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

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by

PIYUSH ANANT

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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 ^{1}H NMR, ^{13}C 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 $FeCl_3$ mediated oxidative polycondensation. All polymers were characterized by ^{1}H NMR, GPC and studied in terms of optical and electrochemical properties. GPC analysis using polystyrene (PS) as standard showed M_n value of 5.4×10^3 gmol^{-1} (PDI = 2.1), 8.4×10^3 gmol^{-1} (PDI = 2.2), 1.16×10^4 gmol^{-1} (PDI = 2.8), and 0.8×10^4 gmol^{-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 ~ 1.2 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 mV, J_{sc} = 1.77 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 ^{1}H NMR, GPC and studied in terms of optical and electrochemical properties. GPC analysis using polystyrene (PS) as standard showed M_n value of 22.4×10^3 gmol^{-1} (PDI = 2.1), 25.4×10^3 gmol^{-1} (PDI = 2.4), 24.0×10^3 gmol^{-1} (PDI = 2.6), and 21.0×10^3 gmol^{-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/cm^2, 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} cm^2/Vs was obtained after annealing.

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