Hall effect in polycrystalline organic semiconductors: the effect of grain boundaries.

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ABSTRACT

Highly crystalline thin films of organic semiconductors are important for applications in high-performance organic optoelectronics. Here we elucidate the effect of grain boundaries on the Hall effect and charge transport properties of organic transistors based on two exemplary benchmark systems: (1) solution processed blends of 2,7-diocetyl[1]benzothieno[3,2-b][1]benzothiophene (C₈-BTBT) small molecules and indacenodithiophene-benzothiadiazole (C₁₆-IDT-BT) conjugated polymer, and (2) large-area vacuum evaporated polycrystalline thin films of rubrene (C₄₂H₂₈). We discover that, despite
the high field-effect mobilities of up to 6 cm$^2$V$^{-1}$s$^{-1}$ and the evidence of a delocalized band-like charge transport, the Hall effect in polycrystalline organic transistors is systematically and significantly underdeveloped, with the carrier coherence factor $\alpha < 1$ (that is, yields an underestimated Hall mobility and an overestimated carrier density). We describe a model based on capacitively charged grain boundaries that explains this unusual behavior. This work significantly advances our understanding of magneto-transport properties of organic semiconductor thin films.

Introduction

Organic semiconductors are suitable for niche applications in flexible electronics, where they have several advantages over traditional inorganic electronic materials. In particular, solution processing of blends of small molecules and polymers can take advantage of the beneficial properties of individual components combined in a single system: a strong propensity of certain small molecules for molecular self-assembly and a superior film-forming ability of polymers$^1$. In organic semiconductor blends, a “vertical” phase separation that usually takes place right after the film deposition is very important$^{1-4}$. It typically leads to a polycrystalline small-molecule layer segregated on top of the film, with the grain boundaries (GB) filled with the polymer, which has been pointed out as the main factor underpinning the improved performance of organic field-effect transistors (OFETs) based on blends, compared to similar devices using only the small molecules. For instance, Hunter et al. recently suggested that intercalation of the conjugated polymer into GB regions likely leads to a better grain connectivity and more efficient inter-grain charge transport.$^2$

We note that various small-molecule/polymer blends were observed to phase separate, leading to such a polycrystalline top layer$^{[4,5]}$, which makes the results reported here generally applicable. For simplicity, below we will call this kind of transistors “blended OFETs”.
Given the recent reports of substantial field-effect mobilities, $\mu_{\text{FET}} > 5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and yet an activated temperature dependence of mobility ($d\mu/dT > 0$) observed in some of the blended OFETs, careful studies of the intrinsic (that is, not dominated by trapping) charge transport properties and understanding the relationship between the microstructure and mobility in blends and other polycrystalline OFETs are necessary. Such studies can be performed via Hall effect measurements, because an observation of a classic Hall effect, for instance, would indicate the presence of band-like, mobile charge carriers that are (at least partially) delocalized in the transistor’s channel.

In this work, we obtained conclusive evidence for coherent charge carrier transport in binary and ternary organic semiconductor blends by performing Hall effect measurements and developing a model that reconciles the longitudinal field-effect and Hall mobilities in this system. The effect of polycrystalline morphology and grain boundaries on the Hall mobility in polycrystalline organic films turns out to be substantial. The binary blends used in our study are composed of 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C$_8$-BTBT) small molecules and indacenodithiophene-benzothiadiazole (C$_{16}$IDT-BT) conjugated polymer. In ternary blends, a C$_{60}$F$_{48}$ molecular dopant is added in small quantities, which improves the field-effect mobility of the blended OFETs. In order to investigate the intrinsic charge carrier mobility in these devices, we used two experimental techniques applied concurrently: longitudinal charge transport measurements in four-probe FETs, and ac-Hall effect measurements. To the best of our knowledge, this is the first observation of a Hall effect in organic semiconductor blends, revealing a band-like transport mechanism and a relatively high intrinsic charge carrier mobility in these systems.

The central novel finding of our work is an observation that the Hall effect in polycrystalline OFETs is systematically “underdeveloped”, even though the longitudinal mobility is high. The Hall effect is called underdeveloped, when the Hall mobility, $\mu_{\text{Hall}}$, is
substantially smaller than the longitudinal field-effect mobility, $\mu_{\text{FET}}$, ($\mu_{\text{Hall}} < \mu_{\text{FET}}$), and respectively the Hall carrier density, $n_{\text{Hall}}$, is systematically greater than the capacitively defined (total) carrier density, $n_{\text{FET}}$, induced in the accumulation channel ($n_{\text{Hall}} > n_{\text{FET}}$). To understand the mechanism of this effect, besides blends, we have also investigated high-quality polycrystalline rubrene thin films with a large grain size previously developed by Fusella et al. These films can be viewed as an ideal polycrystalline organic semiconductor due to the very large grain size of up to $\sim$ 1 mm and crystallographically well-defined grain boundaries, with a highly compact film morphology extended over macroscopically large areas (up to 1 cm$^2$). In OFETs, such rubrene films ensure just a few discrete GBs in the channel and result in relatively high field-effect mobilities, $\mu_{\text{FET}} = 1 - 4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. As the result of our study, we conclude that GBs are the main cause of an underdeveloped Hall effect observed in polycrystalline OFETs. This study emphasizes the importance of microstructure of polycrystalline organic films in defining their magneto-transport properties.

**Results and discussion**

**Figure 1a** shows the chemical structures of the constituents of the blends studied here: small molecule C$_8$-BTBT, conjugated polymer C$_{16}$IDT-BT, and the molecular dopant C$_{60}$F$_{48}$. Deposition of the blend was done according to a recently published protocol, in which annealing of spin-coated films leads to a vertical phase separation, with C$_8$-BTBT crystallized on top of the film. Polarized optical microscopy reveals a close-packed domain structure, with a clear contrast inversion on rotation of polarizers (**Fig. 1b**), signifying a high degree of crystallinity within the grains. It has been previously reported that grains mostly consist of small molecules, while the narrow regions of grain boundaries consist of a mixture of small molecules and polymer, as schematically illustrated in **Fig. 1c**. We find that adding a relatively small amount of C$_{60}$F$_{48}$ dopant (here, up to 1 molar percentage) does not affect the
film’s texture, as can be clearly seen from similar morphologies of the binary (undoped) and ternary (doped) blends (Fig. S1), but noticeably improves the charge transport. In this work, the charge carrier transport at the top surface of these films was explored, because top-gate OFETs were fabricated (Fig. 1d). This allowed investigating the correlation between the film’s microstructure and its transport characteristics. A gate insulator consisting of two layers (900 nm-thick Cytop and 1.33 µm-thick parylene-N) with the total capacitance $C_i = 0.95 \text{nF} \cdot \text{cm}^{-2}$, was used in our OFETs (for fabrication details see Methods).

Figure 1e schematically shows the electric circuitry used for measurements of the field-effect and Hall mobilities. All measurements were performed via a four-probe technique, in which a four-probe voltage, $V_{4p}$, between the voltage probes along the accumulation channel and the source-drain current, $I_{SD}$, are simultaneously measured as a function of the gate voltage, $V_G$, at fixed source-drain voltages, $V_{SD}$, in the linear regime of the transistor’s operation.\textsuperscript{11, 15-17, 18, 19} This allows evaluating the contact-resistance corrected (four-probe) longitudinal channel conductivity, $\sigma_{4p} \equiv (D/W) \cdot \left( I_{SD}/V_{4p} \right) = en_{FET}\mu_{FET}$, where $D$ is the center-to-center distance between the voltage probes along the channel, $W$ is the channel width, $e$ is elementary charge, $n_{FET}$ and $\mu_{FET}$ are the capacitively defined mobile carrier density and longitudinal mobility in the OFET’s channel. Please note that $\sigma_{4p}$ is a sheet conductivity (per square) in Siemens (1 S = 1 Ω$^{-1}$), while $n_{FET}$ is a 2D carrier density in cm$^{-2}$, and $\mu_{FET}$ is in cm$^2$V$^{-1}$s$^{-1}$. This leads to the following expressions for the carrier density and the contact-corrected longitudinal carrier mobility in the channel:

$$n_{FET} \equiv e^{-1}C_i(V_G - V_{th}) \quad \text{and} \quad \mu_{FET} \equiv \frac{D}{W} \cdot \frac{1}{C_i} \cdot \frac{\partial (I_{SD}/V_{4p})}{\partial V_G},$$

(1)

where $C_i$ is the gate-channel capacitance per unit area (in F/cm$^2$), and $V_{th}$ is the threshold voltage.\textsuperscript{11} Even though we find that the contact resistance in the OFETs studied here is not high, the four-probe technique was still used to precisely extract both $\mu_{FET}$ and $\mu_{Hall}$. 

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The Hall mobility $\mu_{\text{Hall}}$ was evaluated by measuring a Hall voltage, $V_{\text{Hall}}$, across the channel (between the Hall probes), when a magnetic field, $B$, is applied perpendicular to the channel carrying a longitudinal source-drain current $I_{SD}$. The Hall measurements were performed via a high-resolution $ac$-Hall technique that has been recently shown to be very effective in evaluating the intrinsic charge transport properties of low-$\mu$ systems such as OFETs.$^{12,13}$ In this method, we use a low-frequency ($< 1$ Hz) small $ac$ magnetic field (r.m.s. $B = 0.23$ T) and a phase-sensitive detection of the corresponding $ac$-Hall voltage by a lock-in amplifier. This $ac$-Hall methodology drastically enhances the signal-to-noise ratio in Hall effect measurements and eliminates the need for very high magnetic fields otherwise necessary for Hall measurements of low-$\mu$ systems. The Hall carrier density $n_{\text{Hall}}$ and the Hall mobility $\mu_{\text{Hall}}$ were determined as:

$$n_{\text{Hall}} \equiv e^{-1} \cdot B \cdot \frac{I_{SD}}{V_{\text{Hall}}} \quad \text{and} \quad \mu_{\text{Hall}} \equiv \frac{\sigma_{ap}}{e n_{\text{Hall}}} = \frac{1}{B} \cdot \frac{D}{W} \cdot \frac{V_{\text{Hall}}}{V_{4p}}$$

(2)

where $V_{\text{Hall}}$ and $B$ are the r.m.s. values of the $ac$-Hall voltage and $ac$ magnetic field, and $I_{SD}$ and $V_{4p}$ are $dc$ values of the source-drain current and four-probe voltage, respectively.$^{12,13}$ Please note that the Hall carrier density above is defined as the number of carriers per unit area ($n_{\text{Hall}}$ is in cm$^{-2}$), while $\mu_{\text{Hall}}$ is as always in cm$^2$V$^{-1}$s$^{-1}$. The first expression above, relating the Hall carrier density with the magnetic field, the source-drain current and the Hall voltage, is obtained by requiring that in a steady state the Lorentz force and the transverse electric force acting on the charge carrier balance each other: $F_L \equiv e \mu_x E_x B = e E_y$, where the subscripts $x$ and $y$ denote the longitudinal and the transverse components in the plane of the accumulation channel, respectively (Fig. 1e). For instance, $\mu_x$ represents the longitudinal FET carrier mobility given by Eq. 1. Thus, the Hall voltage is found as

$$V_{\text{Hall}} \equiv \int_0^W E_x \, dy = \int_0^W \mu_x E_x B \, dy = \frac{B}{e n_{\text{Hall}}} \cdot \int_0^W j_x \, dy = e^{-1} \cdot B \cdot \left(\frac{I_{SD}}{n_{\text{Hall}}}\right)$$

leading to Eq. 2 above.
Figure 2 shows FET and Hall measurements of transistors based on doped and pristine (undoped) blends. All our FETs exhibited linear transfer characteristics, $I_{SD}(V_G)$, with negligible hysteresis (Fig. 2 a, b), indicative of a $V_G$-independent $\mu_{FET}$ and a relatively low concentration of traps in the accumulation channel. We find that at $V_G < -20$ V, approximately 30% of the applied $V_{SD}$ is dropped on the contacts, which results in the contact-corrected four-probe mobility being approximately 1.43 times greater than the corresponding two-probe mobility (Fig. S2). The four-probe mobility of the doped devices is typically in the range $\mu_{FET} = 5 - 6$ cm$^2$V$^{-1}$s$^{-1}$, while the undoped devices show $\mu_{FET} = 2.5 - 3$ cm$^2$V$^{-1}$s$^{-1}$ (Fig. 2 e, f). The reliability factor, $r$, that evaluates the effectiveness of the quoted mobility values in delivering the respective channel conductivities is $r_{lin} = 90\%$ for the doped and 66\% for the undoped devices (for definition of parameter $r$ see Ref. [20]). The main reason for $r < 100\%$ is a non-zero threshold voltage.

One of the central results of this work is a clear observation of a Hall effect in OFETs based on blends, signifying the presence of delocalized charge carriers and coherent band-like transport in these transistors. As shown in Supplementary Fig. S3, the Hall voltage in our OFETs mostly consists of an in-phase component, $V_{H,ip}$, while the out-of-phase component, $V_{H,op}$, is much smaller. Measurements of both the in-phase and out-of-phase components of ac-Hall voltage allow to account for the undesired contribution from the Faraday induction, which can sometimes be present in these measurements, and thus to evaluate the Hall effect correctly. The resultant FET and Hall carrier densities, $n_{FET}$ and $n_{Hall}$, as well as mobilities, $\mu_{FET}$ and $\mu_{Hall}$, of the doped and undoped blends calculated according to Eqs. 1 and 2 are compared in Fig. 2 c, d and Fig. 2 e, f. The first important observation is that doping of the blends with C$_{60}$F$_{48}$ improves both $\mu_{FET}$ and $\mu_{Hall}$ and reduces the OFETs’ threshold voltage. The second important observation is that Hall mobility is noticeably smaller than the longitudinal (FET) mobility, with the so-called charge carrier
coherence factor, $\alpha \equiv \mu_{\text{Hall}}/\mu_{\text{FET}} \equiv n_{\text{FET}}/n_{\text{Hall}}$, in the range 0.33 - 0.45. We stress that such a significant disparity between the Hall and FET mobilities was observed in all blended OFETs studied here, including those with a relatively high longitudinal carrier mobility of $\mu_{\text{FET}} > 5$ cm$^2$V$^{-1}$s$^{-1}$, and it is thus a systematic behavior. Longitudinal mobilities greater than 5 cm$^2$V$^{-1}$s$^{-1}$ are typical for highly ordered crystalline organic semiconductors with a fully coherent band-like charge transport, as, for instance, rubrene ($C_{42}H_{28}$)$^6,^7,^13$, dinaphto-thienothiophene ($C_{22}H_{12}S_2$)$^{21}$ and a few others (see, e.g., Ref. $^{[22]}$). The carrier coherence factor in most high-mobility organic semiconductors is typically very close to unity ($\alpha \approx 1$), which is in sharp contrast with the underdeveloped Hall effect ($\mu_{\text{Hall}} < \mu_{\text{FET}}, n_{\text{Hall}} > n_{\text{FET}}$) observed here in the high-mobility organic blends. Contrary to high-mobility OFETs, most organic transistors with low longitudinal mobilities ($\mu_{\text{FET}} < 1$ cm$^2$V$^{-1}$s$^{-1}$) exhibit $\alpha$ smaller than unity (for instance, $\alpha \sim 0.6$ in pentacene$^8$ and $\sim 0.5$ in TIPS-pentacene$^{23}$). According to the comprehensive model of underdeveloped Hall effect described by Yi et al.,$^{13}$ $\alpha < 1$ is the result of a coexistence of delocalized band-like and hopping carriers that contribute oppositely to the Hall voltage presented across the accumulation channel.

The surprising new observation made in this work is that the blended OFETs exhibit the charge carrier coherence factor noticeably smaller than unity ($\alpha \sim 0.33$), even though their longitudinal field-effect mobility is rather high ($\mu_{\text{FET}} \sim 5$ - 6 cm$^2$V$^{-1}$s$^{-1}$). In addition, it is clear that $\alpha$ is not affected by doping (Fig. 2 e and f). This behavior contradicts our current understanding of the Hall effect in organic semiconductors.$^{13}$ In the current model, hopping and band carriers that coexist in the accumulation channel of OFETs compete in formation of the Hall voltage. While the band carriers experience both the Lorentz force $F_L = e\mu_{\text{FET}}B(V_{4p}/D)$ and the transverse electric force $eE_y$, balancing each other in the transverse direction (along $y$-axis), the hopping carriers only experience the electrostatic force $eE_y$. This leads to a reduced Hall voltage in comparison with the case of only band-like carriers
present in the channel,\textsuperscript{13} with the corresponding carrier coherence factor $\alpha = \mu_{\text{Hall}}/\mu_{\text{FET}} = n_{\text{FET}}/n_{\text{Hall}} < 1$, meaning that Hall effect measurements would result in an underestimated Hall mobility ($\mu_{\text{Hall}} < \mu_{\text{FET}}$) and an overestimated Hall carrier density ($n_{\text{Hall}} > n_{\text{FET}}$). The outcome of this competition in each particular case ultimately depends on the relative populations of band and hopping carriers in the channel, as well as on their effective mobilities, $\mu_{\text{band}}$ and $\mu_{\text{hopping}}$.\textsuperscript{13} The model leads to a general conclusion that for the carrier coherence factor $\alpha$ to be noticeably smaller than unity (an underdeveloped Hall effect), it is necessary (but not sufficient) that the longitudinal mobility of an OFET be low ($\mu_{\text{FET}} \leq 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). On the contrary, when $\mu_{\text{FET}} \geq 5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, the carrier coherence factor must be very close to unity (a fully developed Hall effect should be observed).\textsuperscript{13} According to this model, an organic semiconductor with $\alpha$ as low as 0.33 cannot have the longitudinal mobility $\mu_{\text{FET}} > 5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. We should keep in mind, however, that the model by Yi \textit{et al.} assumes a homogeneous accumulation channel (that is, a channel with a uniform distribution of traps and charges over the entire channel)\textsuperscript{13}. This might not be the case here, in blended OFETs, since the active layer is polycrystalline. Thus, possible effects of grain orientation and grain boundaries must be considered while thinking about the origin of an underdeveloped Hall effect in this system.

The phenomena observed in our work can be explained by considering the effect of capacitively charged grain boundaries, as discussed below. \textbf{Figure 3a} schematically depicts a polycrystalline OFET channel, with several crystalline grains of different crystallographic orientation (shown in the shades of blue) located between the Hall probes (labeled $V_{\text{H}}^+$ and $V_{\text{H}}^-$). We assume for now that each grain is a highly-ordered crystalline semiconductor characterized by a fully band-like coherent charge transport with a high $\mu$ (that is, within each grain, all the charges are delocalized mobile holes, and the density of hopping carriers is negligible). At zero magnetic field ($B = 0$), a uniform accumulation channel with a constant
density $n_0 = e^{-1}C_i(V_G - V_{th})$ of mobile holes is formed in the channel, when $V_G < V_{th}$ is applied (assuming the graduate channel approximation is applicable), which corresponds to the source-drain current $I_{SD} = e n_0 \mu_{FET}(W/L)V_{SD}$ (directed up in Fig. 3a). When a magnetic field is applied (directed into the page in Fig. 3a), each grain acts as a source of transverse electro-motive force (a Hall e.m.f.), because holes within each grain experience a Lorentz force directed to the left that causes a slight redistribution of the hole density in the transverse direction (along the $y$ axis). The resultant excess of holes near the left edge of each grain and the lack of holes near the right edge of the grains are shown in Fig. 3a with “+” and “-” signs, respectively. We emphasize that the minus sign does not represent an electron, but merely indicates that the concentration of holes in this location is lower than the unperturbed background hole density $n_0$. Such a redistribution of the hole density in the transverse direction results in a transverse (Hall) electric field $E_y$ (sometimes approximated as $E_y = V_{Hall}/W$) that balances the Lorentz force $F_L = e \mu_x E_{SD} B$ within each grain, thus leading to a steady state with zero transverse current density $j_y = 0$. This balance leads to the following expression for the transverse electric field within each crystalline grain:

$$E_y^{(i)} = \mu_x^{(i)} E_{SD} B$$

(3)

Here, index $i$ corresponds to a particular grain, $\mu_x^{(i)}$ is the longitudinal mobility in that grain (for transport in the vertical direction in Fig. 3a), and $E_{SD}$ is the source-drain electric field along the channel (along $x$-axis): $E_{SD} = V_{4p}/D$ (or $V_{SD}/L$, if the contact resistance is negligible). This equation immediately suggests that grain boundaries in polycrystalline samples under Hall measurement conditions should be mildly charged. Since the orientation of each grain and the corresponding longitudinal carrier mobilities $\mu_x^{(i)}$ are different (assuming an anisotropic semiconductor), the Lorentz forces generated within each grain should also be different, which would require different transverse electric fields in each grain to balance $F_L$, as indeed suggested by Eq. (3). This would be impossible to realize in
the situation, when only the edges of the accumulation channel are charged, as in Hall effect measurements of homogeneous conductors, because the resultant transverse electric field in the channel would be nearly uniform (that is, the same in each grain) or at least be a smooth function of \( y \).

By assuming charged GBs, it is possible to balance the Lorentz force and the transverse electric force in grains of different orientations. However, as we show below, taking into account different grain orientations still cannot explain the systematically reduced Hall voltage (and \( \alpha < 1 \)) observed here in polycrystalline OFETs. Indeed, considering the set of grains between the Hall probes (Fig. 3a), each having an effective width \( W^{(i)} \) and a transverse electric field \( E_y^{(i)} \) (Eq. 3), the net Hall voltage can be expressed as the sum of the products \( E_y^{(i)} W^{(i)} \): \( V_{Hall} \equiv \mu_{Hall} W B E_{SD} \equiv \sum E_y^{(i)} W^{(i)} = \sum \mu_x^{(i)} W^{(i)} B E_{SD} \), leading to the following expression for the average experimental Hall mobility \( \mu_{Hall} \) expected in such a polycrystalline sample:

\[
\mu_{Hall} = \mu_x^{(1)} \cdot \frac{W^{(1)}}{W} + \mu_x^{(2)} \cdot \frac{W^{(2)}}{W} + \ldots
\]  

(Eq. 4)

It is easy to show that the longitudinal mobility \( \mu_{FET} \) of a polycrystalline channel would also be represented by a similar expression. Indeed, the net source-drain current flowing through the grains shown in the shades of blue in Fig. 3a can be calculated as the sum of the products \( j_x^{(i)} W^{(i)} \): \( I_{SD} \equiv en\mu_{FET} W E_{SD} \equiv \sum j_x^{(i)} W^{(i)} = \sum en\mu_x^{(i)} W^{(i)} E_{SD} \), leading to the following expression for the average longitudinal FET mobility of a polycrystalline sample:

\[
\mu_{FET} = \mu_x^{(1)} \cdot \frac{W^{(1)}}{W} + \mu_x^{(2)} \cdot \frac{W^{(2)}}{W} + \ldots
\]  

(Eq. 5)

Equations 4 and 5 show that \( \mu_{Hall} \) and \( \mu_{FET} \) of a polycrystalline channel are simply given by the weighted average of the longitudinal mobilities of grains, with the weights given by the fraction of the channel width occupied by each grain. When the number of grains is large,
both $\mu_{\text{FET}}$ and $\mu_{\text{Hall}}$ will be simply equal to the orientationally-averaged longitudinal carrier mobility in the grains, $\langle \mu_x \rangle$. This consideration shows that taking into account different grain orientations cannot explain the systematically underdeveloped Hall effect ($\mu_{\text{Hall}} < \mu_{\text{FET}}$) observed in this work, even if the material were strongly anisotropic.

It is reasonable to assume that under Hall measurement conditions, when a Hall e.m.f. is generated within each grain, the excess (or lack) of holes created on the left (right) side of the grain cannot easily recombine with the corresponding lack (or excess) of holes created on the adjacent sides of the neighboring grains (Fig. 3a). Indeed, GBs may not be completely “transparent” for the charge flow, thus representing a barrier for these charges to equilibrate. This can lead to GBs being capacitively charged, that is, having an excess of holes on one side and a lack of them on the other (which is again indicated in Fig. 3a with “+” and “−” signs along the GBs). The corresponding distribution of charge $q(y)$ in the transverse direction (along the horizontal line connecting the Hall probes) is schematically shown in Fig. 3b. The $q = 0$ corresponds to the unperturbed ($B = 0$) background carrier density $n_0$ set by $V_G$. It is easy to see that in such a system the distribution of transverse electric field $E_y$ will have dips at grain boundaries, but will be otherwise nearly constant within the grains, as schematically shown with a blue solid line in Fig. 3c. Here, the regions of constant field correspond to $E_y^{(i)}$ within individual grains given by Eq. 3, and the green dashed line represents the field in the case of a homogeneous channel without GBs. It is clear that integrating such a field profile along $y$ would result in offsets in the potential occurring at each GB. The distribution of the potential $\varphi(y)$ along the horizontal line connecting the Hall probes is shown in Fig. 3d with a blue solid line (the potential gained across a homogeneous channel is shown with a green dashed line). One can see that having capacitively charged GBs results in a smaller net Hall voltage presented across the channel. This effect becomes clearer by drawing an analogy with a charged parallel-plate capacitor, in which another
thinner capacitor is inserted: if the charge polarity of the inner capacitor is opposite, the net voltage on the outer capacitor will be reduced. A more rigorous solution can be obtained by solving a Poisson equation relating the electric field or potential, $E_y$ or $\varphi_y$, with a given spatial distribution of charge $q(y)$: $\frac{\partial^2 \varphi_y}{\partial y^2} = -\frac{\partial E_y}{\partial y} = -q(y)/\varepsilon$, where $\varepsilon$ is the dielectric permittivity (given the symmetry of FET geometry, we can consider only the 1D case). With capacitively charged grain boundaries, solving the Poisson equation with the type of charge distribution shown in Fig. 3 b gives the profiles for $E_y$ and $\varphi_y$ qualitatively similar to those sketched in Fig. 3 c, d. This model suggests that a less developed Hall effect is expected in the case of more strongly charged GBs, which should occur when the barrier height for inter-grain charge flow is higher, or when the disorder at GBs is greater. The barrier height and disorder are expected to be greater for large-angle grain boundaries\textsuperscript{24,27}. The observation that the carrier coherence factor $\alpha$ is independent of doping and the overall mobility level indirectly supports this model. Indeed, since in this case $\alpha$ is governed not by molecular disorder and the degree of carrier delocalization, but simply by the polycrystalline morphology of the film, there is no reason for $\alpha$ to be different, because the morphology of our films is not affected by the small amount of doping used here (see Fig. S1).

To further test our model, we have employed another type of organic semiconductor, large-area polycrystalline rubrene thin films, recently developed by Fusella et al.\textsuperscript{14}. These polycrystalline thin films feature single-crystal grains of rubrene with a very large grain size of up to $\sim$1 mm, with the surface of the grains corresponding to the $(a,b)$ facet of orthorhombic rubrene, separated by crystallographically well-defined grain boundaries. Such films allow for a few or even a single GB in the channel of OFETs, with known crystallographic orientation of each grain. Figure 4 a, c, e shows polarized optical microscopy images of these films, revealing their polycrystalline microstructure. In
particular, a homogeneous birefringence within the grains suggests that each grain is a single crystalline domain, which has been recently confirmed by electron backscattering diffraction.\textsuperscript{14} We therefore expect that the intra-grain charge transport in these samples should be close to fully coherent\textsuperscript{6-8, 13, 20}. We used the well-known angular dependence of optical transmission of linearly polarized light by crystalline rubrene to determine the molecular orientation in each individual grain of these samples (Fig. S4)\textsuperscript{14, 28}, indicated in Fig. 4 by the little blue rectangles elongated along the high-mobility \textit{b}-axis of rubrene (lattice constant 7 Å).\textsuperscript{29} In addition, the molecular orientation within each grain, as well as GB angles are schematically depicted in the models next to the microphotographs in Fig. 4 a, c, e. In these devices, two pairs of Hall probes, labeled A and B, were deposited in addition to the source and drain contacts. These can be used to probe Hall effect at different locations along the channel of the same OFET, where the grain orientation and grain boundaries are different. In the first device (Fig. 4a), each pair, A or B, probes two grains and one grain boundary between them. However, the type of GB is different: G1/G2 probed by pair A is a low-angle (7°) grain boundary, while G3/G4 probed by pair B is a high-angle (77°) grain boundary. In the second device (Fig. 4c), pair A probes a single grain (G1), while pair B probes three grains (G2, G3 and G4) and two grain boundaries between them. The whole channel of the third device (Fig. 4e) consists of just two grains. The Hall probes A measure a single grain (without any GBs), in which the longitudinal transport occurs along the low-\(\mu\) axis (\textit{a}-axis) of rubrene, while the region probed by pair B contains essentially the same grain, but with an inclusion of another grain oriented with its high-\(\mu\) axis (\textit{b}-axis) along the channel.

The corresponding FET and Hall mobilities measured in these polycrystalline rubrene OFETs are shown in Figs. 4 b, d, f, revealing clear differences in the detected \(\mu_{\text{Hall}}\), depending on the grain orientations and the type of grain boundaries between the Hall probes. The raw data for ac-Hall effect measurements can be found in Figs. S5 - S7. It is worth
noting here that the main reason for relatively low $\mu$ in devices in Fig. 4 b and f is the “gauge effect” that occurred when the contacts were thermally evaporated on an unprotected surface of the organic semiconductor in high vacuum (as opposed to the device in Fig. 4d, where the contacts were hand painted with graphite paint$^{30}$). The mobility $\mu_{\text{Hall}}^{(B)}$ obtained by probes B that measure higher angle GBs or a greater number of GBs are typically lower than the longitudinal mobility $\mu_{\text{FET}}$ (Fig. 4 b, d), except for the third device (Fig. 4f). This is similar to our observation in the blended OFETs (Fig. 2), where $\mu_{\text{Hall}}$ is found to be significantly lower than $\mu_{\text{FET}}$. On the contrary, the Hall mobilities measured by probes A, $\mu_{\text{Hall}}^{(A)}$, that test lower angle GBs or fewer GBs in the same OFETs are greater than $\mu_{\text{FET}}$. In the third device (Fig. 4e), the presence of two GBs between the probes B is compensated by the fact that part of the probed region is a grain oriented with its high-$\mu$ axis along the channel, while pair A probes an entirely low-$\mu$ region. This leads to both measurements by pair A and pair B, $\mu_{\text{Hall}}^{(A)}$ and $\mu_{\text{Hall}}^{(B)}$, to be higher than $\mu_{\text{FET}}$ (Fig. 4f). More detailed modeling of these Hall mobilities as a function of GBs’ geometry and angles can be found in Supplementary Fig. S8. Compared to the blended OFETs, where the effect of GBs is more significant and averaged due to the greater number of grains in the channel, the rubrene OFETs allow us to observe both situations with $\mu_{\text{Hall}} < \mu_{\text{FET}}$ and $\mu_{\text{Hall}} > \mu_{\text{FET}}$ within the same device and assign the observed behavior to the specific types of GBs, thanks to a discrete number of them (one to three) in the channel. This experiment clearly shows that Hall mobility measurements in polycrystalline OFETs can depend noticeably on the type of grain boundaries present in the region between the Hall probes.

Finally, we have carried out an additional study that uses high-quality rubrene single crystals with linear defects (“artificial grain boundaries”) intentionally created at the surface before deposition of the gate insulator and gate electrode (Fig. 5). Elongated rubrene crystals with very smooth, mirror-like (a,b)-facets were chosen for this experiment, and
several pairs of Hall probes, labeled P, D1 and D2, were deposited along the channel (the device layout is shown in Fig. 5 a, b). After deposition of contacts, linear defects mimicking a GB were created between the Hall probes D1 and D2, while leaving the surface between the probes P untouched. The defects were created by mechanically “scratching” the crystal’s surface with a tip of a thin metal wire by gently dragging it along the surface in b-axis direction, thus producing a linear defect in the middle of the channel, as schematically shown in Fig. 5a. Although such a defect does not fully represent actual crystallographic GBs as in polycrystalline OFETs above, the static disorder is still a general feature common to grain boundaries. As shown in the photograph of the device (Fig. 5b), we have three pairs of Hall probes in this device, probing the pristine region (P), as well as the two regions with an artificial GB: one with a mild disorder (D1), and another one with a strong disorder (D2). The amount of disorder was varied by the number of scratches applied to the same spot at the surface (see Methods for details).

The Hall mobilities measured in the three regions of this device are shown in Fig. 5c together with the longitudinal mobility of the same FET. The detailed FET and ac-Hall measurements can be found in Figs. S9 - S10. It is evident that the regions with the artificial GB yield lower $\mu_{\text{Hall}}$ compared to that in the pristine region. Furthermore, we have observed an inversion of the carrier coherence factor $\alpha = \mu_{\text{Hall}}/\mu_{\text{FET}}$: it decreases from $\alpha > 1$ in the pristine region to $\alpha < 1$ in the region D2 with a strongly disordered artificial GB. This result is consistent with the model of the effect of grain boundaries on Hall effect described above, indicating that highly disordered grain boundaries may lead to a Hall effect that is more strongly underdeveloped. The results presented in Figs. 4 and 5 highlight the effect of discrete grain boundaries on the Hall effect in OFETs, explaining the origin of an underdeveloped Hall effect in polycrystalline OFETs.
Conclusions

In summary, we have performed the first Hall effect measurements in organic semiconductor blends composed of small molecules and a polymer, revealing coherent (band-like) charge carrier transport in this system. A significant and systematic difference between the longitudinal field-effect mobility and Hall mobility, with the carrier coherence factor $\alpha = \mu_{\text{Hall}}/\mu_{\text{FET}} < 1$, is discovered in polycrystalline blended OFETs. We propose a model that reconciles the relatively high longitudinal mobilities ($\mu_{\text{FET}}$ of up to $6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and yet much smaller Hall mobilities ($\mu_{\text{Hall}}$ of up to $2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) observed in polycrystalline OFETs, based on capacitively charged grain boundaries. The model is supported by additional FET and Hall effect studies of large-grain polycrystalline and single-crystalline rubrene OFETs, where individual well-defined grain boundaries allow us to clearly identify their effect on Hall mobility. These results further advocate for the use of organic single-crystal devices in the studies of truly intrinsic charge carrier transport. Nevertheless, even in polycrystalline films, a mere observation of a Hall signal would already point to the presence of delocalized band-like carriers, which makes Hall effect measurements indispensable for revealing the potential of a studied system in delivering high-mobility charge transport.

Methods

Fabrication of polycrystalline C$_8$-BTBT OFETs: Top-gate bottom-contact FETs were fabricated on glass substrates that were sequentially cleaned in a detergent (DECON 90, 1 vol. % diluted in deionized water), acetone, and isopropanol. For the contacts, 2 nm-thick Ti adhesion layer was first deposited on glass, followed by 20 nm-thick Pt, both sputtered through a contact shadow mask by a DC magnetron sputtering in 5 mTorr of UHP Ar. Channel length and width were $L = W = 1 \text{ mm}$, and the center-to-center distance between the neighboring four-probe voltage probes in the longitudinal direction was $D = 0.34 \text{ mm}$. For
the organic semiconductor, C₈-BTBT was purchased from 1-Material Inc. and used as received, while C₁₆IDT-BT was prepared by following previously reported procedures. The average molecular weight of C₁₆IDT-BT was 66.5 kDa with a dispersity of 2.42. The blend was prepared by dissolving these compounds at a ratio 1:4 C₈-BTBT:C₁₆IDT-BT (10 mg·mL⁻¹) in a 1:1 mixture of tetralin and chlorobenzene. For the doped films, C₆₀F₄₈ was added at 1 molar % of the C₈-BTBT and C₁₆IDT-BT total combined molar mass. The blend was deposited by spin coating the solution heated to 60 °C onto the substrate in nitrogen atmosphere. Following spin coating, the film was annealed on a hotplate at 120 °C for 5 min. Next, a 0.9 μm thick Cytop was grown on top of the C₈-BTBT:C₁₆IDT-BT blend, followed by annealing on a hot plate at 50 °C for 80 min. Subsequently, a 1.33 μm-thick parylene-N was grown on top of Cytop in a custom-designed parylene reactor, thereby resulting in a total gate-channel capacitance $C_i = 0.95$ nF·cm⁻². The FET structures were completed by a 50 nm-thick indium-tin-oxide (ITO) gate sputtered through a shadow mask.

**Fabrication of polycrystalline rubrene OFETs:** Glass substrates coated with ITO, aluminum oxide (100 nm) and tris[4-(5-phenylthiophen-2-yl)-phenyl]amine (TPTPA) (5 nm) were prepared by following the previously published procedure¹⁴. Rubrene (sublimed grade, Sigma Aldrich) was deposited by thermal evaporation (20 nm), followed by annealing on a hot plate at 140 °C for 6 min in a nitrogen atmosphere. An 80 nm-thick adlayer of rubrene was then deposited by thermal evaporation on top of the crystalline template at 1 Å/s at room temperature. Contacts were deposited at the surface of rubrene films either by a thermal evaporation of Ag through a shadow mask or by hand painting with an aqueous suspension of colloidal graphite (Ted Pella). The devices were then sequentially coated with layers of Cytop and parylene-N, followed by the deposition of a 50 nm-thick ITO gate electrode sputtered through a shadow mask, yielding the total gate-channel capacitance $C_i = 2.05$ nF·cm⁻² (for devices with Ag contacts) and 1.74 nF·cm⁻² (for devices with graphite contacts).
Fabrication of single-crystal rubrene OFET with an artificial grain boundary: Rubrene single crystals were grown in a stream of ultra-high purity (UHP) Ar by physical vapor transport. The contacts were hand-painted with an aqueous suspension of colloidal graphite (Ted Pella). After deposition of contacts, linear defects (the so-called “artificial GBs”) were created between the Hall probes by mechanically scratching the crystal’s surface with a tip of a metal wire gently dragged along the surface in \textit{b}-direction for 3-5 times. For an artificial GB with a mild disorder, a 25 \textmu m-thick gold wire was used. For an artificial GB with a stronger disorder, a 100 \textmu m-thick copper wire was used. The devices were then completed by growing a parylene-\textit{N} gate insulator and depositing an ITO gate.

\textit{FET and Hall effect measurements:} All the magneto-transport measurements were performed at room temperature. Keithley Source Meters K2400 and Electrometers K6512 were used for FET measurement. \( V_G \) sweep rate in FET measurements was 0.5 - 1.0 V·s\(^{-1}\). The \textit{ac}-Hall effect measurements were carried out following the previously reported methodology.\(^\text{12} \) An \textit{ac} magnetic field of frequency 0.55 - 0.7 Hz and r.m.s. magnitude \( B_{rms} = 0.2314 \) T was generated by a rotating assembly of permanent Nd magnets. In-phase and out-of-phase Hall voltage signals, \( \Delta V_{H}^{ip} \) and \( \Delta V_{H}^{op} \), were detected by a lock-in amplifier tuned to the frequency of the oscillating magnetic field. The Hall voltage, \( V_{Hall} \), used in Hall mobility calculations was determined as
\[
V_{Hall} = \left[ (\Delta V_{H}^{ip})^2 + (\Delta V_{H}^{op})^2 \right]^{1/2}.
\]

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Figure 1. **OFETs based on blends: materials and devices for Hall effect measurements.** (a) Chemical structures of C$_8$-BTBT small molecule, C$_{16}$IDT-BT conjugated polymer and C$_{60}$F$_{48}$ molecular dopant. (b) Polarized optical microscopy of a spin-cast blend, showing compact polycrystalline morphology of C$_8$-BTBT segregated on top, with a clear polarization contrast inversion. (c) Schematic illustration of the vertical phase separation in C$_8$-BTBT:C$_{16}$IDT-BT blend leading to the formation of ordered crystalline grains (G) of the small molecules separated by disordered regions of grain boundaries (GB). (d) A top-view photograph (left) and a cross-sectional structure (right) of the four-probe top-gate OFETs based on blends used in this work for FET and Hall measurements. (e) Schematics of $ac$-Hall effect measurements in polycrystalline FETs (the gate electrode is omitted for clarity): a low-frequency small magnetic field $B$ is oscillating perpendicular to
the accumulation channel induced at $V_G < 0$, while $dc$ source-drain voltage $V_{SD}$ excites the longitudinal $dc$ source-drain current $I_{SD}$. The longitudinal $dc$ four-probe voltage $V_{4p}$ is measured simultaneously with the transverse $ac$-Hall voltage $V_{Hall}$. The phase sensitive detection with a lock-in amplifier tuned into the frequency of the $B$ field greatly enhances the signal-to-noise ratio in these Hall measurements.
Figure 2. FET and Hall effect measurements of C₈-BTBT:C₁₆IDT-BT blends. The data are shown for OFETs using doped (left panels) and undoped (right panels) blends. The dopant is C₆₀F₄₈. (a, b) Linear-regime transfer characteristics, \(I_{SD}(V_G)\), recorded at several values of \(V_{SD}\) (indicated). (c, d) The carrier densities calculated from the gate-channel capacitance \(n_{FET}\) (dark yellow circles) and Hall effect measurements \(n_{Hall}\) (dark blue squares). (e, f) Charge carrier mobilities extracted from the four-probe FET and ac-Hall effect measurements, \(\mu_{FET}\) and \(\mu_{Hall}\), respectively. The measurement reliability factor is \(r_{lin} = 90\%\) for the doped and 66\% for the undoped devices (for definition of parameter \(r\) see Ref. [20]). The carrier densities and mobilities were calculated via Eqs. (1) and (2). Besides good FET performance, these measurements reveal an intriguing new behavior of polycrystalline OFETs: a Hall effect that is significantly and systematically underdeveloped (\(\mu_{Hall} < \mu_{FET}, n_{Hall} > n_{FET}\)),\(^8\, ^{13}\) despite the relatively high longitudinal mobility (\(\mu_{FET}\) up to 6 cm\(^2\)V\(^{-1}\)s\(^{-1}\)).
Figure 3. The model of capacitively charged grain boundaries in polycrystalline OFETs. (a) Schematic of a polycrystalline film with crystalline grains between the Hall probes (labeled $V_{H,+}$ and $V_{H,-}$). The grains of different crystallographic orientation are colored in different shades of blue. The red and blue arrows represent the longitudinal source-drain current $I_{SD}$ and the Lorentz force $F_L$, respectively. Signs “+” and “-” indicate an excess or a lack of holes in certain areas of the accumulation channel. (b) Schematic distribution of the excess charge $q(y)$ along the horizontal line connecting the Hall probes. $q = 0$ corresponds to the unperturbed carrier density in the channel (at $B = 0$ and $F_L = 0$). (c) The corresponding distribution of the transverse electric field $E_y$ across the channel. Within the grains, the field profile is approximately flat, with slightly different magnitudes due to the different longitudinal mobilities $\mu_x$ and Lorentz forces $F_L = e\mu_x B E_{SD}$ generated within each grain. In the narrow regions of capacitively charged GBs, $E_y$ can be significantly lower. The green dashed line represents the uniform electric field $V_{Hall}/W$ expected in the case of a homogeneous channel without GBs. (d) The corresponding distribution of potential $\phi_y$ along the horizontal line connecting the Hall probes: the green dashed line represents a homogeneous channel without GBs, and the blue solid line takes into account the potential off-sets occurring at capacitively charged GBs.
Figure 4. FET and Hall effect measurements in large-grain polycrystalline rubrene OFETs: the effect of discrete grain boundaries. (a, c, e) Polarized optical micrographs of the three devices showing individual large grains (G1 - G4). The electrodes in the four-probe/Hall-bar geometry can be seen: the source S, the drain D, and the voltage probes A⁺, A⁻, and B⁺, B⁻ (marked with red and yellow triangles). The molecular orientation within individual grains is indicated by the small blue rectangles: the longer side of the rectangle corresponds to the rubrene’s high-mobility axis (the b-axis). The channel of the device in (a) consists of five grains converging at a single nucleation point; the channel of the device in (c) consists of four grains and a single nucleation point; the channel of the device in (e) consists of just two grains. The cartoons on the right schematically show the molecular packing in all the grains (red bars represent tetracene cores of rubrene molecules). (b, d, f) Field-effect mobility $\mu_{\text{FET}}$ (red open circles) extracted from the longitudinal four-probe FET measurements and the Hall mobilities $\mu_{\text{Hall}}$ (squares) extracted from the two pairs (A and B) of the Hall probes for each device, labeled $\mu_{\text{Hall}}^{(A)}$ and $\mu_{\text{Hall}}^{(B)}$, all plotted as a function of $V_G$. The inset schematically shows a cross-section of the device structure.
Figure 5. Hall effect measurements in a single-crystal rubrene OFET with “artificial grain boundaries”. A linear defect, to some extent imitating a grain boundary (“artificial GB”), is created by mechanically scratching the surface of the (a,b)-facet of the crystal between the Hall probes with a sharp tip of a metal wire. (a) Left: top-view layout of the device’s channel with the linear defect (the scratch) made along the channel between the Hall probes indicated with the red line. Right: a sketch of the slipped-stack molecular packing motif with a disordered artificial GB in the middle. (b) A photograph of the actual device (before the deposition of the gate electrode) with three sets of Hall probes labeled P (pristine surface), D1 (surface with a mildly disordered artificial GB) and D2 (surface with a strongly disordered artificial GB). The degree of disorder was varied by the number of scratches applied to the same spot (for details see Methods). (c) Hall mobility $\mu_{\text{Hall}}$ measured in the three regions of the channel (red symbols, with error bars determined from the noise in $V_{\text{Hall}}$) compared to the longitudinal FET mobility $\mu_{\text{FET}}$ measured in the same device (shown as a blue solid line with the hatched area representing the error bar).
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