Supporting Information


Hall Effect in Polycrystalline Organic Semiconductors: The Effect of Grain Boundaries

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SUPPLEMENTARY INFORMATION

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Figure S1. Polarized optical microscope images of spin-cast blends of C$_8$-BTBT small molecule and C$_{16}$IDT-BT conjugated polymer, doped with C$_{60}$F$_{48}$ (a) and pristine (undoped) (b). The films exhibit a clear polarization contrast inversion, revealing a polycrystalline microstructure with similar grain size, texture and morphology in the doped and undoped cases.
Figure S2. Details of four-probe FET measurements of transistors based on C_8-BTBT:C_{16}IDT-BT blends. (a, c) doped, and (b, d) undoped blends. (a, b) Four-probe voltage $V_{4P}$ as a function of the gate voltage $V_G$ measured at several source-drain voltages, $V_{SD} = 1, 3$ and 5 V (indicated). The horizontal solid lines marked “Ideal $V_{4P}$ when Ohmic” correspond to $V_{4P}$ expected in the case of a zero contact resistance (ideal Ohmic device operation). At high $V_G$, the measured $V_{4P}$ approaches 70% of the expected ideal $V_{4P}$. (c, d) Comparison of the corresponding longitudinal field-effect mobilities, $\mu_{FET}$, obtained via four-probe and two-probe measurements, marked $\mu_{4P}$ (dark grey symbols) and $\mu_{2P}$ (red symbols), respectively.
Figure S3. \textit{ac}-Hall effect measurements in OFETs based on C$_8$-BTBT:C$_{16}$IDT-BT blends, (a, b) doped, and (c, d) undoped blends. \(V_H\) is an r.m.s Hall voltage measured across the channel, when an \textit{ac} magnetic field of r.m.s magnitude \(B_{\text{rms}} = 0.2314\) T and frequency in the range 0.56 - 0.7 Hz is applied. The \textit{dc} excitation source-drain current \(I_{SD}\) and the gate voltage \(V_G\) are indicated on top of each panel. Both the in-phase (dark navy squares) and out-of-phase (yellow circles) Hall voltage components are shown. The lower part of each panel shows the corresponding four-probe voltage \(V_{4P}\). The shown two ON-OFF cycles correspond to the \textit{dc} \(I_{SD}\) being intentionally turned ON and OFF in order to determine the baseline of Hall voltage. It is evident that in each case the Hall voltage mostly consists of an in-phase component, signifying that the parasitic Faraday induction contribution is negligible in these measurements, and thus the Hall measurements are reliable.
Figure S4. Identification of molecular orientation in individual grains of polycrystalline rubrene OFETs. The known polarization dependence of the optical absorption coefficient in the orthorhombic rubrene was used for this purpose. The analyzer and polarizer of the optical microscope are fixed at 90° to each other, and the sample is rotated from $\phi = 0$ to 90° ($\phi = 0$ corresponds to the longitudinal channel direction situated horizontally). The minima in transmittance occur when the grain is oriented with its $b$-axis (the high-mobility axis) either along the polarizer ($\phi = 0$) or along the analyzer ($\phi = 90°$). Correspondingly, the maxima in transmittance occur when the grain’s $b$-axis is at $\phi = 45°$. 
Figure S5. *ac*-Hall effect measurements in the large-grain polycrystalline rubrene OFET (shown in Fig. 4 a, b of the main text). R.m.s. Hall voltage, $V_{H}$, measured between probes A$^+$ and A$^-$ (panel a) and probes B$^+$ and B$^-$ (panel b), representing regions A and B of the same channel, respectively. The in-phase (blue squares) and out-of-phase (red circles) Hall voltage signals are shown. The applied gate voltage and the source-drain current in this measurement are $V_G = -45 \text{ V}$ and $I_{SD} = 0.21 \mu\text{A}$.

Figure S6. *ac*-Hall effect measurements in the large-grain polycrystalline rubrene OFET (shown in Fig. 4 c, d of the main text). R.m.s. Hall voltage, $V_{H}$, measured between probes A$^+$ and A$^-$ (panel a) and probes B$^+$ and B$^-$ (panel b). The applied gate voltage and the source-drain current in this measurement are $V_G = -50 \text{ V}$ and $I_{SD} = 0.18 \mu\text{A}$. 
Figure S7. ac-Hall effect measurements in the large-grain polycrystalline rubrene OFET (shown in Fig. 4 e, f of the main text). R.m.s. Hall voltage, $V_H$, measured between probes $A^+$ and $A^-$ (panel a) and probes $B^+$ and $B^-$ (panel b). The applied gate voltage and the source-drain current in this measurement are $V_G = -45$ V and $I_{SD} = 0.26$ $\mu$A.
Figure S8. Verification and quantification of the effect of discrete grain boundaries on the Hall mobility in polycrystalline rubrene OFETs. Here we plot the mobility anisotropy charts (that is, $\mu_a$ vs. $\mu_b$ plots) that are constructed as follows. The Hall mobility $\mu_H$ is modeled as a linear combination of the contributions of individual grains probed by (contained between) the Hall probes, with or without the effect of GBs. When we assume that the contribution of GBs is negligible (such as in panels a and c), the Hall mobilities measured by the two pairs of Hall probes A or B (see device photos in the insets), $\mu_H^{(A)}$ or $\mu_H^{(B)}$, can be each represented by the linear combination of the mobilities of individual grains: $\mu_H = \sum_i w_{Gi} \cdot \mu_{Gi}$, where the coefficients $w_{Gi}$ are the grain widths divided by the total channel width (the relative grain widths), and $\mu_{Gi} = \mu_a \cos^2 \theta_{Gi} + \mu_b \sin^2 \theta_{Gi}$ are the mobilities of individual grains, with $\theta_{Gi}$ being the angle between the grain’s $b$-axis and the longitudinal channel direction. The thin red and blue lines are the solutions for the rubrene’s $a$-axis and $b$-axis mobilities, $\mu_a$ and $\mu_b$, obtained from the above relationship for $\mu_H$ for a given set of measured $\mu_H$, $w_{Gi}$ and grain orientation angles $\theta_{Gi}$. Since two Hall measurements are performed in each FET (by the two pairs of Hall probes, A and B), the obtained values for $\mu_a$ and $\mu_b$ should agree with each other, resulting in an intercept of the red and blue lines on the $\mu_a$ vs. $\mu_b$ chart. This intercept would be the only
solution for $\mu_a$ and $\mu_b$ that satisfies both $\mu_H^{(A)}$ and $\mu_H^{(B)}$ measurements. If the values of $\mu_a$ and $\mu_b$ at the intercept are reasonable and consistent with the known $a$-axis and $b$-axis mobilities of rubrene, then the model given by the above equation can be considered valid. It can be seen that the intercept in panel a corresponds to an unreasonably high anisotropy ratio $\mu_b/\mu_a \sim 10$, inconsistent with the known mobility anisotropy in rubrene ($\mu_b/\mu_a \approx 2 - 3$). In panel c, no intercept at all is reached within the reasonable range of mobilities. This suggests that no reasonable solutions can be found with the assumption of a negligible GB effect. In a model that does account for a GB effect via capacitively charged GBs (shown in panels b and d), the Hall mobility is reduced by each GB present in the channel: $\mu_H = \sum_i w_{Gi} \cdot \mu_{Gi} - \sum_i \mu_{GB} \sin \Delta\theta_{i,i+1}$, where $\Delta\theta_{i,i+1}$ is the GB angle, and $\mu_{GB}$ is an amplitude. The solid red and blue lines in panels b and d are the solution plots of this equation for $\mu_a$ and $\mu_b$ with a varied $\mu_{GB}$ parameter (indicated on top of the panels). The intercepts of these red and blue lines represent the final solution for $\mu_a$ and $\mu_b$, which should lie in the region of correct mobility anisotropy known for rubrene, $\mu_b/\mu_a = 2 - 3$ (highlighted in green). In this case, after taking a GB effect into account, reasonable solutions (the intercepts) exist for a range of amplitudes $\mu_{GB}$.

Figure S9. FET measurements of the single-crystal rubrene OFET shown in Fig. 5 of the main text. The ratio of the channel length to width is $L/W = 4.1$, and the gate-channel capacitance is $C_i = 1.85 \text{nF}\cdot\text{cm}^{-2}$. (a) Linear-regime transfer characteristics, $I_{SD}(V_G)$, recorded at several values of $V_{SD}$ (indicated). (b) Field-effect mobility, $\mu_{FET}$, extracted from the four-probe (dark grey solid squares) and the two-probe (red open circles) measurements of the device. The matching values of these mobilities signify a very small relative contact resistance in this OFET.
**Figure S10.** *ac*-Hall effect measurements in the single-crystal rubrene OFET with an “artificial grain boundary” (see Fig. 5 of the main text). R.m.s. Hall voltage, $V_H$, measured at various locations in the channel between the sets of Hall probes labeled P (panel a), D1 (panel b) and D2 (panel c). The gate voltage and the source-drain current in this measurement are $V_G = -50$ V and $I_{SD} = 0.32$ µA. It is clear that the Hall voltage mostly consists of an in-phase component, which signifies a reliable Hall effect measurement.