Metallic State of Mixed Sequence Oligomer Salt that Models Doped PEDOT

(1The Institute for Solid State Physics, The University of Tokyo, 2Institute for Molecular Science, 3Department of Advanced Materials Science, The University of Tokyo)

Kota Onozuka1, Tomoko Fujino1, Ryohei Kameyama1, Shun Dekura1, Kazuyoshi Yoshimi1, Toshikazu Nakamura2, Tatsuya Miyamoto3, Hiroshi Okamoto3, Hatsumi Mori1

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Conjugated polymers (e.g., doped poly(3,4-ethylenedioxythiophene) (PEDOT)) (Figure 1a, left) are commonly employed materials in organic electronic devices. However, due to the wide molecular-weight distribution, detailed structural information could not be obtained, limiting research on the mechanism of conductivity and methods to control conductivity11. To solve these problems, we reported oligomer models for doped PEDOT (i.e., nO•X, n = 2–3, X = BF4, ClO4, PF6, H2(SO4), Figure 1)22, 33, 44.

In this study, we extended the oligomers by introducing mixed sequences. The multiple units are assembled in a precisely designed sequence that are intrinsic structural determinants of the oligomers. We designed and synthesized 4PS with a sequence of P-S-S-P composed of the oxygen/sulfur-substituted unit S and unit P (Figure 1a, right). The single-crystal XRD analysis of 4PS•(PF6)1.2(solvent)n showed that it forms a pitched π-stack packing structure. The room temperature conductivity σrs of the single crystal was 36 S/cm, a six-order magnitude higher than that of 2O•PF6. Above room temperature, a metallic state was observed. The dramatic improvement of the conductivity can be attributed to the reduction of Coulomb repulsion energy, band filling, and higher dimensionality by introduction of mix sequence.