Design and Synthesis of Push-Pull Functionalized Benzothiadiazole Chromophores

Ph.D. Thesis

By **Yogajivan Rout**



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Design and Synthesis of Push-Pull Functionalized Benzothiadiazole Chromophores

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

> *by* **Yogajivan Rout**



DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE May 2021



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled –" Design and Synthesis of Push-Pull Functionalized Benzothiadiazole Chromophores", in the partial fulfilment 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 28 Dec 2015 to 13 May 2021, under the supervision of Dr.Rajneesh Misra, Professor, Indian Institute of Technology Indore.

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

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

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IIT Indore

DEDICATION TO MY TEACHERS, FAMILY AND FRIENDS

-Yogajivan

Synopsis

2,1,3-Benzothiadiazole (BTD) is a strong electron withdrawing unit, widely employed in organic electronics due to its strong electron affinity (EA) and high reduction potential. BTD is a fused bicyclic-heteroarene in which benzene ring is connected with diazole based five-membered ring, where one of the C atom in the diazole ring is replaced by an S atom (Figure. 1). The 2,1,3-benzothiadiazole unit acts as a powerful electron deficient unit due to the presence of imine functional unit in the diazole ring, and contains four reactive sites (4-, 5-, 6- and 7-positions) (Figure 1), which can be easily functionalized by the incorporation of donor or acceptor units. The substitution of donor or acceptor units at the 4,7positions of BTD unit results in a linear shape, whereas substitution of donor or acceptor units at the 5,6-positions exhibits a butterfly shape. The functionalization at 4,7-positions of BTD unit results in molecular systems with excellent photophysical properties including broad absorption spectra, higher molar absorptivities, better quantum yield and solvatofluorochromic effects, whereas functionalization at the 5,6positions of the BTD core results in inefficient π -conjugation due to high torsional angle. The introduction of donor-acceptor units at 4,7-positions and 5,6-positions of BTD unit offers push-pull systems with excellent solid state photoluminescence quantum yield, which are suitable candidates for organic light emitting diodes (OLEDs). The BTD chromophores exhibit outstanding performance in photovoltaic devices like dye sensitized solar cells (DSSCs), bulk heterojunction organic solar cells (BHJOSCs), nonlinear optics (NLOs), organic field-effect transistors (OFETs), hole transporting materials (HTMs) owing to its high reduction potential and strong electron-withdrawing capacity. The BTD chromophores exhibit strong fluorescence quantum yield and good photostability due to which the chromophores have been used for the detection of metal ions $(Cu^{2+}, Hg^{2+}, Fe^{3+})$ and acetate anions. In the recent

years, BTD based fluorescent chromophores have been utilized as a new class of bio-probes due to its favorable photophysical properties including large stokes shifts and better thermal stability.



Figure 1. The molecular structure of 2,1,3-Benzothiadiazole core. Note that, R_1 , R_2 , R_3 and R_4 are the reactive sites used for π -extensions.

A wide variety of donors (ferrocene, triphenylamine, carbazole, phenothiazine *etc.*) and acceptors (1,1,2,2-tetracyanoethylene 7,7,8,8-tetracyanoquinodimethane and 1,8-naphthalimide, *etc.*) were introduced at 4,7-positions of BTD unit to tune the photonic properties. The photophysical and electrochemical properties of the donor–acceptor functionalized benzothiadiazole derivatives were investigated.

The main objectives of the current work are:

- To design and synthesize donor functionalized benzothiadiazole derivatives for photonic studies.
- To synthesize symmetrical and unsymmetrical benzothiadiazole derivatives by varying the donor/acceptor units at 4- and 7positions.
- To study the effect of donor and acceptor strength on the photophysical and electrochemical properties.

- To tune the HOMO–LUMO gap by using the multi donor and acceptor units in the π-conjugated systems.
- To explore the electronic structure, distribution of electron density over the HOMO and LUMO energy levels and photophysical properties of the donor-acceptor functionalized benzothiadiazole by density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations.



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

Chapter 1: Introduction

This chapter describes the synthesis and functionalization strategies of 2,1,3-Benzothiadiazole derivatives, and their applications in diverse fields.

Chapter 2: Materials and experimental techniques

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

Chapter 3: Aryl substituted unsymmetrical benzothiadiazole chromophores

Chapter 3 describes the design and synthesis of a series of ferrocenyl functionalized unsymmetrical and symmetrical BTDs **2a–2g** *via* [2+2] cycloaddition–retroelectrocyclization reaction utilizing different additional donor groups. The photophysical and electrochemical properties of the BTDs **2a–2g** were systematically studied. The absorption spectra of BTDs **2a–2g** exhibit a strong electronic absorption band in the visible region of the electromagnetic spectrum, which corresponds to the intramolecular charge transfer (ICT). The electrochemical studies of BTDs **2a–2g** exhibit a strong electronic absorption band in the visible region of an additional tetracyanobutadiene (TCBD) acceptor. The computational studies reveal that the incorporation of an additional TCBD unit and systematic variation of terminal donor groups are the key factors to tune the HOMO–LUMO energy levels. The structure of the BTD **2c** was confirmed by single crystal X-ray diffraction analysis.



Figure 3. Normalized electronic absorption spectra of (a) mono-TCBD substituted BTDs 2a-2e and (b) di-TCBD substituted BTDs 2f and 2g in dichloromethane at 1.0×10^{-5} M concentration.

Chapter 4: Design and synthesis of push–pull based triphenylamine and *N*,*N*-dimethylaniline substituted benzothiadiazoles

The usage of multi-modular donor-acceptor chromophores in light harvesting and optoelectronic devices has gained significant interest. A series of triphenylamine and N,N-dimethylaniline functionalized benzothiadiazole derivatives BTD2-BTD4 and BTD6-BTD8 were designed by and synthesized [2+2]cycloadditionretroelectrocyclization reactions of BTD1 and BTD5 with TCNE and TCNQ units. In these derivatives triphenylamine and N,Ndimethylaniline were used as end-capping electron rich unit and benzothiadiazole used as central unit core, was whereas tetracyanobutadiene TCBD and cyclohexa-2,5-diene-1,4-diylideneexpanded TCBD (expanded TCBD) units were used as electron deficient units. The electron-deficient building blocks TCBD and expanded TCBD were introduced in the donor-acceptor systems to tune the photonic properties.



Figure 4. The electronic absorption spectra of (a) **BTD1–BTD4** and (b) **BTD5–BTD8** in dichloromethane $(1 \times 10^{-5} \text{ M})$.

The triphenylamine and *N*,*N*-dimethylaniline functionalized benzothiadiazole derivatives **BTD2–BTD4** and **BTD6–BTD8** exhibit strong and wide electronic absorption band in the visible-near IR regions due to presence of electron-deficient cyano based acceptors units. Electrochemical and computational studies were performed to evaluate their redox potentials and their electronic structures.

Chapter 5: NIR absorbing benzothiadiazole based multimodular push-pull chromophores

A series of symmetrical and unsymmetrical push-pull chromophores BTD1–BTD6 were designed and synthesized in which benzothiadiazole (BTD) was used as a central unit core, phenothiazine and triphenylamine entity as end-capping donor units, 1,1,4,4tetracyanobutadiene (TCBD) and cyclohexa-2,5-diene-1,4-diylideneexpanded TCBD as auxiliary acceptors. The cyano based acceptors TCBD and expanded TCBD were introduced by the [2 + 2]cycloaddition-retroelectrocyclization (CA-RE) reaction of BTD1 and BTD4 with electron acceptors TCNE and TCNQ units to tune the photonic properties. The photophysical properties of BTD1-BTD6 demonstrate that the TCBD and expanded TCBD substituted derivatives BTD2, BTD3, BTD5 and BTD6 exhibit a broad absorption band in the vis-NIR region compared to BTD1 and BTD4 due to strong intramolecular charge transfer (ICT) transition. The electrochemical studies on BTD1-BTD6 explained that the presence of powerful acceptor benzothiadiazole unit and additional cyano based acceptors TCBD and expanded TCBD units tune the HOMO-LUMO energy level significantly. Theoretical calculations revealed that derivatives BTD1-BTD6 show non-planar structure due to the butterfly structure of phenothiazine unit and twisted structure of TCBD and expanded TCBD unit.



Figure 5. The electronic absorption spectra of (a) **BTD1–BTD3** and (b) **BTD4–BTD6** in dichloromethane $(1 \times 10^{-5} \text{ M})$.

The electron density of HOMO for all these derivatives were localized on the phenothiazine unit whereas the LUMO were delocalized over the acceptor (benzothiadiazole, TCBD and expanded TCBD) units. The TCBD derivative **BTD5** shows regioisomeric mixture of **BTD5** and **BTD5**'.

Chapter 6: Design and synthesis of 1,8-Naphthalimides functionalized benzothiadiazole chromophores

A series of multi acceptor based push-pull derivatives **BTD2–BTD5** were designed and synthesized *via* Pd-catalyzed Sonogashira cross-coupling reaction followed by [2+2] cycloaddition–electrocyclic ring-opening reaction in which benzothiadiazole (BTD, A1), naphthalimide (NPI, A2), tetracyanobutadiene (TCBD, A3) or cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD (expanded TCBD, A4) moieties were used as an electron-withdrawing units and triphenylamine (TPA), ferrocene (Fc) units were used as anelectron donating units. The incorporation of cyano based strong acceptors TCBD and expanded TCBD in the naphthalimide functionalized benzothiadiazole derivatives **BTD1** and **BTD4** results with

improved light harvesting properties. The photophysical properties for the benzothiadiazole chromophores **BTD1–BTD5** explained that the chromophore **BTD3** exhibit broad electronic absorption spectra in the near IR regions compared to **BTD1**, **BTD2**, **BTD4** and **BTD5** due to presence of expanded TCBD unit.



Figure 6. The electronic absorption spectra of **BTD1–5** in dichloromethane solvent.

The electrochemical properties reveal that the benzothiadiazole derivatives **BTD1–BTD5** exhibit multiple number of redox waves in the cyclic voltammetry due to the presence of several acceptor units (BTD (A1), NPI (A2), TCBD (A3), expanded TCBD (A4)) and donor units (TPA (D1) and Fc (D2) units). The theoretical calculation demonstrates that the electron density of HOMO energy level is mainly localized on the TPA and Fc units whereas LUMO is delocalized over the acceptors (BTD-NPI, TCBD-BTD and expanded TCBD-BTD) segments.

Chapter 7: Design and synthesis of di-benzothiadiazole based chromophores

Benzothiadiazole based push-pull chromophores **BTD1**, **BTD2** and **BTD3** with structural configuration D'- π -A- π -D- π -A- π -D', D"- π -A- π -D- π -A- π -D" and D"'-A- π -D- π -A-D" were designed and synthesized. In these chromophores, the variation of donor unit and π -linker units are the key factor in tuning the photophysical and electronic properties, which was systematically investigated by the photophysical, electrochemical and computational studies. The photophysical properties of chromophores **BTD1**, **BTD2** and **BTD3** demonstrate that the triphenylamine substituted chromophore **BTD1** exhibits red-shifted wide electronic absorption band compared to the **BTD2** and **BTD3** due to the altering of end-capping donor units. The cyclic voltammogram of **BTD1**, **BTD2** and **BTD3** explained that the presence of benzothiadiazole entity as powerful acceptor in the molecular system enhanced the π -conjugation and tuned the HOMO–LUMO energy levels.



Figure 7. The electronic absorption spectra of **BTD1**, **BTD2** and **BTD3** in dichloromethane $(1 \times 10^{-5} \text{M})$.

The computational studies revealed that there was a good agreement with experimental data. The HOMO energy level of **BTD1** was delocalized over whole molecular system whereas for **BTD2** and **BTD3**, it was mainly localized on phenothiazine entity and LUMO energy level was localized only on acceptor (benzothiadiazole) unit for **BTD1**, **BTD2** and **BTD3**.

Chapter 8: Conclusions and Future Scope.

Chapter 8 summarizes the salient features of the work and the possibilities for the development of new materials for optoelectronic applications.

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- † Papers pertaining to the thesis.
- \$ Authors having equal contribution.

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ACRONYMS

D–A	Donor-acceptor
SCXRD	Single Crystal X-ray diffraction
NMR	Nuclear Magnetic Resonance
PPh ₃	Triphenylphosphin
DMF	Dimethylformamide
DCM	Dichloromethane
Ph	phenyl
IR	Infrared
UV-Vis	UV-Visible Spectroscopy
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
Chapter 1

Introduction

1.1. Background

Push-pull chromophores with extended π -conjugation have emerged as an attractive class of semiconducting materials in the scientific community due to their vast applications in the field of optoelectronics, data storage, OLEDs, and biological studies.^[1] The photonic and electronic properties of the push-pull systems can be easily tuned by altering the strength of donor and acceptor units in the π -conjugated systems.^[2] The introduction of hetero atom based aromatic units in these push-pull chromophores further helps to fine tune the frontiers energy levels.^[3]



Figure 1.1. Schematic representation of push–pull chromophores and their frontier molecular orbital diagram.

Heterocyclic π -conjugated chromophores have been widely employed in various optoelectronic devices to enhance the device performance as well as to improve the photo-thermal and photochemical stability. The most commonly used heterocyclic π conjugated donor and acceptor entities are shown in Chart 1.1.



Chart 1.1. Examples of push and pull moieties.

The combination of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of push and pull units in the push-pull systems result in a set of new HOMO and LUMO energy levels shown in Figure 1.1, which is more tuned compared to individual HOMO and LUMO energy levels of push and pull units and also exhibited narrow energy gap. Thus, the HOMO–LUMO energy gap of organic chromophores can be effectively perturbed by altering the donor and acceptor units in the push-pull systems.^[4] The combination of donor-acceptor entities in various structural architecture like D-A-D, A-D-A, D-A, D- π -A- π -D, A- π -D- π -A, D-A-D-A-D and A-D-A-D-A are of great interest due to easy synthetic modification and can be utilized in several material and biological applications;

[1] Organic light emitting diodes (OLEDs)^[5]

- [2] Dye sensitized solar cells (DSSCs)^[6]
- [3] Bulk heterojunction organic solar cells (BHJ OSCs)^[7]
- [4] Perovskite solar cells (PSCs)^[8]
- [5] Non-linear optics (NLOs)^[9]
- [6] Organic field effect transistors (OFETs)^[10]
- [7] Bio imaging^[11]

1.2. Benzothiadiazole (BTD)

2,1,3-Benzthiadiazole (BTD) is one of the most widely studied chromophore due to its relatively high reduction potential, strong electron-withdrawing capacity, and better thermal stability. ^[12] The BTD unit is a fused bicyclic-heteroarene in which the benzene ring is combined with diazole based five-membered ring where one of the carbon atom in the diazole ring is substituted by the S atom (Figure. 1.2.).



Figure 1.2. Molecular structure and numbering system of 2,1,3-Benzothiadiazole (BTD).

The BTD unit possesses high electron affinity and acts as a n-type electronic material in several optoelectronic applications including bulk heterojunction solar cell, perovskite solar cell, OLEDs and organic field-effect transistors (OFETs) due to the presence of imine functional unit in the diazole ring.^[13] In the BTD unit, 4- and 7-positions can be easily functionalized with various donor-acceptor units, which can further improve the π -conjugation and perturb the HOMO–LUMO gap to a greater extent.^[14] The π -

extended BTD derivatives exhibit excellent features with several benefits, out of which few of the important points are highlighted below;

- (1) BTD contains the heterocyclic five-membered ring (C=N-S-N=C) which endows the core with high electron affinity.
- (2) Donor–acceptor BTD systems exhibit strong absorption with high molar extinction coefficient in the visible region.
- (3) The BTD unit possesses a strong electron-withdrawing character which facilitates intramolecular charge transfer (ICT) in BTD based donor-acceptor chromophores.
- (4) Donor-acceptor BTDs are efficient luminescent materials.
- (5) Donor-acceptor BTD systems exhibit various intermolecular interactions including heteroatom interactions and $\pi \pi$ interactions.
- (6) Donor–acceptor BTD chromophores exhibit excellent thermal and photochemical stability.
- (7) Donor–acceptor BTD systems allow easy synthetic modification there by lowering the HOMO–LUMO gap.
- (8) Donor-acceptor BTD chromophores exhibit large Stokes shifts.

1.3. Classification of donor-acceptor functionalized benzothiadiazole

In the benzothiadiazole unit, there are two reactive sides (4-, 7positions) (Figure 1.2.), which can be easily functionalized by the synthetic modification in order to extend the π -conjugation and modulate the photonic properties.



Figure 1.3. General classification of donor-acceptor substituted benzothiadiazole in this work.

The donor/acceptor substituents were introduced to the benzothiadiazole unit either *via* spacer (π -linker) or without spacer which resulted in formation symmetrical and unsymmetrical chromophores (Figure 1.3).

The mono substituted derivatives were mainly synthesized by the incorporation of donor/acceptor units at the 4- or 7-position of benzothiadiazole unit whereas di-substituted derivatives were synthesized by the reaction of donor/acceptor unit at both 4- and 7-positions.

1.4. Synthesis of Benzothiadiazole derivatives

The benzothiadiazole unit with high reduction potential, intense luminescence properties and strong electron affinity (EA) acts as an excellent candidate for the organic electronic materials as well as biological applications. ^[15] In the past few years, scientific community has widely explored the push-pull functionalized benzothiadiazole chromophores for various applications such as, OLEDs,^[16] dye sensitized solar cells (DSSCs),^[17] bulk heterojunction organic solar cells (BHJOSCs),^[18]perovskite solar cells,^[19] NLOs,^[20] OFETs,^[21]sensing,^[22]bioimaging,^[23] and many

more. The procedure of synthesizing the benzothiadiazole unit is discussed in the following section.

1.4.1. Synthesis of 2,1,3-benzothiadiazole (BTD)

The reaction of commercially available o-phenylenediamine with freshly distilled thionyl chloride in the presence of trimethylamine in dichloromethane solvent resulted in BTD in 93% yield (Scheme 1.1).^[24]



Scheme 1.1. Synthesis of BTD.

1.4.2. Synthesis of 4,7-dibromo-BTD and 5,6-dibromo-BTD

4,7-dibromo-BTD is used as a most common precursor for the synthesis of π -extended donor-acceptor chromophores. 4,7-dibromo-BTD was easily synthesized by reaction of 2,1,3-benzothiadiazole with molecular bromine in hydrobromic acid in 98% yield (Scheme 1.2).^[25]



Scheme 1.2. Synthesis of 4,7-Dibromo-BTD.



Scheme 1.3. Synthesis of 5,6-dibromo-BTD.

5,6-dibromo-BTD is also used as an active precursor for the synthesis of π -extended donor-acceptor chromophores. In this process o-Phenylenediamine **1** was reacted with *p*-toluenesulfonyl chloride (TsCl) in the presence of dry pyridine to form the derivative **2** (Scheme 1.3). The derivative **2** was reacted with bromine in the presence of acetic acid under an ice-cooled temperature to form the derivative **3**, which further reacts with sulphuric acid at 110 °C to form the derivative **4**. The derivative **4** was reacted with thionyl chloride in the presence of dry dichloromethane to form 5,6-dibromo-BTD.^[25]

1.4.3. The substitution of donor and acceptor units at 4,7-positions and 5,6-positions of BTD core

Donor-acceptor functionalization at the 4,7-positions of BTD unit exhibits linear shape π -conjugation however the functionalization at 5,6-positions of BTD core shows butterfly shape π -conjugation. The 5,6-positions of BTD core possesses inefficient π -conjugation due to its higher torsional angle and mainly used in mechanochromic properties and light emitting materials application, whereas 4,7-positions of the BTD core possesses excellent photophysical properties including broad absorption spectra, higher molar absorptivities, better quantum yields, larger solvatofluorochromic effects and also shows low HOMO–LUMO gap. Due to this reason, donor-acceptor substituted 4,7-positions of the BTD unit are commonly used as an active organic electronic materials for various optoelectronic applications such as organic solar cell, OFETs, OLEDs, NLO. ^[15-23]



Figure 1.4. General classification of donor-acceptor substituted at 4,7 and 5,6 positions of BTD.

1.5. Benzothiadiazole fused derivatives

 π -extended and heteroannulated benzothiadiazole chromophores have received enormous attention due to their excellent performance in optoelectronic applications. The π -extended fused benzothiadiazole derivatives have been classified in four different categories due to their complex chemical structures.

(a)Heteroatom substituted benzothiadiazoles



(b) Heteroannulated based tricyclic benzothiadiazole



(c) Heteroannulated based tetracyclic benzothiadiazoles (d) Large π -extended benzothiadiazoles



Chart 1.2. Examples of (a) Heteroatom substituted benzothiadiazoles, (b) Heteroannulated based tricyclic benzothiadiazole, (c) Heteroannulated based tetracyclic benzothiadiazoles, (d) Large π -extended benzothiadiazoles.

In the primary category, benzothiadiazole derivatives contain the fluorine, cyano and nitrogen units. The second, third and fourth category contains the tricyclic fused, tetracyclic fused and large π -extended heteroannulated benzothiadiazoles (shown in chart 1.2.).^[26]

1.6. Synthesis of donor-acceptor benzothiadiazole chromophores

The Palladium-catalyzed cross-coupling reactions are mainly considered as the most common synthetic methods to synthesize the π -extended BTD chromophores. Several cross-coupling reactions (*e.g.* Suzuki coupling, Sonogashira coupling, Stille coupling reaction, Heck coupling) are used, which are summarized in the following sections.

1.6.1. Suzuki Cross-Coupling Reaction

Sun *at el.* designed and synthesized a series of tetraphenylethene substituted benzothiadiazole derivatives 9-11 via Suzuki cross-coupling reaction.^[27]



Scheme 1.4. Synthesis of compounds 9–11.

The reaction of 4,7-dibromobenzothiadiazole with ortho, meta and paranitro phenyl boronic acid (1, 2 and 3) in the presence of $Pd(PPh_3)_4$, K_2CO_3 and in a mixture of THF /H₂O solvent system resulted in the intermediates **5**, **6** and **7** which further reacted with 4,4,5,5-tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2-dioxaborolane (**8**) to synthesize the final products **9–11** in 60–75% yields (Scheme.1.4).

1.6.2. Sonogashira Cross-Coupling Reaction

Pei *et al.* synthesized truxene based π -conjugated dendrimer **3** and **5** *via* Sonogashira cross-coupling reaction and explored the photophysical and electrochemical properties for the organic light emitting diodes.^[28]





Scheme 1.5. Synthesis of compound 3 and 5.

The reaction of 4,7-bis(5-iodothiophen-2-yl)benzo[c][1,2,5]thiadiazole **1** with the monoacetylene dendron **2** and **4** in the presence of $Pd_2(dba)_3$, CuI,

PPh₃ and the solvent trimethylamine/tetrahydrofuran resulted in **3** and **5** in 87% and 76% yield (Scheme.1.5).

1.6.3. Stille Cross-Coupling reaction

The Pd-catalyzed Stille cross-coupling is an important synthetic method for the synthesis of π -conjugated benzothiadiazole chromophores. Reichmanis *et al.* designed and synthesized a series of benzothiadiazole oligothiophene through the Stille cross-coupling reaction for organic fieldeffect transistors (OFETs) as shown in Scheme 1.6.^[29]





Scheme 1.6. Synthesis of compounds 11 and 12.

In these cross-coupling reactions, 2-thienyltributylstannane reacted with 4,7-dibromo-BTD in the presence of $[Pd(PPh_3)_2Cl_2]$ as catalyst and THF as solvent to form the intermediate **3** which followed by several bromination reactions and Stille cross-coupling reactions resulted the intermediates **7** and **8** which further reacted with bithiophene functionalized derivatives **9** and **10** to form final product **11** and **12**.

1.6.4. Heck cross coupling reaction

Sellinger *et al.* designed and synthesized two electron deficient derivatives 5 and 6 via Heck cross-coupling reaction for organic photovoltaics (OPV). $[^{30]}$ In these derivatives 5 and 6, the benzothiadiazole unit was used as central core and N-hexyl-phthalimide and N-hexylnaphthalimide derivatives were used as end capping units. In this process, 4,7dibromobenzothiadiazole reacted with vinyltriethoxysilane in the presence of bis(tritert-butylphosphine)-palladium(0) as catalyst and toluene as solvent at 80 °C for 24 h to form the intermediate 3. The intermediate 3 further reacted with *N*-hexyl-phthalimide and *N*-hexylnaphthalimide in the presence of bis-(dibenzylideneacetone)palladium(0) and tetrabutylammonium fluoride (TBAF) with toluene as solvent at 80 °C for two days to form 5 and 7 respectively in 49% and 21% yields (Scheme.1.7)

14



Scheme 1.7. Synthesis of compounds 5 and 7.

1.7. Other synthetic reactions

1.7.1. Borylation reaction

Turner *et al.* synthesized a series of donor-acceptor based organic semiconductors *via* C–H borylation reaction to investigate the photophysical and electrochemical properties for organic light emitting diodes. In this process thiophene substituted benzothiadiazole derivatives reacted with different Lewis acids including BCl₃ and BBr₃ in the presence of pyridine to form the borylative fused derivative **2** (Scheme 1.8). The intermediate **2** further reacted with Al(alkyl)₃ or Zn(aryl)₂ to form alkyl and aryl substituted fused boracyclic derivatives **3** and **4**. These alkyl and aryl functionalized derivatives dsiplay extended π -conjugation and enhanced stability compared to benzothiadiazole unit.^[31]



Scheme 1.8. Synthesis of compounds 2–4.

1.7.2 Direct C–H Arylation reaction

Scherf *et al.* developed a low bandgap based copolymer **3** for organic photovoltaics. The copolymer was synthesized by the direct arylation reaction of dithiophene derivative (**2**) and 4,7-dibromo-BTD (**1**) in the presence of Pd(OAc)₂ as the catalyst, PCy₃·HBF₄ as the ligand and K₂CO₃ in dimethylacetamide (DMAc) solvent (Scheme 1.9).^[32]



Scheme 1.9. Synthesis of compound 3.

Further Marder *et al.* developed symmetrical and unsymmetrical 4,7-diaryl substituted benzothiadiazole derivatives for optoelectronic applications. [32]



Scheme 1.10. Synthesis of compounds 3a, 3b and 3c.

The 4,7-diaryl substituted benzothiadiazole derivatives **3a**, **3b** and **3c** were synthesized by the direct arylation reaction of 2,1,3-benzothiadiazole (BTD) unit (**1a**), mono and difluoro substituted derivatives (**1b**, **1c**) with 1-bromo-4-methoxybenzene in the presence of $Pd(OAc)_2$, $PtBu_2Me \cdot HBF_4$, pivalic acid, K_2CO_3 , toluene, 120 °C for 3–5 h (Scheme 1.10).

1.8. Applications of benzothiadiazole Derivatives

The donor-acceptor functionalized benzothiadiazole chromophores have received significant attention in the various applications including organic light emitting diodes (OLEDs), photovoltaic devices, batteries as well as in biological studies. Some of the important applications are discussed below.

1.8.1. Organic Light Emitting Diodes (OLEDs)

Benzothiadiazole substituted donor-acceptor chromophores are efficient luminescent materials for OLEDs due to their low cost, high electron affinity, excellent fluorescence quantum yield and high thermal robustness.



Chart 1.3. BTD chromophores for OLEDs.

Promarak *et al.* designed and synthesized four acceptor-donor chromophores where benzothiadiazole was used as central unit, while triphenylamine was used as end-capping unit and n-hexylthiophene as a π -spacer to improve the EQE_{max}. The twisted structural arrangement between n-hexylthiophene and benzothiadiazole unit reduced the π - π interactions resulting in high solid-state emission. Among all chromophores, **2** exhibited excellent device performance with a maximum

external quantum efficiency (EQE_{max}) of 4.15%, maximum luminance of 6842 cd m⁻² and CIE coordinates of (0.65, 0.36) whereas chromophore **1**, **3** and **4** exhibited external quantum efficiency (EQE_{max}) of 1.73%, 0.97% and 2.66%, maximum luminance of 5148 cd m⁻², 706 cd m⁻² and 2334 cd m⁻² and CIE coordinates of (0.67, 0.33), (0.69, 0.31) and (0.66, 0.34), respectively.^[33]

1.8.2. Dye sensitized solar cells (DSSCs)

Dye-sensitized solar cells (DSSCs) have attracted attention of the scientific community due to their low-cost, easy fabrication, high performance and better thermal stability. Zhu *et al.* designed and synthesized chromophore **5** with structural configuration D–A– π –A in which benzothiadiazole was used as auxiliary acceptor to tune the HOMO–LUMO energy gap and improve light stability as well as enhance the light-harvesting capability of sensitizers (shown in Chart 1.4). Chromophore **5** showed excellent power conversion efficiency (PCE) of 8.15% with J_{sc} of 16.91 mA cm⁻², V_{oc} of 672 mV, and *FF* of 0.717. Cao *et al.* synthesized two benzothiadiazole functionalized chromophores **6** and **7** in which dipentyldithieno[3,2-f:2',3'-h]quinoxaline (DPQ) used as π -spacer to improve the photovoltaic performances. Chromophore **6** and **7** showed the power conversion efficiency (PCE) of 6.78% and 7.12% with a J_{sc} of 14.51 mA/cm⁻², V_{oc} 721 mV and FF of 0.65, and J_{sc} of 17.61 mA/cm⁻², V_{oc} 685 mV and FF of 0.59, respectively.^[34]





Chart 1.4. BTD chromophores for DSSCs.

1.8.3. Bulk heterojunction solar cells (BHJ)

The donor-acceptor functionalized benzothiadiazole chromophores are considered as active building block due to its broad absorption spectra and low HOMO–LUMO gap. Zhou *et al.* synthesized triphenylamine substituted benzothiadiazole based p-type donor-acceptor chromophores by the Heck coupling reaction. The photophysical and electrochemical study explained that the incorporation of electron deficient unit at endpositions of triphenylamine tune the HOMO–LUMO gap and showed broad absorption spectra in the UV-Visible region. The chromophore **8** (p-type material) exhibited a power conversion efficiency of 1.96% with a J_{sc} of 5.50 mA/cm⁻² and V_{oc} 0.96 V and FF of 0.37, respectively. Huang *et al.* synthesized two nonfullerene acceptors **9** and **10** with structural configuration A–D–A'–D–A in which BTD unit was used as acceptor in

central core, whereas thiophene substituted derivatives were used as π linkers and two different electron-withdrawing malononitrile units were used as terminal acceptor unit to improve the power conversion efficiency. The photophysical and electrochemical studies explained that both chromophores 9 and 10 showed strong absorption band in the range from visible to near-infrared region and tune the HOMO–LUMO gap due to presence of strong electron withdrawing units at central unit and endcapping positions.



Chart 1.5. Derivatives for BHJ OSCs.

The chromophore **9** and **10** (nonfullerene acceptors) exhibited a power conversion efficiency of 9.3% and 10.5% with a $J_{\rm sc}$ of 18.6 mA/cm⁻², $V_{\rm oc}$ 0.79 V and FF of 0.63, and $J_{\rm sc}$ of 21.0 mA/cm⁻², $V_{\rm oc}$ 0.75 V and FF of 0.66, respectively.^[35]

1.8.4. Perovskite Solar Cells (PSCs)

Palomares *et al.* synthesized BTD based four hole transport materials (HTMs) **11–14** for perovskite solar cell application shown in chart 1.6. The introduction of the phenyl ring in the chromophore **14** leads to a significant decrease of the carrier losses and improved power conversion efficiency drastically.



Chart 1.6. Benzothiadiazole based four hole transport materials **11–14** for PSCs.

The chromophore **14** showed the PCE of 18.09% whereas the chromophores **11**, **12** and **13** exhibited PCE of 17.84%, 13.31% and 11.29%, respectively.^[36]

1.8.5. Nonlinear optics (NLOs)

The high electron affinity and large reduction potential makes the benzothiadiazole unit an attractive candidate for nonlinear optics. Carlott *et al.* synthesized three benzothiadiazole based donor-acceptor chromophores by the Sonogashira cross-coupling reaction in which alkoxy phenyls were used as electron donating unit and benzothiadiazole was used as electron acceptor unit. The hyperpolarizability coefficient β_{CT} for chromophores **15–17** are 460, 2100, 1580 esu⁻¹ cm⁵, respectively. The di-BTD substituted chromophore **16** showed excellent NLO properties compared to chromophores **15** and **17**.^[37]



Chart 1.7. Benzothiadiazole based three chromophores 15–17 for NLO.

1.8.6. Organic thin-film transistor (OTFT)

The multi-acceptor based OTFTs have received significant interest in the recent years due to their applications in memory storage, displays, integrated circuits, radio frequency identification, and sensors. Kelly *et al.* synthesized two acceptor–acceptor linked polymers **18** and **19** in which bisisoindigo and benzothiadiazole were used as electron deficient units. The LUMO energy level of both chromophores **18** and **19** were tuned more significantly due to presence of both electron withdrawing units in the π -conjugated system and showed excellent ambipolar OTFT performance for both **18** and **19** chromophores with hole and electron mobilities up to 4.0×10^{-3} and 1.4×10^{-3} cm² V⁻¹ s⁻¹, respectively. [38]



Chart 1.8. Benzothiadiazole based two chromophores for OTFT.

1.8.7. Sensing

1.8.7.1. Ion Detection in Lithium-Ion Battery

Li *et al.* developed a novel fluorescent organic nanoparticle **20** to detect the specific metal ions in which triazole unit was used as central core and benzothiadiazole was used as branches. ^[39] The fluorescent organic nanoparticle showed excellent selectivity and sensitivity for Fe³⁺ impurity detection in LiFePO₄ which is an active cathode material for lithium ion batteries. The fluorescence intensity of organic nanoparticle did not show any quenching properties when pure LiFePO₄ was dissolved in acid solution, but with the presence of Fe³⁺ impurity the fluorescence intensity started quenching dramatically.



Chart 1.9. Benzothiadiazole based chromophore 20 for ion sensing.

1.8.7.2. Sensor for detection of Hg²⁺

Toxic heavy metal and their derivatives are harmful for human health and environment. It can cause serious damage to the central nervous system and the endocrine system. Zhao *et al.* developed novel near-infrared (NIR) absorbing push-pull organic sensor **21** for detection of Hg^{2+} ion (shown in

Chart 1.10.). ^[40] The sensor showed good binding constant $(2.37 \times 104 \text{ M}^{-1})$ with high selectivity, sensitivity towards the Hg²⁺ due to presence of rhodanine-3-acetic acid as the receptor. The detection of Hg²⁺ ion was confirmed by ¹H NMR titration, HRMS and was also applied in cell imaging, indicating that this chromophore can be a potential candidate for detection of (Hg²⁺) heavy metal in complex living samples.



Chart 1.10. Molecules for heavy metal sensing.

The main objectives of the current work is

- To design and synthesize donor-acceptor functionalized benzothiadiazole chromophores for optoelectronic applications and ultrafast studies.
- To synthesize symmetrical and unsymmetrical benzothiadiazole chromophores by changing the donor/acceptor units at 4- and 7position.
- To study the effect of donor and acceptor strength on the photophysical and electochemical properties.
- To tune the HOMO–LUMO gap by using the multi acceptor units in the π-conjugated systems.
- To investigate the electronic structure, distribution of electron density over the HOMO and LUMO energy levels and photophysical properties of the benzothiadiazole chromophores by using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations.

1.9. Organization of thesis

Chapter 1 of the thesis gives an outline of various design and synthetic strategies of BTD chromophores and their applications in diverse fields.Chapter 2 of the thesis summarizes the instrumentation and general

methods used for the present study.

Chapter 3 of the thesis describes a series of ferrocene-substituted unsymmetrical BTDs and tuning of the photonic properties by using additional acceptor units.

Chapter 4 of the thesis reports the synthesis of TCBD and expanded TCBD substituted triphenylamine-benzothiadiazole systems *via* Pd-catalyzed Sonogashira cross-coupling reactions and [2 + 2] cycloaddition–electrocyclic ring-opening reaction. The significant change on photonic and electrochemical properties was also explored.

Chapter 5 of the thesis describes the design and synthesis of a series of symmetrical and unsymmetrical benzothiadiazole chromophores and their mono substituted TCBD and expanded TCBD derivatives *via* Pd-catalyzed Sonogashira crosscoupling reactions and [2 + 2] cycloaddition–electrocyclic ring-opening reaction. The effect of altering the donor and acceptor strength on the photonic and electrochemical properties was also explored.

Chapter 6 of the thesis describes the design and synthesis of a series of 4ethynyl-1,8-naphthalimide (NPI) substituted benzothiadiazole chromophores and their TCBD and expanded TCBD functionalized derivatives *via* Pd-catalyzed Sonogashira cross-coupling reactions and [2 + 2] cycloaddition–electrocyclic ring-opening reaction. The effect of additional acceptor strength on the photophysical and electrochemical properties was also explored.

Chapter 7 of the thesis describes the design and synthesis of benzothiadiazole substituted donor-acceptor chromophores with structural configuration D'- π -A- π -D- π -A- π -D', D"- π -A- π -D- π -A- π -D" and D"'-A- π -

 $D-\pi$ -A-D''' via Pd-catalyzed Sonogashira cross-coupling reactions. Their photophysical and electrochemical properties were studied.

Chapter 8: of the thesis summarizes the salient features of the work and addressed the future prospects.

1.10. References

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Chapter 2

Materials and experimental techniques

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 procedures.^[1] 2,1,3-Benzothiadiazole, established CuI. $Pd(PPh_3)_4$, tetrabutylammonium $PdCl_2(PPh_3)_2$, ferrocene, hexafluorophosphate $(TBAF_6),$ 4-ethynylaniline, 3-ethynyleniline, ethynyl ferrocene, triphenylamine, and carbazole, 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, tetrahydrofuran (THF), 1,2- dichlorobenzene, dioxane, 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, 77.16 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 were calculated by the steady-state comparative method using following equation,

Where ϕ_F is the emission quantum yield of the sample, ϕ_{st} is the emission quantum yield of the standard, A_{st} and A_u represent the absorbance of the standard and sample at the excitation wavelength, respectively, while S_{st} and S_u are the integrated emission band areas of the standard and sample, respectively, and nD_{st} and nD_u the solvent refractive index of the standard and sample, u and st refer to the unknown and standard, respectively.

2.4. Electrochemical studies

Cyclic voltamograms (CVs) were recorded on CHI620D electrochemical analyzer using Glassy carbon as working electrode, Pt wire as the counter electrode, and Saturated Calomel Electrode (SCE) as the reference electrode. The scan rate was 100 mVs⁻¹. A solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) in CH_2Cl_2 (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 F2.1. 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 obtained free of charge can be via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic 42 Data Centre, 12 union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

2.6. 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]

2.7. References

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Chapter 3

Aryl substituted unsymmetrical benzothiadiazole chromophores

3.1. Introduction

The organic π -conjugated donor-acceptor (D-A) systems are of interest due to its application in organic photovoltaics (OPVs).^[1-4] The optoelectronic properties of the donor–acceptor system can be tailored to a desired extent by altering the donor and acceptor moieties.^[5] In recent years, variety of donor (D) and acceptor (A) systems have been explored, for organic solar cells.^[6]

Benzthiadiazole (BTD) is one of the widely studied strong acceptor in organic electronics due to its high reduction potential and strong electron affinity (EA).^[7] It is extensively utilized for the organic light emitting diodes (OLEDs), two-photon absorbing materials and solar cells.^[8-12] The TCNE is a strong electron acceptor due to the presence of four cyano units, which undergo [2+2] cycloaddition reaction with electron rich alkynes, to form the cyclobutene rings, which undergo retroelectrocyclization reaction to yield donor-substituted TCBD moiety. TCBD substituted derivatives are explored to The tune the HOMO-LUMO energy level, photophysical, electrochemical and thermal properties of D-A molecular systems. The importance of [2+2] cycloaddition reaction is that metal catalysts are not used. Over the past few years, the TCBD substituted push-pull chromophores have been rigorously designed and synthesized between donor-activated alkynes and olefinic electron acceptor to achieve intense electronic absorption bands with strong intramolecular charge transfer interaction, in near-infrared region.^[13] Due to their impressive photophysical, electrochemical properties, these push-pull chromophores have been intensively used in organic solar cells and optical data transmission devices.^[14-17] Ferrocenyl (Fc) derivatives show applications in nonlinear optics, asymmetric catalysis and sensors.^[18,19] Lang and co-workers have developed new methodologies to synthesized ferrocenyl substituted derivatives (planar chiral ferrocences, 2,5-di- and 2,3,4,5-tetraferrocenylsubstituted thiophenes, furans, and pyrroles, 1,2-P,O-substituted ferrocenes) by Friedel–Crafts reactions, Negishi C,C cross-coupling, phospho-Fries rearrangement.^[19] Butenschön and co-workers also have designed and synthesized ferrocenyl derivatives by stereoselective catalytic synthesis and thia-fries rearrangement.^[19] Our group has reported different type of ferrocene derivatives for photonic applications.^[20]

In 1981, Bruce and co-workers have synthesized TCBD substituted chromophores by using metal substituted acetylides and an electrondeficient olefin (TCNE).^[21] These TCBD substituted chromophores shows impressive properties for organic semiconducting materials. Diederich et al. have design and synthesized TCBD linked small molecule for organic semiconducting materials.^[22] Shoji and co-workers have also reported azulene-substituted 1,1,4,4-tetracyanobutadienes as organic electronic materials.^[22g] Michinobu and co-workers have reported various TCBD derivatives,^[23] with a specific attention on the reactivity of alkyne bond by the substitution of various donor groups. They explained that when they used *p*-methoxyphenyl as a weak donor group and *p*-*N*,*N*-dimethylanilino (DMA) as a strong donor group, *p*-methoxyphenyl substituted alkyne bond undergo [2+2] cycloaddition-retroelectrocyclization at 110 °C whereas DMA substituted alkyne proceeded rapidly at 20 °C, which indicates that the strong donor group DMA tune the frontier energy levels to makes the [2+2] cycloaddition-retroelectrocyclization easier.^[24]

Herein, we have synthesized a series of mono/di TCBD substituted BTDs 2a-2g in which TCBD moiety has been explored as an additional acceptor unit, which was incorporated between BTD moiety and various end capping units to explain selectivity (monosubstitution and

disubstitution of TCBD) of [2 + 2] cycloaddition-retroelectrocyclization reaction in presence of distinct electron rich units and also explain the importance of donor strength in [2 + 2] cycloadditionretroelectrocyclization.

3.2. Results and discussions

The synthesis of ferrocenyl functionalized unsymmetrical and symmetrical BTDs 2a-2g are shown in Scheme 3.1 and 3.2. The Sonogashira crosscoupling reactions of 2-bromo-7-ferrocenylethynylbenzo[1,2,5]thiadiazole with respective aryl-acetylenes resulted in BTDs 1a-1g.^[25]



Scheme 3.1. Synthesis of ferrocenyl functionalized unsymmetrical BTDs 2a–2e.



Scheme 3.2. Synthesis of ferrocenyl functionalized BTDs 2f and 2g.

The reaction of BTDs **1a–1e** with excess equivalent TCNE in dichloromethane (DCM) at 40 °C resulted in mono substituted TCBD derivatives **2a**, **2b**, **2c**, **2d** and **2e**, in 87%, 89%, 94%, 93% and 88% yields, respectively, whereas BTDs **1f** and **1g** resulted in di-substituted TCBD derivatives (BTDs **2f** and **2g**) in 92% and 94% yields. The purification of BTD derivatives **2a–2g** were achieved by column chromatography. The BTDs **2a–2g** were well-characterized by ¹H, ¹³C NMR and HRMS techniques. The BTD derivatives are readily soluble in common organic solvents such as dichloromethane, chloroform, tetrahydrofuran, toluene and acetone.

3.3. Photophysical Properties

The electronic absorption spectra of BTDs 2a-2g were recorded in dichloromethane at room temperature (Figure 3.1a and 3.1b), and the data are shown in Table 3.1. The absorption band of BTDs 2a-2e show maxima between 300–356 nm which is attributed to the presence of BTD moiety.^[25]



Figure 3.1. Normalized electronic absorption spectra of (a) mono-TCBD substituted BTDs **2a–2e** and (b) di-TCBD substituted BTDs **2f** and **2g** in dichloromethane at 1.0×10^{-5} M concentration.

The BTDs 2a-2d and 2f displays two distinct absorption band in visible region, the first intense band is in lower wavelength region *i.e.* between

422–539 nm, corresponds to the $\pi \rightarrow \pi^*$ transition, whereas the less intense band in longer wavelength region at 539–633 nm is due to ICT interaction. The BTDs **2e** and BTD **2g** exhibit a strong absorption band in visible region at 539–618 nm attributed to an intramolecular charge transfer (ICT) transition. This was further explained by TD–DFT calculation in dichloromethane phase.

BTD	$\lambda_{abs}[nm]^{[a]}$	$\varepsilon [M^{-1}cm^{-1}]^{[a]}$	$E_{\rm g} [{\rm eV}]^{[{\rm c}]}$
2a	422	68000	2.39
	625	4589	
2b	457	65000	2.42
	634	4789	
2c	442	58700	2.38
	630	33580	
2d	457	56300	2.39
	633	4079	
2e	539	51900	1.97
2f	489	54600	1.83
	624	41656	
2g	618	42700	2.17

Table 3.1. Photophysical, thermal stability and DFT data of BTDs 2a-2g

^aAbsorbance measured in dichloromethane at 1×10^{-5} M concentration, ε : molar extinction coefficient. ^bTheoretical HOMO–LUMO band gap values calculated from DFT calculation.

3.4. Theoretical calculations

The BTDs 2a-2g were theoretically investigated in the gasphases using density functional theory $(DFT)^{[26]}$ and time dependent DFT (TD-DFT) to understand ground state geometry and electronic transitions. Theoretical calculations were performed using the Gaussian 09 programs at the B3LYP/6-31G^{**} level. The HOMO and LUMO energy levels of BTDs **2a** and **2g** are outlined in Figure 3.2. The incorporation of TCBD in BTDs **2a–2g** exhibit twisted backbone skeleton. The HOMO orbitals of BTDs **2a–2d**, **2f** and **2g** are completely localized on ferrocene unit and LUMO on TCBD and BTD unit. The HOMO orbital of BTD **2e** is localized on anthracene. The theoretically calculated HOMO levels of **2a–2g** are -6.02, -5.96, -6.01, -6.02, -5.61, -5.94 and -6.34eV and the corresponding LUMO levels are -3.63, -3.54, -3.62, -3.62, -3.63, -4.12 and -4.18 eV, respectively. The trends of HOMO values of BTDs **2a–2d** are quite similar.

In BTD 2e, the HOMO energy level was raised to -5.61 eV. In the case of BTDs 2f and 2g both LUMO and HOMO were stabilized by incorporation of additional TCBD acceptor.



Figure 3.2. Energy levels diagram of the frontier orbitals of BTDs 2a and 2g estimated by DFT calculations.

The time dependence density functional theory calculation was performed for BTDs 2a-2g at the B3LYP/6-31G** level in DCM solvent to calculate the absorption behavior. On the basis of their oscillator strength (f), the contribution to the molecular orbitals were estimated in the UV/Vis absorptions spectra. The transitions with oscillator strengths, composition and assignments are shown in Table 3.2.

Table 3.2. Calculated electronic transitions for BTDs **2a–2g** in the dichloromethane.

BTD	Wavelength	Composition	f ^a	Assignment
		&		
		Molecular contribution		
2a	438	HOMO-2 \rightarrow LUMO+1(0.68)	0.19	π—π*
	538	HOMO−1→LUMO+1 (0.70)	0.25	ICT
2b	387	HOMO– $6\rightarrow$ LUMO(0.24)	0.15	ππ*
	609	HOMO-2→LUMO (0.30)	0.44	ICT
2c	463	HOMO–1→LUMO+1 (0.64)	0.21	ππ*
	587	HOMO−1→LUMO (0.58)	0.82	ICT
2d	483	HOMO→LUMO+1 (0.68)	0.12	π-π*
	622	HOMO→LUMO (0.63)	0.50	ICT
2e	556	HOMO→LUMO (0.65)	1.03	ICT
2f	437	HOMO–7→LUMO (0.61)	0.30	ππ*
	541	HOMO→LUMO+2 (0.70)	0.19	ICT
2g	492	HOMO-2→LUMO+1(0.11)	0.01	ππ*
	671	HOMO−2→LUMO(0.70)	0.01	ICT
			1	1

 f^{a} oscillator strength.

The absorption spectra for BTD **2e** calculated from TD-DFT calculation are shown in Figure 3.3. The TD-DFT results of BTD **2e** exhibit a strong absorption band originated from HOMO \rightarrow LUMO at 556 nm corresponds to intramolecular charge transfer (ICT) transition.

The position of λ_{max} and orientation of absorption spectra of BTDs **2e** is in good agreement with the experimental data.



Figure 3.3. Experimental (bottom) and TDDFT-predicted (top) UV-Vis absorption spectra of **2e** in DCM.

The UV-Vis regions of BTDs 2a-2d, 2f and 2g dominated by two major absorption bands are shown in Table 3.2 which was explained by TD-DFT calculations. The first absorption band predicted at 538 nm, 609 nm, 587 nm, 622 nm, 541 nm and 671 nm predominantly belongs to HOMO-1 \rightarrow LUMO+1, HOMO-2 \rightarrow LUMO, HOMO−1→LUMO, HOMO→LUMO, HOMO→LUMO+2 and HOMO-2→LUMO transition, which correspond to intramolecular charge transfer (ICT) character, whereas the next absorption band with high intensity at 438 nm, 387 nm, 463 nm, 483 nm, 437 nm and 492 nm dominated by the HOMO- $2 \rightarrow LUMO+1$, HOMO- $6 \rightarrow LUMO$, HOMO-1 \rightarrow LUMO+1, HOMO \rightarrow LUMO+1, HOMO-7 \rightarrow LUMO and HOMO-2 \rightarrow LUMO+1 transition corresponding to $\pi - \pi^*$ character. In experimental as well as theoretical UV/vis spectra, BTD 2e exhibit one electronic transition that corresponds to intramolecular charge transfer (ICT), whereas BTDs 2a2d, 2g and 2f exhibit two electronic transitions related to $\pi - \pi^*$ and, intramolecular charge transfer (ICT) transitions in the visible region.

3.5. Electrochemical Properties

The electrochemical properties of BTDs 2a-2g were investigated by cyclic voltammetry (CV) in dry DCM solution with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte. The glassy carbon, Pt wire and saturated calomel electrode (SCE) were used as working electrode, counter electrode and the reference electrode, respectively. The redox potentials (in volts *vs*. (SCE)) of 2a-2g are summarized in Table 3.3, and the cyclic voltammograms of BTDs 2a-2g are shown in Figure 3.4, Figure 3.5 and Figure 3.6.



Figure 3.4. Cyclic voltammograms of BTDs **2c** in 0.1 M solution of Bu_4NPF_6 in dichloromethane at 100 mV s⁻¹ scan rate versus saturated calomel electrode (SCE) at 25 °C.

The electrochemical properties of BTDs 2a-2g exhibit three reversible reduction waves, the first two reversible reduction waves are attributed to the TCBD unit and a single reduction wave corresponds to the BTD moiety. The BTDs 2a-2g shows two-step reversible reduction wave with one-electron transfer in each step in the region of (-0.109 V to -0.867 V). The first reduction potential values of BTDs 2a-2g reveals that the disubstituted TCBD derivatives of **2g** and **2f** can be easily reduced compared to mono- substituted TCBD derivatives of **2a–2e**, attributed to the strong electron-withdrawing nature of the BTDs **2f** and **2g** derivatives. The reduction potential estimated from the CV spectra for BTDs **2a–2g** are (-0.49 V, -0.86 V, -1.75 V), (-0.40 V, -0.89 V, -1.60 V), (-0.48 V, -0.85 V, -1.73 V), (-0.47 V, -0.82 V, -1.71 V) and (-0.44 V,-0.80 V,-1.63 V), (-0.10 V, -0.26 V, -0.95 V), (-0.12 V, -0.25 V, -1.00 V). A clean inspection of the CV data for BTDs **2a–2d** reveal that all these compounds exhibit one oxidation potential rather than two oxidation potentials, due to weak donor groups but at the same time, the presence of anthracene and triphenylamine, the BTD derivatives of **2e** and **2f** exhibit two oxidation waves.



Figure 3.5. Cyclic voltammograms of BTDs 2f and 2g in 0.1 M solution of Bu₄NPF₆ in dichloromethane at 100 mV s⁻¹ scan rate versus saturated calomel electrode (SCE) at 25 °C.

The BTDs **2a–2e** and **2g** exhibit a oxidation wave corresponding to the ferrocenyl moiety whereas BTD **2e** and **2f** show extra oxidation wave due to anthracene and triphenylamine moiety.



Figure 3.6. Cyclic voltammograms of BTDs **2a**, **2b**, **2d**, **2f** and **2g** in 0.1 M solution of Bu_4NPF_6 in dichloromethane at 100 mV s⁻¹ scan rate versus saturated calomel electrode (SCE) at 25 °C.

BTDS	$E^{1}(V)$	$E^2(V)$	$E^{3}(V)$	$E^{1}(V)$	$E^2(V)$
	Red	Red	Red	Oxid	Oxid
2a	-0.49	-0.86	-1.75	0.78	-
2b	-0.40	-0.89	-1.60	0.87	-
2c	-0.48	-0.85	-1.73	0.79	-
2d	-0.47	-0.84	-1.71	0.79	-
2e	-0.44	-0.80	-1.63	0.80	1.18
2f	-0.10	-0.26	-0.95	0.90	1.23
2g	-0.12	-0.25	-1.00	0.90	-

Table 3.3. Electrochemical properties of BTDs 2a-2g in 0.1 M solution of TBAPF₆ in DCM at 100 mV s⁻¹ scan rate versus SCE electrode

The oxidation potential of ferrocenyl moiety in BTDs 2a-2g are 0.78 V, 0.87 V, 0.79 V, 0.79 V, 0.8 V, 0.90 V and 0.90 V, respectively. The first oxidation potential of 2a-2d follows the order of $2f-2g > 2b > 2e > 2c \sim 2b > 2a$, which shows that the oxidation of ferrocenyl BTDs 2a is easier than BTDs 2b-2g.

3.6. X-ray Analysis

The single crystal of the compound 2c was obtained *via* slow evaporation method by using mixture of methanol and dichloromethane solution at room temperature and is shown in Figure 3.7. The crystal packing diagram of BTD 2c exhibits two different types of interaction which leads to the formation of 2D polymeric structure shown in Figure 3.8 (a) and shows monoclinic space group $P2_1/c$. In the crystal packing diagram, two monomeric units are interlinked through $\pi \cdots \pi$ interaction between centroid of six member ring and five member ring (3.67 Å) to stabilize crystal packing (Figure 3.8 (a). The crystal packing diagram of BTD 2cshows intermolecular interaction between the C-H...N, in Figure 3.8 (b). The important bond lengths and bond angles are listed in the Table 3.4.



Figure 3.7. Single-crystal X-ray structure of BTD **2c** with solvent molecule (Hexane).



Figure 3.8. (a) Packing diagram of BTD 2c with $\pi \cdots \pi$ interaction (b) Packing diagram of ferrocenyl functionalized unsymmetrical BTD 2c along the b-axis.

Identification code	Ligand 1		
Empirical formula	C ₄₄ H ₃₄ FeN ₆ S		
Mr	734.68		
crystal system	Monoclinic		
space group	$P 2_1/c$		
a(Å)	18.9402(4)		
$b(\text{\AA})$	8.5785(2)		
c(Å)	23.1650(6)		
α (deg)	90		
β (deg)	90.691(2)		
γ (deg)	90		
Volume (Å ³⁾	3763.54(15)		
Z	4		
$Dx (Mg m^{-3})$	1.297		
F(000)	1528		
$\mu (\mathrm{mm}^{-1})$	4.037		
θ range for data	3.81 to 71.48		
collection(deg)			
	-23<=h<=22,		
Limiting indices	-6<=k<=10,		
	-28<=l<=27		
Reflections collected	23712		
unique reflections	7236		
R(int)	0.0747		
Completeness to θ	99.6		
Data / restraints / parameters	7236 / 0 / 471		
GOF on F^2	0.915		
D1 and DY [I > 2-(I)]	R1 = 0.0607,		
$\kappa_1 \text{ and } \kappa_2 \left[1 > 2\sigma(1) \right]$	wR2 =0.1706		
D1 and D2 (all data)	R1=0.0770,		
π i and πZ (all data)	wR2 =0.1993		

Table 3.4. Crystal data and structure refinement for BTD 2c

3.7. Experimental Section General Methods

Chemicals were used as received unless otherwise indicated. All the oxygen or moisture sensitive reactions were carried out under argon atmosphere. ¹H NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using residual protonated solvent as an internal standard {CDCl₃, 7.27 ppm}. ¹³C NMR spectra were recorded using a 100 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using the solvent as internal standard {CDCl₃, 77.0 ppm}. The ¹H NMR splitting patterns have been described as "s, singlet; d, doublet; t, triplet and m, multiplet". UV-visible absorption spectra of all compounds were recorded in dichloromethane solution. Cyclic voltammograms and differential pulse voltammograms were recorded on potentiostat 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 for cyclic voltammetry. A solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) in DCM (0.1M) was used as supporting electrolyte.

BTD 2a

In a 100 mL round bottomed flask, TCNE (63 mg, 0.45 mmol) was added to a solution of compound BTD **1a** (222 mg, 0.49 mmol) in CH₂Cl₂ (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 6 h. The solvent was removed in vacuum, and the product was purified by SiO₂ column chromatography with DCM/hexane (2:1, v/v) as eluent to yield BTD **2a** as a dark blue solid (250 mg, Yield: 87%); ¹H NMR (400 MHz, CDCl₃) δ 7.86–7.82 (m, 2H), 7.67–7.66 (m, 2H), 7.43–7.41(m, 3H), 5.51 (s, 1H), 4.91 (s, 1H), 4.68 (s, 1H), 4.68 (s, 1H), 4.48 (s, 1H), 4.39 (s, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 171.3, 161.3, 154.7, 150.6, 132.4, 131.3, 131.0, 130.0, 128.7, 124.2, 123.2, 121.8, 114.0, 113.7, 111.7, 111.3, 101.6, 90.7, 84.8, 79.5, 76.1, 74.9, 74.4, 73.1, 72.7, 70.8; HRMS (ESI-TOF) m/z calculated for $C_{32}H_{16}FeN_6S+K = 611.0138 \ [M+K]^+$, measured 611.0138 $[M+K]^+$.

BTD 2b

In a 100 mL round bottomed flask, TCNE (63 mg, 0.45 mmol) was added to a solution of compound BTD **1b** (235 mg, 0.49 mmol) in CH₂Cl₂ (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 6 h. The solvent was removed in vacuum, and the product was purified by SiO₂ column chromatography with DCM/hexane (2:1, v/v) as eluent to yield BTD **2b** as a dark black solid (270 mg, Yield: 89%); ¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 2H), 7.75 (d, *J* = 12 Hz, 2H), 6.95 (d, *J* = 12 Hz, 2H), 5.49 (s, 1H), 4.90 (s, 1H), 4.68 (s, 1H), 4.48 (s, 1H), 4.38 (s, 4H), 3.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.4, 161.4,161.2, 150.7, 134.2, 131.1, 130.8, 123.7, 114.5, 113.7, 111.8, 111.4, 76.0, 74.9, 73.1, 72.7, 70.8; HRMS (ESI-TOF) m/z calculated for C₃₃H₁₈FeON₆S+Na = 625.0505 [M+Na]⁺, measured 625.0482 [M+Na]⁺.

BTD 2c

In a 100 mL round bottomed flask, TCNE (63 mg, 0.45 mmol) was added to a solution of compound BTD **1c** (260 mg, 0.5 mmol) in CH₂Cl₂ (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 6 h. The solvent was removed in vacuum, and the product was purified by SiO₂ column chromatography with DCM/hexane (2:1, v/v) as eluent to yield BTD **2c** as a dark blue solid (305 mg, Yield: 94%); ¹H NMR (400 MHz, CDCl₃) δ 7.87–7.82 (m, 2H), 7.75 (d, *J* = 8 Hz, 2H), 7.67–7.62 (m, 4H), 7.47 (t, *J* = 8 Hz, 2H), 7.41–7.38 (m, 1H), 5.51 (s, 1H), 5.30 (s, 1H), 4.91 (s, 1H), 4.69 (s, 1H), 4.49 (s, 1H), 4.39 (s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 171.4, 161.3, 154.7, 150.6, 142.8, 140.0, 132.8, 131.3, 131.0, 130.0, 129.1, 128.2, 127.4, 127.2, 124.1, 123.3, 120.6, 114.0, 113.7, 111.7, 111.3, 101.7, 90.7, 85.6, 79.5, 76.1, 74.9, 74.5, 73.1, 72.7, 70.8; HRMS (ESI-TOF) m/z calculated for $C_{32}H_{16}FeN_6S+H = 649.0893$ [M+K]⁺, measured 649.0894 [M+H]⁺.

BTD 2d

In a 100 mL round bottomed flask, TCNE (63 mg, 0.45 mmol) was added to a solution of compound BTD **1d** (247 mg, 0.5 mmol) in CH₂Cl₂ (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 6 h. The solvent was removed in vacuum, and the product was purified by SiO₂ column chromatography with DCM/hexane (2:1, v/v) as eluent to yield BTD **2d** as a dark brown solid (292 mg, Yield: 93%); ¹H NMR (400 MHz, CDCl₃) δ 8.62 (d, J = 4 Hz, 1H), 7.95–7.87 (m, 4H), 7.68–7.50 (m, 4H), 5.52 (s, 1H), 4.91 (s, 1H), 4.69 (s, 1H),), 4.49–4.40 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 171.4, 161.3, 154.9, 150.6, 133.5, 131.9, 131.1, 131.0, 130.8, 128.6, 127.7, 126.2, 125.4, 124.1, 123.4, 119.4, 114.1, 113.7, 111.7, 111.4, 100.25, 90.6, 89.88, 79.6, 76.1, 74.5, 73.1, 72.7, 70.8; HRMS (ESI-TOF) m/z calculated for C₃₂H₁₆FeN₆S+Na = 696.0744 [M+Na]⁺, measured 696.0702 [M+Na]⁺.

BTD 2e

In a 100 mL round bottomed flask, TCNE (63 mg, 0.45 mmol) was added to a solution of compound BTD **1e** (272 mg, 0.5 mmol) in CH₂Cl₂ (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 6 h. The solvent was removed in vacuum, and the product was purified by SiO₂ column chromatography with DCM/hexane (2:1, v/v) as eluent to yield BTD **2e** as a dark violet solid (298 mg, Yield: 88%); ¹H NMR (400 MHz, CDCl₃) δ 8.82 (d, *J* = 8 Hz, 2H), 8.55 (s, 1H), 7.93 (m, 1H), 7.72–7.68 (m, 2H), 7.57 (t, *J* = 8 Hz, 2H), 5.54 (s, 1H), 5.30 (s, 1H), 4.92–4.91 (m, 1H), 4.70–4.69 (m, 1H), 4.50 (m, 1H), 4.42 (s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 171.3, 161.2, 150.6, 133.4, 131.1, 130.4, 130.2, 128.9, 127.7, 126.5, 126.0, 123.8, 123.5, 114.0, 113.6, 111.7, 111.3,99.42, 96.47, 90.2, 79.6, 75.9, 74.7, 74.4, 73.0, 70.8; HRMS (ESI-TOF) m/z calculated for C₃₂H₁₆FeN₆S+Na = 696.0744 [M+Na]⁺, measured 696.0702 [M+Na]⁺.

BTD2f

In a 100 mL round bottomed flask, TCNE (128 mg, 1 mmol)) was added to a solution of BTD **1f** (306 mg 0.50 mmol) in CH₂Cl₂ (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 6 h. After cooling to room temperature, the solvent was removed under vacuum and the product was purified by silica gel column chromatography with DCM/hexane (1:1, v/v) as eluent to yield BTD **2f** as a dark brown solid (400 mg, yield 92%): ; ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 10 Hz, 2H), 7.93 (d, *J* =8 Hz, 1H,), 7.61 (d, *J* = 8.0 Hz, 2H), 7.39–7.35 (m, 4H), 7.25–7.23 (m, 2H), 7.17 (D, J = 8 Hz, 4H), 6.86 (d, J = 8 Hz, 2H), 5.56 (s, 1H), 5.0 (s, 1H), 4.79 (s, 1H), 4.46 (s, 1H), 4.40 (s, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 170.6, 162.6, 162.1, 160.1, 154.1, 151.1, 150.9, 144.5, 132.1, 131.1, 130.3, 129.9, 127.1, 127.0, 120.7, 118.2, 113.9, 113.4, 111.1, 110.8, 110.5, 94.9, 92.8, 79.6, 79.4, 75.6, 74.1, 73.5, 73.0, 70.8.; HRMS (ESI-TOF) m/z calcd for C₅₀H₂₅FeN₁₁S+Na 890.1258 [M + Na]+, measured 890.1250 [M +Na]+.

BTD2g

In a 100 mL round bottomed flask, TCNE (128 mg, 1 mmol)) was added to a solution of BTD **1g** (276 mg 0.50 mmol) in CH₂Cl₂ (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 6 h. After cooling to room temperature, the solvent was removed under vacuum and the product was purified by silica gel column chromatography with DCM/hexane (1:1, v/v) as eluent to yield BTD **2g** as a dark brown solid (380 mg, yield 94%): ; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 10 Hz, 2H), 5.56 (s, 1H), 5.53 (s, 1H), 5.30 (s, 2H), 4.98 (s, 2H), 4.77-4.76 (m, 2H), 4.44 (s, 1H), 4.39-4.37 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 170.6, 170.5, 159.9, 150.8, 129.9, 129.7, 128.9, 113.9, 111.1, 110.8, 93.0, 92.7, 79.5, 79.1, 75.6, 74.1, 73.7, 73.5, 73.0, 70.8, 70.6; HRMS (ESI-TOF) m/z calcd for C₄₂H₂₀Fe₂N₁₀S + Na 831.0186 [M + Na]+, measured 831.0189 [M +Na]+.

3.8. Conclusions

This chapter describes the design and synthesize of a series of arylsubstituted ferrocenyl functionalized unsymmetrical and symmetrical BTDs by formal [2 + 2] cycloaddition-retroelectrocyclization, in which phenyl, *p*-methoxyphenyl, biphenyl, naphthalene and anthracene substituted derivatives show the monosubstitution, whereas triphenylamine and ferrocenyl substituted derivatives shows disubstitution of TCBD in the presence of excess amount of tetracyanoethylene (TCNE). The significance of donor strength to design the mono/ di-substitution of [2 + 2] cycloaddition- retroelectrocyclization reaction was explained successfully by experimental and computational studies. The photophysical and electrochemical properties for all derivatives revealed that the triphenylamine and ferrocenyl substituted derivatives exhibit a strong electronic conjugation in the π -conjugated systems after incorporation of additional TCBD acceptor.

3.9. References

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Chapter 4

Design and synthesis of push–pull based triphenylamine and *N*,*N*-dimethylaniline substituted benzothiadiazoles

4.1. Introduction

Symmetrical and unsymmetrical push–pull functionalized small molecules have attracted considerable interest in optoelectronic applications due to excellent photophysical and electrochemical properties.^[1–10] The use of appropriately positioned, easy to oxidize in electron rich and easy to reduce in electron deficient molecules promote the possibility of push-to-pull charge transfer extending their absorption well into the visible and near-IR regions that can be exploited in organic photovoltaic (OPV) cells.^[10–22] Additionally, the possibility of both hole and electron injection from appropriate semiconducting materials promote their ambipolar organic field effect transistors (OFET) properties.^[23–30]

Extending the simple push–pull dyad concept to build multi-modular systems (having different types of donors and/or acceptors varying in their electron donor and acceptor strengths) would promote multiple intramolecular charge transfer events within the conjugates.^[31–46] An advantage of such phenomenon is in the possibility of extending absorption characteristics covering the visible and near-IR regions and also tune the HOMO-LUMO energy gap. In the multi-modular push-pull systems, the 2,1,3-benzothiadiazole (BTD) unit has gained major attention due to its several advantages such as high reduction potential, strong electron affinity (EA) and broad absorption spectra in the vis-NIR region.^[43–46] The literature reveals that the BTD derivatives widely used as π -conjugated organic materials for the two-photon absorbing materials (TPA), photo-induced intramolecular charge

transfer (ICT), organic light emitting diodes (OLED) and solar cells due to its high reduction potential and excellent thermal stability.^[47–54] In the present study, we have successfully synthesize multi-modular benzothiadiazole based push-pull derivatives **BTD2–BTD4** and **BTD6–BTD8** *via* the [2 + 2] cycloaddition–retroelectrocyclization (CA-RE) reaction in which benzothiadiazole (electron acceptor unit A1) used as central unit core, triphenylamine and *N*,*N*-dimethylaniline (electron donor group D) used as end-capping units, 1,1,4,4tetracyanobutadiene (TCBD, A2) and cyclohexa-2,5-diene-1,4diylidene-expanded TCBD (A3) used as additional acceptor unit to further improve their photophysical and electrochemical properties (Figure 4.1). In this chapter, we have mainly tuned the photonic properties by introducing the cyano based strong electron deficient units (TCBD and expanded TCBD unit) in the π -conjugated systems.



Figure 4.1. Structures of the investigated multimodular systems bearing closely associated with promote charge transfer, TPA, BTD, TCBD, and expanded TCBD electron donor and acceptor entities.

4.2. Results and discussion

Synthesis and characterization of BTD2-BTD4 and BTD6-BTD8

Synthesis of symmetrical and unsymmetrial push-pull chromophores **BTD2-BTD4** and **BTD6-BTD8** are depicted in Scheme 4.1. The benzothiadiazole substituted symmetrical chromophores **BTD1** with

structural configuration D1- π -A1- π -D1 and **BTD5** with structural configuration D2- π -A1- π -D2 were synthesized by the Sonogashira crosscoupling reaction.^[55,56] The TCBD functionalized unsymmetrical chromophores **BTD2** with structural configuration D1-A2-A1- π -D1 and **BTD6** with structural configuration D2-A2-A1- π -D2 were synthesized by the [2 + 2] cycloaddition–retroelectrocyclization reaction of **BTD1** and **BTD5** with one equivalent of TCNE in dichloromethane (DCM) at 40 °C in 89% and 83% yields, respectively.



Scheme 4.1. Synthesis of BTD2–4 and BTD6–8.

The reaction of benzothiadiazole based symmetrical chromophores **BTD1** and **BTD5** with one equivalent of 7,7,8,8-tetracyanoquinodimethane (TCNQ) at 80 °C in dichloroethane results in benzothiadiazole based unsymmetrical push-pull chromophores **BTD3** and **BTD7** in 88% and 92% yields, respectively. The expanded TCBD derivatives **BTD3** and **BTD7** were subjected to [2 + 2] cycloaddition–retroelectrocyclization reaction with TCNE in dichloroethane (DCE), resulted **BTD4** with D1-A2-A1-A3-D1 configuration and **BTD8** with D2-A2-A1-A3-D2 configuration at 80 °C in 90% and 88% yields, respectively. The newly synthesized compounds were purified with thin-layer chromatography while the structural integrity was solved by ¹H and ¹³C NMR and HRMS techniques (see ESI for spectral data).

4.3. Photophysical properties

The triphenylamine and *N*,*N*-dimethylaniline substituted benzothiadiazole chromophores **BTD1** and **BTD5** possess a single absorption band at 484 and 474 nm whereas TCBD and expanded TCBD functionalized derivatives **BTD2–4** and **BTD6–8** exhibit two distinct absorption bands around 436 to 670 nm (shown in the Figure 4.2),



Figure 4.2. The electronic absorption spectra of (a) **BTD1–BTD4** and (b) **BTD5–BTD8** in dichloromethane $(1 \times 10^{-5} \text{ M})$.

in which, the absorption bands in lower wavelength region *i.e.* between 436–545 nm, attributed to the $\pi \rightarrow \pi^*$ transition, whereas the absorption band in higher wavelength region at 550–666 nm corresponds to the intramolecular charge transfer (ICT) interaction, which was further explained by TD-DFT calculation.

 Table 4.1. Photophysical data of symmetrical and unsymmetrical BTD1–

 BTD8

BTDS	$\lambda_{abs}[nm]^a$	$\mathcal{E}[M^{-1}cm^{-1}]$	E_{g}^{opt} (eV)	Theoretical band	
				Gap (eV)	
BTD1	484	15700	2.13	2.35	
BTD2	460	51000	1.62	2.13	
	553	47200			
BTD3	495	64800	1.35	2.04	
	666	50543			
BTD4	480	37452	1.28	1.56	
	616	27461			
BTD5	474	17000	2.15	2.4	
BTD6	436	37000	1.71	2.29	
	547	32000			
BTD7	544	23100	1.32	2.18	
	652	22900			
BTD8	451	35200	1.27	1.75	
	607				

^{*a*}Absorbance measured in dichloromethane at 1×10^{-5} M concentration. λ_{abs} : absorption wavelength. ε : extinction coefficient. E_g^{opt} : optical band gap.

In the presence of expanded TCBD acceptor unit the chromophores **BTD 3** and **7** with structural configuration D1-A3-A1- π -D1 and D2-A3-A1- π -

D2 show a bathochromic of 182 nm and 178 nm compared to the precursors **BTD1** and **BTD5**. After incorporation of TCBD unit to the derivatives **BTD 3** and **7**, the derivatives **BTD 4** and **8** with structural configuration D1-A3-A1- A2-D1 and D2-A3-A1-A2-D2 shows a less bathochromic shift around 132 nm and 133 nm compared to **BTD1** and **BTD5** units, which may be due to more twisted structure after incorporation of TCBD unit (confirmed by the theoretical calculation).

This photophysical result of **BTD1–BTD8** revealed that expanded TCBD unit is used as a strong acceptor compared to TCBD unit and significantly tuned the HOMO–LUMO energy level compared to other derivatives. The optical band gaps calculated for unsymmetrical benzothiadiazoles **BTD1–BTD8** are 2.13 eV, 1.62 eV, 1.35 eV, 1.28 eV, 2.15 eV, 1.71 eV, 1.32 eV and 1.27 eV, respectively (shown in Table 4.1.).

4.4. Electrochemical Properties

In order to explain the electrochemical properties of **BTD1–8**, cyclic voltammetry (CV) was carried out in dry DCM in the presence of n-tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte. In cyclic voltammetry (CV) the Pt wire, saturated calomel electrode (SCE) and glassy carbon were used as counter electrode, the reference electrode and working electrode, respectively. The respective cyclic voltammograms of BTDs **BTD1–8** are depicted in Figure 4.3 and the redox potentials of **BTD1–8** are summarized in Table 4.2.

The triphenylamine and *N*,*N*-dimethylaniline substituted symmetrical benzothiadiazole chromophores **BTD1** and **BTD5** with structural configuration D1- π -A1- π -D1, D2- π -A1- π -D2 display a single reversible reduction wave at -0.86 V and -1.33 V in the cathodic side due to benzothiadiazole unit. Whereas in the anodic side an oxidation peak was observed at 1.04 V and 0.78 V due to triphenylamine and *N*,*N*-dimethylaniline unit.



Figure 4.3. Cyclic voltammograms of **BTD1–BTD8** in 0.1 M solution of Bu_4NPF_6 in dichloromethane at 100 mV s⁻¹ scan rate versus saturated calomel electrode (SCE) at 25 °C.

The TCBD and expanded TCBD functionalized unsymmetrical benzothiadiazole derivatives **BTD2**, **BTD6** and **BTD3**, **BTD7** with structural configuration D1-A2-A1- π -D1, D1-A3-A1- π -D1, D2-A2-A1- π -D2 and D2-A3-A1- π -D2 exhibit three reversible reduction waves whereas both TCBD and expanded TCBD substituted derivative **BTD 4** and **BTD 8** shows five reversible reduction waves with structural configuration D1-A3-A1-A2-D1 and D2-A3-A1-A2-D2. The first two-step reversible reduction waves of **BTD 2** (-0.27 V, -0.65 V), **BTD6** (-0.45 V, -0.81 V) and **BTD3** (-0.33 V, -0.47 V), **BTD7** (-0.29 V, -0.43 V) are attributed to one-electron transfer in each step and correspond to TCBD and expanded TCBD unit. The third reversible reduction of **BTD 2** (-0.89 V), **BTD6** (-1.73 V) and **BTD3** (-1.26 V), **BTD7** (-1.69 V) wave corresponds to benzothiadiazole unit.

BTDS	$E^{1}(V)$	$E^2(V)$	$E^{3}(V)$	$E^4(V)$	$E^{5}(V)$	$E^{1}(V)$	$E^2(V)$
	Red	Red	Red	Red	Red	Oxid	Oxid
BTD1	-0.86					1.04	
BTD2	-0.27	-0.65	-0.89	-	-	1.09	1.29
BTD3	-0.33	-0.47	-1.26	-	-	0.82	0.94
BTD4	-0.28	-0.43	-0.64	-1.01	-1.28	0.76	0.98
BTD5	-1.33					0.78	
BTD6	-0.45	-0.81	-1.73			0.91	1.15
BTD7	-0.29	-0.43	-1.69			0.80	
BTD8	-0.20	-0.34	-0.6	-0.93	-1.08	0.81	

Table 4.2. Electrochemical properties of BTD1-8

Electrochemical analysis was estimated by cyclic voltammetry, in 0.1 M solution of TBAPF_6 in DCM at 100 mV s⁻¹ scan rate versus SCE electrode.

The reduction waves of **BTD4** and **BTD8** revealed that the consecutive four reversible reduction waves at (-0.28 V, -0.43 V, -0.64 V, -1.01 V), (-0.20 V, -0.34 V, -0.6 V, -0.93 V) corresponds to TCBD and expanded TCBD units and the fifth reversible reduction wave at -1.28 V and -1.08 V corresponds to benzothiadiazole unit. In the anodic side, the triphenylamine and *N*,*N*-dimethylaniline substituted symmetrical benzothiadiazole chromophores BTD1 and BTD5 shows a single oxidation wave at 1.04 V and 0.78 V attributed to triphenylamine and N,N-dimethylaniline electron rich unit. The mono TCBD substituted derivative **BTD2** and **BTD6** shows two oxidation waves at (1.09 V, 1.29 V) and (0.91 V, 1.15 V) due to different environment occurred by the assimilation of TCBD unit next to one triphenylamine and N,Ndimethylaniline unit. The triphenylamine functionalized derivative BTD3 and **BTD4** exhibit two oxidation waves at (0.82 V, 0.94 V) and (0.76 V, 0.98 V) corresponds to triphenylamine unit whereas N,N-dimethylaniline functionalized derivative BTD7 and BTD8 exhibit single oxidation at 0.80 V and 0.81 V due to *N*,*N*-dimethylaniline donor unit.

4.5. Theoretical calculation

The density functional theory (DFT) and time dependent (TD-DFT) calculation was performed to investigate the ground state geometries and electronic transitions of **BTD1–8** in the gas-phases by using Gaussian 09 programs at the B3LYP/6-31G** level.^[57] The frontier energy levels of BTD1–8 are illustrated in Figure 4.4 and Figure 4.5. The DFT results explained that, the optimized structure of benzothiadiazole chromophores **BTD1** and **BTD5** exhibit non-planar structure due to the presence of twisted molecular structure of donor units (triphenylamine and *N*,*N*-dimethylaniline) substituted at the end-capping positions whereas the **BTD2–4** and **BTD6–8** shows more nonplanar structure due to the presence of the presence of additional acceptor units (TCBD and expanded TCBD entity).



Figure 4.4. Energy levels diagram of the frontier orbitals of **BTD1–4** estimated by DFT calculations.

The HOMO orbitals of benzothiadiazole based symmetrical chromophores **BTD1** and **BTD5** are delocalized over the whole molecule whereas the major part of LUMO is mainly localized on the BTD unit. In the case of **BTD2–4** and **BTD6–8**, the electron density of HOMO orbitals are mainly localized on triphenylamine and *N*,*N*-dimethylaniline unit and LUMO delocalized over BTD-TCBD, BTD-expanded TCBD and BTD unit segments. The HOMO energy levels of **BTD 1–8** are – 5.03, –5.55, –5.61, –5.83, -4.82, -5.57, -5.62 and -5.93 eV and the corresponding LUMO levels are –2.68, –3.42, –3.57, -4.27, -2.42, -3.28, -3.44 and -4.18 eV respectively.



Figure 4.5. Energy levels diagram of the frontier orbitals of **BTD5–8** estimated by DFT calculations.

The DFT results revealed that the LUMO energy level of **BTD2–4** and **BTD6–8** was lowered after incorporation of additional acceptors TCBD and expanded TCBD units. The **BTD4** and **BTD8** exhibit low band gap compared to other derivatives (**BTD1**, **BTD2**, **BTD3** and **BTD5**, **BTD6**, **BTD7**) due to the presence of both TCBD and expanded TCBD units.

The time-dependent DFT calculation was conducted at the B3LYP/6-31G (d, p) level to explore the electronic absorption spectra of benzothiadiazole based multi modular push-pull chromophores **BTD1–8** in dichloromethane solution. The TD-DFT calculation demonostrate that the benzothiadiazole functionalized symmetrical chromophores **BTD1** and **BTD5** possess an intense absorption band in the visible region around 476 nm and 488 nm, due to intramolecular charge transfer (ICT) transitions.

BTDs	Wavelength	Composition	f^{a}	Assignmen
Chromophores	(nm)	&		t
		Molecular contribution		
BTD1	476	HOMO \rightarrow LUMO (0.63)	1.84	ICT
BTD2	397	HOMO-1→LUMO+1 (0.51)	0.43	$\pi \rightarrow \pi^*$
	486	HOMO→LUMO (0.58)	1.24	ICT
BTD3	470	HOMO-1 \rightarrow LUMO+1(0.58)	0.18	$\pi \rightarrow \pi^*$
	644	HOMO–3→LUMO (0.50)	0.81	ICT
BTD4	468	HOMO→LUMO+1 (0.55)	0.23	$\pi \rightarrow \pi^*$
	557	HOMO→LUMO (0.70)	0.81	ICT
BTD5	488	HOMO→LUMO (0.67)	1.44	ICT
BTD6	500	HOMO→LUMO (0.63)	1.16	$\pi \rightarrow \pi^*$
	384	HOMO-1→LUMO+1 (0.46)	0.41	ICT
BTD7	564	HOMO-1→LUMO+1 (0.59)	1.13	$\pi \rightarrow \pi^*$
	651	HOMO→LUMO+1 (0.65)	0.65	ICT
BTD8	623	HOMO→LUMO (0.66)	0.75	$\pi \rightarrow \pi^*$
	489	HOMO→LUMO+1 (0.60)	0.32	ICT

Table 4.3. Calculated electronic transitions for **BTD1–8** indichloromethane.

 f^{a} oscillator strength.

The TCBD functionalized derivatives (**BTD2** and **BTD6**) exhibits two absorption band in the visible-near IR regions in which the absorption band at lower wavelength region attributed to π - π * transitions and the absorption band at the higher wavelength region corresponds to ICT transitions. Similarly, expanded TCBD derivatives (**BTD3**, **BTD7**) and both TCBD and expanded TCBD derivatives (**BTD4**, **BTD8**) exhibit π – π * transition band and ICT band in the visible-near IR regions. The theoretical results demonstrate that the all derivatives exhibit close agreement with the experimental results (Table 4.3).

4.6.Experimental section

Chemicals were used as received unless otherwise indicated. All the oxygen- or moisture-sensitive reactions were carried out under an argon atmosphere. ¹H NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are reported in δ units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using residual protonated solvent as an internal standard (CDCl₃, 7.26 ppm). ¹³C NMR spectra were recorded using a 100 MHz spectrometer. Chemical shifts are reported in δ units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using the solvent as internal standard (CDCl₃, 77.0 ppm). The ¹H NMR splitting patterns have been described as s, singlet; d, doublet; t, triplet; and m, multiplet. UV-visible absorption spectra of all compounds were recorded in dichloromethane solution. Cyclic voltammograms and differential pulse voltammograms were recorded on a potentiostat using glassy carbon as the working electrode, Pt wire as the counter electrode, and a SCE as the reference electrode. The scan rate was 100 mV s⁻¹ for cyclic voltammetry. A solution of TBAPF₆ in DCM (0.1 M) was used as the supporting electrolyte.

BTD2

In a 100 mL round bottomed flask, TCNE (63 mg, 0.49 mmol) was added to a solution of compound **BTD1** (335 mg, 0.5 mmol) in CH_2Cl_2 (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 6 h. The solvent was removed in vacuum, and the product was purified by SiO₂ column chromatography with DCM/hexane (2:1, v/v) as eluent to yield **BTD2** as a dark violet solid (355 mg, Yield: 89%); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J*=8 Hz, 1H), 7.83 (d, *J*=8 Hz, 1H), 7.65 (d, *J*=8 Hz, 2H), 7.52 (d, *J*=8 Hz, 2H), 7.42–7.30(m, 9H), 7.24–7.10 (m, 11H), 7.03 (d, *J* = 8 Hz, 2H), 6.88 (d, *J* = 9.04 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 164.06, 163.29, 153.81, 150.57, 146.78, 144.68, 135.65, 132.89, 132.22, 131.82, 130.22, 129.72, 127.04, 126.78, 125.76, 124.48, 122.18, 121.83, 121.24, 118.16, 113.64, 113.14, 111.60, 110.91, 92.89, 79.85. HRMS (ESI-TOF) m/z calculated for C₅₂H₃₀N₈S = 821.2206 [M+Na]⁺, measured 821.2163 [M+Na]⁺,

BTD3

In a 100 mL round bottomed flask, TCNQ (150 mg, 0.73 mmol) was added to a solution of compound **BTD1** (335 mg, 0.5 mmol) in DCE (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 6 h. The solvent was removed in vacuum, and the product was purified by SiO₂ column chromatography with DCM/hexane (2:1, v/v) as eluent to yield **BTD 3** as a dark violet solid (384 mg, Yield: 88%); ¹H NMR (400 MHz, CDCl₃) δ 8.35 (d, *J*=8 Hz, 1H), 7.99 (d, *J*=8 Hz, 1H), 7.92 (d, *J*=8 Hz, 1H), 7.62 (d, *J*=8 Hz, 1H), 7.55(d, *J*=8 Hz, 1H), 7.45–7.28 (m, 13H), 7.23–7.13 (m, 11H),7.02 (d, *J* = 8 Hz, 2H), 6.80 (d, *J* = 9.04 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 155.1, 154.9, 152.3, 152.2, 150.2, 147.5, 146.4, 142.0, 149.7, 139.8, 137.3, 135.0, 134.0, 133.8, 131.9, 130.7, 130.5, 128.3, 127.3, 126.5, 126.4, 125.8, 125.3, 124.1, 122.6, 121.6, 119.4, 116.5, 114.6, 114.5, 101.7, 85.8. HRMS (ESI-TOF) m/z calculated for C₅₈H₃₄N₈S = 874.2622 [M], measured 874.2714 [M].

BTD4

In a 100 mL round bottomed flask, TCNE (63 mg, 0.49 mmol) was added to a solution of compound **BTD3** (437 mg, 0.5 mmol) in DCE (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 6 h. The solvent was removed in vacuum, and the product was purified by SiO_2 column chromatography with DCM/hexane (2:1, v/v) as eluent to yield **BTD4** as a dark violet solid (450 mg, Yield: 90%); ¹H NMR (400 MHz, CDCl₃) δ 8.60-8.54 (m, 2H), 8.04 (d, *J*=8 Hz, 1H), 7.86 (d, *J*=8 Hz, 2H), 7.60 (d, *J*=8 Hz, 1H), 7.46-7.19 (m, 20H), 7.11 (d, *J*=8 Hz, 3H), 6.83 (d, *J* = 8 Hz, 2H), 6.76 (d, *J* = 8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 163.5, 154.5, 152.5, 152.2, 152.0, 146.5, 145.7, 137.3, 137.3, 135.0, 133.6, 133.4, 132.8, 131.0, 130.7, 127.9, 127.4, 127.3, 126.7, 126.4, 126.0, 122.5, 119.7, 118.2, 114.5, 114.1, 112.5, 112.0, 82.4. HRMS (ESI-TOF) m/z calculated for C₆₄H₃₄N₁₂S+Na = 1025.2642 [M+Na]⁺, measured 1025.2642 [M+Na]⁺.

BTD6

In a 100 mL round bottomed flask, TCNE (63 mg, 0.49 mmol) was added to a solution of compound **BTD 5** (211 mg, 0.5 mmol) in CH₂Cl₂ (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 6 h. The solvent was removed in vacuum, and the product was purified by SiO₂ column chromatography with DCM/hexane (2:1, v/v) as eluent to yield **BTD6** as a dark violet solid (228 mg, Yield: 83%); ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J*=8 Hz, 1H), 7.78 (d, *J*=8 Hz, 3H), 7.57 (d, *J*=8 Hz, 2H), 6.68 (t, 4H), 3.12 (s, 6H); 3.05 (s, 6H) ¹³C NMR (126 MHz, CDCl₃) δ 164.87, 164.05, 154.74–154.58, 154.33, 151.30, 151.18, 134.13, 132.99, 130.08, 124.92, 123.48, 119.10, 114.58, 113.75, 112.16, 111.82, 111.55, 108.16, 105.85, 90.58, 85.48, 40.25. HRMS (ESI-TOF) m/z calculated for C₃₂H₂₂N₈S = 551.1760 [M+H]⁺, measured 551.1768 [M+H]⁺,

BTD7

In a 100 mL round bottomed flask, TCNQ (150 mg, 0.73 mmol) was added to a solution of compound **BTD5** (211 mg, 0.5 mmol) in DCE (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 6 h. The solvent was removed in vacuum, and the product was purified by SiO_2 column chromatography with DCM/hexane (2:1, v/v) as eluent to yield

BTD7 as a dark violet solid (287 mg, Yield: 92%); ¹H NMR (400 MHz, CDCl₃) δ 7.83–7.69 (m, 2H), 7.54 (d, *J*=8 Hz, 1H), 7.40 (t, 1H), 7.21–7.19 (m, 6H), 6.69–6.58 (m, 4H), 3.07–3.04 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 167.1, 154.7, 154.2, 153.1, 152.9, 152.6, 151.4, 151.2, 150.5, 136.5, 136.1, 134.9, 134.9, 134.7, 134.3, 133.9, 133.7, 132.4, 132.1, 130.6, 130.1, 126.9, 126.0, 125.6, 125.3, 123.8, 123.7, 122.7, 114.9, 114.8, 114.6, 113.0, 112.5, 112.5, 112.3, 112.2, 111.8, 111.7, 108.1, 104.7, 93.5, 90.5, 85.0, 73.2, 72.3. HRMS (ESI-TOF) m/z calculated for C₃₈H₂₆N₈S = 627.2073 [M+H]⁺, measured 627.2056 [M+H]⁺.

BTD8

In a 100 mL round bottomed flask, TCNE (63 mg, 0.49 mmol) was added to a solution of compound **BTD7** (313 mg, 0.5 mmol) in DCE (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 6 h. The solvent was removed in vacuum, and the product was purified by SiO₂ column chromatography with DCM/hexane (2:1, v/v) as eluent to yield **BTD 8** as a dark violet solid (332 mg, Yield: 88%); ¹H NMR (400 MHz, CDCl₃) δ 8.05-7.98 (m, 1H), 7.87 (d, *J*=8 Hz, 1H), 7.78 (d, *J*=8 Hz, 2H), 7.42 (d, *J*=8 Hz, 1H), 7.31–7.27 (m, 3H), 7.22 (d, *J*=8 Hz, 2H), 6.69 (d, *J* = 8 Hz, 2H), 6.63 (d, *J* = 8 Hz, 2H), 3.15 (s, 6H), 3.09 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 166.83, 163.78, 162.19, 154.69, 153.98, 153.12, 151.51, 151.10, 150.50, 136.14, 134.68, 134.36, 133.92, 132.87, 131.34, 130.67, 128.71, 126.10, 125.77, 122.42, 118.16, 114.49, 113.88, 112.60, 112.30, 111.73, 111.29, 110.72, 94.39, 93.54, 75.47, 73.29, 40.31. HRMS (ESI-TOF) m/z calculated for C₄₄H₂₆N₁₂S+H = 755.2196 [M+H]⁺, measured 755.2469 [M+H]⁺.

4.7.Conclusions

A series of push–pull derivatives of **BTD2–4** and **BTD6–8**, in which benzothiadiazole unit was used as the central unit core (electron-acceptor unit (A)), triphenylamine and *N*,*N*-dimethylaniline was used as the end

capping unit (electron- donor group (D)) and tetracyanobutadiene (A2) or expanded TCBD (A3) used as additional acceptor unit. To extend the π conjugation of BTD1 and BTD5, BTD2-4 and BTD6-8 were synthesized cycloaddition-retroelectrocyclization by [2+2]reactions. The photophysical properties of BTD3 and BTD7 exhibit a strong electronic absorption band (ICT) in the near IR regions with high onset value. The BTD2-4 and BTD6-8 shows multi redox waves with low electrochemical band gap which signifies the tuning of HOMO-LUMO energy levels and enhance the π -conjugation. The computational studies demonstrate that there is a good agreement with experimental data. We believe that the molecular design and synthesis of **BTD2–4** and **BTD6–8** gives a new path way to the exploitation of new building blocks in the organic electronics in the future.

4.8.References

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Chapter 5 NIR absorbing benzothiadiazole based multimodular pushpull chromophores

5.1. Introduction

Near-infrared (NIR) absorbing push-pull chromophores have received major attention over the past decade due to its potential applications in the optoelectronics.^[1-3] The NIR absorbing derivatives can be designed by introducing the electron withdrawing units in the π -conjugated systems, which tune the HOMO–LUMO energy levels and shift the absorption spectra towards the NIR region.^[4,5] The hetero atoms based electron withdrawing units were significantly used in the push-pull chromophores to improve the photonic properties, chemical stability, thermal stability, and photo stability.^[6-13]

2,1,3-Benzothiadiazole (BTD) is one of the widely studied strong electron withdrawing unit in organic electronics due to its strong electron affinity (EA) and high reduction potential.^[14-16] The BTD is a fused bicyclicheteroarene in which benzene ring comprised of diazole based fivemembered ring, where one of the C atom in the diazole ring is replaced by an S atom.^[17] Due to the presence of imine functional unit in the diazole ring, BTD shows higher electron affinity and is used as n-type organic electronic materials in the optoelectronic applications. 4- and 7-positions of the BTD unit are easily functionalized with push-pull units to extend the π -conjugation and tune the HOMO–LUMO gap.^[18-22] The push-pull functionalized BTD chromophores exhibit broad absorption spectra in the visible region with high molar extinction coefficient due to the strong intramolecular charge transfer (ICT) in π -conjugated systems.^[23] cell, which showed 4.1% power conversion efficiencies.^[22] Friend and coworkers have also developed several benzothiadiazole derivatives for optoelectronic and organic light emitting diodes.^[17,19] Müllen and coworkers have synthesized BTD substituted push-pull chromophores with altering the electron rich units to investigate the charge carrier mobilities for field-effect transistors.^[20]

Cyano-based chromophores are used as powerful electron acceptors and are widely used in OLEDs, organic field effect transistors and organic solar cells.^[24-28] The cyano-based chromophores like, tetracyanoethylene 7,7,8,8-tetracyanoquinodimethane (TCNE), (TCNO), 6,6dicyanopentafulvenes units have gained significant interest due to their better reactivity towards the electron-rich alkynes, result in highly coloured push-pull (TCBD and expanded TCBD) chromophores with broad absorption spectra and low HOMO-LUMO energy levels.^[29-37] In the past few years, ferrocene (Fc) and N,N-dimethylaniline (DMA) substituted alkyne moieties (electron-rich alkynes) were mainly used for the incorporation of the electron-acceptor (TCNE and TCNQ) units.^[38-40] For the first time, in 1981 Bruce and co-workers have developed TCBD substituted push-pull derivative through the [2 + 2] cycloadditionretroelectrocyclization (CA-RE) reaction of metal substituted acetylides (Ru-acetylide) and an electron-deficient olefin tetracyanoethene (TCNE) units.^[41] In 2007, Diederich and co-workers have explored the expanded TCBD substituted push-pull chromophores, which showed broad absorption band towards the NIR region.^[39] Shoji and co-workers have synthesized 1-azulenyl substituted TCBD and expanded TCBD derivatives and investigate the photophysical and electrochemical properties.^[42] Recently, Bottari et al. developed two new subporphyrins (SubPs) based push-pull chromophores, in which the meso (1) or axial (2) position of macrocycle was functionalized with TCBD unit.^[43,44]

Phenothiazine is a fused tricyclic chromophore, which contains sulfur (S) and nitrogen (N) hetero atoms in the central thiazine ring. The phenothiazine unit is mainly used as strong electron donor in the various applications including OLEDs, NLOs, OFETs, dye sensitized solar cells (DSSCs), bulk heterojunction organic solar cells (BHJOSCs), hole transporting materials (HTMs), sensing, due to low reversible oxidation potential, high chemical and thermal stability and high luminescence and photo-conductivities.^[45-49] Meyer et al. synthesized phenothiazine substituted oligoproline chromophores to investigate the intramolecular electron transfer and also synthesized phenothiazine functionalized Ru complex for mapping the electron transfer pathway in the π -conjugated complex system.^[50,51] Vivo et al. designed and synthesized triarylamine functionalized phenothiazine-based hole-transporting materials for perovskite solar cells which showed 14% power conversion efficiencies with low-cost and eco-friendly PSCs.^[52] The arylamines derivatives such as triphenylamine (TPA) are used as versatile materials (p-type materials) in bulk heterojunction organic solar cells (BHJOSCs), perovskite solar cell, OLEDs and OFETs due to their low oxidation potential and excellent hole-transporting properties.^[53]

In the present study, we have successfully developed a series of multichromophore based push-pull derivatives **BTD1–BTD6** in which benzothiadiazole (BTD, A1) was used as central unit core, phenothiazine (D1) and triphenylamine (D2) entities were used as end-capping donor units, TCBD (A2) and expanded TCBD (A3) were used as additional acceptors shown in Figure 5.1. In the multi-chromophore based push-pull systems, we have introduced cyano based auxiliary acceptors to improve the photonic properties compared to precursors **BTD1** and **BTD4**.



Figure 5.1. Chemical structure of BTD1–BTD6.

5.2. Results and discussion.

Synthesis and Characterizations.

As outline shown in Scheme 5.1, the benzothiadiazole substituted alkyne derivatives **BTD1** and **BTD4** with strong donor units triphenylamine and



Scheme 5.1. Synthesis of symmetrical BTD1 and BTD4 derivatives.

phenothiazine, were synthesized by the Sonogashira cross-coupling reaction of 3-ethynyl-10-propyl-10H-phenothiazine **2** with 4,7-

dibromobenzo[c][1,2,5]thiadiazole **1** and 4-((7-bromobenzo[c][1,2,5]thiadiazol-4-yl)ethynyl)-N,N-diphenylaniline **3**^[54] in 64% and 67% yields, respectively. The synthesis of unsymmetrical chromophores **BTD2**, **BTD3**, **BTD5** and **BTD6** were carried out according to Scheme 5.2.



Scheme 5.2. Synthesis of symmetrical and unsymmetrical benzothiadiazole derivatives BTD1–BTD6.

The benzothiadiazole based unsymmetrical chromophores **BTD2** and **BTD3** with molecular structure D1-A2-A1- π -D1 and D1-A3-A1- π -D1 were synthesized *via* [2 + 2] cycloaddition–retroelectrocyclization (CA-RE) reaction of one equivalent of tetracyanoethylene (TCNE) with **BTD1** in dichloromethane (DCM) at 40 °C and one equivalent of TCNQ with **BTD1** in dichloroethane (DCE) at 80 °C in 87% and 85% yields, respectively. Similarly the tetracyanobutadiene (A2) substituted derivatives **BTD5** and **BTD5'** with molecular structure D2-A2-A1- π -D1 and D2- π -A1-A2-D1 were synthesized by using 1 equivalent of TCNE with **BTD4** in dichloromethane (DCM) at 40 °C result in 60:40 regioisomeric mixtures of **BTD5** and **BTD5'** in 89% yield. The expanded TCBD (A3) substituted derivative **BTD6** (as a single regioisomeric product), with molecular structure D2-A3-A1- π -D1 was synthesized by

using one equivalent of TCNQ with **BTD4** in dichloroethane (DCE) at 80 °C in 88% yield due to the presence of triphenylamine as a better electron donor and activator (Hammett constants σ_p^+ N(C₆H₅)₂ = -0.22)^[55] compared to the phenothiazine unit(Hammett constants σ_p^+ phenothiazine = 0).^[56] The successful synthesis and purification of all symmetrical and unsymmetrical derivatives were confirmed by ¹H and ¹³C NMR and HRMS techniques.

5.3. Electronic Absorption Spectra

The electronic absorption spectra of the push-pull derivatives **BTD1**–**BTD6** in dichloromethane solution are shown in Figure 5.2 and are tabulated in Table 5.1.



Figure 5.2. The absorption spectra of (a) **BTD1–BTD3** and (b) **BTD4– BTD6** in dichloromethane $(1 \times 10^{-5} \text{ M})$ and the derivative **BTD5** corresponds to a mixture of **BTD5** and **BTD5'**.

The benzothiadiazole substituted chromophore **BTD1** with molecular structure D1- π -A1- π -D1 and **BTD4** with structural configuration D2- π -A1- π -D1 exhibits a single absorption band around 477 nm and 485 nm due to strong ICT transition.
Compounds	Photophysical data ^a			Electrochemical data ^b		
	$\lambda_{\max(nm)}$	$\boldsymbol{\varepsilon}(\mathbf{M}^{-1}\mathbf{cm}^{-1})$	$E_{\rm g}^{\rm opt}$	E_{red} (V)	$E_{ox}(\mathbf{V})$	
			(eV)			
BTD1	477	32000	2.13	-1.9	0.77	
BTD2	417	14000	1.51	-0.36	0.68	
	549	15000		-0.76	0.84	
				-1.71		
BTD3	486	27000	1.20	-0.23	0.69	
	666	14000		-0.37	1.28	
				-1.63		
BTD4	485	26000	2.1	-1.22	0.72	
					0.95	
BTD5	460	18000	1.6	-0.38	0.75	
	534	14000		-0.75	1.13	
				-1.71		
BTD6	490	26000	1.28	-0.27	0.5	
	681	21000		-0.39	0.78	
				-1.56		

 Table 5.1. Photophysical and electrochemical data of symmetrical and unsymmetrical BTD1–BTD6

^{*a*}Absorbance measured in dichloromethane at 1×10^{-5} M concentration. λ_{abs} : absorption wavelength. ε : extinction coefficient. E_g^{opt} : optical band gap. ^{*b*}Electrochemical analysis was estimated by cyclic voltammetry, in 0.1 M solution of TBAPF₆ in DCM at 100 mV s⁻¹ scan rate versus SCE electrode. The derivative **BTD5** corresponds to a mixture of **BTD5** and **BTD5'**.

The results explained that the alteration of terminal donor unit (triphenylamine in the place of phenothiazine unit) in the **BTD4** shows a smaller red shift of 8 nm as compared to BTD1 due to better electron donating ability of triphenylamine unit. The TCBD substituted push-pull derivatives **BTD2** with molecular structure D1-A2-A1- π -D1 and **BTD5** with molecular structure D2-A2-A1- π -D1 exhibit π - π * transition in the lower wavelength region around 417 nm and 460 nm whereas the absorption band around 549 nm and 534 nm in the longer wavelength region attributed to ICT transitions. In the π - π * transition, the absorption maxima (λ_{max}) of the **BTD5** exhibits a red shift compared to **BTD2** which may be due to substitution of triphenylamine as better donor unit in the place of phenothiazine unit. When the expanded TCBD unit (a powerful acceptor) assimilated in the push-pull systems, the chromophores BTD3 with molecular structure D1-A3-A1- π -D1 and **BTD6** with molecular structure D2-A3-A1- π -D1 exhibit two absorption bands in the visible and near-IR regions in which the absorption band around 666 nm and 681 nm attributed to ICT transitions and the absorption bands around 486 nm and 490 nm in the lower wavelength region correspond to π - π * transition. The photophysical studies reveal that, the expanded TCBD substituted derivatives BTD3 and BTD6 exhibit 189 nm and 196 nm of red shift compared to derivatives (BTD1 and BTD4) in the ICT band due to incorporation of additional acceptor in the push-pull system.^[57] The results explain that, the presence of cyano-based acceptors TCBD and expanded TCBD shows better performance in the optical properties and tuned the HOMO-LUMO energy levels.^[58] The bathochromic shift in the absorption maxima (λ_{max}) of intramolecular charge transfer (ICT) transitions of **BTD1–BTD6** follows the order **BTD6** > **BTD3** > **BTD2** > **BTD5** > **BTD4** > **BTD1**. The estimated optical bang gaps (E_g^{opt}) for BTD1-BTD6 are 2.13 eV, 1.51 eV, 1.2 eV, 2.1 eV, 1.6 eV and 1.28 eV.

5.4. Electrochemical Properties

The electrochemical behaviour and the HOMO/LUMO energy levels of chromophores **BTD1–BTD6** were calculated by using cyclic voltammetry experiments (in Figure 5.3). The electrochemical data are tabulated in Table 5.1. The electrochemical properties of **BTD1** and **BTD4** were tuned by introducing the auxiliary acceptors (TCBD and expanded TCBD) and altering the terminal donor units. In the cathodic side, the chromophore **BTD1** with molecular structure D1- π -A1- π -D1 and **BTD4** with molecular structure D2- π -A1- π -D1 exhibit a single reversible reduction wave at -1.19 V and -1.22 V due to the presence of benzothiadiazole unit, signifying its acceptor nature whereas in the anodic side, the chromophore **BTD1** exhibit a single reversible oxidation wave at 0.77 V ascribed to both phenothiazine units (D1) and the chromophore **BTD4** show two reversible oxidation waves at 0.72 V and 0.95 V attributed to the triphenylamine and phenothiazine unit.



Figure 5.3. Cyclic voltammograms of **BTD1–BTD6** in 0.1 M solution of Bu_4NPF_6 in dichloromethane at 100 mV s⁻¹ scan rate versus saturated calomel electrode (SCE) at 25 °C. The derivative **BTD5** corresponds to a mixture of **BTD5** and **BTD5'**.

In the cathodic side, the TCBD substituted push-pull chromophores **BTD2** with molecular structure D1-A2-A1- π -D1 and **BTD5** with molecular structure D2-A2-A1-π-D1 revealed three reversible reduction waves at -0.36 V, -0.76 V, -1.71 V and -0.38 V, -0.75 V, -1.71 V due to presence of both electron deficient TCBD and BTD unit. The first two-step reversible reduction waves for both compounds BTD2 and BTD5 belongs to TCBD unit and the third reduction wave corresponds to the benzothiadiazole unit. In the anodic side, the TCBD substituted chromophore **BTD2** with molecular structure D1-A2-A1-π-D1 shows two reversible oxidation waves at 0.68 V, 0.84 V for phenothiazine units due to unsymmetrical environment occurred by the incorporation of TCBD unit next to one phenothiazine unit, whereas **BTD5** with molecular structure D2-A2-A1- π -D1 exhibits two oxidation waves at 0.75 V and 1.13 V due to the presence of two different electron donor units (phenothiazine unit and triphenylamine unit). Similarly, in the cathodic side, the expanded TCBD substituted push-pull derivative BTD3 and BTD6 with molecular structure D1-A3-A1- π -D1 and D2-A3-A1- π -D1 shows three reduction waves at -0.23 V, -0.37 V, -1.63 V and -0.27 V, -0.39 V, -1.56 V in which first twostep reversible reduction waves are attributed to the expanded TCBD unit and the third reduction wave belongs to the benzothiadiazole unit. In the anodic side, the BTD3 and BTD6 exhibit two oxidation waves at 0.69 V, 1.28 V and 0.5 V, 0.78 V due to the donor units (phenothiazine and triphenylamine unit). By considering the onset potentials in both oxidation and reduction side, we have estimated the HOMO energy levels of symmetrical and unsymmetrical push-pull chromophores **BTD1–BTD6** are -4.94, -5.04, -5.05, -4.95, -5.02, -5.01 eV and LUMO energy levels are -3.33, -4.04, -4.15, -3.32, -4.04, -4.15 eV, respectively.

The HOMO and LUMO energy levels estimated for symmetrical and unsymmetrical derivatives **BTD1–BTD6** demonstrated that the LUMO energy levels of **BTD3** and **BTD6** tune more significantly compared to others due to the incorporation of auxiliary acceptor in the push-pull systems. The estimation of band-gap through the electrochemical study is the key factor for the chromophores to be used in optoelectronic applications. The experimental band gaps estimated through the cyclic voltammetry for **BTD1–BTD6** are 1.61, 1.0, 0.9, 1.63, 0.98 and 0.86 eV respectively. The electrochemical band gaps for **BTD1–BTD6** are close comparable to optical band gap (E_g^{opt}) 2.13, 1.51, 1.20, 2.1, 1.6 and 1.28 eV (Table 5.1). The experimental band gaps (electrochemical band) calculated from electrochemical study follow the order **BTD4** > **BTD1** > **BTD2** > **BTD3** > **BTD6**.

5.5. Computational study

The density functional theory (DFT) calculation was performed at the B3LYP/6-31G** level to optimize the electronic structure of BTD1-BTD6 and explained about the electron density distribution over the HOMO and LUMO energy levels.^[59] The optimized electronic structures of BTD1 and BTD4 shows distorted molecular structure due to the presence of phenothiazine unit (as end-capping entity with a butterfly structure) and triphenylamine unit (as end-capping unit with propeller shape). The multi acceptor based push-pull systems BTD2, BTD3, BTD5 and **BTD6** shows more rigid structure compared to **BTD1** and **BTD4** due to the presence of TCBD and expanded TCBD units. The optimized structures and orbital energy diagram of BTD1-BTD6 are shown in Figure 5.4. The theoretical calculation on benzothiadiazole substituted push-pull derivatives **BTD1** with molecular structure D1- π -A1- π -D1 and **BTD4** with molecular structure $D2-\pi$ -A1- π -D1 demonstrated that the electron density of HOMO was spread on end-capping units (phenothiazine and triphenylamine units) while electron density of LUMO was concentrated on the BTD unit and a very negligible amount of LUMOs was on **BTD-PTZ** and **BTD-TPA** segments. In the case of **BTD2** and **BTD3**, the electron density of HOMO was mostly localized on the phenothiazine unit (as strong donor unit) while the majority of electron

density of LUMO was concentrated on **BTD-TCBD** and **BTD-expanded TCBD** segment which is having two electron withdrawing units. Similarly in the case of **BTD5** and **BTD6**, the electron density of HOMO was restricted on phenothiazine unit instead of triphenylamine entity due to the presence of electron withdrawing unit (TCBD and expanded TCBD unit) near to triphenylamine unit, whereas the electron density of LUMO was on **BTD-TCBD** and **BTD-expanded TCBD** segment as combination of powerful acceptor units.



Figure 5.4. Optimized structure, frontier HOMO and LUMO orbitals of **BTD1–BTD6**.

Table	5. 2.	Calculated	electronic	transitions	for	BTD1–BTD6	in
dichlor	ometh	ane.					

BTD	Wavelength	Composition	f^{a}	Assignment
chromophores	(nm)	&		
		Molecular contribution		
BTD1	461	HOMO \rightarrow LUMO (0.63)	1.63	ICT
	419	HOMO−1→LUMO+1	0.18	π-π*
BTD2		(0.48)		
	489	HOMO→LUMO (0.57)	1.06	ICT
	460	HOMO–2→LUMO+1	0.56	ππ*
BTD3		(0.48)		
	703	HOMO \rightarrow LUMO+1 (0.66)	0.38	ICT
BTD4	469	HOMO→LUMO (0.62)	1.74	ICT
	398	HOMO–1→LUMO+1	0.45	ππ*
BTD5		(0.51)		
	465	HOMO \rightarrow LUMO (0.56)	1.12	ICT
	418	HOMO–1→LUMO+1	0.18	ππ*
BTD5'		(0.47)		
	491	HOMO \rightarrow LUMO (0.58)	1.23	ICT
	511	HOMO–2→LUMO (0.59)	0.23	ππ*
BTD6	651	HOMO–1→LUMO+1	0.80	ICT
		(0.57)		
1	1		1	1

 f^{a} oscillator strength.

The theoretically estimated frontier energy levels of multi-acceptor based chromophores **BTD1–BTD6** explained that the LUMO orbitals were strongly influenced with the auxiliary acceptors (TCBD and expanded

TCBD units). The theoretical band-gaps estimated for multi-acceptor based chromophores **BTD1–BTD6** are 2.41, 1.97, 1.67, 2.37, 2.15 and 1.92 eV, respectively. The band gap calculated for multi-acceptor based chromophores **BTD1–BTD6** are close to experimental band gap (E_g^{opt}) 2.13, 1.51, 1.20, 2.1, 1.6 and 1.28 eV (Table 5.1.), but there was small error in the range (0.2–0.7 eV) observed may be due to the solvent effects. In order to investigate the electronic absorption band of the benzothiadiazole substituted push-pull chromophores of **BTD1–BTD6**, we conducted the TD-DFT calculation by using CAM–B3LYP/6-31G** level on optimized ground-state molecular geometries of **BTD1**, **BTD2**, **BTD4**, **BTD5** and **BTD5'** and B3LYP/6-31G** level on **BTD3** and **BTD6** in DCM, which are shown in Table 5.2.

The TD-DFT calculation predicts that the benzothiadiazole substituted push-pull chromophores BTD1 and BTD4 exhibit an intense transition in the visible region around 461 nm and 469 nm (shown in Figure 5.5), which was predominated by HOMO-LUMO energy level due to intramolecular chargetransfer (ICT) transitions whereas the TCBD (BTD2, BTD5 and BTD5') and expanded TCBD (BTD3 and BTD6) derivatives exhibit two intense transition in the visible-near IR regions in which the first transition in the lower wavelength region is attributed to the π - π * transitions and the next transition in the higher wavelength region corresponds to ICT transitions. The electronic absorption spectra calculated from TD-DFT calculations for both regioisomeric derivatives (BTDPTZ5 and **BTDPTZ5**') are in close agreement with each other and also good agreement with experimental data. When we compared the computational study (TD-DFT and DFT data) with experimental data (UV-vis spectra and frontier energy levels estimated from electrochemical study), the results demonstrate that the all derivatives exhibit close agreement with the experimental results.



Figure 5.5. Theoretical absorption spectra of BTD1, BTD3, BTD4 and BTD6.

5.6. Experimental Section

Experimental details Chemicals were used as received unless otherwise indicated. All the oxygen or moisture sensitive reactions were carried out under argon atmosphere and the reflux reactions were performed in an oil

bath. ¹H NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using residual protonated solvent as an internal standard {CDCl₃, 7.26 ppm}. ¹³C NMR spectra were recorded using a 100 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using the solvent as internal standard {CDCl₃, 77.16 ppm}. The ¹H NMR splitting patterns have been described as "s, singlet; d, doublet; t, triplet and m, multiplet". HRMS were recorded on a Bruker-Daltonics micrOTOF-Q II mass spectrometer. UV-visible absorption spectra of all compounds were recorded on a Perkin Elmer Lamba 35 UV-visible spectrophotometer in dichloromethane solution. Cyclic voltammograms and differential pulse voltammograms were recorded on a CHI620D electrochemical analyzer in dichloromethane solvent and potentiostat 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 for cyclic voltammetry. A solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dichloromethane (0.1M) was used as supporting electrolyte.

4,7-bis((10-propyl-10H-phenothiazin-3-

yl)ethynyl)benzo[c][1,2,5]thiadiazol (BTD1) In a 100 mL round bottomed flask 4,7-dibromobenzo[c][1,2,5]thiadiazole derivative 1 (0.146 g, 0.5 mmol, 1 equiv) and 3-ethynyl-10-propyl-10H-phenothiazine 2 (0.278 g, 1.05 mmol, 2.1 equiv) were dissolved in 1:1 (v/v) triethylamine (TEA) (30 ml) and tetrahydrofuran (THF) (30ml). The reaction mixture was purged with argon, and Pd(PPh₃)₄ (0.082 g, 0.071 mmol), and CuI (0.015 g, 0.078 mmol) were added. The reaction mixture was reflux at 60 °C in an oil bath for 6 h. Upon the completion of the reaction, the mixture was evaporated and purified by silica gel column chromatography with hexane/CH₂Cl₂ (1:1) to get the desired compound **BTD1** as a red colored solid. Yield 0.212 g (64%): mp 156–160 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.72 (s, 2H), 7.45–7.40 (m, 4H), 7.18–7.11 (m, 4H), 6.95–6.91 (m, 2H), 6.87–6.81 (m, 4H), 3.83 (t, 4H), 1.89–1.80 (m, 4H), 1.02 (t, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 154.5, 146.2, 144.6, 132.2, 131.4, 130.7, 127.7, 127.5, 125.0, 124.3, 123.0, 117.2, 116.3, 115.8, 115.2, 97.4, 85.7, 49.5, 20.3, 11.4. HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₄₀H₃₀N₄S₃ 662.1627; Found 662.1636.

2-(10-propyl-10H-phenothiazin-3-yl)-3-(7-((10-propyl-10Hphenothiazin-3-yl)ethynyl)benzo[c][1,2,5]thiadiazol-4-yl)buta-1,3diene-1,1,4,4-tetracarbonitrile (BTD2)

In a 100 mL round bottomed flask, TCNE (0.064 g, 0.49 mmol) was added to a solution of compound **BTD1** (0.331 g, 0.5 mmol) in CH₂Cl₂ (50 mL) under an argon atmosphere. The mixture was heated at 40 °C in an oil bath for 6 h. The solvent was removed in vacuum, and the product was purified by SiO₂ column chromatography with DCM/hexane (2:1, v/v) as eluent to yield **BTD2** as dark brown solid (0.344 g, Yield: 87%): mp 130–134 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 8 Hz, 1H), 7.83 (d, J = 8 Hz, 1H), 7.64-7.61 (m, 1H), 7.46-7.38 (m, 3H), 7.18-7.11 (m, 2H), 7.46-7.38 (m, 3H), 7.18-7.11 (m, 2H), 7.46-7.38 (m, 3H), 7.18-7.11 (m, 2H), 7.18-7.11 (3H), 7.05–6.93 (m, 3H), 6.88–6.77 (m, 4H), 3.86–3.79 (m, 4H), 1.89– 1.77 (m, 4H), 1.04–0.99 (m, 6H). ${}^{13}C{}^{1}H{}$ NMR (100 MHz, CDCl₃) δ 163.8, 163.4, 154.7, 151.1, 147.2, 144.2, 142.2, 132.9, 132.0, 131.0, 130.9, 130.7, 128.2, 128.0, 127.8, 127.7, 127.6, 125.5, 125.2, 125.0, 124.5, 124.3, 124.0, 123.5, 123.3, 122.9, 116.3, 115.9, 115.2, 115.0, 113.1, 112.6, 111.8, 111.2, 102.8, 91.3, 85.9, 82.8, 50.0, 49.6, 20.2, 20.1, 11.4, 11.3. HRMS (ESI-TOF) m/z: $[M +H]^+$ calcd for $C_{46}H_{30}N_8S_3$ 791.1828; Found 791.1824.

2-(4-(3,3-dicyano-1-(10-propyl-10H-phenothiazin-3-yl)-2-(7-((10propyl-10H-phenothiazin-3-yl)ethynyl)benzo[c][1,2,5]thiadiazol-4yl)allylidene)cyclohexa-2,5-dien-1-ylidene)malononitrile (BTD3)

In a 100 mL round bottomed flask TCNQ (0.102 g, 0.49 mmol) was added to a solution of **BTD1** (0.331 g, 0.49 mmol) in DCE (50 mL). The mixture was heated at 80 °C in an oil bath for 24 h. After cooling to room temperature, the solvents were removed under vacuum, and the product was purified by silica gel column chromatography with DCM as the eluent to yield **BTD3** as a dark-colored solid (0.368 g, yield 85%): mp 139–143 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8 Hz, 1H), 7.75 (d, J = 8Hz, 1H), 7.42–7.30 (m, 6H), 7.17–7.03 (m, 5H), 6.99–6.92 (m, 3H), 6.87-6.80 (m, 3H), 6.70 (d, J = 8 Hz, 1H), 3.83 (t, 2H), 3.75 (t, 2H), 1.88–1.74 (m, 4H), 1.03–0.97 (m, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 167.0, 154.7, 154.0, 151.3, 149.3, 148.8, 147.0, 144.2, 142.9, 135.7, 135.4, 134.6, 132.2, 132.1, 131.8, 131.0, 130.8, 130.0, 128.8, 127.9, 127.7, 127.7, 127.6, 126.8, 126.7, 126.6, 125.5, 125.1, 124.0, 124.0, 123.3, 123.1, 123.0, 116.1, 115.9, 115.3, 115.2, 115.1, 113.9, 112.6, 112.3, 101.6, 91.1, 58.6, 49.8, 49.6, 29.8, 20.2, 11.4, 11.3. HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₅₂H₃₄N₈S₃ 866.2063; Found 866.2059.

N,N-diphenyl-4-((7-((10-propyl-10H-phenothiazin-3-

yl)ethynyl)benzo[c][1,2,5]thiadiazol-4-yl)ethynyl)aniline (BTD4)

a 100 mL round bottomed flask 3-ethynyl-10-propyl-10H-phenothiazine 2 (0.199)0.75 1.5 mmol. equiv) and 4-((7g, bromobenzo[c][1,2,5]thiadiazol-4-yl)ethynyl)-N,N-diphenylaniline 3 (0.241 g, 0.5 mmol, 1 equiv) were dissolved in 1:1 (v/v) triethylamine (TEA) (30 ml) and tetrahydrofuran (THF) (30ml). The reaction mixture was purged with argon, and Pd(PPh₃)₄ (0.082 g, 0.071 mmol), and CuI (0.015 g, 0.078 mmol) were added. The reaction mixture was reflux at 60 °C in an oil bath for 6 h. Upon the completion of the reaction, the mixture was evaporated and purified by silica gel column chromatography with hexane/CH₂Cl₂ (1:1) to get the desired compound **BTD4** as a red colored solid. Yield 0.224 g (67%): mp 128–132 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.73 (s, 2H), 7.51 (d, J = 8 Hz, 2H), 7.45–7.40 (m, 2H), 7.32–7.28 (m,

5H), 7.17–7.02 (m, 9H), 6.95–6.92 (m, 1H), 6.87–6.81 (m, 2H), 3.83 (t, 2H), 1.89–1.80 (m, 2H), 1.02 (t, 3H). $^{13}C{^{1}H}$ NMR (100 MHz, CDCl₃): δ 154.6, 154.5, 148.8, 147.1, 146.2, 144.5, 133.1, 132.2, 132.1, 131.4, 130.6, 129.6, 127.6, 127.5, 125.4, 125.0, 124.2, 124.0, 123.0, 121.9, 117.4, 117.0, 116.3, 115.7, 115.2, 115.1, 98.3, 97.3, 85.7, 85.1 49.5, 20.3, 11.4. HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₄₃H₃₀N₄S₂ 666.1906; Found 666.1903.

2-(4-(diphenylamino)phenyl)-3-(7-((10-propyl-10H-phenothiazin-3yl)ethynyl)benzo[c][1,2,5]thiadiazol-4-yl)buta-1,3-diene-1,1,4,4tetracarbonitrile (BTD5)

In a 100 mL round bottomed flask, TCNE (0.063 g, 0.49 mmol) was added to a solution of compound **BTD4** (0.333 g, 0.49 mmol) in CH₂Cl₂ (50 mL) under an argon atmosphere. The mixture was heated at 40 °C in an oil bath for 6 h. The solvent was removed in vacuum, and the product was purified by SiO₂ column chromatography with DCM/hexane (2:1, v/v) as eluent to yield BTD5 and BTD5' in 60:40 calculated regioisomeric mixtures as dark brown solid (0.353 g, Yield: 89%): mp 125-128 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 8 Hz, 1H), 7.83 (d, J = 8 Hz, 1H), 7.64 (d, J = 8 Hz, 2H), 7.47–7.35 (m, 6H), 7.24–7.11 (m, 8H), 6.97–6.83 (m, 5H), 3.85 (t, 2H), 3.81 (t, 1H), 1.87–1.78 (m, 2H), 1.31–1.26 (m, 2H), 1.03 (t, 3H), 0.88 (t, 2H). ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃) δ 164.2, 164.0, 154.7, 153.7, 151.1, 147.1, 144.8, 144.2, 132.8, 132.2, 132.0, 131.0, 130.9, 130.2, 127.7, 127.6, 127.0, 126.7, 125.2, 124.0, 124.0, 123.3, 122.1, 118.2, 115.9, 115.2, 113.8, 113.1, 111.9, 111.3, 102.6, 91.5, 85.9, 80.1, 49.6, 34.3, 22.5, 20.2, 14.2, 11.4 HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₄₉H₃₀N₈S₂ 794.2029; found 794. 2107.

2-(4-(3,3-dicyano-1-(4-(diphenylamino)phenyl)-2-(7-((10-propyl-10Hphenothiazin-3-yl)ethynyl)benzo[c][1,2,5]thiadiazol-4yl)allylidene)cyclohexa-2,5-dien-1-ylidene)malononitrile (BTD6) In a 100 mL round bottomed flask TCNQ (0.102 g, 0.49 mmol) was added to a solution of **BTD4** (0.333 g, 0.49 mmol) in DCE (50 mL). The mixture was heated at 80 °C in an oil bath for 24 h. After cooling to room temperature, the solvents were removed under vacuum, and the product was purified by silica gel column chromatography with DCM as the eluent to yield **BTD6** as a dark-colored solid (0.382 g, yield 88%): mp 153–155 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8 Hz, 1H), 7.77 (d, *J* = 8 Hz, 1H), 7.56 (s,1H), 7.45–7.30 (m, 10 H), 7.21–7.12 (m, 10H), 6.99–6.93 (m, 1H), 6.88–6.83 (m, 3H), 3.84 (t, 2H), 1.87–1.80 (m, 2H), 1.03 (t, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 167.7, 154.7, 154.0, 151.7, 151.4, 150.9, 147.0, 145.4, 144.2, 135.9, 135.0, 134.7, 133.9, 132.2, 131.9, 131.0, 130.9, 130.0, 129.7, 127.7, 127.3, 127.0, 126.7, 126.3, 126.0, 125.7, 125.2, 124.0, 123.3, 122.8, 119.1, 115.9, 115.3, 115.2, 114.3, 114.2, 112.2, 101.6, 91.3, 85.6, 75.1, 49.6, 20.2, 11.4. HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₅₅H₃₄N₈S₂ 870.2342; found 870. 2397.

5.7. Conclusions

This chapter describes the design and synthesize of a series of multiacceptor based push-pull chromophores **BTD1–BTD6** *via* [2 + 2] cycloaddition–retroelectrocyclization (CA-RE) reactions in which benzothiadiazole (BTD, A1) was used as central core, phenothiazine (D1) and triphenylamine (D2) entity as end-capping units, TCBD (A2) and expanded TCBD (A3) as additional acceptors. The photophysical, electrochemical and theoretical calculations demonstrate that the presence of cyano based acceptors TCBD and expanded TCBD in the π -conjugated systems tune the photonic properties. The photophysical properties reveal that the expanded TCBD substituted derivatives **BTD3** and **BTD6** shows a broad absorption band in the vis-NIR region compared to the derivatives **BTD1** and **BTD4** due to strong intramolecular charge transfer (ICT) transition. The electrochemical properties of **BTD1–BTD6** explained that the HOMO-LUMO energy levels are strongly influenced by the cyano based acceptors. The theoretical calculation on push-pull derivatives exhibit non-planar structure due to the butterfly structure of phenothiazine unit, propeller structure of triphenylamine unit and twisted structure of TCBD and expanded TCBD unit, further demonstrate that the cyano based acceptors perturb the LUMO energy levels. We have established a new synthetic approach in which a strong acceptor (benzothiadiazole) was introduced in between the two distinct electron donors (phenothiazine and triphenylamine units allied through the acetylene unit) to identify the TCBD substituted regioisomeric mixture of (**BTD5** and **BTD5**') which was confirmed by ¹H and ¹³C NMR. Finally, the studies on the series of multimodular push-pull chromophores **BTD1–BTD6** demonstrate that these chromophores are promising materials for the bulk heterojunction solar cells and show a new pathway to develop the cyano based push-pull chromophores by [2 + 2] cycloaddition–retroelectrocyclization (CA-RE) reactions.

5.8. References

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Chapter 6

Design and synthesis of 1,8-Naphthalimides functionalized benzothiadiazole chromophores

6.1. Introduction

 π -conjugated push-pull chromophores have received substantial attention of the scientific community due to their potential applications in the field of optoelectronic applications.^[1-5] The heteroatom-based derivatives of benzothiazole, benzothiadiazole, diketopyrrolopyrrole, isoindigo, BODIPY, and naphthalimide are explored in the π -conjugated systems to tune the HOMO and LUMO energy levels.^[6-11] The photonic and electronic properties of the organic π -conjugated derivatives can be perturbed by altering the strength of donor or acceptor groups in the π conjugated back bone and π -linkers.^[12-16] Our group is interested to develop heteroatom based push-pull chromophores by modulating the strength of donor and acceptor moieties for the optoelectronic applications.

The push-pull functionalized 2,1,3-benzothiadiazole (BTD) derivatives have been studied in fluorescence imaging, nonlinear optics, light-emitting diodes (OLEDs) and n-type materials due to its high reduction potential and strong electron affinity (EA).^[17-22] Lee and co-workers have developed rhodanine functionalized 2,1,3-benzothiadiazole (BTD) based non-fullerene acceptors for organic solar cell which showed power conversion efficiency up to 8.19%.^[23] Yang *et al.* explored the diketopyrrolopyrrole and isoindigo based 2,1,3-benzothiadiazole (BTD) chromophores for high performance ambipolar semiconducting materials.^[24] Our group has synthesized multi acceptor based benzothiadiazole chromophores for optoelectronic and ultra-fast studies.^[25–27]

On the other hand, the 1,8-Naphthalimide (NPI) derivatives are used in optoelectronic materials, pH sensors, laser dyes, metal sensors and bioimaging due to its high chemical and thermal stability, strong fluorescence quantum yield and good photostability.^[28–30] 1,8-Naphthalimide (NPI) substituted n-type materials possess excellent performance in bulk heterojunction solar cells. Liu and co-workers have developed iminodiacetic acid and picolinic acid based 4-amino-1,8-naphthalimide-based chromophores for detection of Hg²⁺ in aqueous solution and living cells.^[31] Anna and co-workers have designed and synthesized imidazolium functionalized naphthalimide derivatives for bioimaging and anticancer activity.^[32] Our group has developed BODIPY functionalized naphthalimide derivatives for bioimaging applications.^[30]

Tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) are widely used in organic field effect transistors and organic solar cells due to their excellent photophysical and electrochemical properties.^[33–38] The TCNE and TCNQ units undergo [2 + 2] cycloaddition–retroelectrocyclization reaction with electron-rich triphenylamine (TPA), ferrocene (Fc) and *N*,*N*-dimethylaniline (DMA) based alkynes moiety to form donor-acceptor (TCBD and expanded TCBD) based derivatives, which show broad absorption in NIR region.^[33, 34, 36]

In the present study, we have developed a series of multi acceptor based push-pull chromophores **BTD1– BTD5** in which benzothiadiazole (A1) was used as a central unit core, naphthalimide (A2) as end-capping electron deficient unit, tetracyanobutadiene (A3) or expanded TCBD (A4) moiety as additional electron-withdrawing units and triphenylamine and ferrocenyl units as end-capping electron rich unit. Herein we explore the effect of variation of electron rich and electron deficient units on the photophysical, electrochemical and computational studies.

6.2. Results and discussion.

The synthesis of naphthalimide functionalized benzothiadiazole chromophores **BTD2–5** are shown in Scheme 6.1 and 6.2. The triphenylamine substituted benzothiadiazole derivatives **BTD1** with structural configuration D1- π -A1- π -A2 was synthesized by the Sonogashira cross-coupling reaction.^[39]



Scheme 6.1. Synthesis of benzothiadiazole functionalized push-pull derivatives BTD2 and BTD3.

The Sonogashira cross-coupling reaction of $\mathbf{I}^{[40]}$ with 1.3 equiv of acetylene functionalized naphthalimide unit **II** resulted in unsymmetrical benzothiadiazole derivative **BTD4** in 59% yield (Scheme 6.2). The TCBD and expanded TCBD linked naphthalimide substituted benzothiadiazole derivatives **BTD2**, **3** and **5** were synthesized *via* [2 + 2] cycloaddition–retroelectrocyclization reaction. The reaction of TPA and Fc functionalized benzothiadiazole **BTD1** and **BTD4** with TCNE (1 equivalent) in DCM resulted **BTD2** and **5** in 80% and 88% yield, respectively.



Scheme 6.2. Synthesis of benzothiadiazole functionalized push-pull derivatives BTD4 and BTD5.

The expanded TCBD substituted chromophore **BTD3** with structural configuration D1-A4-A1- π -A2 was synthesized by the reaction of 1.2 equivalent of TCNQ with the benzothiadiazole derivative **BTD1** in microwave in dichloroethane (DCE) at 80 °C in 85% yield, whereas the ferrocenyl functionalized benzothiadiazole **BTD4** do not undergo the [2 + 2] cycloaddition–retroelectrocyclization reaction in the presence of excess amount TCNQ. The benzothiadiazole derivatives **BTD2–5** were characterized by ¹H, ¹³C NMR, and HRMS techniques.

6.3. Electronic Absorption Spectra

The optical properties of the naphthalimide functionalized benzothiadiazole derivatives **BTD1–5** were investigated in dilute dichloromethane (DCM) solutions $(1 \times 10^{-5} \text{ M})$ and are depicted in Figure 6.1. The relevant data including absorption maximum (λ_{abs}), extinction

coefficient and optical band gap are summarized in Table 6.1. The triphenylamine and ferrocenyl substituted benzothiadiazole derivatives **BTD1** and **BTD4** exhibit two absorption band at 408 nm and 407 nm due to π - π * transition and the absorption band at 494 nm and 517 nm corresponds to the intramolecular charge transfer (ICT) transition. The TCBD functionalized benzothiadiazole derivatives **BTD2** and **BTD5** exhibit an intense absorption bands around 455 and 416 nm corresponding to strong intramolecular charge transfer (ICT) transition.



Figure 6.1. The electronic absorption spectra of **BTD1–5** in dichloromethane solvent in dichloromethane $(1 \times 10^{-5} \text{ M})$.

In the case of **BTD5**, a shoulder peak was also observed around 582 nm with low intensity, which may be due to the additional ICT transition. The absorption spectra of benzothiadiazole derivatives **BTD2** and **BTD5** shows a blue shift compared to **BTD1** and **BTD4**, due to their non-planar structure which was confirmed by theoretical calculations. The expanded TCBD functionalized derivative **BTD 3** shows a π - π * transition at 418 nm and an intramolecular charge transfer (ICT) transition at 690 nm, respectively. The expanded TCBD derivative **BTD3** exhibits a

considerable bathochromic shift compared to precursor **BTD1** and TCBD functionalized derivative **BTD2** due to its strong donor-acceptor interaction. The optical band gaps for naphthalimide functionalized benzothiadiazole derivatives **BTD1–5** are 2.0 eV, 1.7 eV, 1.4 eV, 1.8 eV and 1.5 eV, respectively.

6.4. Electrochemical Properties

The cyclic voltammetry (CV) was performed to estimate the electrochemical properties and frontier molecular orbitals of the naphthalimide functionalized benzothiadiazole derivatives BTD1-5. The cyclic voltammograms are shown in Figure 6.2 and the electrochemical data are summarized in Table 6.1. The naphthalimide functionalized benzothiadiazole derivatives BTD1-5 exhibit multi-step redox waves due to the reduction of naphthalimide, BTD, TCBD and expanded TCBD acceptor units in the cathodic side, and the oxidation of triphenylamine and ferrocenyl donor unit in the anodic side. The triphenylamine and ferrocenyl functionalized benzothiadiazole derivative BTD1 and BTD4 exhibit two reversible reduction peaks at -1.16 V, -1.28 V and -1.10 V, -1.22 V which corresponds to the benzothiadiazole and naphthalimide unit whereas in the anodic side a oxidation peak was observed in the region of 0.5 V to 1.0 V corresponding to the triphenylamine and ferrocenyl unit. After incorporation of TCBD unit, the benzothiadiazole derivatives BTD2 and **BTD5** shows two additional reversible reduction peaks in the region of -0.3 V to -0.84 V, which is attributed to TCBD unit and the other two reversible reduction waves in the region -0.95 V to -1.4 V corresponds to benzothiadiazole and naphthalimide unit. In the anodic side both TCBD functionalized derivative BTD2 and BTD5 exhibit single oxidation waves corresponding to triphenylamine and ferrocenyl unit.



Figure 6.2. Cyclic voltammograms of **BTD1–5** in 0.1 M solution of Bu_4NPF_6 in dichloromethane at 100 mV s⁻¹ scan rate versus saturated calomel electrode (SCE) at 25 °C.

The expanded TCBD functionalized benzothiadiazole derivative **BTD3** shows four reversible reduction waves in the cathodic side in which first two reversible reduction waves are in the region of -0.2 V to -0.5 V is attributed to the expanded TCBD unit and the next two reversible

reduction waves at -1.17 V and -1.33 V corresponds to the benzothiadiazole and naphthalimide unit.

Table 6.1 .	Photophysical and electrochemical data of naphthalimid	le
BTD1–5		

Compound	Photophysical data ^a			Electrochemical				
				data ^b				
	$\lambda_{ m abs}$	Е	Optical		Ered	(V)		Eox
	(nm)	$\times 10^4$	Band				(V)	
		(M^{-1})	Gap	E_1	E_2	E_3	<i>E</i> ₄	E_1
		cm^{-1})	(eV)					
BTD1	408	4.3	2.0	-	-	-	-	0.96
	494	5.6		1.16	1.28			
BTD2	455	3.7	1.7	-	-	-	-1.4	1.10
				0.45	0.84	1.19		
	418	3.2	1.4	-	-	-	-	0.83
BTD3	690	1.3		0.29	0.46	1.17	1.33	
BTD4	407	4.8	1.8	-	-			0.55
	517	1.0		1.10	1.22			
BTD5	416	4.7	1.5	-	-	-	-	0.83
	582	0.33		0.39	0.74	0.95	1.25	

^a absorbance measured in dichloromethane at 1×10^{-5} M concentration; λ_{abs} :absorption wavelength;; ε : extinction coefficient. ^b electrochemical analysis was estimated by cyclic voltammetry, in 0.1 M solution of TBAPF₆ in DCM at 100 mV s⁻¹ scan rate versus SCE electrode.

The HOMO and LUMO energy levels of naphthalimide functionalized benzothiadiazole **BTD1–5** are -5.29 eV, -5.39 eV, -5.14 eV, -4.87 eV, -

5.18 eV and -3.48, -3.68 eV, -3.72 eV, -3.36 eV, -3.99 eV, respectively. The electrochemical band gap of naphthalimide functionalized benzothiadiazole **BTD1–5** are in good agreement with the optical band gap.

6.5. Computational study

To estimate the molecular geometry and electronic properties of multi modular benzothiadiazole chromophores **BTD1–5**, density functional theory (DFT) calculation was performed by using the B3LYP functional /6-31G** as basis set.^[41] The benzothiadiazole substituted push-pull chromophores **BTD1** and **4** exhibit non-planar structure due to presence of triphenylamine (propeller shape) and ferrocenyl unit.



Figure 6.3. Energy levels diagram of the frontier orbitals of BTD2, 3 and 5 estimated by DFT calculations.

The **BTD2**, **3** and **5** show more twisted structure due to presence of additional nonplanar acceptor units TCBD (A3) and expanded TCBD (A4) unit. The energy level diagram of naphthalimide functionalized

benzothiadiazoles **BTD2**, **3** and **5** are outlined in Figure 6.3. The optimized structures and frontier HOMO and LUMO orbitals of **BTD1–5** are shown in Figure 6.4.

 Table 6.2. Electronic transitions data for naphthalimide functionalized

 benzothiadiazole derivatives BTD1–5 in the dichloromethane

BTDs	Wavelength	Composition	f ^a	Assignment
	(nm)			
BTD1	481	HOMO→LUMO	1.92	ICT
	305	(0.58)	0.4	ππ*
		HOMO→LUMO+2		
		(0.4)		
BTD2	421	HOMO–1→LUMO	1.18	ICT
		(0.61)		
BTD3	656	HOMO−1→LUMO+1	0.62	ICT
	414	(0.68)	0.78	ππ*
		HOMO–2→LUMO+1		
		(0.56)		
BTD4	550	HOMO→LUMO	0.71	ICT
	454	(0.51)	0.67	ππ*
		HOMO→LUMO+1		
		(0.67)		
BTD5	563	HOMO-2→LUMO	0.7	ICT
		(0.89)		

 f^{a} oscillator strength.

The frontier molecular orbitals of **BTD1** and **BTD4** reveals that the HOMO is predominantly concentrated on the TPA and Fc unit, whereas the LUMO is mainly localized on the BTD-NPI units which shows excellent electronic communication in the chromophore **BTD1** and **BTD4**. In the case of TCBD and expanded TCBD functionalized benzothiadiazole
derivatives **BTD2**, **3** and **5**, the electron density of HOMO orbitals is mainly concentrated over the TPA and Fc unit whereas the LUMO is delocalized over the TCBD-BTD and expanded TCBD-BTD segments.

The theoretically estimated HOMO energy levels of benzothiadiazole **BTD1–5** are -5.37 eV, -7.25 eV, -7.05 eV, -5.51 eV, -6.15 eV and LUMO are -3.16 eV, -2.81 eV, -2.88 eV, -2.97 eV and -3.87 eV respectively.



Figure 6.4. Optimized structure, frontier HOMO and LUMO orbitals of BTD1–5.

The time-dependent DFT calculation was performed at the B3LYP/6-31G (d, p) level on optimized napthalimide functionalized benzothiadiazole derivatives **BTD1–5** in dichloromethane to estimate the electronic absorption spectra, which are shown in Figure 6.5 and Table 6.2.

The theoretical calculations demonstrate that the **BTD1** and **BTD5** exhibit two major electronic absorption bands in the uv-vis region in which the absorption spectra in the lower wavelength region belongs to π - π * character and the spectra in the longer wavelength region corresponds to ICT transition.



Figure 6.5. Experimental and theoretical spectra of BTD2 in DCM.

The naphthalimide functionalized benzothiadiazole derivative **BTD2** shows a strong absorption band originated from HOMO–1→LUMO at 421 nm attributed to intramolecular charge transfer (ICT) transition. The orientation of absorption spectra and the position of λ_{max} of benzothiadiazole chromophore **BTD2** is in good agreement with the experimental data as shown in Figure 6.5. The expanded TCBD functionalized benzothiadiazole derivative **BTD3** show two major excited

states, in which the first excited state predicted at 656 nm belongs to a HOMO–1→LUMO+1 transition, which has intramolecular charge transfer (ICT) character. Another excited state with high intensity at 414 nm dominated by the HOMO–2→LUMO+1transition correspond to π – π * character, which is also in good agreement with the experimental data. Overall, the TD-DFT calculations explained that the intramolecular charge transfer (ICT) band of **BTD3** exhibit strong bathochromic shift of ~235 nm as compared to TCBD functionalized **BTD2** chromophore due to presence of expanded TCBD unit which tune the HOMO–LUMO band gap.

6.6. Experimental Section

Experimental details Chemicals were used as received unless otherwise indicated. All the oxygen or moisture sensitive reactions were carried out under argon atmosphere and the reflux reactions were performed in an oil bath. ¹H NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using residual protonated solvent as an internal standard {CDCl₃, 7.26 ppm}. ¹³C NMR spectra were recorded using a 100 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using the solvent as internal standard {CDCl₃, 77.16 ppm}. The ¹H NMR splitting patterns have been described as "s, singlet; d, doublet; t, triplet and m, multiplet". HRMS were recorded on a Bruker-Daltonics micrOTOF-Q II mass spectrometer. UV-visible absorption spectra of all compounds were recorded on a Perkin Elmer Lamba 35 UV-visible spectrophotometer in dichloromethane solution. Cyclic voltammograms and differential pulse voltammograms were recorded on a CHI620D electrochemical analyzer in dichloromethane solvent and potentiostat 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 for cyclic voltammetry.

A solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) in dichloromethane (0.1M) was used as supporting electrolyte.

BTD2

In a 100 mL round bottomed flask, TCNE (63 mg, 0.49 mmol) was added to a solution of compound **BTD1** (339 mg, 0.5 mmol) in CH₂Cl₂ (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 48 h. The solvent was removed in vacuum, and the product was purified by SiO₂ column chromatography with DCM/hexane (2:1, v/v) as eluent to yield **BTD2** as a dark brown solid (322 mg, yield 80%); ¹H NMR (400 MHz, CDCl₃) δ 9.00 (d, J = 8 Hz 1H), 8.71 (d, J = 7 Hz, 1H), 8.64 (d, J = 7.28 Hz, 1H), 8.13–8.04 (m, 3H), 7.95 (t, 1H), 7.70 (d, *J* = 8 Hz, 2H), 7.41–7.37 (m, 4H), 7.20–7.19 (m, 6H), 6.92 (d, J = 8 Hz, 2H), 4.21 (t, J = 8 Hz, 2H), 1.76–1.73 (m, 2H), 1.50–1.45 (m, 2H), 1.00 (t, J = 8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.1, 163.9, 163.7, 163.6, 154.9, 153.8, 151.0, 144.7, 132.6, 132.3, 132.0, 132.0, 131.9, 130.3, 130.2, 128.4, 128.2, 127.0, 126.8, 125.7, 125.6, 123.8, 123.3, 122.3, 122.2, 118.2, 113.7, 113.1, 111.7, 111.0, 97.6, 93.4, 92.8, 79.9,77.4, 40.6, 30.3, 20.5,14.0; HRMS (ESI-TOF) m/z calcd for $C_{50}H_{30}O_2N_8S + K 845.1844 [M + K]^+$, measured $845.1843 [M + K]^+$.

BTD 3

In a 100 mL round bottomed flask, TCNQ (102 mg, 0.49 mmol) was added to a solution of compound **BTD 1** (339 mg, 0.5 mmol) in C₂H₄Cl₂ (50 mL) under an argon atmosphere. The mixture was heated at 100 °C for 10 h in MW. The solvent was removed in vacuum, and the product was purified by SiO₂ column chromatography with DCM/hexane (2:1, v/v) as eluent to yield **BTD3** as a dark brown solid (374 mg, yield 85%); ¹H NMR (400 MHz, CDCl₃) δ 8.99 (d, J = 8 Hz 1H), 8.71 (d, J = 7 Hz, 1H), 8.63 (d, J = 7.28 Hz, 1H), 8.11 (m, J = 8 Hz, 1H), 8.00–7.89 (m, 3H), 7.46 (d, J = 7 Hz, 1H), 7.37–7.29 (m, 8H), 7.22–7.13 (m, 7H), 6.89 (d, J = 8 Hz, 2H), 4.21 (t, J = 8 Hz, 2H), 1.78–1.70 (m, 2H), 1.50–1.44

(m, 2H), 1.00 (t, J = 8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 163.9, 163.7, 154.9, 153.9, 151.8, 151.3, 150.3, 145.4, 135.9, 135.1, 134.5, 133.9, 132.3, 132.0, 131.8, 131.8, 130.3, 130.1, 129.0, 128.3, 128.2, 127.0 126.9, 126.7, 126.4, 126.2, 126.1, 125.8, 123.7, 123.3, 121.2, 119.1, 114.1, 112.6, 112.0, 96.9, 93.4, 92.3, 75.5, 40.6, 30.4, 20.5, 14.0; HRMS (ESI-TOF) m/z calcd for C₅₆H₃₄O₂N₈S + Na 905.2418 [M + Na]⁺, measured 905.2419 [M + Na]⁺.

BTD4

In a 100 mL round bottomed flask Fc-BTD-Br I (100 mg, 0.23 mmol, 1 equiv) and 2-butyl-6-ethynyl-1H-benzo[de]isoquinoline-1,3(2H)dione II (78 mg, 0.28 mmol, 1.2 equiv) were dissolved in 1:1 (v/v) triethylamine (TEA) (30 ml) and tetrahydrofuran (THF) (30ml). The reaction mixture was purged with argon, and PdCl₂(PPh₃)₄ (16 mg, 0.022 mmol), and CuI (4 mg, 0.021 mmol) were added. The reaction mixture was reflux at 60 °C in an oil bath for 6 h. Upon the completion of the reaction, the mixture was evaporated and purified by silica gel column chromatography with hexane/ CH_2Cl_2 (1:1) to get the desired compound **BTD4** as a dark brown solid (83 mg, vield 59%); ¹H NMR (400 MHz, CDCl₃) δ 9.05 (d, J = 8 Hz 1H), 8.69 (d, J = 8 Hz, 1H), 8.61 (d, J = 7.28 Hz, 1H), 8.09 (d, J = 7.28 Hz, 1H), 7.96–7.90 (m, 2H), 7.81 (d, J = 8 Hz, 1H), 4.67 (s, 2H), 4.36–4.32 (m, 6H), 4.22-4.18 (m, 2H), 1.76-1.72 (m, 2H), 1.48-1.44 (m, 2H), 0.99 (t, 3H); 13 C NMR (100 MHz, CDCl₃) δ 164.05, 163.78, 154.67, 154.43, 133.16, 132.73, 131.87, 131.79, 131.63, 131.04, 130.35, 128.16, 127.49, 126.92, 123.09, 122.80, 119.42, 115.14, 99.26, 94.95, 93.80, 82.13, 72.17, 70.42, 69.80, 64.00, 40.49, 30.34, 20.53, 13.99; HRMS (ESI-TOF) m/z calcd for C36H₂₅FeN₃O₂S 619.1012 [M]⁺, measured 619.1019 [M]⁺.

BTD5

In a 100 mL round bottomed flask, TCNE (63 mg, 0.49 mmol) was added to a solution of compound BTD4 (309 mg, 0.5 mmol) in CH₂Cl₂ (50 mL) under an argon atmosphere. The mixture was heated at 40 °C for 48 h. The solvent was removed in vacuum, and the product was purified by SiO₂ column chromatography with DCM/hexane (2:1, v/v) as eluent to yield **BTD5** as a dark brown solid (328 mg, yield 88%); ¹H NMR (400 MHz, CDCl₃) δ 8.96 (d, J = 8 Hz 1H), 8.69 (d, J = 7 Hz, 1H), 8.61 (d, J = 7.28 Hz, 1H), 8.10 (d, J = 8 Hz, 1H), 8 (d, J = 8 Hz, 1H), 7.95–7.88 (m, 2H), 5.56 (s, 1H), 4.94 (s, 1H), 4.71 (s, 1H), 4.50-4.42 (m, 4H), 4.19 (t, 2H), 1.77-1.69 (m, 2H), 1.51-1.42 (m, 2H), 0.99 (t, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.17, 163.90, 163.63, 161.08, 154.85, 150.61, 132.33, 131.98, 131.84, 131.80, 130.87, 130.23, 128.32, 128.15, 125.66, 125.25, 123.76, 123.26, 121.93, 114.03, 113.75, 111.58, 111.25, 97.36, 93.16, 91.31, 79.56, 76.25, 74.97, 74.43, 73.25, 72.81, 70.81, 40.56, 30.32, 29.82, 20.51, 13.97; HRMS (ESI-TOF) m/z calcd for C₄₂H₂₅FeN₇O₂S 748.1213 [M $+ H]^+$, measured 748.1210 [M + H]⁺.

6.7. Conclusions

This chapter describes the design and synthesize of the multi-modular push-pull based unsymmetrical benzothiadiazole derivatives **BTDs2**, **3**, **4** and **5** in which TPA and Fc are used as electron rich units and BTD, NPI, TCBD and expanded TCBD as electron deficient unit to enhance the π conjugation and to tune its optical band gap. The incorporation of cyano based TCBD and expanded TCBD acceptor units in the naphthalimide functionalized benzothiadiazole derivatives **BTDs2**, **3** and **5** show excellent optical properties compared to precursors **BTD1** and **BTD4**. The benzothiadiazole chromophore **BTD3** exhibit broad electronic absorption spectra (ICT) in the near IR region compared to TCBD derivatives

BTDs2, **5** and precursors **BTD1** and **BTD4** due to the presence of powerful electron deficient expanded TCBD unit. These naphthalimide functionalized benzothiadiazole derivatives **BTDs2**, **3** and **4** display interesting electrochemical properties (low electrochemical band gap) which can be useful as n-type semiconducting materials for bulk heterojunction solar cell. The theoretical calculation revealed that, the HOMO energy level of chromophores **BTD2–5** were localized on triphenylamine and ferrocenyl entity whereas the LUMO was delocalized over the BTD-NPI, BTD-TCBD and BTD-expanded TCBD segments.

6.8. Reference

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Chapter 7

Design and synthesis of di-benzothiadiazole based chromophores

7.1. Introduction

The symmetrical and unsymmetrical push–pull organic chromophores have emerged as attractive semiconducting materials in the scientific community due to their applications in optoelectronic devices such as organic dye-sensitized solar cell, bulk heterojunction solar cell and organic light-emitting diodes (OLEDs).^[11] In recent years, push–pull organic chromophores have been designed and synthesized by using various donor-acceptor combination in π -conjugated systems like D-A-D, A-D-A, D- π -A- π -D, A¹- π -A- π -A¹ D¹– π -A- π -D², D–A–D–A–D, and D¹–A–D.^[2] In these push–pull organic chromophores, heterocyclic donor and acceptors were mainly introduced to enhance the photophysical and electrochemical properties.^[3]

Benzthiadiazole (BTD) is known as important building block (as acceptor) in the push-pull organic chromophores (polymers and small molecule), due to its strong electron affinity, high reduction potential, excellent photophysical and electrochemical properties. ^[4] The BTD- organic chromophores are mainly used in organic light-emitting diodes, organic solar cells and organic field effect transistors. ^[5, 6] Our group has reported wide variety push-pull organic derivatives of BTD entity which exhibit a strong and wide electronic absorption band in the visible-near IR regions.^[7] Organic molecules bearing benzothiadiazole unit connected by π -bridges have recently stimulated deep research interest for their ability to undergo photoinduced intramolecular charge transfer and for their important non-linear optical properties.^[8] Phenothiazine (PTZ) is a well-known tricyclic heteroarene with butterfly structure due to the presence of

electron-rich sulfur and nitrogen heteroatoms.^[9] The phenothiazine and its derivatives are mainly used as electron rich component due to its low reversible oxidation potentials produced by sulfur atom. ^[10] Due to these excellent properties, phenothiazine derivatives have been used in numerous applications such as lightemitting diodes (OLEDs) , phosphorescence, thermally activated delayed fluorescence, photovoltaic devices (bulk heterojunction solar cells and dye-sensitized solar cells (DSSCs), respectively), aggregation induced enhanced emission (AIEE), sensors and mechanochromic materials.^[11]





Here, we investigate the photonic properties of multifunctional compounds with the composition of phenothiazine, benzothiadiazole (BTD), triphenylamine and carbazole moieties for energy transfer and charge transfer dynamics properties. In the past few years, there was a numerous studies on organic chromophores consisting of phenothiazine and benzothiadiazole moieties, but still the combination of above moieties are not reported. In this paper, we wish to report multi-modular organic chromophores **PTZBTD1–PTZBTD3** with structural configuration D'- π -

A- π -D- π -A- π -D', D"- π -A- π -D- π -A- π -D" and D"'-A- π -D- π -A-D"' in Figure 7.1. The organic chromophores were synthesized *via* Pd-catalyzed sonogashira cross-coupling reaction in which phenothiazine electron donor (D) unit was used as central unit, TPA (D'), carbazole (D")(with spacer phenyl unit) and carbazole (D"')(without spacer phenyl unit) used as end capping units and benzothiadiazole as powerful acceptor unit to tune the HOMO–LUMO energy levels and extended π -conjugation in the multi-modular organic chromophores. Here we investigate the effect of variation of donor unit and π -linker units on photophysical, electrochemical and computational studies.

7.2. Synthesis

The detailed synthetic route of symmetrical benzothiadiazoles **PTZBTD1**, **PTZBTD2** and **PTZBTD3** are shown in scheme 7. 1.



Scheme 7.1. Synthesis of PTZBTD1, PTZBTD2 and PTZBTD3.

The π -extended small push-pull organic chromophores **PTZBTD1**, **PTZBTD2** and **PTZBTD3** were synthesized *via* sonogashira cross

coupling reaction of the 3,7-diethynyl-10-octyl-10H-phenothiazine with two equivalents of 4-((7-bromobenzo[c][1,2,5]thiadiazol-4-yl)ethynyl)-N,N-diphenylaniline,^[12] 4-((4-(9H-carbazol-9-yl)phenyl)ethynyl)-7bromobenzo[c][1,2,5]thiadiazole^[13] and 4-bromo-7-(9H-carbazol-9yl)benzo[c][1,2,5]thiadiazole^[14] (compound **4**) in 60% , 63% and 65% yields. The chemical structures of **PTZBTD1**, **PTZBTD2** and **PTZBTD3** were confirmed by ¹H and ¹³C NMR and MALDI-TOF mass spectrometry techniques.

7.3. Photophysical Properties

The electronic absorption spectra of multi-modular organic chromophores **PTZBTD1–PTZBTD3** were measured in dichloromethane (DCM) (Figure 7.2) and the optical properties are summarized in Table 7.1.



Figure 7.2. The electronic absorption spectra of **PTZBTD1**, **PTZBTD2** and **PTZBTD3** in dichloromethane $(1 \times 10^{-5} \text{M})$.

In the dilute solution, **PTZBTD1**(triphenylamine substituted push-pull organic chromophore) with structural configuration D'- π -A- π -D- π -A- π -D'

exhibit an intense absorption band around 489 nm due to intramolecular charge transfer (ICT) transition. Similarly, **PTZBTD2** and **PTZBTD3** (carbazole substituted push-pull organic chromophores) with structural configuration D''- π -A- π -D- π -A- π -D'' and D'''-A- π -D- π -A-D''' exhibit a broad absorption band around 469 nm and 467 nm due to intramolecular charge transfer (ICT) transitions.

Table 7.1. Photophysical and electrochemical data of symmetrical	al
PTZBTD1. PTZBTD2 and PTZBTD3	

	Photophysical data ^a			Electrochemica	Electrochemical data ^b		
Compounds	$\lambda_{\max(nm)}$	$\varepsilon (M^{-1} cm^{-1})$	$E_{ m g}^{\;opt}$	E_{red} (V)	E_{red} (V) E_{ox} (
		(eV)	E_{I}	E_1	E_2		
PTZBTD1	489	28000	2.16	-1.19	0.79	0.98	
PTZBTD2	469	9440	2.17	-1.18	0.79	1.02	
PTZBTD3	467	17480	2.28	-1.22	0.79	1.07	

^{*a*}Absorbance measured in dichloromethane at 1×10^{-5} M concentration. λ_{abs} : absorption wavelength. ε : extinction coefficient. E_g^{opt} : optical band gap. ^{*b*}Electrochemical analysis was estimated by cyclic voltammetry, in 0.1 M solution of TBAPF₆ in DCM at 100 mV s⁻¹ scan rate versus SCE electrode.

The photophysical investigation demonstrate that ICT band of the donoracceptor based push-pull organic chromophore **PTZBTD1** exhibit a bathochromic shift of 20 nm relative to **PTZBTD2** and **PTZBTD3** due to extended π -conjugation in donor-acceptor system in which triphenylamine (end-capping unit) used as strong donor unit compared to carbazole unit and also explained that, in the presence of phenyl linkers **PTZBTD2** exhibit a broad absorption spectra (blue color) compared to **PTZBTD3** (green color), whereas the absorption maximum λ_{max} value of both pushpull organic chromophore are same.

The onset values estimated for push-pull organic chromophores **PTZBTD1, PTZBTD2** and **PTZBTD3** in the CH_2Cl_2 solutions is 572, 571 and 543 nm, corresponding to the optical band gaps of 2.16, 2.17 and 2.28 eV, respectively.

7.4. Molecular geometry and frontier orbitals

In order to understand the electronic structures and distribution of frontier molecular orbitals (FMO), we carried out the theoretical calculation (density functional theory (DFT)) at the B3LYP functional /6-31G** basis set. ^[15] In order to reduce computational time for organic chromophores **PTZBTD1–PTZBTD3**, we used methyl substituents instead of the experimental octyl unit.



Figure 7. 3. Optimized structure, frontier HOMO and LUMO orbitals of **PTZBTD1–3**.

The optimized electronic structures of donor-acceptor based organic chromophores **PTZBTD1–3** exhibit non-planar geometry in the π -conjugated push-pull systems due to the presence of phenothiazine unit as

central core with butterfly structure, which was confirmed by optimized structures from Figure 7.3. The energy level diagrams of push-pull organic chromophores **PTZBTD1–3** are shown in the Figure 7.4. The HOMO energy level of **PTZBTD1** with structural configuration D'- π -A- π -D- π -A- π -D' was spread over the whole molecule while LUMO mainly concentrated on both benzothiadiazole (BTD) unit, which indicates that BTD entity exhibit as powerful acceptor in the π -conjugated donor-acceptor system.



Figure 7.4. Energy levels diagram of the frontier orbitals of **PTZBTD1**– **PTZBTD3** estimated by DFT calculations.



Figure 7. 5. Theoretical optical absorption spectra of PTZBTD1–3.

In the case of **PTZBTD2** with structural configuration D"- π -A- π -D- π -A- π -D" and **PTZBTD3** with structural configuration D"-A- π -D- π -A-D", due to the presence of less electron donating unit (carbazole), the electron

density of the HOMO is mainly located on the phenothiazine unit as a strong donor group on the other hand; in the LUMO energy level the electron density is concentrated on BTD unit.

The theoretically calculated HOMO and LUMO energy levels of multimodular organic chromophores **PTZBTD1–PTZBTD3** explained that the terminal donor groups (triphenylamine, carbazole with π -linker and carbazole with without π -linker) are the key factor to tune the **HOMO** and **LUMO** energy levels. The estimations of theoretical band-gap for pushpull organic chromophore **PTZBTD1–PTZBTD3** were 2.29, 2.36 and 2.45 eV respectively. As compared with the optical band gaps (E_g^{opt}) 2.16, 2.17 and 2.28 eV (Table 7. 1), the theoretical band gaps were slightly higher with error 0.2 eV due to the solvent effect in experimental values.

Table 7. 2. Calculated electronic transitions for **PTZBTD 1–3** in dichloromethane

			0		
PTZBTD	Wavelength	Composition	f^{a}	Assignment	
	(nm)	&			
		Molecular contribution			
PTZBTD1	479	HOMO→LUMO (0.521)	2.58	ICT	
PTZBTD2	463	HOMO→LUMO (0.53)	2.64	ICT	
PTZBTD3	440	HOMO→LUMO (0.50)	1.38	ICT	

 f^{a} oscillator strength

In order to understand electronic spectral behaviors of multi-modular organic chromophores **PTZBTD1–PTZBTD3**, we carried out a TD-DFT (time-dependent density functional theory) calculation at the B3LYP/6-31G* level and shown in Figure 7.5. and tabulated in Table 7. 2.

In the TD-DFT calculation, the multi-modular organic chromophores **PTZBTD1–PTZBTD3**) with structural configuration D'- π -A- π -D- π -A- π -D', D"- π -A- π -D- π -A- π -D" and D"'-A- π -D- π -A-D" exhibit a broad absorption band around 479 nm, 463 nm and 440 nm dominated by HOMO–LUMO energy level due to intramolecular charge transfer (ICT) transitions. The absorption spectra for **PTZBTD1–PTZBTD3** calculated from TD-DFT calculation are shown in Figure 7. 5. and good agreement with experimental data.

7.5. Electrochemical properties

The electrochemical studies were performed for multi-modular organic chromophores **PTZBTD1**, **PTZBTD2** and **PTZBTD3** to investigate the effect of donor strength on the redox potentials. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of multi-modular organic chromophores **PTZBTD1**, **PTZBTD2** and **PTZBTD3** were calculated from onset oxidation (E_{ox}) and onset reduction potentials (E_{red}), using the equations $E_{HOMO} = -[(E_{ox} - E_{Fc/Fc}^+) + 4.8]$ eV and $E_{LUMO} = -[(E_{red} - E_{Fc/Fc}^+) + 4.8]$ Ev.

The structural configuration of D'- π -A- π -D- π -A- π -D', D"- π -A- π -D- π -A- π -D" and D"'-A- π -D- π -A-D" with organic chromophores **PTZBTD1**, **PTZBTD2** and **PTZBTD3** exhibit a single quasi-reversible reduction wave at -1.19 V, -1.18 V and -1.22 V in Figure 7.6 correspond to benzothiadiazole unit as strong acceptor. The triphenylamine substituted organic chromophores **PTZBTD1** with structural configuration of D'- π -A- π -D- π -A- π -D' exhibits two oxidation waves at 0.79 V and 0.98 V correspond to phenothiazine and triphenylamine unit. Whereas carbazole substituted organic chromophores **PTZBTD2** and **PTZBTD3** with structural configuration D"- π -A- π -D- π -A- π -D" and D"'-A- π -D- π -A-D" showed two oxidation waves at 0.79 V and 1.07 V due to phenothiazine and carbazole unit.



Figure 7.6. Cyclic voltammograms of **PTZBTD1–PTZBTD3** in 0.1 M solution of Bu_4NPF_6 in dichloromethane at 100 mV s⁻¹ scan rate versus saturated calomel electrode (SCE) at 25 °C.

The LUMO energy levels for phenothiazine based organic chromophores **PTZBTD1**, **PTZBTD2** and **PTZBTD3** are found to be -3.3, -3.29 and -3.24 eV, respectively, whereas HOMO energy levels are -5.26, -5.07 and -5.05 eV, respectively. The electrochemical band gaps of multi-modular organic chromophores **PTZBTD1**–**PTZBTD3** are 1.96, 1.78 and 1.81 eV, respectively. The theoretically estimated HOMO and LUMO energy levels and band gaps of the organic chromophores **PTZBTD1**, **PTZBTD2** and **PTZBTD3** are slightly higher than experimentally calculated values due to interactions of solvent molecules with the chromophores.

7.6. Experimental Section

Synthesis and Characterization. Chemicals were used as received unless otherwise indicated. All the oxygen or moisture sensitive reactions were carried out under argon atmosphere. ¹H NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) using residual protonated solvent as an internal standard {CDCl₃, 7.26 ppm}. ¹³C NMR spectra were recorded using a 100 MHz spectrometer. The ¹H NMR splitting patterns have been described as "s, singlet; d, doublet; t, triplet and m, multiplet". UV-visible absorption spectra of all compounds were recorded in dichloromethane solution. Cyclic voltammograms were recorded on potentiostat 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 for cyclic voltammetry. A solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in DCM (0.1M) was used as supporting electrolyte.

4,4'-(((((10-octyl-10H-phenothiazine-3,7-diyl)bis(ethyne-2,1 diyl))bis(benzo[c][1,2,5]thiadiazole-7,4-diyl))bis(ethyne-2,1diyl))bis(N,N-diphenylaniline) (PTZBTD1)

In a 100 mL round bottomed flask 3,7-diethynyl-10-octyl-10Hphenothiazine 1 (0.15)0.41 and 4-((7g, mmol) bromobenzo[c][1,2,5]thiadiazol-4-yl)ethynyl)-N,N-diphenylaniline 2 (0.49 g, 1.01 mmol) were dissolved in 1:1 (v/v) triethylamine (TEA) (30 ml) and tetrahydrofuran (THF) (30ml). The reaction mixture was purged with argon, and Pd(PPh₃)₄ (0.055 g, 0.047 mmol), and CuI (0.015 g, 0.078 mmol) were added. The reaction mixture was reflux for 12 h. Upon the completion of the reaction, the mixture was evaporated and purified by silica gel column chromatography with hexane/CH₂Cl₂ (1:1) to get the desired compound **PTZBTD1** as a red colored solid. Yield 0.290 g (60%);

¹ H NMR (400 MHz, CDCl₃): δ 7.63 (s, 4H), 7.41 (d, J = 8 Hz, 4H), 7.36– 7.30 (m, 4H), 7.22–7.18 (m, 8H), 7.05–6.97 (m, 12H), 6.94 (d, J = 8 Hz, 4H), 6.75 (d, J = 8 Hz, 2H), 3.77 (t, 2H), 1.74–1.71 (m, 2H), 1.37–1.34 (m, 2H), 1.29–1.20 (m, 8H), 0.78 (t, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 154.58, 148.81, 147.16, 145.23, 133.16, 132.35, 132.12, 131.55, 130.69, 129.61, 125.41, 124.29, 124.00, 121.94, 117.52, 116.94, 116.86, 115.40, 115.10, 98.44, 96.99, 85.99, 85.08, 48.02, 31.88, 29.85, 29.34, 29.31, 26.95, 26.85, 22.77, 14.24 ; MALDI–TOF–MS: m/z: calcd for C₇₆H₅₅N₇S₃ 1161.3681 [M]⁺, measured 1161.547.

3,7-bis((7-((4-(9H-carbazol-9-

yl)phenyl)ethynyl)benzo[c][1,2,5]thiadiazol-4-yl)ethynyl)-10-octyl-10H-phenothiazine (PTZBTD2)

In a 100 mL round bottomed flask 3,7-diethynyl-10-octyl-10Hphenothiazine 1 (0.15 g, 0.41 mmol) and 4-((4-(9H-carbazol-9yl)phenyl)ethynyl)–7–bromobenzo[c][1,2,5]thiadiazole **3** (0.49 g, 1 mmol) were dissolved in 1:1 (v/v) triethylamine (TEA) (30 ml) and tetrahydrofuran (THF) (30ml). The reaction mixture was purged with argon, and Pd(PPh₃)₄ (0.065 g, 0.056 mmol), and CuI (0.015 g, 0.078 mmol) were added. The reaction mixture was reflux for 12 h. Upon the completion of the reaction, the mixture was evaporated and purified by silica gel column chromatography with hexane/CH₂Cl₂ (1:1) to get the desired compound **PTZBTD2** as a colored solid. Yield 0.302 g (63%); ¹H NMR (400 MHz, CDCl₃): δ 8.17 (d, J = 8 Hz, 4H), 7.92 (d, J=8 Hz, 4H), 7.85–7.78 (m, 4H), 7.65 (d, J = 8 Hz, 4H), 7.49–7.44 (m, 12H), 7.32 (t, 4H), 6.87 (d, J=8 Hz, 2H), 3.90 (t, 2H), 1.88–1.81 (m, 2H), 1.49–1.44 (m, 2H), 1.32–1.28 (m, 8H), 0.89 (t, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 154.51, 145.29, 140.61, 138.49, 133.67, 132.75, 132.20, 131.62, 130.71, 127.00, 126.27, 124.28, 123.79, 121.56, 120.48, 117.71, 116.85, 116.76, 115.42, 109.89, 97.46, 96.77, 86.43, 85.93, 48.04, 32.08, 29.85, 29.51,

26.96, 22.84, 14.27 ; MALDI–TOF–MS: m/z: calcd for $C_{76}H_{51}N_7S_3$ 1157.336 [M]⁺, measured 1157.593.

3,7-bis((7-(9H-carbazol-9-yl)benzo[c][1,2,5]thiadiazol-4yl)ethynyl)-10-octyl-10H-phenothiazine (PTZBTD3)

In a 100 mL round bottomed flask 3,7-diethynyl-10-octyl-10Hphenothiazine 1 (0.15 g, 0.41 mmol) and 4-bromo-7-(9H-carbazol-9yl)benzo[c][1,2,5]thiadiazole 4 (0.388 g, 1.026 mmol) were dissolved in 1:1 (v/v) triethylamine (TEA) (30 ml) and tetrahydrofuran (THF) (30ml). The reaction mixture was purged with argon, and $Pd(PPh_3)_4$ (0.082 g, 0.071 mmol), and CuI (0.015 g, 0.078 mmol) were added. The reaction mixture was reflux for 12 h. Upon the completion of the reaction, the mixture was evaporated and purified by silica gel column chromatography with hexane/CH₂Cl₂ (1:1) to get the desired compound **PTZBTD3** as a violet colored solid. Yield 0.259 g (65%); ¹H NMR (400 MHz, CDCl₃): δ 8.20 (d, J = 8 Hz, 4H), 7.99 (d, J = 8 Hz, 2H), 7.85 (d, J = 8 Hz, 2H), 7.53 (d, J = 8 Hz, 2H), 7.48 (s, 1H), 7.42-7.39 (m, 5H), 7.36-7.32 (m, 4H),7.21 (d, J = 8 Hz, 4H), 6.91 (d, J = 8 Hz, 2H), 3.92 (t, 2H), 1.90–1.83 (m, 2H), 1.51–1.46 (m, 2H), 1.34–1.33 (m, 8H), 0.91 (t, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 156.57, 151.81, 145.80, 141.55, 132.90, 132.12, 131.24, 130.57, 128.23, 126.65, 124.82, 124.65, 121.32, 121.10, 117.48, 117.34, 115.95, 111.07, 97.09, 85.97, 48.51, 32.38, 29.81, 27.45, 27.34, 23.27, 14.76 ; MALDI-TOF-MS: m/z: calcd for $C_{60}H_{43}N_7S_3$ 957.274 [M]⁺, measured 957.469.

7.7. Conclusions

This chapter describes the design and synthesize of a series of multifunctional organic chromophores **PTZBTD1–PTZBTD3** with D'- π -A- π -D- π -A- π -D', D''- π -A- π -D- π -A- π -D'' and D'''-A- π -D- π -A-D''' configurations, in which phenothiazine used as central core. Here we have introduced benzothiadiazole (BTD) as powerful acceptor on the both side

of phenothiazine unit to extend the π -conjugation and tuning the HOMO– LUMO energy levels. Photophysical properties demonstrated that **PTZBTD1** shows a bathochromic shift of 20 nm relative to **PTZBTD2** and **PTZBTD3** due to the presence of triphenylamine unit as end-capping unit, which extended π -conjugation in donor-acceptor system. The computational studies revealed that the theoretically calculated absorption spectra of each derivatives was a good agreement with experimental absorption spectra, the HOMO energy level of **PTZBTD1** was delocalized over whole molecular system whereas for **PTZBTD2** and **PTZBTD3**, it mainly localized on phenothiazine entity and LUMO energy level localized only on acceptor (benzothiadiazole) unit for all organic chromophore.

7.8. References

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Chapter 8

Conclusions and Future Scope

8.1. Conclusions

2,1,3-Benzthiadiazole (BTD) is an excellent class of heterocyclic entity containing the diazole based five-membered ring where one of the carbon atom in the diazole ring is substituted by the S atom.^[1] It is an electron deficient organic molecule which acts as strong electro acceptor.^[2] It possesses strong absorption with high molar extinction coefficient and intense luminescence along with a π -conjugated molecular backbone.^[3] The photonic and electronic properties can be easily tuned by functionalizing with different push/pull substituents at 4-, 7- positions of benzothiadiazole unit.^[4] we described the design and synthesize of pushpull benzothiadiazoles and investigated their photophysical, electrochemical and theoretical properties.

In chapter 3, describes the design and synthesize of a series of arylsubstituted ferrocenyl functionalized unsymmetrical and symmetrical BTDs by formal [2 + 2] cycloaddition-retroelectrocyclization, in which phenyl, *p*-methoxyphenyl, biphenyl, naphthalene and anthracene derivatives substituted show the monosubstitution, whereas triphenylamine and ferrocenyl substituted derivatives shows disubstitution of TCBD in the presence of excess amount of tetracyanoethylene (TCNE). The significance of donor strength to design the mono/ di-substitution of [2 + 2] cycloaddition- retroelectrocyclization reaction was explained successfully by experimental and computational studies. The photophysical and electrochemical properties for all derivatives revealed that the triphenylamine and ferrocenyl substituted derivatives exhibit a strong electronic conjugation in the π -conjugated systems after incorporation of additional TCBD acceptor.^[5]

In chapter 4, describes the design and synthesize of a series of unsymmetrical push-pull functionalized benzothiadiazole derivatives, in which benzothiadiazole unit was used as the central unit core (electronacceptor unit (A)), triphenylamine and N,N-dimethylaniline was used as the end capping unit (electron- donor group (D)) and tetracyanobutadiene (A2) or expanded TCBD (3) used as additional acceptor unit. To extend the π -conjugation of benzothiadiazole derivatives, we have introduced tetracyanobutadiene (A') or cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD (A") by [2+2] cycloaddition-retroelectrocyclization reactions. The photophysical properties of expanded TCBD substituted derivatives exhibit a strong electronic absorption band (ICT) in the near IR regions with high onset value. The TCBD and expanded TCBD derivatives show multi redox waves with low electrochemical band gap which signifies the tuning of HOMO-LUMO energy levels and enhance the π -conjugation. The computational studies demonstrate that there is a good agreement with experimental data. We believe that the molecular design and synthesis of unsymmetrical benzothiadiazole derivatives gives a new path way to the exploitation of new building blocks in the organic electronics in the future.^[6]

In chapter 5, describes the design and synthesize of a series of multiacceptor based push-pull chromophores *via* [2 + 2] cycloaddition– retroelectrocyclization (CA-RE) reactions in which benzothiadiazole (BTD, A1) was used as central core, phenothiazine (D1) and triphenylamine (D2) entity as end-capping units, TCBD (A2) and expanded TCBD (A3) as additional acceptors. The photophysical, electrochemical and theoretical calculations demonstrate that the presence of cyano based acceptors TCBD and expanded TCBD in the π -conjugated systems tune the photonic properties. The photophysical properties reveal that the expanded TCBD substituted derivatives show a broad absorption band in the vis-NIR region compared to the precursors due to strong intramolecular charge transfer (ICT) transition. The electrochemical properties for all derivatives explained that the HOMO-LUMO energy levels are strongly influenced by the cyano based acceptors. The theoretical calculation on push-pull derivatives exhibit non-planar structure due to the butterfly structure of phenothiazine unit, propeller structure of triphenylamine unit and twisted structure of TCBD and expanded TCBD unit, further demonstrate that the cyano based acceptors perturb the LUMO energy levels. We have established a new synthetic approach in which a strong acceptor (benzothiadiazole) was introduced in between the two distinct electron donors (phenothiazine and triphenylamine units allied through the acetylene unit) to identify the TCBD substituted regioisomeric mixture by ¹H and ¹³C NMR. Finally, the studies on the series of benzothiadiazole substituted multimodular pushpull chromophores demonstrate that these chromophores are promising materials for the optoelectronic applications and show a new path way to develop the cyano based push-pull chromophores by [2 + 2]cycloaddition-retroelectrocyclization (CA-RE) reactions.

Chapter 6 describes the design and synthesis of a series of unsymmetrical BTDs derivatives *via* [2+2] cycloaddition–retroelectrocyclization reaction. In these chromophores, triphenylamine and ferrocene units were used as electron rich units and benzothiadiazole, 1,8-naphthalimide ,1,1,4,4-tetracyanobutadiene (TCBD) and cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD used as electron deficient unit to tune the HOMO–LUMO gap and broadening the absorption spectra in the near NIR-region. The computational studies revealed that there was a good agreement with experimental data, the HOMO energy level were localized on triphenylamine and ferrocene unit whereas the LUMO delocalized over the benzothiadiazole, 1,8-naphthalimide ,1,1,4,4-tetracyanobutadiene (TCBD) and cyclohexa-2,5-diene-1,4-diylidene-expanded TCBD units.^[7]

In chapter 7 describes the design and synthesize of a series of multifunctional organic chromophores with D'- π -A- π -D- π -A- π -D', D''- π -

A- π -D- π -A- π -D" and D"'-A- π -D- π -A-D"' configurations, in which phenothiazine used as central core. Here we have introduced benzothiadiazole (BTD) as powerful acceptor on the both side of phenothiazine unit to extend the π -conjugation and tuning the HOMO– LUMO energy levels. Photophysical properties demonstrated that triphenylamine susstituted derivative shows a bathochromic shift of 20 nm relative to carbazole substituted derivative due to the presence of triphenylamine unit as end-capping unit, which extended π -conjugation in donor-acceptor system. The computational studies revealed that the theoretically calculated absorption spectra of each derivatives was a good agreement with experimental absorption spectra, the HOMO energy level of triphenylamine susstituted derivative was delocalized over whole molecular system whereas for carbazole substituted derivative, it mainly localized on phenothiazine entity and LUMO energy level localized only on acceptor (benzothiadiazole) unit for all organic chromophores.^[8]

8.2. Future scope

The thesis highlights an important strategy for design and synthesis of various benzothiadiazole based push-pull chromophores to tune the photonic and electronic properties. The HOMO–LUMO band gap of benzothiadiazole chromophores can be perturbed by (a) varying the number of push/pull units, (b) extending the π -conjugation length and (c) varying the π -linker. The incorporation of tetra cyano based strong acceptors TCNE and TCNQ can also enhance the push–pull interactions in the benzothiadiazoles resulting in broad intramolecular charge-transfer at longer wavelength which could be extended to the near infrared region. The benzothiadiazole chromophores with broad absorption spectra in the near infrared region with low HOMO–LUMO band gap could be promising candidate for optoelectronic applications.

8.3. References

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