ADVANCED ELECTRONIC MATERIALS

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Supporting Information

Organic Mixed Ionic Electronic Conductor Nanochannels for Vertical Electrochemical and Ionic Transistors

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Suppl. Mat. S1: Determination of mobility in electronic organic electrochemical transistors

We use the Bernards model to fit the transfer characteristic of the vertical OECTs in saturation regime where $V_D > |V_G - V_T|$ [1]:

$$I_D = \mu_e C^* \frac{Wd}{L} \frac{(V_G - V_T)^2}{2}$$

Where μ_e is the carrier mobility, C^* is the volumetric capacitance of PEDOT:PSS, W, L, and d is the geometric width, length, and thickness of the polymer channel, respectively, and V_G is the gate potential, V_T is the threshold voltage.

The volumetric capacitance is defined as:

$$C^* = \frac{C}{V} = \frac{C}{Ad}$$

where C is the overall capacitance of the channel measured with electrochemical impedance spectroscopy as discussed in the main text, V is the volume of the deposited PEDOT:PSS inside the nanopores, and A is the area of all the nanochannels contacted in parallel by the source and drain electrodes $A = A_S \, n_p \pi r^2$. Here A_S is the area of the evaporated source and drain electrodes (5 mm in diameter), $n_p = 28 \pm 0.7$ pores per 100 μm² is the pore density and r is the radius of a single nanopore. The channel length is given by the thickness of the track-etched membrane.

Suppl. Mat. S2: Determination of mobility in ionic nano-channel transistors

The ionic current density is given by

$$j = \sum_i n_i v_i\, c_i N_A$$

Where n_i represents the charge of the ionic carrier, v_i is velocity and c_i is concentration and N_A is Avogadro's number. For the OMIEC matrix, we assume a single monovalent ion to be the carrier. We substitute the velocity with the definition of the mobility

$$v = \mu_i E$$

The variation in the number density of ions as a function of gate voltage is given by

$$\Delta \rho = \frac{C^*}{n}(V_G - V_T)$$

The total current is obtained by integrating over the cross-section A of the OMIEC transistor channel. For the case of parallel nanochannels this results in an area given by

$$A = n_p \pi r^2 A_S$$

Where n_p is the pore density, r is the pore radius and A_S is the area of source and drain electrodes.

Combining the expressions and introducing the linear channel approximation $E = \frac{V_D}{L}$ we obtain:

$$I_D = \mu_i \frac{c_V}{L} A(V_G - V_T)V_D$$

We simplify by introducing the definition of the volumetric capacitance:

$$c_V = \frac{C}{L\,A}$$

Note that L is the length of the nanochannels.

For the conductivity of the channel, one obtains:

$$G_m = \frac{d\,I_D}{d\,V_D} = \mu_i \frac{C}{L^2}(V_G - V_T)$$

In our analysis, we analyze the slope of the conductance vs gate voltage curve to determine the differential mobility:
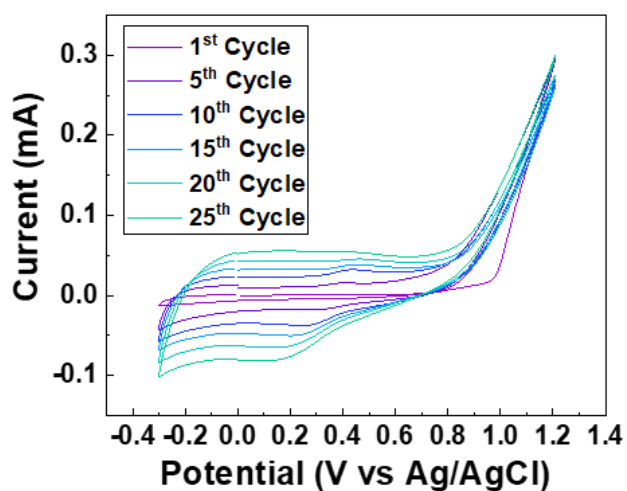
$$\mu_i = \frac{L^2}{C}\frac{d\,G_m}{d\,V_G}$$

Figure S1. Cyclic voltammetry of the PEDOT:PSS within nanoporous membrane during the electropolymerization. The membrane with gold electrode served as the working electrode, and a Pt wire and Ag/AgCl electrode were adopted as the counter electrode and the reference electrode, respectively. A working potential was executed between -0.3 V and 1.2 V at a scan rate of 0.005 V/s.
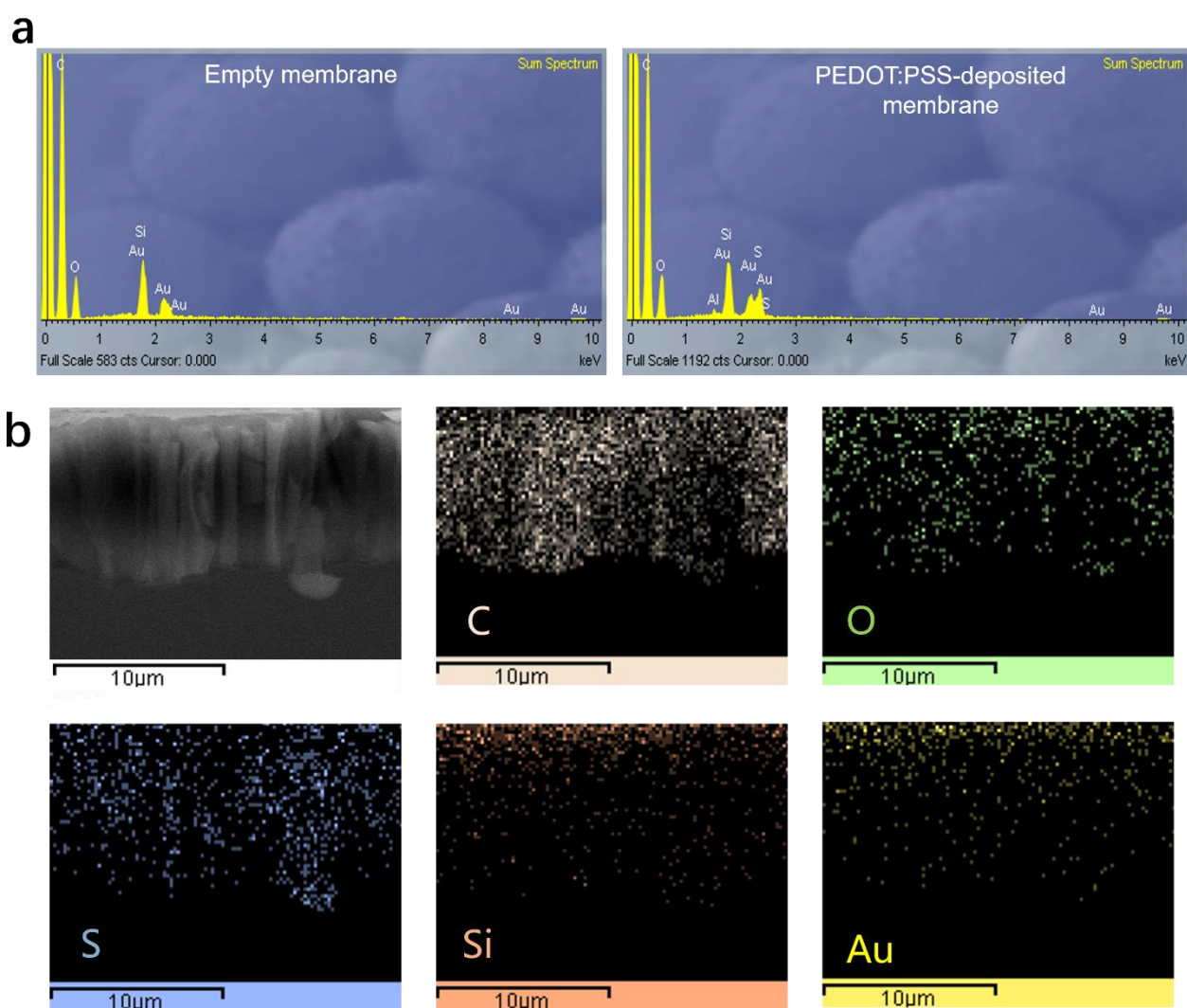

Figure S2. (a) EDX spectrum of the empty membrane and PEDOT:PSS-filled membrane. (b) EDX

analysis of the PEDOT:PSS-filled membrane cross-section. The deposited polymer (PEDOT:PSS) and the porous membrane (polycarbonate) both contain elements C and O. The element S is unique to PEDOT:PSS and absent in the polycarbonate of the membrane. The small amount of element S comes from the PDMS substrate, and the Au is attributed to the evaporated gold layer.
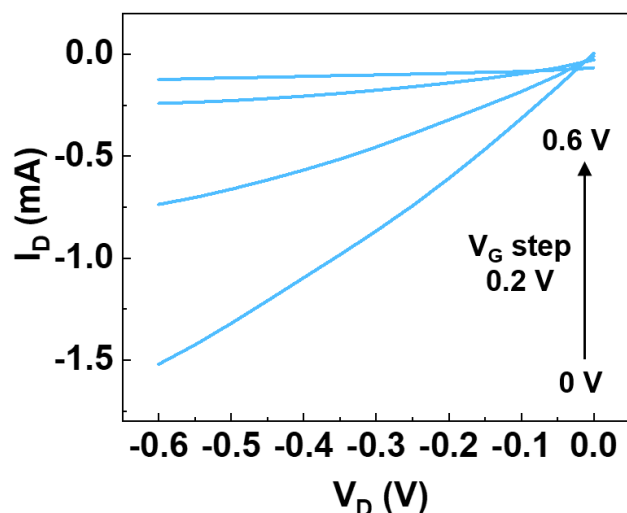

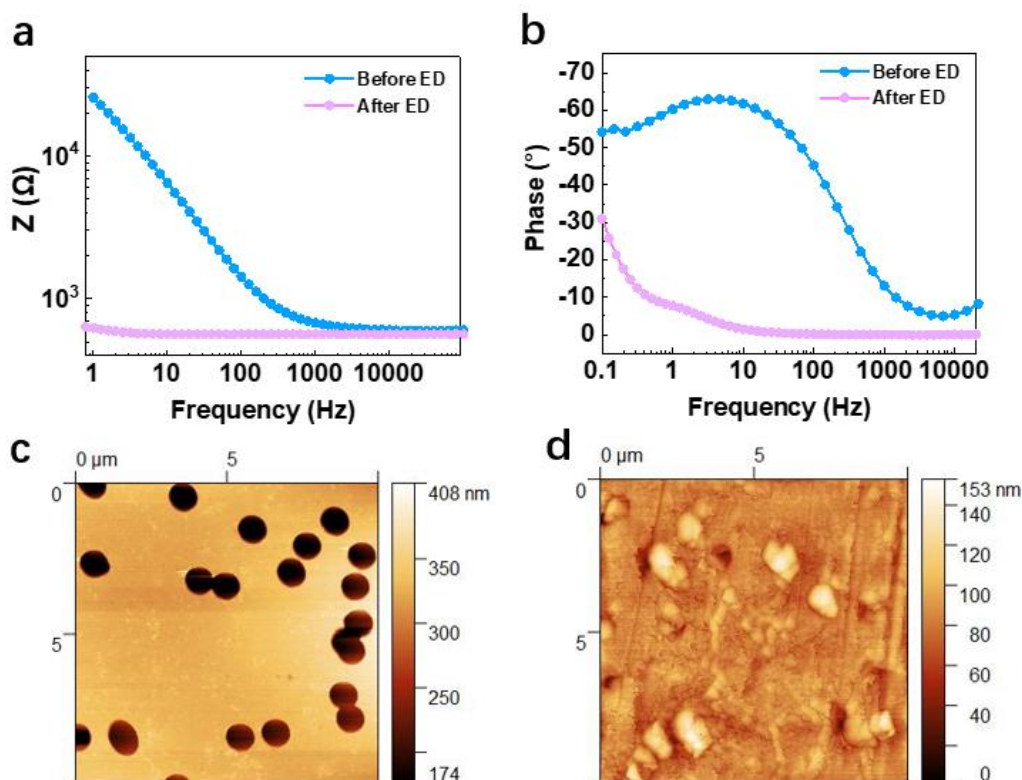**Figure S3.** Output characteristic of the vertical OECTs based on the nanoporous membrane.

Figure S4. (a,b) Electrochemical impedance spectroscopy on PEDOT:Cl filled nanoporous membrane. (a) and (b) represent impedance and phase as function of frequency before and after electrodeposition respectively. (c,d) AFM height images of nanoporous membrane before and after deposition of PEDOT:Cl. From this data, we obtain the parameters that are used in the estimation of

the differential mobility: Channel length (thickness of the membrane) L=10mm; nanopore diameter d=1mm; nanopore density n_p=22 per100 mm^2; EIS capacitance C=0.54 mF
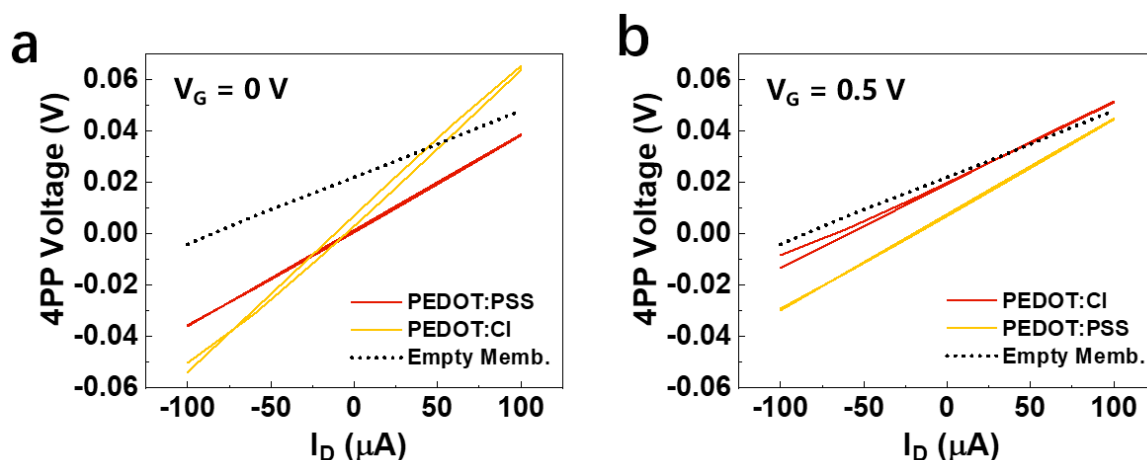

Figure S5. Variation of 4PP voltage with current at (a) V_G = 0 V and (b) V_G = 0.5 V for empty membrane and membranes filled with different OMIECs.
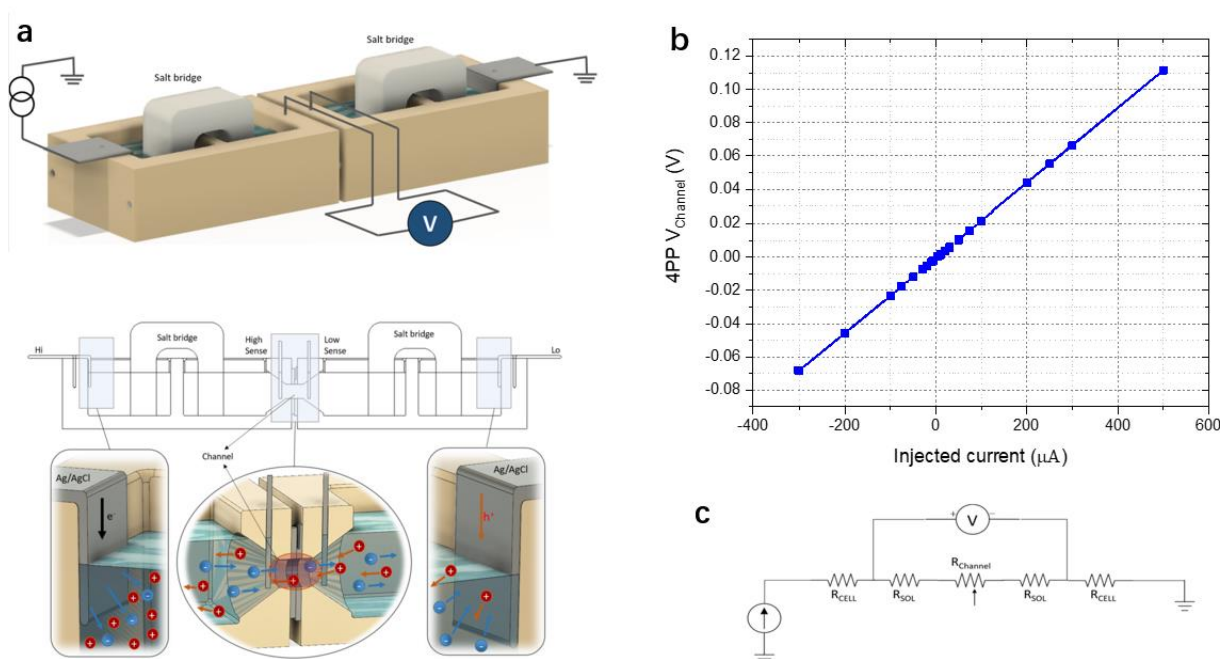

Figure S6. Measurement cell for ionic transport studies. (a) Schematic of the measurement cell for ionic transport characterization. A source measure unit (Keysight 2912B) is used to source a current through the salt bridges and the channel opening. The nanoporous membrane is inserted in the middle of the channel and PDMS o-rings are used to confine the area of the membrane in contact with electrolyte. Two silver wires are positioned in the half-spaces on each side of the membrane and used to measure the potential drop across the membrane using the four-point probe functionality of the source measure unit. In order to apply a gate potential to the membrane, an electrical contact with

silver paste is created on the membrane coated with gold and positioned outside of the O-ring. (b) shows an IV curve obtained without a nanoporous membrane. The result demonstrates that the channel of the measurement cell has an electrolyte resistance of $R_{sol} = 270$ Ω. (c) Equivalent circuit of the measurement configuration. The resistance of the membrane is obtained by $R_m = \frac{V_{4PP}}{I} - R_{sol}$. The conductance plotted in Figure 5 are then obtained by $G_m = \frac{1}{R_m}$.

Supplementary Table

Table S1. The element atomic percentage by EDX analysis for different membranes

Sample	Element (at%)					
	C	O	Si	Au	S	Al
Empty Membrane	77.88	20.21	1.61	0.3	-	-
Deposited Membrane	77.99	19.42	1.42	0.27	0.79	0.11

References
[1]   a) D. A. Bernards, G. G. Malliaras, Adv. Funct. Mater. 2007, 17, 3538; b) Y. Xu, Y. Li, S. Li, F. Balestra, G. Ghibaudo, W. Li, Y. F. Lin, H. Sun, J. Wan, X. Wang, Y. Guo, Y. Shi, Y. Y. Noh, Adv. Funct. Mater. 2020, 30, 1904508.