SYNTHESIS, CHARACTERIZATION AND PHOTOVOLTAIC STUDIES ON THIOPHENE BASED LOW BAND GAP MATERIALS

by

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Submitted

In fulfillment of the requirements of the Doctor of Philosophy to the

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Dedicated

to

Abhi and family

CERTIFICATE

This is to certify that the thesis entitled "**Synthesis, characterization and photovoltaic studies on thiophene based low band gap materials**" being submitted by **Ms. Geeta Saini** to the Indian Institute of Technology, Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. **Ms. Geeta Saini** has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my 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 other university or institute for the award of any other degree and diploma.

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ABSTRACT

Regioregular poly(3-hexyl thiophene), often abbreviated as P3HT, is found to be one of the most promising material in devices. The present research work explored the concept of using arylalkyl (5-octyl-2-thienyl and 4-octylphenyl) based solubilizing groups on the side chain instead of using simple alkyl solubilizing group. This approach has potentially two advantages: firstly, the aryl substituent on the side arm is in conjugation along the main chain and hence can lead to a lower band gap material and secondly, the aryl group on the side arm can enable better chain to chain contact in the solid state leading to enhanced charge carrier transport, an important aspect for improving device efficiency.

To understand the effect of substitution on packing and conjugation several model oligomers (tetra- and hexa thiophenes) were synthesized and characterized. The tetra- and hexa thiophenes were symmetrically substituted by 5-methyl-2-thienyl side groups in varying substitution pattern (H-H, H-T and T-T). The observed UV-data for these oligomeric compounds are comparable to alkyl substituted tetra- and hexathiophenes. X-ray crystallographic studies on the tetramers showed that the H-H coupling leads to a severe twist along the chain leading to poor conjugation.

Several classes of 3- and 3,4-diaryl substituted polythiophenes derivatives have been synthesized and characterized using ^{1}H NMR, UV-vis absorption and emission spectroscopy. The steric interactions induced by disubstitution have been reduced by incorporation of various spacers like bithiophene, ethynylene and vinylene unit. The effect of such conjugated spacers has been studied by UV-vis absorption and emission spectroscopy. It is found that incorporation of such spacers have profound effect on conjugation and band gap. The homopolymer with bithiophene spacer (**P7-P9**)

showed absorption maxima vary between 474-484 nm and M_n value between 4.34 x 10^3 to 5.46 x 10^3 g/mol. In case of polythiophenes derivatives with ethynylene spacer (**P23-P26**) the absorption maxima fall in the range of 436-474 nm and is comparable to P3HT and significantly red shifted compared to poly(3,4-dialkylthiophene) suggesting better conjugation in the polymer backbone after insertion of spacer. GPC analysis using PS standards for this class of polymers showed a M_n of 1.10 x 10^4 to 2.99 x 10^4 g/mol for the various polymers, which corresponds to a degree of polymerization of 23-45 monomer units. The polymers were tested in bulkheterojunction solar cells with PCBM as acceptor with a general structure of glass/ITO/PEDOT:PSS/polymers:PCBM(1:1)/Al and showed poor efficiencies. Among these polymers, **P7** showed best solubility, maximum characteristic current-voltage parameters and a power conversion efficiency of 0.5%. The solar cell performance can be improved by changing the ratios of polymers and PCBM composites or using other acceptors.

Polythiophenes with vinylene moiety (**P29-P32**) showed absorption maxima in the range of 511-595 nm and have excellent solubility in common organic solvents. These materials possess some of the lowest band gap yet reported for thiophene based materials. The GPC analysis using PS standard showed the molecular weight fall in the range of 9.09 x 10^3 to 1.06 x 10^5 g/mol corresponding to degree of polymerization of 13-25 monomers units. The testing of these materials in field effect transistors and solar cells are currently underway.

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