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Infrared signatures of ambipolar injection in narrow gap Donor-Acceptor polymer transistors

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Donor-Acceptor (D-A) copolymers have recently emerged as versatile materials for use in a large variety of device applications. Specifically, these systems possess extremely narrow bandgaps, enabling ambipolar charge transport when integrated in solution-processed field-effect transistors (OFETs). However, the fundamentals of electronic transport in this class
of materials remain unexplored. We present a systematic investigation of ambipolar charge injection in D-A conjugated polymers polybenzobisthiadiazole-dithienopyrrole (PBBTPD) and
polybenzobisthiadiazole-dithienocyclopentane (PBBTCD) using infrared spectroscopy. We observed a significant modification of the absorption edge in both PBBTPD- and PBBTCD-based OFETs under the applied electric field. The absorption edge reveals hardening under electron injection and softening under hole injection. Additionally, we registered localized vibrational resonances associated with charge injection. These findings indicate that several physical processes likely contribute to the field-induced changes in IR transmission spectra, including possibly electron- and hole-induced polaron absorption, and/or electric field-induced modulation of the polymer band edge (the linear Stark effect). Requisite for the latter effect is the existence of a built-in electrical dipole moment, as well as quasi-ordering of the polymer
chains near the semiconductor/insulator interface. Additionally, we carried out microscopic IR measurements to characterize the ambipolar injection profile between electrodes.

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