Multi-Band Charge Transport in Bent-Shaped p-Type Organic Semiconductors

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The multi-band charge transport is a well-known phenomenon in conventional inorganic semiconductors, though it is not commonly observed or investigated in organic semiconductors (OSCs).[1] To date, one of the highest performance p-type OSCs, the bent-shaped decyl-dinaphtho[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene (C_{10}–DNBDT–NW),[2] shows isotropic charge transport that provides resilience to dynamic disorder,[3] and charge-carrier mobility up to 16 $cm^2\ V^{-1}\ s^{-1}$. In this work, we first demonstrate evidence of multi-band charge transport in the high-performance C_{10}–DNBDT–NW, and present the molecular design of a new bent-shaped bis(naphtho[2',3':4,5]thieno)[2,3-*b*:2',3'-*e*]pyrazine (BNTP) π-electron system[4] (Figure 1) to induce more pronounced multi-band charge transport by replacing the central benzene unit of DNBDT with a pyrazine unit. An effective synthetic strategy for the pyrazine-containing extended π-electron system is developed. With rational substituent engineering, the favorable two-dimensional herringbone assembly can be obtained with BNTP, and the decylphenyl-substituted BNTP (C_{10}Ph–BNTP) demonstrates large electronic couplings in the herringbone assembly involving the highest, second highest, and third highest occupied molecular orbitals (HOMO, Second HOMO, and Third HOMO) (Figure 1). C_{10}Ph–BNTP further shows enhanced charge-transport capability with drastically different valence band dispersions when the electronic couplings of all three occupied molecular orbitals are taken into considerations, which results in a high hole mobility up to 9.6 $cm^2\ V^{-1}\ s^{-1}$ in single-crystalline thin-film organic field-effect transistors (Figure 1). Our present study provides a viable molecular design strategy for inducing multi-band charge transports in OSCs.

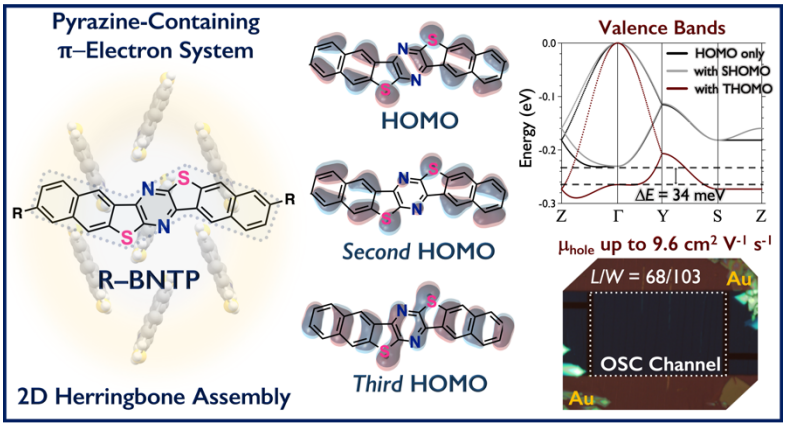

Figure 1 Molecular structure of the novel R–BNTP π-electron system and the distributions of the highest, second highest, and third highest occupied molecular orbitals (HOMO, Second HOMO, and Third HOMO). Valence band structures of R–BNTP when the electronic couplings of different molecular orbitals are taken into considerations, and the microscopic image of the single-crystalline thin-film organic field-effect transistors fabricated using R–BNTP.

References

(1) Kuroda, Y. *et al. Jpn. J. Appl. Phys.* **2019**, *58*, SIIB27. (2) Mitsui, C. *et al. Adv. Mater.* **2014**, *26*, 4546–4551. (3) Fratini, S. *et al. Nat. Mater.* **2017**, *16*, 998–1002. (4) Yu, C. P. *et al. Submitted*