

Supplementary Information for

Beyond 10 MHz Organic Electrochemical Transistors for Printed Multi-valued Logic Circuits

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Details of the Experiment

Appendices S1 and 2

Supplementary Fig. S1 to S24

Supplementary Table S1 to S2

Supplementary References

Materials and methods:

Synthesis of PEDOT:PSS-O (PP2) solution: A mixture of 0.74 g of PEGME (Sigma-Aldrich) and 100 mL of PEDOT:PSS (Clevios PH) solution was allowed to react at 60 °C for 2 h. Subsequently, the mixture was allowed to cool to room temperature, and 0.5 g of imidazole was added to the mixture to neutralize the pH to 7. The prepared mixture was purified by filtration.

Synthesis of PEDOT:PSS-F (PP3) solution: To prepare this solution, 1.2 mmol of 2,2,3,3-tetrafluoropropylmethacrylate (TFPMA, Sigma-Aldrich, 99%) and 4.8 mmol of 4-styrenesulfonic acid sodium salt hydrate were dissolved in 100 mL of DI water. To this solution, 0.065 g of sodium persulfate (initiator) was added. The solution was heated to 80 °C to induce a reaction. After 24 h, the reaction was completed, and the residual sodium persulfate was removed by filtration and ion-exchange. In the prepared P(SS-coTFPMA) solution, 1.26 mmol of 3,4-ethylenedioxythiophene (EDOT, Sigma-Aldrich, 97%) was dissolved. Moreover, 0.0053 g of $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ was added to 2 mL of H_2O and 0.772 g of sodium persulfate was added to 3 mL of H_2O to initiate the polymerization reaction. After 24 h, the resultant products were purified by filtration and ion-exchange. The uniformity of the prepared solution was enhanced through sonication.

Dual-channel electrochemical transistor fabrication: On a substrate, source electrodes and gate contact pads were deposited by evaporation using a shadow mask (Cr/Au = 3 nm/17 nm). Subsequently, the substrate was subjected to UV-ozone treatment. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) solution was spin-coated onto the substrate (1000–4000 rpm), and the system was heated at 150 °C for 2 min. The PEDOT:PSS layer was patterned by conventional photolithography (AZ 5214E) and etched via reactive ion etching (RIE, FEMTO SCIENCE VITA-E). Poly(3-hexylthiophene-2,5-diyl) (P3HT) solution with a crosslinker (2,2-bis(((4-azido-2,3,5,6-tetrafluorobenzoyl)oxy)methyl)propane-1,3-diyl bis(4-azido-2,3,5,6-tetrafluorobenzoate, referred to as 4Bx) was spin-coated and photo patterned on the PEDOT:PSS layer. Au was evaporated to introduce drain electrodes on the PEDOT:PSS-P3HT vertically stacked layer. Ag/AgCl was deposited and patterned on the gate contact pad by spray-coating and used as the reference electrode. A photopatterned ion gel that covered all components served as the electrolyte. The ion gel was prepared by mixing an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIM TFSI, Sigma-Aldrich, 98%), the poly(ethyleneglycol) diacrylate (PEG-DA, Sigma-Aldrich, M_n 575) monomer, and the 2-hydroxy-2-methylpropiophenone (HOMPP, Sigma-Aldrich, 97%) initiator (weight ratio of 21:2:1).

Device characterization: Surface images of Ag/AgCl layer were recorded using a field-emission scanning electron microscope (JEOL 7800F). The thickness and surface morphology of the PEDOT:PSS and P3HT layers were measured using an atomic force microscope (Park Systems NX10). Cyclic voltammetry curves of the PEDOT:PSS films were obtained using a Potentiostat (AMETEK VersaSTAT4) and ferrocene (Sigma-Aldrich, 98%). The electrical properties of the DuECT and logic circuits were measured using a six-arm probe station and a Keithley 4200 semiconductor characterization system.

Appendix S1. V_{ON} calculation based on cyclic voltammetry data:

The reaction to recover the conductivity of the PEDOT:PSS channel, which is lost due to reduction, is $PEDOT + M^+:PSS^- \rightarrow PEDOT^+:PSS^- + M^+ + e^-$. Because the turn-on voltage of the PEDOT:PSS channel layer is the starting point of the oxidation reaction, its value can be estimated by the oxidation potential. Hence, we calculate the HOMO energy level (E_{HOMO}) of PEDOT:PSS by using cyclic voltammetry and estimate the oxidation potential through the HOMO level and standard electrode potentials.

$$E_{HOMO} = [V_{\text{solvent}} - (E_{\text{onset ox}} - E_{1/2(\text{solvent})})]$$

$$\left[E_{H^+/1/2H_2}^\phi \right]_{AVS}^W = 4.44 \text{ V}$$

$$\text{Standard oxidation potential (vs. Ag/AgCl)} = -[E_{HOMO} + 4.44] - 0.197$$

The voltage applied to the channel in the transistor, i.e., the gate electrochemical potential, can be regarded as the sum of the gate voltage and drain voltage. The sum of the drain voltage and oxidation potential is V_{ON} :

$$V_{ON} = -[E_{HOMO} + 4.44] - 0.197 + V_D$$

Appendix S2. Numerical modeling

To calculate the changes in the turn-on voltage with the electrode area covering the channel, we estimate the difference in the electrostatic potential in the channel due to ion penetration. Because the channel thickness is considerably smaller than the channel width, a one-dimensional model is used. The boundary conditions to calculate the electrostatic potentials are set as net ion mobile speed = 0, electrolyte-channel-interface potential = drain voltage = 1 V. The electrostatic potentials are determined using the Poisson equation:

$$\frac{\partial^2 \varphi(x)}{\partial x^2} = -\frac{n_e(x)}{\varepsilon_s \varepsilon_0}$$

where x , φ , n_e , ε_s , and ε_0 represent the position along the x' -axis, electrostatic potential at position x (unit: V), electron density at position x (unit: number/cm³), relative dielectric permittivity of the semiconductor, and vacuum permittivity (8.854×10^{-12} F/m), respectively. Solving the continuity equations and constitutive equations based on the drift-diffusion model yields the electrostatic potential as the position:

$$\begin{aligned} \frac{\partial n_e}{\partial t} &= G - R - \frac{1}{q} \frac{\partial j}{\partial x} \\ j &= q\mu_e \left(n_e \frac{\partial \varphi}{\partial x} + \frac{k_B T}{q} \frac{\partial n_e}{\partial x} \right) \end{aligned}$$

where t , G , R , and j in the continuity equation (top) denote the time, charge generation rate, charge recombination rate, and electron current density, respectively. μ_e and k_B in the drift-diffusion equation (bottom) represent the electron mobility (unit: cm²/Vs) and Boltzmann constant (8.617×10^{-5} eV/K), respectively. In this system, charge generation and recombination can be reasonably disregarded.

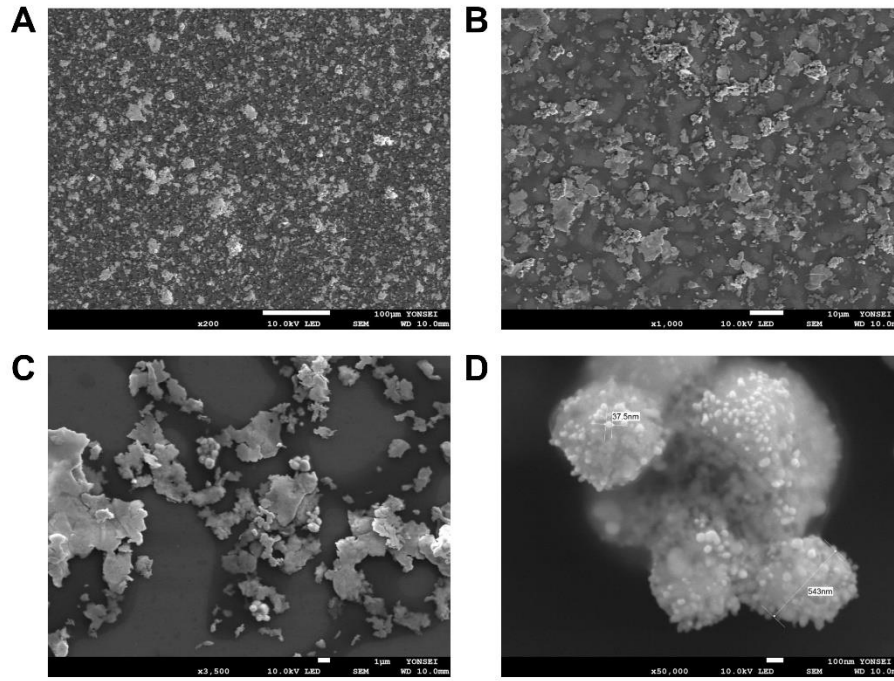


Fig. S1. (A–D) SEM images of sprayed Ag/AgCl on the gate electrode

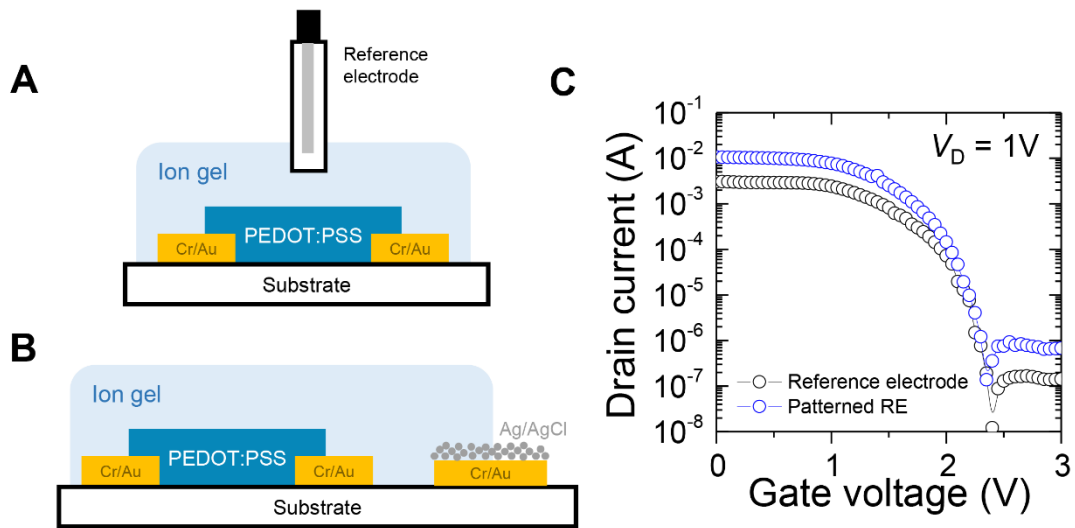


Fig. S2. Schematic of PEDOT:PSS electrochemical transistor based on a (A) conventional reference electrode and (B) sprayed Ag/AgCl electrode for gate electrode. (C) Transfer characteristics for each gate electrode.

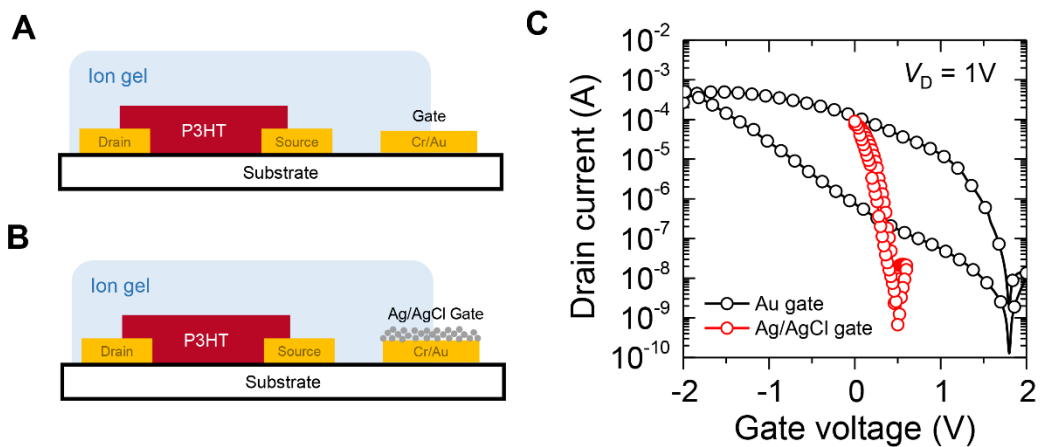


Fig. S3. Schematic of P3HT transistor based on (A) Au gate electrode and (B) sprayed Ag/AgCl gate electrode. (C) Transfer characteristics for each gate electrode.

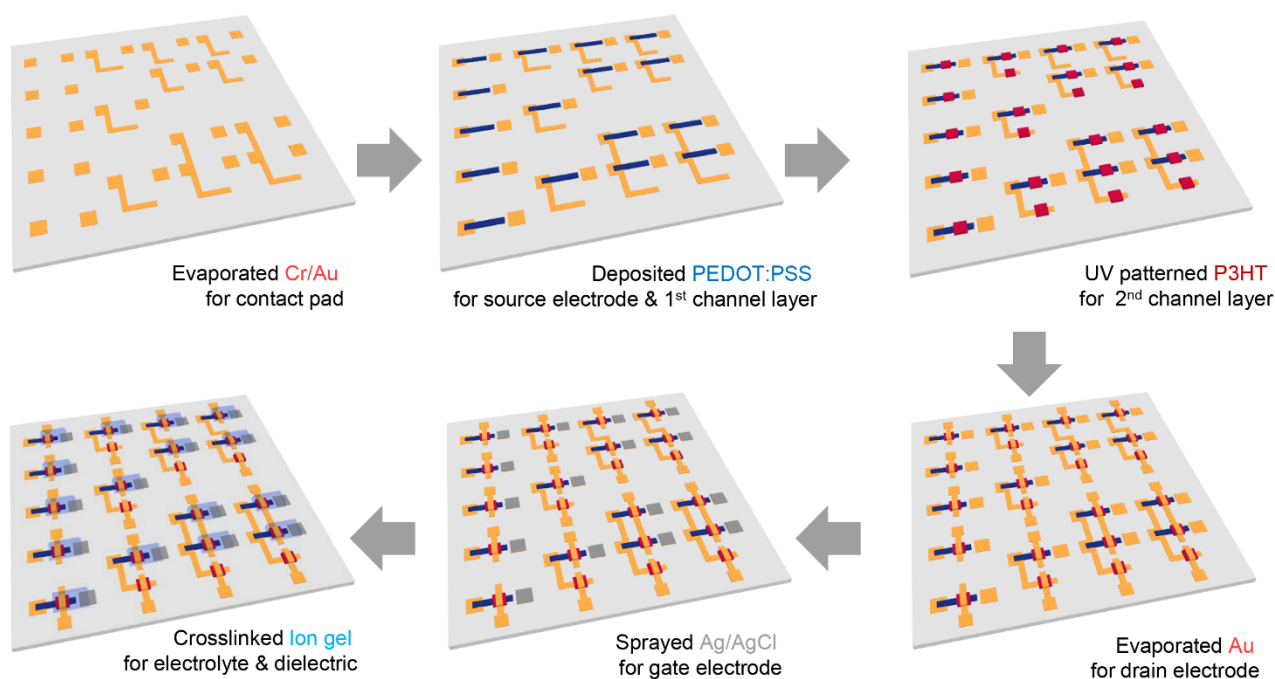


Fig. S4. Fabrication process of DuECT.

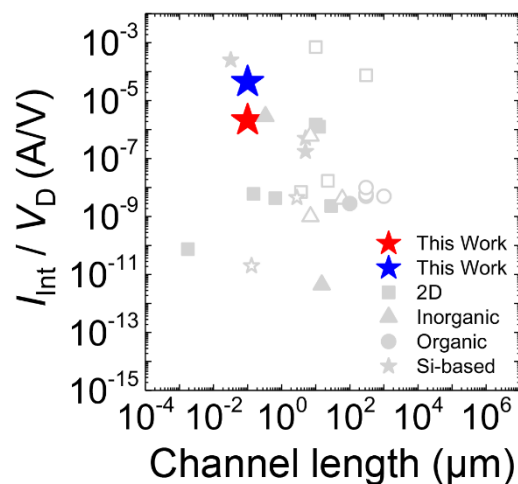


Fig. S5. Intermediate current level schematized by V_D of multivalued logic gates for the existing frameworks and DuECTs.

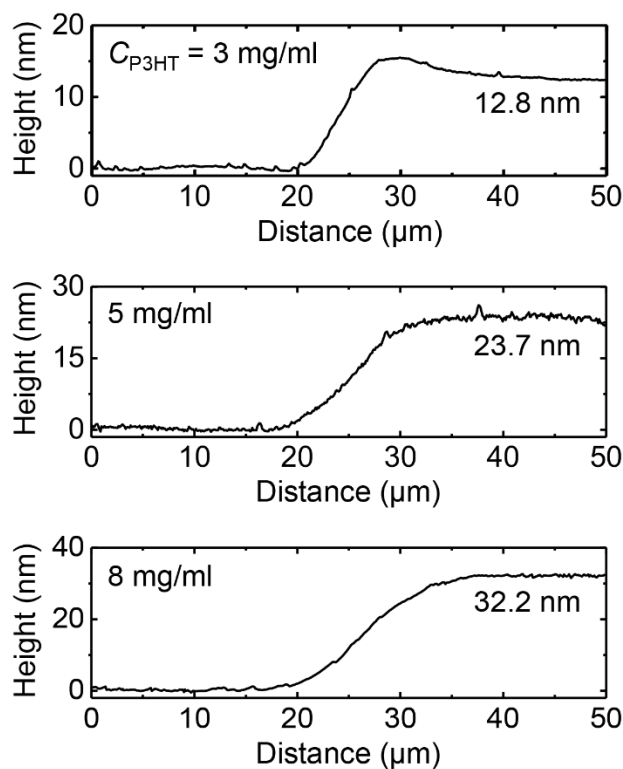


Fig. S6. Cross-section data from atomic force microscopy (AFM) indicating the thickness of spin coating layer for each P3HT concentration.

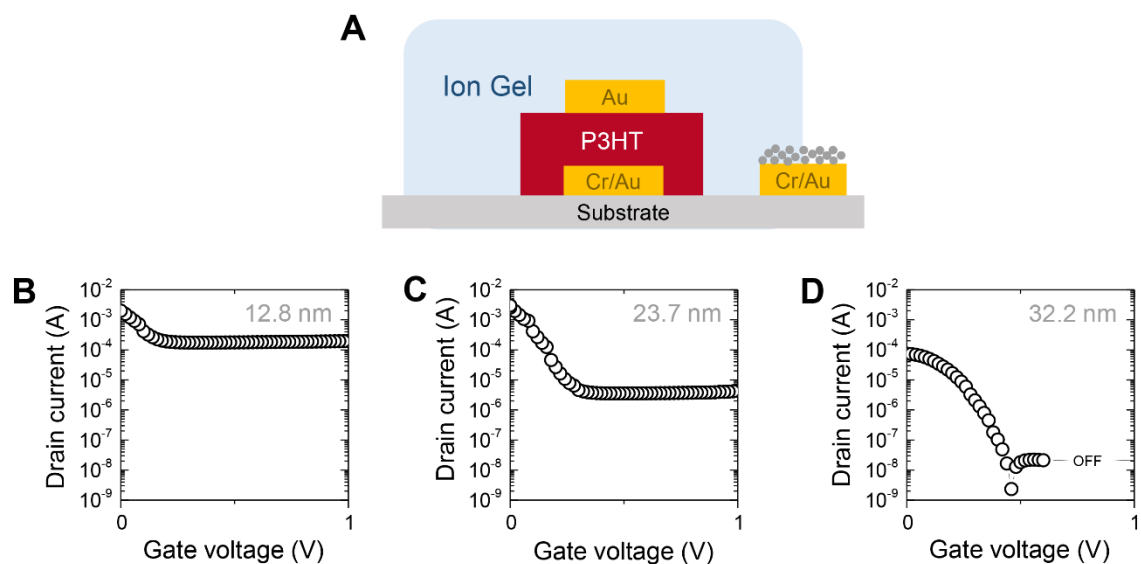


Fig. S7. (A) Schematic of P3HT vertical transistor. (B–D) Transfer characteristics for different thickness values of the P3HT channel layer.

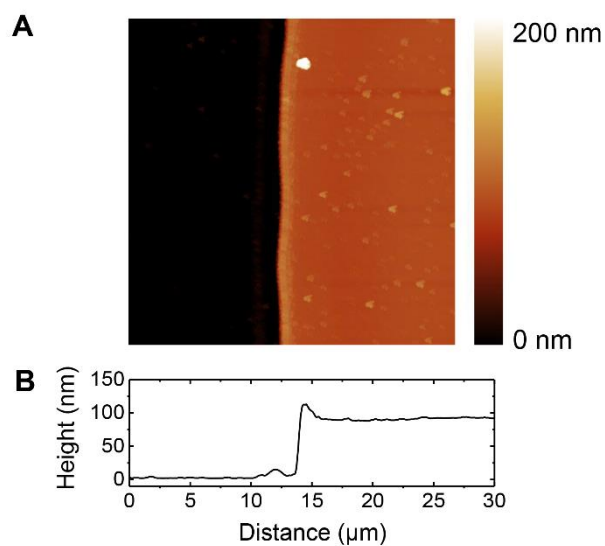


Fig. S8. (A–B) AFM data for thickness of the PEDOT:PSS layer.

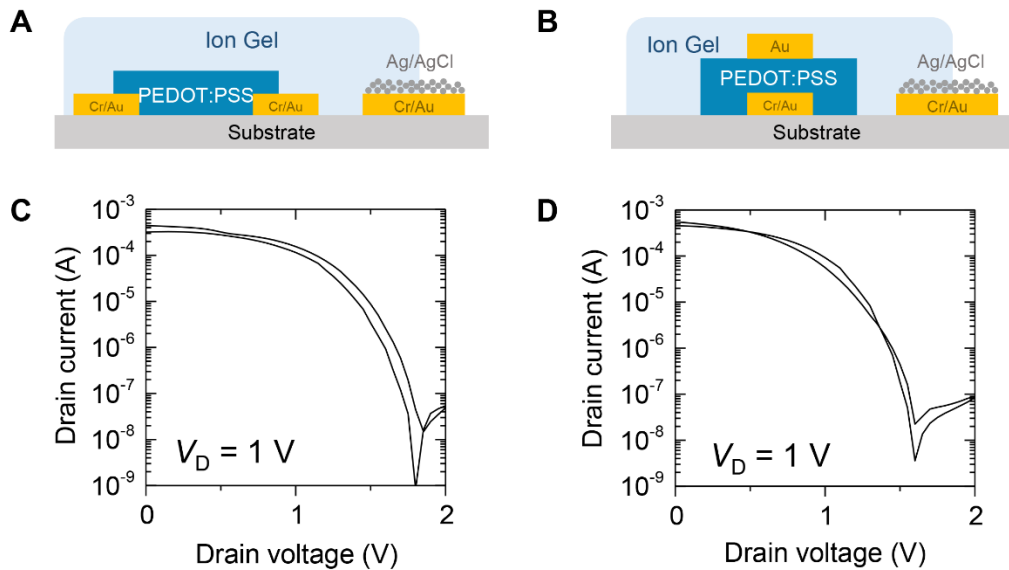


Fig. S9. Schematic of PEDOT:PSS (A) lateral transistor and (B) vertical transistor. Transfer characteristics for (C) lateral structure and (D) vertical structure.

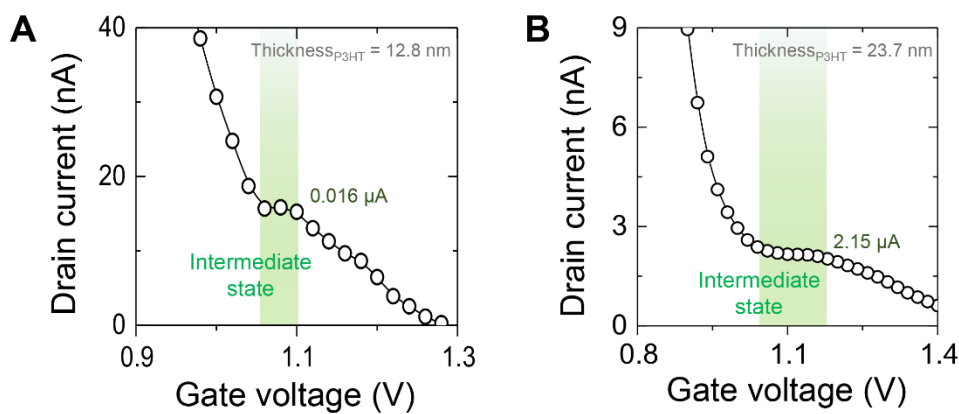


Fig. S10. Linear plot of transfer characteristics for DuECT with P3HT thickness being (A) 12.8 nm and (B) 23.7 nm.

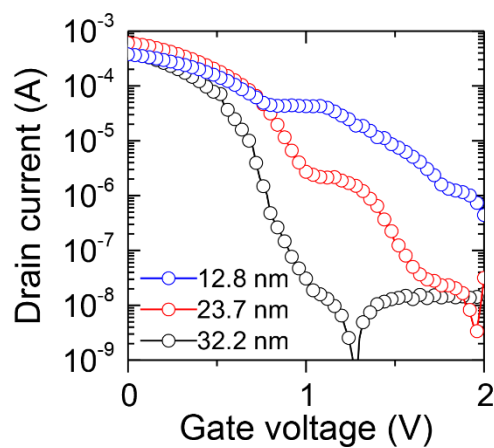


Fig. S11. Semi-log plot of transfer characteristics for different values of P3HT thickness for DuECT.

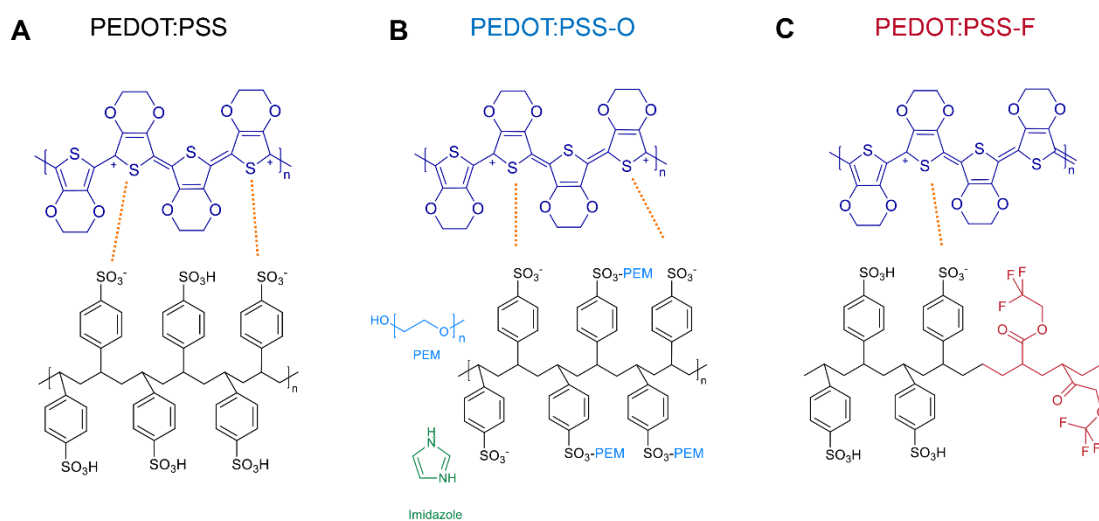


Fig. S12. Chemical structures of (A) PEDOT:PSS, (B) PEDOT:PSS-O and (C) PEDOT:PSS-F as channel materials in DuECTs.

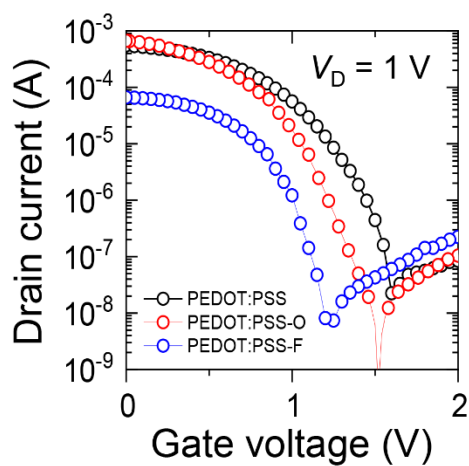


Fig. S13. Transfer characteristics of electrochemical transistors based on different PEDOT:PSS channels.

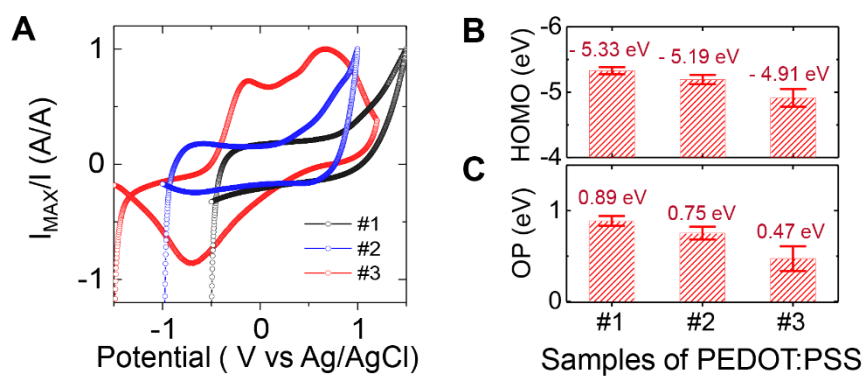
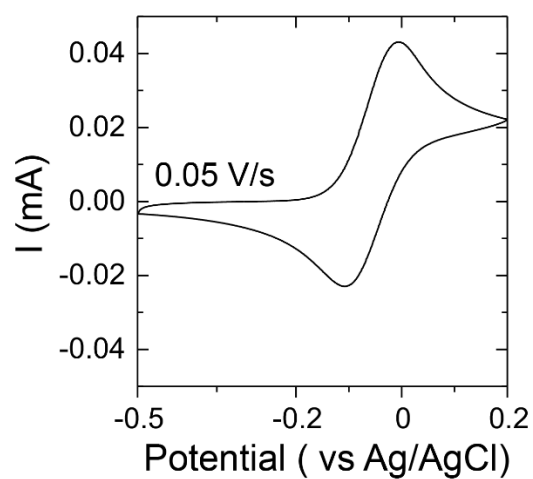


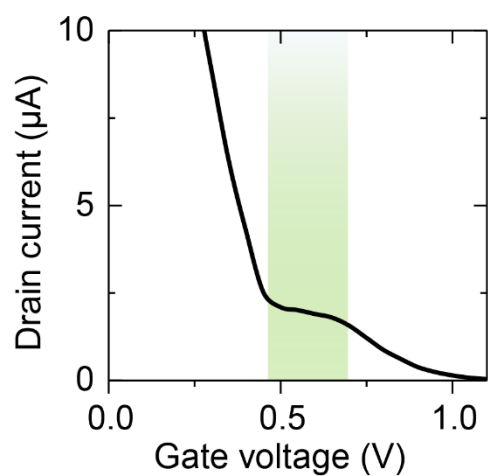
Fig. S14. (A) Cyclic voltammetry data of different PEDOT:PSS polymers. (B) HOMO level derived from cyclic voltammetry data and (C) oxidation potential derived from HOMO level.



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140 **Fig. S15.** Cyclic voltammetry data of the ferrocene solution.

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143 **Fig. S16.** Linear plot of transfer characteristics for DuECT based on the P3HT/PEDOT:PSS-F channel.

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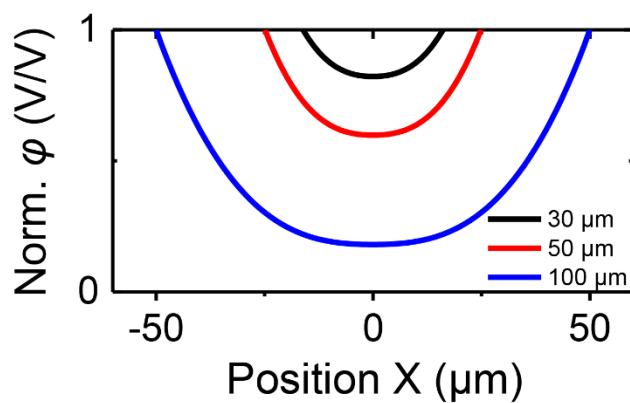


Fig. S17. Normalized electrostatic potential for dual channel under the electrode, determined through numerical calculation.

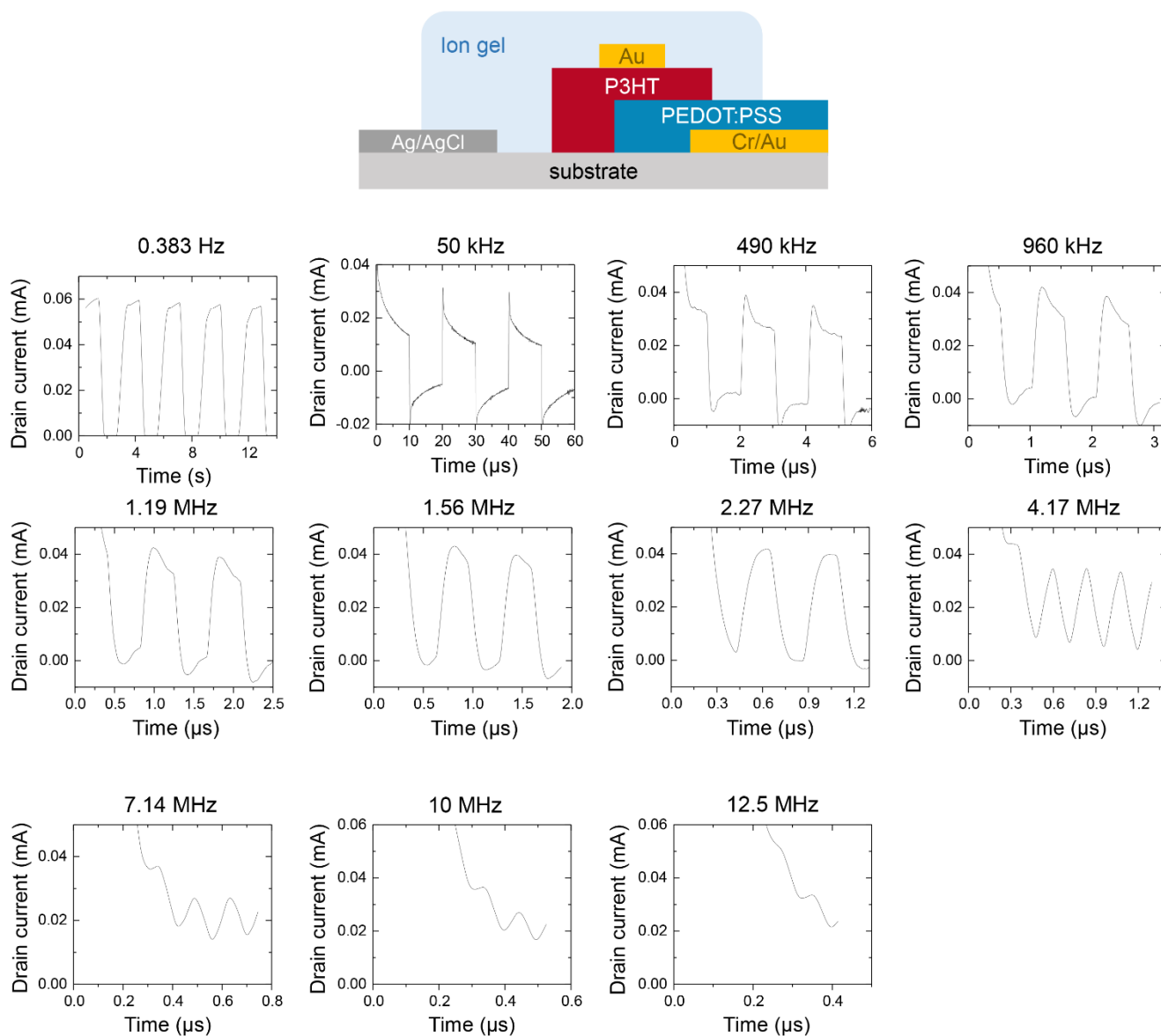


Fig. S18. Device structure and temporal responses of DuECT with various gate pulses.

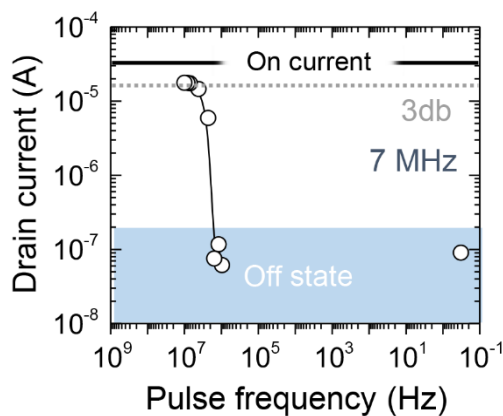


Fig. S19. Current bode plot of DuECT (unpatterned P3HT) operating at $V_D = 1$ V and $V_G = 1$ V.

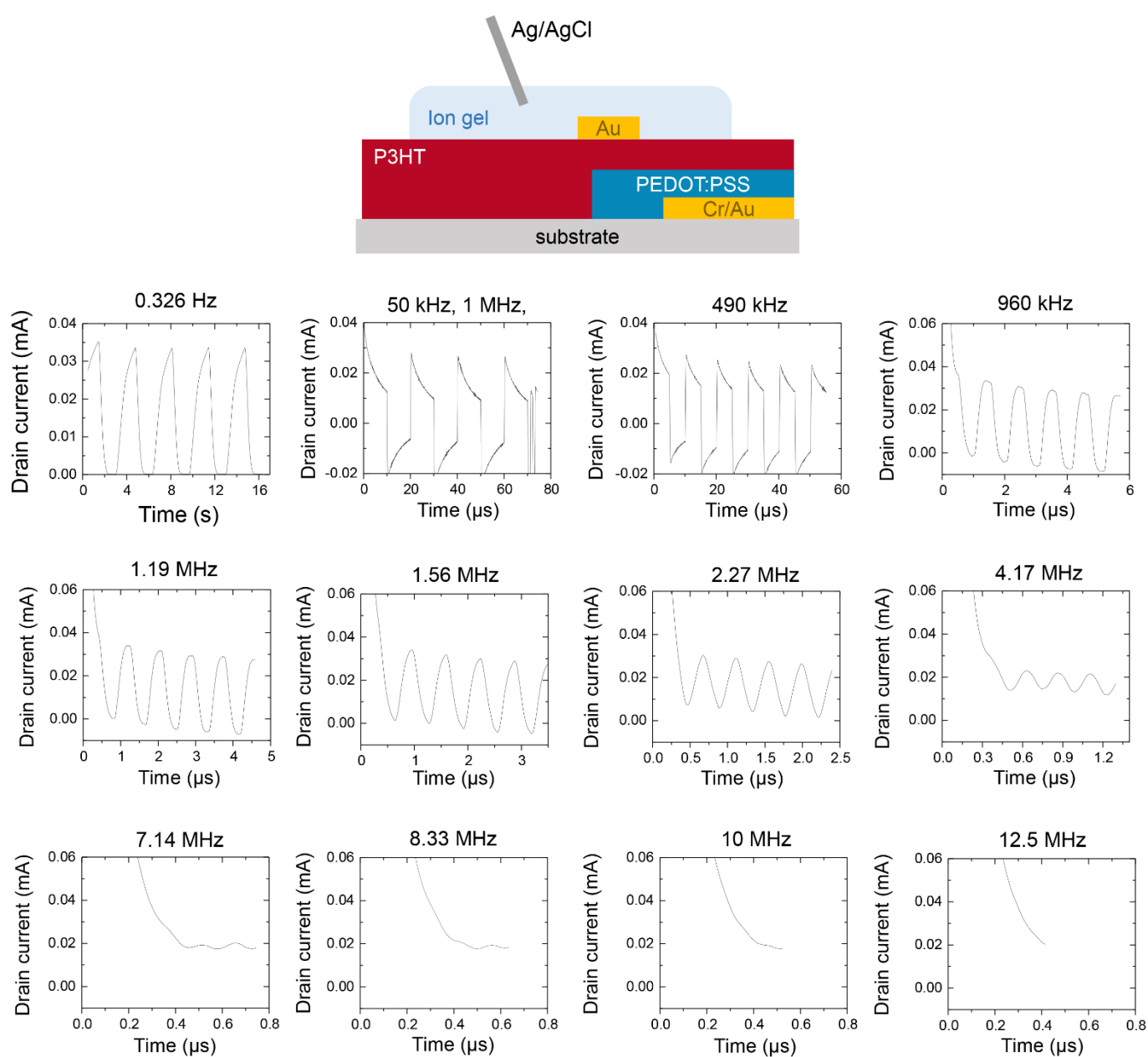


Fig. S20. Temporal responses of DuECT (unpatterned P3HT) with various gate pulses.

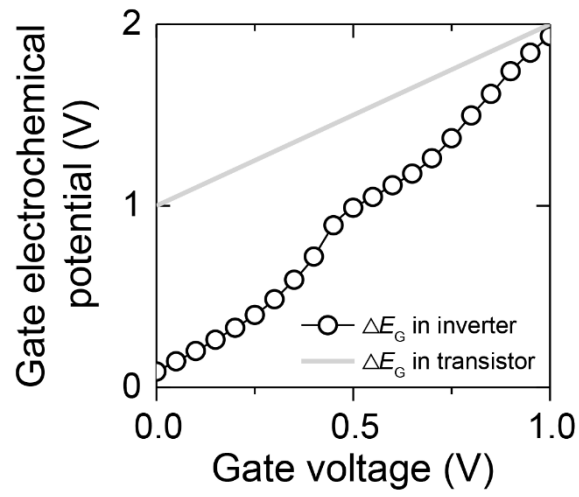


Fig. S21. Gate electrochemical potential applied to the channel on the inverter and transistor.

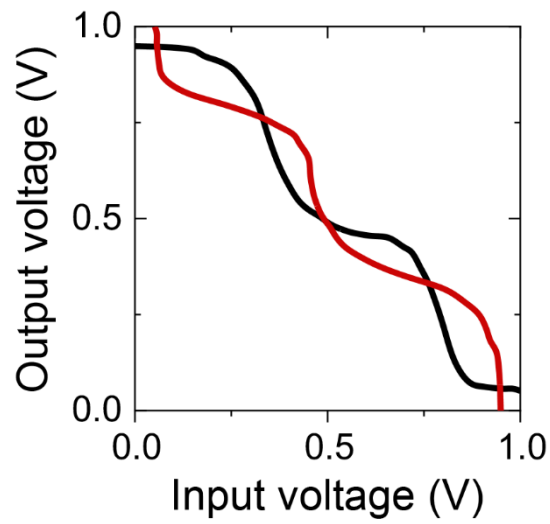


Fig. S22. Plot of symmetric in-out VTC for static noise margins of 0.1283 V and 0.0925 V.

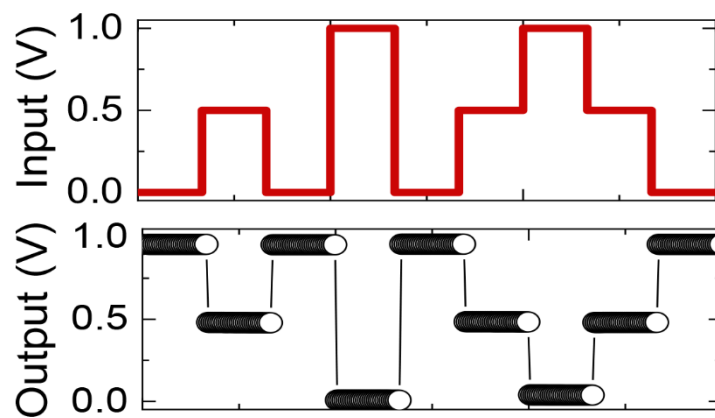


Fig. S23. Output voltages of inverter with varying input voltages.

A

	NMIN		
	0	1	2
0	2	2	2
1	2	1	1
2	2	1	0

B

	NMAX		
	0	1	2
0	2	1	0
1	1	1	0
2	0	0	0

Fig. S24. True tables of **(A)** NMIN and **(B)** NMAX

176 **Table S1.** Operation speeds and channel lengths in OECTs. (* measured based on Fig.s owing to the lack of
177 accurate information.)

Year	Channel material	Electrolyte material	Gate electrode	Channel length (μm)	V_D (V)	V_G (V)	τ_{rise} or f_{-3dB}	Ref.
2004	P3HT	CyEPL	SnO ₂	30	-10	-6	50 Hz	1
2005	PEDOT:PSS	NaCl	Au	50	-0.1	0.4	1 s	2
2007	P3HT	BMIM PF ₆	copper	20	-1	-3	1 ms	3
2008	P3HT	EMIM TFSI		20	-1.5	-2.5	10 kHz	4
2008	P3HT	EMIM TFSI		20	-1	-3	0.2 Hz	5
2009	P3HT	EMIM TFSI		20	-1	-3	500 Hz	6
2011	PEDOT:PSS	PBS	Pt	6	-0.5	0.4	100 us	7
2012	PEDOT:PSS	DMEM	Ag/AgCl	8000	-0.1	0.3	1 s	8
2013	CNT	EMI TCB		10	2	1.2	4.5 us	9
2013	PEDOT:PSS	NaCl	Ag/AgCl	5	-0.4	0.5	39 us	10
2013	PEDOT:PSS	NaCl	Ag/AgCl	10	-0.4	0.5	102 us	10
2014	PTHS	NaCl	Ag/AgCl	10	-0.6	-0.8	38 ms	11
2014	PEDOT:PSS	PBS	Pt or Ag	30	-0.5	0.1	1.5 ms	12
2015	PEDOT:PTHF	KCl	Ag/AgCl	10000		0.5	50 ms	13
2015	PEDOT:PSS	BMIM Otf	PEDOT:PSS	2000*	-1	2	0.2 s	14
2016	TIPS:Pentacene	NaCl		30	-0.4	1.15	0.45 ms	15
2016	p(g2T-TT)	NaCl	Ag/AgCl	10	-0.6	-0.6	420 us	16
2017	P3HT	Pyr14 TFSI		10	-1	-1	18 ms	17
2018	graphene	EMIM TFSI		5000		-4	2.4 s	18
2018	graphene	NaCl	Ag/AgCl	30	0.15	0.02	7.8 kHz	19
2018	PEDOT:PSS	NaCl	Ag/AgCl	0.45	-0.6	-0.8	1.7 kHz	20
2019	PEDOT:PSS	PBS	Ag/AgCl	30		0.3	191.2 us	21
2019	PEDOT:PSS	chitosan		30		0.3	31.7 us	21
2019	PEDOT:PSS	chitosan		12	-0.6	0.1	380 kHz	21
2019	P3HT	EMIM TFSI		0.04	-0.3	-3	1.2 kHz	22
2019	PEDOT:PSS	H ₂ O ₂ , EMEM cell	Ag/AgCl	1000	-0.2	-0.2	3.33 s*	23
2019	PEDOT:PSS	PBS	Ag/AgCl	10		0.1	1.48 ms	24
2020	PBTTT	KCl + BMIM TFSI	Ag/AgCl	20	-0.6	-0.7	3.1 s	25
2020	p(g4T2-T)	NaCl	Ag/AgCl	10	-0.6	-0.6	0.59 ms	26
2020	PEDOT:PSS	chitosan		5	-0.6	-0.4	2.9 us	27
2021	PEDOT:PSS	PBS	Au	30	0.05	0.5	0.6 ms	28

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