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Conjugated molecules

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Summary

The rapid development of conjugated polymeric materials has enable the organic electronic and optoelectronic devices technology (organic field effect transistors, organic solar cells, organic light-emitting diodes, and organic thermoelectric devices) to develop at a rapid pace in the last decades. In order to make these devices suitable for practical applications, stable and efficient devices are required. This also demands new materials with super properties such as an outstanding charge transport, and a high chemical and mechanical stability. Thus, fundamentally understanding the structure-properties relationship is the key to design new materials for these devices.

The scientific goal of this thesis aims to use chemistry approaches to design novel conjugated polymers for specific purposes: 1) enhancing the solubility of intrinsic conjugated polymers in green solvents to replace the highly toxic chlorinated solvent in fabricating organic electronic devices; 2) design and synthesis of n-type conjugated polymers in pursuit of high performance organic thermoelectric devices and for better understanding of the relationship between chemical structures and device performances; 3) investigating novel polymerization strategies to make conjugated polymers. In the meantime, we are also interested in understanding the relationship between the molecular structures and charge transport in single-molecular and molecular-ensemble monolayer tunneling junctions.

In Chapter 2, we report the synthesis and characterization of three new aromatic polyketones with repeating units based on 2,2'-(2,5-dihexyl-1,4-phenylene) dithiophene (PTK), 2,2'-(9,9-dihexyl-9H-fluorene-2,7-diyl)dithiophene (PFTK), and 4,7-bis(3-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (PBTK). These polymers were synthesized with a one-pot Suzuki-Miyaura cross-coupling promoted homopolymerization, which offered good chemical integrity. We systematically investigate bandgap and molecular energy levels of these aromatic polyketones by absorption spectroscopy, cyclic voltammetry and theoretical calculations. As with conventional conjugated polymers, the aromatic polyketones exhibited tunable opto-electroic properties. These new aromatic polyketones possess excellent thermal stability. Especially, they exhibited tunable opto-electronic properties when exposed to acidic conditions.

In Chapter 3, we are developing an alternative to conjugated polyelectrolytes in which "spinless doping" introduces formal charges into the backbones of conjugated polymers without the requisite spin to induce the transition to the metallic state. These conjugated polyions (CPIs) are intrinsic semiconductors that are completely soluble in and processible from polar, protic solvents. In this work, we describes the design, synthesis and optical and electronic properties of two conjugated polymers **CPIZ-B** and **CPIZ-T** that incorporate closed-shell cations into the backbones, balanced by anionic pendant groups by using a three compo-

nents random Suzuki-Miyaura copolymerization to control the electronic structure while retaining sufficient ionic character for processing from polar, protic solvents. Ultraviolet-visible near infrared (UV-Vis-NIR) and electron paramagnetic resonance (EPR) spectroscopy and proof-of-concept bi-layer organic solar cell (OSCs) confirm that spinless doping. We prepared the OSCs by casting films of **CPIZ-T** from mixtures of water and formic acid (HCOOH), acidic solutions being necessary to prevent the cations from being quenched by water. Formic acid is produced on the ton-scale and is widely used for industrial and agricultural applications and as a food additive. It is only flammable at >85 % weight-percent (wt%), making 80:20 v% HCO_2H:H_2O solutions a viable green solvent for processing organic semiconductors.

Molecular doping of conjugated polymers is a key strategy for achieving high-performance organic thermoelectric devices. The relationship between molecular structures of n-type conjugated polymers and thermoelectrics device performance remains vague. In Chapter 4 and Chapter 5, we designed and synthesized a serials of NDI-based n-type conjugated polymers, and systematically investigate the relationship between the chemical architecture and the molecular doping to enhance the performance of the thermoelectric devices.

In Chapter 4, we demonstrate how the type and position of side chains impact the n-doping of donor-acceptor (D-A) copolymers. Four different combinations of linear ethylene glycol-based polar side chains and traditional alkyl side chains are used, and the resultant D-A copolymers are molecularly n-doped by organic dopant with varying doping concentrations. It is found that the polar side chains can greatly improve the mixing of host D-A copolymers with polar dopants as compared to the alkyl side chains, which can increase doping efficiencies up to 10 % to 20 % from 0.25 % in the case of only alkyl side chains used. Additionally, the polar side chains also facilitate the molecular packing of D-A copolymers and increase the mobility by more than an order of magnitude. Because of those advantages of the polar side chains, we achieve an optimized conductivity of 0.08 S/cm in the doped PNDI2TEG-T2DEG with the polar side chains on both D and A moieties. Our work offers an insight into the roles of side chains play in molecular n-doping, which might be general for most conjugated polymers.

In Chapter 5, we demonstrated that the n-type thermoelectric performance of donor-acceptor (D-A) copolymers can be enhanced by a factor of >1000 by tailoring the density of states (DOS) via structure backbone modification. The molecular design is embedding sp^2-N atoms into the donor moiety of an NDI-2T based D-A copolymer (PNDI2TEG-2T). By doing so, a new copolymer named PNDI2TEG-2Tz with improved molecular planarity and the $\pi - \pi$ overlap was obtained. Furthermore, the molecular stacking in the thin film is changed into a preferential edge-on pattern from the original face-on-dominated microstructure. Due to the molecular and microstructural motif, the PNDI2TEG-2Tz exhibits much narrower and denser DOS energy distribution than PNDI2TEG-2T. For this reason, the doped PNDI2TEG-2Tz copolymer exhibits a high electrical conductivity of 1.8 S/cm, which represents over three orders of magnitude enhancement as compared to that of the unmodified D-A copolymer. Additionally, the tailoring of DOS distribution reduces the loss of the Seebeck coefficient, leading to an improved power factor of 4.5 $\mu Wm^{-1}K^{-2}$,

which is a very good result for n-type organic thermoelectric. Our work provides insights into the fundamental understanding of molecular doping and sheds light on designing efficient n-type OTE materials from a new perspective of tailoring the DOS.

Understanding the principles of charge transport through π-molecules spanning two electrodes is of fundamental importance in the field of molecular electronics. The goal of this chapter is two-fold. The first is to present a study on the understanding of the relationships among conjugation pattern, molecular length, and conductance. For this purpose, we employed an bond topology methodology to design and synthesize a series of molecular wires; thieno[3,2-b]thiophene (**TT-1**, linearly conjugation), bithiophene (**BT**, linearly conjugation), thieno[2,3-b]thiophene (**TT-2**, cross-conjugation and an isomer of **TT-1**. We investigated the charge transport of these three molecular wires in tunneling junctions by combining a variety experimental platforms including large area self-assembled monolayers (SAMs) with EGain top contacts and conductive-probe atomic force microscopy (CP-AFM) for SAMs. Through a combination of density functional theory (DFT) and experimental results, we show that cross-conjugation produces quantum interference (QI) features that lead to the lowest conductance and dominate the charge transport.

The second goal is to isolate the specific effects of bond topology and electronegativity on the depth and position of QI features. To address this issue, we designed and synthesized a second series molecules of benzodithiophene derivatives (**BDT-**n); benzo[1,2-b:4,5-b']dithiophene (**BDT-**1, linearly conjugated), benzo[1,2-b:4,5-b']dithiophene-4,8-dione (**BDT-**2, cross-conjugated with quinone), and benzo[1,2-b:5,4-b']dithiophene (**BDT-**3, cross-conjugated and an isomer of **BDT-**1). We investigated the charge transport of this series of molecular wires in tunneling junctions in a variety of experimental platforms. Through a combination of density of functional theory (DFT) and experimental results, we show that cross-conjugation produces a quantum interference feature that leads to lower conductance. The presence of an interference feature and its position can be controlled independently by manipulating bond topology and electronegativity. This is the first study to separate these two parameters experimentally, demonstrating that the conductance of a tunneling junction depends on the position and depth of a QI feature, both of which can be controlled synthetically.