

Electronic Supplementary Information to

Gate voltage impact on charge mobility in end-on stacked conjugated oligomers

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Relation between the transverse and longitudinal electric fields in thin film OFETs satisfying the capacity relation.

In this section we derive the relation between the transversal and longitudinal electric field, which must be fulfilled so that the capacity relation (Eq. 3 of the main text) can be satisfied.

The mutual relation of the transverse and longitudinal electric fields can be estimated from the current conservation law in the longitudinal (x -) direction.

$$J_x = w\mu(V(x,0), E_x(x,0))\sigma(x)E_x(x,0) = const. \quad (S1)$$

In (S1) we assumed that the mobility $\mu(V(x,0), E_x(x,0))$ is a function of the potential $V(x,0)$ and the longitudinal electric field $E_x(x,0)$ in the thin film OFET model. The dependence on $V(x,0)$ includes both the dependence on the transversal electric field across the sample as well as on the accumulated surface charge density $\sigma(x)$ (cf. Eq. 3 of the main text). Next, we assume the current density is equal across the total width w of the sample in the y -direction. Inserting Eq. (3) of the main text to (S1) and taking its derivative along x we find

$$\frac{\partial}{\partial x} J_x = wC \frac{\partial}{\partial x} (\mu(V(x,0), E_x(x,0)) (V(x,0) - V_G) E_x(x,0)) \equiv 0 \quad (S2)$$

Then, introducing notations

$$V_{xG} \equiv V(x,0) - V_G \quad (S3)$$

$$E_x \equiv E_x(x,0) \quad (S4)$$

Eq. (S2) provides

$$-\left(\frac{\partial \mu}{\partial V_{xG}} V_{xG} + \mu\right) E_x E_x + \left(\frac{\partial \mu}{\partial E_x} E_x + \mu\right) V_{xG} \frac{\partial E_x}{\partial x} = 0 \quad (S5)$$

Consequently,

$$\frac{\partial E_x}{\partial x} = \frac{\left(\frac{\partial \mu}{\partial V_{xG}} V_{xG} + \mu\right) E_x^2}{\left(\frac{\partial \mu}{\partial E_x} E_x + \mu\right) V_{xG}} = \frac{\left(\frac{\partial \ln \mu}{\partial \ln V_{xG}} + 1\right) E_x^2}{\left(\frac{\partial \ln \mu}{\partial \ln E_x} + 1\right) V_{xG}} \quad (S6)$$

In the 1d thin film OFET model $\frac{\partial E_y}{\partial y} = 0$, $\frac{\partial E_x}{\partial x} \ll \frac{\partial E_z}{\partial z}$ so that the Poisson equation provides

$$\frac{\partial E_x}{\partial x} = \frac{\left(\frac{\partial \ln \mu}{\partial \ln V_{xG}} + 1\right) E_x^2}{\left(\frac{\partial \ln \mu}{\partial \ln E_x} + 1\right) V_{xG}} \ll \frac{\partial E_z}{\partial z} \approx \frac{\rho(x,0)}{\epsilon_s} \quad (S7)$$

Taking for the right hand side of Eq. (S7) the macroscopic approximation

$$\rho(x,0) = \frac{e \epsilon_{ins}^2 V_{xG}^2}{2KT d^2 \epsilon_s} \quad (\text{Ref. S1}) \text{ we get}$$

$$\frac{\left(\frac{\partial \ln \mu}{\partial \ln V_{xG}} + 1\right) E_x^2}{\left(\frac{\partial \ln \mu}{\partial \ln E_x} + 1\right) V_{xG}} \ll \frac{e \epsilon_{ins}^2 V_{xG}^2}{2KT \epsilon_s^2 d^2} \quad (S8)$$

Utilizing next Eq. (2) of the main text ($E_z(x,0) = -\frac{\epsilon_{ins}(V_{xG})}{\epsilon_s d}$) for the transversal component of the electric field at the bottom we finally arrive at the condition

$$\frac{E_x^2}{E_z^2} \ll \frac{eV_{xG} \left(\frac{\partial \ln \mu}{\partial \ln E_x} + 1 \right)}{2KT \left(\frac{\partial \ln \mu}{\partial \ln V_{xG}} + 1 \right)} .$$

(S9)

Eq. (S9) provides the necessary condition between the longitudinal and transversal electric fields which must be fulfilled for validity of the capacity relation in Eq. 3 of the main text. Assuming that the logarithmic dependence of mobility on applied voltages is of the order of

unity we come to the relation $\frac{E_x^2}{E_z^2} \ll \frac{eV_{xG}}{2KT}$ mentioned in the main text.

The principle of the numerical self-consistent solution of the Gaussian law and current transport within the “simulation box”

In this section we describe the numerical details of the self-consistent solution of the Gaussian law and the current transport inside the “simulation” box.

The “simulation box” consists of a finite number $n_x = 25$ of chains numerated by the index k , while respective chains consist of $n_p = 20$ monomer units numerated by the index i .

$$\nabla \cdot \vec{E} = -\Delta V = \frac{\rho}{\epsilon_s}$$

Therefore, the macroscopic variables, which enter the Gaussian law must be calculated on the discrete state space of points (k,i) . The transcription of the Gaussian law to the discrete variables inside the box is given by Eq. 10 of the main text. For the boundary conditions of the thin film OFET (Eqs. 1-3 of the main text) we find the following: Eq. (1) takes the form

$$V(k, n_p) = V(k, n_p - 1), \tag{S10}$$

for all chains. From Eq. 2 of the main text we get also the condition for the potential $V(k, 1)$ at the bottom of the chain expressed via the potential $V_x(k)$ at the interface between the sample and insulator of the k -th chain.

$$V(k, 1) = \left(1 - \frac{\epsilon_{ins} a_z}{\epsilon_s d} \right) V_x(k) + \frac{\epsilon_{ins} a_z}{\epsilon_s d} V_G . \tag{S11}$$

In Eq. (S11) and below a_x, a_y, a_z are the lengths of the elementary unit (k, i) in respective directions. The interface potential $V_x(k)$ can be, in turn, obtained from the capacity relation (Eq. (3) of the main text) through the total amount of the macroscopic charge $en_I(k)$ per k -th chain (cf. Eq. 6 of the main text) as follows

$$V_x(k) = V_G + \frac{en_I(k)d}{a_x a_y \epsilon_{ins}}$$

(S12)

For setting the boundary conditions for the outer chains, i.e., for $k = n_x$ and $k = 1$ with the externally controlled parameters V_S and V_D (“source” and “drain” potentials) we find

$$-\frac{1}{a_x^2}\{V_S - 2V(n_x, i) + V(n_x - 1, i)\} - \frac{1}{a_z^2}\{V(n_x, i - 1) - 2V(n_x, i) + V(n_x, i + 1)\} = \frac{\rho(n_x, i)}{\epsilon_s}$$

(S13)

$$-\frac{1}{a_x^2}\{V(2, i) - 2V(1, i) + V_D\} - \frac{1}{a_z^2}\{V(1, i - 1) - 2V(1, i) + V(1, i + 1)\} = \frac{\rho(1, i)}{\epsilon_s}$$

(S14)

Eqs. (13-14) say that in performing the “second discrete derivatives” in the Gaussian law

$$-\Delta V = \frac{\rho}{\epsilon_s}$$

on the boundary chains we should extend the potential beyond the boundary chains. For this extended regions we set the potentials V_S and V_D . This approach corresponds to the far field approximation, where the simulation box (micro cavity) is embedded into the potential slope $V_{SD} = V_S - V_D$ of the external electric field. Depending on the particular coupling of the conducting sample to the “real” source and drain contacts, the calibrating of the potential V_S and V_D for the “outer” chains can be in principle varied. For the cases of the “bottom-bottom” or “top-top” contacts, they can be set and fixed just at the bottom or top of the “outer” chains. Alternatively, potentials V_S and V_D could be identified with mean values $V_S \equiv \langle V(n_x) \rangle$ and $V_D \equiv \langle V(1) \rangle$ of the potentials of the outer chains given as

$$V(k) = \frac{\sum_i V(k,i)n(k,i)}{\sum_i n(k,i)}$$

(S15)

Potentials (S15) control then the hopping kinetics between chains with the current

$$J_x = -w\mu(k) \frac{en_I(k)}{a_x \cdot a_y} \cdot \frac{(V(k+1) - V(k))}{a_x} \rightarrow w\mu(V(x), E_x(x,0)) \sigma(x) E_x(x,0) \quad (\text{see Eq.S1}).$$

However, for the “Ohmic” limit ($|V_S - V_D| \ll |V_S - V_G|$) the self-consistent solution of the density –potential distribution is just little sensitive to such variances in the boundary condition definitions .

The eqs. (S10-14) and Eqs. (6, 10) (main text) represent the system of linear algebraic equations between algebraic vectors $[\rho]$ and $[V]$ in the form

$$[\rho] = [M][V] + [const(V_S, V_D)], \quad (\text{S16})$$

where the vector $[const(V_S, V_D)]$ is given by the applied voltages V_S and V_D .

The iterative algorithm in the numerical calculation is:

- (1) Give an initial vector $[\rho]$.
- (2) Obtain a “solution” vector $[V]$ from Eqs. (S10-14) and Eqs. (6, 10) (main text).
- (3) Obtain a new vector $[\rho']$ from Eqs. 4-6 (main text).
- (4) Put the new vector $[\rho']$ to Eq. (S16), then obtain a new vector $[V']$.
- (5) If $[V] = [V']$ we obtain the self-consistent results, otherwise, let $[\rho'] = [\rho]$ and put it back to the procedure (2).
- (6) Eventually, the final $V(k,i)$ and $\rho(k,i)$ are calculated by proceeding the inverse transformation from the algebraic vector space to the two-dimensional (k,i) space.

Reference

[S1] C. H. Kim, Y. Bonnassieux and G. Horowitz, *IEEE Trans. Electron Devices* 2013, **60**, 280