

SUPPORTING INFORMATION

Tailoring the microstructure and charge transport in conjugated polymers by alkyl side-chain engineering

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SPACE CHARGE LIMITED DEVICES

Figure S1: Current-Voltage curves of space-charge-limited hole-only devices [structure: ITO/PEDOT:PSS/Polymer/PEDOT:PSS/Al] using different polymer layers and thicknesses (L). We plotted $I \times L$ as a function of V/L to compare the results obtained at constant electric fields. In this way, differences in current due to a field-dependent mobility can be minimized.

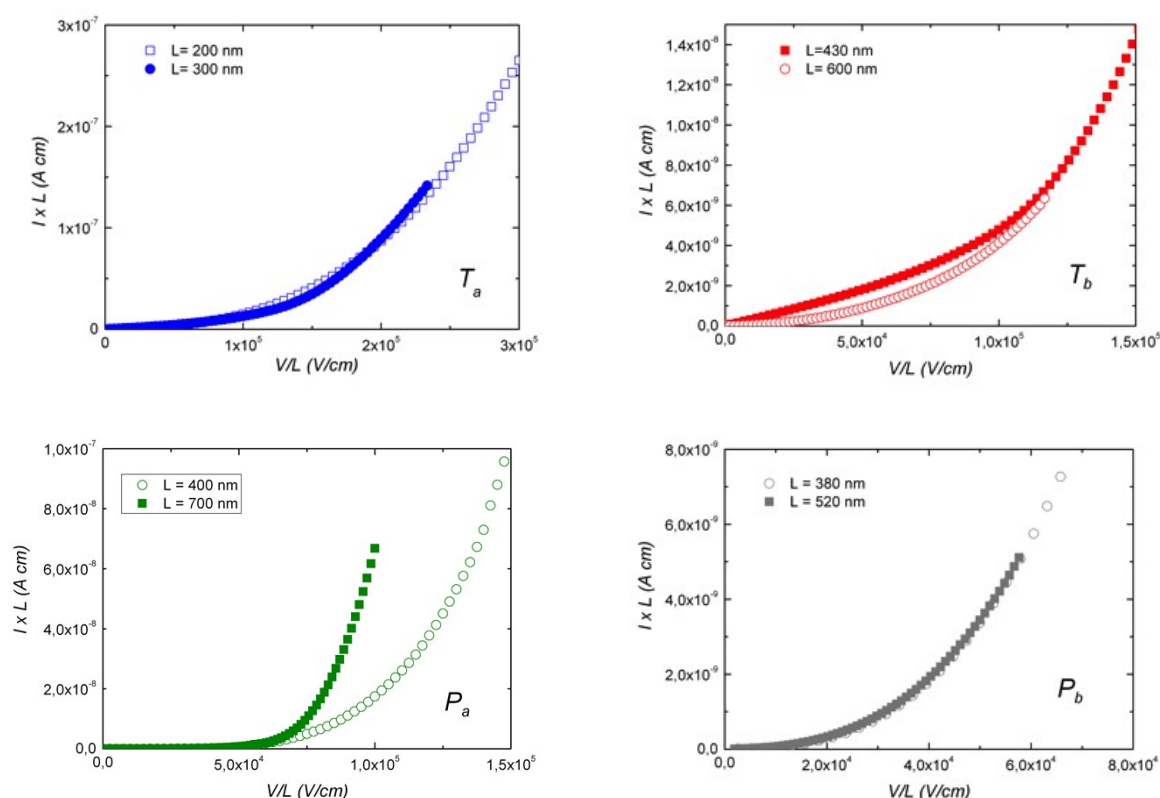
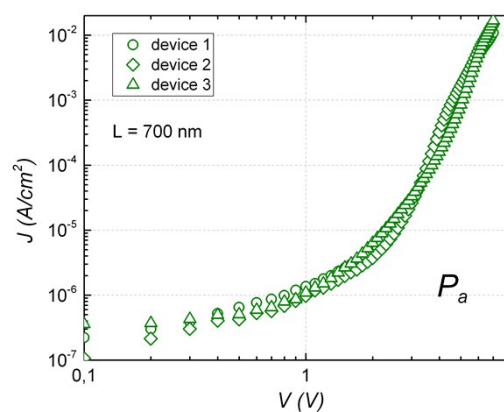
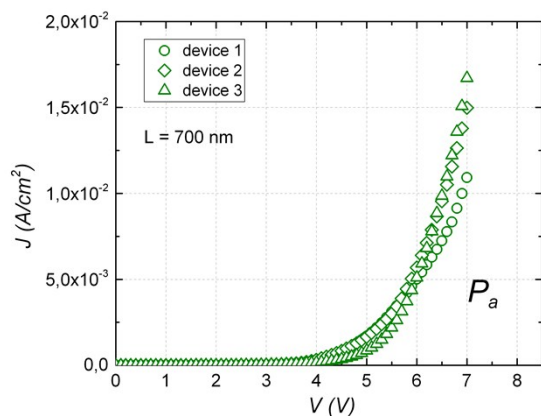


Figure S2: Current-Voltage curves (in linear and logarithmic scale), obtained on several P_a based SCLC devices with a constant film thickness. The results illustrate the significant scattering in SCLC data for this particular polymer.



ORGANIC FIELD EFFECT TRANSISTORS

Figure S3: OFET output characteristics measured at room temperature, with a 20 μ m channel length and 10 mm channel width.

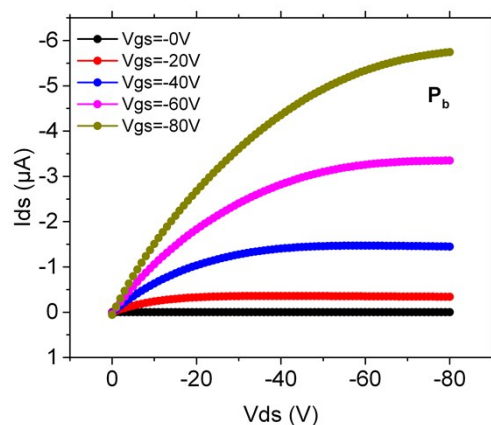
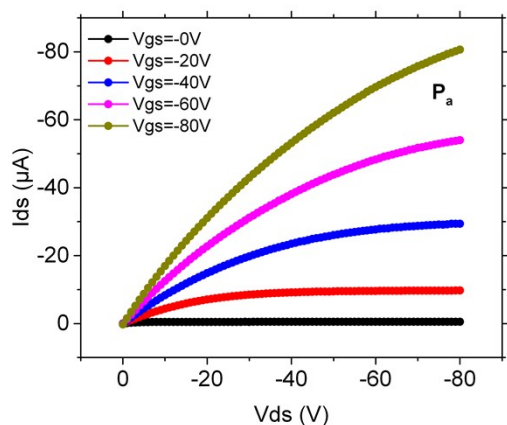
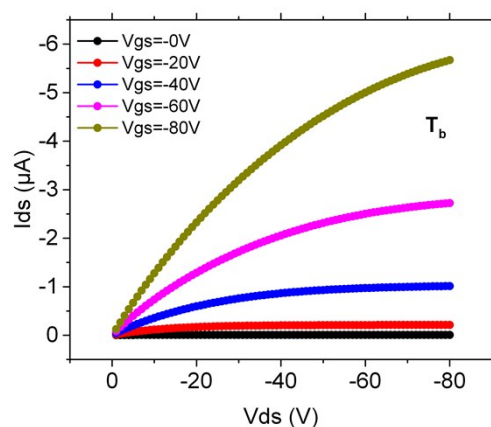
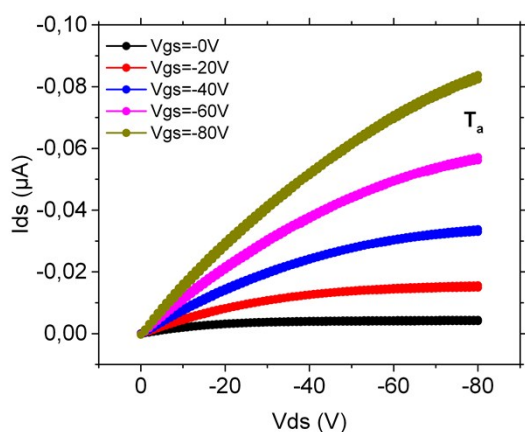
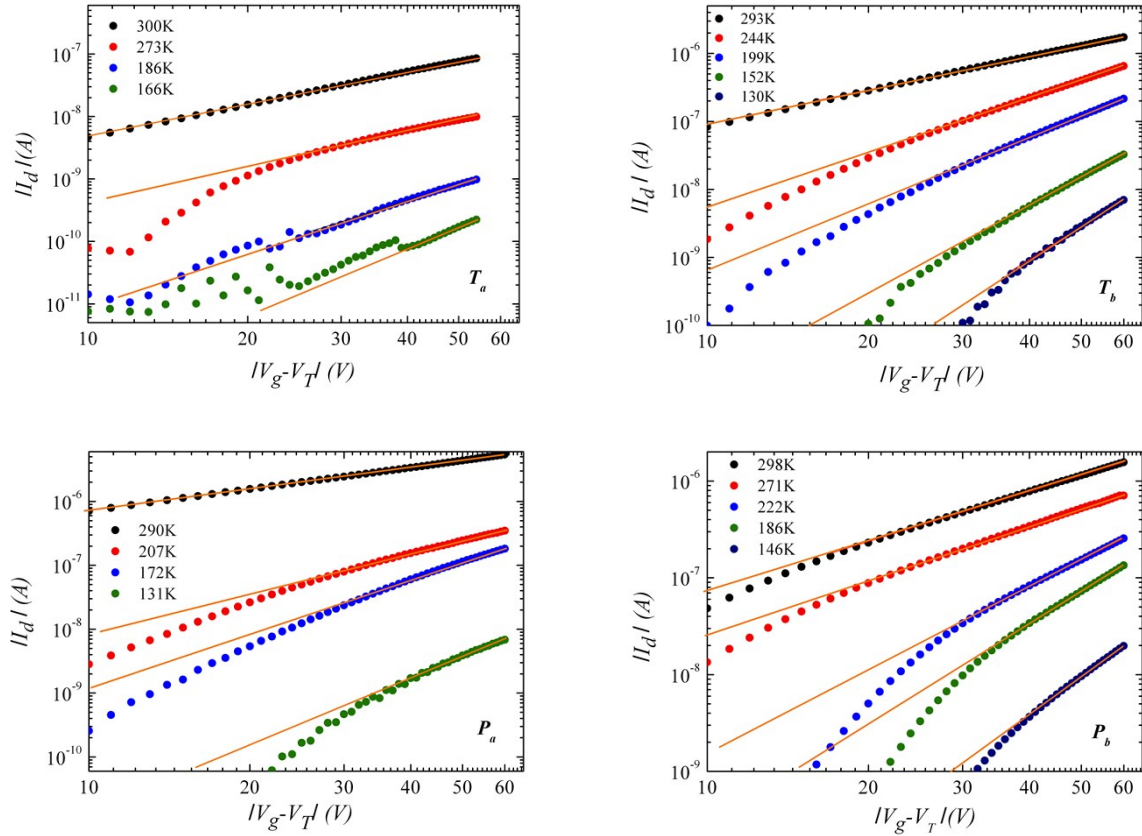


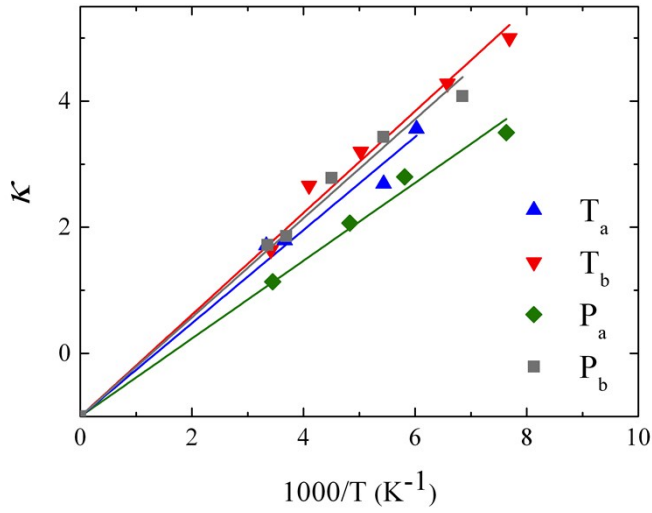
Figure S4: OFET transfer characteristics measured at different temperatures. For each polymer, the threshold voltage was assumed to be independent on temperature, and equal to -6 V for T_a , and zero for T_b , P_a and P_b , respectively. The solid lines are obtained by adjusting the experimental curves to $I_D = c \cdot (V_g - V_T)^k$, with V_T being the threshold voltage and c a constant. According to Vissenberg's transistor model,¹ the fitting parameter k is expected to

vary with temperature as $k = 2 \frac{E_o}{kT} - 1$.



¹a) M. C. J. M. Vissenberg, M. Matters, *Phys. Rev. B* **1998**, 57, 12964 b) J. J. Brondijk, W. S. C. Roelofs, S. G. J. Mathijssen, A. Shehu, T. Cramer, F. Biscarini, P. W. M. Blom, D. M. de Leeuw, *Phys. Rev. Lett.* **2012**, 109, 56601

Figure S5: The fitting parameter k , extracted from the solid lines in Figure S4, are plotted as a function of inverse temperature. The solid lines are obtained by fitting the experimental data to $k = 2\frac{E_o}{kT} - 1$. The corresponding E_o values are given in Table 1 of the main article and are used together with Equation 4 to plot the field-effect mobility as a function of charge carrier density in Figure 4.



GIWAXS

Figure S6: GIWAXS pattern on P_b OFET (a) and SCLC (b) devices

