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Decoupling Dopant Location from Electrical Activity in Organic Transistors by Micro-Raman Mapping

Molecular doping of conjugated polymers creates two coexisting charge-transfer species – the positive polaron on the polymer backbone and the dopant anion – whose spatial distributions are coupled but not identical [1,2]. The anion signature can diminish while backbone holes persist, so the dopant's physical location does not delimit the electrically active region. Micro-Raman mapping resolves this through three distinct fingerprints: the aromatic backbone stretch of pristine PBTTT (1410 cm^{-1}), its quinoidal counterpart from the PBTTT⁺ polaron (1445 cm^{-1}) and the F4TCNQ⁻ anion (1640 cm^{-1}).

We exploit these reporters in a metal-free homojunction OTFT whose S/D electrodes are patterned by vapor-depositing F4TCNQ through a shadow mask into the PBTTT film [3,4]. The three intensity maps across one channel (Fig. 1a) show non-coinciding boundaries: the anion (B) and polaron (C) fronts extend beyond one another, and the effective channel referenced to the pristine map (dotted lines) is narrower than the shadow mask, revealing post-deposition lateral dopant diffusion whose extent depends on film morphology and molecular orientation. Spectra at points A–D (Figure 1b) trace the evolution from the fully doped region through both junctions to the channel center. These Raman-defined boundaries are electrically meaningful: in-operando KPFM potential profiles show the applied bias dropping precisely between them, validating the Raman metric. We are now acquiring time- and condition-dependent Raman maps to extract the lateral diffusion coefficient of F4TCNQ in PBTTT – a quantitative design rule for the minimum accessible channel length in dopant-patterned, metal-free organic electronics.

References

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- [3] I. McCulloch, M. Heeney, C. Bailey et al., *Nat. Mater.*, 5 (2006) 328.
- [4] S.N. Patel, A.M. Glaudell, K.A. O'Hara, E. Lim, M.L. Chabinyc, *Sci. Adv.*, 3 (2017) e1700434.

Figures

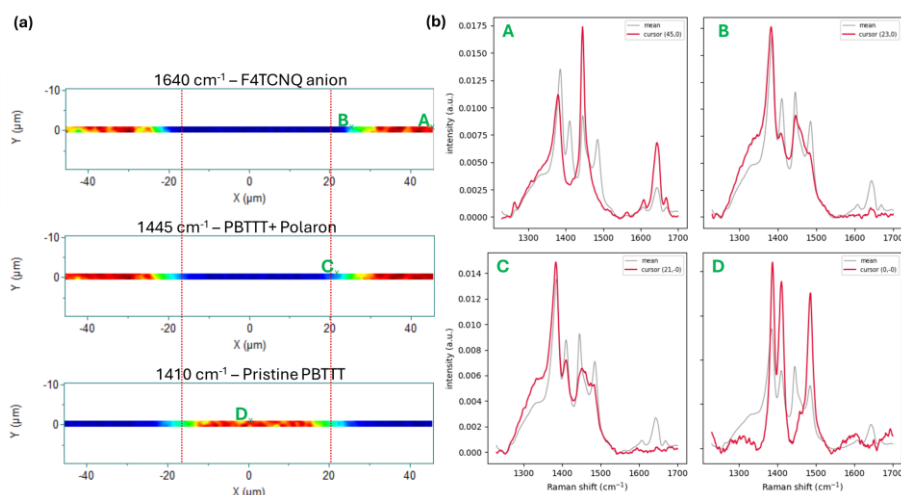


Figure 1: (a) Raman intensity maps of the three marker modes across the OTFT channel; dashed lines: effective channel from the pristine map. (b) Spectra at points A–D compared with the map average (grey)