

Design and Synthesis of Proton-Dopable Organic Semiconductor for Energy Harvesting

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Abstract

Thermoelectric (TE) materials are promising candidates for energy harvesting because of their ability to convert thermal energy into electricity. Organic thermoelectric materials (OTE) have been well developed due to the merits of non-toxicity, high abundance, low-temperature processing, and flexibility. The key to improving the energy harvesting ability of the organic TE materials is to enhance the conductivity and modify the carrier concentration, which requires in-depth study of doping mechanism. Generally, the doping mechanism could divide into charge transfer doping and proton doping (acid doping), according to how charge carriers are generated. Previous works have illustrated the charge transfer doping mechanism, which is meaningful to practical applications. Proton doping is a simple process with good performance, which is easy to modify and control, thus well studied and applied in the preparation of OTE materials. However, the elaboration of the proton doping mechanism varies from one study to another, especially for the research on the commercially available poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), the proton doping mechanism and doping sites are not clear. Some studies attribute the proton doping mechanism to the poly(styrenesulfonic acid) chains removal from PEDOT:PSS films. In contrast, other studies conclude the mechanism of proton adducted into the OTE materials. This study aims to design new OSC molecules for proton-doping mechanism study, investigate whether the materials have the thermoelectric ability, and conclude the influence of molecule structure to thermoelectric properties.

Firstly, an EDOT-ending organic conjugated molecule, 2,5-bis(5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-3-dodecylthiophen-2-yl)thieno[3,2-b]thiophene (BDTTT) was designed and synthesized. Ultraviolet-visible-near-infrared spectroscopy (UV-Vis-NIR) absorption spectrum of BDTTT suggested that the new material could be proton doped. Conductivity of $0.895 \text{ S}\cdot\text{cm}^{-1}$ was obtained from proton-doped film. Proton doping mechanism was determined by the proton nuclear magnetic spectroscopy ($^1\text{H-NMR}$) and density functional theory (DFT) calculation. Results suggested that the most reactive sites are most suitable for proton doping.

Secondly, compared with the general OSCs, which are usually in polymer forms, the BDTTT was fabricated into a thin film and polymerized to achieve performance enhancement. The main peak of UV-Vis-NIR spectra red-shifted from 430 nm to 542 nm, indicating that polymerization occurred and the film was oxidatively doped. By proton doping treatment, the pBDTTT film's conductivity was raised to $24.06 \text{ S}\cdot\text{cm}^{-1}$ and power factor (PF) was $1.40 \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$. Although proton-doped polymer BDTTT indicated thermoelectric ability, further investigations suggested poor thermoelectric performance significantly correlated with the molecular arrangement and structure.

Thirdly, another new molecule 2,5-bis(3-dodecyl-5-(2,2',3,3'-tetrahydro-[5,5'-bithieno[3,4-b][1,4]dioxin]-7-yl)thiophene-2-yl)thieno[3,2-b]thiophene (DTTTT) was

designed and synthesized to examine influence of molecular structure on the properties of proton-doped OSCs. UV-Vis-NIR and NMR spectra indicated that the DTTTT could be proton-doped, the mechanism is the same as BDTTT. The result of DFT calculation suggested that the α -position of DTTTT was more active than BDTTT, indicating that the DTTTT is easier to be proton doped. The PF of the pDTTTT-H₂SO₄ film was 0.186 $\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$, much lower than pBDTTT-TsOH film. The result of UV-Vis-NIR also indicated that polymerization degree of DTTTT is lower than that of BDTTT. Larger molecule volume resulted in a relatively low polymerization degree and shorter chain length. These results indicated that the molecular structure could severely affect the thermoelectric property of OSC materials, and suggested that besides the doping position reactivity, the molecular structure should also be noticed during molecular design.

The findings from this study revealed the actual proton doping mechanism on OTE materials, and the doping sites were specifically identified. The comparison of the properties of the two new molecules revealed the influence of molecular structure on material properties. This study provided a pathway for the designing of proton-dopable OSC materials, EDOT used as an end group could offer an active α -position for proton doping.

Keywords: Thermoelectric; Organic semiconductor; Proton doping.