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Charge Transport and Thermoelectric Properties of Organic Semiconductors

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Summary

Organic semiconductors have emerged as an interdisciplinary research field with significant potential across multiple electronic applications, including organic field-effect transistors, organic photovoltaics, organic light-emitting diodes, and organic thermoelectric devices. To facilitate the rational molecular design of high-performance materials and advance these technologies toward practical implementation, elucidating the fundamental properties of organic semiconductors is crucial.

Our research group has focused on the effects of polar side chains on the fundamental physical processes (e.g. charge transfer, separation, and transport), and corresponding thermoelectric properties of n-type organic thermoelectrics. Besides, we also have developed a new model for the charge carrier behaviors in hopping transport. This thesis builds on previous work regarding organic semiconductors in two perspectives: 1) novel organic thermoelectric materials and understanding of the relationship between chemical structures and thermoelectric performance; 2) experimental observations of Coulomb repulsion and collective screen in organic semiconductors to explain the mechanisms governing electrical property evolution and supplement hopping transport.

Whereas our previous studies examined the influence of polar side chains on thermoelectric performance, the effects of side chain volume and structural variations remain unexplored. In Chapter 3, we characterize and evaluate three novel n-type conjugated polymers as thermoelectric materials, each comprising naphthalenediimide and dialkoxybithiazole units with distinct oligo(ethylene glycol) (OEG) side chains. The incorporation of OEG side chains enhanced host-dopant miscibility. Our findings reveal that, despite inducing slight backbone twisting, increasing the volume of ethylene glycol units in linear side chains maintained enhanced thermoelectric performance due to excellent molecular ordering. Conversely, branched OEG side chains introduce significant steric hindrance, resulting in pronounced backbone twisting. This structural perturbation manifests in disrupted molecular packing within the thin film, adversely affecting molecular doping efficiency and charge transport, ultimately compromising thermoelectric performance. These results demonstrate trade-offs between thermoelectric performance and ethylene glycol side-chain engineering.

Conventional processing methods for organic thermoelectrics, which typically rely on hazardous solvents, constrain the widespread commercial and sustainable application of organic thermoelectric devices. In Chapter 4, we present a novel method for dispersing hydrophobic conjugated polymers in aqueous and ethanolic media. The results demonstrate

that ground-state electron transfer in donor-acceptor blends can dope and disperse a conjugated polymer in these sustainable solvents. The doping mechanism is nucleophilic attack that generates charge carriers by introducing Lewis bases. Both side-chain polarity and solvent selection can modulate the dispersion. This approach enables effective n-type doping in organic semiconductor films, establishing an environmentally sustainable pathway for organic electronics processing.

Based on computational predictions from our group, in Chapter 5, we experimentally explore the reason for the decline in conductivity at high doping level in doped organic semiconductors. Our findings demonstrate that this phenomenon is attributed to Coulomb repulsion rather than morphological changes. We conduct systematic measurements of electrical conductivity and Seebeck coefficient as a function of doping concentration across a series of n-type organic semiconductors. Notably, the carrier density n_x at maximum electrical conductivity is consistent with the carrier density when Seebeck coefficient starts to follow Heike's slope. The correlated dependence of electrical conductivity and Seebeck coefficient on carrier density reveals that electrical conductivity at high doping levels is limited by carrier-carrier repulsion. These experimental findings provide crucial validation for and enhance our existing theoretical framework of hopping transport in doped organic semiconductors.

The Coulomb repulsion in doped organic semiconductors is a collective behavior wherein mobile charge carriers effectively screen dopant molecules. This collective screening mechanism reduces the Coulomb interaction barrier for free carrier generation from dopants. Consequently, the dielectric constant experiences a dramatic enhancement upon doping, a phenomenon termed the "dielectric catastrophe". In Chapter 6, we employ metal-insulator-semiconductor (MIS) devices to investigate dielectric constant variations in both n- and p-type organic semiconductors under different doping concentrations. Different with the traditional utility for carrier density extraction, this study explores the novel application of MIS diodes in dielectric constant measurement for doped organic semiconductors. Our experimental results reveal a remarkable increase in dielectric constant upon doping, ranging from approximately 3.0 to 15.0. This finding validates the existence of the dielectric catastrophe. Combining the conclusion in Chapter 5, we propose that while charge screening enhances free carrier yield, however, this collective behavior can diminish conductivity at high carrier densities due to dominant Coulomb repulsion.