Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information
Theoretical Part – Processing of the Formulas Used for Experimental Data Analysis

Impedance spectroscopy of OLEDs as a tool for estimating mobility and the concentration of charge carriers in transport layers

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Here we will thoroughly discuss an approach that led to the final formula with minimal essential approximations. The derivation procedure was not spontaneous and we didn't follow any universal algorithm. Several approaches were used and various assumptions made until the adequate calculation results were achieved.

Table 1. Symbols, their physical meanings, values and dimensions which they are assigned in this article unless another is specified.

Symbol	Physical meaning	Dimension or value
i	current density	$A \cdot m^{-2}$
U	voltage	V
x	distance	m
μ	charge carrier mobility	$m^2 \cdot V^{-1} \cdot s^{-1}$
n	concentration of charge carriers or charge density	m^{-3}
E	electric field intensity	$V \cdot m^{-1}$
e	electron charge	$1.60 \cdot 10^{-19}$ C
d	layer thickness	m
ε_0	vacuum permittivity	$8.85 \cdot 10^{-12}$ $F \cdot m^{-1}$
ε	relative material permittivity	$F \cdot m^{-1}$
j	imaginary unit	$\sqrt{-1}$
Z, Z_{re}, Z_{im}	impedance (complex value), real and imaginary part	Ω
Y	admittance	Ω^{-1}
C	capacitance normalised by surface area	$F\ m^{-2}$
R	resistance normalised by surface area	$\Omega\ m^2$
δx	thickness of ultrathin discrete thin layer	m
δU	voltage drop in discrete thin layer	V
δn	difference of charge carrier concentrations in two neighbour discrete layers	m^{-3}
Δi	periodic current oscillation (complex value)	i
ΔU	periodic voltage oscillation (complex value)	V
Δn	periodic concentration oscillation (complex value)	n
$\tilde{i}$	current phasor (complex value)	i
$\tilde{U}$	voltage phasor (complex value)	V
$\tilde{n}$	concentration phasor (complex value)	n

The two fundamental formulas describing charge transfer in semiconductors were used: migration current (A1) and Poisson's equation (A2).

$$i = zen\mu \frac{\mathrm{d}U}{\mathrm{d}x}, \tag{S1}$$

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{e}{\varepsilon\varepsilon_0} zn, \tag{S2}$$

Only one type of charge carriers is assumed to prevail in a layer. Therefore the only term *n* will be considered in (S2). Another assumption is concerned with homogeneity of the layer, i.e. charge carrier concentration, mobility and potential gradient is the same in the entire single layer. The diffusion flux of charge carriers is considered negligibly small compared with the flux driven by electric field. It may be not obvious at low voltages but is reasonable for the major part of the spectrum when voltage is higher than 5 V since layer thicknesses are very small ($20 < d < 100$ nm).

The current perturbation signal is supposed to be dependent on voltage and charge density perturbation. The term "oscillation" will be used further instead of "perturbation" for it is sinusoidal. Then Δi function is represented as Taylor series neglecting second and higher order derivatives (S3). Additionally, a capacitive term was taken into account because capacitance behaviour was clearly observed experimentally.

$$\Delta i = \left(\frac{\partial i}{\partial U}\right)\Delta U + \left(\frac{\partial i}{\partial n}\right)\Delta n + C\frac{\partial \Delta U}{\partial t} \tag{A3}$$

Then one has to find a relation between Δn, ΔU and Δi. For that let's consider very thin discrete layer with a thickness δx inside the film posed perpendicular to charge transfer. The impedance will be derived for the one single discrete layer and then generalised to the whole system. Three discrete layers and their parameters are schematically presented in Figure S1.

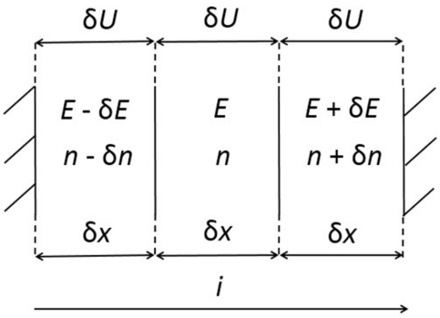

Figure S1. Schematic representation of three neighbour discrete layers and difference of electric field intensity and charge between them.

The contradiction between constant potential gradient and varying electric field intensity ($E = -\mathrm{d}U/\mathrm{d}x = \delta U/\delta x$) may be noticed. However, if the layer thickness and charge carrier concentration are small enough then $\delta E << E$ and $\delta n << n$. Anyway, the slight gradient of *E* and *n* cannot be neglected because it is responsible for capacitive properties of organic layer.

Experimantal observation of capacitance means that oscillation of film charge under ac voltage condition takes place. The capacitive behaviour is stipulated by inconsistent charge transfer between the layers during oscillation.

According to (1) current is proportional to both electric field intensity (potential gradient) and concentration: $i \sim nE$. In stationary state (under dc conditions) current passing through all the borders is the same, otherwise infinite accumulation or depletion of charge would be observed. Therefore equating current passing through neighbour layers (Figure S1) one can write

$$nE = (n + \delta n)(E + \delta E) \tag{S4}$$

that after rearrangement gives relation (A5):

$$\delta n = -\frac{n\delta E}{E+\delta E} \qquad \text{(S5)}$$

Second derivative of voltage on distance can be presented in a discrete form: $\frac{\mathrm{d}E}{\mathrm{d}x} \approx \frac{\delta E}{\delta x}$ and then rearranging (S2) the formula relating δ*E* and *n* is obtained:

$$\delta E = \frac{ez}{\varepsilon\varepsilon_0} n\left(\delta x\right) \qquad \text{(S6)}$$

Substituting δ*E* from (S6) into (S5) one gets (S6):

$$\delta n = -\frac{e}{\varepsilon\varepsilon_0} \frac{zn^2\left(\delta x\right)}{E + \frac{e}{\varepsilon\varepsilon_0} n\left(\delta x\right)} \qquad \text{(S7)}$$

Value *E* in the denominator must be prevailing to obey the condition $\delta n \ll n$. Thus the formula is simplified to (S8).

$$\delta n = -\frac{e}{\varepsilon\varepsilon_0} \frac{zn^2\left(\delta x\right)}{E} = -\frac{e}{\varepsilon\varepsilon_0} \frac{zn^2\left(\delta x\right)^2}{\delta U} \qquad \text{(S8)}$$

Charge corresponding to δ*n* is an accumulated charge of the layer of thickness δ*x*. If $\delta n = 0$ then no capacitive behaviour would be observed experimentally as happens in case of conductors.

The charge density total difference along the layer can be estimated from differential equation (S9).

$$\int_{n_{\min}}^{n_{\max}} \frac{\mathrm{d}n}{n^2} = -\int_0^d \frac{e}{\varepsilon\varepsilon_0} \frac{z}{E} \mathrm{d}x \qquad \text{(S9)}$$

which leads to

$$\Delta n = n_{\max} - n_{\min} = \frac{ezd}{E\varepsilon\varepsilon_0} n_{\max} \cdot n_{\min} \qquad \text{(S10)}$$

The product $n_{\max} \cdot n_{\min}$ can be substituted by square of geometric average n^2.

The capacitance of the layer of thickness *d* equals $C = \frac{\mathrm{d}q}{\mathrm{d}U} = ezd\frac{\mathrm{d}\left(\Delta n\right)}{\mathrm{d}U}$. Deriving (S10) by *U* one gets final formula (S11) relating capacitance, average charge carrier concentration and potential gradient.

$$C = \frac{e^2 z^2 n^2 d}{\varepsilon\varepsilon_0 E^2} \qquad \text{(S11)}$$

Oscillation of charge carrier concentration is directly related to the capacitance:

$$\Delta n = \frac{C\Delta U}{zed} \qquad \text{(S12)}$$

Substituting resulting expressions for Δ*n* into (S3) and deriving (S1) one gets (S13).

$$\Delta i = \left(zen\mu\frac{1}{d}\right)\Delta U + \left(ze\mu\frac{U}{d}\right)\frac{C\Delta U}{zed} + C\frac{\partial \Delta U}{\partial t} \qquad \text{(S13)}$$

When a small ac perturbation signal, $\Delta U = \tilde{U}\exp\left(i\omega t\right)$, is applied, the current and other current- or voltage-dependent parameters oscillate around their steady-state values: $i = i_{dc}+\Delta i$, $n = n_{dc}+\Delta n$, and $U = U_{dc}+\Delta U$. Here index «dc» designates the part which doesn't change with ω frequency.

In general the oscillating potential and the concentrations may be written as harmonic functions of complex non-time-dependent phasors.

$$\Delta U = \tilde{U}\exp(j\omega t),\ \Delta i = \tilde{i}\exp(j\omega t),\ \Delta n = \tilde{n}\exp(j\omega t) \qquad \text{(S14)}$$

Substituting formulas (S14) into (S13) and accomplishing differentiation procedure one gets an equation (S15)

$$\tilde{i} = \left(zen\mu\frac{1}{d}\right)\tilde{U} + \left(\mu\frac{U}{d}\right)\frac{C\tilde{U}}{d} + j\omega C\tilde{U} \qquad \text{(S15)}$$

The last formula is easily rearranged to express impedance of the layer according to (S16) and (S17).

$$Z = \tilde{U}/\tilde{i} \qquad \text{(S16):}$$

$$Z = \frac{1}{zen\mu\frac{1}{d} + \mu\frac{CU}{d^2} + j\omega C} \qquad \text{(S17)}$$

The denominator contains one real and one imaginary term which are attributed to resistor and capacitor respectively. If we assign the real term ($zen\mu\frac{1}{d} + \mu\frac{CU}{d^2}$) as $1/R$ then a simple expression (S18) describing impedance of an equivalent electrical circuit (Figure S2) is obtained.

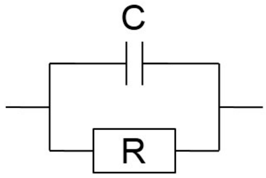

Figure S2. Equivalent electrical circuit of an organic semiconductor layer.

$$Z = \frac{1}{\frac{1}{R} + j\omega C} \qquad \text{(S18)}$$

From spectrum analysis values of R and C can be estimated.

Having three values (i, R, C) three other (n, E, μ) can be calculated (S17)-(S19).

$$n = \frac{iR}{zed}\left(\sqrt{\frac{\varepsilon\varepsilon_0}{d}}C + C\right) \qquad \text{(S19)}$$

$$E = \frac{iR}{d}\left(1 + \sqrt{\frac{dC}{\varepsilon\varepsilon_0}}\right) \qquad \text{(S20)}$$

$$\mu = \frac{d^2}{iR^2C}\frac{1}{\left(1+\sqrt{\frac{dC}{\varepsilon\varepsilon_0}}\right)^2}\sqrt{\frac{dC}{\varepsilon\varepsilon_0}} \qquad \text{(S21)}$$