

Toward Ideal Biointerfacing Electronics Using Organic Electrochemical Transistors

Peiyun Li and Ting Lei*

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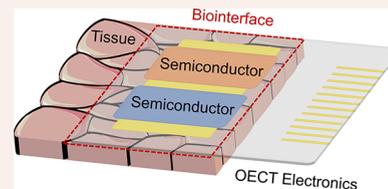
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CONSPPECTUS: The biointerface between biological tissues and electronic devices serves as a medium for matter transport, signal transmission, and energy conversion. However, significant disparities in properties, such as mechanical modulus and water content, between tissues and electronics, present a key challenge in bioelectronics, leading to biointerface mismatches that severely impact their performance and long-term stability. Organic electrochemical transistors (OECTs), fabricated with soft, hydrophilic organic semiconductors, offer unique advantages, including low operating voltage, high transconductance, and compatibility with aqueous environments. These attributes position OECTs as promising candidates for ideal biointerfaces. As neural probes, OECTs have demonstrated superior biocompatibility and signal detection capabilities compared to conventional metal electrodes and inorganic semiconductors. Despite these advantages, the applications of OECT as biointerfaces remain constrained by several limitations, including limited performance, poor stability, mismatches among p-type, n-type, and ambipolar semiconductors, relatively high Young's modulus, and unsatisfactory biointerfacial properties.



In this Account, we summarize our group's efforts to improve both the electronic and biointerfacial properties of OECTs, encompassing structure–property relationship studies, device optimization/fabrication, and biointerface enhancement. To elucidate the structure–property relationship, we explored the material design strategies and device optimization approaches for high-performance OECTs, highlighting the critical role of doped state properties in the OECT system. Recognizing the unique characteristics of OECTs, we designed hydrophilic polymer backbones to replace conventional neutral ones. These hydrophilic ionic backbones foster strong intermolecular interactions, resulting in improved operational stability. Additionally, we demonstrate that constructing high-spin polymers enables the development of high-performance, balanced ambipolar materials. Based on these materials innovations, we advanced fabrication methods of OECT-based logic circuits and fiber-based OECTs, realizing complementary and ambipolar logic circuits, as well as wearable fabric-based biosensors. Finally, we integrated the exceptional biointerface properties of hydrogels with organic semiconductors, pioneering semiconducting hydrogels that exhibit outstanding mechanical, electrical, and biointerfacial properties. These materials enable efficient *in vivo* amplification of electrophysiological signals. The concept and realization of semiconducting hydrogels redefine the scope of OECTs and hydrogel electronics, providing a novel approach to ideal biointerfaces. We hope that the perspectives shared in this Account will inspire the development of next generation bioelectronic devices with enhanced biointerface compatibility and expanded functionalities.

1. INTRODUCTION

Bioelectronic devices are at the intersection of biology and electronics, designed to monitor, modulate, or mimic biological processes, ranging from simple biosensors to complex neural interface.^{1,2} Some bioelectronic devices continuously monitor physiological parameters, for example, glucose levels, heart rate, and neural activity.³ Devices like pacemakers and deep brain stimulators can regulate biological functions by delivering electrical impulses to specific tissues.⁴ Additionally, bioelectronic implants can treat chronic diseases by stimulating tissues or nerves to restore normal function.⁵ The rapid development of bioelectronic devices is driven by the need for advanced diagnostic tools and effective treatments, imposing stringent requirements.⁶ High precision in monitoring and modulation is essential to achieve desired outcomes. Devices must be as small and minimally invasive as possible to reduce discomfort and risk during implantation.⁵ Long-term stability and reliability

are crucial, especially for implants that need to function for years. Materials must be compatible with biological tissues to avoid immune reactions and ensure long-term functionality.

Among these needs, achieving optimal biointerfaces is paramount. There is a huge mismatch between electronics and biological tissue, including water content, mechanical modulus, and ion permeability.⁷ Traditional inorganic materials, including metal and silicon, are rigid, dry, and can conduct electrons.⁸ In contrast, biological tissues are typically

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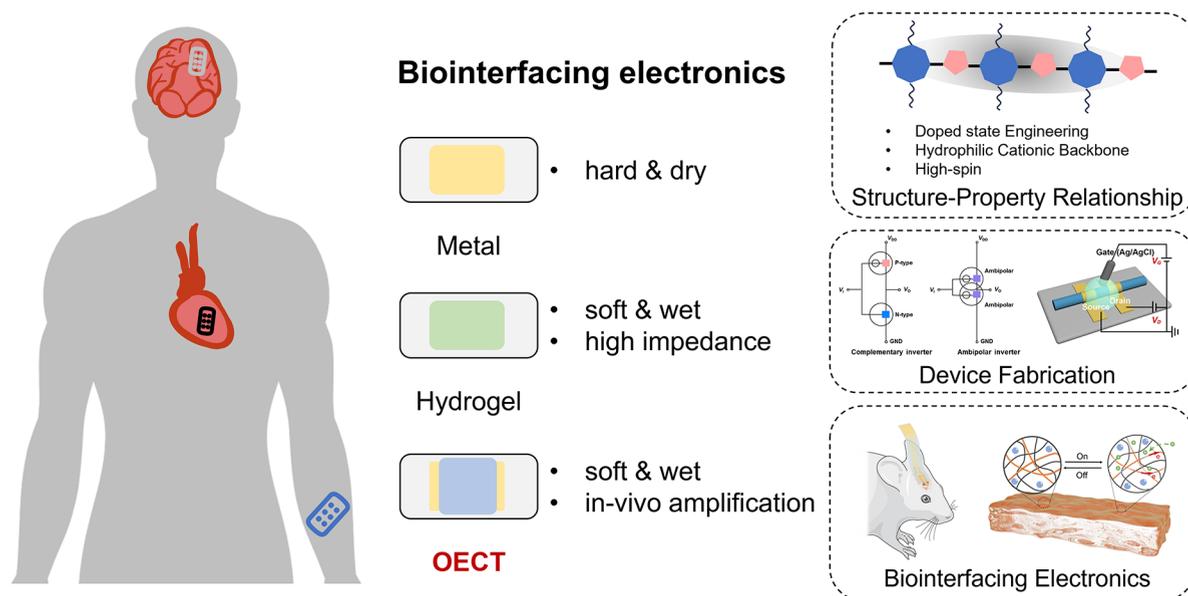


Figure 1. Schematic diagram of bioelectronic devices (left), characteristics of several types of biointerfacing devices (middle), and three major parts in this Account (right). Adapted with permission from ref 19. Copyright 2024 Wiley-VCH Verlag GmbH & Co. Adapted with permission from ref 20. CC BY-NC-ND 4.0. Adapted with permission from ref 21. Copyright 2024 American Association for the Advancement of Science.

soft, hydrous, and can conduct ions. This inherent disparity makes organic materials and electronics intrinsically more compatible with tissues than their inorganic counterparts.⁹ With their versatile structures, organic materials can be used as conductors, semiconductors, and insulators, enabling diverse device functionalities. To date, most front-end bioelectronic devices, such as metal electrodes and hydrogel electrodes,¹⁰ are passive, recording signals without amplification. The small amplitudes of many biosignals limit the signal-to-noise ratio (SNR) of these passive devices. Active devices, such as those based on transistors and logic circuits, are more desirable since they can not only record but also amplify and regulate signals, enhancing SNR and expanding functionalities.

Organic electrochemical transistor (OECT) is a class of thriving active bioelectronic devices that can transduce and amplify ionic signals to electronic signals.¹¹ Unlike other transistors, OECTs operate in aqueous environments with high sensitivity and low operation voltage (usually <0.8 V). The organic semiconductors in OECTs are usually soft, hydrated, and ion-permeable. They can be exposed and directly in contact with biological tissues and have great potential to become ideal biointerfaces.¹² Although OECTs possess notable advantages in bioelectronics, their performance and interfacial properties require further optimization. The lack of effective design strategies and clear structure–property relationships have hindered performance improvement, particularly for n-type and ambipolar devices.^{13,14} Significant mismatches between p-type and n-type semiconductors and the scarcity of high-performance ambipolar semiconductors present a challenge to constructing OECT logic circuits.¹⁵ These limitations hinder the realization of bioelectronic devices with complex functionalities, low power consumption, and stable operation.¹⁴ The mechanical properties of OECT materials, also known as organic mixed ionic-electronic conductors (OMIECs), are relatively soft and can operate in water compared to traditional inorganic materials; however, their mechanical properties still differ significantly from biological tissues.^{16,17} This discrepancy may cause poor

adhesion, rejection, or damage during contact with tissues.¹⁸ Therefore, realizing better biointerfaces for OECTs is also essential.

This Account highlights our group's efforts over the past few years in advancing OECT materials and devices for optimal biointerfacing electronics (Figure 1). We summarize design strategies and the structure–property relationships of OECT materials, including neutral backbone polymers, hydrophilic cationic backbone polymers, and high-spin polymers. Following this, we introduce the fabrication techniques for OECT electronics, focusing on applications such as logic circuits and fiber OECTs. Lastly, we present semiconducting hydrogels that combine the electronic features of organic semiconductors with the mechanical and biological properties of hydrogels. These developments represent significant steps toward achieving ideal biointerface electronics.

2. EXPLORING STRUCTURE–PROPERTY RELATIONSHIPS

The first OECT device dated back to 1984, using polypyrrole as the semiconductor.²² Over the past two decades, poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) is the most widely used OECT material.²³ In recent years, researchers have devoted great efforts to exploring structure–property relationships and developing new material systems. These advancements have enhanced the understanding of OECT mechanisms and led to substantial improvements in device performance.¹⁵

2.1. Engineering p-Type and n-Type Polymers with Neutral Backbones

Early p-type OECT materials were based on polythiophene systems, achieving good performance.²⁴ However, compared to polythiophene systems, donor–acceptor (D-A) conjugated polymers often exhibit higher carrier mobility due to their excellent backbone planarity, low energetic disorder, and strong interchain interactions, making them promising candidates for enhancing OECT performance.²⁵ Despite

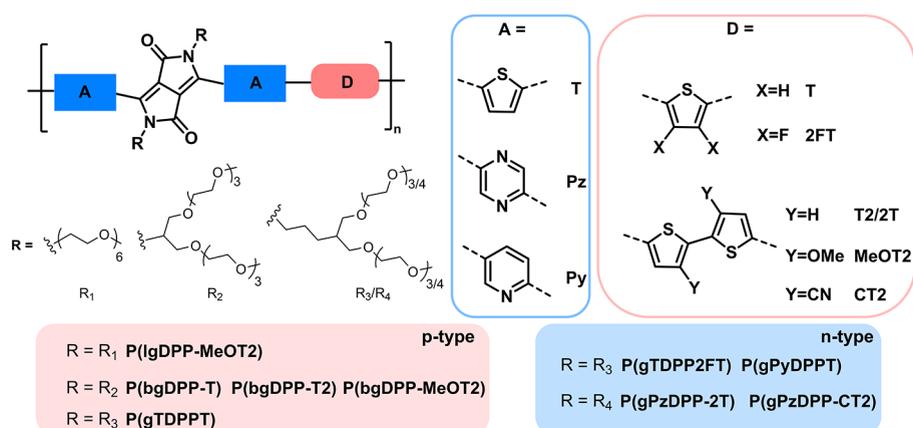


Figure 2. Chemical structures of DPP-based conjugated polymers developed in our group. A determines the type of DPP, including TDPP, PzDPP, and PyDPP. D stands for the donor unit. R is the side chain.

these advantages, early D–A polymers did not demonstrate superior OECT performance. To address this, our group systematically investigated the structure–property relationships of D–A polymers (Figure 2).

First, we chose diketopyrrolopyrrole (DPP) as the acceptor unit to construct D–A polymers, since DPP is one of the most widely used building blocks in organic field-effect transistors (OFETs), largely due to its good planarity and high carrier mobility.²⁵ We evaluated the effects of the donors, side chains, polymerization conditions, and processing solvents.²⁶ The strong electron-donating moiety, MeOT2, increases the HOMO level, lowers the threshold voltage, and exhibits high transconductance. Compared to the linear side chain, the branched ethylene glycol (EG) side chain can improve solubility and facilitate ion transport. Besides, we found that the catalysts and solvents of Stille polymerization should also be optimized for EG side chains to guarantee high molecular weights. We demonstrated for the first time that a polar solvent, hexafluoroisopropanol (HFIP), promotes polymer disaggregation in solution and enhances molecular packing in films for EG side-chain polymers. With these optimizations, the p-type OECTs showed high performances (Table 1) with high mobility, μC^* values, and fast response times. Our findings on the complexity and systematic optimization of OECTs have since been corroborated by subsequent research.¹⁵

Based on our research on p-type materials, our group began to explore n-type polymers. Initially, following conventional wisdom in organic electronics, we assumed that a low lowest unoccupied molecular orbital (LUMO) energy level was critical for designing high-performance and stable n-type OECTs. Therefore, we chose strong electron-deficient pyrazine-flanked DPP (PzDPP)²⁷ as the acceptor and cyano-substituted bithiophene (CT2) (Figure 2) as the donor.²⁸ We also introduced side chains with a farther branching position to provide better molecular packing. Compared to P(gPzDPP-T2), the employment of the cyano (CN) group did lower the LUMO energy level of P(gPzDPP-CT2) and enhance its electron mobility. However, the overall performance is not satisfactory, and P(gPzDPP-CT2) only showed moderate performance with μC^* of $1.72 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ (Table 1).

A computational insight inspired us to reconsider the importance of the LUMO energy level for n-type OECT materials. Density function theory (DFT) calculations revealed that the polaron of P(gPzDPP-CT2) distributed more uniformly than P(gPzDPP-2T). The CN group helps the

Table 1. Summary of the OECT Performance of the Polymers in this Account^{20,21,26,28–30}

Materials	Polarity	μ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	μC^* ($\text{F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$)	V_{th} (V)
P(bgDPP-T)	p	1.6	6	−0.6
P(bgDPP-T2)	p	0.50	42	−0.57
P(lgDPP-MeOT2)	P	2.2	174	−0.87
P(bgDPP-MeOT2)	p	1.6	195	−0.33
P(gPzDPP-2T)	n	0.0016	0.22	0.56
P(gPzDPP-CT2)	n	0.019	1.72	0.32
P(gTDPPPT)	p	0.40	65.1	−0.62
P(gPyDPPT)	n	—	0.07	0.63
P(gTDPP2FT)	n	0.35	54.8	0.64
PNPD	p	0.0019	0.262	−0.67
PANDA2	n	0.33	62.3	0.47
P(PyV)	n	0.25	120	0.55
P(TII-T)	p	0.78	122.2	−0.10
	n	0.08	16.4	0.76
P(TII-2FT)	p	1.07	158.6	−0.39
	n	1.80	147.4	0.64
P(TII-2CT)	P	0.54	96.4	−0.44
	n	0.30	63	0.63

negative polaron distribute more on the thiophene units. This finding suggests that introducing electron-deficient units not only lowers the LUMO energy level but, more importantly, alters the polaron distribution. Inspired by this observation, we analyzed the relationship between performance and LUMO energy levels across various state-of-the-art n-type OECT polymers. Surprisingly, we found no clear correlation between these parameters. This led us to hypothesize that additional key factors, beyond LUMO energy level, influence the performance of n-type OECTs.

Our study began with a simple polymer structure, P(gTDPPPT), which has been demonstrated as a p-type material.²⁹ We systematically modified either the acceptor or donor unit by replacing thiophene with pyridine (Py) in the DPP or introducing two fluorine atoms on the thiophene (2FT) (Figure 2). Our results show that both P(gTDPP2FT) and P(gPyDPPT) exhibit n-type characteristics, but the μC^* of P(gTDPP2FT) reaches $54.8 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$, much higher than the $0.07 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ of P(gPyDPPT) (Table 1). Notably, both polymers have similar LUMO energy levels, suggesting

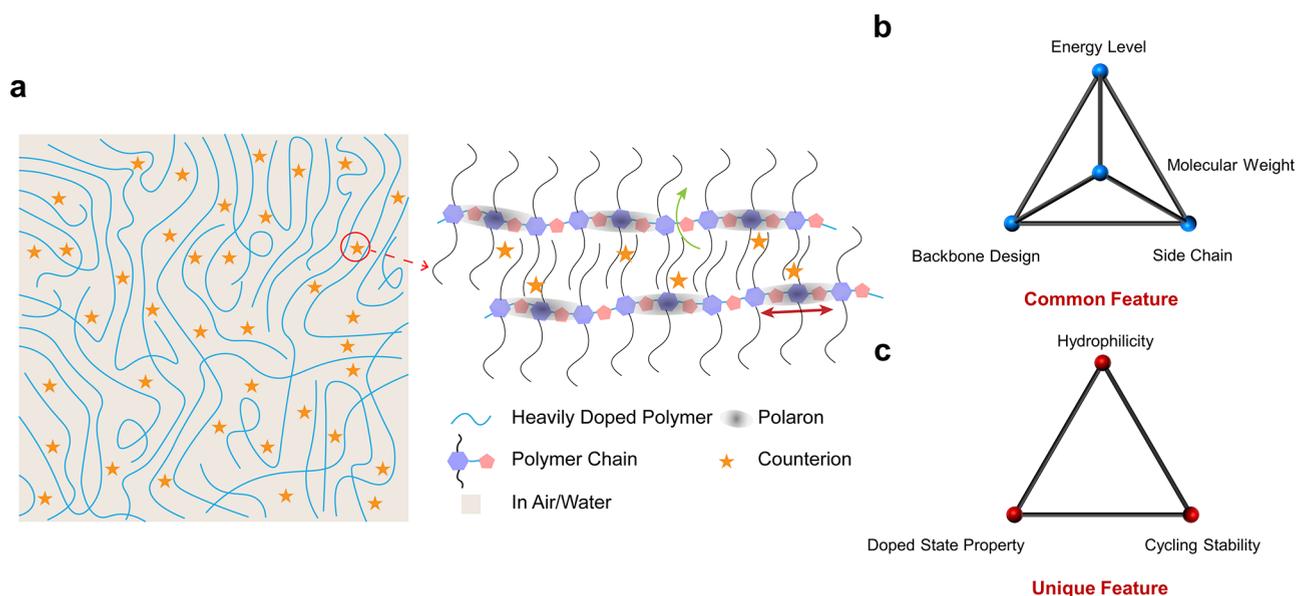


Figure 3. Structure–property relationships in OECT polymers. (a) Schematic diagram of an electrochemically doped OECT polymer system. (b) Summary of the common feature in organic semiconductor polymer design, including energy levels, backbone design, side chain, and molecular weight. (c) Summary of the unique feature in OECT polymer design, including hydrophilicity, doped state property and cycling stability.

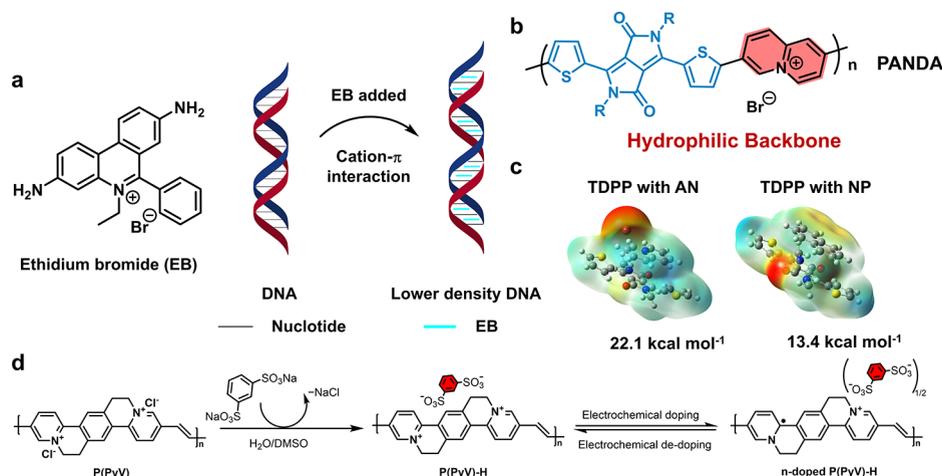


Figure 4. Design of OECT polymers with hydrophilic cationic backbones.³⁰ (a) Insertion of the cationic molecule, EB, into DNA strands, where cation- π interaction plays a major role. (b) Chemical structure of PANDA. (c) DFT-calculated intermolecular interactions between TDPP and AN or NP. (d) Chemical structure of the cationic polymer P(PyV), the dianion exchange reaction, and the electrochemical doping–dedoping processes. Adapted with permission from ref 30. Copyright 2023 Wiley-VCH Verlag GmbH & Co. Adapted with permission from ref 21. Copyright 2024 American Association for the Advancement of Science.

that the difference in performance cannot be attributed to their energy levels alone. Then, we explored the doped state properties of both polymers using DFT calculations. We demonstrated that introducing F atoms enhances the backbone planarity and stabilizes the conformation during electrochemical operation. Moreover, the molecular packing of P(TDPP2FT) becomes more ordered after electrochemical doping. Calculations of doped state properties, including electron energy, charge distribution, and conformation distribution, reveal the origin of the performance differences. P(gTDPP2FT) exhibits the largest energy difference between its neutral and negatively charged states among the three polymers, while P(gPyDPPT) shows the smallest. The negative charges delocalize along the P(gTDPP2FT) chain but localize in the DPP core of P(gPyDPPT). Additionally, the dihedral angles of P(gPyDPPT) remain large in both neutral

and doped states, while the backbone planarity of P-(gTDPP2FT) improves in its doped state compared to its neutral state. These experiments and calculations jointly emphasize the importance of understanding the doped state properties, such as polaron stability, charge distribution, backbone planarity, and conformation stability.

Compared with other organic electronic devices (e.g., OFETs, OPVs, and OLEDs), the semiconductors in OECTs operate in highly doped states, surrounded by ions and water molecules (Figure 3a). This environment not only influences their structure–performance relationship with the conventional paradigms of organic semiconductors but also introduces distinctive characteristics. Our investigations reveal that OECT polymers share several common features with OFET polymers, including energy level, backbone design, side-chain type/length, and molecular weights/distributions (Figure 3b).

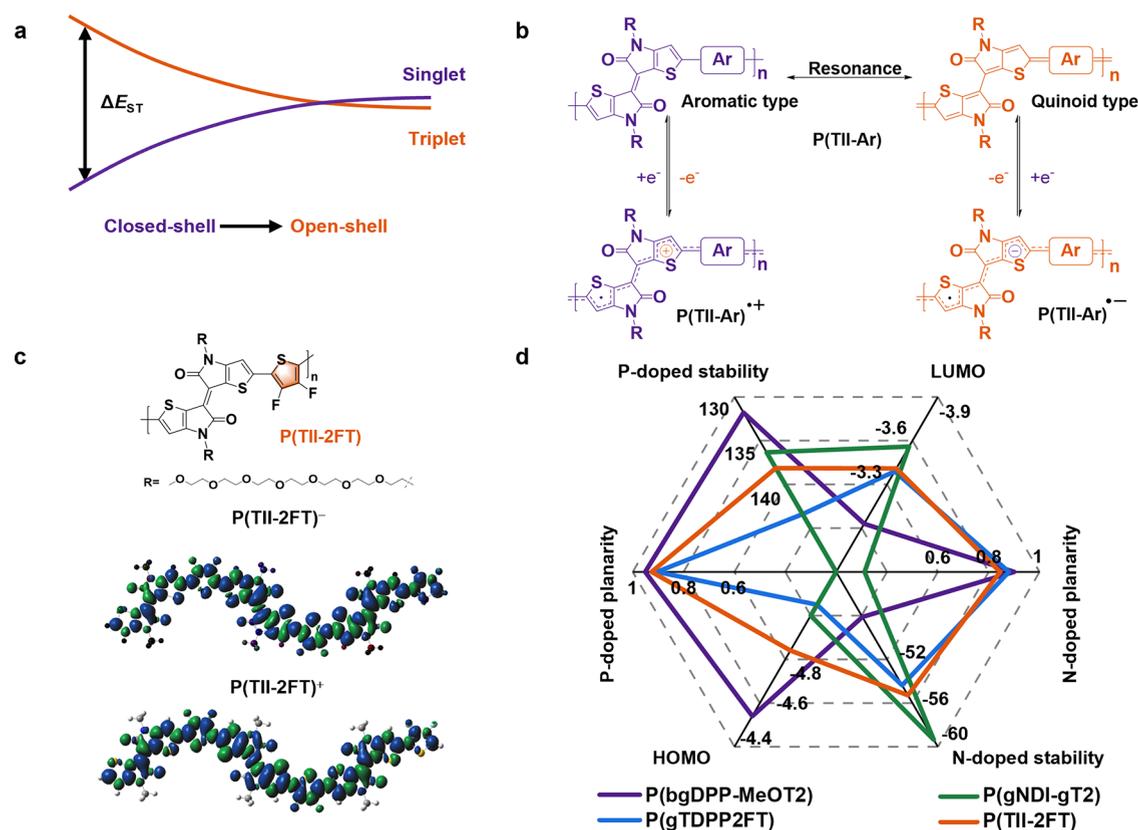


Figure 5. High-spin conjugated polymer design for ambipolar OECT materials.²⁰ (a) Schematic illustration of the transition from a closed-shell to an open-shell state as the energy gap between the singlet and the triplet state decreases. (b) Resonance structures and the amphoteric redox behaviors of P(TII-Ar), encompassing both aromatic type (closed-shell) and quinoidal type (open-shell) structures. The “Ar” represents the comonomers, such as 2FT. (c) Spin density distribution of the positively or negatively charged P(TII-2FT). (d) Comparison of the six parameters affecting the device performance of the four polymers. Adapted with permission from ref 20. CC BY-NC-ND 4.0.

However, beyond these characteristics, special attention must be given to the unique aspects arising from mixed ionic-electronic transport, including hydrophilicity, doped state properties, and redox cycling stability (Figure 3c). We believe that computational screening of polymers based on their doped state properties before synthesis could greatly reduce the trial-and-error cost in OECT material development.

2.2. Hydrophilic Cationic Backbone Polymers

The polymer backbone typically facilitates carrier transport, while the side chain ensures solubility and supports ion transport. In conventional conjugated polymers, the backbones are hydrophobic, which works well in solid-state electronics. However, biological systems are rich in ionic species and function in aqueous environments. Unlike traditional organic semiconductors, biomimetic design should be considered for OECT materials. We propose that hydrophilic conjugated backbones could be interesting. Furthermore, conventional conjugated polymers processed with organic solvents may pose biological toxicity risks due to residual solvent traces, rendering them unsuitable for biointerfacing electronics. To address these challenges, we developed two innovative polymer structures featuring hydrophilic cationic backbones and systematically investigated their unique properties.

Inspired by the DNA dyeing process, during which ethidium bromide (EB) forms strong cation- π interactions with nucleotides and insert into DNA strands (Figure 4a), we hypothesized that cationic units could also form strong π - π interactions, thereby benefiting carrier transport.³⁰ To achieve

cationic backbones, we designed a novel cationic building block, 4a-azonia-naphthalene (AN) bromide (Figure 4b). AN is an isoelectronic analogue of naphthalene (NP) but exhibits significantly stronger electron-withdrawing properties. We synthesized two polymers based on TDPP, incorporating AN and NP as the comonomers, respectively, and named them PANDA and PNPd (Figure 4b). While TDPP with EG side chains and AN are water-soluble, PANDA is not, suggesting the strong intermolecular interactions between its repeating units. Additionally, the binding energy (Figure 4c), rotational barrier, and planarity of TDPP-AN were found to be superior to those of PNPd. Nuclear magnetic resonance experiments further confirmed strong cation- π interactions between TDPP and AN. Moreover, the π - π distance in PANDA is significantly reduced due to enhanced intermolecular interactions compared with PNPd. Unexpectedly, PANDA showed no mass change during electrochemical reduction, and its morphology remains stable during water uptake and ion injection/extraction processes. Compared with PNPd, PANDA demonstrates excellent n-type OECT performance, including high μC^* of $62.3 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ (Table 1), and remarkable stability during long-time cycling. The incorporation of the hydrophilic cationic unit enhances the capacitance of PANDA and the cation- π interaction enables high carrier mobility in the highly doped state. Although the hydrophilic cationic backbone offers many advantages, its precise role and influence on device performance remain incompletely understood, warranting further characterization and investigation in the future.

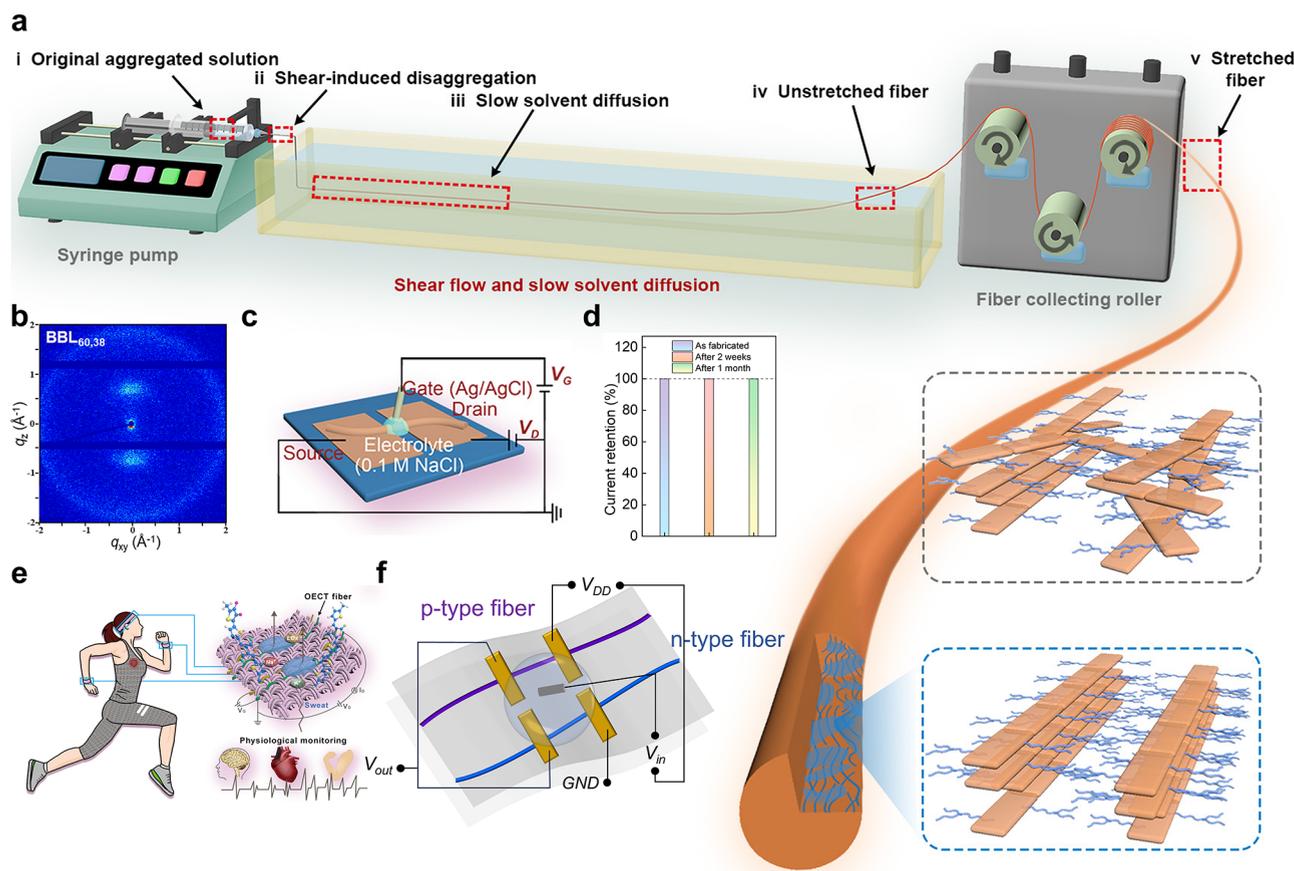


Figure 6. Logic circuits based on complementary and ambipolar OECTs. (a) Schematic of the complementary devices, including transistors, inverters, NAND and NOR gates. (b) Flexible array with 300×300 ambipolar inverters attached to the back of a hand. Scale bar: $100 \mu\text{m}$. (c) Representative voltage transfer characteristic of the ambipolar inverter based on P(TII-2FT) at various supply voltages and the associated voltage gains. (d and e) Corresponding voltage input and output characteristics of the NAND and NOR gates based on P(IgDPP-MeOT2) and P(PyV)-H. Adapted with permission from ref 21. Copyright 2024 American Association for the Advancement of Science. Adapted with permission from ref 20. CC BY-NC-ND 4.0.

Encouraged by the success of PANDA in OECTs and the unique features of cationic backbone polymers, we sought to explore all-cationic conjugated polymers without relying on conventional building blocks such as TDPP. Thus, we designed a novel polymer, P(PyV) (Figure 4d), inspired by previous work.³¹ P(PyV) is a water-soluble cationic polymer devoid of side chains. The incorporation of the double bond enhances the backbone planarity. We also optimized synthetic methods to increase the yield of the ring-closing reaction and minimize defects. However, due to its water solubility, the polymer film gradually dissolves in a 0.1 M NaCl aqueous solution, leading to performance degradation. Addressing the challenge of stabilizing P(PyV) in aqueous environments is a critical next step.

We found that the counteranions (Cl^-) of P(PyV) can be exchanged with 1,3-benzenedisulfonate anions, forming an electrostatically cross-linked network (Figure 4d). This aqueous polymer network is a typical hydrogel and is therefore named P(PyV)-H. The single-network hydrogel P(PyV)-H demonstrates exceptional n-type OECT performance, achieving a high μC^* of $120 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ (Table 1), ranking among the best-performing n-type OECT materials reported to date. P(PyV)-H exhibits a remarkable volumetric capacitance of approximately 485 F cm^{-3} , attributed to its cationic backbone and hydrogel network structure. Upon electrochemical doping, the carrier density reaches 1.75×10^{21}

cm^{-3} , while maintaining excellent electron mobility of $0.25 \text{ cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$. Furthermore, the cationic backbone offers the potential for constructing multineckwork hydrogels, enabling superior biointerfacing properties, which will be discussed in greater detail in subsequent sections.

2.3. Design Strategy for Ambipolar Polymers

In addition to p-type and n-type OECT materials, ambipolar materials are highly valuable for constructing logic circuits, as they significantly simplify fabrication processes.³² However, the performance and stability issues of ambipolar OECT materials remain suboptimal, largely due to the lack of effective design strategies. To address these challenges, we conducted an in-depth exploration of the structure–property relationships in ambipolar materials,²⁰ aiming to provide a comprehensive understanding and guide their development.

As discussed above, the doped state stability and efficient polaron delocalization are critical for high-performance OECTs. We hypothesize that high-spin conjugated polymers, characterized by rich redox behaviors and two electrons occupying two nearly degenerate frontier orbitals capable of reversible electron gain or loss, could achieve stable p-doped and n-doped states while ensuring balanced hole/electron injection and transport behaviors³³ (Figure 5a). To validate this, we choose thienoisindigo (TII) as the polymer building block, owing to its high mobility and strong high-spin

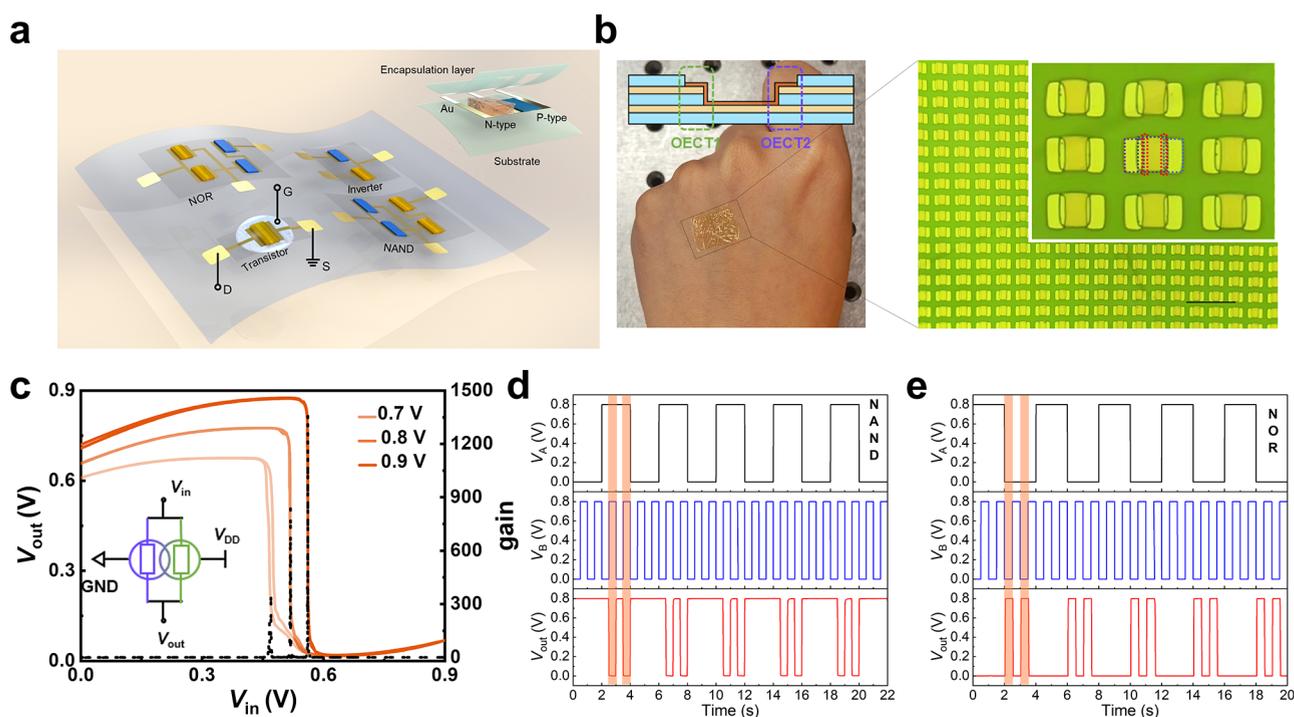


Figure 7. Polymer fibers fabrication and their OECT devices.^{19,42} (a) Schematic illustration of the continuous production of semiconducting polymer fibers using the flow-enhanced crystallization (FLEX) approach. (b) 2D-WAXS pattern of the BBL fibers. (c) Schematic of the fiber-based OECTs. (d) Current retention of a BBL fiber OECT after storing in ambient for up to 1 month. (e) Schematic diagram of the potential wearable applications of the semiconducting polymer fiber OECTs. (f) Diagram of the fiber-based complementary OECT inverters. Adapted with permission from ref 42. CC BY-NC 4.0. Adapted with permission from ref 19. Copyright 2024 Wiley-VCH Verlag GmbH & Co.

characteristics, which facilitates stable ambipolar charge transport after doping (Figure 5b). We designed and synthesized polymer P(TII-2FT) (Figure 5c), featuring strong electron paramagnetic resonance (EPR) signals at room temperature and a triplet high-spin ground state.

For P(TII-2FT), polarons are uniformly distributed across the trimers in both positively and negatively charged states (Figure 5c). It also exhibits superior backbone planarity in doped states. We concluded six key parameters, including HOMO and LUMO energy levels, polaron stability and backbone planarity after oxidation and reduction (Figure 5d). P(TII-2FT) demonstrated remarkable and balanced ambipolar OECT performance, with a p-type μC^* of $158.6 \text{ F cm}^{-1} \text{ V}^{-1}$ and an n-type μC^* of $147.4 \text{ F cm}^{-1} \text{ V}^{-1}$ (Table 1). Furthermore, the devices exhibited exceptional stability, with high current retention after long-term cycling in ambient and negligible performance changes after two months of air storage. These results validate the high-spin design strategy as an effective approach for developing high-performance and stable ambipolar OECT materials. A full analysis of structure–property relationships for all novel OECT materials is beyond the scope of this review, we recommend consulting recent comprehensive reviews for better comparison.^{14,34}

3. FABRICATION OF OECT-BASED ELECTRONIC DEVICES

3.1. OECT-Based Logic Circuits

The processing methods for fabricating individual OECT devices are well-established, including photolithographic patterning, sacrificial layer lift-off, and various printing techniques.³⁵ However, the fabrication of OECT-based logic circuits is more complicated due to the need for precise lead

arrangement and the patterning of multiple organic semiconductors, which are often sensitive to organic solvents and photoresists. Compared to single load-diode type circuits, p-n complementary logic circuits offer significant advantages, such as lower power consumption and higher gain.³⁶ Nevertheless, the processing of complementary circuits, which requires integrating both p-type and n-type semiconductors, adds further complexity to the manufacturing process (Figure 6a). Ambipolar materials, capable of transporting both holes and electrons, provide a promising solution by simplifying manufacturing processes, enhancing device integration, and reducing the overall footprint of logic circuits³² (Figure 6b).

The fabrication of complementary OECT logic circuits includes the patterning of p-type and n-type semiconductors. In our lab, we pattern conventional p-type and n-type OECT polymers, such as P(IgDPP-MeOT2) and P(gTDPP2FT), by a fluoropolymer-protected photolithography and dry-etching technique. For the water-soluble polymer P(PyV), we employed a shadow mask-based spray-coating and ionically cross-linking method (Figure 6a). The inverter based on P(IgDPP-MeOT2) and P(PyV) shows a high gain of 250 V/V and a low power consumption of less than 1 mW. As for the ambipolar inverters based on P(TII-2FT), the semiconducting layer was patterned using a parylene lift-off process (Figure 6b). These inverters achieved a remarkable gain of 809 V/V at a voltage step size of 0.1 mV (Figure 6c), attributed to the balanced and stable electron/hole transport of P(TII-2FT). The NAND and NOR gates, constructed using four transistors, can be fabricated by similar methods as the inverters and exhibit excellent logic-switching behaviors (Figure 6d). Although some researchers have proposed novel methods for fabricating internal-gate OECTs³⁷ and completely vertical

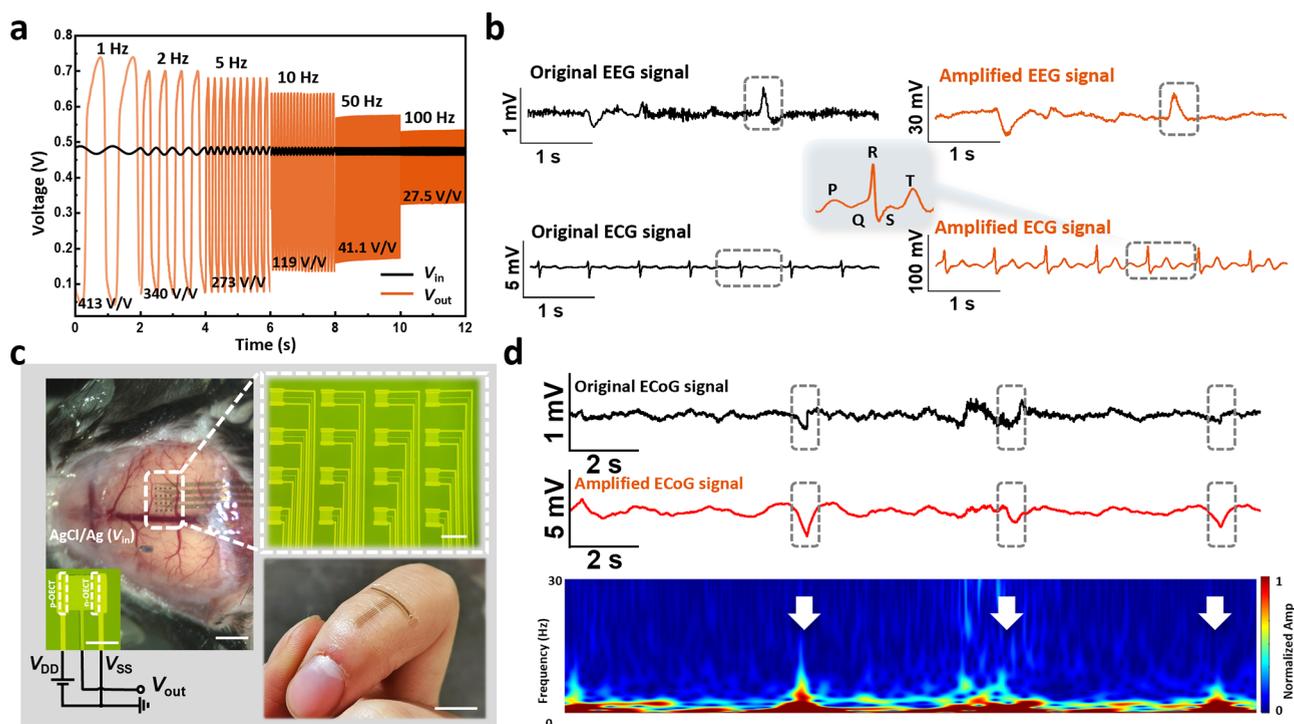


Figure 8. Semiconducting polymer biointerface based on an ambipolar polymer, P(TII-2FT). (a) Dynamic response of the OECT amplifier using small sinusoidal signals at different frequencies. (b) Schematic illustration of the ambipolar OECT amplifier for recording EEG and ECG signals. (c) Photograph of the in vivo ECoG recording and photograph of an ultrathin (10 μm) and flexible amplifier array attached to a finger joint. (d) ECoG signals of the cortex in vivo recorded by a conventional metal electrode or by the P(TII-2FT) amplifier. Adapted with permission from ref 20. CC BY-NC-ND 4.0.

OECTs,³⁸ we focused on planar OECT devices, which maximize the exposure of the semiconductors, making them particularly advantageous for bioelectronic interface applications, a topic that will be discussed in detail later.

3.2. Fiber-Type OECTs and Sensors

Multilayer fiber OECTs have been well explored and exhibit a structure similar to that of thin-film devices, with a cylindrical fiber as the substrate. These devices benefit from well-established processing techniques, ensuring broad material compatibility and delivering performance comparable to that of the thin-film OECTs.³⁹ However, reducing the OECT channel area while maintaining high transconductance poses a significant challenge, particularly for developing miniaturized implantable biosensors. Increasing film thickness helps keep high transconductance, but fabricating homogeneous thick films (>1 μm) remains difficult, especially for conjugated polymers with low solubility and requiring high-boiling-point solvents. Solid-state semiconducting fibers provide a promising solution, as they can reduce the channel size while maintaining a thick and uniform shape. In addition, the three-dimensional micron scale of cells makes micron-scale semiconducting fibers an ideal candidate for creating biologically compatible interfaces.⁴⁰ Fibers with favorable mechanical properties can also be integrated into textiles, enabling a wide range of wearable or implantable bioelectronic devices.⁴¹ However, fabricating robust semiconducting polymer fibers presents considerable challenges. Research on processing techniques for these fibers is still limited, highlighting a critical need for innovation in this area to unlock their full potential.

Our group developed a flow-enhanced crystallization (FLEX) approach for continuously producing tough con-

jugated polymer fibers for OECTs using the wet spinning technique (Figure 7a).^{19,42} By carefully selecting the solvent for OECT polymers, optimizing the coagulation bath conditions, and fine-tuning spinning parameters, we successfully achieved the continuous spinning of various OECT polymers, including p-type P(IgDPP-MeOT2), n-type P(gTDPP2FT), and n-type ladder-type polymer BBL. Unlike the traditional wet-spinning methods that usually require highly concentrated polymer solutions, we found that lowering the OECT polymer solution concentration to provide adequate space for polymer disaggregation, utilizing the strong extensional and shear flows in the spinning needle, replacing the fast bidirectional antisolvent flow to a slower unidirectional flow, and employing poststretching can greatly enhance polymer chain alignment and crystallinity (Figure 7a,b). Note that the ladder-type polymer, BBL, which can only be dissolved in high-boiling-point strong acids, like methanesulfonic acid (MSA), has been challenging to process into thick films (>100 nm). However, our wet-spinning approach enabled the fabrication of BBL fibers with thicknesses over 10 μm . These fibers show remarkable mechanical properties, including high modulus and high toughness, due to their enhanced polymer chain alignment and crystallinity.

Based on these fibers, we fabricated high-performance OECT devices (Figure 7c). These fiber OECTs show outstanding area-normalized transconductance ($g_{m,A} = g_m/WL$). Among them, the BBL fibers showed significantly enhanced μC^* than their thin film counterparts. More importantly, the BBL fiber OECTs showed negligible current degradation after 1500 on–off switching cycles and one month of storage in ambient (Figure 7d). These results surpass the stability of BBL's thin-film devices and other n-type polymers,

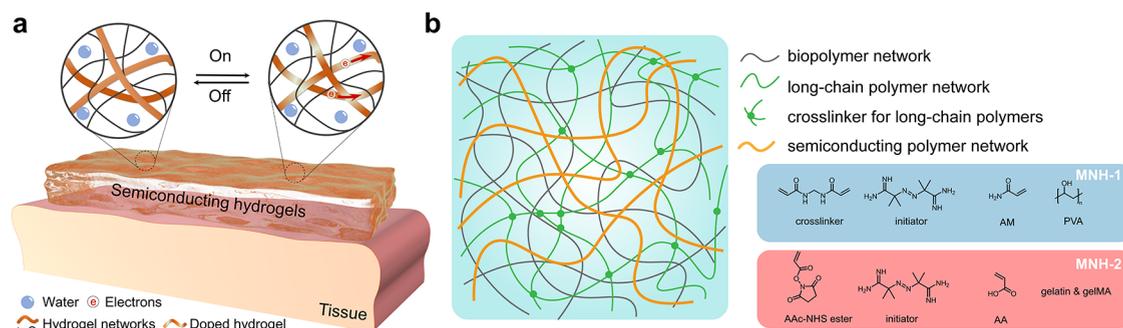


Figure 9. Design of the n-type semiconducting hydrogels.²¹ (a) Conceptual diagram of the working mechanism of a semiconducting hydrogel. (b) Schematic illustration and chemical structures of the multiple network hydrogels: MNH-1 and MNH-2. Adapted with permission from ref 21. Copyright 2024 American Association for the Advancement of Science.

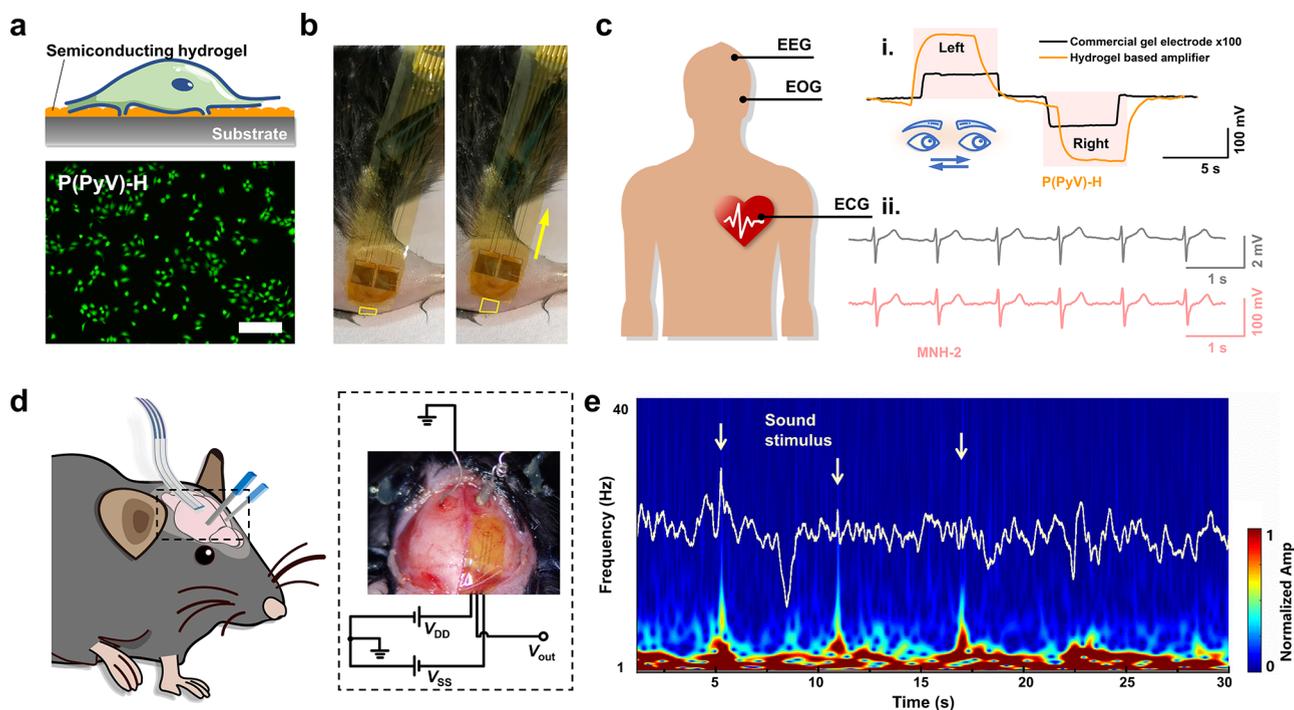


Figure 10. Biointerfacial properties of semiconducting hydrogel-based OECS.²¹ (a) Live/dead staining of HaCaTs. (b) Photographs of OECS devices based on MNH-2 attached to a mouse leg. (c) EOG and ECG signals acquired by the hydrogel amplifiers. (d) Photograph of in vivo ECoG recording and schematic of the electrical wiring. (e) Time domain ECoG signals obtained by the P(PyV)-H-based flexible amplifier and its time-frequency analysis diagram. Adapted with permission from ref 21. Copyright 2024 American Association for the Advancement of Science.

suggesting that fibers could provide better stability due to enhanced polymer chain alignment and tight molecular packing. When used as biosensors, the fiber-based OECSs demonstrated high sensitivity and good selectivity (Figure 7e). We also achieved fiber-based logic circuits using both p-type and n-type OECS fibers (Figure 7f). We believe that fiber-based OECSs hold great potential for exhibiting unique features and applications, particularly in wearable and implantable bioelectronics.

4. BIOINTERFACING ELECTRONICS

Building on the exploration of material structure–property relationships in materials and advancements in device fabrication methods discussed above, this part delves into the development of two types of biointerfacing electronics: semiconducting polymers and semiconducting hydrogels.

4.1. Semiconducting Polymer Biointerface

As previously discussed, ambipolar materials offer significant advantages for constructing logic circuits due to their simplicity and high integration potential. Leveraging P(TII-2FT), we fabricated a vertical-type inverter for on-site biosignal amplification, which effectively amplified sinusoidal small signals in the frequency range of 1 to 100 Hz (Figure 8a). These amplifiers were subsequently used as biointerfacing electronics to collect and amplify various electrophysiological signals. In electrocardiograph (ECG) and electroencephalogram (EEG) tests, our device demonstrated significantly enhanced SNR compared to conventional metal electrodes, with signal intensity amplified over ten times (Figure 8b). Furthermore, highly integrated flexible devices were used to record weak electrocorticograms (ECoG) of mice (Figure 8c). However, due to the high-frequency nature of ECoG signals and the complexities of the biological interface environment, the devices exhibited less pronounced amplification capabilities

in vivo compared to in vitro tests (Figure 8d). These findings highlight the challenges posed by mismatched interfaces between semiconducting polymers and biological tissue, which critically impact the performance of bioelectronic devices and warrant further optimization.

4.2. Semiconducting Hydrogel Biointerface

To overcome the huge mechanical and chemical mismatch between semiconducting polymer and tissues, we turn our attention to hydrogels. Hydrogels are three-dimensional, hydrophilic polymer systems containing large amounts of water, which have been widely used in drug delivery, tissue engineering, and various biological applications.⁴³ Due to their similar mechanical properties, water content, and ion permeability between hydrogels and biology tissues, hydrogels provide excellent biointerfacial properties, making them well-suited for biological integration.⁷ However, traditional hydrogels are ionic conductors or require blending with conductive materials to achieve electronic conductivity. They are not inherently semiconductors, hampering their potential applications in complex electronics that require semiconductor functions such as switching, amplification, rectification, and logic operations.⁴⁴

To create a semiconducting hydrogel (Figure 9a), we employed electrostatic cross-linking of the water-soluble cationic polymer semiconductor P(PyV), yielding a stable hydrogel named P(PyV)-H. Beyond forming single network hydrogels, the water solubility of P(PyV) enables seamless integration with conventional hydrogels to construct multiple network hydrogels (MNHs). These MNHs provide tunable mechanical properties and customizable biological functions. We demonstrated this versatility using two hydrogel systems with primary components of polyacrylamide (PAM) and poly(acrylic acid) (PAA), respectively, designated as MNH-1 and MNH-2 (Figure 9b).

Both MNHs exhibited similar n-type semiconducting behavior to P(PyV)-H, indicating the formation of a continuous charge transport network of P(PyV) with the hydrogel mixture. The MNH-based inverters also functioned effectively as small signal amplifiers, with high amplification for signals in the 1–100 Hz range—performance that is difficult to attain with conventional hydrogels. Beyond their semiconducting properties, the MNHs exhibited excellent mechanical properties. Both were stretchable, capable of withstanding deformation larger than 100%. Additionally, the MNH-2, which incorporates bioadhesive functional groups, demonstrated excellent biointerfacial adhesion properties, which could address the motion artifacts during biosignal recording.

Cell viability tests confirmed the low cytotoxicity and excellent biocompatibility of all the semiconducting hydrogels (Figure 10a). Device interfaced with MNH-2 showed strong bioadhesion on a mouse leg, tolerating stretching and deformation during testing (Figure 10b). These signal amplifiers successfully captured and amplified several electrophysiological signals, including electrooculography (EOG), ECG, EEG, and ECoG (Figure 10c–e). The amplification factors, ranging from 25 to 200 times, were influenced by the signal frequency, interfacial impedance, and ion concentrations in the biofluid, aligning with static test results. Compared with traditional Au and Ag/AgCl electrodes, our semiconducting hydrogel demonstrated superior on-site small signal detecting and amplifying capability with substantially improved SNR. Unlike conventional semiconducting electronic devices, semi-

conducting hydrogels provide a more favorable biological interface, facilitating broad applications in implantable bioelectronics.

In summary, our semiconducting hydrogel-based OECT combines the excellent mechanical and biological properties of hydrogel with the versatile functions of organic semiconductors, presenting a strong candidate for an ideal biointerface. Moreover, the diverse types and chemical modifiability of hydrogels open new opportunities for a wide range of bioelectronic applications, such as hemostasis, drug delivery, self-healing, anti-inflammatory, and antibacterial treatments.⁴³ Looking ahead, additional functionalities, such as acoustic, optical, magnetic, and thermal properties, could be integrated into semiconducting hydrogels, offering multimodal signal transduction, expanded functions, and improved compatibility with biological tissues.

5. CONCLUSION AND OUTLOOK

In this Account, we summarize our recent efforts toward developing an ideal biointerface based on organic electrochemical transistors. This includes studies on the structure–property relationship, device fabrication techniques, and enhancements in biointerfacial properties. We highlight key factors influencing the performance of OECT polymers, including backbone design, side chain engineering, polymerization conditions, and processing solvent effects. A major finding is that the “doped state engineering” strategy is a general approach that benefits both n-type and ambipolar OECT polymers. We have also introduced hydrophilic cationic backbones—previously underexplored in OECTs—thereby expanding the building block library for organic semiconductors.

With these high-performance materials, we have successfully demonstrated multifunctional, low-power, and highly integrated OECT circuits. fiber-based OECTs, produced using our flow-enhanced crystallization method, have significantly advanced the development of bioelectronics with high area-normalized transconductance and excellent stability. These semiconducting polymer-based amplifiers enable effective interfacing with biological tissues for on-site amplification of various electrophysiological signals. Furthermore, the creation of semiconducting hydrogels has endowed hydrogel with semiconducting features, bringing forth an ideal biointerface with superior mechanical and biological properties.

Thanks to global efforts over the past five years, the performance of n-type and ambipolar OECT materials is progressively closing the gap with their p-type counterparts.^{15,45,46} In addition to developing new materials, surface modification presents a versatile strategy to enhance the performance and interfacial functions for OECTs. Adjusting the work function of the metal electrodes can reduce the contact resistance and enhance device performances.⁴⁷ Surface modification or blending with functional groups tailors organic semiconductor biointerfaces, enabling enhanced bioadhesion and sensing capabilities.⁴⁸ Furthermore, new device structures, such as internal gates⁴⁹ and vertical devices,³⁸ have been developed to meet the demands for high speed, high stability, and highly integrated systems. OECTs have already demonstrated considerable success in bioelectronics,⁵⁰ underscoring their unique advantages. Looking to the future, there remain several challenges that need to be addressed in materials, devices, and applications to fully realize the potential of OECTs. We identify the following key challenges:

1. Long-term stability of materials and devices, particularly for n-type and ambipolar devices, continues to be a limiting factor.
2. Achieving large-area processing and highly integrated OECT circuits, while addressing issues such as gate electrode isolation and high-speed operation, is still an ongoing challenge.
3. Fiber-based OECTs face challenges in scalable integration in textiles and lack clear application scenarios that showcase their unique advantages.
4. The development of multifunctional biointerface that go beyond amplifiers to achieve more diverse biological functions requires further exploration.

To overcome the stability issues, several key aspects must be carefully considered, including the chemical stability of the semiconductor during electrochemical doping/dedoping, morphology stability during cycling, and interfacial stability between electrode and channel. Advancing device integration necessitates breakthroughs in large-area, uniform processing, electrolyte patterning, and encapsulation techniques. For fiber-based OECTs, how to leverage textile manufacturing advantages to achieve system-level integration and utilize the fiber-shape advantages in bioelectronics should be further explored. Realizing multifunctional biointerface calls for interdisciplinary collaboration across materials engineering, electronic design, and biological function integration. We believe that addressing these challenges will significantly advance OECT technology, positioning it as a more compelling candidate for the next generation of biointerfacing electronics.

■ AUTHOR INFORMATION

Corresponding Author

Ting Lei – National Key Laboratory of Advanced Micro and Nano Manufacture Technology, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, School of Materials Science and Engineering, Peking University, Beijing 100871, China; orcid.org/0000-0001-8190-9483; Email: tinglei@pku.edu.cn

Author

Peiyun Li – National Key Laboratory of Advanced Micro and Nano Manufacture Technology, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, School of Materials Science and Engineering, Peking University, Beijing 100871, China; orcid.org/0000-0001-7805-527X

Complete contact information is available at:
<https://pubs.acs.org/10.1021/accountsmr.5c00030>

Notes

The authors declare no competing financial interest.

Biographies

Peiyun Li received his B.S. degree in Functional Materials from Huazhong University of Science and Technology in 2019. She joined Lei's group in 2019 and received her Ph.D. degree in Materialogy from Peking University in 2024. Her research focuses on the n-type organic electrochemical transistor materials for bioelectronics.

Ting Lei received his B.S. and Ph.D. degrees from Peking University in 2008 and 2013, respectively. After postdoctoral training at Stanford, he joined Peking University in 2018. He is a Boya

Distinguished Professor in School of Materials Science and Engineering at Peking University. His current research focuses on organic/polymeric semiconductors and their applications in flexible electronics, bioelectronics, and spintronics.

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