

## Supporting Information

### Non-Nernstian Behavior in Organic Electrochemical Transistors: Fundamental Processes and Theory

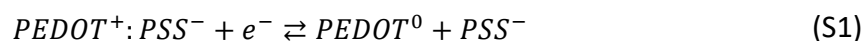
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#### S1. PEDOT:PSS as gate the electrode;

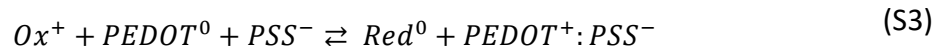
Few applications may require the use of OMEICs as the gate electrode, such as PEDOT:PSS in modified gate electrodes. In this case, a similar approach as given to Ag/AgCl in the main text can be used in the PEDOT:PSS. The electrochemical equilibrium describing the OECT device must be rewritten, accounting to the reaction occurring at the PEDOT:PSS gate electrode described by:



where,  $PEDOT^+$  and  $PEDOT^0$  are the oxidized and reduced species of gate electrode. Considering the OECT with a p-type material in the channel, the same reaction as Equation 6 in the main text can be used:



Coupling the reaction at the gate electrode (Equation S1) to the channel reaction (Equation S2) leads to the global electrochemical reaction (Equation S3), and its respective Nernst Equation (Equation S4):



$$\mathcal{E} = \mathcal{E}_{pol}^\ominus - \mathcal{E}_{PEDOT}^\ominus - \frac{RT}{nF} \ln \frac{[PEDOT^+][Red^0]}{[PEDOT^0][Ox^+]} \quad (S4)$$

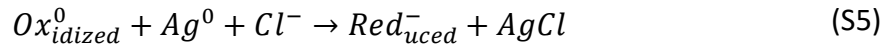
Notice that there is a dependence on the concentrations of the reduced and oxidized species, both in the channel and at the gate electrode. Thus, this electrochemical equilibrium is valid only as long as there are electrochemically active species to sustain the reaction (Equation S3). In this case, certain considerations can be made. The first is to assume, as in the main text, a single-electron reaction, where one charge depleted at the gate electrode results in one charge

created at the channel. The second is assuming that are enough species ate gate electrode to fully oxidize the OECT channel, the concentration of reduced ( $C_{Red^0}$ ) and oxidized at channel ( $C_{Ox^+}$ ) can be considered equal to  $C_{PEDOT^+}$  and  $C_{PEDOT^0}$ , respectively. The model development can then follow the same conditions as for the Ag/AgCl gate electrode.

However, once the species at the gate electrode are fully consumed, the electrochemical equilibrium is no longer valid, a double layer forms at the gate electrode, and additional considerations must be made.

## S2. Model development to an n-type channel polymer;

Considering OECTs with n-type active material, the global electrochemical reaction is given by:



where  $Ox_{idized}^0$  is the polymer on neutral state, and  $Red_{uced}^-$  its reduced state with excess of negative charges. Giving the same treatment as for p-type material, Nernst equation can be written as Equation (S6)

$$\mathcal{E}_{ch} = \mathcal{E}_{pol}^\ominus - \frac{RT}{F} \ln \frac{C_{Red^-}}{C_{Ox^0}} \quad (S6)$$

$$\Delta V_{meas} = \mathcal{E}_{ch} - \mathcal{E}_g = \mathcal{E}_{pol}^\ominus - \mathcal{E}_g - \frac{RT}{F} \ln \frac{C_{Red^-}}{C_{Ox^0}} \quad (S7)$$

$$\Delta V_{meas} = \mathcal{E}_{pol}^{\ominus'} - \frac{RT}{F} \ln \frac{C_{Red^-}}{C_{Ox^0}} \quad (S8)$$

with  $\mathcal{E}_{pol}^{\ominus'} = \mathcal{E}_{pol}^\ominus - \mathcal{E}_g$ .

Here, the density of available states is considered as coming from the contribution of carries concentration ( $\rho_{max}$ ) of reduced and oxidized species as Equation (S9). However, different from the approach to p-type material, in n-type materials the active species carrier's ( $\rho_{Red^-}$ ) corresponds to the reduced one ( $C_{Red^-}$ ):

$$\rho_{max} = C_{Red^-} + C_{Ox^0} \quad (S9)$$

$$\rho_{Ox^0} = \rho_{max} - \rho_{Red^-} \quad (S10)$$

Plugging Equation (S9) and (S10) into Equation (S8) produces :

$$\Delta V_{meas} = \mathcal{E}_{pol}^{\ominus'} - \frac{RT}{F} \ln \frac{\rho_{Red^-}}{\rho_{max} - \rho_{Red^-}} \quad (S11)$$

Equation (S11), can be applied to a local x position of channel, and assume the following format:

$$\Delta V_{x,g} = \mathcal{E}(x) - \mathcal{E}_g = \mathcal{E}_{pol}^{\ominus'} - \frac{RT}{F} \ln \frac{\rho_{Red^-}(x)}{\rho_{max} - \rho_{Red^-}(x)} \quad (S12)$$

Given the local carrier concentration can be written as:

$$\rho_{Red^-}(x) = \frac{\rho_{max} \exp \left[ \frac{F}{RT} (\mathcal{E}_{pol}^{\ominus'} - \mathcal{E}(x) + \mathcal{E}_g) \right]}{1 + \exp \left[ \frac{F}{RT} (\mathcal{E}_{pol}^{\ominus'} - \mathcal{E}(x) + \mathcal{E}_g) \right]} \quad (S13)$$

Here, the local carrier concentration ( $\rho_{Red^-}(x)$ ) is coupled on Ohm's law (Equation (S14)-(S19)).

$$J(x) = -F \mu_e \rho(x) \frac{d\mathcal{E}(x)}{dx} \quad (S14)$$

Considering the contribution from doped and undoped species, Ohm's Law can be rewritten as:

$$J(x) = -F (\mu_{Ox^0} \rho_{Ox^0}(x) + \mu_{Red^-} \rho_{Red^-}(x)) \frac{d\mathcal{E}(x)}{dx} \quad (S15)$$

$$J(x) = -F (\mu_{Ox^0} (\rho_{max} - \rho_{Red^-}(x)) + \mu_{Red^-} \rho_{Red^-}(x)) \frac{d\mathcal{E}(x)}{dx} \quad (S16)$$

$$J(x) = -F (\mu_{Ox^0} \rho_{max} - \mu_{Ox^0} \rho_{Red^-}(x) + \mu_{Red^-} \rho_{Red^-}(x)) \frac{d\mathcal{E}(x)}{dx} \quad (S17)$$

$$J(x) = -F (\mu_{Ox^0} \rho_{max} + (\mu_{Red^-} - \mu_{Ox^0}) \rho_{Red^-}(x)) \frac{d\mathcal{E}(x)}{dx} \quad (S18)$$

Applying the carrier concentration defined in Equation (S13):

$$J(x) = -F \left( \mu_{Ox^0} \rho_{max} + (\mu_{Red^-} - \mu_{Ox^0}) \frac{\rho_{max} \exp \left[ \frac{F}{RT} (\mathcal{E}_{pol}^{\ominus'} - \mathcal{E}(x) + \mathcal{E}_g) \right]}{1 + \exp \left[ \frac{F}{RT} (\mathcal{E}_{pol}^{\ominus'} - \mathcal{E}(x) + \mathcal{E}_g) \right]} \right) \frac{d\mathcal{E}}{dx} \quad (S19)$$

Expressing Equation (S19) in terms of the channel's geometric parameters, with  $w$ ,  $h$ , and  $l$  representing the width, thickness, and length of the channel, respectively:

$$\frac{I_{ds}(x)}{wh} = -F \left( \mu_{Ox^0} \rho_{max} + (\mu_{Red^-} - \mu_{Ox^0}) \frac{\rho_{max} \exp \left[ \frac{F}{RT} (\mathcal{E}_{pol}^{\ominus'} - \mathcal{E}(x) + \mathcal{E}_g) \right]}{1 + \exp \left[ \frac{F}{RT} (\mathcal{E}_{pol}^{\ominus'} - \mathcal{E}(x) + \mathcal{E}_g) \right]} \right) \frac{d\mathcal{E}}{dx} \quad (S20)$$

Integrating Equation (S20) over the channel dimensions (Equation (S21)), the analytical equation that describes drain-source current for OECT steady state operation considering an n-type channel device can be obtained.

$$\int_0^l \frac{I_{ds}(x)}{wh} dx = \int_{\mathcal{E}_s}^{\mathcal{E}_d} F \left( \mu_{Ox^0} \rho_{max} + (\mu_{Red^-} - \mu_{Ox^0}) \frac{\rho_{max} \exp \left[ \frac{F}{RT} (\mathcal{E}_{pol}^{\ominus'} - \mathcal{E}(x) + \mathcal{E}_g) \right]}{1 + \exp \left[ \frac{F}{RT} (\mathcal{E}_{pol}^{\ominus'} - \mathcal{E}(x) + \mathcal{E}_g) \right]} \right) d\mathcal{E} \quad (S21)$$

$$I_{ds} = \frac{wh}{l} \left( \mu_{Ox^0} \rho_{max} F (\mathcal{E}_d - \mathcal{E}_s) + (\mu_{Red^-} \rho_{max} F - \mu_{Ox^0} \rho_{max} F) \frac{RT}{F} \ln \left[ \frac{1 + \exp \left[ \frac{F}{RT} (\mathcal{E}_{pol}^{\ominus'} + \mathcal{E}_g - \mathcal{E}_s) \right]}{1 + \exp \left[ \frac{F}{RT} (\mathcal{E}_{pol}^{\ominus'} - \mathcal{E}_d + \mathcal{E}_s) \right]} \right] \right) \quad (S22)$$

Equation (S22) can be simplified considering that the electrode potentials ( $\mathcal{E}$ ) can be rewritten as the gate ( $\Delta V_{gs}$ ) and drain ( $\Delta V_{ds}$ ) potential applied into the device (Equations (S23) – (S25)).

$$\Delta V_{ds} = \mathcal{E}_d - \mathcal{E}_s \quad (S23)$$

$$\Delta V_{gs} = \mathcal{E}_g - \mathcal{E}_s \quad (S24)$$

$$\Delta V_{dg} = \mathcal{E}_d - \mathcal{E}_g = \Delta V_{ds} - \Delta V_{gs} \quad (S25)$$

The final Equation (S26) describes drain-source current for OECT steady-state operation considering a n-type channel device:

$$I_{ds} = \frac{wh}{l} \left( \mu_{Ox^0} \rho_{max} F \Delta V_{ds} + (\mu_{Red^-} \rho_{max} F - \mu_{Ox^0} \rho_{max} F) \frac{RT}{F} \ln \left[ \frac{1 + \exp \left[ \frac{F}{RT} (\mathcal{E}_{pol}^{\ominus'} + \Delta V_{gs}) \right]}{1 + \exp \left[ \frac{F}{RT} (\mathcal{E}_{pol}^{\ominus'} - \Delta V_{ds} + \Delta V_{gs}) \right]} \right] \right) \quad (S26)$$

In terms of dimensional analysis, the pre-factor product  $\mu \rho_{max} F$  has S·cm<sup>-1</sup> as unity. This, in particular, allows us to rewrite Equation (S26) considering the conductivity of the channel device. The terms related to  $\mu_{Red^-}$  originate the residual conductivity of the channel ( $\sigma_{res}$ ), and those related to  $\mu_{Ox^+}$ , give origin to the actual conductivity of the channel ( $\sigma$ ). The final drain current Equation for the p-type active layer is shown in Equation (S27).

$$I_{ds} = \frac{wh}{l} \left( \sigma_{res} \Delta V_{ds} + (\sigma - \sigma_{res}) \frac{RT}{F} \ln \left[ \frac{1 + \exp \left[ \frac{F}{RT} (\mathcal{E}_{pol}^{\ominus'} + \Delta V_{gs}) \right]}{1 + \exp \left[ \frac{F}{RT} (\mathcal{E}_{pol}^{\ominus'} - \Delta V_{ds} + \Delta V_{gs}) \right]} \right] \right) \quad (S27)$$

### S3. Mathematical development to a p-type channel polymer:

Here we present a calculation from Equation 15 to 21 in the main text.

Through the Ohm's law as below:

$$J(x) = -F \mu_e \rho(x) \frac{d\mathcal{E}(x)}{dx} \quad (S28)$$

and considering the contribution from doped and undoped species, Ohm's Law is rewritten as:

$$J(x) = -F (\mu_{Red^0} \rho_{Red^0}(x) + \mu_{Ox^+} \rho_{Ox^+}(x)) \frac{d\mathcal{E}(x)}{dx} \quad (S29)$$

here  $\mu$  and  $\rho$  are the electronic mobility and carrier density, respectively for reduced ( $Red^0$ ) and oxidized ( $Ox^+$ ) states. Plugging in Equations (S30) and (S31), see below, into Equation (S29), produces Equation (S5) as follows:

$$\rho_{max} = C_{Red^0} + C_{Ox^+} = \rho_{Red^0} + \rho_{Ox^+} \quad (S30)$$

$$\rho_{Red^0} = \rho_{max} - \rho_{Ox^+} \quad (S31)$$

$$J(x) = -F \left( \mu_{Red^0} (\rho_{max} - \rho_{Ox^+}(x)) + \mu_{Ox^+} \rho_{Ox^+}(x) \right) \frac{d\mathcal{E}(x)}{dx} \quad (S32)$$

$$J(x) = -F \left( \mu_{Red^0} \rho_{max} - \mu_{Red^0} \rho_{Ox^+}(x) + \mu_{Ox^+} \rho_{Ox^+}(x) \right) \frac{d\mathcal{E}(x)}{dx} \quad (S33)$$

$$J(x) = -F \left( \mu_{Red^0} \rho_{max} + (\mu_{Ox^+} - \mu_{Red^0}) \rho_{Ox^+}(x) \right) \frac{d\mathcal{E}(x)}{dx} \quad (S34)$$

The carrier concentration was previously defined as (Equation 14 in the main text):

$$\rho(x) = \frac{\rho_{max}}{1 + \exp \left[ -\frac{F}{RT} \left( \mathcal{E}(x) - \mathcal{E}_g - \mathcal{E}_{pol}^{\ominus'} \right) \right]} \quad (S35)$$

Equation (S34) assumes the form of:

$$J(x) = -F \left( \mu_{Red^0} \rho_{max} + \frac{\mu_{Ox^+} \rho_{max} - \mu_{Red^0} \rho_{max}}{1 + \exp \left[ -\frac{\gamma F}{RT} \left( \mathcal{E}(x) - \mathcal{E}_g - \mathcal{E}_{pol}^{\ominus'} \right) \right]} \right) \frac{d\mathcal{E}(x)}{dx} \quad (S36)$$

To obtain the drain-current equation along the channel, Equation (S36) is then expressed in terms of the channel's geometric parameters, with  $w$ ,  $h$ , and  $l$  representing the width, thickness, and length of the channel in centimeters, respectively, and:

$$\frac{I_{ds}(x)}{wh} = -F \left( \mu_{Red^0} \rho_{max} + \frac{\mu_{Ox^+} \rho_{max} - \mu_{Red^0} \rho_{max}}{1 + \exp \left[ \frac{\gamma F}{RT} \left( \mathcal{E}_{pol}^{\ominus'} - \mathcal{E}(x) + \mathcal{E}_g \right) \right]} \right) \frac{d\mathcal{E}}{dx} \quad (S37)$$

$$\int_0^l \frac{I_{ds}(x)}{wh} dx = -F \int_{\mathcal{E}_s}^{\mathcal{E}_d} \left( \mu_{Red^0} \rho_{max} + \frac{\mu_{Ox^+} \rho_{max} - \mu_{Red^0} \rho_{max}}{1 + \exp \left[ \frac{\gamma F}{RT} \left( \mathcal{E}_{pol}^{\ominus'} - \mathcal{E}(x) + \mathcal{E}_g \right) \right]} \right) d\mathcal{E} \quad (S38)$$

Equation (S38) can be readily integrated to produce:

$$I_{ds} = \frac{wh}{l} \left( \mu_{Red^0} \rho_{max} F (\mathcal{E}_d - \mathcal{E}_s) + (\mu_{Ox^+} \rho_{max} F - \mu_{Red^0} \rho_{max} F) \frac{RT}{F} \ln \left[ \frac{1 + \exp \left[ \frac{F}{RT} (\mathcal{E}_d - \mathcal{E}_g - \mathcal{E}_{pol}^{\ominus'}) \right]}{1 + \exp \left[ \frac{F}{RT} (\mathcal{E}_s - \mathcal{E}_g - \mathcal{E}_{pol}^{\ominus'}) \right]} \right] \right) \quad (S39)$$

Considering that the applied potentials on gate ( $\Delta V_{gs}$ ) and drain ( $\Delta V_{ds}$ ) electrodes could be rewritten as function of electrode potentials ( $\mathcal{E}$ ):

$$\Delta V_{ds} = \mathcal{E}_d - \mathcal{E}_s \quad (S40)$$

$$\Delta V_{gs} = \mathcal{E}_g - \mathcal{E}_s \quad (\text{S41})$$

$$\Delta V_{dg} = \mathcal{E}_d - \mathcal{E}_g = \Delta V_{ds} - \Delta V_{gs} \quad (\text{S42})$$

Equation (S39), can assume the form of:

$$I_{ds} = \frac{wh}{l} \left( \mu_{Red^0} \rho_{max} F \Delta V_{ds} + (\mu_{Ox^+} \rho_{max} F - \mu_{Red^0} \rho_{max} F) \frac{RT}{F} \ln \left[ \frac{1 + \exp \left[ \frac{F}{RT} (\Delta V_{ds} - \Delta V_{gs} - \mathcal{E}_{pol}^{\ominus'}) \right]}{1 + \exp \left[ \frac{F}{RT} (-\Delta V_{gs} - \mathcal{E}_{pol}^{\ominus'}) \right]} \right] \right) \quad (\text{S43})$$

In terms of dimensional analysis, the pre-factor product  $\mu \rho_{max} F$  has  $S \cdot \text{cm}^{-1}$  as unity. This, in particular, allows us to rewrite Equation (S43) considering the conductivity of the channel device. The terms related to  $\mu_{Red^0}$  originate the residual conductivity of the channel ( $\sigma_{res}$ ), and those related to  $\mu_{Ox^+}$ , give origin to the actual conductivity of the channel ( $\sigma$ ). The final drain current Equation for the p-type active layer is shown in Equation (S44).

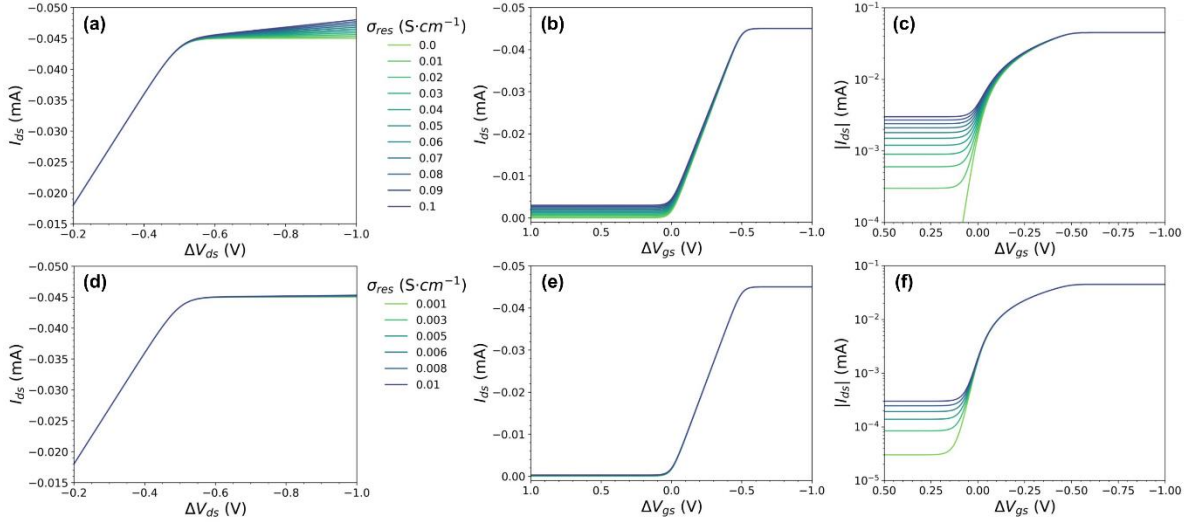
$$I_{ds} = \frac{wh}{l} \left( \sigma_{res} \Delta V_{ds} + (\sigma - \sigma_{res}) \frac{RT}{\gamma F} \ln \left[ \frac{1 + \exp \left[ \frac{\gamma F}{RT} (\Delta V_{ds} - \Delta V_{gs} - \mathcal{E}_{pol}^{\ominus'}) \right]}{1 + \exp \left[ \frac{\gamma F}{RT} (-\Delta V_{gs} - \mathcal{E}_{pol}^{\ominus'}) \right]} \right] \right) \quad (\text{S44})$$

#### S4. Effects of $\sigma_0$ and $\sigma$ over output and transfer curves.

As shown in Figure S1, for the output curves (Figure S1(a)),  $\sigma_{res}$  influences the saturation level. The effect is significant for source-drain curves and with ON/OFF current ratios smaller than  $10^2$  (Figure S1(a)). Since OECTs generally have ON/OFF ratios of  $10^3$  to  $10^6$ , the effects of  $\sigma_0$  on the output curves are considerably reduced.

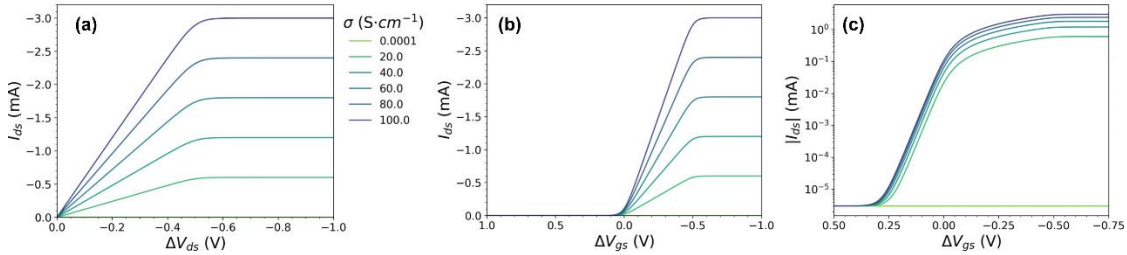
In contrast, for the transfer curves (Figure S1(b-c) and (e-f)),  $\sigma_{res}$  is related to a plateau in the source-drain current for potentials smaller than that for channel doping. On this curve region, for a  $\Delta V_{ds} > 0$  for an oxidation reaction, the channel is in the undoped condition, and the curves can be used to determine resistivity in the channel and estimate  $\sigma_{res}$ . This residual conductivity  $\sigma_{res}$  is used as a fixed input parameter to perform the experimental curves' fittings.

**Figure S1** – Effects of  $\sigma_{res}$  over output (a) and (d) at  $\Delta V_{gs} = -0.5 V$ , transfer (b-c) and (e-f) curves, for different ranges of  $\sigma_0$  in ideal case at  $\Delta V_{ds} = -0.5 V$ . Here were used the following parameters  $w = 1.5 \text{ mm}$ ,  $h = 100 \text{ nm}$ ,  $l = 250 \text{ }\mu\text{m}$ ,  $\sigma = 1.5 \text{ S}\cdot\text{cm}^{-1}$ ,  $\mathcal{E}_{pol}^{\ominus'} = 0 \text{ V}$ ,  $T = 298.15 \text{ K}$ .



$\sigma$  (Figure S2), on the other hand, will directly impact the saturation of the output and transfer curves, as well as the ON/OFF ratio of the devices, making it a relevant parameter mainly for the transduction of ionic signal into the electronic one.

**Figure S2** – Effects of  $\sigma$  over (a) output at  $\Delta V_{gs} = -0.5 V$ , (b) and (c) transfer curves at  $\Delta V_{ds} = -0.5 V$  in ideal case. Here were used the following parameters  $w = 1.5 \text{ mm}$ ,  $h = 100 \text{ nm}$ ,  $l = 250 \text{ }\mu\text{m}$ ,  $\sigma_{res} = 1\text{E-}4 \text{ S}\cdot\text{cm}^{-1}$ ,  $\mathcal{E}_{pol}^{\ominus'} = 0 \text{ V}$ ,  $T = 298.15 \text{ K}$ .



## S5. Non-Nernstian behavior and activity coefficient

As presented in the model development section, the Nernst equation for a monoelectronic reaction can be approximated as:

$$\mathcal{E} = \mathcal{E}_{pol}^{\ominus'} - \frac{RT}{F} \ln \frac{a_{Red^0}}{a_{Ox^+}} \approx \mathcal{E}_{pol}^{\ominus'} - \frac{RT}{F} \ln \frac{C_{Red^0}}{C_{Ox^+}} \quad (\text{S45})$$

Where  $a$  corresponds to the activities for the species ( $Red^0$ ) and oxidized ( $Ox^+$ ). Species activity is related to concentrations through the relationship  $a_i = \gamma_i C_i$ , where  $\gamma_i$  corresponds to the activity coefficient of the species of interest. When  $\gamma_i = 1$ ,  $a_i = C_i$  and the system behaves ideally. On the other hand, equation S38 can be rewritten as a function of activity coefficients:

$$\mathcal{E} = \mathcal{E}_{pol}^{\ominus'} - \frac{RT}{F} \ln \frac{\gamma_{Red^0} C_{Red^0}}{\gamma_{Ox^+} C_{Ox^+}} \quad (\text{S46})$$

Equation S40 is valid for any system (ideal and non-ideal). When for  $\gamma_i = 1$ ,  $a_i = C_i$  and the system behaves ideally. On the other hand, as discussed in the main text, semiconductor polymer systems are known to exhibit non-ideal behavior, and therefore the Nernst equation relates to concentrations as (Equation 23 in the main text):

$$\mathcal{E}_{non-id} = \mathcal{E}_{pol}^{\ominus'} - \frac{RT}{\gamma F} \ln \frac{C_{Red^0}}{C_{Ox^+}} \quad (S47)$$

Correlating equations S39 and S40, we have:

$$\ln \frac{\gamma_{Red^0} C_{Red^0}}{\gamma_{Ox^+} C_{Ox^+}} = \frac{1}{\gamma} \ln \left( \frac{C_{Red^0}}{C_{Ox^+}} \right) \quad (S48)$$

$$\ln \frac{\gamma_{Red^0}}{\gamma_{Ox^+}} + \ln \frac{C_{Red^0}}{C_{Ox^+}} = \frac{1}{\gamma} \ln \left( \frac{C_{Red^0}}{C_{Ox^+}} \right) \quad (S49)$$

$$\ln \frac{\gamma_{Red^0}}{\gamma_{Ox^+}} = \frac{1}{\gamma} \ln \left( \frac{C_{Red^0}}{C_{Ox^+}} \right) - \ln \left( \frac{C_{Red^0}}{C_{Ox^+}} \right) \quad (S50)$$

$$\ln \frac{\gamma_{Red^0}}{\gamma_{Ox^+}} = \left( \frac{1-\gamma}{\gamma} \right) \ln \left( \frac{C_{Red^0}}{C_{Ox^+}} \right) \quad (S51)$$

$$\ln \frac{\gamma_{Red^0}}{\gamma_{Ox^+}} = \ln \left( \frac{C_{Red^0}}{C_{Ox^+}} \right)^{\left( \frac{1-\gamma}{\gamma} \right)} \quad (S52)$$

Applying the property  $e^{\ln(x)} = x$  to equation S45, we obtain the following relationship:

$$\frac{\gamma_{Red^0}}{\gamma_{Ox^+}} = \left( \frac{C_{Red^0}}{C_{Ox^+}} \right)^{\left( \frac{1-\gamma}{\gamma} \right)} \quad (S53)$$

Here it is possible to verify that the activity coefficients for the concentrations of the species involved in the reaction are related to the  $\gamma$  calculated for the model, corresponding to the deviation in concentrations due to the contribution of the ionic environment present in the system.

## S6. Transconductance equations for non-ideal case and dependencies with $\sigma$ , $\gamma$ and $\mathcal{E}_{pol}^{\ominus'}$ ;

The transistor's transconductance ( $g_m$ ) is defined as:

$$g_m = \frac{\partial I_{ds}}{\partial V_{gs}} \quad (S54)$$

and reflects the output gain (amplification) the device is capable of producing. Through our model, one can readily derive Equation S17 and S37 to obtain the transconductances' formulas for  $p$ -type and  $n$ -type OECTs, respectively. The expressions are presented below, and, for the non-ideal case, are dependent on  $\sigma$ ,  $\gamma$  and  $\mathcal{E}_{pol}^{\ominus'}$ , besides the geometrical and voltages dependencies.



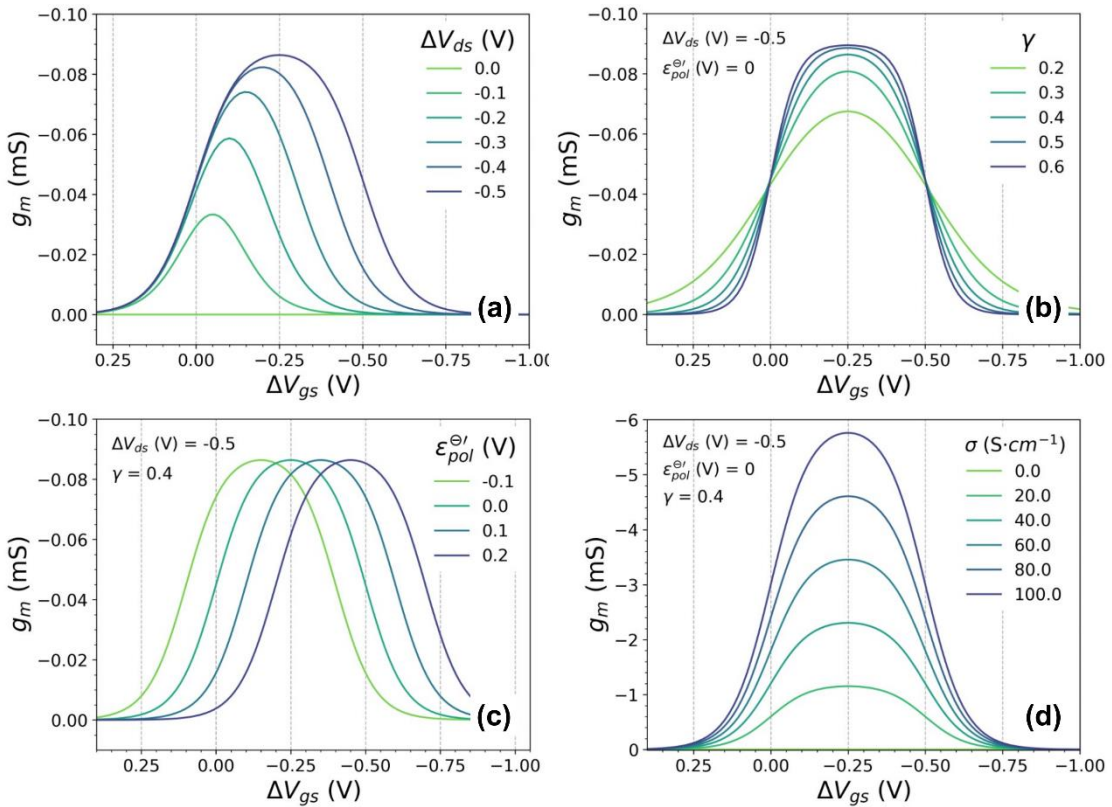
$$\text{p-type} \quad g_m = \frac{wh}{l} \left( (\sigma - \sigma_{res}) \left[ \frac{1}{1 + \exp\left[\frac{\gamma F}{RT}(\Delta V_{gs} + \varepsilon_{pol}^{\ominus'})\right]} - \frac{1}{1 + \exp\left[\frac{\gamma F}{RT}(-\Delta V_{ds} + \Delta V_{gs} + \varepsilon_{pol}^{\ominus'})\right]} \right] \right) \quad (\text{S55})$$

$$\text{n-type} \quad g_m = \frac{wh}{l} \left( (\sigma - \sigma_{res}) \left[ \frac{1}{1 + \exp\left[\frac{\gamma F}{RT}(-\Delta V_{ds} + \Delta V_{gs} + \varepsilon_{pol}^{\ominus'})\right]} - \frac{1}{1 + \exp\left[\frac{\gamma F}{RT}(\Delta V_{gs} + \varepsilon_{pol}^{\ominus'})\right]} \right] \right) \quad (\text{S56})$$

We have used Equation S48 to reconstruct the transconductance's traces, for several conditions as can be seen in Figure S3. In Figure S3(a),  $\gamma$ ,  $\varepsilon_{pol}^{\ominus'}$  and  $\sigma$  were all kept constant, and only  $\Delta V_{ds}$  was varied, simulating transconductance curves derive from transfer curves.

In Figure S3(b) – (d), only one of the fittings parameters was varied at a time. Interestingly to note that each of the parameters affect one particular feature in the transconductance curve:  $\Delta V_{ds}$ , as already from experimental data, varies the  $g_m$  intensities and maximum position. The novelties, here, are the other three curves.  $\gamma$ , (Figure S3 (b)) basically, changes the full width at half maximum (FWHM) of the transconductance curves. While  $\varepsilon_{pol}^{\ominus'}$  (Figure S3 (c)) doesn't affect the FWHM, nor the peak intensity; it only affects, as expected, the peak position. Higher  $\varepsilon_{pol}^{\ominus'}$  would lead to transconductance peaks at higher  $\Delta V_{gs}$ . Finally,  $\sigma$  (Figure S3 (d)) only affect the peak intensity, keeping the FWHM and peak position unvaried. Therefore, our model provides a robust expression with fundamentally justified parameters, that univocally alter a specific feature of the output characteristic of the OECT device.

**Figure S3** - (a) transconductance for non-ideal behavior case for a p-type OECT channel, influence of (b)  $\gamma$ , (c)  $\varepsilon_{pol}^{\ominus'}$  and (d)  $\sigma$  on transconductance at  $\Delta V_{ds} = -0.5$  V. Here were used the following parameters  $w = 1.5$  mm,  $h = 100$  nm,  $l = 250$   $\mu\text{m}$ ,  $\sigma = 1.5$  S $\cdot\text{cm}^{-1}$ ,  $\sigma_{res} = 1\text{E-}4$  S $\cdot\text{cm}^{-1}$ ,  $\varepsilon_{pol}^{\ominus'} = 0$  V,  $T = 298.15$  K, and  $\gamma = 0.4$ .



## S7. Additional statistical parameters of the model fit for experimental data from the literature

A 95% confidence interval was adopted for the fittings of the experimental data presented in the literature. The p-values for the calculated parameters can be found in the Table S1 and Table S2.

Table S1 – p-values calculated for the fit parameters from Flagg *et al*<sup>26</sup> (Figure 5).

	$\sigma$	$\gamma$	$\epsilon_{pol}^{\ominus'}$
<b>TFSI<sup>-</sup></b>	2.315E-65	1.475E-26	4.719E-11
<b>PF<sub>6</sub><sup>-</sup></b>	9.122E-52	1.224E-31	6.900E-29
<b>ClO<sub>4</sub><sup>-</sup></b>	2.095E-79	4.679E-38	3.513E-70
<b>Cl<sup>-</sup></b>	1.170E-49	4.213E-20	7.512E-60

Table S2 - p-values calculated for the fit parameters from Rivnay *et al*<sup>46</sup> (Figure 6).

	$\sigma$	$\gamma$	$\epsilon_{pol}^{\ominus'}$
<b>0%</b>	1.710E-22	9.911E-15	0.048
<b>5%</b>	1.022E-45	1.251E-31	1.068E-36
<b>20%</b>	7.261E-61	1.182E -47	8.959E-48
<b>50%</b>	3.876E-55	1.359E-40	7.042E-50

### S8. Summary of equation and variables

	<i>p</i> -type	<i>n</i> -type
Reaction Direction	$Ox_{idized}^+ + e^- \rightarrow Red_{uced}^0$	$Ox_{idized}^0 + e^- \rightarrow Red_{uced}^-$
Active specie carrier	$\rho = C_{Ox^+}$	$\rho = C_{Red^-}$
Channel current Equation	$I_{ds} = \frac{wh}{l} \left( \sigma_{res} \Delta V_{ds} + (\sigma - \sigma_{res}) \frac{RT}{\gamma F} \ln \left[ \frac{1 + \exp \left[ \frac{\gamma F}{RT} (\Delta V_{ds} - \Delta V_{gs} - \varepsilon_{pol}^{\ominus'}) \right]}{1 + \exp \left[ \frac{\gamma F}{RT} (-\Delta V_{gs} - \varepsilon_{pol}^{\ominus'}) \right]} \right] \right)$	$I_{ds} = \frac{wh}{l} \left( \sigma_{res} \Delta V_{ds} + (\sigma - \sigma_{res}) \frac{RT}{F} \ln \left[ \frac{1 + \exp \left[ \frac{F}{RT} (\varepsilon_{pol}^{\ominus'} + \Delta V_{gs}) \right]}{1 + \exp \left[ \frac{F}{RT} (\varepsilon_{pol}^{\ominus'} - \Delta V_{ds} + \Delta V_{gs}) \right]} \right] \right)$
Transconductance	$g_m = \frac{wh}{l} \left( (\sigma - \sigma_{res}) \left[ \frac{1}{1 + \exp \left[ \frac{\gamma F}{RT} (\Delta V_{gs} + \varepsilon_{pol}^{\ominus'}) \right]} - \frac{1}{1 + \exp \left[ \frac{\gamma F}{RT} (-\Delta V_{ds} + \Delta V_{gs} + \varepsilon_{pol}^{\ominus'}) \right]} \right] \right)$	$g_m = \frac{wh}{l} \left( (\sigma - \sigma_{res}) \left[ \frac{1}{1 + \exp \left[ \frac{\gamma F}{RT} (-\Delta V_{ds} + \Delta V_{gs} + \varepsilon_{pol}^{\ominus'}) \right]} - \frac{1}{1 + \exp \left[ \frac{\gamma F}{RT} (\Delta V_{gs} + \varepsilon_{pol}^{\ominus'}) \right]} \right] \right)$