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Supporting Information

Organic electrochemical transistors from supramolecular complexes of conjugated polyelectrolyte PEDOTS

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1. OECTs



Figure S1. (a) Forward and backward Id/Vg curves relative to the devices of figure 2b. A zoomin of the PEDOTS:DOA 2:1 curve is shown in the inset. (b) Curves of PEDOTS:DOA 1:10 and 1:1 normalised to the maximum current.

A large hysteresis can be observed for the PEDOTS:DOA 1:1 and 1:10 based devices when operated in 0.1 M KCl, with no clear difference in terms of hysteresis between the two. The complete forward/backward sweep for the PEDOTS:DOA 2:1 device is also reported in the figure, showing almost no switching for this device.



Figure S2. Output curves of PEDOTS:DOA 1:1 in 0.1M KCl (a) and PEDOTS:DOA 1:10 in 1 M KCl (b)



Figure S3. Cycling of PEDOTS:DOA 1:1 OECTs in 0.2 M KCl (a) and KCl/CaCl2 (b) performed by switching the Vg between 0 and -0.4 V.

2. Cyclic voltammetry



Figure S4. Effect of the scan rate on the cyclic voltammetry of bare Au IDME electrode, PEDOTS:DOA 1:10 and PEDOTS:DOA 1:1 on IDME, with 2 mM K₃Fe(CN)₆ as redox probe, and KCl at different concentrations as supporting electrolyte. (a) CVs of the three samples in 1 M KCl, at scan rates ranging from 50 to 250 mV/s. (b) Peak currents (i_p) vs. square root of the scan rate ($v^{1/2}$) for the three samples in 1 M KCl. The straight lines represent linear fittings. Linear fittings, performed also for the same samples in 0.1 M KCl and 0.5 M KCl (plots not shown) showed R²>0.99 in all cases. (c, d) Effective area for the three samples in the three different electrolyte concentrations, obtained from the fittings of i_p vs. $v^{1/2}$ by using the Randles–Sevcik equation: $i_p = 2.69 \cdot 10^5 n^{\frac{3}{2}} AD^{\frac{1}{2}} Cv^{\frac{1}{2}}$, where i_p is the peak current, *n* the number of electrons transferred in the redox event, *A* the electrode area, *F* the Faraday constant, *D* the diffusion coefficient of the redox species (7.6·10⁻⁶ cm² s⁻¹ for K₃Fe(CN)₆), *C* the concentration and v the scan rate.

3. Impedance spectroscopy



Figure S5. Impedance spectra of PEDOTS:DOA 1:10 on gold electrode in 0.1 M KCl, 0.2 M KCl and KCl/CaCl₂ (as black, red and blue, respectively); solid lines – results of the fittings with the equivalent circuit shown in Figure 5; bias 0.2 V, 10 mV amplitude.



Figure S6. Impedance spectra of different PEDOTS:DOA films on gold electrode (PEDOTS:DOA 1:10, 1:1 and 2:1 as black, red and blue, respectively) in KCl/CaCl₂; the solid lines represent the fittings with the equivalent circuit shown in Figure 5; bias 0.2 V, 10 mV amplitude.

Table S1. Extended table showing the fitting parameter values extracted by using an equivalent circuit that comprises two CPEs. The capacitance values have been estimated by equation (1). The values of ϕ for CPE_{DL} are close to 1 motivating the circuit reduction to a 4-element circuit (Inset of Fig. 5a). The higher values of capacitance C_{DL} observed for 1:10 and 1:1 films in comparison with the estimated pore capacitance confirms the assignment of first element to the double layer capacitance at the metal/electrolyte interface (bottom of pores). The low (far from 1) values of ϕ for CPE_P illustrate the distributed character of this element, which limits the use of eq. (1) only for estimation purposes.

PEDOTS:	Floctrolyto	во	CE	D v10-6	*	в.,	с г	D v10-6	н
DOA	Electrolyte	K _S , 12	С _Р , μг	P, ×10*	Ψ	κ _Ρ , μ	с _{DL} , μг	r, ×10°	Ψ
	0.1 M KCl	135	0.14	2.3	0.74	3606	0.3	0.30	0.98
1:10	0.2 M KCl	76	0.3	9.1	0.68	606	1.9	4.9	0.89
	0.05 M KCl, 0.05M CaCl ₂	103	0.32	16.3	0.62	336	2.4	3.0	0.98
	0.1 M KCl	121	0.24	4.6	0.72	7834	1.1	7.1	0.79
1:1	0.2 M KCl	81	0.89	20.3	0.67	165	5.5	5.1	1
	0.05 M KCl, 0.05M CaCl ₂	93	0.5	27.4	0.6	251	4.7	3.6	1
	0.1 M KCl	119	0.2	1.4	0.82	8274	0.12	0.5	0.88
2:1	0.2 M KCl	59	0.3	4.8	0.76	1821	0.62	0.1	1
	0.05 M KCl, 0.05M CaCl ₂	87	0.22	0.5	0.6	518	0.23	0.5	0.92

4. Linear sweep voltammetry



Figure S7. Linear sweep voltammetry acquired on 2:1 (A, D and G), 1:1 (B, E and H) and 1:10 (C, F and I) PEDOTS:DOA film-modified gold interdigitated electrodes in 0.1 M KCl (A – C), 0.2 M KCl (D – F) and KCl/CaCl₂ (G – I); scan rates: 5 mV s⁻¹, 50 mV s⁻¹ and 500 mV s⁻¹ as black, red and blue curves, respectively; starting potential: 0.6 V; end potential: -0.3 V.

Linear sweep voltammetry was utilized to investigate both semiconductor transitions and electrocapacitive phenomena on film-modified gold interdigitated electrodes. Besides doping/de-doping transitions (0 V - -0.2 V), all film-modified electrodes showed a linear dependence of current with the scan rate (Fig. S7), as a major criteria for capacitive behavior, recorded in a certain region of potentials (ca. 0.1 V vs Ag/AgCl) far enough from doping/de-doping transitions and faradaic background processes (e.g., oxygen reduction at -0.25 V - -0.3 V). Assuming a minor contribution from underlying gold current collector maintained for all investigated films, the slopes

of scan rate dependencies normalized by the film surface area yielded a capacitance values of 280 μ F cm⁻², 474 μ F cm⁻² and 366 μ F cm⁻² for 1:10, 1:1 and 2:1 PEDOTS:DOA films, respectively. Coherently, 1:1 film showed the largest value of film capacitance due to the balance between wettability and porosity. Assuming an average film thickness of 300 nm, the volumetric capacitances were of 9 F cm⁻³, 16 F cm⁻³ and 12 F cm⁻³ for 1:10, 1:1 and 2:1 PEDOTS:DOA films, respectively.



Figure S8. The scan rate dependencies of currents measured at 0.1 V by linear sweep voltammetry on PEDOTS:DOA films of different compositions (1:1 \blacksquare , 1:10 \bigcirc and 2:1 \blacktriangle) in 0.2 M KCl.

5. Four-electrode electrochemical measurements



Figure S8. Modulation of channel resistance due to doping/de-doping transitions of 1:10 ($\mathbf{A} - \mathbf{C}$) and 2:1 ($\mathbf{D} - \mathbf{F}$) PEDOTS:DOA films in 0.1 M KCl (\mathbf{A} and \mathbf{D}), 0.2 M KCl (\mathbf{B} and \mathbf{E}) and KCl/CaCl₂ (\mathbf{C} and \mathbf{F}) electrolyte solutions. Channel resistance as a function of the gate voltage and at different scan rates in a four-electrode setup. The measurements were performed by varying the voltage at the CE while keeping 50 mV voltage difference between WE1 and WE2.