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Design of Organic Electrochemical Transistors for Bioelectronic Circuits

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Abstract

Bioelectronic devices at the biotic/abiotic interface face a number of key challenges that include device degradation when exposed to biological fluid, their elicited immune response due to mechanical mismatch, and poor signal transduction. Organic electronic materials and their devices, such as organic electrochemical transistors (OECTs) address these shortcomings. They can efficiently transduce ionic signals into electronic currents within the bulk of the device owing to their mixed ionic/electronic transport characteristics. In addition, their operational stability in water, soft mechanical properties (compared to inorganic metals and semiconductors), and diverse fabrication routes have made them attractive choices for biological applications. While single OECTs sensors have made significant contributions to bioelectronics, their integration into more complex circuitry has been limited. The creation of OECT or hybrid circuitry can expand the functionality of bioelectronic devices, allowing for on-site signal amplification or data processing at the interface. Limited circuit implementation arises from shortcomings of current organic mixed ionic/electronic conducting (OMIEC) materials, which often lack stability in oxygenated environments, have low electronic mobilities and relatively slow response times preventing their use in many applications. Moreover, traditional device form factors and fabrication methods hinder the use of multiple OMIECs in one circuit and limit the compactness of the OECTs, which is crucial for future highly localized or high-density recording applications. In this work, I explore new OMIECs, OECT geometries, and fabrication methods to address current shortcomings of state-of-the-art OECTs and show how these materials and approaches can advance OECT circuitry, particularly complementary circuits, for biological applications.

First, I characterize the electronic properties of novel OMIECs to assess their potential for use in OECT-based circuitry. I explore hole-transporting (p-type) and electron-transporting (n-type) OMIECs that are optimized for enhanced stability in oxygenated environments, n-type OMIECs optimized for enhanced electronic mobility, and even small molecules and 2-dimensional polymers for their potential to enable new classes of high performance soft active materials. This work shows systematic synthetic design criteria can be developed to create high performing OMIECs for OECT-based circuits. I then explore a new OECT geometry and configuration that includes two vertical OECTs (vOECTs) arranged opposite to one another such that they share a single sensing site. With this compact device geometry, I demonstrate the first ambipolar OECTbased inverter and show its unique use in an analog application (voltage-to-voltage amplification) to record electrophysiological signals. This concept allows for direct amplification of biosignals at the biotic/abiotic interface without sacrificing device footprint and does not rely on the less desirable current output of single OECT sensors. Next, by taking advantage of OMIEC's bulk properties I demonstrate a new device fabrication paradigm for OECT circuits with the potential to simplify manufacturing. The fabrication method results in self-aligned lasercut OECTs which are compatible with flexible substrates and can be used to create complementary circuits. Lastly, I discuss future directions for new fabrication methods and compact OECT concepts for next generation sensors and circuits.

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List of Abbreviations

- OECT Organic electrochemical transistor
- pOECT Planar organic electrochemical transistor
- vOECT- Vertical organic electrochemical transistor
- OMIEC Organic mixed ionic/electronic conductor
- PEDOT:PSS poly(3,4-ethylenedioxythiophene):polystyrene sulfonate
- EIS Electrochemical impedance spectroscopy
- CV Cyclic voltammetry
- GIWAXS Grazing incidence wide angle x-ray spectroscopy
- PaC Parlyene C
- RIE Reactive Ion Etcher
- SNR Signal-to-noise ratio
- CMOS Complementary-metal-oxide-semiconductor
- S/D Source and drain
- $f_{\text{c}}-Cutoff\ frequency$
- $g_m Transconductance$
- C* Volumetric capacitance
- $I_d Drain \ current$
- V_d Drain bias
- V_g-Gate Bias

This work is dedicated to all the immigrant parents

Your sacrifices were not in vain

We see you, we thank you and we love you

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Chapter 1 Introduction

1.1 Organic Mixed Ionic-Electronic Conductors for Bioelectronics

1.1.1 Background

Bioelectronics is an expansive field with the goal to restore functionality, treat disease and regulate biological processes through the use of electronic devices¹. The first recorded evidence of the field of bioelectronics was in the 1780s when Luigi Galvani was able to make a detached frog leg twitch by applying a small voltage, showing he could induce muscular activity through electrical stimulation²⁻⁴. Since then, bioelectronic devices have been used to monitor glucose in diabetic patients⁵, used as pacemakers and implantable defibrillators to regulate heart rate⁶, and cochlear implants to help restore hearing⁷. Bioelectronics devices have even been used outside of clinical applications to advance the understanding of biological systems; for example, to explore the electrical signaling pathways involved in cell-to-cell communication³. One of the more well-known applications of bioelectronic devices is their use in mapping neural networks to acquire a deeper insight into brain function^{2,3}.

Commonly used bioelectronic devices are typically made with materials such as metals and semiconductors such as silicon which can limit the performance of the device^{8,9}. For instance, metallic electrodes are commonly used for neural recording and stimulation; however, the impedance between the electrode and the biological environment can be high enough to hinder data acquisition, especially when electrode size is shrunken to accommodate for more sensing sites or smaller implant size^{8,10}. In addition, these metallic electrodes will have an elastic modulus that is orders of magnitude larger than that of a cell which is an important property to consider since cells respond to their mechanical environment⁹. This mechanical mismatch will elicit an immune

response⁹. Macrophages and fibroblasts create a fibrous capsule around the implant resulting in an increase in impedance making recording/stimulation more difficult, ultimately resulting in the failure of the device¹¹⁻¹³. In addition, the rigidity of the device does not accommodate for micromotion of the native tissue leading to a constant strain at the device-tissue interface constantly aggravating tissue furthering immune response¹⁴.

1.1.2 Properties of Organic Mixed Ionic-Electronic Conductors

With the materials being one of the major limiting factor, organic semiconductor/conductors, which consist of π -conjugated small molecules and polymers, have gained popularity for their use in bioelectronics from simple uses such as electrode coatings to drive down impedance to more complex ones such as their use as an active material in transducers. One property that makes organic conductors better than hard materials like silicon for bioelectronic applications is that the organic semiconductor is held together with weak Van der Waals interactions rather than covalent bonds making them soft. Another crucial property that makes organic conductors better suited for bioelectronic applications is their ability to uptake and transport ions and interface with electrolyte due to their soft nature, making them organic mixed ionic-electronic conductors (OMIECs) (Fig **1.1**). OMIECs contain a polyelectrolyte ion conducting phase or a hydrophilic side chain that allows ion transport and a conjugated phase that allows electronic transport. OMIECs can be either p-type (hole-transporting), n-type (electron-transporting), or even ambipolar (both hole and electron transporting). They can contain ions to make them intrinsically conductive, such as the commonly used poly(3,4 ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Fig. 1.1), or can uptake ions during device operation, such as the high performing poly(2-(3,3'-bis(2-(2-(2- methoxy)ethoxy)=[2,2'-bithiophen]-5-yl)thieno [3,2-b]thiophene) p(g2T-

TT). OMIECs can also easily be synthetically tuned for the desired application and are solution processible, which is important for biological applications.



Figure 1.1. Mechanism of transport in organic mixed ionic-electronic conductors. Organic mixed ionic-electronic mixed conductors (OMIEC) interface with electrolyte and uptake ions which induces electronic charge transport throughout the bulk of the OMIEC. A commonly used OMIEC PEDOT:PSS intrinsically contains PSS⁻ which acts as a dopant causing the PEDOT⁺ to transport holes along it's backbone. Reproduced with permission¹⁵. Copyright 2012, ACS Publications.

1.2 Organic Electrochemical Transistors for Bioelectronics

Part of this section has been adapted from: "Rashid, R. B., Ji, X., & Rivnay, J. (2021). Organic Electrochemical Transistors in Bioelectronic Circuits. *Biosensors and Bioelectronics*, 113461."

OMIECs have seen tremendous growth in devices called organic electrochemical transistors (OECTs) (Fig. 1.2), which were introduced by Wrighton et al. in 1984¹⁶. OECTs are three terminal devices (gate, source, and drain) with a channel between the source and drain terminals that is typically composed of an OMIEC that is in direct contact with the electrolyte (Fig.1.2a,b)^{17,18}. A small gate bias (V_g) at the electrolyte induces cation/anion injection and drift into the bulk of the OMIEC film, causing it to undergo electrochemical de-doping/doping to ultimately modulate channel conductivity. The drain bias (V_d) will probe the state of conductivity in the active channel, that is determined by the applied gate bias. The response of the OECT (drain current (I_d)) is defined by equation 1 when operating in the saturation regime, which is where I_d is independent of the drain bias^{18,19}. C* is the volumetric capacitance of the OMIEC, μ is the electronic mobility of the OMIEC, W is the width of the channel, d is the thickness of the OMIEC film, L is the length of the channel, and V_{th} is the threshold voltage which is the gate bias at which the OECT goes from OFF to ON. OECTs can have two modes of operation, depletion, and enhancement mode^{17,19}. In depletion mode, the OECT is already conductive at a $V_g = 0V$ and as a bias is applied the channel is dedoped and the OECT is turned OFF, while enhancement mode OECTs operate in the exact opposite manner (Fig. 1.2c).

$$I_d = \frac{\mu C^*}{2} \frac{Wd}{L} \left(V_g - V_{th} \right) \ (1)$$



Figure 1.2. Organic electrochemical transistors. a) An organic electrochemical transistors (OECTs) which consists of three terminals: gate (G), source (S), and drain (D). b) the circuit diagram representation of an OECT. c) Transfer curve showing both accumulation and depletion modes of operation for hole-transporting (p-type) OECTs.

OECTs possess many advantages for biological applications over more traditional electrode-based sensors as well as over other transistor technologies based on inorganic materials, such as the metal-oxide-semiconductor field-effect transistor (MOSFET) and the organic field-effect transistor (OFET) 17,20 . Owing to the mixed ion-electron bulk transport in the OECT channel, these devices can function as ion-to-electron transducers with a high voltage to current transduction (transconductance (g_m) (eq. 2)), and effectively amplify and/or store local input signals 21,22 . As a result, when using OECTs as recording elements, their local amplification property can improve the quality of recorded signals (higher SNR) compared to conventional neural recording

electrodes²³. When compared with MOSFETs or other ion-impenetrable transistors, OECTs can achieve over a 100-fold higher transconductance, improved biocompatibility, reduced mechanical mismatch with biological tissues, and suitable long term electrical stability in aqueous environments ²⁴. While traditional organic field-effect transistors (OFETs) and electrolyte-gated OFETs (EGOFETs) have been demonstrated in many bio-applications ²⁵⁻³⁰, their operation is based on the interfacial charging of either a solid-state dielectric capacitor or an electrical double layer, which limits their transconductance (~ μ S) when compared with OECTs (~mS), which rely on volumetric charging (**Fig.1.3**). The bulk transport of OECTs also allows for a reduction in processing constraints and thus more forgiving/versatile fabrication approaches³¹. Hence, OECTs can readily take on form factors ranging from traditional thin-film electronics to fiber-based textile electronics ³², and active 3D cell-culture or gel scaffolds ^{33,34}.

$$g_m = \frac{Wd}{L} \mu C^* (V_{th} - |V_d|); g_m = \frac{\delta I_d}{\delta V_g}$$
(2)



Figure 1.3. Charging mechanism of different transistor technologies. In a field effect transistor (FET) the gate and the channel are separated by dielectric and when a gate bias is applied it causes charge accumulation at the gate and the channel creating a double-layer capacitor. An electrolyte-gated FET (EGFET) operates in electrolyte and similarly to a FET an interfacial charging phenomenon is observed but at the electrolyte-channel interface. OECTs allow for bulk transport of both ions and electronic carriers resulting in the highest transconductance (g_m) among these technologies. Reproduced with permission¹⁷. Copyright 2018, Nature Publishing Group.

The versatility of OECTs originates from the materials/synthetic tunability and functionalization of organic mixed ionic/electronic conductors (OMIECs)^{21,35-37}, as well as its form factor ¹⁷. The most commonly used OMIEC is the commercially available PEDOT:PSS, which is a p-type (hole transporting) conducting polymer. The commercial availability, high stability and electrical performance as well as ease of fabrication has enabled the general utilization of PEDOT:PSSbased OECTs. However, OECTs based on PEDOT:PSS work in depletion mode (Fig. 1.2c) ³⁸, while different applications may require n-type (electron-transporting) materials or accumulation mode OECTs (both n- and p- type) (Fig. 1.2c), which motivates the development of new materials and composites and fuels new circuit concepts ^{24,39}. In addition to different charge transporting properties, long-term stability of active materials is an area gaining attention, especially for prolonged *in vivo* applications, where unwanted oxidation can cause device failure or produce harmful byproducts through side reactions. Materials development has also focused on the improvement of electronic mobility by inducing secondary doping through additive solvents ⁴⁰; enhancement of volumetric capacitance and ionic mobility through side-chain and backbone engineering ⁴¹; and adjustment of threshold voltage by tuning the electrochemical potential of the gate electrode ⁴². In terms of geometry, it has been shown that electronic properties, like g_m, scale linearly with the geometric factors of the OECT channel (Wd/L, where W, d, L are channel width, thickness, and length, respectively) (eq 2.), which enables the modification of g_m and operating voltage according to the requirements of specific applications ^{43,44}. These fundamental materials and device-centric works have led to materials design principles and higher performing OECTs ²².

The fundamental understanding and optimization of OECTs has led to the development of a myriad of OECT-based sensors ^{20,45-50}. For example, OECT enzymatic sensors were fabricated to detect glucose, lactate, and cholesterol by functionalizing the gate electrode or channel with the corresponding enzyme ^{45,51}. Non-enzymatic sensors such as ion sensors have been demonstrated in OECTs through the use of ion-selective membranes on top of the channel ⁴⁶ or by incorporating chelation sites (such as ionophores) into the channel ⁵². OECTs have also been implemented into arrays for broad band electrophysiological recordings ^{23,53-55}.

1.3 Organic Electrochemical Transistor-based Circuits for Bioelectronics

This section is adapted from: "Rashid, R. B., Ji, X., & Rivnay, J. (2021). Organic

Electrochemical Transistors in Bioelectronic Circuits. Biosensors and Bioelectronics, 113461."

While significant research interest in materials and device level studies has led to the enhancement of transistor-level performance and single-OECT biological sensors, efforts aimed at circuit and systems-level integration of OECTs have paled in comparison. These efforts aim to explore the possibilities of incorporating OECTs into circuits that can achieve more complex functionality when compared to single OECTs, and to move towards technology translation that is relevant and viable for application goals. For example, OECT-based digital circuits that rely on low-cost printing techniques can be used in electrochromic displays, smart electronic labels and point-of-care testing (POCT) tags. In addition, applying OECT-based analog circuits for on-site sensing can highly improve the quality of the measured signal by introducing differential amplifying, noise filtering and reference subtracting functions. Furthermore, intimately incorporating OECT-based digital and neuromorphic circuits with analog sensors can help perform near-sensor or on-sensor data processing. This low-level front-end processing functionality can drastically reduce the abundant data movement and improve the efficiency of high-level data processing by conventional backend electronics ⁵⁶. Therefore, leveraging single OECT or passive matrices towards more complex circuitry will ultimately open a wealth of practical opportunities.

1.3.1 Digital circuits

Digital circuits are electronic circuits that typically designed for use in traditional computing applications to transmit and process binary signals (0's and 1's) contrary to analog circuits which are used to transmit and process continuous signals. Due to the less susceptible nature of digital signal on the distortion, interference and noise during date transmission over analog signal, digital circuits offer an easier, more accurate and reliable handling of the data compared to analog circuit, which is especially important in biological applications where the amplitude of signal is very small making transmission problematic. Owning to the advantages described above, digital circuits have been repurposed as low operational voltage, high sensitivity sensing nodes for biological applications such as ion sensing ^{57,58}. Similar to other organic transistor technologies, individual OECTs are attractive building blocks for digital circuits as they enable low-temperature, solution processible fabrication ^{17,59}. Specifically, OECTs are yet more amenable to low-cost large-area printing techniques due to their bulk transport which relaxes fabrication requirements compared to other transistor technologies³¹. This can further enable design iteration, personalization, and/or mass-production. In addition to the facile fabrication, OECTs' low operational voltage can drive down power consumption which is critical for digital circuits with high integration density. Many OECT-based digital circuits have been developed, starting with the development of OECT-based logic gates as well as more complex digital circuits critical for point of care and disposable diagnostic systems, internet-of-things and asset monitoring applications

Logic gates

The basic building block of digital circuits is the inverter. The first type of OECT-based inverter reported was a resistive ladder-based inverter (Fig. 1.4a) ⁶⁰⁻⁶⁴. Based on the bias on the

OECT the resistor ladder is used to toggle the inverter to either its ON or OFF state. Over time, improvements have been made to the OECT inverter; for example, through novel manufacturing methods, Rothlander et al. were able to reduce the switching time of the inverter by an order of magnitude ⁶³. More complex logic gates have been realized with these resistive ladder-based OECT inverters, such as NAND and NOR gates ⁶⁰⁻⁶⁵. The circuits of these gates are extensions of the inverter circuit shown in Fig. 1.4b⁶⁴. The NAND gate is an inverter with another OECT in parallel with the first one while the NOR gate has another OECT in series with the first one, with each OECT gate having its own input 60-65. High reproducibility across gates has been reported with experimental high and low voltage outputs matching theoretical values ⁶². In addition to using electrical signals as inputs in logic gates, other inputs such as light have also been implemented in AND and OR logic gates ⁶⁶. Due to relaxed fabrication, OECT-based logic gates have been demonstrated with numerous form factors such as in vertical architectures and electronic threads for textile electronics (Fig. 1.4c) ^{67,68}. Moreover, logic gates have even been assembled/fabricated in plants by forming wires within the stem ⁶⁹. The wide variety of logic gate form factors and properties shows its applicability across a broad range of biological applications and design needs.

Alternatives to resistive ladder-based inverters have been demonstrated such as the unipolar inverter which makes use of two identical OECTs ^{58,70}. Using the unipolar inverter, Majak et al. have demonstrated that logic gates can be extended beyond use in circuits for data processing to analog sensing nodes for biological applications (**Fig. 1.4d**). The unipolar inverter was used for cation detection and concentration measurements ⁷⁰. The gate and source of one OECT were shorted together to operate at a reference level and the other was used for detection. A shift in the switching voltage of the inverter (V_{in, switch}) for different electrolyte concentrations was found. This

shift allows the concentration of cation in the solution to be quantified with respect to the reference. It was also demonstrated that the $V_{in, switch}$ shifts differently with different cations (Na⁺, K⁺, Ca²⁺) allowing for detection of the type of cation in the solution. The unipolar sensor is five times more sensitive than other reported single OECTs sensors with a comparable limit of detection ⁷⁰. Romele et al. also leverage the shift in switching voltage with varying electrolyte concentration to explore the fundamental properties of the unipolar inverter ⁵⁸. It was shown that the gain of the inverter increases as the electrolyte concentration of the sensing OECT increases. A gain of 100 was achieved which is the highest reported gain for an OECT-based inverter ⁵⁸. The work with unipolar inverters shows the use of logic gates for biological sensing with the potential for seamless integration into more complex circuitry for extended sensing capabilities or data processing.

The most commonly used inverter in integrated circuits (ICs) is the CMOS inverter which consists of a p-type and n-type MOSFET. When V_{in} is low the p-type transistor is ON and the n-type is OFF so V_{out} is pulled up to V_{DD} and vice versa when V_{in} is high (**Fig. 1.4e**). Complementary circuits are more desirable than single p or n-type circuits due to the lower static power dissipation. Current flow is only present in the CMOS inverter when switching states occurs as only one or the other transistor is on during logic HIGH or LOW. In addition, complementary circuits allow for simplified circuit design with smaller footprints which is crucial for some biological applications (i.e. high-density arrays and implantable probes). The first OECT based complementary inverter has been reported by Sun et al. as seen in **Fig. 1.4e** ⁷¹. The lack of OECT based complementary circuits is due to the lack of high-performing and readily available n-type or ambipolar conjugated polymers ⁷¹. Moreover, for an inverter with ideal performance, the electronic properties, such as mobility and capacitance, of the n and p-type materials must match. However, most p-type

materials used for OECTs surpass the performance of n-type materials ³⁶. To compensate, the geometric dimensions of the n-type OECT can be altered; for example, by increasing channel thickness, making fabrication more complex and harder to integrate with biological implants. Similar to field effect devices, the W/L ratio can also be used to balance n and p OECTs, but at the expense of device footprint. The complementary OECT inverter reported by Sun et al. achieved a gain of 12 with an ideal switching voltage at $V_{DD}/2$. However, the dimensions of the OECTs were relatively large with W= 39 mm and L=20 µm with mismatched thicknesses for n and p-type OECTs. This circuit has the potential to be used as a biological signal transducer (voltage amplifier), unlike single OECT sensors, when operated at the voltage corresponding to peak gain. However, more advancements need to be made regarding n-type materials so that their performance is comparable to current p-type materials. This will allow the geometric dimensions of the OECTs making up the inverter to be reduced without decreasing gain to create logic gates that can interface with biological systems.

The first use of complementary OECT inverter for biological applications was reported by Romele et al ⁵⁷. The high gain of a PEDOT:PSS/BBL based complementary inverter was leveraged for high sensitivity ion detection. As with the unipolar inverters used for ion detection, the change in concentration of the electrolyte shifts the switching threshold of the complementary inverter which is used to detect changes in ion concentration. A sensitivity of 2300 mV V⁻¹ dec⁻¹ (normalized by supply voltage) was reported; the highest ever reported sensitivity for an ionic sensor. In addition to the ability to sense variations in concentrations lower than 20% of relevant cations, detection of concentrations over a range of five orders of magnitude was demonstrated. Clinical relevance was proven by pairing the complementary inverter with an ion-sensitive membrane (ISM) to detect potassium in human serum. The ISM did not affect the performance and sensitivity of the inverter and changes in concentration of other cations in the serum did not cause any considerable shift in the switching voltage. The properties of these complementary inverters can be tuned to either have higher sensitivity over a smaller range of detection or vice versa depending on the supply voltage applied. The compatibility with the ISM, ability to tune properties, the high sensitivity, and high gain show the potential of OECT-based complementary inverters for biological sensing.



Figure 1.4. Overview of OECT-based digital logic gates. a) Resistive-ladder based OECT inverter with the gate terminal of the OECT behaving as the input of the inverter. b) Resistive-ladder based OECT NOR and NAND gates. The NAND gate has two OECTs in parallel and the NOR gate has two OECTs in series. The gates of the two OECTs act as the two individual inputs. c) PEDOT:PSS fibers used to fabricate a resistive-ladder based OECT inverter (circuit in Fig.1.4a). Scale bar is 400 μ m. Reproduced with permission ⁶⁸. Copyright 2007, Nature Publishing Group. d) Unipolar PEDOT:PSS OECT inverter used for reference-based cation sensing leverages switching voltage shift to detect the difference in electrolyte concentration. T₁ is the reference

OECT and T₂ is the sensing OECT. Reproduced with permission ⁷⁰. Copyright 2019, Elsevier. e) Complementary OECT-based inverters made with a P3CPT p-type OECT and a BBL n-type OECT. The inverter shows a nearly ideal switching voltage at $V_{DD}/2$ and voltage transfer characteristics that shift with V_{DD} . Reproduced with permission ⁷¹. Copyright 2018, Wiley-VCH.

Complex digital logic circuits

Logic gates can be paired together to create more complex functionality, such as those widely employed in CMOS architecture. The first type of OECT logic gate-based circuit reported was the ring oscillator which alternates between logic HIGH and LOW (**Fig. 1.5a**)^{60,61}. The OECT-based ring oscillator is composed of an odd number of resistive ladder-based inverters that are connected in series where the output of the last inverter feeds to the input of the first inverter. The ring oscillator can be used to generate clock signals as well as explore the switching speed of logic circuits ^{60,61}.

Hütter et al. reported the first OECT-based digital logic circuits that make use of more complex resistive ladder based-gates, such as NAND gates, for memory circuits ⁶². They reported the first OECT-based flip-flop, which is a circuit that records the input voltage at the rising edge of the clock signal which is then stored until the next rising clock edge. The flip-flop consisted of two inverters and eight NAND gates. This work was extended to a 2-bit shift register, which is made up of two flip-flop and stores the input at the rising edge of the clock in the first bit while the previous state is pushed into the second bit. Shift registers are desirable as they only require two inputs (the clock signal and the input signal) and can easily be extended for the storage of more bits ⁶⁵. However, it was found that the logic level LOW increases in the second flip-flop which ultimately decreases the quality of the signal. This limits the number of flip-flops that can be connected to form the shift register, which is predicted to be six. The authors attribute this decay to the use of PEDOT:PSS-based OECTs as they operate in depletion mode. However, Ersman et

al. recently fabricated a 7-bit shift register (**Fig. 1.5b**) where they only observe a slight difference in voltage between the first and last flip-flop thus surpassing the limit of the shift-register predicted by Hütter et al ^{62,65}. They were able to use the 7-bit shift register to mimic the updating of a 7segment electrochromic display as the number to display could be controlled by the pattern of inputs of seven sequential clock signals ⁶⁵.

Ersman et al. further show the functionality of OECT-based digital circuits by fabricating a 4 to 7-bit decoder using resistive-ladder based gates (Fig. 1.5c)⁶⁵. The decoder was used to address a 7-segment display reducing the number of inputs from seven to four which reduced the number of contact pads required. Most work done to miniaturize devices is focused on the active area rather than the contact pad area ⁶⁵. However, contact pads take up the largest area of the overall device thus reducing the number of contact pads reduces overall area and decreases the complexity of backend electronics. In addition, the decoder has a lower propagation delay than the shift register ⁶⁵. For instance, to drive the electrochromic display, the shift register requires seven full clock cycles while the decoder requires one, making it more efficient. The 4 to 7-bit decoder was integrated on the same substrate as an OECT driven electrochromic display as seen in Fig. 1.5c. The pattern of the four inputs of the decoder turns on a certain selection of OECTs which drives certain parts of the 7-segment display to display the number of interest ⁶⁵. The use of an OECT 2 to 4-bit decoder to select OECTs that can individually drive high-current load devices such as LEDs has also been demonstrated ⁷². The decoder controlled the blinking of the LEDs, even at input frequencies where the ON/OFF ratio achieved was only four ⁷².

While the applications of logic circuitry have focused on simplifying and reducing the footprint of systems used to address low-cost displays and smart tags, which can be used for

applications such as point-of-care testing (POCT) and distributed wearable sensing, these circuits can also be extended for use in other biological applications. Logic circuits could be used to drive/read the individual active node of arrays used for stimulation/recording eliminating the need for each node to have an output line. Thus, the integration of the logic circuits, discussed in this section, into biological applications allows for easier and more effective scale-up which is crucial for multi-analyte, higher resolution sensing and more targeted stimulation.



Figure 1.5. Overview of OECT-based logic circuits. a) Ring oscillator, consisting of five OECT-based inverters (NOT) in series, whose voltage oscillates between logic HIGH and LOW. Reproduced with permission ⁶¹. Copyright 2008, Elsevier. b) OECT-based 7-bit shift register

which consists of 7 flip-flops connected in series fabricated via screen-printing. The two inputs into the shift register are the input and clock signals. c) OECT-based 4 to 7-bit decoder which is comprised of NAND and NOT gates fabricated via screen printing. It allows for the reduction of inputs from 7 to 4. The 4 to 7-bit decoder integrated onto the same substrate as an OECT-driven electrochromic 7-segement display where the combination of 4 inputs into the decoder is used to display the number of interests. Scale bar is 5 mm. Reproduced with permission ⁶⁵. Copyright 2019, Nature Publishing Group.

1.3.2 Analog circuits

Due to the analog nature of biological signals, the development of sophisticated, highperforming OECT-based analog circuits is crucial for signal processing at the abiotic/biotic interface. Signals amplified and processed on-site are more resilient to noise introduced and amplified during data transmission to back-end electronics. In addition, on-site processing can allow for simplified closed loop systems that can provide treatment in response to diagnostic sensing ⁷³. Many OECT-based analog circuits have been developed with varying degrees of complexity for use in biological sensing and will be presented here.

Voltage amplifier

One of the simplest OECT-based analog circuits that has been demonstrated for biological applications is the voltage amplifier which converts the output current of the OECT (I_d) into a voltage. A voltage output is typically more desirable for compatibility with downstream electrophysiology equipment and analysis tools. The circuit consists of a load resistor (R_L) in series with an OECT (**Fig. 1.6a**) ⁴⁴. Rivnay et al. designed a PEDOT:PSS-based OECT to have a peak transconductance at $V_g = 0V$ resulting in only one power supply needed for their voltage amplifier whose gain is defined by equation 1. The experimental gain of the voltage amplifier matches the theoretical gain (eq. 1) and has a similar cutoff frequency to that of a standard OECT, which is crucial for electrophysiological recording.

$$Gain = g_m R_L \tag{1}$$

Braendlein et al. show the potential for OECT voltage amplifiers in biological applications as a preamplifier for electrocardiogram (ECG) recording, and perform an in-depth analysis of how the different regimes of operation (linear vs saturation) affect the performance of the voltage amplifier ⁷⁴. The gain is lower when operated in the linear regime due to the dependence of drain current on V_d. In addition, based on eq. 2 the operation point of the circuit can be held constant when R_L is increased by increasing the supply voltage, which is done to improve the gain of the circuit. This circuit analysis leads to the optimization of the preamplifier circuit for biological signal acquisition. Medical adhesive electrodes interfacing with the human volunteer were externally connected to the voltage preamplifier. A higher gain of the ECG signal when operating the device in the saturation regime rather than the linear regime was achieved and physiologically relevant characteristics from the ECG were extracted (**Fig. 1.6a**). The device in the linear regime showed practically no gain (1 to 1 transduction), while a maximum gain of 30 was achieved by increasing R_L in the saturation regime ⁷⁴.

$$V_{out} = V_{supply} - R_L I_D \tag{2}$$

Venkatraman et al. demonstrated a voltage amplifier with further exploration into different regimes of operation ⁷⁵. Operation in the subthreshold regime was explored, which is observed right as the transistor is turning on, as transconductance efficiency (g_m/I_d) is high because of the exponential relationship between V_g and I_d. By using a poly(2-(3,3'-bis(2-(2-(2-methoxy)ethoxy)ethoxy)-[2,2'-bithiophen]-5-yl)thieno[3,2-*b*]thiophene)(p(g2T-TT))-based OECT, a maximum subthreshold slope of 60 mV dec⁻¹ and a transconductance efficiency of

 60 V^{-1} was achieved. This peak transconductance efficiency was achieved at an I_d of about 10 μ A

rather than typical currents on the order of nA showing the viability of operation in the subthreshold regime. Operating in the subthreshold regime leads to lower power consumption which is crucial for biological implants. In addition, lower power consumption will drive down heat dissipation which can adversely affect the biological tissue/environment that the device is interfacing with. For voltage amplifiers with the same gain, the amplifiers operated in subthreshold region consumed 370 times less power than those operated in saturation. In addition, no difference in the frequency response between the two regions of operation was observed. Moreover, a 5x increase in gain for the subthreshold operated amplifier was observed when using OECTs with the same I_d, meaning the geometric dimensions of the subthreshold operated devices were made larger to compensate for lower currents. The voltage amplifier operated in the subthreshold regime was used as a benchtop preamplifier to measure electroencephalogram (EEG) signals using medical adhesive electrodes. While operating in the subthreshold regime boasts the potential for low power sensing, careful consideration must be taken as devices geometry and R_L must be increased to achieve the same gain. Not only does this increase the overall sensor footprint but will increase the amount of thermal noise generated as well, which is not desirable for biological applications.

Reference based sensing

Two voltage amplifiers connected in parallel with the output voltage defined as the difference between the outputs of the two branches (Wheatstone bridge) allows for reference-based sensing as seen in **Fig.1.6b** ⁷⁶⁻⁷⁸. This type of measurement is beneficial because single OECTs used as biosensors typically experience signal drift in response to factors such as electrolyte evaporation, side reactions due to oxidizable and charged compounds in the solution, and/or surface biofouling ⁷⁷. The differential measurement made with the Wheatstone bridge can remove these perturbations
from the final signal resulting in higher sensitivity and SNR⁷⁷. The first reference-based sensor using PEDOT:PSS-based OECTs was introduced by Svensson et al. ⁷⁶. The difference in the transient behavior of the two OECTs in the bridge is leveraged when the sensing OECT is exposed to electrolytes of different concentrations and the reference OECT is exposed to an electrolyte of a fixed concentration. The OECTs switch at different speeds, with the OECT exposed to the higher concentration switching at a faster speed, causing a difference in voltage between the two branches of the sensor. The reference-based sensor achieved a ten-fold increase in sensitivity when compared to a single OECT sensor.

Reference-based sensing has been used for clinically relevant applications utilizing differences in steady-state instead of transient behavior ⁷⁷. A Wheatstone bridge circuit is used (**Fig. 1.6b**) for lactate sensing as lactate has been linked to the increased metabolic activity of cancer cells ⁷⁹⁻⁸¹. First, the properties of the circuit are tuned by testing the influence of R_L and while R_L increases the gain of the circuit it also increases response time. This shows that the circuit can be tuned for either fast response times or high sensitivity depending on the requirements of the applications ⁷⁷. Lactate sensing is performed by immobilizing an enzyme (lactate oxidase)/electrochemical mediator (ferrocene) complex onto the gate of the sensing OECT ⁴⁵. The same functionalization scheme is performed on the gate of the reference OECT but with a non-specific protein (bovine serum albumin), to ensure similar surface topography of the OECTs. A linear relationship between V_{out} and concentration of lactate up to 30 M is achieved, above which the relationship is noisy due to increased acidity of the sample. The limit of detection is 10⁻⁵ M and lactate can be detected from cell cultures containing as low as 10-100s of peripheral blood mononuclear cells (PBMCs) ⁷⁷. In addition, the reference-based sensor is reusable even after

operating in complex media, when both OECTs are flushed with PBS as seen in **Fig. 1.6b**. The potential in clinical diagnostics is demonstrated when the concentration of lactate from cultures of PBMCs (which are non-cancerous), unstimulated non-Hodgkin's lymphoma cells (NHL), and stimulated NHL cells (which is known to produce higher amounts of lactate) are extracted ⁸². The stimulated NHL cells produce the highest amount of lactate which is in line with the previous finding showing the sensor could be used for cancer detection ⁸².

The Wheatstone bridge was also used as a pH meter in the ranges of 5-7.3, which is a reasonable detection range in biological systems ^{78,83}. Biological systems are particularly sensitive to pH changes thus close monitoring is desired. For instance, during intense physical activity, the pH of sweat decreases due to an increase in lactic acid or during the onset of infection leading to a variation of pH^{83,84}. Current methods require a measurement with respect to a reference electrode whose potential can drift over time, thus requiring frequent and careful calibration of the sensor. Moreover, even if a more stable electrode is chosen such as an IrOx electrode, there is a possibility of a reaction with oxygen during long-term measurements⁸⁵. A differential measurement using OECTs can provide amplification and simultaneously account for such drifts and variations. The difference in the pH of the electrolytes of the two OECTs (Δ pH) closely matches the measurement V_{out} of the Wheatstone bridge. The sensor achieved a sensitivity of -73mV pH⁻¹ with PEDOT:PSS/IrOx gate electrodes, surpassing the sensitivity of pH sensors designed with OFETs (-62mV pH⁻¹)⁸⁶. The clinical relevance of the Wheatstone bridge was demonstrated by sensing pH from human sweat. The participants' sweat was used as the electrolyte of the sensing OECT and solution of a known pH was used as the electrolyte of the reference OECT. The measurements were reproducible and closely matched the measurements made by a commercial pH meter.



Figure 1.6. Overview of OECT-based analog circuits. a) An OECT-based voltage amplifier circuit with a load resistor (R_L) and OECT in series. An OECT-based voltage amplifier used as a preamplifier measuring ECG signals. When the OECT of the amplifier is operated in the saturation regime it results in higher amplification than when operated in the linear regime. Larger load resistors also result in higher gain. Reproduced with permission ⁷⁴. Copyright 2017, Wiley-VCH. B) A Wheatstone bridge consists of two voltage amplifiers in parallel whose output is the difference between the two voltage outputs. The Wheatstone bridge was used as a reference-based sensor for lactate sensing. The output of the sensor matches the difference of the individual outputs of the functionalized (red) and non-functionalized (blue) voltage amplifiers of the bridge and can returns to baseline after washing. Reproduced with permission ⁷⁷. Copyright 2017, Wiley-VCH.

Active arrays

Analog circuits based on the combination of few OECT devices have fulfilled plenty of applications, however, further integration of OECTs into array form is highly desirable in order to achieve large area mapping and/or multi-analyte sensing with high spatial and temporal resolution. There are generally two categories of array devices, passive and active, both of which have been demonstrated using OECTs for biological applications. Compared with passive arrays, active arrays draw more attention because of higher addressing speeds for individual units and device density owing to the reduced number of interconnecting wires. Active arrays of OECTs based on a 1-transistor (1T) design (Fig. 1.7a)⁸⁷ have been demonstrated in optoelectronic applications ^{88,89}. These devices utilized transparent electrodes making them compatible with optical stimulation. (Fig. 1.7b) Additionally, the ultra-thin substrate adopted in these devices enabled an intimate contact with the brain/heart and resulted in a precise mapping of EcoG (Fig. 1.7b) ⁸⁸ or ECG signals⁸⁹. By further modifying the array with a blood compatible coating, the device showed better long-term stability for in vivo use 89. Although active OECT arrays built from 1T designs have been demonstrated in several bio-applications, special biasing schemes need to be adopted in order to address one single element 88 . In addition, the relatively low-density of the devices (3×5, 4×4) in the array limit the spatial resolution when mapping electrophysiological signals. The relatively small ON/OFF ratios and electrolyte gating of the OECTs makes large crosstalk between different elements in the active array hard to avoid.

Hybrid implementation of OECTs with other transistor technologies has enabled technological advances whereby the advantages of OECTs (for sensing applications, for example), is combined with organic or inorganic FETs to achieve fast and low loss switching. Active arrays

based on a 2-transistor (2T) design using OFETs or inorganic transistors as addressing units and OECTs as sensing units can solve the hurdles imposed by the 1T design. This 2T design is analogous to the active matrix addressing scheme generally used in flat panel displays. Pierre et al. have demonstrated a linear active array (1×4) by using ion-selective OECTs (IS-OECTs) for cation detection and indium gallium zinc oxide thin-film transistors (IGZO-TFTs) for multiplexing ⁹⁰. The addressing system of the OECTs was fabricated as a 2 to 4-bit decoder using IGZO-TFTs that were paired with pull-up resistors to form NOT and NAND gates. This multiplexing circuit was demonstrated to be flexible with an increase in threshold voltage being the only parameter to change when flexed which is compensated by the simultaneous increase in the resistance of the pull-up resistors. The decoder accepts two voltage inputs that control four IGZO-TFTs, which can selectively address an individual IS-OECT. The IS-OECTs are connected in a voltage amplifier configuration to convert their ion concentration-dependent response to an output voltage for easy readout, as described earlier in this section. This same design scheme can be readily applied to other potentiometric OECT sensors for multiplexed sensing.

Denser active arrays fully composed of organic transistors have also been constructed. By utilizing OFETs as the active matrix addressing components and the OECTs as electrical signal sensors, Lee et al. have demonstrated a 5×5 active array based on a 2T design (**Fig. 1.7c**)⁵⁹. The addressability of random individual OECT sensors was verified by recording the channel current of OECTs while switching the OFET ON and OFF. Owing to the ultra-thin substrate together with the active array design, this device was able to map the myoelectric signal from the gracilis muscle of an optogenetic mouse after photostimulation (**Fig. 1.7d**). Based on the 2T design strategy, this hybrid, active-matrix sensing array can be further developed with much higher sensing resolution

by decreasing the size of the individual units, which will ultimately lead to improved spatial and temporal resolution. The integration of OECTs with either OFETs or inorganic FETs combined with the relaxed fabrication constraints of OECTs has made it reasonable to believe that the integration of OECTs with the transitional CMOS-techniques is feasible. For example, the OECTs can be fabricated as the sensing nodes on the substrate where the silicon-based circuits have already been fabricated. Since flexible silicon transistors based on a single crystal silicon membrane have been previously demonstrated ⁹¹, it would be possible to incorporate OECTs with silicon transistors for flexible hybrid circuits.



Figure 1.7. Overview of OECT-based active arrays. a) Circuit diagram of an active array based 1T design. A specific biasing scheme is used to address the center device. b) A 4×4 transparent OECT-based active array. A 3×5 version of this array was fabricated on a flexible parylene substrate with an Au grid acting as transparent electrodes. This grid was conformally placed on the cortical surface of an optogenetic mouse for mapping EcoG signals. Scale bar is 1 mm. Reproduced with permission ⁸⁸. Copyright 2017, National Academy of Sciences. c) Circuit diagram of an active matrix based 2T design. d) A 5×5 active-matrix array based on the hybrid integration of OECTs and OFETs. A downsized 2×2 version of this array was placed on the gracilis muscle of an optogenetic mouse to sense the evoked myoelectric potential after photo stimulation. Scale bar is 2 mm. Reproduced with permission ⁵⁹. Copyright 2016, Wiley-VCH.

1.3.3 Advances enabling OECT circuit integration

Certain material modifications that do not involve complex synthesis of novel organic conductors/semiconductors have been explored in OECTs to make their use in integrated circuits possible. In addition, unique OECT geometries, novel fabrication schemes and manufacturing techniques have been developed for more seamless integration of OECTs into more complex circuitry. Those efforts in materials modification and device fabrication will be reviewed in this section.

Materials modification

While PEDOT:PSS is a stable high performing p-type depletion mode OMIEC material, its sole use in OECT-based circuitry can limit functionality. Most integrated circuits are designed with enhancement-mode transistors as they are typically in an OFF state leading to lower power consumption, while depletion-mode transistors need to be biased to stay in OFF state power consumption ^{39,92}. Accumulation mode OMIEC materials have been realized but are not commercially available and can involve complex and costly synthesis ^{39,92-94}. For this reason, PEDOT:PSS has been chemically modified with aliphatic amines, such as *N*-methyl-2,2'diaminodiethylamine, to reduce its intrinsic conductivity through a series of proton and electron transfer reactions which compensate the negative charge on the sulfonate groups and ultimately dedope the polymer ^{93,94}. Accumulation mode OECTs have been demonstrated with the dedoped PEDOT:PSS and resulted in a -0.35V shift in V_{th} and a 15-20x reduction in the drain current at V_g = 0V ⁹⁴.

Another challenge facing the integration of electrolyte-gated transistors such as OECTs into circuits used for bioelectronic applications is the use of ions (electrolyte) for operation. When the

OECTs are operated in biological media the electrolyte will be shared among all the transistors in the circuit preventing independent gating ⁹⁵. Solid-state ion conductors have previously been used to replace traditional electrolytes to independently gate OECTs. For example, a UV cured solid electrolyte based on poly(diallyldimethylammonium chloride) has been used to gate all printed PEDOT:PSS OECTs resulting in response times of 20-30ms and ON/OFF ratios of 10⁵ ⁶⁵. These solid-state OECTs have been used to fabricate numerous logic gates, such as NOT, NAND and NOR, that have made their way into more complex circuits such as decoders and shift registers ^{65,67}. In addition, melanin has been used to independently gate PEDOT:PSS OECTs by injecting protons into the channel to modulate the drain current ⁹⁶. Furthermore, ionic liquids have been implemented for independent gating during lactate sensing ⁹⁷. The mediator ferrocene and lactate oxidase were added to the ionic liquid before UV curing to create a hydrated ion gel. The drain current of the PEDOT:PSS-based OECT decreased as the concentration of the lactate in the added PBS solution interfacing with ion gel increased (10-100 mM) as expected. However, the time needed to reach steady-state with addition of analyte was as long as 10 minutes ⁹⁷.

While solid-state OECTs offer a promising approach for integration, their long response time and difficulties in patterning are limiting factors ⁹⁵. Internally ion gated OECTs (IGT-OECTs) were developed to address these short comings ⁹⁵. IG-OECTs incorporate a hydrated ion reservoir within the conducting polymer channel, which eliminates the need for an external electrolyte and leads to independent gating (**Fig. 1.8a**) ⁹⁵. D-sorbitol is added to the PEDOT:PSS to create the ion reservoirs from the ions present in the PEDOT:PSS dispersion. The g_m scales with volume as expected meaning that the ions are dispersed throughout the entire film preserving the volumetric

capacitance of OECTs, while minimizing ion transit distance (thus time) required to dope or dedope the mixed conductor. A chitosan membrane is used as an ion-permeable membrane to allow for independent gating as it allows for ionic but not electronic conduction. The IGT-OECTs achieved a cutoff frequency of 380 kHz which is orders of magnitude higher than a typical OECT ⁹⁵. In addition, when the response times of IGT-OECTs were compared to that of solid-state OECTs of similar size, the IGT-OECTs were over two orders of magnitude faster. IGT-OECT based NAND and NOR gates were fabricated on flexible substrates to show that independent gating is imperative for computation. A cascaded amplifier was fabricated to show the possibility for electrophysiology recording as multi-stage amplification is required during signal acquisition (Fig. 1.8b). For this example, the first IGT-OECT is set in a voltage amplifier configuration whose output is fed to the second IGT-OECT. The cascaded amplifier produced a gain that is four times larger than a single IGT-OECT ⁹⁵. Similar to the developed depletionmode IGT-OECT (d-IGT), an enhancement-mode IGT-OECT (e-IGT) has been developed to create more sophisticated functionality with circuitry while preserving the individual gating ⁹². The e-IGT is created by adding polyethylenimine (PEI) to the PEDOT:PSS which will decrease its intrinsic conductivity as it binds to the PSS, similar to the work described earlier in this section. A circuit for on-site thresholding to detect epileptic activity using a combination of e-IGTs and d-IGTs was developed. A non-linear rectifier (Fig. 1.8c) is used to suppress lower amplitude non-target signals which decrease the accuracy of detection ⁹². The circuit was placed on the hippocampus of a freely moving epileptic rat and was able to detect epileptic discharges (Fig. 1.8d) and surpassed the performance of traditional detection methods ⁹². This circuit meets the demands of current bioelectronic devices that not only acquire the biological signals but also amplify and process them on-site.



Figure 1.8. Overview of circuits including chemically modified OECTs. a) Cross section of an IGT-OECT. The ion reservoir within the channel, created by the D-sorbitol, providing free-moving ions to dope/dedope the PEDOT:PSS. b) A cascaded amplifier that has two IGT-OECTs connected in series. The output of the amplifier is four times larger than that of a single IGT-OECT. Scale bar is 20 μ m. Reproduced with permission⁹⁵. Copyright 2019, American Association for the Advancement of Science. c) An e-IGT and d-IGT connected in series to create a non-linear rectifier. d) The non-linear rectifier was used to suppress low amplitude non-target signals for more accurate detection of epileptic activity in the hippocampus of a rat. Reproduced with permission ⁹². Copyright 2020, Nature Publishing Group.

Fabrication

More complex logic circuits such as shift registers and decoders are usually made of hundreds of OECTs, which require fabrication techniques like screen printing that can facilitate and ease the mass production of OECTs on flexible substrates, when compared to standard photolithographic techniques ⁹⁸. However, in large-area applications, yield of individual OECTs must be high to

ensure the functionality of the logic circuits. For example, in a logic circuit composed of one hundred OECTs, 99.3% of them must be functional to reach a guaranteed yield of 50% of the complete circuits ⁹⁸. Zabihipour et al. explore the yield and electronic properties of large-scale screen printed OECTs to determine whether it is a viable option for the fabrication of complex logic circuits ⁹⁸. Small PEDOT:PSS OECTs (200x200 µm²) and large PEDOT:PSS OECTs (400x400 µm²) were printed. All 600 small OECTs and 80 large OECTs were operational. The ON/OFF ratio was explored because it is critical for logic circuits as it affects the switching characteristics of the gates. The small OECTs had an average ON/OFF ratio of 7800 while that of the large OECTs was 2250. PEDOT:PSS resistive-ladder based logic gates, which are currently the most commonly used gate for more complex logic circuits, requires a minimum ON/OFF ratio of about 400 to ensure proper switching of states, which both the small and large printed OECTs meet. In addition, the dynamic switching behaviors of the printed OECTs is found to be consistent across OECTs even with slight variations in the transfer characteristics. These results demonstrate that screen-printing is a suitable technique to replace photolithography to mass-produce OECTs on flexible substrates or over large areas with distinctive uniformity and reproducibility, which is critical for complex circuits composed of many OECTs.

The variety of fabrication approaches available for OECTs allows for selection depending on the application of interest. For example, low-cost fabrication may not be a driver for long-term implantable devices as they often have fine features thus requiring more precise fabrication techniques like traditional photolithography. However, for one-time-use diagnostic devices, like, point-of-care testing (POCT) tags, the cost of individual devices needs to be minimized making low-cost printing techniques more favorable.

1.3.4 Wireless implementation

Like many other demonstrated implantable and wearable sensors, most of the devices utilizing OECT-based circuits are still in the proof-of-concept stage. One of the biggest hindrances towards real-life applications is the bulky backend connectivity. As a result, it is important to develop wireless communication strategies to elevate OECT-based circuits into implantable sensors, POCT apparatuses, and personalized medical devices. Both wireless power supplies and wireless data transmission are crucial to integration of OECT-based circuits. Potential wireless power supply and data transmission approaches that have been demonstrated in OECT-based devices will be presented in this section; they include both existing schemes and newly developed concepts which have recently been integrated with OECT-based devices and circuits.

Wireless power harvesting/storage

Biofuel cells are promising energy harvesting elements that can be used to power OECT-based metabolite sensors 99,100 . Tan et al. demonstrated a biofuel cell used for glucose detection that could be extended for detection in other H₂O₂ producing reactions, such as for lactate and ethanol 99 . The fuel cell contains a p(gT2)-based anode and a TTF-TCNQ-based cathode with glucose oxidase (Gox) and glucose in the electrolyte. After the catalytic reaction between Gox and glucose the Gox is reduced and the re-oxidation of Gox can be achieved through electron transfer to the TTF-TCNQ (cathode) or O₂ (forming H₂O₂). The subsequent reaction between H₂O₂ and p(gT2) oxidizes the p(gT2) (anode) and changes the open circuit voltage with respect to the cathode, which can be used to power the OECT. Another biofuel cell using glucose to generate power was proposed by Ohayon et al. which uses a similar mechanism of direct electron transfer but bypasses the formation of H₂O₂ ¹⁰⁰. The cell is comprised of an NDI based material (P-90)

anode immobilized with Gox and a p(EDOT-O-EDOTOH) cathode. Similar to the mechanism discussed above, after the reaction between Gox and glucose, the re-oxidation of the reduced Gox directly transfers electrons to the P-90 anode. These electrons then transit to the cathode through external wiring and allow it to reduce O₂ into H₂O, which can power the OECT. (**Fig. 1.9a**). Since the open circuit voltage of the biofuel cell is dependent on the concentration of metabolite, it can not only be used to power the OECT but also make the OECT into a sensor through tuning the gate voltage by the concentration of metabolite. (**Fig. 1.9b**). To achieve a fully wirelessly powered OECT, a battery can be used as external voltage source to supply the drain voltage while the biofuel cell supplies the gate voltage ¹⁰¹. While these self-powered biosensors have great potential in next-generation biological sensing, the long-term stability of these devices might be of concern. Ohyano et al. performed stability studies that reveal the biofuel cell only retained about 40% of its original power after 30 days but could be operated for another 20 days when the enzyme was replenished ¹⁰⁰.

Conducting polymers (CPs) have also been used to develop supercapacitors (SCs) for powering low-power bioelectronic devices such as OECTs. While SCs have lower specific energy than typical batteries, they feature fast charging/discharging and longer operational lifetime ¹⁰². SCs are typically made with carbon-based materials but integration remains difficult, thus CPs have gained traction due to their flexibility and ease of processing ¹⁰³. One candidate of CPs that can be used in SCs is PEDOT due to its high conductivity, fast response time, and chemical and physical stability ¹⁰⁴. Nikiforidis et al. developed a SC using hydroxymethyl poly(3,4-ethylenedioxythiophene (p(EDOTOH)) electrodes ¹⁰⁵. The electrodes are then embedded into an agarose hydrogel which provides a reservoir of ions and mechanical stability, making it a self-

standing SC. Its operation in biological media and compatibility with miniaturization makes it further suitable for powering bioelectronic devices. The SC demonstrated a power density of 10^5 W kg⁻¹, a fast response time (0.1-30s) and a long self-discharge; a SC charged to 1.5V discharged to 0.67 V over 24 hours when wetted every four hours. In addition, it had a specific capacitance of 75 F g⁻¹ and a volumetric capacitance of 240 F cm⁻³ with a capacitance retention of 75% after 12,000 cycles. The SC was connected to the gate of a PEDOT:PSS-based OECT to modulate the drain current after being charged to varying potentials. A fully self-powered OECT can be achieved by integrating another SC on the drain terminal and has been utilized as Na⁺ ion sensor after implementing an ion selective conducting polymer as active channel.

In addition to biofuel cells and supercapacitors, solar cells offer an alternative for self-powered OECTs as demonstrated by Park et al. (**Fig. 1.9c**)¹⁰⁶. Organic photovoltaics (OPV) were used to power PEDOT:PSS-based OECTs (which are insensitive to light). A finely grated OPV was used which resulted in high-power conversion efficiency and power-per weight that is suitable for wireless applications such as wearables and implantable sensors. The OPV was stable under different mechanical tests and performance was not altered under different angles of illumination which is crucial for functioning conformal devices. The OPV was used to apply the drain voltage of the OECT and the drain current modulation was dependent on the intensity of the light applied to the OPV. The drain current of the OECT showed lower noise levels when powered by the OPV than when powered by a commercial battery. The OPV and OECT were fabricated on the same flexible substrate to create a conformable ECG sensor with an SNR that is three times higher than previously reported sensors (**Fig. 1.9d**)^{45,106}. Since a PEDOT:PSS OECT was used and no DC gate bias was required, as peak transconductance occurs around 0V, making this a

fully wireless powered OECT. While data was still acquired via external wiring, wirelessly powering OECTs makes strides towards fully integrated OECT-based wireless systems.

It is clear from the above implementation that a myriad of opportunities exist to power OECTs using technologies that have previously been developed (batteries, PV, TEG, triboelectrics, etc). The proper choice in power source depends on power requirements, application, and device integration. However, the low power requirements of OECT-based circuits enable a broader range of viable power sources.



Figure 1.9. Power harvesting for wireless OECT integration. a) A two-electrode fuel cell where the anode is functionalized with glucose oxidase for glucose reduction and a cathode that accepts electrons from the anode to reduce O_2 . The resulting potential difference between the two electrodes is used to bias the gate of an OECT. b) Membrane-free fuel cell fueled by glucose with varied concentration can be used to power the OECT in real-time. Reproduced with permission ¹⁰⁰. Copyright 2019, Nature Publishing Group. c) An OPV fabricated on the same substrate as an OECT is used to provide the drain bias of an OECT whose peak transconductance is at Vg = 0V, which results in a single power supply. d) Circuit diagram of the integrated OPV/OECT and recorded ECG signal from an OPV-powered OECT. Reproduced with permission ¹⁰⁶. Copyright 2018, Nature Publishing Group.

Wireless data transmission

In order to achieve fully wireless in vivo or wearable sensing, in addition to wireless power supplies, the ability to wirelessly transmit data is crucial. Sensors enabling wireless data transmission for physical, chemical and electrophysiological sensing ¹⁰⁷ have used various approaches such as radiofrequency identification (RFID)¹⁰⁸, near field communication (NFC) ¹⁰⁹, Bluetooth ^{110,111}, resonant antenna ¹¹² and optical communication ¹¹³. However, majority of those sensors are based on individual electrodes and attention has rarely been paid on integrating wireless data transmission with transistor-based sensors. Ji et al. have demonstrated a portable OECT-based glucose sensor with the ability to detect salivary glucose levels that wirelessly connects to a smartphone via Bluetooth¹¹⁴. A resistor was placed in series with the OECT to create a voltage divider in order to convert the current change into a voltage output at the drain terminal upon the detection of glucose. A Bluetooth detector that measures voltage was integrated between the source and drain terminals to transmit V_d to a smartphone which was then displayed on a phone application. Although the data acquisition and power supply units are relatively bulky, it shows the potential for a fully wireless OECT-based wearable or *in vivo* sensor with further optimization. Similar to the self-powered OECTs described above, integration of OECT sensors and circuits with other existing wireless data transmission protocols can be readily targeted.

1.4 Outlook

This section is adapted from: "Rashid, R. B., Ji, X., & Rivnay, J. (2021). Organic Electrochemical Transistors in Bioelectronic Circuits. *Biosensors and Bioelectronics*, 113461."

The integration of individual OECTs into circuits or systems is still in its infancy, the technological translation of OECT-based circuits needs combined effort from synthetic chemists, material scientists, and engineers in developing new materials, fabrication techniques, modeling approaches and integration strategies. Materials with matched and excellent electrical performance, high environmental and operational stability as well as good reproducibility are highly desired for the development of superior OECTs and circuits. In addition, fabrication processes that can improve the consistency and reproducibility of devices is critical. Assembly techniques or novel fabrication techniques that can seamlessly integrate OECTs with other mature electronic components is crucial. Modeling at the single device and circuit level can allow non-idealities to be taken into consideration leading to a better understanding of device physics and design of novel circuits and systems. Finally, integration of OECT-based circuits with other electronic components can enable new implementation and applications like in-sensor/near sensor computing and processing.

Materials development is one of the most fundamental steps to continue the growth and enhancement of OECT-based devices and circuits, which can benefit from OMIECs with both higher electronic mobility and volumetric capacitance. Further investigation in understanding and balancing the electronic and ionic transport through modification of the conjugation length of the backbone, π - π stacking, and side-chain engineering should be continued ³⁵. Operational

and environmental stability of the materials needs to be addressed and adopted for various application purposes. The stability requirement of the materials could range from minutes for disposable sensors to hours for cell culture-based diagnostics or longer than months for implantable devices. Investigation of the side reactions of the active materials with the operating environment that potentially produce harmful products is also critical. The elimination of these reactions can improve the compatibility and lifetime of OECTs with biological systems. In addition, control of the material synthesis processes is imperative to enhance the batch-to-batch reproducibility of the materials and ultimately the consistency of OECT behavior. Complementary circuits that allow for less complex circuitry, smaller footprints, and lower power consumption are crucial for integrated circuits. In order to fabricate a high-performance OECT based complementary circuit, n-type or ambipolar active materials with comparable electrical behavior and operational stability as p-type active materials is required ³⁶. Furthermore, investigation into composite materials made by blending conducting polymers with additive materials is needed as it may introduce new functionalities such as improved biocompatibility for cell adhesion ¹¹⁵. In order for the library of high performing materials for OECTs to be expanded, investigation of structural and compositional properties during operation by multimodal methods is critical ¹¹⁶, as it may guide materials synthesis and processing, and advance the performance of single devices for circuit utilization.

Novel fabrication techniques can enable new device concepts. The commonly used photolithographic approaches can be sufficient for most applications; however, new fabrication approaches are still desired for developing OECT-based circuits with high density integration and diverse form factors. Printing techniques like ink-jet printing and screen-printing offer easy, low-cost, and large-scale patterning, which permits the large-area roll-to-roll fabrication of circuits with complicated designs. In addition, circuits on fiber substrates are also possible using printing techniques, which can lead to OECT-based circuits for smart textiles. Under the prediction of Moore's Law, although not as aggressive as for silicon electronics (i.e. 7 nm process), higher device density and smaller device size of OECTs (at or below 1 um) is inevitable in the foreseeable future, and desirable for arrayed sensing and for biomarker mapping applications. Vertical OECTs that have conductive channels in the out-of-plane direction can have a decreased channel length, down to sub-micron level and stacked integration along the zdirection, which can significantly enhance the device density per unit area ¹¹⁷. In addition to the fabrication of individual OECTs, techniques that can seamlessly integrate OECTs with other organic/inorganic electronic components is important. This can be achieved by separating the fabrication of the OECTs from the other devices and integrating them later in a modular architecture. Furthermore, new fabrication techniques that can eliminate the thermal and chemical mismatch between the traditional fabrication techniques of OECTs with other electronics needs to be developed to achieve monolithically manufactured circuits and systems for better integration efficiency.

In addition to the development of materials and fabrication approaches, device modeling is critical for understanding and predicting the physics and behavior of components and circuits before spending time and money fabricating and integrating them. On the individual device level, while the Bernards model describes basic operating mechanism and physics of OECTs ¹⁹, non-idealities in devices such as contact resistance, bias stress and parasitic resistance are essential phenomena that need to be accounted for in device models to improve device behavior

prediction. In addition, noise in OECT devices needs to be better understood and accounted for, especially low frequency *1/f* noise, as it can significantly affect the signal to noise ratio of OECT-based sensors ¹¹⁸. *1/f* noise follows a charge-noise model and is caused by the fluctuation of charge carrier density inside the active channel. Relatively few studies have been conducted to investigate the relationship between device geometry and the *1/f* noise through modeling ¹¹⁸⁻¹²⁰, which can provide guidelines for individual device design. In addition to the modeling on the single device level, circuit level modeling is also critical as it can guide the integration of OECT-based circuits with other components at a system level. Modeling approaches/software used for CMOS circuits like Simulation Program with Integrated Circuit Emphasis (SPICE) can be directly applied for OECT circuit design, with effort devoted to adequately describing single OECT device characteristics and non-idealities in such platforms ⁶⁷.

From an application perspective, the development of OECT-based circuits towards multiplexed sensing, enhanced sensing modality and functionality, and closed-loop sensing with real-time feedback are highly desirable. OECT-based active arrays have already been used *in vivo* to measure electrical signals like EEG and electromyography (EMG), while the continuous *in vivo* assessment of chemical and biological molecules can further provide more information on biological processes and patient conditions. Active matrices with OECT sensors in individual pixels are beneficial as they can provide real-time spatial tracking of biochemical and/or biophysical information during cell culture, on the skin surface, or *in vivo*. The biocompatibility of the OECT-based circuits in those *in vivo* applications needs to be carefully examined to avoid harmful immunological response and facilitate long-term implantation and monitoring. Research on biocompatible encapsulation or even intrinsic biocompatible functional materials needs to be

further conducted. Internally ion gated OECTs have shown their potential in high-speed operation and their individual addressability, making them suitable for integration into active matrices as multiplexing units. Although these proposed applications that rely on OECT-based circuits are greatly desirable, circuits and systems based on OECTs alone will not be the way towards advancement. Hybrid integration of OECT-based circuits with other types of devices, like inorganic processing units (i.e. CMOS ASICs), flexible power supplies and wireless data transmission circuits, is a more reliable and practical goal for the near future. Such hybrid integration approaches take advantage of both the versatility of OECTs and the maturity of CMOS technology, which can ultimately allow for diverse application opportunities.

1.5 Dissertation Outline

The main theme for this dissertation is the overall enhancement of OECT performance and fabrication to ease the integration of OECTs into more complex circuitry for biological sensing. This was achieved through the design of new fabrication schemes, compact geometries, and the improvement of OMIEC performance. Chapter 2 will present the OECT performance of newly developed OMIECs that were designed to address current shortcomings that hinder OECT integration. OMIECs included in this chapter aim to enhance operational stability, electronic transport of n-type OMIECs, which currently lag behind their p-type counter parts. Chapter 3 will present the development of a unique OECT geometry pair of cofacial vertical OECTs. In addition, it will demonstrate how pairing this with a novel ambipolar OMIEC creates a complementary inverter in the same area as a typical single OECT sensor. The inverter is then demonstrated as a voltage-to-voltage amplifier for ECG signals, showing the potential of OECT-based circuitry in biological applications. Chapter 4 will present a new fabrication method that

eases the patterning of the OMIEC in the OECT channel. This new method creates self-aligned laser-cut OECT channels which eliminates tedious photolithography steps for rapid prototyping. Lastly, Chapter 5 will present future directions of fabrication techniques that allow the patterning of multiple materials on the same substrate while preserving the high performance of the OECTs.

Chapter 2 Characterization of Organic Mixed Ionic-Electronic Conductors for Organic Electrochemical Transistors

2.1 Introduction

One of the main bottlenecks inhibiting the advancement of OECT-based circuits is electronic properties of currently available OMIECs. N-type OMIECs typically have a much lower mobility volumetric capacitance product (μ C^{*}), a typical figure of merit for OMIECs, when compared to p-type OMIECs. In addition, while n-type OMIECs are especially susceptible to degradation, p-type OMIECs can react with the oxygenated environment as well which ultimately affects device performance and longevity. Most importantly, the presence of n-type and p-type OMIECs with similar threshold voltages is crucial for the development of high performance balanced complementary circuits, as threshold voltage is not a property that can be easily tuned like transconductance.

This chapter presents device performance of a number of novel OMIECs that were evaluated for their potential use in OECTs and OECT-based circuits. This includes a p-type OMIEC for enhanced shelf and electronic stability, a variety of different n-type materials with systematic investigation via backbone and side chain engineering, and new classes of OMIECs such as small molecules and 2D polymers. A broad range of materials are explored here in an effort to discover materials that meet device needs for circuit/sensor implementation, including the latest materials available through collaborative ventures. Moreover, to create an open dialogue with synthetic chemists about what electronic parameters are needed for enhanced OECT performance and OECT-based circuits for practical implementation in bioelectronics. This is an example of device-materials co-design. In the below work, I fabricated and performed OECT and electrochemical measurements to extract electronic properties relevant to performance and stability. All chemical synthesis and data collected that supports our understanding of relative OECT performance, such as GIWAXS and optical spectroscopies, were performed by collaborators. The complete understanding of structure-property relations was elucidated as a collaborative effort.

2.2 Energetic Control of Redox-Active Polymers Toward Safe Organic Bioelectronic Materials

This section is adapted from: "Giovannitti, A., Rashid, R. B., Thiburce, Q., Paulsen, B. D., Cendra, C., Thorley, K., ... & Rivnay, J. (2020). Energetic Control of Redox-Active Polymers toward Safe Organic Bioelectronic Materials. *Advanced Materials*, *32*(16), 1908047."

Organic semiconductors have shown tremendous potential for OECT operation specifically in biological applications as discussed in Chapter 1; however, little attention has been paid to the electrochemical stability of OMIECs. Most work involved in the design and study of OMIECs has focused on how to enhance electronic properties such as g_m , μ , and C* and while those are important factors, electronic stability is a crucial feature for practical use in biological applications, such as long-term *in vivo* measurements. Electrochemical redox stability of OMIECs is accomplished when reversible charging and discharging reactions occur in the absence of noncapacitive faradaic side-reactions between the OMIEC and the electrolyte. The products of such side-reactions may modify the chemical composition of the OMIEC and affect the performance of electrochemical devices. One example of a noncapacitive faradaic reaction is the electron-transfer reaction from the OMIEC to molecular oxygen, also described as the oxygen reduction reaction (ORR). The study of the ORR in OECTs is critical since biological environments are oxygenated. In the absence of an applied potential, a chemical reaction is expected to occur spontaneously when the chemical potential of the products is lower than the reactants, showing the importance of the relationship between the energy levels of the OMIECs and the products of the ORR^{121} . One possible byproduct of this reaction that is of interest is hydrogen peroxide (H₂O₂) which can speed up the degradation of the OECT and harm the surrounding biological environment¹²²⁻¹²⁴.

The ORR yields either H₂O₂ (two-electron process) or water (H₂O) (four-electron process), as well as charging (oxidation) of the OMIEC that acts as the catalyst¹²⁵⁻¹²⁷. The four-electron reaction (O₂ + 2H₂O + 4e⁻ \rightarrow 4OH⁻, E^0 = 1.23 V versus reversible hydrogen electrode (RHE), pH \geq 7) is thermodynamically favorable over the two-electron reaction (O₂+H₂O+2e⁻ \rightarrow HO⁻ ²+OH⁻ E^0 = 0.76 V versus RHE, pH > 7) as shown in **Fig 2.1** However, for some classes of materials, including organic molecules, the reduction of oxygen may terminate at the production of dissolved H₂O₂ instead of the complete reduction to water¹²⁸, due to the rate of the reaction. It is more common for organic materials that the reaction terminates at the production of H₂O₂ due to the H₂O₂ being weakly bound to the surface of the electrode resulting in the rate of desorption to be faster than the next reduction reaction^{127,129,130}.



Figure 2.1. p(gPyDPP-MeOT2) energy level and structure. a) This diagram relates the energy level of p(gPyDPP-MeOT2), PEDOT:PSS and p(g2T-TT) with ionization potential. The material of interest here, p(gPyDPP-MeOT2) is compared to two prototypical p-type OMIECs. η represents the free energy difference between the reactants and the reaction products and shows that for PEDOT:PSS and p(g2T-TT) the ORR producing H₂O₂ is energetically favorable causing it to spontaneously occur while it is not for p(gPyDPP-MeOT2) due to the high IP. b) The chemical structure of p(gPyDPP-MeOT2).

Commonly used OMIECS for OECTs such as PEDOT:PSS and p(g2T-TT) have ionization potentials (IP) that allow them to spontaneously undergo the ORR. However, if an OMIEC is designed with an IP >4.9 then energy would be required for the ORR to occur making it unfavorable and preventing the formation of H₂O₂ (**Fig 2.1**). In this work an OMIEC is designed based on pyridine-flanked diketopyrrolopyrrole (PyDPP) with 3,3'-methoxybithiophene (MeOT2) (P(gPyDPP-MeOT2)) to exhibit a large IP to shift the operational voltage of the OECT such that no ORR occurs in ambient conditions in electrolyte.

p(gPyDPP-MeOT2) OECTs were operated as p-type enhancement mode OECTs with channel dimensions of W = 100 µm and L = 10 µm. The output and transfer curves of the p(gPyDPP-MeOT2) OECT are shown in **Fig 2.2** with no observed hysteresis. The OECT has a threshold voltage (V_{th}) of about -0.35 V, which was extracted by extrapolating from the linear regime of the $\sqrt{|I_D|}$ vs. V_g graph. The device has a normalized peak transconductance ($g_{m,norm}$) of 19.5 ± 2.5 S cm⁻¹ at $V_g = -0.7$ V. The hole mobility of p(gPyDPP-MeOT2) was measured using a frequency-dependent OECT bandwidth measurement (detailed description can be found in methods). A hole mobility of 0.030 ± 0.007 cm² V⁻¹ s⁻¹ (averaged over three devices) at gate potentials of $V_g = -0.7$ V was reported, which is comparable to mobility values reported for other PyDPP copolymers tested in OFETs¹³¹. In addition, the volumetric capacitance (C^*) was extracted using electrochemical impedance spectroscopy (EIS) (**Fig 2.2**). The volumetric capacitance of p(gPyDPP-MeOT2) is 60 F cm⁻³ at an offset potential of 0.7 V versus Ag/AgCl, which is on par with values reported for other donor-acceptor copolymers with glycol sidechains¹²². This resulted in a mobility volumetric capacitance product (μ C^{*}) of 1.8 F cm⁻¹ V⁻¹ s⁻¹.



Figure 2.2. p(gPyDPP-MeOT2) OECT performance. a) The output curve was collected with $\Delta V_g = 0.05 \text{ V}$, 0 V to -0.7V and $\Delta V_d = 0.01$, 0 to -0.4V and a sweep rate of 0.2 V_d /s. b) The transfer curve was collected with $\Delta V_g = 0.01 \text{ V}$, 0V to -0.7V and $V_d = -0.4\text{ V}$ and a sweep rate of 0.2 V_g /s. The right axis shows the I_d on a log scale. c) EIS for p(PyDPP-MeOT2) at potential offsets ranging from 0 to 0.7 V vs Ag/AgCl. Bode plot, phase plot, and effective capacitance (capacitance per area) plot are shown. C_{eff} plots are extracted from fits using the Randle's Circuit (Rs(RP||C). The fit (red dotted line) has an offset of 0.7 V vs. Ag/AgCl in 0.1 NaCl with R_s = 336 Ω , R_p = 1.01 M Ω , C = 6.22 μ F).

Frequency-dependent transconductance measurements show a cut-off frequency >100 Hz (Fig

2.3a), which is of relevance to many electrophysiological processes and can be further improved by downscaling the device dimensions. p(gPyDPP-MeOT2) OECTs showed good stability under gate pulsing conditions. As shown in **Fig 2.3b**, no or little change in the ON current is observed after 400 cycles when applying $V_G = -0.5$ V, while a decrease of 8% and 16% is observed with $V_G = -0.6$ and -0.7 V, respectively.



Figure 2.3. Frequency and stability response of p(gPyDPP-MeOT2) OECTs. a)The frequency response of a p(PyDPP-MeOT2) OECT is shown with a cutoff frequency >100 Hz. The measurement was made by apply a $\Delta 10$ mV sine wave with varying frequencies at the gate with an offset of -0.7V. g_m was extracted from $\Delta I_d / \Delta V_g$. b) The stability of a p(PyDPP-MeOT2) OECT at $V_g = -0.5$, -0.6, -0.7V with a $V_d = -0.4$ V during 400 cycles of ON/OFF switching with 2s ON and 2s OFF.

To study the effects of the ORR, OECT measurements were carried out in 0.1M NaCl solution with high and low oxygen concentrations (**Fig 2.4**) to monitor the changes of the OFF current at open circuit voltage (OCV) conditions after de-doping the polymer, which is when the ORR occurs. PEDOT:PSS and p(g2T-TT) were measured along with p(gPyDPP-MeOT2) for comparison. OECTs were operated in an enclosed electrochemical cell (Redox.me) filled with ~10 mL of a 0.1 M NaCl aqueous solution. The cell was purged with N₂ for ~16 hours to create a low O₂ environment. After purging, the OECT was switched from an equilibrated ON state ($V_g =$ 0 V and $V_d = -0.5$ V for PEDOT:PSS, $V_g = -0.4$ V and $V_d = -0.4$ V for p(g2T-TT), rendering both devices in the saturation regime) to an equilibrated OFF state ($V_g = 0.7$ V for PEDOT:PSS, $V_g =$ 0.4 V for p(g2T-TT), drain voltages remain unchanged). After the OFF state equilibrated for 60 seconds, the Ag/AgCl gate was physically removed from the electrolyte and electrically disconnected. The channel current was then monitored for the 400s to indirectly monitor chemical oxidation of the film that will increase the conductance of the channel. The procedure was repeated on the same devices in an oxygen-rich environment following ~8 hours of sparging with air. For PEDOT:PSS and p(g2T-TT), a spontaneous turn-on of the device is observed which is greater when in the oxygenated environment (**Fig 2.4a,b**). PEDOT:PSS has a faster rise of I_D compared to p(g2T-TT), while p(PyDPP-MeOT2) remains in its low conductive state (**Fig 2.4c**). This supports the hypothesis that p(PyDPP-MeOT2) does not become oxidized in ambient conditions and hence does not form H₂O₂ during device operation.



Figure 2.4. The response of OECTs to low and high O₂ environments. a) PEDOT:PSS OECT with a $V_G = 0$ V followed by $V_G = 0.7$ V for 60 s each (with $V_D = -0.5$ V) before switching to OCV in inert conditions (black line) and ambient conditions (red line) b) p(g2T-TT) OECT with a $V_G = -0.4$ V followed by $V_G = -0.4$ V for 60 s each (with $V_D = -0.4$ V) before switching to OCV in inert conditions (black line) and ambient conditions (red line). c) p(gPyDPP-MeOT2) OECT with a $V_G = -0.7$ V followed by a $V_G = 0$ V for 60 s each (with $V_D = -0.2$ V) before switching to OCV in ambient conditions.

To demonstrate that the ORR yields H_2O_2 , an enzymatic reaction that is selective for H_2O_2 was employed to test the electrolytes that are used for charging and discharging of the polymers for H_2O_2 . Detection was carried out using the peroxidase/dye system (peroxidase horseradish/3,3',5,5'-tetramethylbenzidine) which involved monitoring the dye that had been added to the electrolyte of the OECTs for 10 minutes¹³². H_2O_2 formation was observed for PEDOT:PSS and p(g2T-TT)), whereas no H_2O_2 formation is observed for p(gPyDPP-MeOT2) as observed from the absorption spectra when compared to the control (**Fig 2.5**).



Figure 2.5. Detection of H₂O₂ in OECT electrolyte. a) The absorption spectrum of the dye 3,3',5,5'- tetramethylbenzidine after the addition of the horseradish peroxidase to the electrolyte solution used for the chronoamperometry experiments of PEDOT:PSS, p(g2T-TT) and p(gPyDPP-MeOT2). b) Control experiment showing the absorption spectrum of the dye and enzyme in deionized water as well as the spectrum for the dye after the addition of H₂O₂. In this work, electrochemical side-reactions of state-of-the-art p-type OECT materials were explored, showing that the materials can undergo an ORR during device operation and form the detrimental side-product H₂O₂. A copolymer, p(gPyDPP-MeOT2), was synthesized with an IP>4.9eV which prevented the ORR and production of H₂O₂ when compared to state-of-the-art p-type OMIECs. Although p(gPyDPP-MeOT2) displays a lower μ C* than that of PEDOT:PSS and p(g2T-TT) the strategy of designing OMIECs with higher IPs (deeper highest occupied molecular orbital level (HOMO)) is a viable route for developing stable OECTs, especially for biological applications where hazardous side-products will need to be avoided and low OFF currents of devices are desired for decreased power consumption and higher sensor sensitivity.

2.3 Backbone and Sidechain Engineering for Enhanced OMIECs

2.3.1 Synthetic nuances to maximize n-type organic electrochemical transistor performance in fused lactam polymers

This section is adapted from "Marks, A., Chen, X., Wu, R., Rashid, R. B., Jin, W., Paulsen, B. D., ... & McCulloch, I. (2022). Synthetic Nuances to Maximize n-Type Organic Electrochemical Transistor and Thermoelectric Performance in Fused Lactam Polymers. *Journal of the American Chemical Society*."

As discussed earlier in Chapter 1, the performance of n-type OMIECs typically lag behind that of p-type OMIECs making it challenging to advance the use of OECTs in circuitry^{24,71,133}. In addition to inferior electronic properties such as lower μ_e , n-type materials demonstrate stability issues^{121,134}. This is typically due to their susceptibility to reacting with oxygen and water, making it difficult to incorporate n-type OMIECs into bioelectronic applications, thus the development of high performing n-type OMIECs should be a priority. In this work one of the highest performing n-type OMIEC to date is developed along with a series of OMIECs with varying ratio of hydrophilic to hydrophobic side chain which was done to elucidate design criteria that will optimize electron transporting OECT performance. This series is based on fully fused acceptor-acceptor polylactams $(p(g_7NC_nN))$ (Fig 2.6) repairing the commonly used donoracceptor polymers with ethylene glycol side chains that are typically synthsized using methods that leave residual metal compounds that are difficult to remove, making them potentially toxic in biological applications¹³⁵⁻¹³⁸. In addition the $p(g_7NC_nN)$ polymers are designed with a C=C double bond to link the successive aromatic cores in fused polylactam polymers which enhances rigidity of the polymer backbone and therefore electronic charge carrier mobility¹³⁹.

This series is based on the previously reported $p(g_7NC_{12}N)$ (PgNAN) with further exploration into how the hydrophobic alkyl side chain length affects the OECT performance¹⁴⁰. The alkyl side chains were systematically lengthened from ethyl (C₂H₅) to hexadecyl (C₁₆H₃₃) (**Fig 2.6**). These polymers consist of a naphthalene core (N), a 7-unit ethylene glycol chain on the bis-isatin monomer (g₇) and an alkyl side chain (Cn) tethered to the bis-oxindole monomer unit. The polymers will be refered to Cn for breveity as in **Fig 2.6**.



Figure 2.6. Structure of $p(g_7NC_nN)$ **series.** The chemical structure of $p(g_7NC_nN)$ which is made up of a bis-isatin monomer with a 7-unit ethelyene glycol side chain and a bis-oxindole monomer with an alykl side chain.

The p(g_7NC_nN) was cast as the active material in OECTs and the varying lenth of the alkyl side chain, and the overal hydrophobic content, affected OECT perfromance (**Fig 2.7a,b**). Threshold voltages (V_{th}) tended to increase as the overall alkyl content increased. For p(g_7NC_2N) the threshold voltage was 0.23V whereas for p($g_7NC_{16}N$), this increased to 0.36V (**Fig 2.7C and Table 2.1**). This could be due to the increase in hydrophobicity causing a decrease in ionic transport from C2 to C16 which can manifest as an increase in threshold voltage^{39,141}. p($g_7NC_{10}N$) exhibited the highest drain current and transconductance (**Fig 2.7a,b**). When the peak g_m was normalized by Wd/L across the series, p($g_7NC_{10}N$) had the highest normalized g_m at 0.37 S cm⁻¹ which is an order of magnitude higher than some of the lowest performers within the series such as p(g_7NC_4N) and p($g_7NC_{16}N$) (**Table 2.1**). g_m is also dependent on the commonly used figure merit μ C* so extracting these two electronic parameters can give insight into the

varying performance across the series. Electrochemical impedance spectroscopy (Fig 2.9-2.14) was performed to extract volumetric capacitance (C*) which ranged from 89 to 199 F cm⁻³ (Table 2.1), with C16 exhibiting the lowest C* which once again could be due to the higher degree of hydrophobicity and lower total fraction of conjugated backbone. Interestingly, C2 did not have the highest C* which is what would be expected since it has the lowest degree of hydrophobicity. Instead, C^{*} peaked at C8 meaning that C* is not just related to hydrophilic content. C* remains relatively constant until C10 where C* falls by a factor of 2 which indicates there is a tipping point where the degree of hydrophobic content limits ion transport⁴¹. The electronic mobility increased as the alkyl side chain increased but peaked at 1.20 cm² V⁻¹s⁻¹ for C10 and fell as the side chain length was increased beyond that (Table 2.1). C10 exhibited twice as high a mobility than the other top performers in the series, C8 and the previously reported C12, and exhibited a highest ever mobility reported for an n-type OMIEC (Fig 2.7d)¹³⁴. While the overall high mobility of this series is due to the fused backbone, the variation in mobility within the series is likely due the degree of hydrophobicity affecting swelling and morphological modulation. Furthermore, the preferential stacking microstructure of each polymer is different, which will affect OCET operation as each material's ability to accommodate both ions and water molecules from the electrolyte will also vary. This suggests that the alkyl (C10) side chain in conjunction with the ethylene glycol side chain is optimal for balancing the adverse effects of swelling on electronic transport.



Figure 2.7. $p(g_7NC_nN)$ **OECT performance.** a) The transfer curves of $p(g_7NC_nN)$ OECTs. b) The g_m across different V_g for $p(g_7NC_nN)$ OECTs obtained from the transfer curve. c) The right and left axes show how μC^* and V_{th} are affected by increasing alkyl side chain, respectively. d) How the μ and C* of $p(g_7NC_nN)$ OMIECs compare to other state-of-the-art n-type OMIECS.

Polymer	$^{a}\mu_{e, \text{ OECT}}$ (cm ² V ⁻¹ s ⁻¹)	^b C* (F cm ⁻³)	^c μC* (F cm ⁻¹ V ⁻¹ s ⁻¹)	$dg_{\rm m}'$ (S cm ⁻¹)	^e V _{th} (mV)	^f Device Thickness (cm)
p(g7NC2N)	$(2.00 \pm 0.41) \times 10^{-3}$	$\begin{array}{c} 180 \pm \\ 16 \end{array}$	0.36 ± 0.074	0.067	$\begin{array}{c} 230 \pm \\ 3.3 \end{array}$	$(1.72 \pm 2.61) \times 10^{-4}$
p(g7NC4N)	$(1.46 \pm 0.53) \times 10^{-3}$	126 ± 12	0.18 ± 0.067	0.035	210 ± 2.9	$(4.60 \pm 1.30) \times 10^{-4}$
p(g7NC6N)	$(2.29 \pm 0.70) \\ \times 10^{-3}$	150 ± 4	0.34 ± 0.111	0.065	210 ± 6.4	$(2.92 \pm 0.43) \times 10^{-4}$
p(g7NC8N)	$(6.01 \pm 1.87) \\ \times 10^{-3}$	199 ± 27	1.19 ± 0.371	0.240	250 ± 3.4	$(4.37 \pm 2.30) \times 10^{-5}$
p(g7NC10N)	$(1.20 \pm 0.07) \\ \times 10^{-2}$	$\begin{array}{c} 153 \pm \\ 34 \end{array}$	1.83 ± 0.101	0.370	$\begin{array}{c} 300 \pm \\ 3.0 \end{array}$	$(1.49 \pm 0.26) \times 10^{-4}$
p(g7NC12N) ^[7]	$(6.50 \pm 1.01) \\ \times 10^{-3}$	$ \frac{100 \pm}{6} $	0.66 ± 0.113	0.212	$\overline{328\pm\atop5.3}$	$\overline{(1.51 \pm 2.70) \times 10^{-5}}$
p(g7NC16N)	$(3.80 \pm 0.59) \times 10^{-3}$	86 ± 11	0.33 ± 0.074	0.047	$\begin{array}{c} 360 \pm \\ 10.0 \end{array}$	$(1.33 \pm 2.73) \times 10^{-4}$

Table 2.1. Electronic parameters of p(g7NCnN) OECTs.

^{a)}Electronic mobility extracted from the slope of the transfer curve. ^{b)} Volumetric capacitance extracted from a circuit fit to EIS data. ^{c)} Mobility volumetric capacitance product extracted from the slope of the transfer curve. ^{d)} Peak transconductance normalized by volume of OECT channel. ^{e)} The threshold voltage of the OECTs. ^{f)} The average channel thickness of the tested OECTs. More information on the extraction of these parameters can be found in the methods section.

Since stability is crucial for practical use of OECTs in biological applications, the electrical stability of the polymers was explored by pulsing the gate bias ON (where peak g_m occurs) /OFF at five second intervals repeatedly for approximately thirty minutes (**Fig 2.9-14**). p(g_7NC_2N) and p($g_7NC_{16}N$) did degrade rapidly upon initial cycling but then settled at about 50-75% of the initial current. All the other polymers exhibited stability retaining almost 100% of the current after an initial break in. The stability of these polymers can be attributed to the deeper lowest
unoccupied molecular orbit (LUMO) energy levels (4.2eV), making them less susceptible to reacting with oxygen or water, as discussed in section 2.1.

The last electronic property that is important for evaluating OECTs for biological applications is the cutoff frequency as that dictates what type of biological signals can be recorded. To extract the cutoff frequency a small signal sine wave was applied to the gate bias at different frequencies with the change in drain current recorded (**Fig 2.9-14**). $p(g_7NC_8N)$ exhibited the highest cutoff frequency at 75Hz while the highest performing $p(g_7NC_{10}N)$ had a cutoff frequency of 15Hz. Of the lowest performers of the series, $p(g_7NC_{16}N)$ showed no band bass region at all with the other three polymers exhibiting a cutoff frequency around 20-35Hz. For the majority of the series the cutoff frequency is high enough to do low frequency sensing like ECG, but $p(g_7NC_8N)$ could be used to measure EEG. The cutoff frequency is dependent on the volume of the channel; thus, for example, the thickness of the films could be decreased, to further enhance the cutoff frequency. However, decreases made in width or thickness will drive down the transconductance so OECT geometry must be optimized for the particular application.

To further understand the difference in OECT performance across the series, GIWAXS was performed to get insight into structural differences as the alkyl chain is increased. As the alkyl side chain length increases, the polymer stacking changed from predominantly edge-on (C2, C4, C6, C8) to mixed edge-on and face-on (i.e. isotropic) (C10, C12), and finally to preferentially face-on (C16), as demonstrated in the 2D-GIWAXS patterns (**Fig 2.8**). Devices with isotropic orientation have been shown to improve 3D charge transport in OECTs, which is likely why $p(g_7NC_{10}N)$ exhibits the highest bulk mobility and overall performance^{21,142}.



Figure 2.8. GIWAXs of $p(g_7NC_nN)$ **polymers.** 2D GIWAXS data for thin films of the $p(g_7NC_nN)$ series all spun at an identical spin speed from a 5mg ml⁻¹ chloroform solution.

One of the highest performing n-type OMIEC, $p(g_7NC_{10}N)$, with a high stability and state-of-the art mobility of 1.20 cm² V⁻¹s⁻¹, which can be attributed to the fused polylactam structure, is presented here. In addition, the alkly side chain was varied (C2-C16) to get a deeper understanding of how the ratio of hydrophilic to hydrophobic side chain affects OECT performance. Since the optimal OECT performance is with side chain C10, this tells us that an intermediate hydrophobic side chain length can balance the effects of swelling enabled by the hydrophilic side chain to maintain electronic transport. A majority of the polymers in this series display record stability for electron transporting OMIECs and cutoff frequencies high enough for biological sensing. While it does not perform as well as commonly used p-type OMIECS such as PEDOT:PSS these fused polylactam polymers make strong contenders for n-type OECTs to advance OECT-based circuitry.



Figure 2.9. OECT performance of p(g₇NC₂N). a) The transfer curve was collected with $\Delta V_g = 0.01$ V, 0V to 0.4V and $V_d = 0.4$ V and a sweep rate of 0.2 V_g/s . The right axis shows the g_m across $V_g = 0$ V to 0.4V, which was calculated by $\delta I_d/\delta V_g$. b) The output curve was collected with $\Delta V_g = 0.05$ V, 0 V to 0.4V and $\Delta V_d = 0.01$, 0 to 0.4V and a sweep rate of 0.2 V_d/s . c) The stability at $V_g = 0.4$ with a $V_d = 0.4$ V during 5s ON followed by 5s OFF switching for 30 minutes. d) The frequency response acquired at an offset $V_g = 0.4$. e) EIS at potential offsets 1 ranging from 0 to - 0.4 V vs Ag/AgCl. Bode plot, phase plot, and effective capacitance (capacitance per area) plot are shown.



Figure 2.10. OECT performance of p(g₇**NC**₄**N).** a) The transfer curve was collected with $\Delta V_g = 0.01$ V, 0V to 0.4V and $V_d = 0.4$ V and a sweep rate of 0.2 V_g /s. The right axis shows the g_m across $V_g = 0$ V to 0.4V, which was calculated by $\delta I_d / \delta V_g$. b) The output curve was collected with $\Delta V_g = 0.05$ V, 0 V to 0.4V and $\Delta V_d = 0.01$, 0 to 0.4V and a sweep rate of 0.2 V_d /s. c) The stability at $V_g = 0.4$ with a $V_d = 0.4$ V during 5s ON followed by 5s OFF switching for 30 minutes. d) The frequency response acquired at an offset $V_g = 0.4$. e) EIS at potential offsets ranging from 0 to - 0.4 V vs Ag/AgCl. Bode plot, phase plot, and effective capacitance (capacitance per area) plot are shown.



Figure 2.11. **OECT performance of p(g**₇**NC**₆**N)**. a) The transfer curve was collected with $\Delta V_g = 0.01$ V, 0V to 0.45V and $V_d = 0.4$ V and a sweep rate of 0.2 V_g /s. The right axis shows the g_m across $V_g = 0$ V to 0.45V, which was calculated by $\delta I_d / \delta V_g$. b) The output curve was collected with $\Delta V_g = 0.05$ V, 0 V to 0.45V and $\Delta V_d = 0.01$, 0 to 0.4V and a sweep rate of 0.2 V_d /s. c) The stability at $V_g = 0.45$ with a $V_d = 0.4$ V during 5s ON followed by 5s OFF switching for 30 minutes. d) The frequency response acquired at an offset $V_g = 0.4$. e) EIS at potential offsets ranging from 0 to -0.4 V vs Ag/AgCl. Bode plot, phase plot, and effective capacitance (capacitance per area) plot are shown.



Figure 2.12. OECT performance of p(g7NCsN). a) The transfer curve was collected with $\Delta V_g = 0.01$ V, 0V to 0.5V and $V_d = 0.4$ V and a sweep rate of 0.2 V_g/s . The right axis shows the g_m across $V_g = 0$ V to 0.5V, which was calculated by $\delta I_d/\delta V_g$. b)The output curve was collected with $\Delta V_g = 0.05$ V, 0 V to 0.5V and $\Delta V_d = 0.01$, 0 to 0.4V and a sweep rate of 0.2 V_d/s . c)The stability at $V_g = 0.4$ with a $V_d = 0.4$ V during 5s ON followed by 5s OFF switching for 30 minutes. d) The frequency response acquired at an offset $V_g = 0.45$ e) EIS at potential offsets ranging from 0 to -0.45 V vs Ag/AgCl. Bode plot, phase plot, and effective capacitance (capacitance per area) plot are shown.



Figure 2.13. OECT performance of p(g₇**NC**₁₀**N).** a) The transfer curve was collected with $\Delta V_g = 0.01$ V, 0V to 0.5V and $V_d = 0.4$ V and a sweep rate of 0.2 V_g /s. The right axis shows the g_m across $V_g = 0$ V to 0.5V, which was calculated by $\delta I_d / \delta V_g$. b)The output curve was collected with $\Delta V_g = 0.05$ V, 0 V to 0.5V and $\Delta V_d = 0.01$, 0 to 0.4V and a sweep rate of 0.2 V_d /s. c)The stability at $V_g = 0.45$ V with a $V_d = 0.4$ V during 5s ON followed by 5s OFF switching for 30 minutes. d) The frequency response acquired at an offset $V_g = 0.5$ d) EIS at potential offsets ranging from 0 to -0.5 V vs Ag/AgCl. Bode plot, phase plot, and effective capacitance (capacitance per area) plot are shown.



Figure 2.14. OECT performance of p(g7NC16N). a) The transfer curve was collected with $\Delta V_g = 0.01$ V, 0V to 0.5V and $V_d = 0.4$ V and a sweep rate of 0.2 V_g/s . The right axis shows the g_m across $V_g = 0$ V to 0.5V, which was calculated by $\delta I_d/\delta V_g$. b)The output curve was collected with $\Delta V_g = 0.05$ V, 0 V to 0.5V and $\Delta V_d = 0.01$, 0 to 0.4V and a sweep rate of 0.2 V_d/s . c)The stability at $V_g = 0.5$ with a $V_d = 0.4$ V during 5s ON followed by 5s OFF switching for 30 minutes. d) The frequency response acquired at an offset $V_g = 0.5$ V. e) EIS at potential offsets ranging from 0 to -0.5 V vs Ag/AgCl. Bode plot, phase plot, and effective capacitance (capacitance per area) plot are shown.

2.3.2 Enhancing the backbone coplanarity of n-type copolymers for organic electrochemical transistors

This section is adapted from "Maria I.P., Griggs, S., Rashid, R. B., Paulsen, B., ...& McCulloch, I (2022). Enhancing the backbone coplanarity of n-type copolymers for organic electrochemical transistors. (manuscript in preparation)"

The performance of many currently used OMIECs is jeopardized by the effects of swelling when taking up ions and accompanying water molecules as it can disrupt the connections between crystalline domains resulting in a loss of electronic transport pathway^{143,144}. This phenomenon plagues n-type OMIECs and previous work has been done to address this issue⁴¹. For example, the side chains on the commonly used naphthalene diimide (NDI) unit were modified with alkyl spacers between the backbone and the ethylene glycol side chain to limit the effects of swelling ultimately improving operational stability and electronic mobility¹³⁷. Backbone engineering however can offer more opportunities to promote closer interchain electronic coupling, improve long-range order and therefore increase charge carrier mobility. In this work a naphthodithiophene diimide (NDTI) unit, a thiophene-annulated derivative of NDI, is chosen as the acceptor unit as it offers a more planar backbone than NDI units. The more planar backbone results in extended piconjugation increasing the electron affinity and enhancing stability. The NDTI and NDI (for comparison) units were polymerized with bithiophene units and branched tetraethylene glycol side chains (**Fig 2.15**), which offered better solubility.



Figure 2.15. Structure of NDI-based polymers. The chemical structure of a) P4gNDTI and b) P4gNDI.

To study how the change in polymer backbone affects the uptake of water, electrochemical quartz crystal microbalance with dissipation monitoring (eQCM-D) measurements were performed for P4gNDI and P4gNDTI. First, the mass changed was measured under passive electrolyte uptake, where P4gNDI's mass uptake was large enough to be outside with measurement window of the instrument and P4gNDTI swelled ~57% (**Fig 2.16a,b**). This indicates that substituting NDI with NDTI can decrease polymer swelling due to the enhanced polymer backbone rigidity. Upon doping, P4gNDTI continued to swell reaching additional mass uptake of 24% at -0.4 V and 218% at -0.7 V versus Ag/AgCl as expected due to more hydrated ions being injected into the film to stabilize the reduced species (**Fig 2.16c**).



Figure 2.16. Swelling of NDI-based OMIECs. From the frequency change upon the introduction of 0.1M NaCl the mass change was calculated for a) P4gNDI and b) P4gNDTI. c) The mass change from eQCM-D measurements with applied potentials between 0 and -0.7 V versus Ag/AgCl in 0.1 M NaCl aqueous solution for P4gNDTI.

OECT measurements were carried out with both P4gNDI and P4gNDTI to understand how changes in backbone rigidity affect OECT performance. Both materials exhibited accumulation mode n-type operation (**Fig 2.17**). P4gNDI shows non-ideal OECT characteristics, with hysteresis and degradation of the drain current at gate voltages exceeding 0.45 V (**Fig 2.17**). However, P4gNDTI devices show minimal hysteresis indicating a more reversible ion insertion/injection process. P4gNDTI exhibited a lower threshold voltage (0.20 ± 0.003 V) than P4gNDI ($0.27 \pm$

0.05V) (**Table 2.2**). In addition, P4gNDTI exhibited a higher geometric normalized g_m (0.47 ± 0.06 S cm⁻¹) than P4gNDI ((1.87 ± 0.25) × 10⁻³ S cm⁻¹) (Fig 2.17 and Table 2.2).



Figure 2.17. Performance of NDI-based OECTs. a) The output curve of P4gNDTI was collected with $\Delta V_g = 0.05 \text{ V}$, 0 V to 0.5V and $\Delta V_d = 0.01$, 0 to 0.4V and a sweep rate of 0.2 V_d /s. b) The transfer curve of P4gNDTI was collected with $\Delta V_g = 0.01 \text{ V}$, 0V to 0.5V and $V_d = 0.6\text{V}$ and a sweep rate of 0.2 V_g /s. The right axis shows the g_m across $V_g = 0\text{ V}$ to 0.5V, which was calculated by $\delta I_d / \delta V_g$. c) The output curve of P4gNDI was collected with $\Delta V_g = 0.05 \text{ V}$, 0 V to 0.4V and a sweep rate of 0.2 V_g/s . d) The transfer curve of P4gNDI was collected with $\Delta V_g = 0.05 \text{ V}$, 0 V to 0.47V and $\Delta V_d = 0.01$, 0 to 0.4V and a sweep rate of 0.2 V_d/s . d) The transfer curve of P4gNDI was collected with $\Delta V_g = 0.01 \text{ V}$, 0V to 0.47V and $V_d = 0.6\text{V}$ and a sweep rate of 0.2 V_g/s . The right axis shows the g_m across $V_g = 0.01 \text{ V}$, 0V to 0.47V and $V_d = 0.6\text{V}$ and a sweep rate of 0.2 V_g/s . The right axis shows the g_m across $V_g = 0.01 \text{ V}$, 0V to 0.47V, which was calculated by $\delta I_d / \delta V_g$. e) The stability of P4gNDTI at $V_g = 0.4\text{V}$ with a $V_d = 0.4\text{V}$ during 5s ON followed by 5s OFF switching for 30 minutes.

To understand why Pg4NDTI exhibited a higher g_m than Pg4NDI the material dependent property (μ C*) was extracted from the slope of the transfer curve. P4gNDI exhibited a lower μ C* ((1.61 ± 0.46) × 10⁻³ F V⁻¹ cm⁻¹ s⁻¹) than P4gNDTI (0.27 ± 0.04 F V⁻¹ cm⁻¹ s⁻¹) (**Table 2.2**). To further gain insight into the enhanced performance of P4gNDTI, EIS was performed to extract C* resulting in a C* of 219 F cm⁻³ for P4gNDI and 167 F cm⁻³ for P4gNDTI (**Fig 2.18 and Table 2.2**). The lower C* for P4gNDTI may be expected as the more rigid backbone does not accommodate as much electrolyte uptake as P4gNDI. The higher performance of P4gNDTI is thus due to a higher electronic mobility $((1.42 \pm 0.22) \times 10^{-3} \text{ cm V}^{-1} \text{s}^{-1})$ than P4gNDI $((7.34 \pm 2.11) \times 10^{-6} \text{ cm V}^{-1} \text{s}^{-1})$. Given the lower swelling behavior of P4gNDTI observed by the e-QCM, the higher mobility is likely due to P4gNDTI having the ability to maintain its film microstructure and crystallite interconnectivity during operation in aqueous electrolyte due to a more controlled swelling and lower uptake of hydrated species.^{137,145} In addition, to the high electronic mobility P4gNDTI exhibits good operational stability. After a "break in" drop by $\approx 6\%$ after the first switching cycle, P4gNDTI shows no change in the drain current after 30 min of continuous cycling in aqueous media (**Fig 2.17e**).



Figure 2.18. EIS of NDI-based OMIECs. a) EIS of Pg4NDTI at potential offsets ranging from 0 to -0.5 V vs Ag/AgCl (red to blue) performed in 0.1M NaCl. Bode plot, phase plot, and effective capacitance (capacitance per area) plot are shown. b) EIS of Pg4NDI at potential offsets ranging from 0 to -0.47 V vs Ag/AgCl (red to blue) performed in 0.1M NaCl. Bode plot, phase plot, and effective capacitance (capacitance per area) plot are shown. b) EIS of Pg4NDI at potential offsets ranging from 0 to -0.47 V vs Ag/AgCl (red to blue) performed in 0.1M NaCl. Bode plot, phase plot, and effective capacitance (capacitance per area) plot are shown.

	^a g _m (S cm ⁻¹)	^b V _{th} (V)	сС*	^d µC*	^e μ (cm ² s ⁻¹ V ⁻¹)
			(F cm ⁻³)	(F cm ⁻¹ s ⁻¹ V ⁻¹)	
P4gNDTI	4.68E-2 ±	$0.20 \pm$	$167 \pm$	0.27 ± 3.66E-	1.42E-3 ±
_	6.15E-3	3.27E-3	11.37	2	2.20E-4
P4gNDI	1.87E-4 ±	0.27 ±	219*	1.61E-3 ±	7.34E-6 ±
_	2.46E-5	4.67E-2		4.64E-4	2.11E-6

Table 2.2. Electronic properties of NDI-based OECTs.

^{a)} OECT peak transconductance measured at $V_G = 0.40$ V and normalized by thickness. ^{b)} Threshold voltage extracted from the $\sqrt{I_D}$ versus V_G plot. ^{c)} [μC^*] estimated from the slope of the transfer characteristics. ^{d)} Volumetric capacitance determined from the electrochemical impedance spectra at (V = -0.4 V versus Ag/AgCl). ^{e)} Saturation mobility extracted from the slope of the transfer characteristics.

PgNDTI exhibits one of the highest ever reported electronic mobilities for n-type OECTs and even surpasses the stability of fused lactam-based polymers presented earlier in this chapter. This promising performance of Pg4NDTI demonstrates once again that enhancing backbone coplanarity to mitigate the negative effects of swelling during operation is an effective strategy to enhance electronic transport in n-type OMIECs. 2.3.3 p- to n-Type Mixed Conduction in Isoindigo-Based Polymers through Molecular Design
This section has been adapted from "Parr, Z. S., Borges-González, J., Rashid, R. B., Thorley, K.
J., Meli, D., Paulsen, B. D., ... & Nielsen, C. B. From p-to n-Type Mixed Conduction in Isoindigo-Based Polymers through Molecular Design. Advanced Materials, 2107829."

While polythiophenes^{146,147}, diketopyrrolopyrrole-^{138,142,148,149} and naphthalene diimide-^{24,41} based OMIECs have been extensivley studied for OECTs, isoindigo based OMIECs have not, even though they show potential due to their versatile and highly efficient charge transporting motifs¹⁵⁰. Here isoindigo and analogs that replace the tranditional benzene ring with pyridine (7,7'diazaisoindigo) and thiophene (thienoisoindigo) are explored as OMIECs for enhanced OECT performance. The lactam nitrogens are functionalized with an amphipathic side chain, which is composed of a five-methylene spacer and a terminal triethylene glycol unit, to allow for ion injection into the bulk of the film^{150,151}. By replacing the benzene the torsional twist can be reduced resulting in a more planar backbone and higher OECT performance due to more efficient charge transport. 7,7'-diazaisoindigo (AIG) and thienoisoindigo (TIG) result in less steric respulsions due to fewer repulsive H-H interactions and lactam oxygen/aryl hydrogen interactions resulting in dihedral angles (ϕ_1 , ϕ_2) that are either 0° or 180° unlike with isoindigo (IG). The three motifs (IG, AIG, and TIG) were then copolymerized with either an electron-rich thiophene (T) unit or electrondeficient 2,1,3-benzothiadiazole (BT) unit, to create a series of six isoindigo-based copolymers (Fig 2.19). This series has allowed for the development of efficient p-and n-type OMIECS for OECTs and has given way for struture-property realtionships that can be used for the developent of future OMIECs.



Figure 2.19. Structure of isoindigo-based polymer series. a) The isoindigo (IG), 7,7'diazaisoindigo (AIG) and thienoisoindigo (TIG) scaffolds with important dihedral angles (ϕ_1 and ϕ_2) and steric interactions (grey shading) highlighted on the isoindigo scaffold. The isoindigo, 7,7'-diazaisoindigo and thienoisoindigo scaffolds co-polymerized with b) a electron-rich thiophene (T) unit c) an electron-deficient 2,1,3-benzothiadiazole (BT) unit. R=(CH₂)₅(OCH₂CH₂)₃OCH₃.

The electrochemical properties of the isoindigo series were explored with cyclic voltammetry (CV) in 0.1M NaCl. From the electron-rich polymers, TIG-T showed clear and reversible oxidative behavior with good current density (**Fig 2.20a**) and an onset of oxidation at 0.3 V. IG-T and AIG-T showed almost no electrochemical response; however, IG-T did show a small non-reversible oxidative event at 0.95V (**Fig 2.20a**). For the electron-deficient polymers, TIG-BT showed both reversible oxidation and reduction events at an onset of 0.35V and -0.8V, respectively (**Fig 2.20b**). Once again, AIG-BT and IG-BT showed no strong electrochemical

response, but a non-reversible faradic event can be seen for AIG-BT with no clear onset (Fig

2.20b).



Figure 2.20. CV of isoindigo-based polymer series. a) Top: IG, AIG, TIG co-polymerized with thiophene. Bottom: rescaled to show the oxidative behavior of IG-T. b) CV of Top: IG, AIG, TIG co-polymerized with 2,1,3-benzothiadiazole Bottom: rescaled to show the oxidative and reductive behavior of AIG-BT. All measurements were done on drop-casted films from 5 mg ml⁻¹ chloroform solution onto glassy carbon in 0.1 M aqueous NaCl solution at a scan rate of 100 mV s⁻¹; each polymer film was cycled ten times with scan numbers 2-10 shown here.

The polymers were then employed in OECTs to assess their electronic properties. All films were dropcasted and operated in 0.1M NaCl with an external Ag/AgCl gate. For the electron-rich polymers, no drain current was observed for AIG-T which was expected based on the CV. IG-T showed p-type operation with peak drain currents around 4 μ A, a V_{th} of ~ -0.7V and a peak transconductance (g_m) of 23 mS cm⁻¹ (**Fig 2.21a**). TIG-T also showed p-type operation but with much better performance, in good accorandance with observations made by the CV. TIG-T had a peak drain current of ~12mA with a V_{th} of -0.2V and a peak g_m of 52 S cm⁻¹(**Fig 2.21b**). For the electron-deficient polymers, no drain current was observed for IG-BT which is in agreement with

the CV. TIG-BT however showed p-type operation with mA drain currents, smilar to TIG-T. TIG-BT had a peak g_m 23 S cm⁻¹ and a V_{th} of ~ -0.35V (**Fig 2.21c**). AIG-BT showed n-type operation with a peak drain current of 6µA, a V_{th} of ~ 0.55V, and a peak g_m of 29 mS cm⁻¹ (**Fig 2.21d**). The operational stability of the polymers was tested by pulsing the gate voltage from OFF to an ON voltage close to where peak g_m occurs which was at 0.7 V, -0.8 V, -0.5 V, and -0.7 V for AIG-BT, IG-T, TIG-T and TIG-BT respectively. IG-T showed rapid deterioration of OECT performance whereas TIG-BT and TIG-T showed good stability with less than 10% loss of drain current over the 30-minute cycling period (**Fig 2.21**). Interestingly, the drain current of AIG-BT increased during cycling but seemed to plateau. Increasing current makes devices just as hard to implement for biological applications as decreasing current, total stability is ideal.



Figure 2.21. OECT performance of isoindigo-based series. a) **IG-T.** The transfer curve was collected with $\Delta V_g = 0.01$ V, 0V to -0.8V and $V_d = -0.4$ V and a sweep rate of 0.05 V_g /s. The right axis shows the g_m across $V_g = 0$ V to -0.8V, which was calculated by $\delta I_d / \delta V_g$. The output curve was collected with $\Delta V_g = 0.05$ V, 0 V to -0.8V and $\Delta V_d = 0.01$, 0 to -0.4V and a sweep rate of 0.05 V_d /s. The stability at $V_g = -0.8$ V with a $V_d = -0.4$ V during 5s ON followed by 5s OFF switching for 30 minutes. b) **TIG-T.** The transfer curve was collected with $\Delta V_g = 0.01$ V, 0V to -0.75V and $V_d = -0.4$ V and a sweep rate of 0.2 V_g /s. The right axis shows the g_m across $V_g = 0$ V to -0.75V, which was calculated by $\delta I_d / \delta V_g$. The output curve was collected with $\Delta V_g = 0.05$ V, 0 V to -0.75V, which was calculated by $\delta I_d / \delta V_g$. The output curve was collected with $\Delta V_g = 0.05$ V, 0 V

to -0.75V and $\Delta V_d = 0.01$, 0 to -0.4V and a sweep rate of 0.2 V_d /s. The stability at $V_g = -0.5$ V with a $V_d = -0.4$ V during 5s ON followed by 5s OFF switching for 30 minutes. c) **TIG-BT.** The transfer curve was collected with $\Delta V_g = 0.01$ V, 0V to -0.8V and $V_d = -0.4$ V and a sweep rate of 0.2 V_g /s. The right axis shows the g_m across $V_g = 0$ V to -0.8V, which was calculated by $\delta I_d / \delta V_g$. The output curve was collected with $\Delta V_g = 0.05$ V, 0 V to -0.8V and $\Delta V_d = 0.01$, 0 to -0.4V and a sweep rate of 0.2 V_d /s. The stability at $V_g = -0.7$ V with a $V_d = -0.4$ V during 5s ON followed by 5s OFF switching for 30 minutes. d) **AIG-BT.** The transfer curve was collected with $\Delta V_g = 0.01$ V or 0.75 V and $V_d = 0.4$ V and a sweep rate of 0.05 V_g /s. The right axis shows the g_m across $V_g = 0$ V to 0.75 V, which was calculated by $\delta I_d / \delta V_g$. The output curve was collected with $\Delta V_g = 0.01$ V, 0V to 0.75 V, which was calculated by $\delta I_d / \delta V_g$. The output curve was collected with $\Delta V_g = 0.01$ V, 0V to 0.75 V, which was calculated by $\delta I_d / \delta V_g$. The output curve was collected with $\Delta V_g = 0.01$ V, 0V to 0.75 V, which was calculated by $\delta I_d / \delta V_g$. The output curve was collected with $\Delta V_g = 0.01$ V, 0V to 0.75 V, which was calculated by $\delta I_d / \delta V_g$. The output curve was collected with $\Delta V_g = 0.05$ V, 0 V to 0.75 V and $\Delta V_d = 0.01$, 0 to 0.4V and a sweep rate of 0.05 V_d /s. The stability at $V_g = 0.7$ V with a $V_d = 0.4$ V during 5s ON followed by 5s OFF switching for 30 minutes.

	^a g _m (S cm ⁻¹)	^b C* (F cm ⁻³)	°μ (cm ² s ⁻¹ V ⁻¹)	^d μC* (F cm ⁻¹ s ⁻ ¹ V ⁻¹)	eV _{th} (V)
IG-T	2.32E-2±4.0E- 3	76.2±6.94	2.66E-3± 4.53E-4	2.03E-1± 3.45E-2	-0.69±1.6E- 3
TIG-T	52.20 ± 10.07	121.0± 11.89	1.10 ± 2.18 E-1	132.0±26.23	-0.20± 1.08E-2
TIG-BT	22.65±10.80	82.1 ± 7.91	6.14E-1± 3.08E-1	55.31±27.74	-0.34± 8.36E-3
AIG-BT	2.92E-2± 6.24E-3	83.5±8.45	1.38E-3± 3.82E-4	1.15E-1± 3.19E-2	0.55± 2.69E-3

Table 2.3. Electronic properties of isoindigo-based OECT series.

^{a)}Transconductance values measured at V_g values of -0.8 V (**IG-T**), -0.6 V (**TIG-T**), -0.75 V (**TIG-BT**), and 0.75 V (**AIG-BT**); values normalized by active layer dimensions Wd/L; ^{b)} Volumetric capacitance extracted from electrochemical impedance spectroscopy measurements; ^{c)}Electronic mobility extracted from the transistor characteristics in the saturated regime; ^{d)} Mobility volumetric capacitance product calculated from the slope of g_m as a function of $(Wd/L)(V_{th} - V_g)$. ^{e)} Threshold voltage extracted from extrapolation of the linear regime of the $\sqrt{|I_d|}$ vs V_g . Average values were extracted from either 5 or 6 measured devices.

To extract the important material dependent figure of merit μ C^{*}, electrochemical impedance spectroscopy (EIS) was performed to extract C^{*} (**Fig 2.22**). IG-T, AIG-BT and TIG-BT all had a similar volumetric capacitance of about 80 F cm⁻³ while TIG-T had a higher C^{*} at 120 F cm⁻³ (**Table 2.3**). Mobility was extracted from the OECT characteristics in the saturated regime with TIG-T and TIG-BT having relatively high mobilities, 1.1 and 0.6 cm² s⁻¹ V⁻¹ respectively (**Table** **2.3**). The μ C^{*} of TIG-T (132 F cm⁻² s⁻¹ V⁻¹) is comparable to that of other commonly used higher performing p-type OMIECs such as the glycolated polythiophene p(g2T-T)^{22,146}. IG-T had a lower hole mobility at $3 \cdot 10^{-3}$ cm² s⁻¹ V⁻¹ resulting in a lower μ C^{*} (0.2 F cm⁻¹ s⁻¹ V⁻¹) than that of the TIG based polymers, which is to be expected as it had the least planar backbone. AIG-T had an electron mobility of $1.5 \cdot 10^{-3}$ cm² s⁻¹ V⁻¹. While the μ C^{*} of n-type OMIECs is typically lower than that of p-type OMIECs, AIG-BT's μ C^{*} (0.1 F cm⁻¹ s⁻¹ V⁻¹) is comparable to or better than the glycolated naphthalenediimide-based^{24,41} systems and is only slightly lagging behind newly developed n-type OMIECs^{140,152}.



Figure 2.22. EIS of isoindigo-based OMIECs. EIS at potential offsets vs Ag/AgCl ranging from a) 0 to 0.8 V for IG-T. b) 0.to 0.75 V for TIG-T c) 0 to 0.8 V for TIG-BT d) 0 to -0.7V for AIG-BT vs Ag/AgCl. Bode plot, phase plot, and effective capacitance (capacitance per area) plot are shown.

To understand the difference in OECT characteristics grazing incidence wide-angle x-ray scattering (GIWAXS) was performed on thin films (**Fig 2.23**). The OMIECs all exhibited populations of both face-on (out-of-plane π -stack) and edge-on (in-plane π -stack) crystallites, with T containing copolymers favoring face-on and BT copolymers favoring of edge-on

crystallites. IG and AIG based copolymers were more susceptible to being either edge-on or face-on when paired with T or BT respectively, but TIG copolymers favored a mix of edge-on or face-on regardless of being paired with T or BT. This may be one of the reasons for the high performance of the TIG copolymers because transport in OECT is volumetric rather than interfacial. Since TIG-T and TIG-BT show very similar microstructure with high in-plane lamellar ordering, the slightly higher performance of TIG-T might be due to the lower ionization potential (IP), which is manifested as a lower threshold voltage (Table 2.4). The lower performance (lower mobility) of the IG-T could be due to its lack of chain ordering as evidenced by the broad shoulders in the lamellar spacing (h00) in Fig 2.24a,b. While a more ordered structure was observed for IG-BT than IG-T this did not manifest as a higher performing OECT as expected due to the prohibitively large IP preventing the OECT from turning on (Table 2.4). AIG-T and AIG-BT both displayed high lamellar ordering (h00) as shown by the multiple scattering peaks (Fig 2.24). In addition, AIG-BT was expected to have the most planar backbone and thus it has three orders of nicely resolved lamellae scattering. The highly rigid backbone coupled with the high electron affinity (EA) (Table 2.4) is likely the reason for the good n-type performance from AIG-BT based OECTs. While TIG-BT did show high EA as well, its barrier to rotation is smaller and is more structurally flexible but a rigid backbone is a design criterion for high performing n-type OMIECs as displayed by other higher performers like BBL and other n-type OMIECs discussed in this chapter^{71,140}. The reasoning for AIG-T not being able to operate as a p-type OMIEC may be due to the higher IP as well, making it inaccessible within the water window (Table 2.4).

	^a Ionization	^b Electron Affinity	
	Potential (IP) (eV)	(EA) (eV)	
IG-T	5.66	2.75	
IG-BT	5.88	2.74	
TIG-T	4.92	2.80	
TIG-BT	5.02	2.98	
AIG-T	5.77	2.96	
AIG-BT	6.00	3.02	

Table 2.4. Electronic properties of isoindigo polymers.

The ^a)ionization potential (IP) and ^b)electron affinity (EA) were calculated as the difference in single point energies of the charged and neutral species.



Figure 2.23. GIWAXS of isoindigo-based polymers. a) IG-T, b) IG-BT, c) AIG-T, d) AIG-BT, e) TIG-T, f) TIG-BT showing preferential face-on stacking for thiophene (T) copolymers and edge-on stacking for benzothiadiazole (BT) copolymers. All films were cast from a 5mg/ml (in CHCl₃) and spun at 1500 rpm.



Figure 2.24. Linecuts of isoindigo-based polymers. In-plane (q_r) and out-of-plane (q_z) line cuts of thiophene copolymers, (a) and (b), and benzothiadiazole copolymers, (c) and (d), respectively. Lamellar (h00) and π peaks (010) labeled accordingly.

This work shows that TIG and AIG motifs can be used to create high performing OECTs with peak mobilities that are on the same order of magnitude of the highest performing OMIECs currently available. TIG-based polymers display very narrow optical band gaps, low IPs and high EAs making them possible candidates for both p- and n-type, and thus ambipolar, operation in aqueous mediums. AIG's rigid backbone and high electron affinity make it a good choice for high perfroming n-type OECTs. AIG-based systems provide a good platform for exploring this further; for instance, with new comonomers providing so-called conformational locking by taking advantage of noncovalent interactions. The exploration of iosindigo motifs and different monomers can help develop a wide library of OMIECs that is needed to further OECT-based ciruitry.

2.4 Exploring More Crystalline Active Materials for Mixed Conduction

2.4.1 A Semiconducting Two-dimensional Polymer as an Organic Electrochemical Transistor Active Layer

This section is adapted from "Rashid, R. B., Evans, A. M., Hall, L. A., Dasari, R. R., Marder S. R., ...& Rivnay, J. (2022). A Semiconducting Two-dimensional Polymer as an Organic Electrochemical Transistor Active Layer. *Advanced Materials* (accepted)."

Two dimensional polymers (2DPs), particularly those synthesized from solution polymerization often known as covalent organic frameworks (COFs), have the potential to address current limitations faced by OMIECs and ultimately enhance OECT performance. 2DPs are network polymers whose structure and porosity are likely to resist structural changes under operation and swelling, which can lead to more operationally stable OECTs. In addition, 2DPs contain welldefined pores that can aid ion injection and mobility throughout the bulk of the OMIEC which can enhance response time, an issue that plagues some OMIECs. The pores could even be tuned and functionalized to create ion selective OECTs for biological sensing. Most previously reported 2DP semiconductors observe low conductivities but a new 2DP TIIP was reported with an intrinsic conductivity of 3.5 X 10^{-5} S m⁻¹.¹⁵³ 2DP films are typically defect prone and difficult to pattern over micron-scale devices needed for biological applications; however, recent examples of interfacial, direct-growth, or additive manufacturing film production exemplify that high-quality 2DP films are rapidly becoming available.¹⁵⁴⁻¹⁶⁰ The structural properties of 2DPs and recent advances made on 2DP semiconductors make them worthy of interrogation for OECTs.

Here, textured thin films of the previously reported semiconducting 2DP TIIP were fabricated. They are produced by imine condensation of N,N'-dibutyl-6,6'-diformylthienoisoindigo and 1,3,6,8-tetra(aminophenyl)pyrene (**Fig. 2.25**). Through a combination of spectroscopic and electrochemical techniques, TIIP is shown to be intrinsically semiconducting with addressable oxidative potentials. Film synthesis conditions and microfabrication techniques were developed to deposit micron-resolution TIIP films with metal interconnects and insulation to obtain 2DP-coated electrodes and OECTs with semiconducting 2DP transistor channels (**Fig 2.25**). Such film assembly and device fabrication showed that TIIP enables a volumetric charge of C* of 32 F/cm³, on par with prototypical conducting polymer OMIECs.⁴³ The performance of OECT devices based on TIIP active layers revealed a modest peak transconductance (g_m) of 0.14 S cm⁻¹, a μ C* of 1.75 F cm⁻¹ V⁻¹ s⁻¹, and allowed for device-scale mobility determination of 0.05 cm² V⁻¹ s⁻¹. These advances in patterning 2DPs and characterizing their performance in electrochemical devices will enable broader investigations of the optoelectronic properties of this emerging macromolecular architecture.



Completed 2DP-based device

Figure 2.25. Structure and fabrication of TIIP. TIIP direct polymerization and patterning by dry peel-off to produce transistor structures.

First the electrochemical response of TIIP is assessed to ensure the redox accessibility required for OECT operation. Due to the harsh synthetic conditions of TIIP films that are incompatible with indium tin oxide substrates, polycrystalline 2DP powder films were studied first. The cyclic voltammetry shows that TIIP exhibits two oxidative peaks at +0.6 V and +1.25 V (vs Fc/Fc⁺) (**Fig 2.26a**). The irreversibility of these oxidative features is likely due to the poor adhesion of oxidized TIIP to the conductive carbon used to perform this measurement, this is in contrast to the reversibility and low hysteresis of the OECT devices presented herein. The reductive features in the CV were dismissed due to the high probability of unstable OECT operation in ambient conditions. Electron spin resonance (ESR) SEC collected during an oxidative sweep showed the formation of a paramagnetic species at 0.8 V (vs Ag/Ag⁺) with a *g* value of 2.0024, consistent with the formation of an organic radical (**Fig. 2.26b**). The increasing intensity of ESR signal with

increasing bias demonstrates that oxidative bias leads to hole injection into the TIIP film. The ESR and CV data show that TIIP has the potential for operation in OECTs in ambient conditions.



Figure 2.26. Oxidative accessibility of TIIP. a) Cyclic voltammogram of TIIP at 100 mV/s swept in the reductive direction first showing two oxidative processes. b) Electron spin resonance spectroelectrochemistry of TIIP from +0.6 to +1.2 V showing the formation of a radical upon oxidation. Experiments conducted at room temperature in a 0.1 M TBAPF₆/MeCN electrolyte.

To evaluate the electrical properties of patterned TIIP films, aqueous electrolyte-gated devices were investigated. Polymer-coated microelectrodes are useful for characterizing the electrochemical properties of TIIP in a form factor most relevant to OECTs. Electrochemical impedance spectroscopy of a TIIP-coated electrode operating in 0.1 M NaCl was used to extract capacitance. The impedance spectra were fit to a circuit model consisting of a resistor in series with a resistor and constant phase element (CPE) in parallel ($R_s(R||Q)$) (**Fig. 2.27a**). While the impedance spectra did not fit a circuit model consisting of ideal elements as other OECT materials do, a CPE is commonly used to describe porous materials.¹⁶¹ A pseudo capacitance was extracted from the CPE using $Y_0^{(1/n)} R^{(1/n-1)}$ where $Y_0 = 2.96 \mu S^n$ and n = 0.79. This approach yielded a value of 0.8 mF cm⁻² at 0.8 V and showed a 20-fold increase in effective capacitance when switching the gate bias from the neutral to oxidized state. These data suggest that the film charging is not limited to the electrolyte-TIIP interface, and that the bulk of the 2DP participates in

electrochemical charging, consistent with OMIECs used in electrolyte-gated devices. Assuming the full thickness of the TIIP allows for film oxidation at these biases, the effective volumetric capacitance (C*) of the TIIP films would be 32 F cm⁻³ at 0.8 V. Since the uniformity of charging within the film, both in the bulk, and as a function of penetration depth, is not well explored, this reported C* value might increase as polymerization and fabrication methods improve. Nevertheless, this C* value is on par with other OECT materials such as the prototypical conducting polymer PEDOT:PSS, and lower than homopolymer OMIECs.^{22,162}

The output and transfer characteristics shown in **Fig 2.27c,d** show *p*-type (hole transport) operation $(V_g, V_d < 0V)$, which is consistent with the findings of the ESR-SEC. The output curve shows clear linear and saturation regimes typical of transistor operation. TIIP OECTs demonstrated a normalized peak transconductance (g_m) of 0.14 S cm⁻¹ at -0.8 V, which was extracted from the slope of the transfer curve $(\delta I_d/\delta V_g)$. The threshold voltage $(V_{th} = 0.71 \text{ V})$ was extracted from the extrapolation of the linear regime of the $\sqrt{|I_d|}$ vs V_g plot. Electronic mobility (μ_e) was then extracted using the equation $g_m = \frac{wd}{l} \mu C^* (V_g - V_{th})$ and was 0.05 cm² V⁻¹ s⁻¹. This results in a μC^* of 1.75 F V⁻¹cm⁻¹ s⁻¹.

In benchmarking TIIP against existing OMIEC-channel materials used in OECTs, the present devices exhibit modest figure of merit values. Top performing *p*-type polymer OECT materials achieve μ C*>100 F V⁻¹ cm⁻¹ s⁻¹, but the performance of TIIP is on par with the best *n*-type OECT active materials, which will likely be the limiting device in future circuits. With its more crystalline morphology, it may be more appropriate to compare 2DPs with crystalline small-molecule OMIECs (or potential assemblies of 2D materials) rather than linear polymers. From this perspective, TIIP outperforms or performs similarly to other crystalline OECT materials such as

small molecule materials and composites; for example, a small molecule n-type fullerene-based OMIEC demonstrated a μ C* of 7 F V⁻¹ cm⁻¹ s⁻¹, which is within a factor of four of the TIIP OMIEC performance presented here.¹⁶³ 2DP-based OMIECs may indeed fill a critical gap in the field: providing a synthetic design strategy to combine the advantages of small molecule OMIECs (including precision chemical control and crystalline ordering) with the more established high performance of linear polymer-based OMIECs. Currently, TIIP shows mobility ~20 times lower than top performing linear polymers, which could be readily improved with advances in thin film formation and processing. However, the higher volumetric capacitances are the main reason linear polymers outperform TIIP. This may likely be due to facile ion intercalation from amorphous regimes into semicrystalline pathways, however 2DPs or COFs have the potential for enhanced ion transport due to their porous architecture and synthetic tunability thereof.



Figure 2.27. Performance of TIIP OECTs. a)Electrochemical impedance spectroscopy of TIIPcoated electrodes at potential offsets of 0.3 V to 0.8 V vs Ag/AgCl. The dotted green fits are from (R_s(R_p||Q)), which makes use of a constant phase element (Q). A pseudo capacitance was extract from the circuit leading to a fit of R_s = 246 Ω . R_p = 8.9 M Ω , and C = 7.1 µF. b)Output curve (ΔVg = 0.05 V, 0 V to -0.8 V and Vd : 0 to -0.4 V) of a OECT. c) Transfer curve (ΔVg = 0.01 V, 0 V to -0.8 V and Vd = -0.4 V) on a log and linear scale of a TIIP OECT. OECT characteristics of a 100 µm x 10 µm (W x L) device, ~300 nm thick. Inset: Optical micrograph of TIIP OECT described above.

These results show that the 2DP TIIP films enable micron-scale operational transistors with respectable mobilities of 0.05 cm² V⁻¹ s⁻¹. While this value is approximately two orders of magnitude lower than the highest performance conjugated linear polymers, macroscale measurements of 2DP semiconductor performance are an important step towards evaluating the potential of macromolecular sheets as semiconductors, which have been shown to have high mobilities through nanoscale spectroscopy measurements and density functional theory calculations. ^{153,164-169}

Demonstrated 2DP-based OECT fabrication and device-performance foreshadows a new OMIEC design paradigm. Now that 2DP-based OECT performance has been established, it will be more straightforward to explore the systematic optimization of these materials for OECTs. However, at present, the performance of these devices falls short of their potential. Presumably, the discontinuous, defect-prone films that are presently available limits the potential of 2DPs as semiconductors. Undeniably, defect prevalence, mesoscale ordering, and macroscale morphology will influence ionic injection, electrolyte transport, and long-range electronic mobilities. While we observe direct evidence for bulk film charging in this work, it is unclear whether this ion injection occurs via defects or through the designed porosity of the framework. In line with this question is whether the charging observed is limited to defect/amorphous regions interfacing with crystalline 2DPs domains (as is the case with alkylated conjugated polymer:polymer electrolyte blend OMIECs, or some nano-fibrillar materials), or if charge carrier distribution is more uniform throughout the bulk. Future investigations into film formation/processing will answer these questions and allow for rapid iteration in 2DP development as active materials for OECTs and other microelectronic components.

In this work we demonstrated that a two-dimensional polymer, TIIP, can be polymerized, pattered, and operated as a micron-scale electrochemical transistor. TIIP films were deposited by direct polymerization, followed by dry PaC liftoff, which produced devices with well-defined channel dimensions. The device shows low hysteresis operation and bulk modulation of channel conductance, consistent with OECT operation. The measured electrical characteristics reveal charging of 0.8 mF cm⁻², approximated as 32 F cm⁻³ volumetric capacitance, with a hole mobility of 0.05 cm² V⁻¹ s⁻¹.

These findings show that 2DPs are a viable and distinct new class of OECT active layers. The ideal OMIEC design calls for an anisotropic material where ionic injection and transport is orthogonal to the transistor channel and electronic transport occurs within the plane of the channel, bridging a source and drain electrode. Semiconducting 2DPs nominally meet these requirements extremely well. Because the 2DP backbone (and thus the electronic structure) and pore functionality are orthogonal and can be aligned, it should be possible to systematically engineer OMIECs with tailored conductivities, capacitances, response times, and selectivity. As these synthetic design parameters are uncovered, we anticipate that 2DP transistors will also be optimized for other OMIEC devices such as chemical sensing or neuromorphic computing. To realize this development, it will be critical to understand and control the microscale structure of 2DPs including their domain size and defect density. While this study does not address these challenges in full, it is a proof-of-principle demonstration that maturing synthetic and fabrication techniques are reaching the required fidelity to enable these explorations.

2.4.2 Semiconducting Small Molecules as Active Materials for p-Type Accumulation Mode Organic Electrochemical Transistors

This section is adapted from "Parr, Z. S., Rashid, R. B., Paulsen, B. D., Poggi, B., Tan, E., Freeley, M., ... & Nielsen, C. B. (2020). Semiconducting Small Molecules as Active Materials for p-Type Accumulation Mode Organic Electrochemical Transistors. *Advanced Electronic Materials*, *6*(6), 2000215."

(P4E4) (Fig 2.28) and subsequently blended with 10% high molecular weight polyethylene

oxide (PEO) to overcome the low viscosity of the small molecule solution and enhance charge injection into the film.



Figure 2.28. Chemical Structure of small molecules. Chemical structure of a) P2E2. B) P4E4.

The electrochemical conditions of the small molecules relevant to OECT behavior were probed using solid-state cyclic voltammetry (CV) in aqueous electrolyte (0.1M NaCl). The CV in **Fig 2.29a** shows that the PTTP-C6 with the hydrophobic side chains was not able to oxidize as the resistance to ion injection was too high to allow oxidation below the electrolysis potential of water. However, when the triethylene side chains were added PTTP allowed ion injection into the film showing a nonreversible oxidation event with a high onset of oxidation of 0.93 V versus Ag/Ag⁺ (**Fig 2.29a**), proving that the addition of the hydrophilic side chains aids ion injection. P2E2 and P4E4 show reversible oxidation with an onset of 0.34V and 0.22V respectively; in addition, they showed stability over many CV cycles (**Fig 2.29b,c**). The P2E2:PEO films exhibited almost identical behavior to that of the neat film but showed greater long-term stability when cycled (**Fig 2.29b**). The P4E4:PEO films exhibited an onset of oxidation ~0.1V lower than that of the neat film. The blended film also exhibited higher current density than that of the neat

film (**Fig 2.29c**). The early onset of oxidation and reversible redox behavior makes them possible OMIECs for OECTs.



Figure 2.29. Cyclic voltammetry of small molecules. Thin film CV of neat molecule and molecule:PEO blend films drop-cast onto a glassy carbon electrode from 5 mg mL⁻¹ chloroform solutions. Cyclic voltammograms recorded at 100 mV s⁻¹ in 0.1 M aqueous NaCl after two cycles apart from PTTP for which the first cycle is reported. a) PTTP-C6 and PTTP, b) P2E2 and P2E2:PEO, c) P4E4 and P4E4:PEO.

P2E2, P4E4, P2E2:PEO, and P4E4:PEO were tested as OECTs which were operated in 0.1M

NaCl with a Ag/AgCl pellet used as the gate. The devices were cycled three times before

recording transistor characteristics to ensure stable recordings. With P2E2-based OECTs no

current across a number of devices was observed even when cast with different spin-coating

conditions. However, the blended P2E2:PEO-based OECTs did turn on but with a low Id of 6nA

(Fig 2.30a,b). The P2E2:PEO-based OECT device exhibited a threshold voltage V_{th} of -0.28 V,

matching the expected onset of oxidation from the CV, but a reliable gm could not be extracted

due to the poor performance. For P4E4-based OECTs, the devices did turn on and an Id of

around 20nA was achieved with an ON/OFF ratio of 10^{1} (**Fig 2.30c,d**). The devices showed some hysteresis which could be mitigated by cycling of the devices and performing measurements at a slower sweep rate. The P4E4-based OECTs were able to achieve a $g_{\rm m}$, of 0.14 μ S at a gate voltage of -0.65 V. The highest performing OECTs were the P4E4:PEO-based OECTs (**Fig 2.30e,f**). The devices had an average peak transconductance of 0.65 μ S at a gate voltage of -0.47 V and ON/OFF ratios around 10^{2} for an average device thickness of 31 nm. The μ C* product was found to be 0.81 F V⁻¹ cm⁻¹ s⁻¹ in the saturation regime for P4E4:PEO while the inferior performance of the neat P4E4-based device prevented a reliable extraction of the μ C* product. Consistent with the CV, the OECTs with the PEO blend turned on at lower bias ($V_{\rm th}$ of -0.15 V) than the neat P4E4-based devices ($V_{\rm th}$ of -0.32 V). The relatively low currents observed for both neat P4E4 and its PEO blend made it difficult to extract the OECT charge carrier mobility (μ).


Figure 2.30. OECT characteristics of semiconducting small molecules. All output curves were collected with $\Delta V_g = 0.05$ V, 0 V to -0.6V and $\Delta V_d = 0.01$, 0 to -0.4V and a sweep rate of 0.02 V_d /s. All transfer curves were collected with $\Delta V_g = 0.01$ V, 0V to -0.8V and $V_d = -0.4$ V and a sweep rate of 0.02 V_g /s. a) Output curve of P2E2:PEO-based OECT. b) Transfer curve of P2E2:PEO-based OECT. c) Output curve of P4E4-based OECT. d) Transfer curve of P4E4based OECT. e) Output curve of P4E4:PEO based OECT. f) Transfer curve of P4E4:PEO based OECT.

To understand the difference in the P2E2 and P4E2 OECTs and the neat and blended devices, grazing incident wide angle X-ray diffraction scattering (GIWAXS) was performed to assess the microstructure of the films. The 2D GIWAXs pattern for the P2E2 and P2E2:PEO films show discrete spots indicating an fiber textured (isotropic in plane, with strong out of plane anisotropy) polycrystalline film while the P4E4 scatters much more like a semicrystalline film which allows for more ion intercalation which is necessary for OECT operation (**Fig 2.31**)¹⁵. The poor performance of the P2E2-based OECTs is likely due to the staggered crystal packing in the solid state where molecules exhibit minimal π -stacking and therefore negligible electronic charge transport.



Figure 2.31. GIWAXS of small molecules. GIWAXS data for films all spun from a 5mg ml⁻¹ chloroform solution a) P2E2. b) P2E2:PEO. c)P4E4. d) P4E4:PEO.

While the performance of the OECTs presented here do not compare to the state-of-the-art active materials used, the first p-type accumulation mode small molecule OECT is presented. Like most small molecule systems, bulk properties are more strongly dependent on grain boundaries and the stability of such defects. In addition, the molecular structure of the small molecules can be readily affected by ion intercalation, which may adversely affect stability. In this work, mobility was not reliably extracted due to the poor OECT performance; however, with further optimization small molecules have the potential to be good candidates for new mixed ionic-electronic conduction materials and are worthy of further investigation.

2.5 Methods

2.5.1 Microfabrication

OECTs were fabricated using methods described previously but will be briefly mentioned below and illustrated in Fig 2.32. S1813 or nLOF 2035 photoresist was spun onto a glass wafer at 3500 rpm for 30s and baked at 110 °C for 1min (steps 1-2). It was then exposed to UV light using a SUSS MJB4 mask aligner and developed in AZ400 K (1:4 dilution) or AZ 300MIF developer (steps 3-4). A 5nm chromium or titanium layer was then deposited followed by a 100nm gold layer using a metal deposition system (AJA) (step 5). The wafer was then left for overnight liftoff in Microposit 1165 (MicroChem) or acetone (step 6). Two layers of Paralyene C (an insulation layer and a sacrificial layer) were then deposited with a thin layer of a 2% micro90 solution spun between them (steps 7-9). To pattern the sacrificial layer AZ P4620 photoresist was then spun onto to the glass at 3000 rpm for 1min and baked at 110 °C for 2min (step 10). It was then exposed to UV light using a SUSS MJB4 mask aligner and developed in AZ400 K (1:4 dilution) developer (steps 11-12). Using a reactive ion etcher (RAMCO), the channels of the OECTs were etched at 160W with 50 sccm of O2 and 10 sccm of CHF3 for ~25minutes (step 13-14). Lastly, the OMIEC were spun or dropcasted onto the substrate followed by the peeling of the sacrificial layer of PaC, leaving the OMIEC only in the channels (steps 15-16).

2.5.2 Electrical Measurements

All electrical OECT Measurements were taken with a National Instruments PXIe-1082 system using custom made LabView Programs as previously described. To obtain output and transfer curves 2 NI PXIe-4143 source measuring units were used. To obtain stability measurements a square pulse was applied to the gate using NI PIXe 6363 DAQ while current was recorded using NI PXIe-4143. Transconductance as a function of frequency was obtained in similar manner but with a small amplitude sine wave (10 mV) applied at the gate while recording current using NI PXIe-4081 digital multimeters. All measurements were taken using an external Ag/AgCl pellet electrode as the gate in a 0.1M NaCl solution. Transconductance was calculated from the transfer curve using $(\delta I_D/\delta V_g)$ Mobility was calculated one of two ways. 1. Mobility was extracted from the slope of the transconductance $g_m = \frac{wd}{t} \mu C^* (V_g - V_{th})$. 2. Mobility was extracted by first extracting hole/electron transit time (τ) by matching gate and drain current derived impedance measurements using custom a Matlab script. From transit time mobility was calculated using (μ = L²/ τ V_d), where L is the length of the OECT channel. All thickness measurements were taken with a Veeco Dektak-8 profilometer.

Impedance, phase shift and effective capacitance data was generated using electrochemical impedance spectroscopy (EIS) (AutoLab). A Ag/AgCl wire was used as a reference electrode, a Pt mesh was used as the counter electrode and an electrode with the OMIEC coating it (fabricated on the same substrates as the OECTs) was used as the working electrode (fabricated with the same methods described above). EIS was performed in a 0.1M NaCl solution with a 10mv sine wave, with frequencies from 0.1 Hz to 0.1 MHz, applied to the to the working electrode with an offset. To extract volumetric capacitance (C^{*}), a Randall's circuit (R(R|C)) was fit to the impedance spectra to extract the capacitance which was then normalized the volume of the film on the working electrode.



Figure 2.32. Microfabrication of OECTs. Flow chart of the dry peel off process used to pattern OECT channels and electrodes for EIS. It makes use of photolithography and a sacrificial layer of parylene C.

2.6 Conclusion

This chapter presented the following polymers with their unique characteristic:

- 1. P(gPyDPP-MeOT2): p-type accumulation mode (deep lying HOMO for stable operation)
- p(g₇NC₂N) p(g₇NC₁₆N): n-type accumulation mode (fused lactam-based polymers for higher electronic mobility and stability)
- 3. P4gNDI: n-type accumulation mode (poor performer used for comparison)
- P4gNDTI: n-type accumulation mode (rigid backbone for higher electronic mobility and stability)
- 5. TIG-T: p-type accumulation mode (thienoisoindigo-based polymer thiphene unit)
- TIG-BT: p-type accumulation mode (thienoisoindigo-based polymer with 2,1,3benzothiadiazole (BT) unit)
- 7. IG-T: p-type accumulation mode (isoindigo-based polymer with thiophene unit)
- AIG-BT: n-type accumulation mode (7,7'-diazaisoindigo-based polymer with 2,1,3benzothiadiazole (BT) unit)
- 9. TIIP: p-type accumulation mode (2DP)
- 10. P2E2:PEO: p-type accumulation mode (small molecule)
- 11. P4E4: p-type accumulation mode (small molecule)
- 12. P4E4:PEO: p-type accumulation mode (small molecule)

This work created a robust library showing what novel materials are available for OECT-based circuits, which join an already rich library of materials of previously reported materials. Even with the advances of the electronic properties of OMIECs displayed here there are still challenges present that hinder their integration into OECT-based circuitry. For instance, while P(gPyDPP-MeOT2) displays high stability its higher threshold voltage makes it harder to integrate with commonly used n-types that exhibit lower threshold voltages. The fused lactam polymer series, NDI-based polymer pair, and the isoindigo-based polymer series do contain polymers that are high performing; however, the OECT polymer films were dropcasted and not spin coated, to produce thicker films for higher performance. Dropcasted films can have device performance variability across devices on the same substrates and are harder to reproduce from substrate to substrate as it is an imprecise technique making it impractical for biological applications. Moreover, if thicker films produced by dropcasting are required to provide a transconductance of interest it can reduce the cut off frequency once again making it unfeasible for certain biological applications. However, these works on polymers have given synthetic chemists an insight into how structural changes affect the electronic performance of OECTs, opened the opportunity for new OECT-based circuits and has expanded upon previous state-ofthe-art OMIECs by continuing to explore side chain and backbone engineering of new comonomer units. In addition to the work done on linear polymers, the work on small molecules and 2DPs serve to demonstrate proof-of-concepts that may open up new classes of OMIECs. While they are further from implementation the results show promise and are worth further investigation.

Finally, it is important to understand that when choosing an OMIEC for integration into a certain application electronic performance and even stability are not the only factors to consider. Reproducibility and compatibility with the fabrication process are just as important for integration of OMIECs into OECT-based circuitry. High performing circuits that cannot be reproduced in a systematic manner will not advance OECTs for bioelectronic applications.

Chapter 3 Ambipolar Inverters Based on Cofacial Vertical Organic Electrochemical Transistor Pair for Bio-signal Amplification

This chapter was adapted from: "Rashid, R. B., Du, W., Griggs, S., Maria, I. P., McCulloch, I., & Rivnay, J. (2021). Ambipolar inverters based on cofacial vertical organic electrochemical transistor pairs for biosignal amplification. *Science Advances*, *7*(37), eabh1055."

3.1 Introduction

Bioelectronic recordings traditionally decouple front end signal transduction (biochemical, biophysical and electrophysiological detection) from downstream signal processing (amplification, filtering, or feature detection)^{56,173}. Minimizing the physical distance and improving system integration between components responsible for signal transduction and processing can improve recorded signal quality, simplify implementation, and more readily enable practical wireless systems^{92,174}. The typical approach for on-board signal processing requires silicon CMOS circuits in the form of packaged or bare die silicon integrated circuits or, alternatively, front-end co-localization of sensors and CMOS circuits¹⁷⁴⁻¹⁷⁹. Imparting additional functionality to a sensing node is an approach gaining significant attention as it may lead to yet more integrated, higher performing and lower power systems^{56,92,176}. Additional functionality can include multimodal or multimarker sensors that allow for measurement of simultaneous complementary biomarkers at the same sensing site or on-site analog signal processing^{92,180-182}. Such on-site or in-sensor signal processing could further provide instantaneous feedback and enable future low power closed-loop devices that perform diagnostic and treatment functions^{73,183}. Achieving active sensing nodes often requires tradeoffs between

performance/functionality and physical footprint, which can for example yield lower density arrays, and requires fabrication and assembly approaches not easily achievable with flexible or conformable form factors^{56,59,176}. To realize compact form factors and development of sophisticated circuitry at a sensing site, organic electrochemical transistors (OECTs) have the potential to allow for thhis goal due to their bulk ionic/electronic transport offering high gain and relaxed fabrication.

As described in Chapter 1 the complementary inverter (NOT gate) is one of the fundamental building blocks of digital circuits and can even be used to enhance analog signal processing⁷¹. The inverter can provide voltage-to-voltage amplification, which is not offered by a single OECT sensor, and can eliminate the potential noise associated with resistor-based OECT voltage amplifiers^{75,77}. However, despite the high performance of OECTs researchers have not been able to realize geometries or fabrication schemes of OECT-based inverters that make them feasible for use in practical biological settings^{57,62,65,71,72}. As described in Chapter 1, the difficulty of fabricating two different active materials with mismatched electronic performance makes it difficult to create micron-scale inverters using traditional OECT geometries, photolithography and manufacturing techniques.

Vertical OECTs (vOECTs) present a compelling route to decrease transistor footprint and increase recording density. In vOECTs the source and drain (S/D) contacts are stacked on top of each other vertically rather than laterally on a planar 2D surface (pOECT)¹¹⁷. The interest in vOECTs is not only due to their smaller device footprints but also to their enhanced electronic properties^{18,117}. Higher transconductance and cutoff frequency can be attained with vOECTs with the same or smaller area than a pOECT^{17,18,43,117}. The length of a vOECT channel is nominally

defined by the thickness of an insulating interlayer between the S/D contacts for vOECTs while it is the planar distance between the two for pOECTs, typically defined photolithographically for micron-scale OECTs¹¹⁷. The thickness of the insulation can be reliably made submicron while still pinhole free while the pOECTs are limited by photolithography capabilities and alignment requirements when fabricating via standard photolithography. The first account of vOECTs used vias to connect the source and drain contacts that were printed on opposite sides of the substrate¹⁸⁴. More recently micron-scale, photolithographically patterned vOECTs were demonstrated by Donahue et. al which showed both the scaling behavior and promising cut-off frequency of this OECT device format¹¹⁷.

In this work we target a compact form factor amplifying (voltage-to-voltage) sensing node based on an OECT inverter. We make use of vOECTs in a novel cofacial pair configuration, that has two vOECTs facing one another sharing a single channel. This approach defines an inverter in the same footprint as a single pOECT. The compact configuration does not allow p- and n-type organic mixed conducting ionic-electronic materials (OMIECs) to be patterned separately, necessitating demonstration of an OECT complementary inverter based on an ambipolar OMIEC¹³⁶. The use of vOECTs allows for the preservation of high gain with reduced area; the cofacial OECT inverter demonstrated a peak gain of about 28. To validate the cofacial OECT inverter as a voltage amplifier we recorded electrocardiograms (ECG) from healthy subjects with a gain of 10. Finally, we further lay out potential barriers to implementation due to degradation and associated p/n imbalance.

3.2 Results

3.2.1 Cofacial OECT pair fabrication and characterization

To achieve a small footprint for the active sensing node, we take advantage of the vertical form factor of vOECTs. By simultaneously patterning two vOECTs along opposite side walls of a single active area we form a cofacial pair of OECTs that will later form the basis for a complementary inverter (**Fig 3.1a,b**). These structures are fabricated photolithographically, whereby two metallic layers separated by an insulating layer of Parylene C (PaC) serve as the source and drain contacts and interconnects. In this case, the thickness of the separating PaC layer roughly defines the vOECT channel length (~600 nm), whereas the width of the OECTs, and the spacing between the cofacial vOECT pair is defined photolithographically by the etched area, as noted in **Fig 3.1a**. The on-chip inverter structure requires the bottom contacts to be shorted such that the two vOECTs are in series – this shorted terminal serves as the output signal for the inverter, as discussed below. Full fabrication details can be found in the Methods section.



Figure 3.1. Vertical and planar OECTs in a cofacial pair configuration. a) Cross section schematic of the cofacial pair showing materials, dimensions, and contacts for individual OECT wiring, as well as for the on-chip inverter. Shown above is the chemical structure of $p(C_4-T_2-C_0-EG)$ b) A tilted SEM micrograph of the cross section of the cofacial pair of OECTs. Focused ion beam (FIB) milling was used to expose the cross section, necessitating a thick layer of Pt deposited on top of the completed device. Scale bar = 1µm c) Transfer curves of all the possible p-type ($\Delta V_g = 0.01$ V, 0V to -0.8V and $V_d = -0.4$ V) and n-type ($\Delta V_g = 0.01$ V, 0V to 0.6V and $V_d = 0.4$ V) OECTs (2 pOECTs, 2 vOECTs, and the 2 vOECTs in series) of the cofacial pair. d) Output curves of the p-type ($\Delta V_g = 0.05$ V, 0 V to 0.6V and $V_d : 0$ to -0.8V and $V_d : 0$ to -0.4V) and n-type ($\Delta V_g = 0.05$ V, 0 V to 0.6V and $V_d : 0$ to -0.8V and $V_d : 0$ to -0.4V) and n-type ($\Delta V_g = 0.05$ V, 0 V to 0.6V and $V_d : 0$ to 0.4V) bottom and top pOECTs of the cofacial pair. e) Output curves of the p-type ($\Delta V_g = 0.05$ V, 0 V to -0.8V and $V_d : 0$ to -0.4V) and n-type ($\Delta V_g = 0.05$ V, 0 V to 0.6V and $V_d : 0$ to 0.4V) left and right vOECTs of the cofacial pair.

In order to take advantage of the cofacial pair format, the individual operation of the vertical devices (vOECTs) was compared to traditional microfabricated pOECTs. In this work, an OMIEC with both hole and electron transport capability under electrochemical modulation in

aqueous electrolyte is desired. The donor-acceptor polymer $p(C_4-T2-C_0-EG)$, featuring a naphthalenetetracarboxylic diimide unit with hybrid alkyl-glycol side chains and a triethylene glycol-substituted bithiophene unit has recently demonstrated ambipolar charge transport in OECTs and therefore meets the above requirements (**Fig. 3.1a**)¹³⁶. The characteristics of this material were validated in a traditional pOECT configuration by analyzing current/voltage (I-V) characteristics and electrochemical impedance data. Traditional single-layer planar 100 µm /10 µm (W/L) pOECTs with 50 nm active layer thicknesses were tested to extract the parameters of $p(C_4-T2-C_0-EG)$ (**Fig 3.2a-d**). The summary of parameters shown in **Table 3.1**, which matches those previously reported, shows that while the transconductance (g_m), mobility (μ_c) (extracted from I_d-V_g, transfer characteristics), and volumetric capacitance (C^{*}) (from EIS) are similar when operated as hole and electron (p- and n-type) OECTs, the threshold voltages (V_{th}) are not.

Table 3.1. Electronic properties of p(C₄-T2-C₀-EG) pOECTs

	g_m (S/cm)	$V_{th}\left(\mathbf{V} ight)$	C^* (F/cm ³)	μ (cm ² /Vs)
p-channel	$\begin{array}{c} 2.73 \times 10^{\text{-2}} \pm \\ 1.69 \times 10^{\text{-2}} \end{array}$	$-0.60 \pm 9.11 \times 10^{-3}$	90.8 ± 17.03	$\begin{array}{c} 1.48 \times 10^{-3} \pm \\ 9.08 \times 10^{-4} \end{array}$
n-channel	$\begin{array}{c} 3.07 \times 10^{\text{-2}} \pm \\ 1.82 \times 10^{\text{-2}} \end{array}$	$\begin{array}{c} 0.30 \pm 4.76 \times \\ 10^{\text{-2}} \end{array}$	125 ± 34.60	$1.28 imes 10^{-3} \pm 7.74 imes 10^{-4}$

This table summarizes the transconductance (g_m) normalized by geometric dimensions (Wd/L), threshold voltage (V_{th}), volumetric capacitance (C^*), and mobility (μ_e) of the ambipolar material p(C₄-T₂-C₀-EG) in both the n- and p-operation. Transistor characteristics were extracted from N=6, errors reported are standard deviations.



Figure 3.2. p(C₄-T2-C₀-EG) pOECT performance. a) Transfer curve ($\Delta V_g = 0.01$ V, 0V to - 0.8V and $V_d = -0.4$ V) on a log and linear scale of a p-type pOECT. b) Output curve ($\Delta V_g = 0.05$ V, 0 V to -0.8V and $V_d : 0$ to -0.4V) of a p-type pOECT. c) Transfer curve ($\Delta V_g = 0.01$ V, 0V to 0.6V and $V_d = 0.4$ V) on a log and linear scale of a n-type pOECT. d) Output curve ($\Delta V_g = 0.05$ V, 0 V to 0.6V and $V_d : 0$ to 0.4V) of a n-type pOECT. e) The wiring diagram of a complementary OECT-based comprised of two complementary pOECTs externally wired to one another on the same substrate. f) The voltage transfer characteristic of the inverter described in e) ($\Delta V_g = 0.01$ V, 0V to 0.6V and $V_{DD} = 0.8$ V) and the corresponding gain ($\delta V_{out}/\delta V_{in}$) with a peak gain of around 8.

To test the operation of the vOECTs, the top and bottom contacts were chosen as the source and drain respectively, while the gate was a Ag/AgCl electrode immersed in a 0.1M NaCl electrolyte. The resulting transfer and output I-V characteristics can be seen in **Fig 3.1C,D,E**. Choosing top right and top left contacts as the source and drain terminals is a measure of the two vOECTs in series. As such, separate photolithographically fabricated test structures with the bottom contact

not shorted were employed to test both planar device configurations (**Fig 3.1C,D**). The channel length of the pOECTs is defined as the total OMIEC channel distance between the two contacts. The top pOECT of the pair has a length of 6.2μm while the bottom pOECT has a length of 5 μm (**Fig 3.1**). Both the vOECTs and the pOECTs have a channel width of 100μm and a channel thickness of 150nm (this thickness is measured at the bottom of the photolithographically defined region, as an accurate determination of film thickness on the side walls is limited). As seen by the output and transfer curves in **Fig 3.1C,D,E** the drain current of the vOECTs is ~10 times higher than that of the pOECTs, for both p- and n-type, which is on par with the geometric scaling of the OECT channels, assuming comparable device thickness (i.e. current scaling roughly matches channel length scaling). To confirm the series measurement of the vOECTs with the on-chip shorted output, we separately shorted two isolated vOECTs together in series to confirm peak current is ~1/2 the maximum current in the 2 vOECTs (**Fig 3.3**), as expected. The transfer characteristics of the vOECTs of a cofacial pair with the bottom contacts not shorted (**Fig 3.3**) is comparable to the vOECTs with the shorted bottom contacts (**Fig 3.1C**).



Figure 3.3. $p(C_4-T_2-C_0-EG)$ vOECTs with isolated bottom contacts. a) P-type transfer curves of all possible OECT combinations (2 pOECTs, 2 vOECTs, and the 2 vOECTs in series) in a cofacial pair with isolated bottom contacts ($\Delta V_g = 0.01$ V, 0V to -0.8V and $V_d = -0.4$ V). b) N-type transfer curves of all possible OECT combinations (2 pOECTs, 2 vOECTs, and the 2 vOECTs in series) in a cofacial pair with isolated bottom contacts ($\Delta V_g = 0.01$ V, 0V to -0.8V and $V_d = -0.4$ V). b) N-type transfer curves of all possible OECT combinations (2 pOECTs, 2 vOECTs, and the 2 vOECTs in series) in a cofacial pair with isolated bottom contacts ($\Delta V_g = 0.01$ V, 0V to 0.6V and $V_d = 0.4$ V).

3.2.2 Cofacial Ambipolar Complementary Inverter

A traditional complementary inverter is typically made by separately wiring two different transistors, a p-type transistor and a n-type transistor (**Fig 3.4a**)^{57,71}. The source of the p-type OECT is connected to V_{DD} while the source of the n-type OECT is wired to ground. The gates of the two OECTs are wired together externally to create a common input. Then the drain terminals of both OECTs are wired together externally to read V_{out} .

To achieve such an inverter within the footprint equivalent to that of a single planar OECT, we employ the cofacial pair of vOECTs as described above. The use of an ambipolar material such as p(C₄-T2-C₀-EG) is critical in this case, as patterning opposing side walls to separately define a p-type and n-type material is not possible. In the cofacial configuration, the shared electrolyte and Ag/AgCl gate contacts both channels which couples the input of the two OECTs. A proposed revised circuit diagram that better reflects the arrangement of the cofacial pair is shown in **Fig 3.4b**.



Figure 3.4. OECT cofacial pair complementary inverter. a) The wiring diagram for an OECT-based complementary inverter with two OECTs independently gated. b) The condensed wiring diagram of an OECT complementary inverter based on a cofacial pair of vOECTs. c) Schematic cross section of a cofacial pair wired as a complementary inverter and a top view microscopic image of the cofacial inverter. d) The voltage transfer characteristics of the cofacial pair inverter ($\Delta V_{in} = 0.01$ V, 0 to 0.6 V and $V_{DD} = 0.7$, 0.75, and 0.8 V). The corresponding gain ($\delta V_{out}/\delta V_{in}$) with peak gains of 15, 18, and 28 for $V_{DD} = 0.7$, 0.75, and 0.8 V, respectively. e) The frequency response of the cofacial pair. The inset shows a sinusoidal input ($\Delta V_{in} = 0.01$ V with an offset of 0.23V at 1.5Hz and $V_{DD} = 0.8$ V) with the corresponding amplified output.

With an ambipolar material one vOECT can behave as the p-type OECT and the other the n-type OECT depending on the effective V_g at each channel. The source terminal of the p-type OECT is connected to V_{DD} and the source terminal of the n-type OECT is connected to ground, which are

the top contacts of the vOECTs. The shorted bottom contacts of each OECT behave as the drain terminals where the output of the inverter (V_{out}) is recorded (Fig 3.4c). The voltage transfer characteristics (VTCs) of the cofacial inverter pair was recorded with varying V_{DD} (0.7, 0.75, 0.8) (Fig 3.4d). The gain of the inverter was extracted from the voltage transfer characteristics $(\delta V_{out}/\delta V_{in})$ and increased as V_{DD} increased, reaching a peak gain of about 28 at $V_{DD}=0.8V$ (Fig **3.4d**). At $V_{in} = 0.26V$ with $V_{DD} = 0.8V$, $I_{DD} = 72nA$, resulting in a power consumption of about 57.7nW. The inverter characteristics indicate that the inverter is not balanced: the peak gain at $V_{DD}=0.8V$ is at $V_{in}=0.26V$ rather than $V_{in}=V_{DD}/2=0.4$ V. Since the cofacial configuration requires that channel dimensions be equivalent, this mismatch is due to the inherent imbalance in the ptype and n-type transport and charging of $p(C_4 - T_2 - C_0 - EG)$. Since μ_e , and C* are similar for both the p-type and n-type swing (**Table 3.1**) the difference in V_{th} ($\Delta |V$ th| ~0.3 V) was determined to be the root cause in the shift in the switching voltage of the cofacial inverter from the ideal $V_{\rm DD}/2$. The transfer characteristics of the individual vOECTs of this cofacial pair are shown in Fig 3.5. Due to the large difference in the V_{th} of the p-type and n-type swings of $p(C_4-T_2-C_0-EG)$ used in this cofacial configuration the two vOECTs are not in saturation during the transition region of the VTC as is typical of complementary inverters. When V_{in} is large enough for the ntype vOECT of the pair to enter saturation the p-type vOECT has already left saturation, meaning that operation in linear or sub-threshold regime is likely. Across an array of five cofacial pairs the gain varies from 17 to 25 at a V_{in} of 0.23 to 0.26V (Fig 3.6).



Figure 3.5. $p(C_4-T2-C_0-EG)$ OECT performance of cofacial pair. a) P-type transfer curves of all possible OECT combinations (2 pOECTs, 2 vOECTs, and the 2 vOECTs in series) in a cofacial pair with shorted bottom contacts ($\Delta V_g = 0.01$ V, 0V to -0.8V and $V_d = -0.4$ V) on a log and linear scale. b) N-type transfer curves of all possible OECT combinations (2 vOECTs and the 2 vOECTs in series) in a cofacial pair with shorted bottom contacts ($\Delta V_g = 0.01$ V, 0V to -0.8V and $V_d = -0.4$ V) or a log the 2 vOECTs in series) in a cofacial pair with shorted bottom contacts ($\Delta V_g = 0.01$ V, 0V to -0.8V and $V_d = -0.4$ V) or a log and the 2 vOECTs in series) in a cofacial pair with shorted bottom contacts ($\Delta V_g = 0.01$ V, 0V to 0.6V and $V_d = 0.4$ V) on a log and linear scale.



Figure 3.6. Reproducibility of p(C₄-T2-C₀-EG) cofacial inverters. a) The voltage transfer characteristics of an array of 5 cofacial complementary inverters ($\Delta V_g = 0.01$ V, 0V to 0.6V and $V_{DD} = 0.8$ V. b) The corresponding gain ($\delta V_{out}/\delta V_{in}$) with peak gains that vary from 17 to 25.

The AC characteristics of the inverter show a cutoff frequency of about 16Hz (**Fig 3.4e**). The inset shows a sinusoidal input of 10 mV with an offset of 0.23 V at a frequency of 1.5Hz resulting in a gain of about 13 observed at the output for this frequency. The frequency response of the individual p and n-type vOECTs of the cofacial pair compared to the frequency response of the cofacial inverter swept from low to high and high to low frequencies can be seen in **Fig 3.7**. Based on the directional sweeps, the frequency response of the p-type vOECT at low frequencies is indictive of degradation, complicating analysis. Accounting for this degradation, it appears that both the p-type and n-type vOECTs show comparable cut-offs, which is in agreement with the finding that their C* values are similar (**Table 3.1**). The frequency response of the inverter, which is lower than the individual vOECTs, may be limited by this degradation and/or other known effects limiting digital inverter switching speed in the transition region.



Figure 3.7. Frequency response of $p(C_4-T_2-C_0-EG)$ cofacial inverter. a) The input of the cofacial inverter swept from low to high frequency (solid) and from high to low frequency (dashed) ($V_{in} = 0.23 \text{ V}, \Delta 0.01 \text{ V}; V_{DD} = 0.8 \text{ V}$). b) The input of the n-type vOECT of the cofacial pair swept from low to high frequency (solid) and from high to low frequency (dashed) ($V_g = 0.6 \text{ V}, \Delta 0.01 \text{ V}; V_d = 0.4 \text{ V}$). c) The input of the p-type vOECT of the cofacial pair swept from low to high frequency (dashed) ($V_g = -0.8 \text{ V}, \Delta 0.01 \text{ V}; V_d = -0.4 \text{ V}$). It is evident that the p-type vOECT suffers from degradation, most evident in the low frequency regime.

Next, the stability of the inverter was explored by applying the input bias where peak gain occurs, $V_{in} = 0.15$ V and monitoring the change in V_{out} over time with a V_{DD} = 0.8V (**Fig 3.8**). After holding the inverter at $V_{in} = 0.15$ V for about thirteen minutes the recorded gain of ~10 before the time study dropped to ~5 at that bias. The peak gain of the inverter had shifted to $V_{in} = 0.12$ V and had dropped to 8. In addition, the input of the inverter was pulsed from 0 to 0.6 V

with a $V_{DD} = 0.7$ V (**Fig 3.9**). The V_{high} and the V_{low} of the inverter during pulsing decrease and increase, respectively. The transfer curves of the individual vOECTs of the pair and the VTC of the inverter were collected before and after pulsing. Before pulsing the gain of the inverter was around 13 at a V_{in} of 0.14 V; however, after pulsing the gain at the same V_{in} had dropped to 7.5. After pulsing the peak gain shifted from 0.14 V to 0.12 V and had dropped slightly to 12.5. We believe that the imbalance in the decay of the μ C* and thus drain currents of both the n- and p-type vOECTs contribute to the observed shift and decrease in peak gain.



Figure 3.8. Response of p(C₄-T2-C₀-EG) cofacial inverter over time. a) The cofacial inverter was held at a constant $V_{in}=0.15V$ ($V_{DD}=0.8V$) where the peak gain of the inverter is observed. The V_{out} of the inverter starts at 0.45V and decays to 0.21V over the course of 13 minutes. b) The voltage transfer characteristics of the cofacial pair before being held at $V_{in}=0.15V$ and after ($\Delta V_g = 0.01 V$, 0V to 0.6V and $V_{DD} = 0.8V$). There is an observed shift in the switching voltage of the VTC; the peak gain has shifted from $V_{in}=0.15V$ to $V_{in}=0.12V$. c) The corresponding gain ($\delta V_{out}/\delta V_{in}$) before and after pulsing with an observed shift of the peak gain and has decreased by about 5.



Figure 3.9. Stability of p(C₄-T2-C₀-EG) cofacial inverter. a) Pulsing the input of the cofacial pair from 0 to 0.6V ($V_{DD} = 0.7V$) for about 4 minutes and the resulting output. The V_{out,low} increases while the V_{out,high} decreases. b) The voltage transfer characteristics of the complementary inverter before and after pulsing ($\Delta V_g = 0.01 \text{ V}$, 0V to 0.6V and $V_{DD} = 0.7\text{V}$). There is an observed shift in the switching voltage of the VTC. c) The corresponding gain ($\delta V_{out}/\delta V_{in}$) before and after pulsing with an observed shift of the peak gain. d) P-type transfer curves ($\Delta V_g = 0.01 \text{ V}$, 0V to -0.7V and $V_d = -0.4\text{V}$) of one of the vOECTs in the cofacial pair before and after pulsing. e) N-type transfer curves ($\Delta V_g = 0.01 \text{ V}$, 0V to 0.6V and $V_d = 0.4\text{V}$) of one of the vOECTs in the cofacial pair before and after pulsing pair before and after pulsing.

3.2.3 Cofacial Inverter Pair as a Voltage Amplifier

To demonstrate the utility of the cofacial complementary inverter pair for amplifying biosignals, the concept was used as a benchtop preamplifier to record electrocardiograph (ECG) signals. One adhesive medical electrode was connected to the Ag/AgCl gate (input) of inverter and the other was connected to a voltage supply set to an offset bias where peak gain occurs, 0.26 V, for this cofacial inverter (**Fig 3.10a**). The output ECG had a peak-to-peak amplitude of

around 5 mV (**Fig 3.10b**). The potential difference between the two medical electrodes was measured for comparison which resulted in a peak-to-peak amplitude around 0.5 mV (**Fig 3.10c**). This measured gain of ~10 is consistent with the AC measurements noted above. Other differences in the ECG traces such as noise levels might be attributed to the low cutoff frequency of the inverter as compared to the direct voltage measurement using a digital multimeter (DMM).



Figure 3.10. ECG signal amplification using cofacial pair complementary inverter. a) The wiring diagram of the cofacial pair inverter when used as a voltage preamplifier. 3M adhesive medical electrodes are placed below the clavicle on both the right and left side with one being connected to a DC offset and the other connected directly to the input of the inverter on a benchtop. b) The ECG signal recorded from the output of the cofacial pair inverter. c) The ECG signal recorded directly between the adhesive medical electrodes using a benchtop digital multimeter.

3.3 Discussion

The concept of a cofacial arrangement of OECTs presented here enables an ambipolar inverter where the composite OECTs are co-localized in a manner which allows for a compact geometry. When implemented with vOECTs, the inverter active area spans the same footprint as a single planar OECT. vOECTs not only offer compact geometry but when compared to pOECTs of the same area and thickness there is a ten-fold increase in the drain current (**Fig 3.1**). Geometric dimensions affect the gain of the inverter, as the gain is directly proportional to g_m^{57} . Shorter length channels can result in a higher gain and while the thickness of the channel can be increased to compensate for longer channel lengths it increases the response time making it less suitable for electrophysiological recordings⁵⁷. It is difficult to directly compare the inverter of the cofacial pair and an inverter based on 2 pOECTs wired together externally due to the challenges in measuring and controlling the film thickness of the vOECT channels. However, an inverter with pOECTs with the same area (10 x100 µm) as the cofacial inverter pair with the channel material, p(C4-T2-C0-EG), shows a peak gain of 8 (**Fig 3.2**) compared to 28 for the cofacial vertical configuration (**Fig 3.4**).

The ambipolar inverters demonstrated herein using $p(C_4-T2-C_0-EG)$ are not perfectly balanced (n vs. p channel) which can be problematic for digital logic applications. In this cofacial configuration it would not be feasible to independently change the dimensions (i.e. length and thickness) of the individual p-type and n-type vOECTs to achieve a balanced inverter; however, the resulting VTCs may be beneficial in analog applications. Since V_{th} of the p-type OECT is higher than the V_{th} of the n-type OECT, the input voltage at which peak gain occurs is shifted closer to V_{in} = 0V which means that the offset required when recording biological signals is smaller, reducing power consumption. In addition, the use of an ambipolar material may present some difficulties for digital logic circuits as the inverter does not fully pull up to V_{DD} or pull down to ground. This is due to the p- and n-type OECTs not fully turning off, as seen from the transfer curves of the vOECTs (**Fig 3.5**), as they enter an ambipolar regime of operation^{24,185-¹⁸⁸. This feature in the VTC has also been observed in previously reported OFET-based ambipolar inverters¹⁸⁷⁻¹⁸⁹.} The developed cofacial OECT complementary inverter is used as a proof-of-concept for an onboard voltage amplifier to record electrophysiological signals. This single inverter can be used to replace traditionally used voltage dividers to reduce the overall footprint of the active sensing node. While the cutoff frequency of the inverter is high enough to record low frequency biological signals such as ECG, the geometry can be further modified to reduce response time to ensure no attenuation of higher frequency activity. This includes shorter channel widths and decreasing the thickness of the insulating layer between the source and drain contacts of the vOECTs by reducing PaC thickness or targeting thinner conformal oxide layers in order to achieve shorter vOECT channel length. This approach may add challenges in fabrication, reproducibility, and increase contribution of parasitic lead resistance and/or short channel effects¹¹⁷. Another route to achieve higher frequency cutoff is to decrease the channel thickness which, however, is likely to decrease the gain of the inverter⁵⁷. As with single OECT sensors it appears that a balance must be navigated between gain and response time. Another consideration when using an inverter is the allowable input window when operating about the bias where peak gain occurs. When gain increases the linear window of operation decreases so the amplitude of the biological signal of interest must be considered when designing the inverter; a balance between high gain and minimal distortion should be achieved. Based on the VTC of the cofacial inverter presented here (Fig 3.4d), the maximum input signal amplitude resulting in minimal output distortion is around 40mV which allows for the recording of many biological signals that fall in the μ V to mV range such as the ECG, EEG and even ECoG recordings^{23,75}.

Finally, while the in-sensor signal amplification of this cofacial pair inverter concept presents numerous advantages, significant barriers must be addressed before practical adoption

in bioelectronics. First, reproducibility must be improved regardless of fabrication approach. Without inverter-to-inverter reproducibility, an array of such active sensing nodes will require a different V_{DD} and/or V_{in} offset in order to achieve the same gain. Second, the stability of the $p(C_4-T2-C_0-EG)$ herein prevents this inverter from achieving long term use, critical for both *in vivo* and wearable applications. This work suggests that both n- and p-type performance of this particular material degrade on both extended switching, and during continuous operation at the V_{in} of peak gain. Device degradation affects both the individual OECT characteristics, affecting peak gain of the inverter, but more significantly exacerbates loss in gain at the chosen operating point by causing a shift in the switching voltage. The understanding of both of these effects is limited also by the lack of significant ambipolar OMIEC candidate^{24,136}. Further work is needed to understand the mechanism of degradation and to improve the stability of ambipolar materials. Existing studies exploring stability and degradation mechanisms will inform these efforts¹²².

3.4 Conclusion

Here we present an OECT-based ambipolar inverter which fits within the same area as a typical micron-scale planar OECT by employing a cofacial pair of vertical OECTs. The compact geometry and the peak gain of 28 of these cofacial ambipolar inverters makes them good candidates for direct voltage-to-voltage amplification. We demonstrate the use of the cofacial inverter as a voltage amplifier by recording ECG signals. The signals recorded from the output of the inverter showed a 10x amplitude when compared to direct voltage recordings using a digital multimeter. While we outline barriers that must be overcome for this device concept, the cofacial inverter concept herein presents a promising approach towards on-site and in-sensor amplification. This co-localization of a simple circuit using vertical OECTs may be further

applicable to other on-site signal processing functions including rectification and reference-based differential biochemical detection on flexible and conformal bioelectronic arrays. This active sensing scheme can therefore be used to achieve functional back-end processing at or near the biotic/abiotic interface for use in far-reaching bio-integrated devices.

3.5 Methods

3.5.1 Device Fabrication

The cofacial inverters were fabricated using a dry peel off process reported previously but will be mentioned here briefly^{75,190}. To define the first layer of gold AZnLOF 2035 was spun onto clean microscope slides at 3500rpm and then baked at 110°C for one minute. The slides were then exposed to UV light using an MJB4 mask aligner, post exposure baked at 110°C for one and half minutes and developed in AZ300MIF for 30 seconds. The slides were then placed in an AJA ebeam where 5nm of Cr and 100nm of Au were deposited and then left in acetone for liftoff for thirty minutes. A 0.65µm thick Paralyene C (PaC, SCS Coatings) insulation layer was then deposited in the presence of the adhesion promoter A 174 using a SCS Labcoter II. Another gold layer was patterned on top of the insulation layer using the same steps mentioned above. Once the final insulation layer was deposited an anti-adhesive was spun on and a sacrificial layer of PaC was deposited. To pattern the active sites and contact pads AZP4620 was spun on at 3000rpm and baked at 110°C for two minutes. It was then exposed to UV light using an MJB4 mask aligner and developed in 1:4 AZ 400K. The slides were then placed in a Samco RIE to selectively etch the PaC using CHF₃ and O₂.

The polymer $p(C_4-T_2-C_0-EG)$ was synthesized following a previously reported protocol¹³⁶. Then $p(C_4-T_2-C_0-EG)$ was spun on at 900rpm from a 5mg/ml solution and the sacrificial layer was

mechanically peeled off leaving the material only in the channel. Standard pOECTs were made using the same steps but without a second gold layer. thickness measurements were performed using a Veeco Dektak-8 stylus profilometer. Cross sectional scanning electron microscopy images were taken using a JEOL 4700F FIB/SEM. First 20nm of bulk platinum (Pt) was sputter coated then 1µm of local Pt was deposited to prevent ion beam damage. The cross sections were milled using a FIB at 30kV with currents up to 10nA. The samples were mounted at 45° and tilted at 20° for SEM imaging at 10kV. Microscopic images were taken using a Zeiss Scope.A1 and AxioCam 105 color.

3.5.2 Electrical Characterization

OECT and inverter measurements were made with an NI PXIe 1082 using custom LabView code. In addition, all measurements were done in 0.1M NaCl using a Ag/AgCl electrode as an external gate. Output curves and transfer curves were collected by using source measuring units (SMUs)(NI PXIe-4143). For the p-type measurements, the output curves were collected using a V_d from 0 to -0.4V and a V_g from 0 to -0.8V and transfer curves were collected using a constant V_d = -0.4V while varying V_g from 0 to -0.8V. For the n-type measurements, the output curves were collected using a V_d from 0 to 0.4V and a V_g from 0 to 0.6V and transfer curves were collected using a constant V_d = 0.4V while varying V_g from 0 to 0.6V.

The threshold voltage (V_{th}) of the p-type and n-type OECTs were extracted from a linear extrapolation of the $\sqrt{|I_d|}$ vs V_g plot. Electrochemical Impedance Spectroscopy (EIS) was performed using a potentiostat (Metrohm Autolab) to extract volumetric capacitance (C*). A three-electrode configuration was used with a 10mV sine wave with offsets from 0.5 to 0.8V for the p-type direction and -0.2 to -0.5V for the n-type direction. The spectra were recorded from 0.1 to 10⁵ Hz. A Randall's circuit (R(R|C)) was fit to the impedance spectra to extract the effective capacitance which was normalized by film volume to find volumetric capacitance (C*). Mobility of both the holes and electrons were extracted using the following equation $g_m =$

$$\frac{wa}{L}\mu C^*(V_g-V_{th}).$$

The voltage transfer characteristics (VTCs) of the inverter were collected using the SMUs to apply V_{DD} and V_{in} and a digital multimeter (DMM) (NI PXIe-4081) was used to measure V_{out} . The VTCs were collected by sweeping V_{in} from 0 to 0.6V while holding V_{DD} constant at 0.7, 0.75, or 0.8V. Gain was calculated by taking the derivative of the VTC ($\delta V_{out}/\delta V_{in}$). AC measurements on the inverter were performed by applying an input of 10mV sinusoidal signal with an offset at the peak gain of the inverter at varying frequencies using the NI PXIe 6363. Stability studies were performed by pulsing V_{in} from 0 to 0.6V in 5s intervals using the NI PXIe 6363.

ECG was measured by placing two adhesive 3M dot electrodes right below the clavicle on the right side and left side of the subject. One 3M electrode was wired directly to the Ag/AgCl gate of the inverter (on the benchtop) while the other 3M electrode was wired to a bias (NI PXIe 6363). For comparison, the two 3M dot electrodes were wired directly to the DMM. The signals were acquired at 1 kHz and filtered using a bandstop filter of 55-65Hz then a bandpass filter of 0.1 to 100Hz. All ECG measurements were taken in compliance with institutional review board guidelines and with informed written consent before subject participation.

Chapter 4 Self-aligned, Laser-cut Organic Electrochemical Transistors

This chapter was adapted from "Rashid, R. B., Ciechowski, R. J., & Rivnay, J. (2020). Selfaligned, laser-cut organic electrochemical transistors. *Flexible and Printed Electronics*, *5*(1), 014007."

4.1 Introduction

Fabrication of OECTs has been achieved with a variety of techniques with different approaches catering to a specific niche: large area, complex circuits, and bio-integration with each of these requiring different demands.¹⁷ The property of mixed conduction, and the associated bulk transport known to dominate OECT opens up the possibility for new approaches to OECT fabrication, and can add value to both the format and performance of OECT devices.³¹

Photolithographic techniques allow for the patterning of metal interconnects, active OECT channels and the insulation layers (required for operation of device arrays in electrolytes and complex biological settings) of OECTs down to the sub-micron scale. One technique traditionally used to fabricate OECTs is a dry peel-off process that involves multiple photolithography steps, physical vapor deposition of multiple parlyene C (PaC) layers, and dry etching.^{23,38,75} Such a technique is advantageous because it allows for simultaneous patterning of the active channel and the insulation layer, and does not expose the organic semiconductor to harsh plasma or solvent environments. Other techniques involving photolithography eliminate the use of PaC to pattern the active material and instead directly blanket deposit the active material and etch outside the channel area.¹⁹¹ Further, some approaches employ fluorinated photoresists (orthogonal resists) that do not

interact with the active material but protect it from solvent exposure and plasma during etching, and can subsequently be used to insulate contacts and interconnects.¹⁹²

Non-photolithographic techniques have been explored for OECTs in cases where large area, low cost, or rapid prototyping are of critical importance.^{61,193} Many of these approaches target traditional extrusion or ink-based processing and patterning. Manufacturing techniques such as screen printing have even been used to make OECTs for use in logic circuits,⁶² leading to demonstrations of an inverter using resistors and OECTs. Complementary inverters tend to be more efficient due to lower power consumption but require the ability to pattern multiple active materials.⁷¹ Laser manufacturing techniques have been used in the fabrication of myriad electronic components.¹⁹⁴⁻¹⁹⁶ Some efforts into laser-based patterning of OECTs have been made on flexible substrates but the technique resulted in a heat affected zone due to the decomposition of the PEDOT as it was polymerized onto the substrate before cutting.¹⁹⁷ Blaudeck et al. used a combination of manufacturing techniques including screen printing to pattern contacts and insulation, and laser cutting to create the channel followed by inkjet printing to pattern PEDOT:PSS into the channel.³¹ Although this technique was able to produce OECTs with good electrical properties, such as high ON/OFF ratios, the yield of the array was very low (25%).³¹ It further required overfilling of the channels with PEDOT:PSS to compensate for manufacturing errors.³¹

Herein, we present a method to pattern OECTs combining the use of laser patterning, and surface energetics to produce devices with self-aligned insulation. Laser cutting is used to simultaneously define a channel length as well as an opening in the insulator stack that is self-aligned. The insulation stack is capped with a hydrophobic material, in this case Teflon AF 2400, that allows

material to be "dragged and dropped", with a controlled volume deposited into laser-cut perforations. The benefits of laser cutting the channels goes beyond faster or more streamlined fabrication and elimination of photolithography steps; this approach provides for micron-scale channel lengths and lower parasitic capacitance due to the elimination of the overlap of the active material with the source and drain contacts.¹⁸ In addition, the application of this manufacturing technique can be extended for use in complementary circuits as it allows for readily implemented deposition of different materials in adjacent channels without the need for special equipment or additional patterning steps. Although this paper makes use of traditional photolithography to pattern interconnects and contact pads, the self-aligning insulation layer and laser-cut channels are compatible with additive manufacturing techniques to pattern contacts, thus completely eliminating the use of photolithography. Finally, we show that this technique is amenable to fabrication of flexible arrays with free standing OECTs that can be used for bidirectional sensing in bioelectronic devices.

4.2 Results and Discussion

4.2.1 Fabrication Scheme and Optimization of Self-Aligned Laser-cut OECTs

The non-traditional fabrication employed herein relies on pre-assembly of a substrate/interconnect/insulator stack. Metallic interconnects were, in this work, patterned photolithographically and arranged in an array of 2 x 12 on a glass slide, coated with Parylene C, and then cast with Teflon AF2400. The channels of all the OECTs used herein were patterned by laser cutting the loop portion of a continuous interconnect creating a source and drain electrode which resulted in a channel length of about $L=25 \,\mu\text{m}$, which is the smallest cut width that could be achieved with the laser system employed in this work. The channel width was defined by the width of the metallic interconnect, which was fully cut by the laser, $W=700 \,\mu\text{m}$. The hydrophobic top surface of the material stack allowed for a small droplet of diluted PEDOT:PSS dispersion to be physically dragged across surface and wicked into the perforation formed by the laser cut, which is significantly more hydrophilic, allowing a facile and defined deposition of the active channel material (**Fig 4.1 and Fig 4.2**).



Figure 4.1. OECT fabrication flow. a) Flow diagram describing the fabrication process. 1. Assembly of the substrate, patterned gold interconnects, insulator stack (including the hydrophobic, Teflon AF capping layer). 2. Laser cutting/ablation to create the channel and self-align the contacts/insulation, 3. Deposition of the channel materials, in this case PEDOT:PSS, by physically dragging across the channel. 4. Baking to complete the transistor structure, 5. Exposing to electrolyte and operating as a common source OECT. b) Selection of laser power for optimal formation of channels, ensuring complete cutting through the gold with minimal damage to the glass substrate underneath. Starting from the left the respective powers are 0.1, 0.5, 1.0, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0W. Top: reflection, bottom: transmission mode optical micrographs. The horizontal metallic interconnect is 700µm in width.

Critical to the fabrication procedure are the parameters employed for laser cutting, which are instrumental to ensure a complete cut through the materials stack while minimizing damage to the rigid carrier and debris around channel edge. The main parameter that was optimized was the power of the laser. Powers of 5.0 W (the maximum power of the laser) down to 0.1 W were employed and inspected (**Fig 4.1b**). The cuts were evaluated by the amount of damage done to the glass carrier below, the amount of damage to the self-aligned insulation on top, and the amount of debris left over; this qualitative determination led to a power of 2.0W as the optimal setting given the properties of the laser and materials stack (materials and thicknesses). Very low powers did not result in complete ablation of the metal interconnect, and thus did not define a channel, and while 1.0 W may have resulted in less damage to the glass, more cracking to the hydrophobic layer was qualitatively observed. Higher laser power resulted in less debris and cracking but more damage to the glass. A cross-sectional SEM image of the channel (**Fig 4.3**) shows the relative dimensions and the laser induced damaged morphology.


Figure 4.2. Surfaces energetics of self-aligned OECTs (a) The top coating of Teflon AF provides a hydrophobic surface, with a measured contact angle of 123° This enables a droplet of solution/dispersion to be readily dragged across the surface, and over a laser cut perforation (which will act as a hydrophilic well into which the solution will wick, solvent will evaporate, and a thin film layer will be deposited). (b) a dry device laser cut channel. (c) a droplet of water on top, and (d) the remaining water pinned in the channel after the droplet has been dragged away. (scale bar in b applies to b,c,d)

4.2.2 Performance of Self-Aligned Laser-cut OECTs

OECT performance and reproducibility was subsequently tested, initially investigating the array on a rigid carrier substrate (glass slide, as in **Fig 4.1**). **Fig 4.4a,b** shows output (I_d - V_d) and transfer (I_d - V_g) characteristics of a typical device. The distributions of electrical properties were analyzed by first looking at the maximum drain currents achieved at $V_g = 0$ V and $V_d = -0.6$ V leading to a mean current of 0.88 ± 0.31 mA (**Fig 4.4c**). Transconductance is a device measure of voltage to current sensitivity, and defined as $g_m = \partial I_d / \partial V_g = (Wd/L) \mu C^*(V_{th} - V_g)$ where W,

d, L are the effective channel width, thickness, and length of the channel, μ is the electronic charge carrier mobility, and C^* is the volumetric capacitance.^{22,43} The distribution of g_m of the OECTs at $V_g = 0$ V and $V_d = -0.6$ V (Fig 4.4d) results in a mean of 2.82 ± 0.78 mS. The transconductance of the OECTs presented in this work are within a factor of ten lower than PEDOT:PSS OECTs prepared using standard photolithographic techniques; however, they are nearly identical to other reported, similar sized OECTs.^{43,198} Finally, the threshold voltage (V_{th}) of the OECT at V_d = -0.6 V (saturation) was extracted by extrapolating the linear region of the $I_{\rm d}^{1/2}$ - $V_{\rm g}$ plot, as shown in Fig **4.4b inset**. The mean $V_{\rm th}$ was 0.53 ± 0.068 V. The slight variability in electrical properties across the array might be due to variation in thickness of the active material (variability in the active material casting) and variability in the laser cut (size, depth, amount of debris created -- affecting droplet pinning and total deposited material) (Fig **4.3**). The average thickness of the PEDOT:PSS measured across the devices on the array was 115.50 ± 50.30 nm, the broad distribution of which may account for the observed variability. Based on these results, there is a need for this fabrication method to be further optimized for reproducibility. Different ablation techniques, such as femtosecond laser or focused ion beam, may be appropriate to achieve higher quality channels which may lead to improved reproducibility.



Figure 4.3. Tilted cross section SEM micrograph of a representative laser cut channel. This micrograph shows the relative cross section dimensions of the device and the laser induced damage to the material stack on the periphery of the device. Debris found hanging off the glass substrate is due to the incomplete cleavage of the PaC and Teflon AF layers during the mechanical cleaving of the sample for SEM.

To demonstrate generality, we target other active materials, and show that the described approach can also be compatible with non-aqueous based materials such as glycolated thiophene materials cast from chlorinated solvents, such as p(g2T-TT) (**Fig 4.5**) providing the possibility for fabrication of accumulation mode materials and complementary circuits.³⁹ These data show that OECTs patterned using the present approach can be of high quality and moderate reproducibility as they are forgiving to the lack of precision and quality associated with such manufacturing techniques, due the OECTs reliance on bulk charge transport rather than interfacial transport. This same property of OECTs has previously allowed for more unique form factors. For example, Müller *et. al* were able to create woven electrochemical transistors on silk fibers by dying the silk with an organic conductor.¹⁹⁹ Moreover, Wan et. al used porous PEDOT:PSS scaffolds as the active material in an OECT channel which showed comparable performance to traditionally spin coated films.³⁴



Figure 4.4. Electrical characteristics of laser-cut OECT array. a) Output curve ($\Delta V_g = 0.05 \text{ V}$, 0 V to 0.6V), b) transfer curve ($V_d = -0.6 \text{ V}$) of the OECTs with laser-cut channels on a rigid substrate. The right axis (red) shows the resulting transconductance trace. Inset: saturation regime extraction of threshold voltage (V_{th}). Histograms of electrical characteristics across a single array (N=24 devices), including (c) I_d (at $V_g = 0\text{ V}$ and $V_d = -0.6\text{ V}$) showing an asymmetric distribution with mean 0.88 ± 0.31 mA, (d) g_m (at $V_g = 0\text{ V}$ and $V_d = -0.6\text{ V}$) with a mean of 2.82 ± 0.78 mS, and (e) V_{th} resulting in a mean of 0.53 ± 0.068 V.



Figure 4.5. p(g2T-TT) laser-cut OECT performance. Typical output curve ($\Delta V_g = 0.05$ V, 0.4 V to -0.4 V and $V_d : 0$ to -0.4 V), left, and transfer curve ($\Delta V_g = 0.01$ V, 0.4 V to -0.4 V and $V_d = -0.4$ V), right, for p(g2T-TT) on a rigid array with the self-aligning insulation layer and laser cut channels. All electrical measurements were taken with the same methods described in the Materials and Methods section.

4.2.3 Flexible Self-Aligned Laser-cut OECTs

To show that laser-cut channels and the self-aligned insulation layer are compatible with unique form factors we created arrays on a flexible substrate as seen in Fig 4.6a. Fabrication was similar to that of the array on the rigid substrate but had a substrate layer of PaC, and was first delaminated from the glass, followed by the conducting polymer being patterned by dragging a droplet of diluted PEDOT:PSS dispersion across the suspended laser-cut channels. Previous work has explored the mechanical robustness of conformal PaC arrays.³⁸ While, in this work, we have not tested the robustness of such free-standing arrays under mechanical loading/deformation, it is possible that the perforation of the substrate and added substrate-channel interfaces may be potential sources of stress concentration and defect nucleation. Two different types of PEDOT:PSS channels are found to be formed using this approach: through-hole, where only the side walls of the channel are coated, and free standing films as seen in Fig 4.6b. This is confirmed by visual inspection and through device characteristics: the maximum drain current seen in the output curves of the two different OECTs in Fig 4.6c,d. The through-hole OECT achieved approximately a thirty-fold lower current at $V_g = 0$ V and $V_d = -0.6$ V than the free standing OECT due to a lower effective Wd/L geometric factor, whereby the active channel is defined by a residual film deposited on the side wall of the laser-cut hole, with a channel length tracking the perimeter of the cut from the respective edges of the metal contacts as seen in Fig 4.6e. It is believed that these two formats have advantages in different applications. If high transconductance is needed, for example; when recording low amplitude neural signals then the free-standing films would be suitable.²⁰⁰ In this case, low molecular weight species, ions, and water could readily transport through the freestanding film, potentially aiding in masking probes from immune response.²⁰¹ If a more mesh-like structure is desired that allows for both fluid flow and cell/tissue ingrowth, allowing for more

regenerative applications, then the through-hole OECTs may be suitable.²⁰² In this work, the goal was not to target one format over the other, however, it is postulated that fine control of surface energetics, ink viscosity/concentration and volume can be used as knobs to favor a particular version of these flexible OECTs. In the present work, the variability and reproducibility of the free-standing arrays was poor – **Fig 4.6**, for example shows a through-hole and free standing OECT side by side. Creating higher reproducibility of free standing films across the array might be achieved if PEDOT:PSS is deposited and crosslinked before delamination from the rigid carrier substrate.²⁰³





а

b

free-standing

Figure 4.6. Self-aligned, laser patterned flexible arrays. a) Micrograph of a flexible array of planar laser-patterned OECTs. b) Schematic cross-sections of the two flexible OECT forms achieved herein: a free-standing OECT and a through-hole OECT depending, which are defined by the nature of PEDOT:PSS channels after deposition/drying (materials color coding is the same as in Fig 4.1a). Output curves ($V_g: 0 - 0.6V, \Delta = 0.05V$) of (c) free standing and (d) through-hole OECTs. e) Micrograph of two adjacent OECTs of each type.

4.2.4 Self-aligned Laser-cut Cofacial Inverter

The self-aligned laser-cut fabrication scheme can be scaled up to create vOECTs by adding a second layer of gold on top of the first as discussed in chapter 3 (**Fig 4.7a**). Once the channel is ablated the cofacial pair is created which can be used in conjunction with the ambipolar material discussed in chapter 3 (p(C₄-T2-C₀-EG)) to create an inverter. While the devices do not provide the clean cuts of a vertical side wall as depicted in the schematic, they yield operational cofacial pair complementary inverters (**Fig 4.7d**) which operate under the same principles as those in Chapter 3. In the case of the self-aligned, laser cut devices the exact and uniform dimensions of the separate devices are not readily discernable due to the ill-defined device topography and the variations in active material thickness owing (effectively) to a drop casting method. These same factors likely contribute to the difference in performance between the self-aligned laser-cut and photolithographically defined inverters. The damaged laser cut sidewalls of the channel might change the effective length of the vOECT channels and affect material contact with the source and drain contacts, as opposed to the photolithographically defined channels which have smoother vertical sidewalls (**Fig 4.7c**).

The self-aligned, laser-cut cofacial inverter shows that OECT-based circuits are compatible with direct write fabrication techniques, which is enabled by the relaxed fabrication constraints of OECTs owing to their bulk transport properties. This fabrication method can address the issue of patterning p- and n-type materials in separate channels when an ambipolar material is not available owing to the Teflon AF topcoat. This feature may allow for sperate materials be dragged and dropped into adjacent perforations of the materials stack. Separate pand n-type materials may be desirable for digital circuits to ensure the complete switching to the logic level HIGH and LOW, but not necessary for analog applications. Thus, self-aligning vOECTs for complementary logic gates can be integrated into more complex logic circuits such as decoders, that are typically comprised of hundreds of OECTs and resistors to make up unipolar gates, to enhance performance and potentially reduce the overall footprint. Despite the potential advantages presented by the laser-cut patterning approach, further development and optimization of the process are needed. To improve the performance and reproducibility of the self-aligned OECTs different ablation methods such as femtosecond laser-cutting and focused ion beam milling can be used. Excessive local heating and associated damage must be minimized, for example using shorter duration pulses and exploring processing and post-processing conditions for ablation of the particular materials stack, in order to enhance the topography of the channels.



Figure 4.7. Laser-cut and self-aligned cofacial complementary inverter pair. a) The crosssection schematic of a laser-cut cofacial pair. The stack has an added hydrophobic coating to aid in the selective deposition of $p(C_4-T2-C_0-EG)$ in the laser cut trench. B) Optical micrograph of the self-aligned laser cut cofacial pair. The dotted red outline denotes the shorted bottom contacts of the vOECTs where V_{out} of the inverter is recorded. The dashed purple box outlines the top contacts of the vOECTs of the inverter that are connected to V_{DD} and ground. Scale bar = 5 µm C) A tilted SEM micrograph of the cross section of the cofacial pair of OECTs. FIB milling was used to expose the cross section, requiring deposition of a thick Pt layer. Scale bar = 200 µm D) The voltage transfer characteristics of the cofacial pair inverter ($\Delta V_{in} = 0.01$ V, 0 V to 0.6 V and $V_{DD} = 0.8$ V) and the corresponding gain ($\delta V_{out}/\delta V_{in}$) with a peak gain of about 12.

4.3 Conclusions

In this work we present a novel method to fabricate OECTs based on laser cutting the channels and using a self-aligning hydrophobic insulation layer. This technique takes advantage of the relaxed design constraints imparted by bulk rather than interfacial transport of charge carriers of OECT devices. This method allows for the reduction or complete elimination of photolithography steps typically used with micron scale devices as the active material can simply be ink deposited by dragging a droplet into the channel. It also offers a decrease in parasitic capacitance due to the self-alignment of the insulation and the source/drain contacts, since the channel is made via laser cutting rather than photolithography causing the overlap between the channel and source/drain contacts to be eliminated. This method can open the door to simplified fabrication of complementary circuits, or multi-analyte sensor arrays due to the ease at which different materials can be patterned on the same array. We have shown that this fabrication technique is compatible with flexible substrates and allows for the production of through-hole and free-standing films which may otherwise be challenging to achieve with traditional lithography. Such unique OECT form factors present unique opportunities in biological sensing and stimulation within cell/tissue culture or in in vivo environments. Lastly, we show the potential for the self-aligned laser-cut fabrication scheme to be used to create compact form factors, such as the vOECT cofacial pair presented here, to create OECT-based circuits.

4.4 Methods

4.4.1 Fabrication

Clean microscope slides were thoroughly cleaned using ultrasonication in acetone, IPA, and deionized water. For fabrication of arrays on rigid substrates, gold was patterned directly onto the glass. For free-standing, flexible arrays, a 2µm thick parlyene C substrate layer was deposited in a SCS LabCoater II parlyene deposition system. To pattern gold interconnects, S1813 photoresist (Shipley) was spun onto the microscope slides at 3500 rpm for 30 seconds and baked at 110°C for 1 minute. The resist was then patterned using an MBJ4 SUSS Mask Aligner and developed in AZ

400K 1:4 for 30 seconds. Chromium/Gold (5nm/100nm) was subsequently deposited (AJA metal deposition system), and patterned by liftoff in Micoposit 1165 (Microchem) to define interconnects and contact pads. The slides were then sonicated and rinsed with acetone to complete liftoff and placed in the parlyene coater where $\sim 2\mu m$ of PaC was deposited with an adhesion promoter. Teflon AF 2400 (Chemours) was then spun onto the slides at 1500 rpm and baked at 210°C. Using an LCS Laser Cutter, the channels were cut, setting the power of laser to 2.0W, number of repetitions to 1, and the frequency to 40kHz. PEDOT:PSS (Hereaus Clevios PH1000) dispersion was formulated with 5% ethylene glycol, 1% wt GOPS, and 2 drops of DBSA (Sigma Aldrich), and subsequently diluted by half in deionized water. PEDOT:PSS dispersion was diluted because deposition of a pinned droplet of 1.25 wt% effectively resulted in a local drop casting and thus a thick film. As such, the size of the laser-cut and the dispersion concentration are the main route to control total deposited channel material. For the OECTs fixed on the glass substrate, the PEDOT:PSS was dragged across the array to fill the channels and left to bake at 140°C for 30 mins. For the flexible arrays, the array was first soaked in DI to allow the array to delaminate from the glass carrier. The PEDOT:PSS was then dragged across the free standing array and baked at 140°C for 30 mins. The laser-patterned self-aligned cofaical pairs were made using the same steps but a sacrificial PaC layer was deposited on the glass slide first and after the final insulation layer was deposited onto the second layer of gold, a layer of Teflon AF 2400 was spun onto the slide at 1500 rpm and baked at 210°C for 20 minutes. Then using an LCS laser cutter the channels were cut using a power of 2W, a frequency of 40kHz with one repetition. A droplet of $p(C_4-T_2-C_0-EG)$ was then pinned onto the Teflon coating and dragged and dropped into the ablated channel.

To estimate the thickness of the PEDOT:PSS deposited in the channels, thickness of the channel before and after deposition was measured with difference between the two yielding a film thickness. All thickness measurements were performed on a Veeco Dektak-8 profilometer. Inspection and lateral dimension extraction were performed using a Zeiss Scope.A1 and AxioCam 105 color. First SEM image (Hitachi SU830) of pOECT cross-section were collected after a 9nm osmium coat (SPI). Cross sectional scanning electron microscopy images of cofacial pair were taken using a JEOL 4700F FIB/SEM. First 20nm of bulk platinum (Pt) was sputter coated then 1µm of local Pt was deposited to prevent ion beam damage. The cross sections were milled using a FIB at 30kV with currents up to 10nA. The samples were mounted at 45° and tilted at 20° for SEM imaging at 10kV.

4.4.2 Electrical Measurements

All electrical OECT Measurements were performed with a National Instruments PXIe-1082 system using custom LabView programs as previously described. Output curves and transfer curves were obtained using two source-measure units (SMUs) (NI PXIe-4143). All measurements were done in 0.1 M NaCl using a Ag/AgCl pellet as an external gate. Output curves were measured by applying a V_d of 0V to -0.6V and a V_g of 0V to 0.6V with a sweep rate of 0.2 V/s. Transfer curves were measured by holding V_d constant at -0.6V and applying a V_g of 0.6V to 0V. All testing was performed in ambient conditions in an open lab setting.

Chapter 5 Future Directions and Conclusion

5.1 Introduction

This chapter will present proof-of-concepts that can continue to advance OECT-based circuits for bioelectronics. First, I expand upon the Teflon coated laser cut vOECTs presented in Chapter 4 to show the potential use for patterning multiple OMIECs on the same substrate to enable fabrication of complementary circuits. Next, I explore the development of new fabrication processes to produce high quality and reproducible complementary circuits. I expand the traditional dry sacrificial peel off method, described in Chapters 2 and 3, to include a second sacrificial layer to allow for two OMIECs to be patterned sequentially. Furthermore, I explore the use of a 3D printed cellulose nanofiber (CNF) hydrogel to protect OECT channels during multi-OMIECs casting for complementary OECT circuits. Next, I test a method to address the electronic mismatch between n- and p-type OMIECs by decreasing the intrinsic conductivity of the p-type OMIEC. Facile chemical modifications such as the one shown in this chapter addresses the mismatch without needing to alter device geometry or synthetically design lower preforming p-type OMIECs. Finally, I demonstrate a new OECT geometry that allows for higher amplification and sensing in a more compact geometry.

5.2 Self-aligned, Laser-cut Complementary Circuits

The self-aligned, laser-cut cofacial pair presented in Chapter 4 offers a simplified fabrication method for inverters and while the example presented in Chapter 4 makes use of an ambipolar OMIEC as a proof-of-concept the method can be extended for use in complementary circuits with unipolar transporting channel materials. Ambipolar inverters present electronic properties that negatively affect the performance of the inverter; for example, ambipolar inverters never completely pull up or down due to the unique ambipolar regime of operation which leads to nondiscrete HIGH and LOW levels and higher power dissipation^{186,187,204}. While complementary circuits made of a separate p- and n-type OECTs address this issue, patterning multiple OMIECs on the same substrate at the micron scale presents materials and fabrication challenges. To facilitate the patterning of both p- and n-type OMIECs researchers have investigated the use of printing methods such as screen printing. Yang et al. present a complementary inverter based on BBL and $p(g_42T-T)$ OECTs with a gain of 25 and a gain of ~200 when two inverters are cascaded. However, due to the large dimensions of the individual OECTs (W x L = 2 mm x 200 µm) the response time of the device was long, with the BBL OECT limiting the response at 145 ms.²⁰⁵ Thus, while printing methods allow for ease of patterning multiple OMIECs further optimization is required to create micron scale devices to ensure the response time is sufficient for biological and computational applications. The fabrication method presented in Chapter 4, which allowed for micron scaled devices, eases the patterning of multiple OMIECs by allowing them to be dragged and dropped in neighboring channels (**Fig 5.1**).



Figure 5.1. Cross section of a laser-cut OECT-based complementary inverter. This figure shows an expanded cross section of figure 4.7a showing how the Teflon coating allows for easy drag and drop of different OMIECs in neighboring channels for complementary inverters.

OMIECs discussed in chapter 2 were used to create the complementary inverter with the laser cut OECTs. PgNAN (C12) (5mg/ml) and TIG-BT (0.5mg/ml) were used for the n- and p-type OECTs respectively. These two materials were chosen as they offer similar threshold voltages, which is a property that cannot be easily tuned. Since the drag and drop method offered by the Teflon coating does not easily allow for control of thickness like spin coating, TIG-BT was diluted. The dilution achieves thinner effective film thickness, to offer a better matching of electronic properties such as current, transconductance, and response time.



Figure 5.2. Laser cut OECT-based complementary inverter. a) The transfer curve of 15 TIG-BT vOECTs. All transfer curves were collected with $\Delta V_g = 0.01$ V, 0V to -0.8V and $V_d = -0.4$ V and a sweep rate of 0.2 V_g /s. b) The transfer curve of 15 PgNAN (C12) vOECTs. All transfer curves were collected with $\Delta V_g = 0.01$ V, 0V to 0.4V and $V_d = 0.4$ V and a sweep rate of 0.2 V_g /s. c) The voltage transfer characteristics of PgNAN, TIG-BT inverter. $\Delta V_{in} = 0.01$ V, 0V to 0.4V and $V_{DD} = 0.8$ V)

The individual TIG-BT and pgNAN lasercut vOECTs showed poor reproducibility across the array with some vOECTs not turning on (**Fig 5.2a,b**). However, the TIG-BT and pgNAN devices that showed comparable drain current were wired in an inverter configuration (**Fig 5.2c**). While some

inverting characteristics are shown, the inverter was unable to pull up to 0.8 V, which is likely due to poor performance of the TIG-BT vOECT causing high channel resistance. Moreover, the switch from HIGH to LOW was not as sharp as typical complementary inverters which is likely due to the high resistance of the PgNAN vOECTs preventing the inverter from pulling down.

To enhance the performance of the laser cut complementary inverter, the ablation was optimized by replacing picosecond laser cutting with femtosecond (fs) laser cutting. As seen in the SEM images in Chapter 4, the channel side wall roughness may be creating unreliable channel length which could be a contributing factor to the reproducibility issues, which the fs ablation may correct. (**Fig 5.3**). In addition, the higher resolution possible with the fs laser allows for smaller cuts leading to shorter channel lengths (~5 μ m rather than 25 μ m), which can decrease device footprint and decrease parasitic charging (**Fig 5.3**). The less laser damaged devices however did not translate into higher performing devices. The main issue faced with the fs laser ablation was the shorting of the vertical channels during ablation.



Figure 5.3. Femtosecond laser-cut vOECTs. The microscopic image shows the quality of OECT channel after femtosecond ablation. Scale bar is 200 µm.

To further advance the performance of the Teflon coated devices, pOECTs could be explored with

fs laser cutting rather than vOECTs. In addition, further tuning of fs laser cutting parameters or

exploration of post ablation processing to remove metallic residues could correct for shorted vertical contacts. Moreover, while not cost-effective or scalable, other ablation techniques could be explored such as focus ion beam, to explore the fundamentals of this device concept. While channel topography is a contributing factor to device performance and reproducibility, material selection and film quality are as well. The TIG-BT was diluted to a low concentration which may have promoted the formation of discontinuous non-homogenous films as evidenced by the higher rate of non-functioning vOECTs than the PgNAN vOECTs. Thus, the availability of OMIECs with better matched electronic properties might help with reproducibility of laser cut OECT inverters.

5.3 Microfabricated OECT-based Complementary Inverters

5.3.1 Using a Double Parylene C Sacrificial layer approach for Complementary Inverters

To enhance the reproducibility of micron-scale complementary inverters with both OECTs on a single substrate, photolithographic techniques may still be the most reliable way to achieve this. To achieve patterning of both n- and p-type OMIECs on the same substrate, the fabrication method used in chapters 2 and 3 is extended to add a subsequent sacrificial PaC layer that is etched to expose the desired active areas after one of the OMIECs has been patterned using the first sacrificial layer (**Fig 5.4**). This method has the potential for higher reproducibility as the OMIECs are spin coated rather than dropcasted which typically leads to more uniform film formation across devices. BBL₁₅₂ (which will be mentioned as BBL) is chosen as the initial n-type OMIEC owing to its electronic stability, performance, and to its ability to withstand delamination during patterning of the second OMIEC²⁰⁶. p(g2T-T) is selected as the p-type OMIEC as its threshold voltage is similar to that of BBL and is electrical stable¹⁴⁶. However, it does exhibit higher electrical performance than BBL. To remedy the mismatch in electronic performance between

BBL and p(g2T-T), p(g2T-T) was diluted to 1 mg/ml and spun at 2000rpm. Similarly, to TIG-BT in section 5.2, when p(g2T-T) is diluted to low concentrations the OECTs exhibit low reproducibility. The transfer curves in **Fig 5.5** represent the best pair of vOECTs (100 μ m x 1 μ m) with drain terminals shorted on board but the p-type vOECT exhibited a drain current that is ~7 times higher than that of the n-type.



glass slide

Figure 5.4. Fabrication scheme of complementary inverter using a double sacrificial layer. Continuing from the fabrication scheme in Figure 2.33. In steps 14-16 the n-type OMIEC is patterned via spin coating followed by peeling the first sacrificial PaC layer. The p-type channels are protected as the PaC is not yet etched there. In step 17 the anti-adhesive soap and the second PaC sacrificial layer are deposited. In steps 18-21 the p-type channel is patterned via photolithography and dry etching while the n-type channel is protected. In steps 22-23 the p-type OMIEC is patterned via spin coating followed by peeling the second sacrificial PaC layer.



Figure 5.5. vOECT characteristics of complementary pair fabricated via double sacrificial layer. a) The transfer curve of a p(g2T-T) vOECT. Transfer curve was collected with $\Delta V_g = 0.01$ V, 0V to -0.6V and $V_d = -0.6$ V. b) The transfer curve of a BBL vOECT. The transfer curve was collected with $\Delta V_g = 0.01$ V, 0V to 0.5V and $V_d = 0.5$ V.

The voltage transfer characteristics of the inverter demonstrate a working inverter with a peak gain of 14 at a V_{in} of 0.45 V which is shifted from the ideal $V_{DD}/2$ (**Fig 5.6**). The higher performance of the p-type causes the inverter to pull down later and not as effectively which can also limit the gain as the slope of the transition will not be as steep. This example demonstrates that matching p-type and n-type performance is not only crucial for digital logic but analog applications that require high gain as well.



Figure 5.6. Inverter characteristics using the double sacrificial method. a) The voltage transfer characteristics of the BBL, p(g2T-T) based inverter ($\Delta V_{in} = 0.01$ V, 0 to 0.4,0.55,0.6 V and $V_{DD} = 0.4$, 0.55, and 0.6 V). b) The corresponding gain ($\delta V_{out}/\delta V_{in}$) with peak gains of 9, 13, and 14 for $V_{DD} = 0.4$, 0.55, and 0.6 V, respectively.

The stability of the inverter was tested to ensure that the location of the peak gain does not shift during the measurement which is crucial for analog applications. This was done by pulsing the inverter from $V_{in} = 0$ to 0.42V, which is the location of peak gain at $V_{DD} = 0.55V$, for ~1 second at each V_{in} . As seen in **Fig 5.7a** the V_{out} increases at first but begins to plateau after 30 seconds at ~0.18V. In addition, the VTC and the gain curves before and after the pulsing are overlapping (**Fig 5.7b,c**) showing that over this duration of inverter operation or stressing, the inverter characteristics are stable, which is promising for bioelectronic sensing applications.



Figure 5.7. Stability of inverter fabricated via double sacrificial layer patterning. a) Pulsing the input of the complementary pair from 0 to 0.42 V ($V_{DD} = 0.55$ V) and the resulting output. The V_{out,low} increases until it plateaus while the V_{out,high} stays constant. b) VTC before and after pulsing showing no change ($\Delta V_{in} = 0.01$ V, 0 to 0.55 V and $V_{DD} = 0.55$ V). c) The corresponding gains ($\delta V_{out}/\delta V_{in}$) before and after pulsing showing no change in magnitude or location of peak gain.

5.3.2 Using a 3D Printed Hydrogel for Complementary Inverters

While section 5.3.1 presents a promising fabrication method for OECT-based complementary inverters, it can be time consuming and can add costs since it requires additional PaC deposition, photolithography and etch steps. To expedite and simplify the fabrication process, a hybrid microfabrication and printing technique is developed. It uses the fabrication methods described in chapters 2 and 3 to define the contacts and channels and employs a 3D printed (Biox, Cellink) cellulose-based hydrogel (cellulose nanofiber) to mask one area of the design, while casting subsequent inks (**Fig 5.8**). The hydrogel is used to protect one side of channels while the first OMIEC is spin coated and is then removed with DI. The hydrogel is then printed on top of the first OMIEC that was cast to protect it while the second OMIEC is spin coated and is once again removed. Finally, the sacrificial PaC layer defining the micron scale OECTs is peeled off leaving the n-type OMIEC on one side and the p-type OMIEC on the other. This fabrication methods preserves the ability to spin coat the OMIECs for high reproducibility without the added microfabrication steps in 5.3.1.



Figure 5.8. Fabrication scheme of complementary inverter using a hydrogel. The contacts of the vOECTs and the channels are defined using the same fabrication method described in Chapter 3 resulting in the device in step 1. In step 2 a cellulose nanofiber-based hydrogel is 3D printed onto on side of the devices to protect half the channels. In step 3 the n-type OMIEC is spin coated on top of the devices. In step 4 the hydrogel is removed with DI and mechanical scrubbing. In step 5 the hydrogel is printed on top of the n-type channels to protect them while the p-type OMIEC is spun on in step 6. In step 7 the hydrogel is removed once again with DI and the sacrificial PaC is removed leaving the OMIECs in the channels with n-type on one side and p-type on the other.

BBL and p(g2T-T) were once again used as the n- and p-type OMIECs respectively and the transfer curves for the individual vOECTs (100 µm x 1 µm) with shorted drains are seen in **Fig 5.9**. In this case, there was a mismatch between the n-type and p-type vOECTs with p(g2T-T) exhibiting a drain current that is about 4 times larger than that of the BBL.



Figure 5.9. vOECT characteristics of complementary pair patterned with a hydrogel. The transfer curve of a p(g2T-T) vOECT. Transfer curve was collected with $\Delta V_g = 0.01$ V, 0V to - 0.6V and $V_d = -0.6$ V. b) The transfer curve of a BBL vOECT. The transfer curve was collected with $\Delta V_g = 0.01$ V, 0V to 0.5V and $V_d = 0.5$ V.

The VTC of the inverter begins to switch at a V_{in} closer to the ideal value of $V_{DD}/2$ (Fig 5.10a,b); for example, for $V_{DD} = 0.55V$ the peak gain occurs at 0.26 V(Fig 5.10c). In addition, since there is better balance, the inverter is able to fully pull down and completely switch off to 0V. The stability of the inverter was tested by pulsing V_{in} from 0V to 0.55V (holding for ~5 seconds at each voltage) which resulted in the inverter pulling up and down completely to the same level at every pulse showing the potential for stable digital and computational applications.



Figure 5.10. Inverter characteristics using the hydrogel method. a) The voltage transfer characteristics of the BBL, p(g2T-T) based inverter ($\Delta V_{in} = 0.01$ V, 0 to 0.2, 0.3, 0.4, 0.5 and 0.55 V and $V_{DD} =$ to 0.2, 0.3, 0.4, 0.5 and 0.55 V). b) The corresponding gain ($\delta V_{out}/\delta V_{in}$) with peak gains of 5.7, 8.8, 11.5, 13 and 15.5 for $V_{DD} =$ to 0.2, 0.3, 0.4, 0.5 V, respectively c) Pulsing the input of the complementary pair from 0 to 0.55 V ($V_{DD} = 0.55$ V) and the resulting output. The V_{out,low} and V_{out,high} stay constant.

5.3.3 Reducing the Conductivity of p-type OMIECs

The major limiting factor for producing high quality reproducible complementary inverters in sections 5.3.1 and 5.3.2 is the mismatch in electrical characteristics between the p- and n-type OMIECs. Typically, the thickness of the p-type OECTs is reduced to decrease its electrical properties but reducing thickness of films cast from solutions with concentrations typically used (5mg/ml) results in the p-type OMIECs still being too conductive so the concentration of the solution is decreased to create even thinner films²⁰⁶. However, with this technique, reproducibility

of the p-type OMIEC is compromised not only from substrate to substrate but from device to device on the same substrate as well, due to the potential formation of discontinuous films. While the development of high performing n-type OMIECs progresses, simple modifications to decrease the conductivity of the p-type OMIEC can be explored. Sodium hypochlorite (NaClO) has been previously used to decrease the conductivity of PEDOT:PSS by 10 orders of magnitude.²⁰⁷ The NaClO treatment leads to overoxidation of the PEDOT:PSS, disrupting polymer conjugation by breaking bonds associated with delocalized hole transport in the thiophene backbone, thus decreasing electronic conductivity. It has even been demonstrated that treatment in NaClO can lead to material loss due to chain scission.²⁰⁷ To create more balanced inverters, the p-type OMIEC presented in sections 5.3.1 and 5.3.2 is treated in NaClO to purposefully degrade electronic properties in order to better match those of BBL.

p(g2T-T) was spin coated from a 5mg/ml solution onto 100x10 µm planar OECTs which resulted in mA currents (**Fig 5.11**). The OECTs were then dipped into a 0.1% sodium hypochlorite solution for 5 seconds followed by placement in a DI bath. Post treatment, the drain current of all the pOECTs did decrease (**Fig 5.11**) but the change in drain current did not follow any trend. It seems that the OECTs with higher initial drain current decreased by a smaller percentage than those with lower initial drain currents (**Table 5.1**). In addition, there was an outlier as one of the OECTs did not turn on at all post treatment. This could be due to penetration rate of the sodium hypochlorite solution.



Figure 5.11. Decreasing the conductivity of p(g2T-T). Transfer curves of p(g2T-T) OECTs before and after being dipped in 0.1% sodium hypochlorite solution. All transfer curves were collected with $\Delta V_{\rm g} = 0.01$ V, 0V to -0.6V and $V_{\rm d} = -0.6$ V.

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	I ₀ (mA)	I _f (mA)
D1	3.24	2.79
D2	2.98	2.11
D3	1.62	0.14
D4	1.18	DEAD
D5	1.89	0.088

Changes in drain current of p(g2T-T) OECTs before (I_o) and after (I_f) being submerged in a 0.1% sodium hypochlorite solution. No trend for reproducibility is achieved.

To ensure the reproducibility of the decrease in drain current when dipped in the NaClO solution, the concentration of the solution could be further decreased. Currently, the devices were only dipped in the solution for 5 seconds but if the concentration of the NaClO solution decreased the devices could be left in the solution for longer leading to more room for error and higher reproducibility, which has been previously demonstrated. This will ensure that the process is reaction limited rather than diffusion limited.²⁰⁷ By decreasing the concentration of the NaClO solution the film would be shorter than the time scale of conductivity decay giving more control over the process.²⁰⁷

5.4 Annular OECTs

High transconductance is important for biological sensing as it can lead to high signal-to-noise ratio (SNR) and higher sensitivity during signal acquisition.²³ However, the inherent electronic properties of the active channel materials, such as mobility (μ) and volumetric capacitance (C*) are not the only parameters that affect the performance (transconductance and response time) of the OECT as seen in eq. 1, where W is width, d is thickness, L is length, *V*_{th} is the threshold voltage and *V*_d is the drain bias.^{17,18}

$$g_m = \frac{Wd}{L} \mu C^* (V_{th} - |V_d|) \ (1)$$

Based on eq.1 the geometric area of the OECT affects its performance meaning that its dimensions can be used to optimized or enhance performance. However, parameter changes can come with undesirable consequences; for example, increasing the width (W) will increase g_m but it will also increase the overall area of the sensing OECT which will cause a decrease in number of sensing units (or transistor density) in order to retain a constant overall device size. The thickness of the OECT (*d*) can be increased to increase g_m but increasing the thickness may increase the charging time (higher *C*) which can limit potential target applications.¹⁸ The length of the OECT channel (*L*) can be decreased to increase g_m and unlike increasing the width and thickness it neither increases the overall area of the devices nor increases the response time. However, in a planar configuration where the source and drain (S/D) terminal of the OECT (pOECT) are next to one another (**Fig 5.12a,b**) the length is typically limited to ~5um due to the traditional photolithography techniques used in an academic cleanroom.¹¹⁷ To overcome the limitations found with photolithography vertical OECTs (vOECTs), where the source and drain contacts are stacked on top of one another (**Fig 5.12c,d**), can be used as the length of the channel is defined by the thickness of the insulation between the S/D terminals (**Fig 5.12c**), as demonstrated in Chapter 3.

Another geometry in a vertical configuration that has yet to be explored extensively is the annular OECT (**Fig 5.12e**), which is where, similar to previously fabricated vOECTs, the S/D contacts are stacked on top of one another, and the length of the OECT channel is the thickness of the insulation between the S/D metal layers. However, in the annular configuration the contacts are circular instead of rectangular (avOECTs). The benefit of avOECTs over vOECTs or pOECTs is that in the same area more functionalities can be added to the OECT without increasing the device area which is crucial for bioelectronic applications. For example, avOECTs can be used for regenerative applications as the free space can allow for cell and neuronal growth through the OECT. In addition, the circular nature of the contacts has the potential to eliminate any edge effects or fringing fields that can be exhibited with the rectangular contacts.



Figure 5.12. OECT geometries. a) A pOECT with the length defined by the lateral distance between the S/D contacts which is dictated by the limitations of photolithography. b) The cross section of a pOECT. c) A vOECT with the length defined as the vertical distance between the S/D contacts which is dictated by the thicknesses of the insulating PaC. c) The cross section of a vOECT showing the length of the channel. d) An avOECT with the length defined as the vertical distance between the circular S/D contacts which is distance dictated by the thicknesses of the insulating PaC.

pOECTs, vOECTs and avOECTs were all fabricated (using similar methods described in chapter 3) on the same substrate to accurately evaluate the difference in the performance. All the OECTs had a width of 100 μ m while the pOECTs had a length of 10 μ m and the vOECTs/avOECTs had a length of 0.65 μ m. The OMIEC used was p(g2T-T) (5 mg/ml) and was spun at 1500 rpm to ensure uniform films particularly along the sidewall of the vOECTs and avOECTs. The output curve (**Fig 5.13a**) shows that the avOECT behave as expected and when compared to vOECTs of the same length and width (**Fig 5.13b**) they observe similar drain currents.



Figure 5.13. Electronic characteristics of avOECTs. The output curve of the avOECT was collected with $\Delta V_g = 0.05 \text{ V}$, 0 V to -0.5V and $\Delta V_d = 0.01$, 0 to -0.5V and a sweep rate of 0.2 V_d /s. b) The transfer curves of pOECTs, vOECTs and avOECTs were collected with $\Delta V_g = 0.01$ V, 0V to -0.5V and $V_d = -0.5V$ and a sweep rate of 0.2 V_g /s with I_d on a log scale.

As seen in **Fig 5.12e**, avOECTs have free space in the circular area defined by the S/D contacts which can be used to add other sensing elements to increase the functionality without increasing the area of the device. For example, the gate terminal can be added to that free space and functionalized for biochemical sensing applications, such as glucose detection, creating an entire sensing element in the same area as a typical OECT (**Fig 5.14**). This concept also ensures that the sensing gate electrode has a uniform distance from the channel.



Figure 5.14. Schematic of avOECT biochemical sensor. The schematic shows how a gate electrode can be added to the free space and can potentially be functionalized to create biochemical sensors.

5.5 Conclusion and Outlook

The primary goal of the work presented in this dissertation is to explore novel materials, geometries, and fabrication schemes for OECTs to advance their use in more complex circuitry for biological sensing; specifically, the complementary inverter as it is the building block of many circuits. In chapter 2, I characterize novel OMIECs for their potential use in complementary circuits and even explore the potential of new classes of active materials. The OMIECs included high stability p-type and n-type OMIECs, high electron mobility OMIECs, small molecules and 2D polymers. In chapter 3, I design a cofacial pair of vertical OECTs to create the smallest OECTbased inverter to date and perform the first ever demonstration of voltage-to-voltage amplification with an OECT-based inverter. In chapter 4, I develop a novel fabrication scheme that uses selfaligned laser-cut OECT channels to ease fabrication of OECTs and OECT circuits. In chapter 5, I present proof-of-concepts and future directions for fabrication schemes and new geometries to ease the patterning of multiple OMEICs on a single substrate and enhance sensing. As the development of higher performing OMIECs, particularly n-type OMIECs, continues to advance they can be seamlessly integrated in the fabrication schemes and OECT geometries developed in this dissertation to create more reproducible stable circuit performance required for biological applications. In particular, the μ C* of n-type OMIECs needs to be improved to match that of high performing p-type OMIECs available. In addition, when designing new OMIECs the threshold voltage of the OMIEC needs to be considered more heavily and designed to match already available OMIECs as threshold voltage is not a property that can be easily tuned. To further ease the fabrication of large complementary circuits new manufacturing and printing techniques that offer better resolution for smaller OECT channel dimensions, such as aerosol jet printing, should be explored.

Continuing the advancement of OECT-based circuits is crucial for enhancing the functionality of signal acquisition and processing at the abiotic/biotic interface. For example, OECT-based logic gates can be functionalized for analyte detection which can produce diagnostic decisions to be used further downstream for drug delivery or electrical stimulation, effectively creating closedloop systems. In addition, logic circuits such as decoders can be used for multiplexed reading and driving of sensors, ultimately decreasing the footprint of the overall device. While circuits such as the decoder already exist, replacing the commonly used resistive ladder-based gates with complementary gates may enhance circuit performance, decrease number of circuit components and circuit area making them more suitable for bioelectronic applications. Complementary circuits can also be used in neuromorphic circuits to mimic brain function for smart soft robotics and brainmachine interface applications²⁰⁸. While the circuits and concepts presented here are completely OECT based, OECTs are not meant to completely replace traditionally used inorganic processing units, wireless power supplies and Bluetooth components but rather complement them. OECTs boast the advantage of being able to intimately interact with the biological environment while the inorganic processing units offer operating speeds that far surpass that of OECTs preventing switching losses. To take advantage of both technologies, hybrid circuits will be the practical goal forward.

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Education		
Northwestern University Ph.D., Biomedical Engineering, GPA: 3.875	Expected 06/2022	
Linköping University Fulbright and American Scandinavian Association Fellow (visiting	09/2021-05/2022 Ph.D. student in Sweden)	
Northwestern University, Kellogg School of Management Management for Scientists and Engineers Certificate	08/2020	
University of California, Santa Cruz (UCSC) Bachelor of Science, Bioengineering, Electrical Engineering minor	06/2017 CPA: 3 85 (Magna	
Cum Laude, Tau Beta Pi)	, OTA: 5.05 (Magna	
Cum Laude, Tau Beta Pi) Research Experience		
Cum Laude, Tau Beta Pi) <u>Research Experience</u> Graduate Research Assistant, J. Rivnay Lab Department of Biomedical Engineering at Northwestern University	09/2017-present	
Cum Laude, Tau Beta Pi) <u>Research Experience</u> Graduate Research Assistant, J. Rivnay Lab Department of Biomedical Engineering at Northwestern University • Designed, fabricated and tested novel bioelectronic sensors usin transistors in applications of electrophysiology and biochemica • Developed new microfabrication schemes to enhance efficiency compact sensor geometries	09/2017-present ng organic electrochemical l sensing y and enable unique and	
Cum Laude, Tau Beta Pi) Research Experience Graduate Research Assistant, J. Rivnay Lab Department of Biomedical Engineering at Northwestern University Designed, fabricated and tested novel bioelectronic sensors usin transistors in applications of electrophysiology and biochemica Developed new microfabrication schemes to enhance efficiency compact sensor geometries Performed research on Department of Defense funded project h presenting quarterly updates Led collaborations with numerous chemical synthesis groups w	09/2017-present og organic electrochemical l sensing y and enable unique and hitting targets on time and	

coordinating with 15 faculty, post docs and graduate students across 4 different institutions

Research Assistant, Dr. Ali Yanik's Lab

Department of Electrical Engineering at UCSC

- Developed and fabricated multiple novel microfluidic channels to explore *V. cholerae* biofilm formation
- Secured funding for senior thesis project and managed collaboration with the Microbiology an Environmental Toxicology Dept.

06/2015-06/2017

Leadership Experience

Mentor, Science Club

Science in Society, Northwestern University

- Mentored weekly group science experiments (4 middle school students) to teach critical thinking skills in STEM
- Collaborated with program coordinators to design a study to explore faculties' attitude towards outreach

Mentor, Morning Mentoring

Science in Society, Northwestern University

- Designed custom curriculum for weekly 1 on 1 tutoring sessions with middle school students in collaboration with students' teachers
- Created worksheets to assess the progress of 40 students in mathematics

Head Undergraduate Research Mentor, Rivnay Lab

Department of Biomedical Engineering, Northwestern University

- Trained 3 undergraduate students to perform wet lab skills, data analysis, and design experiments
- Acquired 2 competitive grants (\$10,000) for students through the undergraduate research office

Teaching Experience

Teaching Assistant

Department of Biomedical Engineering, Northwestern University

- Collaborated with professor to design virtual class that would increase student engagement in a 50 person class
- Aided 3 student groups in refining and practicing their final presentations to which those groups were awarded an A on the project

Tutor/Reader

Baskin School of Engineering, UCSC

- Class tutored/graded: Linear Algebra, Ordinary Differential Equations, and Programming in C, Bioethics
- Prepared lesson plans for group tutoring sessions of up to 40 students

09/2017-present

06/2018-present

09/2017-present

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04/2020-06/2020

01/2015 - 06/2017

Honors and Awards		
• Fulbright Scholar Finalist (\$13,000)	09/2021-06/2022	
 American Scandinavian Association Fellow (\$22,790) 	09/2021-06/2022	
• Research Progress Award from BME Dept. (\$500)	05/2021	
Simpson Querry Institute Photo Contest Winner	12/2019	
• Conference Travel Grant from TGS (\$600)	09/2018	
• Koret Scholar (Research Funding \$3000)	01/2017-06/2017	
Tau Beta Pi Engineering Honors Society	05/2017-present	

Publications and Patents

- 1. Adam Marks Xingxing Chen, Ruiheng Wu, **Reem B. Rashid**, Wenlong Jin, Bryan D. Paulsen, Maximilian Moser, Xudong Ji, Sophie Griggs, Dilara Meli, Helen Bristow, Nicola Gasparini, Simone Fabiano, Jonathan Rivnay and Iain McCulloch. "Synthetic nuances to maximize n-type organic electrochemical transistor and thermoelectric performance in fused lactam polymer." *Journal of the American Chemical Society* (2022).
- Reem B. Rashid[†], Austin M. Evans[†], Lyndon A. Hall, Raghunath R. Dasari, Seth R. Marder, Deanna M. D'Allesandro, William R. Dichtel, Jonathan Rivnay. "A Semiconducting Two-dimensional Polymer as an Organic Electrochemical Transistor Active Layer." *Advanced Material* (accepted)(2022).
- Zachary S. Parr, Jorge Borges-González, Reem B. Rashid, Karl J. Thorley, Dilara Meli, Bryan D. Paulsen, Joseph Strzalka, Jonathan Rivnay, and Christian B. Nielsen. "From pto n-Type Mixed Conduction in Isoindigo-Based Polymers through Molecular Design." *Advanced Materials*: 2107829 (2022).
- Reem B. Rashid[†], Xudong Ji[†], and Jonathan Rivnay. "Organic electrochemical transistors in bioelectronic circuits." *Biosensors and Bioelectronics* 190 (2021): 113461.
- Reem B. Rashid, Weiyuan Du, Sophie Griggs, Iuliana P. Maria, Iain McCulloch, and Jonathan Rivnay. "Ambipolar inverters based on cofacial vertical organic electrochemical transistor pairs for biosignal amplification." *Science advances* 7, no. 37 (2021): eabh1055.
- 6. Jonathan Rivnay, **Reem B. Rashid**, Robert J. Ciechowski. "Vertical Organic Electrochemical Transistor Pairs" *U.S Patent App*, Filed:3/5/21 (Patent application submitted awaiting issuance)
- Chen, Xingxing, Adam Marks, Bryan D. Paulsen, Ruiheng Wu, Reem B. Rashid, Hu Chen, Maryam Alsufyani, Jonathan Rivnay, and Iain McCulloch. "N-type Rigid Semiconducting Polymers Bearing Oligo (Ethylene Glycol) Side Chains for High Performance Organic Electrochemical Transistors." *Angewandte Chemie International Edition* (2020).
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Mode Organic Electrochemical Transistors." *Advanced Electronic Materials* 6, no. 6 (2020): 2000215.

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- Reem B. Rashid, Robert J. Ciechowski, and Jonathan Rivnay. "Self-aligned, laser-cut organic electrochemical transistors." *Flexible and Printed Electronics* 5, no. 1 (2020): 014007.
- 11. Flagg, Lucas Q., Connor G. Bischak, Jonathan W. Onorato, Reem B. Rashid, Christine K. Luscombe, and David S. Ginger. "Polymer crystallinity controls water uptake in glycol side-chain polymer organic electrochemical transistors." *Journal of the American Chemical Society* 141, no. 10 (2019): 4345-4354.
- Parr, Zachary S., Roman Halaksa, Peter A. Finn, Reem B. Rashid, Alexander Kovalenko, Martin Weiter, Jonathan Rivnay, Jozef Krajcovic, and Christian B. Nielsen. "Glycolated Thiophene-Tetrafluorophenylene Copolymers for Bioelectronic Applications: Synthesis by Direct Heteroarylation Polymerisation." *ChemPlusChem* (2019).

Oral and Poster Presentations

1.	Asilomar Bioelectronics Symposium, Pacific Grove, CA	09/2018
2.	Biomedical Engineering Department Recruitment Day, Evanston, IL	02/2018,2019
3.	Biomedical Engineering Department Research Day, Chicago, IL	05/2019, 2021
4.	Fall MRS Conference, Virtual	12/2020

Skills

• AutoCAD, microfabrication, soft lithography, LabView, transistor/semiconductor physics, PCB design (Eagle)