Synthesis of N-Heterocycle Based Conjugated Materials For Potential Electronic Applications

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ABSTRACT

Nitrogen containing polymers have been extensively studied as active materials in various organic electronic devices such as OLEDs, organic solar cells and OFETs. 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. A review of literature shows that although various reports on N-heterocycle based polymers are available, they are all synthesized by indirect methods and often require multi step synthesis. This is in part due to a lack of readily available methods to synthesize suitably functionalized N-heterocycle based difunctional monomers which can be readily coupled to build extended conjugated frameworks.

In this thesis work, the development of precursor routes to functionalized N-heterocyclic monomers based on quinoline, isomeric biquinolines, diazepine and cinnoline derivatives are reported. Also, facile coupling of these units with small molecules are demonstrated. 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. Single crystal X-ray studies on these coupled products provided valuable information on the conformation and bulk packing of these materials. The precursor approach avoids non-selective functionalization after monomer synthesis and the difunctional monomers can be directly coupled with other conjugated moieties in high yields to build extended conjugated materials.

A series of copolymers based on these N-heterocyclic monomers with various aromatic moieties such as thiophene, fluorene, 2,1,3-benzothiadiazole and cyclopentadithiophene were synthesized using either Suzuki polycondensation reaction or direct-arylation polycondensation reaction. The resulting copolymers were characterized $^1$H NMR, DSC, TGA, Cyclic Voltammetry, UV-vis absorption, and emission spectroscopy. Based on the optical and electrochemical properties of the developed materials, they were tested for application in electronic devices in some cases.