SYNTHESIS OF FLUORENE AND CYCLOPENTADITHIOPHENE BASED DONOR-ACCEPTOR TYPE LOW BAND GAP CROSS-CONJUGATED POLYMERS FOR SOLAR CELL APPLICATIONS

BHAVNA SHARMA

CENTRE FOR POLYMER SCIENCE AND ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

BHAVNA SHARMA

Centre for Polymer Science and Engineering

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Dedicated to Papa and

Flight Lieutenant Himanshu

CERTIFICATE

This is to certify that the thesis entitled "**Synthesis of Fluorene and Cyclopentadithiophene based donor-acceptor type low band gap cross-conjugated polymers for solar cell applications**" being submitted by **Ms. Bhavna Sharma** 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 her. **Ms. Bhavna Sharma** has worked under my guidance and supervision and has fulfilled the requirements for the submission of her 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.

Dr. Josemon Jacob
Professor
Centre for Polymer Science and Engineering
Indian Institute of Technology Delhi
Hauz Khas, New Delhi, India – 110016

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ABSTRACT

Research in the field of conjugated polymers is of great interest with increase in the need of developing cost-effective renewable energy sources. These materials are widely used as active materials for various applications in electronic devices. The organic polymers used in photovoltaics have the potential of achieving cost-effective and easier methods for energy production from light. Since, [6,6]-phenyl-C_{71}-butyric acid ester ($PC_{71}BM$) is one of the perfect electron acceptors, most of the efforts are being focused on the development of donor polymers with low band gap for improvement of efficiency in solar cells. Cyclopenta[2,1-b:3,4-b′]dithiophene (CPDT) and fluorene based conjugated polymers are found to be promising materials to be used for polymer solar cells. Most of the conjugated polymers known have conjugation in main chain only. Introduction of ethylene bridge at the bridging carbon atom, leads to cross-conjugation in the polymeric chains where conjugation is present in main chain as well as side chain. These polymers were typically synthesized using traditional carbon-carbon coupling methods such as Suzuki, Stille and Kumada type cross-coupling. These conventional methods have some disadvantages such as involvement of greater number of steps for monomer synthesis; toxicity due to the organotin reagents in Stille cross-coupling; tedious purification methods etc. Direct arylation polymerization (DAP) is a newly emerging technique for the synthesis of conjugated polymers which overcomes many of the issues associated with the above mentioned polymerization methods. In this work, focus is on the development of CPDT and fluorene based cross-conjugated polymers with low band gap and high molecular weight. These polymers were synthesized by direct arylation polymerization to obtain high molecular weight.

The synthesized polymers were then characterized and their efficiency was tested in solar cell applications. To achieve this objective, the following approach was used.

In the first chapter, optimization studies were done to achieve high molecular weight for the poly[2,6-(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-b;3,4-b′]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] **(PCPDTBT)** by Pd-catalyzed direct arylation polymerization method. Optimization studies were done for **PCPDTBT** synthesis for determining the suitable reaction conditions so as to produce high molecular weight polymers are essential which were then applied to synthesize more CPDT based conjugated and cross-conjugated polymers. The polymerization between alkylated CPDT as donor and benzothiadiazole as acceptor were carried out under varying conditions of solvent, base, concentration and temperature to obtain polymers **P1-P15**. The highest number average molecular weight of 69.3 kg mol^{-1} for **PCPDTBT**. Bulk heterojunction solar cells were fabricated by blending **PCPDTBT** with $PC_{71}BM$ in different ratios and the polymer showed efficiency of 1.94%. The above optimized conditions were used to synthesize **P16** with CPDT as donor and quinoxaline as acceptor with molecular weight of 46.1 kg mol^{-1} which was further characterized and tested in solar cells.

In the second chapter, CPDT based conjugated polymers **P17** and **P18** were synthesized with different acceptors based on the above optimized conditions. Also, cross-conjugated polymers **P19**, **P20** and **P21** were synthesized using cross-conjugated monomer of CPDT (4-(bis((2-ethylhexyl)thio)methylene)-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophene) and different acceptors. All the polymers were fabricated with acceptor $PC_{71}BM$ in different ratios. Among these polymers, **P18** and **P20**, shows better efficiency of 1.86% and 1.37%, respectively.

In third chapter, fluorene based cross-conjugated polymers were synthesized, where cross-conjugated derivative of fluorene ((2, 7-dibromo-9*H*-fluoren-9-ylidene)methylene)bis((2-

ethylhexyl)sulfane) was used as donor and polymerized with different acceptors to obtain various donor-acceptor type polymers for application in solar cells and OLEDs. Firstly, for application in solar cells, random copolymers **P22a** and **P23a** were synthesized by Yamamoto polymerization in good yields. Polymers **P22b**, **P22c**, **P23b** and **P23c** were synthesized by DAP polymerization. The polymer **P23b** was used for fabrication in BHJ solar cells as it has highest molecular weight of 43.1 kg mol^{-1}, so that good polymeric films can be formed. In preliminary device testing PCE was found to be 1.4 % with **P23b**:$PC_{71}BM$. Four more fluorene based cross-conjugated polymers were synthesized which were used in OLEDs. Homopolymer **P24**, random copolymers **P25** and **P26** were synthesized by Yamamoto polymerization while alternating copolymer **P27** was synthesized by Suzuki polycondensation. These new polymeric materials were used in the application for OLEDs.

Altogether, a simple, cost-effective and environmentally safe method was used for the development of high molecular weight conjugated and cross-conjugated polymers for solar cell applications. The concept of cross-conjugated polymers is used here to avoid the unwanted steric hindrance by introduction of ethylene bridge between the side chain and the main chain, so that the polymers obtained possess coplanarity for smoother charge flow.

सार

संयुग्मित पॉलिमर के क्षेत्र में अनुसंधान लागत प्रभावी नवीकरणीय ऊर्जा स्रोतों के विकास की आवश्यकता में वृद्धि के साथ बहुत रुचि है। इन सामग्रियों का उपयोग इलेक्ट्रॉनिक उपकरणों में विभिन्न अनुप्रयोगों के लिए सक्रिय सामग्री के रूप में व्यापक रूप से किया जाता है। फोटोवोल्टाइक्स में इस्तेमाल किए जाने वाले कार्बनिक पॉलीमर को ऊर्जा उत्पादन से प्रकाश से लागत प्रभावी और आसान तरीके प्राप्त करने की क्षमता है। चूंकि, [6,6] -फेनील-सी 71-एटीआई एसिड एस्टर (पीसी 71 बीएम) एकदम सही इलेक्ट्रॉन स्वीकार्यों में से एक है, अधिकतर प्रयास सौर सेल में दक्षता में सुधार के लिए कम बैंड अंतर वाले दाता पॉलिमर के विकास पर केंद्रित हैं। साइक्लोपेंटा [2,1-बी: 3, 4-बी] डायथियोफेंने (सीपीडीटी) और फ्लोरियन आधारित संयुग्मित पॉलिमर पॉलीमर सौर कोशिकाओं के लिए इस्तेमाल होने वाली होनहार सामग्री पाए जाते हैं। ज्ञात संयुग्मित पॉलिमर के अधिकांश मुख्य श्रृंखला में संयुग्मन केवल हैं ब्रिजिंग कार्बन परमाणु पर एथिलीन पुल का परिचय, बहुलक श्रृंखलाओं में पार-संयुग्मन की ओर जाता है जहां संयुग्मन मुख्य श्रृंखला में साथ ही साइड चेन में मौजूद होता है। इन पॉलिमर को आम तौर पर पारंपरिक कार्बन-कार्बन युग्मन विधियों जैसे सुजुकी, स्टेल और कुमादा प्रकार क्रॉस-युग्मन का उपयोग करके संश्लेषित किया गया था। इन पारंपरिक तरीकों में कुछ नुकसान हैं जैसे मोनोमर संश्लेषण के लिए अधिक से अधिक कदमों की भागीदारी; स्टेल क्रॉस-युग्लेशन में अंगोनेटिन अभिकर्मकों के कारण विषाक्तता; थकाऊ शुद्धि विधियों आदि। डायरेक्ट एरिलेशन पॉलिमिराइज़ेशन (डीएपी) संयुग्मित पॉलिमर के संश्लेषण के लिए एक नई उभरती हुई तकनीक है जो उपर्युक्त polymerization के तरीकों से जुड़े कई मुद्दों पर काबू पाती है। इस काम में, कम बैंड अंतर और उच्च आणविक भार वाले सीपीडीटी और फ्लोरिन आधारित क्रॉस-संयुग्मित पॉलिमर के विकास पर ध्यान केंद्रित किया गया है। इन पॉलिमर को उच्च आणविक वजन प्राप्त करने के लिए सीधे एरिलेशन पॉलीमराईकरण द्वारा संश्लेषित किया गया था। संश्लेषित पॉलिमर तब चित्रित किए गए थे और उनकी दक्षता सौर सेल अनुप्रयोगों में जांच की गई थी। इस उद्देश्य को प्राप्त करने के लिए, निम्नलिखित दृष्टिकोण का इस्तेमाल किया गया था।

पहले अध्याय में, पॉली के लिए उच्च आणविक भार हासिल करने के लिए अनुकूलन अध्ययन किया गया [2,6- (4,4-बीआईएस (2-एथिलेहेक्सिल) -4 एच-साइक्लोपेंटा [2,1-बी; 3,4-बी '] डायथियोफिनेई) लाल्ट -4,7-(2,1,3-बेंजोथियाडियाजोल)] (पीसीपीडीटीबीटी) पीडी-उत्प्रेरित डायरेक्ट एरिलेशन पॉलिमाइज़ेशन विधि द्वारा। उपयुक्त प्रतिक्रिया की स्थिति निर्धारित करने के लिए पीसीपीडीटीबीटी संश्लेषण के लिए ऑप्टिमाइज़ेशन अध्ययन किया गया ताकि उच्च आणविक वजन पॉलिमर का उत्पादन करना जरूरी हो, जो तब अधिक सीपीडीटी आधारित संयुग्मित और पार संयुग्मित पॉलिमर को संश्लेषित करने के लिए लागू किया गया था। दाता और बेंज़ोथियाडियाजोल के रूप में एलिकेलेटेड सीपीडीटी के बीच पॉलिमराइजेशन को विलायक, आधार, एकाग्रता और तापमान पॉलिमर P1-P15 प्राप्त करने के लिए अलग-अलग शर्तों के तहत किया गया था। पीसीपीडीटीबीटी के लिए 69.3 किलो मोल-1 के उच्चतम औसत औसत आणविक वजन। बल्क हेटरोज्क्शन सौर कोशिकाओं को पीसीएडीडीटीबीटी को पीसीएडीबीटी के साथ विभिन्न अनुपातों में सम्मिलित किया गया और बहुलक ने 1.94% की दक्षता दिखायी। उपरोक्त अनुकूलित शर्तों का उपयोग P16 को सीडीडीटी के साथ दाता और क्विनॉक्सलाइन के रूप में 46.1 किलोग्राम-एमओएल -1 के आणविक भार के साथ स्वीकार्य के रूप में संश्लेषित करने के लिए किया गया था, जिसे सौर कोशिकाओं में और विशेषता और परीक्षण किया गया था।

दूसरे अध्याय में, सीपीडीटी आधारित संयुग्मित पॉलिमर P17 और P18 को ऊपर अनुकूलित शर्तों के आधार पर विभिन्न स्वीकार्यकों के साथ संश्लेषित किया गया था। इसके अलावा, पार-संयुग्मित पॉलिमर P19, P20 और P21 को सीपीडीटी (4- (बीआईएस (2-एथिलेहेक्सिल) थियो) मिथिलीन के क्रॉस-संयुग्मित मोनोमर का उपयोग करके संश्लेषित किया गया था -4 एच-साइक्लोपेंटा [1,2-बी: 5,4- बी '] डाइथियोफेंने) और विभिन्न स्वीकर्ता सभी पॉलिमर स्वीकार्य पीसी 71 बीएम से अलग अनुपात में निर्मित किए गए थे। इन पॉलिमर में, P18 और P20, क्रमशः 1.86% और 1.37% की बेहतर दक्षता दिखाते हैं।

तीसरे अध्याय में फ्लोरियन आधारित क्रॉस-संयुग्मित पॉलिमर को संश्लेषित किया गया था, जहां फ्लोरेंस के पार-संयुग्मित व्युत्पन्न ((2, 7-डायब्रोमो-9 एच-फ्लोरोएन-9-य्लिडेन) मिथाइलन) बीआईएस ((2-एथिलेहेक्सिल) सल्फ़ान) के रूप में इस्तेमाल किया गया था दाता और सौर कोशिकाओं और ओएलईडीएस में आवेदन के लिए

विभिन्न दाता-स्वीकर्ता प्रकार के पॉलिमर प्राप्त करने के लिए विभिन्न स्वीकारकर्ताओं के साथ बहुलक। सबसे पहले, सौर कोशिकाओं में आवेदन के लिए, यादृच्छिक सहपॉलिमरों P22a और P23a अच्छी पैदावार में यामामोटो पॉलिमराइजेशन द्वारा संश्लेषित किया गया। पॉलिमर P22b, P22c, P23b और P23c डीएपी बहुलकीकरण द्वारा संश्लेषित किया गया। बहुलक P23b का उपयोग बीएचजेएस सौर कोशिकाओं में किया गया था क्योंकि यह 43.1 किलोग्राम के सबसे अधिक आणविक वजन 1 है, ताकि अच्छा बहुलक फिल्में बनाई जा सकें। प्रारंभिक डिवाइस परीक्षण में पीसीई को P23b: पीसी 71 बीएम के साथ 1.4% पाया गया। चार और फ्लोरिन आधारित क्रॉस-संयुग्मित पॉलिमर संश्लेषित किए गए थे जिनका उपयोग ओएलईडीएस में किया गया था। समपॉलिमर P24, यादृच्छिक सहपॉलिमरों P25 और P26 यममोतो पॉलिमराइजेशन द्वारा संश्लेषित किया गया था जबकि वैकल्पिक सहपॉलिमर P27 सुजुकी बहुलकीकरण द्वारा संश्लेषित किया गया था। ओएलईडी के लिए आवेदन में ये नई बहुलक सामग्री का उपयोग किया गया था।

कुल मिलाकर, एक सरल, लागत प्रभावी और पर्यावरण की दृष्टि से सुरक्षित पद्धति का उपयोग सौर सेल अनुप्रयोगों के लिए उच्च आणविक वजन संयुग्मित और क्रॉस संयुग्मित पॉलिमर के विकास के लिए किया गया था। साइड चेन और मुख्य श्रृंखला के बीच एथिलीन पुल के जरिए अवांछित स्टेरिक बाधा से बचने के लिए क्रॉस संयुग्मित पॉलिमर की अवधारणा का उपयोग किया जाता है, ताकि पॉलिमर प्राप्त हो सकें।

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CHAPTER 2 **27**

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LIST OF ABBREVIATIONS

PSC	Polymer Solar Cell
OLED	Organic Light Emitting Diode
FF	Fill Factor
V_{oc}	Open Circuit Voltage
J_{sc}	Short Circuit Current Density
PCE	Power Conversion Efficiency
D-A	Donor-acceptor
BHJ	Bulk Heterojunction
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
E_g	Band Gap
E_g^{opt}	Optical Band Gap
CPDT	Cyclopentadithiophene
EL	Electroluminescence
ITO	Indium Tin Oxide
EA	Electron Affinity
IP	Ionization Potential

PEDOT-PSS	Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
$PC_{71}BM$	[6,6]-phenyl-C_{71}-butyric acid ester
DMSO	Dimethylsulfoxide
DMF	Dimethylformamide
DCM	Dichloromethane
THF	Tetrahydrofuran
NMP	N-methyl-2-pyrrolidone
CN	Chloronaphthalene
DIO	Diiodothiophene
ODT	Octanedithiol
MT	Methanol Treatment
NBS	N-bromosuccinimide
NMR	Nuclear Magnetic Resonance
AFM	Atomic Force Microscopy

LIST OF CHEMICAL FORMULAS

K_2CO_3	Potassium Carbonate
Cs_2CO_3	Cesium Carbonate
NaH	Sodium Hydride
Na_2SO_4	Sodium Sulpahte
KOH	Potassium Hydroxide
C_4H_9KO	Potassium tert-butoxide
$NaBH_4$	Sodium Borohydride
Et_3N	Triethylamine
EtOH	Ethanol
CS_2	Carbon disulphide
$Pd(OAc)_2$	Palladium acetate
Pd_2dba_3	Tris(dibenzylideneacetone)dipalladium(0)
$Pd(PPh_3)_4$	Tetrakis(triphenylphosphine)palladium(0)
$Ni(COD)_2$	Bis(cyclooctadiene)nickel(0)
HCl	Hydrochloric acid
TBAB	Tetra-n-butylammonium bromide