High performance ambipolar organic mixed ionic-electronic conductor for adaptive logic circuits and neuromorphic electronics

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Organic mixed ionic-electronic conductors (OMIECs) are central to bioelectronic applications such as biosensors¹, health monitoring devices and neural interfaces², and have facilitated efficient next-generation brain-inspired computing³ and biohybrid systems⁴. Most OMIECs are hole-conducting (p-type) materials, while complimentary logic circuits and various biosensors require electron-conducting (n-type) materials too^{5,6}. Here we show an ambipolar mixed ionic-electronic polymer that achieves high on/off ratios with high ambient p- and n- type stability. We highlight the versatility of the material by demonstrating its use as a neuromorphic memory element, an adaptable ambipolar complementary logic inverter, and a neurotransmitter sensor. The ambipolar operation of this material allows for straightforward monolithic fabrication and integration, and opens a route towards more sophisticated complex logic and adaptive circuits.

The success of many organic bioelectronic applications results from the reduced interface impedance and the extraordinarily high electrochemical transconductance in OMIECs^{7,8}. These and other unique properties such as biocompatibility, low voltage operation, simple fabrication processing, stretchable and flexible materials, and the extensive capabilities in tailoring molecular structures and functions via chemical synthesis has opened a wide variety of possible bioelectronic applications such as neural probes⁷ and sensors for ions⁹, metabolites⁵, bacteria¹⁰, and viruses¹¹. Furthermore, the huge dynamic range and electrochemical doping nature of these polymers has produced tuneable analogue neuromorphic devices^{3,12} with high stability¹³ resulting in proof-of-principle circuits^{14,15} as well as biohybrid systems directly modulated by neurotransmitters secreted locally⁴. Current applications are often based on the commercially available poly(3,4-ethylene-dioxythiophene): polystyrene sulfonate (PEDOT:PSS), which is a p-type (hole) conductive polymer that operates in depletion-mode. This means that the material is conductive and can be turned off by applying a gate potential. Enhancement-mode p-type devices exist, notable by design¹⁶ or by dedoping of PEDOT:PSS with small molecule amines¹⁷. However, in order to form logic gates, complementary circuits, and energy storage devices, a combination of p- and n-type materials is required⁶. Besides, n-type OMIECs are essential for detecting metabolites like glucose and lactase in enhancement mode organic electrochemical transistors (OECTs)⁵.

Despite various efforts to explore n-type materials, to date the amount and the performance of n-type OMIECs is still inferior compared to its p-type counterpart. The key issue is that (doped) n-type materials in general are extremely unstable when exposed to air, combined with the challenge of achieving high electron mobility. Another challenge is to obtain OMIECs that can be doped by both cations and anions and can conduct both holes and electrons. One strategy to design n-type conjugated polymers is copolymerizing an electron deficient moiety (acceptor), such as naphthalenediimide (NDI), with an electron rich moiety (donor) like thiophene. These donor-acceptor (D-A) polymers are often modified with hydrophilic ethylene glycol (EG) type side chains for applications as aqueous electrolyte gated transistors, glucose sensing, and biofuel applications¹⁸. The EG chains support highly efficient electrochemical doping within the whole volume and enables low voltage (<1V) operation, which is essential when using an aqueous electrolyte. In order to properly operate stable devices in water, a LUMO level below -4eV is required for n-type polymers to avoid side reactions with water and oxygen¹⁹. High performance n-type OMIECs require balancing the ions and electron mobility, while maintaining unperturbed crystalline structures upon electrochemical doping²⁰. It has been reported that embedding sp²-N into polymer backbones results in a more planar structure, enhancing the π - π stacking, and increasing the electron mobility^{21,22}. Capitalizing on these properties, the material we present here is an NDI-bithiozale D-A copolymer (referred to as P-3O, shown in Fig. 1a) functionalized with EG side chains, for stable operation both in aqueous environments as well as with a solid electrolyte.

An all-solid-state environment is desirable in applications associated with electronic circuitry, logic circuits, and neuromorphic computing, as the operation of circuits in aqueous environments can lead to interference with the surrounding electronics as well as neighboring devices. From a technological point of view the use of liquid electrolytes limits the high-density integration of devices.²³ The solid electrolyte consists of an ionic liquid (1-ethyl-3-methylimidazolium bis(trifluorosulfonyl)imide, EMIM:TFSI) within a polymer matrix (poly(vinylidene fluoride-co-hexafluoropropylene), PVDF-HFP)²⁴. Figure 1a shows the architecture of the solid electrolyte-gated device. The devices can be designed with a side gate which simplifies the fabrication by avoiding a complex layer-by-layer process to construct a stacked structure. Figure 1b and 1c give the output and transfer characteristics of the P-3O OECT showing a near-symmetric ambipolar electrical behaviour when operated in ambient environment with a solid gel-electrolyte. The polymer achieves an on/off ratio of 10⁴ and shows stable operation for more than 20,000 cycles for both p- and n-type in ambient conditions, see Figure 1d and 1e. This all-solid-state device allows for straightforward fabrication and facile integration of large circuitry such as an array architecture often used in neuromorphic computing or integrated adaptable electronic circuits.

Figure 1| Solid-state ion-gated transistor. **a)** Schematic of the ion gel side-gated organic electrochemical transistor. Chemical structures of the conjugated D-A polymer P-3O and ion gel. **b)** Ambipolar output curve. **c)** Ambipolar semi-log transfer curve carried out in ambient environment. **d)** n-type and **e)** p-type operational stability measurement of the ion gel gated transistor. The drain current (I_{ds}) was monitored when applying a 5s gate voltage pulse $|V_G|=0.8$ V (interval time of 5 s) for 21600 pulse cycles ($|V_{ds}|=0.1$ V).

We demonstrate this capability by fabricating an adaptive memory device, an electrochemical random-access memory (EC-RAM) based on P-3O. The EC-RAMs adopt a similar configuration as solid-state electrochemical transistors and maintains non-volatile memory by employing an open gate circuit in combination with a current limiting resistor (see Fig. 2a). The conductance can be randomly accessed over a large range and in an analog fashion, allowing these devices to act as synaptic weights in hardware artificial neural networks, enabling parallel computation¹⁵ and increasing the energy efficiency. Organic EC-RAMs are able to operate at low voltage and with high write speeds (20 ns pulse).²⁵ The P-3O EC-RAMs function in n-type mode (positive read and write voltage) and can access over 2^5 conductance states across two orders of magnitude, in linear fashion, and with high state retention (see Fig. 2). Figure 2b shows a state retention of 5 minutes in nitrogen atmosphere. Due to the presence of oxygen and water, encapsulation is needed for operating in ambient conditions (see Fig. S19). The state retention can be further improved by optimising the device geometry and purifying the ion gel. The n-type P-3O-based EC-RAM exhibits comparable performance to p-type polymer based EC-RAMs such as PEDOT:PSS¹³, p(g2T-TT)²⁵, and P3HT²⁶. Even though the P-3O polymer is ambipolar, the p-type mode (negative read and write voltage) EC-RAM decays faster even in nitrogen atmosphere (see Fig. S20) which might indicate that the energetic barrier for back diffusion of the anions (TFSI⁻) is low²⁷. The n-type EC-RAMs can be further integrated in large crossbar arrays to emulate the synaptic weights in an artificial neural network. We simulate the behaviour of such an array, in its performance to recognize and

classify handwritten digits (see Supplementary Information). The linear and symmetric behaviour of potentiation and depression of the conductance (see Fig. 2e) results in efficient training and inference of the neural network. Figure 2f shows that for both the small and large handwritten digits dataset the accuracy of training an EC-RAM is comparable to the ideal numeric accuracy, which is the theoretical limit for this algorithm.

Figure 2| Solid-state ion-gated EC-RAM. **a)** Schematic of the EC-RAM with a resistor in series to limit the gate current, used to access different conductance states. **b)** State retention in a N_2 environment for 5 minutes at different conductance states over two orders of magnitude. **c)** Behaviour over time when tuned to different discrete conductance states. **d)** 14 cycles of 32 conductance states showing linear potentiation and depression (pulse width 300 ms and delay 500 ms with a 1 GOhm resistor). **e)** Heat map of the change in conductance across the conductance range for both potentiation and depression with the colour representing the cumulative distribution function (CDF) at each conductance state. **f)** Training results of the simulation showing the accuracy of the ideal numerical and experimentally derived neural network for 40 epochs classifying 8x8 pixel (small) and 28x28 pixel (large) handwritten digits²⁸.

Due to the excellent performance of the P-3O ambipolar polymer that spans across multiple different functional areas, complex and integrated circuits can be realized while remaining a straightforward monolithic fabrication process. Since both the p- and n-type transfer curves

have a near-identical behaviour (shown in Fig. 1c), we can fabricate an inverter, a fundamental building block of electronic circuits (see Fig. 3). Inverters are used in both digital circuits, as logic gates, and in analogue circuits as voltage amplifiers since it inverts the applied input voltage (V_{in}) from a high to low voltage and vice versa (see Fig. 3a and b). At the transition region it shows a high gain which makes an organic inverter find relevant and wide applications in several fields, including for example printed electronics, imperceptible and wearable electronics, sensors and bioelectronics^{29–31}. Figure 3a shows the performance of the solid-state ambipolar inverter with a gain of 12 at $V_{DD} = 0.8V$, along with Figure 3b presenting the logic NOT gate operation where a high input results in a low output voltage. To highlight opportunities for more advanced bioelectronic applications as well as future personalized and adaptive systems operating locally, we combine the ambipolar inverter with the EC-RAM in order to realize an adaptable, or trainable, circuit, without increasing fabrication complexity. The neuromorphic inverter configuration (shown in Fig. 3c) allows for interactive tuning of the gain, a characteristic feature used to extract, for example, electrophysiological signals². The conductance of the EC-RAM can be altered in a similar fashion as described before. The conductance states that are presented in Figure 3d modulate the inverter behaviour and result in a shift of the inverter gain peak (see Fig. 3e).

Conventional complementary circuits based on a combination of a p- and n-type material commonly require multiple or complex fabrication steps. Using our ambipolar conductive polymer we can significantly decrease this complexity by monolithic fabrication including the added neuromorphic traits. This expands the capabilities of the complementary circuits in bioelectronics and sensors, in which OMIECS have already proven to be powerful due to their large volumetric ionic capacitance that allows for a significant amplification when transducing biological signals. In biological, aqueous, environments stable p-type OMIECs are common, whereas high performance n-type materials, in terms of stability and electrical behaviour, are not. However, for biosensors detecting anions or some metabolites like glucose, stable n-type materials are crucial.

Figure 3| Solid-state ambipolar inverter. a) Ambipolar inverter behaviour at different V_{DD} voltages with below the corresponding gain ($|dV_{out}/dV_{in}|$) and the inset representing the

schematic inverter circuit. **b)** Complementary logic gate behaviour of a NOT gate with $V_{DD} = 0.8V$ and the input V_{in} pulsing between 0 and 0.9V for 6s. **c)** Illustration of a neuromorphic inverter including an EC-RAM in series with the gate of the ambipolar inverter. **d)** Read out of the different conductance states of the EC-RAM with **e)** the corresponding behaviour of the neuromorphic inverter ($V_{DD} = 0.8V$).

We studied the behaviour of a 100 mM NaCl aqueous electrolyte gated OECT using P-3O as the active channel, and Ag/AgCl as the gate electrode (shown in Fig. 4a). In this configuration P-3O also exhibits ambipolar behaviour in transistor performance (see Fig. 4b and 4c for the output and transfer curves), which indicates that the polymer could also be doped by both cations (Na^+) and anions (Cl^-). In n-type mode, the P-3O polymer works exceptionally well with stable on/off ratio of ~ 4 orders of magnitude for more than 21600 cycles, shown in Figure 4d. After continuously operating more than 60 hours, the on-current only exhibits a slight decrease (approximately 25%) but maintains the on/off ratio in similar orders of magnitude (see Fig. S13). The remarkable stability is a result of the precise tailoring of the energy levels (LUMO - 4.30 eV, see Fig. S10 and Table S1) with respect to oxygen and water¹⁹. Despite extremely high stability for p-type in ion-gel, the material performance in liquid electrolytes in p-type mode is less (see Fig. S14), showing 2 orders of magnitude on/off ratio for over 2 hours operation. The aqueous electrolyte operated ambipolar inverter and the tuning of it using the EC-RAM is demonstrated in Figure S22 and S24. We further show the exceptional n-type performance of the P-3O polymer in aqueous electrolyte by demonstrating its behaviour as a neurotransmitter sensor (see Fig. 4e) which has potential in advanced biohybrid systems⁴. We adopted a Au side-gated device configuration in Figure 1a and monitored the drain current at a drain potential of $V_{ds}=0.1V$, while oxidizing the dopamine at the gate electrode by applying a gate potential of $V_g=0.6V$. A faradaic gate current was observed when different concentrations of dopamine analyte were added (Fig. 4e bottom panel), which lowers the potential drop at the Au gate and electrolyte interface, leading to more effective gating at the channel (See Fig. S15). Meanwhile, the drain current increases in response to increased dopamine concentrations (Fig. 4e top panel and Fig. S16, S17). These results prove the interaction of P-3O as an excellent electron conductor with neurotransmitters like dopamine, showing its potential in adaptive biohybrid applications.

Figure 4| Aqueous operation of the P-3O based devices. **a)** Schematic of aqueous electrolyte gated OECT. **b)** Ambipolar P-3O OECT output curve. **c)** Ambipolar P-3O OECT semi-log transfer curve. **d)** N-type OECTs ($V_g=0.8V$, $V_{ds}=0.5V$) operation stability in 100mM NaCl aqueous electrolyte for 21600 pulse cycles. A gate voltage pulse V_g was applied for 5 s with an interval time of 5 s. **e)** Au side-gated OECTs for dopamine sensing. The output drain current I_{ds} , gate current I_{gs} were monitored when adding different concentration of dopamine into the 100 mM NaCl (aq.) electrolyte at $V_{ds}=0.1V$ and $V_g=0.6V$. A glass well was glued to the device using PDMS to retain the electrolyte. Starting with 40 μL 100 mM NaCl aqueous solution. 10 μL analyte solution was added into the well each time.

Due to the intrinsic ionic-electronic coupling, OMIECs exhibit great potential not only in bridging electronics and biological systems, but also in constructing non-volatile memory devices for hardware artificial neural networks (ANNs). In this work, we have presented the capability to integrate individual devices into circuits for potential applications like adaptive biosensors and brain-inspired computing, utilizing the ambipolar NDI-thiazole conjugated polymer P-3O. The remarkable characteristics of this semiconducting polymer, including symmetric p- and n-type behaviour, high performance and ambient stability, allows for straightforward monolithic fabrication and integration of single devices, including transistors, neuromorphic memory and sensors, as well as logic gates and trainable circuits for next-generation adaptive and personalized bioelectronic applications.

Experimental

Materials. The P-3O synthesis details and characterization are described in the Supplementary Information. Chloroform, 1-ethyl-3-methylimidazolium bis(trifluorosulfonyl)imide, poly(vinylidene fluoride-co-hexafluoropropylene), and dopamine hydrochloride are purchased from Sigma-Aldrich and used as received. The ion gel solution was prepared following the reported method²⁴ without further baking the ionic liquid. Ionic liquid (EMIM:TFSI) and poly(vinylidene fluoride-co-hexafluoropropylene) (4:1 w/w) were dissolved in acetone with the following proportions: 17.6 wt% ionic liquid, 4.4 wt% polymer and 78 wt% solvent. The resulting ion gel solution was stirred at 40 °C for at least 30 min. The interdigitated microelectrodes IDA-Au-6 (channel length L 5 μm , individual channel width w 1.8 mm, number of pairs 30, number of channels n 59, total channels width $W=n \cdot w=10.62$ cm) are purchased from MicruX technologies.

OECTs, EC-RAMs Fabrication and Characterization. The polymer solutions were prepared in chloroform at the concentration of 5 mg/mL. The interdigitated microelectrodes were treated with UV ozone over 15 mins, following spin-coating the polymer solutions at 1000 rpm for 30s. The samples were annealed on the hotplate at 100 °C for 30 mins. For side gate devices, the gate and active channel were separated by excimer laser ablation. The ion gel solution was drop casted on the top of the active area and dried in the fume hood. For EC-RAM measurements, the devices were stored in the nitrogen atmosphere glovebox. The electrical characterization of OECTs is recorded by a Keithley sourcemeter SMU 2602B, which is controlled by the software Arkeo developed by Cici research. The EC-RAMs are recorded by Keithley 2602B with Labview and the inverter data is acquired with a NI DAQ USB-6363 and with Keithley SMU 2636B controlled with Matlab software.

Data availability

The data are available from the authors on reasonable request.

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Author contributions

Y.Z., G.Y., J.S., and Y.v.d.B initiated the idea. Y.v.d.B. supervised the project. G.Y., J.S., and R.C.C. designed the polymer. G.Y. synthesized and characterized the polymer. Y.Z, E.R.W.D. and Y.v.d.B. designed the experiments. Y.Z, E.R.W.D performed device fabrications and the measurements. T.S. performed the CrossSim simulation. Y.Z., E.R.W.D. and G.Y. prepared the manuscript. Y.Z., E.R.W.D and Y.v.d.B. wrote the manuscript. All the authors contributed to the comments and suggestions on the final manuscript.

Competing financial interests

The authors declare no competing financial interests.

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Supplementary Information

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1. Synthetic Procedures

1-1 Synthesis and characterization of materials

Reagents

All reagents and solvents were commercial and were used as received. 2,6-dibromo-1,4,5,8-naphthalene tetracarboxylic diimide was purchased from TCI. 4,4'-bis(octyloxy)-2,2'-bis(trimethylstannyl)-5,5'-bithiazole (**2Tz**) was purchased from SunaTech. 2-(2-(2-methoxyethoxy)ethoxy)ethanamine and bis(2-(2-(2-ethoxyethoxy)ethoxy)ethyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (**NDI-30**) were synthesized according to literature procedures ^{S1-S2}.

Characterization

¹HNMR and ¹³CNMR were performed on a Varian Unity Plus (400 MHz) instrument at 25 °C, using tetramethylsilane (TMS) as an internal standard. NMR shifts are reported in ppm, relative to the residual protonated solvent signals of CDCl₃ (δ = 7.26 ppm) or at the carbon absorption in CDCl₃ (δ = 77.23 ppm). Multiplicities are denoted as: singlet (s), doublet (d), triplet (t) and multiplet (m). High Resolution Mass Spectroscopy (HRMS) was performed on a JEOL JMS 600 spectrometer. FT-IR spectra were recorded on a Nicolet Nexus FT-IR fitted with a Thermo Scientific Smart iTR sampler. Thermal properties of the polymers were determined on a TA Instruments DSC Q20 and a TGA Q50. DSC measurements were executed with two heating-cooling cycles with a scan rate of 10 °C min⁻¹. TGA measurements were done from 20 to 800 °C with a heating rate of 20 °C min⁻¹. Cyclic voltammetry (CV) was carried out with a CH-Instruments 760e Electrochemical Workstation in a three-electrode configuration where the working electrode was glassy carbon electrode, the counter electrode was a platinum wire, and the pseudo-reference was a Ag/Ag⁺ reference electrode that was calibrated against ferrocene (Fc/Fc⁺). Cyclic voltammograms for the polymer films deposited on the glassy carbon working electrode in CHCN₃ solution containing Bu₄NPF₆ (0.1 mol L⁻¹) electrolyte at a scanning rate of 100 mV s⁻¹.

Figure S1: Synthetic route for NDI based monomer **NDI-30**.

Synthesis of **NDI-30**

2-(2-(2-methoxyethoxy)ethoxy)ethanamine (600 mg, 3.38 mmol, 4 eq) was added to a suspension of 2,6-dibromo-1,4,5,8-naphthalene tetracarboxylic diimide (360 mg, 0.845 mmol, 1 eq) in 10 mL of glacial acetic acid and heated to 120°C for 4 h. The reaction mixture was then cooled to room temperature and added to water, then extracted with CH₂Cl₂. The organic phase was washed with brine, dried over anhydrous sodium sulfate and removed solvent by rotary evaporator. The crude product was purified by silica gel column chromatography with CH₂Cl₂/acetone as the eluent afforded target compound as a bright yellow solid.

NDI-30: ¹HNMR (400 MHz, CDCl₃): δ 8.97 (s, 2H), 4.46 (t, J = 5.6 Hz, 4H), 3.84 (t, J = 6.0 Hz, 4H), 3.73-3.67 (m, 4H), 3.65-3.52 (m, 8H), 3.52-3.42 (m, 4H), 3.31 (s, 6H). ¹³CNMR (100 MHz, CDCl₃): δ 163.47, 163.37, 141.66, 130.97, 130.40, 127.96, 126.74, 74.51, 73.16, 72.74, 70.22, 61.64, 42.67. HRMS(ESI) Calcd. for C₂₈H₃₂Br₂N₂O₁₀Na₁ [M+Na]⁺: 739.02954, found: 739.03025.

a)

b)

Figure S2: a) ^1H NMR and b) ^{13}C NMR spectra of **NDI-30**

Figure S3: HRMS spectra of **NDI-30**

Figure S4: Synthetic route for NDI-Tz based low band gap conjugated polymer P-3O.

Synthetic procedures for the NDI-Tz (PNDI-3O) based polymers

To a dry three-neck flask, NDI based monomer **NDI-3O** (0.1 mmol, 71.6 mg) and thiazole based monomer **2Tz** (0.1 mmol, 75 mg) were added under argon followed by tris(dibenzylideneacetone) dipalladium [$\text{Pd}_2(\text{dba})_3$] (8 mg) and tri(*o*-tolyl)phosphine [$\text{P}(\text{o-tolyl})_3$] (12 mg). The flask and its contents were subjected to 3 pump/purge cycles with N_2 followed by addition of anhydrous, degassed chlorobenzene (5 mL) via syringe. The reaction mixture was stirred at 120 °C for five days. After cooling to room temperature, the deeply gray coloured reaction mixture was dropped into 100 mL vigorously stirred methanol (containing 5 mL 12 M hydrochloric acid). After stirring for 4 hours, the precipitated solid was collected by filtration. The solid polymers were redissolved in chloroform and reprecipitated into methanol. After filtration, the polymers were subjected to sequential Soxhlet extraction. The sequential solvents were methanol, hexane and chloroform. Impurities and low-molecular-weight fractions were removed by methanol and hexane. Finally, the polymer solution in chloroform was concentrated to give the polymers as dark solid. ^1H NMR (400 MHz, CDCl_3): δ 10.38-8.79 (m, 2H), 5.08-2.66 (m, 34H), 2.12-0.62 (m, 30H). IR (cm^{-1}): 668, 692, 719, 763, 790, 896, 950, 982, 1064, 1104, 1176, 1208, 1245, 1297, 1314, 1366, 1441, 1487, 1564, 1647, 1698, 2854, 2920.

Figure S5: ^1H NMR spectra of NDI based polymer (P-3O).

Figure S6: IR spectra of NDI based polymer (P-3O).

Figure S7. MALDI-TOF-MS spectra of NDI based polymer P-30.

1-2 Thermal properties

Figure S8: Thermogravimetric (TGA) analysis plots and DSC analysis plots for NDI based polymers (P-30).

1-3 Absorption properties

Figure S9: The absorption of NDI based polymers (P-30) in dilute CHCl_3 (10^{-5} M) and thin film state.

1-4 Electrochemistry properties

Figure S10. Cyclic voltammograms of the conjugated polymer P-3O thin films deposited on the glass carbon working electrode in CHCN_3 solution containing Bu_4NPF_6 electrolyte.

Table S1. Optical and electrochemical data for the polymer P-3O.

Polymer	$\lambda_{\text{max}}^{\text{film}}$ [nm]	$\lambda_{\text{onset}}^{\text{film}}$ [nm]	$E_{\text{g}}^{\text{opt. (a)}}$ [eV]	HOMO (b)[eV]	LUMO (c)[eV]	$E_{\text{onset}}^{\text{ox.}}$ [V]	$E_{\text{onset}}^{\text{red.}}$ [V]	E_{g}^{ec} [eV]
P-3O	973	1225	1.01	-5.53	-4.30	0.43	-0.80	1.23

(a) $E_{\text{g}}^{\text{opt.}} = 1240 / \lambda_{\text{onset}}^{\text{film}}$

(b) $\text{HOMO} = - (5.10 + E_{\text{onset}}^{\text{red.}}) \text{ eV}$

(c) $\text{LUMO} = - (5.10 + E_{\text{onset}}^{\text{ox.}}) \text{ eV}$

2. OECTs

2-1 Ion gel gated OECTs

a)

b)

Figure S11. Comparison of P-3O ion gel OECT n-type transfer curve ($V_{\text{ds}}=0.1\text{V}$) before and after bias stress stability over 21600 cycles (pulse 5s, interval 5s, over 60 hours). a) Linear plot, b) Semi-log plot.

Figure S12. Comparison of P-3O ion gel OECT p-type transfer curve ($V_{ds} = -0.1V$) before and after bias stress stability over 21600 cycles (pulse 5s, interval 5s, over 60 hours). a) Linear plot, b) Semi-log plot.

2-2 Aqueous electrolyte OECT

Figure S13. Comparison of P-3O 100mM NaCl aqueous OECT transfer curve ($V_{ds} = 0.6V$) before and after bias stress stability over 21600 cycles (pulse 5s, interval 5s, over 60 hours). a) Linear plot, b) Semi-log plot.

Figure S14. P-type ($V_g = -0.7V$, $V_{ds} = -0.1V$) OECTs operation stability in 100mM NaCl aqueous electrolyte. A gate voltage pulse V_g was applied for 5 s with an interval time of 5 s. The device became unstable after 950 cycles and broke down eventually.

2-3 Dopamine sensing

Figure S15. **Dopamine sensing mechanism.** Dopamine (DA) can be electrochemical oxidized to its quinone form (DQ). This schematic illustrates the potential drop across the Au gate OECTs system. When a gate potential (higher than the oxidation potential of DA) is applied, Dopamine is oxidized electrochemically at the Au gate electrode. The oxidation of DA generates Faradaic currents, which lower the potential drop across the Au/electrolyte interface, leading to more effective gating at the active channel.

Figure S16. Comparison of P-3O Au side-gated OECT transfer curve ($V_{ds}=0.1V$) with and without 1 M dopamine in 100mM NaCl aqueous electrolyte.

Figure S17. Comparison of P-3O Au side-gated OECT output curve a) with 1 M dopamine, b) without dopamine in 100mM NaCl aqueous electrolyte.

3. EC-RAMs

Figure S18. Linear plot of P-3O EC-RAMs n-type conductance state retention over time (5 mins).

Figure S19. The retention time comparison of P-3O EC-RAM devices **n-type** operation in ambient and N₂ atmosphere glovebox. The conductance state decays faster when oxygen and water present ($V_{ds}=0.1V$).

Figure S20. The retention time of P-3O EC-RAM devices **p-type** operation in N_2 atmosphere glovebox. The conductance state decays very fast ($V_{ds} = -0.1V$).

4. Ambipolar inverter

4.1

The ambipolar inverter is realized by connecting two single ion-gated transistors with a shared ion gel or aqueous electrolyte. One of the two channels of the Keithley SMU 2636B is used to supply the input voltage (V_{in}) whereas the other channel is used for the potential at V_{DD} . Each of these voltages including the output voltage (V_{out}) is recorded with a DAQ NI USB-6353. The operation with either a solid ion gel or aqueous electrolyte shows the transition from a high to low output at a different input value. This correlates to the different values of the threshold voltage obtained from the transfer curve (Figure S11 and S13). The higher gain for aqueous electrolyte gated inverters can be explained by the higher on/off ratio for the individual OECT devices. Due to the increased conductance at the gate-electrolyte interface the voltage drop across this interface is reduced and the gating at the channel is more effective compared to the ion-gel gated equivalent.

Figure S21. Solid state ambipolar inverter behavior for increasing V_{DD} (0.65V to 0.80V). Input voltage V_{in} is scanned from -0.3V to 1.1V and back (0.01V/s).

Figure S22. Aqueous gated ambipolar inverter behavior for increasing V_{DD} (0.70V to 0.80V). Input voltage V_{in} is scanned from -0.2V to 0.5V and back (0.01V/s).

4.2

The neuromorphic ambipolar inverter is configured in a similar fashion as the regular ambipolar inverter described in SI.4.1, with the difference that the EC-RAM channel is in series with the gate (previously V_{in}) of the regular inverter. The conductance state of the EC-RAM is modified with Keithley SMU 2602B using LabView software.

Figure S23. Solid-state neuromorphic inverter behavior for $V_{DD} = 0.70$ V, $V_{DD} = 0.75$ V, and $V_{DD} = 0.80$ V with each scan a decreasing EC-RAM conductance. Input voltage V_{in} is scanned from -0.3V to 1.0V and back (0.01V/s). For the sweep at the lowest conductance value V_{in} is scanned to 1.4V in order to completely turn the inverter output off.

Figure S24. Aqueous neuromorphic inverter behavior for $V_{DD} = 0.70V$, $V_{DD} = 0.75V$, and $V_{DD} = 0.80V$ with each scan a decreasing EC-RAM conductance. Input voltage V_{in} is scanned from $-0.1V$ to $0.5V$ and back ($0.01V/s$).

5. EC-RAM based neural network simulation

In order to verify the EC-RAM's ability to function as the weight in a neural network, the classification performance of crossbar array of these devices is examined. A model of a crossbar array is simulated using CrossSim (Sandia National laboratories)^{S5} with the same network architecture as described in the reference [S3,4]. The small (8×8 pixel)^{S6} and large (28×28 pixel)^{S7} MNIST handwritten digits datasets are used and classified with a $64 \times 36 \times 10$ and $784 \times 300 \times 10$ network structure, respectively.

The experimental weights are extracted from the conductance modulation measurement (Figure 2d) with 14 potentiation and depression cycles of 32 measured states. In the simulation the weights are offset by 50% to introduce negative weight values and the total range is clipped by 25% (maximum and minimum) to enable operation in the most linear regime. Both datasets are trained for 40 epochs with a sigmoid activation function. To validate the efficacy of the EC-RAM based crossbar array the experimentally derived weights are compared to the ideal numeric weights. The numeric analyses simulate the perfect EC-RAM, i.e. no read/write noise and no nonlinearity. Clipping is also disabled for the numeric analysis which removes all restrictions on maximum and minimum weight values allowing operation across the full range. The write noise and nonlinearity that is used in the experimental analyses is directly derived from the data shown in Figure 2e. The update value (conductance) consists of the average update step ΔG_0 (at a specific conductance state where CDF = 0.5) plus the contribution of the write noise which is randomly sampled from the cumulative distribution function (CDF). The nonlinearity of the device is included as well since the average (ΔG_0) changes over the conductance domain. In this way, the measurement data accounts for both write noise and nonlinearity. Read noise is not taken into consideration as this is independent of the EC-RAM performance.

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