Design, Synthesis and Characterization of Bisthiazole Based Donor-Acceptor Molecular Systems

By RAMESH MARAGANI



DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE MAY, 2017

Design, Synthesis and Characterization of Bisthiazole Based Donor-Acceptor Molecular Systems

A THESIS

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

> *by* **RAMESH MARAGANI**



DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE MAY, 2017



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Design**, **Synthesis and Characterization of Bisthiazole Based Donor–Acceptor Molecular Systems** 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, 2014 to May, 2017 under the supervision of Dr. Rajneesh Misra, Associate Professor.

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.

Signature of the student with date (RAMESH MARAGANI)

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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Date:	Date:	Date:

ACKNOWLEDGEMENTS

The work described in this thesis would not have been possible without my close association with numerous people who were always there when I required them the most. I take this opportunity to acknowledge them and extend my sincere gratitude for helping me make this Ph.D. thesis a possibility.

I would like to begin with the person who made the biggest difference in my life, my mentor and supervisor, Dr. Rajneesh Misra. He has been there, in front of my eyes throughout my Ph.D., motivating and inspiring every bit of me towards new possibilities in life. He has been a living role model to me, taking up new challenges every day, tackling them with all his grit and determination and always thriving to come out victorious. It's his vigor and hunger to perform in adverse situation, which has inspired me to thrive for excellence and nothing less. His excellent supervision, advice and guidance from the very early stage made the completion of this study possible. I am indebted to him for his support, motivation and better understanding.

I express my heart-felt gratitude to Dr. Shaikh M. Mobin for single crystal X-ray support and his valuable guidance. I would also like to extend my gratitude to my PSPC members Dr. Shaikh M. Mobin and Dr. Santosh K Vishvakarma for their valuable suggestions and guidance.

With great pleasure, I express my respect to Prof. Pradeep Mathur (Director, Indian Institute of Technology Indore) for his unending encouragement and providing all the facilities at Indian Institute of Technology Indore.

I am grateful to Dr. Satya S. Bulusu (Head, Discipline of Chemistry, Indian Institute of Technology Indore) for his suggestions and guidance in various aspects. I am also grateful to Dr. Suman Mukhopadhyay, Dr. Tridib K. Sarma, Dr. Anjan Chakraborty, Dr. Sampak Samanta, Dr. Biswarup Pathak, Dr. Sanjay Singh and Dr. Chelvam Venkatesh for their guidance and help during various activities.

I would like to acknowledge all the teachers I learnt from since my childhood, I would not have been here without their guidance, blessing and support.

I extend my profound thanks to my group members, Dr. Bhausaheb, Dr. Prabhat Gautam, Dr. Sheshashena Reddy, Mrs. Rekha, Dr. Thaksen, Yuvraj, Madhurima, Yogajivan, Bijesh, Rama Krishna and Jeevan for their generous cooperation and help to make my work successful.

It has been wonderful to work with many friends and labmates together during my Ph.D., and I would like to record my thanks to Dr. N. Rajendra, Dr. Maruthi Konda, Mr. Ramesh Reddy, Mr. Siva, Dr. Karthik Thirumala, Dr. Sonam and Mr. Anoop.

My heart-felt thanks to my splendid juniors at IIT Indore for their generous co-operation and help.

I am also thankful to all my friends who helped me directly-indirectly during my Ph. D. I am thankful to Ms. Sarita Batra, Mr. Kinney Pandey, Mr. Ghanshyam Bhavsar and Mr. Manish Kushwaha for their technical help and support.

I would like to express my thanks to IIT Indore for infrastructure and Council of Scientific and Industrial Research (CSIR), New Delhi for my Fellowship and all others who helped and supported me directly or indirectly.

I thank the Almighty for giving me the strength and patience to work through all these years.

Finally, I would like to acknowledge the people who mean world to me, my father Appaiah Maragani, mother Rambai Maragani, brothers Krishna Maragani, Sridhar Maragani, Ganesh Maragani, my sister-in-laws and my wife Lavanya Maragani, I don't imagine a life without their love and blessings.

RAMESH MARAGANI

DEDICATED TO

MY TEACHERS, FAMILY AND FRIENDS

- RAMESH MARAGANI

SYNOPSIS

The electron withdrawing thiazole rings of bisthiazole (BTz) are constructing unit of various π -conjugated donor–acceptor (D–A) molecular systems. The electron receiving nature of the thiazole ring is recognized due to the presence of electron-withdrawing nitrogen of the imine (–C=N). BTz is a good acceptor and its donor–acceptor (D–A) derivatives exhibit high fluorescence quantum yield, high photochemical and thermal stability. The photophysical and electrochemical properties of BTz based Donor–Acceptor system is a function of their HOMO–LUMO gap. The BTz based donor-acceptor systems are used in Organic photovoltaics (OPVs), Aggregation induced emission (AIE), Organic field effect transistors (OFETs), Mechanochromism, and Nonlinear optics (NLO).

The HOMO–LUMO gap of D–A, D– π –A, D- π -A- π -D and D-A₁-A-A₁-D systems can be tuned by varying spacer length of π -bridge. The BTz based D–A systems with strong intramolecular charge-transfer and low HOMO–LUMO gap is favorable for dye sensitized solar cells (DSSCs). A variety of donors (triphenylamine, ferrocene, *etc.*) and acceptors (TCNE, cynoacetic acid, malononitrile, *etc.*) have been explored in the design and synthesis of donor–acceptor systems.



Figure 1. Bisthiazole (BTz).

The substitution of the donors and acceptors at 3 and 3'-positions of the BTz perturbs the photonic properties of bisthiazole derivatives significantly. In order to tune the HOMO–LUMO gap of bisthiazole derivatives, the BTz unit was functionalized with various donors, spacers and acceptors in symmetrical manner.

The influence of substitution of various D/A systems on the photophysical and electrochemical properties was studied.

The main objectives of the present study are:

- To synthesize donor-substituted symmetrical BTz of the type D–A, D–π– A, D-A₁-A-A₁-D and D–π–A–π–D and to study the effect of extension of π-conjugation length on the photophysical and electrochemical properties.
- To design and synthesize ferrocenyl-substituted symmetrical BTz by addition of the various π -spacers, linkers and their effect on HOMO–LUMO gap.
- To study the influence of various D/A units on photophysical, thermal and electrochemical properties.

Chapter 1: Introduction

This chapter describes the synthesis and functionalization approaches of BTz derivatives, and their applications in different fields.

Chapter 2: Materials and Experimental Techniques

Chapter 2 summarizes the general experimental methods, characterization techniques and details of instruments used for characterization.

Chapter 3: C₂-Symmetric Ferrocenyl Bisthiazole: Synthesis, Photophysical, Electrochemical and DFT Studies

Chapter 3 describes a series of donor–acceptor ferrocenyl substituted bisthiazole, synthesized by the Pd-catalyzed Suzuki, Heck, and Sonogashira cross-coupling reactions. Their photophysical, electrochemical and computational studies reveal strong donor–acceptor interaction.



Chapter 4: CS-Symmetric Triarylborane Substituted Bisthiazole for Selective Detection of F– and CN– ions

Chapter 4 summarizes the synthesis of triarylborane substituted bisthiazole by using Sonogashira cross-coupling reaction for selective detection of F^- and CN^- ions in the presence of Cl^- , Br^- , Γ^- and NO_2^- anions. The detection limits for F^- and CN^- was found to be 5.7 ×10⁻⁶ M and 2.1×10⁻⁶ M respectively. The time dependent density functional theory (TD-DFT) calculation at 6-31g (d, p)/B3LYP level on the bisthiazole triarylborane was studied for F^- and CN^- ions.



Chapter 5: $(D-\pi-A)_2-\pi$ -D-A Type Ferrocenyl Bisthiazole Linked Triphenylamine Based Molecular Systems for DSSC: Synthesis, Experimental and Theoretical Performance Studies

Chapter 5 describes the design and synthesis of ferrocenyl (donor) bisthiazole linked triphenylamine (donor) based donor- π -acceptor- π -donor-acceptor [(D- π -A)₂- π -D-A] type dyes by using Pd-catalyzed Sonogashira cross-coupling and Knoevenagel condensation reactions. Their photophysical, electrochemical and computational studies reveal strong donor-acceptor interaction. The Dye sensitized solar cells (DSSCs) based on **D1** and **D2** exhibit the power conversion efficiency (PCE) of 6.33% and 5.03% respectively.



Chapter 6: C_s-Symmetric Donor-Acceptor Systems of Bisthiazole: Synthesis, Photophysical, Electrochemical Properties and Computational Studies

Chapter 6 reports the design and synthesis of C_s -Symmetric D- π -A- π -D and D-A₁-A-A₁-D bearing a variety of electron donating and electron withdrawing groups by using Pd-catalyzed Sonogashira cross-coupling and [2+2]cycloaddition-retroelectrocyclization reactions. Their photophysical and electrochemical properties were explored which show strong donor-acceptor interaction. The [2+2] cycloaddition-retroelectrocyclization reaction pathway was studied by theoretical calculations, which reveals that when terminal positions of bisthiazole are substituted by donor groups are favorable for the [2+2] cycloaddition reaction whereas when bisthiazole substituted by electron withdrawing groups are unfavorable for [2+2]cycloadditionretroelectrocyclization reaction.



Chapter 6: Donor-Acceptor Triphenylvinyl and Tetraphenyl Conjugates: Synthesis, Aggregation-induced emission, Aggregation-caused quenching and TD-DFT Studies.

Triphenylvinyl (TPV) substituted bisthiazole **4** and tetraphenylethylene (TPE) substituted triphenylamine oxazole **5** were designed and synthesized by the Pd-catalyzed Suzuki cross-coupling reaction. The TPV **4** shows Aggregation-induced emission (AIE) behavior and TPE **5** shows aggregation-caused quenching (ACQ) effect in THF/water mixture due to the $\pi \rightarrow \pi$ stacking. The thermal stability of the TPV **4** and TPE **5** are reported, in which TPE **5** show better thermal stability as compared to TPV **4**.



Chapter 8: Conclusions and Future Scope.

Chapter 8 summarizes the salient features of the work and its future prospects to develop the new materials for optoelectronic applications.

LIST OF PUBLICATIONS

- Maragani R., Misra R*., Roy M. S., Singh M. K., Sharma G. D*. (2017), (D-π-A)₂-π-D-A Type Ferrocenyl Bisthiazole Linked Triphenylamine Based Molecular Systems for DSSC: Synthesis, Experimental and Theoretical Performance Studies, *Phys. Chem. Chem. Phys.*, 19, 8925-8933 (DOI: 10.1039/c7cp00612h).[†]
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[†]Papers pertaining to the thesis.

CONFERENCE PRESENTATION

 Research workshop and Conference Indian Institute of Technology (IIT), Indore, India - Technischen Universität, Berlin, Germany (1-11-2016 and 4-11-2016). I have given talk in collaboration with Prof. Dr. Holger Butenschön (Leibniz Universität Hannover) on Ferrocene Based Molecular Wires.

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ACRONYMS

D–A	Donor-acceptor	
NLO	Nonlinear Optical	
P^{H}	The negative logarithm of hydronium	
	ion concentration (- $log10[H_3O^+]$)	
SCXRD	Single Crystal X-ray diffraction	
PXRD	Powder X-ray diffraction	
NMR	Nuclear Magnetic Resonance	
PPh ₃	Triphenylphosphin	
DMF	Dimethylformamide	
DCM	Dichloromethane	
TGA	Thermogravimetric Analysis	
Ph	phenyl	
IR	Infrared	
UV-Vis	UV-Visible Spectroscopy	
•••	Represents interaction	
Calcd.	Calculated	
CDCl ₃	Chloroform-d	
ESI-MS	Electrospray Ionization- Mass	
	Spectrometry	
EtOH	Ethanol	
MeOH	Methanol	
THF	Tetrahydrofuran	
TLC	Thin Layer Chromatography	
TEA	Triethylamine	

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
Introduction

1.1. Background

In donor-acceptor systems, the donor groups (D) donates electrons and transports holes, whereas the acceptor groups (A) withdraws electrons and transports electrons. In donor-acceptor materials the electrons comes from the donor to acceptor, during this process of electron transfer, the electrons are excited from HOMO to LUMO energy level which leads to charge separation and it results in the formation of charge-transfer absorption band in UV-vis region. The strength of charge transfer absorption band can be improved by the addition of π -spacers and π -linkers between the donor and acceptor groups (Figure 1.1).



Figure 1.1. Schematic presentation of charge-transfer phenomenon in a donoracceptor system with π -linker.

The tuning of charge transfer band in donor and acceptor systems have been attracted in material science applications such as Organic photovoltaics (OPVs) and Organic field effect transistors (OFETs).¹⁻¹⁰

The π -donors such as fluorene, anthracene, carbazole, triphenylamine, phenothiazine and metallocene (ferrocene) *etc*. are reported as a electron donors as shown in Figure 1.2.¹¹⁻²⁰



Figure 1.2. Different type of donors.

The acceptor group generally consist of electron–withdrawing imine groups (-C=N-) for example benzothiadiazole (BT), quinoxaline (QX), pyridylthiadiazole (PT), bisthiazole (BTz), benzobisthiazole (BBTz), benzotriazole (BTA), Isoindigo (II), *etc.* (Figure 1.3). Based on their electron-withdrawing ability, these acceptor units are often classified into three categories: weak, medium and strong acceptors. Generally, the electron withdrawing capability is decided by the LUMO level of the unit. The lower LUMO energy level correspond to stronger electron-withdrawing groups.²¹⁻²⁹



Figure 1.3. Different type of acceptors.

Accordinding to the molecular orbital (MO) theory the donor groups have more HOMO–LUMO gap as compared to the acceptor. However the donor-acceptor systems show less HOMO–LUMO gap as compared to the donor as well as acceptor units (Figure 1.4).³⁰



Figure 1.4. Effect of molecular orbital couplings of donor and acceptor systems on HOMO–LUMO gap.

1.2. Bisthiazole (BTz)

Bisthiazole (BTz) is a heterocyclic core where two thiazole moieties are covalently connected through carbon atoms (Figure. 1.5.).³¹



Figure 1.5. The molecular structure of bisthiazole

The structure of bisthiazole reveals anti conformation with respect to hetero atoms, which is supported from the single crystal X-ray structure of ferrocenyl substituted bisthiazole derivative as shown in the Figure 1.6.³¹



Figure 1.6. Single crystal X-ray structure of ferrocenyl substituted bisthiazole derivative.

According to IUPAC nomenclature the numbering for the atoms of the two thiazole rings are shown in the Figure 1.7.



Bisthiazole

Figure 1.7. Nomenclature for the bisthiazole (BTz) ring system.

Bisthiazole (BTz) is an electron acceptor moiety. It can be considered as a 12π electron heteroaromatic system. Structural modifications of the bisthiazole compound through 3 and 3' position results in bisthiazole derivatives with several characteristic features as following:

(1) The heterocyclic five-membered ring (C=N-S-N=C) is a good electron acceptor and exhibits high electron affinity.

(2) BTz derivatives exhibit absorption in the UV–region with high molar extinction coefficient.

(3) BTz derivatives show well-ordered crystal structures with intermolecular interactions such as heteroatom contacts and π - π interactions.

(4) BTz based donor-acceptor (D–A) systems exhibit excellent photochemical and thermal stability.

1.2.1. Classification of symmetrical bisthiazole: Four different types of symmetrical bisthiazole have been classified based on the substitution at the 3- and 3'- positions of the bisthiazole system. The substitutions of same donor groups or linker units on both the positions of the bisthiazole core results in symmetrical BTz as shown in Figure 1.8.



Figure 1.8. Different types of symmetrical bisthiazole (BTz) (a) linear symmetrical bisthiazole donor-acceptor system; (b) linear symmetrical bisthiazole donor - π - acceptor system; (c) nonlinear symmetrical bisthiazole donor - π - acceptor system; (d) nonlinear symmetrical bisthiazole donor - π - acceptor system.

1.2.2. Synthesis of bisthiazole: The reaction of 1-bromooctan-2-one with dithiooxamide in ethanol solvent under reflux condition for 24 h followed by workup results dark brown oil which upon column chromatography on SiO₂ using ethyl acetate/hexane (1:8 v/v) as eluent resulted bisthiazole as light-brown oil. The bromination of the resultant bisthiazole with N-bromosuccinimide (NBS) in acetic acid results dibromo bisthiazole in good yields (Scheme 1.1).³²



Scheme 1.1. Synthetic scheme for the preparartion of bisthiazole (BTz) and its bromo derivative.

1.3. Synthesis of other bisthiazole derivatives:

The common synthetic methodology for the synthesis of different type of bisthiazole based derivatives is summarized in the following sections.

1.3.1. 2,6-diphenylbenzo[1,2-d:4,5-d']bis(thiazole):

The widely used procedure for the preparation of benzobisthizole derivatives involves the arrangement of a sulphur atom between the two *para*-amine groups. The reaction of *vicinal* diamine derivatives polyphosphoric acid (PPA) in presence of nitrogen atmosphere is most general method for the synthesis of 2,6-diphenylbenzo[1,2-d:4,5-d']bis(thiazole) (Scheme 1.2).^{33,34}



Scheme 1.2. Synthesis of BTz derivatives via 1,2-diamines.

1.3.2. 2, 5-diphenyl-3a,6a-dihydrothiazolo[5,4-d]thiazole:

The preparation of fused bisthizole derivatives involves the introduction of a thione between the two *ortho*-amine groups (dithiooxamide). The reaction of *vicinal* diamine and respective aldehyde derivatives in presence of *n*-propanol at

reflux for 4 h. This is most general method for the synthesis of 2,5-diphenyl-3a, 6a-dihydrothiazolo[5,4-d]thiazole (Scheme 1.3).^{35,36}



Scheme 1.3. Synthesis of BTz derivatives *via* 1,2-diamines.

1.3.3. Cross-coupling of 5,5'-dibromo-4,4'-dihexyl-2,2'-bithiazole:

The synthesis of 5,5'-dibromo-4,4'-dihexyl-2,2'-bithiazole derivatives has been done by using Pd-catalyzed cross-coupling reaction of the 5,5'-dibromo-4,4'- dihexyl-2,2'-bithiazole unit with the different type of aryl groups.

Suzuki Coupling: The design and synthesis of donor–acceptor 5,5'-dibromo-4,4'dihexyl-2,2'-bithiazole derivatives *via* the Pd-catalyzed Suzuki cross-coupling reaction is one of the most commonly used procedure. This procedure usually involves the reaction of 5,5'-dibromo-4,4'-dihexyl-2,2'-bithiazole and arylboronic acids or esters in the presence of palladium catalysts such as *tetrakis*(triphenylphosphine)palladium(0) [Pd(PPh₃)₄] in the presence of a sodium and potassium carbonates or tetrabutylammoniumbromide as a base. The reaction yields are generally high. Y. Lin *et al.* synthesized donor-substituted BTz derivatives by the reaction of 4,7-dibromo-BTz with arylboronic acids (Scheme 1.4).³⁷



Scheme 1.4. Synthesis of BTz derivatives *via* Suzuki cross-coupling reaction of dibromo- BTZ.

Alternatively the Suzuki cross-coupling reaction have also been carried out with the pinacol esters of BTz in good yields (Scheme 1.5).³⁷



Scheme 1.5. Synthesis of BTz derivatives *via* Suzuki cross-coupling reaction of pinacol esters of BTz.

Stille Coupling: The synthesis of BTz derivatives via the Pd-catalyzed Stille coupling reaction is alternative procedure for the synthesis of donor-acceptor bisthiazole. Curtis et al. has introduced stannyl group at one side of the bisthiazole ring as shown Scheme 1.6. Bisthiazole stannyl compound was treated presence with dibromo thiophene derivative in the of bis(triphenylphosphine)palladium(II) dichloride $[Pd(PPh_3)_2Cl_2],$ triphenyl phosphine ligand. These reactions show reasonable to high yield Scheme 1.6. ³⁸



Scheme 1.6. Synthesis of BTz derivatives via Stille coupling of dibromo- BTz.

Sonogashira Coupling: The Pd-catalyzed Sonogashira cross-coupling is also a significant procedure for the design and synthesis of donor–acceptor π -conjugated BTz. The normal conditions for Sonogashira coupling involves the reaction of the 5,5'-dibromo-4,4'-dihexyl-2,2'-bithiazole and the alkyne derivative with catalytic amounts of *bis*(triphenylphosphine)palladium(II) dichloride [Pd(PPh_3)₂Cl₂], and copper(I) iodide in the presence of an organic base (triethylamine or diisopropylamine). A common example is shown in Scheme 1.7.³⁹



Scheme 1.7. Synthesis of BTz derivative *via* Sonogashira cross-coupling reaction of dibromo- BTz with alkyne moiety.

Heck Coupling: The Heck cross-coupling of 5,5'-dibromo-4,4'-dihexyl-2,2'bithiazole is a less commonly used procedure for the design of donor–acceptor bisthiazoles as compared to the Suzuki, Stille and Sonogashira cross-coupling reactions. Nevertheless it is a significant procedure for incorporation of C=C bond for various optoelectronic applications. This procedure frequently utilizes the reaction of 5,5'-dibromo-4,4'-dihexyl-2,2'-bithiazole with alkenes catalyzed by palladium(II) acetate/tetrabutylammoniumiodide in the presence of a base as shown in Scheme 1.8.⁴⁰



Scheme 1.8. Synthesis of linear shaped BTz derivative via Heck coupling.

Formylation reaction:

The formylation reaction is also a significant procedure for the design and synthesis of donor–acceptor π -conjugated BTz. The normal conditions for formylation reaction involves the solution of 4-(5'-bromo-4,4'-dihexyl-[2,2'-bithiazol]-5-yl)-N,N-diphenylaniline and n-BuLi in THF at -78^oC. After stirring for 1 h, a solution of N-formylmorpholine (N-FMP) in THF was added. After additional stirring for 1 h at -78^oC, the mixture was allowed to warm to room temperature overnight. The final solution was acidified with 1M HCl solution and stirred for 45 min at room temperature. The aqueous phase was extracted with dichloromethane, and the organic layer was dried over magnesium sulfate. After evaporation of the solvent, the final crude product was purified by column chromatography on silica gel (PE/CH₂Cl₂=1:1, ν/ν) to yield an orange solid (Scheme 1.9).⁴¹



Scheme 1.9. Synthesis of BTz formylation derivative.

1.4. Applications of bisthiazole derivatives.

The donor–acceptor bisthiazole derivative based molecular systems have been explored for a extensive diversity of applications. Some of the common applications are described below:

1.4.1. Nonlinear optics (NLO): There has been substantial attention in the improvement of organic nonlinear optical materials. The bisthiazole (BTz) moiety is an constructing block for NLO materials due to its reduction potential. Jiang *et al.* has designed a varity of donor-substituted BTz s reported as a NLO materials (Figure 1.9).⁴²



Figure 1.9. Molecular structures of triphenylamine-substituted BTz derivative.

The π -conjugated donor–acceptor organic materials with large two-photon absorption (TPA) cross-sections are prospective applicant for several applications such as optical limiting, two-photon laser scanning fluorescence imaging, threedimensional optical data storage, and photodynamic therapy.⁴³⁻⁴⁸ The fluorophores with large TPA cross-sections are reported in the literature.⁴⁹⁻⁵² Jiang *et al.* designed and synthesized a different type of triphenylamine substituted BTz derivatives and explored their two-photon absorption properties. The TPA cross-section was significantly high in C₃-symmetric type BTz derivatives as compared to the corresponding one-dimensional sub-units (Figure 1.10).⁵³



Figure 1.10. Molecular structures of two-photon absorbing BTz derivatives.

1.4.3. Dye sensitized solar cells (DSSCs):

O'Regan and Grätzel have explored the dye-sensitized solar cell (DSSC) in $1991.^{54}$ They have reported polypyridyl ruthenium (II) complex adsorbed on a nano particulate TiO₂ surface show good efficiency in DSSC. In DSSC experiment the donor-acceptor materials HOMO-LUMO gap (E_g) is an important factor because the power conversion efficiency depends majorly on this factor. ⁵⁵⁻

Recently Hua *et al.* reported a series of BTz-substituted triphenylamine derivatives for DSSCs and achevied maximum power conversion efficiency

7.51%. The structure of BTz-substituted triphenylamine derivatives are shown in the Figure 1.11.⁶⁰



Figure 1.11. Structures of BTz -substituted triphenylamine for DSSCs.

Similar type of BTz-substitued triphenylamine compounds (Figure 1.12) 61 have been synthesized by Tian *et al.* and achieved power conversion efficiency over 5.73 % .



Figure 1.12. Structures of BTz -substituted triphenylamine for DSSCs.

1.4.4. Bulk heterojunction (BHJ) solar cells:

The conjugated organic dyes and fullerene derivatives are frequently used in bulk heterojunction (BHJ) solar cells.⁶² The strong charge transfer band donor-acceptor systems are useful for making bulk heterojunction (BHJ) solar cell devices. The BHJ solar cell exhibits more resourceful than the dye-sensitized solar cell (DSSC). Friend *et al.* and Heeger *et al.* first time reported bulk heterojunction (BHJ) solar cells in 1995.^{63,64} The molecular systems having low HOMO-LUMO gap are commonly used as the donor materials with fullerene derivatives as acceptors for BHJ solar cells.

A variety of low band gap BTz based donor-acceptor molecules have been designed and synthesized due to its strong electron affinity. Zhan *et al.* reported a novel donor–acceptor–donor type donor molecule 4,4'-((4,4'-dihexyl-[2,2'-bithiazole]-5,5'-diyl)bis(thiophene-5,2-diyl)) bis (N,N-diphenylaniline) based on the electron-accepting BTz unit as shown in Figure 1.13, which shows power conversion efficiency (PCE) up to 2.61%.⁶⁵



Figure 1.13. Structures of BTz -substituted triphenylamine based small molecule for BHJ solar cell.

Yang *et al.* utilized 8-(trideca-1,3,5,8,10,12-hexayn-7-yl)benzo[1,2-b:3,4b':6,5-b"] (BTT) unit on the BTz unit to synthesize low HOMO–LUMO gap polymer. The BHJ solar cells based on the BTT-derivative showed a PCE of 5.06 % (Figure 1.14).⁶⁶



Figure 1.14. Structures of the BTz -substituted triphenylamine based small molecule for BHJ solar cell.

Seki *et al.* has synthesized benzothiadiazole (BTD) based BTz polymer derivative having low HOMO–LUMO (1.74 eV) gap, which show poor PCE of 0.15 % in BHJ solar cells (Figure 1.15).⁶⁷



Figure 1.15. Structures of BTD -substituted BTz based polymerl molecule for (BHJ) solar cell.

Lin *et al.* has synthesized cyclopentadithiophene (CPDT) based BTz polymer derivative having low HOMO–LUMO (1.74 eV) gap, which shows PCE of 2.79 % in BHJ solar cells (Figure 1.16).⁶⁸



Figure 1.16. Structures of BTz -substituted CPDT based polymerl molecule for (BHJ) solar cell.

1.4.5. Organic field-effect transistors (OFETs).

Organic field-effect transistors (OFETs) have been considered one of the emerging field of interest in optoelectronic applications. ⁶⁹⁻⁷³ The Koezuka group reported for the first time the use of organic materials in the Organic field-effect transistor (OFET) devices.⁷⁴ Recently Zhan *et al.* reported benzo[1,2-b:4,5-b0]dithiophene (BDT) substituted bisthiazole unit in OFET devices and they reported a good charge carrier mobility of 0.194 cm² V⁻¹S⁻¹ for this polymer as shown Figure 1.17.⁷⁵



Figure 1.17. Structures of BTz -substituted CPDT based polymerl molecule for OFETs.

Li *et al.* also reported a thiophene based bisthiazole compound (Figure 1.18) 76 which shows good charge carrier mobility up to 0.0077 cm² V⁻¹S⁻¹.



Figure 1.18. Structures of BTz -substituted CPDT based polymer molecule for OFETs.

1.4.6. Sensing: Fluorescent sensing of metal ions in solution as well in biological medium are of great concern because of their biological relevance.^{77,78} Recent literature reveals the use of BTz derivatives as a fluorescent sensor of heavy metal ions.^{79,80} Geng *et al.* reported the use of 4,4'-dibutyl-5,5'-di(pyridin-4-yl)-2,2'-bithiazole as a fluorescent sensor for iron (III) ion. The molecular structure of 4,4'-dibutyl-5,5'-di(pyridin-4-yl)-2,2'-bithiazole and its iron complex is shown in Figure 1.19.⁸¹



Figure 1.19. Structures of (a) 4,4'-dibutyl-5,5'-di(pyridin-4-yl)-2,2'-bithiazole and (b) its iron complex.

1.5. Organization of thesis

Chapter 1: This chapter gives an outline of the special features, classification and various synthetic strategies for the design of BTz and its derivatives, and their applications in diverse fields.

Chapter 2: This chapter summarizes the instrumentation and general methods used for the present study.

Chapter 3: This chapter describes a series of ferrocene-substituted symmetrical BTz and extended the conjugation length between the donor and the acceptor to tune the photonic properties.

Chapter 4: This chapter reports triarylborane functionalised bisthiazole for the selective detection of F^- and CN^- anions.

Chapter 5: This chapter describes the synthesis of a series of triphenylamine linked ferrocenyl bisthiazole based molecules of the type $(D-\pi-A)_2-\pi$ -D-A and their applications as a materials in dye sensitized solar cells (DSSCs).

Chapter 6: Chapter 6 reports the design and synthesis of C_s -symmetric D- π -A- π -D and D-A₁-A-A₁-D bearing a variety of electron donating and electron withdrawing groups by using Pd-catalyzed Sonogshira cross-coupling and [2+2] cycloaddition-*retroelectrocyclization* reactions.

Chapter 7: The chapter 7 describes the design and synthesis of triphenylvinyl (TPV) substituted bisthiazole **4** and triphenylvinyl (TPV) substituted triphenylamine oxazole **5** by using Pd-catalyzed Suzuki cross-coupling reaction. Their photophysical, aggregation induced emission (AIE), aggregation-caused

quenching (ACQ) properties and computational studies were thoroughly explored in this chapter.

Chapter 8: This chapter summarizes the noticeable features of the work and addressed the future projections.

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2.1. Introduction

This chapter describes the materials, general synthetic procedures, characterization techniques and the instrumentation employed in this thesis.

2.2. Chemicals for synthesis

The common solvents used for syntheses were purified according to established procedures.^[1] 1-bromooctan-2-one, dithiooxamide, CuI, Pd(PPh₃)₄, PdCl₂(PPh₃)₂, ferrocene, tetrabutylammonium hexafluorophosphate (TBAF₆), 4-3-ethynyleniline, ethynyl ferrocene, triphenylamine, ethynylaniline, and cyanoacetic acid. malononitrile, tetrabutylammonium fluoride. tetrabutylammonium chloride, tetrabutylammonium iodide, tetrabutylammonium bromide, tetrabutylammonium cyanide, tetrabutylammonium nitrate, (2bromoethene-1,1,2-triyl)tribenzene, POCl₃, K₂CO₃ were procured from Aldrich chemicals USA. Silica gel (100-200 mesh and 230-400 mesh) were purchased from Rankem chemicals, India. TLC pre-coated silica gel plates (Kieselgel 60F254, Merck) were obtained from Merck, India. Dry solvents dichloromethane, 1,2-dichloroethane, chloroform, Dimethylformamide, tetrahydrofuran (THF), triethylamine and methanol were obtained from spectrochem and S. D. Fine chem. Ltd. All the oxygen or moisture sensitive reactions were performed under nitrogen/argon atmosphere using standard schlenk method. The solvents and reagents were used as received unless otherwise indicated. Photophysical and electrochemical studies were performed with 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

¹H NMR (400 MHz), and ¹³C NMR (100 MHz) spectra were recorded on the Bruker Avance (III) 400 MHz, using CDCl₃ and acetone-d₆ as solvent. Chemical shifts in ¹H, and ¹³C NMR spectra were reported in parts per million (ppm). In ¹H NMR chemical shifts are reported relative to the residual solvent peak (CDCl₃, 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. ¹³C NMR chemical shifts are reported relative to the solvent residual peak (CDCl₃, 77.36 ppm).

2.3.3. UV-Vis spectroscopy

UV-Vis absorption spectra were recorded using a Varian Cary100 Bio UV-Vis and Perkin Elmer 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 (ϕ_F)

The fluorescence quantum yields (ϕ_F) of compounds **1-4** were calculated by the steady-state comparative method using following equation,

 $\oint_{F} = \oint_{st} \times Su/S_{st} \times A_{st} / A_{u} \times n_{2}D_{u}/n_{2} \text{ Dst} \dots (Eq. 1)$

Where ϕ_F is the emission quantum yield of the sample, ϕ_{st} is the emission quantum yield of the standard, Ast and Au 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) and Differential Pulse Voltamograms (DPVs) were recorded on CHI620D electrochemical analyzer using Glassy carbon as working electrode, Pt wire as the counter electrode, and Saturated Calomel Electrode (SCE) as the reference electrode. The scan rate was 100 mVs⁻¹. A solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) in CH₂Cl₂ (0.1 M) was employed as the supporting electrolyte.

2.5. Single crystal X-ray diffraction studies.

Single crystal X-ray diffraction studies were performed on SUPER NOVA diffractometer. The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on $F^{2.1}$. The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions, and refined with isotropic temperature factors, generally 1.2Ueq of their parent atoms. The CCDC numbers contain the respective supplementary crystallographic data. These data can be obtained free of charge www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge via Crystallographic 42 Data Centre, 12 union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

2.6. Powder X-ray diffraction (PXRD) studies.

The XRD measurements were performed using Rigaku SmartLab, Automated Multipurpose X-ray diffractometer. The X-rays were produced using a sealed tube and the wavelength of the X-ray was 0.154 nm (Cu K-alpha).

2.7. Computational calculations

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

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C₂-Symmetric Ferrocenyl Bisthiazoles: Synthesis, Photophysical, Electro chemical and DFT Studies

3.1. Introduction

The design, synthesis and applications of small molecule based donoracceptor systems are monotonically increasing due to their importance in the field of Organic photovoltaics (OPVs), Organic field effect transistors (OFETs), Aggregation induced emission (AIE), Mechanochromism and Nonlinear optics (NLO).¹⁻⁹ The photonic and electronic properties of the donor-acceptor systems can be tuned by altering the strength of donor, acceptor or spacer.¹⁰ Our group has explored variety of ferrocneyl functionalized donor-acceptor systems for the Nonlinear optics, and Organic photovoltaics.^{11, 12}

The electron withdrawing thiazole ring is an important building block in a variety of π -conjugated D-A molecular systems.¹³ The electron accepting nature of the thiazole is attributed to the presence of electron-withdrawing nitrogen of the imine (-C=N).¹⁴ Very recently we have reported ferrocenyl functionalized thiazole and their 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) derivatives, which exhibits strong intramolecular charge transfer (ICT).¹⁵ The bisthiazole unit with two thiazole rings connected together is a stronger acceptor unit and exhibits improved charge transfer and lowers the HOMO–LUMO gap.¹⁶ In this chapter we reported the ferrocenyl functionalized donor-acceptor systems with different

spacer length on both ends of the bisthiazole. We also describe the synthesis of C_2 -symmetric ferrocenyl substituted bisthiazoles containing alkyl side chains, which would improve the solubility. The effect of systematic variation of the conjugation length on the photophysical, electrochemical and thermal properties and the HOMO-LUMO gap was explored.

3.2. Results and discussion

The ferrocenyl substituted bisthiazoles (Fc-bisthiazoles) **3–8** were synthesized by the Suzuki, Heck and Sonogashira cross-coupling reactions of 5,5'-dibromo-4,4'-dibutyl-2,2'-bisthiazole (**2**) with ferrocenyl boronic acid, vinyl ferrocenyl and the ferrocenyl substituted ethyne derivatives respectively. The starting material 5,5'-dibromo-4,4'-dibutyl-2,2'-bisthiazole (**2**) was synthesized by reported procedure (Scheme 3.1).¹⁷



Scheme 3.1. Synthesis of bisthiazole (a).

The 5,5'-dibromo-4,4'-dibutyl-2,2'- bisthiazole (2) was reacted with ferrocenyl boronic acid (c) under the Suzuki coupling reaction condition which resulted 59

compound **3** in 55% yield. The Heck coupling reaction of bisthiazole (**2**) with vinyl ferrocenyl (**d**) in the presence of $Pd(OAc)_2$, and tetrabutylammonium iodide (NBu₄I) resulted in *trans* ferrocenyl substituted bisthiazole **4** in 62% yield. The Sonogashira cross–coupling reaction of bisthiazole (**2**) with ethynylferrocene (**e**), 4–ferrocenylphenylacetylene (**f**), and 3-ferrocenylphenylacetylene (**g**) resulted in **5**, **6**, and **7** in 71%, 65%, and 52% yields respectively. The Pd–catalyzed Sonogashira cross-coupling of 4-ethynyl-4'-(ferrocenyl)-biphenyl (**h**) with bisthiazole (**2**) resulted compound **8** in 37% yield (Scheme 3.2). All the compounds were well characterized by ¹H, ¹³C–NMR, and HRMS techniques. The compounds **3** and **5** were also characterized by the single crystal X-ray technique.


Scheme 3.2. Synthesis of ferrocenyl substituted bisthiazoles 3–8.

3.3. Thermal properties

The thermal properties of the ferrocenyl substituted bisthiazoles 2–8 were explored using thermogravimetric analysis (TGA) at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere (Figure 3.1). The decomposition temperature for 10% weight loss in the ferrocenyl bisthiazoles 3–8 was above 250 °C, whereas the bisthiazole 2 show 10% weight loss at 230 °C. The thermal stability of the ferrocenyl bisthiazoles follows the order 8 > 4 > 6 > 7 > 5 > 3 > 2. The ferrocenyl bisthiazole 8 show more stable as compared to the other compounds.



Figure 3.1. TGA plots of ferrocene substituted bisthiazole 2–8.

3.4. Photophysical properties

The electronic absorption spectra of the ferrocenyl substituted bisthiazoles 2–8 were recorded in dichloromethane at room temperature, and the photophysical data are listed in Table 3.1. The Fc-bisthiazoles 3–8 show strong absorption band between 353–423 nm corresponding to $\pi \rightarrow \pi^*$ transition. The Fc-bisthiazole 4 exhibit significant red shift as compared to the Fc-bisthiazoles 3 and 5–8. The Fc-

bisthiazoles 3, 4 and 5 exhibits metal to ligand charge transfer (MLCT, ferrocene \rightarrow bisthiazole) band between 490–524 nm.¹⁸ The Fc-bisthiazole 4 shows strong intramolecular charge transfer as shown in Figure 3.2.¹⁸ The red shift in the absorption maxima for $\pi \rightarrow \pi^*$ absorption band follows the order 4 > 8 > 7 > 6 > 5 > 3 > 2.



Figure 3.2. Normalized electronic absorption spectra of the ferrocenyl substituted bisthiazole conjugates (a) **2–5** and (b) **6-8** in dichloromethane.

3.5. Electrochemical propetries.

The electrochemical behavior of the ferrocene substituted bisthiazoles **3–8** were investigated by the cyclic voltammetric analysis in dry dichloromethane solution at room temperature using tetrabutylammoniumhexafluorophosphate (TBAPF₆) as a supporting electrolyte. The electrochemical data are listed in Table 3.1 and the representative cyclic voltammogram is shown in Figure 3.3. All potentials were corrected to be referenced against Fc/Fc⁺, as required by IUPAC.¹⁹⁻²¹ The cyclic voltammograms of the ferrocenyl substituted bisthiazoles **3–8** show reversible oxidation wave of ferrocene/ferrocenium.¹⁶ The ferrocenyl group in the compounds **3–8** show higher oxidation potential as compared to the free ferrocene. The Fc-bisthiazoles **3–8** shows one irreversible reduction wave corresponding to the bisthiazole acceptor. The oxidation potential of the ferrocenyl moiety in the ferrocenyl substituted bisthiazoles follows the order **4** > **5** > **3** > **8** > **6** > **7**. The trend exhibit that the ferrocene substituted bisthiazole with



vinyl linkage exhibits stronger electronic communication as compared to other derivatives.

Figure 3.3. The Cyclic voltammograms of the Fc-bisthiazoles 3-8 at 0.01 M concentration in 0.1 M Bu_4NPF_6 in dichloromethane recorded at 100 mVs⁻¹ scan speed.

Compounds	$\lambda_{max}[nm]$	Eoxid	E _{red}	T_d
	$(\varepsilon[Lmol-cm^{-1}])^{a}$	(V)	(V)	
2	353(65070)	-	-	225
3	372 (70300) 490	0.11 ^b	-1.37 ^c	293
4	425 (72355) 524	0.18 ^b	-1.36 ^c	400
5	398 (76800) 494	0.16 ^b	-1.35 ^c	310
6	417 (82025)	0.07 ^b	-1.36 ^c	315
7	407 (78648)	0.06 ^b	-1.33 ^c	344
8	422 (94357)	0.10 ^b	1.39 °	459
Ferrocene	-	0.00	-	-

Table 3.1. Photophysical, electrochemical, and thermal properties of the ferrocenyl substituted bisthiazole conjugates **2–8**.

^aMeasured in dichloromethane at 4×10^{-6} M concentration. ^b Recorded by cyclic voltammetry, in 0.1 M solution of Bu₄NPF₆ in DCM at 100 mV s⁻¹ scan rate, vs SCE Electrode.

3.6. Time dependent density functional (TD-DFT) studies:

In order to understand the photophysical and electrochemical properties of the ferrocenyl substituted bisthiazoles, the time dependent density functional (TD-DFT) calculation was performed on Fc-bisthiazoles **3**, **4** and **5**. The quantum chemical calculations were performed using the Gaussian 09 program.²² The structures of **3**, **4**, and **5** were optimized using B3LYP. The solvent calculations were carried out in the dichloromethane (DCM) using the polarized continuum model (CPCM) of Gaussian 09 software. The 6-31G** basis set for C, N, H and LANL2DZ for Fe was used for all the calculations.^{22, 23}

The TDDFT predicted vertical excitation energies for Fc-bisthiazoles **3–5** are shown in Figure 3.4 along with individual experimental UV-vis spectra. The major intense transitions in the Fc-bisthiazoles **3–5** are π - π * in nature. The strong absorption band calculated at B3LYP level are 415, 395 and 397 nm for **3**, **4** and **5** respectively. The experimental values for these transition are 372, 398, 425 nm for **3**, **4** and **5** respectively, which show good agreement with the experimental values.



Figure 3.4. The comparison of experimental and calculated (TD-DFT at B3LYP level) absorption spectrum of Fc-bisthiazole **3**, **4** and **5** in DCM solution.

The predicted vertical transitions and oscillator strengths in Fc-bisthiazoles 3–5 are listed in Table 3.2. In Fc-bisthiazole 3 the transition is dominated by a HOMO \rightarrow LUMO transition 75% and oscillator strength is 0.647. In Fc-bisthiazole 4 and 5, the HOMO-4 \rightarrow LUMO transition contribute to the lowest excited state by 99%, which belongs to π - π * transition. The Fc-bisthiazole 4 show one more major contribution (95%) between HOMO-2 \rightarrow LUMO, which corresponding to the intramolecular charge transfer (ICT) transition at 433 nm as shown in Figure 3.5.



Figure 3.5. The major transitions in Fc-bisthiazole 4.

Table 3.2. Computed vertical transition energies and their Oscillator strengths (f) and major contributions for the Fc-bisthiazoles **3**, **4** and **5**

Fc-bisthiazoles	TD-DFT/ B3LYP (DCM)			
	λ _{max}	f	Major contribution (%)	
3	415 nm	0.647	HOMO→LUMO (75%)	
4	397 nm	1.1693	HOMO−4→LUMO (99%)	
	433 nm	0.1895	HOMO−2→LUMO (95%)	
5	395 nm	1.2172	HOMO−4→LUMO (99%)	

The Figure 3.6 shows the electron density distribution of the HOMO and LUMO of the Fc-bisthiazole **3**, **4** and **5** obtained using DFT/B3LYP method. The HOMOs in the Fc-bisthiazoles **3** and **5** are delocalized over the ferrocenyl and thiazole

groups, whereas the LUMOs are located on the thiazole moiety. The Fcbisthiazole **4** show HOMO delocalized over the ferrocenyl group only while the LUMO are located on the thiazole groups. Thus, the electron densities transfer in Fc-bisthiazole **4** from ferrocenyl group (HOMO) to thiazole (LUMO) group, which indicates strong charge transfer from HOMO to LUMO as compared to the Fc-bisthiazoles **3** and **5**. The HOMO-LUMO gap is lower in compound **4** as compared to the compounds **3** and **5** due to the incorporation of the vinyl group.



Figure 3.6. The energy level diagram of the frontier molecular orbitals of the Fcbisthiazoles **3**, **4** and **5** calculated using B3LYP level of DFT theory.

3.7. Single crystal X-ray diffraction studies



Figure 3.7. (a) Single crystal X-ray structure of the Fc-bisthiazoles 3 and 5.

The single crystal of Fc-bisthiazoles **3** and **5** was obtained via slow evaporation of dichloromethane solution at room temperature, which crystallizes into the centrosymmetric triclinic space group P^{-1} (Figure 3.7). The single crystal X-ray structures of Fc-bisthiazoles **3** and **5** shows Skew-eclipsed conformations as shown in Figure 3.8.



Figure 3.8. Single crystal X-ray structures Skew-eclipsed conformations through b-axis (a) Fc-bisthiazole **3** and (b) Fc-bisthiazole **5**.

The crystal packing diagram of **5** reveals intermolecular N···H interactions between the two adjacent molecules, which are interconnected via thiazole ring to hydrogen of the hexyl chain. The C–H··· π interaction between hydrogen (H1) and alkyne carbon (C6) (C–H··· π , 2.885 Å) leads to the formation of 2-D network (Figure 3.9)



Figure 3.9. Packing diagram of Fc-bisthiazole **5**, forming 2-D network through *b*-axis. The secondary interactions are shown by the dashed lines.

3.8. Experimental section

All reagents were obtained from commercial sources, and used as received unless otherwise stated. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker Avance (III) 400 MHz instrument by using CDCl₃ as solvent. ¹H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl₃, 7.26 ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), and m (multiplet), and the coupling constants, J, are given in Hz. ¹³C NMR chemical shifts are reported relative to the solvent residual peak (CDCl₃, 77.36ppm) and Cp= cyclopentadienyl ring protons. Thermogravimetric analyses were performed on the Mettler Toledo Thermal Analysis system. UV-visible absorption spectra were recorded on a Cary-100 Bio UV-visible spectrophotometer. Cyclic voltamograms (CVs) were recorded on a CHI620D electrochemical analyzer using glassy carbon as the working electrode, Pt wire as the counter electrode, and the saturated calomel electrode (SCE) as the reference electrode. The scan rate was 100 mV s-1. A solution of tetrabutylammonium hexafluorophosphate (TBAPF_6) in CH₂Cl₂ (0.1 M) was employed as the supporting electrolyte. DCM was freshly distilled from CaH_2 prior to use. All potentials were experimentally

referenced against the saturated calomel electrode couple but were then manipulated to be referenced against Fc/Fc+ as recommended by IUPAC. Under our conditions, the Fc/Fc+ couple exhibited $E^{\circ} = 0.38$ V versus SCE. HRMS was recorded on a Bruker-Daltonics micrOTOF-Q II mass spectrometer. The single crystal X-ray structure of the Fc-bisthiazoles **3** and **5** CCDC numbers are 1441410 and 1441409.

X-ray crystallography. Single crystal X-ray structural studies of **3** and **5** were performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 293(2) K using graphite-monochromoated Cu K α radiation ($\lambda_{\alpha} = 1.54184$ Å). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on F^{2} .¹

General procedure for the preparation of Fc-bisthiazoles 3-8

Synthesis of Fc-bisthiazoles 3

In the presence of argon atmosphere a solution of bisthiazole **2** (0.1 g, 0.2 mmol) and ferrocene boronic acid (0.140 g, 0.44 mmol), Pd(PPh₃)₄ (0.011 g, 0.01 mmol) and CS₂CO₃ (0.098 g, 0.3 mmol) were dissolved in the mixture of and THF (8 ml), and DMF (2 ml), and stirred for 24 h at 160 °C, after completion of the reaction, the reaction mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography on silica gel, using hexane/DCM (90:10) to get **3** as a red solid (0.08 g, 55%); ¹H NMR (400 MHz, CDCl3): $\delta = 4.57$ (s, 4H), 4.37 (s, 4H), 4.19 (m, 7H), 2.84 (t, 4H), 1.78 (t, 4H), 1.42 (m, 12H), 0.91 (m, 6H), ppm; ¹³C NMR (100 MHz, CDCl3): $\delta = 157.20$, 153.67, 105.84, 70.12, 69.33, 69.24, 31.73, 30.22, 29.25, 28.88, 22.65, 14.15 ppm; HRMS (ESI-TOF): m/z calculated for C₃₈H₄₄Fe₂N₂S₂ 704.1641 [M+] found 704.1642.

Synthesis of Fc-bisthiazoles 4

In the presence of argon atmosphere a solution of bisthiazole **2** (0.1 g, 0.2 mmol) and vinyl ferrocene (0.094 g, 0.44 mmol), Pd(OAc)₂ (0.02 g, 0.08 mmol), K₂CO₃ (0.112 g, 0.8 mmol) and tetrabutylammonium iodide (0.075 g, 0.2 mmol) were dissolved in DMF (5 ml), and stirred for 24 h at 100 °C, after completion of the reaction, the reaction mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography on silica gel, using hexane/DCM (85:15) to get **4** as a red solid (0.095 g, 62%); ¹H NMR (400 MHz, CDCl3): $\delta = 6.78$ (q, 4H), 4.47 (s, 4H), 4.34 (s, 4H), 4.16 (m, 8H), 2.82 (t, 4H), 1.77 (q, 4H), 1.39 (m, 12H), 0.92 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl3): $\delta = 154.53$, 133.75, 130.67, 115.44, 82.66, 69.53, 69.37, 66.99, 31.71, 29.74, 29.61, 29.04, 22.65, 14.14 ppm; HRMS (ESI-TOF): m/z calculated for C₄₂H₄₈Fe₂N₂S₂ 756.1984 [M+] found 756.1954.

Synthesis of Fc-bisthiazoles 5

In the presence of argon atmosphere a solution of bisthiazole **2** (0.1 g, 0.2 mmol) and the ethynyl ferrocene (0.093, 0.44 mmol) in dry THF (20ml), added triethylamine (5 ml), Pd(PPh₃)₄ (0.013 g, 0.01 mmol), stirred for 16 h at 100 °C, after completion of the reaction, the reaction mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography on silica, using hexane/ DCM (85:15) to get **5** as a red solid (0.110 g, 71 %); ¹H NMR (400 MHz, CDCl3): δ = 4.55 (d, 4H), 4.32 (m, 12H), 2.92 (t, 4H), 1.84 (q, 4H), 1.41 (m, 12H), 0.93 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl3): δ = 162.25, 158.15, 128.61, 116.28, 98.53, 71.59, 70.12, 69.36, 31.65, 30.52, 29.14, 29.01, 22.67, 14.18 ppm; HRMS (ESI-TOF): m/z calculated for C₄₂H₄₄Fe₂N₂S₂ 753.1706 [M+H] found 753.1719.

Synthesis of Fc-bisthiazoles 6-8

In the presence of argon atmosphere a solution of bisthiazole **2** (0.1 g, 0.2 mmol) and the corresponding ethynyl ferrocene (0.44 mmol) in dry THF (20ml), added triethylamine (5 ml), $Pd(dba)_2$ (0.018 g, 0.03 mmol), and $AsPh_3$ (0.009 g, 0.03 mmol) stirred for 24 h at 80 °C, after completion of the reaction, the reaction

mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography on silica.

Fc-bisthiazole 6: compound eluted using hexane/ DCM (80:20) to get **6** as a yellow solid (0. 120 g, 65 %). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.50 (q, 8H), 4.70 (s, 4H), 4.39 (s, 4H), 4.06 (m, 8H), 2.97 (t, 4H), 1.86 (q, 4H), 1.46 (m, 12H), 0.93 (m, 6H) ppm. ¹³C NMR (CDCl₃, 100 MHz, ppm): 162.87, 158.72, 140.74, 131.47, 125.91, 83.97, 80.01, 69. 77, 69.53, 66. 59, 31.62, 29.71, 29.12, 28.93, 22.64, 14.14 ppm. HRMS (ESI-TOF): m/z calculated for $C_{54}H_{52}Fe_2N_2S_2$ 904.2268 [M+] found 904.2288.

Fc-bisthiazole 7: compound eluted using hexane/ DCM (80:20) to get **7** as a yellow solid (0. 096 g, 52 %). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.62 (s, 2H), 7.51 (d, J = 8 Hz, 2H), 7.39 (t, 2H), 7.33 (t, 2H), 4.69 (s, 5H), 4.37 (s, 5H), 4.08 (m, 8H), 2.99 (t, 4H), 1.88 (q, 4H), 1.47 (m, 12H), 0.92 (m, 6H) ppm. ¹³C NMR (CDCl₃, 100 MHz, ppm): 163.17, 158.89, 140.05, 135.17, 128.90, 128.55, 122.56, 115.66, 99.13, 84.12, 79.15, 69.70, 69.26, 66.56, 31.62, 30.52, 29.12, 28.94, 22.65, 14.13 ppm. HRMS (ESI-TOF): m/z calculated for C₅₄H₅₂Fe₂N₂S₂ 904.2268 [M+] found 904.2289.

Fc-bisthiazole 8: compound eluted using DCM to get **8** as a red solid (0. 085 g, 37 %). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.66 (q, 16H), 4.54 (s, 5H), 4.27 (m, 13H), 2.98 (t, 4H), 1.85 (q, 4H), 1.44 (m, 12H), 0.93 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz, ppm): 163.24, 158.92, 131.92, 126.96, 126.87, 80.90, 71.48, 70.03, 68.96, 31.62, 30.52, 29.15, 28.93, 22.65, 14.17 ppm. HRMS (ESI-TOF): m/z calculated for C₇₀H₆₀Fe₂N₂S₂ 1104.2896 [M+] found 1104.3015.

3.9. Conclusions

In summary, we have described the synthesis of ferrocenyl functionalized bisthiazole systems. Their photonic, electronic, and thermal properties can be tuned by varying the spacer length. The Fc-bisthiazole **4** shows good electronic communication between the ferrocenyl groups to bisthiazole acceptor as compared to others. These results show the design of new materials with varying

spacers for various optoelectronic applications. The optical and electrochemical properties of Fc bisthiazoles were explained from the TD-DFT calculations. The optical limiting properties of these materials are currently ongoing in our laboratory.

3.10. References

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 $C_{2h}\mbox{-}Symmetric Triarylborane Substituted Bisthiazole for Selective Detection of <math display="inline">F^-$ and $CN^-\mbox{-}ions$

4.1. Introduction

In recent years considerable attention has been paid in the design and synthesis of anion probes due to their application in wide range of chemical, environmental, industrial and biological processes.¹ The fluoride ion with highest electron charge density is primarily used in dental care and the treatment of osteoporosis.^{2,3} However, excessive amounts of fluoride ions in human body result in dental and skeletal injuries, bone diseases, lesions of the thyroid, liver and other organs.⁴ On the other hand cyanide ion is widely used in synthetic fertilizers, dyes and textiles, petrochemical elution. pesticides. automobiles. pharmaceuticals and electroplating.⁵ Therefore there is a need of sensor which can detect these anions. The literature reveals that a variety of triarylborane based molecular systems has been explored in organic electronics.⁶ The triarylborane containing molecular systems have empty p_{π} -orbital on the boron centre which can effectively communicate with the neighbouring π -electron system.⁷ This makes triarylborane derivatives a potential candidate for optoelectronics applications.⁸⁻²⁰ The triarylborane molecular systems exhibit high Lewis acidity and steric hindrance due to the bulky mesityl groups. The acidity of the triarylborane moiety can be tuned by substituting the electron donating and electron withdrawing groups.²¹ The electron-withdrawing group conjugated with the triarylborane increases the Lewis acidity of the triarylborane. Our research group is involved in the design and synthesis of anion sensors based on triarylborane containing molecular systems. Recently we have reported F and CN ion sensing behaviour of triarylborane functionalised naphthalimide, pyrazabole, BODIPY and porphyrin.²² In this chapter we reported triarylborane functionalised bisthiazole for sensing of anions. The bisthiazole is a strong acceptor and have been explored in Organic

photovoltaics (OPVs), dye sensitised solar cells (DSSC).²⁴ Bisthiazole is a strong acceptor drags electron density from triarylborane unit and increases its Lewis acidity.

4.2. Results and discussion

The triarylborane substituted bisthiazole **1** was synthesized by the Pd–catalysed Sonogashira cross–coupling reaction of bisthiazole as shown in Scheme 1. The starting material 5, 5'-dibromo-4, 4'-dihexyl-[2,2']bithiazolyl (d) and (4–ethynyl phenyl)–dimesitylborane (e) was synthesized by the reported procedures.^{23, 24}

The triarylborane substituted bisthiazole **1** was synthesized by the Sonogashira cross–coupling reaction of bisthiazole d with (4–ethynylphenyl)dimesitylborane e using the Pd(PPh₃)₄ as a catalyst in tetrahydrofuran (THF) solvent, triethylamine as a base at 100 °C for 24h, which resulted the triarylborane substituted bisthiazole 1 in 74% yield (Scheme 4.1). The triarylborane substituted bisthiazole 1 was characterised by ¹H NMR, ¹³C NMR and HRMS techniques. In the ¹H NMR spectra of triarylborane substituted bisthiazole **1**, the aromatic protons of triarylborane exhibit one doublet between 7.49 ppm and 7.54 ppm and one singlet at 6.84 ppm.



Scheme 4.1. Synthesis of triarylborane substituted bisthiazole dyad 1.

4.3. Photophysical properties



Figure 4.1. (a) Normalized electronic absorption and (b) emission spectra (λ_{ex} 416 nm) of triarylborane substituted bisthiazole **1** (2.1×10⁻⁵ M) in THF solvent.

The electronic absorption and emission spectra of **1** was recorded in THF. The triarylborane substituted bisthiazole **1** show red shifted absorption band at 416 nm compared to the bisthiazole intermediate **d** (353 nm) which can be attributed to the π - π * electronic transition. The triarylborane substituted bisthiazole **1** show emission maximum at 474 nm and 503 nm and the quantum yield of 0.26 (Figure 4.1).

Anion binding studies: The anion sensing ability of the triarylborane substituted bisthiazole 1 was investigated by the absorption and emission studies, using various anions (F^- , CI^- , Br^- , Γ , NO_2^- and CN^-). The anions were used in their tetrabutylammonium salts in THF solvent. The absorption and emission studies show no significant change in the presence of CI^- , Br^- , I^- and NO_2^- anions (Figure 4.2), while F^- and CN^- exhibit profound effect.



Figure 4.2. Effect of anions on the absorption spectrum of **1** $(2.1 \times 10^{-5} \text{ M})$ in THF solvent.

Upon addition of fluoride ion the intensity of absorption band at 416 nm gradually decreased and shifted to 429 nm (Figure 4.3). One isobestic point was observed at 446 nm. The bisthiazole triarylborane dyad **1** exhibits fluorescence at 474 nm and 503 nm upon excitation at 410 nm in THF solvent. The emission studies show no significant change in the presence of Cl⁻, Br⁻, I⁻ and NO₂⁻ anions, whereas F⁻ and CN⁻ show significant effect (Figure 4.3).



(a) (b) **Figure 4.3.** The bisthiazole triarylborane dyad **1** (a) Effect of anions on the fluorescence spectrum of **1** ((2.1×10^{-5} M)) (λ_{ex} 473 nm) (b) UV light in the presence of different anions in THF solvent.

Upon addition of fluoride ion to **1**, its emission intensities at 474 nm and 503 nm gradually decreased and become a broad emission centred at 511 nm. The addition of F^- ion results in red shifted in emission at 511 nm and fluorescence was quenched by 2.3 folds (Figure 4.4).



Figure 4.4. (a) Absorption and (b) fluorescence titration spectra of triarylborane substituted bisthiazole 1 ($2.1 \times 10-5$ M) with TBAF in THF solvent.

The effect of other anions in the presence F^- sensing there is no spectral change as shown in Figure 4.5.





Fig ure**4.5.** Effect of other anions in the presence 1 + F in THF solvent.

After addition of cyanide ion, there was a gradual decrease in the intensity of the absorption band at 416 nm and a new band at 510 nm was developed (Figure 4.6 (a)). One isosbestic point was observed at 453 nm. Upon addition of cyanide ion to 1, its emission intensities at 474 nm and 503 nm gradually decreased and become a broad emission peak centring at 506 nm. The fluorescence was quenched upto 2.9 folds (Figure 4.6 (b)).



Figure 4.6. (a) Absorption and (b) fluorescence titration spectra of bisthiazole triarylborane 1 ($2.1 \times 10-5$ M) with TBACN in THF solvent.

The effect of other anions in the presence CN– sensing there is no spectral change as shown in Figure 4.7.





Figure 4.7. Effect of other anions in the presence $1+ CN^{-}$ in THF solvent. The detection limit of 1 for F– and CN– was calculated based on the fluorescence titration data and found to be $5.7 \times 10-6$ M and $2.1 \times 10-6$ M respectively (Figure 4.8)



Figure 4.8. Job's plot of **1** (a) TBAF and (b) TBACN in THF solution. The absorbance was collected at 416 nm.

The binding constant of the complex formed in solution was estimated by using the standard Benesi–Hildebrand equation 1.

$$\frac{1}{I - I_o} = \frac{1}{I_1 - I_o} + \frac{1}{(I_1 - I_o)K_a[M]}$$
 Eq. 1

Where I_0 is the intensity before addition of anion, I is the intensity in the presence of F^-/CN^- , I_1 is intensity upon saturation with anion, and K_a is the binding constant of the complex formed. The binding constant towards the F^- and CN^- ion were found 11,100 M⁻¹ and 12,464 M⁻¹ using the above equation (Figures 4.9 and 4.10).



Figure 4.9. Benesi–Hildebrand plot of **1** by plotting $1/(I_0-I)$ as a function of $1/[F^-]$ for the calculation of binding constant (K). Here I refer to the fluorescence intensity of **1** at 424 nm at a given F^- concentration and I_o corresponds to the initial fluorescence intensity of **1** at 424 nm in the absence of F^- .



Figure 4.10. Benesi–Hildebrand plot of **1** by plotting $1/(I_0-I)$ as a function of $1/[CN^-]$ for the calculation of binding constant (K). Here I refer to the fluorescence intensity of **1** at 424 nm at a given CN^- concentration and I_o corresponds to the initial fluorescence intensity of **1** at 424 nm in the absence of CN^- .

In order to gain further insight into the F– and CN– binding, 1H-NMR titration studies were performed on 1. In order to gain further insight into the F[–] and CN[–] binding, ¹H-NMR titration studies were performed on **1**. The comparison of ¹H– NMR spectra of **1** before and after addition of fluoride anion is shown in Figure 4.11.

The aryl protons of triarylborane show one doublet at 7.54 ppm and one singlet 6.84 ppm. After addition of 0.4 equivalent of fluoride anion one new peak was observed at 6.57 ppm and it was gradually increased upto 2 equivalents then saturated. On the other hand the intensity of doublet at 7.54 ppm and singlet 6.84 ppm was decreased. In the case of cyanide sensing aryl protons of triarylborane singlet signal at 6.84 ppm was shielded upon addition of cyanide anion and it was observed at 6.59 ppm (Figure 4.12).



Figure 4.11. ¹H–NMR titration spectra of bisthiazole triarylborane dyad 1 with TBAF in $CDCl_{3}$.



Figure 4.12. ¹H–NMR titration spectra of bisthiazole triarylborane dyad 1 with TBACN in $CDCl_3$

The detail explanation of ¹H–NMR titration is given supporting information. From the chart 1 and figure 4 it can be observed the phenyl protons (H-1) singlet signal at 6.84 ppm are shielded upon addition of fluoride anion and the new signal is observed at 6.57 ppm. The signal at 6.57 ppm corresponds to the H-1 protons. Due to the shielded nature of phenyl protons (H-1) singlet signal at 6.84 ppm, these protons intensity is decreased and new the same protons new signal appeared at 6.57 ppm. From the chart 1 and figure 4 it can be observed the phenyl protons (H-1) singlet signal at 6.84 ppm are shielded upon addition of fluoride anion and the new signal is observed at 6.57 ppm. The signal at 6.57 ppm corresponds to the H-1 protons. Due to the shielded nature of phenyl protons (H-1) singlet signal at 6.84 ppm, these protons intensity is decreased and new the same protons new signal appeared at 6.57 ppm (chart 3.1).



Chart 3.1. The triarylborane substituted bisthiazole 1.

4.4. Time dependent density functional (TD-DFT) studies:

In order to understand the anion sensing behaviour of the bisthiazole substituted triarylborane **1** the time dependent density functional (TD-DFT) calculation was performed. The quantum chemical calculations were performed using the Gaussian 09 program.²⁵ The structures of **1**, **1-F**, and **1-CN** were optimized using B3LYP level The 6-31G** basis set for C, N, H, B, S used for all the calculations.

The solvent calculations were carried out in the tetrahydrofuran (THF) using the polarized continuum model (CPCM) of Gaussian 09 software.²⁶

The **1**, **1-F** and **1-CN** experimental and computed (TD–DFT: B3LYP) (UV–vis) absorption data are represented in Figure 4.13. The strong absorption band of **1**, **1-F** and **1-CN** calculated at B3LYP levels are 495 nm, 524 nm and 507 nm respectively. The experimental values for this transition are 416 nm, 428 nm and 503 nm for **1**, **1-F** and **1-CN** respectively. The experimental values are in good agreement with the TD–DFT/B3LYP values.



Figure 4.13. The comparison of experimental and calculated (TD-DFT at B3LYP level) absorption spectrum of bisthiazole triarylborane dyad **1**, **1-F** and **1-CN** in THF solution.

In bisthiazole triarylborane dyad 1 the HOMO \rightarrow LUMO transition contributes to the lowest excited state by 98% and oscillator strength is 2.73. After addition of fluoride ion the 1-F shows HOMO-1 \rightarrow LUMO+1 transition contribute to the lowest excited state by 30% and in case of 1-CN shows major contribution (59%) between HOMO-1 \rightarrow LUMO+1 (Table 4.1) and these transitions are shown Figure 4.14.

Table 4.1. Computed vertical transition energies and their Oscillator strengths (*f*) and major contributions for the **1**, **1**-**F** and **1**-**CN**.

Bisthiazole	TD-DFT/ B3LYP (DCM)		
triarylborane	λ _{max}	f	Major contribution (%)
1	495 nm	1.7002	HOMO→LUMO (98%)
1F	524 nm	0.3902	HOMO-1 \rightarrow LUMO+1 (30%)
1CN	507 nm	1.6259	HOMO-1→LUMO+1 (59%)



Figure 4.14. The major transitions of bisthiazole triarylborane dyad 1, 1-F and 1-CN.

The electrostatic potential surface of bisthiazole substituted triarylborane dyad 1, **1-F** and **1-CN** are shown in Figure 4.15. In **1** the bisthiazole groups show negative potential (-0.011) whereas the triarylborane moiety show positive potential (+0.011) confirming bisthiazole is acting as a acceptor. Since Boron is electron deficient, the addition of F- should increase the electron density on Boron which was confirmed by the negative potential (-0.019) of triarylborane unit from the electrostatic potential surfaces of bisthiazole triarylborane dyad **1F**.



Figure 4.15. The electrostatic potential surfaces of bisthiazole triarylborane dyad 1, 1-F and 1-CN.

The Figure 4.16 shows the energy level digram of the frontier molecular orbitals (FMO) of bisthiazole triarylborane dyad **1**, **1-F** and **1-CN** obtained using computational calculation. The HOMO-LUMO gap in **1**, **1-F** and **1-CN** is a function of anion groups. In bisthiazole triarylborane dyad **1** the HOMO-LUMO gap is 2.84 eV. After addition of F^- anion the HOMO and LUMO energy gap was decreased to 0.15 eV. The addition of CN^- further reduced the HOMO-LUMO gap to 0.13 eV. The HOMO-LUMO gap in bisthiazole triarylborane dyad **1**, **1-F** and **1-CN** follows the order **1CN** > **1F** >1.



Figure 4.16. The energy level diagram of the frontier molecular orbitals of bisthiazole triarylborane dyad **1**, **1-F** and **1-CN** calculated using B3LYP level of DFT theory.

4.5. Experimental section

All the chemicals were purchased from commercial sources and used without further purification. Triethylamine was received from commercial source, and distilled on KOH prior to use. ¹H NMR and ¹³C NMR spectra were performed on 400 MHz and 100 MHz Bruker Ultra shield (Avance–III) Nano Bay spectrometer. All the spectra were recorded at 298K.¹H NMR data are reported as follows: s: singlet, d: doublet, t: triplet, bs: broad singlet and coupling constants, *J*, are given in Hz. Chemical shifts in ¹H NMR and ¹³C NMR spectra were reported in parts per million (ppm) with TMS (0 ppm) and CDCl₃ (7.27 ppm ,77.00 ppm) as standards. TLC analysis was carried out using silica gel 60 F₂₅₄ plates. UV–vis absorption spectra of all compounds were recorded in THF on a carry–100 Bio UV–visible Spectrophotometer. Emission spectra were taken in a fluoromax-4p fluorimeter from Horibayovin (model: FM–100). The excitation and emission slits were 2/2 nm for the emission measurements. All the measurements were done at 298K. For UV–visi and fluorescence titrations the

anion (F⁻, Cl⁻, Br⁻, Γ⁻, NO₂⁻ and CN⁻) stock solutions were prepared in THF in the order of 10^{-3} M. The triarylborane naphthalimide **1** stock solution was prepared (C=1mM) in THF. Working solutions of **1** and anions were freshly prepared from stock solutions. The fluorescence quantum yield (Φ) was calculated using Quinine sulfate (Φ=0.54) as reference. Column chromatography was performed on Merck silica gel (230-400 mesh). The anions were used in their tetrabutylammonium salts. The relative fluorescence quantum efficiency, (Φ), is evaluated by employing Quinine sulfate as standard (Φ=0.54) following the equation 1.²⁷

$$\Phi = \Phi_{std} \left(\frac{I_{unk}}{I_{std}}\right) \left(\frac{A_{std}}{A_{unk}}\right) \left(\frac{\eta_{unk}}{\eta_{std}}\right)^2 \dots 1$$

Where Φ_{unk} , Φ_{std} , I_{unk} , I_{std} , A_{std} , A_{unk} , η_{unk} and η_{std} are the fluorescence quantum efficiency, the integral of the emission intensities, the absorbance at the excitation wavelength and the refractive indexes of the corresponding solvents of the unknown samples and the standard respectively.

Absorption and fluorescence titration spectra of triarylborane substituted bisthiazole 1 (2.1×10^{-5} M) with TBAF in THF solvent for the binding constant of the complex formed in solution has been estimated by using the standard Benesi–Hildebrand equation 2.²⁸

$$\frac{1}{I - I_o} = \frac{1}{I_1 - I_o} + \frac{1}{(I_1 - I_o)K_a[M]}$$
 Eq. 2

Where I_0 is the intensity before addition of anion, I is the intensity in the presence of F^{-}/CN^{-} , I_1 is intensity upon saturation with anion, and K_a is the association constant of the complex formed. The detection limit of **1** as a fluorescent sensor for the analysis of fluoride and cyanide were determined from the plot of fluorescence intensity as a function of the concentration of fluoride and cyanide respectively. The detection limits of fluoride and cyanide ions using 1 were determined from the following equation: DL = K SD/S, where K=3; SD is the standard deviation of the blank solution; S is the slope of the calibration curve.²⁹

General procedure for the Synthesis of 5,5'-Bis-{4-[bis-(2,4,6-trimethylphenyl)-boranyl]-phenylethynyl}-4,4'-dihexyl-[2,2']bithiazolyl 5,5'-1: Dibromo-4,4'-dihexyl-[2,2']bithiazolyl **d** (100 mg, 0.20 mmol), (4– ethynylphenyl)dimesitylborane (156 mg, 0.44 mmol) were dissolved in dry THF (20ml), added triethylamine (5 ml), Pd(PPh₃)₄ (0.013 g, 0.01 mmol), stirred for 24 h at 100 °C, after completion of the reaction, the reaction mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography on silica, using hexane/ DCM (75:25) to get 1 as a yellow solid (0.130 g, 62 %); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.54$ (g, 8H), 6.84 (s, 8H), 2.96 (t, 4H), 2.33 (s, 12H), 2.02 (s, 24H), 1.83 (t, 4H), 1.35 (m, 12H), 0.89 (t, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 163.57$, 159.10, 140.87, 139.00, 136.15, 130.81, 128.28, 125.69, 115.52, 99.32, 81.96, 31.59, 29.76, 28.91, 23.50, 22.64, 21.30, 14.18 ppm; HRMS (ESI): calcd. for C₇₀H₇₈N₂S₂B₂ 1055.5706 [M+] found 1055.5709.

4.6. Conclusions

In summary, we have designed and synthesized new bisthiazole triarylborane based fluorescent chemosensor for the selective detection of F^- and CN^- anions. The bisthiazole triarylborane selective detects F^- and CN^- ions the presence of CI^- , Br^- , Γ , NO_2^- ions and exhibits colorimetric and fluorometric response. The computational and Photophysical properties show strong electronic communication between the triarylborane and bisthiazole unit. The NMR titration studies further confirmed the selective detection of F^- and CN^- anions. The ease of synthesis and simplicity in sensing of triarylborane bisthiazole can be used for onsite anion sensing of F^- and CN^- anions.

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5.1. Introduction

Dye sensitized solar cells (DSSCs) have attracted enormous attention from the scientific community¹ for the past two decades due to their advantages, such as providing lightweight colored and flexible devices with certified power conversion efficiencies of $11.4\%^2$ and $14.3\%^3$. One of the key components in the DSSC is the sensitizer which controls light harvesting and charge separation.^{4,5} DSSCs based on metal containing sensitizers, including ruthenium dyes,^{6,7} Znporphyrins,^{8,9} and perovskites,^{10,11} have achieved remarkable power conversion efficiencies (PCE) so far, but their practical uses are still limited due to their high cost, scarcity and environmental problems. However, the use of metal free organic dves as sensitizers is fascinating because of their easier synthetic routes and versatile structure tallying with energy levels, along with superior light harvesting ability due to their high absorption coefficients.^{12–14} The structure of the organic dyes plays a key role in perturbing their optical and electrochemical properties and hence the photovoltaic properties of DSSCs to induce effective intramolecular charge transfer (ICT) for charge separation. The concept of donor- $(\pi$ -bridge)acceptor (D– π –A) has been widely exploited, offering molecules capable of absorbing a wide range of the solar spectrum.^{15,16} Organic dyes with triphenylamine (TPA) donors with different p-conjugated linkers, including aromatic and heteroaromatics and cyanoacrylic acid as anchor/acceptor, are promising to attain better DSSC performance.¹⁷⁻²⁰ Moreover, as Diau et al. have reported, push-pull type porphyrin dyes incorporating ethynyl units in their backbone can effectively promote strong coupling at the interface of TiO₂ and

broaden the light harvesting region, resulting in better photovoltaic performances.²¹

Ferrocene based molecular systems exhibit interesting optical and electrochemical properties and have been explored as donor units in the sensitizers for DSSCs.²² Singh et al. have used some ferrocene based dithiocarbamate sensitizers for DSSCs.^{10,11,23} Recently, the same research group reported on ferrocenyl bearing Ni(II) and Cu(II) dithiocarbamates in DSSCs and achieved a PCE of 3.87%.²⁴

We are interested in exploiting ferrocene as an antenna in dye sensitized solar cells (DSSCs). The choice of using ferrocene derivatives as sensitizers is due to their well-defined reversible redox process and strong electron donating properties. Recently we have used two ferrocenyl substituted triphenylamine based donor–acceptor dyes as sensitizers and achieved an overall PCE of 4.96%.²⁵ In order to increase the efficiency of DSSC in ferrocene based dyes, we have designed and synthesized triphenylamine linked ferrocenyl bisthiazole based donor–acceptor dyes **D1** and **D2**. The DSSCs fabricated with **D1** and **D2** as sensitizers showed overall PCEs of 6.33% and 5.03%, respectively. The higher PCE for **D1** may be attributed to the strong binding of the anchoring cyanoacrylic acid with the TiO₂ surface as compared to the dicyanovinyl unit in **D2**.

5.2. Results and discussion



Scheme 5.1. Synthesis of bisthiazole.



Scheme 5.2. Synthesis of compound C.



Scheme 5.4. Synthesis of compound 2.



Scheme 5.5. Synthesis of dye D1.



Scheme 5.6. Synthesis of dye D2.

The ferrocenyl bisthiazole linked triphenylamine based donor-acceptor dyes **D1** and **D2** were synthesized by the Suzuki cross-coupling and Knoevenagel condensation reactions. The starting materials 5,5'-dibromo-4,4'-dibutyl-2,2'-bisthiazole (**a**)²⁶ (Scheme 5.1) and 4-(bis(4-ethynylphenyl)amino) benzaldehyde (**c**)²⁷ (Scheme 5.2)were synthesized by the reported procedures (Scheme 5.3). The 5-bromo-4,4'-dihexyl-5'-(ferrocenylethynyl)-2,2'-bithiazole (**1**) was synthesized by sonogshira cross-coupling of 5,5'-dibromo-4,4'-dibutyl-2,2'-bisthiazole (**a**) and ethnyl ferrocene (**b**) which resulted mono substituted ferrocenyl bisthiazole (**1**) in 50% (Scheme 5.4). The compound **2** was synthesized by the Sonogashira cross-

coupling reaction of 5-bromo-4,4'-dihexyl-5'-(ferrocenylethynyl)-2,2'-bithiazole (1) with 4-(bis(4-ethynylphenyl)amino) benzaldehyde which resulted compound 2 in 62% yield. The dyes **D1** and **D2** were synthesized by Knoevenagel condensation reaction of 2 with cyanoacetic acid and malononitrile in dichloromethane and acetic acid mixture (1:1 ratio) in the presence of NH₄OAc which resulted **D1** and **D2** in 72% and 75% yields respectively (Scheme 5.5 and 5.6). All the compounds were well characterized by ¹H, ¹³C–NMR, and HRMS techniques.

5.3. Photophysical properties

The electronic absorption spectrum of **D1** and **D2** in dilute dichloromethane (DCM) solution is shown in Figure 5.1 and the data are summarized in Table 5.1. As shown in Figure 5.1, both **D1** and **D2** exhibited similar absorption profiles with two distinct bands.



Figure 5.1. Normalized absorption spectra of dyes (a) D1, (b) D2 in DCM solution and $onTiO_2$ film.

The major absorption bands at 423 nm and 426 nm of dyes **D1** and **D2** are attributed to mixed ICT/p–p* transition of the chromophores, which was further confirmed by TD-DFT calculations. The optical absorption spectra of dyes on TiO₂ films are shown in Figure 5.1 (a) and (b) (red colour). The absorption peaks

are red-shifted and broadened as compared to those in solution and are located at 484 nm and 492 nm for **D1** and **D2**, respectively. The broadening of the absorption spectra is a result of the interaction between TiO_2 and the sensitizers, and is beneficial for light harvesting.²⁷

Table 5.1. Photophysical, electrochemical, and theoretical properties of thetriphenylamine linked bisthiazole based donor-acceptor dyes **D1** and **D2**.

				Electro	Theoretical
Dyes	λ_{\max} (nm)	E _{oxid} (V)	E _{red} (V)	chemical	band gap
	and			band	(eV)
	$\varepsilon (M^{-1} \text{ cm}^{-1})^{a}$			gap (eV)	
D1	426 (86726) ^a	0.073 ^b	-1.55 ^d	E _{HOMO} = -4.95	
		0.51 ^c		E _{LUMO} = -3.51	2.68
				$E_{gap}=1.44$	
D2	429 (88459) ^a	0.078 ^b	-1.48 ^d	E _{HOMO} = -4.96	
		0.60 ^c		E _{LUMO} = -3.56	2.65
				Egap=1.40	

^aMeasured in dichlomethane; ^bThe oxidation value of ferrocene unit, ^cThe oxidation value of triphenyl unit, ^dThe half wave reduction values of bisthiazole group.

5.4. Electrochemical properties

The electrochemical properties of the ferrocenyl bisthiazole linked triphenylamine based donor–acceptor dyes **D1** and **D2** were studied by cyclic voltammetry (CV) measurement. The electrochemical data of dyes **D1** and **D2** are listed in Table 5.1, and the representative cyclic voltammograms are shown in Figure 5.2. The cyclic voltammograms of dyes **D1** and **D2** show two oxidation waves and one reversible reduction wave. The first reversible oxidation wave belongs to the ferrocene unit and the second quasi-reversible oxidation wave corresponds to the triphenylamine unit.

The reduction wave corresponds to the bithiazole group. The highest occupied molecular orbital (HOMO) energy levels of the dyes were estimated from the

onset oxidation potential (Eox onset) i.e. HOMO = q(Eox onset + 4.8) eV and are shown in Table 5.1. The HOMO energy levels for both the dyes (- 4.95 eV and - 4.96 for **D1** and **D2**, respectively).

are more negative than the iodide/triiodide redox potential (- 4.8 eV), indicating that the dye generation in DSSCs may be readily proceed by electron transfer from the redox solution. The lowest unoccupied molecular orbital (LUMO) energy levels are estimated from the onset reduction potential (E_{red} onset) LUMO = q(E_{red} onset + 4.8) eV LUMO = -q(E_{red} + 4.8) eV and are shown in Table 5.1. The LUMO energy levels are -3.51 eV and -3.56 eV for **D1** and **D2**, respectively, and are higher than the conduction band edge of TiO₂ (- 4.2 eV), indicating there is sufficient driving force for electron injection from the excited dye to the TiO₂.



Figure 5.2. Cyclic voltammograms of the dyes D1 and D2 at $(1.0 \times 10^{-4} \text{ M})$ concentration in dichloromethane recorded at a scan rate of 100 mVs⁻¹.

5.5. Theoretical calculations.

In order to understand the photophysical and electrochemical properties of the ferrocenyl bisthiazole linked triphenylamine based donor-acceptor dyes **D1** and **D2**, the density functional theory (DFT) and time dependent density functional (TD-DFT) calculation was performed. The structures of dye **D1** and **D2** were optimized by DFT in B3LYP/6-31G** and photophysical properties were studied by TD-DFT in dichloromethane solvent (CPCM model) using Gaussian 09 at the CAM-B3LYP for C, H, N, S, O and Lanl2DZ for Fe level.²⁸

The TD-DFT predicted vertical excitation energies for dyes **D1** and **D2** are shown in Figure 5.3, along with individual experimental UV-vis spectra.

The major intense transitions in dyes **D1** and **D2** are mixed ICT/ π - π * transitions in nature. The strong absorption band calculated at CAM-B3LYP level are 424 nm, 423 nm respectively. The experimental values for these transitions are 426 nm, 429 nm respectively, which show good agreement with the experimental values.



Figure 5.3. The comparison of experimental and calculated (TD-DFT at CAM-B3LYP level) absorption of dyes **D1** and **D2** in DCM solution.

The predicted vertical transitions and oscillator strengths in dyes **D1** and **D2** are listed in Table 5.2. In Dyes **D1** and **D2** the transitions are dominated by a HOMO-1 \rightarrow LUMO transition 21%, 16 % and oscillator strengths are 3.3863, 3.403 respectively (Table 2). The absorption band calculated (CAM-B3LYP) in this region (424 nm, 423 nm) confirms that the molecular orbitals (MOs) associated with these transitions are ferrocene (donor) to acrylic acid (acceptor) and attributed to mixed ICT/ π - π * transition from HOMO-1 \rightarrow LUMO as shown in Figure 5.4 and 5.5.



Figure 5.4. The calculated π - π * and ICT transitions and transition band between HOMO-1 to LUMO+1 at 424 nm of dye **D1** using CAM-B3LYP Theory.





5.6. Theoretical photovoltaic calculations

The theoretical values of HOMO, HOMO-1 and LUMO energy levels for **D1** are shown in Figure 5.6 and the HOMO and HOMO-1 energy levels are almost the same. In DSSCs, the HOMO to LUMO or HOMO-1 to LUMO transitions are not important. Only the binding of dye with the TiO₂ surface and electron injection from the LUMO of the dye into TiO₂ are important.²⁹



Figure 5.6. The frontier molecular orbitals of the dye D1.

The HOMO energy levels of these dyes **D1** and **D2** are more negative compared to the redox potential of the electrolyte I_3 /I and also the LUMO energy levels of these dyes are more positive than the conduction band of TiO₂ (_4.2 eV), which is desirable for photoelectron injection. The electron injection is possible by both dyes **D1** and **D2** as the LUMOs of both dyes are above the CB of TiO₂, as shown in Figure 5.7.



Figure 5.7. Molecular energy level diagram of **D1** and **D2** including the redox energy level of I_3^{-1}/I .

The photovoltaic applications of dyes **D1** and **D2** were studied by using the DFT and TD-DFT theory. The power conversion efficiency (η) was calculated according to the eq (1):²⁹

Where P_{in} is the incident power density, J_{sc} is the short-circuit current, V_{oc} is the open-circuit current, and *FF* denotes the fill factor.

The theoretical values of open-circuit V_{oc} was calculated from the following eq (2). These values are sufficient for a possible efficient electron injection. The dyes **D1** and **D2** show good open-circuit in TiO₂ (Table 5.2). As per calculation dye **D2** having more open-circuit current as compared to the dye **D1** due to the lower HOMO level.³⁰

Dy	λ_{max}	Main configurations	oscillator	LHE = 1-	
e			strength	10 ^{-f}	V _{oc} /TiO ₂
D1	424	HOMO-1→LUMO	3.386	0.999	0.78
	nm	(21%)			
D2	423	HOMO−1→LUMO	3.403	0.999	0.89
	nm	(16%)			

Table 5.2. Theoretical light harvesting efficiency (LHE) values of dyes **D1** and**D2**.

 $V_{\rm oc} = |E_{\rm HOMO} (\text{Donor or dye})| - |E_{\rm LUMO} (\text{Acceptor}) \text{ of } \text{TiO}_2| - 0.3$ (2)

The short-circuit current (J_{sc}) in solar applications are determined by the following equation (3).

 $J_{sc} = \int LHE(\lambda) \phi_{inject}.\eta_{collect}. d\lambda$ ------(3)

Where LHE is the light harvesting efficiency at a given wavelength, ϕ_{inject} is the electron injection efficiency and $\eta_{collect}$ is the charge collection efficiency. In this $\eta_{collect}$ is a constant. As a result, the enhancement of J_{sc} should focus on improving the LHE and ϕ_{inject} . In the eq. (2) if LHE is directly proportional to J_{sc} also increased. According to eqn (4), we have calculated the light harvesting efficiency (LHE) of dyes **D1** and **D2**, in which both dyes are showing same LHE values (Table 5.2).³⁰

LHE =
$$1 - 10^{-f}$$
 ------ (4)

Where *f* is the oscillator strength of the dye corresponding to λ_{max} ,

 ϕ_{inject} is the electron injection efficiency, and $\eta_{collect}$ is the charge collection efficiency. It is reasonable to assume $\eta_{collect}$ to be constant for the same DSSC with only different dyes. ϕ_{inject} is related to the free energy of electron injection (ΔG_{inject}) and is expressed by following equation (5)

 $\phi_{inject} \alpha f (\Delta G_{inject}) ------ (5)$

Therefore, the more negative $\Delta Ginject$ the greater will be the electron injection efficiency. $\Delta Ginject$ can be calculated as the difference between excited state oxidation potential ($E_{OX}^{dye^*}$) of the dye and the ground state reduction potential (E_{CB}) and ΔE stands for the electronic vertical transition energy associated with the λ_{max} (Table 5.3).³¹

Table 5.3. The calculated excited and ground state oxidation potential $(E_{OX}^{dye^*}$ and $E_{OX}^{dye})$, the electronic vertical transition energy (DE) associated with the λ_{max} of the dyes.

Dyes	$\lambda_{max/nm}$	ΔΕ	$E_{OX}^{dye}(eV)$	E _{OX} ^{dye*}	(AGinject)
		(eV)		(eV)	
D1	426	2.91	5.28	2.37	-1.83
D2	429	2.89	5.39	2.50	-1.70

$$E_{OX}^{dye^*} = E_{OX}^{dye} - \Delta E \dots (6)$$

$$\Delta G_{inject} = E_{OX}^{dye^*} - E_{CB} \dots (7)$$

Overall theoretical DSSc calculation reveals that the open-circuit (V_{oc}) and light harvesting efficiency (LHE) of dyes **D1** and **D2** shows almost same performance. But the key parameter of electron injection $_{\Delta Ginject}$ from E_{LUMO} of dye to CB of TiO₂ is more flexible in the case of dye **D1** (-1.83) as compared to the dye **D2** (-1.70) (Figure 5.7), which is good agreement with experimental results.

5.7. Experimental photovoltaic properties

We have fabricated DSSCs based on these two dyes as sensitizers. The electrolyte is composed of 0.6 M 1, 2-dimethyl-3-propylimidazolium/0.05 M I₂/0.1 M LiI and the cell effective area was 0.16 cm^2 . TiO₂ electrodes were sensitized with 0.1 mM dye solution for 12 hours. First of all we have fabricated the DSSCs dipping the photoanode in a pristine dye solution, but the overall PCE was very low in the range of 2.5% may be due to the aggregation problem. Therefore, Co-adsorption with chenodeoxycholic acid (CDCA) was also examined to prevent aggregation of the dyes on TiO₂. The current-voltage characteristics of the DSSCs were measured under the illumination of stimulated AM1.5 G (100 mW/cm²) are shown in Figure 5.8 (a) and the photovoltaic parameters are compiled in Table 5.4.

Table 5.4. Photovoltaic parameters of DSSCs sensitized with dye D1 and D2.

Dyes	$J_{sc}(mA/cm^2)$	V _{oc} (V)	FF	PCE (%)
D1	11.56	0.74	0.74	6.33
D2	9.98	0.69	0.72	5.03

DSSC sensitized with **D1** showed overall PCE of 6.33 % with J_{sc} of 11.56 mA/cm², Voc of 0.74 and FF of 0.74. However, the **D2** sensitized DSSC exhibit lower PCE of 5.03%, with Jsc of 9.98 mA/cm², V_{oc} of 0.69 V and FF of 0.72. Since the molecular structure of both **D1** and **D2** is same except anchoring units,



Figure 5.8. (a) Current-voltage characteristics and (b) IPCE spectra of dyes D1 and D2.

the difference in the photovoltaic parameters may be related to the strength of binding of dyes with TiO₂ surface. As shown in Figure 5.8 (b), the incident photon to current conversion efficiency (IPCE) spectra, **D1** based DSSC showed higher values of IPCEs throughout the entire wavelength regions than that for **D2** counterpart. The Jsc values estimated from the integration of IPCE spectra of the DSSCs are about 11.47 mA/cm² and 9.84 mA/cm² for **D1** and **D2**, respectively. The lower value of J_{sc} and FF for the **D2** based DSSCs may be related to the inefficient adsorption of dye on the TiO₂ surface because of the presence of DCV anchoring unit, which directly influences the electron injection.³²

The IPCE value is given by IPCE=LHEx_{ϕ inj}x_{ϕ reg}x_{η cc}, where LHE is light harvesting efficiency of the DSSC, LHE=1-10^{-A}, A is the absorbance of the photoanode, ϕ_{inj} and ϕ_{reg} are the electron injection and regeneration efficiencies, respectively, and η_{cc} is the charge collection efficiency.

Nyquist and Bode spectra are measured by electrochemical impedance spectroscopy (EIS) in dark condition under a forward bias -0.70 V, to get information about the interfacial charge transfer processes at the interfaces in the DSSCs such as charge recombination at the TiO2/dye/electrolyte interface, electron transport in the TiO₂ electrode, I_3^- transport in electrolyte.³³ The Nyquist plots and Bode phase plots for the DSSCs sensitized with **D1** and **D2** are shown in Figure 5.8 (a) and (b) respectively. The semicircle observed in the middle frequency range of Nyquist plots (Figure 5.9 (a)) is proportional to the interfacial charge transfer resistance (Rct) at the $TiO_2/dye/electrolyte$ interface. It can be seen that the Rct is higher for the **D1** based DSSC as compared to **D2** counterpart. The DSSC with larger Rct can suppress the charge recombination and reduce the dark current and thereby improving the Voc.³⁴



Figure 5.9. (a) Nyquist plots and (b) Bode phase plots for the DSSc of dyes D1 and D2.

Therefore, the larger value of Rct for **D1** sensitized DSSC reflects that slower rate of recombination rate of injected photoelectrons in TiO₂ with $I_3^$ species which can be attributed to the more amount of dye loading. The lower frequency peak in the Bode plot (Figure 5.9 (b)) implies longer lifetime (τ_e) of injected electron in TiO₂ according to the relation $\tau_e = 1/(2\pi f)$ (f is the peak frequency of lower-frequency range in Bode plots). A longer electron lifetime corresponds to a lower dark current. The DSSC based on **D1** has the longer electron lifetime, which implies the most effective suppression of the back reaction between the injected electrons and the electrolyte, resulting in the improvement of the Voc, although its HOMO energy level is lower than that for **D2**.

5.8. Experimental section

All reagents were obtained from commercial sources, and used as received unless otherwise stated. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker Avance (III) 400 MHz instrument by using CDCl₃ as solvent. ¹H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl₃, 7.26 ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), and m (multiplet), and the coupling constants, J, are given in Hz. ¹³C NMR chemical shifts are reported relative to the solvent residual peak (CDCl₃, 77.36ppm). UV-visible absorption spectra were recorded on a Cary-100 Bio UV-visible spectrophotometer. Cyclic voltamograms (CVs) were recorded on a CHI620D electrochemical analyzer using glassy carbon as the working electrode, Pt wire as the counter electrode, and the saturated calomel electrode (SCE) as the reference electrode. The scan rate was 100 mV s-1. A solution of tetrabutylammonium hexafluorophosphate (TBAPF6) in CH₂Cl₂ (0.1 M) was employed as the supporting electrolyte. DCM was freshly distilled from CaH2 prior to use. All potentials were experimentally referenced against the saturated calomel electrode couple but were then manipulated to be referenced against Fc/Fc+ as recommended by IUPAC. Under our conditions, the Fc/Fc+ couple exhibited $E^{\circ} =$ 0.38 V versus SCE. HRMS was recorded on a Bruker-Daltonics micrOTOF-Q II mass spectrometer.

Device fabrication and characterization

The fabrication of DSSC as well as the TiO₂ photoanodes and counter electrodes were carried out following of our earlier work.²⁵ The thickness of the TiO2 electrode is 12-13 μ m. Each dye was dissolved in a mixture of DCM:EtOH (1:1) with 20 mM CDCA which was used as sensitized solution with a concentration of 5x10-4 M). The prepared TiO₂ photoanodes were dipped into the dye solution for 12 h, risen with ethanol and dried in ambient conditions. The redox electrolyte used for the DSSCs and device characterization are as reported in over earlier communication²⁵.

General procedure for the preparation of dyes D1 and D2.

Synthesis of compound 1

In the presence of argon atmosphere a solution of bisthiazole **2** (0.5 g, 1.01 mmol) and the ethynyl ferrocene (0.18 g, 0.85 mmol) in dry THF (20ml), added triethylamine (5 ml), Pd(PPh₃)₄ (0.013 g, 0.01 mmol), stirred for 16 h at 75 °C, after completion of the reaction, the reaction mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography on silica, using hexane/ DCM (45:55 *v/v*) to get **1** as a red solid (0.450 g, 71 %); ¹H NMR (400 MHz, CDCl₃): $\delta = 4.54$ (d, J = 4 Hz, 2H), 4.31 (s, 2H), 4.27 (m, 4H), 2.91 (t, 2H), 2.77 (t, 2H), 1.81 (t, 2H), 1.73 (t, 2H), 1.42 (m, 12H), 0.92 (t, 6H), ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 161.75$, 98.30, 71.25, 69.77, 69.02, 31.28, 31.25, 28.73, 28.62, 28.36, 22.30, 22.26, 13.76 ppm; HRMS (ESI-TOF): m/z calculated for C₃₀H₃₅BrFeN₂S₂ 624.0750 [M+] found 624.0748.

Synthesis of compound 2

In the presence of argon atmosphere a solution of compound **1** (0.42 g, 0.67 mmol) and compound (c) (0.1 g, 0.31 mmol) in dry THF (20 ml), added triethylamine (5 ml), Pd(PPh₃)₄ (0.013 g, 0.01 mmol), stirred for 16 h at 80 °C, after completion of the reaction, the reaction mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography on silica, using hexane/ DCM (10:90 *v*/*v*) to get **1** as a red solid (0.250 g, 57 %); ¹H NMR (400 MHz, CDCl₃): δ = 9.90 (s, 1H), 7.79 (d, *J* = 8 Hz, 2H), 7.51 (d, *J* = 8 Hz, 2H), 7.17 (m, 6H), 4.54 (s, 4H), 4.31 (m, 11H), 2.95 (t, 8H), 1.83 (t, 8H), 1.43 (m, 24H), 0.93 (t, 12H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 190.44, 163.08, 162.27, 159.08, 157.89, 152.03, 146.30, 132.89, 131.38, 125.27, 122.02, 118.79, 116.60, 115.23, 98.75, 98.26, 80.52, 71.58, 70.10, 69.36, 64.14, 31.61, 30.49, 29.09, 28.89, 22.64, 14.14 ppm; HRMS (ESI-TOF): m/z calculated for C₈₃H₈₃Fe₂N₅S₄O 1406.4258 [M+] found 1406.4258.

General procedure for the preparation of dyes D1 and D2

Under argon atmosphere the mixture of compound 2 (0.1 g, 0.21 mmol), active methylene group (0.026 g, 0.31 mmol) was dissolved in DCM (2 ml), acetic acid (4 ml), added NH₄OAc (0.050 g, 0.64 mmol), stirred for 16 h at 100 $^{\circ}$ C, after completion of the reaction, reaction mixture was concentrated under reduced pressure, purified by column chromatography on neutral alumina.

Dye D1: compound eluted using methanol/DCM (4:98) to get **D1** as a dark orange solid (0. 055 g, 52 %). %); ¹H NMR (400 MHz, CDCl₃): $\delta = 8.03$ (s, 1H), 7.88 (d, J = 4 Hz, 2H), 7.47 (d, J = 8 Hz, 4H), 7.14 (d, 6H), 4.54 (s, 4H), 4.30 (m, 10H), 2.92 (t, 8H), 1.81 (t, 8H), 1.35 (m, 24H), 0.91 (t, 12H) ppm; ¹³C NMR (100 MHz, CDCl3): $\delta = 165.14$, 162.25, 158.81, 157.95, 149.32, 134.43, 132.73, 132.59, 128.13, 128.02, 123.72, 116.53, 114.94, 98.82, 97.64, 89.09, 71.57, 70.10, 69.63, 64.16, 31.61, 30.49, 29.09, 28.89, 22.63, 14.13 ppm; HRMS (ESI-TOF): m/z calculated for C₈₆H₈₄Fe₂N₆S₄O₂ 1472.4238 [M+] found 1472.4943.

Dye D2: compound eluted using methanol/ DCM (2:98) to get **D2** as a dark orange solid (0. 060 g, 58 %). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.95$ (s, 1H), 7.78 (d, J = 8 Hz, 2H), 7.56 (m, 4H), 7.18 (m, 6H), 4.54 (s, 4H), 4.31 (m, 12H), 2.92 (t, 8H), 1.81 (t, 8H), 1.41 (m, 24H), 0.91 (t, 12H) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 162.39$, 162.25, 159.09, 149.59, 149.35, 132.13, 132.03, 131.33, 118.24, 116.30, 93.72, 90.02, 80.29, 71.57, 70.09, 69.34, 64.16, 31.61, 30.48, 29.08, 28.46, 22.54, 14.13 ppm; HRMS (ESI-TOF): m/z calculated for C₈₆H₈₃Fe₂N₇S₄ 1455.4442 [M+] found 1455.4398.

5.9. Conclusions

In summary, we have designed and synthesized triphenylamine linked ferrocenyl bisthiazole based donor-acceptor dyes **D1** and **D2** and applied as sensitizers for DSSCs. The effects of acylic acid and malononitrile acceptor groups on the optical, electrochemical and photovoltaic properties were investigated. The computational properties also reveals that in all dyes (**D1** and **D2**) having ferrocene (donor) to acceptor intramolecular charge transfer transitions (HOMO-1 \rightarrow LUMO). The DSSC based on dye **D1** yielded a PCE of

6.33% while dye D2 showed a PCE of 5.03%. The J_{sc} of dye D1 is greater than dye D2 which can be attributed to the broader absorption profile of dye D1 and promising value of IPCE as compared to the dye D2.

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Chapter 6

C_s-Symmetric Donor-Acceptor Bisthiazoles: Synthesis, Photophysical, Electrochemical and Computational Studies

6.1. Introduction

The tuning HOMO-LUMO gap play important role in material applications such as such as optoelectronic properties, solid-state packing and charge transport characteristics in a various molecular devices.¹⁻⁴ The tetracyano quinodimethane (TCNQ) and tetracyanoethene (TCNE) are strong electron acceptors useful to tuning of HOMO-LUMO gap, which is useful for improving the power conversion efficiency of dye-sensitized solar cells (DSSCs) and bulk heterojunction (BHJ) solar cells properties.⁵

The bisthiazole is a electron withdrawing unit due to the presence of electronwithdrawing nitrogen of the imine (–C=N) which plays a key role in the construction of π -conjugated donor-acceptor (D-A) molecular systems.⁶ Various strong acceptors, such as Tetracyanoquinodimethane (TCNQ), tetracyanoethene (TCNE) and cyanoethynylethenes (CEEs) has been attached to strong donors as well as acceptors.^{7,8} These donor-acceptor systems exhibit efficient intramolecular charge transfer (ICT) interactions and shows strong non-linear optical properties.^{9,10} The incorporation of TCNQ, TCNE in D-A system results in higher reduction potential and red shift absorbtion in the UV-Vis spectrum which leads to the tuning of optoelectronic properties.^{11,12}

The [2 + 2] cycloaddition-retroelectrocyclization of TCNE with electron-rich acetylides, results in TCDB derivatives.^{13, 14} In case of electron-rich acetylides when terminal positions are attached by electron withdrawing groups, the cycloaddition *retroelectrocyclization* reaction is difficult due to the lower HOMO and higher LUMO energy level of TCNE which leads to no reaction.¹⁵

In this chapter we have discussed the donor and acceptor substituted bisthiazole systems, where donor substituted bisthiazole undergoes [2+2]

cycloaddition-retroelectrocyclization reactions with tetracyanoethene (TCNE), whereas acceptor substituted bisthaizole does not undergo any rection.

6.2. Results and discussion

The bisthiazole donor-acceptor systems **1–5** were designed and synthesized by the Sonogashira cross-coupling and [2+2] cycloaddition-retroelectrocyclization reactions. The starting materials 5,5'-dibromo-4,4'-dibutyl-2,2'-bisthiazole (**a**) was synthesized by reported procedure.¹⁶ The Sonogashira cross–coupling reaction of 5,5'-dibromo-4,4'-dibutyl-2,2'-bisthiazole (**a**)¹⁶ with ethynylferrocene (**b**), 4-ethynyl-N,N-diphenylaniline (**c**), and 2-butyl-6-ethynyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**d**) resulted in **1**¹⁷, **2**¹⁸, and **3** in 71%, 65%, and 52% yields respectively. The [2+2] cycloaddition-retroelectrocyclization reactions of **1–3** with TCNE at 100 °C for 16 h resulted in **4**, **5** in 71%, 65% yield respectively and there was no product formation in case of compound **3**. The bisthiazole **1–5** were well characterized by ¹H, ¹³C–NMR, and HRMS techniques (Scheme 6 1)



Scheme 6.1. Synthesis of bisthiazole donor-acceptor systems 1–5.

The reaction of 5,5'-dibromo-4,4'-dibutyl-2,2'-bisthiazole (**a**) with ethynyl ferrocene and ethynyl triphenyamine results bisthiazole **1** and bisthiazole **2** respectively which favor cycloaddition reaction with TCNE as shown by negative Gibbs free energy parameter -0.081 Kcal/Mol and -0.073 Kcal/Mol calculated by computational studies respectively as shown in Figure 6.1.

In case of naphthalimide substituted bisthiazole **3** the TCNE reaction was unsuccessful which showed positive Gibbs free energy (0.009 Kcal/Mol).¹⁹ This conforms that when bisthiazole terminal positional are substituted by donor groups are favorable whereas bisthiazole substituted by electron withdrawing groups are not favorable for [2+2] cycloaddition-retroelectrocyclization reactions (Figure 6.1).



Figure 6.1. The Gibbs free energy differences of the bisthiazoles 1-3 by using 6-311+ g(d,p)/B3LYP at 373 K in Dichloroethane solvent.

In triphenylamine substituted bisthiazole (2) the HOMO energy level (-5.00 eV) is near to the LUMO level (-4.56 eV) of TCNE, therefore mixing of HOMO orbital of bisthiazole 2 and LUMO orbital of TCNE is possible in cycloaddition reaction. On the other hand in bisthiazole substituted by ethnyl naphthalimide (3), the orbital mixing between the TCNE and bisthiazole 3 is not favourable for cyclo addition reaction because of the HOMO energy level (-5.85 eV) is far from LUMO level (-4.56 eV) of TCNE as compared to the bisthiazole 2 (Figure 6.2).²⁰



Figure 6.2. The HOMO and LUMO molecular orbitals of compound 2, TCNE and compound 3 by using 6-311+ g(d,p)/B3LYP at 373 K in Dichloroethane solvent.

6.3. Thermal stability. The thermal stability of the donor-acceptor bisthiazoles 1-5 were explored using thermogravimetric analysis (TGA) at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere (Figure 6.3). The decomposition temperature for 10% weight loss in bisthiazole derivatives 1-5 was above 200 °C. The bisthiazole **3** showed good thermal stability as the 10% weight loss is at higher (307 °C) as compared to the other bisthiazole derivatives. The overall thermal stability of the bisthiazole derivatives follows the order 4 > 5 > 2 > 3 > 1.



Figure 6.3. TGA plots of donor-acceptor bisthiazole 1–5.

6.4. Photophysical properties:

The electronic absorption spectra of bisthiazoles 1-5 were recorded in dichloromethane at room temperature, and the photophysical data are listed in Table 6.1. The donor-acceptor bisthiazoles 1-3 show strong absorption band within 398–450 nm range corresponding to $\pi \rightarrow \pi^*$ transition. The incorpoaration of TCNE in 1 and 2 results bisthiazoles 4 and 5 with distinct photophysical properties compared to stating analogues. The compound 4 show two major absorption at 356 nm and 424 nm corresponding to $\pi \rightarrow \pi^*$ transition and intramolecular charge transfer (ICT) transition respectively with a weak d-d transition at 621 nm (Figure 6.4). Whereas compound 5 shows a strong absorption maximum at 457 nm due to ICT transition (Figure 6.4).



Figure 6.4. Normalized electronic absorption spectra of the donor-acceptor conjugated bisthiazoles 1–5 in dichloromethane

$\lambda_{max}[nm]$	Eoxid	E _{red}	$Td(^{\circ}C)^{f}$
$(\varepsilon[Lmol-cm^{-1}])^{a}$	(V)	(V)	
398 (76800)	0.16 ^b	-1 35 ^d	225
378 (70800)	0.10	-1.55	223
494			
437 (70300)	0.65 ^c	1.07 ^d	282
+37 (10300)	0.05	-1.07	202
450 (72355)	-	-1.08 ^e	276
		1	
		-1.65°	
356 (76800)	0.38 ^b	-0.89 ^e	307
40.4		1 4 - e	
424		-1.45	
621			
457	-0.82°	-0.49^{e}	293
		1.01 ^e	
		-1.01	
	$\lambda_{max}[nm] \\ (\epsilon[Lmol-cm-1])^{a} \\ 398 (76800) \\ 494 \\ 437 (70300) \\ 450 (72355) \\ 356 (76800) \\ 424 \\ 621 \\ 457 \\ 457 \\ $	$\lambda_{max}[nm]$ E_{oxid} $(\epsilon[Lmol-cm^{-1}])^a$ (V) 398 (76800) 0.16^b 494 - 437 (70300) 0.65^c 450 (72355) - 356 (76800) 0.38^b 424 - 621 - 457 -0.82^c	$\lambda_{max}[nm]$ EoxidEred(ϵ [Lmol-cm ⁻¹]) ^a (V)(V)398 (76800)0.16 ^b -1.35 ^d 494437 (70300)0.65 ^c -1.07 ^d 450 (72355)1.65 ^e 356 (76800)0.38 ^b -0.89 ^e 4241.45 ^e 6210.49 ^e 457-0.82 ^c -0.49 ^e -1.01 ^e 1.01 ^e

Table 6.1. Photophysical, electrochemical and thermal stability data of thebisthiazole derivatives 1–5.

^aMeasured in dichlomethane; ^bThe oxidation potential of ferrocene unit, ^coxidation potential of triphenyl unit and ^dThe half wave reduction potential of bisthiazole group and half wave reduction potential of TCBD. ^fDecomposition temperatures for 10 % weight loss at a heating rate of 10 °C min⁻¹, under nitrogen atmosphere.

6.5. Electrochemical propetries. The electrochemical behavior of donoracceptor conjugated bisthiazole derivatives 1-5 were investigated by the cyclic voltammetric analysis in dry dichloromethane solution at room temperature using

tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) as a supporting electrolyte. The electrochemical data are listed in Table 6.1, and the representative cyclic voltammograms are shown in Figure 6.5. All potentials were corrected to be referenced against Fc/Fc⁺, as required by IUPAC.²¹ The cyclic voltammograms of the bisthiazole 1 show reversible oxidation wave corresponding to ferrocene and 2 show irreversible oxidation wave belonging to triphenylamine unit respectively and both 1 and 2 show one reversible reduction wave corresponding to bisthiazole unit. The bisthiazoles 3 shows two reversible reduction peaks which belongs to bisthiazole and napthalimide unit respectively. The TCNE substituted bisthiazoles **4** and **5** shows higher oxidation values, the first reversible oxidation wave at 0.38 V belongs to ferrocene and other one irreversible oxidation wave at 0.82 V belongs to triphenylamine unit respectively. The bisthiazole 4 and 5 each show two quasi reversible reduction waves corresponding to TCNE. The TCNE substituted bisthiazole 5 with triphnylamine linkage exhibits stronger electronic communication as compared to other derivatives.



Figure 6.5. Cyclic voltammograms of (a) bisthiazole derivative 1 (b) bisthiazole derivative 4 at $(1.0 \times 10^{-4} \text{ M})$ concentration in dichloromethane recorded at a scan rate of 100 mVs⁻¹.

6.6. Time dependent density functional (TD-DFT) studies:

In order to understand the photophysical and electrochemical properties of donoracceptor bisthiazoles **1–5**, the time dependent density functional (TD-DFT) calculation was performed. The quantum chemical calculations were performed using the Gaussian 09 program.²¹ The solvent calculations were carried out in the dichloromethane (DCM) using the polarized continuum model (CPCM) of Gaussian 09 software and 6-31G**/B3LYP and CAM- B3LYP basis set for C, N, H, S was used for all the calculations.²²

The TDDFT predicted vertical excitation energies of bisthiazoles 1 and 4 are shown in Figure 6.6 along with individual experimental UV-vis spectra. The major intense transitions in bisthiazoles 1-3 are π - π * in nature. The strong absorption band calculated at CAM-B3LYP level are 402, 329 and 428 nm for 1, 2 and 3 respectively. The experimental values for these transition are 398, 437, 450 nm for 1-3 respectively. After incorporation TCNE in bisthiazoles 4 and 5 show major intense transitions at 411 nm and 406 nm belongs to intramolecular charge transfer (ICT), which show good agreement with the experimental values.

The predicted vertical transitions and oscillator strengths in bisthiazoles 1–5 are listed in Table 6.2. In bisthiazole 1 and 2 the transition is dominated by a HOMO- $2\rightarrow$ LUMO transition 49%, 15% and oscillator strength is 0.757, 3.3134 respectively. In bisthiazole 3, the HOMO-1 \rightarrow LUMO+1 transition contribute to the lowest excited state by 12%, which belongs to π - π * transition. The bisthiazole 4 show major contribution (56%) between HOMO-4 \rightarrow LUMO, which corresponding to the intramolecular charge transfer (ICT) transition at 433 nm and bisthiazole 5 show major transition between HOMO-1 \rightarrow LUMO +2 (44%) which belongs intramolecular charge transfer (ICT) transition at 406 nm.



Figure 6.6. The comparison of experimental and calculated (TD-DFT at CAM-B3LYP level) absorption spectrum of (a) bisthiazole **1** and (b) bisthiazole **4** in DCM solution.

Table 6.2. Computed vertical transition energies and their Oscillator strengths (f) and major contributions for the Fc-bisthiazoles **3**, **4** and **5**.

Bisthiazoles 1-5	TD-DFT/ CAM-B3LYP (DCM)			
	λ _{max}	f	Major contribution (%)	
1	402 nm	0.757	HOMO−2→LUMO (49%)	
2	329 nm	3.3134	HOMO−2→LUMO (15%)	
3	428 nm	2.7668	HOMO-1 \rightarrow LUMO +1 (12%)	
4	411nm	0.922	HOMO-1 \rightarrow LUMO +2 (56%)	
	310 nm	0.2084	HOMO−4 →LUMO (12%)	
5	406 nm	1.7057	HOMO-1 \rightarrow LUMO +2 (44%)	

The bisthiazole **4** shows two major intense absorption bands at 310 nm and 411 nm, due to transition occurring from HOMO-4 \rightarrow LUMO and HOMO-1 \rightarrow LUMO+2 respectively. The frontier molecular orbitals further supports these transitions HOMO-4 \rightarrow LUMO belongs to π - π * and HOMO-1 \rightarrow LUMO+2

corresponds to the intramolecular charge transfer (ICT) from ferrocne (Donor) to TCBD (acceptor) as shown in Figure 6.7.



Figure 6.7. The major transitions in bisthiazole derivative 4.

In the optimized structure of bisthiazole derivatives **2** and **5**, the triphenylamine groups show almost planar conformation with respect to bisthiazole rings and the dihedral angle between them is 0.78°. The incorporation of the 1,1,4,4-tetracyanobuta-1,3-dienes (TCBD) groups results in loss of planarity in bisthiazole derivative **5** and the dihedral angle between the triphenylamine groups and bisthiazole rings is 84.62° (Figure 6.8).



Figure 6.8. Comparison of the dihedral angle of the optimized structures of (a) bisthiazole **2** (b) bisthiazole **5**.
The Figure 6.9 shows the electron density distribution of the HOMO and LUMO of the bisthiazoles **1**–**5** obtained by using DFT/B3LYP method. The HOMO in the bisthiazole derivatives **1** and **4** is delocalized over the ferrocenyl groups and LUMO is delocalized over thiazole groups and TCBD groups respectively. In bisthiazole **2** and **5** the HOMO is delocalized over the TPA and bisthaizole group whereas the LUMO is delocalized on the thiazole and TCBD groups respectively. In case of bisthaizole **3** the HOMO and LUMO is delocalized over the napthalimide and bisthiazole groups. Thus, the electron density transfer in bisthiazole **4** and **5** from ferrocenyl and TPA groups (HOMO) to thiazole and TCBD (LUMO) groups, which indicates strong charge transfer from HOMO to LUMO as compared to other bisthiazole systems. The HOMO-LUMO gap is lower in bisthiazole **5** as compared to other bisthiazoles due to the incorporation of TCBD as a strong acceptor.



Figure 6.9. The energy level diagram of the frontier molecular orbitals of the bisthiazole derivatives 1–5 calculated using B3LYP level of DFT theory.

6.7. Experimental section

General experimental procedures. All reagents were obtained from commercial sources, and used as received unless otherwise stated. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker Avance (III) 400 MHz instrument in CDCl₃ with TMS as internal standard. ¹H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl₃, 7.26 ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), and m (multiplet), and the coupling constants, J, are given in Hz. ¹³C NMR chemical shifts are reported relative to the solvent residual peak (CDCl₃, 77.36 ppm). Thermogravimetric analyses were performed on the Mettler Toledo Thermal Analysis system. UV-visible absorption spectra were recorded on a Cary-100 Bio UV-visible spectrophotometer. Cyclic voltamograms (CVs) were recorded on a CHI620D electrochemical analyzer using glassy carbon as the working electrode, Pt wire as the counter electrode, and the saturated calomel electrode (SCE) as the reference electrode. The scan rate was 100 mV s-1. A solution of tetrabutylammonium hexafluorophosphate (TBAPF6) in CH_2Cl_2 (0.1 M) was employed as the supporting electrolyte. DCM was freshly distilled from CaH_2 prior to use. All potentials were experimentally referenced against the saturated calomel electrode couple but were then manipulated to be referenced against Fc/Fc+ as recommended by IUPAC. Under our conditions, the Fc/Fc+ couple exhibited $E^{\circ} = 0.38$ V versus SCE. HRMS was recorded on a Bruker-Daltonics micrOTOF-Q II mass spectrometer.

General Procedure for the preparation of bisthiazole derivatives 1-3

Under argon atmosphere to a solution of 5,5'-dibromo-4,4'-dibutyl-2,2'bisthiazole (**a**) (0.1 g, 0.2 mmol) and the corresponding ethynyl derivative (0.44 mmol) in dry THF (20 ml) was added triethylamine (5 ml), Pd(PPh₃)₄ (0.018 g, 0.03 mmol), and reaction mixture was stirred for 16 h at 85 °C. After completion of the reaction, the reaction mixture was concentrated under reduced pressure and the crude compound was purified by column chromatography on silica. **bisthiazole 1:** This compound was eluted using hexane using hexane/ DCM (85:15 ν/ν) as a red solid (0.110 g, 71 %); ¹H NMR (400 MHz, CDCl3): δ = 4.55 (d, 4H, Cp'), 4.32 (m, 12H, Cp), 2.92 (t, 4H, CH₂), 1.84 (q, 4H, CH₂), 1.41 (m, 12H, CH₂-CH₂-CH₂), 0.93 (m, 6H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl3): δ = 162.25, 158.15, 128.61, 116.26, 98.53, 71.59, 70.12, 69.36, 31.65, 30.52, 29.14, 29.01, 22.67, 14.18 ppm; HRMS (ESI-TOF): m/z calculated for C₄₂H₄₄Fe₂N₂S₂ 753.1706 [M+H] found 753.1719.

bisthiazole 2: This compound was eluted using hexane/ DCM (75:25 v/v) as a yellow solid (0. 126 g, 71 %). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.38 (d, J = 8 Hz, 4H), 7.30 (m, 8H), 7.14 (m, 12H), 7.03 (d, J = 8 Hz, 4H), 2.93 (t, 4H), 1.83 (q, 4H), 1.45 (m, 12H), 0.9 (t, 6H) ppm. ¹³C NMR (CDCl₃, 100 MHz, ppm): 162.55, 158.48, 148.47, 147.03, 132.40, 132.17, 129.47, 125.19, 123.82, 121.98, 115.96, 115.06, 99.34, 79.17, 31.60, 29.11, 28.91, 28.70, 22.62, 14.13 ppm. HRMS (ESI-TOF): m/z calculated for C₅₈H₅₄N₄S₂ 871.3864 [M+H] found 871.3863.



Figure 6.10. Cyclic voltammograms of bisthiazole derivative **2** at $(1.0 \times 10-4 \text{ M})$ concentration in dichloromethane recorded at a scan rate of 100 mVs-1.



Figure 6.11. The comparison of experimental and calculated (TD-DFT at CAM-B3LYP level) absorption spectrum of bisthiazole **2** in DCM solution.

bisthiazole 3: compound eluted using hexane/ DCM (80:20) to get **3** as a orange solid (0. 115 g, 63 %). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.69 (t, 4H), 8.61 (d, J = 8 Hz, 2H), 7.99 (d, J = 8 Hz, 2H), 7.90 (t, 2H), 4.23 (t, 4H), 3.10 (t, 4H), 1.93 (t, 4H), 1.77 (t, 4H), 1.50 (m, 12H), 1.02 (t, 6H), 0.90 (t, 6H) ppm. ¹³C NMR (CDCl₃, 100 MHz, ppm): 166.48, 164.72, 163.88, 163.62, 159.87, 131.74, 130.73, 130.30, 127.72, 126.49, 123.22, 122.67, 114.99, 96.17, 89.20, 40.41, 30.95, 30.23, 29.66, 22.63, 20.41, 14.12 ppm. HRMS (ESI-TOF): m/z calculated for C₅₄H₅₄N₄S₂O₄ 886.3581 [M+] found 886.3989.



Figure 6.12. Cyclic voltammograms of bisthiazole derivative **3** at $(1.0 \times 10-4 \text{ M})$ concentration in dichloromethane recorded at a scan rate of 100 mVs-1.



Figure 6.13. The comparison of experimental and calculated (TD-DFT at CAM-B3LYP level) absorption spectrum of bisthiazole **3** in DCM solution.

General Procedure for the preparation of bisthiazole derivatives 4 and 5

A solution of alkyne derivative (0.1 g, 0.13 mmol) and TCNE (0.36 mmol) in dichloroethane was stirred for 16 h at 100 $^{\circ}$ C. After completion of the reaction, the reaction mixture was concentrated under reduced pressure, then the crude compound was purified by column chromatography on silica.

bisthiazole 4: This compound was eluted using hexane/ DCM (80:20 ν/ν) as a gray solid (0. 066 g, 49 %). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 5.62 (d, J = 8 Hz, 3H), 5.14 (d, J = 8 Hz, 2H), 4.95 (s, 2H), 4.52 (m, 9H), 2.79 (t, 4H), 1.86 (q, 4H), 1.43 (m, 12H), 0.85 (t, 6H) ppm. ¹³C NMR (CDCl₃, 100 MHz, ppm): 31.61, 31.58, 30.95, 29.40, 28.72, 22.52, 14.07 ppm. HRMS (ESI-TOF): m/z calculated for C₅₄H₄₄Fe₂N₁₀S₂ 1008.1873 [M+] found 1008.1888.

bisthiazole 5: This compound was eluted using hexane/ DCM (80:20 v/v) as a dark brown solid (0. 055 g, 42 %). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.65 (d, J = 8 Hz, 4H), 7.45 (m, 8H), 7.30 (m, 12H), 6.98 (d, J = 8 Hz, 4H), 2.85 (t, 4H), 1.89 (q, 4H), 1.41 (m, 12H), 0.90 (t, 6H). ¹³C NMR (CDCl₃, 100 MHz, ppm): 165.33, 163.56, 162.66, 159.13, 154.27, 144.27, 131.88, 130.22, 126.99, 118.19, 112.62, 111.33, 110.68, 89.91, 32.98, 31.62, 29.47, 28.79, 22.55, 14.07 ppm. HRMS (ESI-TOF): m/z calculated for C₇₀H₅₄N₁₂S₂ 1149.3928 [M+Na] found 1149.3922.



Figure 6.14. Cyclic voltammograms of bisthiazole derivative **5** at $(1.0 \times 10-4 \text{ M})$ concentration in dichloromethane recorded at a scan rate of 100 mVs-1



Figure 6.15. The comparison of experimental and calculated (TD-DFT at CAM-B3LYP level) absorption spectrum of bisthiazole **5** in DCM solution.

6.8. Conclusions

In summary, we have described the synthesis of donor –acceptor conjugated bisthiazole derivatives 1-5. Their photophysical, electrochemical properties and thermal stability can be tuned by varying the donor and acceptor groups. The bisthiazole derivative 5 shows good electronic communication between the TPA

groups and TCBD acceptor as compared to others. The optical and electrochemical properties of the bisthiazole derivatives were explained from the TD-DFT calculations. The [2+2] cycloaddition-retroelectrocyclization reaction pathway has been studied by theoretical calcualtions. These studies show that, the terminal positions of the bisthiazole substituted by electron donor groups are favorable for the TCNE reaction whereas bisthiazole terminals substituted by electron withdrawing groups are unfavorable for [2+2] cycloaddition-retroelectro cyclization reactions. The optical limiting properties of these materials are currently ongoing in our laboratory.

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Chapter 7

Donor-Acceptor Triphenylvinyl and Tetraphenyl Conjugates: Synthesis, Aggregation- Induced Emmission, Aggregation-Caused Quenching and TD-DFT Studies

7.1. Introduction

The donor-acceptor molecular systems has been widely studied in the field of material applications such as Organic photovoltaics (OPVs), Aggregation induced emission (AIE), Organic field effect transistors (OFETs), Mechanochromism, and Nonlinear optics (NLO).¹⁻¹⁰ In aggregation-induced emission (AIE) the aggregation of luminogens show a constructive role in improving the light-emission efficiency. It provides a unique platform for the investigation of essentially useful luminescent materials.¹¹⁻¹³A variety of AIE-active luminogens with tunable emission colors and high quantum yields in the solid state have been reported, which exhibits technological applications in a broad range of fields including microchip, energy and bioscience technology.^{14,15} Quenching of emission which is mainly caused by the "formation of aggregates", commonly known as "aggregation-caused quenching" (ACQ)^{16,17} lacks in practical applications like organic light-emitting diodes, solid-state lasers, etc. ¹⁸⁻²¹ due to the quenching of emission in solid state.

The electron receiving nature of the thiazole ring is recognized due to the presence of electron-withdrawing nitrogen of the imine (–C=N) and functionality ²² and has been widely used in the construction of π -conjugated D-A molecular systems.²² We have recently reported Aggregation induced emission of thiazoles of tetraphenyl (TPE) derivatives.⁸ In this chapter, we report a bisthiazole compound **4** with two triphenylvinyl (TPV) units which exhibits aggregation

induced emission (AIE) phenomena and tetraphenyl (TPV) substituted triphenylamine-oxazole **5** exhibits aggregation-caused quenching emission (ACQ) phenomena.

7.2. Results and discussion

The triphenylvinyl (TPV) substituted bisthiazole (**4**) and tetraphenylethylene oxazole (**5**) were synthesized by the Suzuki cross-coupling reactions of 4,4,5,5-tetramethyl-2-(1,2,2-triphenylvinyl)-1,3,2-dioxaborolane (**1**) with bromosubstituted bisthaiazole (**2**) and oxazole (**3**) derivatives respectively. All the starting materials, 4,4,5,5-tetramethyl-2-(1,2,2-triphenylvinyl)-1,3,2-dioxaborolane (**1**), 5,5'-dibromo-4,4'-dibutyl-2,2'-bisthiazole (**2**) and 4-(5-(4-bromophenyl)-1,3,4-oxadiazol-2-yl)-N,N-diphenylaniline (**3**) were synthesized by reported procedures.²³⁻²⁵

The 5,5'-dibromo-4,4'-dibutyl-2,2'- bisthiazole (2) was reacted with 4,4,5,5tetramethyl-2-(1,2,2-triphenylvinyl)-1,3,2-dioxaborolane (1) under the Suzuki coupling reaction condition which resulted 4,4'-dihexyl-5,5'-bis(1,2,2triphenylvinyl)-2,2'-bithiazole 4 in 60% yield. The 4,4,5,5-tetramethyl-2-(1,2,2triphenylvinyl)-1,3,2-dioxaborolane (1) was treated with 4-(5-(4-bromophenyl))-(4-bromophenyl)1,3,4-oxadiazol-2-yl)-N,N-diphenylaniline (3) in the presence of $Pd(PPh_3)_4$ catalyst, THF:MeOH (2:1 ν/ν) mixture as a solvent and K₂CO₃ used as a base resulted N,N-diphenyl-4-(5-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,4-oxadiazol-2yl)aniline 5 in 65% yield (Scheme 7.1). All the compounds were well characterized by ¹H, ¹³C–NMR, and HRMS spectroscopic techniques.



Scheme 7.1. Synthesis of TPV 4 and TPE 5.

7.3. Thermal stability

The thermal stability of the **4** and **5** were studied using thermogravimetric analysis (TGA) at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere (Figure 7.2). The TPE-oxazole derivative **5** shows better thermal stability (10% weight loss at 252 °C) as compared to the TPV substituted bisthiazole **4** (10% weight loss at 226 °C).



Figure 7.1. TGA plots of TPV 4 and TPE 5.

7.4. Photophysical properties

The electronic absorption spectra of the triphenylvinyl (TPV) systems 4 and tetraphenylethylene **5** were recorded in tetrahydrofuran (THF) at room temperature and the photophysical data are listed in Table 7.1. The triphenylvinyl (TPV) substituted bisthiazole derivative **4** and TPE-oxazole derivative **5** shows absorption band between 291–365 nm corresponding to $\pi \rightarrow \pi^*$ transition.

The TPV bisthiazole **4** exhibits significant (76 nm) blue shift as compared to TPV oxazole **5**. The TPE **5** exhibits red shift in the absorption maxima ($\pi \rightarrow \pi^*$) as compared to the TPV **4**. The TPV **4** and TPE **5** show fluorescence maxima at 404 nm and 449 nm respectively (Figure 7.3).



Figure 7.2. Normalized electronic spectra of the TPV **4** and TPE **5** (a) UV-vis spectra and (b) fluorescence spectra in THF.

Table 7.1.	Photophysical	and thermal	properties of	of the TP	V 4 and TPE 5
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Compounds	$\lambda_{max}[nm]$	Emission	$T_d(^{\circ}C)^b$
	$(\varepsilon[\text{Lmol-cm}^{-1}])^{a}$	$\lambda_{max}[nm]^{a}$	
4	291 (78361)	404	226
	347		
5	365 (75073)	449	252

^aMeasured in tetrahydrofuran (THF). ^bDecomposition temperatures for 10% weight loss at a heating rate of 10 $^{\circ}$ C min⁻¹, under nitrogen atmosphere.

Aggregation-induced emission phenomenon:

The AIE phenomenon of TPV **4** was studied in THF–water medium with different water fractions. The emission spectrum of TPV **4** shows Aggregation-induced emission (AIE) behavior upto 60% water fraction (f_w), further addition of water results in fluorescence quenching due to the $\pi \rightarrow \pi$ stacking.²⁶ The quantitative estimation of the AIE process was obtained by calculating the

fluorescence quantum yield for TPV **4** in the mixtures of water and THF in various proportions using 9, 10-diphenylanthracene as standard. In pure THF solution the TPV **4** exhibits fluorescence quantum yield 0.04, which was increased to 0.52 at 60% water fraction and then again decreased to 0.001 at 90% water fraction. The fluorescence images of TPV **4** in THF–water medium with different water fractions under UV illumination are shown in Figure 7.4 which clearly shows different AIE behavior.²⁷



Figure 7.3. (a) Emission spectra of TPV **4** (10^{-5} M) in THF/H₂O medium with different volume fractions of water. ($\lambda_{ex} = 292$ nm) (b) Fluorescence images of **4** in the presence of different THF/Water fractions under UV light.

Aggregation-caused quenching phenomenon:

The aggregation behavior of TPE **5** was investigated in THF/water mixture. The emission spectra of TPE **5** show significant bathochromic shift on increasing water fraction (f_w) from 0% – 60%. On increasing water fractions (f_w) from 60% – 90%, TPE **5** show blue shift in emission. The quenching in emission intensity due to the aggregation-caused quenching (ACQ) effect which is assigned to be charge transfer from TPA to TPE through oxazole ring as shown in Figure 7.5.^{26,27}



Intramolecular charge transfer

from triphenylamine to TPE through oxazole bridge



Figure 7.4. a) Emission spectra of TPE **5** (10^{-5} M) in THF/H₂O medium with different volume fractions of water. ($\lambda_{ex} = 366$ nm). (b) Fluorescence images of **4** in the presence of different THF/Water fractions under UV light. (c) Charge transfer from TPA to TPE through oxazole ring.

7.5. Time dependent density functional (TD-DFT) studies:

In order to understand the photophysical properties of TPV **4** and TPE **5** the density functional theory (DFT) and time dependent density functional (TD-DFT) calculation was performed. The structures **4** and **5** were optimized using B3LYP. The solvent calculations were carried out in the tetrahydrofuran (THF) using the

polarized continuum model (CPCM) of Gaussian 09 software. The 6-31G** basis set for C, H, N, S was used for all the calculations.^{28, 29}

The TPV core in **4** and **5** shows non planar conformation with respect to bisthiazole and oxazole ring. The dihedral angle between Tetraphenyl and bisthiazole is 114.87°, whereas angle between Tetraphenyl and oxazole rings was found to be 122.65° (Figure 7.6).



Figure 7.5. Geometry optimized structures of the TPV **4** and TPE **5** with Gaussian 09 at the TD-DFT, B3LYP/6-31G** level of theory.

The TD-DFT predicted vertical excitation energies of **4** and **5** are shown in Figure 7.7, along with individual experimental UV-vis and emission spectra. The major intense transitions in the TPV **4** and TPE **5** are π - π * in nature. The strong absorption band calculated at CAM-B3LYP level are 374 nm and 344 nm for **4** and **5** respectively. The experimental values for these transitions are 291 nm and 385 nm for **4** and **5** respectively. These results show good agreement with the experimental values (Table 7.2).



Figure 7.6. Comparison of experimental and calculated (TD-DFT at CAM-B3LYP level) absorption spectrum of (a) bisthiazole **4** and (b) bisthiazole **5** in DCM solution.

Table 7.2. Computed vertical transition energies and their Oscillator strengths (f) and major contributions for the TPV **4** and TPE **5**.

Compounds	TD-DFT/ B3LYP (DCM)			
	λ_{max}	f	Major contribution (%)	
4	374 nm	1.0295	HOMO→LUMO (86%)	
5	344 nm	1.8168	HOMO →LUMO (82%)	

The Figure 7.8 shows the electron density distribution of the HOMO and LUMO of the TPV 4 and TPE 5 obtained using DFT/B3LYP method. The HOMO and LUMO in the TPV 4 is delocalized over the TPE and thiazole groups respectively. The TPE oxazole 5 shows HOMO delocalized over the TPA group only while the LUMO is located on the oxazole and TPE groups. Thus, the electron density transfer in TPE system 5 from TPA group (HOMO) to oxazole and TPE (LUMO) group, which indicates strong charge transfer from HOMO to LUMO as compared to the TPV system 4. The HOMO-LUMO gap is lower in TPV system 4 as compared to the TPE system 5 due to the incorporation of TPA as a strong donor.



Figure 7.7. The energy level diagram of the frontier molecular orbitals of the TPV **4** and TPE **5** calculated using B3LYP level of DFT theory.

7.6. General procedure for the preparation of TPV 4 and TPE 5

Synthesis of TPV system 4

In argon atmosphere a solution of compound **2** (0.10 g, 0.02 mmol) and compound **1** (0.17 g, 0.04 mmol) in dry THF (10 ml), methanol (5 ml), water (2 ml) was added K₂CO₃ (0.35 g, 0.25 mmol) followed by Pd(PPh₃)₄ (0.03 g, 0.003 mmol) and the mixture was stirred for 16 h at 90 °C. After completion of the reaction, the reaction mixture was concentrated under reduced pressure and the crude compound was purified by column chromatography on silica, using hexane/ DCM (75:25 ν/ν) as eluent to get **4** as a white solid (0.12 g, 70%); ¹H NMR (400 MHz, CDCl₃): δ = 7.32 (m, 30H), 2.52 (t, 4H), 1.49 (t, 4H), 1.28 (m, 12H), 0.85 (t, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 157.73, 151.42, 143.70, 142.37, 140.15, 137.63, 137.31, 130.67, 130.36, 130.03, 129.47, 128.27, 128.05, 127.54, 127.29, 126.85, 32. 61, 31.19, 31. 16, 26.45, 22.32, 14.11 ppm; HRMS (ESI-TOF): m/z calculated for C₅₈H₅₆N₂S₂ 845.3958 [M+H] found 845.3944.

Synthesis of TPE systems 5

In argon atmosphere a solution of compound **3** (0.1 g, 0.025 mmol) and compound **1** (0.136 g, 0.035 mmol) in dry THF (10 ml), methanol (5 ml), water (2 ml) was added K₂CO₃ (0.350 g, 0.25 mmol) followed by Pd(PPh₃)₄ (0.035 g, 0.003 mmol) and mixture was stirred for 16 h at 90 °C. After completion of the reaction, the reaction mixture was concentrated under reduced pressure and the crude compound was purified by column chromatography on silica, using hexane/ DCM (85:15 ν/ν) as eluent to get **5** as a green solid (0.09 g, 54%); ¹H NMR (400 MHz, CDCl₃): δ = 7.97 (dd, *J* = 8 Hz, 2H), 7.86 (d, *J* = 8 Hz, 2H), 7.35 (t, 6H), 7.18 (m, 23H) ; ¹³C NMR (100 MHz, CDCl₃): δ = 164.00, 150.92, 146.70, 139.99, 131.36, 129.81, 129.61, 127.99, 125.67, 124.38, 121.17 ppm; HRMS (ESI-TOF): m/z calculated for C₄₆H₃₃N₃O₁ 644.2696 [M+H] found 644.2718.

7.7. Conclusions

In summary, we have described the synthesis of C_1 , C_2 -symmetric TPV 4 and TPE 5. Their photonic, computational and thermal properties were studied. The TPV 4 shows aggregation-induced emission (AIE) behavior and TPE 5 shows aggregation-caused quenching (ACQ) effect in THF/water medium. The TD-DFT calculation reveals that TPE 5 shows good electronic communication between the TPA group to oxazole acceptor. These results show the design of new materials for optoelectronic applications.

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Chapter 8

Conclusions and Future Scope

8.1. Conclusions

The bisthiazole (BTz) unit is a good acceptor and its derivatives exhibit red shifted absorption, high fluorescence quantum yield and high thermal stability.^{1,2} The photonic properties of BTz derivatives can be tuned by various π -linkers, π -donors and π -acceptors.³ We have functionalized BTz with various donor/acceptor units in symmetrical fashion to tune photophysical and electrochemical properties.⁴

In Chapter 3, the BTz were functionalized with ferrocenyl donor unit at the 3- and 3'-positons through various π -spacers and π -linkers. Their photophysical, electrochemical and computational studies reveal strong donor-acceptor interaction.⁵

In Chapter 4, Triarylborane substituted bisthiazole was designed and synthesized by the Sonogashira cross-coupling reaction for selective detection of F^- and CN^- ions in the presence of Cl^- , Br^- , I^- and NO_2^- anions. The detection limit for F^- and CN^- were found to be 5.7×10^{-6} M and 2.1×10^{-6} M respectively. The time dependent density functional theory (TD-DFT) calculation at B3LYP on the bisthiazole triarylborane was studied for F^- and CN^- ions.⁶

Chapter 5 describes the design and synthesis of ferrocenyl (donor) bisthiazole linked triphenylamine (donor) based donor- π -acceptor- π -donor-acceptor [(D- π -A)₂- π -D-A] type dyes by using Pd-catalyzed Sonogshira cross-coupling and Knoevenagel condensation reactions. Their photophysical, electrochemical and computational studies reveal strong donor-acceptor interaction. The Dye sensitized solar cells (DSSCs) based on **D1** and **D2** exhibit the power conversion efficiency (PCE) of 6.33% and 5.03% respectively.⁷

In chapter 6 the C_s-Symmetric D- π -A- π -D and D-A₁-A-A₁-D bearing a variety of electron donating and electron withdrawing groups were designed and

Sonogashira cross-coupling synthesized via Pd-catalyzed and [2+2]cycloaddition-retroelectrocyclization reactions. Their photophysical, electrochemical properties and computational studies were explored which show strong donor acceptor interaction. In this chapter [2+2] cycloadditionretroelectrocyclization reaction pathway has been studied by computational calcualtions, which reveals that when bisthiazole terminal positions are substituted by donor groups are favorable for the cycloaddition reaction while bisthiazole substituted by withdrawing groups are unfavorable for [2+2] cycloaddition-retroelectrocyclization reactions.

Chapter 7 describes the design and synthesis of triphenylvinyl (TPV) substituted bisthiazole **4** and tetraphenylethylene (TPE) substituted triphenylamine oxazole **5** by using Pd-catalyzed Suzuki cross-coupling reaction. Their photophysical, aggregation induced emission (AIE), Aggregation-caused quenching (ACQ) properties and computational studies were studied. The TPV **4** shows Aggregation-induced emission (AIE) behavior and TPE **5** shows complete aggregation-caused quenching (ACQ) effect in THF/water mixture due to the $\pi \rightarrow \pi$ stacking. The thermal stability of the TPV **4** and TPE **5** are reported, in which TPE **5** show good thermal stability as compared to TPV **4**.

8.2. Future scope

- The thesis highlights the tuning of HOMO–LUMO gap of a series of donor-acceptor small molecules reported. The HOMO–LUMO gap of the donor-acceptor molecules can be tuned by changing the π -linkers. The increase of donor/acceptor strength results in significant tuning of the optical (HOMO–LUMO) gap as well photophysical, electrochemical and dye-sensitized solar cells (DSSCs).⁸⁻¹⁵
- The triarylborane substituted bisthiazole selectively detects F⁻ and CN⁻ ions in the presence of Cl⁻, Br⁻, I⁻ and NO₂⁻ anions which makes them useful in sensing applications.¹⁶⁻¹⁸

8.3. References

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