transfer (ICT) from donor to DPP respectively. The di-TCBD bridged derivatives FcDPP 5 and FcDPP 8 exhibited red shifted absorption maxima relative to mono-TCBD bridged derivatives FcDPP 4 and FcDPP 7 due to increase in donor-acceptor interaction. The similar trends were observed while comparing the mono-TCBD bridged derivatives (FcDPP 2, FcDPP 4 and FcDPP 7) with their acetylene linked deriartives (FcDPP 1, FcDPP 3 and FcDPP 6) due to strong donor-acceptor interactions. The synthesized ferrocene-based DPP derivatives (FcDPP) exhibit distinct photophysical properties that arise from variations in their molecular structures and donor-acceptor interactions. In terms of absorption wavelengths ( $\lambda_{abs}$ ), FcDPP 2 displays the highest values both in solution (710 nm) and thin film (786 nm), indicating its efficient light absorption across a broad spectrum. On the other hand, FcDPP 7 shows the largest difference between its solution-phase (720 nm) and thin-film (761 nm) absorption maxima, potentially due to aggregation effects in the solid state. The molar extinction coefficients ( $\varepsilon$ ) reflect the efficiency of light absorption by the compounds. FcDPP 6 exhibits the highest  $\varepsilon$  values indicative of strong light-absorbing properties resulting from its molecular structure. Conversely, FcDPP 8 shows comparably lower  $\varepsilon$ values, suggesting relatively weaker light absorption efficiency. The optical band gap (E<sub>c</sub>) values provide insights into the energy required for electronic transitions within the molecules. FcDPP 4 possesses the low optical band gap (1.35 eV), indicating its potential for efficient charge transport and utilization in photovoltaic devices. On the other hand, FcDPP 2 exhibits the high optical band gap (1.45 eV), suggesting its role as a potential electron acceptor in organic solar cells. The optical band gap and theoretical HOMO-LUMO gap of ferrocene-based derivatives FcDPPs 1-8 were calculated from onset absorption and density functional theory calculations respectively and the data are listed in Table 5.1. The incorporation of additional TCBD group significantly lowers the optical band gap and theoretical HOMO–LUMO gap.



Figure 5. 3. Normalized UV-vis absorption spectra of FcDPPs 5 and 7 in different solvents.

The solvent dependent absorption spectra of **FcDPPs 1–8** was recorded in toluene, dichloromethane (DCM), tetrahydrofuran (THF), ethylacetate (EAA) and N, N-dimethylformamide (DMF) shows negative solvatochromism. The absorption curve undergoes blue shift as the polarity of solvent increases from toluene to DMF as shown in Figure 5.3.

FcDPP	$\lambda_{abs}(nm)^a$	$\lambda_{abs}(nm)^b$	3	Ec	E <sup>d</sup> (eV)
			(×10 <sup>4</sup> M <sup>-</sup>	(eV)	
			<sup>1</sup> cm <sup>-1</sup> ) <sup>a</sup>		
FcDPP 1	620	679	0.47	1.76	2.05
	580	626	0.39		
FcDPP 2	710	786	1.04	1.45	1.74
FcDPP 3	626	659	1.26	1.75	2.02
	586	610	1.01		
FcDPP 4	728	724	0.99	1.35	1.63
FcDPP 5	736	768	1.42	1.44	1.71
	685	704	1.22		
	479	495	1.20		
FcDPP 6	628	671	2.50	1.72	2.03
	590	616	2.13		
FcDPP 7	720	761	0.69	1.40	1.78
	465	476	0.79		
FcDPP 8	733	780	0.59	1.48	1.75
	686	701	0.51		
	471	497	0.73		

**Table 5. 1.** The optical and theoretical/computational properties of **FcDPPs 1-8**.

<sup>a</sup> Absorbance measured in DCM solution;  $\epsilon$ : extinction coefficient; <sup>b</sup>absorbance measured in film; <sup>c</sup>Optical band gap; <sup>d</sup>Theoretical band gap.

# **5.4. Electrochemical Properties**

The electrochemical properties of ferrocene based DPP derivatives **FcDPP 1–FcDPP 8** were explored by cyclic voltammetry (CV) technique in dichloromethane solvent using 0.1M tetrabutylammonium hexafluorophosphate ( $Bu_4NPF_6$ ) as supporting electrolyte. The CV plots of **FcDPP 1–FcDPP 8** are shown in Figure 5.4. and the corresponding electrochemical data are listed in Table 5.2.

The ferrocene-based DPP derivatives **FcDPP 1–FcDPP 8** exhibit multiple oxidation waves between 0.54-1.67 V corresponding to the donor units (ferrocene, thiophene and *N*-phenyl carbazole/triphenylamine/*N*, *N*-dimethyl aniline). The acetylene bridged ferrocene-based derivatives **FcDPP 1**, **FcDPP 3** and **FcDPP 6** exhibit one reduction waves corresponding to mono-anion formation of DPP. The TCBD bridged derivatives **FcDPP 2**, **FcDPP 4**, **FcDPP 5**, **FcDPP 7** and **FcDPP 8** exhibit three reduction waves in which first two reduction waves between -0.35 – -0.87 V corresponds to the reduction of TCBD moiety into mono- and di- anion and the remaining wave corresponds to the reduction of DPP moiety. The oxidation of ferrocene becomes difficult in mono- and di-TCBD functionalized ferrocene derivatives (**FcDPP 2**, **FcDPP 4**, **FcDPP 5**, **FcDPP 7** and **FcDPP 8**) relative to corresponding acetylene bridged derivatives (**FcDPP 2**, **FcDPP 3** and **FcDPP 6**) due to introduction of strong electron acceptor group (Tetracyanobutadiene) whereas reduction becomes easier upon incorporation of acceptor group as shown in Table 5.2.

	<i>E</i> <sup>3</sup>	$E^2$	<i>E</i> <sup>1</sup>	$E^{1}$	$E^2$	$E^3$	$E^4$
FcDPP	Red	Red	Red	Oxid	Oxid	Oxid	Oxid
	<b>(V</b> )	<b>(V</b> )	( <b>V</b> )	<b>(V</b> )	( <b>V</b> )	<b>(V</b> )	(V)
FcDPP 1	-	-	-1.73	0.55	0.89	1.31	1.67
FcDPP 2	-1.83	-0.71	-0.43	0.81	1.04	1.34	1.64
FcDPP 3	-	-	-1.12	0.54	0.81	1.04	1.41
FcDPP 4	-1.82	-0.71	-0.44	0.55	0.88	1.10	1.48
FcDPP 5	-1.75	-0.84	-0.35	0.87	1.11	1.24	1.67
FcDPP 6	-	-	-1.72	0.55	0.73	0.94	-
FcDPP 7	-1.64	-0.65	-0.46	0.56	0.77	1.11	1.32
FcDPP 8	-1.60	-0.87	-0.35	0.86	1.28	1.57	-

**Table 5. 2.** The electrochemical properties<sup>a</sup> of ferrocene-based derivatives **FcDPP 1–FcDPP 8**.

<sup>a</sup>The electrochemical analysis was performed in a 0.1 M solution of  $Bu_4NPF_6$ in dichloromethane at 100 mVs<sup>-1</sup> scan rate, versus SCE at 25 °C. The trend in the first oxidation potential of **FcDPP 1–FcDPP 8** follows the order: **FcDPP 3<FcDPP 1≈FcDPP 4≈FcDPP 6<FcDPP 7<FcDPP 2<FcDPP 8<FcDPP 5**. The trend in the first reduction potential of **FcDPP 1–FcDPP 8** follows the order: **FcDPP 5≈FcDPP 8<FcDPP 2<FcDPP 4<FcDPP 7< FcDPP 3<FcDPP 6<FcDPP 1**.





**Figure 5. 4.** Cyclic voltammograms of **FcDPPs 1–8** in dichloromethane solvent using 0.1 M tetrabutylammonium hexafluorophosphate ( $Bu_4NPF_6$ ) as supporting electrolyte.

# 5.5. Theoretical Calculations

# **Density Functional Theory**

The density functional theory (DFT) calculation was carried out to understand the geometry, and the electronic structure of the asymmetrical ferrocene functionalized DPP **FcDPPs 1–8** using the Gaussian09W program.<sup>[24]</sup> The long alkyl chains on lactam ring were replaced by ethyl group to reduce the computation time. The DFT calculations were performed B3LYP/6-31G\*\* for C, H, N, S, O and Lanl2DZ for the Fe. The frontier molecular orbitals (FMOs) of **FcDPPs 3–8** are shown in Figure 5.5.



**Figure 5. 5.** The electron density distribution and the HOMO-LUMO gap in **FcDPPs 3–8**.

The electron density at highest occupied molecular orbitals (HOMOs) of **FcDDP 1, FcDPP 3, FcDPP 6 and FcDPP 8** are distributed on the whole molecule whereas the electron density in their lowest unoccupied molecular orbitals (LUMOs) are localized mainly on the acceptor units (DPP). The delocalization of HOMOs on donors (triphenylamine/Ferrocene/*N, N*-dimethylaniline/*N*-phenyl carbazole) as well as acceptor (DPP/TCBD) and LUMOs on acceptors only

(DPP/TCBD units) shows the typical D–A interaction and charge transfer from donor to acceptor in **FcDPP 2**, **FcDPP 4**, **FcDPP 5** and **FcDPP 7**. The HOMO energy level in **FcDPP 1** is -4.81 eV and the LUMO energy level in TCNE is at -4.56 eV while after the incorporation of one TCBD group in **FcDPP 1** the HOMO energy level gets more stabilized in **FcDPP 2** (-5.38 eV), Thus the energy level difference between the HOMO of **FcDPP 2** and the LUMO of TCNE is higher as compared to the energy level difference between the HOMO of TCNE as shown in Figure 5.6. This hinders the further reaction of TCNE group with **FcDPP 2** and could be the possible reason for not getting **FcDPP 3** even on elevated temperature.



**Figure 5. 6.** HOMO-LUMO gap calculations of **FcDPP 1**, **2** and TCNE.

The calculated HOMO energy levels for **FcDPPs 1-8** are -4.81, -5.38, -4.64, -5.14, -5.81, -4.55, -5.22, -5.84 eV and the corresponding LUMO levels are -2.76, -3.64, -2.62, -3.51, -4.09, -2.52, -3.44, -4.09 eV respectively. The theoretically calculated HOMO-LUMO gap follow the trend **FcDPP 1>FcDPP 6>FcDPP 3>FcDPP 7>FcDPP 8>FcDPP 2>FcDPP 5>FcDPP 4**.

#### **Time Dependent Density Functional Theory (TD–DFT)**

The time dependent density functional theory (TD-DFT) calculation was performed in order to get the idea of electronic transitions in DPP based derivatives with ferrocene as one end capping donor FcDPPs 1-8. The major electronic transitions in FcDPPs 1-8 calculated from TD-DFT with composition and oscillator strengths are shown in Table 5.3. The major charge transfer transition in FcDPPs 1-8 occur from HOMO- $2 \rightarrow LUMO+5$ , HOMO→ LUMO, HOMO-2→LUMO+5, HOMO→LUMO, HOMO-1→LUMO, HOMO→LUMO, HOMO→LUMO+1 and HOMO-1→LUMO respectively while the other transitions in FcDPP 1, FcDPP 3, FcDPPs 6-8 occurs from HOMO→LUMO, HOMO→LUMO, HOMO-3→LUMO+3, HOMO $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO respectively corresponds to  $\pi$ - $\pi^*$  transitions. The theoretical HOMO-LUMO gaps of FcDPPs 1–8 is in good agreement with the optical band gaps as shown in Table 5.1.

Compound	Wavelength	Composition	Oscillation
	(nm)		Strength (f <sup>a</sup> )
FcDPP 1	642	HOMO→LUMO (0.65)	1.67
	599	HOMO-2→LUMO+5 (0.30)	0.23
FcDPP 2	586	HOMO $\rightarrow$ LUMO (0.70)	0.89
FcDPP 3	654	HOMO→LUMO (0.68)	1.96
	601	HOMO-2→LUMO+5 (0.31)	0.12
FcDPP 4	804	HOMO→LUMO (0.70)	1.48
	642	HOMO-1→LUMO (0.68)	0.15
	882	HOMO→LUMO (0.62)	0.015
FcDPP 5	736	HOMO-1→LUMO (0.63)	1.16
	648	HOMO→LUMO (0.68)	1.78
FcDPP 6	599	HOMO-3→LUMO+3 (0.39)	0.12

**Table 5. 3.** Major electronic transitions of **FcDPPs 1–8** calculated by TD-DFT.

FcDPP 7	599	HOMO→LUMO (0.70)	0.63
	501	HOMO→LUMO+1 (0.69)	0.24
FcDPP 8	789	HOMO-1→LUMO (0.67)	0.04
	733	HOMO→LUMO (0.68)	1.10

 $f^{\rm a}$ =oscillation strength

# **5.6. Experimental Section:**

# **General methods**

The chemicals were used as received unless otherwise indicated. All the moisture sensitive reactions were performed under argon atmosphere using the standard Schlenk method. <sup>1</sup>H NMR (400 MHz/500 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded by using CDCl<sub>3</sub> as the solvent. The <sup>1</sup>H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl<sub>3</sub>, 7.26 ppm). The multiplicities are given as: s (singlet), d (doublet), m (multiplet), and the coupling constants, *J*, are given in Hz. The <sup>13</sup>C NMR chemical shifts are reported with relative to the solvent residual peak (CDCl<sub>3</sub>, 77.0 ppm). HRMS was recorded on a mass spectrometer (ESI-TOF). The absorption spectra of DPPs were recorded on UV-visible Spectrophotometer in dichloromethane. Cyclic voltammograms (CVs) were recorded on an electrochemical analyzer using glassy carbon as working electrode, Pt wire as the counter electrode, and SCE as the reference electrode.

#### Synthesis of FcDPP 1

In 100 mL round bottom flask, dibromo–DPP (0.250 g, 0.34 mmol) and ethynyl ferrocene (0.064 g, 0.30 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.017 g, 0.015 mmol) and CuI (0.006 g, 0.030 mmol) were then added. The reaction mixture was stirred overnight at 60 °C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (3:2) as an eluent to get **1** in 62% yield and then in 100 mL round bottom flask, **1** (0.150g, 0.16 mmol) and 9-(4-ethynylphenyl)-9H-carbazole (**a**) (0.043 g, 0.16 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.009 g, 0.008 mmol) and CuI (0.002 g, 0.014 mmol) were then added. The reaction mixture was stirred overnight at 80 °C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (3:2) as an eluent to get **FcDPP 1** in 60% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.93 (2H, s), 8.16-8.14 (2H, m), 7.80-7.78 (2H, m), 7.63-7.61 (2H, m), 7.46-7.44 (4H, m), 7.33-7.22 (4H, m), 4.56 (4H, s), 4.33-4.28 (5H, m), 4.10-4.08 (4H, m), 1.77 (4H, s), 1.51-1.26 (28H, m), 0.87 (6H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 161.4, 161.2, 140.5, 139.7, 138.7, 138.5, 136.9, 135.4, 133.5, 133.2, 132.4, 130.9, 130.2, 129.5, 128.2, 127.0, 126.3, 123.8, 121.2, 120.6, 120.5, 109.9, 109.0, 108.5, 98.6, 97.1, 83.4, 78.9, 71.8, 70.3, 69.7, 63.9, 42.5, 32.1, 32.0, 30.2, 29.7, 29.5, 29.4, 27.0, 22.8, 14.3; HRMS (ESI) m/z calcd for C<sub>66</sub>H<sub>67</sub>FeN<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: 1053.4020 [M<sup>+</sup>] found 1053.4009; UV/vis (Dichloromethane)  $\lambda_{max}$  620 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (0.47×10<sup>4</sup>).

#### Synthesis of FcDPP 2

**FcDPP 1** (0.100g, 0.10 mmol) and tetracyanoethylene (0.015g, 0.12 mmol) were dissolved in 50 mL round bottom flask containing anhydrous dichloromethane under argon atmosphere. The reaction mixture was allowed to stirred for 6 h at room temperature. The solvent was removed under vaccum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (1:4) as an eluent to get **FcDPP 2** in 80% yield.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ in ppm): 9.17-9.16 (1H, m), 9.00-8.99 (1H, m), 8.16-8.14 (2H, d, *J*=10 Hz), 7.80-7.78 (2H, d, *J*=10 Hz), 7.65 (3H, m), 7.63-7.49 (1H, m), 7.48-7.41 (3H, m), 7.34-7.30 (2H, m), 7.22

(1H, s), 5.58 (1H, s), 5.07 (1H, s), 4.88 (1H, s), 4.53-4.36 (5H, m), 4.28 (1H, s), 4.10-4.03 (4H, m), 1.73-1.72 (4H, m), 1.42-1.25 (28H, m), 0.89-0.86 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 172.0, 161.4, 160.6, 155.0, 142.8, 141.5, 139.7, 138.9, 138.0, 137.8, 136.4, 135.7, 135.1, 133.7, 133.3, 131.1, 130.0, 127.0, 126.3, 123.8, 120.8, 120.6, 113.7, 113.0, 112.7, 112.5, 109.8, 109.4, 98.8, 83.1, 79.5, 78.7, 76.3, 76.0, 75.2, 72.9, 72.6, 71.7, 70.4, 42.9, 42.7, 34.3, 32.0, 30.5, 30.1, 29.7, 29.6, 29.4, 29.3, 27.0, 26.9, 22.8, 22.5, 14.3, 14.2; HRMS (ESI) m/z calcd for C<sub>72</sub>H<sub>67</sub>FeN<sub>7</sub>O<sub>2</sub>S<sub>2</sub>: 1181.4144 [M<sup>+</sup>] found 1181.3984; UV/vis (Dichloromethane)  $\lambda_{max}$  710 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (1.04×10<sup>4</sup>).

#### Synthesis of FcDPP 3

In 100 mL round bottom flask, dibromo–DPP (0.250 g, 0.34 mmol) and ethynyl ferrocene (0.064 g, 0.30 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.017 g, 0.015 mmol) and CuI (0.006 g, 0.030 mmol) were then added. The reaction mixture was stirred overnight at 60°C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (3:2) as an eluent to get 1 in 62 % yield and then in 100 mL round bottom flask, 1(0.150 g, 0.16 mmol) and 3(4-ethynyl-N, N-diphenylaniline) (0.044 g, 0.16 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and Pd(PPh<sub>3</sub>)<sub>4</sub>(0.009 g, 0.008 mmol) and CuI (0.002 g, 0.014 mmol) were then added. The reaction mixture was stirred overnight at 80 °C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (3:2) as an eluent to get FcDPP 3 in 62% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.90 (2H, m), 7.70 (2H, m), 7.37 (4H, m), 7.30 (4H, m), 7.12 (4H, m), 7.08 (2H, m), 4.55(2H, s), 4.30

(5H, m), 4.07 (4H, s), 1.75 (4H, m), 1.35 (28H, m), 0.86 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 158.68, 158.66, 146.1, 144.3, 136.7, 136.5, 136.3, 133.0, 129.7, 127.7, 127.4, 127.2, 126.9, 126.7, 125.1, 125.0, 122.8, 122.2, 121.4, 119.1, 111.9, 111.5, 106.0, 96.1, 95.7, 69.1, 67.0, 61.3, 39.85, 39.83, 31.7, 31.3, 29.4, 29.3, 29.1, 28.9, 27.8, 27.68, 27.64, 27.5, 27.2, 27.18, 27.15, 27.11, 27.07, 27.02, 26.8, 26.75, 26.70, 26.65, 26.4, 26.1, 24.39, 24.38, 23.43, 23.40, 20.18, 20.16, 11.6; HRMS (ESI) m/z calcd for C<sub>66</sub>H<sub>69</sub>FeN<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: 1055.4180 [M<sup>+</sup>] found 1055.4177; UV/vis (Dichloromethane)  $\lambda_{max}$  625 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (3.8×10<sup>4</sup>).

# Synthesis of FcDPP 4

**FcDPP 3** (0.10 g, 0.09 mmol) synthesized as per reported procedure<sup>23</sup> and tetracyanoethylene (0.014g, 0.11 mmol) were dissolved in 50 mL round bottom flask containing anhydrous dichloromethane under argon atmosphere. The reaction mixture was allowed to stirred for 3 h at room temperature. The solvent was removed under vaccum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (1:4) as an eluent to get **FcDPP 4** in 62% yield.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, *δ* in ppm): 9.16-8.97 (3H, m), 7.72-7.63 (2H, m), 7.38-7.30 (6H, m), 7.14-7.12 (4H, m), 7.10-6.91 (3H, m), 5.56 (1H, s), 5.06 (1H, s), 4.87 (1H, s), 4.57-4.52 (4H, m), 4.36-4.29 (2H, m), 4.07-4.03 (4H, m), 1.73-1.70 (4H, m), 1.41-1.27 (28H, m), 0.89-0.85 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm):171.9, 161.4, 160.4, 151.8, 149.1, 146.8, 139.7, 138.4, 137.7, 136.0, 135.0, 134.8, 133.8, 132.7, 132.4, 131.8, 130.1, 129.6, 129.0, 126.9, 126.8, 125.5, 124.2, 121.3, 118.1, 113.8, 113.6, 113.0, 112.9, 112.6, 112.5, 108.9, 100.8, 81.8, 79.4, 78.3, 76.09, 75.9, 75.0, 72.8, 72.4, 71.8, 71.6, 70.2, 69.9, 42.7, 42.5, 31.9, 30.4, 29.9, 29.7, 29.5, 29.3, 29.2, 26.8, 22.7, 14.1; HRMS (ESI) m/z calcd for C<sub>72</sub>H<sub>69</sub>FeN<sub>7</sub>O<sub>2</sub>S<sub>2</sub>: 1206.4196 [M+Na]<sup>+</sup> found 1206.4199; UV/vis (Dichloromethane)  $\lambda_{max}$  728 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (0.99×10<sup>4</sup>).

# Synthesis of FcDPP 5

**FcDPP 3** (0.144 g, 0.14 mmol) and tetracyanoethylene (0.034 g, 0.27 mmol) were dissolved in 50 mL round bottom flask containing anhydrous dichloromethane under argon atmosphere. The reaction mixture was allowed to stirred for 5 h at room temperature. The solvent was removed under vaccum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (1:9) as an eluent to get **FcDPP 5** in 85% yield.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, *δ* in ppm): 9.15-9.08 (2H, m), 7.75-7.66 (4H, m), 7.42-7.38 (4H, m), 7.29 (2H, s), 7.23-7.21 (4H, m), 6.93-6.90 (2H, m), 5.61 (1H, s), 5.09 (1H, s), 4.89 (1H, s), 4.53-4.45 (5H, m), 4.36-4.29 (1H, m), 4.05-4.03 (4H, m), 1.72-1.68 (4H, m), 1.41-1.24 (28H, m), 0.89-0.87 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm):171.5, 161.9, 160.6, 157.4, 154.1, 144.3, 139.4, 139.3, 138.7, 138.6, 138.2, 138.0, 137.9, 137.6, 136.7, 136.5, 131.8, 130.2, 126.9, 120.7, 118.0, 113.5, 113.4, 112.7, 112.6, 112.0, 111.5, 81.7, 80.0, 79.3, 75.7, 75.2, 72.9, 72.6, 71.5, 42.8, 31.9, 30.2, 29.7, 29.5, 29.4 29.3, 29.2, 26.8, 26.7, 22.7, 14.1; HRMS (ESI) m/z calcd for C<sub>78</sub>H<sub>69</sub>FeN<sub>11</sub>O<sub>2</sub>S<sub>2</sub>: 1334.4321 [M+Na]<sup>+</sup> found 1334.4209; UV/vis (Dichloromethane) λ<sub>max</sub> 736 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (1.42×10<sup>4</sup>).

#### Synthesis of FcDPP 6

In 100 mL round bottom flask, **1** (0.175 g, 0.19 mmol) and 4-ethynyl-N,N-dimethylaniline (**b**) (0.028 g, 0.19 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.009 g, 0.008 mmol) and CuI (0.002 g, 0.014 mmol) were then added. The reaction mixture was stirred overnight at 80°C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (3:2) as an eluent to get **FcDPP 6** in 65% yield.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.97-8.88 (2H, m), 7.43-7.41 (2H, d, *J*=10 Hz), 7.32-7.31 (2H, m), 6.68-6.66 (2H, d, *J*=10 Hz), 4.55

(3H, s), 4.32-4.28 (6H, m), 4.09-4.05 (4H, m), 3.02 (6H, s), 1.78-1.74 (4H, m), 1.44-1.26 (28H, m), 0.87 (6H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 161.4, 161.3, 150.7, 139.4, 138.9, 136.0, 135.5, 133.0, 132.4, 132.1, 130.4, 129.7, 129.6, 129.4, 111.9, 108.7, 108.6,108.4, 100.2, 98.3, 81.0, 78.9, 71.8, 70.3, 69.7, 64.0, 53.6, 42.5, 40.3, 32.0, 30.2, 29.7, 29.4, 27.0, 22.8, 14.3; HRMS (ESI) m/z calcd for C<sub>56</sub>H<sub>65</sub>FeN<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: 954.3761 [M+Na]<sup>+</sup> found 954.3623; UV/vis (Dichloromethane)  $\lambda_{max}$  628 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (2.50×10<sup>4</sup>).

#### Synthesis of FcDPP 7

**FcDPP 6** (0.08 g, 0.08 mmol) and tetracyanoethylene (0.011g, 0.08 mmol) were dissolved in 50 mL round bottom flask containing anhydrous dichloromethane under argon atmosphere. The reaction mixture was allowed to stirred for 15 minutes at room temperature. The solvent was removed under vaccum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (1:4) as an eluent to get **FcDPP 7** in 68% yield.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, *δ* in ppm): 9.14 (1H, s), 9.04 (1H, s), 7.81-7.77 (3H, m), 7.36 (1H, s), 6.73-6.71 (2H, d, *J*=10 Hz), 4.57 (2H, s), 4.35 (2H, s), 4.28 (5H, s), 4.10 (4H, s), 3.17 (6H, s), 1.75 (4H, s), 1.54-1.26 (28H, m), 0.88-0.86 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 162.1, 161.5, 160.6, 157.9, 154.6, 143.1, 140.0, 138.4, 138.0, 137.3, 135.3, 135.2, 132.8, 132.7, 132.6, 128.8, 117.9, 114.3, 113.4, 113.2, 112.4, 109.0, 100.7, 79.9, 78.9, 74.8, 71.9, 70.4, 70.0, 63.5, 53.6, 42.9, 42.6, 40.3, 32.0, 31.9, 30.5, 30.1, 30.0, 29.7, 29.6, 29.4, 29.3, 26.9, 22.8, 14.3, 14.2; HRMS (ESI) m/z calcd for C<sub>62</sub>H<sub>65</sub>FeN<sub>7</sub>O<sub>2</sub>S<sub>2</sub>: 1082.3884 [M+Na]<sup>+</sup> found 1082.3863; UV/vis (Dichloromethane)  $\lambda_{max}$ 720 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (0.69×10<sup>4</sup>).

# Synthesis of FcDPP 8

**FcDPP 6** (0.100 g, 0.11 mmol) and tetracyanoethylene (0.028 g, 0.22 mmol) were dissolved in 50 mL round bottom flask containing anhydrous dichloromethane under argon atmosphere. The reaction mixture was allowed to stirred for 1 h at room temperature. The solvent

was removed under vaccum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (1:9) as an eluent to get **FcDPP 8** in 90% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ in ppm): 9.14-9.08 (2H, m), 7.80-7.65 (4H, m), 6.74-6.72 (2H, m), 5.61 (1H, s), 5.09 (2H, s), 4.89 (1H, s), 4.53-4.46 (5H, m), 4.03 (4H, s), 3.18 (6H, s), 1.70-1.69 (4H, m), 1.47-1.11 (28 H, m), 0.88-0.81 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ in ppm): 171.6, 161.6, 160.7, 160.6, 158.1, 155.0, 154.7, 139.6, 139.3, 139.2, 138.5, 138.4, 137.9, 136.9, 136.5, 132.6, 117.7, 114.2, 113.6, 113.4, 112.9, 112.8, 112.7, 112.5, 112.2, 111.6, 81.9, 80.1, 79.4, 75.3, 74.6, 73.0, 72.7, 71.7, 42.9, 40.3, 32.0, 29.8, 29.6, 29.5, 29.4, 29.3, 26.9, 22.8, 14.2; HRMS (ESI) m/z calcd for C<sub>68</sub>H<sub>65</sub>FeN<sub>11</sub>O<sub>2</sub>S<sub>2</sub>: 1210.4008 [M+Na]<sup>+</sup> found 1210.3927; UV/vis (Dichloromethane)  $\lambda_{max}$  733 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (0.59×10<sup>4</sup>).

### **5.7.** Conclusions

In conclusion, we have designed and synthesized ferrocene based DPP derivatives FcDPPs 1-8 by the Pd-catalyzed Sonogashira crosscoupling reactions followed by followed by [2+2] cycloadditionelectrocyclization ring opening reaction. Their photophysical and electrochemical properties were investigated which shows that the incorporation of TCBD groups red shifts the absorption, exhibit additional two reduction potentials and lowers the HOMO-LUMO gap. Mono-TCBD incorporation took place on acetylene linked N, Ndimethyl aniline side (FcDPP 6) indicating strong donor strength of N, N-dimethylaniline unit in comparison to the ferrocene where as in FcDPP 1 and FcDPP 2, the attack of first TCNE took place at triple bond linked to ferrocene side indicating strong donor strength of ferrocene relative to triphenylamine and N-phenyl carbazole unit. The electrochemical study exhibits multiple oxidation waves in ferrocene based DPP derivatives due to oxidation of various donor units (Ferrocene/thiophene/N-phenyl carbazole/Triphenylamine). The broad absorption in visible region, multiple redox potentials and low HOMO-

LUMO gap indicates that these molecules are potential candidate for optoelectronic applications.

# 5.8. References

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# Chapter 06: Phenothiazine Based Diketopyrrolopyrrole Derivatives Functionalized with Different Donors

# **6.1. Introduction**

Over the past two decades, there has been significant development in donor-acceptor (D-A) conjugated materials, particularly for their applications in organic electronics.<sup>[1-4]</sup> These materials have garnered attention due to their unique electronic structures and versatile properties, which can be tailored through strategic design. One effective strategy involves the synthesis of conjugated donor-acceptor system that incorporate electron-rich donor and electron-deficient acceptor segments linked by a bridging unit.<sup>[5-9]</sup> This molecular architecture allows for precise control over the physical and optoelectronic properties of the small molecules by chemically modifying the donor, acceptor, or the linking group.<sup>[10-15]</sup> By fine-tuning these structural elements, researchers can achieve materials with desired characteristics such as enhanced charge carrier mobility, improved stability, and optimized energy levels for efficient charge transport.<sup>[16,17]</sup> Donoracceptor based Small organic molecules (SOMs) are of interest for their ability to facilitate intrachain push-pull charge transfer, a mechanism that underpins their utility in organic electronics. This mechanism enables the synthesis of highly conjugated SOMs with minimized energy gaps, thereby extending their absorption spectrum into the visible and near-infrared regions. Such extended absorption profiles are crucial for applications requiring efficient light harvesting, such as in photovoltaic devices.<sup>[18-22]</sup> Among the various acceptor groups, Diketopyrrolopyrrole (DPP) derivatives have emerged as a promising building block. The planar structure of DPP facilitates strong  $\pi$ - $\pi$ interactions, which is essential for promoting efficient charge transport and such molecular systems have demonstrated excellent performance
in various electronic devices, owing to their electron-deficient nature and superior light absorption properties.<sup>[23]</sup> Initially utilized as pigments in inks and coatings, DPP derivatives gained attraction in organic electronics following advancements in their synthesis for solutionprocessable semiconductors around 2008.<sup>[24-28]</sup> By incorporating electron-donating moieties such as N-phenyl carbazole, triphenylamine, and N, N-dimethylaminophenyl, researchers can further modulate the electronic structure of DPP-based materials. These donor units not only introduce a push-pull effect within the molecular framework but also allow precise adjustment of energy levels, charge carrier mobility, and photophysical properties, thereby optimizing performance in specific electronic applications. In this study, our focus is on the design and synthesis of a series of small organic molecules P-1-P-6 via Sonogashira cross-coupling reactions with DPP as the electron-deficient acceptor unit, complemented by various donor units including *N*-phenyl carbazole, triphenylamine, and N, N-dimethylaminophenyl, with phenothiazine serving as the central core (Figure 6.1). The synthesis of these complex molecular architectures is achieved through the Sonogashira cross-coupling reaction, a versatile method known for its ability to construct carbon-carbon bonds under mild conditions. This approach allows for the efficient assembly of  $\pi$ -conjugated systems with tunable electronic properties, essential for exploring structure-property relationships in organic semiconductors. By systematically varying the donor strength and position within these molecular designs, our study aims to provide insights into how these modifications impact the optoelectronic properties of the resulting materials.



**Figure 6. 1.** Structure of phenothiazine functionalized diketopyrrolopyrrole **P-1–P-6**.

## 6.2. Result and Discussions

The Sonogashira cross-coupling reactions of **1** with various aryl alkynes, including 9-(4-ethynylphenyl)-9H-carbazole (a), 4-ethynyl-N, Ndiphenylaniline (b), and 4-ethynyl-N, N-dimethylaniline (c) using Pd(PPh<sub>3</sub>)<sub>4</sub> as a catalyst, CuI as a co-catalyst, THF as a solvent, and triethylamine as base, at a temperature of 60 °C for 8h gives 2, 3 and 4 respectively in 50-60% yields (Scheme 6.1). Further reactions of intermediates 2, 3 and 4 with 3-ethynyl-10-propyl-10H-phenothiazine (5) via Sonogashira cross-coupling reaction using  $Pd(PPh_3)_4$  as a catalyst, CuI as a co-catalyst, toluene as a solvent, and triethylamine as base, at a temperature of 90 °C for 12h gives mono-substituted derivatives of phenothiazine P-1-P-3 respectively in yields 65-75% (Scheme 6.2). Similarly, the Sonogashira cross-coupling reactions of intermediates 2, 3 and 4 with 3,7-diethynyl-10-propyl-10Hphenothiazine (6) using Pd(PPh<sub>3</sub>)<sub>4</sub> as a catalyst in the presence of CuI in toluene as solvent and triethylamine as base at 90 °C for 12h gives disubstituted derivatives of phenothiazine P-4–P-6 respectively in yields 50-65% (Scheme 6.3).



Scheme 6. 1. Synthesis of Diketopyrrolopyrrole based intermediates 2–4.



Scheme 6. 2. Synthesis of phenothiazine functionalized DPPs P-1–P-3.

The phenothiazine based DPP derivatives (**P-1–P-6**) were purified by repeated silica gel column chromatography and recrystallization technique. **P-1–P-6** are readily soluble in common organic solvents such as dichloromethane, ethyl acetate, tetrahydrofuran, toluene *etc* and were fully characterized by common spectroscopic techniques (<sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS/MALDI).



Scheme 6. 3. Synthesis of phenothiazine functionalized DPPs P-4–P-6.

# **6.3.** Photophysical Properties

The electronic absorption spectra of phenothiazine based DPP derivatives **P-1–P-6** were recorded in  $10^{-5}$  M DCM solution (Figure 6.2.) and the corresponding data are listed in Table 6.1.



Figure 6. 2. Electronic absorption spectra of P-1-P-6 in  $10^{-5}$  M DCM.

The phenothiazine based DPP derivatives P-1-P-6 exhibit broad absorption band in the range of 300-800 nm in DCM covering Vis-NIR region as shown in Figure 6.2. They exhibit two major absorption bands; both correspond to the  $\pi$ - $\pi$ \* transitions. The mono-substituted phenothiazine-based derivatives (P-1-P-3) exhibit absorption maxima at 620 nm, 626 nm and 629 nm whereas di-substituted phenothiazinebased derivatives (P-4-P-6) exhibit their absorption maxima at 625 nm, 625 nm and 629 nm. This shows that phenothiazine based DPP derivatives P-1-P-6 exhibit similar absorption maxima values even on increasing the length of conjugation this might be because of break of conjugation between the two arms due to non-planarity in di-substituted phenothiazine derivatives (P-4-P-6). When the end-capped donor in DPP functionalized phenothiazine molecules (P-1-P-6) was switched from N-phenyl carbazole to N, N-dimethylamino phenyl group, the absorption bands shifted to a longer wavelength (red shift). This shows a strong interaction between the donor-acceptor interactions in P-3 and **P-6**. The molar extinction coefficients  $(\varepsilon)$  reflect the efficiency of light absorption by the compounds. The derivative P-4 exhibits the highest  $\varepsilon$ values indicative of strong light-absorbing properties Conversely, P-6 shows comparably lower  $\varepsilon$  values, suggesting relatively weaker light absorption efficiency.



Figure 6. 3. Normalized UV-vis absorption spectra of P-1 and P-4 in different solvents.

The optical band gap and theoretical HOMO-LUMO gap of phenothiazine-based derivatives **P-1–P-6** were calculated from onset absorption and density functional theory calculations respectively and the data are listed in Table 6.1. The substitution of end-capping group linked to phenothiazine by strong donor (N, N-dimethylaminophenyl) slightly lowers the optical band gap and theoretical HOMO–LUMO gap. The solvent dependent absorption spectra of **P-1–P-6** was recorded in toluene, chloroform, dichloromethane (DCM), tetrahydrofuran (THF), and N, N-dimethylformamide (DMF) shows no significant change in the absorption bands thus indicating absence of any charge transfer band as shown in Figure 6.3.

Compound	$\lambda_{abs}(nm)$	3	E <sup>a</sup> (eV)	E <sup>b</sup> (eV)
		(×10 <sup>4</sup> M <sup>-1</sup> cm <sup>-</sup>		
		1)		
P-1	620	4.7	1.85	2.01
	579	4.0		
	341	3.2		
P-2	626	6.1	1.83	1.99
	586	5.2		
	351	3.9		
P-3	629	2.8	1.80	1.99
	591	2.4		
	339	1.7		
P-4	625	15.0	1.78	1.97
	589	13.1		
	342	10.2		
P-5	625	3.9	1.76	1.95
	589	3.6		
	352	4.2		
P-6	629	2.2	1.75	1.95
	589	1.9		
	339	1.4		

**Table 6. 1.** The optical and theoretical/computational properties of **P**-**1**–**P**-**6**.

Absorbance measured in DCM solution;  $\epsilon$ : extinction coefficient; <sup>a</sup>Optical band gap; <sup>b</sup>Theoretical band gap.

## **6.4. Redox Properties**

The redox properties of phenothiazine-based DPP derivatives **P-1–P-6** were explored by cyclic voltammetry (CV) technique in dichloromethane solvent using 0.1M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) as supporting electrolyte. The CV plots of **P-1–P-6** are shown in Figure 6.4. and the corresponding electrochemical data are listed in Table 6.2.



**Figure 6. 4.** Cyclic voltammograms of **P-1–P-6** in dichloromethane solvent using 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) as supporting electrolyte.

The phenothiazine-based DPP derivatives **P-1–P-6** exhibit multiple oxidation waves between 0.40–1.05 V corresponding to oxidation of various donor units (*N*-phenyl carbazole / triphenylamine/*N*, *N*-dimethyl amino phenyl/thiophene) in which derivatives **P-1–P-3** exhibits three oxidation waves corresponding to oxidation of different end capping donor (*N*-phenyl carbazole / triphenylamine/N, N-dimethyl amino phenyl); phenothiazine and thiophene of DPP while in case of **P-3–P-6** only two oxidation waves were observed. These derivatives exhibit one reversible reduction wave in the range of -1.05 - -1.35 corresponding to reduction of DPP into mono-anion formation as shown in Figure 6.5. In both mono- and di-substituted phenothiazine-based DPP derivatives (**P-1–P-6**), it was observed that it is easier to oxidize *N*, *N*-dimethyl amino

phenyl (**P-3** and **P-6**) and triphenylamine end-capped phenothiazine derivatives (**P-2** and **P-5**) as compared to *N*-phenyl carbazole end-capped derivatives (**P-1** and **P-4**) thus reduction becomes difficult in **P-3** and **P-6**. The trend in the first oxidation potential of **P-1–P-6** follows the order **P-4**> **P-5**> **P-6**> **P-1**> **P-2** $\approx$ **P-3**. The trend in the first reduction potential of **P-1–P-6** follows the order: **P-3**> **P-2**> **P-1**> **P-6**> **P-5**> **P-4**.

Compound	$E^{1}$	$E^{1}$	$E^2$	<b>E</b> <sup>3</sup>	
	Red	Oxid	Oxid	Oxid	
	( <b>V</b> )	( <b>V</b> )	( <b>V</b> )	( <b>V</b> )	
P-1	-1.26	0.42	0.59	0.92	
P-2	-1.33	0.41	0.69	1.04	
P-3	-1.34	0.41	0.67	0.98	
P-4	-1.08	0.89	1.20	-	
P-5	-1.12	0.87	1.20	-	
P-6	-1.13	0.76	1.19	-	

**Table 6. 2.** The electrochemical properties<sup>a</sup> of phenothiazine based DPPs **P-1–P-6.** 

<sup>a</sup>The electrochemical analysis was performed in a 0.1 M solution of  $Bu_4NPF_6$ in dichloromethane at 100 mVs<sup>-1</sup> scan rate, versus Ag/AgCl at 25 °C.

#### **6.5.** Theoretical calculations

#### **Density Functional Theory**

The density functional theory (DFT) calculation was carried out to understand the geometry, and the electronic structure of the phenothiazine-based DPP derivatives **P-1–P-6** using the Gaussian 09W program.<sup>[29]</sup> The long alkyl chains on lactam ring were replaced by ethyl group to reduce the computation time. The DFT calculations were performed B3LYP/6-31G (d, p) for C, H, N, S and O. The frontier molecular orbitals (FMOs) of **P-1–P-6** are shown in Figure 6.5.



**Figure 6. 5**. Frontier molecular orbitals of phenothiazine based DPPs **P-1–P-8** calculated by DFT using B3LYP/6-31G (d, p) for C, H, N, S, O.

The phenothiazine-based DPP derivatives **P-1–P-6** exhibit non-planar geometry. The electron density of highest occupied molecular orbitals (HOMOs) of phenothiazine-based DPP derivatives **P-1–P-6** are distributed on the whole molecule whereas their lowest unoccupied molecular orbitals (LUMOs) are localized mainly on the acceptor unit (DPP core), this indicates presence of donor-acceptor interactions as shown in Figure 6.5.





The calculated HOMO energy levels for **P-1–P-6** are -4.78, -4.62, -4.53, -4.81, -4.64, -4.54 eV and the corresponding LUMO levels are -2.77, -2.63, -2.54, -2.84, -2.69, -2.59 eV respectively. The theoretically calculated HOMO-LUMO gap follow the trend **P-1**>**P-2** $\approx$ **P-3**>**P-4**>**P-5** $\approx$ **P-6**.

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

The time dependent density functional theory (TD–DFT) calculation was performed in order to get the idea of electronic transitions in phenothiazine-based DPP derivatives **P-1–P-6**. The major electronic transitions in **P-1–P-6** calculated from TD–DFT with composition and oscillator strengths are shown in Table 6.3.

Compound	Wavelength	Composition	Oscillation	
	( <b>nm</b> )		Strength (f <sup>u</sup> )	
P-1	608	HOMO→LUMO (0.70)	1.69	
	366	HOMO-1 $\rightarrow$ LUMO+1 (0.51)	0.18	
P-2	617	HOMO $\rightarrow$ LUMO (0.71)	1.83	
	396	HOMO-3→LUMO (0.51)	0.24	
P-3	614	HOMO→LUMO (0.70)	1.74	
	396	HOMO-2→LUMO (0.50)	0.41	
P-4	720	HOMO→LUMO (0.67)	3.07	
	678	HOMO→LUMO+1 (0.68)	0.92	
P-5	658	HOMO→LUMO (0.63)	2.39	
	607	HOMO-1→LUMO (0.61)	0.82	
P-6	736	HOMO→LUMO (0.65)	3.36	
	698	HOMO $\rightarrow$ LUMO+1 (0.58)	1.16	

Table 6. 3. Major electronic transitions of P-1–P-6 calculated by TD-DFT.

*f*<sup>a</sup>=oscillation strength

The break of conjugation between the two arms in phenothiazine substituted DPPs (P-4-P-6) due to non-planar structure can also be illustrated by FMOs obtained via computational calculations. This may be the probable reason for the similar absorption bands for the mono-(P-1-P-3) and di- substituted (P-4-P-6) phenothiazine-based dimer DPP derivatives. The major electronic transition in P-1–P-6 occur from HOMO $\rightarrow$ LUMO corresponds to  $\pi$ - $\pi$ \* transitions while the other transitions in P-1-P-6 occurs from HOMO-1→ LUMO+1, HOMO- $3 \rightarrow LUMO$ , HOMO-2 $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO+1, HOMO- $1 \rightarrow LUMO$ , HOMO→LUMO+1 respectively corresponds to intramolecular charge transfer transitions. The theoretical HOMO-LUMO gaps of **P-1–P-6** is in good agreement with the optical band gaps as shown in Table 6.1. The absorption spectra of P-1 and P-2 calculated from TDDFT are shown in Figure 6.7.



Figure 6.7. Theoretical absorption spectra of P-1 and P-2.

## **6.6. Experimental section:**

## **General methods**

The chemicals were used as received unless otherwise indicated. All the moisture sensitive reactions were performed under argon atmosphere using the standard Schlenk method. <sup>1</sup>H NMR (400 MHz/500 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded by using CDCl<sub>3</sub> as the solvent. The <sup>1</sup>H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl<sub>3</sub>, 7.26 ppm). The multiplicities are given as: s (singlet), d (doublet), m (multiplet), and the coupling constants, *J*, are given in Hz. The <sup>13</sup>C NMR chemical shifts are reported with relative to the solvent residual peak (CDCl<sub>3</sub>, 77.0 ppm). HRMS was recorded on a mass spectrometer (ESI-TOF). The absorption spectra of DPPs were recorded on UV-visible Spectrophotometer in dichloromethane. Cyclic voltammograms (CVs) were recorded on an electrochemical analyzer using glassy carbon as working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode.

In a 250 mL round-bottom flask, 1 (0.500 g, 0.68 mmol) and N-(4ethynylphenyl) carbazole (0.182 g, 0.68 mmol) were dissolved in anhydrous tetrahydrofuran (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 15 min and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.039 g, 0.034 mmol), and CuI (0.006 g, 0.030 mmol) were then added. The reaction mixture was stirred overnight at 65°C. After completion, the reaction mixture was allowed to cool to room temperature. The solvent was removed under vacuum and the crude was purified by silica gel column chromatography with hexane/CH<sub>2</sub>Cl<sub>2</sub> (3:1) as an eluent to get 2 in 40% yield and then in a 100 mL round-bottom flask, 2 (0.200 g, 0.22 mmol) and 3-ethynyl-10-propyl-10H-phenothiazine (0.058 g, 0.22 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 15 min and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.017 g, 0.015 mmol), and CuI (0.006 g, 0.030 mmol) were then added. The reaction mixture was stirred overnight at 90°C. After completion, the reaction mixture was allowed to cool to room temperature. The solvent was removed under vacuum and the crude was purified by silica gel column chromatography with hexane/ $CH_2Cl_2$  (3:1) as an eluent to get **P-1** in 68% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.97-8.90 (2H, m), 8.15-8.13 (2H, m), 7.77-7.75 (2H, d, J = 8 Hz), 7.61-7.59 (2H, m), 7.47-7.43 (5H, m), 7.33-7.27 (5H, m), 7.16-7.10 (2H, m), 6.94-6.83 (2H, m), 6.79-6.77 (1H, m), 4.10-4.05 (4H, m), 3.82-3.79 (2H, m), 1.85-1.74 (6H, m), 1.29-1.27 (28H, m), 1.03-1.01 (3H, m), 0.88-0.85 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 161.2, 161.1, 146.1, 144.3, 140.4, 139.4, 138.7, 138.3, 135.9, 135.4, 133.3, 133.1, 132.7, 130.9, 130.8, 130.0, 129.3, 128.2, 127.5, 127.4, 126.9, 126.1, 124.9, 123.9, 123.7, 122.9, 121.1, 120.4, 115.7, 115.6, 115.0, 109.7, 108.8, 108.5, 97.8, 97.0, 83.2, 82.4, 49.4, 42.4, 31.9, 30.1, 29.7, 29.6, 29.3, 26.9, 22.7, 20.1, 14.1, 11.3; HRMS (ESI) m/z calcd for C<sub>71</sub>H<sub>72</sub>N<sub>4</sub>O<sub>2</sub>S<sub>3</sub>: 1108.4812 [M<sup>+</sup>] found 1108.4816; UV/vis (Dichloromethane) λ<sub>max</sub> 620 nm, ε [M<sup>-1</sup>cm<sup>-1</sup>] (4.7×10<sup>4</sup>).

In 100 mL round bottom flask, 1 (0.250 g, 0.34 mmol) and 4-ethynyl-N, N-diphenylaniline (0.072 g, 0.27 mmol) were dissolved in anhydrous THF (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.017 g, 0.015 mmol) and CuI (0.006 g, 0.030 mmol) were then added. The reaction mixture was stirred overnight at 60 °C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (3:2) as an eluent to get 3 in 55% yield and then in 100 mL round bottom flask, 3 (0.150 g, 0.16 mmol) and 3-ethynyl-10propyl-10H-phenothiazine (0.042 g, 0.16 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.009 g, 0.008 mmol) and CuI (0.002 g, 0.014 mmol) were then added. The reaction mixture was stirred overnight at 90°C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (3:2) as an eluent to get P-2 in 72% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.94-8.93 (2H, m), 7.38-7.27 (10H, m), 7.14-7.01 (8H, m), 6.99-6.91 (3H, m), 6.86-6.78 (2H, m), 4.07-4.03 (4H, m), 3.83-3.79 (2H, m), 1.86-1.71 (6H, m), 1.36-1.26 (28H, m), 1.03-1.00 (3H, m), 0.88-0.85 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 161.2, 148.7, 146.9, 146.1, 144.3, 139.1, 138.9, 135.7, 135.6, 132.7, 132.6, 130.9, 130.1, 130.0, 129.9, 129.5, 129.4, 129.0, 127.5, 127.4, 125.4, 124.9, 124.0, 123.9, 122.9, 121.6, 115.8, 115.6, 115.1, 114.5, 108.6, 108.5, 98.7, 97.7, 82.4, 81.8, 49.4, 42.4, 31.9, 30.0, 29.7, 29.6, 29.4, 29.3, 29.2, 26.9, 22.7, 20.1, 14.1, 11.3; HRMS (ESI) m/z calcd for C<sub>71</sub>H<sub>74</sub>N<sub>4</sub>O<sub>2</sub>S<sub>3</sub>: 1110.4968 [M<sup>+</sup>] found 1110.4959; UV/vis (Dichloromethane)  $\lambda_{max}$  626 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (6.1×10<sup>4</sup>).

1 (0.250 g, 0.34 mmol) and 4-ethynyl-N, N-dimethylaniline (0.039 g, 0.27 mmol) were dissolved in a 100 mL round bottom flask containing anhydrous THF (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 min followed by addition of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.017 g, 0.015 mmol), and CuI (0.006 g, 0.030 mmol). The reaction mixture was stirred overnight at 60°C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (3:2) as an eluent to get 4 in 50% yield. 4 (0.150 g, 0.19 mmol) and 3-ethynyl-10-propyl-10H-phenothiazine (0.050 g, 0.19 mmol) were dissolved in a 100 mL round bottom flask containing anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 min followed by addition of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.017 g, 0.015 mmol), and CuI (0.006 g, 0.030 mmol). The reaction mixture was stirred overnight at 90°C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (1:1) as an eluent to get P-**3** in 70% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 8.97-8.96 (1H, d, J=4Hz), 8.93-8.92 (1H, d, J=4 Hz), 7.42-7.40 (2H, m), 7.34-7.29 (4H, m), 7.17-7.10 (2H, m), 6.95-6.78 (3H, m), 6.67-6.65 (2H, m), 4.08-4.04 (4H, m), 3.84-3.80 (2H, m), 3.01 (6H, s), 1.86-1.71 (6H, m), 1.36-1.25 (28H, m), 1.04-1.00 (3H, m), 0.80-0.85 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 161.3, 161.1, 150.6, 146.0, 144.3, 139.4, 138.6, 135.9, 135.4, 132.9, 132.7, 131.9, 130.8, 130.3, 130.2, 130.0, 129.3, 128.8, 127.5, 127.4, 124.9, 124.0, 122.9, 115.8, 115.6, 115.1, 111.7, 108.6, 108.2, 100.2, 97.6, 82.4, 80.9, 49.4, 42.4, 40.1, 31.9, 30.1, 29.7, 29.5, 29.3, 29.2, 26.9, 22.7, 20.1, 14.1, 11.3; HRMS (ESI) m/z calcd for C<sub>61</sub>H<sub>70</sub>N<sub>4</sub>O<sub>2</sub>S<sub>3</sub>: 986.4655  $[M^{+}]$ 986.4655: UV/vis found (Dichloromethane)  $\lambda_{\text{max}}$  629 nm,  $\in [M^{-1}\text{cm}^{-1}]$  (2.8×10<sup>4</sup>).

In 100 mL round bottom flask, 3,7-diethynyl-10-propyl-10Hphenothiazine (0.01 g, 0.03 mmol) and **2** (0.055 g, 0.06 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.004 g, 0.004 mmol) and CuI (0.001 g, 0.007 mmol) were then added. The reaction mixture was stirred overnight at 90°C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with DCM as an eluent to get **P-4** in 52% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.97-8.94 (4H, m), 8.15-8.13 (4H, d, *J*=8Hz), 7.78-7.76 (4H, m), 7.62-7.59 (5H, m), 7.47-7.31(15H, m), 7.00 (2H, s), 6.79-6.73 (4H, m), 4.10-4.05 (8H, m), 3.80 (2H, s), 1.84-1.75 (10H, m), 1.46-1.25 (56H, m), 1.05-1.00 (3H, m), 0.88-0.86 (12H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 161.2, 161.1, 140.4, 135.4, 133.3, 133.1, 132.8, 131.0, 130.8, 126.9, 126.1, 123.7, 120.4, 115.3, 109.7, 108.8, 42.4, 31.9, 31.8, 30.3, 30.1, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.9, 22.7, 19.9, 14.1, 11.2; MALDI calcd for  $C_{127}H_{129}N_7O_4S_5$ : 1977.753 [M<sup>+</sup>] found 1977.839; UV/vis (Dichloromethane)  $\lambda_{max}$  625 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (15.0×10<sup>4</sup>).

#### Synthesis of P-5

In 100 mL round bottom flask, 3,7-diethynyl-10-propyl-10Hphenothiazine (0.010 g, 0.03 mmol) and **3** (0.056 g, 0.06 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.004 g, 0.004 mmol) and CuI (0.001 g, 0.007 mmol) were then added. The reaction mixture was stirred overnight at 90°C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with DCM as an eluent to get **P-5** in 59% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.95-8.93 (4H, m), 7.53 (2H, s), 7.38-7.33 (8H, m), 7.32-7.27 (12H, m), 7.25-7.01 (12H, m), 7.00-6.99 (4H, m), 4.08-4.05 (8H, m), 3.83-3.81 (2H, m), 1.85-1.74 (10H, m), 1.45-1.23 (56H, m), 1.05-1.01 (2H, m), 0.94-0.83 (12H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 161.2, 161.1, 148.7, 146.9, 145.0, 142.9, 139.3, 139.2, 138.9, 135.7,135.5, 135.2, 132.8, 132.6, 131.0, 129.9, 129.5, 128.6, 125.3, 124.1, 123.9, 123.5, 121.6, 115.9, 114.4, 114.0, 108.6, 108.5, 97.3, 42.2, 34.9, 34.7, 34.5, 33.8, 31.9, 31.6, 31.4, 30.2, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.9, 26.9, 22.7, 20.0, 14.1, 11.2; MALDI calcd for C<sub>127</sub>H<sub>133</sub>N<sub>7</sub>O<sub>4</sub>S<sub>5</sub>: 1979.902 [M<sup>+</sup>] found 1979.836; UV/vis (Dichloromethane)  $\lambda_{max}$  625 nm,  $\in$  [M<sup>-1</sup>cm<sup>-1</sup>] (3.9×10<sup>4</sup>).

#### Synthesis of **P-6**

In 100 mL round bottom flask, 3,7-diethynyl-10-propyl-10Hphenothiazine (0.010 g, 0.003 mmol) and **4** (0.048 g, 0.006 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.004 g, 0.004 mmol) and CuI (0.001 g, 0.007 mmol) were then added. The reaction mixture was stirred overnight at 90°C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with DCM as an eluent to get **P-6** in 62% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 8.98-8.97 (2H, d, *J*=8 Hz), 8.92 (2H, s), 7.43-7.41 (4H, d, *J*=8 Hz), 7.35-7.31 (4H, m), 7.23-7.21 (2H, m), 6.82-6.76 (4H, m), 6.74-6.66 (4H, m), 4.08-4.05 (8H, m), 3.82-3.79 (2H, m), 3.02 (12H, s), 1.85-1.72 (10H, m), 1.44-125 (56H, m), 1.05-1.01 (3H, m), 0.99-0.85 (12H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 161.3, 161.1, 140.4, 136.0, 135.8, 135.3, 133.0, 132.9, 132.8, 131.9, 130.9, 130.0, 129.3, 128.9, 128.5, 127.7, 126.9, 126.1, 124.1, 123.9, 123.7, 120.4, 115.3, 111.7, 108.2, 71.8, 49.6, 42.4, 40.2, 40.1, 31.9, 30.3, 30.1, 29.7, 29.6, 29.4, 29.3, 29.2, 27.7, 26.9, 22.7, 19.9, 19.2, 14.1, 11.2; ; MALDI calcd for C<sub>107</sub>H<sub>125</sub>N<sub>7</sub>O<sub>4</sub>S<sub>5</sub>: 1732.842 [M<sup>+</sup>] found

1732.988; UV/vis (Dichloromethane)  $\lambda_{max}$  629 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (2.2×10<sup>4</sup>).

## 6.7. Conclusions

In conclusion, we have designed and synthesized phenothiazine-based DPP derivatives P-1-P-6 by the series of Pd-catalyzed Sonogashira cross-coupling reactions. Their photophysical and redox properties were investigated which shows that the incorporation of strong donor (N, Ndimethylaminophenyl) red shifts the absorption, exhibit low oxidation potentials and lowers the HOMO-LUMO gap. The phenothiazine based DPP derivatives P-1-P-6 exhibit similar absorption bands even on increasing the length of conjugation this might be because of break of conjugation between the two arms due to non-planarity in di-substituted phenothiazine derivatives. The electrochemical study exhibits multiple oxidation waves in phenothiazine-based DPP derivatives due to oxidation of various donor units (thiophene/N-phenyl carbazole/Triphenylamine/N, N-dimethylaminophenyl). The broad absorption in visible region, multiple redox potentials and low HOMO-LUMO gap indicates that these molecules are potential candidate for optoelectronic applications.

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# Chapter 07: Ferrocenyl-diketopyrrolopyrroles functionalized mono-, di- and tri- substituted triphenylamine derivatives: A comparative study

#### 7.1. Introduction

Harnessing solar energy for the production of clean and renewable fuels is critical to addressing future energy demands. Organic electronic devices, such as organic field-effect transistors (OFETs)<sup>[1-5]</sup> and organic solar cells (OSCs),<sup>[6-9]</sup>have emerged as significant players in this endeavor. These devices utilize organic small molecules with extensive  $\pi$ -conjugation based on donor-acceptor (D-A) frameworks, which are extensively researched for their wide range of optoelectronic applications, including OSCs, nonlinear optical (NLO) switches.<sup>[10,12]</sup> sensors,<sup>[13,14]</sup> fluorescent near-infrared (NIR) probes,<sup>[15-17]</sup> and data storage devices.<sup>[18,19]</sup> Diketopyrrolopyrrole (DPP) stands out due to its  $\pi$ -conjugated bicyclic di-lactam structure, making it one of the most utilized organic dyes. DPP is favored for its straightforward synthesis, excellent thermal stability, strong electron-accepting properties, planarity, high fluorescence quantum yield, and robust photostability.<sup>[20-</sup> <sup>22</sup> These features make DPP a highly suitable candidate for diverse optoelectronic applications. Despite its poor solubility in organic solvents caused by strong  $\pi$ - $\pi$  interactions and hydrogen bonding, Nalkylation of DPP significantly enhances its solubility in common organic solvents.<sup>[23-27]</sup> Additionally, DPP-based materials demonstrate high charge-carrier mobility and efficient light absorption across a broad spectrum, including the visible region. Combining the donor thiophene with the acceptor DPP (resulting in dithienyl DPP) produces small organic molecules that absorb visible light, which is crucial for solar energy applications.<sup>[28-30]</sup> A crucial method for synthesizing DPP derivatives involves Sonogashira coupling, a powerful and widely used cross-coupling reaction in organic chemistry. The Sonogashira coupling reaction is highly valued for its ability to form carbon-carbon bonds

under relatively mild conditions, offering high functional group tolerance and enabling the construction of complex molecular architectures. In the context of DPP-based materials, Sonogashira coupling facilitates the introduction of various substituents, enhancing the solubility, electronic properties, and overall performance of the resulting compounds.<sup>[31-33]</sup>The nature of donor used for the design of efficient small organic molecules significantly influences the D–A interaction. Ferrocene is widely used donor unit for the synthesis of various organic molecules based on D–A framework due to its excellent thermal, photochemical stability and strong NLO response.<sup>[34, 35]</sup>

Zhang et al. reported a series of star-shaped molecules with fused aromatic ring 1,3,5-tri(thiophen-2-yl) benzene (TTB), 2,4,6tri(thiophene-2-yl)-1,3,5-triazene (TTT) as core for OSCs.<sup>[36-39]</sup> Triphenylamine (TPA) is widely used as an electron donor to design efficient D-A based molecules. In recent years, many star-shaped small molecules based on TPA as a central core have been widely studied for organic photovoltaics.<sup>[40,41]</sup> The sp<sup>3</sup> hybrid N atom of triphenylamine breaks the electronic conjugation between three arms, However its special propeller structure is easy to form amorphous material and contact closely with fullerene acceptor which leads to poor phase separation and charge recombination and enhance the charge dissociation efficiency.<sup>[42,43]</sup> Herein we have designed and synthesized mono-, di- and tri- substituted DPP and ferrocenyl-DPP based derivatives with TPA as a central core TPA-DPPs 1-6 by the Pdcatalyzed Sonogashira cross-coupling reactions in order to investigate the effect of number of DPP and ferrocenyl-DPP units on the photophysical and electrochemical properties. The effect of increasing the number as well as change of end capping group has also been investigated.



Figure 7. 1. Chemical structures of DPP and ferrocenyl-DPP based derivatives **TPA–DPPs 1–6**.

## 7.2. Results and discussion

The mono-, di- and tri- DPP substituted triphenylamines TPA-DPPs 1-3 were synthesized by the palladium catalyzed Sonogashira crosscoupling reaction of 1, 2 and 3 with 1.0, 2.0 and 3.0 equivalents of monobromo DPP (DPP-Br) in 75%, 60% and 65% yield respectively (Scheme 7.1). Recently we have reported the synthesis and solar cell properties of TPA-DPP 1 and we have taken it here for the sake of comparison.<sup>[32]</sup> The mono-, di- and tri- ferrocenyl-DPP based derivatives with TPA as central core (TPA-DPPs 1-6) were synthesized by palladium catalyzed Sonogashira cross-coupling reactions of 1, 2 and 3 (with 1.0, 2.0 and 3.0 equivalents of mono bromo ferrocenyl-DPP in 60%, 62% and 65% yield respectively (Scheme 1). The DPP and ferrocenyl DPP functionalized TPA derivatives (TPA-**DPPs 1–6**) were purified by repeated silica gel column chromatography and recrystallization techniques. TPA-DPPs 1-6 are readily soluble in common organic solvents and were fully characterized by common spectroscopic techniques (<sup>1</sup>H NMR, <sup>13</sup>C NMR, HRMS and MALDI).



Scheme 7. 1. Synthesis of DPP and ferrocenyl-DPP based derivatives with triphenylamine as central core **TPA–DPPs 1–6**.

## 7.3. Photophysical properties

The electronic absorption spectra of DPP and ferrocenyl-DPP based derivatives with TPA as central core **TPA-DPPs 1–6** were recorded in dichloromethane solution and as film at room temperature (Figure 7.2.) and the corresponding data are listed in Table 7.1.



**Figure 7. 2.** Normalized UV-vis absorption spectra of DPP and ferrocenyl-DPP based derivatives with TPA as central core **TPA–DPPs 1–6** in DCM solution and as film.

The absorption spectra of TPA-DPPs 1-6 exhibit broad absorption bands covering visible region from 450 nm-700 nm in DCM solution and from 500 nm-900 nm in film prepared using spin coater. The absorption bands in solution at shorter wavelength region (around 500 nm) and longer wavelength region (around 600 nm) correspond to the  $\pi$ - $\pi$ \* transition. The DPP based derivatives **TPA-DPPs 1-3** exhibit absorption bands at 583 nm, 586 nm and 586 nm whereas ferrocenyl-DPP based derivatives TPA-DPPs 4-6 exhibit their absorption bands at 625 nm, 627 nm and 627 nm respectively. This shows that the di- and tri-substituted DPP (TPA-DPPs 2 and 3) and ferrocenyl-DPP (TPA-DPPs 5 and 6) based derivatives with TPA as central core show negligible red shift since  $sp^3$  hybridized N atom of TPA breaks the conjugation between three arms of core. Increasing the number of substitutions by end capping groups resulted in the red shift of absorption to small extent but the incorporation of additional ferrocenyl unit red shift the absorption by~ 40 nm.

TPA-	$\lambda_{abs}(nm)^a$	$\lambda_{abs}(nm)^b$	3	Ec	Ed	Te
DPP			$(\times 10^4 \mathrm{M}^{-}$	(eV)	(eV)	(°C)
			<sup>1</sup> cm <sup>-1</sup> ) <sup>a</sup>			
ТРА-	583	610	2.3	1.83	2.23	359
DPP 1	551	570	2.8			
TPA-	586	614	1.9	1.78	2.09	377
DPP 2	552	570	1.6			
ТРА-	586	612	4.9	1.75	2.06	306
DPP 3	554	566	4.3			
TPA-	625	662	3.8	1.66	2.01	343
DPP 4	586	608	2.6			
TPA-	627	656	4.6	1.65	1.96	233
DPP 5	586	608	3.3			
TPA-	627	653	5.2	1.53	1.93	426
DPP 6	587	607	4.1			

**Table 7. 1.** The optical properties of DPP and ferrocenyl–DPP based derivatives with TPA as central core **TPA–DPPs 1–6**.

<sup>a</sup> Absorbance measured in DCM solution;  $\epsilon$ : extinction coefficient; <sup>b</sup>absorbance measured in film; <sup>c</sup>Optical band gap; <sup>d</sup>Theoretical band gap; <sup>e</sup>Decomposition temperatures at 5% weight loss at a heating rate of 10 <sup>o</sup>C min<sup>-1</sup> under a nitrogen atmosphere.

The optical band gap and theoretical HOMO-LUMO gap of DPP and ferrocenyl-DPP based derivatives **TPA–DPPs 1–6** were calculated from onset absorption and density functional theory calculations respectively and the data are listed in Table 7.1. The incorporation of additional ferrocenyl unit significantly lowers the optical band gap and theoretical HOMO–LUMO gap. The absorption band get broadened up to 1000 nm in thin film compared to in solution due to aggregation in solid state. The emission spectra of **TPA–DPPs 2–6** were recorded in dichloromethane at room temperature (Figure 7.3). The DPP functionalized TPA (**TPA–DPPs 1–3**) are highly emissive in nature. Fluorescence quantum yield for **TPA–DPPs 1–6** are 0.34, 0.61, 0.30, 0.04, 0.06 and 0.02 respectively using Rhodamine 6G in ethanol as

standard which shows quenching of fluorescence takes place in ferrocenyl DPP functionalized TPA (**TPA–DPPs 4–6**).



**Figure 7. 3.** Emission spectra of DPP based derivatives **TPA–DPP 2–6** in DCM.

#### 7.4. Thermogravimetric analysis

The thermogravimetric analysis of **TPA–DPPs 1–6** were carried out under nitrogen atmosphere and their thermograms are shown in Figure 7.4. The DPP and ferrocenyl–DPP functionalized TPA derivatives **TPA–DPPs 1–6** exhibit good thermal stability. The thermal stability follows the order **TPA–DPPs 6** > 2 > 1 > 4 > 3 > 5 indicating that trisubstitued ferrocenyl DPP derivative **TPA–DPP 6** exhibits high thermal stability as compared to its mono- (**TPA–DPP 4**) and di- substituted (**TPA–DPP 5**) analogues. The di- substituted DPP derivative (**TPA– DPP 2**) exhibits high thermal stability as compared to its mono- (**TPA–DPP 3**).



Figure 7. 4. Thermogravimetric analysis of TPA–DPPs 1–6 under a nitrogen atmosphere.

## 7.5. Lifetime measurements

We conducted lifetime measurements to gain a better insight about the lifetime of excited state of DPP and ferrocenyl–DPP derivatives of TPA (**TPA–DPPs 1–6**) as shown in Figure 7.5. The average lifetime of **TPA–DPP 1–3** are 0.36 ns, 0.52 ns and 0.23 ns (Figure 7.5). Di-substituted DPP functionalized TPA (**TPA–DPP 2**) exhibit longer excited state lifetime as compared to their mono- and tri substituted DPP functionalized TPA (**TPA–DPP 1** and **3**).



Figure 7. 5. Time resolved decay curves of TPA–DPPs 1–3 at 620 nm.

## 7.6. Electrochemical properties

The electrochemical properties of the DPP and ferrocenyl-DPP based derivatives with triphenylamine as central core **TPA–DPPs 1–6** were explored by cyclic voltammetry and differential pulse voltammetry (CV

and DPV) techniques in dichloromethane solvent using 0.1M tetrabutylammonium hexafluorophosphate ( $Bu_4NPF_6$ ) as supporting electrolyte. The CV and DPV plots of **TPA–DPPs 2, 4, 5 and 6** are shown in Figure 7.6. The corresponding electrochemical data are listed in Table 7.2.

DPP based derivatives with TPA as central core **TPA-DPPs 1–3** exhibit three oxidation and one reduction waves. The two oxidation waves between 0.5-1.5V corresponds to oxidation of two asymmetric thiophene units and other due to oxidation of triphenylamine unit while one reduction waves (-1.0 - -1.5V) correspond to the reduction of DPP unit. The ferrocenyl-DPP based derivatives **TPA–DPPs 4–6** exhibit four oxidation and one reduction wave. First oxidation wave at around 0.64Vcorresponds to the oxidation of ferrocene unit and the next two oxidation waves between 0.7-1.5V correspond to the oxidation of asymmetric thiophene units and fourth oxidation wave corresponds to oxidation of TPA unit.





Figure 7. 6. CV (black line) and DPV (red line) curves of **TPA–DPPs** 2, 4, 5 and 6.

In DPP substituted TPA derivatives (**TPA–DPPs 1–3**), it has observed that it is difficult to oxidize disubstituted DPP derivative of TPA (**TPA–DPP 2**) as compared to its tri– (**TPA–DPP 3**) and mono–substituted analogues (**TPA–DPP 1**). In case of ferrocenyl–DPP substituted TPA (**TPA–DPPs 4–6**), it has observed that first oxidation potentials of mono–, di– and tri–substituted ferrocenyl–DPP derivatives of TPA (**TPA–DPPs 4, 5** and **6**) are nearly same ~0.64V but reduction becomes difficult on increasing the number of ferrocenyl–DPP unit. The reduction potential of **TPA–DPPs 1–6** indicates that it is difficult to reduce DPP functionalized TPA derivatives (**TPA–DPPs 1–3**) as compared to ferrocenyl DPP analogs (**TPA–DPPs 4–6**).

	$E^1$	$E^1$	$E^2$	$E^3$	$E^4$
TPA-DPP	Red	Oxid	Oxid	Oxid	Oxid
TPA-DPP 1	-1.51	0.86	1.03	1.79	-
TPA-DPP 2	-1.40	1.00	1.28	1.83	-
TPA-DPP 3	-1.46	0.94	1.09	1.80	-
TPA-DPP 4	-1.53	0.63	0.93	1.07	1.83
TPA-DPP 5	-1.50	0.64	0.98	1.14	1.84
TPA-DPP 6	-1.56	0.64	0.98	1.22	1.83

**Table 7. 2.** The electrochemical properties of DPP and ferrocenyl– DPP based derivatives with TPA as central core **TPA–DPPs 1–6**.

The electrochemical analysis was performed in a 0.1 M solution of  $Bu_4NPF_6$ in DCM at 100 mVs<sup>-1</sup> scan rate, versus Ag/Ag<sup>+</sup> at 25 °C.

## 7.7. Theoretical calculations

## **Density Functional Theory (DFT)**

The density functional theory (DFT) calculation was carried out to understand the geometry, and the electronic structure of the DPP and ferrocenyl-DPP based derivatives with triphenylamine as central core **TPA–DPPs 1–6** using the Gaussian09W program.<sup>[44]</sup> The geometry optimizations were carried out in the gas phase. The DFT calculations were performed at B3LYP/6-31

+G\*\* for C, H, N, S, and O and Lanl2DZ for the Fe level of theory. The frontier molecular orbitals (FMOs) of **TPA–DPPs 1–6** are shown in Figures 7.7, 7.8 and 7.9.


**Figure 7. 7.** The FMOs of DPP and ferrocenyl-DPP based derivatives **TPA–DPPs 1** and **4** estimated by DFT calculations.

The electron density of highest occupied molecular orbitals (HOMOs) of DPP and ferrocenyl-DPP based monomers (**TPA–DPPs 1** and **4**) and dimers (**TPA-DPPs 2** and **5**) are distributed on the whole molecule whereas their lowest unoccupied molecular orbitals (LUMOs) are localized mainly on the DPP core (Figures 7.7 and 7.8).



**Figure 7. 8.** The FMOs of DPP and ferrocenyl-DPP based derivatives **TPA–DPPs 2** and **5** estimated by DFT calculations.

The HOMOs of both DPP and ferrocenyl–DPP based derivatives **TPA–DPPs 3** and **6** are distributed on the whole molecule whereas LUMO and LUMO+1 are localized mainly on two strands of the DPP core (Figure 7.9). The localization of LUMO and LUMO+1 on DPP core indicates the acceptor nature of DPP in **TPA–DPPs 3** and **6**. The

localization of HOMOs on triphenylamine and LUMOs on DPP shows the typical D–A interaction and charge transfer from triphenylamine to DPP in **TPA–DPPs 3** and **6**.



Figure 7. 9. The FMOs of DPP and ferrocenyl–DPP based trimers **TPA–DPPs 3** and 6 estimated by DFT calculations.

## **Time Dependent Density Functional Theory (TD–DFT)**

The time dependent density functional theory (TD–DFT) calculation was performed in order to get the idea of electronic transitions in DPP and ferrocenyl–DPP based derivatives with triphenylamine as central core **TPA–DPPs 1–6**. The major electronic transitions in **TPA–DPPs 1–6** calculated from TD–DFT with composition and oscillator strengths are shown in Table 7.3.

The strong electronic transitions from HOMO $\rightarrow$ LUMO in longer wavelength region were observed in **TPA–DPPs 1–6** which corresponds to the ICT from triphenylamine to DPP whereas other short wavelength transitions due to  $\pi - \pi^*$  transition were observed in **TPA–DPPs 1–6** (Table 7.3). The derivatives **TPA–DPPs 3** and **6** exhibit additional transition in longer wavelength region from HOMO $\rightarrow$ LUMO+1 due to ICT. The localization electron density in HOMOs of DPP and ferrocenyl–DPP based trimers **TPA–DPPs 3** and **6** on whole molecule (on three arms along with triphenylamine) and distribution of LUMOs on two arms shows there is only communication between two arms (Figure 7.9). This may be the probable reason for the similar absorption bands for the DPP and ferrocenyl–DPP based dimer analogues (**TPA–DPPs 2** and **5**). The HOMO–LUMO gap values obtained from DFT calculations shows that the incorporation of additional ferrocenyl unit lowers the HOMO-LUMO gap in **TPA–DPPs 1–6** which found to be in good agreement with the optical band gap values from the onset absorption (Table 7.1).

Compound	Wavelength	Composition	Oscillation
	( <b>nm</b> )		Strength (f <sup>a</sup> )
TPA-DPP 1	479	HOMO $\rightarrow$ LUMO (0.70)	0.56
TPA-DPP 2	655	HOMO→LUMO (0.70)	1.83
	583	HOMO-1→LUMO+1	0.71
		(0.69)	
	582	HOMO-1→LUMO (0.59)	0.53
TPA-DPP 3	652	HOMO $\rightarrow$ LUMO (0.70)	1.32
	651	HOMO→LUMO+1 (0.70)	1.38
	596	HOMO-2→LUMO (0.48)	0.52
TPA–DPP 4	654	HOMO $\rightarrow$ LUMO (0.68)	1.96
	699	HOMO $\rightarrow$ LUMO (0.69)	2.63
TPA-DPP 5	627	HOMO-1→LUMO+1	0.66
		(0.65)	
	632	HOMO-1→LUMO (0.55)	0.59
	706	HOMO→LUMO (0.69)	1.75
TPA-DPP 6	704	$HOMO \rightarrow LUMO + 1(0.69)$	2.27
	648	HOMO-1→LUMO+1	0.67
		(0.51)	
	649	HOMO-1→LUMO (0.67)	0.47

**Table 7. 3.** Major electronic transitions of **TPA–DPPs 1–6** calculated by TD-DFT.

# 7.8. Experimental Section:

# **General methods**

The chemicals were used as received unless otherwise indicated. All the moisture sensitive reactions were performed under argon atmosphere using the standard Schlenk method. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded by using CDCl<sub>3</sub> as the solvent. The <sup>1</sup>H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl<sub>3</sub>, 7.26 ppm). The multiplicities are given as: s (singlet), d (doublet), m (multiplet), and the coupling constants, J, are given in Hz. The <sup>13</sup>C NMR chemical shifts are reported with relative to the solvent residual peak (CDCl<sub>3</sub>, 77.0 ppm). HRMS was recorded on a mass spectrometer (ESI-TOF) and MALDI-TOF spectrometer. The absorption spectra of DPPs were recorded on UVvisible Spectrophotometer in dichloromethane. The TGA analyses were performed on the thermal analysis system at the heating rate of 10 °C per minute under a nitrogen atmosphere. Cyclic voltammograms (CVs) and differential voltammograms (DPVs) were recorded on an electrochemical analyzer using glassy carbon as working electrode, Pt wire as the counter electrode, and saturated  $Ag/Ag^+$  as the reference electrode. For lifetime measurements, we used a picosecond TCSPC instrument obtained from Horiba (Fluorocube-01-NL). The samples were excited at 480 nm using a picosecond diode laser (model: PicoBrite-375L), and the decays were collected at 620 nm. We used a filter on the emission side to eliminate the scattered light. The signals were collected at magic angle (54.751) polarization using a photomultiplier tube (TBX-07C) as the detector. The full width half maximum (fwhm) of the instrument response function of our setup is ~140 ps. Data analysis was performed using IBH DAS version 6 decay analysis software. Throughout all the measurements, we maintained the temperature (T) at 20°C. The decays were fitted with a multiexponential function.

#### Synthesis of TPA-DPP 2

In 100 mL round bottom flask, DPP-Br (0.250 g, 0.37 mmol) and **2** (4ethynyl-*N*-(4-ethynylphenyl)-*N*-phenylaniline) (0.055 g, 0.18 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and  $Pd(PPh_3)_4$  (0.017 g, 0.015 mmol) and CuI (0.006 g, 0.030 mmol) were then added. The reaction mixture was stirred overnight at 80°C. After completion of reaction the reaction mixture was allowed to cool down at room temperature. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (1:1) as an eluent to get **TPA–DPP 2** in 60 % yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.92 (4H, m), 7.65 (2H, d, J=4 Hz), 7.42 (5H, m), 7.34 (4H, m), 7.16 (3H, m), 7.08 (5H, m), 4.08 (8H, s), 1.75 (8H, m), 1.26 (56H, m), 0.87 (12H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 161.3, 147.7, 140.1, 135.45, 135.40, 133.6, 132.7, 129.7, 128.8, 128.6, 126.0, 125.9, 124.8, 123.2, 123.0, 116.0, 107.8, 98.0, 42.3, 31.8, 30.07, 30.05, 29.9, 29.7, 29.6, 29.5, 29.4, 29.29, 29.25, 29.18, 29.11, 26.8, 22.6, 14.1; MALDI m/z calcd for C<sub>90</sub>H<sub>107</sub>N<sub>5</sub>O<sub>4</sub>S<sub>4</sub> : 1449.7206 [M<sup>+</sup>], found 1450.552; UV/vis (Dichloromethane)  $\lambda_{max}$  586 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (1.9×10<sup>4</sup>).

## Synthesis of TPA-DPP 3

In 100 mL round bottom flask, **DPP-Br** (0.250 g, 0.37 mmol) and **3** (tris(4-ethynylphenyl) amine) (0.038 g, 0.12 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.017 g, 0.015 mmol) and CuI (0.006 g, 0.030 mmol) were then added. The reaction mixture was stirred overnight at 80°C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (1:3) as an eluent to get **TPA–DPP 3** in 65% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.91 (6H, m), 7.65 (3H, d, *J*=4 Hz), 7.47 (8H, m), 7.38 (2H, m), 7.29 (2H, m), 7.27 (2H, m), 7.10 (6H, m), 4.07 (12H, s), 1.75 (12H, m), 1.25 (83H, m), 0.87 (19H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 161.32, 161.30, 147.0, 140.2, 138.9, 135.5, 135.3, 133.89, 133.87, 132.94, 132.93, 130.9, 130.4, 129.8, 128.7, 128.6, 124.26, 124.22, 124.1, 117.3, 108.5, 107.9, 97.6, 82.6, 53.4, 42.3, 33.4, 31.9, 30.1, 30.0, 29.74, 29.71, 29.68, 29.64, 29.5, 29.48, 29.42, 29.41, 29.3, 29.2, 26.9, 26.8, 22.7, 14.1; MALDI m/z calcd for C<sub>126</sub>H<sub>153</sub>N<sub>7</sub>O<sub>6</sub>S<sub>6</sub> : 2053.0240 [M<sup>+</sup>], found 2053.109; UV/vis (Dichloromethane)  $\lambda_{max}$  586 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (4.9×10<sup>4</sup>).

#### Synthesis of TPA-DPP 4

In 100 mL round bottom flask, dibromo–DPP (0.250 g, 0.34 mmol) and ethynyl ferrocene (0.064 g, 0.30 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.017 g, 0.015 mmol) and CuI (0.006 g, 0.030 mmol) were then added. The reaction mixture was stirred overnight at 60 °C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (3:2) as an eluent to get Fc-DPP-Br in 62 % yield and then in 100 mL round bottom flask, Fc-DPP-Br (0.150 g, 0.16 mmol) and 1(4-ethynyl-N, N-diphenylaniline) (0.044 g, 0.16 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.009 g, 0.008 mmol) and CuI (0.002 g, 0.014 mmol) were then added. The reaction mixture was stirred overnight at 80°C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (3:2) as an eluent to get TPA-DPP 4 in 60% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 8.90 (2H, m), 7.70 (2H, m), 7.37 (4H, m), 7.30 (4H, m), 7.12 (4H, m), 7.08 (2H, m), 4.55(2H, s), 4.30

(5H, m), 4.07 (4H, s), 1.75 (4H, m), 1.35 (28H, m), 0.86 (6H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 158.68, 158.66, 146.1, 144.3, 136.7, 136.5, 136.3, 133.0, 129.7, 127.7, 127.4, 127.2, 126.9, 126.7, 125.1, 125.0, 122.8, 122.2, 121.4, 119.1, 111.9, 111.5, 106.0, 96.1, 95.7, 69.1, 67.0, 61.3, 39.85, 39.83, 31.7, 31.3, 29.4, 29.3, 29.1, 28.9, 27.8, 27.68, 27.64, 27.5, 27.2, 27.18, 27.15, 27.11, 27.07, 27.02, 26.8, 26.75, 26.70, 26.65, 26.4, 26.1, 24.39, 24.38, 23.43, 23.40, 20.18, 20.16, 11.6; HRMS (ESI) m/z calcd for C<sub>66</sub>H<sub>69</sub>FeN<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: 1055.4180 [M<sup>+</sup>] found 1055.4177; UV/vis (Dichloromethane)  $\lambda_{max}$  625 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (3.8×10<sup>4</sup>).

# Synthesis of TPA-DPP 5

In 100 mL round bottom flask, **Fc-DPP-Br** (0.150 g, 0.16 mmol) and **4** (4-ethynyl-*N*-(4-ethynylphenyl)-*N*-phenylaniline) (0.024 g, 0.08 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.009 g, 0.008 mmol) and CuI (0.002 g, 0.014 mmol) were then added. The reaction mixture was stirred overnight at 80 °C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (1:1) as an eluent to get **TPA-DPP 5** 62% in yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.92 (4H, m), 7.70 (1H, s), 7.43 (5H, m), 7.34 (5H, m), 7.15 (2H, m), 7.07 (4H, m), 4.55 (4H, s), 4.30 (11H, m), 4.07 (8H, s), 1.76 (8H, s), 1.33 (56 H, m), 0.87 (12H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 161.3, 161.2, 147.8, 139.3, 138.8, 135.7, 135.5, 132.8, 132.3, 130.3, 129.9,129.8, 129.5, 128.9, 126.0, 123.2, 116.1, 108.7, 108.4, 98.4, 98.1, 82.3, 69.6, 63.9, 42.4, 42.3, 32.0, 31.9, 30.1, 29.7, 29.6, 29.4, 29.3, 26.9, 22.7, 14.1; MALDI m/z calcd for  $C_{114}H_{123}Fe_2N_5O_4S_4$ :1866.7190 found 1866.521; UV/vis (Dichloromethane)  $\lambda_{max}$  627 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (4.6×10<sup>4</sup>).

#### Synthesis of TPA-DPP 6

In 100 mL round bottom flask, **Fc-DPP-Br** (0.150 g, 0.16 mmol) and 3 (tris(4-ethynylphenyl) amine) (0.017 g, 0.052 mmol) were dissolved in anhydrous toluene (20 mL) and triethylamine (5 mL). The reaction mixture was degassed with argon for 20 minutes and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.009 g, 0.008 mmol) and CuI (0.002 g, 0.014 mmol) were then added. The reaction mixture was stirred overnight at 80°C. The reaction mixture was allowed to cool down at room temperature after completion of reaction. The solvent was removed under vacuum and the crude product was purified by repeated silica gel column chromatography with hexane/DCM (1:3) as an eluent to get **TPA-DPP 6** in 65% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ* in ppm): 8.91(6H, m), 7.46 (7H, m), 7.37 (2H, m), 7.11 (9H, m), 4.55 (6H, s), 4.30 (17H, m), 4.07 (12H, s), 1.76 (12H, m), 1.34 (84H, m), 0.87 (18H, m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *δ* in ppm): 161.3, 139.4, 138.7, 135.7, 135.4, 133.9, 133.0, 132.9, 132.3, 130.4, 130.0, 129.5, 124.3, 124.2, 124.1, 108.8, 108.4, 98.4, 97.7, 82.7, 71.7, 70.2, 69.6, 63.8, 42.4, 42.3, 31.9, 30.1, 29.7, 29.6, 29.5, 29.4, 29.3, 26.9, 22.7, 14.2; MALDI m/z calcd for C<sub>162</sub>H<sub>177</sub>Fe<sub>3</sub>N<sub>7</sub>O<sub>6</sub>S<sub>6</sub> : 2677.0166 [M<sup>+</sup>] found 2677.042; UV/vis (Dichloromethane)  $\lambda_{max}$  627 nm,  $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>] (5.2×10<sup>4</sup>).

### 7.9. Conclusions

In conclusion, we have designed and synthesized DPP and ferrocenyl– DPP based derivatives with TPA as central core **TPA–DPPs 2, 4, 5** and **6** by the Pd–catalyzed Sonogashira cross-coupling reactions. Their photophysical and electrochemical properties were investigated which shows that the incorporation of additional ferrocenyl unit red shifts the absorption, exhibit additional low oxidation potential and lowers the HOMO–LUMO gap. As the number of DPP or ferrocenyl-DPP units increases on TPA slightly red shifts the absorption. They possess good thermal stability and long excited state lifetime

between the range of 0.2–0.5ns. The electrochemical study exhibits additional low voltage oxidation peak in ferrocenyl–DPP based derivatives due to oxidation of ferrocenyl unit. The broad absorption in

visible region, multiple redox potentials and low HOMO–LUMO gap indicates that these molecules are potential candidate for optoelectronic applications.

# 7.10. References

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# 8.1. Conclusions

Diketopyrrolopyrrole (DPP) and its derivatives have emerged as crucial building blocks in the field of electronic devices.<sup>[1-3]</sup> The basic structure of DPP consists of a core unit featuring two amine groups and carbonyl functionalities, flanked by aromatic groups. This configuration imparts strong electron-deficient character to DPP, making it potential candidate for constructing donor-acceptor (D-A) conjugated materials.<sup>[4]</sup> The significance of DPP derivatives lies in their ability to exhibit strong  $\pi$ - $\pi$ interactions and aggregation between neighbouring DPP moieties. These properties are essential for altering the electronic and optoelectronic properties of materials derived from DPP.<sup>[5]</sup> Such materials have found wide-range of applications in electronic devices including organic photovoltaics (OPVs) <sup>[6, 7]</sup> memory devices, <sup>[8]</sup> organic field-effect transistors (OFETs),<sup>[1]</sup> and sensors. <sup>[9]</sup> As research progresses, understanding the synthetic methods for preparing DPP derivatives becomes increasingly crucial. Straightforward synthesis that ensures stability, while maintaining high electrical and optical performance, pave the way for continued innovation and application development. The photonic and electronic properties can be easily tuned by functionalizing thiophene-flanked DPP with different push/pull substituents. We described the design and synthesize of push-pull Diketopyrrolopyrrole and investigated their photophysical and electrochemical properties.

Chapter 3, describes the design and synthesis of symmetrical and unsymmetrical acetylene bridged *N*-phenyl carbazole based diketopyrrolopyrroles by the Pd-catalyzed Sonogashira cross-coupling and Stille coupling reactions. A comparative study of isomeric *N*-phenyl carbazole (*meta-* and *para-* isomers), attached to the DPP is performed. The *N*-phenyl carbazole based DPP monomers exhibit absorption in the visible region whereas the corresponding dimers show broad absorption

towards near-infrared (NIR) region with lowering of HOMO-LUMO gap. The *para-N*-phenyl carbazole based DPPs show red shifted absorption compared to their *meta*-substituted analogues. The emission spectra revealed that DPP monomers are fluorescent in nature whereas quenching of fluorescence was observed in DPP dimer. The thermogravimetric analysis shows higher thermal stability for *meta-N*-phenyl carbazole based DPPs as compared to their *para*-based analogues. Monomers of carbazole based DPPs are thermally more stable as compared to their dimers. The electrochemical study reveals multiple oxidation waves related to donor moieties (such as thiophene and carbazole) and one reduction wave corresponding to DPP unit.<sup>[10]</sup>

In Chapter 4, we describe the design and synthesis of a series of symmetrical and unsymmetrical push-pull functionalized diketopyrrolopyrrole (DPP) derivatives. In these compounds, the DPP unit serves as the central electron-acceptor core, while triphenylamine and N, N-dimethylaminophenyl act as electron-donor end groups. Additionally, tetracyanobutadiene (TCBD) was incorporated as an extra acceptor unit to extend the  $\pi$ -conjugation through [2+2] cycloadditionretroelectrocyclization reactions. The photophysical properties of TCBD-substituted derivatives reveal a strong electronic absorption band in the near-infrared region, indicative of intramolecular charge transfer (ICT). These TCBD-based derivatives exhibit multiple redox waves and a low electrochemical energy gap, highlighting the tuning of HOMO-LUMO energy levels and enhanced  $\pi$ -conjugation. Computational studies align well with the experimental data, supporting our findings. We believe that the molecular design and synthesis of these symmetrical and unsymmetrical DPP derivatives pave the way for new building blocks in future organic electronics applications.<sup>[11]</sup>

In Chapter 5, we describe the design and synthesis of a series of small organic molecules by incorporating DPP as an acceptor unit and ferrocene, triphenylamine, N-phenyl carbazole and N, N-dimethylaminophenyl as donor units. We used the Sonogashira cross-

coupling reaction to achieve efficient coupling of these units, followed by [2+2] cycloaddition-retroelectrocyclization to access  $\pi$ -conjugated systems with tunable electronic properties. The photophysical and electrochemical properties of these molecules were investigated, revealing that the incorporation of TCBD groups causes a red shift in absorption, exhibits additional reduction potentials, and lowers the HOMO-LUMO gap. Mono-TCBD incorporation occurred on the acetylene-linked N, N-dimethylaniline side, indicating the strong donor strength of N, N-dimethylaniline compared to ferrocene. Conversely, the first TCNE attack took place at the triple bond linked to the ferrocene side, indicating the strong donor strength of ferrocene relative to triphenylamine and N-phenyl carbazole units. The electrochemical study shows multiple oxidation waves in ferrocene-based DPP derivatives due to the oxidation of various donor units (ferrocene/thiophene/N-phenyl carbazole/triphenylamine). The broad absorption in the visible region, multiple redox potentials, and low HOMO-LUMO gap indicate that these molecules are potential candidates for optoelectronic applications. By systematically varying the donor strength and position, we anticipate gaining insights into the impact of these modifications on the optoelectronic properties of the resulting materials.

In Chapter 6, we describe the design and synthesis of a series of small organic molecules based on functionalizing the active sites of phenothiazine with various donor end-capped diketopyrrolopyrrole (DPP) derivatives. These molecules incorporate DPP as the electron-deficient acceptor unit, complemented by various donor units such as *N*-phenyl carbazole, triphenylamine, and *N*, *N*-dimethylaminophenyl, with phenothiazine serving as the central core. The synthesis of these complex molecular architectures is achieved through the Sonogashira cross-coupling reaction, a versatile method known for constructing carbon-carbon bonds under mild conditions. This approach allows for the efficient assembly of  $\pi$ -conjugated systems with tunable electronic properties, essential for exploring structure-property relationships in organic semiconductors. Our investigation into their photophysical and

redox properties reveals that the incorporation of a strong donor (N, Ndimethylaminophenyl) results in a red shift in absorption, exhibits low oxidation potentials, and lowers the HOMO-LUMO gap. The phenothiazine-based DPP derivatives display similar absorption bands even with increased conjugation length, possibly due to the break in conjugation between the two arms caused by non-planarity in disubstituted phenothiazine derivatives. The electrochemical study shows multiple oxidation waves in phenothiazine-based DPP derivatives due the oxidation of various donor units (thiophene/Nto phenylcarbazole/triphenylamine/N,N-dimethylaminophenyl) and one reduction wave corresponding to the formation of a mono-anion of DPP. The broad absorption in the visible region, multiple redox potentials, and low HOMO-LUMO gap indicate that these molecules are potential candidates for optoelectronic applications. By systematically varying the donor strength and position within these molecular designs, our study aims to provide insights into how these modifications impact the optoelectronic properties of the resulting materials.

Chapter 7, describes the designed and synthesized mono-, di- and trisubstituted DPP and ferrocenyl-DPP based derivatives with TPA as a central core by the Pd-catalyzed Sonogashira cross-coupling reactions in order to investigate the effect of number of DPP and ferrocenyl-DPP units on the photophysical and electrochemical properties. The effect of increasing the number as well as change of end capping group has also been investigated. Their photophysical and electrochemical properties were investigated which shows that the incorporation of additional ferrocenyl unit red shifts the absorption, exhibit additional low oxidation potential and lowers the HOMO-LUMO gap. As the number of DPP or ferrocenyl-DPP units increases on TPA slightly red shifts the absorption. They possess good thermal stability and long excited state lifetime between the range of 0.2-0.5 ns. The electrochemical study exhibits additional low voltage oxidation peak in ferrocenyl-DPP based derivatives due to oxidation of ferrocenyl unit. The broad absorption in visible region, multiple redox potentials and low HOMO-LUMO gap

indicates that these molecules are potential candidate for optoelectronic applications.<sup>[12]</sup>

#### 8.2. Future scope

The thesis underscores a pivotal strategy in the design and synthesis of Diketopyrrolopyrrole-based push-pull chromophores aimed at finetuning of their photonic and electronic properties. DPP chromophores HOMO–LUMO band gap can be effectively modulated through several approaches: (a) adjusting the number of push/pull units, (b) extending the  $\pi$ -conjugation length, and (c) varying the  $\pi$ -linker structure. Furthermore, by incorporating strong acceptors such as tetracyano TCNE, derivatives like the push-pull interactions within Diketopyrrolopyrrole intensified, leading are to enhanced intramolecular charge-transfer at longer wavelengths, potentially near-infrared (NIR) extending into the region. These Diketopyrrolopyrrole based chromophores exhibit broad absorption spectra in the Vis-NIR region along with a reduced HOMO-LUMO band gap, rendering them highly promising for future optoelectronic applications. Moving forward, further exploration could focus on optimizing synthetic methodologies to enhance the efficiency and scalability of these chromophores, as well as exploring their performance in practical device applications such as organic photovoltaics and photodetectors. Additionally, investigating their stability under different environmental conditions and their compatibility with various substrate materials could broaden their potential utility in advanced optoelectronic technologies.

## 8.3. References

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