Design and synthesis of 1,1,4,4-tetracyanobutadiene (TCBD) based donor-acceptor D-A pyrazabole systems

M.Sc. Thesis

By

Nitin Rajesh

DISCIPLINE OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY INDORE

June 2020

Design and synthesis of 1,1,4,4-tetracyanobutadiene (TCBD) based donor-acceptor D-A pyrazabole systems

A THESIS

Submitted in partial fulfillment of the

requirements for the award of the degree

of

Master of Science

by

Nitin Rajesh

DISCIPLINE OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY INDORE

June 2020

INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Design and synthesis of 1,1,4,4-tetracyanobutadiene (TCBD) based donor-acceptor D-A pyrazabole systems** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2019 of joining the M.Sc. program to March 2020 of M.Sc. Thesis submission under the supervision of Prof. Rajneesh Misra, Professor, IIT Indore.

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

Nitin Rajesh
25/12/2020

Signature of M.Sc. Student with date (Nitin Rajesh)

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

Signature of the Supervisor of M.Sc. thesis (Prof. Rajneesh Misra)

Nitin Rajesh has successfully given her M.Sc. Oral Examination held on 25-06-20.

Tushar kanti Mukherjee

Signature of Supervisor of M.Sc. thesis | Convener, DPGC

Signature of PSPC Member #1 | Signature of PSPC Member #2

Date: | Date:

ACKNOWLEDGEMENTS

With incredible joy, I need to communicate my profound feeling of appreciation to my supervisor Prof. Rajneesh Misra, for giving me a wonderful opportunity to pursue research and believing in my research abilities. His steady direction, backing and inspiration have been colossally useful to finish this M.Sc. venture. His energy and devotion have consistently roused me. Further, I might want to thank my PSPC individuals Dr. Biswarup Pathak and Dr. Satya S. Bulusu for their significant proposals and backing.

I wish to offer my thanks to Prof. Neelesh Jain, Director, IIT Indore for his ceaseless consolation, help and backing in each viewpoint. I am appreciative to Dr. Biswarup Pathak (Head, Discipline of Chemistry, Indian Institute of Technology Indore). I am likewise appreciative to Dr. Anjan Chakraborty, Dr. Tridib Kumar Sarma, Dr. Suman Mukhopadhyay, Dr. Apurba Kumar Das, Dr. Sampak Samantha, Dr. Sanjay Singh, Dr. Tushar Kanti Mukherjee, Dr. Chelvam Venkatesh, Dr. Shaikh M. Mobin, Dr. Satya S. Bulusu, Dr. Amrendra Kumar Singh, Dr. Abhinav Raghuvanshi, Dr. Deepak Kumar Roy, Dr. Selvakumar Sermadurai, Dr. Umesh A. Kshirsagar help during different exercises. I might want to stretch out my true gratitude to my guide Anupama Ekbote and for her sort and agreeable nature and help in managing challenges. I stretch out my profound gratitude to my gathering individuals Dr. Yuvraj Patil, Madhurima Poddar, Yogajivan Rout, S. Bijesh, Charu Popli, Indresh Singh Yadav, Faizal Khan, Manju Sheokand, Dilip Pinjari, Pankaj Kumar Gupta, Mohd. Wazid, Nikhilji Tiwari for their benevolent co-activity and help to make my work effective. I might likewise want to thank the specialized staff from Sophisticated Instrumentation Center (SIC), IIT Indore, Mr. Kinny Pandey, Mr. Ghanshyam Bhavsar and Mr. Manish Kushwaha for their understanding and convenient specialized help without which it was difficult to proceed with my work. I for one need

to stretch out my gratitude to my clump mates who were consistently there and never let me down during these M.Sc. days.

Here, it is to be uniquely referenced that, it has been brilliant to work with numerous PhD seniors during my M.Sc. Above all none of this would have been conceivable without the help of my family and I profoundly offer my affection and thanks to my folks. At long last, I might want to communicate my gratitude to IIT Indore for framework and all other people who helped and bolstered me legitimately or in a roundabout way.

Nitin Rajesh

Discipline of Chemistry, IIT Indore

DEDICATED TO MY PARENTS AND MY TEACHERS……

For their support in every stage of my life!

ABSTRACT

In this work, we have designed and synthesized donor-acceptor D-A pyrazabole (PY-A) systems using different donors like triphenylamine (TPA-D), phenothiazine (PTZ-D') and ferrocene (Fc-D'') with the help of Sonogashira cross-coupling reaction. The 1,1,4,4-tetracyanobutadiene (TCBD, A′) derivatives of the D-A pyrazabole systems are formed followed by a [2 + 2] cycloaddition–retroelectrocyclization reaction on treatment with tetracyanoethylene (TCNE). The incorporation of TCBD act as an acceptor (A′) can further modulate the donor-acceptor strength, electronic and photophysical properties of the pyrazabole systems. The opted design helps up in opening new possibilities for development of near infrared (NIR) absorbing systems with various opto-electronic systems.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF SCHEMES

NOMENCLATURE

π	Pi
Λ	Wavelength
Δ	Chemical shift
Nm	Nanometre
Mmol	Millimole
mL	Millilitre
Rt	Room temperature
Ev	Electron volt
V	Volt

ACRONYMS

TPA	Triphenylamine
Fc	Ferrocene
PPh_3	Tri-phenylphosphine
DCM	Dichloromethane
NBS	N-Bromosuccinimide
DFT	Density functional theory
HRMS	High-resolution mass spectroscopy
$CDCl_3$	Chloroform-d
CuI	Copper iodide
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
Et_3N	Triethylamine
D-A	Donor-acceptor
D-π-A- π-D	π- bridged donor acceptor
DMSO	Dimethyl sulfoxide
$PdCl_2(PPh_3)_2$	Dichlorobis(triphenylphosphine) palladium (II)
NMR	Nuclear magnetic resonance
PTZ	Phenothiazine
PY	Pyrazabole
TCNE	Tetracyanoethylene
TCBD	1,1,4,4-tetracyanobutadiene
TMS	Tetramethylsilane

Chapter 1 Introduction

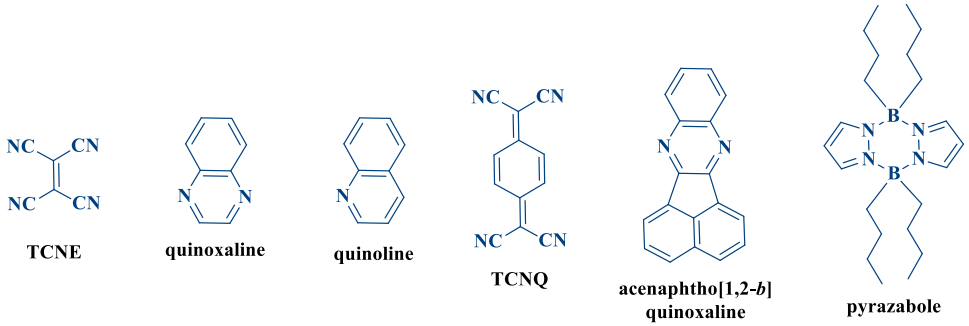
1.1. General Introduction

In recent years, donor–acceptor molecular systems have gained significant interest due to their potential applications in organic photovoltaics (OPVs), nonlinear optics, organic light emitting diodes (OLEDs), solid-state emission, stimuli responsive device, biological studies and other optoelectronic devices *[1-9]*. The donor-acceptor molecules possess an electron rich species attached to an electron deficient species which allows intramolecular charge transfer (ICT) within the system *[10]*. The optical and electronic properties of donor-acceptor systems can be finely tuned by simple modifications such as alteration of the donor or acceptor ability or by the addition of different π linkers which have a direct effect on the ICT process *[11-12]*. In the donor-acceptor molecules, the donor moiety is used to be increase in HOMO level whereas the acceptor moiety is used to decrease in the LUMO level *[13-14]*. The integration of donor and acceptor units result in narrow HOMO-LUMO gap and a wide absorption spectrum *[15]*. Therefore, the D-A systems are majorly used in organic electronics and photovoltaic devices *[16]*.

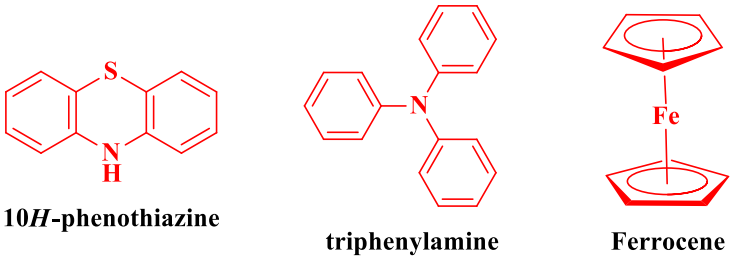
The use of π linkers is a very effective approach in controlling the photophysical and electronic properties of D-A systems. Organic donor-π-acceptor (D-π-A) compounds have been extensively studied experimentally and theoretically. The commonly used donors are triarylamines *[17]* (TPA), carbazole, ferrocence *[18]* (Fc), thiophene, oligothiophenes and phenothiazine (PTZ) *[19-20]*, whereas pyrazabole (PY), TCNE (tetracynoethylene), TCNQ (tetracynoquinodimethane), diarylborons *[21-22]*, quinolone, and quinoxaline *[23]*, are commonly used as electron-accepting moieties. The incorporation of donor and acceptor units' reveal endow the molecules with noteworthy intramolecular charge transfer (ICT) behavior which is revealed in their

UV–vis absorption and photoluminescence (PL) spectra *[24-25]*. The use of different donors can easily alter the electrochemical behavior of D-A compounds *[13]*.

ACCEPTOR



DONOR



In this work we have selected, pyrazabole (PY) as our central acceptor unit. Pyrazabole system are a new kind of boron heterocyclic systems, which are can be easily functionalized at the pyrazole carbon as well as boron atom and are very stable. The pyrazabole system is a nitrogen-boron heterocyclic compound and acts as a weak acceptor *[26-28]*. The tetra coordinated boron atom has a negative charge which is neutralized by nitrogen atoms, and the whole molecule become neutral and can be synthesized by the dimerization of two pyrazole rings The pyrazabole core can exist in either of this different confirmations like flat, chair or boat which is controlled by the charecter of the substituent linked with the boron atom and pyrazabole core *[26]*. The substitution of

pyrazabole unit with various donor groups on the pyrazabole moiety results in different donor-acceptor architectures i.e. D-A, D-A-D, D-π-A, D-π-A-π-D *etc.* serving as excellent candidates in organic photovoltaics, photonics, sensors, stimuli responsive materials etc. These properties of pyrazabole have been exploited in our proposal by design and synthesis of pyrazabole functionalized donor-acceptor systems incorporating various donor systems such as ferrocene *[18]*, triphenylamine *[17]*, and phenothiazine *[19-20]*. The various donors are attached to pyrazabole by coupling reactions and the donor-acceptor ability was tuned by introducing acetylenic linkage. To further increase the acceptor strength of pyrazabole moiety, 1,1,4,4-tetracyanobutadiene (TCBD, A′) was introduced followed by a [2 + 2] cycloaddition–retroelectrocyclization reaction with tetracyanoethylene. 1,1,4,4-tetracyanobutadiene (TCBD, A′) also act as a strong acceptor because of four cyano group.

We have chosen different donors like Triphenylamine (TPA-D), Phenothiazine (PTZ-D′) and Ferrocene (Fc-D″) for formulating the whole molecule. All these three donors are extensively known to possess good electron donating ability. Phenothiazine is a well-known heterocyclic moiety comprising of nitrogen and Sulphur atom which was first synthesized by Bernthsen in 1883 *[19-20]*. It has low oxidation potential and high thermal and electrical stability. Triphenylamine is a star shaped molecule which also has an excellent electron donating ability. It was first synthesized by Merz and Weith in 1873. It shows high hole mobility with non-coplanar structure which helps in restraining intermolecular aggregation *[18]*. Ferrocene is a sandwich shaped donor which was first synthesized by Kealy and Pauson in 1951. It also shows the reversible oxidation at low potential *[17]*. All these donors show wide range of applications in organic photonics, organic electronics, solid state emission and as NIR

absorbing Dyes, when joined with different acceptors All the molecules were well represented by ^{1}H-NMR and HRMS.

1.2. Aim and Strategy of our work

The work was designed with an aim of precise tuning of the donor-acceptor ability of pyrazabole systems by incorporation of different donors, introduction of acetylenic linkage and utilization of strong acceptor like TCBD. The molecular strategy was designed to study the optical and electronic properties of different TCBD substituted D-A pyrazabole systems such as TPA (D), PTZ (D') and Fc (D'') substituted Pyrazabole. A series of D-π-A-π-D, D-A'-A-π-D, D-A'-A-A'-D were synthesized by utilization of pyrazabole as acceptor (A) and TPA, PTZ and Fc as donor and TCBD as acceptor (A'). Further, ^{1}H NMR and Mass spectroscopic techniques was used to determine the structure of the compounds.

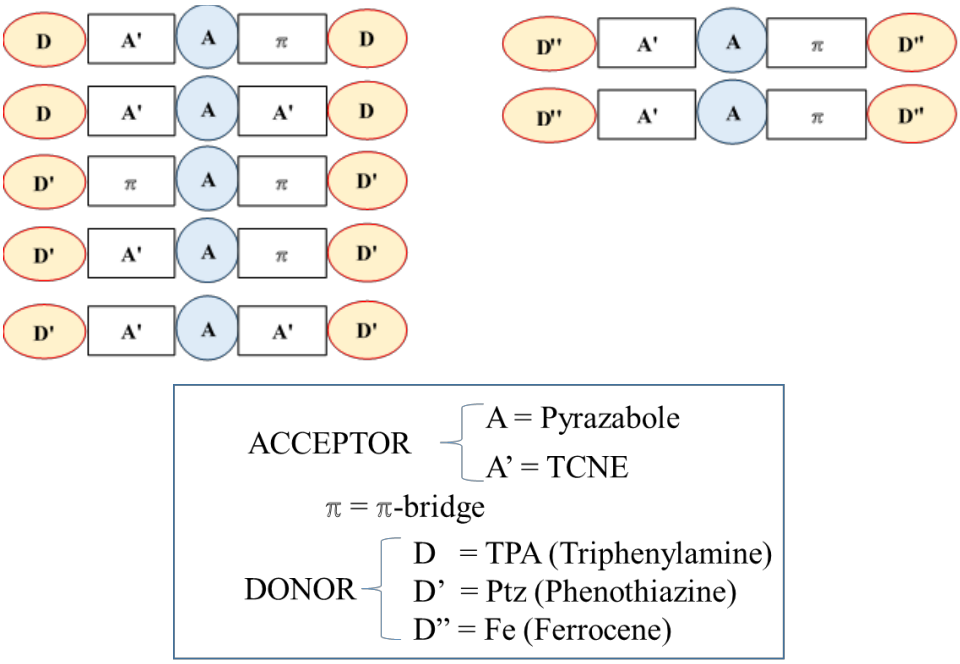
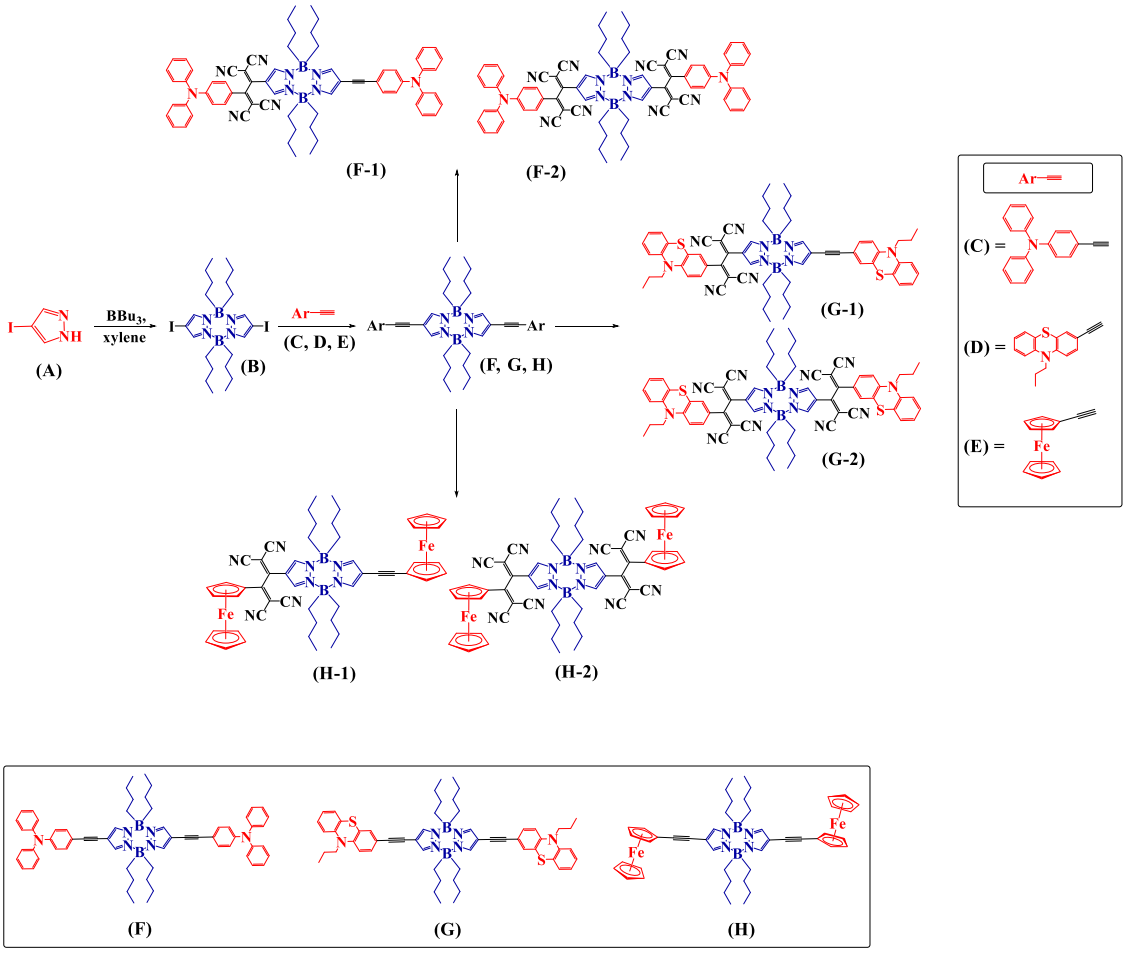


Figure 1: Structure and molecular framework of different donor-acceptor system.



Scheme 1: Overall Scheme

Chapter 2 Experimental Section

2.1. Chemicals, reagents and methods

All Chemicals which were used for synthesis and purification of compounds, were pure. These chemical includes phenothiazine (PTZ), bromine (Br_2) (Sigma-Aldrich, 99.5%), ferrocene (Sigma-Aldrich, 98%), TPA (Sigma-Aldrich, 99SS%), iodopropane (Sigma-Aldrich, 99%), iodoimidazole, BBu_3, xylene (Spectrochem, >99%), TCNE (Sigma-Aldrich, 98%), TCNQ (Sigma-Aldrich, 98%), DCM (Spectrochem), DCE (Spectrochem), hexane (Spectrochem), CuI (Sigma-Aldrich, ≥99.5%), $Pd(PPh_3)_2cl_2$ (Sigma-Aldrich, 99%), Et_3N (Sigma-Aldrich, ≥99%), THF, DMF (Spectrochem, >95%), Dioxane (Spectrochem, ≥99.5%), NaOH, $POCl_3$ (Spectrochem, >99%), $AlCl_3$ (Sigma-Aldrich, 99.99%).

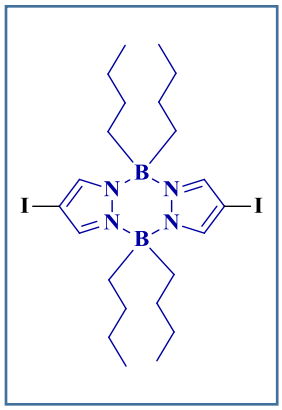
Mainly we are dealing with C-C coupling reactions (Sonogashira and Suzuki). All these reactions are mostly moisture sensitive reactions, so all the oxygen and wet sensitive reactions were performed in inert (nitrogen/argon) atmospheric conditions. ^{1}H-NMR spectra of all compounds were recorded using a Bruker AV 400 MHz spectrometer. Chemical shifts are described in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using left-over protonated able to make payment as an internal standard {$CDCl_3$ and DMSO-d6}. The splitting patterns in ^{1}H-NMR spectrum explained by the symbol as “s, singlet; d, doublet; t, triplet and m, multiplet.” Mass spectrometric analyses were done on Bruker-Daltonics, microTOF-Q II mass spectrometer.

2.2. General Procedure for the Preparation of the Precursors

The precursors B, C, D, E, F and H were synthesized as per reported procedure *[29-32]*.

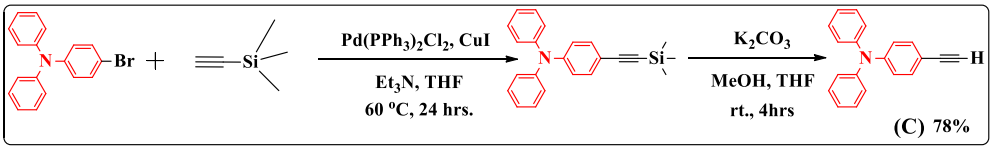
2.2.1. Synthesis of central acceptor

2.2.1.1. Synthesis of B *[31]*. The intermediate 4,4,8,8-Tetrabutyl-2,6-diiodopyrazabole (B) was synthesized by condensation reaction, a mix of 4-iodopyrazole 'A' (5.0 g, 25.7 mmol) and 100 mL of xylene, 25 ml of a 1M solution of tributylborane in THF was added and refluxed at 120 ℃ for 12 hrs. After taking away the able to make payment under rotavap, the coming out product 'B' was washed with methanol to give in a white solid (5.6 g 3, 68.5%).



2.2.2. Synthesis of adjacent Donor

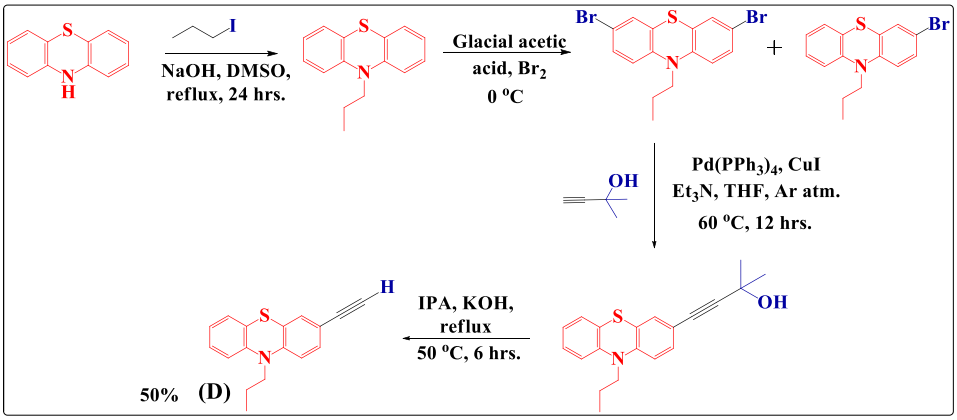
2.2.2.1. Synthesis of C *[29]*. 4-ethynyl-N,N-diphenylaniline was synthesized by earlier reported procedure, first monobromo derivative of triphenylamine (2 g, 6.168 mmol) was reacted with trimethylsilylacetylene (1.5 ml, 9.25 mmol) by Sonogashira cross-coupling reaction. The intermediate N,N-diphenyl-4-((trimethylsilyl)ethynyl)aniline (2.76 g, 5.186 mmol), was deprotected by K_2CO_3 (4.3 g, 31.1 mmol) with 1:1 solution of methanol and THF to obtain light yellow solid 4-ethynyl-N,N-diphenylaniline at rt. with the yield of 78%.



Scheme 2: Synthesis of **C**

2.2.2.2. Synthesis of D *[30]*: 3-ethynyl-10-propyl-10H-phenothiazine was synthesized by four different steps. First 10H-phenothiazine (2 g, 10 mmol) moiety was reacted with propyliodide (3.56 g, 20.9 mmol) by alkylation method in presence of NaOH (3.2 g, 80 mmol), 50 ml DMSO and heated under reflux for 24 hrs. Then the reaction mixture was discharged into water and ethyl acetate (300 mL) was used to extract the organic phase. After that the organic part of the system was self-controlled and dried over anhydrous

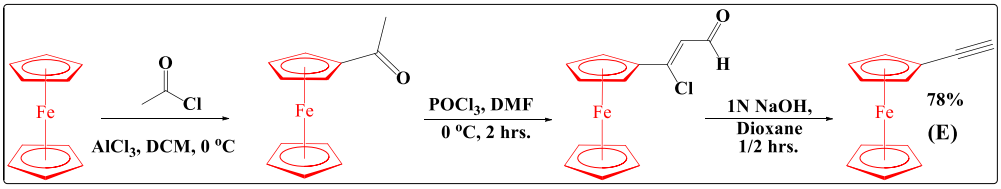
$MgSO_4$. After taking away the solvent rotavap, the rest was made clean by column chromatography using silica and DCM-hexane (1:9; v/v) as the filtrate to give a colorless viscous liquid (2.15 g, 85%). After this the alkylated product was employed bromination reaction, 10-propyl-10H-phenothiazine (2 g, 8.28 mmol) was dissolved in 13 ml $CHCl_3$ and a solution of NaOH (0.496 g, 12.42 mmol) in 50 ml glacial acetic acid was added to the above mixture. Then at last bromine (0.42 ml, 8.28 mmol, in 10 mL glacial acetic acid) was added dropwise at 0 °C. The mix was stirred at 0 °C till the complete addition of bromine took place. After this mix was removed and workup with water and DCM, and the organic layer was dried over $MgSO_4$. At last we got a light yellow liquid of mono-bromo alkylated PTZ (3-bromo-10-propyl-10H-phenothiazine) with the yield of 69% and then this mono-bromo PTZ derivative was reacted with 2-methylbut-3-yn-2-ol (1.5equi.) at 60 °C for 12 hrs. by Sonogashira cross-coupling reaction after this the deprotection of propan-2-ol by TPA, KOH at 50 °C and we got our desired product at the end.



Scheme 3: Synthesis of **D**

2.2.2.3. Synthesis of E *[31]***:** Ethynylferrocene was also synthesized by three steps starting from ferrocene (Fc). Firstly, Fc was functionalized to monoacetyl ferrcene by alkylation process, in which a solution of $AlCl_3$ (2.2 g, 16.3 mmol) in 10 ml DCM was added to 2-neck RB, stirred it on magnetic stirred with the addition of acetylchloride (1.1 ml) dropwise, then a mixture

of Fc (2.8 g, 15 mmol and 10 ml DCM) was added to the above solution and stirred the whole mixture for half an hour and we got dark violet color mixture which was further quenched and the organic layer was extracted with DCM, at last resulted in monoacetyl ferrocene (orange color, m.p. = 82 ℃) with the yield of 81.72%. Further a solution of monoacetyl ferrocene (1.7 g, 7.45 mmol) in DMF (10 ml) was added to a three neck RB at 0 ℃ after this a red complex solution of $POCl_3$ (3 ml) in DMF (10 ml) was added dropwise to the above mixture at 0 ℃ by Vilsmeier-Haack reaction and the change of color was observed from dark brown to deep blue and at last the complete solution was quenched with sodium acetate, after that the product which was extracted with hexane, (1-chloro-2-formylvinyl)ferrocene (2 g, 7.2 mmol) dissolved in 1N NaOH in 30 ml 1,4-Dioxane and the complete solution was refluxed for half an hour and at the end our desired product ethynylferrocene was obtained with the yield of 78%.



Scheme 4: Synthesis of **E**

2.2.3. Synthesis of Donor Acceptor molecules

2.2.3.1. Synthesis of F *[32]***: 'F'** was synthesized as earlier reported procedure, in which 4,4,8,8-Tetrabutyl-2,6- diiodopyrazabole **'B'** and 4-ethynyl-N,N-diphenylaniline **(C)** undergoes Pd-catalysed Sonogashira cross-coupling reaction in presence of CuI as co-catalyst, trimethylamine (Et_3N) as a base and THF as solvent in inert condition. ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 4H), 7.76–6.99 (m, 20H, TPA aromatic H), 1.18 (d, 8H, *J* = 8Hz), 0.88–0.78 (m, 20H), 0.655 (d, 8H, *J* = 8Hz).

2.2.3.2. Synthesis of H *[31]***:** Similar procedure as in **'F'** was used in the synthesis of **'H'** in which 4,4,8,8-Tetrabutyl-2,6- diiodopyrazabole **'B'** and

Ethynylferrocene **'E'** undergoes Pd-catalysed Sonogashira cross-coupling reaction in presence of CuI as co-catalyst, trimethylamine (Et_3N) as a base and THF as solvent in inert condition. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 4H), 4.51 (s, 4H), 4.30 (t, 13H, *J* = 8Hz), 1.26 (t, 8H, J = 8Hz), 0.79 (m, 20H), 0.68–0.64 (m, 8H). Observed mass $[M]^+$ = 800.35 Calculated mass $[M]^+$ = 800.35.

2.3. Synthesis of Final Compounds

The [2 + 2] cycloaddition−retroelectrocyclization reaction of pyrazabole **F**, **G** and **H** with TCNE resulted in mono and di substituted TCBD-functionalized pyrazabole **F-1**, **G-1**, **H-1** (mono substituted TCNE) and **F-2**, **G-2**, **H-2** (di substituted TCNE) respectively.

2.3.1. Synthesis of F-1 and F-2: For obtained the mono substituted TCBD-functionalized pyrazabole **'F-1' by** [2 + 2] cycloaddition−retroelectrocyclization reaction from pyrazabole **'F'**. The TCNE was used to be 1.1 equivalents with respect pyrazabole **'F'** in presence of DCM and the whole reaction is conducted at rt. for 4 hrs. caused to result in pyrazabole **'F-1'** with the yield of 66.72%. On the other side for obtained the di substituted TCBD-functionalized pyrazabole **'F-2'** from **'F'**, TCNE was used to be 2 equivalents with respect to pyrazabole **'F'** at 60 °C for 12 hrs. caused to result in pyrazabole **'F-2'** with the yield of 78.34%. **(F-1)** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 2H), 7.72 (s, 2H), 7.635 (d, 2H, *J* = 1.2Hz), 7.40 (d, 4H, *J* = 8Hz), 7.34 (d, 2H, *J* = 8Hz), 7.31–7.27 (m, 6H), 7.21 (t, 4H, *J* = 8Hz), 7.05 (t, 4H, *J* = 8Hz), 7.12 (d, 2H, *J* = 8Hz), 7 (d, 2H, *J* = 8Hz), 6.92 (d, 2H, *J* = 8Hz), 1.16 (t, 8H, *J* = 4Hz), 0.78–0.67 (m, 28H). Observed mass $[M+Na]^+$ = 1069.57 Calculated mass $[M+Na]^+$ = 1069.58. **(F-2)** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 4H, *J* = 4Hz), 7.62 (d, 4H, *J* = 8Hz), 7.40 (t, 8H, *J* = 8Hz), 7.29 (d, 4H, *J* = 8Hz), 7.21 (d, 8H, *J* = 8Hz), 6.92 (t, 4H, *J* = 4Hz), 1.16 (t, 8H, *J* = 8Hz), 0.77–0.71 (m, 28H). Observed mass $[M+Na]^+$ = 1097.5894 Calculated mass $[M+Na]^+$ = 1197.59.

2.3.2. Synthesis of G: Phenothiazine functionalized pyrazabole **'G'** was synthesized by Pd-catalysed Sonogashira cross-coupling reaction between diiodopyrazabole (B) and 3-ethynyl-10-propyl-10H-phenothiazine (D) in presence of CuI as co-catalyst, trimethylamine (Et_3N) as a base and THF as solvent in inert atmosphere. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 4H), 7.26 (s, 4H), 7.12 (d, 4H, *J* = 8Hz), 6.92–6.86 (m, 6H), 6.79 (d, 2H, *J* = 8Hz), 3.81 (t, 4H, *J* = 8Hz), 1.81 (t, 4H, *J* = 8Hz), 1.18 (d, 4H, *J* = 8Hz), 1.01 (s, 6H), 0.78 (m, 20H), 0.67 (t, 8H, *J* = 8Hz). Observed mass $[M]^+$ = 910.5246 Calculated mass $[M]^+$ = 910.52.

2.3.3. Synthesis of G-1 and G-2: For obtained the mono substituted TCBD-functionalized pyrazabole **'G-1' by** [2 + 2] cycloaddition−retroelectrocyclization reaction from pyrazabole **'G'**. The TCNE was used to be 1.1 equivalents with respect pyrazabole **'G'** in presence of DCM and the whole reaction is conducted at rt. for 4 hrs. caused to result in pyrazabole **'G-1'**. On the other side for obtained the di substituted TCBD-functionalized pyrazabole **'G-2'** from **'G'**, TCNE was used to be 2 equivalents with respect to pyrazabole **'G'** at 60 °C for 12 hrs. caused to result in pyrazabole **'G-2'**. **(G-1)** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 2H), 7.72 (s, 2H), 7.65 (d, 1H, *J* = 8Hz), 7.36–6.78 (m, 13H). 3.87–3.80 (p, 4H, *J* = 8Hz), 1.85 (q, 4H, *J* = 8Hz), 1.42–1.26 (m, 6H), 1.04 (t, 8H), 0.88–0.70 (m, 28H), **(G-2)** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 4H), 7.64 (d, 2H, *J* = 8Hz), 7.33 (s, 2H), 7.18 (s, 2H), 7.03 (t, 4H, *J* = 8Hz), 6.87 (t, 4H, *J* = 8Hz), 3.85 (t, 4H, *J* = 8Hz), 1.85 (q, 4H, *J* = 8Hz), 1.28–1.14 (m, 8H), 1.04 (t, 6H, *J* = 8Hz), 0.71 (m, 28H).

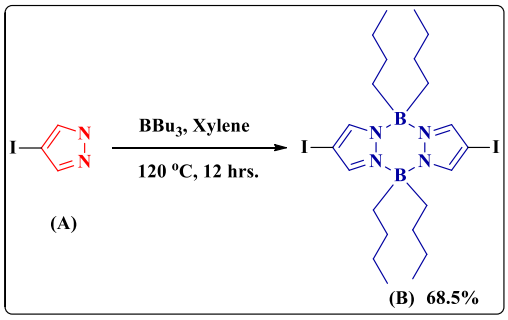
2.3.4. Synthesis of H-1 and H-2: For obtained the mono substituted TCBD-functionalized pyrazabole **'H-1' by** [2 + 2] cycloaddition−retroelectrocyclization reaction from pyrazabole **'H'**. The TCNE was used to be 1.1 equivalents with respect pyrazabole **'H'** in presence of DCM and the whole reaction is conducted at rt. for 4 hrs. caused

to result in pyrazabole **'H-1'**. On the other side for obtained the di substituted TCBD-functionalized pyrazabole **'H-2'** from **'H'**, TCNE was used to be 2 equivalents with respect to pyrazabole **'H'** at 60 °C for 12 hrs. caused to result in pyrazabole **'H-2'**. **(H-1)** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 2H), 7.67 (s, 2H), 5.715 (d, 2H, *J* = 4Hz), 5.09 (t, 1H, *J* = 4Hz), 4.83 (t, 1H), 4.47 (s, 3H), 4.255 (d, 7H, *J* = 4Hz), 1.25 (t, 8H, *J* = 4Hz), 0.88–0.63 (m, 28H). **(H-2)** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 4H), 5.72 (d, 2H, *J* = 8Hz), 5.10 (s, 2H), 4.83 (s, 2H), 4.52 (s, 10H), 4.22 (d, 2H, *J* = 8Hz), 1.09–1.02 (m, 8H), 0.81–0.53 (m, 28H).

Chapter 3 Results and discussion

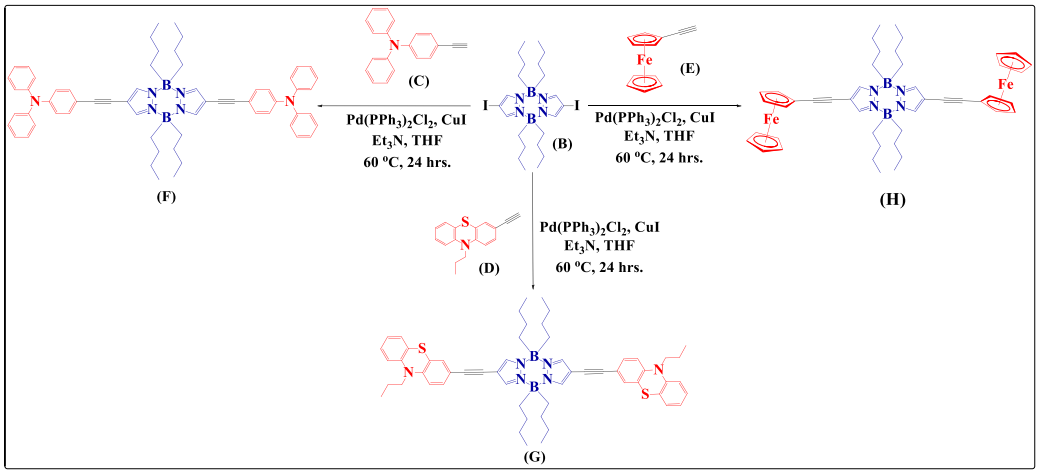
3.1. Synthesis of Donors (D), Acceptors (A), Donor-Acceptor (D-A) system and characterization

The synthesis of TCNE substitued Pyrazabole compounds D-A systems '**B**' to **'H-2'** are shown in different schemes one by one. The diiodopyrazabole '**B**' was synthesized by condensation reaction between 4-iodopyrazole in presence of xylene and tributyborane at 120℃, according to following earlier reports. The compound '**B**' was obtained with 68.5% yield.



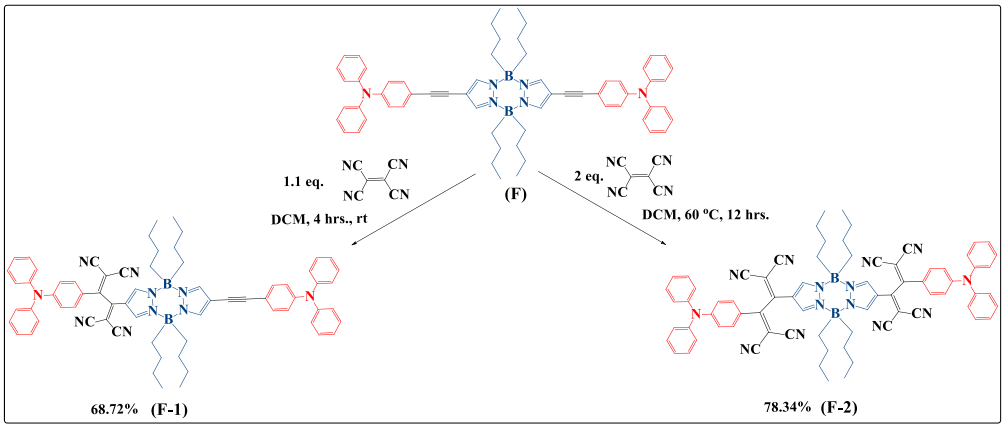
Scheme 5: Synthesis of **B**

The Sonogashira cross-coupling reactions of diiodopyrazabole '**B**' with 2.1 equivalent of 4-ethynyl-N,N-diphenylaniline **'C'**, 3-ethynyl-10-propyl-10H-phenothiazine **'D'** and Ethynylferrocene **'E'** resulted in formation of symmetrical pyrazabole systems **'F'**, **'G'** and **'H'** respectively of architecture like D-π-A-π-D.

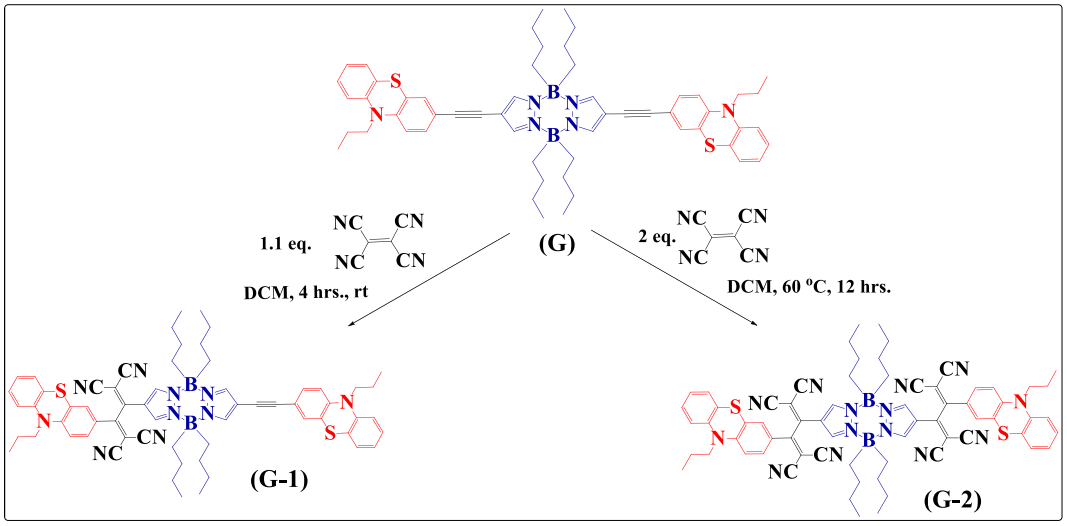


Scheme 6: Synthesis of **'F'**, **'G'** and **'H'**

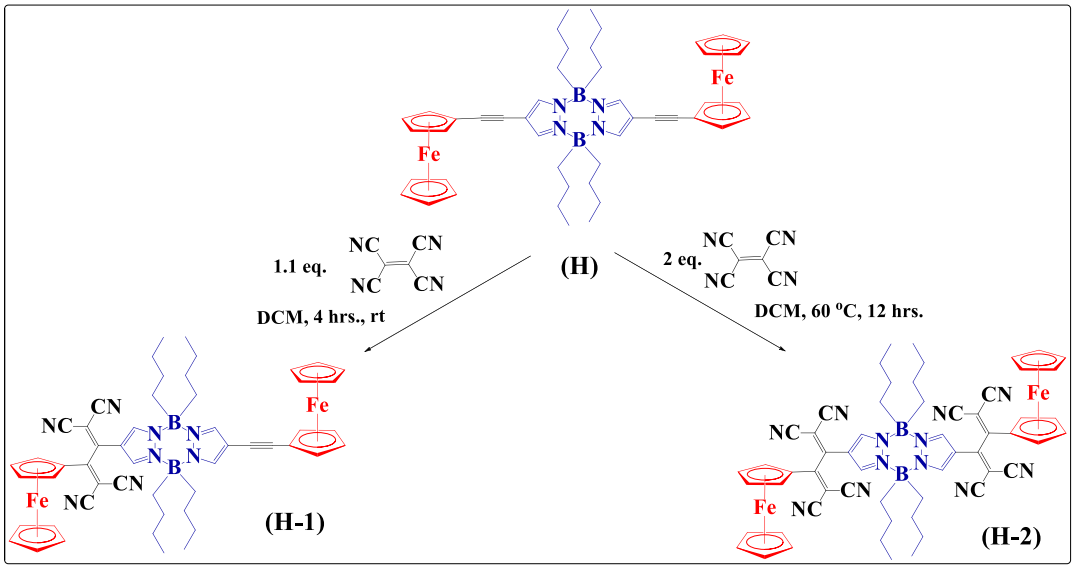
The [2 + 2] cycloaddition−retroelectrocyclization reaction of pyrazabole **'F'**, **'G'** and **'H'** with TCNE resulted in TCBD functionalized mono-di pyrazabole **F-1, F-2, G-1, G-2, H-1 and H-2**. 1.1 equivalent of TCNE with pyrazabole **'F'**, **'G'** and **'H'** in methylenedichloride (DCM) at room temperature resulted in mono substituted TCNE pyrazabole **'F-1'**, **'G-1'** and **'H-1'**, whereas the reaction of 2 equivalents of TCNE with pyrazabole **'F'**, **'G'** and **'H'** at 40°C resulted in di substituted TCNE pyrazabole **F-2**, **G-2** and **H-2** respectively.



Scheme 7: Synthesis of **'F-1 and F-2'**.



Scheme 8: Synthesis of **'G-1 and G-2'**.



Scheme 9: Synthesis of **'H-1 and H-2'**

The purification of all pyrazabole compounds were carried out by column chromatography, and all the compounds were characterized by ^{1}H NMR and Mass spectra.

3.2. Photophysical properties:

The photophysical properties of TCBD substituted TPA pyrazaboles (**F-1** and **F-2**) were studied using electronic absorption spectroscopy. A solution of **F-1** and **F-2** in 10^{-5} M DCM solution was used studying the photophysical properties. The UV-vis spectra (**Figure 2**) of **F-1** and **F-2** displayed absorption bands between 250-350 nm corresponding to the π-π* transitions. The molecules also showed absorption bands in the higher wavelength region (500-600 nm) which could be ascribed to the intramolecular charge transfer (ICT) occurring from the donor to acceptor moieties. The ICT band in molecules **F-1** and **F-2** is red-shifted as compared to the ICT band in molecule *[32]*. The addition of TCBD increases the acceptor strength by tuning of LUMO level which further shifts the ICT of TCBD derivatives to longer wavelength.

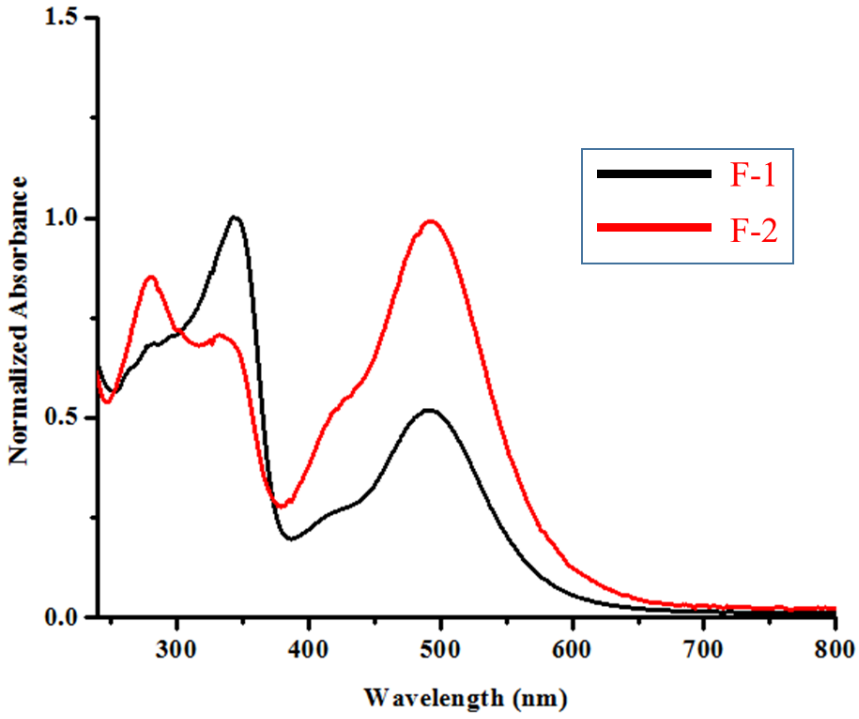


Figure 2: Absorption spectra of **F-1** and **F-2** in 10^{-5} M DCM solution.

Chapter 4: Conclusion and Future Prospective

4.1. Conclusion: We have successfully synthesized donor-acceptor D-A pyrazabole (PY-A) using different donors like TPA, PTZ and Fc with the help of Sonogashira cross- coupling reaction followed by the addition of TCNE by cycloaddition–retroelectrocyclization reaction. The incorporation of TCBD act as an acceptor (A′) can further modulate the donor-acceptor strength, which is shown by the red shift in ICT band of **F-1** and **F-2**. All these molecules were characterized using ^{1}H and Mass spectroscopic techniques. This scheme can be further used for the development of opto-electronics, NIR-absorbing Dyes.

APPENDIX A

^{1}H and Mass Spectra

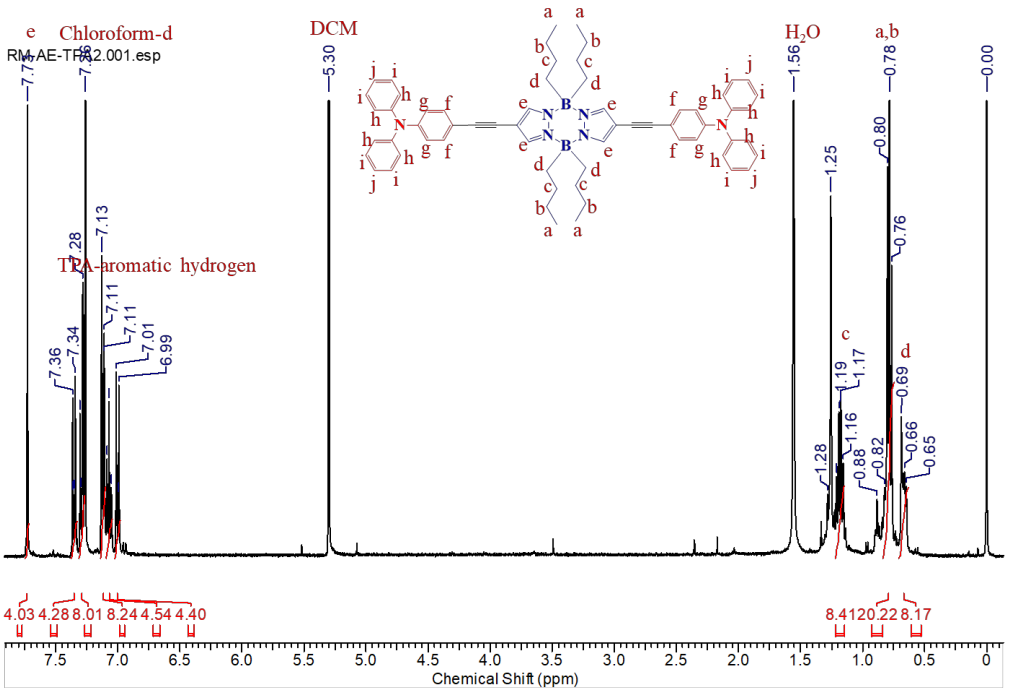
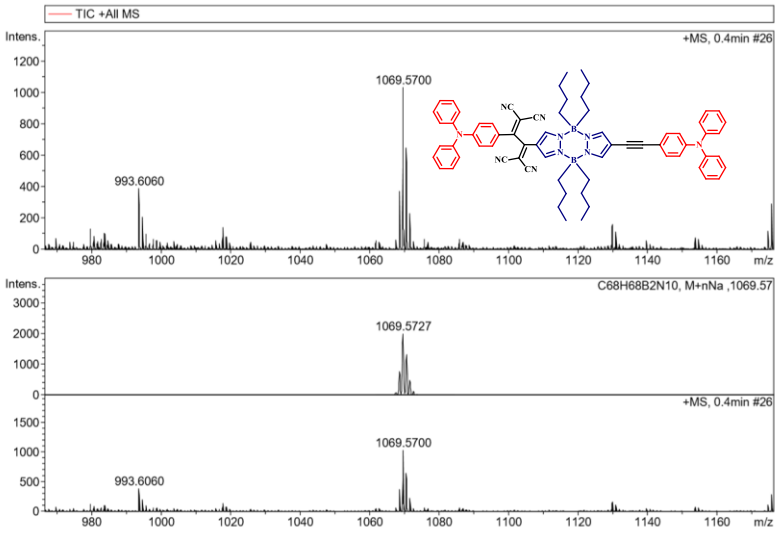


Figure 3: ^{1}H NMR spectrum of **F.**



Mol. Wt. of TP1 = 1046.58 g/mol

$(M+Na)^+$ peak = 1069.57

Figure 4: Mass spectrum of **F-1.**

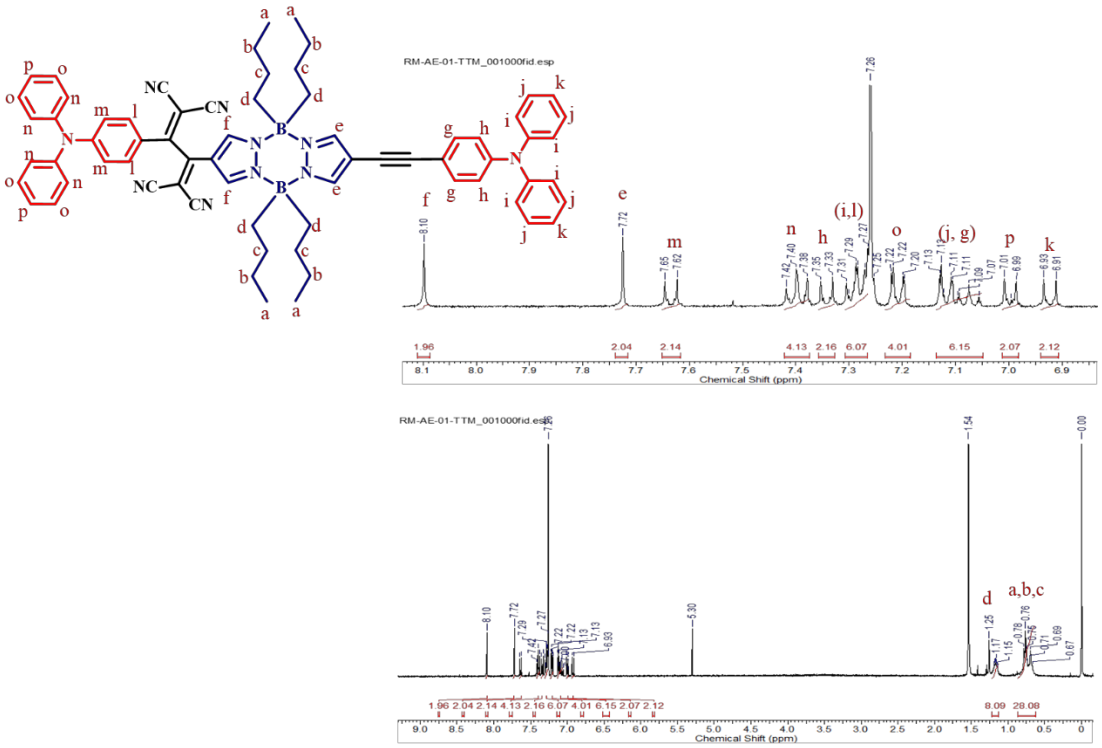


Figure 5: ^{1}H NMR spectrum of **F-1.**

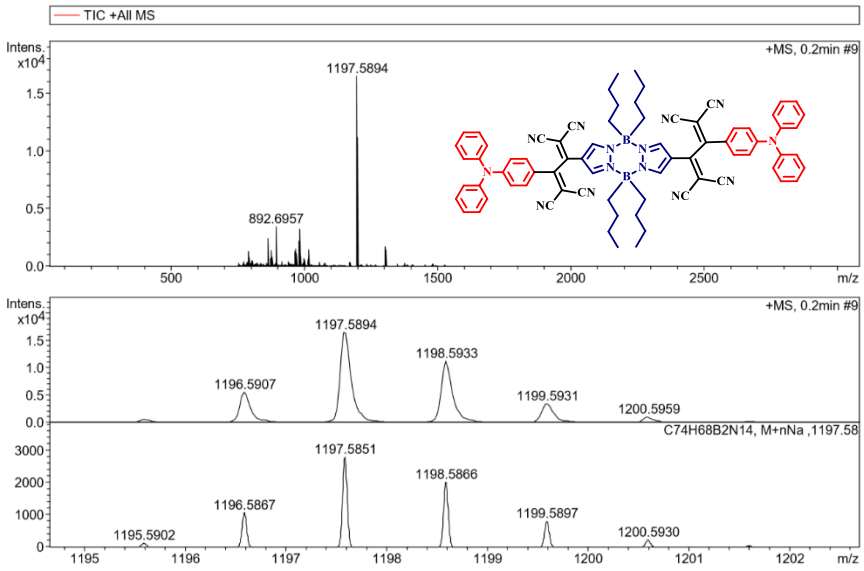


Figure 6: Mass spectrum of **F-2.**

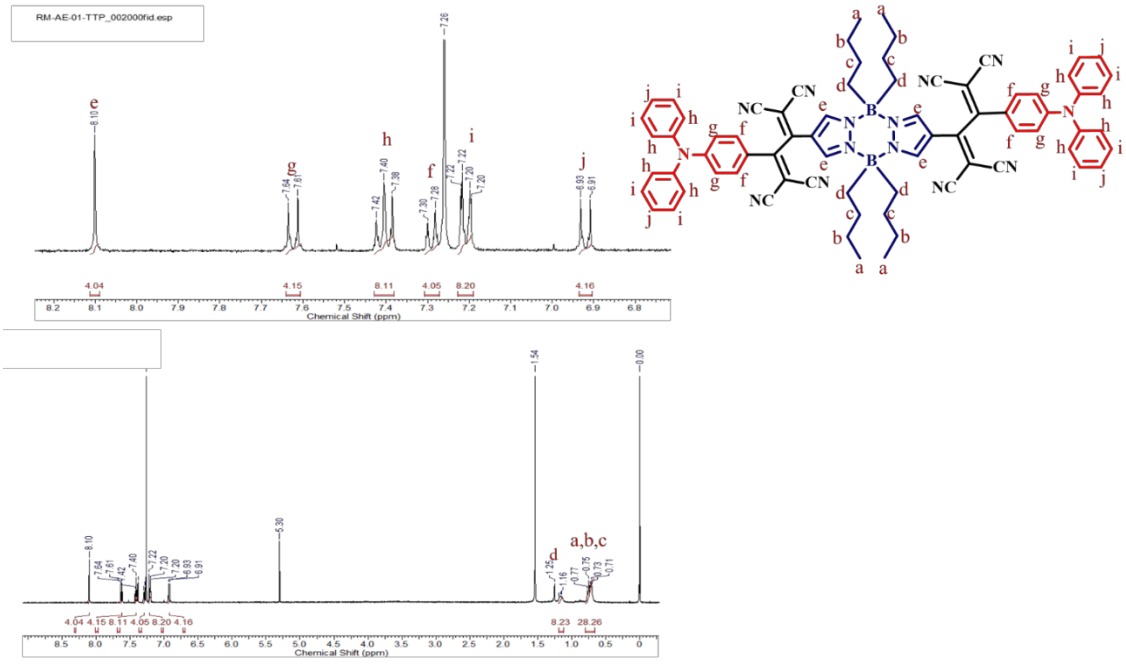


Figure 7: ^{1}H NMR spectrum of **F-2.**

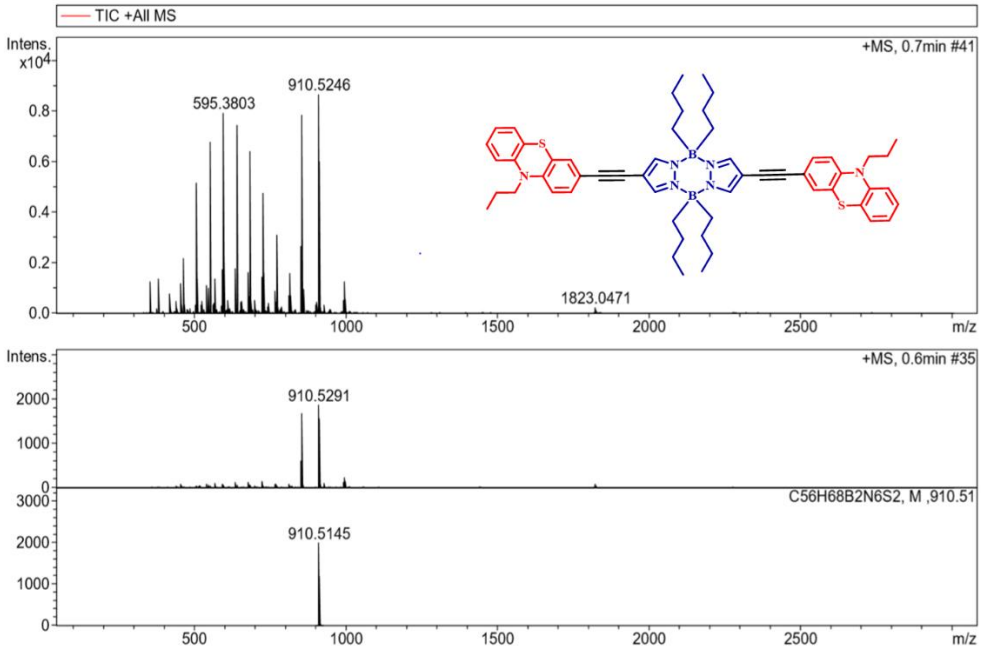


Figure 8: Mass spectrum of **G.**

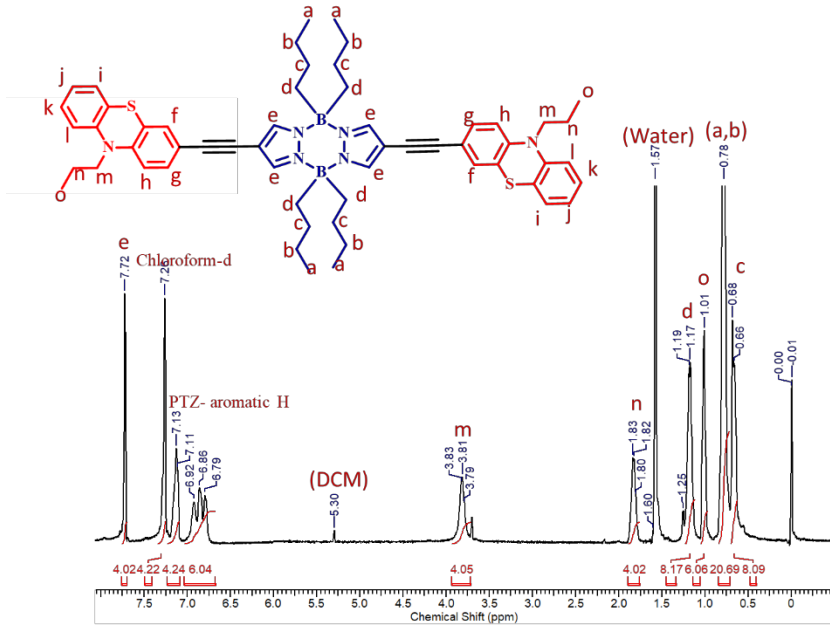


Figure 9: ^{1}H NMR spectrum of **G.**

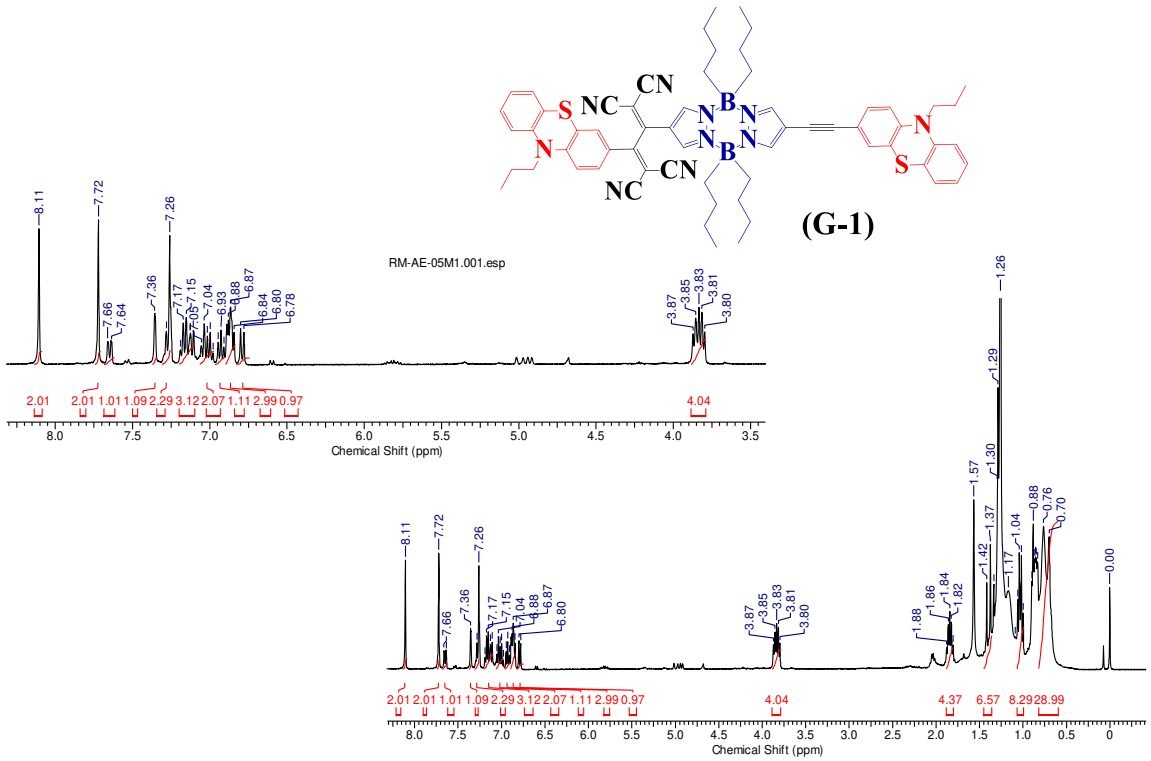


Figure 10: ^{1}H NMR spectrum of **G-1.**

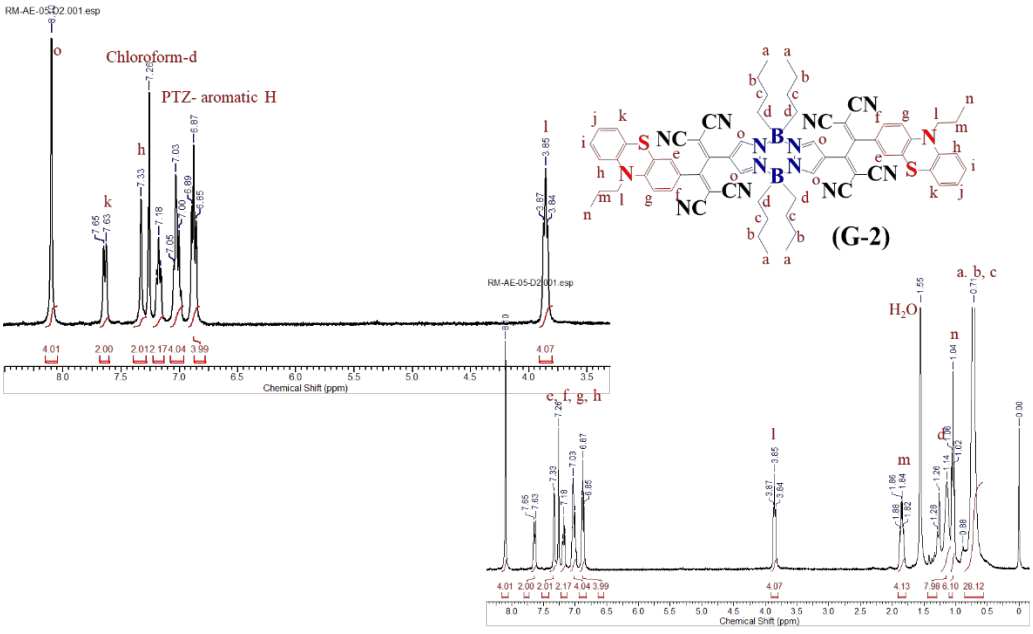


Figure 11: ^{1}H NMR spectrum of **G-2.**

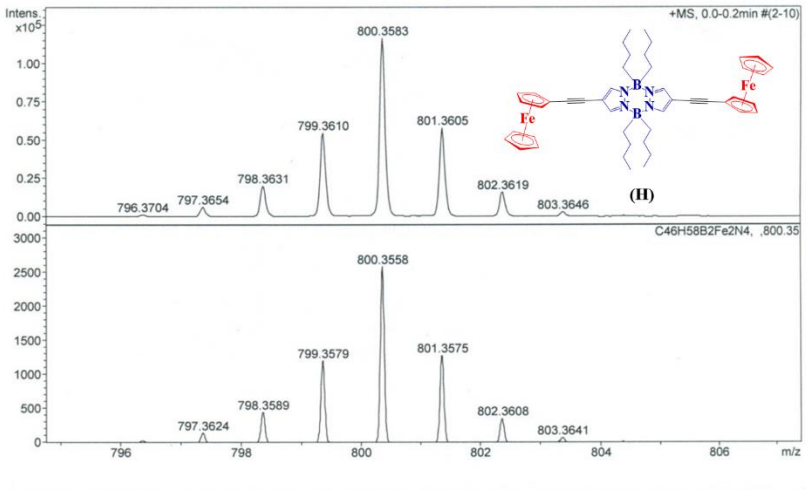


Figure 12: Mass spectrum of **H.**

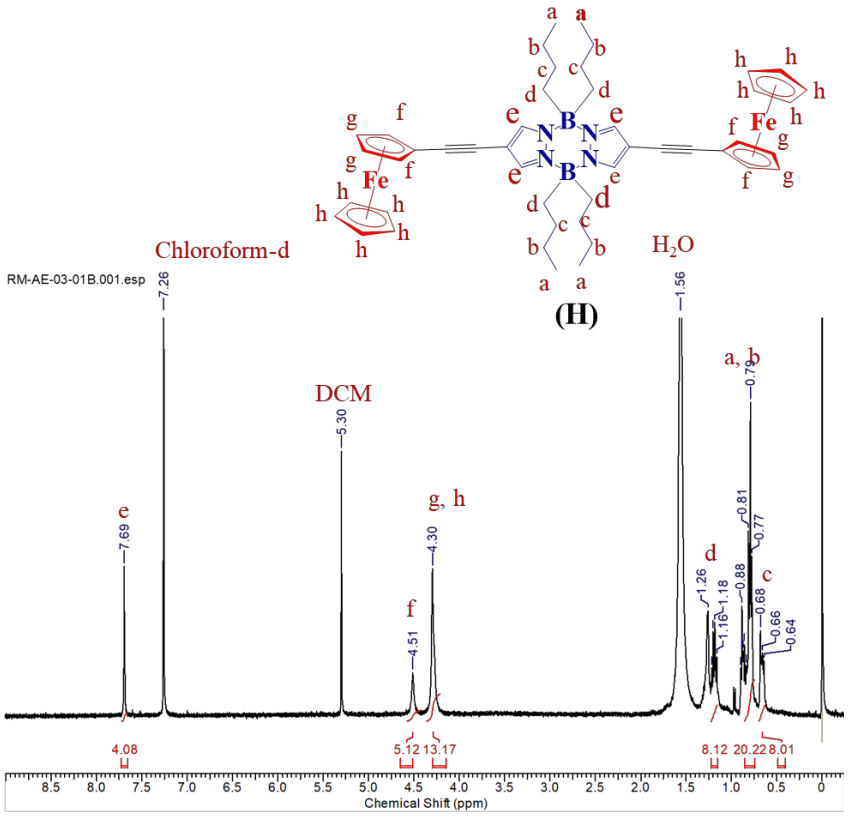


Figure 13: ^{1}H NMR spectrum of **H.**

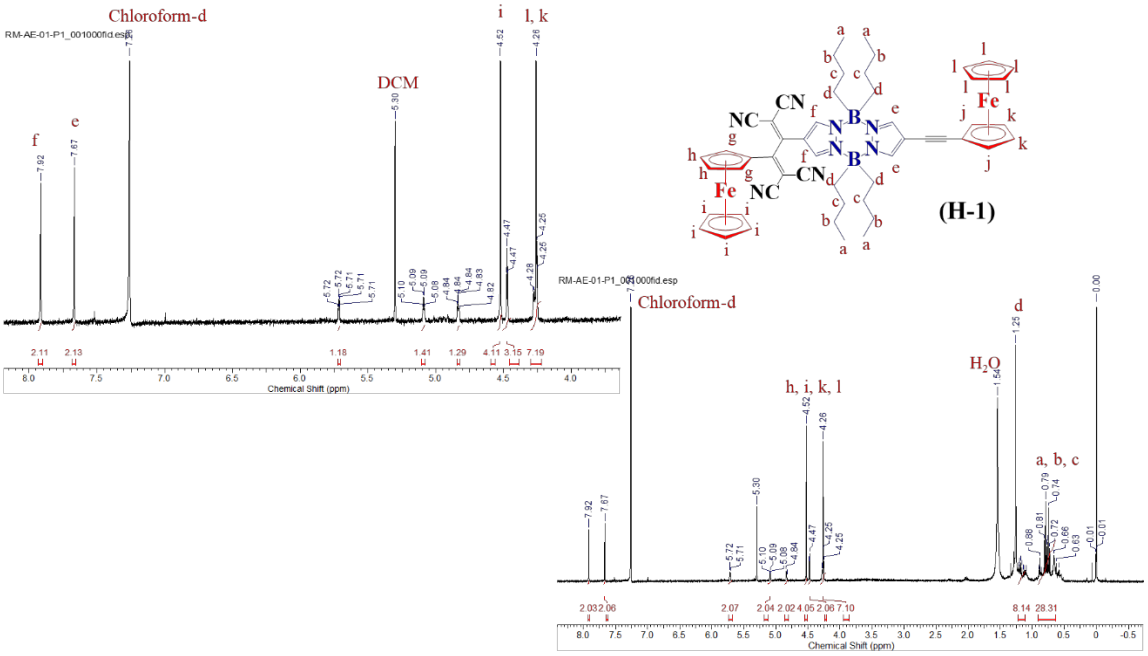


Figure 14: ^{1}H NMR spectrum of **H-1.**

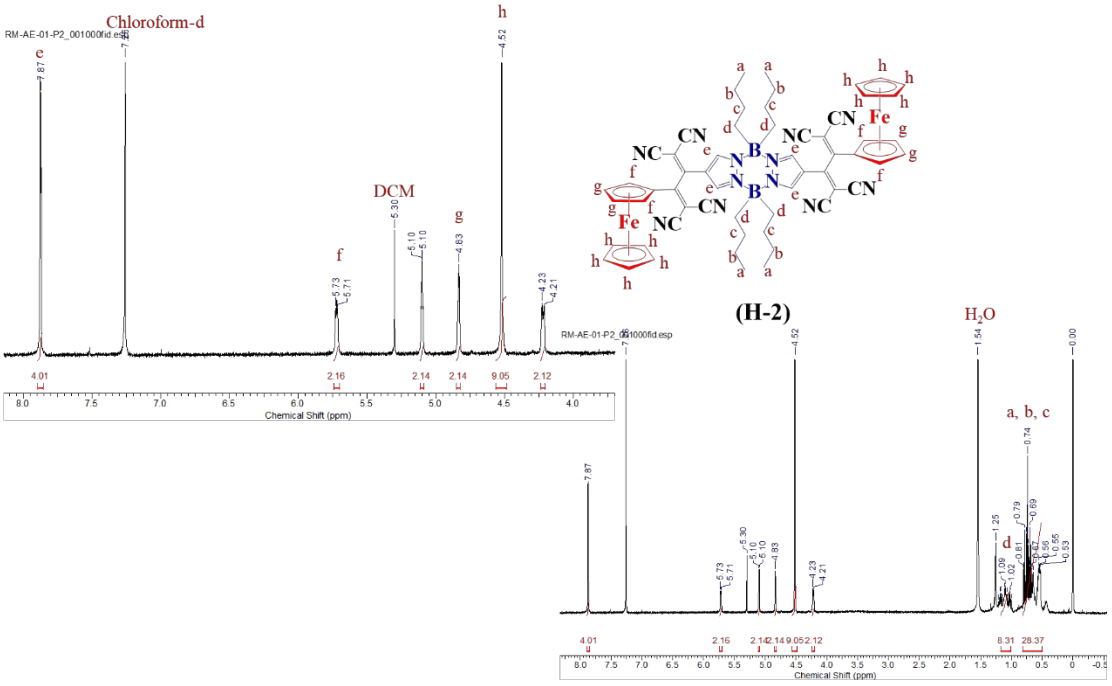


Figure 15: ^{1}H NMR spectrum of **H-2.**

References:

(1) Chen W., Cao T. (2009), Development of Novel Conjugated Donor Polymers for High-Efficiency Bulk-Heterojunction Photovoltaic Devices, Acc. Chem. Res., 42, 1709-1718.

(2) Mishra A., Ma C., B“auerle P. (2009), Functional Oligothiophenes: Molecular Design for Multidimensional Nanoarchitectures and Their Applications, Chem. Rev., 109, 1141-1276.

(3) Winzenberg K. N., Kemppinen P., Scholes F. H., Collis G. E., Shu Y., Birendra Singh T., Bilic A., Forsyth C. M., Watkins S. E. (2013), Indan-1,3-dione electron-acceptor small molecules for solution-processable solar cells: a structure–property correlation, Chem. Commun., 49, 6307-6309.

(4) Patil Y., Misra R., Keshtov M. L., Sharma G. D. (2016), 1,1,4,4-Tetracyanobuta-1,3-diene Substituted Diketopyrrolopyrroles: An Acceptor for Solution Processable Organic Bulk Heterojunction Solar Cells, J. Phys. Chem. C, 120, 6324–6335.

(5) Patil Y., Misra R., Sharma A., Sharma G. D. (2016), D–A–D–π–D–A–D type diketopyrrolopyrrole based small molecule electron donors for bulk heterojunction organic solar cells, Phys. Chem. Chem. Phys., 18, 16950–16957.

(6) Weder C. (2011), Mechanoresponsive Materials, J. Mater. Chem., 21, 8235−8236.

(7) Kishimura A., Yamashita T., Yamaguchi K. and Aida T. (2005), Rewritable Phosphorescent Paper by the Control of Competing Kinetic and Thermodynamic Self-Assembling Events, Nat. Mater., 4, 546−549.

(8) Ciardelli F., Ruggeri G. and Pucci A. (2013), Dye-containing polymers: methods for preparation of mechanochromic materials, Chem. Soc. Rev., 2013, 42, 857−870.

(9) Farinola G. M. and Ragni R. (2011), Electroluminescent materials for white organic light emitting diodes, Chem. Soc. Rev. 2011, 40, 3467−3482.

(10) Panja S. K., Dwivedi N. (2016), Tuning The Intramolecular Charge Transfer (ICT) Process in Push-Pull System: Effect of Nitro group, RSC Adv., 6, 105786-105794.

(11) Cao D., Peng J., Hong, Y., Fang, X., Wang, L., Meier, H. (2011), Enhanced Performance of the Dye-Sensitized Solar Cells with Phenothiazine-Based Dyes Containing Double D−A Branches, Org. Lett., 13, 1610.

(12) Kulkarni A. P., Wu P. T., Kwon T. W., Jenekhe S. A. (2005), Phenothiazine-Phenylquinoline Donor−Acceptor Molecules: Effects of Structural Isomerism on Charge Transfer Photophysics and Electroluminescence, J. Phys. Chem. B, 109, 19584.

(13) Leu W. C. W., Hartley C. S. (2013), A Push–Pull Macrocycle with Both Linearly Conjugated and Cross-Conjugated Bridges, Org. Lett., 15, 3762.

(14) Gholami M., Tykwinski R. R. (2006), Oligomeric and Polymeric Systems with a Cross-conjugated π-Framework, Chem. Rev., 106, 4997.

(15) Perepichka D. F., Bryce M. R. (2005), Molecules with Exceptionally Small HOMO–LUMO Gaps, J. Mol. Electron., 44, 5770–5373.

(16) Armin A., Hambsch M., Kim K., Burn P. L., Meredith P., Namdas E. B. (2014), Thick junction broadband organic photodiodes, Laser Photonics Rev., 8, 924–932.

(17) He C., He Q., Yang X., Wu G., Yang C., Bai F., ShuaI Z., Wang L., Li Y. (2007), Synthesis and Photovoltaic Properties of a Solution-Processable Organic Molecule Containing Triphenylamine and DCM Moieties, J. Phys. Chem. C 2007, 111, 8661–8666.

(18) Patil Y., Misra R., Singhal R., Sharma G. D. (2016), Ferrocene-diketopyrrolopyrrole based non-fullerene acceptors for bulk heterojunction polymer solar cells, J. Mater. Chem. A, 5, 13625-13633.

(19) Pappenfus T. M., Schneiderman D. K., Casado J., Navarrete J. T., Delgado M. C. R., Zotti G., Vercelli B., Lovander M. D., Hinkle L. M., Bohnsack J. N., Man K. R. (2011), Oligothiophene Tetracyanobutadienes: Alternative Donor−Acceptor Architectures for Molecular and Polymeric Materials, Chem. Mater., 23, 823-831.

(20) Hart A. S., K C C. B., Subbaiyan N. K., Karr P. A., D'Souza F. (2012), Phenothiazine-sensitized Organic Solar Cells: Effect of Dye Anchor Group Positioning on the Cell Performance, ACS Appl. Mater. Interfaces, 4, 5813.

(21) Chang Y. J., Chou P.-T., Lin Y.-Z., Watanabe M., Yang C.-J., Chin T.-M., Chow T. J. (2012), Organic dyes containing oligo-phenothiazine for dye-sensitized solar cells, J. Mater. Chem., 22, 21704.

(22) Reutenauer P., Kivala M., Jarowski P. D., Boudon C., Gisselbrecht J−P., Gross M., Diederich F. (2007), New strong organic acceptors by cycloaddition of TCNE and TCNQ to donor-substituted cyanoalkynes, Chem. Commun., 4898−4900.

(23) Zang J., Cai w., Huang F., Wang E., Zhang C., Liu S., Wang M., Duan C., Yang T. (2011), Synthesis of Quinoxaline-Based Donor−Acceptor Narrow-Band-Gap Polymers and Their Cyclized Derivatives for Bulk-Heterojunction Polymer Solar Cell Applications, Macromolecules, 44, 4, 894-901.

(24) Najaru S. M., Patil M. K., Nadef A., Inamdar S., Khari I. A. M. (2020), Photophysical, thermal properties, solvatochromism and DFT/TDDFT studies on novel conjugated D-A-π-A-D form of small

molecules comprising thiophene substituted 1,3,4-oxadiazole, J. Mol. Sci., 1199.

(25) Ekbote A., Jadhav T., Misra R. (2017), T-shaped donor-acceptor-donor type tetraphenylethylene substituted quinoxaline derivatives: Aggregation induced emission and mechanochromism, New. J. Chem., 41, 9346-9353.

(26) Jadhav T., Maragani R., Misra R., Sreeramulu V.,Rao D. N., Mobin S. M. (2013), Design and synthesis of donor–acceptor pyrazabole derivatives for multiphoton absorption, Dalton Trans., 4340–4342.

(27) Jadhav T., Dhokale B., Patil Y., Misra R. (2015), Aggregation induced emission and mechanochromism in tetraphenylethene substituted pyrazabole, RSC Adv., 5, 68187–68191.

(28) Trofimenko S. (1967), Boron-pyrazzole chemistry. I. Prrazaboles, J. Am. Chem. Sci., 89, 3165.

(29) Zou L., Liu Z., Yan X., Liu Y., Fu Y., Liu J., Huang Z., Chen X., and Qin J. (2009), Star-Shaped D-π-A Molecules Containing a 2,4,6-Tri(thiophen-2-yl)-1,3,5-triazine Unit: Synthesis and Two-Photon Absorption Properties, Eur. J. Org. Chem, 5587-5593.

(30) Wu Y., Guo H., Shao J., Zhang X., Ji S., Zhao J. (2011), Synthesis of Ethynylated Phenothiazine Based Fluorescent Boronic Acid Probe, J. Fluoresc., 21, 1143–1154.

(31) Misra R., Jadhav T., MobinS. M. (2014), Ferrocenyl pyrazaboles: Design, Synthesis, Structure, and Properties Probe, Dalton Trans., 43, 2013–2022.

(32) Patil Y., Jadhav T., Dhokale B., Butenschen H., Misra R. (2017), Donor Substituted Pyrazabole Monomers and Dimers: Design, Synthesis and Properties, Chemistry Select., 2, 415–420.