

Metallic Behavior of Mixed-sequence Oligo(alkylenedioxythiophene) Salt

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Conjugated polymers (e.g., doped poly(3,4-ethylenedioxythiophene) (PEDOT)) are commonly employed materials in organic electronic devices. However, the wide molecular-weight distribution has hampered the acquisition of detailed structural information, limiting study on the conductivity mechanism and methods to control conductivity (Figure 1). We recently developed single-molecular-weight oligomer models for doped PEDOT (i.e., $n\mathbf{O}\cdot\mathbf{X}$, $n = 2-3$, $\mathbf{X} = \text{BF}_4, \text{ClO}_4, \text{PF}_6$)^(1,2) composed of 3,4-ethylenedioxythiophene unit \mathbf{O} . The characteristic richness in structure-controlling factors of these oligomer-based materials, including the chain lengths and sequences, encouraged us to establish a method for precise controlling of conductivity based on the molecular structures. We first demonstrated the effects of elongating chain lengths in oligo EDOT systems; $3\mathbf{O}\cdot\text{PF}_6$ (CH_2Cl_2)_n exhibited improved conductivity, with a room-temperature conductivity σ_{rt} of 1.0×10^{-3} S/cm compared to $2\mathbf{O}\cdot\text{PF}_6$ (2.3×10^{-5} S/cm).⁽²⁾

In this study, we report on the combined effects of chain lengths and sequences on the conductivities of the charge transfer salts. We designed and synthesized $4\mathbf{PS}$ with a sequence of P-S-S-P composed of the oxygen/sulfur-substituted unit \mathbf{S} and bulky 3,4-propylenedioxythiophene unit \mathbf{P} (Figure 1b). The single-crystal XRD analysis of the charge transfer salt $4\mathbf{PS}\cdot\text{PF}_6(\text{solvent})_n$ showed that donors are stacked in a head-to-head manner, possibly due to the presence of bulky \mathbf{P} unit at the termini, to form a pitched π -stack packing structure. The first-principles calculation based on the single-crystal structure suggested the considerable intracolumnar and minor intercolumnar transfer integral suggesting its quasi-1D electronic structure. The σ_{rt} of the single crystal was 36 S/cm, a six-order magnitude higher than that of $2\mathbf{O}\cdot\text{PF}_6$, and, above room temperature, decrease in the conductivity upon heating, i.e. a metallic behavior, was observed (Figure 1c). The dramatic improvement of the conductivity can originate in the elongated oligomer length and mix sequence that may reduce the Coulomb repulsion energy between carriers, as well as the higher dimensionality.

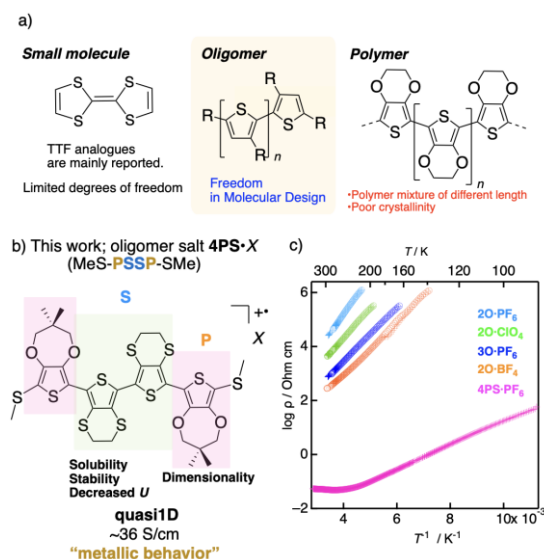


Figure 1. (a) comparison small molecule, oligomer and polymer (b) Structures of new oligomer salts $4\mathbf{PS}\cdot\text{PF}_6(\text{solvent})_n$ (c) $\rho-T^{-1}$ plot of $4\mathbf{PS}\cdot\text{PF}_6(\text{acetone})_n$ measured with a AC voltage.

References

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