SYNTHESIS OF N-HETEROCYCLE BASED CONJUGATED MATERIALS FOR POTENTIAL ELECTRONIC APPLICATIONS

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by

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Dedicated to my

family

CERTIFICATE

This is to certify that the thesis entitled "**Synthesis of N-heterocycle based conjugated materials for potential electronic applications**" being submitted by **Ms. Manisha Tomar** 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. Manisha Tomar** 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.

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ABSTRACT

N-containing polymers have been extensively studied as active materials in various organic electronic devices such as OLEDs, organic solar cells and FETs. Either p- or n-type semiconducting materials can be generated depending on the nature of incorporation of the nitrogen atom in the monomer unit. Among the various classes widely investigated include oxadiazole, pyridine, quinoxaline, carbazole, isoquinoline, benzimidazole, triazole etc. The present work deals with the synthesis and characterization of various N-heterocycle based difunctional monomers, polymers and copolymers. A precursor approach has been developed in this work to generate various difunctional monomers with bromine atoms at the desired positions for coupling, thereby avoiding non-selective post-synthesis bromination.

In the first section, the synthesis and characterization of various functionalized quinoline and biquinoline based materials are described. Two regio isomers of biquinoline, namely 8,5′-dibromo-5,8′-biquinoline and 5,5′-dibromo-8,8′-biquinoline, were synthesized to see the effect of orientation on conjugation and packing. The synthesized molecules were coupled with 9,9-dimethylfluorene and thiophene to prepare a series of model compounds for the corresponding polymers and X-ray crystallographic studies on some of these gave insight into the mode of packing in these materials. The synthesized molecules were characterized by ^{1}H and ^{13}C NMR, elemental analysis, mass spectroscopy, UV-vis absorption and emission spectroscopies and in some cases, by X-ray crystallography. The absorbance and emission maxima for the model compounds based on quinoline/biquinoline with fluorene (**13-16**) lie in the range of 328 nm to 341 nm, and 414 nm to 433 nm, respectively. The absorbance and emission maxima for the model compounds based on quinoline/biquinoline with thiophene (**24-28**) lie in the range

of 345 nm to 420 nm, and 448 nm to 497 nm, respectively. The absorption position for model compound based on quinoline is red-shifted as compared to model compounds based on biquinoline units. Also, absorption maxima for model compounds based on biquinoline core is slightly dependent on the linkage between the two quinoline units and absorption position of model compound based on 5,8′-biquinoline unit **15** is at a slightly longer wavelength compared with that of model compound containing 8,8′-biquinoline unit **16,** suggesting that **15** adopts, on average, a more planar conformation in solution.

In the next section, the synthesis of a series of alternating copolymers containing either quinoline or isomeric biquinoline unit (5,8′-biquinoline and 8,8′-biquinoline) and 9,9-dialkylfluorene (**P1a-P3b**) in the backbone using Pd catalyzed Suzuki polycondensation reaction are described. The absorbance maxima for **P1a-P3b** lie in the range of 344 nm to 365 nm. All the copolymers emit in the blue region with an emission maxima centered in the range of 430 nm to 448 nm. The optical band gaps of the copolymers were found to be in the range of 2.78 eV to 2.89 eV. However, due to low solid state quantum yield, these polymers were not tested in OLED devices. Further, a series of random copolymers based on quinoline/8,8′-biquinoline with 9,9-dioctylfluorene and thiophene/benzothiadiazole using palladium catalyzed Suzuki cross-coupling reaction were synthesized. The absorbance maxima and emission maxima for these polymers (**P8-P11**) lie in the range of 411 nm to 436 nm, and 460 nm to 533 nm, respectively. Polymers having **TBT** unit and either quinoline (**P6**) or 8,8′-biquinoline unit (**P7**) in the polymer backbone synthesized using Pd catalyzed direct arylation polycondensation reaction exhibit absorbance maxima centered at 494 nm and 481 nm, respectively. Polymers containing **CPDT** and 2,1,3-benzothiadiazole unit with either quinoline (**P12**) or 8,8′-biquinoline unit (**P13**) in the polymer backbone showed absorbance maxima centered at 664 nm and 649 nm, respectively. Among all the synthesized polymers **P6**, **P7**, **P12** and

P13 showed lowest electrochemical band gap of 1.98 eV, 1.87 eV, 1.39 eV and 1.27 eV, respectively.

3,9-Dibromo-6-aryl-5*H*-dibenzo[d,f][1,3]diazepine was synthesized by a simple and fast one-step reaction with benzaldehyde in the presence of I_2/K_2CO_3 using *t*-butanol as the solvent. In order to increase the solubility, an alkyl chain was introduced into the molecule by reacting with 4-octylbenzaldehyde and 4-octyloxybenzaldehyde. 3,9-Dibromo-6-phenyl-5*H*-dibenzo[d,f][1,3]diazepine was coupled with thiophene (**45**), 2,1,3-benzothiadiazole (**46**), and 9,9-dimethylfluorene (**47**) to prepare a series of model compounds using standard Suzuki coupling reaction which were characterized by ^{1}H NMR, ^{13}C NMR, mass spectroscopy, UV-Vis absorption spectroscopy, fluorescence spectroscopy, and by X-ray crystallography. The absorbance and emission maxima for **45**, **46** and **47** lie in the range of 304 nm to 356 nm, and 436 nm to 527 nm, respectively. A new route toward the synthesis of 3,8-dibromobenzo[c]cinnoline was developed and it coupled with 3-octyllthiophene to synthesize a model compound which was used as a monomer for the synthesis of copolymers.

In the last section, two polymers based on 3,9-dibromo-6-phenyl-5*H*-dibenzo[d,f][1,3]diazepine were synthesized. **P14**, an alternating copolymer containing 3,9-dibromo-6-aryl-5*H*-dibenzo[d,f][1,3]diazepine unit and 9,9-dialkylfluorene in the backbone exhibit absorption and emission maxima centered at 350 nm and 487 nm, respectively, whereas **P15**, a random copolymer containing 3,9-dibromo-6-aryl-5*H*-dibenzo[d,f][1,3]diazepine with 2,1,3-benzothiadiazole and 9,9-dialkylfluorene in the backbone showed absorption and emission maxima centered at 432nm and 542 nm, respectively. Benzo[c]cinnoline was explored as a new candidate for application in organic materials and a series of donor-acceptor type copolymers (**P16 - P20**) containing benzo[c]cinnoline with various donor and acceptor moieties in the backbone were

synthesized and characterized. The absorbance maxima for **P16**-**P20** lie in the range of range of 494 nm to 649 nm. The electrochemical band gap of the copolymers as determined by cyclic voltammetric measurements are found to be in range of 1.95 eV to 1.4 eV. The HOMO energy levels (-5.23 eV to -5.80 eV) of these polymers are located quiet below the LUMO energy level of **PCBM** (LUMO = -4.3 eV) and can generate reasonable V_{oc}. Device studies on these materials are currently underway.

Overall, simple and direct precursor routes have been developed to access a host of nitrogen containing heterocylces which were shown to undergo facile coupling with various aromatic moieties to generate materials with extended conjugation. Incorporation of N-heterocycles generates polymeric materials with deeper lying HOMO levels, typically -5.7 to -5.9 eV and can serve as a useful tool to tune HOMO energy levels.

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LIST OF ABBREVIATIONS

D-A	Donor-acceptor
BHJ	Bulk Heterojunction
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
E_g	Band gap
ICT	Internal Charge Transfer
CPDT	Cyclopentadithiophene
BDT	Benzodithiophene
OLED	Organic Light Emitting Diode
EL	Electroluminescence
ITO	Indium Tin Oxide
MEH-PPV	Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]
EQE	External Quantum Efficiency
EA	Electron affinity
IP	Ionization potential
TPBI	1,3,5-tri(phenyl-2-benzimi-dazolyl)-benzene
PEDOT-PSS	Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
OPV	Organic photovoltaic
DMSO	Dimethylsulfoxide
DMF	Dimethylformamide
DCM	Dichloromethane

THF	Tetrahydrofuran
NBS	N-bromosuccinimide
TLC	Thin layer chromatography
NMR	Nuclear Magnetic Resonance
n-BuLi	Normal-butyl lithium
TBT	Thiophene-benzothiadiazole-thiophene unit
DPP	Diketopyrrolopyrole

LIST OF CHEMICAL FORMULAS

Na_2SO_4	Sodium Sulphate
Na_2CO_3	Sodium Carbonate
KOH	Potassium Hydroxide
H_2SO_4	Sulphuric acid
HNO_3	Nitric Acid
HCl	Hydrochloric acid
$Pd(dppf)Cl_2$	1,1' Bis(diphenylphosphino)ferrocene]dichloropalladium(II)
$FeCl_3$	Ferric Chloride
NaOH	Sodium Hydroxide
$Ni(dppp)Cl_2$	Propane 1,3-bis(dphenylphosphino) Nickel
$Pd(PPh_3)_4$	Tetrakis(triphenylphosphine)palladium(0)