

SYNTHESIS AND CHARACTERIZATION OF 4,4'-BIS(2,1,3-BENZOTHIADIAZOLE) BASED CONJUGATED MATERIALS FOR ELECTRONIC APPLICATIONS

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by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy
to the



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Dedicated to my Mother and my Late Father

CERTIFICATE

This is to certify that the thesis entitled "**Synthesis and Characterization of 4,4'-bis(2,1,3-benzothiadiazole) based Conjugated Materials for Electronic Applications**" being submitted by **Mr. Piyush Anant** to the Indian Institute of Technology Delhi, New Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by him. **Mr. Piyush Anant** has worked under my guidance and supervision and has fulfilled the requirements for the submission of his thesis, which to our knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any University or Institute for the award of any other degree or diploma.

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ABSTRACT

Low band gap donor-acceptor alternating conjugated polymers have received considerable interest as active materials for organic photovoltaics (OPVs), light emitting diodes (OLED), and electrochromic devices. Typical donor-acceptor conjugated polymers are made of electron-deficient nitrogen containing aromatic heterocycles (**2,1,3-benzothiadiazole**, [1,2,5]-thiadazolo[3,4-*g*]quinoxaline, and benzo[1,2-*c*: 3,4-*c'*]bis[1,2,5]-thiadiazole, etc.) as effective acceptors and electron rich derivatives (thiophene, fluorene, alkoxybenzene, carbazole, etc.) as effective donors. The low band gap of these types of copolymers based on 2,1,3-benzothiadiazole are due to the strong quinoid form, which contributes to the low band gap due to more stable 1,2,5-thiazole which is formed. These polymers have high electron affinity due to the nitrogen atoms in the thiadiazole rings and the short intermolecular contacts between *S* and *N* resulting in strong inter-chain interaction.

The present work used the concept of using the **4,4'-bis(2,1,3-benzothiadiazole)** unit as an effective electron acceptor. A new route towards the synthesis of 7,7'-dibromo-4,4'-bis(2,1,3-benzothiadiazole) was developed using standard Suzuki coupling. 7,7'-Dibromo-4,4'-bis(2,1,3-benzothiadiazole) was coupled with 9,9-dioctylfluorene, 2,2'-bis(9,9-dioctylfluorene) and alkyl substituted thiophenes using Suzuki cross-coupling to prepare a series of model compounds (**BFFB**, **BBFBB**, **FBBF**, **3TBB3T**, **4TBB4T**, and **5TBB5T**), which were characterized by ¹H NMR, ¹³C NMR, mass spectroscopy, UV-Vis absorption spectroscopy, fluorescence spectroscopy, and in some cases by X-ray crystallography. The absorbance maxima of BFFB, BBFBB, and FBBF lie in the range of 425-436 nm, whereas the absorbance maxima of 3TBB3T, 4TBB4T, and 5TBB5T are more red shifted and lie in the range of 432-472 nm.

A series of copolymers based on 4,4'-bis(2,1,3-benzothiadiazole) with 9,9-dioctylfluorene and alkyl thiophenes {**poly[BFB]**, **poly[BFFB]**, **poly[3TBB3T]**, and **poly[4TBB4T]**} were also synthesized either by Ni(0) mediated Yamamoto polycondensation or FeCl₃ mediated oxidative polycondensation. All polymers were characterized by ¹H NMR, GPC and studied in terms of optical and electrochemical properties. GPC analysis using polystyrene (PS) as standard showed M_n value of $5.4 \times 10^3 \text{ g mol}^{-1}$ (PDI = 2.1), $8.4 \times 10^3 \text{ g mol}^{-1}$ (PDI = 2.2), $1.16 \times 10^4 \text{ g mol}^{-1}$ (PDI = 2.8), and $0.8 \times 10^4 \text{ g mol}^{-1}$ (PDI = 2.5) for poly [BFB], poly[BFFB], poly[3TBB3T], and poly[4TBB4T], respectively. The absorbance maxima of poly [BFB], poly[BFFB], poly[3TBB3T], and poly[4TBB4T], are at 450, 458, 486, and 520 nm, respectively. The electrochemical band gap of the copolymers were determined by cyclic voltammetry measurements, and were found to be $\sim 1.2 \text{ eV}$. The polymers were tested in solar cell with regioregular rr-P3HT (BASF Sepiolid P200) as an electron donor, and blended with polymer in 1:1 ratio. **Poly[4TBB4T]** showed the highest efficiency of 0.27 % with $V_{oc} = 346 \text{ mV}$, $J_{sc} = 1.77 \text{ mA/cm}^2$, and $FF = 0.37$, after annealing it at 130 °C for 15 minutes.

Another series of copolymers based on 4,4'-bis(2,1,3-benzothiadiazole) and vinylene spacers in the main polymer chain was synthesized and characterized. The copolymers {**poly[BFB-vinylene]**, **poly[BFFB-vinylene]**, **poly[3TBB3T-vinylene]**, and **poly[4TBB4T-vinylene]**} were characterized by ¹H NMR, GPC and studied in terms of optical and electrochemical properties. GPC analysis using polystyrene (PS) as standard showed M_n value of $22.4 \times 10^3 \text{ g mol}^{-1}$ (PDI = 2.1), $25.4 \times 10^3 \text{ g mol}^{-1}$ (PDI = 2.4), $24.0 \times 10^3 \text{ g mol}^{-1}$ (PDI = 2.6), and $21.0 \times 10^3 \text{ g mol}^{-1}$ (PDI = 3.1) for poly[BFB-vinylene], poly[BFFB-vinylene], poly[3TBB3T-vinylene], and poly[4TBB4T-vinylene], respectively. The absorbance maxima of poly [BFB-vinylene], poly[BFFB-vinylene], poly[3TBB3T-vinylene], and poly[4TBB4T-vinylene], are 492, 495, 500, and 592 nm,

respectively. The electrochemical band gap of the copolymers were determined by cyclic voltammetry measurements, and were found to be in the range of 1.0 - 1.25 eV. The polymers were tested in solar cell with regioregular rr-P3HT (BASF Sepiolid P200) as an electron donor, and blended with polymer in 1:1 ratio. **Poly[4TBB4T-vinylene]** showed the highest efficiency of 0.04 % with $V_{oc} = 336$ mV, $J_{sc} = 0.25$ mA/cm², and FF = 0.45, after annealing it at 130 °C for 15 minutes.

A series of p- and n-type materials with pyrene substituted at 1-, 3-, 6-, 8- positions with either 2,1,3-benzothiadiazole (**36**) or alkylthiophenes (**43-45**) was synthesized for application in field effect transistors (FETs). The absorbance maximum of **36**, **43**, **44**, and **45** were observed at 410, 410, 452, and 458 nm, respectively. **45** was dye cast into films and evaluated for its hole transporting behavior, and the mobility of 1.9×10^{-5} cm²/Vs was obtained after annealing.

TABLE OF CONTENTS

	Page No.
Abstract	i
List of Figures	v
List of Tables	ix
List of Schemes	xi
List of Charts	xiii
List of Abbreviations	xv
Chapter 1 Introduction and Literature Survey	1
1.1 Overview of π -conjugated materials	1
1.1.1 Types of low band gap polymers	4
1.2 Metal catalyzed coupling reaction	6
1.2.1 Suzuki condensation	6
1.2.2 Yamamoto condensation	7
1.2.3 Stille coupling	7
1.3 Optoelectronic devices	8
1.3.1 Organic Thin Field Effect Transistors (OTFETs)	8
1.3.1.1 Basic operation of OFETs	8
1.3.1.2 Materials used in OFETs	9
1.3.2 Polymeric Solar Cells	12
1.3.2.1 Basic working principles of a solar cell	13
1.3.2.2 Solar cell device parameters	15
1.3.2.3 Materials used in solar cell devices	15
1.3.2.4 Device structure	17

1.3.2.5	Current challenges	18
1.3.3	Organic Light Emitting Diodes (OLEDs)	19
1.4	Motivation of this work	20
1.4.1	2,1,3-Benzothiadiazole: A promising material for electronics	20
1.4.2	Synthesis of 4,4'-bis(2,1,3-benzothiadiazole) based materials	22
1.4.3	Synthesis of pyrene based materials for FETs	23
1.5	Format of the thesis	24
Chapter 2	Synthesis of 7,7'-dibromo-4,4'-bis(2,1,3-benzothiadiazole) and its coupling with various conjugated moieties as model compounds for polymers	27
2.1	Introduction	27
2.2	Results and Discussion	28
2.2.1	Synthesis	28
2.2.1.1	Synthesis of 7,7'-dibromo-4,4'-bis(2,1,3-benzothiadiazole)	28
2.2.1.2	Synthesis of model compounds based on 4,4'-bis(2,1,3-benzothiadiazole) and 9,9-dioctylfluorene	30
2.2.1.3	Synthesis of model compounds based on 4,4'-bis(2,1,3-benzothiadiazole) and alkyl substituted thiophenes	33
2.2.2	X-ray crystallographic study of model compounds	36
2.2.3	Photophysical properties	39
2.2.3.1	Optical properties of 2,1,3-benzothiadiazole and 4,4'-bis(2,1,3-benzothiadiazole)	39
2.2.3.2	Optical properties of compounds based on 4,4'-bis(2,1,3-benzothiadiazole) and 9,9-dioctylfluorene	40
2.2.3.3	Optical properties of compounds based on 4,4'-bis	

	(2,1,3-benzothiadiazole) and alkyl thiophenes	42
2.3	Conclusions	45
2.4	Experimental Section	46
Chapter 3	Synthesis and characterization of 4,4'-bis	
	(2,1,3-benzothiadiazole) based copolymers with	
	9,9-dioctylfluorene and alkyl substituted thiophenes	63
3.1	Introduction	63
3.2	Results and Discussion	66
3.2.1	Synthesis	66
3.2.2	Photophysical properties	68
3.2.3	Electrochemical properties and determination of band gaps	72
3.2.4	Organic solar cell performance	72
3.2.5	Morphology of the blend	75
3.2.6	Photo Induced Absorption (PIA) spectroscopy	76
3.3	Conclusions	77
3.4	Experimental Section	77
Chapter 4	Synthesis and characterization of 4,4'-bis	
	(2,1,3-benzothiadiazole) based copolymers with vinylene spacer	81
4.1	Introduction	81
4.2	Results and Discussion	84
4.2.1	Synthesis	84
4.2.2	Photophysical properties	86
4.2.3	Electrochemical properties and determination of band gaps	88
4.2.4	Organic solar cell performance	89
4.3	Conclusions	91

4.4	Experimental Section	92
Chapter 5	Synthesis and characterization of pyrene centered materials for applications in FETs	97
5.1	Introduction	97
5.2	Results and Discussion	99
5.2.1	Synthesis	99
5.2.1.1	Synthesis of 1,3,6,8-tetrakis(2,1,3-benzothiadiazol-4-yl)pyrene	99
5.2.1.2	Synthesis of boronate esters of thiophene	100
5.2.1.3	Synthesis of pyrene and thiophene based oligomers	101
5.2.2	X-ray crystallographic study of oligomers	102
5.2.3	Differential Scanning Calorimetry	103
5.2.4	Photophysical properties	104
5.2.5	Field effect transistor device studies	107
5.3	Conclusions	109
5.4	Experimental Section	109
Chapter 6	Summary and Conclusions	119
	References	123
	Appendices	131
	List of Publications	139
	Bio-data	