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Electronic Supplementary Information to the article "**On methodology of characterization of organic field effect transistors with charge concentration dependent mobility**"

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Content:

1) Estimate of parameters of Eq. 1 (main text) based on molecular-scale modelling [S1].
2) Derivation of the 1-D drift-diffusion equation with mobility dependent on charge concentration. Derivation of the current-voltage characteristics for constant mobility (independent on charge concentration) and estimation of electric fields and their divergences at contacts. Discussion about the limits of the drift-diffusion equation model stemming from the model itself.

1) Concentration dependence of the hole mobility

Figure 8 in Ref. S1 shows the calculated hole mobility as a function of the hole concentration and energetic disorder in crystalline (a) and amorphous (b) phase. Calculation was done for an external electric field 10^7 V/m oriented in the π-stacking direction in the crystalline phase and along one of the axes in the amorphous phase (see Fig. 6 in Ref. S1). These numerical results can be very well approximated using the empirical formula by Eq. 1 in main text. The calculated fitting parameters are shown in Table S1.

σ(ε)	***A*** **[cm²/(Vs)]**	n_p **[cm⁻³]**	***p***	n_q **[cm⁻³]**	***q***
Crystalline phase					
0.00	7.4666E+00	1.0000E+21	0.0000E+00	1.4876E+20	1.8113E+00
0.05	4.1903E+00	3.0903E+20	5.1794E-01	1.8891E+20	2.1624E+00
0.10	8.8461E-02	1.7743E+18	7.8083E-01	1.8049E+20	2.3514E+00
0.15	6.0150E-04	5.6824E+17	1.2901E+00	2.4758E+20	3.2053E+00
0.20	3.2024E-06	4.5555E+17	1.9221E+00	3.1579E+20	4.9237E+00
Amorphous phase					
0.00	5.0453E-05	1.4026E+20	5.7812E-01	1.7771E+20	2.1038E+00
0.05	1.4039E-05	8.4350E+18	6.0926E-01	1.5140E+20	2.0024E+00
0.10	5.6641E-07	7.3534E+17	8.7079E-01	1.5041E+20	2.0603E+00
0.15	1.0748E-08	3.6617E+17	1.3293E+00	1.6018E+20	2.3811E+00
0.20	1.6462E-10	3.2395E+17	1.8930E+00	1.6021E+20	2.7525E+00

Table S1: Optimized parameters of the empirical formula Eq. 1 in main text describing the concentration dependence of the hole mobility μ'_{cryst} in the crystalline phases of P3HT oriented in the π-stacking direction and of the hole mobility μ'_{amorph} in the amorphous phase

oriented along one of the axes shown in Fig. 6 of Ref. S1. Calculations were done for different values of the local energetic disorder *σ(ε)*.

2) Thin layer model

This section is related to the part of the main article, which solves the 1-D kinetic transport of the so called "surface charges", which due to the symmetry of the OFET reduces the problem to 1-D one. Here, we will first derive the drift-diffusion equation for 1-D systems with explicitly dependent mobility on charge concentration, next we show a correct analytical solution of the 1-D drift-diffusion equation with constant mobility without contact resistances and also we show consequences stemming from the exact solution, together with a possible approximation and its limitations.

Let x is the coordinate along the active channel toward the drain contact and z is the coordinate perpendicular to the plain of the conducting channel. Thin layer model of hole transport assumes that the equivalent surface charge density $\sigma(x)$ is given by the integration of volume charge density $\rho(x,z)$ in the Poisson equation ($\mathrm{div}\, E = \rho(x,z)/\varepsilon$) in the direction z perpendicular to the transporting layer, i.e. $\sigma(x) \equiv \int \rho(x,z)dz$. Moreover, it is assumed that divergences of electric field perpendicular to the conducting layer are dominant and divergences in the direction of the conducting layer are negligible. Then we get for the equivalent surface charge density $\sigma(x)$ the following capacitor relation

$$\sigma(x) = C(V(x) - V_G + V_T), \tag{S1}$$

where C is the capacity of the insulating layer. In the calibration of the gate voltage V_G also the work function of the gate and potential drops at interfaces of insulator should be taken into account. This is reflected by the potential shift of the threshold voltage V_T. The latter also includes trapped (very deep traps) surface charges that do not contribute to the current but which had to be included in the integration of the Poisson equation. Therefore, the expression CV_T includes trapped surface charges as well as shift of the gate level due to its work function and effects at interfaces. The source-to-drain-current I_{SD} in the thin capacitor model includes both drift and diffusion currents. If we denote by E_x the component of the electric field along the conductive channel the drift term equals to $w\int_0^t \mu(\rho)\rho E_x(x,z)dz$, where t is the thickness of the conducting layer inside the OFET. Linearizing the distribution of the component E_x perpendicularly to the conducting channel $E_x(x,z) \approx E_x(x,0) + z\frac{\partial}{\partial z}E_x(x,0)$, we find for the drift term

$$w\int_0^t \mu(\rho)\rho . E_x(x,z)dz \approx w\int_t^t \mu(\rho)\rho . \{E_x(x,0) + z\frac{\partial}{\partial z}E_x(x,0)\}dz = w\mu(\sigma)\sigma E_x(x,0) + w\frac{\partial}{\partial z}E_x(x,0)\int_0^t \mu(\rho)\rho z dz \quad . \tag{S2}$$

Here, in the first term of the expansion we introduced $\mu(\sigma(x)) \equiv \frac{1}{\sigma(x)}\int_0^t \mu(\rho(x,z))\rho(x,z)dz$ as mobility dependent on equivalent surface charge concentration $\sigma(x)$ controlled by the instant potential $V(x) - V_{\mathrm{G}} + V_{\mathrm{T}}$ through Eq. (S1). The latter becomes obvious after realizing that the distribution of volume charge density $\rho(x,z)$ along the direction z is fully controlled by the equilibrium between the drift and diffusion current along the z direction. Solving that, it can be analytically found that the charge distribution is fully controlled by the component $E_z(x,0)$ of electric field at the boundary, which is exactly given by $V(x) - V_{\mathrm{G}} + V_{\mathrm{T}}$, and whence also by $\sigma(x)$ through the capacity relation (S1). For the estimate of mutual contribution of both terms we can write

$$\frac{w\int_0^t \mu(\rho)\rho z\frac{\partial}{\partial z}E_x(x,0).dz}{w\int_0^t \mu(\rho)\rho E_x(x,0)dz} = \frac{\frac{\partial}{\partial z}E_x(x,0)\int_0^t \mu(\rho)\rho.z.dz}{E_x(x,0)\int_0^t \mu(\rho)\rho.dz} \leq \frac{\frac{\partial}{\partial z}E_x(x,0)\int_0^t \rho.z.dz}{E_x(x,0)\int_0^t \rho.dz} = \frac{\frac{\partial}{\partial z}E_x(x,0)}{E_x(x,0)}.\bar{z} = \frac{\frac{\partial}{\partial x}E_z(x,0)}{E_x(x,0)}.\bar{z} = \frac{\frac{-\varepsilon_D}{\varepsilon_{P3HT}d}\frac{\partial}{\partial x}(U(x)}{-\frac{\partial}{\partial x}(U(x) - \ldots}\bar{z} = \frac{\varepsilon_D}{\varepsilon_{P3HT}d}\bar{z}$$

(S3)

In the inequality of (S3) we used the fact that $\mu(\rho(z)) \geq \mu(\rho(s))$ for $z < s$ due to the mobility increase with charge concentration. We also introduced "mean thickness $\bar{z}$" of charge conducting channel in the conductive channel $\bar{z} \equiv \int \rho z dz/\sigma$. For the numerator we also utilized the relation $rot\,\vec{E} = 0$, which yields $\frac{\partial}{\partial z}E_x(x,0) = \frac{\partial}{\partial x}E_z(x,0)$ and that at the boundary $E_z(x,0) = \frac{-\varepsilon_D(V(x) - V_{\mathrm{G}} + V_{\mathrm{T}})}{\varepsilon_{P3HT}d}$. Next, taking into account permittivities of conductive polymer and insulating dielectrics satisfy $\varepsilon_{P3HT} \approx 4.2$ and $\varepsilon_D \approx 3.9$ and that the "mean thickness $\bar{z}$" of the order of few nm is significantly shorter than the thickness of the insulating dielectric dielectrics d = 230 nm, the right hand side in (S3) $\to 0$ and for the drift current we can write

$$I_{drift} \approx -w\mu(\sigma)\sigma\frac{\partial}{\partial x}(V(x) - V_{\mathrm{G}} + V_{\mathrm{T}}). \qquad \text{(S4)}$$

On the other hand, for the diffusion term we can write

$$I_{diffusion} \approx - \int_0^t D(\rho)\frac{\partial \rho(x,z)}{\partial x}dz = - D(\bar{\sigma}(x))\frac{\partial}{\partial x}\int_0^t \rho.dz = - D(\bar{\sigma}(x)).\frac{\partial}{\partial x}\sigma \approx - \frac{k_B T}{e}\mu(\sigma(x))\frac{\partial}{\partial x}\sigma .$$

(S5)

In the last equation we have used the mean value theorem for integration and the Einstein relation $\frac{D(\sigma(x))}{\mu(\sigma(x))} \sim \frac{k_B T}{e}$. Morever, we can generalize Eq. S4 (and similarly Eq. S5) even for mobility $\mu(z,\rho(x,z))$ also explicitly dependent on the coordinate z, which would account also for surface effects. Then in Eq. S4 (or S5) $\mu(\sigma(x)) \equiv \frac{1}{\sigma(x)}\int \mu(z,\rho(x,z))\rho(x,z)dz$ would be used.

Exact solution of the drift-diffusion with constant mobility

Let's assume for simplicity that in the drift-diffusion equation (S4) controlling the current flowing between the source and drain along the 1-D chain, the mobility μ is not dependent on the equivalent surface charge density σ. Eq. (S4) then takes the form

$$I_{SD} = -w\sigma(x)\mu\frac{\partial V(x)}{\partial x} - wD\frac{\partial \sigma(x)}{\partial x} . \quad \text{(S6)}$$

Substituting for $U(x)$ from Eq. S1 we get

$$I_{SD} = -\frac{w\mu}{C}\sigma(x)\frac{\partial}{\partial x}\sigma(x) - Dw\frac{\partial}{\partial x}\sigma(x) = -\frac{w\mu}{C}\frac{\partial}{\partial x}\left(\frac{\sigma(x)^2}{2} + \frac{CD}{\mu}\sigma(x)\right) =$$
$$= -\frac{w\mu}{C}\frac{\partial}{\partial x}\{\frac{1}{2}\left(\sigma(x) + \frac{CD}{\mu}\right)^2 - \frac{1}{2}\left(\frac{CD}{\mu}\right)^2\} = -\frac{w\mu}{2C}\frac{\partial}{\partial x}\left(\sigma(x) + \frac{CD}{\mu}\right)^2 . \quad \text{(S7)}$$

Utilizing that the current I_{SD} is constant, i.e., independent on x, along the chain the last equation S6 can be integrated to the solution

$$I_{SD}x + K = -\frac{w\mu}{2C}\left(\sigma(x) + \frac{CD}{\mu}\right)^2 , \quad \text{(S8)}$$

with the integration constants K. After utilizing S1 we get

$$I_{SD}x + K = -\frac{w\mu}{2C}\left\{C\left(V(x) - V_G + V_T\right) + \frac{CD}{\mu}\right\}^2 . \quad \text{(S9)}$$

Utilizing the Einstein-Smoluchowski relation, Eq. S9 takes a form

$$I_{SD}x + K = -\frac{w\mu C}{2}\left(V(x) - V_G + V_T + \frac{\mathrm{kT}}{\mathrm{e}}\right)^2 . \quad \text{(S10)}$$

The last term in Eq. S10 kT/e $\approx$ 0.025 V and it correspond to the correction obtained from the diffusion current. In manifold articles this term is neglected. Below, we will see that it is actually a very critical factor in the saturation regime at the drain. The equation above contains two constants of integration: the current "I_{SD}" and the constant "K". Both of them

can be obtained from boundary conditions of the potential at both contacts: $V(x=0) = V_S$ (source) and $V(x=L) = V_D$ (drain), respectively. Namely,

$$K = -\frac{w\mu C}{2}(V_S - V_G + V_T + \frac{kT}{e})^2 , \qquad (S11)$$

$$I_{SD}L + K = -\frac{w\mu C}{2}(V_D - V_G + V_T + \frac{kT}{e})^2 . \qquad (S12)$$

Finally, we arrive at the relation

$$I_{SD} = -\frac{w\mu C}{2L}\{\left(V_{SG} - V_{SD} + V_T + \frac{kT}{e}\right)^2 - \left(V_{SG} + V_T + \frac{kT}{e}\right)^2\} . \qquad (S13)$$

Eq. S13 directly expresses the dependence of the current I_{SD} as a function of applied source-to-drain ($V_{SD} = -V_D + V_S$) and source-to-gate ($V_{SG} = -V_G + V_S$) voltages. In the Ohmic limit for small source-to-drain voltage V_{SD} we get the linear regime

$$I_{SD} \sim w\mu C(V_{SG} + V_T + \frac{kT}{e})\frac{V_{SD}}{L} . \qquad (S14)$$

On the other hand, Eq. (S13) takes its maximum for

$$V_{SD} = V_{SG} + V_T + \frac{kT}{e} . \qquad (S15)$$

However, there is a limitation that cannot be neglected. As for holes $V_{SG} > 0$, earlier then the voltage V_{SD} takes the value as shown in Eq. S15 for values $V_{SD} = V_{SG} + V_T$ (and $V_D = V_G - V_T$), the surface concentration $\sigma(x)$ disappears at the drain contact, because due to the Eq. S1 $\sigma(L) = 0$ and the current takes the value

$$I_{SD} = \frac{w\mu C}{2L}\{\left(V_{SG} + V_T + \frac{kT}{e}\right)^2 - \left(\frac{kT}{e}\right)^2\} = \frac{\mu w C}{2L}\{\left(V_{SD} + \frac{kT}{e}\right)^2 - \left(\frac{kT}{e}\right)^2\} . \qquad (S16)$$

For increasing value of the source-to-drain voltage V_{SD} and fixed value of source-to-gate voltage V_{SG} the local charge density at the drain remains $\sigma(L) = 0$ and this value is a new "boundary condition" to the differential equation S8, instead of the value of drain voltage V_D. The solution for the current I_{SD} in the saturation regime thus reads as

$$I_{SD}^{saturation} = \frac{w\mu C}{2L}\{\left(V_{SG} + V_T + \frac{kT}{e}\right)^2 - \left(\frac{kT}{e}\right)^2\} . \qquad (S17)$$

Hole concentration:

From the relation

$$I_{SD}x + K = -\frac{w\mu}{2C}\left(\sigma(x) + \frac{CD}{\mu}\right)^2 = -\frac{\mu w}{2C}\left(\sigma(x) + \frac{\mathrm{k}TC}{\mathrm{e}}\right)^2 \qquad \text{(S18)}$$

we get

$$\sigma(x) = -\frac{\mathrm{k}TC}{\mathrm{e}} + \sqrt{\frac{2(I_{SD}x + K)C}{-w\mu}}, \qquad \text{(S19)}$$

which is not a linear function along the channel. In the same way, also the drop of the potential along the channel is not a linear function. The derivative $\left|\frac{\partial}{\partial x}\sigma(x)\right|$ along the channel increases and particularly near the drain significantly increases in the saturation regime.

Diffusion current: From Eq. (S19) we get

$$-Dw\frac{\partial\sigma(x)}{\partial x} = \frac{I_{SD}kT}{e}\frac{C}{\sqrt{\frac{2(I_{SD}x + K)C}{-\mu w}}} = I_{SD}\frac{kT}{e}\frac{C}{\left(\sigma(x) + \frac{kT}{e}C\right)} = I_{SD}\frac{kT}{e}\frac{1}{\left(V(x) - V_G + V_T + \frac{kT}{e}\right)},$$

(S20)

where for both channel ends ($x = 0$, source) and ($x = L$, drain) we find:

$$-Dw\frac{\partial\sigma(x)}{\partial x}\bigg|_{x=0} = I_{SD}\frac{\frac{\mathrm{k}T}{\mathrm{e}}}{V_{\mathrm{SG}} + V_{\mathrm{T}} + \frac{\mathrm{k}T}{\mathrm{e}}}$$

(S21)

From (S21) we observe that the diffusion current at the source is always negligible. On the other hand for the diffusion current at the drain we find

$$-Dw\frac{\partial\sigma(x)}{\partial x}\bigg|_{x=L} = I_{SD}\frac{\frac{\mathrm{k}T}{\mathrm{e}}}{V_{\mathrm{DG}} + V_T + \frac{\mathrm{k}T}{\mathrm{e}}} = I_{SD}\frac{\frac{\mathrm{k}T}{\mathrm{e}}}{V_{\mathrm{SG}} - V_{SD} + V_T + \frac{\mathrm{k}T}{\mathrm{e}}}.$$

(S22)

Diffusion current at the drain is also always negligible **except for the saturation regime,** where $V_{\mathrm{SD}} \geq V_{\mathrm{SG}} + V_{\mathrm{T}}$. Then we find

$$- D\frac{\partial\sigma(x)}{\partial x}\Big|_{x=L} \to I_{SD}\ . \qquad \text{(S23)}$$

Thus, in this limit the current I_{SD} is fully diffusion controlled at the drain. Physically, within the 1-D model the current is controlled by the charge concentration gradient $\frac{\partial\sigma(x)}{\partial x}$ for distances from drain where $V(x) - V_G + V_T \approx \frac{kT}{e} = 0.025\ eV$.

Electric field:

Utilizing Eq. S9 we find for the component of electric field E_x along the conductive channel

$$E_x = -\frac{\partial V(x)}{\partial x} = \frac{I_{SD}}{\sqrt{w\mu C}}\frac{1}{\sqrt{2(-I_{SD}x - K)}} = \frac{I_{SD}}{w\mu C}\frac{1}{(V(x) - V_G + V_T + \frac{kT}{e})}$$

(S24)

At x = 0 (source):

$$-\frac{\partial V(x)}{\partial x}\Big|_{x=0} = \frac{I_{SD}}{w\mu C}\frac{1}{(V_{SG} + V_T + \frac{kT}{e})}\ .$$

(S25)

If $V_{SD} \to 0$ (the Ohmic limit) we obtain

$$-\frac{\partial V(x)}{\partial x}\Big|_{x=0} = \frac{V_{SD}}{L}, \qquad \text{(S26)}$$

which means that at the source the intensity of electric field corresponds to the mean slope of the source-to-drain potential V_{SD}. On the other hand, in the saturation regime we get

$$-\frac{\partial V(x)}{\partial x}\Big|_{x=0} \approx \frac{(V_{SG} + V_T)}{2L},$$

(S27)

indicating that at the source the intensity of electric field corresponds to the half of the source-to-gate potential $(V_{SG} + V_T)/2$.

At x = L (drain):

$$-\frac{\partial V(x)}{\partial x}\Big|_{x=L} = \frac{I_{SD}}{w\mu C}\frac{1}{V_{DG} + V_T + \frac{kT}{e}}\ .$$

(S28)

If $V_{\mathrm{SD}}\rightarrow 0$ (the Ohmic limit) then we get

$$-\frac{\partial V(x)}{\partial x}\bigg|_{x=L}=\frac{V_{\mathrm{SD}}}{L}, \tag{S29}$$

corresponding to the mean slope of the source-to-drain potential V_{SD}. On the other hand, in the saturation regime we get

$$-\frac{\partial V(x)}{\partial x}\bigg|_{x=L}\approx\frac{(V_{SG}+V_{\mathrm{T}})^2}{2L\frac{\mathrm{k}T}{\mathrm{e}}}.$$

(S30)

For $V_{SG}+V_{\mathrm{T}}$ = 5 V and L = 5 μm, which corresponds to moderate values of the applied gate voltage we obtain from Eq. S30 $-\frac{\partial V(x)}{\partial x}\Big|_{x=L}\approx 2\ \mathrm{x}\ 10^7\mathrm{V/m}$. On the other hand, for high values of gate voltage $V_{SG}+V_{\mathrm{T}}$ = 25 V and L = 5 μm we obtain $-\frac{\partial V(x)}{\partial x}\Big|_{x=L}\approx 5\ \mathrm{x}\ 10^8\mathrm{V/m}$. However, such a high value of the internal electric field is hardly possible in organic materials, since it would cause an electrical breakdown of the sample.

Divergence of electric field:

For the divergence of the component E_x along the conductive channel we obtain from (S24)

$$\frac{\partial E_x}{\partial x}=-\frac{\partial^2 V(x)}{\partial x^2}=-\frac{{I_{SD}}^2}{\sqrt{w\mu C}}\frac{1}{\sqrt{2(-I_{SD}x-K)}} \tag{S31}$$

At x = L (drain) in saturation regime:

$$\frac{\partial E_x}{\partial x}=-\frac{\partial^2 V(x)}{\partial x^2}\bigg|_{x=L}\approx\frac{1}{L^2}\frac{(V_{\mathrm{SG}}+V_{\mathrm{T}})^4}{(\frac{\mathrm{k}T}{\mathrm{e}})^3} \tag{S32}$$

If we restricted the Poisson equation just to the dimension along the channel, this divergence would produce a carrier density $n(x)$/e

$$\frac{n(x)}{\mathrm{e}}\approx\frac{\epsilon}{\mathrm{e}L^2}\frac{1\,(V_{\mathrm{SG}}+V_{\mathrm{T}})^4}{(\frac{\mathrm{k}T}{\mathrm{e}})^3}.$$

(S33)

For the relative permittivity $\varepsilon = 4.2$, $L = 5$ μm and $V_{SG} + V_T = V_{SD} = 10$ V, the carrier density would be ca 5 x 10^{21} cm^{-3}, which is comparable to the full density of all HOMO states for P3HT (ca 4 x 10^{21} cm^{-3}).

On the basis of calculated electric fields and their divergences at the drain we conjecture the model based purely on the capacity relation (S11) of the thin layer model controlled by the drift-diffusion equation (S4-S5) fails at the drain in the saturation regime. Our model presented in the main text, which eliminates these unphysical artifacts, includes the contact resistances connected in the series to the 1-D model. Nevertheless, these estimates of calculated electric fields and their divergences at the drain in "an ideal 1-D model" indicate possibility of non-trivial effects near contact even for OFET simulation based on macroscopic kinetic theory for charge transfer.

3. Profiles of electric field intensity and charge concentration in transversal direction (perpendicular to the channel length)

For given value of the potential difference $V(x) - V_G + V_T$ the transversal component of the electric field intensity $E_z(x,0)$ at the bottom at the conducting layer is strictly determined. If in the transversal direction the drift and diffusion currents are in equilibrium and the Poisson equation is reduced just to the transversal direction also the distribution of the transversal electric field intensity and charge concentration is unambiguously determined as follows

$$E_z(z) = Gtg\{\frac{eGz}{2KT} + arctg\{\frac{E(0)}{G}\}\} = G\frac{\left(tg\{\frac{eGz}{2KT}\} + \frac{E_z(0)}{G}\right)}{1 - tg\{\frac{eGz}{2KT}\}\frac{E_z(0)}{G}} \qquad \text{(S34)}$$

$$\rho(z) = \varepsilon_{P3HT}\frac{\partial E_z}{\partial z} = \frac{\varepsilon_{P3HT}e}{2KT}\frac{G^2}{cos^2(\frac{eGz}{2KT} + arctg\{\frac{E_z(0)}{G}\})} > 0 ,$$

(S35)

with the constant G determined from the "gate" boundary condition.

$$Gtg\{\frac{eGt}{2KT}\} = -E_z(0) = \frac{\left(V(x) - V_G + V_T\right)}{\varepsilon_{P3HT}}C \qquad \text{(S36)}$$

which can be easily obtained from Eq. (S34) under the condition that at the opposite site to the insulating dielectrics the transversal electric field vanishes, i.e., $E_z(t) = 0$. Utilizing Eqs. (S34-S36) we can also estimate the factor $\frac{\varepsilon_D \bar{z}}{\varepsilon_{P3HT}d}$ in Eq (S3) for the ratio of the first order and zeroth order terms in the Taylor expansion as follows

$$\frac{w\int_0^t \mu(\rho)\rho z\frac{\partial}{\partial z}E_x(x,0)dz}{w\int_0^t \mu(\rho)\rho E_x(x,0)dz} \le \frac{\varepsilon_D\ \bar{z}}{\varepsilon_{P3HT}d} = \frac{\varepsilon_D}{\varepsilon_{P3HT}}\frac{\int_0^t \rho(z)zdz}{d\int_0^t \rho(z)dz} = \frac{kT}{e}\frac{ln(1+(\frac{E_z(0)}{G})^2)}{(V(x)-V_G+V_T)} \approx$$

$$\approx \frac{kT}{e}\frac{ln\left[1+(\frac{2}{\pi}\left\{\frac{\varepsilon_D}{\varepsilon_{P3HT}}\frac{(V(x)-V_G+V_T)}{2\frac{kT}{e}}\frac{t}{d}+1\right\})^2\right]}{(V(x)-V_G+V_T)}$$

(S37)

In Eq. (S37) we utilized Eqs. (S34-S35) in performing integration and for the obtained result we used that Eq. (S36) provides $-\frac{E_z(0)}{G} \approx \frac{2}{\pi}\left\{\frac{\varepsilon_D}{\varepsilon_{P3HT}}\frac{(V(x)-V_G+V_T)}{2\frac{kT}{e}}\frac{t}{d}+1\right\}$ for $V(x)-V_G+V_T > 1V$. When parameters of the studied OFET, i.e., $\varepsilon_{P3HT} \approx 4.2$, $\varepsilon_D \approx 3.9$, d = 230 nm and t = 230 nm are inserted into Eq. (S37) we find for the limit of the upper boundary $\frac{\varepsilon_D\ \bar{z}}{\varepsilon_{P3HT}d}$ values as shown in Table S2. We find that the "thin layer" OFET model is valid for values of $V(x)-V_G+V_T$ of the order of units in V.

$V(x)-V_G+V_T$	$\frac{\varepsilon_D\ \bar{z}}{\varepsilon_{P3HT}d}$
1 V	0. 088
2 V	0.06
3 V	0.046
4 V	0.038
5 V	0.033

Table S2: The upper boundary limit $\frac{\varepsilon_D\ \bar{z}}{\varepsilon_{P3HT}d}$ for the ratio of the first and zeroth order expansion terms in Eq. (S3).

Distributions of both quantities in Eqs. (S34-35) for parameters of FET setup are shown in Fig. S1 up to 10 nm. We observe that the transversal electric field intensity reduces to 10 % of its boundary value within just "few" nm so that the also the "equivalent surface charge" $\sigma(x)$ is concentrated just within just "few" nm to the bottom of the channel. The effect is more pronounced for higher values of gate voltage drop. We also note that within thin layer the charge concentration can be the order of ca $0.01 \div 0.1\ nm^{-3}$, which was shown in [S1] to be in the range of mobility increase. Next, we also note that within this "thin layer" also transversal electric field intensities are very high. Namely, for $V(x)-V_G+V_T \ge 20\ V$, the transversal

electric field intensity $E_z(z)$ is of the order of ca $10^8 V.m^{-1}$. Both these high charge concentration and electric field intensities, as well as the variability of the mobility dependence along the transversal direction must be taken into account for rigorous molecular scale modelling. We find

$$\mu(V(x)) \equiv \frac{1}{(C(V(x)-V_{\mathrm{G}}+V_{\mathrm{T}}))}\int_0^t \mu_{molecular-scale}(z,\rho(x,z),E_z(x,z))\rho(x,z).dz) \quad , \tag{S38}$$

where inputs $\rho(x,z)$ and $E_z(x,z)$ are given by Eqs. (S34-35) and molecular scale mobility $\mu_{molecular-scale}$ can critically depend on local morphology, and therefore, for its evaluation suitable model must be chosen, which exactly matches given morphology

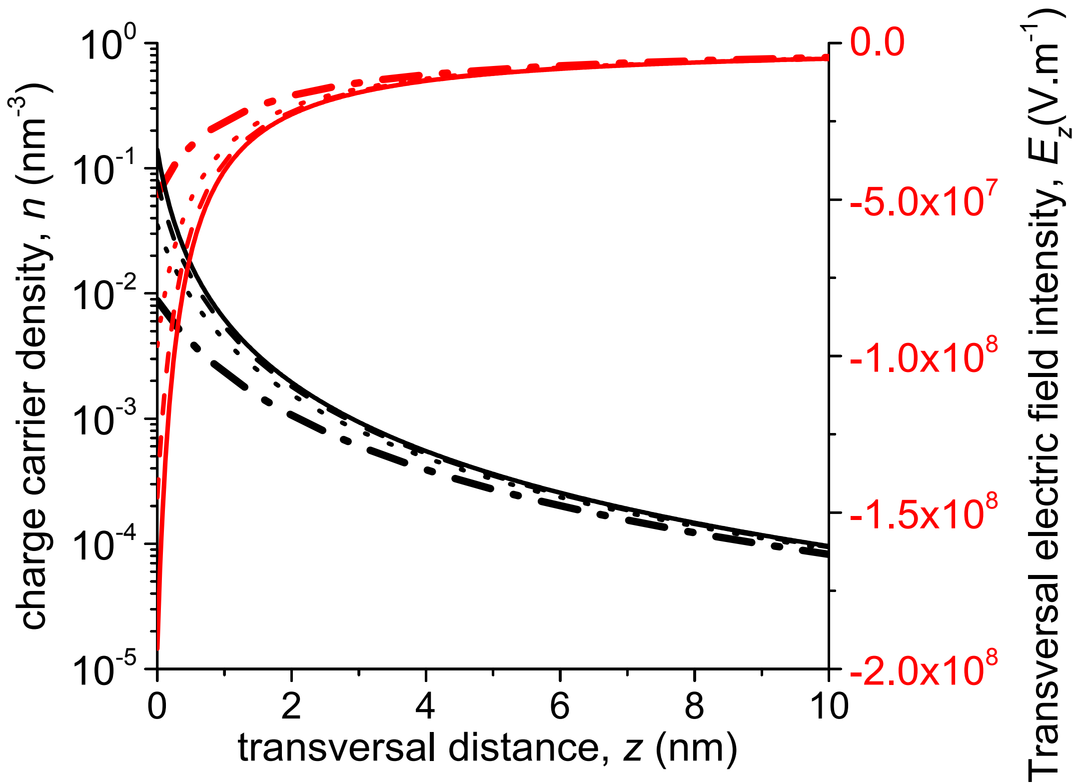

Fig. S1: Transversal electric field intensity and charge concentration distribution along transversal direction of the conducting channel for various applied gate voltage $(V(x)-V_{\mathrm{G}}+V_T)$: 40 V (solid line), 30 V (dash line), 20 V (dotted line), 10 V (dash-dotted line).

4. Examples of mobility dependences on gate voltage for P3HT samples prepared under different conditions.

For the sake of illustration of mobility dependence on gate voltage we show in Fig S2 several other dependences for samples prepared under various different conditions than shown in the main text:

In all additional samples a poly(3-hexylthiophene), P3HT, M_w=44000, regioregularity 96 %, obtained from LISICON was used. The thin polymeric layers were cast on Si(n^+)/SiO_2 substrates in ambient air conditions. The Si(n^+)/SiO_2 substrates were purchased from

Fraunhofer Institute for Photonic Microsystems, Dresden, Germany (SiO_2 thickness 230 nm, with corresponding gate capacitance C = 15 nF.cm^{-2}, 30 nm thick Au electrodes with 10 nm ITO undercoat, channel width W = 1 cm and channel lengths L = 5 µm, 10 µm, 15 µm and 20 µm), respectively.

a) dip-coated … high. The thin active layer was deposited from a fresh solution of P3HT in toluene (10mg/ml) at sample withdrawing speed 4mm/min onto the previously silanizated substrate surface with octadecyltrietoxysilane (OTS) purchased from Sigma-Aldrich. The OTS modified substrate surface has increased hydrophobicity compared to bare substrate; water contact angel is around 90° while for fresh not treated substrate it is around 60°. The final active layer was annealed on the hot plate for 1h at 150°C in N_2 glovebox atmosphere and then slowly cooled dawn in order to improve layer crystallinity. The threshold voltage $U_T = -15\ V$ was found independent on the channel length L.

b) dip-coated … low. The 20 nm thin active layer was deposited from fresh solution in dichlorobenzene (5mg/ml) at sample withdrawing speed 4mm/min onto the bare (not treated) substrate. The threshold voltage $U_T = -16\ V$ was found independent on the channel length L

c) spin-coated … The 120 nm thick active layer was deposited from a fresh solution of P3HT in chloroform (10mg/ml) by spin-coating at 1000 rpm for 30s onto the bare (not treated) substrate. threshold voltage $U_T = -12\ V$, independent on the channel length

We observed that the mobility dependences can be generally very different either in absolute values of mobility changes by several order of magnitudes or in their profiles. This is given by the variability of the dependence $\mu_{molecular-scale}(z,\rho(x,z),E_z(x,z))$ with respect to the charge concentration ρ and transversal electric field E_z for concrete morphology.

In the estimation of the mobility dependences we took the identical methodological concept as indicated in the main text, utilizing identical equations for separation of mobility and contact resistances for given gate voltage, with threshold voltage estimation from the conductance $g_{s-Ohmic}$ (Eq. 13 in the main text) in the Ohmic limit for each channel length. For the latter one we found it independent on the channel length.

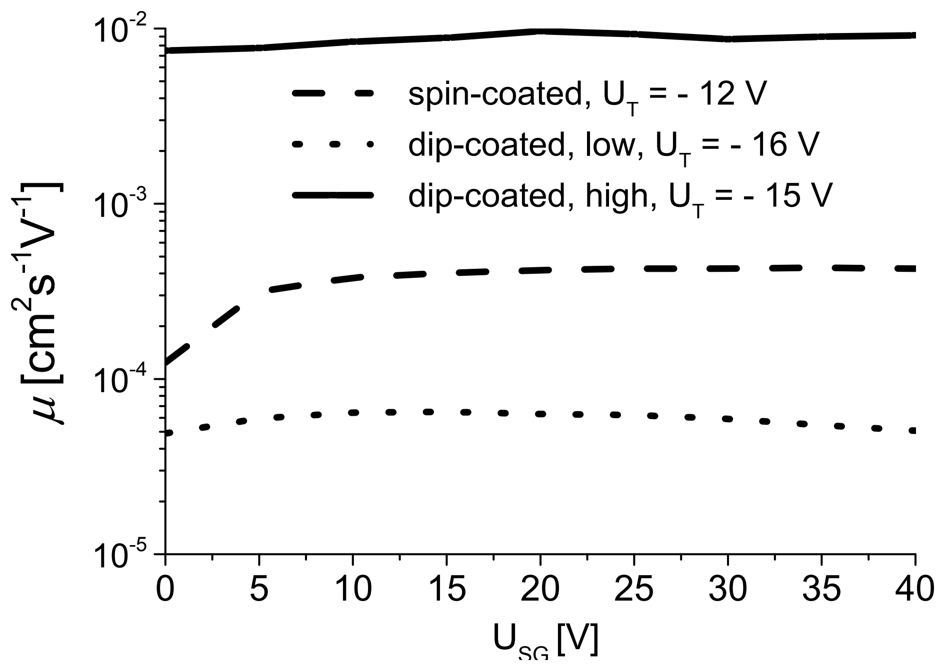

Fig. S2: Mobility dependences for P3Ht samples prepared under different conditions.

References

[S1] P. Toman, M. Menšík, W. Bartkowiak, J. Pfleger, Phys. Chem. Chem. Phys. 19 (2017) 7760