

**Strategies for Optimizing Hydrophobic Semiconducting Polymers for OECTs:
Modifications and Additives**

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ABSTRACT

Organic electrochemical transistor (OECT) are widely explored for advanced applications, including implantable bioelectronics and neuromorphic computing. These devices rely on organic mixed ion-electron conductors (OMIECs) as active channel materials, enabling ionic and electronic charge transport. However, OMIECs face challenges such as excessive swelling, degrading electrical performance, and synthetic constraints. To overcome these limitations, hydrophobic semiconducting polymers, when engineered, present a promising alternative.

In the first part of this thesis, organometallic polymers are explored as channel materials for OECTs. Three novel ruthenium (Ru)-polymetallaynes with distinct bridging ligands—2,2'-dodecylbithiophene (BT), cyclopentadithiophene (CPDT), and dithienopyrrole (DTP)—were designed and synthesized. Varying from BT to CPDT introduces ligand planarity, while transitioning to DTP achieves redox-matching between the metal and ligand oxidation potentials, enhancing metal-metal (M-M) interactions. This leads to multiple oxidation states, resonance stabilization (comproportionation constant (K_c) = 2×10^5), and improved state retention (90% over 30 minutes) in electrochromic devices. The OECT device performance improves from BT to CPDT and is best for DTP, supporting the redox-matching principle. This demonstrates the potential of this strategy for developing OMIECs and introducing functions like non-volatility, which is useful for neuromorphic non-volatile memory devices.

OECTs require active materials that enable both electrical and ionic transport. While several semiconducting polymers, such as poly(3-hexylthiophene) (P3HT), offer good electrical conductivity, their hydrophobic nature limits ion transport, hindering OECT performance. In the second and third parts of this thesis, enhanced ion transport in such polymers is achieved using two metal-containing additives: (1) 20 mol%-doped poly(vinylferrocene) (PVF⁺), a redox-active and hydrophilic polymer, and (2) poly(ethylene glycol)-functionalized gold nanoparti-

cles (PEG-AuNPs).

In the second part, PVF^+ was blended with hydrophobic P3HT, resulting in phase separation, with P3HT forming the continuous domain, as confirmed by electron microscopy. The continuous P3HT domain preserves the electron transport pathway. The hydrophilicity of PVF^+ enhances ion penetration efficiency, as shown by cyclic voltammetry (CV) and spectroelectrochemical (SEC) analysis, which reveals a higher number of P3HT polarons in the blend compared to pure P3HT, and OECT devices exhibit shorter response times with higher PVF^+ content. grazing incidence wide-angle X-ray scattering (GIWAXS) shows suppressed face-on P3HT crystallite formation, enhancing ion diffusion.

In the third part, gold nanoparticles (AuNPs) are explored since the enhancement of charge carrier mobility (μ) in composites has been demonstrated. Moreover, AuNP offer flexibility for surface modification, introducing hydrophilic sites into the channel and facilitating ion penetration. Incorporating hydrophilic AuNP into P3HT improves both ionic and electrical performance in OECTs. The enhancement of μ is attributed to crystal contraction in the composites as revealed by GIWAXS. Electrical impedance spectroscopy and SEC analysis show increased volumetric capacitance (C^*) and more efficient doping of P3HT in the composite, respectively. This leads to a high μC^* value ($98 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ at 5 wt% PEG-AuNP), comparable to state-of-the-art OMIECs. Furthermore, composite OECTs exhibit shorter response times than P3HT-based devices, likely due to the hydrophilic sites on PEG-AuNP, enhancing ion transport. This approach is also applicable to other hydrophobic semiconductors, such as poly(2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl)thieno[3,2-b]thiophene)) (PDPP-TT).

In conclusion, this thesis explores advanced materials, including Ru polymetallaynes and composites of hydrophobic semiconducting polymers with metal-containing additives, to enhance OECT performance. These strategies introduce unique properties, such as non-volatility, suitable for high-capacity memory appli-

cations, and leverage the advantages of well-understood hydrophobic polymers. Incorporating metal-containing additives leads to balanced improvements in electrical and ionic performance, significantly expanding the range of OMIEC available for tailored applications.

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LIST OF ABBREVIATIONS

Δ_o	crystal field splitting
ΔE	potential difference
$\Delta E_{a,c}$	difference of the anodic peak of oxidation and the cathodic back-reduction peak
$\Delta T\%$	transmittance changes
μ	charge carrier mobility
μ_h	hole charge carrier mobility
μ_{lin}	μ at linear regime
μ_{sat}	μ at saturation regime
τ	response time
τ_{off}	turn-off time
τ_{on}	turn-on time
[EMIM][TFSI]	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
AC	alternating current
ACA	advancing contact angle
AFM	atomic force microscopy
Ag/Ag ⁺	non-aqueous silver/silver ion
Ag/AgCl	silver/silver chloride
AgCl	silver chloride
AgOTf	silver trifluoromethanesulfonate
AIBN	azobisisobutyronitrile

AO	atomic orbital
Au	gold
AuNP	gold nanoparticle
BBL	poly(benzimidazobenzophenanthroline)
Br ⁻	bromide ion
BT	2,2'-dodecylbithiophene
BTD	benzothiadiazole
C	carbon
C*	volumetric capacitance
C-C	carbon-carbon single bonds
C=C	carbon-carbon double bonds
CB	conduction band
Cl ⁻	chloride ion
CPDT	cyclopentadithiophene
CPE-K	poly[2,6-(4,4-bis-potassium butanylsulfonate-4H-cyclopenta-[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)]
CV	cyclic voltammetry
DFT	density functional theory
DPP	diketopyrrolopyrrole
DTP	dithienopyrrole
E _B	thermal energy barrier
E _g	bandgap
E _{onset}	onset of oxidation potential
E _{ox}	oxidation potential
EC	electrochromic

EDL	electrical double layer
EDOT	3,4-ethylenedioxythiophene
EG	ethylene glycol
EGOFET	electrolyte-gated organic field-effect transistor
EGT	electrolyte-gated transistor
EIS	electrical impedance spectroscopy
EPR	electron paramagnetic resonance
Fc	ferrocene
Fc ⁺	ferrocenium
Fc/Fc ⁺	ferrocene/ferrocenium
Fe	iron
Fe ₂ (SO ₄) ₃	iron(III) sulfate
g _{av}	average EPR g-value
g _{m,n}	geometry-normalized g _m
g _{m,max}	peak g _m
g _m	transconductance
GIWAXS	grazing incidence wide-angle X-ray scattering
GOPS	glycidylxypropyl trimethoxysilane
GPC	gel permeation chromatography
H	hydrogen
H _{AD}	electronic coupling between acceptor and donor
HAuCl ₄	chloroauric(III) acid
HMDS	hexamethyldisilazane
HOMO	highest occupied molecular orbital
I _g	gate current
I _{d,lin}	I _d at the linear regime

$I_{d,sat}$	I_d at the saturation regime
I_d	drain current
IS	inner-sphere
ITO	indium tin oxide
IVCT	intervalence charge transfer
K_c	comproportionation constant
LCAO	linear combination of atomic orbitals
LF	Ligand field
LMCT	ligand-to-metal charge transfer
LUMO	lowest unoccupied molecular orbital
M-M	metal-metal
MLCT	metal-to-ligand charge transfer
MO	molecular orbital
MV	mixed-valence
N	nitrogen
n-Bu ₄ NPF ₆	tetra-n-butylammonium hexafluorophosphate
NDI	naphthalene diimide
nec-	non-endcapped
NIR	near-infrared
NMR	nuclear magnetic resonance
O	oxygen
O ²⁻	oxo
OECD	organic electrochromic device
OECT	organic electrochemical transistor
OFET	organic field-effect transistor
OLED	organic light-emitting diode

OMIEC	organic mixed ion-electron conductor
OPV	organic photovoltaic
OS	outer-sphere
OSC	organic semiconductor
OSCP	organic semiconducting polymer
p	injected charge carrier density
P3DDT-b-PMMA	poly(3-dodecylthiophene)-block-poly(methyl methacrylate)
P3EHT-b-PEO	poly(3-(2'-ethylhexyl)-thiophene)-block-poly(ethylene oxide)
P3HT	poly(3-hexylthiophene)
P3HT-b-PEO	poly(3-hexylthiophene)-block-poly(styrenesulfonate)
PBTTT	poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene]
PCBM	[6,6]-phenyl-C ₆₁ -butyric acid methyl ester
Pd	palladium
PDI	polydispersity
PDPP-TT	poly(2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl)thieno[3,2-b]thiophene))
PEDOT	poly(3,4-ethylenedioxythiophene)
PEDOT-S	poly(3,4-ethylenedioxythiophene) derivative
PEDOT:PSS	poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PEG	poly(ethylene glycol)
PEG-AuNP	poly(ethylene glycol)-functionalized gold nanoparticle

PSS	polystyrene sulfonate
Pt	platinum
PTHS	poly(6-(thiophene-3-yl)hexane-1-sulfonate) tetrabutylammonium
PVA	poly(vinyl alcohol)
PVDF-HFP	poly(vinylidene fluoride-co-hexafluoropropylene)
PVF	poly(vinylferrocene)
PVF ⁺	20 mol%-doped poly(vinylferrocene)
py	pyridine
RCA	receding contact angle
Ru	ruthenium
S	sulfur
SEBS	polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene
SEC	spectroelectrochemical
SEM	scanning electron microscopy
SMU	source-measure unit
SS	subthreshold swing
TEM	transmission electron microscopy
TFSI ⁻	bis(trifluoromethanesulfonyl)imide
THF	tetrahydrofuran
Ti	titanium
UV-vis-NIR	Ultraviolet-visible near-infrared
V _d	drain potential
V _g	gate potential
V _{th}	threshold potential

VB	valence band
VF	vinylferrocene

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Chapter 1

Introduction

1.1 Organic electronics

In the 1970s, Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa made a ground-breaking discovery in materials science with a conjugated polymer, polyacetylene, that would later earn them the 2000 Nobel Prize in Chemistry.[1, 2] When doped with iodine, polyacetylene – featuring an alternating arrangement of single and double bonds (π -conjugation) – achieves conductivity as high as $2 \times 10^4 \text{ S cm}^{-1}$ at room temperature.[3] Since then, scientific interest in conjugated polymers has surged, as evidenced by a large number of publications (>32000 articles) according to a Google Scholar search with the keyword “conjugated polymers”.

This discovery paved the way for the field of organic electronics, an interdisciplinary domain bridging physics, chemistry, materials science, and electronics. One of the main focus points in the field is on developing high-performance organic semiconducting polymers known for their solution processability, mechanical flexibility, and lightweight nature. These properties facilitate the large-scale fabrication of organic electronic devices, including organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), and organic electrochromic devices (OECDs).

The development of organic semiconducting polymers has paved the way for a diverse range of electronic applications, extending beyond traditional devices like OFETs. Apart from the above-mentioned emerging technologies, electrolyte-

gated transistors (EGTs) have garnered significant attention in the last decade due to their unique ability to couple ion and electron transport. EGTs exhibit high capacitance and, therefore, operate at low potential and possess exceptional transconductance (transconductance (g_m)), making them highly suitable for detecting weak biological signals in bioelectronic applications. Additionally, unlike conventional inorganic semiconductors, organic semiconducting polymers used in EGTs do not form insulating oxide layers during operation in the presence of electrolytes, ensuring stable performance and efficient ion penetration. These advantages position EGTs as a versatile platform for next-generation bioelectronics, neuromorphic computing, and other advanced technologies.

1.2 Electrolyte-gated transistors (EGTs)

1.2.1 Device architecture

Since the first demonstration of EGT by Wrighton in 1984 using a polypyrrole channel (a five-terminal device, shown in **Figure 1.1**),[4] these devices have received immense interest due to their versatility across a wide range of applications, including label-free (bio-)sensing[5, 6, 7] to cutting-edge neuromorphic technologies[8, 9, 10, 11].

EGTs have since evolved into three-terminal devices composed of source, drain, and gate electrodes. The source and drain electrodes could be made of gold (Au) or conductive polymers, while the gate terminal could be a polarizable (e.g., Au, and platinum (platinum (Pt))) or non-polarizable (e.g., silver/silver chloride (silver/silver chloride (Ag/AgCl)) pellet) electrode, and the channel conductance can be modulated by the application of gate potential.[12]

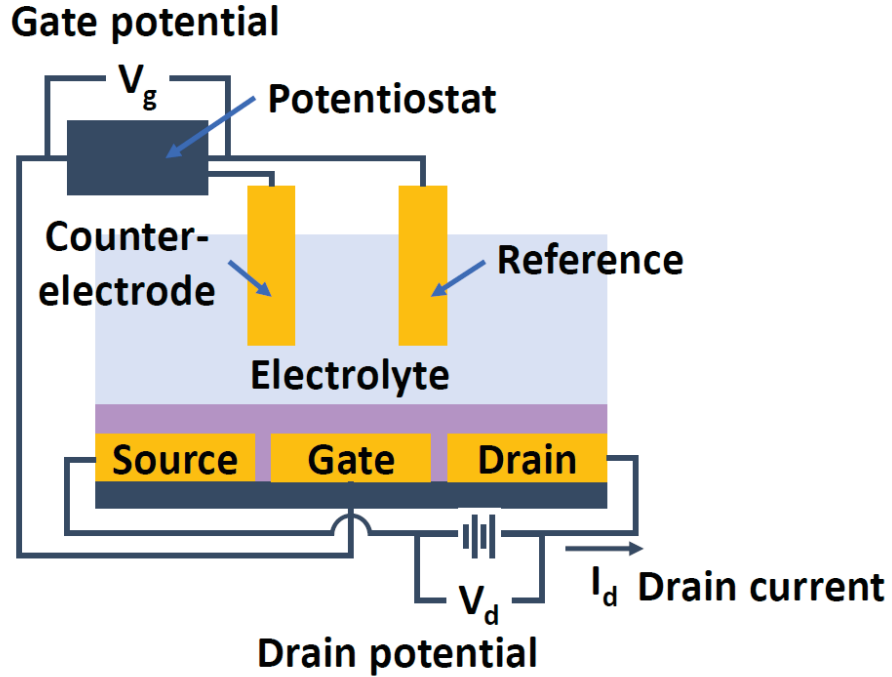


Figure 1.1: First demonstration of a 5-terminal electrolyte-gated transistor (EGT) with the use of polypyrrole as the semiconducting channel (Condition: 0.1 M n-Bu₄NClO₄). Reproduced with permission from Ref [4].

Unlike conventional OFETs, which use a dielectric layer to electrically separate the gate terminal and the semiconductor channel, EGTs replace the dielectric layer with an electrolyte or water layer (illustrated in **Figure 1.2**).

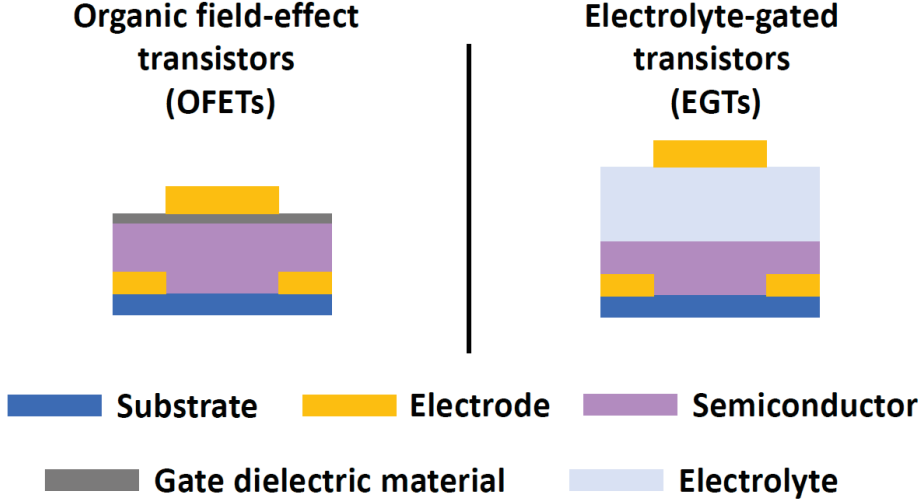


Figure 1.2: Device components/architectures of OFET (left) and EGT (right).

This design, leveraging the high capacitance of the electrolyte, allows operation at low voltages (e.g., ± 1 V), [13, 14] enabling applications in biosensing without the risk of cell damage. Furthermore, the semiconducting channel in EGTs sometimes exhibits higher charge carrier mobility compared to conventional OFETs with the same channel material, possibly due to reduced electrostatic potential fluctuation at high charge carrier densities in the presence of electrolyte. [15] Note that this is a hypothesis that still remains ambiguous, and further experimental investigations are still needed.

EGTs can be constructed using various configurations, including top-gate and lateral (coplanar) gate architectures (**Figure 1.3**). In the top-gate configuration, the gate terminal is positioned above the source-drain channel plane, offering convenient implementation for device characterization since challenges such as gate alignment are avoided during fabrication. Conversely, the lateral-gate configuration places the gate terminal on the same plane as the source-drain channel. In this

configuration, multiple-gate configuration, which is required in various applications such as integrated sensing platforms and neuromorphic circuits, can be realized.[16]

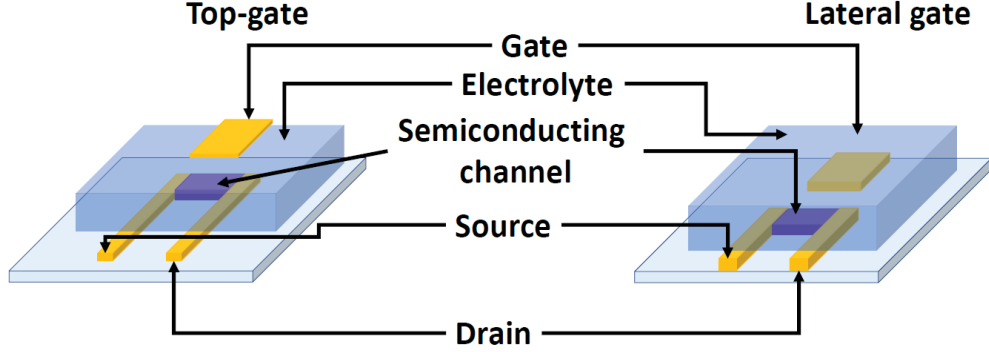


Figure 1.3: Different configurations of EGT: top-gate (left) and lateral-gate (right) configuration.

1.2.2 Operation mechanism and device metrics

Furthermore, EGTs can be categorized into two main device types – electrolyte-gated organic field-effect transistors (EGOFETs) and organic electrochemical transistors (OECTs), which differ in the operation mechanisms due to different electrolyte-channel interactions

1.2.2.1 Electrolyte-gated organic field-effect transistors (EGOFETs)

Figure 1.4 shows different commonly observed operation mechanisms of EGOFETs, including p-type and n-type accumulation mode operations. In p-type accumulation mode operation, the application of a negative gate potential (V_g) smaller than the threshold potential (V_{th}) induces the migration of cations in the electrolyte toward the gate/electrolyte interface, while anions accumulate at the electrolyte/channel interface. This compensates for the generated charge carriers (i.e., holes) at the channel surface. Consequently, a thin conductive channel of hole charge carriers is formed, transitioning the channel from a high-resistance state (i.e., off-state) to a low-resistance state (i.e., on-state) when a constant negative

drain potential (V_d) is applied across the channel. In n-type accumulation mode operation, a positive V_g larger than V_{th} is applied at the gate, inducing the migration of electrolytic anions toward the gate/electrolyte interface. Simultaneously, cations accumulate at the electrolyte/channel interface, compensating the generation of charge carriers (i.e., electrons) at the surface of the channel and transitioning the channel from off-state to on-state when a positive V_d is applied across the channel.

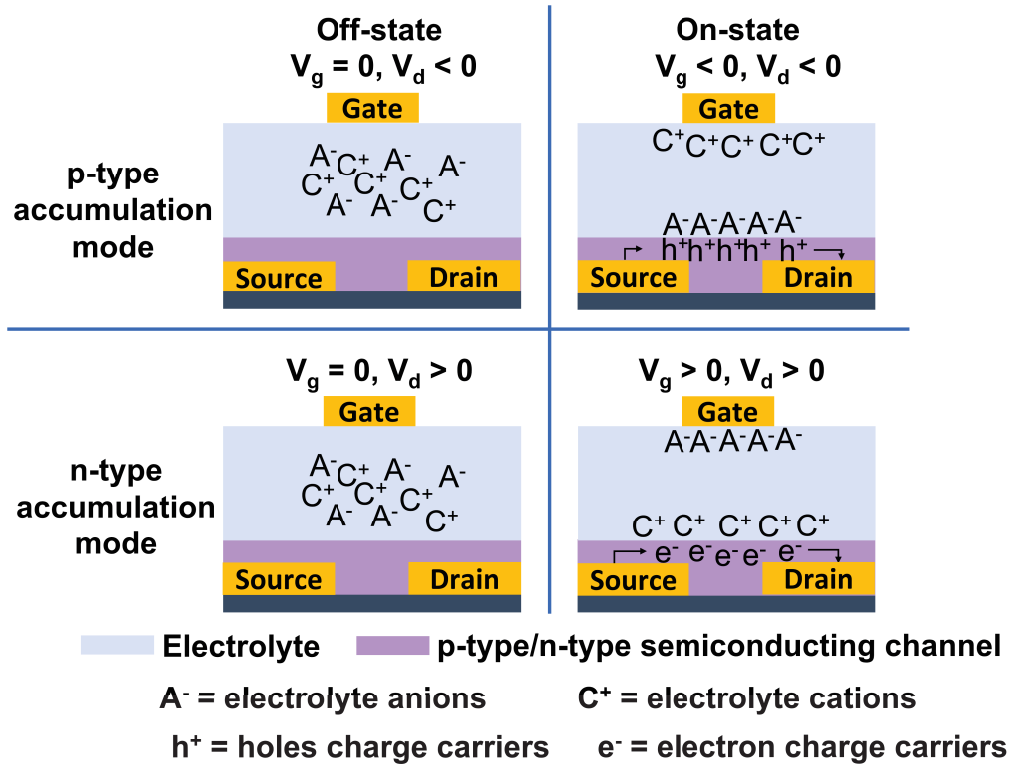


Figure 1.4: Graphical illustration of p-type and n-type operation in accumulation mode electrolyte-gated organic field-effect transistors (EGOFETs).

Due to the weak interaction between the channel and electrolyte, ion penetration is minimal, with ions and charge carriers primarily accumulating at the electrolyte/channel interface, forming an electrical double layer (EDL). This EDL formation model can be applied to EGTs with hydrophobic semiconducting materials as the channel in general. Taking p-type accumulation operation mode as an example (Figure 1.5), since the EGOFET operation mechanism resembles that

of OFET, which primarily relies on interfacial charge accumulation or depletion at the channel under an electric field from the gate terminal, the steady-state drain current (I_d) behavior at the linear regime ($I_{d,lin}$) and at the saturation regime ($I_{d,sat}$) can be modeled by **Equation 1.1** and **Equation 1.2**, respectively:[14]

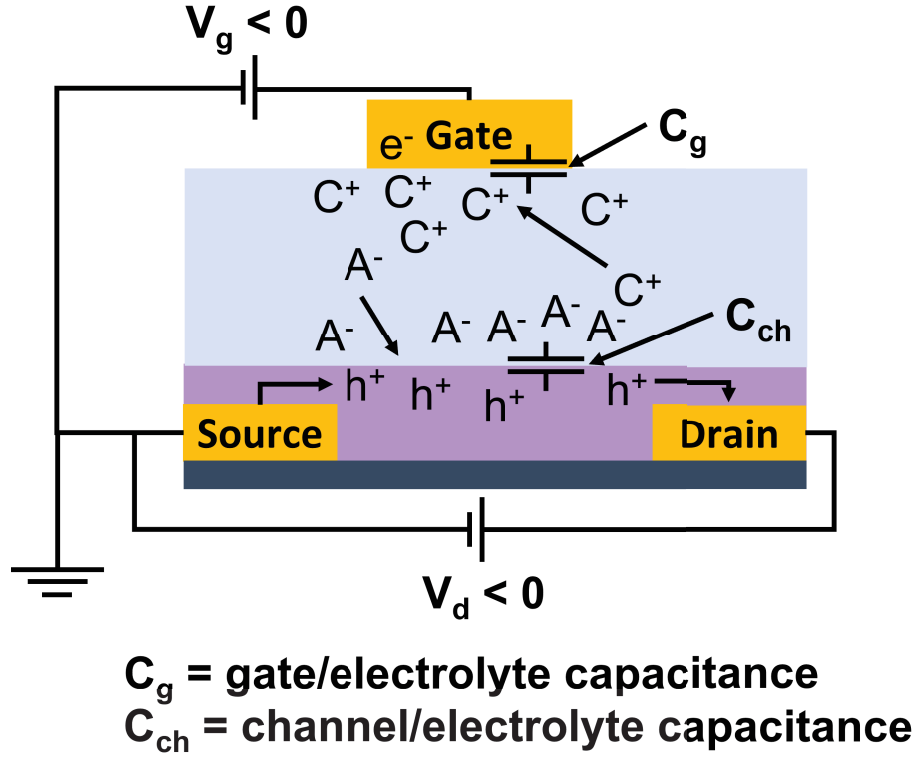


Figure 1.5: Depiction of operation mechanism for EGOFETs. It involves the formation of EDL at the gate/electrolyte and the electrolyte/channel interfaces, and the accumulation of charge carriers (e.g., holes) at the electrolyte/channel interface.

$$I_{d,lin} = -\frac{W}{L} \mu_{lin} C \left(V_g - V_{th} - \frac{V_d}{2} \right) V_d \quad \text{when } |V_g - V_{th}| \geq |V_d| \quad (1.1)$$

$$I_{d,sat} = -\frac{W}{2L} \mu_{sat} C (V_g - V_{th})^2 \quad \text{when } |V_g - V_{th}| \leq |V_d| \quad (1.2)$$

, where W and L are channel width and length, respectively, μ_{lin} and μ_{sat} are charge carrier mobility (μ) at linear and saturation regimes, respectively, and C is

the capacitance per unit area (When a polarizable gate is used, $C = \left(\frac{C_{\text{ch}} + C_g}{C_{\text{ch}} \times C_g} \right) A_{\text{ch}}^{-1}$, where C_{ch} is the capacitance at the channel/electrolyte interface, C_g is the capacitance at the gate/electrolyte interface and A_{ch} is the channel area; when a non-polarizable gate is used, $C = C_{\text{ch}} A_{\text{ch}}^{-1}$).

With the help of the above-mentioned equations and the device's current-voltage characteristics, important device parameters, including on-off ratio, subthreshold swing (SS), V_{th} , μ , and transconductance (g_m), can be extracted.[17, 18] The on-off ratio, derived from the transfer curve, where V_d is kept constant (negative in the case of a p-type channel), V_g is swept (in the negative range), and I_d is measured, indicating the distinction between the device's on-state and off-state. The highest I_d at the on-current and the lowest I_d at the off-state are used to calculate the on-off ratio. A high on-off ratio is preferable for clear state differentiation. SS quantifies the voltage required to achieve a 10-fold increase in I_d , which is expressed in V dec^{-1} and defined as $\text{SS} = \frac{\partial V_g}{\partial \log_{10} I_d}$. It indicates how sharply a device can be switched on.

V_{th} is also determined from the transfer curve by extrapolating the linear fit of $I_{d,\text{lin}}$ and $\sqrt{I_{d,\text{sat}}}$ to $I_d = 0$ in the linear and saturation regimes, respectively. In EGOFET, V_{th} can be influenced by factors such as gate potential,[19, 20] electrolyte humidity[21], and Ohmic loss at the electrolyte/channel interface during operation.[22]

μ , a parameter of how efficiently charge carriers move in the channel, can be calculated from the $\frac{\partial I_d}{\partial V_g}$ and $\frac{\partial \sqrt{I_d}}{\partial V_g}$ in the linear and saturation regimes as shown in the following **Equation 1.3** and **Equation 1.4**, respectively:

$$\mu_{\text{lin}} = \frac{\partial I_{d,\text{lin}}}{\partial V_g} \left(\frac{L}{C W V_d} \right) \quad \text{when } |V_g - V_{\text{th}}| \geq |V_d| \quad (1.3)$$

$$\mu_{\text{sat}} = \left(\frac{\partial \sqrt{I_{d,\text{sat}}}}{\partial V_g} \right)^2 \left(\frac{2L}{C W} \right) \quad \text{when } |V_g - V_{\text{th}}| \leq |V_d| \quad (1.4)$$

g_m , which can be calculated from the slope of the transfer curve, indicates signal amplification efficiency and the extent of ion-channel interaction in EGOFETs.

In EGOFETs with weak ion-channel interaction, g_m values typically fall in the micro-Siemens range.[23, 24]

However, some studies suggest that ion penetration could still occur although hydrophobic semiconducting materials were utilized,[25, 26, 27] resulting in the oxidation of the channel materials in the presence of counteranions and leading to a “mixed-mode” operation mechanism.[28]

1.2.2.2 Organic electrochemical transistors (OECTs)

Among all EGTs, OECTs have gained significant attention over the last decade. As a subset of EGTs, OECTs are distinguished by their use of hydrophilic, swellable, and ion-permeable semiconducting materials, namely, organic mixed ion-electron conductors (OMIECs), as channel materials during the operation in aqueous medium.[18, 29] With high solution processability, biocompatibility, stability in physiological environments, and efficient ion-channel interaction,[18, 29] these materials make OECTs ideal for applications in implantable bioelectronics[30] and bio-interfacing.[31] In the following sections, the operation mechanism and device metrics of OECTs will be discussed.

Unlike EGOFETs, which rely on EDL formation at the electrolyte/channel interface, OECT channels are ion-permeable. Upon applying a V_g , electrolytic ions are injected into the channel via swelling, resulting in volumetric doping (or redox reactions). This generates polarons or bipolarons within the semiconducting channel volume, implying that the Faradaic reaction occurs at the channel, as supported by many in-operando spectroscopic characterizations.[32, 33], as illustrated in **Figure 1.6**, for different operation mechanisms, including p-type and n-type accumulation mode and p-type depletion mode, which are akin to those of the EGOFETs. Additionally, there is another option for OECT to operate in depletion mode when poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is used as the channel material. Since the PEDOT moiety is doped by the PSS moiety, this composite initially exhibits an on-state when the V_g is

zero. Upon applying a positive V_g , electrolytic anions will migrate toward the gate electrode while the electrolytic cations are injected into the PEDOT:PSS channel, compensating the negatively charged polystyrene sulfonate (PSS) ion and, thus, dedoping the poly(3,4-ethylenedioxythiophene) (PEDOT) moiety. As a result, the channel will be at an off-state.

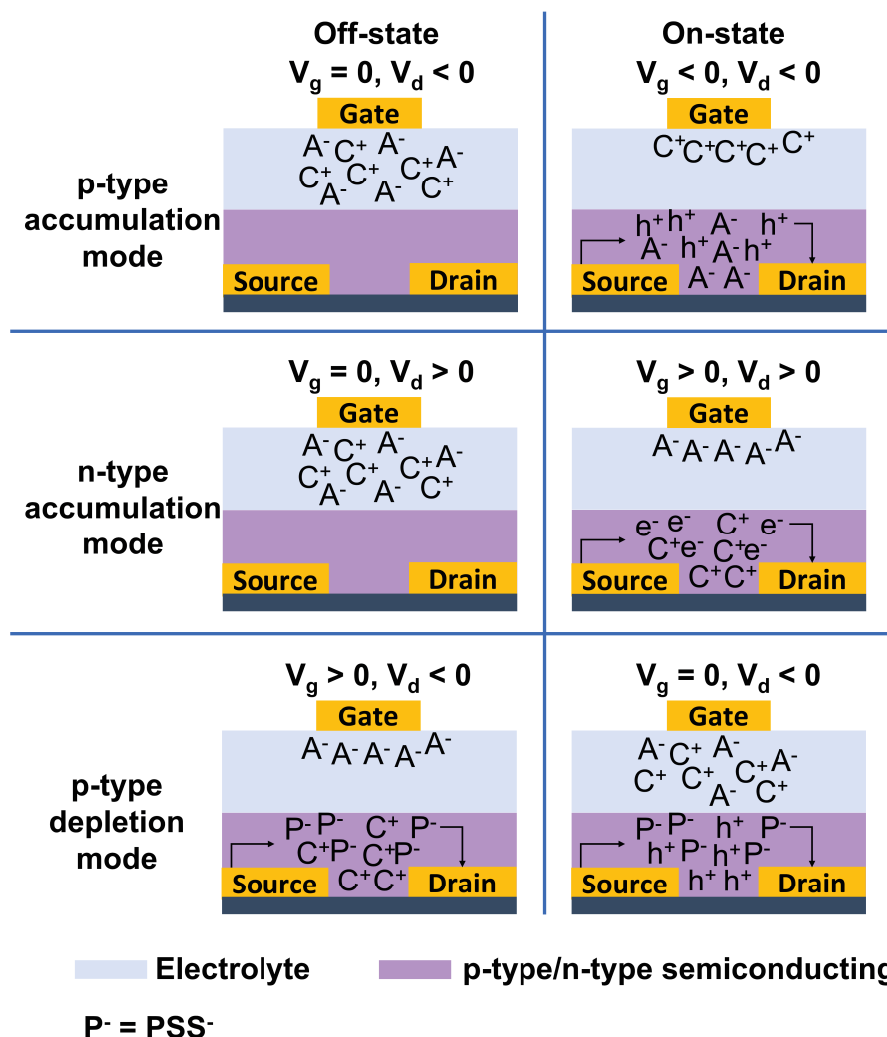


Figure 1.6: Schematic illustrations of common organic electrochemical transistor (OECT) operation mechanisms, including p-type accumulation mode, n-type accumulation mode, and p-type depletion mode operations.

Taking p-type accumulation mode OECT as an example (as illustrated in **Figure 1.7**), the steady-state I_d behavior of OECTs in both linear and saturation regimes can be modeled by the Bernards and Malliaras model with the long-channel approximation as shown in **Equation 1.5** and **Equation 1.6**: [34, 35, 36]

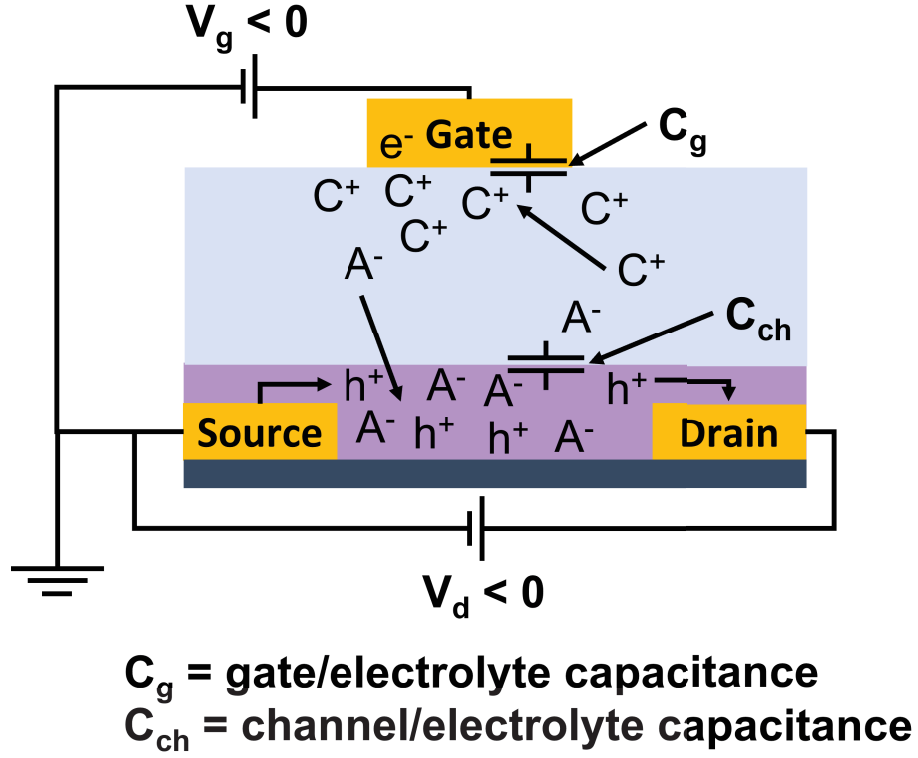


Figure 1.7: Illustration of operation mechanism for OECT, where anions are injected into the semiconductor channel when a negative gate potential (V_g) is applied, accompanied by the oxidation of the channel material.

$$I_{d,lin} = \frac{W_d}{L} \mu C^* \left(V_g - V_{th} - \frac{V_d}{2} \right) V_d \quad \text{when } |V_g - V_{th}| \geq |V_d| \quad (1.5)$$

$$I_{d,sat} = -\frac{W_d}{2L} \mu C^* (V_{th} - V_g)^2 \quad \text{when } |V_g - V_{th}| \leq |V_d| \quad (1.6)$$

,where C^* represents the volumetric capacitance of the channel and d is the channel thickness.

Accordingly, g_m in the both linear and saturation regime can be calculated by the

derivative of **Equation 1.5** and **Equation 1.6** with respect to V_g as shown in **Equation 1.7** and **Equation 1.8**, respectively:[36, 37]

$$g_m = \frac{\partial I_{d,lin}}{\partial V_g} = -\frac{W_d}{L} \mu C^* V_d \quad (1.7)$$

$$g_m = \frac{\partial I_{d,sat}}{\partial V_g} = \frac{W_d}{L} \mu C^* |V_{th} - V_g| \quad (1.8)$$

Key OECT parameters, such as on-off ratio, g_m , and V_{th} , are evaluated similarly to EGOFETs.[37] It is noteworthy that the g_m values in OECTs can reach the milli-Siemens range due to the volumetric response in the channel,[18] making them capable of sensing weak physiological signals such as nervous signals.[38] Another important metric for OECT is the material-specific parameter μC^* , which is the product of μ and volumetric capacitance (C^*)[39] and it offers a convenient evaluation and comparison of different OMIECs (**Figure 1.8**).

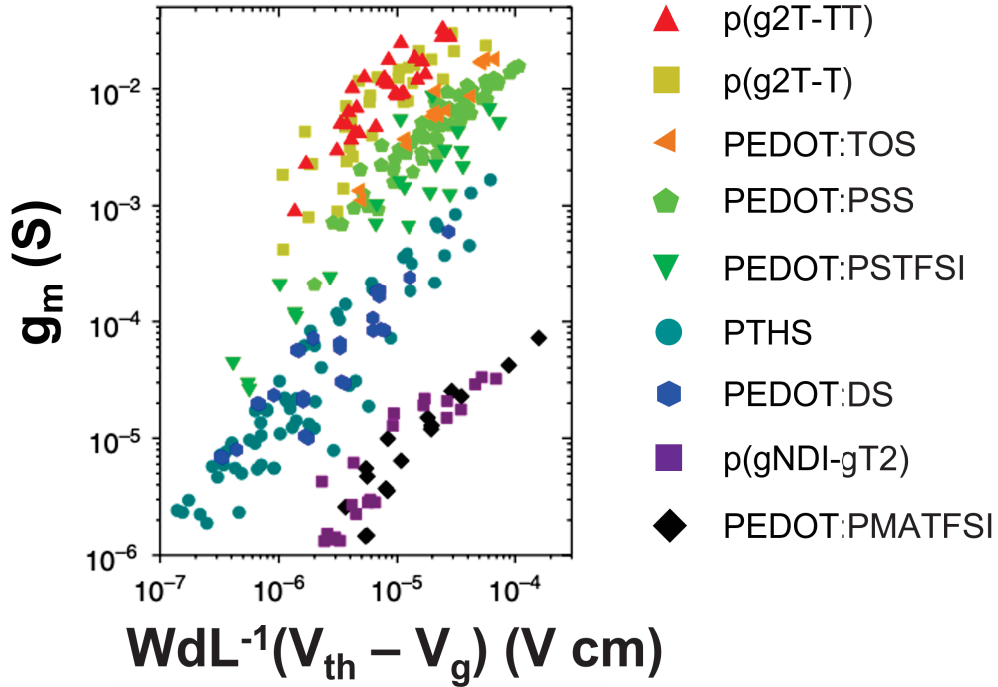


Figure 1.8: Peak transconductance ($g_{m,max}$) vs WdL^{-1} plots of different organic mixed ion-electron conductors (OMIECs). Reprint with permission from ref [36].

It is typically extracted from the transfer curve of an OECT device with varying geometry. The peak g_m ($g_{m,\max}$) at a corresponding operation condition $|V_{\text{th}} - V_g|$ is obtained. By varying the channel geometry, $g_{m,\max}$ vs $\frac{W_d}{L} |V_{\text{th}} - V_g|$ can be plotted, and μC^* is calculated from the slope of the linear fit.[37, 39] Finally, the response time (τ) for transient behavior, indicative of the ion-channel interaction efficiency,[28] can be measured by applying V_g in the form of a square wave and recording the change of I_d simultaneously. τ can be calculated either from the time required for I_d to rise/decay from 10% to 90% of its maximum value or from the exponential fitting of the rising/decaying I_d .

1.2.3 Semiconducting channel materials

1.2.3.1 Organic semiconductors (OSCs) single crystals

Single-molecule-based organic semiconductors (OSCs) are a class of carbon (C)-based materials with alternating carbon-carbon single bonds (C-C) and carbon-carbon double bonds (C=C) within a molecule. In these materials, the sp^2 -hybridized carbon atomic orbitals (AOs) interact with the adjacent sp^2 -hybridized carbon AOs to form σ (bonding) and σ^* (antibonding as denoted by the asteroid) molecular orbitals (molecular orbitals (MOs)), while the remaining p_z -orbitals of C atoms form π and π^* MOs (shown in **Figure 1.9**). The MO are filled with electrons according to the Aufbau principle and Hund's rule, creating the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and the interaction between HOMO and LUMO gives rise to conjugation (or resonance).

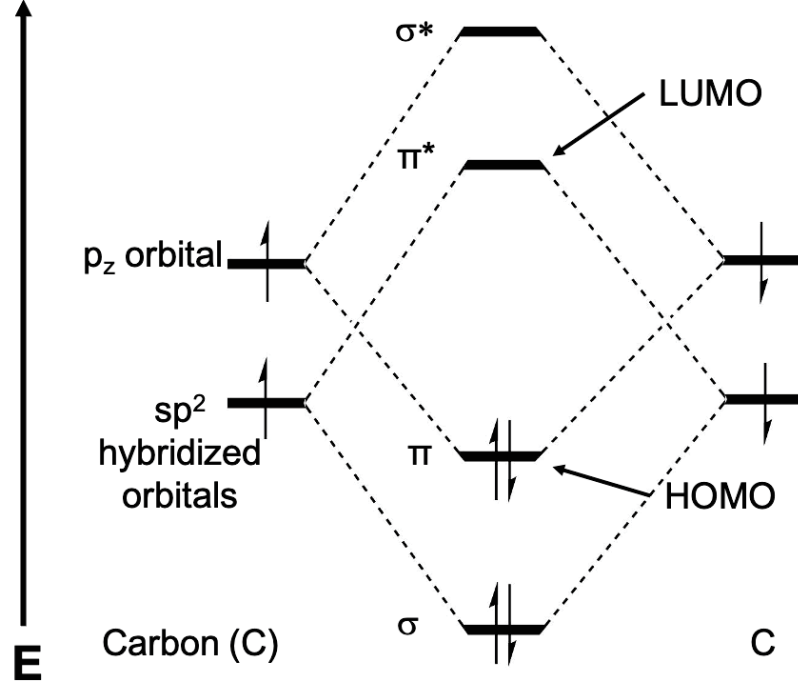


Figure 1.9: Illustration of the molecular orbitals (MOs) interaction between two sp^2 -hybridized C atoms and the formation of σ , π (highest occupied molecular orbital (HOMO)), π^* (lowest unoccupied molecular orbital (LUMO)), and σ^* MOs.

Typical examples of single crystals investigated in EGOFET include rubrene [40, 41] and pentacene, which are both known for their high hole charge carrier mobility (μ_h) in conventional OFET.[42, 43, 44], While these materials can exhibit high μ_h , their intrinsic brittleness limits their applications in, for example, flexible electronics.[40] Therefore, the polymeric forms of conjugated organic materials become a more versatile alternative.

1.2.3.2 Organic semiconducting polymers (OSCPs)

Organic semiconducting polymers (OSCPs), composed of elements, such as C, hydrogen (H), and heteroatoms (e.g., nitrogen (N), oxygen (O), or sulfur (S)) are widely utilized in EGOFETs. Their numerous possibilities for structural modification result in high solution processability and mechanical deformability.[45, 46]

Therefore, they have garnered significant interest within the research community. In order to understand a conjugated polymer's properties, such as optical absorption and ionization potential, a band diagram is often used to visualize the phenomena. Starting from 1,3-butadiene, as illustrated in **Figure 1.10**, the interaction between four carbon p_z orbitals forms four MOs (Ψ_1 to Ψ_4) with different numbers of nodal planes (dotted lines between the nodes) according to Hückel theory.

The energy level of the MOs is governed by the number of nodal planes in the MO (the less nodal plane, the more bonding character it has and, hence, more stable and of lower energy level). When the number of repeating units and conjugation length increase, a valence band (VB), which is formed by bonding MOs and accommodates the HOMO, and a conduction band (CB), which is formed by antibonding MOs and accommodates the LUMO, are formed. The energy gap between the VB and CB is the bandgap (E_g) of the material.

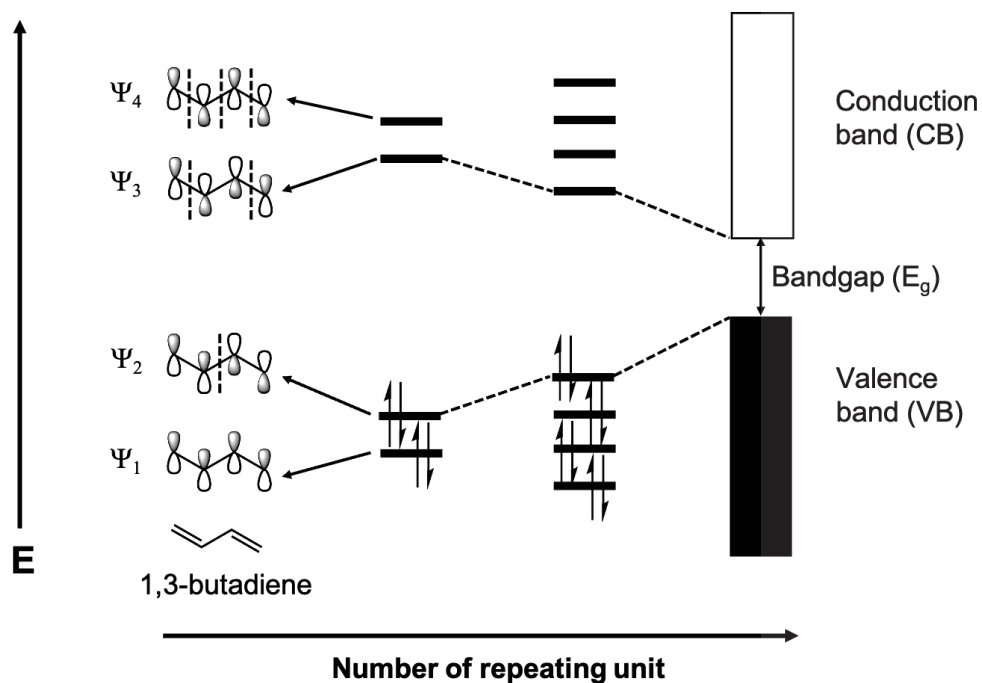


Figure 1.10: Exemplary MO diagram of 1,3-butadiene and the formation of conduction band (CB) and valence band (VB) when the repeating unit increases.

Depending on the HOMO-LUMO energy level, OSCPs can either exhibit p-type, in which hole transport through high-lying HOMO is supported, n-type, in which electron transport through low-lying LUMO is supported, or ambipolar behavior, in which both electron and hole transport are supported. Typical examples include the prototypical poly/oligothiophene,[47, 48, 49] poly[2,5-bis(3-tetradecylthiophen-2-yl) thieno[3,2-b]thiophene] (PBTTT)[50] and diketopyrrolopyrrole (DPP)-based polymers[51, 52] for p-type OSCPs, and naphthalene diimide (NDI)-based polymers and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) for n-type OSCPs,[53] as shown in **Figure 1.11**.

Conventional semiconducting polymers have been widely used in printed and flexible EGTs due to their excellent processability and mechanical flexibility. However, their predominantly hydrophobic nature often hinders ion transport, a critical device metric that governs the operation efficiency of EGTs.

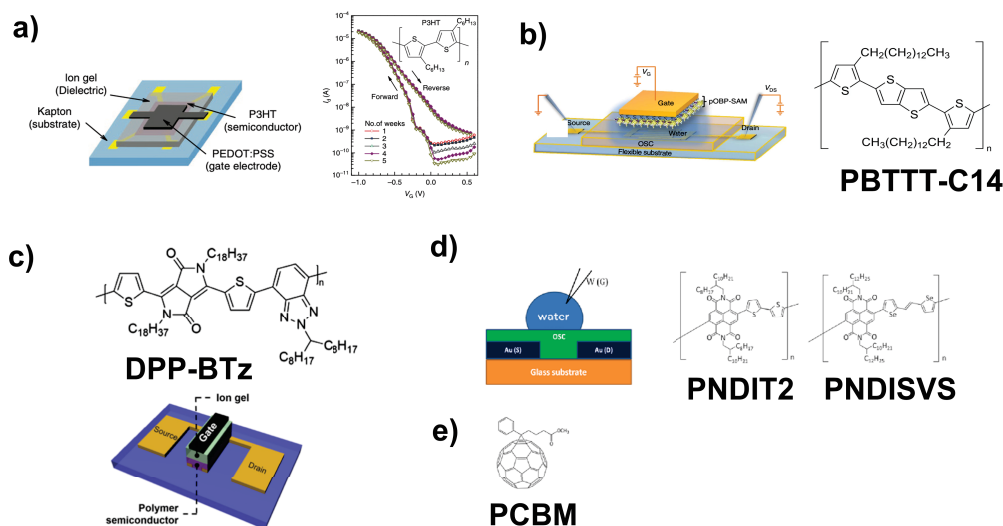


Figure 1.11: Examples of p-type organic semiconducting polymers (OSCPs), including a) polythiophene-based OSCP, b) PBTTT-based OSCP, and c) DPP-based OSCP, and n-type OSCPs including d) NDI-based OSCPs and e) PCBM. Reprinted with permission from ref [49][50][51][53].

To address these limitations, researchers have increasingly turned to another class of materials known as OMIECs. Unlike traditional OSCPs, OMIECs are

designed with hydrophilic properties that promote rapid ion transport. This is typically achieved by incorporating polar or ionic side chains into the polymer backbone. These modifications not only preserve the inherent electronic conductivity of the conjugated backbone but also create pathways that facilitate the movement of ions, which will be discussed in the next section.

1.2.3.3 Organic mixed ion-electron conductors (OMIECs)

OMIECs are distinctive polar and redox-active semiconducting materials that enable the mediation of both electron and ion transport. Their unique properties often stem from the presence of hydrophilic and charged side chains, which foster strong interactions with electrolytes and facilitate ion permeation into the channels. Consequently, OMIECs, which allow for volumetric doping and lead to substantial improvements in signal amplification (high g_m) and device response speed, find extensive application in OECTs, making them highly attractive for various aforementioned advanced applications. In this section, various types of OMIECs – block copolymers, conjugated electrolytes, composites/blends, and conjugated polymers with polar side chains will be introduced.[29]

Block copolymers

OMIEC with a block co-polymer structure consist of semiconducting polymer segments covalently connected to polyelectrolyte or polar polymer segments.[54, 55, 56] **Figure 1.12** shows some of the examples of block co-polymers, including poly(3-hexylthiophene)-block-poly(styrenesulfonate) (P3HT-b-PEO), poly(3-(2-ethylhexyl)-thiophene)-block-poly(ethylene oxide) (P3EHT-b-PEO) and poly(3-dodecylthiophene)-block-poly(methyl methacrylate) (P3DDT-b-PMMA). This structure gives rise to phase separation in the solid state, which results in the segregation of electronically and ionically conductive phases. By manipulating segment ratios, diverse morphologies can be achieved, making block co-polymers versatile for various functional roles. However, their OECT performance remains underexplored as most studies have focused on spectroscopic and morphological investigations for the two-terminal electrochromic or light-emitting devices.

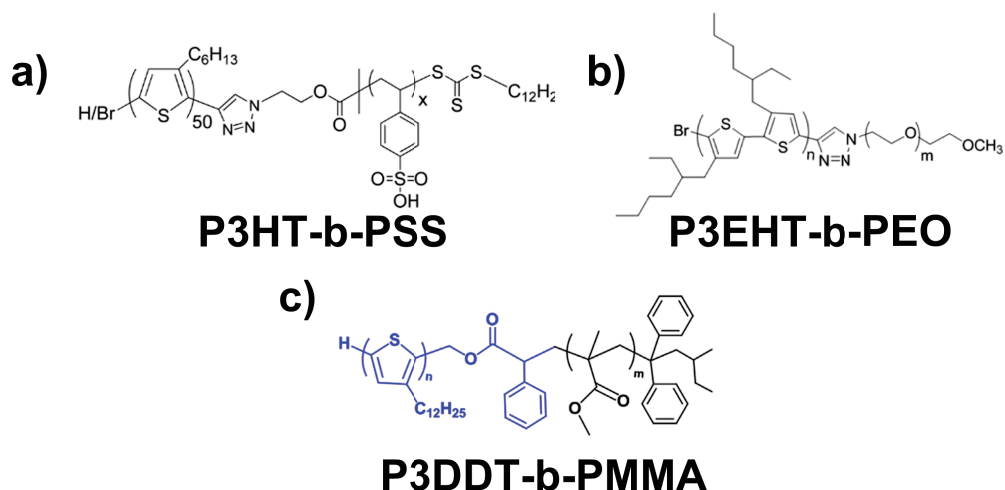


Figure 1.12: Examples of block co-polymers such as a) P3HT-b-PEO, b) P3EHT-b-PEO, and c) P3DDT-b-PMMA.

Conjugated polyelectrolytes

Conjugated polyelectrolyte features conjugated semiconducting backbones with tethered side chains with ionic terminal,[57, 58, 59, 60, 61] thereby exhibiting electrolyte-like behavior (examples shown in **Figure 1.13**).

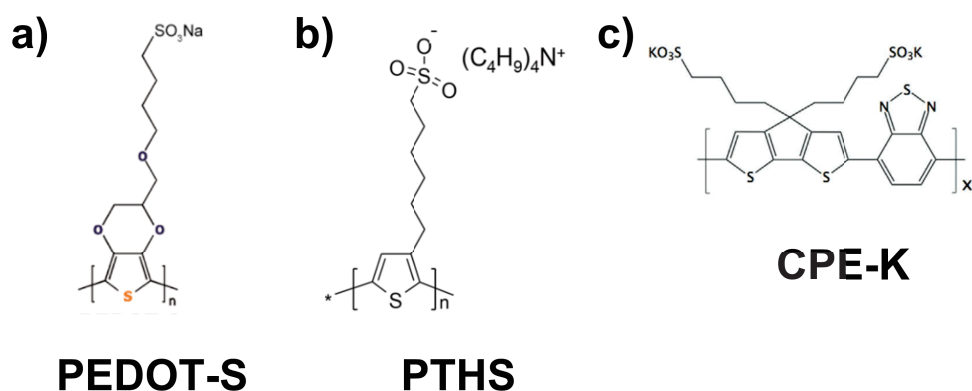


Figure 1.13: Examples of polyelectrolytes a) PEDOT-S, b) PTHS and CPE-K. Reprinted with permission from ref[57][58][62].

These ionic side chains not only enhance solution processability but also act as self-dopants, stabilizing generated polarons. Examples include poly(3,4-ethylenedioxythiophene) derivative (PEDOT-S) ($g_m = 16.2$ mS, $W = 1125$ μ m,

$L = 20 \text{ }\mu\text{m}$, $d = 75 \text{ nm}$), which contains sodium sulfonate terminal group at the side chains.[59, 62] PEDOT-S-based OECT device operates in depletion mode as the PEDOT:PSS OECTs. However, due to its high water solubility, it also compromises film stability during operation, leading to inferior OECT performance compared to PEDOT:PSS-based OECTs. In order to solve the film stability and depletion mode operation problems, poly(6-(thiophene-3-yl)hexane-1-sulfonate) tetrabutylammonium (PTHs) was designed and fabricated into OECT devices ($g_m = 0.4 \text{ mS}$, $W = 250 \text{ }\mu\text{m}$, $L = 5 \text{ }\mu\text{m}$, $d = 60 \text{ nm}$).[57] A more recent example is poly[2,6-(4,4-bis-potassium butanysulfonate-4H-cyclopenta-[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (CPE-K), where the potassium sulfonate groups are covalently bound to the donor-acceptor (D-A) type conjugated backbone consist of cyclopentadithiophene CPDT and benzothiadiazole (BTD) units.[58] The observed CPE-K OECT g_m is $> 60 \text{ mS}$ ($W = 270000 \text{ }\mu\text{m}$, $L = 8 \text{ }\mu\text{m}$, $d = 3 \text{ }\mu\text{m}$).

Composites/blends

PEDOT:PSS is a widely studied blend-based OMIEC[63, 64, 65, 66] thanks to its commercial availability. In fact, it is the only commercially available OMIEC due to its facile synthesis. It is synthesized from 3,4-ethylenedioxythiophene (EDOT) using an acid template (i.e., polystyrene sulfonic acid) and oxidants (e.g., iron(III) sulfate ($\text{Fe}_2(\text{SO}_4)_3$)), resulting in a water-dispersed blend of PEDOT:PSS.[67] Morphologically, PEDOT:PSS films exhibit phase separation into hydrophobic PEDOT-rich and hydrophilic PSS-rich domains, as shown in **Figure 1.14**. [68, 69, 70, 71], The neighboring PSS acts as a charge-compensating dopant for PEDOT conjugated backbones, enabling high conductivity in its pristine form (i.e., $< 1 \text{ S cm}^{-1}$ for Clevios PH1000)[72]. In OECT operation, PEDOT:PSS devices typically function in depletion mode. When $V_g = 0 \text{ V}$, the channel remains conductive due to the presence of hole charge carriers in PEDOT chains. By applying a positive V_g , anions are attracted toward the gate electrode, while cations are injected into the channel. This course of ion motion neutralizes the

negative charges on PSS and de-dopes PEDOT chains, resulting in reduced channel conductivity.

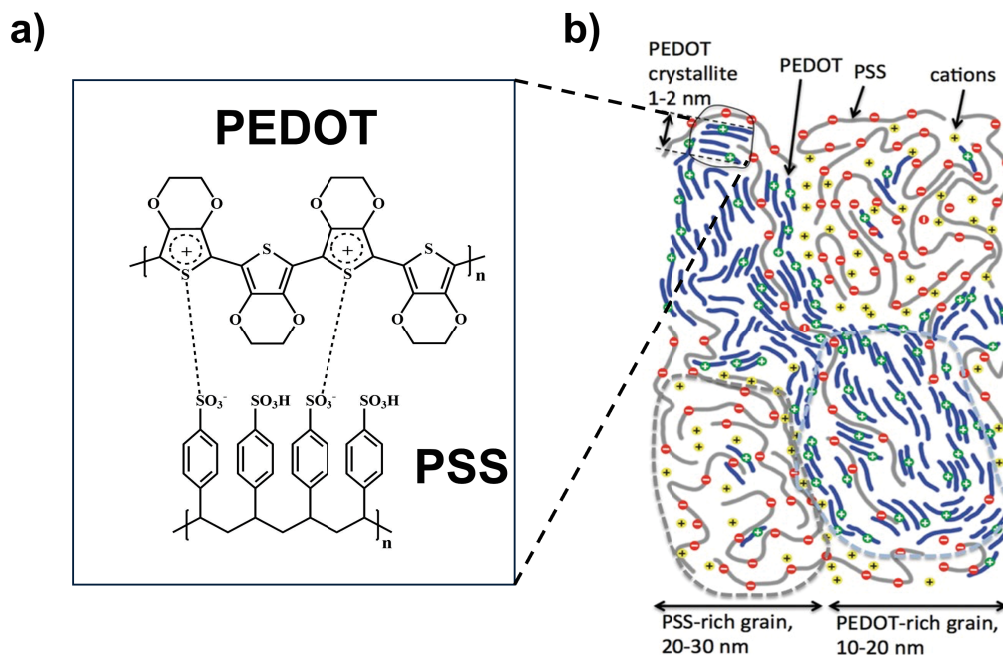


Figure 1.14: molecular structure of PEDOT:PSS in the absence of injected cations and b) morphology model of PEDOT:PSS (blue line: PEDOT, grey line: PSS) when cations (yellow) are injected. There are PEDOT-rich and PSS-rich phases. The majority of the cations are injected into the PSS-rich phase. The graph is adopted with permission from ref[68].

Conjugated polymers with polar side chains

In this category, the most recently developed and the most promising materials are the ethylene glycol (EG) functionalized conjugated polymers, where the EG side chains are covalently attached to the conjugated polymer backbone, as shown in **Figure 1.15**. With this EG functionalization approach, the use of solvent additives can be avoided, therefore enabling a much more facile fabrication procedure.[73] More importantly, the presence of EG side chains allows for significant swellability and efficient ion transportation within the material. Consequently, high C^* and, therefore, high g_m can be achieved. To date, the best performing EG functionalized OMIECs are p-type OMIECs, such as P(g2T2-g4T2) and

P(g1T2-g5T2), which benchmarks the μC^* values at 522 and $496 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$, respectively, and the g_m values at $6.5 \pm 1.6 \text{ mS}$ ($W = 100 \text{ }\mu\text{m}$, $L = 10 \text{ }\mu\text{m}$ and $d = 45 \text{ nm}$) and $10.2 \pm 1.2 \text{ mS}$ ($W = 100 \text{ }\mu\text{m}$, $L = 10 \text{ }\mu\text{m}$ and $d = 65 \text{ nm}$), respectively[74] While significant progress has been made in developing high-performance p-type OMIECs, the development of n-type OMIECs is relatively limited, primarily due to the instability problem when operating in aqueous conditions. Only recently, breakthroughs in n-type OMIEC development have been made, introducing several promising n-type materials, such as P(gNDI-gT2)[75] and ladder-type poly(benzimidazobenzophenanthroline) (BBL)[76], benchmarking g_m of $21.7 \text{ }\mu\text{S}$ ($W = 100 \text{ }\mu\text{m}$, $L = 10 \text{ }\mu\text{m}$ and $d = 350 \text{ nm}$) and 9.7 mS ($W = 39 \text{ mm}$, $L = 20 \text{ }\mu\text{m}$ and $d = 180 \text{ nm}$), respectively.

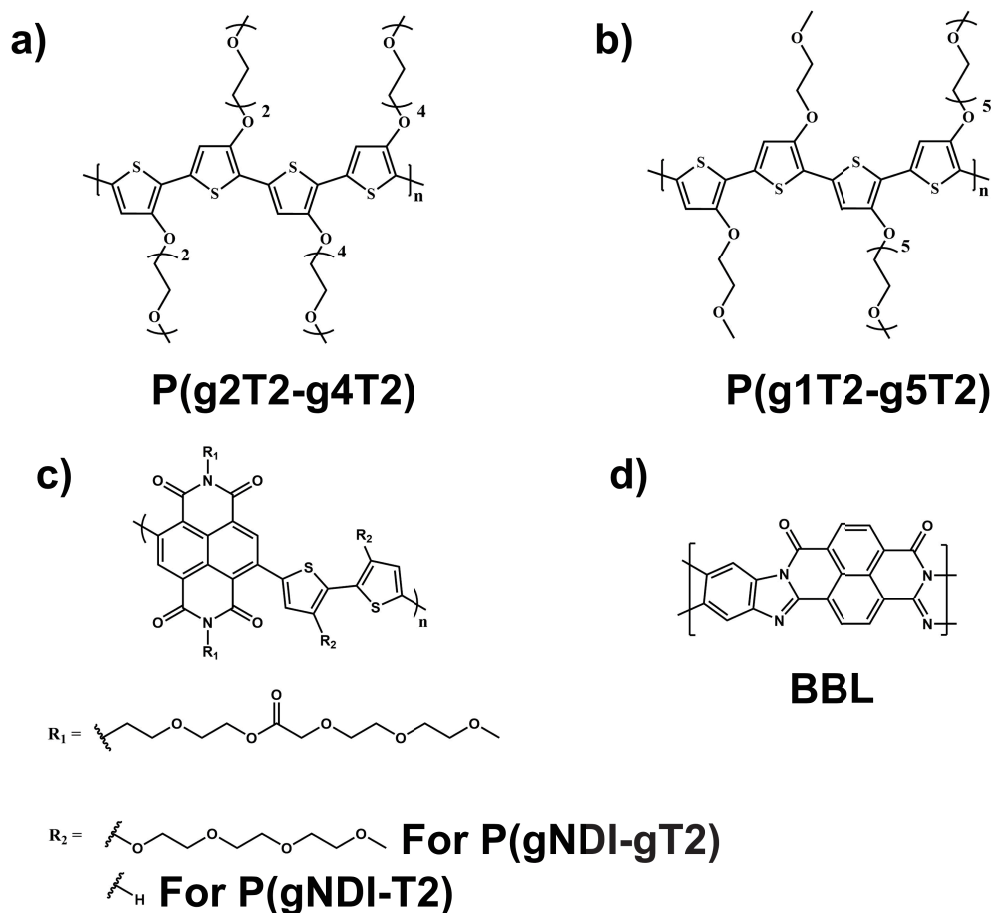


Figure 1.15: Chemical structures of high-performance p-type OMIEC examples, including a) P(g2T2-g4T2) and b) P(g1T2-g5T2), and n-type OMIECs, including c) P(NDI-gT2) and P(gNDI-T2) and d) BBL. Reproduced with permission from ref[74][75][76].

1.2.4 Current challenges and the search for suitable materials/systems

In EGOFETs, conventional semiconducting materials and polymers exhibit slow response times due to their hydrophobic nature. While these materials effectively facilitate electron transport, their poor interaction with aqueous electrolytes limits ion penetration. This weak ion transport reduces the efficiency of electrochemical gating, leading to delayed device operation.

Although PEDOT:PSS is the most studied OMIEC, since pristine PEDOT:PSS is mechanically unstable in aqueous medium (i.e., water), delamination can occur.[77] Therefore, crosslinking additives (e.g., 5 v/v% glycidyloxypropyl trimethoxysilane

(GOPS)) are deployed in order to stabilize the film during device fabrication and operation. However, the use of additives can deteriorate electronic and ionic transportation.[78, 79] Furthermore, PEDOT:PSS operates in depletion mode, meaning that the channel stays on when the V_g is not applied, which can lead to high power consumption during device operation.

EG functionalization of conjugated polymers can significantly improve ion permeability and ion transportation in the channel material. Nevertheless, it comes with two main disadvantages: (I) excessive swelling during the operation could disrupt the connection between crystallites[80], and (II) the challenging chemical synthesis and purification due to their strong interaction with both polar and non-polar solvents.[81]

Consequently, since the existing material systems pose various problems, it highlights the importance of searching for alternative material systems that can circumvent these problems.

Therefore, in this thesis, two alternative solutions will be explored:

- (I) Using metallopolymers as the OECT channel materials.
- (II) Engineering conventional hydrophobic OSCPs by blending hydrophilic additives

Regarding (I), metallopolymers could serve as channel materials. However, there is a distinct lack of studies regarding their OECT performance. With appropriate selections of metal centers and organic ligands, redox activity can be integrated into the system, enabling control over device operation potential.[82] The change of metal center oxidation states will lead to the change of other physical properties, such as the conductivity of the materials, yielding high conductivity, which indicates high μ values, and making them alternative options beyond the typical OMIECs mentioned earlier. Furthermore, metal centers are intrinsically bulky due to the need for auxiliary ligands for the stabilization of metal centers, leading to the formation of an amorphous morphology due to decreased interaction among the polymer backbones and restricted polymer chain rotation. Consequently, this

could facilitate efficient ion diffusion from the electrolyte for charge compensation during redox reactions. Overall, it could result in enhancement in both electrical and ionic performance in OECTs.

Regarding (II), conventional OSCP s have a number of favorable properties, such as established synthesis, excellent electrical performance, and commercial availability. However, their hydrophobic nature hampers ion transport behavior, making them a less favorable choice compared to existing OMIECs for channel materials. To address this issue, hydrophilic additives can be utilized to engineer the hydrophobic OSCP s. By improving surface hydrophilicity or creating hydrophilic channels, efficient ion transport and, consequently, enhanced ion-channel interaction can be achieved, potentially boosting OECT ionic performance in terms of better C^* values and shorter device response time compared to the OECTs with unmodified hydrophobic OSCP channels.

1.2.4.1 Organometallic polymers - fundamentals of organo-metallic compounds

Metallopolymers are an emerging class of materials that combine metal and organic semiconducting polymer moieties. With the combination of metal and organic parts, they provide unique and valuable properties such as spin-orbit coupling and stimuli responsiveness while still offering the flexibility for structural modification and the possibility for energy efficient solution processibility,[83] making them promising candidates for (opto)electronics applications.

Ligand field (LF) theory

In order to explain the optical and chemical properties of metal complexes, it is necessary to understand the charge transfer events that take place. Ligand field (LF) theory is a commonly adopted theory to explain the interaction between the atomic orbitals (AOs) of the metal center and the molecular orbitals (MOs) of

the organic ligands. This interaction is described using the linear combination of atomic orbitals (LCAO), resulting in the formation of MOs that are characteristic of the corresponding metal complexes. With the aid of LF theory, physical properties, such as magnetic and optical properties, and chemical properties, such as the coordination geometry, of organometallic/metal-organic compounds can be predicted. For example, $[\text{Fe}(\text{py})_6]^{2+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ are of different magnetic properties. As shown in the MO diagram in **Figure 1.16**, since pyridine (py) ligands contain π^* anti-bonding MOs, it acts as a π -acceptor and allows for strong interaction with the d_π orbitals of iron (Fe) metal (d_{xy} , d_{xz} , and d_{yz}). As a result, the d_π orbitals are stabilized, and the LF splitting between d_π and d_{σ^*} (d_{z^2} and $d_{x^2-y^2}$) (i.e., crystal field splitting (Δ_o)) becomes larger than the electron pairing energy. Consequently, the electrons are paired up in the d_π orbitals, and $[\text{Fe}(\text{py})_6]^{2+}$ is in a low-spin state (i.e., diamagnetic). On the contrary, since H_2O bears two pairs of non-bonding lone pair electrons on the oxygen atom, the low-lying non-bonding MOs can only weakly interact with d_{σ^*} orbitals of the Fe metal. Hence, the d_{σ^*} is not destabilized too much, and the LF splitting is smaller than the electron pairing energy, leading to the high spin state (i.e., paramagnetic) in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$.

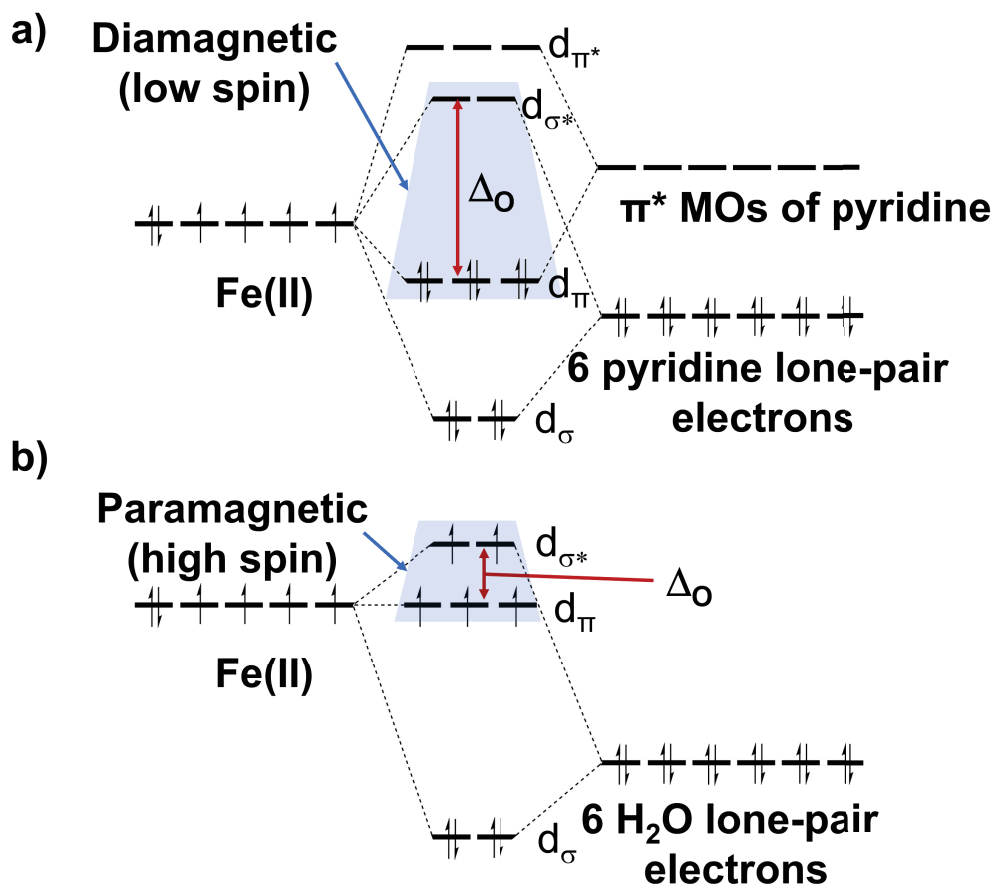


Figure 1.16: Molecular orbital (MO) diagrams of a) $[\text{Fe}(\text{py})_6]^{2+}$ and b) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$. The former complex is diamagnetic (at low spin state) due to the large crystal field splitting (Δ_o) and vice versa for the latter case. Only the frontier MOs are shown for a clear illustration.

Intramolecular charge transfer - ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT)

With LF theory, one can intuitively comprehend the charge transfer events, i.e., ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT), that are responsible for the optical and chemical properties of a metal complex.[84, 85] As illustrated in **Figure 1.17**, in the presence of π -donating ligands with high-lying filled π -orbitals, such as oxo (O^{2-}) and bromide ion (Br^-) ions, electrons from the π -orbitals can transfer to empty or half-occupied metal orbitals (i.e., d_{π} (or t_{2g}) or d_{σ^*} (or e_g^*)), thus leading to LMCT.

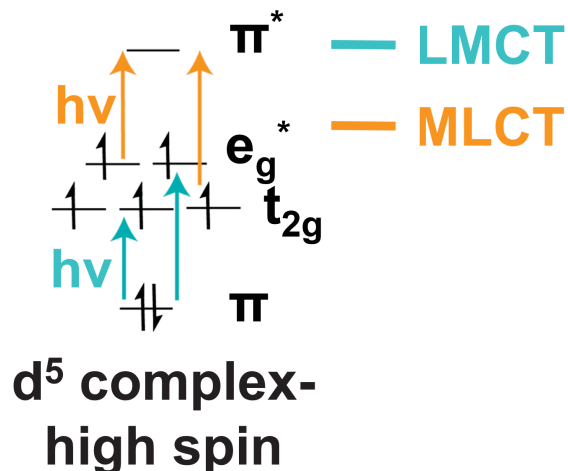


Figure 1.17: Illustration of ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT) adopted in d⁵ complex adopted with permission from ref[85].

Meanwhile, in the presence of π -accepting ligands with low-lying π^* -orbitals, such as bipyridine ligands,[86] electrons from metal orbitals (i.e., e_g^* or t_{2g}) can transfer to the ligand π^* -orbitals, allowing for MLCT.

Intermolecular charge transfer - outer-sphere (OS), inner-sphere (IS) charge transfer, and intervalence charge transfer (IVCT)

Apart from the intramolecular charge transfer, intermolecular charge transfer among metal centers or complexes is also of great significance, especially in solid-state for electronic applications. Intermolecular charge transfer among organometallic complexes can be classified into two different mechanisms – outer-sphere (OS) and inner-sphere (IS) charge transfer mechanisms. According to the definition, OS and IS charge transfer are both the electron transfer from the donor moiety to the acceptor moiety, whereas the donor-acceptor interaction in the former case is minimal and in the latter case is significant due to the presence of bridging ligand between two metal centers.[87] Therefore, OS charge transfer is conceived as a through-space charge transfer (i.e., hopping), while IS charge trans-

fer is conceived as a through-bond charge transfer when the donor and acceptor wavefunctions overlap. Marcus-Hush theory can be adopted for the description of OS mechanism (in non-adiabatic condition, where electronic coupling between acceptor and donor (H_{AD}) is weak) and IS mechanism (in adiabatic condition, where H_{AD} is strong) (**Figure 1.18**).

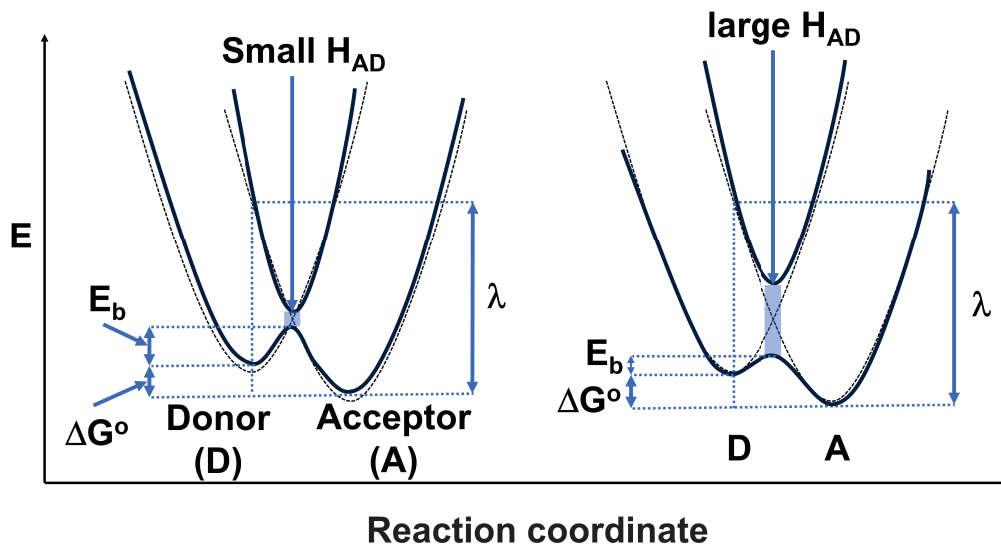


Figure 1.18: Graphical illustration of Marcus-Hush theory. E_b is the thermally-activated electron transfer energy barrier from donor (D) to acceptor (A). λ is defined as the reorganization energy. ΔG° is the Gibbs free energy. Left: the potential surface of the charge transfer reaction when the electronic coupling between acceptor and donor (H_{AD}) is smaller. Right: the potential surface of the charge transfer reaction when H_{AD} is large.

With the help of Marcus-Hush theory, different classes of mixed-valence (mixed-valence (MV)) compounds can be distinguished (namely, class I – III) depending on the relative H_{AD} and reorganization energy (λ) magnitude (weakest in class I, strongest in class III) according to the Robin-day classification regarding MV compounds[88] (**Figure 1.19** shows the example of potential surfaces of symmetrical (same metal center) class I-III MV compounds).

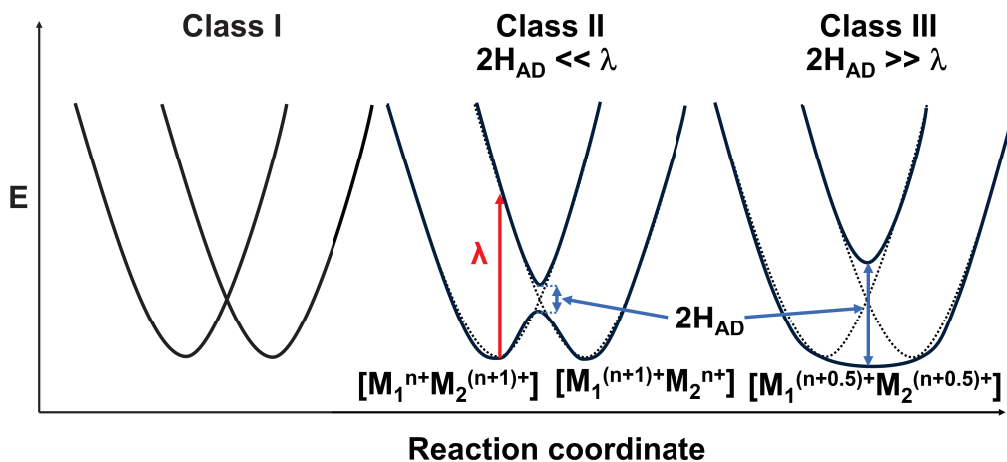


Figure 1.19: Potential surface of class I-III mixed-valence (MV) compounds.

In class I MV compounds, due to the weak interaction between the redox active metal centers (hereafter denoted as redox sites), the oxidation states at different centers are distinctive, and there would be no interconversion of oxidation states between two metal centers (namely, M_1 and M_2). In class II MV compounds, since there is a weak interaction between the redox sites, although the oxidation states of the metal centers are still different, interconversion of oxidation states between redox sites can occur. Thus, class II MV systems are considered localized systems. In class III MV compounds, due to strong interaction between two redox sites, the two redox sites are merged into one state, eliminating the thermal energy barrier (E_B) and forming a delocalized system. In this case, the oxidation states of the metal centers are indistinguishable and non-integral.

In class II and class III MV compounds, intervalence charge transfer (IVCT),

charge transfer between metal centers that only differ in oxidation states, can take place, and therefore, an IVCT absorption band can be observed. Furthermore, when the metal centers are bridged via conjugated ligands, the electronic coupling can take place via a direct through-bond mechanism or indirect through-space superexchange mechanism (**Figure 1.20**). Both mechanisms can be described by the interaction of frontier orbitals (i.e., d_π orbitals from the metal centers and π and π^* orbitals from the bridging ligand) depending on the degree of orbital overlap between the two metal centers via the bridging ligand. In practice, both mechanisms can contribute to the IVCT.

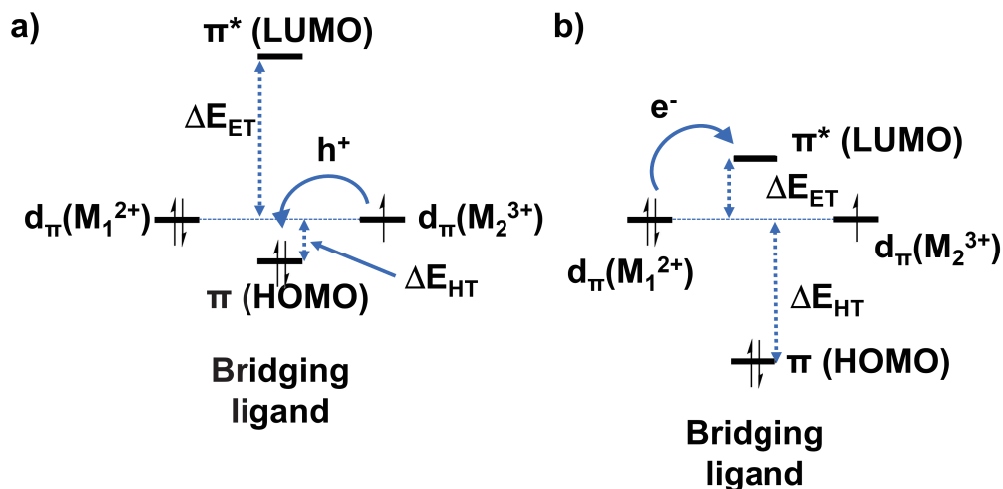


Figure 1.20: Sketch of energy diagram of electronic coupling for a) hole transfer mechanism and b) electron transfer mechanisms. ΔE_{ET} and ΔE_{HT} represent electron and hole transfer energy, respectively.

Classification of conjugated organometallic polymers - Wolf type I-III

To harness different functionalities, a wide variety of metallopolymer with varying structural arrangements of metal complexes and polymer backbones have been studied.[89, 90] To elucidate the utility of metallopolymer with different positioning of metal complexes, a concise classification scheme is necessary. A widely accepted classification scheme is the Wolf classification,[91, 92] which classifies metallopolymer into three categories of metallopolymer, namely Wolf type I-III (**Figure 1.21**). From Wolf type I to Wolf type III, the interaction between metal center and conjugated polymer backbone, as well as the interaction between metal centers, increases.[93, 92]

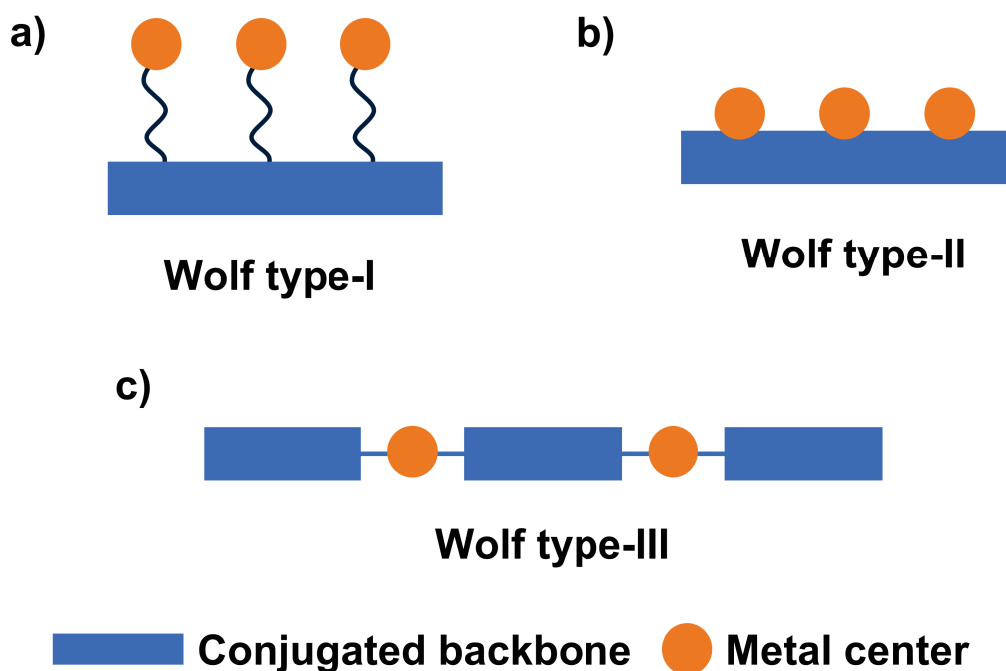


Figure 1.21: Wolf classification of different metallopolymer. Reproduced with permission from ref[93].

In Wolf type-I metallopolymer, there is no/negligible interaction between the metal centers and the polymer backbone. This includes conjugated or non-conjugated polymer with tethered metal complexes via aliphatic chains.[94] In this case, the polymer backbone acts as a host for the functional metal complex.

Wolf type-II metallopolymers are a class of metallopolymers that contain metal complexes tethered to a conjugated backbone via conjugated linkage or directly coordinated peripheral to the conjugated polymer backbone. In this case, the introduction of metal complexes can influence the material properties (e.g., conductivity and UV absorption pattern) by enhancing backbone planarity upon chelation and introducing additional metal center-based absorption bands (e.g., MLCT). However, M-M interaction is usually not observed due to the presence of bridging ligands with large molecular distances.

For Wolf type-III metallopolymers, the metal centers are integrated into the conjugated backbone through covalent or coordinative bonds. The metal centers are crucial not only for maintaining structural integrity but also for directly participating in the charge delocalization pathway. They play a significant role in mediating intrachain charge transfer. Consequently, there is a notable alteration in the electronic and optical properties of the metallopolymers, especially when the oxidation state of the metal centers changes.[95] These features make Wolf type-III metallopolymers ideal candidates for redox-responsive applications.

1.2.4.2 Engineering of hydrophobic OSCPs for enhanced OECT performance - current strategies and beyond

Apart from developing novel materials, another promising strategy would be to engineer existing high-performance OSCPs for OECT applications. Recently, more research has been dedicated to investigating the modification of hydrophobic OSCPs for enhanced OECT performance, thanks to their outstanding electrical performance, well-studied synthesis, and good commercial availability. To enhance the OECT performance of hydrophobic channels, especially their ionic performance, such as C^* and τ , different approaches regarding the control of channel morphology, channel microstructure, and device layout have been reported.

Control of channel morphology

Precise control of channel morphology can significantly enhance ion injection/diffusion efficiency. Jackson et al. demonstrated that the balance of amorphous and crystalline ratios in P3HT can influence ion distribution and injection kinetics.[96] They demonstrated that while ions preferentially enter the crystalline regions, as revealed by the photoinduced force microscopy characterizations, the presence of amorphous regions at an optimal ratio can significantly facilitate the ion injection kinetics, as suggested by the spectroelectrochemical (SEC) analysis.

Flagg et al. fabricated OECT devices with P3HT using additive-induced directional crystallization and a blade-coating technique.[97] By manipulating the coating directions (i.e., parallel and perpendicular to the source-drain channel), the orientation of the crystals was successfully controlled, forming long ribbon structures in the range of μm . The OECT devices with parallel P3HT crystals obtained from parallel blade-coating exhibited an order of magnitude improvement in steady-state figure-of-merit μC^* ($717 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$) compared to those with isotropic P3HT crystals ($56 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$), thus demonstrating the utility of this method.

Control of channel micro/mesostructures

One of the common strategies developed in recent years is controlling the micro/mesostructure of OECT channels, such as porosity. Huang et al. and Zhang et al. utilized an environmentally friendly and facile method, breath figures, to fabricate a series of porous OECT channels composed of P3HT, PDPP-TT, P(g2T-T), PNDI-T2, and so on.[98, 99] The introduction of porosity into the channel significantly enhanced ion diffusion efficiency, as indicated by the prominently shortened OECT response time, significantly increased C^* values, and the dramatic enhancement of geometry-normalized g_{m} , reaching the value of 374 S cm^{-1} , which exceeds some of the existing OMIECs.

Liu et al. took this approach further by fabricating porous P3HT/polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS) and P(T2g-T)/SEBS blends.[100] By leveraging the elastomeric property of SEBS, remarkable mechanical behavior was observed. Additionally, by stacking several porous layers on top, OECT metrics, i.e., g_m , experienced a 2-3 fold increase.

During the thesis writing, a new approach to pattern the channel material was proposed by Yan et al.[101] In this study, P3HT was patterned into tiny lines parallel to the source-drain channel. By controlling the line width and line interval, lateral area increases, thereby assisting ion injection into the channel. Subsequently, improved device τ and g_m were observed, enabling physiological signal monitoring with a significantly enhanced signal-to-noise ratio.

Modification of OECT device layouts

Beyond material engineering, device engineering strategies have also been explored to optimize ion injection in hydrophobic channels. Bischak et al. and He et al. demonstrated that incorporating an ion-gel interlayer containing bis(trifluoromethanesulfonyl)imide (TFSI⁻) ions between the aqueous electrolyte and the channel can facilitate ion exchange during the ion injection process.[102, 103] Unlike chloride ion (Cl⁻), which are highly hydrated and less compatible with hydrophobic semiconducting polymers such as P3HT and PBTTT, TFSI⁻ ions are more hydrophobic and, therefore, exhibit a greater affinity for these materials. This improved compatibility enhances ion injection efficiency, leading to more effective channel doping, as confirmed by SEC analysis, along with faster device response times and increased g_m .

Strategy beyond current approaches – hydrophilic additives

The strategies highlighted above clearly strive to improve ion injection efficiency or kinetics in hydrophobic channels. However, upon closer inspection of the current

material systems, it becomes evident that the most effective method for enhancing ion injection efficiency lies in increasing the hydrophilicity of a material. This is supported by numerous examples in OMIECs where polar EG side chains are covalently attached to the conjugated polymer backbone, yielding some of the best-performing OECT materials to date.

However, the synthesis of OMIECs is challenging due to the difficulty of handling and purifying polar and hygroscopic monomers. Furthermore, excessive swelling during operation could deteriorate long-term electrical performance. Given these challenges, alternative methods to incorporate hydrophilicity, such as blending hydrophilic additives, should be considered.

Blending additives with readily available hydrophobic matrix materials allows for the modulation of local hydrophilicity in the blends/composites without significant synthetic effort. This provides good tunability for optimizing OECT performance by simply adjusting the additive/OSCP ratios. Meanwhile, using hydrophobic OSCPs as matrix materials avoids excessive swelling during operation, potentially providing long-term device stability. Therefore, with all these advantages, this approach is adopted in this thesis to enhance the OECT performance of hydrophobic channels.

1.3 Aim and motivation

While metallopolymers have been extensively studied for applications in in-situ conductivity measurements, sensors, and electrochromic (EC) devices, their potential in OECT applications remains largely unexplored. Consequently, their performance in EGTs is not yet fully understood. Therefore, the first part focuses on Wolf type-III Ru-based polymetallaynes, which are particularly interesting due to their intrinsic redox activity (i.e., from Ru^{2+} to Ru^{3+}) and the potentially high conductivity resulting from direct orbital overlap between the Ru-acetylide and organic bridging ligand moieties. Recent advancements in dehydro-halogenation

synthesis have made Ru-polymetallaynes more accessible, overcoming previous synthetic limitations.[104] Thus, the first part of this research involves the synthesis and characterization of three Ru-polymetallaynes with systematic structural modifications (namely, P1, P2, and P3), followed by the fabrication and evaluation of their EC and OECT devices.

To further advance OECT technologies, the second and third parts of this study focus on blending and composite approaches using well-established semiconducting polymers, such as P3HT, combined with carefully selected additives. 20 mol%-doped poly(vinylferrocene) (PVF^+) is incorporated due to its hydrophilicity,[105] which is expected to enhance ion uptake and transport within the channel. By increasing hydrophilicity, this study aims to examine its impact on key OECT performance metrics, particularly those related to ionic processes, such as transient behavior. Additionally, PVF^+ consists of bulky ferrocene (Fc) units that is likely to exhibit an amorphous morphology, which is beneficial to ion injection kinetics by facilitating efficient ion penetration and transport within the polymer matrix.[96] Furthermore, PEGylated gold nanoparticles (PEG-AuNP) are introduced not only for their hydrophilic nature, which facilitates ion transport, but also for their ability to strengthen polymer backbone interaction.[106] This dual effect could lead to a more balanced enhancement in both electronic and ionic properties, ultimately improving overall OECT performance and offering much higher freedom of choice for OMIEC design.

Chapter 2

Synthesis and characterizations of Ruthenium (Ru)-polymetallaynes and their applications in organic electrochemical transistor (OECT) devices

2.1 Introduction

Metallopolymers have attracted significant attention for various applications, such as sensors, electrochromic (EC) displays, and data storage/processing technologies. Among the most commonly studied organometallic moieties are the cyclometalated complexes, including multinuclear $\text{Ru}(\text{tpy})_2$ centers that are linked by redox-active triphenylamine bridging ligands (**Figure 2.1**).[107, 108]

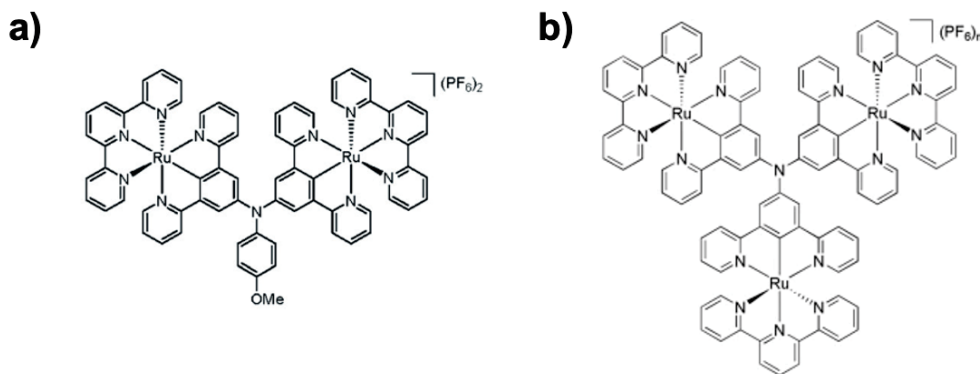


Figure 2.1: Examples of $\text{Ru}(\text{tpy})_2$ moieties that can exhibit multiple oxidation states. Reprinted with permission from ref[107][108]

These moieties exhibit good stability and multiple oxidation states under different electrochemical potentials. Upon application of electrochemical potential,

a change of coloration accompanying the defined change of oxidation states will be resulted, generating different optical output signals and making them promising candidates for a wide variety of higher-capacity memory compared to conventional binary memory systems and efficient data storage/processing applications such as flip-flop-flap ternary memory.[109]

Although these aforementioned organometallic moieties are of good electrochemical stability, their thin film states are of low solubility due to the lack of solubilizing side chains, limiting the precise control over the film morphology to tailor for different applications. More importantly, low conductivity is usually observed due to the non-planar configuration and, therefore, the charge mediation via indirect orbital overlap. This implies low charge carrier mobility in this class of materials according to Ohm’s law (**Equation 2.1**). As a result, their applications in devices such as OECTs are limited.

$$\text{Conductivity} = e (n \mu_e + p \mu_h) \quad (2.1)$$

,where e represents elementary charge, n , and p represent electron and hole concentrations, respectively. μ_e and μ_h represent electron and hole mobility, respectively. Alternatively, Wolf type-III rigid-rod polymetallaynes could be another option worth the attention.[110, 89] In polymetallaynes, metal centers are covalently bound to sp-hybridized acetylenic carbons, affording a stable structure for different studies. Meanwhile, efficient and direct charge transfer through the metal orbitals via through-bond orbital overlap or through-space superexchange mechanisms is possible in polymetallaynes,[111, 112] offering considerable potential for organic electronic applications.[113]

Since the first polymetallayne synthesis via Sonogashira-Hagihara-type coupling was demonstrated,[114, 115] it has fueled the exploration of various metal-polymetallaynes. Nowadays, the most commonly seen examples of polymetallaynes are platinum (Pt) or palladium (Pd)-based polymetallaynes (namely, Pt-polymetallaynes and Pd-polymetallaynes).[89] Their functional roles in a wide

range of applications, such as OFETs, OLEDs, OPVs, and optical power limiters are studied. However, due to the lack of redox activity in these metal centers, the σ -bond character of the Pt-C bond makes them essentially molecular insulators.[116]

On the other hand, the introduction of earlier transition metals (i.e., group 8 metals) such as iron (Fe) or ruthenium (Ru) could afford even more functionality in the materials. Upon incorporation of Ru centers into the metal-acetylide moiety, it yields highly conductive materials, as shown recently.[113] Moreover, since Fe or Ru centers are redox active, they can undergo reversible redox reactions (e.g., $\text{Ru}^{2+}/\text{Ru}^{3+}$).[117, 118] Redox activity exposes this group of materials to a much wider range of functionalities, such as non-volatile memory due to the change of charge state,[119, 82] and potentially redox-based devices such as organic electrochemical transistor (OECTs).

Despite their potential, group 8 metal-based polymetallaynes remain underexplored, presumably due to the lack of reliable, straightforward synthetic routes. Therefore, developing a facile synthetic approach for Ru-polymetallaynes would greatly benefit rational and systematic modification of chemical structures. Previously, we demonstrated a dehydrohalogenation strategy to synthesize Ru-polymetallaynes (i.e., P1, where bithiophene (BT) conjugated ligands bridge Ru centers) (as shown in **Figure 2.2**).[104]

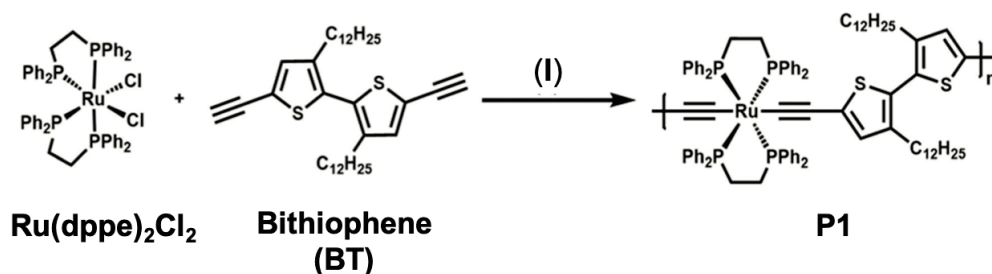


Figure 2.2: Previously reported dehydrohalogenation polymerization of P1. Reaction condition (I): sodium hexafluorophosphate, triethylamine, dichloromethane, 45°C, 3 days. Reproduced with permission from ref[104].

This synthetic route (i.e., dehydrohalogenation polymerization) can realize further structural modifications to synthesize other Ru-polymetallaynes. Namely, P2 (Ru centers are bridged by cyclopentadithiophene (CPDT), ligands) and P3 (Ru centers are bridged by dthienopyrrole (DTP), ligands) are designed to enhance the planarity of bridging ligands and also achieve redox-matching, a design principle known to enhance metal-metal (M-M) interaction by aligning the energy levels of metal and organic bridging ligand orbitals (as shown in **Figure 2.3**),[120] thus providing both multiple stable oxidation states via resonance stabilization and enhanced conductivity in the mixed-valence (MV) state through an inner-sphere (IS) charge transfer pathway.

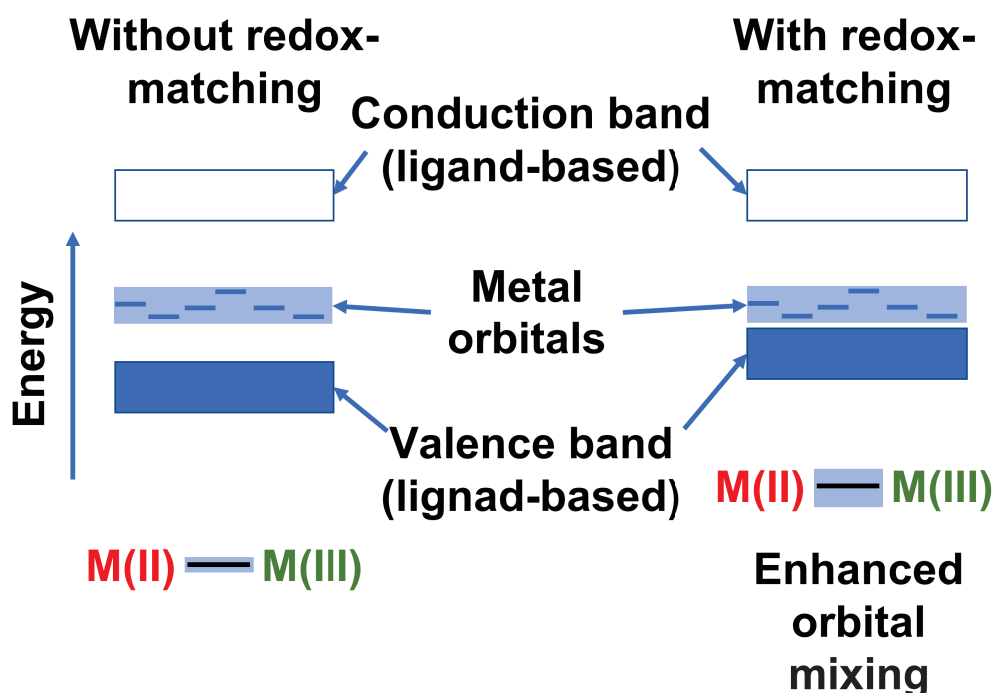


Figure 2.3: Graphical illustration of redox-matching. Since the oxidation potentials of the bridging ligand and metal centers are of a smaller difference, the energy levels of the ligand-based valence band and the metal orbitals are more aligned, enabling both inner sphere and outer sphere charge transfer pathways and, therefore, enhanced orbital mixing and M-M interaction.

The following sections focus on structural, spectroscopic, and EC characterizations to elucidate the properties of these materials. density functional theory

(DFT) calculations suggest that oxidized P3 may be a Robin-Day class II-III MV system (please refer to section 1.2.4.1 for more details of Robin-Day classification). Additionally, EC device studies support multilevel EC memory effects. Finally, the OECT performance of Ru-polymetallaynes and their thin-film morphology are explored, revealing device performance that aligns with the redox-matching model, where the IS charge transfer pathway enhances conductivity in the MV state, particularly in P3 compared to P1 and P2.

2.2 Results and discussion

2.2.1 Synthesis

In comparison to the BT in P1, the CPDT in P2 and the DTP in P3 are more rigid and planar (**Figure 2.4** for the structures of P1-P3).

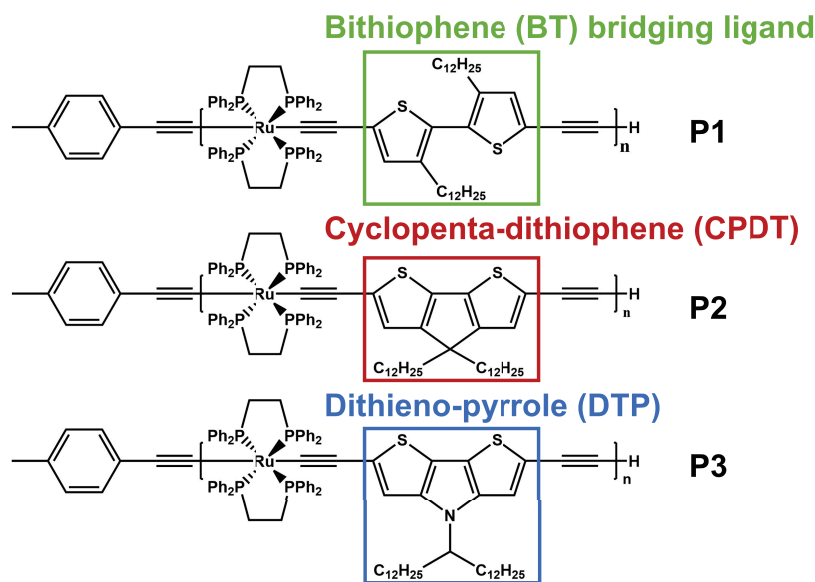


Figure 2.4: Chemical structures of P1, P2, and P3

This increase in rigidity stems from our previous study on P1, where we observed differences in the $\text{Ru}^{2+}/\text{Ru}^{3+}$ oxidation behavior between thin film and solution states (e.g., $\text{Ru}^{2+}/\text{Ru}^{3+}$ oxidation peak separation and, therefore, se-

quential oxidation events were observed in solution state but not in the thin film).[104] This difference is likely due to the higher degree of freedom for bond rotation in the solution state, which allows more significant rotation around the carbon-carbon (C-C) single bond of the BT moiety (**Figure 2.5**). In contrast, in thin-film conditions, this rotation is restricted. Therefore, it adopts a less planar but more energetically stable conformer in thin film[121] and a more planar conformation on average, and, therefore, stronger M-M interactions in the solution state. This observation suggests that reducing the torsion angle of the bridging ligands could improve electronic communication between metal centers in the solid state. Therefore, we incorporated the more planar CPDT bridging ligand into P2 to enhance the M-M interaction.

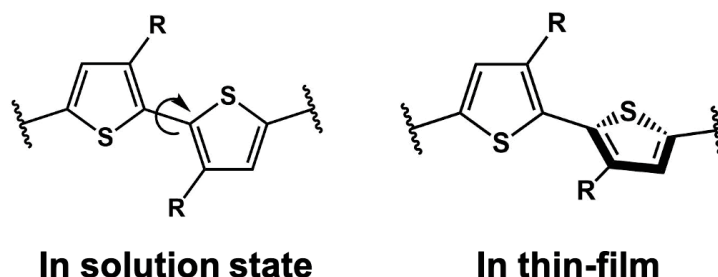


Figure 2.5: Different conformations of the BT unit in solid and solution states. In the solution state, the C-C bond can rotate with a higher degree of freedom. Meanwhile, in solid-state (thin-film), the two thiophene rings can be locked with a torsion angle.

Additionally, the introduction of DTP in P3 aimed to achieve redox-matching, a strategy known to improve M-M interaction. This technique involves matching the oxidation potential (E_{ox}) of the metal centers and the bridging ligands (See **Figure 2.3**).[120] Since DTP is more electron-rich than BT and CPDT, and therefore of lower E_{ox} , [122] it was incorporated through a simple dehydrohalogenation polymerization, ensuring that the M-M distance remained relatively unchanged. As a result, any influence on M-M interaction can be attributed to the planarity of the bridging ligand and redox-matching rather than the change in

the molecular distance of the bridging ligand as observed in electropolymerization polymetallaynes.[110]

Consequently, both P2 and P3 exhibit enhanced M-M interaction, metal oxidation peak separation, and additional stable oxidation states (i.e., MV states). Notably, by examining P2 and P3, the resonance stabilization of the MV state in P3, facilitated by redox-matching, can be elucidated.

The synthesis of P1 was successfully replicated from prior work. For P2 and P3, polymerization required higher temperatures, and anhydrous tetrahydrofuran (THF) was used as the solvent (see **Figure 2.6** for the synthetic route).

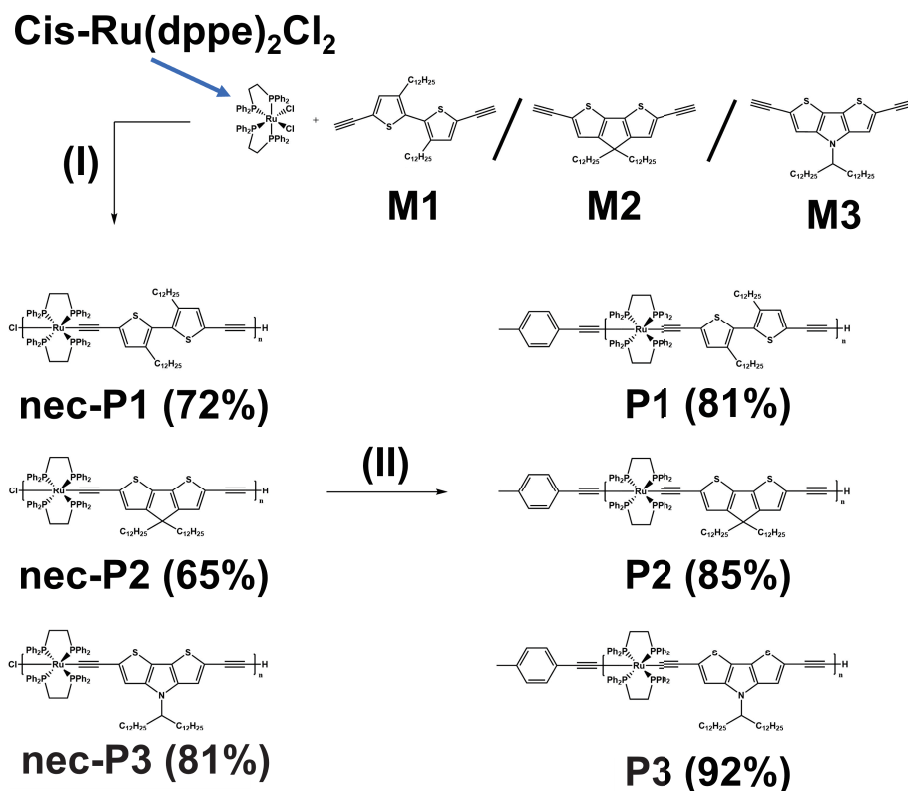


Figure 2.6: Synthetic routes for P1, P2, and P3. (I) **non-endcapped (nec)-P1**: sodium hexafluorophosphate (NaPF₆), triethylamine (NEt₃), dichloromethane (DCM), 45°C in inert atmosphere (N₂), 2 days; **nec-P2**: NaPF₆, NEt₃, tetrahydrofuran (THF), 70°C in N₂, 2 days; **nec-P3**: NaPF₆, NEt₃, THF, 70°C in N₂, 5 days (II) **P1**: 4-ethynyltoluene, NaPF₆, NEt₃, DCM, 45°C in N₂, 24 h; **P2**: 4-ethynyltoluene, NaPF₆, NEt₃, THF, 70°C in N₂, 24 h; **P3**: 4-ethynyltoluene, NaPF₆, NEt₃, THF, 70°C in N₂, 24 h. Adopted with permission from ref[82].

Both P2 and P3 were only obtained after precipitation in an alkaline solution, as confirmed by ^1H and ^{31}P nuclear magnetic resonance (NMR) spectra of P3 before and after alkaline solution treatment, suggesting the formation of protonated intermediates during the reaction (See **Appendix B.1 and B.2**).^[123] End-capping with 4-ethynyltoluene was performed to more accurately determine the degree of polymerization by NMR spectroscopy, which yielded values of 50, 9, and 15 for P1, P2, and P3, respectively, as determined from the integral ratios between the thiophene protons and end-group protons (i.e., tolyl and acetylenic protons, see **Appendix B.3 to B.5**).

2.2.2 Electrochemical and spectroelectrochemical (SEC) studies

Electrochemical and spectroelectrochemical (SEC) measurements, coupling of cyclic voltammetric (CV) measurement, and Ultraviolet-visible near-infrared (UV-vis-NIR) spectroscopic measurement or electron paramagnetic resonance (electron paramagnetic resonance (EPR)) spectroscopy were employed to identify different cationic radicals formed during redox processes for P1, P2, and P3. From CV measurements, it was observed that the electrochemical behavior of the P1 thin film differs from that of P2 and P3. **Figure 2.7** displays the CV of the three polymers.

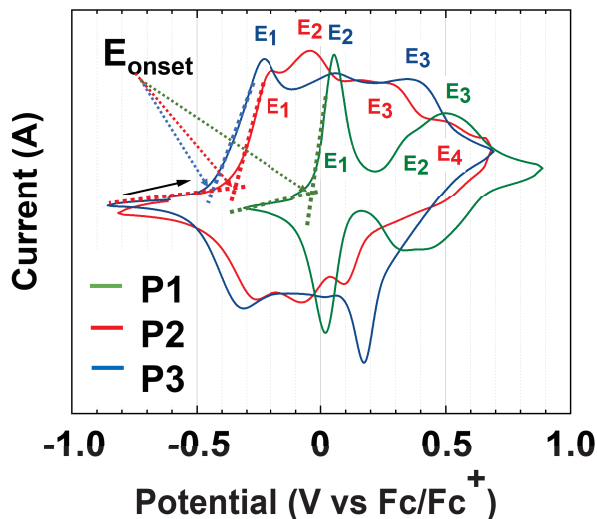


Figure 2.7: Cyclic voltammetric (CV) graphs of P1 (green line), P2 (red line), and P3 (blue line). The CV characterizations were carried out in 0.1 M tetrabutylammonium hexafluorophosphate ($n\text{-BU}_4\text{NPF}_6$) in acetonitrile (ACN) with the platinum (Pt) disc as working electrode, Pt wire as counter electrode, and non-aqueous silver/silver ion (Ag/Ag^+) as reference electrode. The redox potentials are referenced to the ferrocene/ferrocenium (Fc/Fc^+) redox couple as an internal reference.

The applied potential was referenced to the internal ferrocene/ferrocenium (Fc/Fc^+) redox couple. The onset of oxidation potential (E_{onset}) exhibited a significant cathodic shift from P1 ($-0.03\text{ V vs. Fc}/\text{Fc}^+$), P2 ($-0.35\text{ V vs. Fc}/\text{Fc}^+$)

to P3 (-0.44 V vs. Fc/Fc^+), indicating an extended delocalization of charge,[124] presumably due to the enhanced M-M interaction upon the introduction of ligand planarity in P2 and electron-rich DTP units for redox-matching in P3.

For P1, a sharp oxidation peak ($E_1 = 0.05$ V) is followed by two broad peaks ($E_2 = 0.35$ V and $E_3 = 0.5$ V). In situ, EPR analysis showed that the first oxidation corresponds to the $\text{Ru}^{2+}/\text{Ru}^{3+}$ process, while the latter peaks are associated with oxidation of the BT bridging ligand. At the first oxidation (E_1), it exhibited an anisotropic EPR signal ($g_x = 2.002$, $g_y = 2.026$, $g_z = 2.067$; average EPR g -value ($g_{\text{av}} = 2.032$), indicating the formation of Ru^{3+} species (**Figure 2.8**).

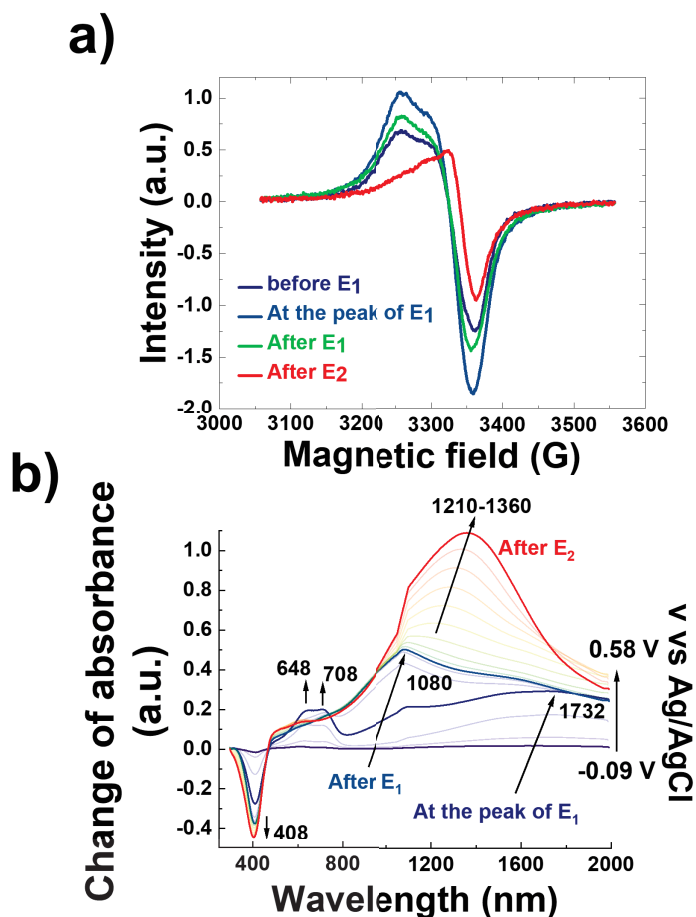


Figure 2.8: In situ a) electron paramagnetic resonance (EPR) and b) Ultraviolet-visible near-infrared (UV-vis-NIR) spectra of P1. ΔA = change of absorbance.

The lower g-value anisotropies compared to other typical Ru^{3+} complexes suggest that the spin density is partially transferred from the Ru^{3+} center to the thiophene moiety,[125] implying weak M-M interaction in P1. The UV-vis-NIR SEC data support this by showing the formation of two types of charged cationic radicals upon oxidation (i.e., cationic radical I: 648, 708, and 1732 nm at the peak of E_1 and cationic radical II: 1080 nm after E_1). This phenomenon can be attributed to Ru^{3+} species with mixed coplanar and twisted bithiophene geometries, allowing for weak M-M interaction in P1. Hence, spin density can be partially transferred to the BT moiety, resulting in comparably lower g-values anisotropies. Note that after E_1 , the intensity of the anisotropic EPR signal decreased. This suggests the potential formation of diamagnetic spin coupling of the Ru^{3+} species. At higher E_{ox} (i.e., after E_2), it exhibited a new isotropic EPR signal (g-value = 2.01). The g-value indicates that the radical species generated at the potential is predominantly organic-based. Therefore, the radical species at high E_{ox} are significantly contributed by the oxidation of BT moiety and this oxidation can be ascribed to the ligand-based oxidation. A red-shifting absorption band in the range of 1210-1360 nm was observed from the UV-vis-NIR spectra.

For P2 and P3, multiple redox events were observed, as shown in **Figure 2.7**. In the case of P3, the CV showed three oxidation events ($E_1 = -0.24$ V, $E_2 = -0.06$ V, and $E_3 = 0.36$ V). The first two peaks (E_1 and E_2) correspond to the sequential $\text{Ru}^{2+}/\text{Ru}^{3+}$ oxidation, and the EPR signals reveal rhombic symmetry ($g_x = 2.043$, $g_y = 2.022$, and $g_z = 2.002$; $g_{\text{av}} = 2.022$), indicating the formation of Ru^{3+} (**Figure 2.9**).

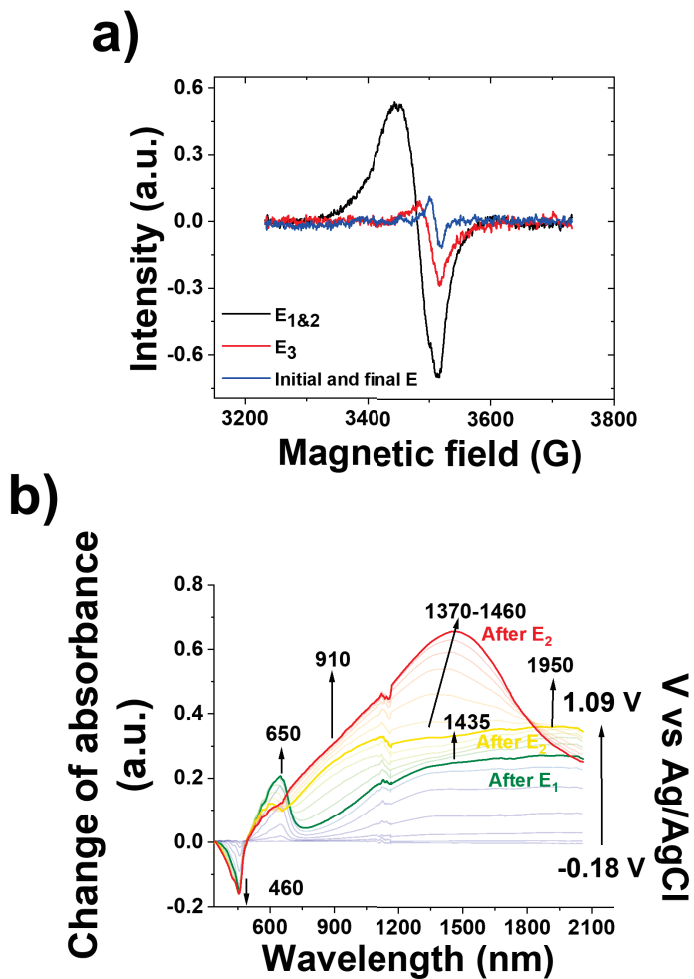


Figure 2.9: In situ a) EPR and b) UV-vis-NIR spectra of P3.

Additionally, UV-vis-NIR spectroscopic data reveal the formation of an MV state between E_1 and E_2 (i.e., MV compound: 650, 1435, and 1950 nm between E_1 and E_2). The observed separation between E_1 and E_2 in P3 (i.e., potential difference (ΔE) = 0.29 V) suggests a stable intermediate oxidation state, likely

due to enhanced M-M interactions, is facilitated by the rigid and redox-matched DTP ligand ($K_c \approx 2 \times 10^5$, calculated according to the **Equation 2.2**).[126] This further enhances charge delocalization in the MV compound,[127, 128] which could contribute to resonance stabilization.

$$K_c = e^{\left(\frac{\Delta E_F}{RT}\right)} \quad (2.2)$$

, where F is the Faraday's constant. R is ideal gas constant and T is temperature in K.

Further oxidation (i.e., E_2) resulted in the same rhombic EPR signal but with lower intensity (See **Figure 2.10**), which can be explained by the diamagnetic spin coupling of two Ru^{3+} centers. According to the UV-vis-NIR spectra, the formation of another radical species was observed after E_2 , giving rise to an absorption band at 910 nm. The final oxidation event (E_3) resulted in an isotropic EPR signal ($g = 2.009$), indicating the formation of an organic cationic radical (i.e., DTP^+). The UV-vis-NIR spectra exhibited a strong near-infrared (NIR) absorption band that shifts progressively upon oxidation.

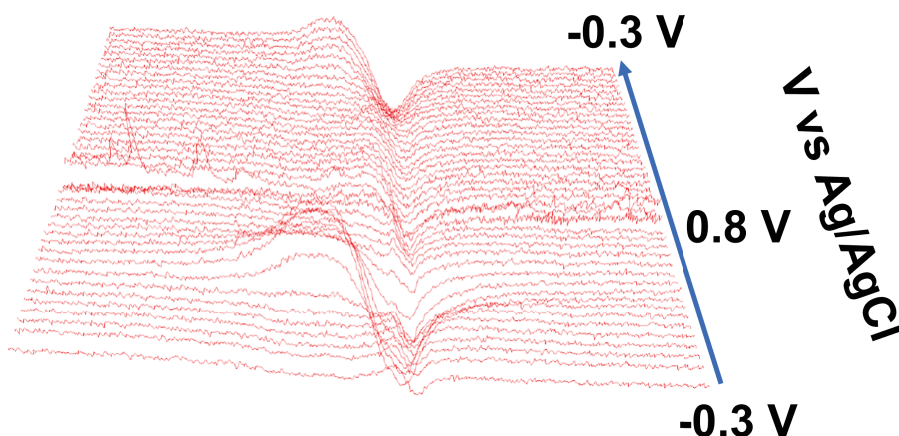


Figure 2.10: Compilation of P3 EPR spectra from -0.3 V to 0.8 V and then from 0.8 V to -0.3 V. At around 0.25 V vs silver/silver chloride (Ag/AgCl), at which the mixed-valence (MV) compound was generated, the intensity of the rhombic anisotropic EPR signal is of the highest intensity.

P2 showed a similar electrochemical behavior to P3, as shown in **Figure 2.11**. After E_1 and E_2 , an anisotropic signal was observed from the EPR spectrum ($g_x = 2.047$, $g_y = 2.021$, and $g_z = 2.002$; $g_{av} = 2.023$), indicating that both E_1 and E_2 are Ru^{2+}/Ru^{3+} oxidation with significant contribution from the organic bridging ligand. K_c value of P2 is estimated to be 1×10^3 . Further oxidation up to E_4 resulted in an isotropic EPR signal with g -value = 2.010. This can be attributed to the formation of organic-based cationic radical species that gave rise to an absorption band at 1317 nm.

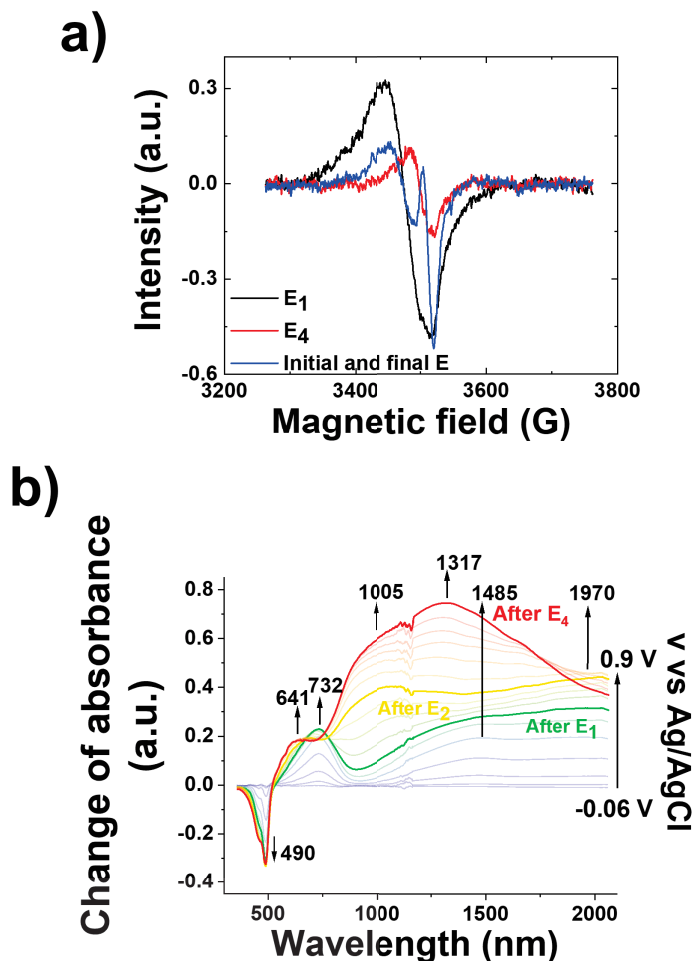


Figure 2.11: In situ a) EPR and b) UV-vis-NIR spectra of P2.

Note that all polymers exhibited EPR signals at the beginning and end of the CV scan (E.g., 'Initial and final E' as indicated in **Figure 2.9a** and **2.11a**).

P1 g-value = 2.018; P2 g-value = 2.005; P3 g-value = 2.004). The initial and final EPR signals from P2 and P3 were isotropic and of lower values, implying charge trapping in the organic bridging ligand. Meanwhile, the initial and final EPR signals of P1 were slightly anisotropic, indicating charge trapping at the Ru centers occurred. These results are in line with the redox-matching model, as shown earlier, where the metal orbitals in P1 are higher lying than the highest occupied molecular orbital (HOMO) of bridging ligand and, therefore, the Ru centers are preferentially oxidized. On the other hand, the bridging ligand HOMOs in P2 and P3 are closer or even overlap with the Ru metal orbitals. Therefore, electrons are initially removed from the organic moieties, exhibiting an organic radical species and isotropic EPR signal. Nevertheless, the EPR and UV-vis-NIR responses indicate that P2 and P3 exhibit a more efficient charge delocalization than P1. Moreover, the HOMO energy level of P1, P2, and P3 were found to be -5.05, -4.73, and -4.66 eV, respectively, according to **Equation 2.3**.^[129]

$$\text{HOMO} = (-5.1 + E_{\text{onset}} - E_{1/2, \text{Fc}/\text{Fc}^+}) \text{ eV} \quad (2.3)$$

, where $E_{1/2, \text{Fc}/\text{Fc}^+}$ is the halfway potential of Fc/Fc⁺ redox couple.

2.2.3 Theoretical calculations

To further understand the nature of MV compounds in P1–P3 (i.e., whether they are Robin-Day class-I, class-II, or class-III), DFT calculations were performed on dinuclear model complexes MC-BT and MC-DTP, moieties where weak and prominent M–M interaction were previously observed, respectively. **Figure 2.12** shows the structures of the model complexes.

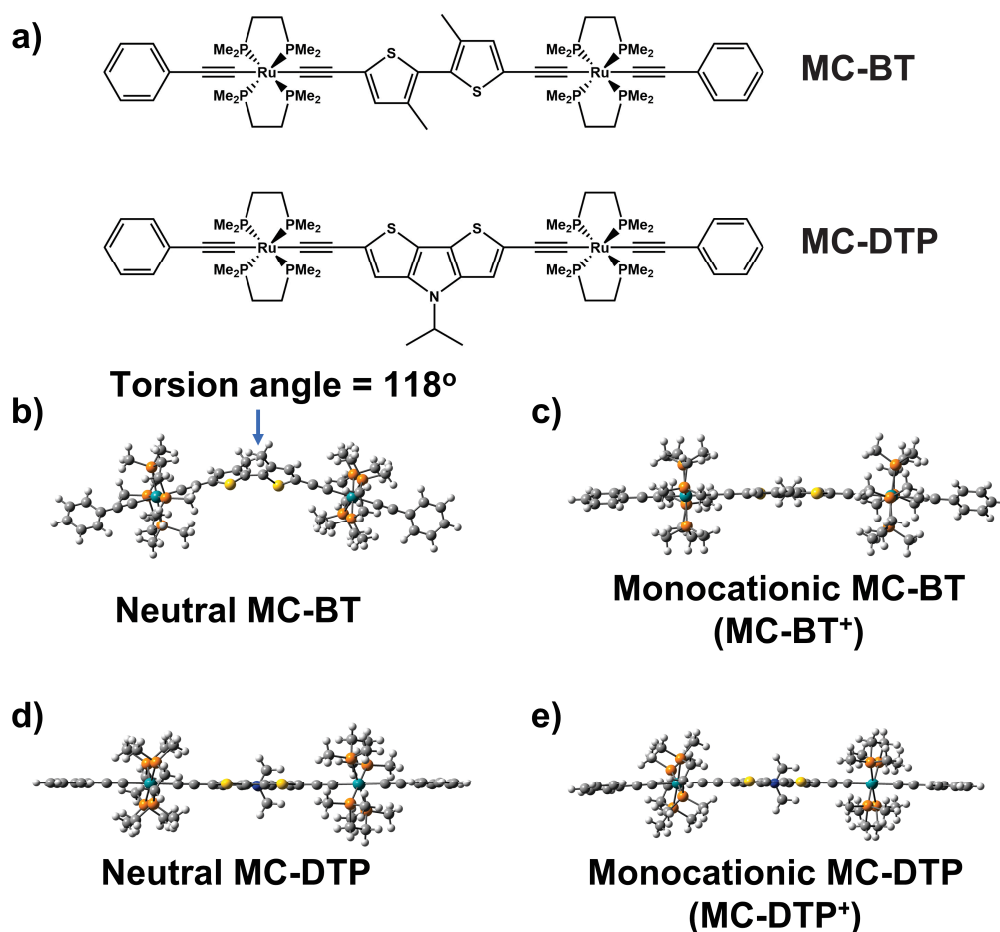


Figure 2.12: a) Structures of model complexes MC-BT and MC-DTP. DFT optimized geometries of b) MC-BT, c) monocationic MC-BT (MC-BT⁺), d) MC-DTP, and e) monocationic MC-DTP (MC-DTP⁺).

These calculations revealed the geometries of the neutral and monocationic states of MC-BT and MC-DTP. After optimization, neutral MC-BT exhibited a torsion angle of 118° at the BT bridging ligand. In contrast, neutral MC-DTP

exhibited an expected planar geometry since the DTP unit has a conjugated fused-ring structure. This suggests that P1 exhibits weaker M-M interactions and behaves as a class-I MV compound. Therefore, this explains the single $\text{Ru}^{+2}/\text{Ru}^{+3}$ oxidation peak observed in CV measurements.

Moreover, the theoretically calculated HOMO-LUMO energy level and the frontier orbitals of the model complexes (both neutral and monocationic) were obtained (**Figure 2.13**), further confirming the electron-rich character of DTP moiety due to the higher lying HOMO level of MC-DTP (-3.29 eV) compared to that of MC-BT (-3.97 eV).

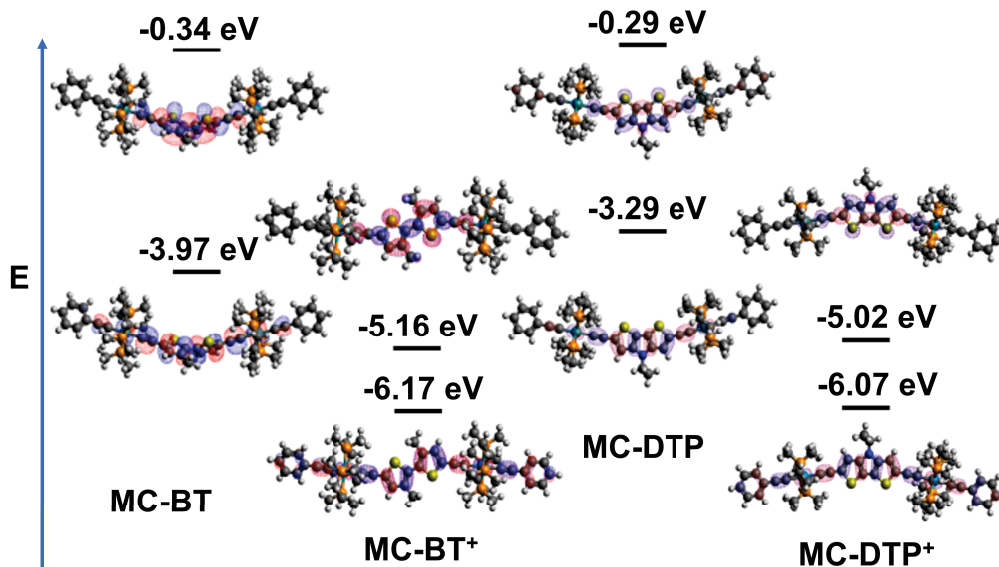
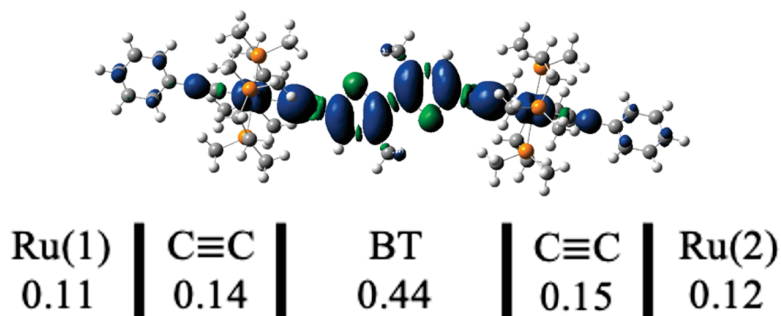


Figure 2.13: HOMO-LUMO energy level of MC-BT, MC-BT⁺, MC-DTP, and MC-DTP⁺ frontier orbitals.

To understand the spin distribution upon oxidation and to classify the poly-metallaynes, spin density distribution calculations on the monocationic model complexes (i.e., MC-BT⁺ and MC-DTP⁺) were performed. Spin density distributions for the monocationic states of both model complexes (MC-BT⁺ and MC-DTP⁺) show significant contributions from the bridging ligands, with 44% on BT and 46% on DTP (**Figure 2.14**).

MC-BT⁺



MC-DTP⁺

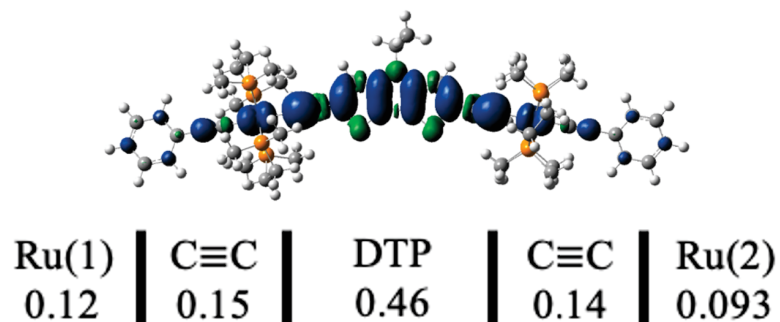


Figure 2.14: Spin density distribution of MC-BT⁺ and MC-DTP⁺.

The two Ru centers in both model complexes contribute evenly to the spin density (11% and 12% in MC-BT⁺ and 9% and 12% in MC-DTP⁺). This evidence supports the notion that both polymers could exhibit strong bridging ligand-mediated M-M interactions upon oxidation. Therefore, P1 and P3 will likely form stable class II-III MV compounds in their MV states. However, according to the CV measurements, the absence of peak separation in P1 oxidation indicates that it might form class I-II MV compounds, implying minimal M-M interaction. This discrepancy could stem from the geometrical deviation between theoretical and experimental conditions. In theoretical calculation, the geometry the calculations were based on was optimized and relatively planar, thereby allowing for better charge mediation between two Ru centers. However, in practice, the P1 thin film

consists of a mixture of planar and non-planar conformers, thus distorting orbital overlap and through-bond charge mediation across the two Ru centers.

2.2.4 Solid-state electrochromic (EC) memory device characterizations

Based on the SEC results, all three polymers exhibited significant changes in absorption in the visible and NIR regions upon oxidation. P2 and P3 showed more stable MV states, owing to enhanced M-M interactions and charge delocalization, making them suitable candidates for EC memory devices. As described in the Experimental Section, Solid-state EC devices were fabricated using P1, P2, and P3.

The applied potentials for the EC devices were determined based on the absorption maxima observed in the SEC experiments (Figure 2.15).

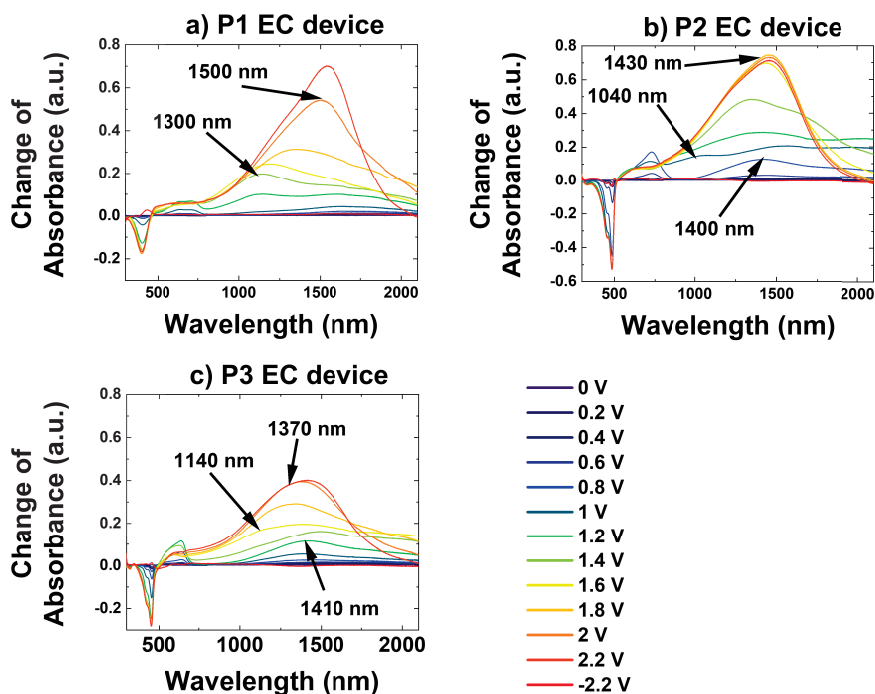


Figure 2.15: UV-vis-NIR absorption spectra of a) P1 electrochromic (EC) device, b) P2 EC device, and c) P3 EC device at different potentials.

P2 and P3 EC devices operated at lower voltages than the P1 EC device (i.e., P1 EC devices operated at 1.6V and 2V to achieve E_1 and E_2 and E_3 ,

respectively; P2 EC devices operated at 0.8 V, 1 V, and 1.6 V to achieve E_1 , E_2 , and $E_{3/4}$, respectively; P3 EC devices operated at 1.2 V, 1.6 V, and 2 V to achieve E_1 , E_2 , and E_3 , respectively), suggesting lower power consumption.

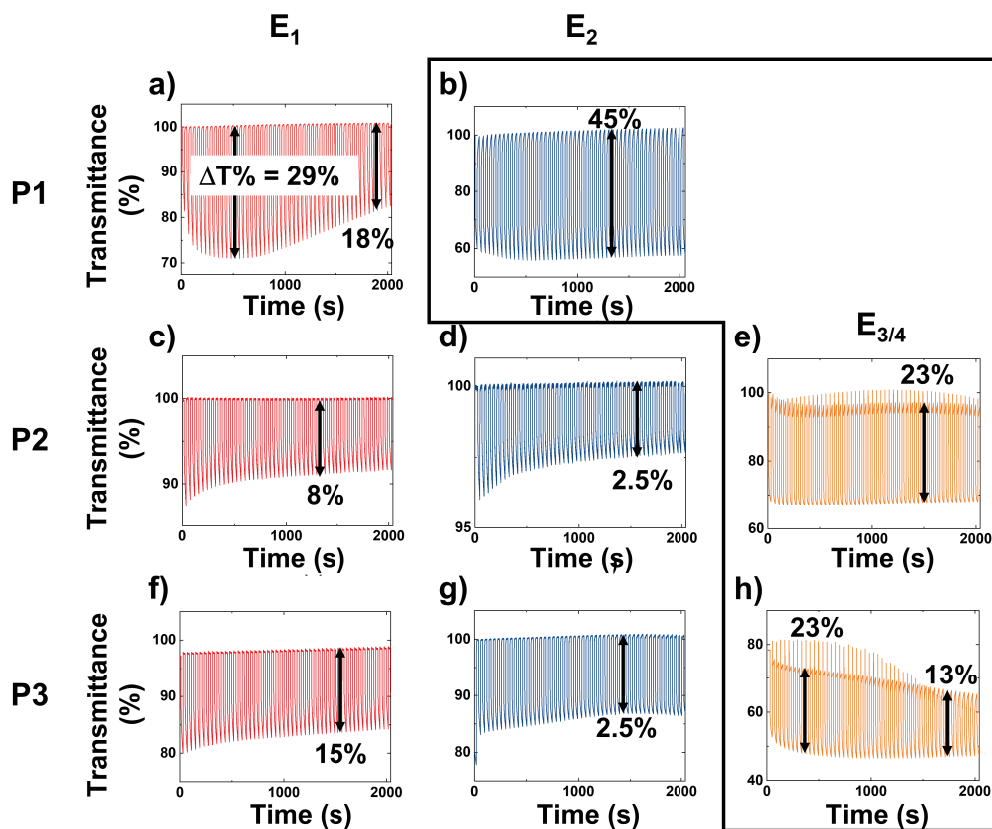


Figure 2.16: Cyclic stability of P1, P2, and P3 EC devices at different oxidation states. Each row represents measurements from the same device (i.e., P1, P2 and P3 EC devices), and each column represents the sequence of oxidation events (i.e., E_1 , E_2 , and E_3). The measurements that are not circled originated from metal-based oxidation, while those circled by a solid line represent organic-based oxidation. For all measurements, 50 cycles of 20 s 'off-pulses' (-2.2 V for all EC devices, resulting in high transmittance ($T\%$)) and 20 s 'on-pulses' (which results in lower $T\%$) were applied to the devices. For a) and b), the on-pulses were 1.6 and 2 V, respectively, and the monitoring wavelengths were 1130 and 1500 nm, respectively. For c), d), and e), the on-pulses were 0.8, 1, and 1.6 V, respectively, and the monitoring wavelengths were 1400, 1040, and 1430 nm. For f), g), and h), the on-pulses were 1.2, 1.6, and 2 V, respectively, and the monitoring wavelengths were 1410, 1140 and 1370 nm, respectively.

The cyclic stability of these EC devices was tested, and 20 seconds of writing and erasing potentials were applied to the EC devices. -2.2 V was utilized as the erasing potential for all EC devices (**Figure 2.16**). P2 and P3 EC devices exhibited enhanced cyclic stability performance for metal-based oxidation compared to P1 EC device (E_1 for all polymers and E_2 for P2 and P3) in terms of transmittance changes ($\Delta T\%$) over 50 cycles ($\Delta T\%$ decrease of E_1 = from 29% to 18% for the P1 EC device, from 12% to 8% for P2, from 20% to 15% for P3; $\Delta T\%$ decrease of E_2 = from 4% to 2.5% for P2, from 14% to 13% for P3). Furthermore, the cyclic stability of ligand-based oxidation was also characterized. Interestingly, P3 showed a more drastic decrease in $\Delta T\%$ than P1 and P2 over 50 cycles (i.e., $\Delta T\%$ decreased from 23% to 13% for P3, while those of P1 and P2 remained around 45% and 23%, respectively). It is probably due to the prominent charge trapping that occurred in P3, which aligns with the EPR results in the previous section.

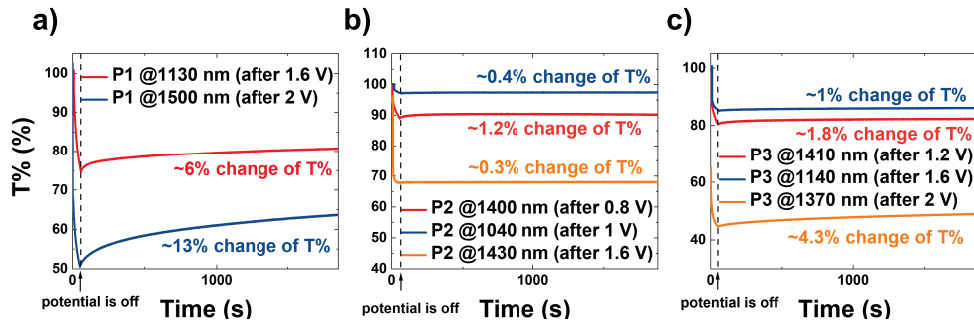


Figure 2.17: State retention characterizations of a) P1, b) P2, and c) P3 EC devices. Potentials of 50 seconds were applied to the EC devices to achieve various oxidation states, followed by turning off the potential and monitoring with the corresponding absorption maxima for 30 minutes.

State retention tests revealed that P2 and P3 can retain their oxidation states better than P1 over a certain period, i.e., 30 minutes (**Figure 2.17**). In this characterization, different oxidation states of the polymers were achieved by applying 50 seconds of the corresponding potentials, followed by monitoring the absorption maxima in an open circuit. P1 exhibited $\Delta T\%$ of 6% (monitored by 1130 nm wavelength) and 13% (monitored by 1500 nm) for E_1 and E_2 , respectively. Mean-

while, P2 exhibited $\Delta T\%$ of 1.2% (monitored by 1040 nm), 0.4% (monitored by 1400 nm), and 0.3% (monitored by 1430 nm) for E₁, E₂, and E_{3/4}, respectively, and P3 exhibited $\Delta T\%$ of 1.8% (monitored by 1410 nm), 1% (monitored by 1140 nm), and 4.3% (monitored by 1370 nm) for E₁, E₂, and E₃, respectively. This highlights the improved memory performance of P2 and P3 compared to P1 due to the enhanced M-M interaction and, therefore, resonance stabilization, demonstrating the potential of these polymers for use in low-power, high-performance memory devices.

2.2.5 2.2.5. Morphological, electrical, and SEC characterizations of P1, P2, and P3 OECT devices

The enhancement of M-M interaction in Robin-Day class II-III polymetallaynes (i.e., P2 and P3) not only improved resonance stabilization but also lowered the device operation potential, as reflected in their EC device characterizations. Beyond enhanced resonance stabilization and lowered operation potential, these M-M interactions also contribute to improved conductivity, particularly in the MV state of the metallopolymers. Additionally, the presence of bulky Ru centers is expected to facilitate efficient ion uptake and transport, providing more free volume for ion movement. Consequently, all these features suggest that Ru-polymetallaynes can be utilized as an OECT channel material, albeit the scarcity of utilization of metallopolymers in OECT channels.

To investigate the morphology of these polymers, grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were conducted. The results (**Figure 2.18**) revealed that both P1, P2, and P3 thin films exhibited amorphous morphology with isotropic polymer chain orientation.

This behavior is consistent with their rigid-rod backbone structures and/or the presence of sterically bulky Ru(dppe)₂ centers, which limit polymer backbone mobility, hinder interchain interaction, and thus suppress crystallite formation.

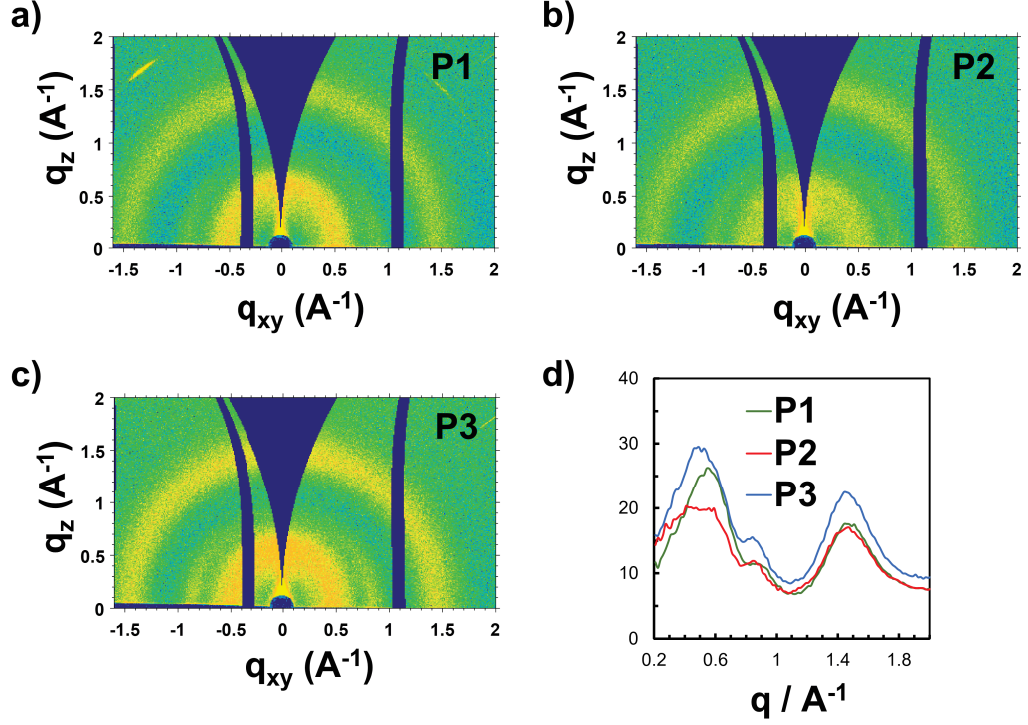


Figure 2.18: Grazing incidence wide-angle X-ray scattering (GIWAXS) reflection patterns of a) P1, b) P2, and c) P3 thin films. d) is the GIWAXS line-cut profile of the reflection patterns.

Nevertheless, since the amorphous structure can facilitate ion diffusion, which is one of the key functionalities in organic mixed ion-electron conductors (OMIECs), P1, P2, and P3 were fabricated into OECT devices, and their preliminary OECT performance was evaluated.

The transfer characteristics of the P1-P3 OECT devices were examined. The devices were fabricated on substrates featuring patterning source-drain electrodes with a 3-micron gap passivated by a layer of SiO_2 . 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) was used as the electrolyte, and a silver/silver chloride (Ag/AgCl) pellet with silver wire was used as the gate electrode.

As shown in **Figure 2.19a**, both P2 and P3 OECTs exhibited significantly higher on-state drain current (I_d), on-off ratios, and transconductance (g_m) compared to P1 OECT, with maximum g_m values of $0.35 \mu\text{S}$ for P2 OECT and $0.67 \mu\text{S}$ for P3 OECT.

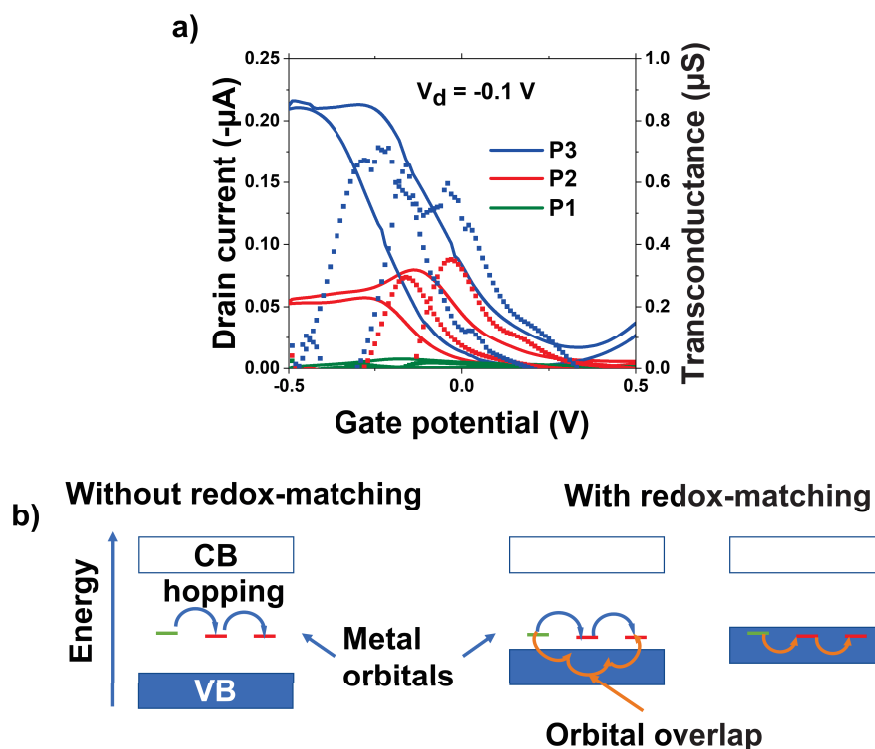


Figure 2.19: a) Transfer characteristics (drain current (I_d) vs gate potential (V_g)) of P1 (green line), P2 (red line), and P3 (blue line) organic electrochemical transistors (OECTs) and the corresponding transconductance (g_m) (scattered plot). b) Schematic explanation of the redox-matching principle for the enhanced OECT performance of P2 and P3 compared to P1.

This can be explained by the effect of redox-matching (as shown in **Figure 2.19b**), which promotes the more efficient inner-sphere charge transfer pathway compared to outer-sphere charge transfer (e.g., hopping).

To further investigate the charge transport properties and redox behavior of P3, SEC analysis was performed. The UV-vis-NIR spectra of the P3 film (**Figure 2.20**) confirmed that the on-state of the OECT device corresponds to the MV state of the polymer, as evidenced by the emergence of absorption bands at 640 nm and 1400 nm when a potential of 0.5 V was applied under the same experimental conditions as the OECT measurements.

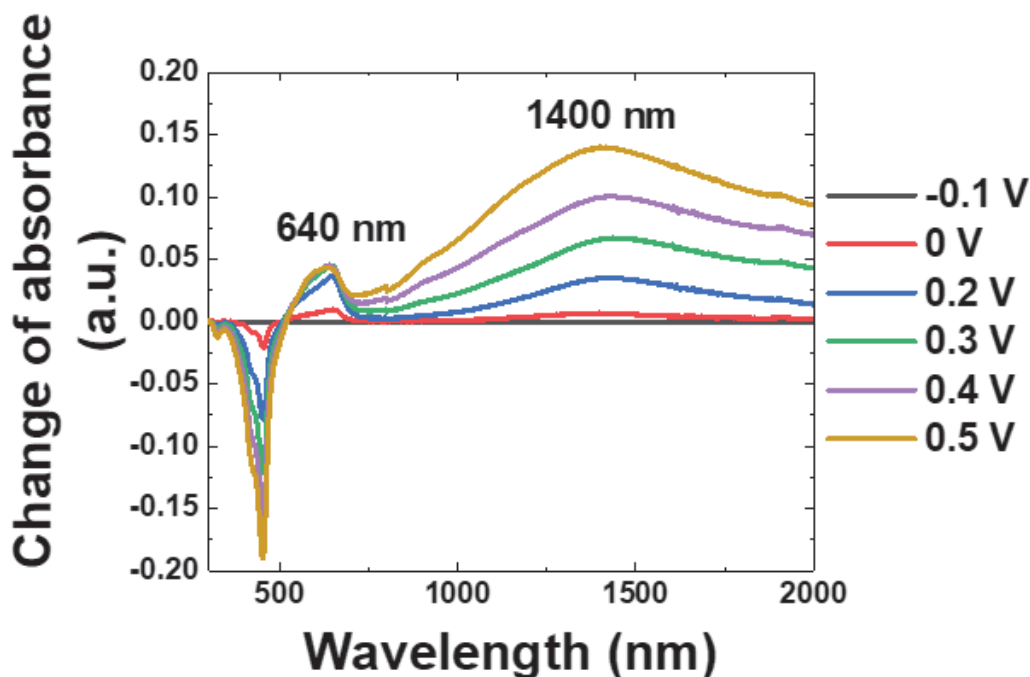


Figure 2.20: Spectro-electrochemical (SEC) analysis of P3 at different potentials (Condition: working electrode = indium tin oxide (ITO), counter electrode = Pt, reference electrode = Silver/silver chloride (Ag/AgCl) pellet. Electrolyte = 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]).

This observation indicates that charge transport in P3 is facilitated by enhanced M-M interactions upon the incorporation of redox-matching, which promotes a more efficient inner-sphere charge transfer (i.e., orbital overlap) at the MV state on top of a less efficient outer-sphere charge transfer (e.g., hopping).

These combined experiments of EC and OECT characterizations demonstrate that P2 and P3 benefit from M-M interactions, which stabilize the redox-active states and improve charge transport. Additionally, the presence of sterically bulky Ru

centers may create free volume within the amorphous polymer network, facilitating ion uptake and charge compensation. These factors contribute to the enhanced OECT performance.

2.2.6 Conclusion

In this chapter, three novel, solution-processable Ru-polymetallaynes (namely, P1, P2, and P3) were developed and analyzed. Their molecular structures were verified, and number-average molecular weights with degrees of polymerization were estimated using NMR, resulting in values of 50, 9, and 15, respectively. Electrochemical and SEC studies showed all three polymers exhibited strong NIR absorption. Specifically, P2 and P3 demonstrated metal-based oxidation $\text{Ru}^{2+}/\text{Ru}^{3+}$ peak separation, indicating improved M-M interactions due to enhanced bridging ligand planarity and, in the case of P3, better redox-matching between the metal centers and organic components. This intensified M-M interaction facilitated the formation of stable Robin-Day class II–III MV compounds in P2 and P3, as supported by the K_c values obtained from the electrochemical characterization and further corroborated by DFT calculations. Solid-state EC devices constructed from these polymers revealed low operational potentials for multicolor switching (-2.2 V to 2 V) and enhanced state retention, with the metal-based cationic states in P2 and P3 maintaining over 98% stability after 30 minutes. These results suggest that reinforcing M-M interactions in P2 and P3 can substantially enhance optical memory characteristics (i.e., state retention ability). Moreover, preliminary results showed the potential of P3 for OECT application by utilizing the more conductive MV state compared to P1 and P2 ($g_{m,\text{max}} = 0.67 \mu\text{S}$ for P3 and $0.35 \mu\text{S}$ for P2, no clear g_m is determined for P1), which could be explained by the redox-matching principle, demonstrating its utility for OMIEC design.

In the future, we can focus on exploiting the non-volatility in P2 and P3 observed in the EC devices to develop OECT-based memory, exhibiting both digital and

analogous resistive switching behavior. In particular, analogous switching would be important for associative learning and high-capacity neuromorphic memory with simple electrical circuits.[10] However, further device optimization is needed, such as using interdigitated electrodes to increase channel width and realize large signal amplification. As a result, more distinct conductance states can be achieved.

2.2.7 Contribution

Dr. Evgenia Dmitrieva from IFW Dresden performed the SEC analysis (i.e., EPR and UV-vis-NIR coupling with CV). Dr. Olga Guskova from IPF Dresden performed the theoretical calculations. Dr. Ningwei Sun from IPF Dresden assisted the EC device characterizations. 3-micron channel substrates were fabricated by Dr. Heiko Reith's group from IFW Dresden.

Chapter 3

Blending of doped poly(vinylferrocene) (PVF) with poly(3-hexylthiophene) (P3HT) for enhanced electrochemical transistors (OECTs) performance

3.1 Introduction

Electrolyte-gated transistors (EGTs) represent a class of three-terminal devices that utilize an electrolyte as the gate, in contrast to the gate dielectric layer found in traditional organic field-effect transistors (OFETs). Within this category, organic electrochemical transistors (OECTs) stand out as particularly promising, employing organic mixed ion-electron conductors (OMIECs)—hydrophilic semi-conducting materials—as the channel materials to enable efficient interactions between the channel and electrolytic ions through swelling[29, 28, 130] while supporting electron transport through the conjugated backbone simultaneously. This facilitates volumetric doping, leading to high volumetric capacitance (C^*), high charge carrier mobility (μ), and, therefore, high transconductance (g_m) according to **Equation 1.8**,[131] making OECTs highly suitable for biosensing applications.[132, 133]

Beyond C^* , μ , and g_m , the device turn-on time (turn-on time (τ_{on})), primarily governed by the device geometry and electrolytic ion mobility as described by the Bernards and Malliaras model,[34] benefits from using hydrophilic OMIECs, enabling efficient ion injection and mobility. The high response speed is crucial for applications such as real-time biosensing[12] and rapid neuromorphic computing[134, 8, 135], enabling broad bandwidth operation and a high signal-to-noise

ratio.

Current strategies for designing OMIECs frequently involve incorporating charged or polar side chains, such as ethylene glycol,[29, 136, 75] or copolymerizing semi-conducting polymers with polymer electrolytes or polyelectrolytes.[137, 56] These approaches have led to OMIECs with high μC^* values - a material-specific metric combining charge carrier mobility and volumetric capacitance - and short response time.[138] However, the lack of mechanistic study on the synthesis of OMIECs and the hygroscopicity of the monomers makes the control of polymer parameters, purification and handling challenging.[81] Eventually, it poses significant barriers to their practical application. Thus, alternative approaches for designing OMIECs are necessary.

One promising alternative is hydrophobic organic semiconducting polymers (OS-CPs), which incorporate alkyl side chains. These materials offer well-established synthetic pathway and good electrical properties. However, their hydrophobicity significantly impairs interaction with polar electrolytic ions, leading to poorer ion penetration, lower C^* values, and slower response speeds in OECT devices compared to typical OMIECs.[28] To address these limitations, researchers have explored modifications to the channel’s micro- and mesostructure,[98, 100, 97] control of channel crystallinity,[96] or device architecture.[103, 102]

Another simple yet effective approach would be blending hydrophobic materials with other polar or hydrophilic materials to create polar domains for efficient ion-channel interactions while retaining hydrophobic OSCP domains for electron transport. However, many hydrophilic materials, such as poly(vinyl alcohol) (poly(vinyl alcohol) (PVA)) and poly(ethylene glycol) (poly(ethylene glycol) (PEG)), are water-soluble, leading to potential performance degradation in aqueous environments due to dissolution.

Ferrocene (Fc), a versatile organometallic moiety, could offer a potential solution for channel modification. Its well-established properties, including high electrochemical stability and accessible redox potential, make it a valuable component in

various fields, such as electrochemical referencing,[139, 140] (bio)sensing,[141, 142] and surface modification.[105, 143] Importantly, the redox transition of ferrocene to ferrocenium (Fc^+) enhances surface hydrophilicity, which is critical for applications such as OECTs that rely on efficient ion-channel interactions. Thus, blending Fc^+ -containing materials with hydrophobic OSCP s could improve channel wettability and hydrophilicity, potentially enhancing ionic performance in OECT devices.

To the best of our knowledge, the integration of organometallic moieties (e.g., Fc and Fc^+) into OECT channels has been minimally explored. In this study, the feasibility of using blends of 20 mmol% chemically doped polyvinylferrocene (PVF^+) with regioregular poly(3-hexylthiophene) (P3HT) as OECT channel materials was investigated. Electrical characterizations (e.g., transfer, output, and response time measurements) were conducted to evaluate the influence of PVF^+ on device performance. Additionally, spectroelectrochemical (SEC) analyses were performed to identify cationic radicals and polarons generated under various bias conditions. Various morphological characterizations, including contact angle measurements, grazing incidence wide-angle X-ray scattering (GIWAXS) measurements and atomic force microscopy (AFM) were adopted to elucidate the influence of PVF^+ on thin-film properties.

3.2 Results and discussion

3.2.1 synthesis and structural characterizations

Poly(vinylferrocene) (PVF) was synthesized via free radical polymerization of vinylferrocene (VF) using azobisisobutyronitrile (AIBN) as the radical initiator following a reported protocol.[144] The process is illustrated in **Figure 3.1**, and the chemical structure was characterized by nuclear magnetic resonance (NMR) spectroscopy (see Appendix B.6). The observed broad multiplet signals from 3.96 - 4.23 ppm and around 2.04 ppm indicate the formation of the polymeric form of VF.

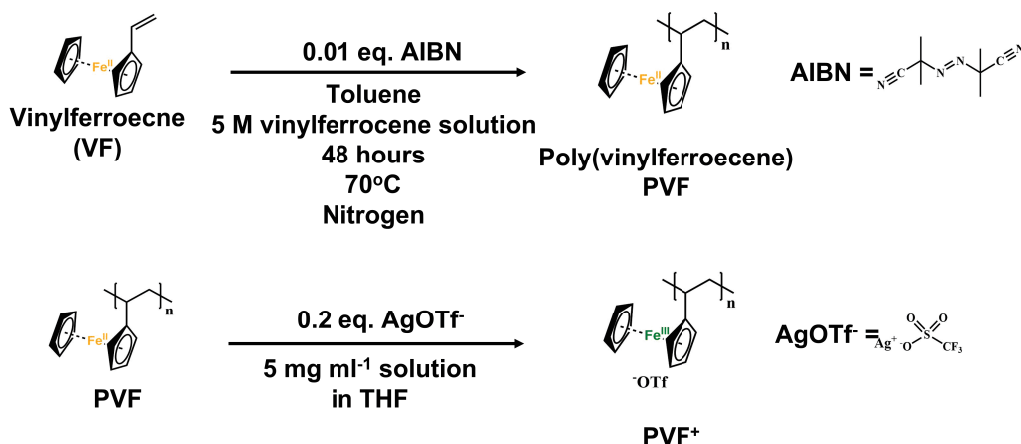


Figure 3.1: Synthetic route to poly(vinylferrocene) (PVF) and the doping condition to obtain 20 mol%-doped poly(vinylferrocene) (PVF⁺).

Soxhlet extraction was subsequently performed, and the tetrahydrofuran (THF) fraction was collected. Gel permeation chromatography (gel permeation chromatography (GPC)) analysis revealed that the number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), and polydispersity (PDI) were 12 kDa, 17 kDa, and 1.4, respectively (see Appendix B.7 and Table B.1). Although PVF is typically processed in halogenated organic solvents such as chloroform, GPC results indicated decomposition when chloroform was used as the eluent (Appendix B.8). This decomposition was attributed to photolysis in the presence of halogenated solvents.[144] To avoid the decomposition of PVF during the preparation procedure, another solvent system had to be sought. THF could be a good option since it not only dissolves PVF but also induces aggregation of P3HT polymer chains, leading to high crystallinity and, therefore, potentially improved electrical performance.[145] Consequently, THF was selected as the processing solvent for PVF and its blends with P3HT in this study.

However, PVF is known for its break-in effect, or memory effect, which is due to the inefficient ion diffusion into the pristine material during the electrochemical cycle.[146] To circumvent or minimize this effect, chemical doping of PVF can be employed to pre-configure the material, allowing for a more efficient ion diffusion

into the thin film. In poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), the blending of hydrophobic PEDOT and hydrophilic PSS results in phase separation, allowing for the preservation of crystallinity in the PEDOT-rich domain and, therefore, electronic transportation.[68] Similarly, phase separation would be expected when mixing hydrophobic P3HT with hydrophilic doped PVF, thus maintaining the electronic interaction in the P3HT-rich domain and minimizing electrical and ionic performance trade-offs.

To achieve PVF doping, silver trifluoromethanesulfonate (AgOTf) was employed as the dopant (details provided in the Experimental Section). Successful doping of PVF in THF was confirmed via UV-vis absorption spectroscopy (as denoted by PVF^+ in **Figure 3.2**), as evidenced by a reduction in absorbance at 446 nm (associated with the metal-to-ligand charge transfer (MLCT) of Fc) and the emergence of an absorption peak at 630 nm (ligand-to-metal charge transfer (LMCT) of Fc^+).[147]

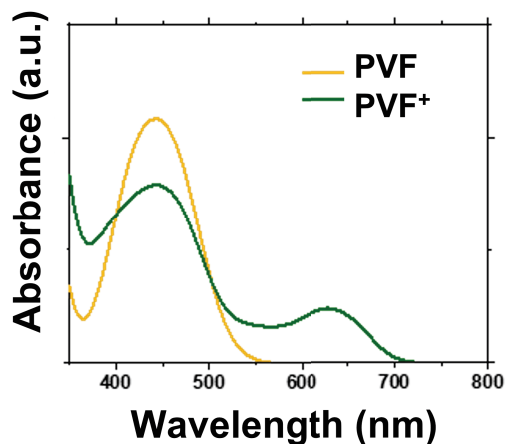


Figure 3.2: Ultraviolet-visible (UV-vis) absorption spectra of PVF (yellow line) and PVF^+ (green line).

Approximately 20% of Fc groups were converted to Fc^+ since 0.2 molar equivalents of AgOTf were added to the PVF solution, resulting in a corresponding 20% decrease in absorbance intensity. The doping level at 20% was optimized

to maximize the number of Fc^+ groups on the PVF polymer chain, enhancing hydrophilicity while preserving solubility in common organic solvents like THF for high processability.

3.2.2 Electrical characterizations

To evaluate the influence of the PVF⁺ content on the ionic and electrical performance of PVF⁺/P3HT blend channels, OECTs were fabricated using pure P3HT, 5PVF⁺ (5 wt% PVF⁺ and 95 wt% P3HT), 10PVF⁺ (10 wt% PVF⁺ and 90 wt% P3HT), 25PVF⁺ (25 wt% PVF⁺ and 75 wt% P3HT), and 50PVF⁺ (50 wt% PVF⁺ and P3HT) as channel materials. Electrical characterizations included transfer, output, and response time measurements were performed, with 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) as the electrolyte and an silver/silver chloride (Ag/AgCl) pellet as the gate electrode. Detailed fabrication procedures are described in the Experimental Section. **Figure 3.3** illustrates the transfer characteristics and the g_m of the OECT devices.

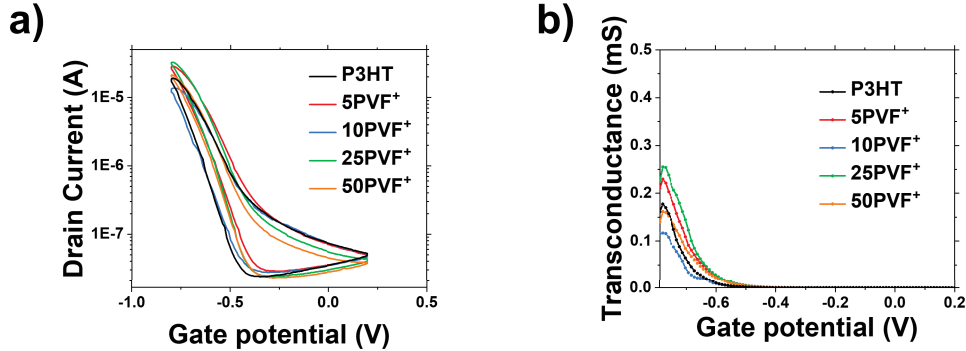


Figure 3.3: The transfer characteristics of poly(3-hexylthiophene) (P3HT) (black line), 5PVF⁺ (red line), 10PVF⁺ (blue line), 25PVF⁺ (green line), and 50PVF⁺ (orange line) organic electrochemical transistors (OECTs) and b) the corresponding g_m . Scan rate = 0.024 V s^{-1} (channel width = $300 \mu\text{m}$, channel length = $300 \mu\text{m}$, electrolyte = 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]), gate electrode = silver/silver chloride (Ag/AgCl). Drain potential (V_d) = -0.6 V .

A gate potential (V_g) range of 0.2 V to -0.8 V was applied, while the drain potential (V_d) was held constant at -0.6 V to ensure the channel operated in the saturation regime, as confirmed by output characteristics, as shown in **Figure 3.4**.

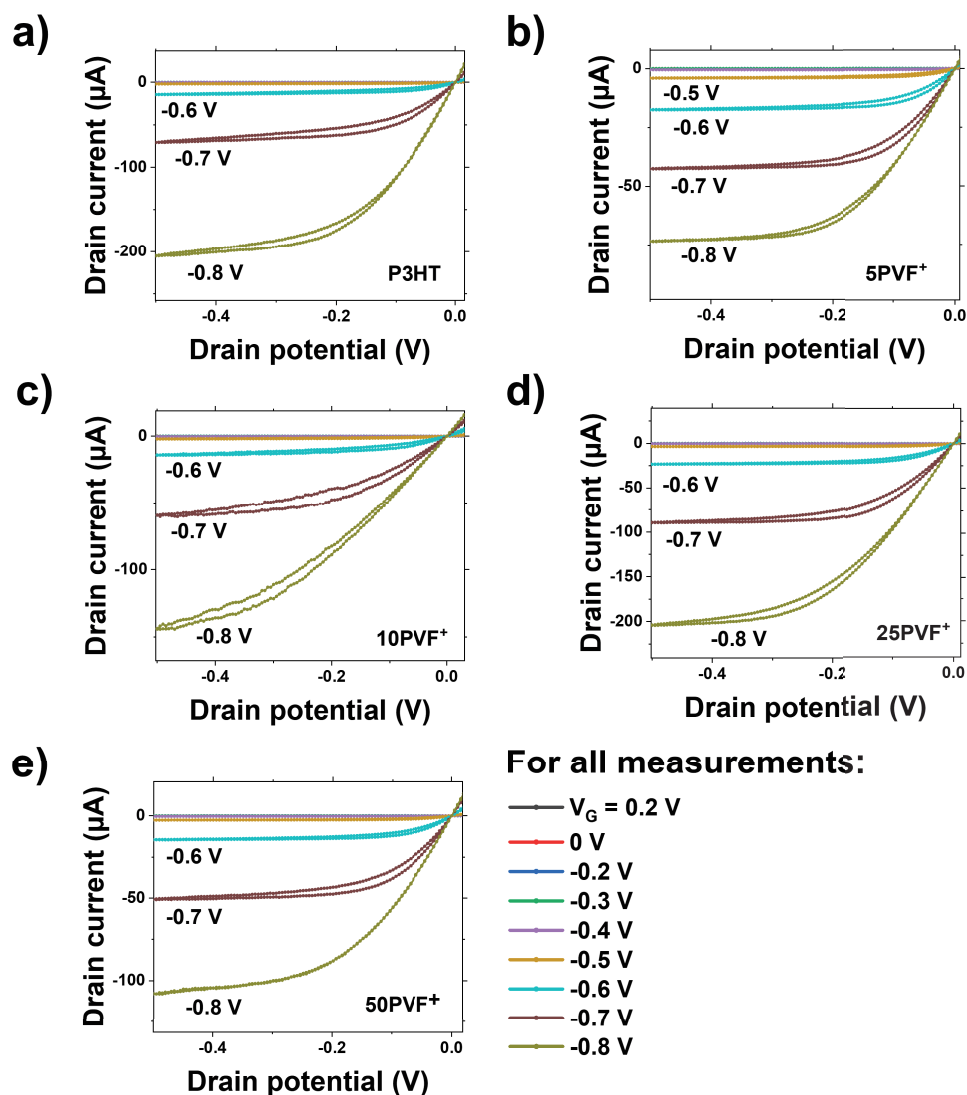


Figure 3.4: Output characteristics of a) P3HT, b) 5PVF⁺, c) 10PVF⁺, d) 25PVF⁺, and e) 50PVF⁺ OECTs. Scan rate = 0.012 V s⁻¹. Channel width = 1800 μm , channel length = 300 μm . Electrolyte = [EMIM][TFSI]. Gate electrode = Ag/AgCl pellet.

The on-off ratios were determined to be 370 (P3HT), 570 (5PVF⁺), 270 (10PVF⁺), 750 (25PVF⁺), and 550 (50PVF⁺), with corresponding maximum g_m values ($g_{m,\text{max}}$) of 0.18 mS, 0.23 mS, 0.12 mS, 0.26 mS, and 0.16 mS, respectively.

These results indicate that blending up to 50 wt% PVF⁺ into the channel does not compromise the electrical performance. The threshold voltages (V_{th}) were -0.62 V, -0.58 V, -0.59 V, -0.58 V, and -0.57 V for P3HT, 5PVF⁺, 10PVF⁺, 25PVF⁺, and 50PVF⁺, respectively. The slight decrease in V_{th} in all of the blend OECTs suggests that a more facile oxidation of P3HT occurred in the OECT devices.[80] Furthermore, the introduction of PVF enabled more efficient ion penetration, as evidenced by τ_{on} measurements. Alternating V_g (0 V for 22 s and -0.8 V for 22 s) were applied to the Ag/AgCl gate electrode, and the resulting drain current (I_d) was fitted using an exponential decay function to determine τ_{on} values. The τ_{on} for the P3HT OECT was 6.79 ± 1.91 s, while the 5PVF⁺, 10PVF⁺, 25PVF⁺, and 50PVF⁺ OECTs exhibited significantly shorter times of 5.20 ± 1.61 s and 5.52 ± 0.82 s, 3.92 ± 0.78 s, and 4.36 ± 1.02 s, respectively (**Figure 3.5**). This substantial reduction in τ_{on} for the blend film channels confirms faster ion penetration from the electrolyte into the channel.

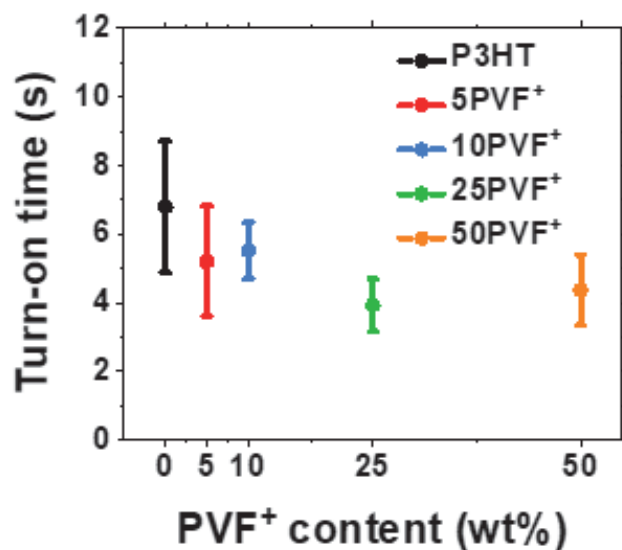


Figure 3.5: Turn-on time (τ_{on}) of P3HT, 5PVF⁺, 10PVF⁺, 25PVF⁺, and 50PVF⁺ OECTs.

The electrical characterization results are summarized in **Table 3.1**.

Sample	$g_{m,max}$ (mS)	on-off ratio	V_{th} (V)	τ_{on} (s)
P3HT	0.18	370	-0.62	6.79 ± 1.91
5PVF ⁺	0.23	570	-0.58	5.20 ± 1.61
10PVF ⁺	0.12	270	-0.59	5.52 ± 0.82
25PVF ⁺	0.26	750	-0.58	3.92 ± 0.78
50PVF ⁺	0.16	550	-0.57	4.36 ± 1.02

Table 3.1: Summary of the measured parameters from the electrical characterizations.

Here, the typical trade-off of electrical performance was not observed upon incorporating the insulating PVF⁺ polymer, even at high PVF⁺ content.[36] Therefore, further investigation of the blends, including gate current (I_g) analysis, electrochemical studies (section 3.2.3.), spectroelectrochemical analysis (section 3.2.4.), and morphological studies (section 3.2.5.), would be worth conducting to understand the electrical behavior.

First of all, I_g analysis was conducted. Upon integration of I_g according to **Equation 3.1**[148, 149] starting from the V_{th} , the injected charge carrier density (p) at different V_g can be calculated, as shown in **Figure 3.6**.

$$p = \frac{\int I_g dV_g}{reAd} \quad (3.1)$$

, where r is scan rate of V_g during transfer characterization (i.e., 0.025 V s^{-1} , e is elementary charge, A is area of channel in contact with electrolyte ($\approx 0.3 \text{ cm}$ in diameter), d is film thickness measured from ellipsometry ($23 \pm 0.1 \text{ nm}$ for P3HT, $26.3 \pm 0.1 \text{ nm}$ for 5PVF⁺, $26.1 \pm 0.1 \text{ nm}$ for 10PVF⁺, $22 \pm 0.1 \text{ nm}$ for 25PVF⁺ and $21.8 \pm 0.1 \text{ nm}$ for 50PVF⁺).

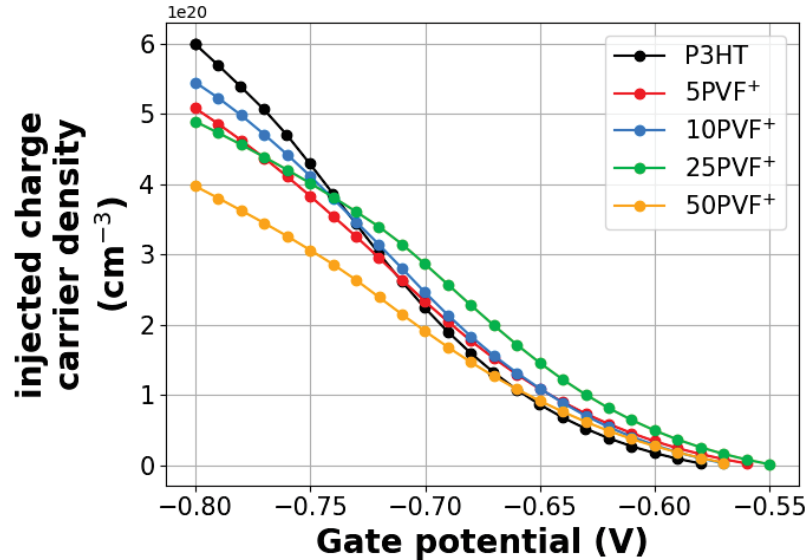


Figure 3.6: Injected charge carrier density (p) vs gate potential (V_g) plots of different blend OECS.

It was observed that the density of injected charge carriers was in the order of 10^{20} , which is in good agreement with the reported values regarding P3HT-based OECS.[49] Moreover, p seemed to correlate with the amount of P3HT at the channel since it decreased with higher PVF⁺ content, suggesting that a considerable amount of carrier density is contributed by the P3HT moiety.

However, despite the decrease in p with higher PVF⁺ content, the μ , which was calculated from **Equation 3.2**, [148, 150] showed an increase at the on-state (i.e., -0.8 V) from 0.014 cm⁻¹ V⁻¹ s⁻¹ for P3HT to 0.03 cm⁻¹ V⁻¹ s⁻¹ for 25PVF⁺ and 0.024 cm⁻¹ V⁻¹ s⁻¹ for 50PVF⁺ (**Figure 3.7**). This increase in μ might be the reason for the absence of an OECT performance trade-off, as this can compensate for the loss of injected charge carriers at the channel. Nevertheless, further experiments are required to understand the enhancement in μ in the blend channels.

$$I_d = \frac{Wd}{L} V_d \mu e p \quad (3.2)$$

, where W is channel width, L is channel length, and e is the elementary charge.

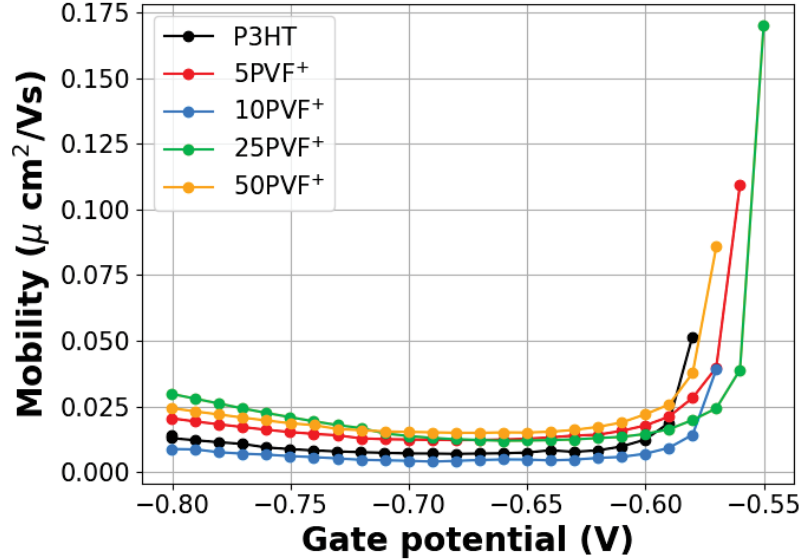


Figure 3.7: Charge carrier mobility (μ) vs V_g plots of different blend OECTs.

3.2.3 Electrochemical characterizations

To elucidate the electrochemical properties of the blends, the cyclic voltammetric (CV) behavior of the respective films was measured. As shown in **Figure 3.8**, the P3HT oxidation peak was observed at approximately 0.74 V vs Ag/AgCl. In comparison, the current response of the oxidation peak at 0.23 V vs Ag/AgCl increases with the PVF⁺ content. Therefore, it is assigned to be the PVF oxidation peak.

Additionally, an improved electrochemically reversibility was found when the

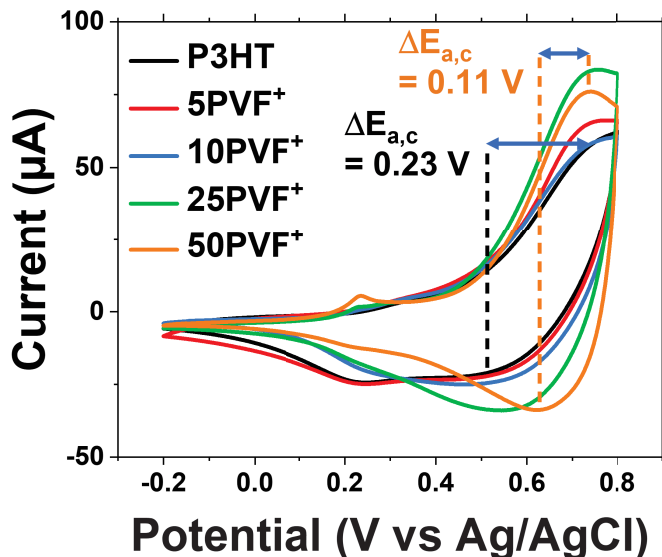


Figure 3.8: Cyclic voltammetric (CV) graphs of the blend films. Working electrode = platinum (Pt) disc; counter electrode = Pt wire; reference electrode = Ag/AgCl pellet; electrolyte = [EMIM][TFSI]; Scan rate = 0.05 V s⁻¹; the mass of material = 0.02 mg.

PVF⁺ content increased, as the difference of the anodic peak of oxidation and the cathodic back-reduction peak ($\Delta E_{a,c}$) became smaller with higher content of PVF (i.e., $\Delta E_{a,c}$ decreases from 0.23 for P3HT to 0.11 for 50PVF⁺). Since irreversibility could be due to ion accumulation at the redox-active electrode,[151]the improved reversibility at high PVF⁺ content can be attributed to the reduced ion trapping when the hydrophilic domain formed by PVF⁺ facilitated the ion transportation in the film.

3.2.4 Spectroelectrochemical (SEC) characterizations

To gain further insight into the functional role of PVF⁺, spectro-electrochemical (SEC) analyses were conducted. To yield a more significant contrast in the change of absorption, only P3HT and 50PVF⁺ will be discussed. **Figure 3.9** shows the normalized absorption spectra (at 520 nm) for P3HT and 50PVF⁺ thin films.

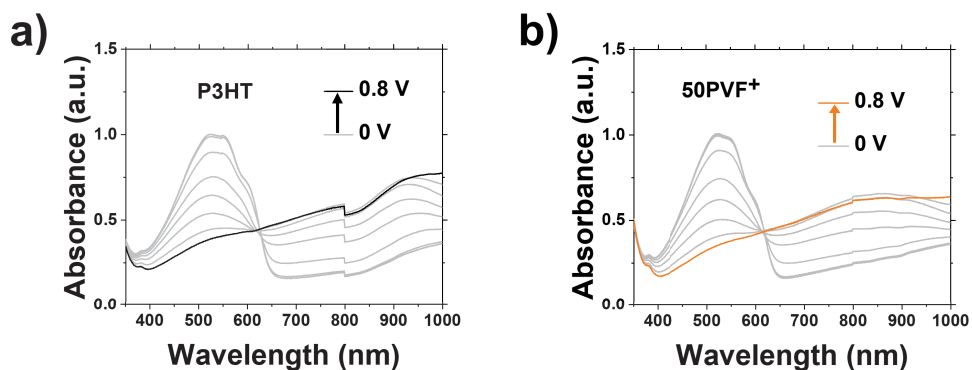


Figure 3.9: Spectroelectrochemical (SEC) analysis of a) P3HT and b) 50PVF⁺. Working electrode = indium tin oxide (ITO). Counter electrode = Pt wire. Reference electrode = Ag/AgCl pellet. Electrolyte = [EMIM][TFSI].

At 0 V applied to the indium tin oxide (ITO) working electrode, both films exhibited a maximum absorption at 520 nm, corresponding to the π - π^* transition in P3HT. When a higher potential (0.8 V) was applied, the π - π^* absorption intensity decreased across all thin films. However, the magnitude of this decrease differed between the P3HT film and the 50PVF⁺ films. Specifically, in P3HT, the π - π^* absorption intensity decreased by 61% upon applying 0.8 V (absorbance = 0.39), while the blend films exhibited a more significant decrease in absorbance upon applying 0.8 V (65% decrease, absorbance = 0.35). Furthermore, at 0.8 V, an absorption band at 790 nm was observed in both P3HT and 50PVF⁺, indicating the formation of polarons in both samples. In P3HT thin film, the absorbance value was 0.58, while that of 50PVF⁺ is 0.62.

These qualitative results indicate that a higher number of P3HT moieties undergo doping in the blend films when the devices are in the on-state (-0.8 V). This

enhancement of P3HT doping efficiency can be attributed to the incorporation of hydrophilic PVF⁺, which provides a pathway for ion transportation and improves ion transport efficiency within the channel. This also provides consolidated evidence for the increase in μ in the blend OECTs: although the overall p of the blends becomes lower due to the lower concentration of P3HT moiety in the channel, more polarons are generated at the P3HT moiety upon the incorporation of PVF⁺, thereby increasing the local p at the P3HT moiety and enhancing the μ in the blend OECTs.

3.2.5 Surface and morphological characterizations

The incorporation of PVF⁺ resulted in increased hydrophilicity of the films. Contact angle measurements showed a significant decrease in the advancing water droplet contact angle from 118.0° for pure P3HT films to 102.8°, 104.9°, 61.3° and 61.0° for 5PVF⁺, 10PVF⁺, 25PVF⁺ and 50PVF⁺ blend films (**Figure 3.10**), respectively, indicating enhanced wettability with a higher proportion of PVF⁺ in the blends.

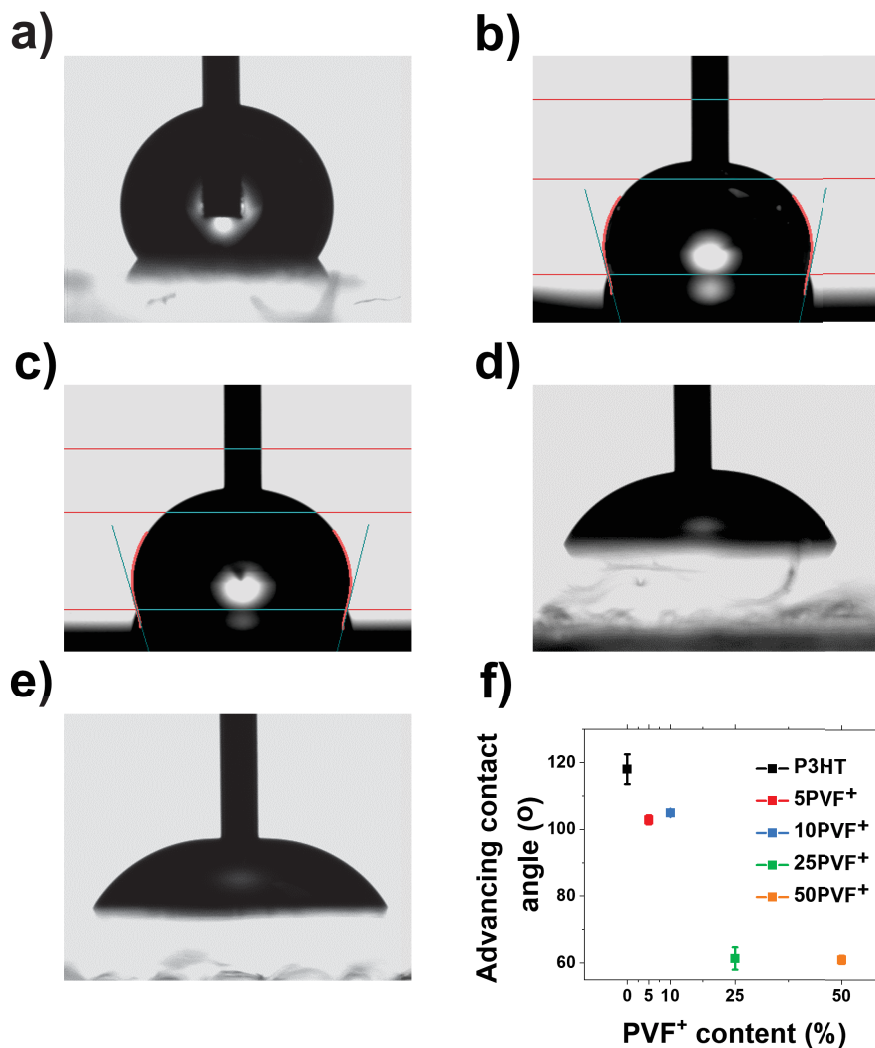


Figure 3.10: Screenshots of contact angle measurements on various thin film surfaces - a) P3HT, b) 5PVF⁺, c) 10PVF⁺, d) 25PVF⁺, and e) 50PVF⁺. f) summarizes the results of contact angle measurements.

This increase in hydrophilicity suggests that improved ion-channel interaction in the blend film channels is possible, potentially enhancing OECT performance by enhancing channel doping and improving the transient behavior, i.e., τ_{on} . However, receding contact angle measurements for the blend films could not be obtained, which is likely due to the samples' significant aggregation and, therefore, high surface roughness, as indicated by the AFM measurement (**Figure 3.11**).^[152] From 25PVF⁺ to 50PVF⁺, the decrease in contact angle is minimal. This implies the domination of the hydrophilic PVF⁺ domain starting from the PVF⁺ content at 25 wt%.

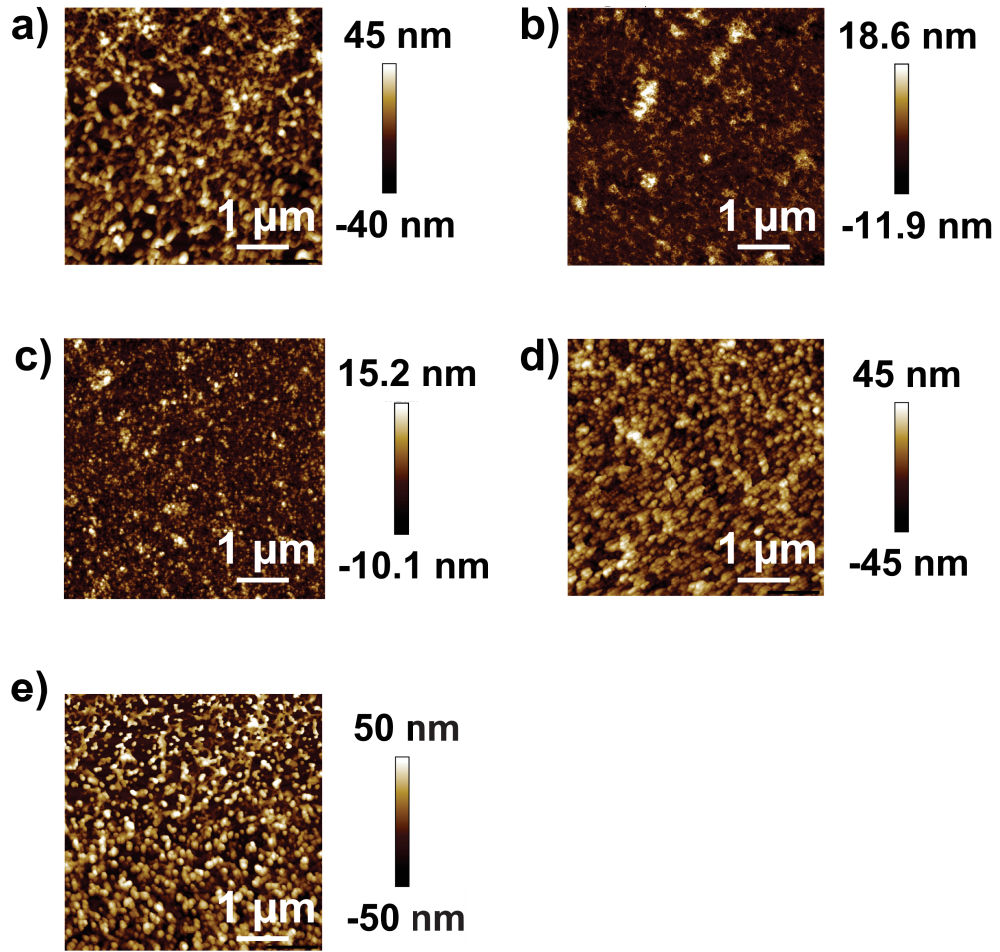


Figure 3.11: Atomic force microscopy (AFM) images of a) P3HT, b) 5PVF⁺, c) 10PVF⁺, d) 25PVF⁺, and e) 50PVF⁺ thin films. The bars at the lower right corner are 1 μm.

To further understand the reason for the observed improvement in τ_{on} , GI-WAXS measurements were conducted. In the P3HT thin film, reflections of π - π stacking (010) and lamellae stacking, (100) and (200), were observed, showing a mixture of face-on and edge-on orientations of the P3HT crystallites (see **Figure 3.12**). The blend films (i.e., 5PVF⁺, 10PVF⁺, 25PVF⁺, and 50PVF⁺) demonstrated prominent differences from the P3HT thin film in the GIXWAS reflection pattern.

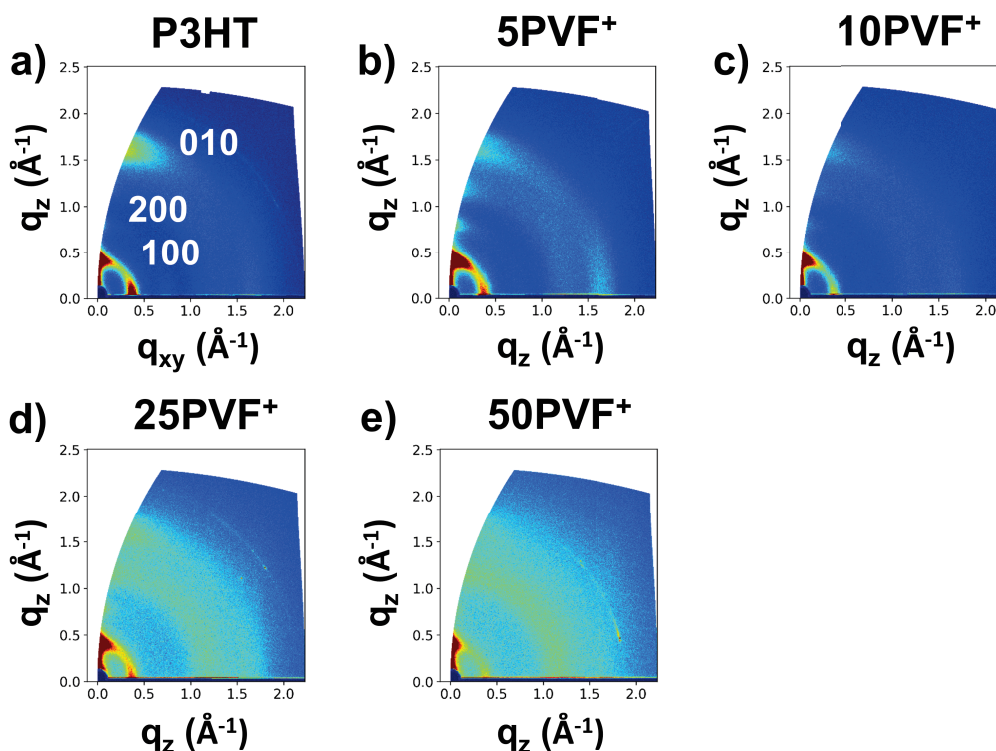


Figure 3.12: Grazing incidence wide-angle X-ray scattering (GIWAXS) reflection patterns of a) P3HT, b) 5PVF⁺, c) 10PVF⁺, d) 25PVF⁺, and e) 50PVF⁺ thin films.

An isotropic reflection at $1.175 \text{ \AA}^{-1}$ ($d = 5.35 \text{ \AA}$) was observed in the blend films, presumably a new isotropic crystalline phase that does not have a lattice distance typical of the P3HT crystal system. Since PVF is regarded as an amorphous polymer due to the presence of bulky Fc side groups, this isotropic reflection could be assigned to the PVF-rich phase. To determine this, scanning electron

microscopy (SEM) and transmission electron microscope (TEM) were employed to elucidate any phase separation and elemental distribution in the blend thin films. **Figure 3.13a-d** show the SEM images of all the blend films. All films exhibited rough surfaces, with particle sizes of around 100 nm. As shown in **Figure 3.13e-f**, further TEM investigation of these particles reveals high iron (Fe) content and slightly lower sulfur (S) content.

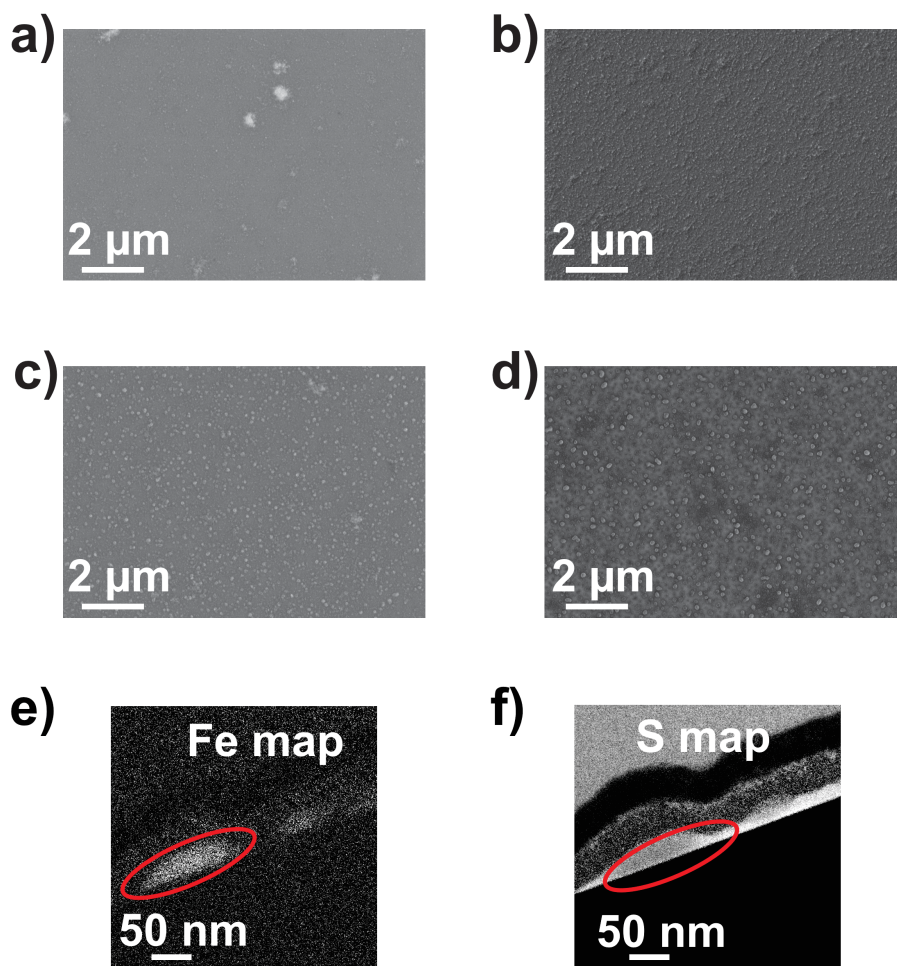


Figure 3.13: Scanning electron microscopy (SEM) images of a) 5PVF⁺, b) 10PVF⁺, c) 25PVF⁺, and d) 50PVF⁺ thin films. e) and f) are the transmission electron microscopy (TEM) images of 50PVF⁺ at the same position as circled in red.

Therefore, these particles are identified as the PVF-rich domain, while the continuous domain is the P3HT-rich domain. This could explain the enhanced

electrical performance since the electrically conductive pathway through the continuous P3HT-rich domain is retained.

Additionally, in both blend thin films, the reflections indicating face-on orientation ((010) in q_z direction and (100) in q_{xy} direction) is considerably reduced as compared to the (100) reflection in q_z -direction, which resembles edge-on orientation. For the 5PVF⁺ film, the azimuthal tube cuts show a ca. 2 times reduction of face-on P3HT crystallites compared to the pristine P3HT film, while the in-plane edge-on reflection intensity is similar to that of the P3HT thin film (**Figure 3.14**). A similar phenomenon was also observed in 10PVF⁺ (ca. 2.8 times decrease in face-on P3HT crystallites), 25PVF⁺ (ca. 3.5 times decrease in face-on P3HT crystallites), and 50PVF⁺ thin films (ca. 8 times decrease in face-on P3HT crystallites).

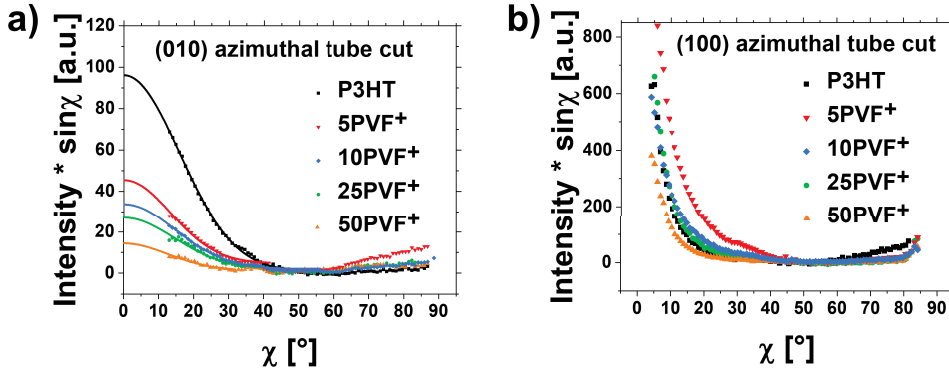


Figure 3.14: Azimuthal tube cuts of a) (010) and b) (100) GIWAXS reflection of different blend thin films.

This indicates that the formation of face-on crystallites is suppressed upon blending PVF⁺, leading to the presence of a higher percentage of edge-on crystallites in the blends,[153] and therefore, facilitating the ion transportation from the electrolyte to the channel[154] and further contributing to the enhancement of ionic performance in the blend OECT devices.

3.3 Conclusion

Chemically doped PVF⁺ was blended with P3HT at different weight ratios. The incorporation of PVF⁺ results in the enhancement of OECT performance, including μ , and shorter τ_{on} . The blend films exhibited improved P3HT doping efficiency, as supported by the CV characterization and SEC analysis). The faster response time in the blend OECTs (i.e., 3.92 s for 25PVF⁺), revealed by the response time characterizations, can be ascribed to the enhanced hydrophilicity according to the contact angle measurements and the suppression of face-on P3HT crystallites according to the GIWAXS measurements, further allowing for a higher percentage of edge-on oriented P3HT crystallites, favoring ion penetration into the channel. SEM and TEM measurements confirmed the dispersion of the PVF-rich domain in the continuous P3HT-rich domain. Thus, the electron transport is supported, showing higher μ in 25PVF⁺ and 50PVF⁺ compared to P3HT. This explains the absence of electrical performance compromisation. Overall, this study provides a facile approach for design of OMIECs with readily available materials (i.e., PVF and P3HT), exhibiting improved ionic (i.e., higher P3HT doping efficiency and shorter τ_{on}) and electrical performance (i.e., improved μ), and thereby showing no deterioration of OECT performance. This opens up a much wider choice of OMIEC materials, making OECTs' real-world application more possible.

3.4 Contribution

Dr. Eva Bittrich performed the GIWAXS and ellipsometry measurements and analyzed the results with Prof. Mahmoud Al-Hussein. Dr. Petr Formanek conducted the SEM and TEM measurements and analysis. Oliver Ditzer performed the AFM measurements. Ronja Thümmeler performed the contact angle measurements.

Chapter 4

Boosting organic electrochemical transistor (OECT) performance with PEGylated gold nanoparticles (PEG-AuNP) in hydrophobic channels

4.1 Introduction

From Chapter III, we have demonstrated the high promise of a blending approach and found that using hydrophilic 20% chemically-doped poly(vinylferrocene) (PVF⁺) as an additive to the hydrophobic channel enhances the organic electrochemical transistors (OECT) performance in terms of doping efficiency, faster response time (τ_{on}), as well as charge carrier mobility (μ). Therefore, this work lays the foundation for the use of other blends or composites as channel materials to achieve an improved OECT performance.

From the last study, although the blending approach did improve the above-mentioned metrics, the injected charge density was decreased, therefore hindering the further improvement of OECT performance. In fact, the overall OECT performance of a material is governed not only by electrical performance but also by ionic performance. This can be understood from the figure of merits, μC^* , the product of μ , which governs electron transport property, and volumetric capacitance (C^*), which gives information to the channel-ion interaction ability. It is a material-specific parameter independent of other factors, such as device geometry and operational conditions, thereby providing an intuitive estimation of a material's steady-state OECT performance.[39]

To date, some of the best-performing organic mixed ion-electron conductors

(OMIECs) are the conjugated semiconducting polymers with polar oligo(ethylene glycol) side chains, exhibiting μC^* as high as $522 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for p(g2T2-g4T2) (please refer to the Introduction section for the chemical structure).[74] In this class of materials, the interacting conjugated polymer backbone can support electron transport, showing satisfactory μ values. At the same time, the polar ethylene glycol (EG)-rich domain can efficiently accommodate ions via swelling once in contact with electrolytes, allowing for volumetric doping of the channel and, thus, resulting in high C^* , transconductance (g_m) and short τ_{on} in the range of millisecond.

Despite the high performance of EG-modified OMIECs in OECTs, their synthesis is not as facile as the conventional hydrophobic organic semiconducting polymers (OSCP), presumably due to the hygroscopic nature of the monomers.[81] As a result, the purification of monomers is challenging, affecting the monomer purity. This again makes the control of polymer parameters such as polydispersity challenging. Moreover, OMIECs mediate ion diffusion via swelling during operation.[155, 156] Although it incurs efficient ion injection and transport, excessive swelling could occur, leading to defects formation and degradation of operational stability.[80]

To overcome the obstacles, other materials or systems should be explored. Among all materials, conventional hydrophobic OSCPs that contain alkyl side chains could be a promising choice, thanks to the well-established mechanistic studies on hydrophobic OSCPs synthesis and their good electrical performance, exhibiting charge carrier mobility as high as $7.76 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, [157] which is comparable to their inorganic counterparts such as polycrystalline silicon. However, despite the reduced swelling, these materials are, in general, not utilized for OECT applications, such as implantable bioelectronics, due to their hydrophobicity and, therefore, weak interaction with the aqueous medium in a physiological environment. Nevertheless, considering their outstanding electrical properties, established synthetic routes, and commercial availability, the adaptation of hydrophobic OS-

CPs in the OECT channel would symbolize a significant advancement. Therefore, much effort has been dedicated to enabling hydrophobic OSCP in OECT.

Huang et al. demonstrated that manipulating the porosity of the channel materials via the breath figure method leads to a significant increase in surface area and a boost of a series of OECT parameters, including g_m , C^* , and τ_{on} . [98] However, the control of porosity, such as the distribution of pores and pore sizes, is challenging since it requires precise control of fabrication parameters to reproduce the same condensed water droplet position and sizes for uniform porosity. As the OECT performance depends on the porosity, this imposes a challenge to OECT device performance reproducibility. Another approach is the interlayer approach, as demonstrated by Bischak et al. and, recently, He et al., which involves the use of an interlayer between the hydrophobic channel and aqueous electrolyte. [102, 103] The interlayer is composed of an ionic liquid, such as 1-ethyl-3-methylimidazolium-bis(trifluoromethyl sulfonyl)imide, [EMIM][TFSI], embedded in a gel matrix, such as poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP). During the p-type accumulation mode operation, ion exchange could occur. The small aqueous electrolytic ions, such as chloride (Cl^-) will be injected into the interlayer, and the large polarizable anions in the interlayer, i.e., $TFSI^-$, will be injected into the hydrophobic channel. Since polarizable anions can interact with the OMIEC channel more efficiently, the ion exchange occurring at the interlayer leads to the enhancement of OECT performance. However, since the ionic liquid is miscible with an aqueous medium, the release of ionic liquid to the electrolyte could potentially deteriorate the long-term operational stability and release potentially harmful substances to the physiological environment. Since each of the existing approaches poses different drawbacks, it consolidates the need to adopt other strategies for engineering hydrophobic channels.

Gold nanoparticles (AuNPs) might provide a reliable alternative for hydrophobic channel engineering. Studies demonstrated that AuNP composites of OMIEC or semiconducting polymers can increase μ by photo-annealing [158] or enhancing

polymer packing through backbone planarization.[106] Moreover, the established chemistry for AuNPs enables facile surface modification via ligand exchange,[159] allowing for the control of surface hydrophilicity. This could provide hydrophilic sites at the channel, thus facilitating ion diffusion and realizing increased C^* . In addition, by optimizing the size of the AuNPs and the matrix thickness, the surface of AuNPs can be partially exposed, thus providing uniform and hydrophilic AuNPs/OSCP interfacial area for mediating ion transport.

Upon careful examination of the existing OMIECs, attaching poly(ethylene glycol) (PEG) side chains is the most promising method, affording high-performance channel materials due to the enhanced ion conductivity. While it is synthetically difficult to attach these polar side chains onto conjugated polymer backbones, it is much easier to place these side chains onto the AuNP surface.

Therefore, in this chapter, different weight ratios of poly(ethylene glycol)-functionalized gold nanoparticle (PEG-AuNPs) are mixed with commercially available semiconducting polymers (i.e., poly(3-hexylthiophene) (P3HT)), and the OECT performances are evaluated.[160] Last but not least, PEG-AuNPs are also mixed with another semiconducting polymer (poly(2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl)thieno[3,2-b]thiophene (PDPP-TT))), demonstrating the versatility of this material engineering approach.

4.2 Results and discussion

4.2.1 Synthesis and purification

In this chapter, hydrophilic PEG-AuNPs, which acts as a nanoparticle filler to support ion transport, was incorporated into high-performance OSCPs, which act as polymer matrix to support electron transport. Citrate-stabilized AuNPs (45 nm) was synthesized via a step-growth method, followed by ligand exchange with thiol-PEG to obtain PEG-AuNPs. From the Transmission electron microscope (TEM) images in **Figure 4.1a**, the formation of a 2 nm-thick PEG shell was

observed. After ligand exchange,[159] the AuNPs were extracted with chloroform in order to obtain a homogenous solution when mixed with the P3HT solution (also in chloroform) so that an even distribution of PEG-AuNP is achieved (**Figure 4.1b**). For the polymer matrix, we selected two well-explored, commercially

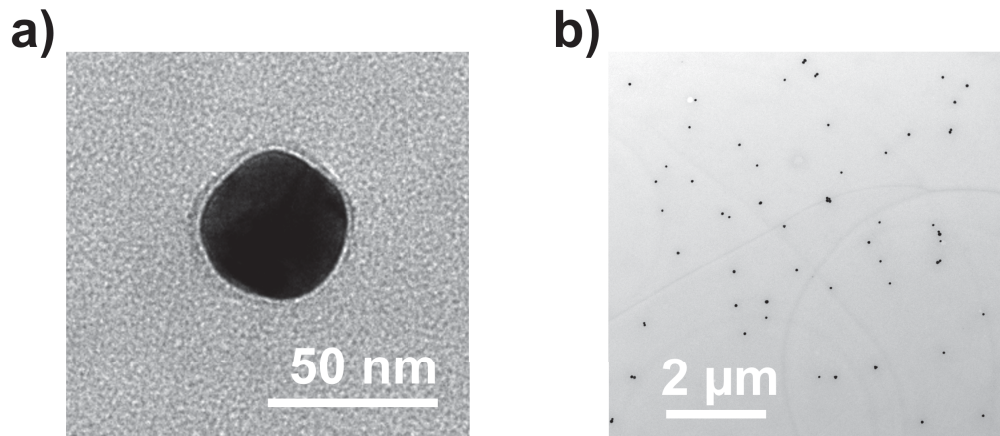


Figure 4.1: A zoomed-in transmission electron microscopy (TEM) image of an poly(ethylene glycol)-functionalized gold nanoparticle (PEG-AuNP) (diameter = 45 nm, PEG-shell thickness $\approx$ 2 nm) and the TEM image of drop-casted film of the composite with 5 wt% PEG-AuNP and 95 wt% poly(3-hexylthiophene) (P3HT).

available OSCPs—P3HT and PDPP-TT—known for their established electrical properties. Before they were used in any characterization or fabrication, the OSCPs underwent purification via Soxhlet extraction with methanol and acetone, followed by extraction with chloroform.

4.2.2 Electrical characterizations

In order to determine the most optimal ratio of PEG-AuNP and P3HT for the best overall OECT device performance, composites with varying PEG-AuNP weight ratios were prepared and employed as the channel materials in OECT devices (100 wt% P3HT denoted as pure P3HT; 5 wt% PEG-AuNP in 95 wt% P3HT denoted as 5 wt% AuNP/P3HT; 10 wt% PEG-AuNP in 90 wt% P3HT denoted as 10 wt% AuNP/P3HT; 20 wt% PEG-AuNP in 80 wt% P3HT denoted as 20 wt%

AuNP/P3HT). Electrical characteristics such as transfer characteristics, output characteristics, operational stability, and device response speed were evaluated. From the electrical characterizations, device parameters such as g_m , on-off ratio, threshold voltage (V_{th}), τ_{on} , and turn-off time (turn-off time (τ_{off})) were extracted. Transfer curves of all the composite OECTs were obtained (**Figure 4.2a, c, e, g**).

The measurement was carried out with a gate potential (V_g) range from 0.2 V to -0.8 V, and the drain current (I_d) was recorded. 0.1 M NaCl_(aq) was used as the electrolyte and a silver/silver chloride (Ag/AgCl) pellet was used as the gate electrode. A -0.6 V of drain potential (V_d) was applied to the channel to ensure the device operation in the saturation regimes, as indicated by the output characteristics (**Figure 4.2b, d, f, h**).

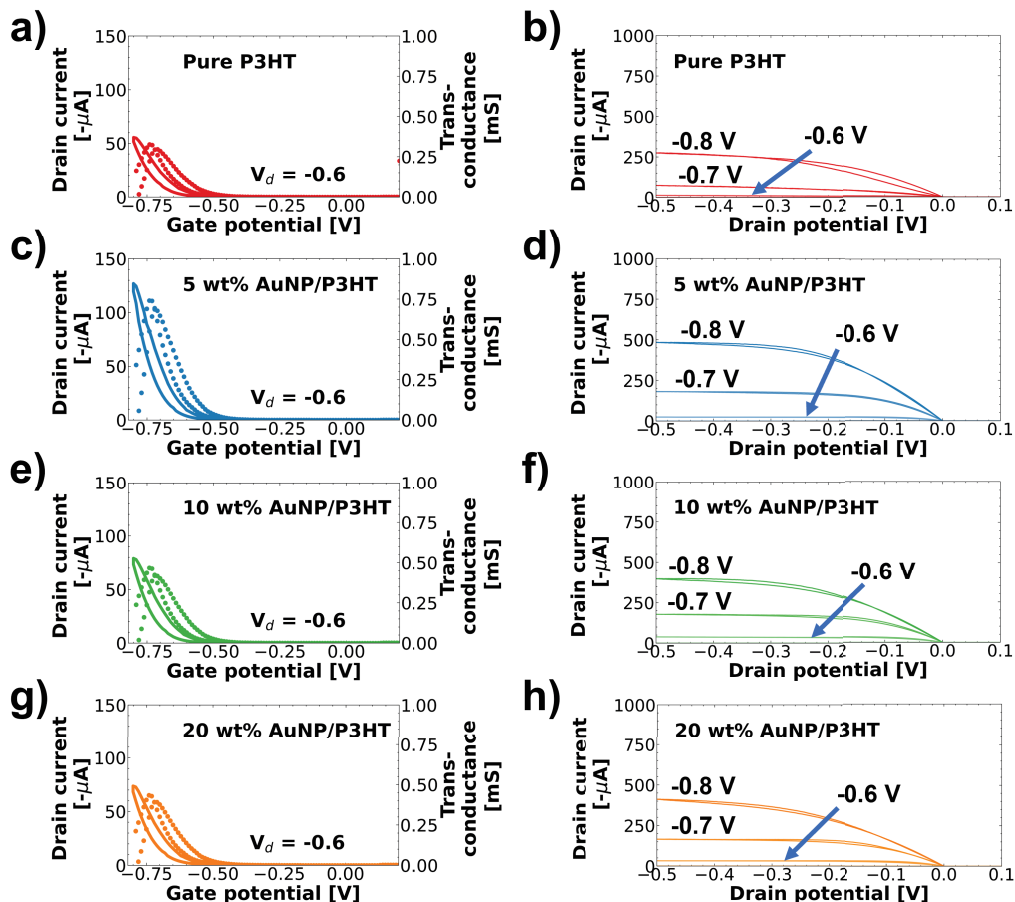


Figure 4.2: Transfer characteristics of organic electrochemical transistors (OECTs) with a) pure P3HT, c) 5 wt% AuNP/P3HT, e) 10 wt% AuNP/P3HT, and g) 20 wt% AuNP/P3HT channels at drain potential (V_d) = -0.6 V, and the corresponding output characteristics in b), d), f) and h). Channel width = 1800 μm . The dotted lines in the transfer characteristics represent the transconductance (g_m), while the solid lines represent the drain current (I_d). Channel length = 100 μm . Scan rate for transfer characterization = 0.024 V s^{-1} . Scan rate for output characterization = 0.004 V s^{-1} . Electrolyte = 0.1 M $\text{NaCl}_{(\text{aq})}$. Gate electrode = silver/silver chloride (Ag/AgCl) pellet.

From the transfer curves, V_{th} , g_m , and on-off ratio can be assessed directly. V_{th} of the P3HT and composite OECTs were estimated according to the suggested method in the literature.[37] As illustrated in **Figure 4.3a**, a slight alteration of V_{th} was observed for 5 wt% AuNP/P3HT, indicating the 5 wt% AuNP/P3HT OECTs channels can be modulated by a lower gate voltage. Meanwhile, it was observed that the g_m values increased from 0.3 mS for P3HT OECTs to higher than 0.7 mS for 5 wt% AuNP/P3HT OECTs, while the on-off ratios demonstrated

a 2-fold increase from P3HT OEECTs to 5 wt% AuNP/P3HT OEECTs. For a reliable comparison, geometry-normalized g_m (geometry-normalized g_m ($g_{m,n}$)) were extracted from all the peak g_m values. As shown in **Figure 4.3b**, the $g_{m,n}$ values of 5 wt% AuNP/P3HT OEECTs (median $\approx 17 \text{ S cm}^{-1}$) are 2 to 3-fold higher than those of P3HT (median $\approx 7 \text{ S cm}^{-1}$), 10 wt% AuNP/P3HT (median $\approx 9 \text{ S cm}^{-1}$) and 20 wt% AuNP/P3HT (median $\approx 5 \text{ S cm}^{-1}$) OEECT devices. This symbolizes a significant improvement in ion/electron transport properties for the 5 wt% AuNP/P3HT composite thin film. Further increment of PEG-AuNP weight ratios in the composites OEECT channels (i.e., 10 wt% AuNP/P3HT and 20 wt% AuNP/P3HT) does not lead to observable improvement in g_m .

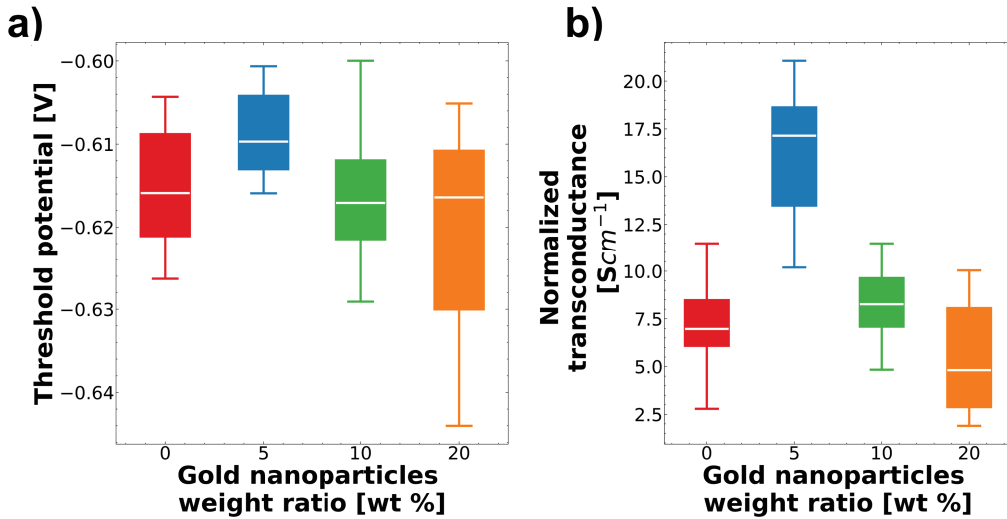


Figure 4.3: a) Threshold potential (V_{th}) and b) geometry-normalized transconductance ($g_{m,n}$) of all composite OEECT devices.

Furthermore, μC^* values for each composite were obtained from the plots of g_m vs $WdL^{-1}(V_{th}-V_g)$, where W represents the channel width, d represents the channel thickness, L represents the channel length, and the slopes of the linear fit lines represent the μC^* values and are shown in **Figure 4.4**. According to the linear fit, the μC^* value of P3HT is $37.57 \pm 10.87 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$, while those of 5 wt% AuNP/P3HT, 10 wt% AuNP/P3HT, and 20 wt% AuNP/P3HT are $97.55 \pm 10.21 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$, $74.02 \pm 8.55 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$, and 74.07

$\pm 9.04 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$, respectively (Please see **Table 4.1** for the summary of measured metrics)

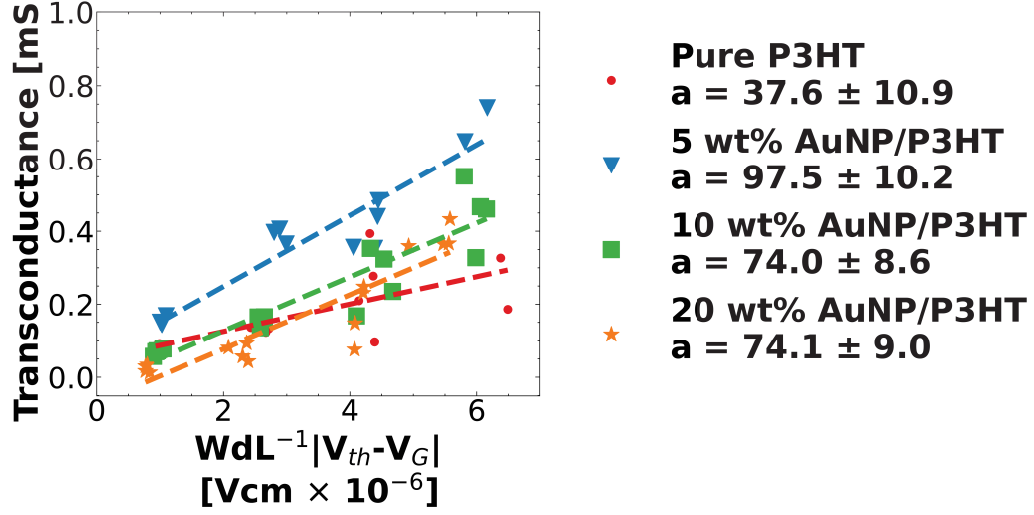


Figure 4.4: Transconductance (g_m) vs $WdL^{-1}\mu C^* |V_{th} - V_g|$ plots of all the composite OECTs, where W = channel width, d = channel thickness, L = channel length, μ = charge carrier mobility, C^* = volumetric capacitance and V_g = gate potential.

PEG-AuNP weight ratios (%)	on-off ratio	V_{th} (V)	$g_{m,n}$ (S cm^{-1})	μC^* ($\text{F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$)
0	800	-0.62	6.97	37.57 ± 10.87
5	1600	-0.61	17.15	97.55 ± 10.21
10	1100	-0.62	8.27	74.02 ± 8.55
20	1400	-0.62	4.81	74.07 ± 9.04

Table 4.1: Measured OECT metrics of different AuNP/P3HT composites.

Since the increase in μC^* observed in 5 wt% AuNP/P3HT can be contributed by both μ and C^* , it is necessary to understand which factors contribute more to the enhanced μC^* . To achieve this, EIS measurement is needed. EIS allows us to extract parameters such as capacitance by fitting the impedance data with a suitable equivalent circuit.

In this case, the Randles circuit was adopted in the impedance measurement to extract the capacitance data of different composites (see Figure 4.5).

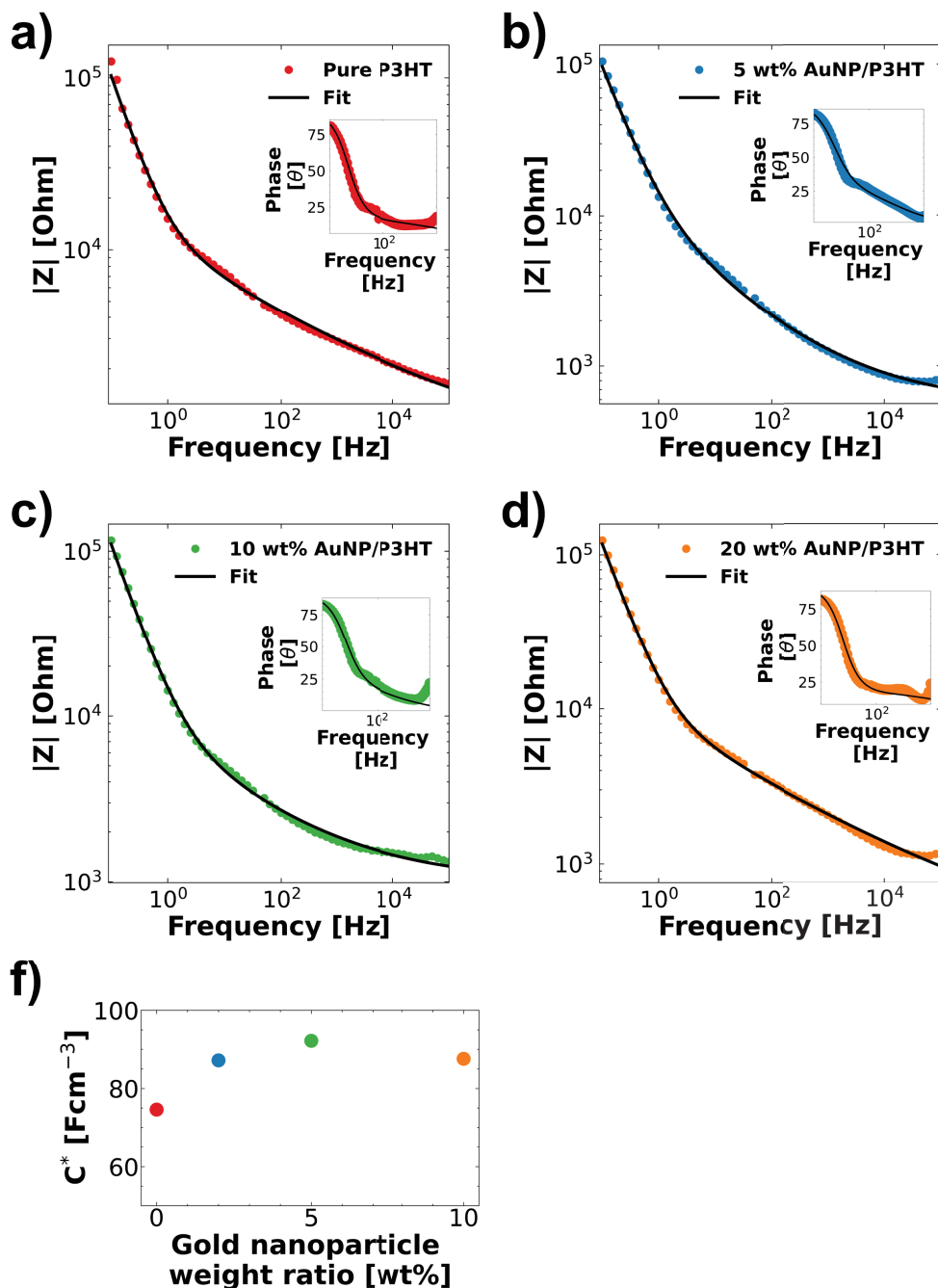


Figure 4.5: Electrical impedance spectroscopy (EIS) measurements of a) P3HT, b) 5 wt% AuNP/P3HT, 10 wt%/P3HT, and d) 20 wt% AuNP/P3HT OECTs. Insets are the phase vs frequency plots with the corresponding fits. e) shows the plot of C^* vs PEG-AuNP content. Electrolyte = 0.1 M NaCl_(aq). Gate electrode = Ag/AgCl pellet.

The C^* of the composites was calculated by dividing the extracted capacitance by the film volumes and is shown in **Figure 4.5e**. An increase in C^* from 74.59 F cm^{-3} for pure P3HT to 87.20 F cm^{-3} for 5 wt% AuNP/P3HT. With higher loading of PEG-AuNP, the C^* values further increased to 92.17 F cm^{-3} for 10 wt% AuNP/P3HT and 87.58 F cm^{-3} for 20 wt% AuNP/P3HT. A small decrease of C^* was observed from 10 wt% AuNP/P3HT to 20 wt% AuNP/P3HT. It might be due to the formation of gold nanoparticle islands at high PEG-AuNP loading (i.e., 20 wt%), thereby reducing the PEG-AuNP/P3HT interfacial area. (This will be discussed in section 4.2.4 Surface and morphological characterizations). This further evidences the dependence of C^* on the PEG-AuNP/P3HT interfacial area, thus supporting the idea that the PEG shell between AuNP and P3HT facilitates ion diffusion and allows for the generation of more charges in the composites compared to P3HT.

The μ at saturation regime (μ_{sat}) of different composite OECT were calculated according to the Bernards and Malliaras model for steady-state OECT behavior (**Equation 4.1**):

$$\mu_{\text{sat}} = \frac{2LW}{dC^*} \left(\frac{\partial I_d}{\partial V_g} \right)^2. \quad (4.1)$$

A profound increase in μ_{sat} was observed from P3HT OECTs to 5 wt% AuNP/P3HT OECTs (i.e., $5.35 \pm 1.95 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for P3HT OECTs versus $9.69 \pm 2.02 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for 5 wt% AuNP/P3HT OECTs). This shows that the incorporation of PEG-AuNP not only enhances the ion transport from the electrolyte to the channel but also enhances the electron transport within the channel. The enhancement of μ_{sat} for 5 wt% AuNP/P3HT is presumably due to the reduced π - π and lamellae distances as indicated by grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements, which will be discussed in section 4.2.4. However, when the PEG-AuNP loading further increased (i.e., 10 wt% AuNP/P3HT and 20 wt% AuNP/P3HT), a decrease in μ_{sat} was observed, although the same π - π and lamellae distance reductions were also observed in these two composite thin films. This might be explained by the charge-trapping

property of AuNPs as observed in many organic non-volatile devices, where the introduction of AuNPs leads to inhibition of current injection[161], thereby exhibiting the reduction of charge carrier mobility.

Furthermore, the operational stability of the P3HT and composite OECT devices was characterized. A square wave of potential was applied to the gate electrode (22 s at -0.8 V to switch on the channels and 22 s at 0.2 V to switch off the channels), and -0.4 V was applied across the source-drain channels. At least 40 on-off cycles were measured for all the OECT devices (Figure 4.6).

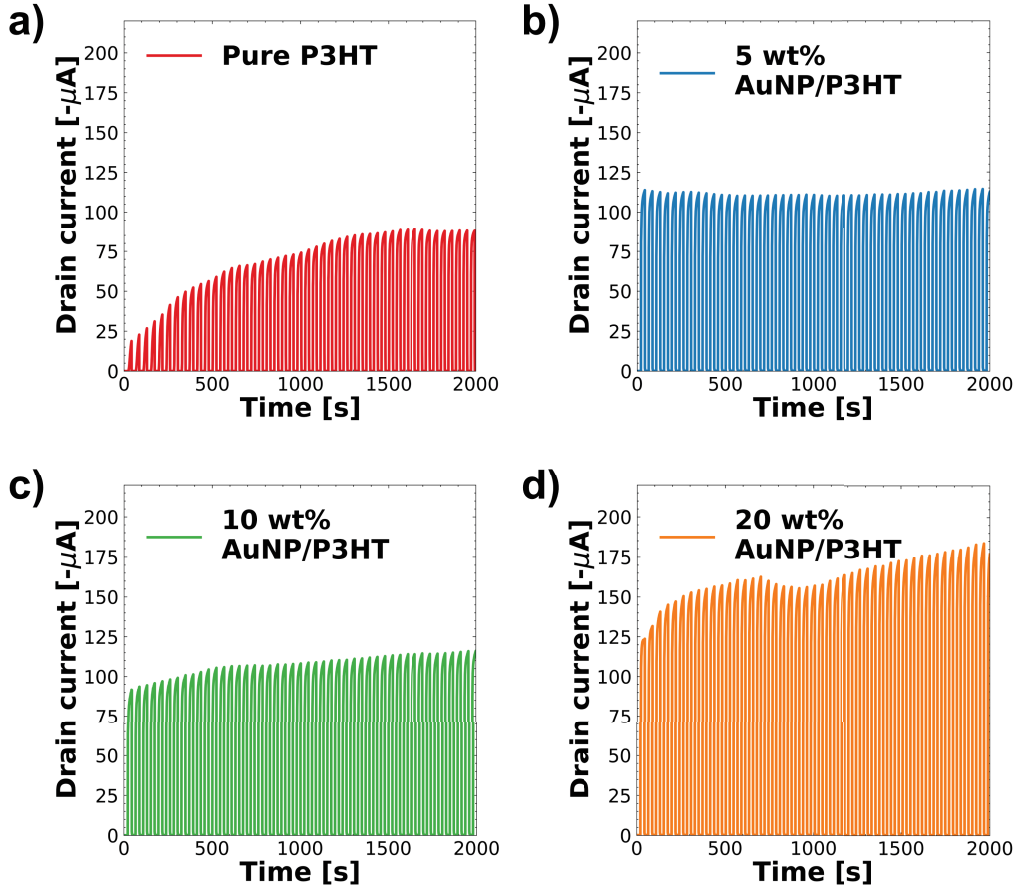


Figure 4.6: Operational stability characterization of OECTs with a) pure P3HT, b) 5 wt% AuNP/P3HT channels, c) 10 wt% AuNP/P3HT, and d) 20 wt% AuNP/P3HT. The devices are switched on with $V_g = -0.8$ V (duration = 22 s) and switched off with $V_g = 0.2$ V (22 s). Channel width = 300 μm. Channel length = 100 μm. Electrolyte = 0.1 M NaCl_(aq). $V_d = -0.4$ V for all operational stability characterizations.

In **Figure 4.6**, the 5 wt% AuNP/P3HT OECT device demonstrated constant on-off cycles throughout the course of measurement, while the P3HT OECT device demonstrated an increase in on-state I_d over the first 30 cycles, followed by a plateau of on-off cycles. Moreover, both 10 wt% AuNP/P3HT and 20 wt% AuNP/P3HT OECTs exhibited more stable on-off cycles compared to P3HT OECT. These results suggest that the incorporation of hydrophilic PEG-AuNP into P3HT provides an interlayer for fast ion diffusion and channel doping. Therefore, fewer cycles are needed for the on-off I_d to reach equilibrium. On the other hand, in P3HT OECT, the penetration of ions through the hydrophobic channel may be slower. Therefore, more on-off cycles were needed for the on-state I_d to reach an equilibrium. Exponential fitting was performed on the I_d in order to extract the τ_{on} and τ_{off} of the P3HT and the composite OECTs, as shown in **Figure 4.7**. It is found that all the composite OECTs exhibited significantly shorter τ_{on} (4.50 ± 0.11 s, 5.56 ± 0.25 s, and 4.49 ± 0.17 s for 5 wt%, 10 wt% and 20 wt% AuNP/P3HT OECTs, respectively) compared to the P3HT OECT (15.46 ± 0.81 s). The same phenomenon was also observed in the characterizations of τ_{off} (2.31 ± 0.07 s, 1.81 ± 0.07 s, 1.35 ± 0.09 s, and 1.13 ± 0.06 s for P3HT, 5 wt%, 10 wt% and 20 wt% AuNP/P3HT OECTs, respectively). These results further support the functional role of PEG-AuNP in facilitating ion diffusion. **Table 4.2** summarizes the extracted parameters from OECT response time characterizations, EIS measurement, and the calculated μ_{sat} .

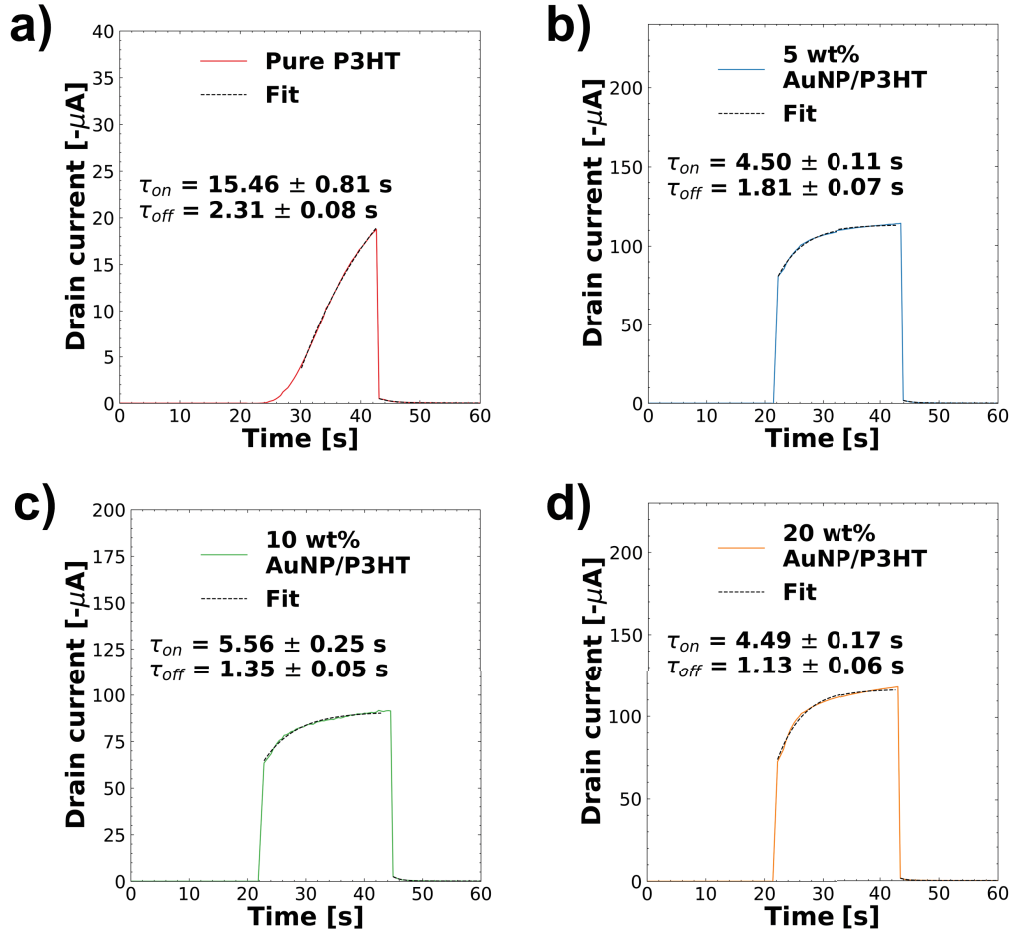


Figure 4.7: Estimation of the turn-on time (τ_{on}) and turn-off time (τ_{off}) values of OECTs with different composite channels. The dotted black line represents the exponential decay fit.

PEG-AuNP weight ratio (%)	τ_{on} (s)	τ_{off} (s)	C^* (F cm^{-3})	$\mu_{sat} \times 10^{-3}$ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
0	15.46 ± 0.81	2.31 ± 0.07	74.59	5.35 ± 1.95
5	4.50 ± 0.11	1.81 ± 0.07	87.20	9.69 ± 2.02
10	5.56 ± 0.25	1.35 ± 0.09	92.17	4.80 ± 1.04
20	4.49 ± 0.17	1.13 ± 0.06	87.58	3.12 ± 1.69

Table 4.2: Summary of τ_{on} , τ_{off} , C^* , and estimated μ_{sat} from Bernards and Malliaras model.

4.2.3 Spectroelectrochemical characterizations

To investigate how AuNPs influence the electrochemical doping efficiency of P3HT during operation, spectro-electrochemical (SEC) analysis was conducted on both pure P3HT and 5 wt% AuNP/P3HT thin films. UV-vis absorption spectra were recorded for composite films with varying AuNP/P3HT ratios. Up to 10 wt% AuNP content, no noticeable variations in absorption profile or intensity were detected compared to pure P3HT (**Figure 4.8**).

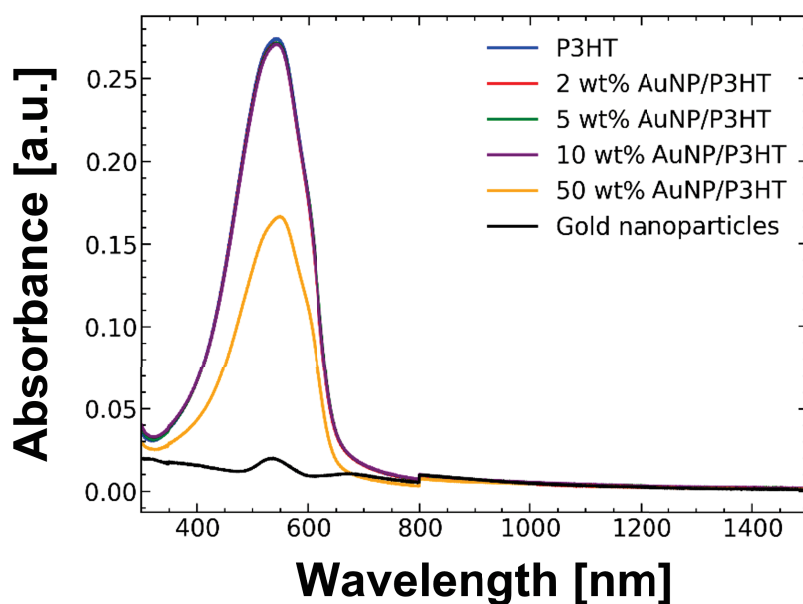


Figure 4.8: Thin film ultraviolet-visible (UV-vis) absorption spectra of pure P3HT and composites with different AuNP/P3HT weight ratios (i.e. 2, 5, 10, and 50 wt%)

However, when a gate voltage was applied in the presence of a 0.1 M NaCl electrolyte, a distinct difference emerged between pure P3HT and the 5 wt% AuNP/P3HT film (**Figure 4.9**). The reason for emphasizing only the comparison of P3HT and 5 wt% AuNP/P3HT thin films is that the 5 wt% AuNP/P3HT OECT exhibited the best overall performance according to different electrical characterizations. For pure P3HT, the π - π^* absorption at 520 nm dropped from 1 to 0.7 upon applying 0.8 V versus Ag/AgCl, while polaron absorption around

800 nm increased from 0.15 to 0.36, indicating oxidation of P3HT.[34, 35] In contrast, under the same bias conditions, the 5 wt% AuNP/P3HT film exhibited a more pronounced reduction in π - π^* absorption (1 to 0.55) and a stronger rise in polaron absorption (0.05 to 0.41). At 0.8 V, the ratio of π - π^* to polaron absorption in the composite film (0.55 vs. 0.41) was significantly lower than in pure P3HT (0.7 vs. 0.36), indicating a higher efficiency of oxidation in the 5 wt% AuNP/P3HT film. This suggests that the inclusion of AuNPs facilitates more effective volumetric doping of P3HT, aligning with the previously observed enhancement in C^* values in the composite films.

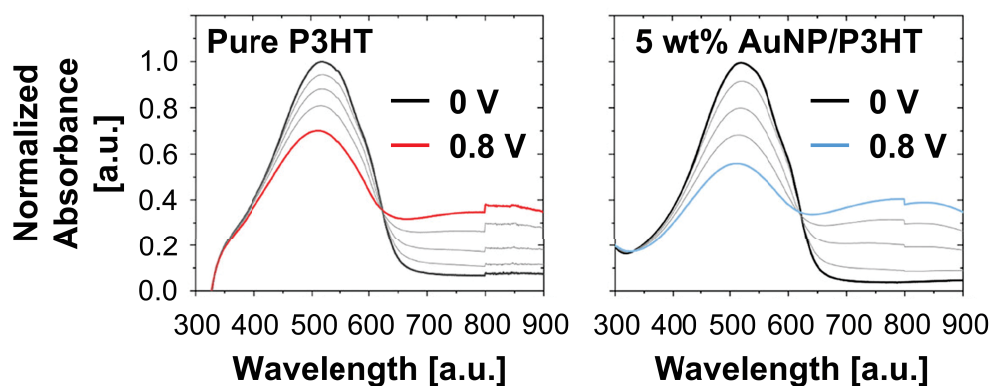


Figure 4.9: Spectro-electrochemical (SEC) analysis of a) pure P3HT and b) 5 wt% AuNP/P3HT thin films. Condition: working electrode = indium tin oxide (ITO); counter electrode = platinum (Pt) wire; reference electrode = Ag/AgCl pellet. Electrolyte = 0.1 M NaCl_(aq).

4.2.4 Surface and morphological characterizations

Contact angle measurements were performed to confirm the formation of hydrophilic channels upon the incorporation of PEG-AuNP into the P3HT matrix. Since the film thicknesses of the composite films are lower than the diameter of the PEG-AuNP, as estimated from AFM, the embedded PEG-AuNPs are expected to be partially exposed to the electrolyte, forming a hydrophilic interlayer for ion mediation. Therefore, with a higher loading of PEG-AuNP, we expect the surface hydrophilicity to be modified, which should be reflected from the contact angle measurements. **Table 4.3** lists the measured advancing contact angle (ACA) and receding contact angle (RCA). A decrease in both ACAs and RCAs of all the sample thin films was observed, indicating the formation of a hydrophilic surface and, therefore, providing an ion-permeable channel between the AuNP/P3HT interface.

Thin films	Average ACA	Standard deviation of ACA	Average RCA	Standard deviation of RCA
P3HT	99.79	1.07	92.99	1.00
5 wt% AuNP/P3HT	94.08	7.61	90.89	2.39
10 wt% AuNP/P3HT	99.12	1.55	90.44	2.00
20 wt% AuNP/P3HT	83.74	3.19	59.24	5.25

Table 4.3: Table of the advancing contact angle (ACA) and receding contact angle (RCA) values of different composite thin films.

The stability of PEG-AuNPs in the P3HT matrix during electrochemical cycles was also characterized. This characterization can enable us to ascribe the enhancement of OECT performance to the presence of PEG-AuNP instead of the formation of porous microstructure, which could also lead to the enhancement of OECT performance, as mentioned in the introduction section. To achieve that, two 5 wt% AuNP/P3HT films were prepared. While one was not subjected to any treatment, the other one was subjected to cycles of gate potentials square waves

(-0.8 V versus Ag/AgCl for 2 s, followed by 0 V versus Ag/AgCl for 2 s, 10 cycles), followed by soaking for 30 minutes in Millipore water and rinsing thoroughly with fresh Millipore water. For a clearer illustration, two 50 wt% AuNP/P3HT thin films (50 wt% of PEG-AuNP and 50 wt% of P3HT) were also prepared, and one of the films was subjected to the above-mentioned treatment procedure. No removal of PEG-AuNP was observed according to the AFM characterizations (**Figure 4.10**). These results suggest that the enhancement of OECT performance originated from the PEG-AuNP/P3HT composite system.

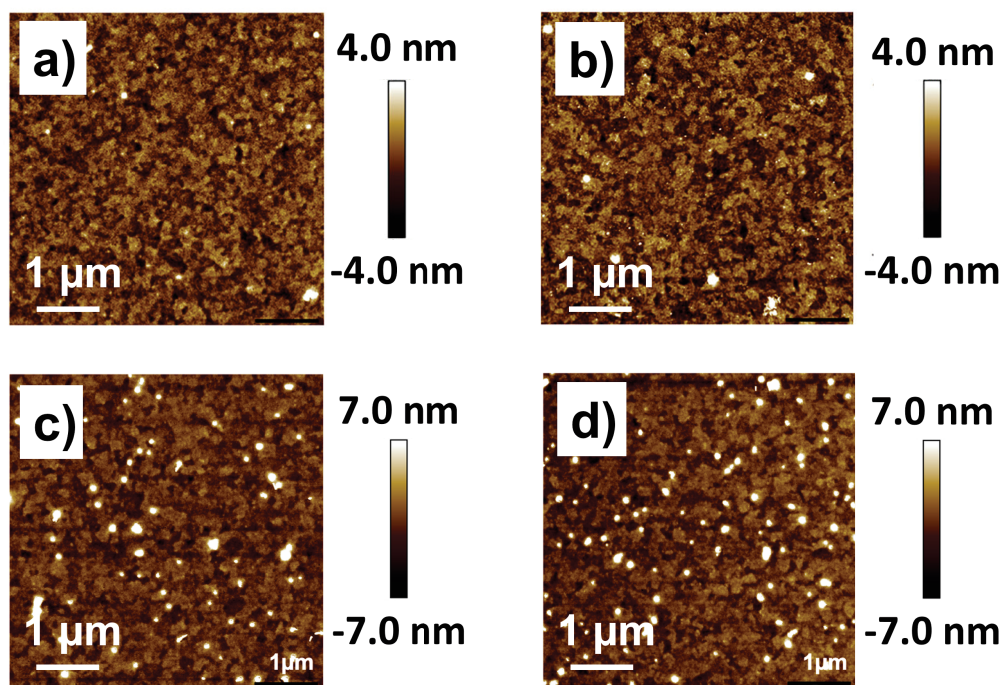


Figure 4.10: a) Pristine and b) treated 5 wt% AuNP/P3HT thin films. c) Pristine and d) treated 50 wt% AuNP/P3HT. No loss of AuNPs was observed after 10 V_g cycles (-0.8 V for 2 s, followed by 0 V for 2 s), followed by 30 minutes of soaking in Millipore water.

Furthermore, GIWAXS was employed to elucidate the film morphology so that further understanding of the enhanced ion and electron transport behavior in the composite OECTs can be achieved. According to the 2D GIWAXS reflection patterns, as shown in **Figure 4.11**, both P3HT, 10 wt% AuNP/P3HT, and 20 wt% AuNP/P3HT thin films exhibited (100) and (200) lamellae distance reflection in both in-plane and out-of-plane orientation with respect to the substrate, while (010) π - π stacking distance mainly appeared in the out-of-plane orientation, suggesting that the majority of the P3HT crystallites adopt a face-on orientation in these sample thin films.

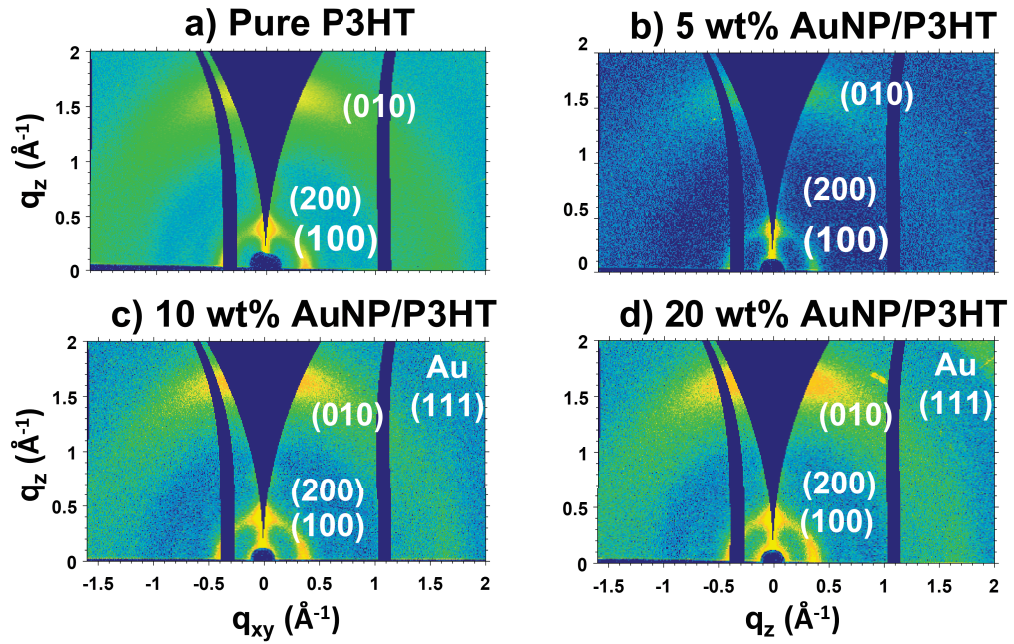


Figure 4.11: Grazing incidence wide-angle X-ray scattering (GIWAXS) reflection patterns of a) pure P3HT, b) 5 wt% AuNP/P3HT, c) 10 wt% AuNP/P3HT and d) 20 wt% AuNP/P3HT

To further analyze the P3HT crystallite orientation relative to the substrates, azimuthal tube cuts of the (010) reflection in the range of 0° to 90° were extracted from the 2D GIWAXS reflection patterns (**Figure 4.12**). Note that the P3HT crystallites in 5 wt% AuNP/P3HT thin film appeared more isotropic due to the exhibition of a relatively more even distribution of intensity compared to the other sample thin films. This more random orientation of P3HT crystallites in 5 wt% AuNP/P3HT could explain the facilitated channel-ion interaction, as indicated by the higher C^* compared to P3HT, faster OECT response time, and the constant on-off switching in the operational stability characterization.

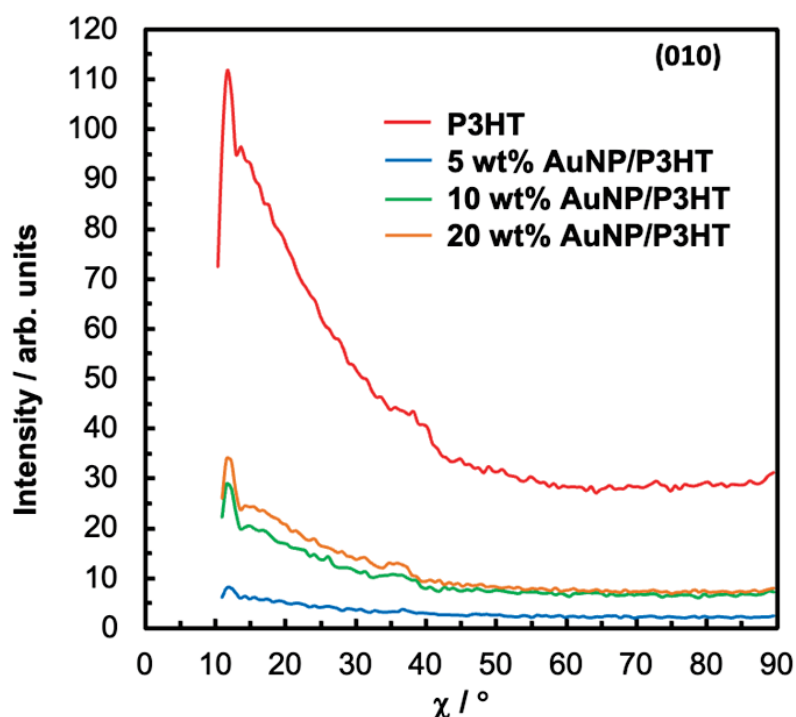


Figure 4.12: Azimuthal tube cut of (010) reflection of various composite thin films.

Moreover, an Au(111) reflection was observed when the PEG-AuNP content was higher than 10 wt% in P3HT (**Figure 4.13**), which could be due to the formation of AuNP aggregates/islands in the P3HT matrix.

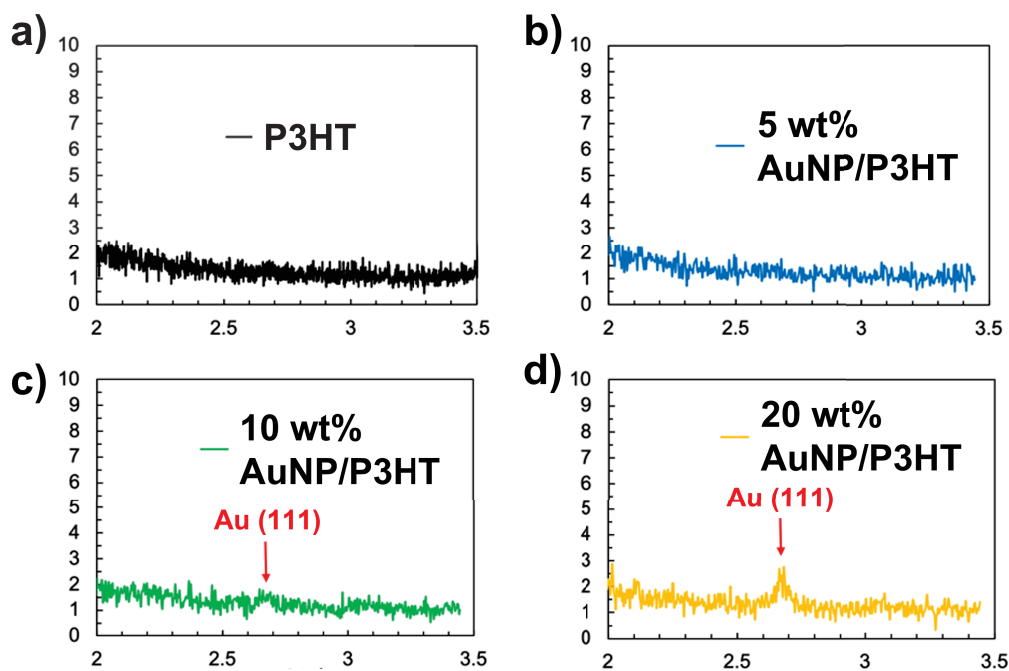


Figure 4.13: X-ray diffraction patterns of a) pure P3HT, b) 5 wt% AuNP/P3HT, c) 10 wt% AuNP/P3HT and d) 20 wt% AuNP/P3HT. The (111) reflection of gold aggregates at $q \approx 2.7 \text{ \AA}^{-1}$ is indicated in the 10 wt% and 20 wt% composite films.

To confirm that, high-resolution AFM was conducted to investigate the distribution of PEG-AuNP. From **Figure 4.14**, $2 \times 2 \mu\text{m}$ AFM images of 5 wt% AuNP/P3HT, 10 wt% AuNP/P3HT, and 20 wt% AuNP/P3HT thin films are displayed. The images indicate that in 10 wt% AuNP/P3HT and 20 wt% AuNP/P3HT thin films, a more profound formation of PEG-AuNP islands occurred. As a result, the PEG-AuNP/P3HT interfacial area could be reduced, providing a possible explanation for the small decrease in C^* from 10 wt% AuNP/P3HT to 20 wt% AuNP/P3HT in the EIS measurements since the ion penetration efficiency can be hampered by the reduced PEG-AuNP/P3HT interfacial area.

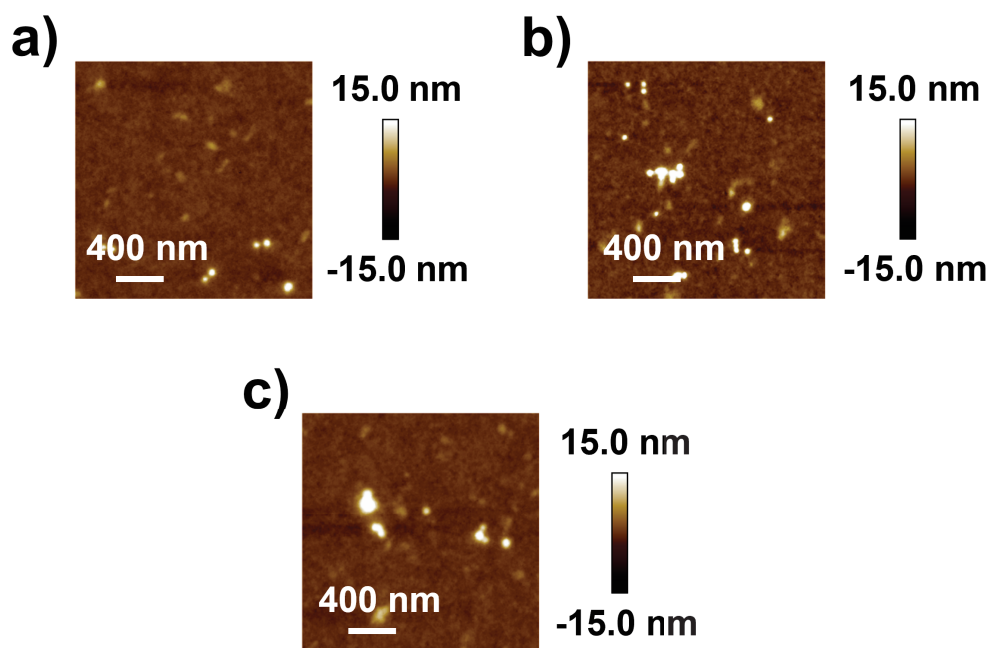


Figure 4.14: High-resolution atomic force microscopy (AFM) images of a) 5 wt% AuNP/P3HT, b) 10 wt% AuNP/P3HT and c) 20 wt% AuNP/P3HT thin films.

Lastly, in order to unveil the underlying reasons for the enhanced charge carrier mobility, as observed and estimated earlier, crystallite parameters such as π - π and lamellae distances were evaluated. It was found that the π - π distance and lamellae distance of both 5 wt% AuNP/P3HT, 10 wt% AuNP/P3HT, and 20 wt% AuNP/P3HT thin films became smaller (i.e., 3.77 Å and 16.68 Å, 3.79 Å and 16.69 Å, and 3.79 Å and 16.61 Å, respectively) compared to those of P3HT thin film (i.e., 3.88 Å and 17.26 Å, respectively), indicating enhanced interaction between the conjugated polymer backbones and thus resulting in higher μ compared to P3HT (see **Table 4.4** for the summary of thin film characterizations). While the reason for such crystallite contraction is still unclear, it is postulated that the enhanced polymer backbone interaction is promoted by the interfacial stress, as suggested by the difference in hydrophilicity and, therefore, different surface tension according to the contact angle measurements.

Samples	d_{100} (Å)	d_{010} (Å)	Film thickness (nm)
P3HT	17.26	3.88	32.8
5 wt% AuNP/P3HT	16.68	3.77	27.7
10 wt% AuNP/P3HT	16.69	3.79	24.8
20 wt% AuNP/P3HT	16.61	3.79	22.0

Table 4.4: Summary of lamellar distance (d_{100}) and π - π distance (d_{010}) in different composite films (i.e. pure P3HT, 5 wt% AuNP/P3HT, 10 wt% AuNP/P3HT and 20 wt% AuNP/P3HT).

4.2.5 AuNP/PDPP-TT OECTs - demonstration of the versatility of the composite strategy

To assess the versatility of our approach across different polymer systems, OECT devices were fabricated using pure PDPP-TT, 2 wt% AuNP/PDPP-TT (2 wt% PEG-AuNP in 98 wt% PDPP-TT), 4 wt% AuNP/PDPP-TT (4 wt% PEG-AuNP in 96 wt% PDPP-TT), and 6 wt% AuNP/PDPP-TT (6 wt% PEG-AuNP in 94 wt% PDPP-TT) as channel materials, and their $g_{m,n}$ and μC^* values were measured. The addition of 2 wt% PEG-AuNPs led to a substantial rise in $g_{m,n}$ from 9.09 S cm^{-1} for the pure PDPP-TT to 22.68 S cm^{-1} for the 2 wt% AuNP/PDPP-TT composite (Figure 4.15).

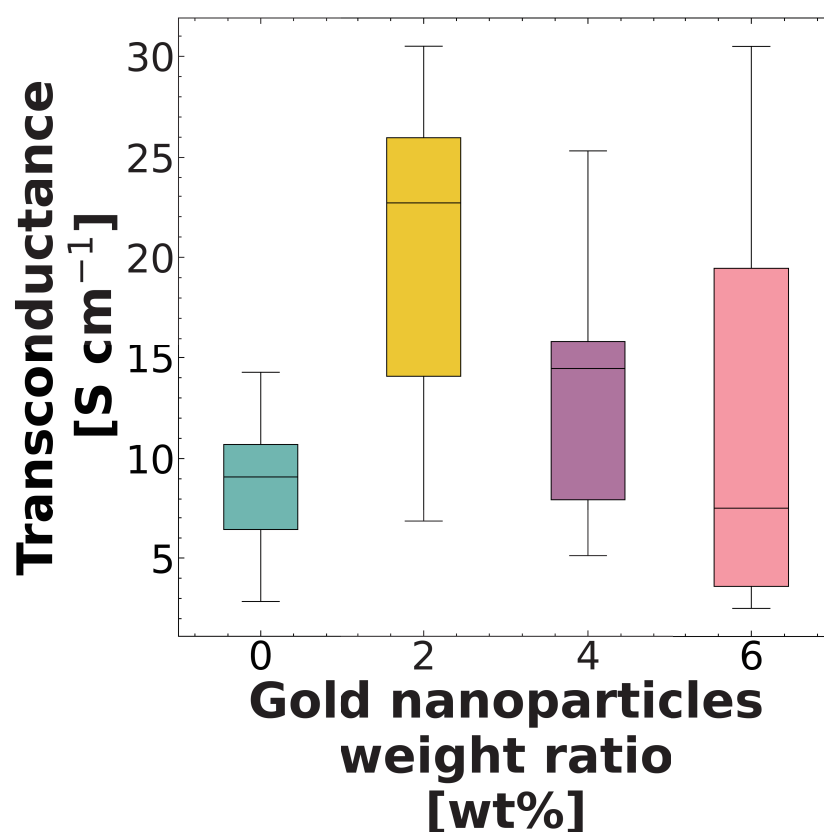


Figure 4.15: Box plot of $g_{m,n}$ of the AuNP/PDPP-TT composite OECTs with different PEG-AuNP content. The peak g_m values were extracted from at least 8 OECT devices. Channel width = $1800 \mu\text{m}$. Channel length = $100 \mu\text{m}$. Electrolyte = $0.1 \text{ M NaCl}_{(\text{aq})}$. Gate electrode = Ag/AgCl pellet.

Furthermore, the μC^* value increased from $42.9 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for pure PDPP-TT to $169.9 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for the 6 wt% AuNP/PDPP-TT composite (**Figure 4.16**). These results confirm that this composite strategy can be successfully applied to other hydrophobic semiconducting polymers.

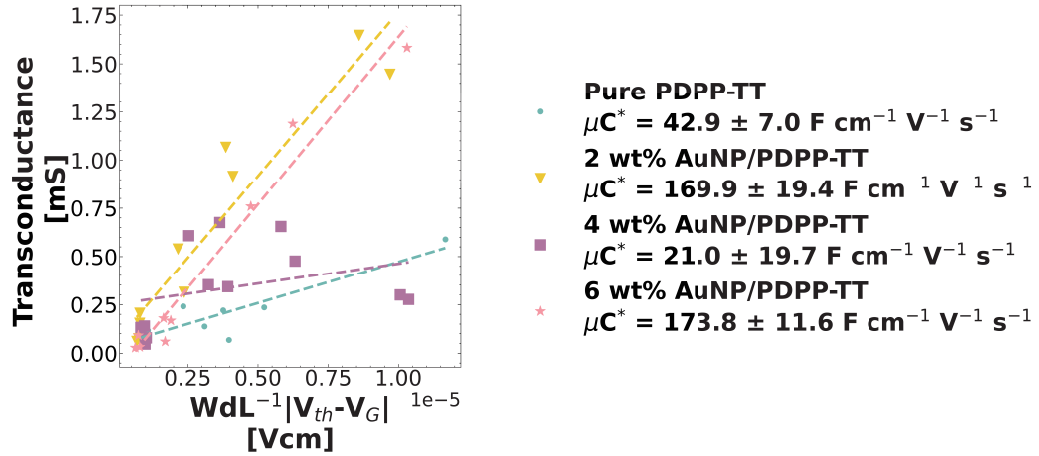


Figure 4.16: g_m vs $\frac{Wd}{L} \mu C^* |V_{th} - V_g|$ plots of all the composite PDPP-TT and AuNP/PDPP-TT OECTs.

4.3 Conclusion

This study provides a facile and effective approach (i.e., incorporation of PEG-AuNP with OSCPs) to improve overall OECT performance of hydrophobic channels, including electrical performance and device transient behavior. Upon mixing PEG-AuNP with P3HT, notable enhancement in overall OECT performance. Extensive characterizations, including electrical characterizations, electrical impedance measurements, response time characterizations, SEC, GIWAXS, and contact angle analysis, were carried out, revealing that PEG-AuNPs not only introduce hydrophilicity to the composite channels but also influence the thin film morphology depending on the PEG-AuNP concentration. This morphological modification can facilitate more efficient ion transport and induce efficient P3HT doping. Additionally, all composite thin films (i.e., 5 wt% AuNP/P3HT, 10 wt% AuNP/P3HT, and 20 wt% AuNP/P3HT) exhibit a crystallite contraction (reduced

π - π and lamellae distances), enabling us to explain the higher μ_{sat} values in 5 wt% AuNP/P3HT compared to P3HT. Consequently, these combined effects result in a profound improvement in $g_{\text{m,n}}$, and OMIEC figure-of-merit μC^* , boosting the overall OECT performance. Enhancing OECT performance while avoiding complicated structural modification can broaden the scope of viable semiconducting materials (e.g., PDPP-TT) for OMIEC design and OECT applications. This will open up a much wider library of material choices and make OECT applications more available in the future.

4.4 Contribution

Mr. Oliver Ditzer and Ms. Qiong Li performed the AFM and high-resolution AFM measurements, respectively. Mr. Ali Solgi conducted the electrical impedance measurements. Mr. Haoran Zhang synthesized the PEG-AuNP. Ms. Ronja Thümmeler performed the contact angle measurements. Prof. Mahmoud Al-Hussein conducted the GIWAXS measurements and data analysis. Dr. Ningwei Sun performed the SEC analysis.

Chapter 5

Summary and outlook

5.1 Summary

5.1.1 Metallopolymers

In chapter II of this work, three novel ruthenium (Ru)-polymetallaynes were synthesized which were designed with specific structural modifications to probe their structure-property relationships (i.e., increased bridging ligand planarity from P1 to P2 and introducing redox-matching from P2 to P3). As a result, the metal-metal (M-M) interaction was enhanced from P1 to P3, as indicated by the peak separation phenomenon in electrochemical characterizations. Also, the formation of stable mixed-valence (MV) species in P2 and P3 was found, as reflected by the enhanced comproportionation constant (K_c) in P2 ($K_c = 1 \times 10^3$) and P3 ($K_c = 2 \times 10^5$), and the enhanced delocalization according to density functional theory (DFT) calculations. The enhanced stabilization effect in the oxidized states in P2 and P3 translated to enhanced state retention in the P2 and P3 electrochromic (EC) devices compared to the P1 EC devices. Preliminary organic electrochemical transistor (OECT) devices were also fabricated with P1, P2, and P3, revealing OECT performances that align with the redox-matching principle, where the increased alignment of metal and organic moiety orbitals leads to a shift of the charge transfer pathway to a more efficient inner sphere route (i.e., orbital overlap).

5.1.2 Engineering of hydrophobic channels for enhanced OECT performance

With the aim to make OECT technology more available, in chapter III of this thesis blends from commercially available and prototypical poly(3-hexylthiophene) (P3HT) and chemically oxidized poly(vinylferrocene) (PVF⁺) were used as channel material. PVF⁺ was used as an additive and blended with P3HT at different weight ratios in order to enhance the hydrophilicity of the channel. Upon blending, more efficient doping was observed according to the cyclic voltammetric (CV) and spectroelectrochemical (SEC) characterizations, where more reversible redox reaction was observed, and more P3HT polarons were generated with higher content of PVF⁺, respectively. Scanning electron microscope (SEM) and transmission electron microscope (TEM) experiments revealed phased separation, with the P3HT domain being continuous in the blends. These evidence could explain the higher hole charge carrier mobility (μ_h) as estimated from the gate current (I_g) analysis. An improvement in OECT transient behavior with higher PVF⁺ content was also observed, which is attributed to the increased hydrophilicity according to the contact angle measurements and the face-on P3HT crystallites suppression, as revealed by grazing incidence wide-angle X-ray scattering (GIWAXS) measurements, which leads to a higher ratio of edge-on and isotropic P3HT crystallites in the blends, further facilitating ion transport into the blend channels.

In Chapter IV, PEGylated gold nanoparticles (PEG-AuNPs) were chosen as an additive to the P3HT matrix based on two reasons: (I) their hydrophilic surface allows for efficient ion uptake and transport through the PEG interlayer at the OECT channel (II) studies suggest that gold nanoparticles (AuNPs) can influence polymer backbone packing, which may lead to improved charge carrier mobility (μ). This can result in an overall improvement in OECT performance, as suggested by the material-specific figure-of-merit μC^* . By incorporating PEG-AuNP, this study showed that the approach simultaneously enhances both the ionic and electrical performance of a hydrophobic channel at an optimal PEG-AuNP

ratio (i.e., 5 wt% PEG-AuNP in 95 wt% P3HT), as supported by the increased volumetric capacitance (C^*) according to electrical impedance spectroscopy (EIS) measurement, a more thorough P3HT doping in the composite according to the SEC analysis, faster OECT response time (τ_{on} and τ_{off}), and enhanced μ_{h} in the composite compared to pure P3HT. The more efficient ion transport behavior in the composite can be explained by the introduction of hydrophilic channels in hydrophobic P3HT and, in the case of 5 wt% PEG-AuNP composite, the more isotropic orientation of P3HT crystallites. Meanwhile, crystallite contraction (reduction in π - π and lamellae distances) in the composites could explain the enhancement in hole mobility. Consequently, it resulted in the overall OECT performance as indicated by the increase in μC^* values (from $38 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for P3HT to $98 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for 5 wt% AuNP/P3HT composite). Last but not least, PEG-AuNP/PDPP-TT composites OECTs were also fabricated, exhibiting a boost in μC^* values (from $43 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for PDPP-TT to $174 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ for 6 wt% AuNP/PDPP-TT composite) and demonstrating the versatility of this approach to other semiconducting polymers.

5.2 Outlook

While non-volatile OECT devices are of great promise in the field of neuromorphic applications, such as associative learning and neuromorphic non-volatile memory, the development of novel non-volatile materials is still vastly unexplored. As observed from the P2 and P3 EC devices, P2 and P3 exhibited an enhancement of state retention ability compared to P1 due to the enhancement of M-M interaction and resonance stabilization, allowing for the retention of an oxidation state for a certain time and making them good candidates for non-volatile memory applications. Here, especially variations of the peripheral ligand sphere would be interesting: On one hand, a reduction of the ligand bulkiness could increase the π - π stacking; on the other hand, the electron density of the metal centers could be tuned. However, less bulky phosphine ligands generally suffer from low

stability, and other known ligand systems do not support the necessary trans-acetylide structure. Guidance from computational calculations could lead to new designs combining ambient stability, trans-acetylide layout, and favorable electron densities. Finally, the design of a stable monomer that allows – ideally reversible – electropolymerization could yield a new class of materials for the controlled dendritic growth of OECT channels stimulated by alternating current (AC), a fascinating and highly promising sub-field in neuromorphic computing. To further improve OECT device performance, such as on-off ratio and transconductance (g_m), more structural modification could be carried out. In the future, with suitable device layout optimization, research in the direction of OECT-based rewritable non-volatile memory devices with the use of metallopolymers can be conducted. Hopefully, in the future, the use of the novel Ru-polymetallaynes could not only fuel the field of non-volatile materials research but also enable the advanced non-volatile memory applications.

For the engineering of hydrophobic materials, while PVF⁺ as an additive only mediates anions, which may only be suitable for modifying a p-type OECT channel, other stable anionic such as viologen-based polyelectrolytes can be considered for the modification of n-type OSCPs, enhancing their OECT performance. Furthermore, the neutral hydrophilic PEG-AuNPs can mediate both cations and anions, making this approach suitable for modifying both p-type and n-type channels. In fact, the development of n-type materials is still falling behind that of p-type materials, mainly due to their instability in aqueous and ambient conditions. Although recent progress in the search for stable n-type OMIECs has been made, offering several different stable structures that can operate in the presence of electrolytes and oxygen, in general, their OECT performance metrics, such as g_m and μC^* , are still not comparable to those of p-type OMIECs. Therefore, the incorporation of PEG-AuNPs could potentially yield a series of high-performance n-type OMIECs, enabling technologies such as OECT-based complementary circuits. Moreover, since AuNPs offer exceptional surface modification flexibility, different structures,

such as various OSCPs, can be incorporated as the surface ligand on AuNP, which allows for more options for microstructure control (e.g., self-assembled layer), introducing unprecedented properties into OECT applications.

Chapter 6

Experimental section

6.1 Synthesis and characterizations of ruthenium (Ru)-polymetallaynes and their applications in electrochromic and organic electrochemical transistor (OECT) devices

All the experimental procedures (except sections 6.1.10 and 6.1.11) and methods in this chapter are extracted from the reported literature.[104, 82]

6.1.1 Materials and synthesis

Synthesis of bridging ligands (i.e., 2,2'-dodecylbithiophene (BT), cyclopentadithiophene (CPDT), and dithienopyrrole (DTP)) was performed according to the reported procedure. The polymerization of P1, P2, and P3 was conducted according to the reported dehydrohalogenation polymerization. All the chemicals were used without further purification.

P1: Cis-Ru(dppe)₂Cl₂ (0.3 g, 0.31 mmol) and 3,3'-didodecyl-5,5'-diethynyl-2,2'-bithiophene (M1) (0.17 g, 0.31 mmol) were dissolved in anhydrous dichloromethane (DCM) (55 mL) in a reflux set-up, followed by the addition of sodium hexafluorophosphate (NaPF₆) (0.16 g, 0.96 mmol) and triethylamine (NEt₃) (0.53 mL, d = 0.73 g cm⁻³, 3.8 mmol). The reaction mixture was heated at 45°C for two days, and the resulting solution was filtered through celite, precipitated in methanol three times, and precipitated in n-hexane, affording a brownish-yellow solid (non-endcapped (nec-)P1, 0.34 g, 72%). 4-Ethynylthiophene (0.36 mL, d = 0.92 g cm⁻³, 2.6 mmol) and nec-P1 (0.18 g, 0.12 mmol) was dissolved in anhydrous DCM (35 mL)

in a reflux set-up. NaPF₆ (0.18 g, 1 mmol) and NEt₃ (0.36 mL, $d = 0.73 \text{ g cm}^{-3}$, 2.6 mmol) were added to the reaction mixture. The reaction mixture was heated at 45°C overnight under nitrogen flow. The resulting solution was filtered through celite, precipitated in methanol three times, and precipitated in n-hexane, affording a brownish-yellow solid (0.14 g, 81%). ¹H NMR (500 MHz, CD₂Cl₂, δ): 7.54 (m, 16H), 7.26 (m, 8H), 7.11 (m, 16H), 6.28 (br s, 2H), 2.70 (br s, 8H), 2.61 (m, 4H), 1.69 (m, 4H), 1.44–1.28 (m, 36H), 0.87 ppm (m, 6H). ³¹P NMR (202 MHz, CD₂Cl₂, δ): 51.8 (m), 52.7 ppm (s). FT-IR: 2039 cm⁻¹ (vcuc). $M_{n,\text{GPC}} = 58 \text{ kg mol}^{-1}$, $M_w = 205 \text{ kg mol}^{-1}$, PDI = 3.53. $M_{n,\text{NMR}} = 72 \text{ kg mol}^{-1}$.

P2: 2,6-Diethynyl-4,4-didodecyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (M2) (0.44 g, 0.79 mmol) was dissolved in anhydrous tetrahydrofuran (THF, 60 mL) and transferred to the Schlenk flask with cis-Ru(dppe)₂Cl₂ (0.76 g, 0.79 mmol). Additional tetrahydrofuran (THF) (36 mL) was added into the flask, followed by the addition of NaPF₆ (0.41 g, 2.4 mmol) and NEt₃ (1.33 mL, $d = 0.73 \text{ g cm}^{-3}$, 9.44 mmol). The reaction mixture was heated at 70°C in an inert atmosphere for two days. The resulting solution was filtered through celite, precipitated in 0.5% w/v potassium hydroxide/methanol solution, suspended and stirred in methanol for 30 minutes, and precipitated in n-hexane, affording deep brown solid (nec-P2, 0.74 g, 65%). 4-ethynyltoluene (0.96 mL, $d = 0.92 \text{ g cm}^{-3}$, 7.60 mmol) and nec-P2 (0.40 g) were dissolved in anhydrous THF (80 mL) in a reflux set-up. NaPF₆ (0.40 g, 2.33 mmol) and NEt₃ (0.96 mL, $d = 0.73 \text{ g cm}^{-3}$, 6.93 mmol) were added to the reaction mixture. The reaction mixture was heated at 70°C overnight under nitrogen flow. The resulting solution was filtered through celite, precipitated in 0.5% w/v potassium hydroxide/methanol, stirred rigorously in methanol for 30 min, and precipitated in n-hexane, affording brownish yellow solid (0.34 g, 85%). ¹H NMR (500 MHz, CD₂Cl₂, δ): 7.55 (m, 16H), 7.25 (m, 8H), 7.09 (m, 16H), 6.20 (br s, 2H), 2.70 (br m, 8H), 1.83 (br m, 4H), 1.25 (m, 36H), 0.86 ppm (m, 6H). ³¹P NMR (202 MHz, CD₂Cl₂, δ): 52.29 (m), 52.97 ppm (s). FT-IR: 2029 cm⁻¹ (vcuc). $M_{n,\text{GPC}} = 66 \text{ kg mol}^{-1}$, $M_w = 211 \text{ kg mol}^{-1}$, PDI = 3.19. $M_{n,\text{NMR}} = 13 \text{ kg mol}^{-1}$

Anal. Calc. For $C_{89}H_{101}P_4RuS_2$: C: 73.22; H: 6.97; S: 4.39. Found: C: 72.38; H: 6.72; S: 4.50.

P3: 2,6-Diethynyl-4-(pentacosan-13-yl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (M3) (0.26 g, 0.46 mmol) was dissolved in anhydrous THF (40 mL) and transferred to the Schlenk flask with $cis\text{-}Ru(dppe)_2Cl_2$ (0.44 g, 0.46 mmol). Additional THF (17 mL) was added into the flask, followed by the addition of $NaPF_6$ (0.24 g, 1.4 mmol) and NEt_3 (0.76 mL, $d = 0.73\text{ g cm}^{-3}$, 5.5 mmol). The reaction mixture was heated at 70°C in an inert atmosphere for five days. The resulting solution was filtered through celite, precipitated in 0.5% w/v potassium hydroxide/methanol solution, stirred rigorously in methanol for 30 min, and precipitated in n-hexane, affording deep brown solid (nec-P3, 0.53 g, 81%). 4-Ethynyltoluene (1.1 mL, $d = 0.92\text{ g cm}^{-3}$, 8.6 mmol) and nec-P3 (0.47 g, 0.32 mmol) were dissolved in anhydrous THF (35 mL) in a reflux set-up. $NaPF_6$ (0.47 g, 2.8 mmol) and NEt_3 (1.1 mL, $d = 0.73\text{ g cm}^{-3}$, 8.1 mmol) were added to the reaction mixture. The reaction mixture was heated at 70°C overnight under nitrogen flow. The resulting solution was filtered through celite, precipitated in 0.5% w/v potassium hydroxide/methanol solution, stirred rigorously in methanol, and precipitated in n-hexane, affording a brownish-yellow solid (0.43 g, 92%). 1H NMR (500 MHz, CD_2Cl_2 , δ): 7.59 (m, 16H), 7.28 (m, 8H), 7.12 (m, 16H), 6.21 (br s, 2H), 4.06 (br s, 1H), 2.72 (br m, 8H), 2.05-1.92 (m, 4H), 1.25 (m, 36H), 0.86 ppm (m, 6H). ^{31}P NMR (202 MHz, CD_2Cl_2 , δ): 52.29 (m), 52.97 ppm (s). FT-IR: 2029 cm^{-1} (vcuc). $M_{n, GPC} = 78\text{ kg mol}^{-1}$, $M_w = 233\text{ kg mol}^{-1}$, PDI = 2.99. $M_{n, NMR} = 22\text{ kg mol}^{-1}$. Anal. Calc. For $C_{89}H_{101}P_4RuNS_2$: C: 72.5; H: 6.91; S: 4.35; N: 0.95. Found: C: 70.6; H: 6.59; S: 5.13; N: 1.15.

6.1.2 Nuclear magnetic resonance (NMR) spectroscopy

NMR spectra were recorded on a Bruker Avance III 500 spectrometer operating at 500.13 MHz for 1H and 202.46 MHz for ^{31}P using the standard pulse sequences included in the TOPSPIN 3.2 software package. The 1H NMR spectra were

referenced on the solvent signal (CD_2Cl_2 : δ (^1H) = 5.31 ppm). All chemical shifts are reported in ppm.

6.1.3 Gel permeation chromatography (GPC)

GPC measurements were carried out on an Agilent 1100 Series (Agilent, USA) normal temperature size exclusion chromatograph equipped with a refractive index detector and a PL Gel MIXED-B column (Polymer Laboratories, UK). Chloroform was used as eluent, and the flow rate was 1 mL min^{-1} . The measurements were carried out at 40°C . Number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity (PDI) were determined based on calibration with polystyrene standards obtained from Polymer Standards Service (PSS, Germany).

6.1.4 Fourier transform-infrared (FT-IR) spectroscopy

FT-IR spectra were obtained on an FT-IR Spectrometer Vertex80v with Golden Gate Diamant ATR Unit (SPECAC) and MCT-detector. The detection range was from $4000\text{--}600\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . For each spectrum, 100 scans were accumulated.

6.1.5 Elemental analysis (EA)

EA was carried out on EuroEA Elemental Analyser. The combustion process was carried out at 1000°C with 15 mL of oxygen. The calibration type was selected as single-point (K-Factor) regression.

6.1.6 Cyclic voltammetry (CV)

CV was recorded on IVIUM multichannel potentiostat under nitrogen flow with an in-house three-electrode system consisting of a platinum (Pt) disc working electrode, Pt wire counter electrode, and non-aqueous silver/silver ion (non-aqueous silver/silver ion (Ag/Ag^+)) pseudo-reference electrode. During CV measurements, 0.1 M tetra-n-butylammonium hexafluorophosphate tetra-n-butylammonium hexafluorophosphate ($\text{n-Bu}_4\text{NPF}_6$) was used as the supporting electrolyte. Ferrocene/-ferrocenium (Fc/Fc^+) was used as the internal reference. All measurements were carried out at the scan rate of 50 mV s^{-1} .

6.1.7 In Situ electron-paramagnetic resonance (EPR) and ultraviolet-visible near-infrared (UV-vis-NIR) Spectroelectrochemical (SEC) Measurements

The spectroelectrochemical experiments were conducted within the optical EPR cavity (ER 4104OR, Bruker, Germany). EPR spectra were recorded using the EMX X-band CW spectrometer (Bruker, Germany). An NMR teslameter (ER036TM, Bruker, Germany) was used for precise g value determination. The UV-vis-NIR spectra were obtained with the Avantes spectrometer AvaSpec-2048 $\times$ 14-USB2 with the CCD detector, and the AvaSpec-NIR256-2.2 equipped with an InGaAs detector, employing the AvaSoft 7.5 software (Avantes, The Netherlands). An Avantes Avalight-DH-S-BAL light source was utilized. Both the EPR and UV-vis-NIR spectrometers are connected to a HEKA potentiostat PG 390, which triggers both spectrometers. Triggering is executed via the PotMaster v2 $\times$ 90 software package (HEKA Elektronik, Germany). In situ UV-vis-NIR spectra are depicted as difference spectra (ΔA). The spectrum of the polymer in its uncharged state (measured at the initial potential) served as the reference spectrum, and each UV-vis-NIR spectrum was collected relative to the neutral (uncharged) state at the initial potential. All EPR and UV-vis-NIR spectroelectrochemical ex-

periments were carried out at room temperature (298 K). For standard in situ EPR/UV-vis-NIR spectroelectrochemical experiments, a three-electrode EPR flat cell was employed. An indium tin oxide (ITO) coated glass (specific surface conductivity of $20\ \Omega\text{sq}^{-1}$, Merck) acted as the working electrode, a silver chloride (AgCl)-coated silver wire served as the reference electrode, and a platinum wire as the counter electrode. All potentials are referenced to the Fc/Fc^+ redox couple as an internal standard. A supporting electrolyte of 0.1 M TBAPF₆ in acetonitrile was used. The cell assembling and measurements were conducted under an inert (nitrogen) atmosphere. Polymer films on the electrodes were prepared by drop coating from a dichloromethane solution.

SEC analysis for elucidation of OECT operation was performed with ITO stripes ($76\text{ mm} \times 5\text{ mm}$) as working electrode. $40\ \mu\text{L}$ 5 mg mL^{-1} polymer solutions in THF were spin-coated onto the ITO stripes (2000 rpm, 120 s). A Pt wire was used as a counter electrode, and a silver/silver chloride (Ag/AgCl) pellet with a silver wire (Science Products GmbH) as a reference electrode. 1-Ethyl-3-methylimidazolium bis(fluoro sulfonyl)imide ([EMIM][TFSI]) was used as a supporting electrolyte.

6.1.8 Density functional theory (DFT) calculations

All structures were optimized using the DFT/B3LYP(6-31G(d)) and LANL2DZ basis set for Ru, as implemented in Gaussian 09 Rev. D01.[162] This combination of functional and basis sets has been successfully utilized for Ru complexes with organic ligands.[163, 164, 165, 166, 167] Subsequent harmonic frequency calculations for each model complex and charge state reveal no imaginary frequencies, indicating that the obtained geometries correspond to their local minima.

6.1.9 Fabrication and Characterization of the EC Devices

The gel electrolyte was prepared by mixing 1.5 g of lithium perchlorate (LiClO_4), 2.5 g of polymethyl methacrylate (PMMA, $M_w = 120,000$), 10 mL of propylene carbonate, and 10 mL of acetonitrile (ACN). The mixture was stirred overnight

until it became homogeneous. ACN was removed under vacuum overnight until there were no more bubbles. ITO substrates were cleaned by sonication in acetone and isopropanol for 10 minutes each and dried with nitrogen flow. The devices were fabricated in an inert and moisture-free atmosphere. A 10 mg mL^{-1} polymer solution in dichloromethane was prepared and filtered using a $0.45 \mu\text{m}$ syringe filter. A volume of $100 \mu\text{L}$ of the polymer solution was spin-coated onto a clean ITO substrate at 1000 rpm for 120 s. Afterward, the polymer films were dried under vacuum for 30 minutes. A 0.05 mm thick homemade PTFE frame was placed on top of the polymer film to define the active area. The gel electrolyte was then deposited within the PTFE frame. Another clean ITO substrate was placed on top of the gel electrolyte. Finally, the device was sealed with UV glue. The EC device characterization was carried out with Metrohm Autolab PGSTAT204. The working electrode was connected to the ITO substrates with the polymer thin film. The counter and reference electrodes were connected to the opposite ITO substrate. UV-vis-NIR spectra of the devices after applying different potentials were recorded on a Cary 7000.

6.1.10 Fabrication and characterizations of OECT devices

The silicon oxide (SiO_2)-passivated test substrates were fabricated by photolithography procedure, leaving only a 1800×3 -micron channel exposed. The substrates were sonicated in acetone and isopropanol for 10 minutes each, followed by air plasma surface cleaning. After that, the substrates were immediately transferred into a petri dish with $200 \mu\text{L}$ of hexamethyldisilazane (HMDS). After 15 minutes, the substrates were heated at around 100°C for another 15 minutes. $50 \mu\text{L}$ 5 mg mL^{-1} polymer solution in THF was spin-coated onto the substrates (2000 rpm, 120 s) with an Ossila vacuum-free spin-coater and dried under vacuum for two hours. All the OECT measurements were performed in an ambient atmosphere on a probe station (MPI), with [EMIM][TFSI] as the electrolyte and Ag/AgCl pellet with a silver wire as the gate electrode. Keithley 2612b source-measure

unit (SMU) (Keithley Instruments, USA) was used to source the gate potential (V_g) and drain potential (V_d) while measuring drain current (I_d). The SMU was controlled by SweepMe! Software (sweep-me.net). For all transfer measurements, the V_d was maintained at -0.1 V, and each gate voltage step was set to 0.01 V with a software delay time of 0.1 s. The range of V_g applied was between 0.5 and -0.5 V for all the OECTs.

6.1.11 Grazing incidence wide-angle X-ray scattering (GI-WAXS) measurements

The polymer solutions were spin-coated on HMDS-treated silicon substrates (for the spin-coating parameters and HMDS treatment procedure, please see section 6.1.10) and dried under vacuum for two hours. The as-cast thin film samples were used for the measurements without thermal annealing. GIWAXS experiments were performed using the Ganesha 300XL+ system (SAXSLAB ApS, Lyngby/-Denmark). The instrument is equipped with a Pilatus 300K detector, a Cu X-ray source operated at 50 kV/0.6 mA ($\lambda = 1.5408 \text{ \AA}$), and a three-slit collimation system. An incident angle of 0.2° and a sample-to-detector distance of 102.2 mm were used. The data were analyzed using the GIXSGUI program.

6.2 Blending of doped poly(vinylferrocene) (PVF) with poly(3-hexylthiophene) (P3HT) for enhanced electrochemical transistors (OECTs) performance

6.2.1 Materials and synthesis

Regioregular P3HT purchased from Ossila was subjected to Soxhlet purification with methanol, acetone, followed by THF. Vinylferrocene (VF) was purchased from abcr GmbH and was used without further purification. Azobisisobutyronitrile (AIBN) was recrystallized in warm methanol and stored in an inert atmosphere. **Poly(vinylferrocene) (PVF)** was synthesized via free radical polymerization according to the reported procedure. Vinylferrocene (4.37 g, 19.99 mmol) and AIBN (66 mg, 0.40 mmol, 0.02 eq.) were added into a 25 mL pressure flask in a glovebox under an inert atmosphere. 4 mL of anhydrous toluene was added into the flask so that a 5 M vinylferrocene (VF) solution in toluene was prepared. The flask was sealed and heated at 70°C for two days. After that, the resultant gel-like orange solution was precipitated in 300 mL of methanol. The orange solid was collected by vacuum filtration (3.1 g, yield = 71%). Soxhlet purification was performed in the order of methanol, acetone, hexane, and THF. The THF fraction was collected and concentrated by vacuum, followed by precipitation in 200 mL methanol. The yellow solid was collected by vacuum filtration and dried overnight under vacuum. ^1H NMR (400 MHz, CDCl_3 , δ): 4.23-3.96 (m, 9H, ferrocenyl-H), 2.04 (m, 3H, Alkyl-H).

PVF⁺ was obtained via chemical doping. 50 mg of PVF was dissolved in 10 mL of THF. 12 mg of silver trifluoromethanesulfonate (AgOTf) was added into the PVF solution while the solution was rigorously stirred. The dark green solution was filtered through a 0.45 μm PTFE syringe filter and stored in an inert atmosphere before use.

6.2.2 NMR

NMR spectra were recorded on a Bruker Avance III 500 spectrometer operating at 500.13 MHz for ^1H using the standard pulse sequences included in the TOPSPIN 3.2 software package. The ^1H NMR spectra were referenced on the solvent signal (CDCl_3 : $\delta (^1\text{H}) = 7.26$ ppm). All chemical shifts are reported in ppm.

6.2.3 GPC

1 PL MIXED-B-LS (300×7.5 mm) with $10\text{ }\mu\text{m}$ PSgel (Agilent Technologies) was used as the column. Chloroform, DCM, and THF were used as the eluents in different measurements. The adopted RI detector and pump system with degasser were both from Serie 1100 (Agilent Technologies). All solution sample solutions were prepared at the concentration of 3 mg mL^{-1} . Approximately $30\text{ }\mu\text{L}$ of sample solution was extracted for each measurement. All measurements were carried out at 25°C with a flow rate of 1 mL min^{-1} .

6.2.4 UV-vis-NIR spectroscopy

UV-vis-NIR spectra of the PVF thin film, PVF^+ thin film, and the blend thin films were recorded on the Cary 7000.

6.2.5 SEC characterization

$40\text{ }\mu\text{L}$ of 5 mg mL^{-1} blend solutions were spin-coated on $76\text{ mm} \times 5\text{ mm}$ ITO stripes (2000 rpm, 120 s). The SEC characterizations were carried out with Metrohm Autolab PGSTAT204. $[\text{EMIM}][\text{TFSI}]$ was used as the supporting electrolyte. Ag/AgCl pellet with a silver wire was used as the reference electrode. Pt wire was used as the counter electrode and the polymer-coated ITO stripes were used as the working electrodes in each measurement. UV-vis-NIR spectra at different

applied potentials were recorded on Cary 7000.

6.2.6 CV

CV was recorded on Metrohm Autolab PGSTAT204 with an in-house three-electrode system consisting of a Pt disc working electrode, Pt wire counter electrode, and a Ag/AgCl pellet with a silver wire reference electrode. During CV measurements, [EMIM][TFSI] was used as the supporting electrolyte. 20 μL of each blend solution (1 mg mL^{-1}) was drop-casted on the Pt disc working electrode. All measurements were carried out at the scan rate of 50 mV s^{-1} .

6.2.7 Contact angle measurement

The blend thin film samples were prepared by spin-coating 50 μL 5 mg mL^{-1} PVF⁺/P3HT solutions (with 0 wt%, 5 wt%, 10 wt%, 25 wt%, and 50 wt% PVF⁺) in THF on the HMDS-treated quartz-coated glass substrates at 2000 rpm for 120 s (please see section 6.1.10 for HMDS surface treatment procedure). Contact angle measurement was performed on an OCA 40 Micro Automatic Contact Angle Meter and analyzed with SCA 20 (DataPhysics Instruments GmbH, Filderstadt, Germany). The device was equipped with a 7-fold zoom lens with integrated fine focus ($\pm 4\text{ mm}$), a microscopic lens (20-fold with 7.5 to 55 magnifications; field of view with 1/2-inch standard camera 0.85×0.64 to $0.116 \times 0.087\text{ mm}$) and an image processing system (CCD camera with a resolution of 768×576 pixels, frame grabber compatible with Euronorm CCIR, 60 images per second). Milli-Q grade water was used. Dynamic contact angle measurements were performed by first dispensing a volume of 5 μL of a water droplet, followed by dispensing another 5 μL ($0.25\text{ }\mu\text{L s}^{-1}$) and withdrawing 5 μL ($0.25\text{ }\mu\text{L s}^{-1}$). Frames used for calculations were selected according to the droplet movement periods. Advancing and receding contact angles were calculated using average ranges of leaning tangents.

6.2.8 OECT fabrication and characterizations

Quartz-coated glass substrates were sonicated in acetone and isopropanol for 10 min each. After that, source-drain electrodes (i.e., titanium (Ti) = 5 nm, gold (Au) = 30 nm) were defined by E-beam evaporation through a shadow mask. Photolithography was performed with the use of SU-8 2002 so that only the contact pads of the source/drain electrodes and a defined area at the channel were exposed. The photolithography procedure and parameters are adopted from the data sheet provided by the company. Finally, blend solutions with different PVF⁺/P3HT ratios were spin-coated spin-coating onto the patterned substrates (Please see section 6.2.7 for the spin-coating parameters).

Transfer, output, and transient behavior characterizations were evaluated under ambient conditions on a probe station (MPI) connected to a Keithley 2612b SMU (Keithley Instruments, USA). An Ag/AgCl pellet with a silver wire was used as the gate electrode. [EMIM][TFSI] was used as the supporting electrolyte. The SMU was controlled by the SweepMe! software (sweep-me.net). For all transfer measurements, the V_d was maintained at -0.6 V, and each V_g step was set to 0.01 V with a software delay time of 0.1 s. For all output measurements, the V_d step was set to 0.002 V with a software delay time of 0.1 s. The range of applied V_d was between 0.5 V and -0.5 V, while the V_g was constant. For the turn-on time (τ_{on}) measurements, V_g was alternating between -0.8 V and 0 V (22 s each) in order to achieve on and off states, respectively. A constant V_d (i.e., -0.4 V) was applied to the channel.

6.2.9 GIWAXS measurements

The blend solutions were spin-coated on HMDS-treated silicon substrates (for the spin-coating parameters and HMDS treatment procedure, please see section 6.2.7 and 6.1.10, respectively) and dried under vacuum for two hours. The as-cast thin film samples were used for the measurements without thermal annealing.

GIWAXS measurements were performed using the Ganesha 300 XL+ (SAXSLAB, Copenhagen, Denmark) with monochromatic Cu-K α radiation ($\lambda = 1.542 \text{ \AA}$), and a 300k Pilatus area detector (pixel resolution: $0.172 \times 0.172 \text{ }\mu\text{m}^2$). The angle of incidence was fixed at 0.2° , the scanning time at 7200 s, and the sample-to-detector distance was set to 110 mm. Alignment of the sample was performed at GISAXS conditions at a detector-sample distance of 1060 mm. GIWAXS data analysis was done with a self-developed Python script to transform the detector data to a spherical projection (q_{xy} , q_z) and to evaluate cake cuts $I(q)$ and tube cuts $I(\chi)$. The intensity data of tube cuts were corrected for the local background, and (010) tube cuts were fitted to Gaussian functions. All films had similar thicknesses of $(22 \pm 1) \text{ nm}$, as determined by spectroscopic ellipsometry. Thus, tube cuts were used for the evaluation of relative P3HT crystallite amounts in face-on and edge-on orientation in the films.

6.2.10 Atomic force microscopy (AFM)

The blend polymer solutions were spin-coated on HMDS-treated quartz-coated glass/silicon substrates with the aforementioned HMDS surface treatment procedure and spin-coating parameters. The surface morphology of the films was examined using ScanAsyst mode on a Bruker FastScan AFM equipped with a ScanAsyst Air Probe. Nanoscope Analysis 2.0 software was used for the analysis.

6.3 Boosting OECT performance with PEGylated nanoparticles in hydrophobic channels

All the experimental procedures and methods in this chapter are extracted from the reported literature.[160]

6.3.1 Synthesis of PEGylated gold nanoparticles (PEG-AuNPs)

PEGylated-AuNP: citrate stabilized AuNPs were first synthesized by a step-growth method. Before the start of the synthesis, all glassware and stir bars were cleaned with aqua regia and rinsed three times with Millipore water. The procedure began with the preparation of seeds. First, 150 mL of 2.2×10^{-3} M sodium citrate solution was heated to boiling (100°C) in a 1 L conical flask under stirring. 1 mL of 25×10^{-3} M chloroauric(III) acid (HAuCl_4) was quickly added. After 10 minutes, the solution changed to a pink color, indicating seed formation. The solution was cooled to 90°C , and 1 mL of 25×10^{-3} M HAuCl_4 was added. After stirring for 30 minutes at 90°C , another 1 mL of 25×10^{-3} M HAuCl_4 was added and stirred for 30 minutes. 82.8 mL of Millipore water and 3.12 mL of 60×10^{-3} M sodium citrate solution were added to the flask. The temperature was maintained at 90°C , and 1.56 mL of 25×10^{-3} M HAuCl_4 was added and stirred for 30 minutes. Then, another 1.56 mL of the HAuCl_4 solution was added and stirred at 90°C for 30 minutes. For Step 3, 130.9 mL of Millipore water and 4.94 mL of 60×10^{-3} M sodium citrate solution were added, and the solution was kept at 90°C . Then, 2.47 mL of 25×10^{-3} M HAuCl_4 was added and stirred for 30 minutes, and this operation was repeated once. In Step 4, 207 mL of Millipore water and 7.8 mL of 60×10^{-3} M sodium citrate solution were added to the flask, and the solution was maintained at 90°C , followed by the addition of 3.9 mL of 25×10^{-3} M HAuCl_4 . After stirring for 30 minutes, another 3.9 mL of 25×10^{-3} M HAuCl_4 was added, and the solution was stirred for an additional 30 minutes. Finally, in Step 5, 327.4 mL of Millipore water and 12.36 mL of 60×10^{-3} M

sodium citrate solution were added. The solution was kept at 90°C, and 6.18 mL of 25×10^{-3} M HAuCl₄ was added and stirred for 30 minutes. Another 6.18 mL of 25×10^{-3} M HAuCl₄ was then added, and the solution was stirred for another 30 minutes, resulting in a final volume of 957.53 mL and around 50 nm AuNPs. After obtaining the desired size of citrate-AuNPs, a ligand exchange was carried out by using thiol-PEG (6 kDa). 1 mL of chloroform with 10 mg mL⁻¹ thiol-PEG was added to 10 mL of aqueous AuNP solution (2.0 mg mL⁻¹ Au), followed by vented for 2 minutes. After adding 5 mL of methanol and another 1 mL of chloroform, the mixture was shaken and vented again for 2 minutes. Subsequent shaking overnight secured the complete ligand exchange. Then, the PEG-AuNPs in the chloroform phase were purified by three centrifugation–redispersion cycles (500 rcf for one hour, redispersion in chloroform).

6.3.2 OECT fabrication and characterizations

The photolithographic patterning procedure of OECT substrates with SU-8 passivation was the same as in section 6.2.8. Finally, the composite solutions with different PEG-AuNP/P3HT ratios were spin-coated onto the patterned substrates (2000 rpm, 120 s). The devices were physically separated from each other by scratching. Transfer, output, and operational stability characterizations were evaluated under ambient conditions on a probe station (MPI) connected to a Keithley 2612b SMU (Keithley Instruments, USA). A Ag/AgCl pellet with silver wire was used as the gate electrode. 0.1 M NaCl_(aq) was used as the supporting electrolyte. The SMU was controlled by the SweepMe! software (sweep-me.net). For all transfer measurements, the V_d was maintained at -0.6 V, and each V_g step was set to 0.01 V with a software delay time of 0.1 s. The range of V_g applied was between 0.2 and -0.8 V for the P3HT-based composite OECTs and between 0.1 and -1 V for the PDPP-TT-based composite OECTs. For all output measurements, the V_d step was set to 0.002 V with a software delay time of 0.1 s. The range of applied V_d was between 0.5 and -0.5 V while the V_g was constant. For all

operational stability measurements, V_g was alternating between -0.8 V and 0.2 (22 s each) in order to achieve on and off states, respectively. A constant V_d (i.e., -0.4 V) was applied to the channel.

6.3.3 Electrical impedance spectroscopic (EIS) measurement

EIS measurements were conducted using a Metrohm Autolab PGSTAT302N (Filderstadt, Germany) in the potentiostatic mode. The measurements were performed with an RMS amplitude of 25 mV and a DC offset of 0.8 V. The scan range for the measurements spanned from 10^5 to 10^{-1} Hz.

6.3.4 SEC analysis

ITO-coated glass substrates were cleaned by sonicating in acetone and isopropanol for 10 min each. After that, the 5 mg mL^{-1} pure P3HT and 5 wt% AuNP/P3HT solutions were diluted 50 times and drop-casted onto the ITO substrates. The as-cast films were dried under a vacuum for one hour. 0.1 M $\text{NaCl}_{(\text{aq})}$ solution was used as the supporting electrolyte. The SEC characterization was carried out with Metrohm Autolab PGSTAT204. The working electrode was connected to the ITO substrates coated with a polymer thin film. The counter electrode was connected to a Pt wire. The reference electrode was connected to an Ag/AgCl pellet via silver wire. UV-vis-NIR spectra of the devices after the application of different potentials were recorded on Cary 7000.

6.3.5 Contact angle measurement

The thin film samples were spin-coated on HMDS-treated quartz-coated glass substrates with the spin-coating parameters mentioned in section 6.3.2. Contact angle measurement was performed on an OCA 40 Micro Automatic Contact Angle Meter and analyzed with SCA 20 (DataPhysics Instruments GmbH, Filderstadt,

Germany). The device was equipped with a 7-fold zoom lens with integrated fine focus (± 4 mm), a microscopic lens (20-fold with 7.5 to 55 magnifications; field of view with 1/2in. standard camera 0.85×0.64 to 0.116×0.087 mm) and an image processing system (CCD camera with a resolution of 768×576 pixels, frame grabber compatible with Euronorm CCIR, 60 images per second). Every 13th frame was used for analysis. Milli-Q grade water was used. Dynamic contact angle measurements were performed by first dispensing a volume of 5 μ L of a water droplet, followed by dispensing another 5 μ L ($0.25 \mu\text{L s}^{-1}$) and withdrawing 5 μ L ($0.25 \mu\text{L s}^{-1}$). Frames used for calculations were selected according to the droplet movement periods. Advancing and receding contact angles were calculated using average ranges of leaning tangents.

6.3.6 GIWAXS measurements

50 μ L of 5 mg mL⁻¹ composite solutions (i.e., P3HT, 5 wt% AuNP/P3HT, 10 wt% AuNP/P3HT, and 20 wt% AuNP/P3HT) were spin-coated onto HMDS-treated substrates with the abovementioned spin-coating parameters and HMDS surface treatment procedure. The as-cast thin film samples were used for the measurements without thermal annealing.

GIWAXS experiments were performed using the Ganesha 300XL+ system (SAXS-LAB ApS, Lyngby/Denmark). The instrument is equipped with a Pilatus 300K detector, a Cu X-ray source operated at 50 kV/0.6 mA ($\lambda = 1.5408 \text{ \AA}$), and a three-slit collimation system. An incident angle of 0.2° and a sample-to-detector distance of 102.2 mm were used. The data were analyzed using the GIXSGUI program. The radially integrated line profiles of the GIWAXS patterns were fitted using individual Gaussian functions. The lamellar spacing and coherence length were then calculated from the (100) peak position, q_{100} , and full width at half maximum, Δq_{100} , according to the following equations: $2\pi/(q_{100})$ and $2\pi/(\Delta q_{100})$, respectively. For in-plane and out-of-plane line cuts, the intensity was averaged over an azimuthal range of 0° - 17° and 71° - 88° , respectively.

6.3.7 AFM measurements

Polymer solutions with different weight ratios of AuNP were spin-coated on HMDS-treated silicon substrates with the same spin-coating parameters and HMDS surface treatment procedure as mentioned above. The surface morphology of the films was examined using ScanAsyst mode on a Bruker FastScan AFM equipped with a ScanAsyst Air Probe. Nanoscope analysis 2.0 software was used for analysis. To determine the thickness of the films, areas of the samples were removed by scratching, and the step height of the scratches was measured at three different locations on the film and averaged.

6.3.8 Transmission electron microscopy (TEM)

TEM images were obtained using a Zeiss Libra 120 with an accelerating voltage of 120 kV. Samples were prepared by placing a 2 μ L droplet of the diluted AuNP/P3HT solution on TEM grids (Cu, 200 Mesh, coated with carbon film; Science Services GmbH).

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APPENDICES

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Chemical derivatization of an array of three gold microelectrodes with polypyrrole: fabrication of a molecule-based transistor

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High-Mobility Low-Hysteresis Electrolyte-Gated Transistors with a DPP-Benzotriazole Copolymer Semiconductor

Author: Seung Ju Lee et al
Publication: Macromolecular Research
Publisher: Springer Nature
Date: May 29, 2020

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A High Transconductance Accumulation Mode Electrochemical Transistor

Author: Sahika Inal, Jonathan Rivnay, Pierre Leleux, et al

Publication: Advanced Materials

Publisher: John Wiley and Sons

Date: Oct 13, 2014

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Organic Electrochemical Transistors Based on the Conjugated Polyelectrolyte PCPDTBT-SO3K (CPE-K)
Author: Thuc-Quyen Nguyen, Guillermo C. Bazan, Dirk Leifert, et al
Publication: Advanced Materials
Publisher: John Wiley and Sons
Date: Jul 12, 2020
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Highly Stable Conjugated Polyelectrolytes for Water-Based Hybrid Mode Electrochemical Transistors
Author: Olle Inganäs, Niclas Solin, Roger Gabrielsson, et al
Publication: Advanced Materials
Publisher: John Wiley and Sons
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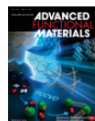
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Understanding the Capacitance of PEDOT:PSS

Author: Igor V. Zozoulenko, Xavier Crispin, Magnus Berggren, et al

Publication: Advanced Functional Materials

Publisher: John Wiley and Sons

Date: May 15, 2017

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Side Chain Redistribution as a Strategy to Boost Organic Electrochemical Transistor Performance and Stability

Author: Iain McCulloch, Sahika Inal, Eleni Stavrinidou, et al

Publication: Advanced Materials

Publisher: John Wiley and Sons

Date: Aug 5, 2020

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**SPRINGER NATURE****N-type organic electrochemical transistors with stability in water****Author:** Alexander Giovannitti et al**Publication:** Nature Communications**Publisher:** Springer Nature**Date:** Oct 7, 2016*Copyright © 2016, The Author(s)***Creative Commons**

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**Complementary Logic Circuits Based on High-Performance n-Type Organic Electrochemical Transistors****Author:** Simone Fabiano, Magnus Berggren, Robert Forchheimer, et al**Publication:** Advanced Materials**Publisher:** John Wiley and Sons**Date:** Jan 10, 2018*© 2018 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim***Order Completed**

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A new era of LMCT: leveraging ligand-to-metal charge transfer excited states for photochemical reactions

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Ann Marie May  and Jillian L. Dempsey 

Author affiliations

Abstract

Ligand-to-metal charge transfer (LMCT) excited states are capable of undergoing a wide array of photochemical reactions, yet receive minimal attention compared to other charge transfer excited states. This work provides general criteria for designing transition metal complexes that exhibit low energy LMCT excited states and routes to drive photochemistry from these excited states. General design principles regarding metal identity, oxidation state, geometry, and ligand sets are summarized. Fundamental photoreactions from these states including visible light-induced homolysis, excited state electron transfer, and other photoinduced chemical transformations are discussed and key design principles for enabling these photochemical reactions are further highlighted. Guided by these fundamentals, this review outlines critical considerations for the future design and application of coordination complexes with LMCT excited states.

A new era of LMCT: leveraging ligand-to-metal charge transfer excited states for photochemical reactions

A. M. May and J. L. Dempsey, *Chem. Sci.*, 2024, **15**, 6661 DOI: 10.1039/D3SC05268K

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Recent advances in metallopolymer-based drug delivery systems

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Gulzhian I. Dzhardimalieva , Lev N. Rabinskiy , Kamila A. Kydralieva  and Igor E. Uflyand 

Author affiliations

Abstract

Metallopolymer (MPs) or metal-containing polymers have shown great potential as new drug delivery systems (DDSs) due to their unique properties, including universal architectures, composition, properties and surface chemistry. Over the past few decades, the exponential growth of many new classes of MPs that deal with these issues has been demonstrated. This review presents and assesses the recent advances and challenges associated with using MPs as DDSs. Among the most widely used MPs for these purposes, metal complexes based on synthetic and natural polymers, coordination polymers, metal-organic frameworks, and metallo dendrimers are distinguished. Particular attention is paid to the stimulus- and multistimuli-responsive metallopolymer-based DDSs. Of considerable interest is the use of MPs for combination therapy and multimodal systems. Finally, the problems and future prospects of using metallopolymer-based DDSs are outlined. The bibliography includes articles published over the past five years.

Recent advances in metallopolymer-based drug delivery systems

G. I. Dzhardimalieva, L. N. Rabinskiy, K. A. Kydralieva and I. E. Uflyand, *RSC Adv.*, 2019, **9**, 37009 DOI: 10.1039/C9RA06678K

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A Molecular Platform for Multistate Near-Infrared Electrochromism and Flip-Flop, Flip-Flap-Flop, and Ternary Memory
Author: Yu-Wu Zhong, Jiannian Yao, Jian-Hong Tang, et al
Publication: Angewandte Chemie International Edition
Publisher: John Wiley and Sons
Date: Jul 3, 2015
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Multistate Redox Switching and Near-Infrared Electrochromism Based on a Star-Shaped Triruthenium Complex with a Triarylamine Core
Author: Jian-Hong Tang et al
Publication: Scientific Reports
Publisher: Springer Nature
Date: Oct 12, 2016
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 **Synthesis of Novel Ruthenium-Polymetallaynes and Their Application in Multistate Electrochromic Memory**
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 Publication: Advanced Materials Technologies
 Publisher: John Wiley and Sons
 Date: Aug 5, 2022
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Boosting OECT Performance with PEGylated Gold Nanoparticles in Hydrophobic Channels

Author: Franziska S.-C. Lissel, Ningwei Sun, Hans Kleeemann, et al

Publication: Advanced Functional Materials

Publisher: John Wiley and Sons

Date: Nov 26, 2024

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B Appendix B - supporting information

B.1 chapter 2 - Synthesis and characterizations of Ruthenium (Ru)-polymetallaynes and their applications in organic electrochemical transistor (OECT) devices

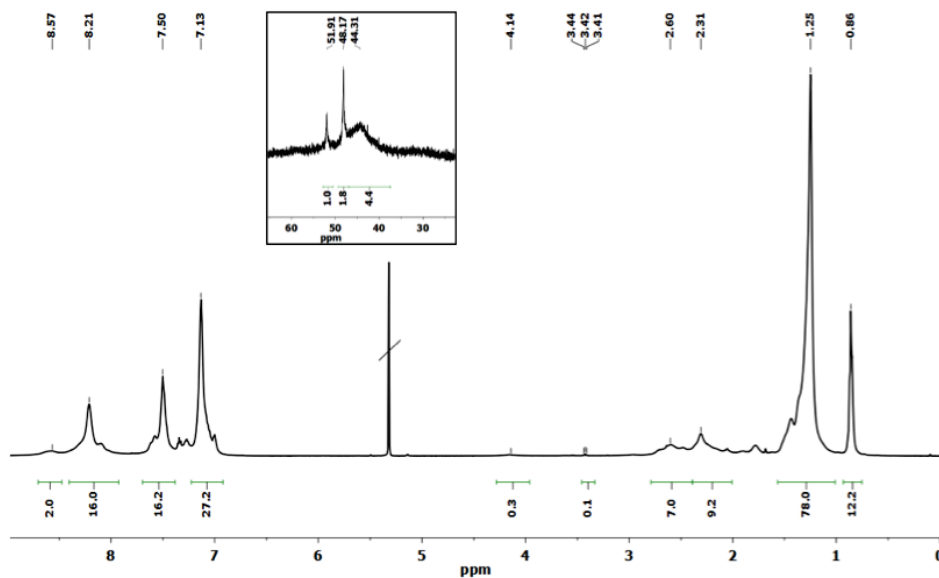


Figure B.1: ^1H NMR spectrum of nec-P3 before precipitation in alkaline solution (Inset: ^{31}P NMR spectrum of nec-P3 before precipitation in alkaline solution).

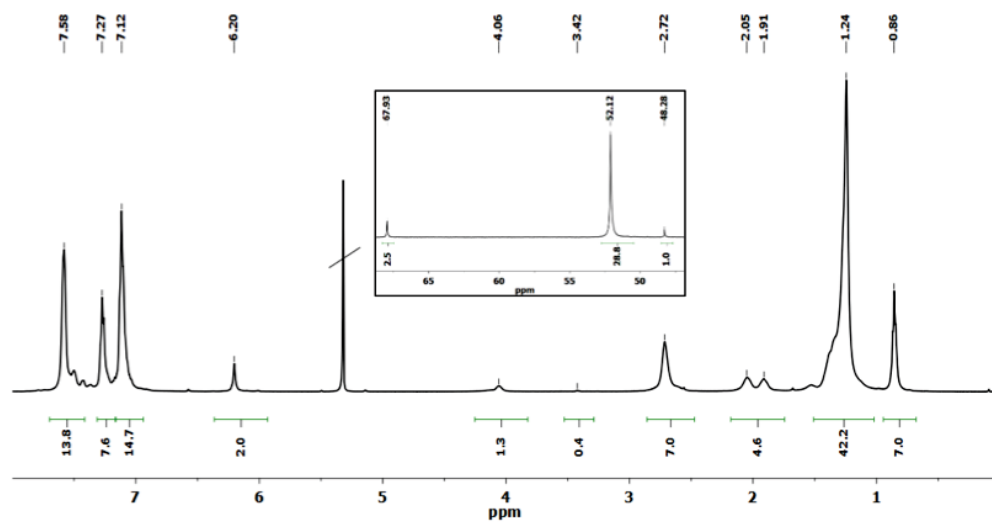


Figure B.2: ^1H NMR spectrum of nec-P3 after precipitation in alkaline solution (Inset: ^{31}P NMR spectrum of nec-P3 before precipitation in alkaline solution).

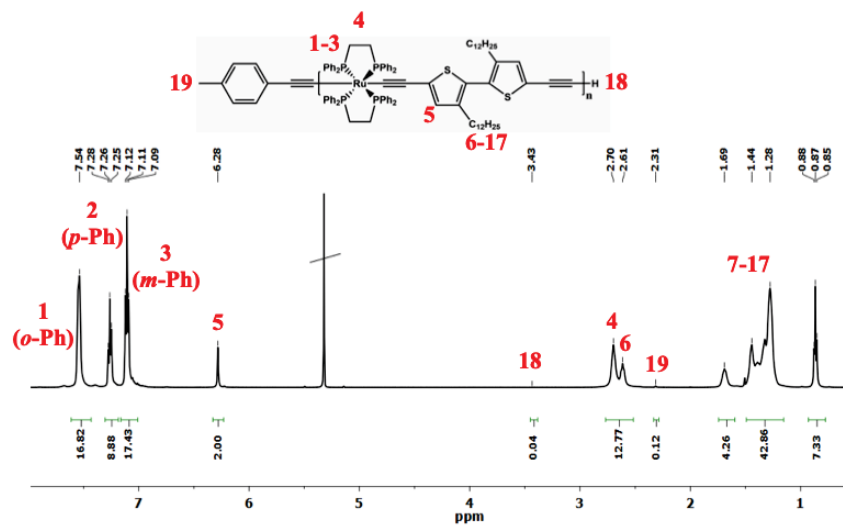


Figure B.3: ^1H NMR spectrum of P1.

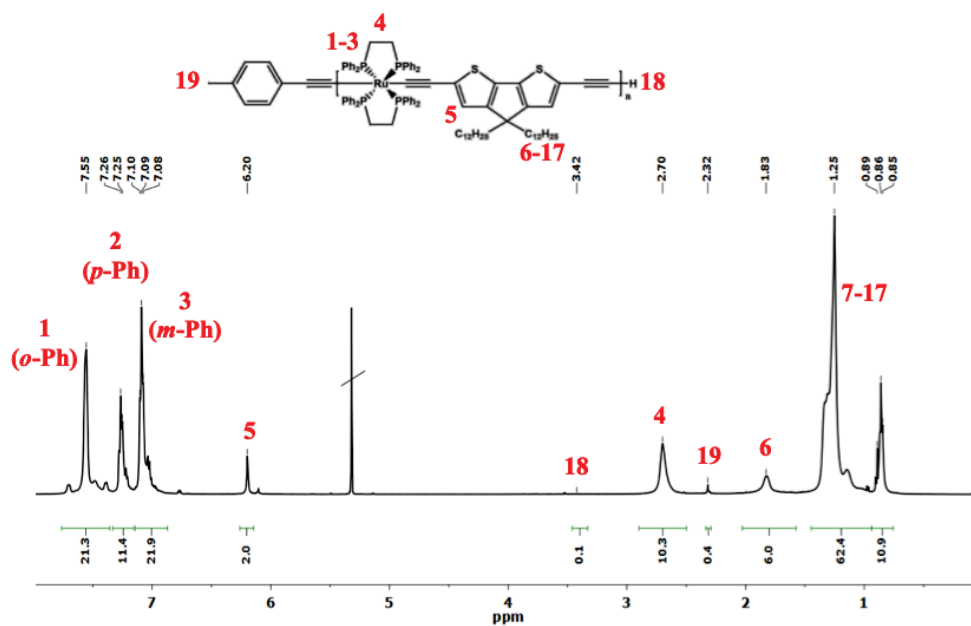


Figure B.4: ¹H NMR spectrum of P2.

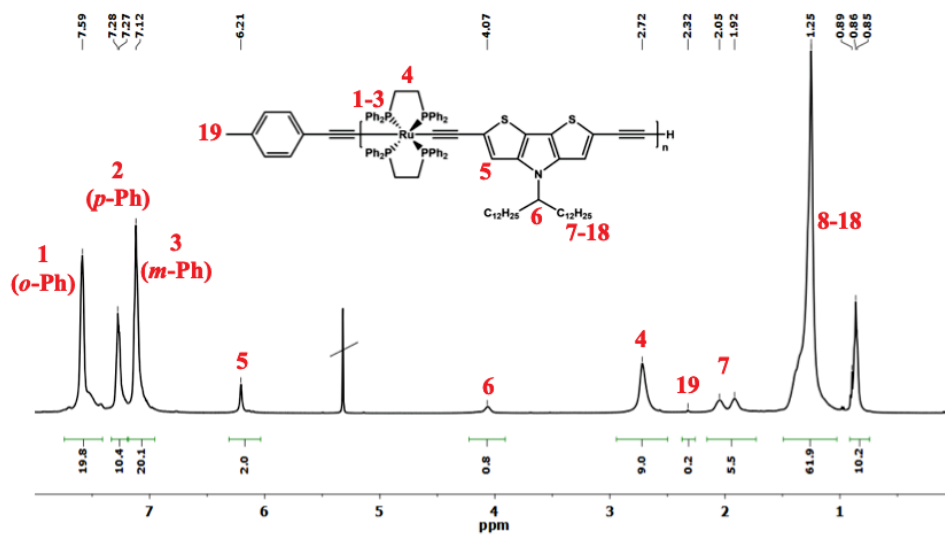


Figure B.5: ¹H NMR spectrum of P3.

$$\text{degree of polymerization (d.p.)} = \frac{I_{\text{thiophene}}}{I_{\text{acetylenic}} + \frac{I_{\text{tolyl}}}{3}} \quad (\text{B.1})$$

For P1:

$$I_{\text{thiophene}} = 2;$$

$$I_{\text{acetylenic}} = 0.04$$

$$I_{\text{tolyl}} = 0.12$$

$$\text{d.p.} \approx 50$$

For P2:

$$I_{\text{thiophene}} = 2;$$

$$I_{\text{acetylenic}} = 0.1$$

$$I_{\text{tolyl}} = 0.4$$

$$\text{d.p.} \approx 9$$

For P3:

$$I_{\text{thiophene}} = 2;$$

$$I_{\text{acetylenic}} \approx 0.067 \text{ (due to non-uniform baseline)}$$

$$I_{\text{tolyl}} = 0.2$$

$$\text{d.p.} \approx 15$$

B.2 Blending of doped poly(vinylferrocene) (PVF) with poly(3-hexylthiophene) (P3HT) for enhanced electrochemical transistors (OECTs) performance

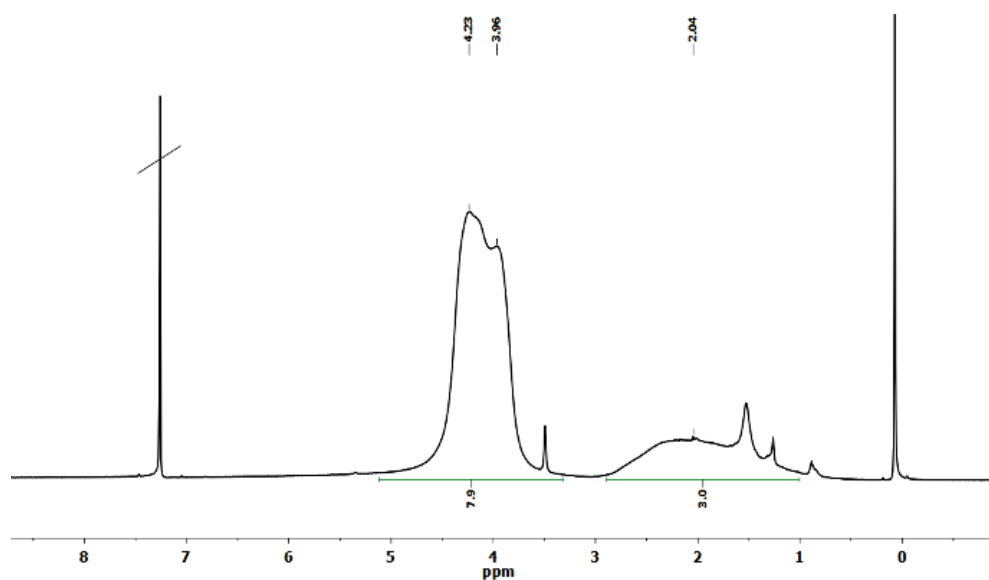


Figure B.6: ^1H NMR spectrum of P3. The broad multiplet at around 2.04 ppm is assigned to be the alkyl proton while the multiplet at 3.96 - 4.23 ppm is assigned to be the protons on ferrocene unit.

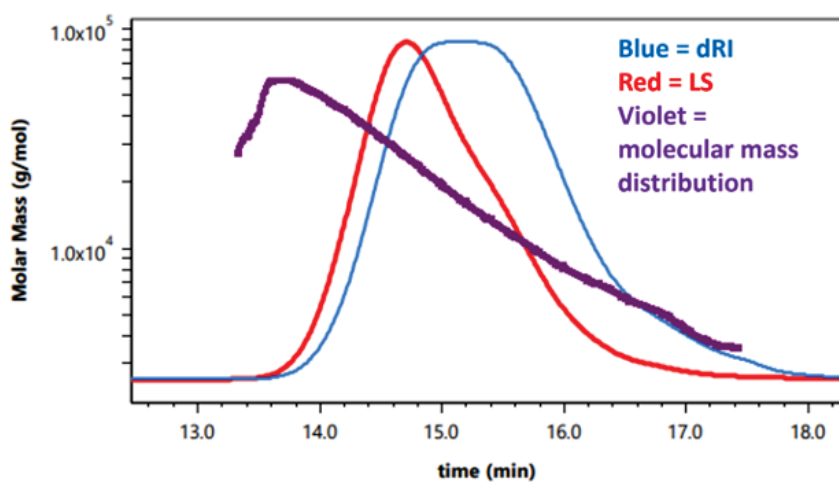


Figure B.7: GPC graphs of PVF with THF as the eluent at 40° .

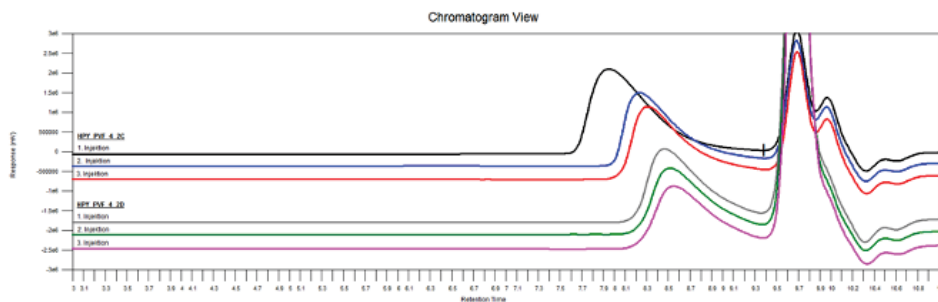


Figure B.8: GPC results from the measurements with chloroform (black line: first injection; blue line: second injection after 1 hour; red line: third injection after another 1 hour) and dichloromethane (grey line: first injection; green line: second injection after 1 hour; pink line: third injection after another 1 hour) as the eluents. A shift to the smaller molecular weight was observed in both cases, indicating a decomposition of PVF in the presence of halogenated solvents.

Entry	M_n (g mol^{-1})	M_w (g mol^{-1})	Polydispersity (M_w/M_n)
First measurement	12100	17100	1.41
Second measurement	12000	17100	1.42
Third measurement	12100	17100	1.42

Table B.1: Number-averaged molecular mass (M_n), weight-averaged molecular mass (M_w) and polydispersity (PDI) of the synthesized PVF.

C List of publications

- **Po Yuen Ho**, Hartmut Komber, and Kilian Horatz, Takuya Tsuda, Stefan C. B. Mannsfeld, Evgenia Dmitrieva, Ulrike Kraft, Henning Sirringhaus, Franziska Lissel, "Synthesis and characterization of a semiconducting and solution-processable ruthenium-based polymetallayne", *Polym. Chem.*, 2020, 11, 472
- **Po Yuen Ho**, Evgenia Dmitrieva, Ningwei Sun, Olga Guskova, Franziska S.-C. Lissel, "Synthesis of Novel Ruthenium-Polymetallaynes and Their Application in Multistate Electrochromic Memory", *Adv. Mater. Technol.*, 2022. 7. 2200316
- **Po Yuen Ho**, Oliver Ditzer, Ali Solgi, Haoran Zhang, Ronja Thümmmler, Mahmoud Al-Hussein, Hans Kleemann, Ningwei Sun, Franziska S.-C. Lissel, "Boosting OECT Performance with PEGylated Gold Nanoparticles in Hydrophobic Channels", *Adv. Funct. Mater.*, 2025, 35, 2412559
- **Po Yuen Ho**, Oliver Ditzer, Ronja Thümmmler, Tommy Meier, Eva Bittrich, Mahmoud Al-Hussein, Hans Kleemann, Ningwei Sun, Franziska S.-C. Lissel, "Blending doped PVF with P3HT for enhanced OECT performance", *Manuscript in preparation*
- R. Kuhrt, **P. Y. Ho**, M. Hantusch, F. Lissel, O. Blacque, M. Knupfer, B. Büchner, "Synthesis and charge transfer characteristics of a ruthenium-acetylide complex", *RCS Adv.*, 2020, 10, 43242
- T.-H. Kao, Z. Qiao, **P. Y. Ho**, O. Ditzer, N. Sun, B. Voit, F. Lissel, "Synthesis of linear unsubstituted poly(4,4'-triphenylamine) via Suzuki-Miyaura coupling of an asymmetric AB monomer", *J. Polym. Sci.*, 2022, 60, 1899
- Z. Qiao, K. Horatz, **P. Y. Ho**, A. Mitrofanov, C. Zhou, N. Sun, F. Lissel, "Carboxylic groups via postpolymerization modification of polythiophene and their influence on the performance of a polymeric MALDI matrix", *Macromol. Chem.*

