

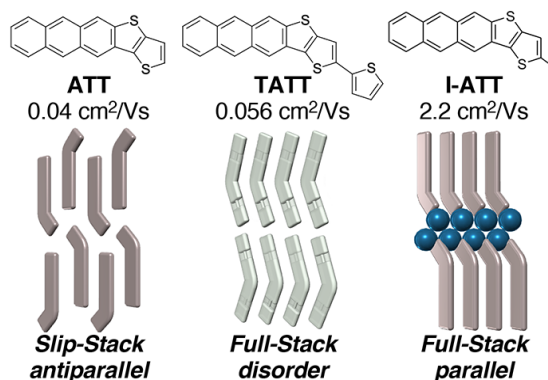
Control of Molecular Orientation in Organic Semiconductors Using Weak Iodine–Iodine Interactions

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Organic field-effect transistor (OFET) materials require high molecular orientation for efficient charge transport in thin films. In this study, we report the semiconductor characteristics of asymmetric thienoacene (ATT; anthra[2,3-*b*]thieno[2,3-*d*]thiophene) derivatives that exhibit both high solubility and high molecular orientation.¹ Herein, we systematically investigated the crystal structure changes and charge transport properties of asymmetric thienoacenes(ATT), the thienyl derivative (TATT), and the monoiodinated derivative (I-ATT)².

TATT and I-ATT were synthesized via the regioselective α -lithiation of ATT. OFET devices of I-ATT fabricated by drop-casting method showed higher p-type semiconductor characteristics than those of ATT and TATT (ATT: 0.04 cm²/Vs, TATT: 0.056 cm²/Vs, and ATT: 2.2 cm²/Vs). Single crystal X-ray diffraction analysis revealed that ATT formed a slip-stack antiparallel structure and TATT formed a full-stack disorder structure with enhancement of molecular symmetry and dispersion force. In contrast, I-ATT formed a full-stack parallel structure with a large orbital overlapping. These results suggest that a weak iodine–iodine interaction as an intermolecular force stabilizes the molecular arrangement favorable for charge transport. Thin film X-ray diffraction, which was fabricated in the same manner as the OFET device, gave profiles characteristic of the in-plane herringbone structure and the end-on orientation in the out-of-plane direction in all molecules. The d-spacing calculated from the out-of-plane direction corresponded to one molecular length for ATT and TATT, and head-to-head dimers for I-ATT. These results indicate that the iodine–iodine interaction is effective for controlling molecular orientation in solution-processable OFET materials.



1) Y. Ogawa, *et al.*, *ACS Appl. Mater. Interfaces* **2017**, 9, 9902–9909.

2) A. Matsunaga, *et al.*, *J. Phys. Chem. Lett.* **2021**, 12, 111–116.