

n-Type semiconductors for organic electrochemical transistor applications

Simiao Yu, Christina J. Kousseff, Christian B. Nielsen^{*}

Department of Chemistry, Queen Mary University of London, London E1 4S, UK

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ABSTRACT

Over the last decade, the organic electrochemical transistor (OECT) has appeared as a powerful platform for developing organic bioelectronic applications such as electronic biosensors and neuromorphic devices. The rapidly growing interest in this field has spurred the development of new active bioelectronic materials that are tailor-made to fulfil the mixed ionic-electronic conduction requirements of the OECT. While p-type (hole-transporting) organic semiconductors quickly appeared with impressive mixed conduction properties, their electron-transporting counterparts, n-type organic semiconductors have lagged severely in terms of OECT performance metrics. Here, we review recent progress on the development of n-type organic semiconductors, including both small-molecule and polymer systems, for OECT applications and discuss the bioelectronic applications that have emerged from the materials development.

1. Introduction

The last few decades have witnessed a tremendous success in organic semiconductors (OSCs) due to their unique advantages of solution-processability, chemical versatility and light weight, in addition to their mechanical flexibility. With these strengths, organic semiconductors are widely used as the active layer in many electronic applications such as organic photovoltaics (OPVs) [1–3], organic field effect transistors (OFETs) [4,5] and bioelectronic devices [6,7]. Among these applications, organic electrochemical transistors (OECTs), which are used as bioelectronic devices, have gradually become a major research focus in the field of organic bioelectronics in the last few years.

The OECT is an electrolyte-gated transistor, which was proposed by Wrighton and his colleagues for the first time in 1984 [8]. In an OECT, the bulk active layer is electrochemically doped/de-doped during operation with concurrent charge compensation from the electrolyte. In recent years, the applications of OECTs in chemical and biological sensors have attracted much attention. Sensors based on OECTs have many advantages over those based on conventional OFETs. Firstly, the sensor based on OECTs works at low voltage (<1 V), which can effectively prevent the occurrence of hydrolysis [9]. Secondly, it can work in aqueous media and can be integrated on different substrates for real-time applications of chemical and biological sensors. Moreover, OECT devices are small in size, and gate electrodes and channels can be fabricated separately. The transistor-based sensor is a combination of sensor and amplifier, so the device has high sensitivity and low detection

limit [10].

An OECT device as schematically illustrated in Fig. 1 has three electrodes, which are source, drain, and gate electrode, an organic semiconductor film and a substrate. The organic semiconductor film is in contact with the electrolyte, through which the gate electrode is in contact with this active layer. Electronic charges are injected into the bulk semiconductor film from the source electrode, resulting in a change to its doping state and conductivity, meanwhile, ions from the electrolyte move into the organic semiconductor film to compensate the electronic charges [11]. The charge carrier density in the semiconductor layer is controlled by the voltage applied to the gate electrode. Two metal electrodes, source and drain electrode, are directly connected with the semiconductor layer to control the direction of electronic charge carriers. And the substrate is the structural support of the whole device.

The working principle of the OECT is described as follows, which can be generalized as gate voltage (input) controls drain current (output). The operation of an OECT device is regulated by voltages applied to the gate electrode (gate voltage, V_G) and drain electrode (drain voltage, V_D). The V_G controls the ion implantation into the channel and the doping state of the organic semiconductor film. The V_D induces the drain current (I_D). I_D is proportional to the number of mobile electrons or holes in the channel, thus the doping state of organic semiconductor film can be detected [10]. The conductivity of organic semiconductors can be adjusted through the voltage drop between the gate/electrolyte interface and the voltage drop between the electrolyte/channel interface, which is the basis for OECTs to convert a biochemical signal into

^{*} Corresponding author.

E-mail address: c.b.nielsen@qmul.ac.uk (C.B. Nielsen).

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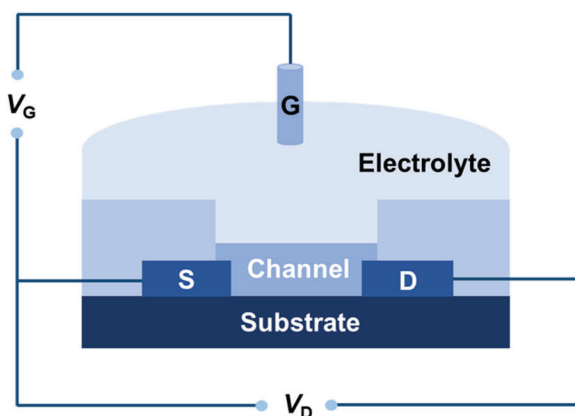


Fig. 1. The typical structure of an organic electrochemical transistor. S = source electrode, D = drain electrode, G = gate electrode, V_G = gate voltage, V_D = drain voltage.

electrical signal amplification. The performance of OECTs can be displayed using transconductance (g_m), defined in Eq. (1)[12]:

$$g_m = (w \cdot d / l) \cdot \mu \cdot C^* \cdot (V_{Th} - V_G) \quad (1)$$

where w , d , l refers to channel width, thickness and length, respectively; μ refers to charge carrier mobility; C^* refers to volumetric capacitance; V_{Th} refers to threshold voltage and V_G refers to gate voltage. Through this equation, we can conclude that g_m can be modulated via modifying channel dimensions (w , d and l), channel materials (μ and C^*), or the nature of the gate electrode [13,14]. In addition, some other features like stability, switching times and on-off ratios may influence performance. Normally, we can measure the I_D of devices over a period by applying a constant or pulsed applied voltage load to characterize the device stability [15]. Switching times are used to measure the device transient response. On (τ_{ON}) and off (τ_{OFF}) times can be estimated as the time required to reach 90% and 10% of I_D for fully switched on and off devices, respectively, which are proportional to channel thickness [15]. Also, a mono-decay exponential function can be used to fit the relaxation of the I_D , with the characteristic time corresponding to the transient response of the OECT [16]. Plus, high on-off ratios could result in high sensitivity [17].

Since 1984, OECTs have attracted much interest due to their ability to track biological activities. Many researchers have achieved sensing and detection of various ions by using OECTs as detection methods [18–20]. In addition, OECTs also play an important part in various bioelectronic devices for healthcare-related uses and biomedical research [21]. For example, OECTs are used in electrophysiology to measure cell activity or in conjunction with cell cultures for drug screening [22]. Also, OECTs can be used as biological sensors for the detection of electrolytes and metabolites [23–25] which are of great importance for human health.

In this review, we summarize the development of n-type polymers and small molecules for OECTs in the last few years. The quick development of this field during the past two decades could be attributed to the synthetic methods, various materials design strategies and device engineering protocols. With the emergence of novel materials, detailed structure-property relationships of n-type channel materials and reasons for their excellent performance will be discussed. In addition, a variety of different applications for n-type OECTs will be presented. Furthermore, the outlook on the scope and challenges in this field will be also discussed.

2. Materials in OECTs

2.1. Overview

Material selection is important for OECTs to achieve good performance, and the operation of OECTs depends on channel materials capable of conducting ions as well as electronic charge carriers (mixed conduction). Channel materials are typically made of organic semiconductors. Compared with inorganic materials, organic semiconductors are solution-processable, enabling low-cost processing. Chemical modification can be easily conducted at the molecular level. What's more, organic semiconductors have high potential for biocompatibility, which can be further modified by incorporating biomolecular side groups, making them ideal channel materials [26].

Based on the property of the dominant charge carrier within the molecular backbone, organic semiconductors can be divided into two categories, p-type and n-type semiconductors. Generally, p-type materials are hole transporting semiconductors, while n-type materials are electron transporting semiconductors. The molecular design of p- and n-type semiconductors typically utilizes electron-withdrawing and electron-donating building blocks and combinations thereof (such as alternating donor-acceptor motifs) to allow for facile charge injection through optimization of frontier energy levels [27]. The development of n-type OECT materials lagged far behind the p-type materials for many years until a novel material based on the naphthalene diimide (NDI) monomer was designed and synthesized in 2016 [28]. One research area that has benefited from n-type OECTs is biological sensing devices such as enzymatic sensing of metabolites [9]. In addition, access to n-type materials enabled the development of complementary logic circuits [10].

For a long period of time, molecular design has played an essential role in developing organic semiconductors for OECT devices. Previous research was mainly concentrated on the design of polypyrrole [8,29] or polyaniline [30,31] for OECTs. However, it encountered some bottlenecks. Ever since poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was successfully used for OECT applications in 2002 [32], considerable efforts have been devoted to developing novel channel materials. The first consideration is backbone planarity. Planar backbones could offer tight π -stacking, facilitate π -electron delocalization and enhance intermolecular charge transport [33,34]. One approach is incorporating aromatic fused ring building blocks into the conjugated backbone [33]. Some electron-deficient units, such as naphthalene diimide (NDI) [35] isoindigo (IID) [36] or diketopyrrolopyrrole (DPP) [37] have been selected to design stable organic n-type materials. An alternative strategy is introducing noncovalent intramolecular interactions within the aromatic backbones [38], so that channel materials could obtain high charge-carrier mobility, which makes them good candidates for application in OECTs. Another consideration is energy levels. The main reason for the slow development of electron-transporting materials is ambient instability. According to de Leeuw et al., this instability results from the propensity of organic π -radical anions to interact with water and/or oxygen in the atmosphere [39]. A lowest unoccupied molecular orbital (LUMO) energy level deeper than -4.0 eV is beneficial to n-type materials to operate stably in an ambient environment [40].

Side chain engineering is also considered as an effective molecular design method to boost the performance of organic semiconductors for OECTs. Some hydrophilic or ion-transporting side chains are chosen to modify conjugated polymers. Ethylene glycol side chains, for example, are widely used among these classes of channel materials. Much research is focusing on changing the length of the ethylene glycol chain or using mixed alkyl/ethylene glycol solubilizing chains to control excessive swellability while maintaining mixed ionic/electronic conduction capability [41–44]. In addition, some other side chain designs are conducted, such as exploring the optimal length as well as branching points of this ethylene glycol chains in order to balance solubility with

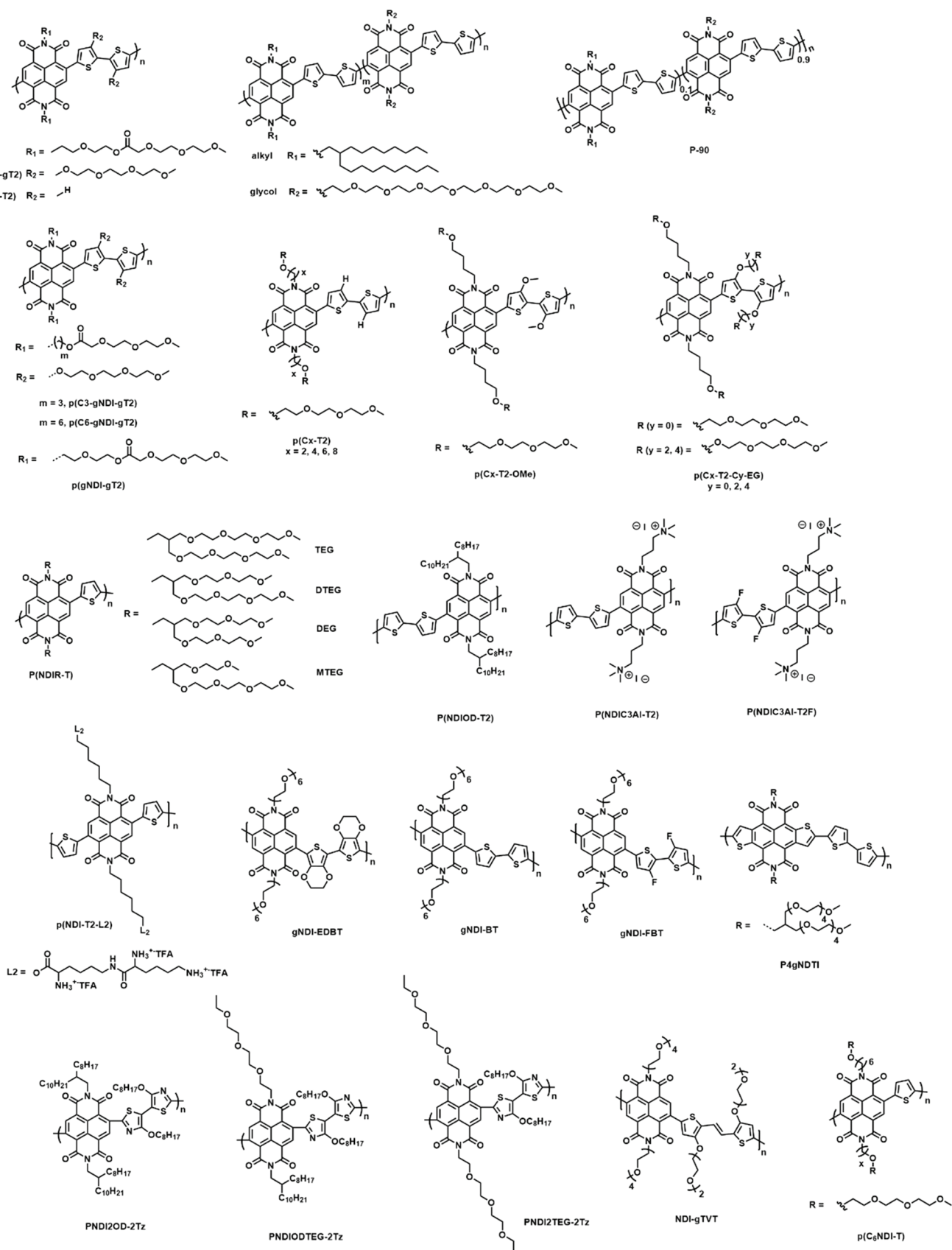


Fig. 2. Chemical structures of the NDI-based polymers used as OEET channel materials.

backbone packing. What's more, different hydrophilic side chains have also been developed to design novel channel materials [45].

Therefore, n-type channel materials for OECTs should be designed with high electron affinity, low ionization potential as well as the ability of ion penetration. Besides, high mobility is an important feature for materials so that OECTs can yield efficient current modulation [46].

2.2. Polymers

2.2.1. Naphthalene diimide (NDI) derivatives

Naphthalene diimide (NDI) is one of the most famous electron-accepting building blocks for constructing organic semiconductors due to its coplanar molecular structure, suitable optical absorption range, high electron affinity and good charge carrier mobility, which are widely applied for OPV and OFET devices, among other applications [47,48]. The NDI unit, which was copolymerized with thiophene-based donor units, was reported as a potential n-type material for OECTs for the first time in 2016. When both building blocks were functionalized with ethylene glycol chains, the copolymer was obtained and used to design the ambipolar OECT, which could work in aqueous media and show high stability during pulse measurements over two hours. Analogously, a series of copolymers based on NDI and bithiophene units were developed with different glycol side chain percentages with respect to the alkyl side chain [49]. In this research, OECT devices can only work when using the copolymers functionalized with more than 50% of the glycol side chain as the active layers, due to the improving reversibility of the redox reactions with higher glycol chain densities. Furthermore, the copolymers exhibit high electron mobilities when functionalizing with alkyl side chains, whereas the electron mobility slumps when over 25% of the alkyl side chains are replaced by polar glycol side chains. **P-90** (90% of glycol side chains) exhibited the highest performance among all these polymers, with a normalized g_m of 0.210 S cm^{-1} and an electron mobility of $2.38 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. After that, n-dopant tetra-n-butylammonium fluoride (TBAF) was used as a molecular dopant and morphology-additive to enhance the transconductance of **P-90** [50]. When adding 40 mol% of TBAF, OECT devices achieved the highest transconductance and good operational stability.

As mentioned above, side chain engineering is an important method to boost device performance. In the previous research, such as the polymer **p(gNDI-gT2)**, there are two carbons between the NDI backbone and ethylene glycol motifs. On the basis of this polymer structure, an alkyl spacer was introduced into the side chains of the NDI unit. Two new n-type polymers featuring propyl (**p(C3-gNDI-gT2)**) and hexyl (**p(C6-gNDI-gT2)**) spacers were designed and synthesized [51]. The presence of alkyl spacers limits the harmful over-swelling of the polymer in aqueous electrolytes and allows reversible redox reactions to occur at low potentials. Ultimately, **p(C6-gNDI-gT2)**-based OECT devices achieved good operational stability, with on-currents stable for over two hours at alternating gate potentials between 0 V and 0.6 V. Substitutions on donor units have also been shown to have an impact on the properties of NDI-based copolymers in OECT applications. As shown in Fig. 2, both the acceptor unit NDI and donor unit bithiophene were functionalized with various ethylene glycol chains. A carbon spacer between the ethylene glycol moiety and imide nitrogen atom is proved to influence the film order and crystallinity, and consequently the electron mobility. Besides, the performance of the n-type device was hampered when the bithiophene core was functionalized with a methoxy group or an ethylene glycol side chain. The best performing material is the polymer **p(C6-T2)**, with a six-carbon spacer on the side chains of the NDI unit and no substitutions on the bithiophene unit, which exhibited a maximum transconductance of 2.28 S cm^{-1} [52].

In addition to linear ethylene glycol side chains, branched oligo (ethylene glycol) chains (OEG) were used to construct NDI-based n-type molecules. Recently, Kim et al. designed and synthesized a series of new polymers with branched side chains of different lengths via Stille coupling with a thiophene unit [53]. When using eco-friendly solvents

instead of toxic halogenated solvents to fabricate OECT devices, branched OEG side chains provide sufficient solubility. All polymers exhibited superior solution processability in ethanol/water. In a follow-up study, asymmetric branched OEG chains were investigated [54]. Compared with a 3-(2-(2-methoxyethoxy)ethoxy)-2-((2-(2-methoxyethoxy)ethoxy)methyl)propyl (DEG) chain, a 13-((2-methoxyethoxy)methyl)-2,5,8,11-tetraoxatetradecan-14-yl (MTEG) chain has the same ethylene glycol content but the structure is asymmetric. Since the ethylene glycol part of the MTEG chain is located further from the NDI backbone, side chain flexibility improved and there may be less constraint from the rigid backbone [55]. It is well known that more ethylene glycol content in the molecule leads to stronger swelling characteristics. The shorter and asymmetric MTEG chains resulted in improved interactions among polymer backbones with reduced swelling capability. Simultaneously, close connections between crystalline domains hence enabled charge transport in the material, which led to an improvement in OECT performance. **P(NDIMTEG-T)** in chloroform-processed OECTs obtained a μC^* of $0.18 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ while **P(NDIDEG-T)** exhibited a μC^* of $0.16 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$. When processing in an ethanol/water mixture, the charge carrier mobility of **P(NDIMTEG-T)**-based devices increased substantially due to the enhanced edge-on orientation of crystalline structures, and thus achieved a high μC^* of $0.56 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$.

Some other hydrophilic side chains are chosen as alternatives to ethylene glycol chains to design bio-functional n-type polymers. **p(NDI-T2-L2)**, for example, was a novel material functionalized with lysine-based side chains where TFA group is trifluoroacetic acid [45]. Here, **p(NDI-T2-L2)** serves a dual purpose, supporting a lipid bilayer and performing well in OECT channels. The polymer is able to interact with zwitterionic vesicles and supply adequate hydrophilicity for high volumetric capacitance at the same time; this demonstrated the initial instance of an n-type OECT interacting with a biomimetic platform. Kiriy et al. developed new NDI-based polymers **P(NDIC3AI-T2)** and **P(NDIC3AI-T2F)** with cationic side groups [56]. Electron-deficient group fluorine atoms were introduced into thiophene units to improve the electron affinity of the polymer. **P(NDIC3AI-T2F)** showed the highest n-doping capabilities among the three polymers, due to the charge-stabilizing interactions between negatively charged backbones and ammonium groups under the n-doped state. Besides, the n-doped **P(NDIC3AI-T2F)** exhibits a conductivity of up to $10^{-2} \text{ S cm}^{-1}$ in the ambient environment.

Apart from side chain modification, donor functionalization is used to influence the electron mobility and electrochemical redox behaviour for n-type donor-acceptor type copolymers [57]. In 2022, Yue's group chose three different donor moieties 2,2'-bithiophene (BT), 2,2'-bis(3,4-ethylenedioxy)bithiophene (EDBT) and 3,3'-difluoro-2,2'-bithiophene (FBT) to copolymerize with NDI unit [58]. The copolymer **gNDI-FBT** with weak electron-donating moiety FBT showed high electrochemical stability in aqueous solution with 98% of the initial capacity remaining between +0.2 and -0.6 V, probably resulting from the bipolaron delocalization brought on by the addition of electron-withdrawing fluorine atoms. **gNDI-FBT** has suitable molecular packing, which is beneficial to ion-electron transport. Good performance of OECT devices based on **gNDI-FBT** were achieved as well, with a high volumetric capacitance of 197 F cm^{-3} and a low threshold voltage of 0.19 V.

Very recently, three novel non-fused conjugated polymers comprising NDI and dialkoxybithiazole have been reported as n-type channel materials [59]. Unlike bithiophene, bithiazole has an electron-deficient nature, which could increase the electron affinity of the molecule and thus improve charge carrier mobility and electrochemical doping [60,61]. Different amounts of ethylene glycol chains were introduced into the NDI unit. All three polymers showed low-lying LUMO energy levels. In particular, **PNDI2TEG-2Tz**, with two ethylene glycol side chains, showed the lowest LUMO level of -4.35 eV among the three polymers, probably because glycol ethers have inductive effects on electronic structures [62,63]. As a result, OECT devices based on

PNDI2TEG-2Tz achieved good electron mobility up to $3.16 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the highest performance compared with **PNDI2OD-2Tz** and **PNDIODEG-2Tz**. Furthermore, operational stability was measured, with no degradation appearing until 1000 cycles in aqueous electrolyte. Thienylenevinylene (**TVT**) is another electron-donating unit that can be used to design n-type donor-acceptor (D-A) conjugated polymers with the **NDI** unit [64]. Both **NDI** and **TVT** units were functionalized with ethylene glycol chains and the polymer **NDI-gTVT** was synthesized by Stille coupling. It can be used as channel material of n-type OECTs.

Backbone engineering is another design method to modify the channel materials. McCulloch et al. used a new core-extended **NDI**, naphthodithiophene diimide (**NDTI**) unit as the building block to synthesize n-type polymers [65]. Compared with **NDI**, **NDTI** has a more coplanar structure and extended π -system, which could increase the electron affinity of the polymer. Polymer **P4gNDTI** prepared by copolymerization of a branched ethylene glycol chain-functionalized **NDTI** with bithiophene, via Stille coupling. **P4gNDTI** exhibited high electron affinity and easy electrochemical reduction in aqueous environment, which was proved by cyclic voltammetry and spectroelectrochemical measurements. Additionally, the introduction of the **NDTI** unit controlled the swelling ability of the polymer due to the improved backbone planarity. Therefore, a μC^* of $0.27 \pm 0.04 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ and good shelf-life stability over four weeks were achieved for **P4gNDTI** based OECT devices, showing the importance of backbone planarity in device performance.

2.2.2. BBL

A ladder-type polymer poly(benzimidazobenzophenanthroline) (**BBL**) was demonstrated as an efficient and stable n-type material for OECTs by Fabiano and his colleagues in 2018, which became another classic n-type channel material [66]. Compared with the **NDI**-based polymers mentioned above, **BBL** has a highly planar and rigid π -conjugated system, which could facilitate intramolecular transfer, leading to high charge mobility within the polymer. Besides, **BBL** has high electron conductivity and electron affinity. Accumulation mode OECT devices based on **BBL** exhibit high transconductance (up to 9.7 mS) and good stability in aqueous media during pulse measurements over one hour of operation. Remarkably, neither I_D nor g_m of **BBL**-based devices had changed after three months of storage in an ambient environment, showing excellent stability. **BBL**-based n-type OECTs can be well integrated with p-type OECTs to make electrochemical complementary inverters, enabling high amplification with low power consumption. Compared with another typical n-type **NDI**-based polymer **P-90** [67], there are no hydrophilic side chains in the molecular structure of **BBL**, so the conjugated backbone takes up more space, leading to a superior charge storage capacity which is almost three times that of **P-90**. In spite of swelling and ion uptake, the rigid structure of **BBL** preserves the integrity of the electron conduction path. But for **P-90**, the presence of ionic interactions with side chains and water undermines the crystallite connectivity required for effective charge transport. OECT device parameters exhibited that **BBL** is the superior n-type material, with a higher electron mobility of $2.14 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a higher volumetric capacitance of 731 F cm^{-3} , which provides a new strategy of designing rigid-backbone, side chain-free molecules for n-type OECT applications.

Following the groundbreaking work of developing **BBL**, Fabiano's group has carried out a series of further studies on this remarkable polymer. In 2021, a type of **BBL**-based n-type conductive ink was developed [68], which was doped with an insulating polymer poly(ethyleneimine) (**PEI**) [69]. The conductive ink composed of **BBL:PEI** nanoparticles can be deposited by the spray-coating technique. When blended with 50 wt% of linear **PEI** and annealed, the electrical conductivity of the films reached 8 S cm^{-1} , which is a significant improvement over pure **BBL** films ($10^{-5} \text{ S cm}^{-1}$), probably due to the electron-donating secondary amine groups that donate electrons in **PEI** chains [70,71]. Another attempt is to use multi-walled carbon

nanotubes (**MWCNTs**) together with **BBL** to develop n-type OECTs [72]. **MWCNTs** have high electrical conductivity, resulting in an effective charge percolation path in the **BBL** channel. As a result, an enhanced transistor transient response time of 15 ms and high normalized transconductance of up to 0.34 S cm^{-1} for **BBL:MWCNT**-based OECTs were achieved.

Molecular weight, an important characteristic parameter for polymers, determines the properties of materials such as charge transport. Hence, four **BBL** polymers with various viscosity-average molecular weights (M_v) from 4.9 to 51 kDa (repeating units were calculated from 15 to 152) were synthesized via managing the polycondensation reaction time [73]. The GIWAXS data reveals that the π - π stacking distance decreases as the molecular weight of **BBL** increases, leading to a stronger π - π interaction of the higher molecular weight polymer. Also, enhanced lamellar packing crystallinity was found for higher molecular weight **BBL** by its lower paracrystalline disorder, so that intermolecular charge transport improved. When used as OECT channel materials, **BBL**₁₅₂-based OECTs exhibited the best performance among these polymers, with a high geometry-normalized transconductance of 11.1 S cm^{-1} , fast temporal response of 0.38 ms and low threshold voltage of 0.15 V, which highlight the significance of molecular weight in enhancing conjugated polymer-based OECT device performance.

BBL can also be used for all-polymer bulk heterojunction (BHJ) OECTs to obtain ambipolar transportation. Leong's group developed a new side chain-free, p-type ladder polymer 6*H*-pyrrolo[3,2-*b*:4,5-*b'*]bis[1,4] benzothiazine (**PBBTL**), which was blended with the n-type ladder polymer **BBL** [74]. The BHJ structure provided a continuous network between the **PBBTL** and **BBL** interfaces. For the blend **PBBTL:BBL** (3:1), both components form pure nanosized domains, and these non-interfering crystallites could promote efficient electron and hole transport. Both cationic and anionic penetration and transport could occur in the channel. Hence, very promising ambipolar properties of **PBBTL:BBL**-based OECTs were achieved, with a balanced μC^* of $2.72 \pm 1.04 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for p-type operation and $1.36 \pm 0.81 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for n-type operation.

2.2.3. Fused acceptor-acceptor polymers

Fused polylactam polymers, a very important category of materials in OFETs, have been investigated for bioelectronic applications. There is an electron-deficient bis-lactam motif along the molecular backbone, which increases electron affinity. The repeat units are linked together by carbon-carbon double bonds and intermolecular interactions can be promoted by these carbonyl groups [75–77]. In 2021, McCulloch's group reported two n-type polymers **PgNaN** and **PgNgN**, with a rigid backbone and oligo(ethylene glycol) (**OEG**) side chains, by a metal-free aldol-condensation polymerization [78]. Due to the acceptor-acceptor structure, a low-lying LUMO energy level less than -4.0 eV is present in both polymers, leading to better electron transport and stability. The carbon-carbon double bonds ensure a fully rigid π -electron system with no torsion of the molecular backbone, enabling high electron mobility of up to $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the OECT device. The difference between the two polymers is the various density of **OEG** side chains. **PgNaN**, comprising both **OEG** chains and alkyl chains, showed a preferable hydrophilic/hydrophobic behaviour, leading to the polymer with both sufficient ionic diffusion and suppressive swelling. As a result, **PgNaN**-based OECT devices exhibited better performance with a μC^* of $0.662 \pm 0.113 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$, compared to $0.037 \pm 0.016 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for **PgNgN**. Based on the polymer **PgNaN**, McCulloch's group modified the structure by changing the alkyl side chain length from ethyl (C_2H_5) to hexadecyl ($\text{C}_{16}\text{H}_{33}$) [79]. OECTs based on the polymer with decyl chains **p(g₇NC₁₀N)** exhibited the best μC^* of $1.83 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ among all the polymers, probably due to the mixed edge-on and face-on microstructure of **p(g₇NC₁₀N)**, which was shown by GIWAXS. In addition, this series of polymers **p(g₇NC_nN)** can also be used as channel materials for organic thermoelectric devices. When doping with (4-(1,3-dimethyl-2,3-dihydro-1*H*-benzimidazol-2-yl)phenyl)dimethylamine

(N-DMBI), **p(g₇NC₄N)** with short alkyl chains showed the highest thermoelectric performance, with an electrical conductivity of 7.67 S cm^{-1} and a power factor of $10.4 \mu\text{W m}^{-1} \text{ K}^{-2}$.

Another example of metal-free aldol-condensation polymerization is using a lactone building block to construct n-type donor-acceptor polymers [80]. Similarly, lactone is a strong electron-deficient building block, which can afford low LUMO energy levels below -4.0 eV and a rigid backbone. Polymers **p(C-T)** and **p(N-T)** showed close π - π stacking distances and mixed edge-on and face-on orientation, which was revealed by GIWAX data, leading to high electron mobility of $0.069 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $0.059 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively. AFM data showed that both **p(C-T)** and **p(N-T)** had a porous microstructure and disordered amorphous microstructure, which could promote effective ion-to-electron coupling and achieve good device performance.

2.2.4. Isoindigo (IID) derivatives

Isoindigo (IID) is a crucial functional group used in conjugated aromatics owing to a series of unique advantages, such as good chemical stability and electron affinity. Two five-membered electron-withdrawing lactam rings are combined by an exocyclic double bond, which can operate to deepen the LUMO energy level [36]. Yue et al. used the isoindigo unit to copolymerize with the electron donating group 3,4-ethylenedioxythiophene (EDOT) and obtained a series of D-A copolymers, which have low ionization potential for stable operation in an aqueous environment [81]. Various side chains including branched alkyl chains, linear and branched ethylene glycol (EG) chains, and hybrid alkyl-ethylene glycol chains were introduced to the lactam nitrogen positions. When using linear EG chains instead of branch EG chains, both transconductance and device stability of **PIBET-O** based devices increased. The most promising performance was achieved when choosing hybrid side chains (**PIBET-AO**), in which the alkyl contribution improved the substrate adhesion and operational stability of the devices, and the EG moieties ensured efficient ion injection simultaneously. The alkyl chains are very close to the molecular backbone, which is thought to contribute to the improved stability of **PIBET-AO** by preventing changes in film morphology.

Apart from introducing different hydrophobic or hydrophilic side chains on the lactam nitrogen, replacing the benzene moiety with various peripheral aromatic rings is another strategy to modify the isoindigo building block [82,83]. Recently, our group used pyridine and thiophene as peripheral aromatic units and designed new isoindigo-based building blocks, 7,7'-diazaisoindigo (AIG) and thienoisindigo (TIG) [84]. Thiophene (T) and 2,1,3-benzothiadiazole (BT) were chosen to copolymerize with the new isoindigo-based building blocks. Among these six polymers, only **AIG-BT** showed n-type OECT operation. Both pyridine and BT monomers are electron-deficient, which provided the large electron affinity of the polymer, leading to good electron injection and n-type operation in an aqueous environment. Besides, **AIG-BT** has a highly planar and rigid polymer backbone, which is very important for n-type operational stability. An electron mobility of $1.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a μC^* value of $0.12 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ were obtained for devices using **AIG-BT** as the channel materials, indicating that **AIG** is a very promising building block for n-type semiconductors.

2.2.5. Diketopyrrolopyrrole (DPP) derivatives

Diketopyrrolopyrrole (DPP), which has a bis-lactam structure, is a very famous electron deficient building block in constructing organic semiconductors [37]. The fused-ring structure contributes backbone planarity. So far, most channel materials based on the DPP moiety for OECTs are p-type [85,86]. In 2021, a DPP-based polymer **2DPP-OD-TEG** was developed for ambipolar OECTs [87]. **2DPP-OD-TEG** exhibited suitable LUMO and highest occupied molecular orbital (HOMO) energy levels, which match well with the electrochemical window of water, resulting in stable p-type and n-type OECT operation in an aqueous environment. **2DPP-OD-TEG**-based OECTs showed balanced p-type and

n-type performance. Very recently, two polymers, **P(gPzDPP-2T)** and **P(gPzDPP-CT2)**, were designed and synthesized using a pyrazine-functionalized DPP moiety (**PzDPP**) and bithiophene unit [88]. The **PzDPP** unit was chosen due to its very low LUMO energy level. When introducing cyano groups on the bithiophene unit, which is a strong electron-withdrawing group used for decreasing the LUMO energy level of the molecule, the bithiophene moiety would have a greater proportion of negative polarons, resulting in polaron redistribution on the molecular backbone. Branched ethylene glycol chains with a branching position farther away from the lactam nitrogen atom were used to ensure a close π - π stacking distance [89]. As a result, a very impressive performance of **P(gPzDPP-CT2)**-based OECT devices was achieved, with a high electron mobility of $1.9 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and high μC^* of $1.72 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$, providing a new design strategy to improve charge carrier mobility.

Some p-type OECT materials could be switched to n-type OECT materials through modifications at the molecular level. In 2022, Lei's group introduced fluorine atoms on thiophene units so that p-type polymer **P(gTDPPT)** changed into n-type polymer **P(gTDPP2FT)** [90]. Calculations of the properties of the polymers' doped states showed that compared with **P(gTDPPT)**, the negative charges of **[P(gTDPP2FT)]⁻** are more delocalized, leading to more balanced charge distribution on the whole polymer chain, hence **[P(gTDPP2FT)]⁻** has better stability. Very high n-type OECT performance based on polymer **P(gTDPP2FT)** were achieved with a μC^* of $54.8 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ and mobility of $0.35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, showing the importance of the doped state engineering.

2.2.6. Bithiophene imide (BTI) derivatives

Another electron-withdrawing building block that is widely used to design n-type semiconductors is bithiophene imide (BTI), which is based on the combination of bithiophene and imide. The bithiophene unit offers planarity and efficient π - π stacking, while the strongly electron-deficient imide unit increases the electron affinity of the building block [91]. The imide nitrogen position could be functionalized with various substitutions to ensure the solubility of the polymer. In 2021, Guo et al. designed two BTI-based donor-acceptor type polymers which can be used as channel materials in OECTs [92]. **f-BTI2TEG-T** and **f-BTI2TEG-FT** were synthesized by a Stille coupling-based polycondensation of the BTI and thiophene/difluorothiophene units. Branched ethylene glycol side chains were chosen to ensure sufficient polymer solubility for device fabrication. Compared with the non-fluorinated **f-BTI2TEG-T**, **f-BTI2TEG-FT** exhibited a lower LUMO energy level of -3.82 eV due to the fluorine atoms, so that electron injection could be facilitated and the potential stability window in aqueous electrolytes could be improved. Furthermore, **f-BTI2TEG-FT** showed reduced crystallinity, leading to better ion penetration into the polymer but decreased electron mobility [89,93]. When used as channel materials for OECTs, both polymers exhibited high electron mobility over $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and remarkable μC^* of $15.2 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for **f-BTI2TEG-FT**-based devices was obtained ($2.3 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for **f-BTI2TEG-T**), which showed excellent OECT performance. After that, Guo's group chose thienylene-vinylene-thienylene (TVT) as an alternative to copolymerize with BTI unit [94]. Similarly to the two polymers mentioned above, both **f-BTI2g-TVT** and **f-BTI2g-TVTCN** were developed as n-type channel materials. Cyano-functionalization was used to modify the donor unit, which could lower LUMO energy level of the molecule. OECTs using **f-BTI2g-TVTCN** as the active layer exhibited very promising performance, with a $g_{m,norm}$ of 12.8 S cm^{-1} and μC^* of $41.3 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$, closing the gap with p-type OECTs.

2.3. Small molecules

Small-molecule semiconductors are another category of materials which have shown great potential applications in organic electronics, due to the advantages of well-defined molecular weight, ease of

synthesis and purification, and high crystallinity, compared to their polymer counterparts [95,96]. In recent years, some research has begun to focus on the use of small molecule materials in OECT applications. The first n-type small molecule was developed by Ginger et al. in 2019, using fullerene derivatives as the building block [97]. Fullerene and its derivatives are some of the most successful electron-deficient building blocks in OPVs and OFETs [98,99], which had not yet been used in OECTs. In this paper, fullerene with glycolated side chains, 2-(2,3,4-tris(methoxytriglycol) phenyl) [60] fulleropyrrolidine (**C60-TEG**) was designed and synthesized. When used as active layer material for OECT devices, a C^* of $220 \pm 50 \text{ F cm}^{-3}$, and a μC^* of $7.0 \pm 2.0 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ were achieved. The mobility μ is $3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is roughly two orders of magnitude lower than the best value of fullerene-based field effect transistors. In addition to becoming the first small molecule OECTs, **C60-TEG** also showed that many of the design strategies for conjugated polymers are applicable to the design of small-molecule semiconductors.

While the development of **C60-TEG** is groundbreaking, fullerene derivatives suffer from some intrinsic defects, such as high production costs, thermal instability and low electronic mobility, which has limited their practical applications [100]. In order to solve the shortcomings of fullerene derivatives, some researchers have focused on investigating non-fullerene small molecules for n-type OECT applications. In 2022, a series of non-fullerene small molecules based on perylene diimide (**PDI**) were designed and synthesized (**PDI-3EG**, **4Cl-PDI-3EG**, and **4Cl-PDI-4EG**) [101]. **PDI** has been well-known as an exceptional electron-accepting building block for constructing organic semiconductors, due to its large coplanar molecular structures, high electron affinity and good charge carrier mobility [102,103]. Yue and her colleagues modified the **PDI** building block on both imide nitrogen positions and bay positions simultaneously. Polar ethylene glycol chains of different lengths were introduced at the imide positions to improve the molecular ion penetration capacity while maintaining the conjugated cores which enables electronic conductivity. Chlorination at the bay positions lowered the LUMO energy level of molecules. Compared with **PDI-3EG**, both **4Cl-PDI-3EG** and **4Cl-PDI-4EG** showed LUMO energy levels of -4.08 eV (below -4.0 eV), which is helpful to improve the oxidative stability in OECT devices. Rational design of molecular structures led to superior device performance. Devices based on chlorinated **PDI** with short ethylene glycol chains (**4Cl-PDI-3EG**) showed a μC^* of $0.20 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ and a $g_{m,norm}$ of $4.84 \times 10^{-2} \text{ S cm}^{-1}$ while **4Cl-PDI-4EG** with longer ethylene glycol chains exhibited a low threshold voltage of 0.05 V , high volumetric capacitance C^* value of 320 F cm^{-3} , and a $g_{m,norm}$ of $4.52 \times 10^{-2} \text{ S cm}^{-1}$. Besides, **4Cl-PDI-4EG**-based OECTs showed good operational stability with no degradation over one hour.

After **PDI**-based small molecules, Yue et al. designed other non-fullerene small molecules, **gNR** and **hgNR**, with two electron-withdrawing units, naphthalene bis-isatin and rhodamine [104]. Similar to other small molecules for OECTs, ethylene glycol chains were introduced at the lactam nitrogen positions to ensure ion transport. Through incorporating the rhodamine unit into the molecular core, a sulfur...oxygen noncovalent intramolecular interaction is formed between the sulfur atom on the rhodamine unit and the oxygen atom on the lactam ring; plus, a hydrogen bond is found between the oxygen atom on the rhodamine unit and the hydrogen on the naphthalene, which was proved by density functional theory calculations. A highly planar and rigid core was achieved, leading to efficient electron mobility up to $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (**gNR**). A $g_{m,norm}$ of 0.4 S cm^{-1} and a μC^* of $2.6 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ were achieved for **gNR** based OECT devices, which can be comparable to the cutting-edge n-type polymers used in OECTs. Besides, the addition of an alkyl spacer can increase the stability of OECT devices, although both electronic and ionic transports could be reduced to some extent.

Another new design strategy was used to develop new channel materials for ambipolar OECTs, blending n-type and p-type materials

together to form a bulk-heterojunction (BHJ) structure, which is a very common structure in organic photovoltaics [74]. An n-type fullerene-based small molecule, **PrC₆₀MA**, and a p-type polymer polythiophene, **p(g2T-TT)**, were chosen to make the BHJ blend [105]. Compared to the direct synthesis of a new material, using a BHJ blends allows the optimization of two components each. Besides, BHJ morphology, with its significant interpenetrating network, results in appropriate film integrity and electrical stability. When using the blend ratio of **PrC₆₀MA:p(g2T-TT)** 95:5 (w:w) as the channel, OECT devices exhibited good performance and stability with almost no current degradation after 100 cycles in alternating polarities.

3. Applications of n-type OECTs

The effective mixed ionic-electronic conduction of these materials within an OECT framework sets the groundwork for their utilization in biological applications. The inherent properties of ion penetration into the bulk of the channel provide the necessary characteristics, such as stable aqueous interfacing, extended operation time, high transconductance, and signal amplification, to make OECTs highly appropriate for high sensitivity, long term biological applications [106]. Thus far, the majority of organic materials successfully applied for this purpose have been p-type, mainly attributed to the relative instability of n-type materials in air. However, in many cases for OECT-based sensing, it is preferable to operate an n-type system, as electron release intrinsic to biological processes can interact with electron-deficient moieties, providing a direct and efficient pathway for signal transduction in response to relevant analytes. In addition, the development of n-type materials which can match the electrical output and stability of their p-type counterparts is critical for access to OECT-based complementary circuits, which could deliver high-speed, low power operation, with enhanced signal to noise ratios [107].

Furthermore, of the p-type examples of OECT frameworks for biological applications, an overwhelming proportion utilize the successful, high-performance material poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (**PEDOT:PSS**). While highly effective, stable and biocompatible, and thus ubiquitously seen across bioelectronics, **PEDOT:PSS** operates in depletion mode, due to the stabilization of the hole current by surrounding negatively charged **PSS** at no applied gate voltage [9,108]. It is preferable, however, to employ materials that function in accumulation mode. These are more energy efficient due to their maintenance of an OFF state in the absence of gate bias, turning ON upon interaction with an analyte; thereby presenting superior ON/OFF ratios at low biases with a high signal-to-noise ratio [109,110]. Thus, in recent years, pioneering examples of n-type OECTs which combine this accumulation modality with biologically relevant electron transporting characteristics have been presented to achieve the sensing of biological analytes and processes, while the development of n-type or ambipolar materials for use in all-organic complementary circuits and inverters has been realized; examples of these are highlighted below.

3.1. Biological sensing

Due to the ability of n-type materials to stabilize electrons on their backbone, the first generation of n-type OECTs for biological sensing have capitalized on a selective biological process which produces electrons, that is, the enzymatic oxidation of sugar species by their respective oxidases. This highly specific interaction causes the release of two electrons which can be sequestered directly by the polymer, resulting in a fast and sensitive effect on current output. In 2018, the first application of an n-type polymer for enzymatic sensing was presented by Inal et al., who applied the polymer **P-90** (Fig. 2) to sense lactate when coupled with the enzyme lactate oxidase (LOX) (Fig. 5a). The OECT demonstrated an increase in channel current upon lactate oxidation to pyruvate as a result of increased charge carrier density; this selective capability is informed by features of the polymer's structure. The conjugated,

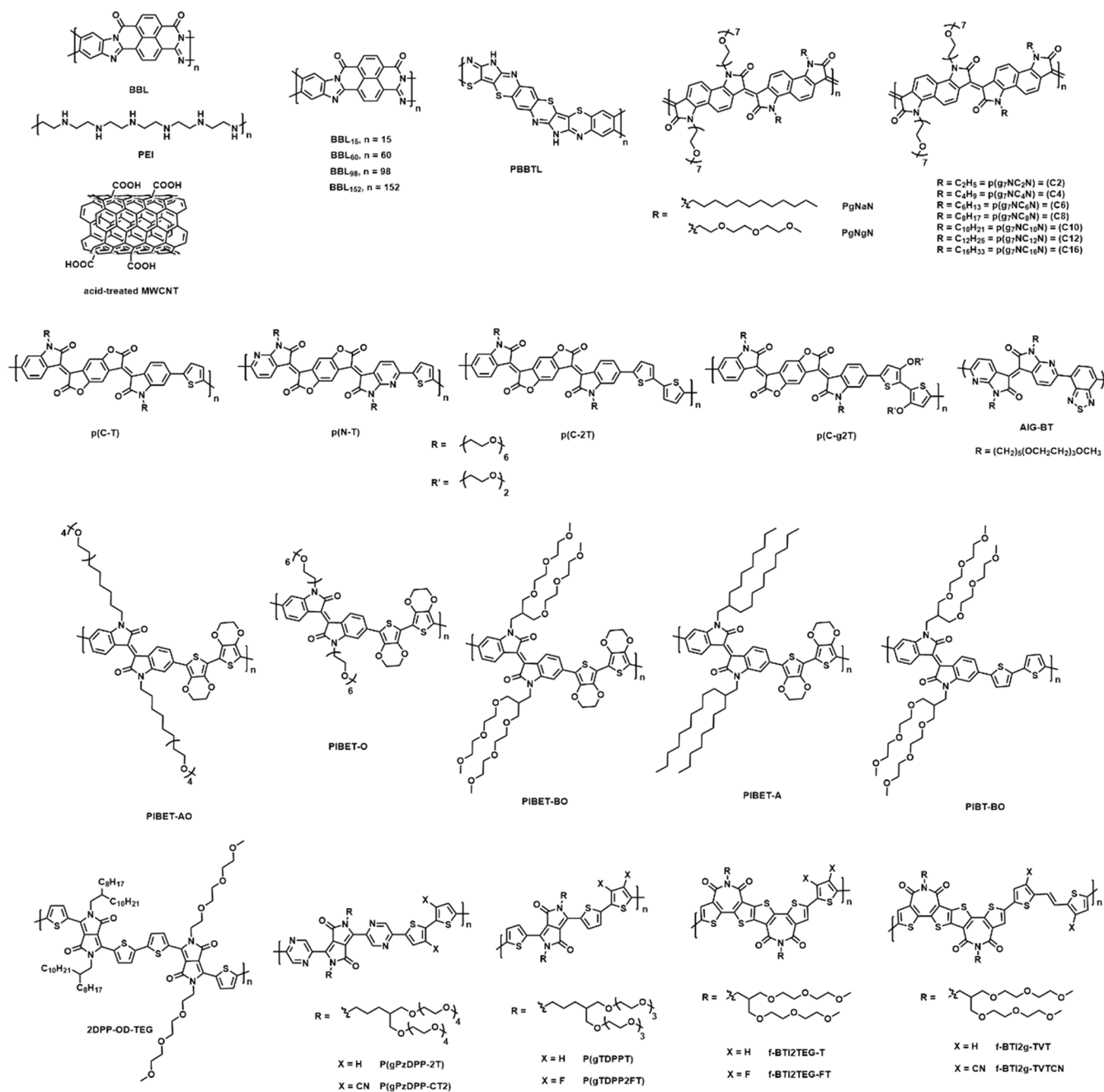


Fig. 3. Chemical structures of n-type polymers used as OECT channel materials.

electron-deficient **NDI** motif acts as both electron acceptor and redox mediator. Meanwhile, the high proportion of glycol side chains not only enable sufficient swellability in water, permitting electrochemical activity and ion diffusion in aqueous media, but also provide a polar environment which causes the enzyme to interact in close proximity to the polymer; this averts the need for an electron transfer mediator and allows facile functionalization by drop-casting directly on the polymer film. The device exhibited a specific, reversible response to lactate to a limit of 10 μM ; this work also marked the first accumulation mode OECT for biological sensing, and laid the groundwork for a series of exciting developments in the following years [111].

The following year, this approach was adapted to detect glucose, this time featuring glucose oxidase (GOx) as the corresponding selective enzyme. Harnessing a similar mechanism to the above, the oxidation of glucose to gluconolactone by GOx releases 2 electrons which are

stabilized by the **P-90** backbone, resulting a current increase in response to glucose concentration. In this case, an additional simple modification to the processing of the material was undertaken in order to further enhance OECT performance: based on the principle that crystallinity, and hence, charge carrier mobility, can be improved with the introduction of a small quantity of a “bad” solvent to the polymer solution [112], Inal et al. demonstrated a three-fold improvement of trans-conductance and greater ON current by incorporating 15% acetone in the **P-90** solution alongside chloroform. The resulting film was characterized by increased roughness and extensive ion penetration, with a higher degree of in-plane backbone ordering, and thus volumetric capacitance and charge carrier mobility were enhanced in comparison to an all-chloroform control. The device exhibited a low detection limit of 10 nM and a dynamic range exceeding 8 orders of magnitude [113]. Following that, the same group successfully harnessed the power of this

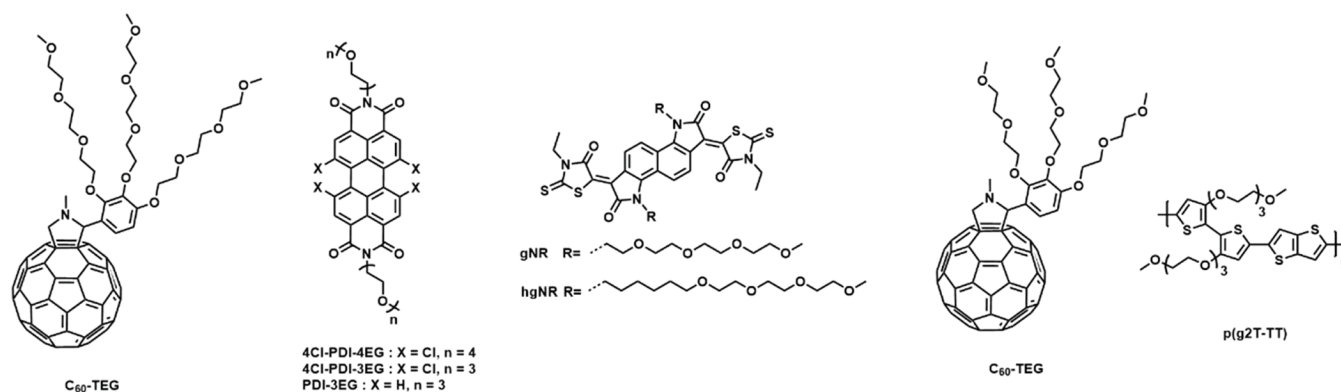


Fig. 4. Chemical structures of n-type small molecules and their blends used as OECT channel materials.

process, pairing a GOx-adsorbed **P-90** anode with a p-type organic cathode to generate a glucose-fueled power supply; electrons sequestered by **P-90** via GOx are transferred by an external circuit to the p-type electrode, whereupon the catalytic reduction of O₂ by the p-type polymer **p(EDOT-co-EDOTOH)** generates water; the coupling of these systems generates electrical energy [114]. Here, the introduction of glucose to the system is shown to correspond to an increase in open circuit voltage and maximum power density, the latter of which was maximized at the biologically relevant glucose concentration of 10 mM, proved effective in human saliva, and was sufficient to power an OECT, thus unlocking the potential for enzymatic fuel cells as self-powered sensors [115]. In 2021, another step towards lab-on-a-chip operation was presented: combining the sensitive and straightforward sensing platform of the **P-90**/GOx OECT framework with the reduced perturbation, low volume requirement, and continuous flow of a microfluidic channel, it is possible to achieve real time monitoring, high transconductance, and a detection limit as low as 1 nM [116].

Beyond the sensing of sugars, adaptations to the recent breakthroughs in n-type OECT platforms have the potential to be applied in many and diverse biological settings; once such instance is the application of **p(C₆NDI-T)** (Fig. 2) by Inal et al., to detect aggregates of amyloid- β , which can be indicative of Alzheimer's disease. An OECT was fabricated incorporating an isoporous membrane with a high affinity for amyloid- β aggregates; this feature, integrated with a microfluidic channel, enabled label-free detection of amyloid- β aggregates in 1 μ L volumes of human serum down to a femtomolar concentration. At a positive gate bias, the introduction of positively charged aggregates to the membrane causes increased cation flow into the polymer channel, while at a negative gate bias, the flow of anions to the channel is reduced. Thus, due to the combined effects of its accumulation mode operation and n-type characteristics, the **p(C₆NDI-T)**-based device demonstrated a lower power consumption, higher ON/OFF ratio, and superior sensitivity in comparison to both the highly popular p-type depletion-mode material **PEDOT:PSS**, and an accumulation mode p-type polymer, **p(g0T2-g6T2)** [117].

A timely example is the application of the same polymer in the channel of an OECT which is gate-functionalized with the relevant antibody recognition domain ("nanobody") to achieve the highly sensitive detection of the SARS-CoV-2 spike glycoprotein, necessary to identify cases of COVID-19. Application of alternating current electrothermal flow (ACET) directed the analyte to the sensor surface to achieve ultrarapid response times. Furthermore, when compared to a state-of-the-art p-type material, **p(g₃C₂T2-T)**, the n-type device displayed a three orders of magnitude lower detection limit, as little as 100×10^{-18} M, due to the high capacitance of **p(C₆NDI-T)** [118].

Another pioneering example of biological monitoring is the modification of the polymer **NDI-T2** to include charged lysine side chains (**NDI-T2-L2**, Fig. 2) whose hydrophilic and biocompatible characteristics enabled the successful interfacing of the channel material with a

supported lipid bilayer. The first case of a biofunctionalized n-type polymer for lipid interfacing, this setup enabled the activity of a pore-forming protein to be monitored: at increasing concentrations of Gramicidin A, cation permeability through the pores and into the **NDI-T2-L2** channel caused an increased in ON current, with high operational stability in air and water (Fig. 5b) [45].

The lag in the development of small-molecular n-type OECT materials in comparison to their polymeric counterparts is thus far also reflected in their relative lack of representation within applications in bioelectronics. However, the superior simplicity of their synthetic modification, purification and processability on a large scale, alongside their controllable molecular weight, structural replicability and generally high crystallinity (and hence mobility), ensures that small molecules remain much desired components for use in biological sensors [95,119]. In 2022, the first such OECT has been realized by Yue et al., employing an n-type small molecule in an OECT to sense H₂O₂. Similarly to the polymers discussed in this section so far, the successful material is based on a rylene diimide, although in this case, it is the extended core of the perylene diimide (**PDI**) which is used in place of naphthalene diimide (**NDI**). Ion penetration is encouraged by glycolated side chains, while the chlorinated bay positions of the core lower the LUMO to encourage electron injection and enhance ambient stability [120,121]. The best performing material of the series discussed in Section 2.3, **4Cl-PDI-4EG** (Fig. 4), was applied as both the channel and gate material in an OECT; at the gate, it was functionalized with MnO₂ nanoparticles (NPs), whose role is the catalysis of H₂O₂ decomposition. Under a positive bias, this oxidation event delivers two electrons to the gate, causing an increase in channel current; the device achieved a detection limit of 0.75 μ M [101].

3.2. Complementary circuits

In addition to the detection of biologically relevant molecules, the ability to monitor and mimic electrophysiological processes, such as heart impulses, eye movements, and synaptic behaviors, is highly desirable. Detection of such tiny impulses requires excellent signal amplification with a high signal-to-noise ratio and good biological interfacing, for which OECT systems are ideal. Particularly, complementary inverters featuring both p- and n-type components are required to obtain the necessary high-gain, amplifying functionality at low power operation. Until recently, the development of all-organic systems for this purpose had been impeded by the relative delay in production of n-type materials which match the sufficiently low threshold voltage, high transconductance, and aqueous-stable operation of their p-type counterparts [107]. In 2018, the first such high-gain, all-OECT complementary logic circuit was reported by Fabiano et al., featuring **BBL** (Fig. 3) as the active n-type material. The planarity and rigidity of the ladder-type **BBL** allows the material to achieve a higher conductivity than traditional donor-acceptor n-type polymers due to extended charge carrier delocalization; this enables the transconductance to match that of a

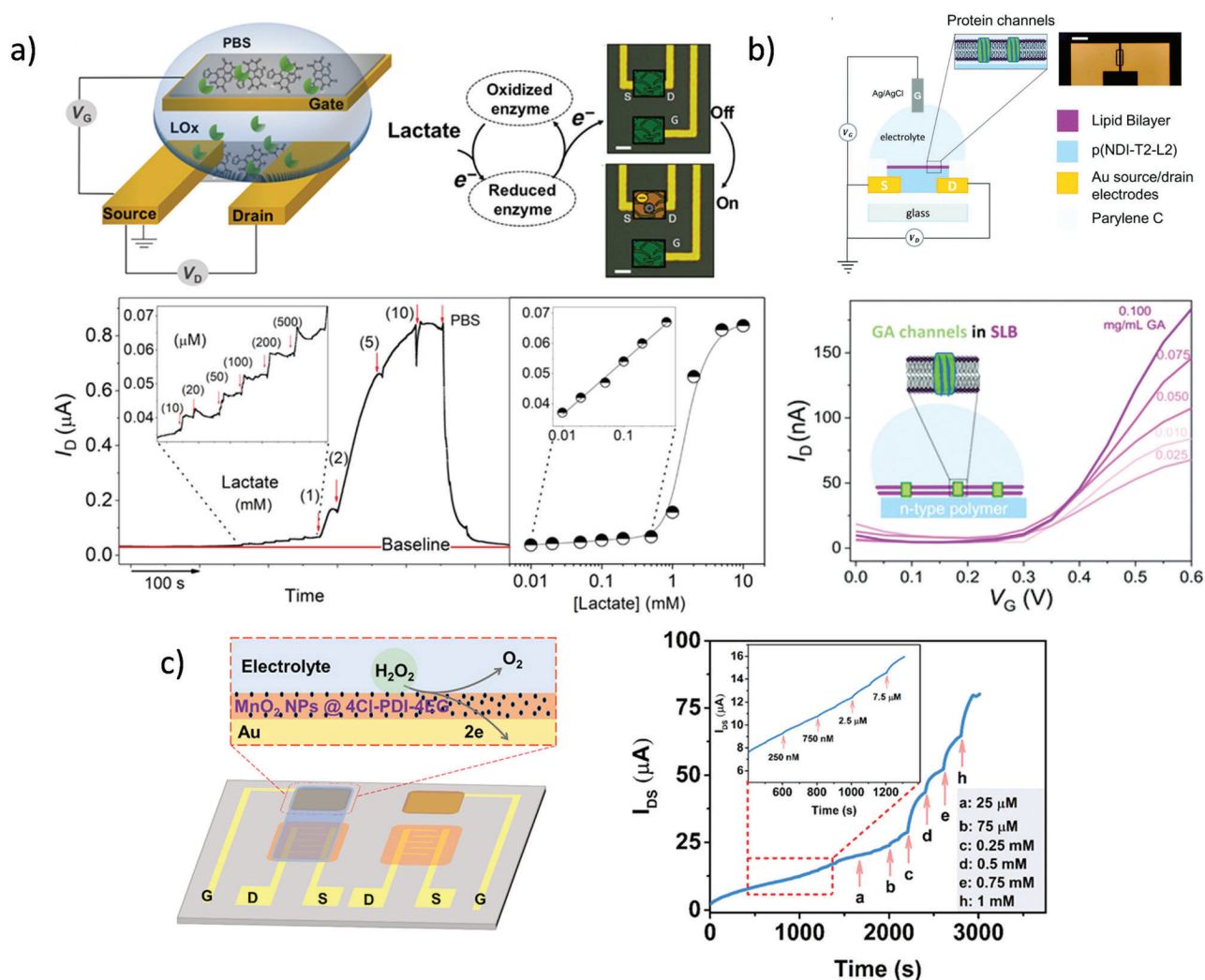


Fig. 5. Applications of n-type materials in OECT-based biological sensing platforms. a) P-90/LOx-based sensor for lactate, with an illustration of the corresponding lactate oxidation and transfer of electrons to the n-type channel; source-drain current response of OECT to increasing lactate concentration. From Pappa et al., *Sci. Adv.*, 4 (2018) eaat0911 [106]. © The Authors, some rights reserved; exclusive licensee AAAS. Distributed under a CC BY-NC 4.0 license <http://creativecommons.org/licenses/by-nc/4.0/>. Reprinted with permission from AAAS. b) Schematic representation of NDI-T2-L2-based OECT with supported lipid bilayer; transfer curves showing drain current increase in response to increasing Gramicidin A channels. Adapted with permission from reference [45]. Copyright The Royal Society of Chemistry (2020). c) Planar gate H_2O_2 sensor featuring 4Cl-PDI-4EG/MnO₂ NPs; channel current response to increasing H_2O_2 concentrations. Adapted with permission from reference [101]. Copyright 2022 American Chemical Society.

p-type material. Thus, in combination with the p-type polymer P3CPT, an inverter was presented which demonstrated a switching voltage and noise margin among the best in the field [66]. Subsequent breakthroughs in the design of these systems include: the combination of BBL with poly(ethyleneimine) (PEI) to achieve n-type depletion mode OECT operation, enabling the fabrication of an inverter featuring PEDOT:PSS, the one of best-performing p-type materials currently dominating the field of organic bioelectronics [68]; the development of ambipolar materials such as 2DPP-OD-TEG (Fig. 3), which can act as the active material in a single-component logic circuit, far reducing the complexity of manufacture due to the patterning of a single channel [87]; and the combination of n- and p-type blends in a bulk-heterojunction (BHJ) structure, such as the ladder polymers BBL and PBBTL [74] or the fullerene-based small molecule PrC₆₀MA (Fig. 4) with p(g2T-TT) [105], which introduces a highly controllable, adaptable approach to OECT inverters. In 2022, Fabiano et al. presented a printed, scalable complementary circuit based on BBL:PSSNa alongside p(g₂T-T):PQ-10, which operated in enhancement mode, demonstrating record-high voltage gain and detecting voltage signals as low as 100 μ V [122].

Very recently, the advances made in this field have paved the way for

all-organic OECT complementary circuits to be applied successfully for the detection of biological processes for the first time. In 2021, Rivnay et al. applied the ambipolar, NDI-based donor-acceptor polymer p(C₄-T2-C₀-EG) (Fig. 2) as both the p- and n-type OECT components of a cofacial inverter which was able to amplify electrocardiogram (ECG) signals with a gain of 10 [123]. The following year, Leong et al. took the bulk-heterojunction approach to signal amplification, mixing BBL with the new p-type ladder polymer PBBTL; high control over mixing and phase separation gave a bicontinuous network with balanced ambipolar properties. The resulting BHJ inverter was applied to amplify electrooculography (EOG) signals: very weak (ca. 1.5 mV) [124] potential variations caused by left/right or up/down eye movements. These were successfully amplified to give an output voltage change of approximately 80 mV, enabling the device to track eye movement [74].

Finally, the ability to emulate the low-energy synaptic plasticity of neural networks, such as those found in the human brain, has long been a goal of electronics and materials communities: the potential for rapid, energy efficient, complex logical computation and memory on a small scale is the key to a new generation in artificial intelligence. While organic semiconductors represent a promising class of materials for this

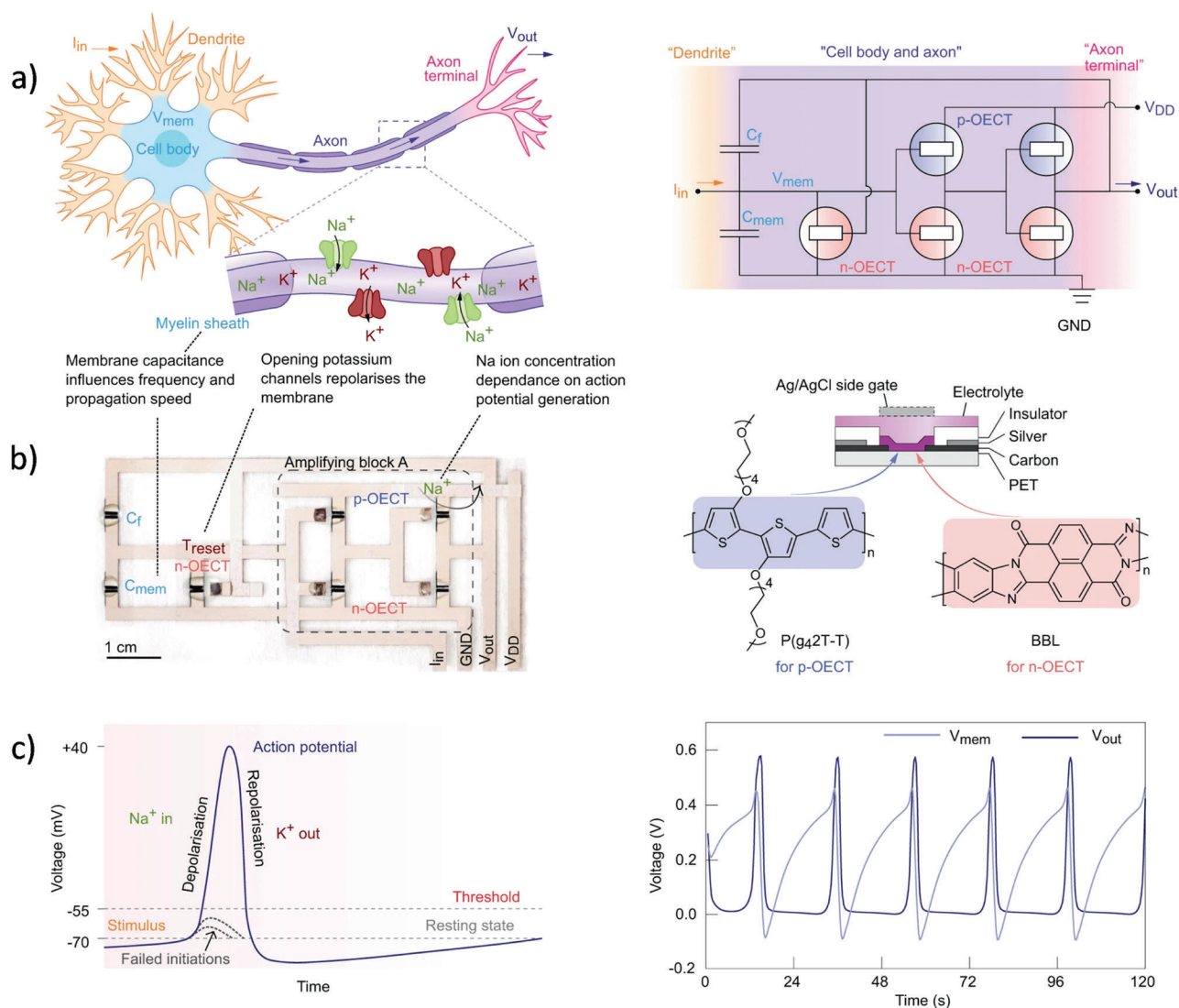


Fig. 6. a) Comparison of a biological neuron and the OECT-based artificial neuron by Fabiano et al.; b) printed organic electrochemical neuron with the structure of the p-type (P(g42T-T)) and n-type (BBL) constituents; c) the phases of nerve cell action potential compared to the spiking activity of the OECT-based neuron. Copyright Springer Nature, Fabiano et al., under CC BY license <https://creativecommons.org/licenses/by/4.0/>. Reproduced with permission from ref [127].

prospect, due to their flexibility, biocompatibility, and synthetic tunability, there is still a long way to go to reach the necessary performance, scale and processability required for state-of-the-art applications in neuromorphic computing [125,126]. Once again, the development of n-type materials for this purpose has trailed behind that of the p-type components; however, both are critical for the fabrication of complementary circuits required to achieve neuronal mimicry. In 2022, a few groups have debuted n-type materials for these systems, which take steps towards achieving the stability, low operating voltage and high conductivity requirements which had been lacking in the past. For example, van de Burgt et al. synthesized a series of planar NDI-dialkoxybithiazole(2Tz) copolymers (Fig. 2) which demonstrated improving OECT performance and stability relative to the increasing number of glycolated side chains, as a result of the hydrophilicity, ionic interaction, and low LUMO that these moieties imbue. The best-performing of these materials, PNDI2TEG-2Tz, was incorporated into an electrochemical resistive random-access memory device (EC-RAM), whereupon good conductance state retention over two orders of magnitude was observed, opening the door to its potential use in neuromorphic computing [59]. He et al. demonstrated a three-terminal artificial synapse using a novel polymer, NDI-gTVT (Fig. 2), which

features an NDI acceptor unit with a thienylenevinylene donor. At a positive bias, lithium ions embedded within the polyethylene oxide dielectric are removed from this matrix and penetrate the n-type polymer layer, aided by interaction with the glycolated side chains. This process mimics the path of neurotransmitters crossing a synaptic cleft to initiate a nerve impulse; the device presented a low voltage, high current density (ca. 10 kA cm^{-2}), alongside paired-pulse facilitation and long-term plasticity [64]. Finally, Fabiano et al. combined BBL with the p-type polymer P(g42T-T) to present an all-organic, printed complementary circuit to generate actions potentials mimicking the firing of nerve pulses; at the transition voltage, amplifier gain is rapidly increased, contributing to a feedback loop similar to that of a biological neuron (Fig. 6); furthermore, input current-controlled high frequency spiking of the artificial neuron was able to induce lobe closure upon device bio-integration with a Venus Flytrap [127].

4. Summary and outlook

Ever since the first n-type material for OECTs came out in 2016, this field has received wide attention and developed rapidly. The quick development could be attributed to focused synthetic efforts and

Table 1
Summary of n-type polymer-based OECT performance parameters.

Materials	V_{th} [V]	$g_{m,norm}$ [S cm ⁻¹]	μC^* [F cm ⁻¹ V ⁻¹ s ⁻¹]	μ [cm ² V ⁻¹ s ⁻¹]	C^* [F cm ⁻³]	τ (ON) [ms]	Reference
p(gNDI-gT2)	0.28	0.1085	-	-	397	5	[28]
P-75	-	0.141	-	1.46×10^{-4}	188.0	-	[49]
P-90	-	0.210	-	2.38×10^{-4}	198.2	-	[49]
P-100	-	0.204	-	1.96×10^{-4}	192.4	-	[49]
P-90:TBAF (40%)	0.22	0.0905	-	1.8×10^{-4}	143	24	[50]
p(gNDI-gT2)	0.26	0.13	0.06	2.2×10^{-4}	221	-	[51]
p(C3-gNDI-gT2)	0.25	0.34	0.13	9.2×10^{-4}	72	-	[51]
p(C6-gNDI-gT2)	0.37	0.37	0.16	6.3×10^{-4}	59	-	[51]
p(C4-T2-OMe)	0.46 ± 0.030	0.10	0.07 ± 0.011	3.87×10^{-4} ± 6.46×10^{-5}	170	-	[52]
p(C4-T2-C0-EG)	0.32 ± 0.007	0.31	0.22 ± 0.016	1.16×10^{-3} ± 8.60×10^{-5}	188	24.6	[52]
p(C4-T2-C2-EG)	0.30 ± 0.003	0.02	0.01 ± 0.002	4.99×10^{-5} ± 9.75×10^{-6}	200	6.2	[52]
p(C4-T2-C4-EG)	0.33 ± 0.009	0.01	0.006 ± 0.001	5.34×10^{-5} ± 9.81×10^{-6}	116	12.5	[52]
p(C2-T2)	0.27 ± 0.004	0.40	0.20 ± 0.015	3.97×10^{-4} ± 3.05×10^{-5}	492	6.3	[52]
p(C4-T2)	0.24 ± 0.002	0.63	0.30 ± 0.0003	1.90×10^{-3} ± 1.88×10^{-6}	158	7.5	[52]
p(C6-T2)	0.30 ± 0.003	2.28	1.29 ± 0.117	4.74×10^{-3} ± 4.31×10^{-4}	272	9.6	[52]
p(C8-T2)	0.37 ± 0.002	0.15	0.13 ± 0.074	3.76×10^{-4} ± 2.17×10^{-4}	342	12.7	[52]
P(NDITEG-T) (Chloroform)	0.25	0.021	0.03	0.16×10^{-3}	181.7	-	[54]
P(NDIDTEG-T) (Chloroform)	0.21	0.063	0.08	0.34×10^{-3}	232.7	-	[54]
P(NDIDEG-T) (Chloroform)	0.20	0.135	0.16	0.66×10^{-3}	240.1	-	[54]
P(NDIMTEG-T) (Chloroform)	0.22	0.143	0.18	0.71×10^{-3}	250.8	-	[54]
P(NDITEG-T) (Ethanol/water)	0.26	0.031	0.04	0.24×10^{-3}	165.8	-	[54]
P(NDIDTEG-T) (Ethanol/water)	0.18	0.135	0.21	0.94×10^{-3}	221.5	-	[54]
P(NDIDEG-T) (Ethanol/water)	0.15	0.359	0.51	2.12×10^{-3}	239.9	-	[54]
P(NDIMTEG-T) (Ethanol/water)	0.18	0.378	0.56	2.23×10^{-3}	250.9	-	[54]
p(NDI-T2-L2)	0.22	-	0.31	-	95	-	[45]
gNDI-EDBT	0.52	0.003	0.02 ± 0.01	3.96×10^{-4}	50.5	377.6	[58]
gNDI-BT	0.30	0.019	0.09 ± 0.01	5.69×10^{-4}	158.3	102.3	[58]
gNDI-FBT	0.19	0.036	0.12 ± 0.02	6.10×10^{-4}	196.6	45.5	[58]
PNDIODETEG-2Tz	0.75	-	-	-	-	5.7 s	[59]
PNDI2TEG-2Tz	0.54	0.493	1.16 ± 0.28	3.16×10^{-3}	≈ 367	< 100	[59]
P4gNDTI	0.20 ± 0.003	0.47 ± 0.06	0.27 ± 0.04	$(1.42 \pm 0.22) \times 10^{-3}$	167 ± 11.4	-	[65]
BBL	0.21	0.359	-	7×10^{-4}	-	900	[66]
BBL	0.19	0.815	1.99	2.14×10^{-3}	731	5.2	[67]
P-90	0.24	0.009	0.0343	7.45×10^{-5}	261.5	41	[67]
BBL:MWCNT (10:1)	-	0.335	1.06	1.41×10^{-3}	753.8	37	[72]
BBL ₁₅	0.27	0.617	1.94	$(3.59 \pm 0.23) \times 10^{-3}$	540 ± 20	0.89	[73]
BBL ₆₀	0.21	1.92	4.90	$(9.42 \pm 0.88) \times 10^{-3}$	520 ± 32	0.52	[73]
BBL ₉₈	0.18	4.04	10.2	$(2.05 \pm 0.15) \times 10^{-2}$	499 ± 19	0.43	[73]
BBL ₁₅₂	0.15	11.1	25.9	$(4.40 \pm 0.34) \times 10^{-2}$	589 ± 26	0.38	[73]
PBBTL:BBL	0.26	0.43 ± 0.24	1.36 ± 0.81	$(0.81 \pm 0.48) \times 10^{-2}$	168	1.72	[74]
PgNaN	0.37 ± 0.01	0.212	0.662 ± 0.113	$(6.50 \pm 1.01) \times 10^{-3}$	100 ± 6	127	[78]
PgNgN	0.21 ± 0.02	0.007	0.037 ± 0.016	$(1.89 \pm 0.23) \times 10^{-4}$	239 ± 97	-	[78]
p(g7NC ₂ N)	$(230 \pm 3.3) \times 10^{-3}$	0.067	0.36 ± 0.074	$(2.00 \pm 0.41) \times 10^{-3}$	180 ± 16	-	[79]
p(g7NC ₄ N)	$(210 \pm 2.9) \times 10^{-3}$	0.035	0.18 ± 0.067	$(1.46 \pm 0.53) \times 10^{-3}$	126 ± 12	-	[79]
p(g7NC ₆ N)	$(210 \pm 6.4) \times 10^{-3}$	0.065	0.34 ± 0.111	$(2.29 \pm 0.70) \times 10^{-3}$	150 ± 4	-	[79]
p(g7NC ₈ N)	$(250 \pm 3.4) \times 10^{-3}$	0.240	1.19 ± 0.371	$(6.01 \pm 1.87) \times 10^{-3}$	199 ± 27	-	[79]
p(g7NC ₁₀ N)	$(300 \pm 3.0) \times 10^{-3}$	0.370	1.83 ± 0.101	$(1.20 \pm 0.07) \times 10^{-2}$	153 ± 34	-	[79]
p(g7NC ₁₂ N)	$(328 \pm 5.3) \times 10^{-3}$	0.212	0.66 ± 0.113	$(6.50 \pm 1.01) \times 10^{-3}$	100 ± 6	-	[79]
p(g7NC ₁₆ N)	$(360 \pm 10.0) \times 10^{-3}$	0.047	0.33 ± 0.074	$(3.80 \pm 0.59) \times 10^{-3}$	86 ± 11	-	[79]
p(C-T)	0.43	0.80 ± 0.16	6.7 ± 0.9	0.069	97 ± 9	-	[80]
p(N-T)	0.25	0.72 ± 0.23	4.3 ± 0.6	0.059	73 ± 9	-	[80]
p(C-2 T)	0.44	0.14 ± 0.04	1.0 ± 0.3	0.019	53 ± 9	-	[80]
PIBET-AO	0.44 ± 0.02	1.3	-	-	-	590	[81]
PIBET-O	0.44 ± 0.01	1.0	-	-	-	620	[81]
PIBET-BO	0.62 ± 0.01	0.8	-	-	-	762	[81]
PIBET-A	0.86 ± 0.06	0.5	-	-	-	18.9 s	[81]
PIBT-BO	0.80 ± 0.01	1.4	-	-	-	1.1 s	[81]

(continued on next page)

Table 1 (continued)

Materials	V_{th} [V]	$g_{m,norm}$ [S cm ⁻¹]	μC^* [F cm ⁻¹ V ⁻¹ s ⁻¹]	μ [cm ² V ⁻¹ s ⁻¹]	C^* [F cm ⁻³]	$\tau_{(ON)}$ [ms]	Reference
AIG-BT	0.55	0.029 ± 0.006	0.12 ± 0.03	$1.4 \times 10^{-3} \pm 4 \times 10^{-4}$	83.5 ± 8.5	-	[84]
2DPP-OD-TEG	0.89 ± 0.01	0.73	7	4.78×10^{-2}	146	500	[87]
P(gPzDPP-2 T)	0.56	-	0.22	1.6×10^{-3}	134	22.7	[88]
P(gPzDPP-CT2)	0.32	-	1.72	1.9×10^{-2}	91	3.0	[88]
P(gTDPP2FT)	0.64 ± 0.01	-	54.8	0.35	156 ± 24	1.75	[90]
f-BTI2TEG-T	0.68	0.27	2.30	0.044	52	332	[92]
f-BTI2TEG-FT	0.53	4.60	15.20	0.034	443	272	[92]
f-BTI2g-TVT	0.9	0.27	1.50	0.014	110 ± 19	68	[94]
f-BTI2g-TVTCN	0.68	12.8	41.3	0.24	170 ± 22	52	[94]

Table 2

Summary of n-type small molecule-based OECT performance parameters.

Materials	V_{th} [V]	$g_{m,norm}$ [S cm ⁻¹]	μC^* [F cm ⁻¹ V ⁻¹ s ⁻¹]	μ [cm ² V ⁻¹ s ⁻¹]	C^* [F cm ⁻³]	$\tau_{(ON)}$ [ms]	Reference
C60-TEG	0.556 ± 0.006	0.0146	7.0 ± 2.0	$3 \times 10^{-2} \pm 1 \times 10^{-4}$	220 ± 50	80 ± 10	[97]
4Cl-PDI-4EG	0.05	0.0452	0.13 ± 0.05	$4.18 \pm 0.18 \times 10^{-4}$	303 ± 17	215	[101]
4Cl-PDI-3EG	0.26	0.0484	0.17 ± 0.03	$(8.07 \pm 0.71) \times 10^{-4}$	198 ± 25	282	[101]
PDI-3EG	0.34	0.0164	0.08 ± 0.02	$(3.79 \pm 0.10) \times 10^{-4}$	207 ± 8	130	[101]
gNR	0.35 ± 0.01	$(402 \pm 10) \times 10^{-3}$	2.5 ± 0.1	0.013	198 ± 12	195	[104]
hgNR	0.29 ± 0.01	$(263 \pm 3) \times 10^{-3}$	1.2 ± 0.04	0.009	129 ± 3	128	[104]
PrC ₆₀ MA	0.620	6.1	21.7	-	-	-	[105]
PrC ₆₀ MA:p(g2T-TT) (95:5)	0.649	3.0	11.8	-	-	20 ± 3	[105]

implementation of various materials design strategies including a high degree of backbone planarity and judicious tuning of frontier energy levels. Some molecular design strategies for n-type materials in OFETs have been borrowed, such as using electron-deficient building blocks or introducing electron-withdrawing groups onto the chromophores, leading to promising device performance. Besides, detailed structure-property relationships of n-type channel materials are studied at the same time continuously increasing the understanding. Whereas the first n-type OECT materials displayed electron mobilities on the order of 10^{-5} cm² V⁻¹ s⁻¹, the best-performing materials now have electron mobilities above 0.1 cm² V⁻¹ s⁻¹ with corresponding μC^* figure-of-merit values above 40 F cm⁻¹ V⁻¹ s⁻¹. Albeit still more than an order of magnitude lower than the best-performing p-type materials, the gap in device performance between p- and n-type OECT materials has narrowed significantly over the last few years.

In terms of their applications within OECT frameworks for biological sensing, n-type materials have until very recently been markedly absent from the field, due largely to their inherent ambient instability and generally poorer performance than p-type materials, which obstructed progress for a long time. However, the last few years have witnessed a turning point, in which new n-type materials are being applied as biological sensing components in OECTs for the first time, thanks to the debut of a new generation of materials which overcome these issues by structural design. This includes the development of aqueous stable, efficient n-type materials whose electron-accepting characteristics can be exploited alongside enzymes for biological sensing; in addition, the attainment of mobility and conductivity values which approach p-type counterparts has enabled an advancement in the production of all-organic OECT-based complementary inverters. This takes the field a step closer to mimicking the energy efficiency, complexity and plasticity of biological synapses, to achieve the complex processing and memory required for the advancement of artificial intelligence technologies.

Looking forward, the rapid development of both small-molecule and polymeric n-type semiconductors with highly efficient mixed ionic-electronic properties bodes well for continued development. As such, we envision that this ongoing push for further improving the n-type OECT performance metrics through molecular design will continue to narrow the performance gap between p- and n-type OECT materials. A major challenge still exists around the ambient and operational stability

of these materials and the potential for detrimental side reactions with water and oxygen.

As higher-performing materials start to appear and become available for device implementation, we expect further progress with bio-electronic applications to follow. For instance, improving on the design features established so far, we anticipate more examples of n-type materials tailored to sense specific analytes, biomarkers and biological processes. The continued enhancement of performance through new materials development and device engineering combined with the low power requirements also open the door to wearable and real-time sensing and monitoring technologies to be developed further and edge closer to marketable products. The flexibility and potential for aqueous stability and high biocompatibility of these materials and their devices mean that they also hold the potential to be applied in vivo in the future. (Tables 1 and 2).

5. CRediT authorship contribution statement

Simiao Yu: Data curation, Writing – original draft preparation, Writing – review & editing. **Christina J. Kousseff:** Data curation, Writing – original draft preparation, Writing – review & editing. **Christian B. Nielsen:** Conceptualization, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

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