Charge modulation spectroscopy of solution-processable field-effect transistors

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**NANYANG
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UNIVERSITY**

**CHARGE MODULATION
SPECTROSCOPY OF SOLUTION-
PROCESSABLE FIELD-EFFECT
TRANSISTORS**

CHIN XIN YU

**SCHOOL OF PHYSICAL &
MATHEMATICAL SCIENCES**

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**Charge Modulation Spectroscopy of
Solution-Processable
Field-Effect Transistors**

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List of abbreviations

CH ₃ NH ₃ PbI ₃ / MAPbI ₃	Methylammonium Lead Iodide
CMM	Charge Modulation Microscopy
CMS	Charge Modulation Spectroscopy
D-A	Donor-Acceptor
DPPT-TT	Poly(N- alkyldiketopyrrolo -pyrrole dithienylthieno[3, 2-b]thiophene)
EA	Electroabsorption
EL	Electroluminescence
F8BT	Poly(9,9-dioctylfluorene-alt-benzothiadiazole)
FET	Field-Effect Transistor
FTIR	Fourier Transform Infra-Red
FWHM	Full-Width-at-Half-Maximum
GIXS	Grazing-Incidence X-Ray Scattering
HOMO	Highest Occupied Molecular Orbital

IRAV	Infra-Red Active Vibrational
IR-CMS	Infrared Charge Modulation Spectroscopy
LED	Light-Emitting Diode
LE-FET	Light-Emitting Field-Effect Transistor
LUMO	Lowest Unoccupied Molecular Orbital
MIS	Metal-Insulator-Semiconductor
NEXAFS	Near Edge X-Ray Absorption Fine Structure
P(NDI2OD-T2)	Poly { [N, N9- bis(2- octyldodecyl)- naphthalene- 1, 4, 5, 8- bis(dicarboximide)- 2, 6- diyl]- alt- 5, 5' -(2, 2'- bithiophene) }
P3HT	Regioregular Poly(3-hexylthiophene)
PC	Photocurrent
PEI	Polyethylenimine
PIA	Photo-Induced Absorption
PIR	Photo-Induced Reflectance
PMMA	Poly(methyl methacrylate)
RAIRS	Reflection-Absorption Infrared Spectroscopy
SAM	Self-Assemble Monolayer
SEM	Scanning Electron Microscope
TIPS-P	Triisopropyl-Silylethynyl Pentacene

Abstract

Recent development of cost-effective, flexible, and large area optoelectronic devices has increased demand for high-performance, solution-processable field-effect transistors (FETs) to drive active devices and circuits. Among the materials of choice to realize solution-processable FETs are organic conjugated polymers and hybrid organic-inorganic perovskite semiconductors, gifted by high charge carrier mobilities and compositionally tunable optoelectronic properties. Given the complexity of such systems compared to conventional inorganic semiconductors, the implementation and optimization of polymer and perovskite FETs requires deep understanding of their charge transport properties as well as their device physics. In this thesis work, we studied prototypical solution-processable semiconducting materials for unipolar, ambipolar, and light-emitting FETs. We employed charge modulation spectroscopy (CMS), a unique electrical pump-optical probe technique that allows selective unipolar excitation and *in situ* probing of charge transport characteristics of operating devices, with spatial resolution down to optical diffraction limit. By analyzing charge-induced absorption and vibrational features of polymer FETs, we were able to determine local charge carrier concentrations and distributions, and elucidate their relationship with structural characteristics of the active layers. Moreover, using an ambipolar hybrid organic-inorganic perovskite as active material, we realized the first perovskite light-emitting FET. Our results lay down the path for developing mathematical device models as well as optimizing the molecular design of organic and hybrid organic-inorganic semiconductors for the

development of high-performance, solution-processable FETs, as well as high brightness light-emitting devices like gated light-emitting diodes and electrical injection lasers.

Chapter 1

Introduction

Understanding of the electronic properties of solution-processable semiconductors is crucial towards commercialization of this class of materials. The motivation to explore and improve the performance of these materials is primarily driven by the simple and fast fabrication methods enabled by the solution processability, which is essential for achieving cheap and high throughput fabrication of electronic devices on flexible substrates, especially for large area application. Besides, the ease of tuning the optoelectronic properties through modifying the chemical structure and composition provides various possibilities to develop electronic devices such as photovoltaic cells, light-emitting diodes (LEDs), field-effect transistors (FETs), and active matrix displays.

A variety of solution-processable functional materials are available, such as oxide semiconductors, organic semiconductors, and hybrid perovskites. Among them, organic conjugated polymers and hybrid perovskites are the best materials of choice, given their high charge carrier mobilities and compositionally tunable optoelectronic properties. For conjugated polymers, the adoption in various devices such as FETs and solar cells, as well as the synthesis of new materials are helped by comprehensive studies of the dynamics of charge carrier generation and transport developed over the past 40 years. Meanwhile, solution-processed hybrid perovskites, benefited from the maturity of existing research studies for developing

organic optoelectronic devices, emerged as the fastest improving photovoltaic materials with a remarkable demonstration of 22.1% power conversion efficiency,¹ despite it was just first demonstrated in 2009.² The photophysics of this class of materials is complicated by the quasi-amorphous (or poly-crystalline) structure that appears to be neither fully disordered nor fully crystalline, which increases the difficulties for implementing mathematical and physical models to predict the structure-properties relationships, especially for organic semiconductors. Hence, experimental characterization of these materials is timely and important to better understand the nature of electronic excitations, which are largely dependent on fabrication conditions.

Conventionally, all optical characterization techniques such as photo-induced transient absorption³⁻⁵ have been commonly established to interrogate charge carrier generation, while electro-optical techniques such as fast transient photocurrent⁶ and pulse-radiolysis time-resolved-microwave-conductivity⁷ are used to study the “early time” charge transport physics. Charge modulation spectroscopy (CMS) is an electro-optic technique where polaronic absorption features and bleaching characteristics of charge carrier at the semiconductor-dielectric interface are probed. Developed as a complementary characterization technique to all optical photo-induced absorption (PIA) spectroscopy, CMS, a technique that is implemented directly on a functional device, is adapted to study the charged excitations in organic conjugated polymers as well as some aspects of device physics.⁸⁻¹³ Unlike Kelvin probe¹⁴ or second harmonic generation microscopy,¹⁵ intensity of CMS signals correlates directly to the carrier concentration accumulated in FET, allowing the direct visualization of carrier distribution for studying working mechanism of the device.

The aim of this thesis work is to study the charge transport as well as charged-excitation physics in solution-processable materials, *i.e.* organic conjugated

polymers and hybrid organic-inorganic perovskites. More specifically, we explore different charged excitation spectroscopic signatures, including polaronic excited states, electroabsorption, and infra-red active vibrational (IRAV) modes, to study the carrier injection and charge distribution, as well as to examine the structure-properties relation at the semiconductor-dielectric interface of different unipolar and ambipolar FETs. Besides, the nature of the charge carrier species (such as intermolecular *vs.* intramolecular polarons, free carriers *vs.* polarons) is explored by analyzing these spectral features. To obtain this information, various unipolar and ambipolar FETs are fabricated to be examined by CMS. Prototypical conjugated polymer materials such as regioregular poly(3-hexylthiophene), (P3HT), poly { [N,N9-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,59-(2,29-bithiophene) } , (P(NDI2OD-T2)), and poly(N-alkyldiketopyrrolo-pyrrole dithienylthieno[3,2-b]thiophene), (DPPT-TT), are used as active materials for FETs to address these goals. The ambipolar charge transport in hybrid perovskites $\text{CH}_3\text{NH}_3\text{PbI}_3$ is also studied by FET characterization and CMS, and is exploited to achieve light emission from FETs.

To address the above goals, this thesis is organized in the following structure:

Chapter 1 will first be providing a short overview on the solution-processable materials used in this thesis, *i.e.* organic conjugated polymers and hybrid organic-inorganic perovskites. The working principle and current-voltage characteristics of various types of FETs, *i.e.* unipolar p- and n-channel, ambipolar, and light-emitting FETs, are described subsequently, following by an introduction to charge modulation spectroscopy (CMS) and microscopy (CMM). Then, various spectroscopic signatures in organic conjugated polymers, such as polaron-induced absorption, IRAV modes, and electroabsorption, are also briefly overviewed.

Chapter 2 explores the unique IRAV modes in conjugated polymers as well as FET

current-voltage characteristics to study unipolar p- and n-channel FETs. Prototypical p-channel P3HT FETs are fabricated to map the carrier distribution in different operating regimes of FET, while n-channel P(NDI2OD-T2) FETs are used to examine the effect of hydrophobic surface treated gate dielectric on the field-effect charge transport, as well as the molecular orientation at the semiconductor-dielectric interface.

In Chapter 3 we proceed to study ambipolar FETs with DPPT-TT as active material. CMM is incorporated to elucidate the contribution of polaronic absorption and electroabsorption from different areas of the FET active channel. Besides, maps of carrier density in unipolar linear and saturation, and ambipolar regimes are also recorded and discussed.

Chapter 4 deals with field-effect transport as well as electroluminescence properties of hybrid perovskite light-emitting FETs. CMS and photo-induced absorption studies were also performed to provide insights about the charge carrier species in hybrid perovskite.

Lastly, a conclusion of the thesis is provided, following by a short overview on some potential future work.

Chapter 2

Materials and methods

This chapter describes the materials and the characterization techniques used in this thesis work. An overview of solution-processable materials are first provided, following by a description of the working principle as well as the current-voltage relationship of unipolar and ambipolar FET, which are essential parts for performing charge modulation spectroscopy (CMS). Then, a literature and technical reviews of charge modulation spectroscopy and microscopy (CMM) are briefly overviewed. Lastly, charge excitations in conjugated polymers are introduced, along with the concept of polaron and its associated spectroscopic signatures.

2.1. Solution-processable materials

Recent development in solution-processable materials offers opportunities to develop cost-effective electronics on flexible substrates. Such advantage is enabled by the easy and low temperature processing without the needs of using high vacuum deposition techniques. Typically, deposition of solution-processable materials can be performed by lab-scale fabrication techniques (such as spin-coating, drop-casting, ink-jet printing, etc.) as well as factory-scale manufacturing methods (such as roll-to-roll printing, screen printing, etc.). There are a variety of solution-processable active semiconducting materials available for fabricating FETs, including metal oxides, organic small molecules, organic conjugated polymers, and

hybrid perovskites. Metal oxides, such as ZnO ¹⁶⁻¹⁸ and CuO ,^{19, 20} are crystalline semiconductors with band transport properties that resemble conventional inorganic semiconductors such as Si and GaAs. Despite showing high carrier mobilities,^{21, 22} the processing of materials requires high-temperature annealing, which prohibits deposition on common plastic substrates. Besides, metal oxides are often weak in mechanical flexibility, which limits their application for flexible electronics. Unlike metal oxides, organic small molecules have been utilized as active materials of FETs to drive flexible active matrix displays.²³ Charge transport in organic small molecules is governed by the reorganization energy and the transfer integral, which are determined by the molecular structure and the intermolecular packing of the organic crystals.²⁴ To achieve high mobility FET transport, small reorganization energy and large transfer integral are required. Besides, the static structural and energetic disorders, originated from defects that are results of different processing and purification-related effects, should be minimized to optimize charge transport at the semiconductor-dielectric interface. Conventional organic small molecules are not soluble and can only be solubilized upon substitution of functionalized derivatives. A prototypical material of soluble organic small molecules is TIPS-P (triisopropyl-silylethynyl pentacene), a small molecule with triisopropyl-silylethynyl groups substituted on the central 6- and 13-position of a pentacene core molecule. TIPS-P thin films, deposited by spincoating technique, are highly crystalline with edge-on orientation of two-dimensional, brick-wall, cofacial π - π stacking motif, exhibit high charge carrier mobilities exceeding $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^{25, 26}

In this thesis, we focus on studying organic conjugated polymers and hybrid perovskites as the nature of their charge transport in semi- or poly- crystalline structures requires experimental studies to provide insight towards understanding their structure-properties relation. Besides, both organic conjugated polymers and

hybrid perovskites are also high carrier mobility semiconducting materials with interesting properties, such as robust bendable mechanical flexibility, low temperature solution processability, and easy compositional tuning, which make them amongst the most promising solution-processable materials for manufacturing cost-effective and large area flexible optoelectronic devices. The subsequent section introduces various prototypical materials used in this thesis work.

2.1.1. Organic conjugated polymers

Organic conjugated polymers, also known as π -conjugated polymers, are “quasi-one-dimensional” semiconducting materials with anisotropic optical properties and carrier mobilities. The origin of electronic structure in organic conjugated polymers is related to the sp^2 hybridization of the carbon atoms in the each oligomer unit. The σ -bonds of carbon hold the molecular structure together, while the alternating π -bonds are responsible for the semiconducting properties.^{27, 28} Here we selected and studied prototypical p-type, n-type, and ambipolar conjugated polymers to carry out our studies. The next few paragraphs provide a brief overview on the conjugated polymers used in this thesis (Figure 2.1).

P3HT (regioregular poly(3-hexylthiophene), Figure 2.1A), a polythiophene made soluble by substituting alkyl side chains to the polymer backbone, is a prototypical conjugated polymer used photovoltaic applications with efficiency exceeding 5%.²⁹ The mobility of P3HT FETs with self-assemble monolayer treated SiO_2 dielectric can reach $0.24 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,³⁰ and even higher with electrolyte gate dielectric.^{31, 32} The charge transport in P3HT is largely affected by the molecular weight and the fabrication conditions,^{30, 33-36} which dictate the crystalline quality of the semiconductor domains. The crystalline domain of P3HT, enabled by the self-assemble property, has lamellar stacking structure formed by interdigitated alkyl side-chains and π - π stacking with adjacent polymer chains (Figure 2.2A). While

charge transport is still favorable along the direction of polymer backbone (intrachain transport), this packing geometry enhances interchain transport through improving interchain interactions from π - π stacking. It is commonly understood that promotion of edge-on orientation with π - π stacking parallel to the substrates (Figure 2.2B), allowing the formation of larger and better crystalline semiconductor domains with enhanced interconnectivity between grains of crystallized semiconductor domains, is very critical to achieve better charge transports for thiophene-based conjugated polymers.^{30, 33-36} However, this seems not necessary for P(NDI2OD-T2).

P(NDI2OD-T2) (poly- { [N,N9-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene) } , Figure 2.1B) is an n-type

Figure 2.1 — Molecular structures of conjugated polymers. (A) P3HT. (B) P(NDI2OD-T2). (C) DPPT-TT.

Figure 2.2 — Packing structures of P3HT. (A) Schematic of lamellar stacking and π - π stacking directions of P3HT. (B, C) Edge-on (B) and face-on (C) orientations of lamellar structures on substrates.

donor-acceptor (D-A) conjugated copolymer with record electron mobility for printed n-channel polymer FETs.^{37, 38} Unlike P3HT, the microstructure of P(NDI2OD-T2) thin films have preferable formation of a disorder matrix with face-on (Figure 2.2C) orientated crystalline domains.³⁹ This is consistent with the demonstrated high bulk mobility⁴⁰ in diode structures and low contact resistance in staggered structure FETs.⁴¹ Conventional perception from thiophene-based conjugated polymer studies, suggesting that edge-on packing is preferable over face-on texture to provide enhanced charge transport properties through facilitating hopping of charge carriers between neighboring conjugated segments,⁴² does not agree with the measured high mobility from P(NDI2OD-T2) FET.³⁸ However, it was also found that edge-on orientation is preferred by the first few layers of the top surface of thermally annealed spin-coated thin film, while face-on orientation is still preferred in the bulk;^{43, 44} this could explain the measured high mobility for top-gated bottom-contact devices. Through proper manipulation and alignment of P(NDI2OD-T2) aggregated segments to the preferable charge transport direction, *i.e.* along the polymer backbone, electron mobility of P(NDI2OD-T2) FETs can reach up to $6.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in high gate bias regime.⁴⁵ Besides, the hole mobility of $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with balanced ambipolar charge transport has also been demonstrated with P(NDI2OD-T2) by utilizing high- κ dielectric gate insulators.⁴⁶ The charge transport in P(NDI2OD-T2) has been identified to be predominantly intra-molecular in nature, meaning that interchain delocalization of polarons is not necessary to achieve high mobility ($\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). This characteristics of charge delocalization within a single polymer chain is unique to high mobility D-A conjugated polymers, where D-A molecular design of larger and more planar repeating units allows better linear conformation of the molecule to endure side-chain disorder, which provides excellent charge transport regardless of the thin film morphologies.^{47, 48}

DPPT-TT (poly(N-alkyldiketopyrrolo-pyrrole dithienylthieno[3, 2- b]thiophene), Figure 2.1C) is another example of high mobility conjugated polymers by D-A design approach with record mobility $\sim 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for printed p-channel FETs.⁴⁹ Note that recent reports have shown that this mobility value may be overestimated by as much as an order of magnitude⁵⁰ due to the non-idealities in transfer characteristics of FET devices that arise from the rapidly changing contact resistance relative to the slowly varying channel resistance.⁵¹ Nevertheless, several independent reports have confirmed high ambipolar mobilities⁵²⁻⁵⁴ ($\mu_e = 0.1\text{-}1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and $\mu_h \sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and balanced⁵² transport properties. This D-A copolymer utilizes the donor-acceptor interaction of DPP (diketopyrrolo-pyrrole) and TT (dithienylthieno[3,2-b]thiophene) moieties for enhancing the intermolecular interactions as well as crystalline packing to facilitate interchain charge transport.^{49, 55, 56} As spun and thermally annealed DPPT-TT thin films have edge-on oriented, in-plane liquid crystalline texture with a π - π stacking distance of $\sim 0.38 \text{ nm}$ ^{52, 53, 57} or shorter ($< 0.35 \text{ nm}$).⁴⁹ A large “quasi-domain” ($\sim 1 \mu\text{m}$) with rigid backbone lying parallel to the substrate plane,⁵⁷ as well as a shortening π - π stacking distance⁴⁹ to further enhance interchain charge hopping might be the origin of the high mobility transport in this material.

2.1.2. Hybrid organic-inorganic perovskites

Perovskite is a crystal structure that can be described by a general formula of ABX_3 . In the case of hybrid organic-inorganic perovskites (later to be referred as hybrid perovskites), X is a halide anion, B is an organic cation, and A is a metal cation. Basic 3-dimensional perovskite crystal structures are constructed by organic cations B occupying the 12-fold coordinated sites between the corner-sharing metal halide (AX_6) octahedra (Figure 2.3A). To predict the stability of the crystal structure, we can refer to rationalized parameter such as Goldschmidt tolerance

factor t ,⁵⁸ which is defined as $t = \frac{R_{A-X}}{\sqrt{2}R_{B-X}} = \frac{R_A - R_X}{\sqrt{2}(R_B - R_X)}$; where R_{A-X} is the distance between A and X , and R_{B-X} is the distance between B and X ; R_A , R_B , and R_X denoted the ionic radii of A , B , and X , respectively. A cubic crystal structure has t lying in the range between 0.89 and 1.0, while a lower value gives tetragonal (Figure 2.3B) or orthorhombic (Figure 2.3C) structures. When $t > 1$, the three-dimensional $B-X$ network can be destabilized, leading to the multilayer structure of “2-dimensional” perovskite crystals.

One of the archetypal hybrid perovskites is $\text{CH}_3\text{NH}_3\text{PbI}_3$ (methylammonium lead iodide or MAPbI_3), which has been widely studied for photovoltaic applications⁵⁹⁻⁶³ and is currently regarded as the fastest improving solar cells with a record power conversion efficiency of 22.1% achieved in less than 7 years.¹ Owing to easy solution processing and cost-effective fabrication, hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ has also been actively exploited for different applications, such as light-emitting diodes,⁶⁴⁻⁶⁶ water splitting,⁶⁷ and optical-pumped lasers.⁶⁸⁻⁷¹ $\text{CH}_3\text{NH}_3\text{PbI}_3$ is a 3-dimensional perovskite with a tetragonal structure at room temperature (Figure 2.3B) and exhibits a phase transition to lower-temperature orthorhombic structure below ~ 160 K (Figure 2.3C).^{72, 73} The atomic structures of hybrid perovskites are more complex than inorganic perovskites due to the presence of noncentrosymmetric

Figure 2.3 — Crystal structures of 3-dimensional perovskites. (A) Cubic crystal structure of 3-dimensional perovskites.⁶⁰ (B) Room temperature tetragonal and low temperature orthorhombic structures of hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$.

organic molecules that can possess many possible orientations. For $\text{CH}_3\text{NH}_3\text{PbI}_3$, the orientations of CH_3NH_3^+ cations are randomly distributed in the room temperature tetragonal phase, while only in the low temperature orthorhombic phase organic cations are frozen with fixed orientation.⁷⁴ Organic cations CH_3NH_3^+ play a major part in stabilizing the perovskite structure and changing the lattice constant, but not very decisive in determining basic electronic structures, which are largely decided by the lead iodide network as the states contributed by the organic molecules are far from the band edges.⁷⁵

Similar to GaAs, $\text{CH}_3\text{NH}_3\text{PbI}_3$ is a direct band-gap material with strong optical absorption in the visible to near infrared region, which is one of the major attributes for the exceptional high photovoltaic efficiency obtained with sub-micron thickness of active materials.⁷⁶ Besides, the ambipolar charge transport properties⁷⁷⁻⁷⁹ and the long carrier diffusion length ($\sim\mu\text{m}$ to $\sim\text{mm}$)⁸⁰⁻⁸³ in $\text{CH}_3\text{NH}_3\text{PbI}_3$ have also been commonly recognized as the reasons behind high efficiency perovskite solar cells. Moreover, solution-processed $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films have high mobility, which was experimentally determined to be $8\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ and $66\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ by terahertz spectroscopy⁸⁴ and Hall effect measurement,⁸⁵ respectively. Theoretical calculations also predicted a high mobility and small effective mass of holes and electrons for $\text{CH}_3\text{NH}_3\text{PbI}_3$,^{86, 87} where the latter is also experimentally confirmed.⁸⁸⁻⁹¹

However, the commercialization of hybrid perovskite solar cells is hampered by their impractical stability upon exposure to ambient moisture as well as their anomalous hysteretic current-voltage behavior.⁹² While encapsulation can be an easy solution to effectively isolate the active materials from moisture or water, hysteresis in current-voltage characteristics is a serious issue for correctly extracting solar cell efficiency.⁹² Effects such as ferroelectricity of methylammonium cation,⁹³ ion drifting,⁹⁴ polarization effect,⁹² and the filling of trap states⁹⁵ have been associated to the observed hysteresis behavior.

Previously, FETs with tin(II)-based 2D hybrid perovskites as active materials have achieved impressive field-effect mobility ($> 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and on/off ratio ($> 10^6$).⁹⁶⁻⁹⁹ From existing literature, rare examples of three-dimensional perovskite FETs can be found,¹⁰⁰⁻¹⁰⁴ which might be due to the strong hysteresis due to ionic transport. Nevertheless, hybrid perovskites remain an attractive class of materials for fabricating light-emitting field-effect transistors (LE-FETs), due to the high photoluminescence efficiency⁶⁹ and tunable band gap, from visible to infrared.^{85, 105}

The nature of charge carrier in hybrid perovskites was also found to be primarily associated to photo-excitation intensity.^{73, 106} Upon weak photo-excitation, free charge carriers are primarily generated,⁷³ suggesting that the role of heterojunction interface is to extract charges rather than dissociating excitons,⁷³ consistent with the good efficiency of hybrid perovskite solar cells without hole transporting layer.¹⁰⁷ At higher photo-excitation intensity, photoexcited species change from free carriers to predominantly excitons.⁷³ Recently, Zhu *et al.* proposed that charge carriers in hybrid perovskites should be treated as “large polarons”, which are commonly observed in a wide range of polar solids such as inorganic perovskites, ferroelectric materials, and ionic crystals.¹⁰⁸ This proposal is supported by the observation of inverse temperature-dependent mobility¹⁰⁹⁻¹¹¹ and photo-induced giant dielectric constant effect.¹¹² The theory might also provide explanations for the discrepancy between theoretical predicted high mobility and experimental extracted low mobility. On the other hand, the origin of bright and broadband emission from 2-dimensional hybrid perovskites is still heavily discussed. Although superior light emission characteristics, a result of the intrinsic layered configuration of 2D hybrid perovskites, are expected from the strong confinement of exciton within the inorganic interlayers,^{96, 113, 114} the extreme broadband emission is untypical of narrow emission from excitonic states. The broadband emission in 2D hybrid perovskites has also been related to energy transfer from inorganic

framework to organic linker,¹¹⁵ distributed trap states or formation of self-trapped excitons.¹¹⁶⁻¹¹⁸ Through a combination of optical spectroscopy and density functional theory studies, Cortecchia *et al.* recently reveals that the emissive species might be a self-localized polaron originated from polaronic excitons localized within the inorganic lattice.¹¹⁹

2.2. Solution-processable field-effect transistors

The first working (point-contact) transistor is demonstrated in 1947,^{120, 121} for which the Nobel prize in physics was subsequently awarded to William B. Shockley, John Bardeen, and Walter H. Brattain in 1956. The operation mechanism of field-effect transistors was first proposed in 1930¹²² but it was first demonstrated only in 1960.¹²³ The first FET was a silicon-based metal-oxide-semiconductor FET (MOSFET),¹²³ which is also commonly known as MISFET (metal-insulator-semiconductor FET) or IGFET (insulated gate FET). The demonstration of field-effect in organic semiconductors can be traced back to the 1970,^{124, 125} but the first functional organic FET (OFET) was only reported in 1986.¹²⁶ Typically, OFETs adopt the thin film transistor (TFT) configuration, which was previously used with low conductivity materials, such as amorphous hydrogenated silicon (aSi:H).¹²⁷ To date, the highest field-effect mobility of OFETs fabricated by solution processing is up to $43 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ($25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ on average),¹²⁸ which surpasses the required minimum mobility of $1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for OFET-driven organic LED displays.¹²⁹ The solution-processability of organic semiconductors allows cheaper fabrication of devices compared to conventional crystalline semiconductors, especially for applications where large area is needed. Besides, the robustness of organic electronics fabricated on flexible substrates, as firstly demonstrated in 1990,¹³⁰ also provides technological interests for commercialization of organic electronic products.

This section introduces the basic working principle and the current-voltage characteristics of unipolar and ambipolar FETs, including light-emitting FETs (LE-

FETs). Hole and electron transport in different operating regimes of unipolar and ambipolar FETs will also be described.

2.2.1. Working principle of field-effect transistor

The structure of a field-effect transistor (FET) is shown in Figure 2.4A. A typical FET consists of three electrodes (namely source, drain, and gate), an active thin semiconductor layer, and an insulating dielectric layer. The dielectric layer is sandwiched between the gate electrode and the semiconductor layer to form a metal-insulator-semiconductor (MIS) structure, while the semiconducting layer separates source and drain electrodes of width W (channel width) by a distance L (channel length).

Figure 2.4 illustrates the basic operating principle of unipolar FETs. Typically the source electrode acts as the charge-injecting electrode and is always grounded ($V_s =$

Figure 2.4 — Working principle of an unipolar FET. (A) Linear FET operating regime. (B) Beginning of the saturation operating regime. The black arrow denotes the pinch-off point. (C) Saturation operating regime. The pinch-off point moves towards the source electrode.

0 V), while voltage biases of V_g (or V_{gs}) and V_d (or V_{ds}) are applied to gate and drain electrodes, respectively. For n-channel (p-channel) FETs, a positive (negative) V_{gs} is applied to inject electrons (holes) from the grounded electrodes to induce an electron (hole) accumulation layer at the semiconductor-dielectric interface (Figure 2.4A). The density of induced accumulated electron (hole) at the semiconductor-dielectric interface is proportional to V_{gs} and to the capacitance per unit area C_i of the dielectric. However, induced charges have to first fill deep traps at the interface, and only additional induced charges are mobile and contribute to current in FET after all the deep traps at the interface are filled. On the other hand, accumulation of charges at the interface can occur at $V_{gs} = 0$ V due to an internal potential created by doping (donor or acceptor) states and interface dipoles.^{131, 132} Therefore, a threshold voltage V_{th} is defined to account for the charge filling of the deeps traps or for the doping states and interfacial dipoles, where the density of induced mobile charges at the interface is now proportional to the effective gate voltage $V_{gs} - V_{th}$ instead of simply V_{gs} .

When $V_{ds} = 0$ V, the charge concentration is distributed evenly in the FET induced channel (Figure 2.4A). Applying a small drain-source bias ($V_{ds} \ll V_{gs} - V_{th}$) will form a linear gradient of carrier density from the source to drain electrode (Figure 2.4B). This corresponds to the linear operating regime of the FET, where I_{ds} is proportional to V_{ds} . When $V_{ds} = V_{gs} - V_{th}$, the induced channel is “pinched off” at the drain electrode, as indicated with a black arrow in Figure 2.4B, due to the zero local potential at the drain electrode. A further increase in V_{ds} results in the formation of a depletion region next to the drain electrode since local potential of the region is below V_{th} . This corresponds to the saturation operating regime of the FET, where I_{ds} does not increase substantially by applying higher V_{ds} : the extra kinetic energy gained by propagating charges is balanced off by travelling across an expanding depletion region (Figure 2.4C).

2.2.2. Current-voltage characteristics

In general, the current-voltage relationship of a typical FET is described by using the gradual channel approximation method.¹³³⁻¹³⁵ Note that this approximation method is only valid for FETs with large channel length, typically $L > 10 d_{\text{dielectric}}$ (thickness of dielectric layer), to ensure that the carrier distribution within the channel is determined by the field created by V_{gs} .^{136, 137} This is to prevent a domination of space-charge limited bulk current at the saturation operating regime where “on” and “off” states of the FET cannot solely be determined by V_{gs} .¹³⁸⁻¹⁴³ Besides, the approximation does not account for gate voltage-dependent mobility and for the non-ohmic contacts between the source (drain) electrode and the semiconductor layer.

If the above mentioned conditions are satisfied, the current-voltage relation of FETs follows:

$$I_{\text{ds}} = \frac{W}{L} \mu C_i [(V_{\text{gs}} - V_{\text{th}}) V_{\text{ds}} - \frac{1}{2} V_{\text{ds}}^2] \quad (2.1)$$

Where W is the channel width, L the channel length, μ the mobility, and C_i the capacitance per unit area. Equation 2.1 shows that the drain-source current I_{ds} is dependent on drain-source voltage V_{ds} and gate-source voltage V_{gs} . This means that one can define two basic FET current-voltage characteristics, namely the output and the transfer characteristics. The former is obtained by measuring I_{ds} as a function of V_{ds} at different fixed V_{gs} , while the latter is attained by acquiring I_{ds} as a function of V_{gs} at different fixed V_{ds} . Figure 2.5 and Figure 2.6 show typical FET characteristics we obtained from n- and p-channel organic FETs, respectively.

In the linear operating regime (Figure 2.4A), where the source-drain bias is much smaller than the effective gate bias, *i.e.* $V_{\text{ds}} \ll V_{\text{gs}} - V_{\text{th}}$, Equation 2.1 can be simplified to:

$$I_{ds,lin} = \frac{W}{L} \mu_{lin} C_i (V_{gs} - V_{th,lin}) V_{ds} \quad (2.2)$$

Equation 2.2 states that the linear drain-source current $I_{ds,lin}$ is linearly proportional to both V_{ds} and V_{gs} ; thus, linear mobility μ_{lin} and linear threshold voltage $V_{th,lin}$ can be extracted from a linear fitting of the FET transfer characteristics (I_{ds} vs. V_{gs}).

In the saturation operating regime (Figure 2.4B and Figure 2.4C) pinch-off of the channel occurs at the drain electrode when $V_{ds} = V_{gs} - V_{th}$, and the drain-

Figure 2.5 — Current-voltage characteristics of P(NDI2OD-T2) n-channel FET. (A, B) Output (A) and transfer (B) characteristics of P(NDI2OD-T2) FET. The inset of (B) shows the schematic configuration of P(NDI2OD-T2) FET. The thickness of PMMA and SiO₂ are both 500 nm. Saturation threshold voltage is extracted to be 8.5 V.

Figure 2.6 — Current-voltage characteristics of P3HT p-channel FET. (A, B) Output (A) and transfer (B) characteristics of P3HT FET. The inset of (B) shows the schematic configuration of P3HT FET. The thickness of P3HT, PMMA, and SiO₂ are 100 nm, 500 nm, and 500 nm, respectively. Saturation threshold voltage is extracted to be 4.1 V.

source current does not substantially increase and saturates at $I_{ds,sat}$. By assuming that the channel shortening at the drain electrode due the depletion region is negligible, the saturation current $I_{ds,sat}$ can be obtained by substituting $V_{gs} - V_{th}$ into V_{ds} in Equation 2.2, which yields:

$$I_{ds,sat} = \frac{W}{2L} \mu_{sat} C_i (V_{gs} - V_{th,sat})^2 \quad (2.3)$$

Equation 2.3 shows that the saturation drain-source current $I_{ds,sat}$ has a quadratic dependence on $V_{gs} - V_{th}$. The saturation mobility μ_{sat} and saturation threshold voltage $V_{th,sat}$ can therefore be extracted from the linear fitting of $(I_{ds,sat})^{1/2}$ vs. V_{gs} plot.

2.2.3. Ambipolar and light-emitting field-effect transistors

Ambipolar transport, *i.e.* the capability to transport holes and electrons simultaneously, is considered to be a generic feature of many undoped organic semiconductors.¹⁴⁴ This property was also observed in hydrogenated amorphous silicon (a-Si:H) and carbon nanotubes, with the former being the first demonstration of ambipolar FET¹⁴⁵ and the latter being the first carbon-based material for which ambipolar transport and associated light emission were reported.¹⁴⁶

Typically, conventional organic FETs rarely show n-channel behavior due to high injection barrier of electron, which arises from the mismatch of the LUMO (lowest unoccupied molecular orbital) level (2-3 eV) with the work function of conventionally convenient-test gold electrode (4.8-5.1 eV). Improvement of electron injection can be achieved by using low work function electrodes, such as calcium and magnesium, which unfortunately are not stable in ambient environment. The mismatch between the LUMO of the organic semiconductor and the work function of gold electrodes can be generally reduced by increasing the electron affinity to lower the LUMO by adding strong electron withdrawing group such as fluorine,

cyano, or diimide moieties.¹⁴⁷ This also improves the environmental stability of the organic semiconductor against degradation by oxygen and moisture. However, radical anions remain thermodynamically unstable, thus a kinetic barrier is required to prevent the diffusion of water and air into the active channel region during device operation. Besides, the observation of n-channel behavior is strongly depended on the nature of the semiconductor-dielectric interface. Passivation of hydroxyl groups at the interface is proven to be crucial for n-channel transport in OFET since hydroxyl groups act as electron traps, which would shift the threshold voltage for electron-accumulation to unusual high voltage range,¹⁴⁴ especially for materials with low electron affinities.¹⁴⁸

One of the challenges in fabricating ambipolar FETs is to obtain efficient injection of both holes and electrons into the active channel, especially for organic semiconductor with bandgap of 2-3 eV. Any single component electrode will limit the injection of at least one carrier. For the coplanar FET configuration (bottom-contact, bottom-gate), carrier injection is limited by the contact area of the side wall of drain-source contacts, despite having a direct contact between the injecting electrodes and the accumulation layer. In contrast, the staggered FET configuration (top-contact, bottom-gate or top-gate, bottom-contact) utilizes the effective lengthening of the channel by injecting carriers from the large overlapped area of the source/drain electrode with the gate electrode, other than from the edge of electrode. This leads to current crowding effects that decrease contact resistance, which is important for devices with high injection barriers.¹⁴⁴ Typically, efficient injection of both carriers can be achieved by using asymmetric contacts, which consist of different high and low work function electrodes, to allow alignment of the HOMO (highest occupied molecular orbital) and the LUMO levels of the active material to the respective injecting electrode.^{149, 150} Besides, the use of low bandgap materials as active layers can also lower the injection barrier, leading to almost no

contact resistance for holes and electrons.¹⁵¹

One of the technological interests of ambipolar FETs is the realization of light-emitting FETs (LE-FETs), devices that integrate electronic switching and light-emitting properties. Compared to LEDs, LE-FETs provide spatial control of the emission area that allows emission away from metal electrodes, improving the external quantum efficiency by reducing the escape of carriers into the electrode without recombination, and exciton quenching by metal.¹⁵² The recombination rate is significantly improved by the two-dimensional carrier accumulation at the semiconductor-dielectric interface that permits high current density in LE-FETs ($1 - 10 \text{ A cm}^{-2}$) than in LEDs ($10^{-3} - 10^{-2} \text{ A cm}^{-2}$). It has been demonstrated that the external quantum efficiency of LE-FETs can outperform an optimized LED structure with the same material,¹⁵³ therefore LE-FET can potentially be an useful device for integrated electro-optical switches as well as electrically pumped lasers.

From a fundamental point of view, ambipolar FETs and LE-FETs provide opportunities to understand the physics of these materials and devices. Particularly, LE-FETs provide a useful platform for studying recombination physics in organic semiconductors by exploiting the efficient radiative recombination of holes and electrons. The spatial control of light emission from the FET active channel allows direct visualization of ambipolar transport characteristics,¹⁵² and proves the presence of separate hole and electron channels in series within the active FET channel when operating in ambipolar injection conditions, as proposed by Schmechel *et al.*¹⁵⁴ and Smits *et al.*¹⁵⁵ A simple ambipolar model provided by Schmechel *et al.*,¹⁵⁴ as described in the next section, is typically applied to analyze ambipolar FET characteristics.

Operating principle of ambipolar and light-emitting FET

Figure 2.7 shows schematics of the working principle of ambipolar FETs in electron

accumulation mode; typical output and transfer characteristics of ambipolar FETs are shown in Figure 2.8. Note that the illustration of local potential at gate, source, and drain electrodes with respect to each other in Figure 2.7 is simplified, and does not precisely describe the actual distribution of potential along the FET active channel.

When ambipolar FETs operate in electron accumulation mode, electrons and holes are injected from source and drain, respectively. This requires the local gate potential at source ($|V_{gs}|$) and drain ($|V_{gd}|$, defined as $|V_{gs} - V_{ds}|$) electrodes to be higher than the threshold voltages of injecting electrons ($|V_{th,e}|$) and holes ($|V_{th,h}|$), respectively. No currents are injected into the active layer when $|V_{gs}| < |V_{th,e}|$ and $|V_{gd}| < |V_{th,h}|$.

Figure 2.7 — Working principle of ambipolar and light-emitting FETs, with illustration of local potential at gate, source, and drain electrodes in electron accumulation mode. (A) Unipolar linear FET operating regime. (B) Unipolar saturation FET operating regime. (C) Ambipolar injection FET operating regime. Injection of holes when local gate potential at drain electrode ($|V_{gd}|$) is higher than the threshold voltage of hole accumulation $|V_{th,h}|$. In light-emitting FETs, holes and electrons recombine radiatively to emit light (indicated with purple arrow) at the meeting point (recombination zone) of electron and hole channels. (D) Hole only injection regime with positive gate bias. The local gate potential at drain electrode V_{gd} is defined as $V_{gs} - V_{ds}$.

When $|V_{gs}| > |V_{th,e}|$ and $|V_{gd}| \ll |V_{th,h}|$ and $|V_{ds}| < |V_{gs} - V_{th,e}|$, as shown in Figure 2.7A, the current-voltage characteristics will follow:

$$|I_{ds}| = \frac{WC_i}{L} \mu_e \left((V_{gs} - V_{th,e}) - \frac{V_{ds}}{2} \right) V_{ds} \quad (2.4)$$

This corresponds to the unipolar linear FET operating regime where a uniform electron density distribution is induced at the active layer by applying positive V_{gs} that is higher than threshold voltage of electron accumulation $|V_{th,e}|$ (Figure 2.7A). Similar to Equation 2.1, $|I_{ds}|$ in Equation 2.4 is linearly dependent on $|V_{ds}|$ when $|V_{ds}| \ll |V_{gs} - V_{th,e}|$. Thus, similar to unipolar n-channel FETs, increasing $|V_{ds}|$ higher than $|V_{gs} - V_{th,e}|$ drives the FET from the linear to the unipolar saturation operating

Figure 2.8 — Current-voltage characteristics of F8BT (Poly(9,9-dioctylfluorene-alt-benzothiadiazole)) ambipolar FET. (A, B) Output (A) and transfer (B) characteristics of F8BT FET. The inset in panel (B) shows the molecular structure of F8BT.

regime (Figure 2.7B). If $|V_{gd}| < |V_{th,h}|$, the current-voltage characteristics is given by:

$$|I_{ds}| = \frac{WC_i}{2L} \mu_e (V_{gs} - V_{th,e})^2 \quad (2.5)$$

Similar to Equation 2.3, Equation 2.5 does not depend on V_{ds} , and I_{ds} does not increase significantly at a fixed V_{gs} . Mobility of ambipolar FETs is usually extracted from this equation due to the ease of performing linear fitting on $(I_{ds})^{1/2}$ vs. V_{gs} plot and clearer identification of saturation than linear operating regime from FET output characteristics. By further increasing $|V_{ds}|$, holes are injected from the drain electrode if $|V_{gd}| > |V_{th,h}|$ (Figure 2.7C). In the case of light-emitting FETs, the injected holes recombine radiatively with electrons to emit light (also known as electroluminescence, EL), as indicated with a purple arrow in Figure 2.7C.

A further increase in drain-source voltage improves hole injection, pushing the emission further away from the drain (or closer to source) electrode. In this regime, the current-voltage relation can be described with:

$$|I_{ds}| = \frac{WC_i}{2L} \{ \mu_e (V_{gs} - V_{th,e})^2 + \mu_h (V_{ds} - (V_{gs} - V_{th,h}))^2 \} \quad (2.6)$$

Note that Equation 2.6 assumes that holes and electrons recombine with infinite recombination rate at the position where two channels meet.^{134, 152, 154} In the case of $|V_{gs}| < |V_{th,e}|$ and $|V_{gd}| \geq |V_{th,h}|$ (Figure 2.7D), only holes are injected despite of the positive gate bias applied. This reduces Equation 2.6 to:

$$|I_{ds}| = \frac{WC_i}{2L} \mu_h (V_{ds} - (V_{gs} - V_{th,h}))^2 \quad (2.7)$$

Equation 2.7, which resembles the second term of Equation 2.6, shows that $|I_{ds}|$ has quadratic dependence on $(V_{ds} - (V_{gs} - V_{th,h}))$, which leads to a diode-like current behavior of the output characteristics (Figure 2.8A). For transfer characteristics

(Figure 2.8B), the semi-logarithmic plot displays a V-shape curve with one arm representing electron transport and the other indicating hole transport, which can be described by Equation 2.5 and Equation 2.7 depending on V_{gs} .

By assuming that the hole and electron are accumulated in saturation under the ambipolar injection regime, in which the accumulation length of hole (L_h) and electron (L_e) channel are added up to the total channel length ($L = L_h + L_e$), we can obtain:

$$|I_{ds,sat}| = \frac{WC_i}{2L_{e/h}} \mu_{e/h} (V_{g,eff} - V_{th,e/h})^2 \quad (2.8)$$

Where $V_{g,eff}$ is the effective gate voltage at respective hole and electron injection electrode. In ambipolar operating regime, hole and electron current are equally injected ($|I_{ds,sat}| = |I_e| = |I_h|$). Thus, with equation 2.8, we can obtain the ratio of the length of accumulated hole and electron channel:

$$\frac{L_e}{L_h} = \frac{\mu_e (V_{gs} - V_{th,e})^2}{\mu_h (V_{gd} - V_{th,h})^2} \quad (2.9)$$

Note that equation 2.9 assumes electron and hole are injected from source and drain respectively. The assumption in deriving equation 2.8 and 2.9 are commonly used in predicting the recombination/light-emitting zone of ambipolar LE-FET.^{134, 156, 157} Nevertheless, there are several other notable models^{154, 155, 158} that also provides qualitative description about the ambipolar operation as well as the device physics of the ambipolar FET in the existing literature.

2.3. Charge modulation spectroscopy and microscopy

In this section, charge modulation spectroscopy (CMS) and microscopy (CMM) will be introduced, as they are the optical techniques mainly used to characterize FET devices in this thesis. The underlying principles of this technique as well as

the implications of the results will be illustrated. Details of the experimental setup and measurement method are available in the appendix.

2.3.1. Charge modulation spectroscopy

CMS is an advanced electro-optic technique to study charge excitations in organic semiconductors.^{9, 12, 159-167} Conventionally, the technique is developed as a complementary to photo-induced absorption (PIA)^{11, 168-170} and photocurrent (PC) spectroscopy^{6, 171, 172} experiments to study charge injection and accumulation in conjugated polymers. PIA is a fully optical characterization method, which relies on optical excitation (photo doping) and optical probing, while PC probes the current response of conjugated polymers upon photo-excitation; both are typically employed to study photovoltaic materials. In comparison, CMS is an electrical pump-optical probe technique that allows *in situ* and contactless probing of the charge carrier density in operating semiconductor devices, such as organic FETs. CMS is very sensitive to detect the thin accumulation of charge carriers at the semiconductor-dielectric interface, allowing the quantification of carrier concentration.^{162, 163} Besides, CMS also allows selective probing of either negative or positive polarons by applying appropriate gate bias to induce hole or electron accumulation (interfacial doping) at the semiconductor-dielectric interface of FETs.^{54, 173} By varying the angle of probing with respect to the normal plane of substrate plane, CMS experiments can differentiate spectroscopic species of active materials from substrate's modes.^{165, 166, 174} In addition, a synchronous excitation light source as the modulated voltage's allows studying of the quenching of photoluminescence from active materials^{165, 166} as well as the charge injection properties from different electrodes.¹⁷⁴

CMS probes the polaronic absorption (see section 2.4 for details) and bleaching features of injected charges without associated counterions.^{8, 9, 11, 165-167} Typically, CMS is probed in the near infrared spectral region,^{8, 9, 54, 159, 175-177} where polaronic

features can possibly be masked by electroabsorption from the Stark effect (see section 2.4 for details).⁹ However, when probed in the mid-infrared, CMS also detects infra-red active vibrational (IRAV) modes (see section 2.4 for details) of conjugated polymers, a specific and unique signature of polarons, allowing a more direct assessment of charge carrier present at the semiconductor-dielectric interface.^{162, 163, 178, 179}

CMS spectra are obtained by plotting the normalized change in optical probing intensity (*i.e.* intensity of detected transmitted/reflected probe beam) as a function of photon energy or wavelength. There are two different approaches to acquire CMS spectra: phase-sensitive, lock-in amplifier technique (to be referred as “lock-in technique”) and quasi-static, on-off acquisition technique (to be referred as “on-off technique”). For the former technique, a modulating bias $V_{DC} \pm V_{AC}$ is applied to the gate electrode of the FET. The direct component (DC) of the applied gate bias induces carrier accumulation at the semiconductor-dielectric interface, while the alternating component (AC) modulates the density of induced mobile carrier. The change in carrier density modulates the intensity of the probing monochromatic light. The intensity change in transmission (δT) or reflectance (δR), modulated by the change in carrier density, can be demodulated by using a phase-sensitive lock-in amplifier. The CMS spectra are obtained by normalizing the intensity change in transmission (or reflectance) to the original transmission spectrum $\frac{\Delta T}{T} = \frac{\delta T}{T}$ (or reflectance $\frac{\Delta R}{R} = \frac{\delta R}{R}$). In the on-off technique, the CMS spectra are acquired by collecting transmission (T) or reflectance(R) spectra with (T_{on} or R_{on}) and without (T_{off} or R_{off}) charge accumulation. The charge accumulation is obtained by applying ON voltage (V_{on}) and OFF voltage (V_{off}) to induce and to deplete carrier accumulation at the semiconductor-dielectric interface, respectively. The CMS

spectra are then derived by calculating $-\frac{\Delta T}{T} = -\frac{T_{on} - T_{off}}{T_{off}}$ or $-\frac{\Delta R}{R} = -\frac{R_{on} - R_{off}}{R_{off}}$.

In comparison, lock-in technique resolves both in-phase and quadrature phase of the signal, where the former provides information about different spectroscopic signatures related to mobile charges,^{8, 9, 175, 176} while the latter provides additional information on the presence of long-lived species.^{9, 180} However, this technique is typically applied to probe spectroscopic features in visible and near infrared range, as the use of a monochromatic probe requires a strong light source and a monochromator with highly efficient diffraction gratings. Conventionally, Fourier transform infra-red (FTIR) spectrometer is used to perform measurements in mid-infrared, to overcome the disadvantage of weak intensity of typical mid-IR sources.^{181, 182} CMS with on-off technique benefits from broadband probing characteristic of FTIR spectroscopy, which may also incorporate a lock-in amplifier at the expense of more complicated signal processing.^{181, 182} On the other hand, the signal-to-noise ratio of the on-off technique relies on the sensitivity of detector. This often requires substantial averaging thus a longer acquisition time to obtain spectra with large signal-to-noise ratio compare to the lock-in technique.^{9, 183, 184}

Figure 2.9 — Charge modulation spectroscopy measurements of DPPT-TT FETs. (A) CMS spectra of a top-gate bottom-contact FET acquired with lock-in amplifier technique. The continuous and dashed lines are the in-phase and quadrature phase of the measured signals, respectively. (B) CMS spectra of a bottom-gate bottom-contact FET acquired with accumulation on-off technique.

Nevertheless, the on-off technique is proven to be sensitive to slow and trapped charges, which also makes it a unique acquisition technique, for instance, to study water-induced and oxygen-induced instabilities in organic semiconductors.^{183, 184}

Figure 2.9 shows the typical CMS spectra acquired with the lock-in technique (Figure 2.9A) and the on-off technique (Figure 2.9B).

2.3.2. Charge modulation microscopy

With CMS coupled to a confocal microscope, charge modulation microscopy (CMM) can be used to map the carrier distribution across FET channel with diffraction limited spatial resolution (Figure 2.10).^{163, 175, 176, 178, 179} By performing polarization-dependent CMM (p-CMM, Figure 2.11),¹⁷⁶ the orientation of charged transition dipole moments can be resolved (Figure 2.12). Previously, Martino *et al.* revealed that charges mainly populate regions with ordered polymer chains through a series of CMM measurements and DFT calculations.¹⁷⁶ A subsequent work also unveiled that charges tend to occupy pre-aligned polymer chains.¹⁸⁵

Moreover, a similar technique was also utilized to acquire the spatial distribution of electric-field in the active channel of FETs by biasing the FETs into full depletion

Figure 2.10 — Carrier distribution mapped by CMM. (A) Maps of charge density distribution across the FET channel in electron accumulation mode ($V_{gs} = 30 \text{ V} \pm 20 \text{ V}$) with different applied V_{ds} . (B) Corresponding line profiles of carrier distribution, as shown in (A).

Figure 2.11 — Polarization-dependent CMM in electron accumulation mode of a DPPT-TT FET. The $\Delta T/T$ maps are obtained by applying $V_{gs} = 40 \text{ V} \pm 20 \text{ V}$ to the gate while grounding both source and drain electrodes. A probing wavelength of 820 nm was chosen as it is the maximum of the bleaching characteristics in the CMS spectrum (Figure 2.9A). The polarization directions indicated in the maps are measured with respect to the direction of the FET active channel.

Figure 2.12 — Analysis of polarization-dependent CMM. The maps of different parameters are obtained by fitting the polarization-dependent CMM (as shown Figure 2.11) with a cosine square equation $I_{(x,y)} = M_{(x,y)} \cos^2(\beta_{(x,y)} - \theta) + C_{(x,y)}$. C is the fraction of the signal independent of the probing light polarization, M is the amplitude of modulation, and β is the direction of preferential alignment of the polymeric backbones. R^2 is the r-squared value of the fitting in each pixel. Equation

$$A_{(x,y)} = \frac{M_{(x,y)}}{M_{(x,y)} + 2C_{(x,y)}}$$

is used to obtain the degree of order in each pixel. The CMM

$\Delta T/T$ map with 0 degree polarization probe is also provided for easy comparison.

regime¹⁸⁰ instead of accumulation. Besides, such microscopy technique also allows studying the charge injection landscape of an FET.¹⁶³

Conventional CMM is performed by using a static and focused light source to raster scan the FET sample,^{163, 175, 176, 180} which requires long acquisition duration especially for large probing areas. In a recent demonstration, a CCD (charge-coupled device) camera was incorporated to simultaneously acquire the 2-dimensional charge distribution along FET active channel.¹⁸⁶ Such technique is typically used to perform thermoreflectance imaging.^{187, 188}

2.4. Spectroscopic signatures of conjugated polymers

Typical organic semiconductors have intrinsically low electrical conductivity owing to the relatively low charge density and carrier mobility.¹⁸⁹ A conventional method to enhance charge transport properties in semiconductors is doping,¹⁹⁰ which can generally increase the conductivity by few orders of magnitude. Unlike in conventional inorganic semiconductors, the terminology “oxidation” and “reduction” is used when referring to p-type and n-type doping in organic semiconductors. p-type or n-type doping affects the π -electrons in polymers. Charge carriers induced by doping are delocalized over single or multiple polymer chains depending on the nature of the structure-properties relations.^{9, 11, 42, 191} The common doping methods used for organic semiconductors are summarized in below:

Chemical doping requires exposure of organic semiconductors to oxidizing or reducing agents. Typically, reducing agents such as alkali metals are used to achieve n-type doping, while p-type doping is obtained with iodine and bromine. The doping process however produces extra counter-ions left by the reduced oxidizing or the oxidized reducing agents, which compensate the doping charges. Chemical doping effect is permanent, but can be reversed by “inverse-doping”.

Photo-doping generates charges through excitation of electrons into higher excited

states by photon absorption and subsequent charge separation. This doping method produces a local oxidation accompanied by local reduction. This effect is temporary, since the excited charge carrier species will eventually relax or decay to the ground or trap states. Photo-doping is the basic excitation mechanism of photo-induced absorption and photocurrent measurements.

Interfacial doping is achieved through injecting charge carriers directly into the organic semiconductor. In this case, holes and electrons are injected to the π and π^* bands of an organic semiconductor, respectively. p-type doping removes electrons (same as adding holes), while electrons are added for n-type doping. Compared to other doping methods, interfacial doping does not produce counterions. Similar to photo-doping, interfacial doping is temporary and lasts only while a biasing voltage is applied. Interfacial doping is the principal mechanism to perform CMS studies on carrier injection and accumulation at semiconductor-dielectric interfaces.

2.4.1. Polaronic signatures

Polarons are originated from self-trapping of charge carriers due to its strong interaction with phonons. It can also be visualized as charged quasi particles that are localized within potential wells stem from a localized lattice distortion. (Note that delocalized polarons are not considered here) In general, polarons can be found in various classes of materials, including molecular crystals, polar and ionic solids, and polymers.¹⁰⁸ Polarons in solids can be generally categorized into “large polaron” and “small polaron”, subjected to the electron-phonon interaction range and size. (Other species, such as bipolaron, polaron-excitons, etc. are not discussed here). Hence, description of polarons in conjugated polymers, as illustrated in subsequent paragraphs, should be accounted as “small polaron”, since it is localized species with a short range phonon interaction and a relative smaller size to the

lattice constant.

Figure 2.13A shows p-type doping of a poly(alkylthiophene) chain, where polarons are formed upon introduction of extra charges. The polymer lattice is distorted by changing the configuration in the vicinity of the charges, thus splitting the polymer backbone into regions with different ground states to accommodate the extra charges induced by doping. For the case of poly(thiophene), the non-degenerate ground states are the lower energy neutral (Figure 2.13B) and higher energy quinoid (Figure 2.13C) states. The lattice distortion caused by doping is restrained within a few monomeric units, hence polarons are self-localized carrier species.

For the ideal case of an infinitely long neutral polymer chain, HOMO and LUMO states are delocalized along the polymer chain with substantial dispersion and bandwidths of several electron volts.¹⁹² These HOMO and LUMO states are equivalent to the valence band (VB) and the conduction band (CB), respectively, of inorganic semiconductors. Figure 2.14A shows the typical energy levels of non-degenerate ground state conjugated polymers. The energy difference between the HOMO and the LUMO energy levels is referred as the bandgap E_g of the conjugated polymers, while π - π^* transitions refer the promotion of electrons from π bonding orbital to π^* antibonding orbital through excitations. In a neutral

Figure 2.13 — Doping in organic semiconductors. (A) p-doping of poly(alkylthiophene). (B, C) Neutral (B) and quinoid (C) groundstates of polythiophene.

conjugated polymer, states are forbidden within the bandgap.

Upon oxidation of a conjugated polymer chain, *i.e.* removal of an electron from the HOMO orbitals, a positive polaron is formed (Figure 2.14B) along with introduction of extra states within the bandgap. This allows extra polaronic transitions (P1 and P2) that are reduced in energy compare to the bandgap of the organic semiconductor. These transitions are signatures of polarons localized within a polymer chain as a result of intramolecular charge transfer. P1 can be probed in mid-infrared region while P2 are typically observed in visible or near infrared region.

Other than intramolecular charge transfer, intermolecular charge transfer may also occur by “jumping” or “hopping” of charges from one polymer chain to another. This is an essential process for allowing charge transport in molecular systems below percolation threshold and polymer chains with finite length. For P3HT, polarons are delocalized over several π -stacked chains rather than confined to a single chain,¹⁹³ due to high degree of interchain interaction. Figure 2.14C shows

Figure 2.14 — Polaron transitions in non-degenerated ground state organic semiconductors. (A, B, C) Schematic of the energy levels of a neutral polymer chain (A), a polaron on an isolated chain (B), and a polaron delocalized over two co-facial chains (C).

that polaronic levels are further split into another two states in the case of polaron delocalized over two cofacial polymer chains. Thus, two additional allowed polaronic transitions (DP1 and DP2) are introduced on top of P1 and P2.¹⁹⁴ DP1 is red-shifted compared to the P1 transition, while DP2 is blue-shifted compared to the P2 transition.

2.4.2. Vibrational signatures

Other than polaronic absorption, introduction of charge carriers into organic semiconductors is also manifested by the appearance of infrared active vibrational (IRAV) modes in the mid-IR region.²⁷ The IRAV modes arise from conversion of even parity Raman modes to odd parity IR modes due to the breaking of local translational symmetry in the presence of extra charge carriers. IRAV modes also show one-to-one correspondence to the strongest vibrational modes from IR and Raman spectra.^{179, 195} The intensity of IRAV modes is directly proportional to charge density, which makes it a sensitive and selective signature for probing charge carriers in conjugated polymers.¹⁹⁵

The origin of IRAV modes is related to the perturbation from the extra charge carriers, which causes localized optical-phonon modes to split off. The frequencies of IRAV modes are determined by the characteristic pinning potential of restoring forces that are against the translation of charges, where the pinning potential corresponds to the lowest frequency mode.^{196, 197} Amplitude mode formalism was first developed to predict the frequencies and oscillator strengths of the resonance of the Raman-active A_g modes.¹⁹⁷ An effective conjugation coordinate (ECC) model was later developed by Zerbi *et al.* to interpret the activation of IRAV modes and the phonon dispersion behavior by accounting the molecule geometry changes due to excitation of molecules from ground state to the excited state.¹⁹⁸ Amplitude mode formalism was then extended to describe the overlapping of anti-resonances and quantum interferences of IRAV modes with the polaronic transitions in the

PIA spectra.¹⁹⁹ Recently, Yin *et al.* utilized first principles response calculation to describe the quantitative assignment of IRAV modes (frequencies and intensities) by taking the ground, charged, and singlet excited-state vibrational normal modes into account.¹⁹⁵

2.4.3. Electroabsorption and Stark effect

Electroabsorption (EA) is a characteristic absorption feature in semiconductors due to the presence of an external electric field. The external electric field interacts with the dipoles in the semiconductor, resulting in the alignment of dipole moments to the same or opposite direction of the external electric field. In a homogenous electric field, the alignment of dipole moments splits the field-free level into two symmetric energy levels (Figure 2.15), where the lower and higher energy levels correspond to the directions of dipole moments pointing to the same and opposite directions of the electric field, respectively. Therefore, the absorption edge of a semiconductor is shifted to lower energies or higher wavelengths.^{9, 200} The splitting of energy levels due to the external electric field is known as Stark effect. The shift of energy levels is given by

$$\Delta E = \vec{\mu}F + \frac{1}{2} \vec{p}F^2 \quad (2.10)$$

The first term of the Equation 2.8 represents a linear shift in energy due to the interaction with permanent dipole moments $\vec{\mu}$, which is also known as linear Stark effect. Typically, an ideal centrosymmetric nondegenerate polymer has no dipole moment, but permanent dipoles can ensue from disorder, charge transfer states, or defects.²⁰⁰⁻²⁰² However, this term is effectively zero when considering the average over isotropic and randomly oriented molecules, $\langle \vec{\mu}F \rangle = 0$. The second term of Equation 2.8 arises from the interaction between induced dipole moments and the external electric field, which has quadratic dependence. The effect is also known as

the quadratic Stark effect. In this case the amount of energy shift depends on the dipole polarizability, $\bar{\rho}$, and the strength of the external electric field.

According to perturbation theory, an EA spectrum is given by a linear combination of absorption spectrum with all orders of field perturbations. Therefore, the main spectral contributions stem from the first and second orders of the field dependence.^{9, 200} Hence the change in absorption $\Delta\alpha$ due to EA should be equal to:

$$\Delta\alpha = \left\langle \frac{\partial\alpha}{\partial E} \Delta E \right\rangle + \frac{1}{2} \left\langle \frac{\partial^2\alpha}{\partial^2 E} \Delta E^2 \right\rangle \quad (2.11)$$

The first term is mainly contributed by the quadratic Stark effect, since the linear Stark effect is effectively zero when considering the average over isotropic and randomly oriented molecules. However, the term $\bar{\mu}F$ does not necessarily provide zero net contribution to the second term of Equation 2.9, as isotropic averaging of the squared of the term gives $\langle (\bar{\mu}F)^2 \rangle = 1/3(\mu F)^2$. Hence, the first derivative of

Figure 2.15 — Stark effect. (A, B) Schematic of the energy levels of field-free polymer chain (A) and the splitting of energy levels due to the presence of electric field (B).

the absorption corresponds to the quadratic Stark effect, while the second derivative of the absorption corresponds to the linear Stark effect. The change in absorption $\Delta\alpha$ shall then follow:

$$\Delta\alpha = \frac{1}{2} \left[-\Delta P \frac{\partial\alpha}{\partial E} + \frac{1}{3} \mu^2 \frac{\partial^2\alpha}{\partial^2 E} \right] F^2 \quad (2.12)$$

As shown in Equation 2.10, $\Delta\alpha$ has quadratic dependence on external electric field. For typical EA measurement, an electric field of $F = F_{AC} + F_{DC}$ is applied to the sample. In non-injecting bias condition, the EA signal response shall experimentally follow the simplified equation:

$$\Delta \frac{T}{T}(\lambda) = \chi(\lambda) \left[\frac{F_{AC}^2}{2} (1 + \cos(2\omega t)) + 2F_{AC}F_{DC} \cos(\omega t) + F_{DC}^2 \right] \quad (2.13)$$

Where λ is the wavelength, χ is the electric susceptibility tensor, F_{AC} and F_{DC} are the alternating (AC) and direct (DC) components of the electric field, ω is the modulation angular frequency $2\pi f$ (f is modulation frequency), and t is time. This means that the first harmonic (1ω) of the signal is proportional to both the AC and DC component of electric field, while the second harmonic (2ω) of the signal is only proportional to the square of the AC component.

In principle, EA and CMS spectra can be acquired by using the same setup. The latter is obtained by biasing the device into full accumulation, while the former is biased in full depletion to avoid signal screening from injected free carriers.⁹ Notably, for organic light-emitting diodes, EA experiments are very useful and effective to measure the internal field as well as the built-in potential in the device.²⁰³⁻²⁰⁵

Chapter 3

Unipolar field-effect transistors

In this chapter, we implement IR-CMS to study the carrier distribution in an operating p-channel FET and the structure-properties relation of semiconductor-dielectric interface with an n-channel FET. In the first section of the chapter, a simple on-off IR-CMS approach, with incorporation of a tabletop FTIR-confocal setup, is used to probe low-energy polaron bands and infra-red active vibrational (IRAV) modes. Thanks to high specificity and strong oscillator strength of IRAV modes, IR-CMS is utilized to quantify charge carrier density and to map polaron distribution across the FET channel. To perform this study, we used a prototypical p-channel material P3HT as the active material to validate our IR-CMS setup with tabletop FTIR-confocal system, as it is one of the most studied organic conjugated polymers for studying photophysics in organic semiconductors.^{30, 33-36} Upon establishing the IR-CMS measurement with a prototypical p-channel materials, we proceed to demonstrate that IR-CMS can be utilized to study structure-properties relation of an n-channel material, as most structure-transport characteristics has only been performed with p-channel materials. In the second section of the chapter, we choose P(NDI2OD-T2) as it is a high mobility material that has been used as prototypical materials for studying n-channel conjugated polymer system.^{37-41, 43, 46, 175, 183, 184, 206-226} Specifically, we study the influence of gate dielectric hydrophobicity, adjusted by chemical modification of gate dielectric with different self-assemble

monolayers, on the charge transport properties of n-type P(NDI2OD-T2) bottom-gated FETs. The charge transport properties of such devices are studied with FET characterization. Finally, we implemented IR-CMS to resolve the molecular orientation at the semiconductor-dielectric interface by analyzing the normal IR modes of the conjugated polymers.

3.1. p-channel P3HT transistors

In this section, we explore the benefits of large oscillator strength of IRAV modes and the low energy polaron bands to elucidate the carrier distribution across a p-channel FET in different operating bias regimes. Optimization of charge transport properties in FETs relies on understanding primary charged excitations in conjugated polymers as well as on device physics. Conventionally, photoinduced absorption (PIA)^{11, 168-170} and photocurrent^{6, 171, 172} spectroscopy are used to study charge injection and accumulation in conjugated polymers for photovoltaic application. In comparison, charge modulation spectroscopy (CMS) is developed as a complementary technique to study charge excitations in organic semiconductors, typically for FET devices.^{8, 9, 11} Unlike chemical or photo-induced absorption, CMS detects polaron induced absorption and bleaching features of injected charges, without the associated counterions.^{9, 12, 159-164} Besides, CMS allows sensitive detection of polarons in nanometer-thick accumulation layer¹⁸³ as well as a quantitative estimate of the charge carrier density¹⁶³ in selective hole or electron accumulation mode.^{54, 173}

A spatial map of CMS local features across FET channel provides information on injection landscape and charge distribution in different operating regimes.^{160, 164} Charge modulation microscopy (CMM) was previously implemented in visible and near-IR to obtain information on different structural conformation and carrier distribution.^{175, 176} Here we explore the advantage of the unique vibrational signatures of charge carriers in conjugated polymer FETs by performing CMM in

the mid-infrared.^{9, 11, 163}

By coupling CMS to a confocal microscope, we spatially record CMS by acquiring the difference in reflectance with and without charge accumulation. Unlike other CMS techniques, where the change in optical signal is acquired with phase-sensitive lock-in amplifier, our on-off technique allows probing the quasi-static behavior of the FET. This approach was proven sensitive to slow and trapped charges when implemented in visible and near-IR to study water-induced and oxygen-induced instabilities in P(NDI2OD-T2).¹⁸³ CMM in mid-IR has previously been demonstrated with bright synchrotron radiation, where limited spatial resolution required V-shape transistor channel to study the charge injection length scale.^{163, 227} In comparison, our approach utilizes a simple confocal microscope, with diffraction-limited resolution, coupled to a table-top FTIR, to quantify charge density and to map polaron distribution in a working conventional FET device. As a proof-of-principle, we adopted P3HT, one of the most studied prototypical polymer for photovoltaic application,²²⁸ as the active material to study carrier distribution in FET devices and aging effects in ambient conditions.

3.1.1. Transistor characteristics and vibrational modes of P3HT

To perform CMS measurement, P3HT was chosen as the active material to fabricate FETs. Figure 3.1 shows the current-voltage characteristics of the fabricated P3HT FETs and the respective device configuration (figure inset). The P3HT FET displays textbook output characteristics (Figure 3.1A) with saturation mobility and threshold voltage of $3.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 4.1 V, respectively, as extracted from transfer characteristics (Figure 3.1B). The relatively low mobility of P3HT compared to previous publications ($> 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)³⁰ is related to the use of PMMA to reduce the gate leakage current (Figure 3.4B).^{229, 230} The low hysteresis and ideal FET characteristics of these P3HT FETs, however, make them suitable

Figure 3.1 — Current-voltage characteristics of P3HT FET. (A, B) Output (A) and transfer (B) characteristics of P3HT FET. The inset of (B) shows the schematic configuration of P3HT FET and the molecular structure of P3HT. The thickness of P3HT, PMMA, and SiO_2 is 100 nm, 500 nm, and 500 nm, respectively. Extracted saturation threshold voltage is 4.1 V. Measurements were performed in inert gas environment.

for CMS measurements.

Since the FET device is not transparent in spectral region of interest, we perform CMS (Figure 3.2A) only in reflectance. Typical CMS reflectance spectrum shows similar spectral signatures as photo-induced absorption in transmission (Figure 3.2B) and reflection modes (Figure 3.2C), indicating the equivalence between interfacial doping and photo-doping by charge accumulation and optical excitation, respectively. This validates the approach to use back reflectance geometry for CMS measurement on mid-IR opaque substrates. The IRAV modes, as seen in CMS and PIA spectra (indicated with dashed lines in Figure 3.2), show one-to-one correspondence to the IR (Figure 3.2D) and Raman (Figure 3.2E). IRAV modes originate from the breaking of symmetry related to the strong coupling between self-localized polarons on the local chain distortion and the polymer backbone, which converts even parity Raman modes into odd parity IRAV modes.^{9, 169, 231} In typical P3HT with relatively high mobility, IRAV modes appear as sharp Fano antiresonances in PIA and CMS spectra, and overlap with the low energy polaron band around $1100 \pm 500 \text{ cm}^{-1}$.^{11, 232, 233} Besides, IRAV modes also reveal the charge

Figure 3.2 — Comparison of CMS IRAV modes with PIA, PIR, IR and Raman spectra. (A) CMS reflectance acquired in ambient environment with $V_{\text{on}} = -50$ V, $V_{\text{off}} = 25$ V, and $V_{\text{ds}} = 0$ V. (B, C) Photo-induced absorption (B) and photo-induced reflectance (C) of P3HT thin film. Spectra are acquired at 78 K with $\lambda_{\text{ex}} = 532$ nm and laser excitation intensity $I = 30$ mW/cm². (D, E) Infrared absorption (D) and Raman (E) spectra. Dashed lines indicate the main vibrational modes and the corresponding numbering on the top panel (A) refers to their mode assignment in Table 3.1.

carrier oscillations along the polymer chain and possess large oscillator strength.^{169, 234, 235} Therefore, they can be utilized as a selective and sensitive signature for probing the density and distribution of polarons in CMM experiments.

While analytical theory has previously been established to study Fano antiresonance features of IRAV modes in conjugated polymers such as frequencies, oscillator strengths, and relative intensities,^{197, 233} here we model the IRAV features by employing first principle density functional theory (DFT) calculations. The main transitions of experimental and calculated infrared and Raman modes, together with IRAV modes of PIA and CMS are summarized in Table 3.1. The details of the first principle study are published in ref. 195.

Table 3.1 — Assignment of main vibrational transition modes in P3HT. The table summarizes the experimental and calculated (bracket) IR modes, IRAV modes of PIA and CMS, and Raman modes of P3HT.

Modes No	IR (cm ⁻¹)	Assignments	PIA-IRAV (cm ⁻¹)	CMS-IRAV (cm ⁻¹)	Raman (cm ⁻¹)	Assignments

1					599 (595)	C _α -S-C _α ring deformation
2			678		678 (661)	C _α -S-C _α symmetric deformation
3	726 (720)	Hexyl rocking vibration	725	726	727	C _α -S-C _α asymmetric deformation
4	817 (815)	C _β -H out-of plane vibration	817	821		
5			1002		1005	C _β -C _{alkyl} stretching
6			1084	1033, 1066	1090	C _α -H and C _β -H bending
7	1378 (1386)	Terminal CH ₃	1375	1379	1383 (1358)	C _β -C _β symmetric stretching
8	1456 (1451)	C _α =C _β symmetric stretching	1450	1450	1450 (1430)	C _α =C _β symmetric stretching
9	1512 (1500)	C _α =C _β asymmetric stretching	1512	1514	1512 (1512)	C _α =C _β asymmetric stretching

3.1.2. Carrier density quantification and distribution

To calibrate the spectral density to the accumulated charge concentration, we consecutively acquired the FET transfer characteristics (Figure 3.3A) and CMS spectra (Figure 3.3B) in ambient environment. The duration between subsequent runs is about 30 minutes. Exposure to oxygen and moisture is known to cause oxidation of the P3HT thin film, hence creation of trap states.²³⁶⁻²³⁸ Besides, oxidation also induces doping, which results in the change of FET operating mode from normally OFF (zero drain-source current at $V_{gs} = 0$ V) to normally ON.^{229, 238,}

²³⁹ This is reflected by the shift in threshold voltage ΔV_{th} , with respect to the pristine device, that eventually saturates (Figure 3.3A). Similarly, when acquiring consecutive CMS spectra with gate voltages $V_{on} = -60$ V and $V_{off} = 100$ V and drain-source bias of 0 V, the IRAV intensity increases and saturates (Figure 3.3B), as observed for the antiresonance peak around 1730 cm^{-1} related to the C=O double bond.²⁴⁰ This proves the sensitivity of CMS measurements to the chemical changes as well as the change in charge carrier density in the FET channel induced by electrostatic doping. To quantify these effects, the effective spectral density of

Figure 3.3 — Characterization of aging effects in P3HT FET operating continuously in ambient condition. (A) Successive FET transfer characteristics measured with $V_{ds} = -60$ V. (B) Successive CMS spectra acquired in ambient environment with $V_{on} = -60$ V, $V_{off} = 100$ V, and $V_{ds} = 0$ V. (Each spectrum is offset by 10^{-3} for clarity). (C) Dependence of doping-induced effective carrier density ($N_{eff} = \int |-\Delta R / R| d\omega$, integrated from 680 to 1700 cm^{-1}) and ΔV_{th} on number of run. (D) Linear dependence between ρ_{2D} and $N_{eff,doping}$. This relation is applied to quantify polaron density from CMS measurements. The fitting of the slope is $(1.57 \pm 0.12) \times 10^{16}$ carriers/ m^2 per wavenumber (cm^{-1}).

IRAV modes $N_{\text{eff}} = \int |\Delta R / R| d\omega$ ^{162, 163} is calculated by summing the absolute value of CMS spectra in the spectral region containing IRAV modes, *i.e.* from 680 to 1700 cm^{-1} wavenumbers, as confirmed by DFT calculations (Table 3.1). As plotted in Figure 3.3C, the doping-induced effective spectral density is obtained by subtracting the subsequent effective spectral density values to the value obtained by the device in pristine condition (run #1), *i.e.* $N_{\text{eff,doping}} = N_{\text{eff}} - N_{\text{pristine}}$. The similar behavior between $N_{\text{eff,doping}}$ and ΔV_{th} (Figure 3.3C) suggests a shared common cause, which is most likely due to the chemical-induced doping of the device that increases polarons density. Previously the saturation of N_{eff} , as observed in Figure 3.3C, was related to either the gate leakage current of the FET or to the induced metal-insulator transition at high carrier densities.¹⁶³ Here we reduced the gate leakage ($I_{\text{gs}} \sim -1$ nA at $V_{\text{gs}} = -80$ V, Figure 3.4B) by including the additional PMMA layer on top of SiO_2 . Besides, our CMS spectra do not display monotonic, Drude-like absorption of delocalized polaron states in the far-IR, which is expected when metal-insulator transition occurs.¹⁶² This suggests that metal-insulator transition in P3HT does not take place at carrier densities lower than 10^{16} holes/ m^2 , the maximum achievable carrier concentration in this work.

Figure 3.4 — Control CMS and gate leakage measurements. (A) Control CMS measurements on devices with (blue) and without (black and red) P3HT active layer. (B) Gate leakage of P3HT FET. The curve is obtained with $V_{\text{ds}} = 0$ V.

Moreover, we can individually estimate the doping-induced carrier density by using a simple capacitive model, $\rho_{2D} = \frac{\kappa\epsilon_0}{ed} \Delta V_{th}$, where the capacitance per unit area $\frac{\kappa\epsilon_0}{ed}$ of gate dielectric (500 nm of PMMA + 500 nm of SiO₂) is estimated to be ~ 2.8 nF cm⁻². This enables us to calculate the carrier density ρ_{2D} as a function of measured ΔV_{th} at each run. We further plotted ρ_{2D} as a function of corresponding $N_{\text{eff,doping}}$ (Figure 3.3D) to obtain the correlation between the effective spectral density of IR/V modes and the accumulated carrier concentration in the FET active channel. Here we assume that the charge carrier density ρ_{2D} is linearly proportional to effective spectral density $N_{\text{eff,doping}}$ (Figure 3.3D) because of two reasons: First, it is known that, from chemical doping^{162, 163} and photo-doping^{168, 169, 232, 233} experiments, differential signal is linearly dependent to the (photo- or chemical) doping density at low doping densities such as those electrically induced in our experiments; Second, non-linearity of the differential signal could occur due to a metal-insulator transition, where the differential spectra of a high density doping of P3HT thin film are signified by appearance of monotonic, Drude-like absorption of delocalized

Figure 3.5 — Control CMS and FET measurements. (A) Three consecutive CMS reflectance measurements in ambient environment. Spectra are acquired with $V_{ds} = 0$ V and gate modulation of $V_{on} = -60$ V and $V_{off} = 40$ V. (B) Three consecutive transfer measurements of FET in ambient condition at $V_{ds} = -60$ V. The table in the inset of panel (B) summarizes the extracted mobilities and threshold voltages.

polaron states in the far-IR, for which we have no evidence in our CMS spectra. A proportionality constant of 1.57×10^{16} carriers/m² per wavenumber (cm⁻¹) is obtained from a linear fitting of the data in Figure 3.3D. This gives a direct numerical correlation of integrated signal of CMS spectra to charge carrier density in the FET channel.

Other than obtaining an estimate for the accumulated carrier density, we performed hyperspectral mapping to record the spatial distribution of charge carriers across the active channel of the FET by CMM. CMM mapping has previously been demonstrated in the visible and near-IR spectral regions,¹⁷⁵ while such mapping in mid-IR required large-area devices and V-shaped electrodes to obtain the charge injection landscape.^{163, 164} Here we utilized a high-sensitivity FTIR confocal microscope to perform hyperspectral mapping of carrier concentration across the FET channel with conventional parallel source-drain electrodes. Charge

Figure 3.6 — Three-dimensional representation of carrier distribution across the P3HT FET at different applied V_{ds} . The 2D charge carrier density (ρ_{2D} , z -axis) is obtained by analyzing IR-CMS spectra. x_d denotes the distance from the drain electrode. The CMS mapping is acquired with gate modulation biases of $V_{on} = -60$ V and $V_{off} = 80$ V. The color map is represented in logarithmic scale. The channel length of the FET device is 150 μm .

Figure 3.7 — CMS reflectance mapping across the P3HT FET channel. (A, B) CMS mapping with drain-source bias of 0 V (A) and -120 V (B) with gate modulation biases of $V_{\text{on}} = -60 \text{ V}$ and $V_{\text{off}} = 80 \text{ V}$.

density mapping of various V_{ds} between 0 V and -120 V ($V_{ds} = 0, -30, -60, -90, -120 \text{ V}$) are obtained by fixing the gate modulation at $V_{\text{on}} = -60 \text{ V}$ and $V_{\text{off}} = 80 \text{ V}$. By keeping the V_{off} above the threshold voltage of the device ($V_{\text{off}} < V_{th} \sim 100 \text{ V}$ for this particular device), the acquired CMS spectra do not change over time and depend only on induced carrier density within each modulation cycle, despite of slight oxidation of the active material throughout the measurement in ambient

environment. This is evidenced by the stability of the observed CMS spectra and FET saturation mobility over time despite of the obvious threshold voltage shift (Figure 3.5).

Figure 3.6 shows the 3-dimensional plot of charge carrier density (ρ_{2D}) across the P3HT FET channel (shown as a function of distance from drain electrode x_d) at different applied V_{ds} . ρ_{2D} are deduced from the linear correlation obtained in Figure 3.3D and calculation of N_{eff} of IRAV modes (Figure 3.7, only measurements with $V_{ds} = 0$ V and -120 V are shown). The spot size of the probe beam is ~ 40 μm , and steps of 20 μm are used to scan the IR beam across the FET channel. From Figure 3.6, we observe a notable drop of carrier density when x_d is higher than 100 μm and lower than 40 μm . This can be attributed to the higher reflection of the IR beam illuminating partially/fully the metallic electrodes, which gives a signal convoluted with the actual differential reflectance from the active channel of the FET. To improve spatial resolution, the beam spot size could be reduced down to its diffraction limit. However, this would result in lower signal-to-noise ratio and longer acquisition time (the entire mapping with conditions used took ~ 3 hours).

When the applied V_{ds} is lower than -90 V, we observe a fairly constant carrier density of $\sim 3 \times 10^{16}$ carriers/ m^2 distributed along the FET channel. For higher V_{ds} biases, *i.e.* $V_{ds} \geq -90$ V, the polaron distribution is modulated closer to the drain electrode, where the density is lower. This is due to the decrease of the local potential close to the drain when V_{ds} is applied, and results in carrier density depletion, similar to previously reported CMM studies.^{160, 175}

3.2. n-channel P(NDI2OD-T2) transistor

In this section, we exploit the unique IRAV modes in conjugated polymers as well as FET current-voltage characteristics to study the effect of gate dielectric surface

treatment on the n-channel transport of bottom-gated P(NDI2OD-T2) FETs. In FETs, charge transport occurs at the nanometer-thick charge accumulation layer, which is strongly affected by the engineering of the semiconductor-insulator interface.⁴² Understanding the structure-properties relations^{39, 45, 47, 215, 225} at different length scales helps developing high mobility ($\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) FETs.^{38, 45, 49, 215} For top gated FET devices, low dielectric constant materials are typically chosen to favor charge transport in FETs.^{42, 159, 241} Meanwhile, surface passivation is proven to be important for bottom gated FETs, especially in devices with SiO_2 substrates. The passivation of trap states from hydroxyl group on SiO_2 was shown to lead to improvement in device performance and generally to ambipolar charge transport in conjugated polymers.¹⁴⁴ Amongst the surface passivation techniques, the use of self-assemble monolayers (SAM) is a facile and effective method to improve charge transport as well as air stability.^{131, 132, 242-245} Treatment with organosilane molecules typically increases hydrophobicity of the SiO_2 surface. For PB16TTT^{242, 243} and P3HT,^{30, 33-36} carrier mobility was found to be monotonically dependent on the surface hydrophobicity of SiO_2 . For thiophene-based conjugated polymers such as P3HT, the improvement of mobility is related to the formation of larger and better crystalline semiconductor domains allowed by the promotion of edge-on orientation and π - π stacking parallel to the substrates, as well as to the better interconnectivity between grains of crystallized semiconductor domains on low surface energy surfaces.^{33-36, 246} However, this relation is not generally true as the performance of high molecular weight P3HT was also insensitive to the treatment.^{36,}

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Despite of the plethora of studies on p-type conjugated polymers, fewer efforts have been devoted to understanding the effect of surface energies on the charge transport of an n-channel conjugated polymer. Here we chose a high performance n-type conjugated polymer P(NDI2OD-T2)(Poly{ [N,N9-bis(2-octyldodecyl)- naphthalene-

1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,59-(2,29-bithiophene) } , Polyera Ink N2200, molecular structure shown in the inset of Figure 3.8D), to study charge transport dependence on different surface treatments of SiO₂. The microstructure of P(NDI2OD-T2) thin film was initially found to form a disorder matrix with crystalline domains showing preferable face-on orientation, as revealed by grazing-incidence X-ray scattering (GIXS) analysis.³⁹ The face-on texture of thin films is conventionally understood to be unfavorable for charge carrier transport, although field-effect mobility measurements suggested otherwise.³⁸ This is in contrast to the conventional perception that edge-on packing provides enhanced charge transport properties facilitating hopping of charge carriers between neighboring conjugated segments.⁴² It has also been shown that bulk orientation changes from face-on to edge-on upon melt treatment with slow cooling, resulting in a drop in mobility measured with electron only diode, while field-effect mobility of bottom-gated FETs remains similar.^{43, 225} Near edge X-ray absorption fine structure (NEXAFS) spectroscopy was employed to show that the first few layers of thermally annealed spin-coated thin films have edge-on orientation on the top surface, while face-on orientation is still preferred in the bulk of the film.^{43, 44} This microstructure is consistent with the demonstrated high bulk mobility⁴⁰ in diode structures and low contact resistance in staggered structure FETs.⁴¹ However, the semiconductor-dielectric interface, which hosts the active charge transport layer, is buried underneath for bottom gated FETs. Therefore, selective structural information on the molecules cannot be accessed through techniques such as GIXS, NEXAFS, and atomic force microscopy.^{38, 43, 44} To unveil structure-function relationships at the active channel of FETs, we performed IR-CMS on the FET with different surface hydrophobicity induced by SAM molecule treatment. By probing the low energy polaron band and infrared active vibrational (IRAV) modes, we were able to resolve the relative orientation of the conjugated polymer segments relative to the substrate by examining the normal modes of IRAVs assigned by complementary

Raman and IR absorbance measurement. The change in molecular orientation is also correlated with charge transport and activation energy extracted from temperature-dependent FET measurements.

3.2.1. Self-assemble monolayer treatment

SAM molecule treatment on SiO_2 surface can modify the surface energy. Typically, these SAM molecules consist of end substituents of hydrophilic and hydrophobic components, with the former being physically adsorbed or chemically bonded to SiO_2 surface and the latter forming a lower energetic surface.^{248, 249} Here we used hexamethyldisilazane (HMDS)²⁵⁰ and octyltrichlorosilane (OTS)²⁵¹ (their molecular structures are shown in the inset of Figure 3.8E and Figure 3.8F, respectively) to modify the surface tension of the SiO_2 and study the effects of these modifications on P(NDI2OD-T2) FET performance. For the case of HMDS, two OH groups on the SiO_2 surface are passivated by methyl-terminated groups.²⁵⁰ With similar mechanism, OTS passivates the SiO_2 surface with octyl-terminated groups.²⁵¹

The effectiveness of the SAM treatment can be easily tested by examining the surface hydrophobicity with contact angle measurements (Figure 3.8A to Figure 3.8C).²⁴³ The degree of surface energy is directly indicated by the measured contact angle, where high contact angle is formed on surfaces with low surface energy.²⁵² As shown in Figure 3.8, the measured contact angle of deionized water on untreated, HMDS-, and OTS-treated SiO_2 are 59, 93, and 110 degree, respectively, similar to the previous results reported in the literature.^{33, 242, 243, 246}

We further examine the effect of the different SAM treatments by studying the field-effect charge transport of high performance n-channel materials, P(NDI2OD-T2), with a bottom-contact bottom-gate FET configuration (see inset of Figure 3.8D). The output characteristics of P(NDI2OD-T2) FETs with different SAM treated SiO_2 are shown in Figure 3.8D to Figure 3.8F, while Figure 3.8G to Figure

3.8I show the transfer characteristics. We observe a nonlinear current dependence at low drain-source voltage in all output characteristics, indicating that contact resistance is not negligible in all FET devices, regardless of the different SAM treatments. The origin of contact resistance is related to the imperfect alignment of the HOMO/LUMO of the active materials to the work function of the electrode, which forms a potential barrier for charge carriers injection.²⁵³ To minimize the influence of contact resistance, we extracted the mobility from the transfer characteristics measured in the saturation regime ($V_{ds} = 60$ V), where resistance due to space charge effect is likely to dominate over the contact resistance.¹³⁴ The

Figure 3.8 — Characterization of SAM surface treatments. (A, B, C) Contact angle measurements of 5 µl of deionized water on non-treated (A), HMDS-treated (B), and OTS-treated (C) SiO₂ dielectrics. (D, E, F) Output characteristics of P(NDI2OD-T2) FETs with non-treated (D), HMDS-treated (E), and OTS-treated (F) SiO₂ dielectrics. (G, H, I) Transfer characteristics of P(NDI2OD-T2) FETs at drain-source of 60 V with non-treated (G), HMDS-treated (H), and OTS-treated (I) SiO₂ dielectrics. The extracted mobilities are summarized in Table 3.2. The inset of panel (D) shows the molecular structure of P(NDI2OD-T2) and the FET configuration. The insets of panel (E) and (F) show the molecular structures of the SAM molecules HMDS and OTS, respectively. The channel length and width of the P(NDI2OD-T2) FETs are 100 µm and 20 mm, respectively.

Table 3.2 — Summary of n- channel saturation mobilities and threshold voltages of P(NDI2OD-T2) FETs with different surface treated SiO_2 dielectrics. The values are extracted from transfer characteristics measurements shown in Figure 3.8(G, H, and I). Statistical differences of mobilities and threshold voltages from difference devices are available in Figure 3.9.

Treatment	Saturation Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Saturation Threshold Voltage (V)
Non-treated	0.02	8.5
HMDS	0.06	7.4
OTS	0.15	16.9

Figure 3.9 — Statistical analysis. (A, B) Statistical analysis of mobility (A) and threshold voltage (B) extracted from untreated (contact angle = 59 deg), HMDS (contact angle = 93 deg), and OTS (contact angle = 110 deg). The values are obtained over averages of 16 devices with channel length of 80 or 100 μm and channel width of 20 mm.

mobilities extracted from conventional gradual channel approximation analysis¹³⁴ are 0.02, 0.06, and 0.15 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for non-treated, HMDS, and OTS treated surfaces, respectively. The threshold voltages are also summarized in Table 3.2, while statistical differences of mobility and threshold voltage are reported in Figure 3.9. The mobility of HMDS-treated FETs is about thrice of that of the untreated devices, while mobility of FETs with OTS treatment is improved by almost an order of magnitude; the latter value is close to mobilities of P(NDI2OD-T2) bottom gated FETs reported in the literature.^{225, 254} We note that the FET mobility is

Figure 3.10 — p-type saturation and n-type linear transfer characteristics of P(NDI2OD-T2) FETs with differently treated SiO₂ surfaces. (A) p-type transfer characteristics in saturation regime ($V_{ds} = -60$ V). The extracted mobilities and threshold voltages are summarized in Table 3.3. (B) n-type transfer characteristics in linear regime ($V_{ds} = 5$ V). The extracted mobilities and threshold voltages are summarized in Table 3.4. The channel length and width are 20 μm and 20 mm, respectively.

higher with a more hydrophobic SiO₂ surface, similar to previous studies of FETs with p-type PB16TTT as active material.^{242, 243} Besides, the hydrophobic surface treatment also improves the hole transport (Figure 3.10A and Table 3.3). Due to the fact that the drain-source current is found to be smaller than the gate leakage current (not reported), the hole mobility could not be extracted for the FET with untreated SiO₂. For HMDS- and OTS-treated devices, the saturation hole mobilities are $0.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $2.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Thus, the SAM treatment, simultaneously enhances electron and hole transport in P(NDI2OD-T2), a finding that cannot be attributed to chemical doping, as a dopant only improves transport of one carrier type and deteriorates the opposite kind.²³⁴

To quantify the effectiveness of trap passivation by the SAM treatment, we extracted the sub-threshold slope from the transfer characteristics in the linear regime (Figure 3.10B). Table 3.4 summarizes the linear mobilities and threshold voltages, as well as the extracted sub-threshold slopes. The sub-threshold slope provides a characteristic assessment of the filling of trap states by induced charges

Table 3.3 — Summary of p-channel saturation mobilities and threshold voltages of P(NDI2OD-T2) FETs with different surface treated SiO₂ dielectrics. Values are extracted from the transfer characteristics shown in Figure 3.10A.

Treatment	Saturation Mobility (cm ² V ⁻¹ s ⁻¹)	Saturation Threshold Voltage (V)
Non-treated	-	-
HMDS	0.5×10^{-4}	-68.1
OTS	2.1×10^{-4}	-62.5

Table 3.4 — Summary of n-channel linear mobilities, threshold voltages, and sub-threshold slopes of P(NDI2OD-T2) FETs with different surface treated SiO₂ dielectrics. Values are extracted from the transfer characteristics shown in Figure 3.10B.

Treatment	Linear Mobility (cm ² V ⁻¹ s ⁻¹)	Linear Threshold Voltage (V)	Sub-threshold slope (V/dec)
Non-treated	3.7×10^{-3}	3.5	2.6
HMDS	2.3×10^{-3}	16.9	2.4
OTS	6.6×10^{-3}	32.2	2.1

before conduction of mobile carriers becomes allowed, providing an estimate of the trap density on each SiO₂ surface investigated.²⁵⁵ Besides, systematic study of sub-threshold slopes also helps determining the contamination caused at the semiconductor-dielectric interface by certain fabrication conditions.²⁵⁶ From the linear transfer characteristics, sub-threshold slopes are determined to be 2.1, 2.4, and 2.6 V dec⁻¹ for OTS, HMDS, and untreated device, respectively. This suggests that trap density is lower when SiO₂ surfaces are treated with SAM molecules, indicating that reduction in trap density plays a role in the observed improvement of hole and electron transport in modified FETs.

Unlike the extracted saturation mobility, the linear mobility is higher in the case of FETs with untreated surface than in devices with HMDS-treated surface, while

OTS-treated devices have the highest linear mobility. This can be attributed to the different contact resistance of the two FET devices (see output measurement Figure 3.8), which is likely related to different morphologies on semiconductor-electrode interface because of different treatments.^{134, 253} We note that, in each type of device, the extracted linear mobilities are consistently lower than the respective saturation mobilities. This can be due to underestimation of the extracted linear mobility when using the gradual channel approximation method in the presence of significant contact resistance (see output measurement Figure 3.8).²⁵³

3.2.2. Field-effect mobility activation energy and its implications

In this section, we examine the activation energy (E_A) of FETs with different SiO₂ treatments by performing temperature-dependent FET measurements (Figure 3.11). The mobility drops as the operating temperature is lowered, indicating that charge transport is limited by thermally activated processes, typical of most conjugated polymer systems.²⁴¹ All devices with different SiO₂ treatments display Arrhenius-like dependence, and the extracted E_A are 0.07, 0.11, and 0.13 eV for OTS, HMDS, and untreated devices, respectively. A lower E_A for FETs with higher surface hydrophobicity indicates smaller energetic disorder experienced by charge carrier at

Figure 3.11 — Temperature dependent mobilities of P(NDI2OD-T2) FETs with different SiO₂ surface treatments and transmittance of 500 nm thick PMMA thin film. (A) Arrhenius plot and extraction of activation energies of P(NDI2OD-T2) FETs with different surface treatments. The equation in the inset is used to extract the activation energies E_A . (B) Transmission spectrum of 500 nm thick PMMA thin film.

the SAM treated semiconductor-dielectric interface. Previously, dipolar dielectric surfaces were known to cause carrier localization through electronic polarization, which broadens the of localized polaron states, as indicated by the increase in mobility activation energy^{42, 159, 241} Typically, HMDS and OTS treatments result in well-defined and ordered dielectric surface for subsequent semiconductor deposition. Besides, the hydrophobic surface by HMDS or OTS treatments is less polar,²⁴¹ which may lower the energetic disorder of the interface and favor charge transport.

3.2.3. Molecular orientation of P(NDI2OD-T2)

For thiophene-based organic semiconductors, hydrophobic surface treatment typically improves charge transport by promoting the π - π stacking of polymer chains parallel to the substrates plane for two-dimensional delocalization of polarons, particularly in bottom gated FET configuration.^{33-36, 246} Previously, GIWAXS and NEXAFS were employed to study the carrier transport in P(NDI2OD-T2) with different thin film morphologies, where insights on the crystalline packing in bulk and top surface can be retrieved.^{43, 45, 175} Unfortunately, these techniques are not effective for examining bottom gated devices, where the active semiconductor-dielectric interface lays beneath.

We performed IR-CMS to address the effect of surface treatment on the molecular orientation of the semiconductor at the different semiconductor-dielectric interfaces. CMS spectra are acquired by calculating the normalized change in reflectance with and without carrier accumulation at the semiconductor-dielectric interface ($-\Delta R/R$). To reduce the oxidation of P(NDI2OD-T2), we deposited a PMMA encapsulation layer (~ 500 nm) with high optical transmittance (see Figure 3.11B).

Figure 3.12 shows the IR-CMS spectra of P(NDI2OD-T2) FET with different SiO₂ surface treatments, while statistical distributions of CMS spectra from different measurements are available in Figure 3.13. All IR-CMS spectra show band

absorption with peak around 980 cm^{-1} accompanied by Fano antiresonances from 1050 cm^{-1} to 1800 cm^{-1} . The band absorption is related to the absorption of allowed sub-bandgap states enabled by the presence of polarons,^{8, 9, 168, 179} while the Fano anti-resonant features are infra-red active vibrational (IRAV) modes, Raman-active

Figure 3.12 — Comparison of IR-CMS with infrared and Raman spectra. (A) CMS reflectance spectra of P(NDI2OD-T2) FETs with different SiO_2 surface treatments. The spectra are collected with $V_{\text{ds}} = 0\text{ V}$ and gate modulation of $V_{\text{on}} = 100\text{ V}$ and $V_{\text{off}} = 0\text{ V}$. Statistical distributions of CMS spectra from different measurements are available in Figure 3.13. (B, C) Raman (B) and infrared absorption (C) spectra of P(NDI2OD-T2) thin film. The spectra are divided into region I, II, and III for the ease of data interpretation. The dashed lines represent the two major modes, polarized along and perpendicular to the polymer backbone.

modes converted into IR modes due coupling of self-localized polarons to the polymer backbone and local chain distortion.^{168, 169} This means that IR/V modes are related to charge oscillations along the polymer chain, and can also be used to probe the molecular orientation of conjugated polymer chain.¹⁷⁹ Previously, a combination of grazing angle reflection-absorption IR spectroscopy (RAIRS) and IR transmission spectroscopy were employed by Giussani *et al.* to resolve the orientations of NDI2OD and T2 moieties of P(NDI2OD-T2) with respect to the substrate surface.^{207, 214} By analyzing the normal mode intensity of the respective moieties, they concluded that as-cast or thin films of P(NDI2OD-T2) annealed below the melting temperature display a face-on orientation with the polymer backbone lying on the substrate plane, featuring T2 units oriented almost flat and parallel to the surface with a slight tilted NDI2OD units. In our study, the lack of data below 800 cm⁻¹ prevented access to the spectral information about the normal modes of T2 units.²¹⁴ Therefore, to simplify the following discussion, the NDI2OD and T2 moieties are assumed to be coplanar.

As shown in Figure 3.12A, the IR-CMS spectra display different spectroscopic features for devices with different SiO₂ treatments. The polaron band intensity is the highest for the OTS-treated devices, which is possibly related to a larger induced carrier density that also leads to high mobility in FET measurements (Figure 3.8). Both devices with non-treated and HMDS-treated surface have similar band intensity, although mobility is higher for the latter case. This might be related to the use of on-off measurement technique which does not have the selectivity to probe selectively mobile charges.¹⁷⁹ Similar polaronic band features (peak position and bandwidth) are observed for all three devices with different treatments, suggesting that a common nature and energetic landscape are shared among them. This is also consistent with a previous study showing that polaronic species have intra-molecular nature in D-A conjugated polymer P(NDI2OD-T2).²⁵⁷

Figure 3.13 — Statistical distribution. (A,B,C) Distribution of 3 different CMS spectra acquired from OTS (A), HMDS (B), and untreated (C) SiO_2 devices. (D) Distribution of CMS spectra as shown in A, B, and C plotted in a single schematic. The spectra are collected with $V_{\text{ds}} = 0$ V and gate modulation of $V_{\text{on}} = 100$ V and $V_{\text{off}} = 0$ V.

It has also been demonstrated that high mobility D-A conjugated polymers possess the capability to delocalize charge carrier within a single molecule, without the need to extend to neighboring chains. This is owing to the molecular design that utilizes larger and more planar repeating units to promote a linear conformation of the molecule to endure side-chain disorder, which allows excellent charge transport properties regardless of the film microstructure.^{47, 48} This is further supported by the high field-effect mobilities ($> 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) obtained in our FETs fabricated with spin-coated films, without employing procedures to improve mobility by enhancing the interfacial alignment relative to the preferential carrier propagation direction^{45,}

Despite the similarities shown in the low energy polaron band, IRAV features are different for devices with different SiO₂ treatments. IRAV modes in IR-CMS are not in a perfect one-to-one correspondence with IR and Raman features, which can be attributed to the overlap of IR and Raman modes (Figure 3.12B and Figure 3.12C). Our Raman and IR spectra are similar to data reported by Giussani *et al.*, who performed first principle calculations to interpret the IR and Raman modes.²¹⁴ For the simplicity of discussion, analysis of IRAV modes is divided into three spectral regions (see Figure 3.12).

In the spectral region 1100-1300 cm⁻¹, namely Region I in Figure 3.12, the spectra show identical signatures, but with different spectral intensity. This region shows antiresonance strength (dip intensity) with similar trend to the field-effect mobility, with OTS being the strongest while HMDS and untreated device appearing similar, which can be primarily attributed to the difference in charge density induced by different interfaces.

In the spectral region between 1300-1600 cm⁻¹, indicated as region II in Figure 3.12, IRAV modes are the most distinct for the OTS-treated device, while the untreated device appears to be completely featureless. According to a previous IR and Raman study on P(NDI2OD-T2) thin films, the corresponding spectral region can be dominated by the Raman Я-modes, *i.e.* bond length alternation oscillations, that consist of C=C / C-C bonds stretching/shrinking, either confined on the T2 or NDI2OD unit or delocalized on the whole NDI2OD-T2 monomer.²¹⁴ The same study also shows that corresponding IR modes in this spectral region mainly arise from the C=C / C-C bonds stretching as well as CH and CH₂ bending localized on the NDI2OD unit.²¹⁴ In fact, when compared to the corresponding spectral region in IR and Raman spectra (Figure 3.12B and Figure 3.12C), neither of the IRAV modes from IR-CMS spectra (Figure 3.12A) show a direct one-to-one correspondence to either of the Raman or IR modes. This can be due to the overlapping of multiple

Raman and IR modes of the macromolecule conjugated polymers in this spectral region, results in featureless modes that stem from convoluted signals. Nevertheless, the IRAV modes still manifest a charge density dependence, in which the OTS-treated device shows stronger dip intensity, while HMDS-treated and non-treated devices are alike.

Unlike region I and II, region III of IR-CMS, corresponding to the spectral region between 1600 - 1900 cm^{-1} , shows a direct one-to-one correspondence between IRAV and IR modes. As indicated with dotted lines in Figure 3.12, the IRAV modes centered around 1666 cm^{-1} and 1706 cm^{-1} correspond to IR modes (Figure 3.12C). These modes at 1666 cm^{-1} and 1706 cm^{-1} were previously identified as localized anti-symmetric C=O stretching normal modes, polarized along the backbone direction of NDI2OD unit, and the localized symmetric C=O stretching normal modes, polarized along the side chain direction of NDI2OD unit.²¹⁴ The fact that these modes have orthogonal polarization allows resolving the preferential orientation, *i.e.* face-on *vs.* edge-on orientation, of the conjugated polymer by analyzing the relative intensity of the two modes.²¹⁴ As shown Figure 3.12A, the dip intensity ratio between 1666 cm^{-1} and 1706 cm^{-1} modes changes with different treatment. The ratio is the highest for the OTS device and the lowest for the untreated device. A higher ratio implies that the molecules prefers a relative edge-on orientation, since weakening of the 1706 cm^{-1} band is due to the rotation of some polymer segments out of the substrate plane. Conversely, a face-on orientation would result in a stronger dip for the 1706 cm^{-1} band, since the absorption of this mode is favored only when the molecular segment is lying flat on the substrate. For the HMDS-treated device, similar IRAV dip strength is observed for both modes, indicating that the orientation of the conjugated polymer is between those of the OTS-treated and the untreated devices. The change of intensity ratio is unlikely originated from specific intermolecular interactions in the solid state, since no shift in frequency

accompanies the change of intensity. A moderate frequency shifts ($2\text{-}5\text{ cm}^{-1}$), related to intermolecular interactions involving alkyl chains, was previously observed in the high frequency region ($2700\text{-}3000\text{ cm}^{-1}$) when passing from solution to film. However, we do not observe any IRAV signature in this spectral region in IR-CMS, likely due to the insulating nature of the alkyl side chains, similar to the previous studies conducted with P3HT as the active materials.^{9, 179} It is also worth noting that the IR-CMS spectra are collected using a confocal objective with numerical aperture of 0.5, hence the signal comprises collective information over 30 degree ($\arcsin 0.5$) from the substrate plane direction. Nevertheless, the obtained spectra still provide the relative change in preferential molecular orientation of the conjugated polymer, changing from face-on to edge-on while turning the hydrophilic SiO_2 surface into hydrophobic (see Figure 3.14).

Figure 3.14 — Schematic of possible molecular orientation of P(NDI2OD-T2) on different SAM-treated SiO_2 surface.

Correlation between molecular orientation and charge transport properties

Section 3.2.1 shows that the SAM treatment increases the hole and electron carrier mobilities of the active materials with increasing hydrophobicity of the SiO_2 surface. The improvement in ambipolar charge transport is also supported by the reduction of sub-threshold slope from linear transfer characteristics which indicates a lower density of traps at the dielectric interface with a higher hydrophobicity surface. Section 3.2.2 further reveals that a lower energetic disorder for a higher hydrophobicity SiO_2 surface that can be due to a lower dipolar surface that reduces

the electronic polarization and localized polaron states at the semiconductor-dielectric interface.²⁴¹ The morphology of P(NDI2OD-T2) thin film was initially found to form a disorder matrix with crystalline domains showing preferable face-on orientation, as revealed by grazing-incidence X-ray scattering (GIXS) analysis.³⁹ The face-on texture of thin films is understood to be favorable for charge transport in bulk vertical than thin film planar direction, although field-effect mobility measurements suggested otherwise.³⁸ However, our FET and CMS characterization suggests that the improvement of field-effect transport is associated with the relative edge-on molecular orientation upon the hydrophobic treatment. This is also consistent with the demonstration of bulk orientation changes from face-on to edge-on upon melt treatment with slow cooling, resulting in a drop in mobility measured with electron only diode, while field-effect mobility of bottom-gated FETs (with OTS treatment) remains similar.^{43, 225} This suggests that field-effect transport in FET only occurs at the semiconductor-dielectric interface¹³⁴ and the nanostructure at the interface can be different than the one in the bulk. This also consistent with the near edge X-ray absorption fine structure (NEXAFS) spectroscopy measurement that reveals the first few layers of thermally annealed spin-coated thin films have edge-on orientation on the top surface, while face-on orientation is still preferred in the bulk of the film.^{43, 44} The result of CMS measurement is consistent with conventional perception that edge-on packing provides enhanced charge transport properties facilitating hopping of charge carriers between neighboring conjugated segments.⁴² Hence the improvement of the field-effect transport, upon the hydrophobic treatment, is likely due to the preferable relatively edge-on molecular orientation that enhances the carrier hopping between neighboring crystalline domains.

3.3. Conclusions

In conclusion, we utilized IR-CMS to examine the carrier distribution along the

active channel of p-channel FETs in different operating regimes, and the effect of SAM treatment of SiO_2 on molecular orientation at the semiconductor-dielectric interface in n-channel bottom gated FETs. In the first part of the chapter, we have discussed mid-IR CMS of polaronic absorption features and IRAV modes of P3HT. The IRAV modes were compared with IR and Raman modes, and their features were assigned by DFT calculations. We employed a simple capacitive model to correlate the IRAV modes of CMS spectra to charge carrier density by analyzing the contribution of oxidation-induced or electrostatically-induced charge carriers in the same gate bias modulation schemes. We concluded that there is no sign of metal-insulator transition at the maximum carrier densities of $\sim 3 \times 10^{16}$ holes/ m^2 achieved. Benefiting from its high sensitivity and selectivity, we have used CMS reflectance mapping to obtain the carrier density distribution along the active channel of the FET in different operating regimes. In the second part of the chapter, HMDS and OTS were used to tune the hydrophobicity of SiO_2 from a relative hydrophilic untreated surface to a hydrophobic OTS-treated surface. FET measurements revealed an increase in electron mobility with increasing hydrophobicity of the SiO_2 surface. Surface treatment also improves hole transport, suggesting that the enhancement in ambipolar charge transport originates from the decrease in carrier trap density, accessed by the sub-threshold slope of transfer characteristics in the linear regime. Temperature-dependent FET mobility measurement revealed a lower extracted E_A with higher hydrophobicity surface, suggesting that the SAM treatment reduces energetic disorder. The extracted E_A is also consistent with FET mobility measurements, where improvement of mobility may also be attributed to the narrower density of localized polaron states due to less polar hydrophobic surface by HMDS and OTS treatments. These effects were further studied with IR-CMS by accessing the low energy polaron band and the IRAV modes. The low energy polaron band shows higher intensity with increasing hydrophobicity, consistent with the higher mobility obtained from FET

measurements. Through the analysis of the relative intensity of normal modes of the NDI2OD unit, IRAV modes further reveal a transformation from face-on to edge-on orientation with respect to substrate surface upon HMDS and OTS treatment. Overall, these studies prove the effectiveness of combining conventional electrical measurements with broadband electro-optic CMS measurements in conjugated polymer FETs to determine relationships between transport properties and the polymer morphology/structure.

This chapter has shown that IR-CMS is a useful technique to reveal charge carrier distribution in mid-IR, as well as to provide information about the molecular orientation of the conjugated polymers in both p-type and n-type transistors. A prototypical p-type P3HT has been utilized to reveal the relationship between carrier density and IRAV intensity in mid-infrared, which is conventionally address in visible and near infrared region.^{175, 176} IR-CMS has been utilized to correlate structure-properties relation of p-type materials,^{8, 9, 11} here we utilized it to improve our understanding of the charge transport in n-type P(NDI2OD-T2) donor-acceptor copolymer. The research works in this chapter focused on unipolar conjugated polymer materials, in which their charge transport has also been considered as ambipolar in nature.¹⁴⁴ The CMS study of both electron and hole transport in unipolar materials could have been limited by the orders of magnitude difference in carrier mobilities. Hence, a high and balanced carrier mobility donor-acceptor copolymer, DPPT-TT, will be studied with CMS to address the nature of ambipolar charge transport in the conjugated polymer in Chapter 4.

Chapter 4

Ambipolar field-effect transistors

In Chapter 3, unipolar p-type P3HT polymer and n-type P(NDI2OD-T2) donor-acceptor (D-A) copolymer have been studied. D-A copolymers are a unique class of semiconducting materials which was partly developed to enhance electron transport and stability,¹³⁴ as for P(NDI2OD-T2) in Chapter 3, and to achieve ambipolar transport properties for different organic electronic applications.^{49, 57, 135, 191, 259, 260} In this chapter, we adapted a prototypical high mobility D-A copolymer DPPT-TT (poly(N-alkyldiketopyrrolo- pyrrole dithienylthieno[3,2-b]thiophene), Figure 4.1A) as the active material to study the transport characteristics, charge distribution, and device physics of an ambipolar organic field-effect transistor by the means of charge modulation spectroscopy (CMS) and microscopy (CMM). Benefiting from high spatial resolution of confocal microscopy, specific spectral contributions to the macroscopic CMS spectra from channel center and electrode edges can be explicitly isolated. Besides, carrier distributions along the active FET channel, in unipolar and ambipolar regimes, are also recorded. Incorporation of a high spatial resolution optical probe in our CMS experiments helps to correctly assign spectral features as well as recording the actual carrier distribution in an operating FET. This is a new experimental perspective to interrogate the nature of carrier species in high-mobility ambipolar semiconducting polymers.

4.1. Field-effect transistor characteristics

We adopted D-A copolymer DPPT-TT as active material for the ambipolar FET fabrication. DPPT-TT is known for its high carrier mobilities and balanced ambipolar transport characteristics,^{49, 52, 53} which are mostly attributed to the D-A pair that allows inducing a closely packed and ordered stacking of polymer chains.⁴⁹ The FET devices are optimized in a bottom-contact, top-gate configuration

Figure 4.1 — Current-voltage characteristics of DPPT-TT FET. (A) The schematic configuration of DPPT-TT FET, and molecular structures of the active layer DPPT-TT and electron injection layer PEI. (B, C) Output (B) and transfer (C) characteristics of DPPT-TT FET with channel length and width of 20 μm and 20 μm , respectively.

(Figure 4.1A) for CMS and CMM measurements. To obtain ambipolar FETs with balanced hole and electron mobilities, we adopted a surface modifier, polyethylenimine (PEI, Figure 4.1A), to enhance the injection of electrons from the Au source/drain contacts. This partly reduces the hole injection compared to the FET devices optimized for hole transport.²⁶¹ The use of PEI as electron injection layer increases the contact resistance for hole injection, as reflected by the non-linear current dependence at low drain-source bias in output characteristics (Figure 4.1B) under hole accumulation regime (negative gate bias), in comparison to the better linearity in the electron accumulation regime (positive gate bias). The electron and hole saturation mobilities are determined to be 0.27 and 0.10 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively, by performing standard transistor analysis (gradual channel approximation method) to the recorded FET transfer characteristics (Figure 4.1C). In comparison to previous reported mobilities (0.1-1.0 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for electron mobility and 1-10 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for hole mobility),^{49, 52-54} the obtained mobilities are lower, which we attribute to different device configurations¹³⁴ and fabrication procedures as well as the different molecular weight²⁶² of the copolymers used in this work. Given the good and balanced mobilities, the fabricated FETs are nonetheless suitable for performing CMS and CMM measurements to exploit charge transport properties in unipolar and ambipolar injection regimes. Besides, the high contact resistance for hole injection provides unique opportunities to study and identify spurious spectroscopic signatures which overlap with polaronic absorption and bleaching features.

4.2. Spectral signatures in the near-infrared and visible regions

CMS probes charge-induced excitation features in organic semiconductors.^{173, 263} For this instance, the induced carrier accumulated at the semiconductor-dielectric interface, by a direct-component (DC) gate bias, is modulated by an alternating component (AC) gate voltage. Lock-in amplifier is then used to record the change

in transmittance of the probing photons due the modulated free carriers.

Charge modulation spectroscopic signatures of DPPT-TT

To explore the individual hole and electron transport characteristics in DPPT-TT, the normalized differential transmission ($\Delta T/T$) are measured in hole and electron accumulation (subsequently indicated as h - and e -accumulation, respectively) gate bias regimes. The macroscopic CMS spectra (Figure 4.2A), obtained by probing the entire FET device area (spot diameter ~ 1 mm), shows bleaching characteristics ($\Delta T/T > 0$) around 1.46 eV to 2.25 eV originating from the depletion of ground state absorption, and charge-induced absorption ($\Delta T/T < 0$) of the polaronic sub-gap optical transitions at lower energies. In the bleaching region, the peaks at 1.50 eV and 1.69 eV together with the shoulder at 1.86 eV resemble the DPPT-TT absorption spectrum (Figure 4.2A, blue). In the infrared spectral region (1.13 eV to 1.46 eV), different spectral features can be observed for CMS spectra in h - and e -accumulation modes. Previously, DPPT-TT FETs with higher hole than electron field-effect mobility was employed to study the origin of these spectral signatures.⁵⁴ Three identified spectral features at 0.8 eV, 1.11 eV, and 1.38 eV were assigned to transitions within a monomer unit, a staggered dimer stacking, and a cofacial dimer stacking, respectively, through a combination of photo-induced absorption, chemical-induced absorption, and density functional theory calculation studies.⁵⁴ From these studies, it is understood that two-dimensional delocalization of positive and negative polarons within at least two neighboring polymer chains, fostered by the strong intermolecular coupling, is responsible for the high ambipolar carrier mobilities in DPPT-TT.⁵⁴ When comparing our CMS spectra in the low energy region, a sharp and intense negative peak at 1.44 eV is observed in h -accumulation, while the same feature is weaker in e -accumulation. In comparison to previous reported cofacial dimer stacking peak at 1.38 eV,⁵⁴ this peak is blue-shifted by 0.06 eV, and overlaps with the absorption tail of DPPT-TT. Nevertheless, a charge-

Figure 4.2 — Optical properties of DPPT-TT. (A) Macroscopic CMS spectra, acquired by probing the whole FET device area, in hole (black, $V_{gs} = -40 \text{ V} \pm 10 \text{ V}$) and electron (red, $V_{gs} = 40 \text{ V} \pm 10 \text{ V}$) accumulation regime. Spectra were taken with grounded source and drain ($V_s = V_d = 0 \text{ V}$). The blue curve is the absorption spectrum of the DPPT-TT thin film. (B) Local CMS spectra at FET channel center, acquired by using high resolution confocal microscope, in h -accumulation (black, $V_{gs} = -50 \text{ V} \pm 20 \text{ V}$) and e -accumulation (red, $V_{gs} = 40 \text{ V} \pm 20 \text{ V}$). (C) Local CMS spectra at electrode edge, collected with $V_{gs} = -40 \text{ V} \pm 20 \text{ V}$ and $V_{ds} = 0 \text{ V}$, in 1st harmonic (black) and 2nd harmonics (red). The second derivative of absorption is shown in blue curve. (D) Schematics of optical probing area of CMS spectra, indicated with yellow arrow(s), shown in (A), (B), and (C) (from top to bottom, respectively). The in-phase and quadrature phase signals are denoted with solid and dashed curves, respectively.

induced absorption band from 1.13 eV to 1.37 eV can be observed in both h - and e -accumulation CMS spectra.

The overall bleaching and charge-induced band intensity is stronger in e -accumulation than h -accumulation, a fact that can be due to the higher

accumulated charge density at the semiconductor-dielectric interface in e -accumulation. Besides, the stronger band and bleaching intensity can also be attributed to the shifted threshold voltages for holes and electrons, which are a direct consequence of applying PEI as electrode surface modifier to improve electron injection at the cost of increasing injection barrier for holes. The similarity between strong absorption peak at 1.44 eV in h -accumulation CMS spectrum and the reported absorption peak at 1.38 eV in ref. 54, suggests that this peak may result from the different superposition with bleaching features in the two cases. Such a peak is however very weak in the e -accumulation CMS spectrum (Figure 4.2A, red), which prompted us to assess the local CMS spectra along the FET channel to further analyze the origin of these peaks.

To obtain the local CMS spectra from small area, a confocal microscope¹⁷⁵ (spot size ~ 600 nm at 835 nm probing wavelength) is used to acquire the optical probing signal. As shown in Figure 4.2B, CMS spectra collected from the center of the FET channel display similar charge-induced absorption features in h - and e -accumulation regimes, which appear as a single broad and flat band spanning from ~ 1.38 eV to 1.13 eV (Si detector limit). These local CMS spectra do not resemble the macroscopic CMS spectra shown in Figure 4.2A, but are similar to the previously reported photo-induced absorption of DPPT-TT.⁵⁴ However, when collecting the local CMS spectra in h -accumulation mode at the electrode edge (Figure 4.2C, black curve acquired at first harmonic, 1ω), a distinct negative peak around 1.43 eV is observed, as seen in the macroscopic CMS spectrum in h -accumulation regime (Figure 4.2A, black curve). Nevertheless, local CMS spectra collected at the center of the channel and at the electrode edge show similar bleaching characteristics.

To understand the origin of the difference in the observed charge-induced absorption features from FET channel center and electrode edges, the second

harmonic (2ω) of the $\Delta T/T$ signal at the electrode edge is acquired. Similar to 1ω spectrum, the 2ω spectrum collected at the electrode edge (Figure 4.2C, red curve) displays a negative peak appears at 1.43 eV. When acquiring at 2ω , the modulated charge signal is not recorded since it is linearly dependent on the amplitude of the gate modulation. In this case, spectral features in 2ω spectra shall only come from field-dependent electroabsorption (EA) optical transitions. Moreover, the negative peak feature at 1.43 eV is also similar to the second derivative of DPPT-TT thin film absorption spectrum (Figure 4.2C, blue curve), implying that profound EA signals contributed to the CMS spectrum acquired at the electrode edge in comparison to local spectra collected at the channel center. The EA band is originated from the Stark shifts of the neutral polymer optical transitions due to the presence of a polarization field. In our case the presence of EA may be a direct result of a deficient hole injection at the electrode due to the use of PEI surface modifier, which gives rise to weak screening of the induced field by gate bias.^{9, 200} Therefore, the observed negative peak at 1.43 - 1.44 eV in macroscopic CMS spectra (Figure 4.2A) as well as in local 1ω and 2ω CMS spectra collected at electrode edge (Figure 4.2C) is most likely an EA feature. Moreover, the 2ω spectrum collected from the electrode edge (Figure 4.2C, red) displays a blue-shifted zero-crossover from the bleaching characteristics to charge-induced absorption in comparison to the 1ω spectrum (Figure 4.2C, black). This can be explained by the fact the 1ω spectrum is a superposition of signals from polaronic absorption and EA, while the 2ω spectrum depends uniquely on EA. Besides, a non-zero quadrature phase signal is also observed in 1ω CMS spectrum collected at the electrode edge (Figure 4.2C). This can be attributed to the presence of long lived charge species,¹⁸⁰ which is accounted in the acquired quadrature phase signal.

Control experiments with DPPT-TT diode

To reaffirm the origin of EA contributions in macroscopic CMS measurements, we implemented Stark spectroscopy on a DPPT-TT metal-insulator-semiconductor (MIS) diode (inset of Figure 4.3A). To acquire only EA signals from DPPT-TT MIS diode, the total voltage ($|V_{DC}| + |V_{AC}|$) applied should be in the no-current-injection range, *i.e.* from -1.5 V to 1.5 V (see current-voltage characteristics of DPPT diode, Figure 4.3A). Figure 4.3B shows the acquired 1ω (black curve) and 2ω (red curve) spectra from the DPPT-TT diode. Both spectra appear to display similar spectral features as the local CMS spectra obtained by probing at the electrode edge. The weak quadrature phase signals (dashed lines, Figure 4.3B) in both 1ω and 2ω spectra suggest that the acquired signals could solely be attributed to the field dependence of the ground state optical transitions. Here we confirm that EA signals are prevalently found in CMS spectra collected at the electrode edge (Figure 4.2C), and it also superimposed with the polaronic absorption in macroscopic CMS spectra (Figure 4.2A). This spurious interference from EA has

Figure 4.3 — Control CMS experiments with DPPT-TT diode. (A) Current-voltage measurement of DPPT-TT diode. The inset shows the diode configuration. (B) CMS (black) and electro-absorption (red) of DPPT-TT MIS diode. The in-phase and quadrature phase signals are denoted with solid and dashed curves, respectively. Spectra were acquired with grounded ITO (indium tin oxide) and $1\text{ V} \pm 0.25\text{ V}$ bias to Au. Similar spectra can be obtained when switching biases between the two electrodes.

strong implication on assigning proper CMS spectroscopic signatures as well as interpreting the nature of charge carrier species in D-A copolymers, *e.g.* intra- *vs.* inter-chain polarons.^{191, 257}

4.3. Carrier injection and contact resistance

Being associated to the polarization electric field, the EA signal can be utilized to study the effect of contact resistance on the FET device characteristics. Contact resistance in FETs stems primarily from the reduction of injection efficiency due to the formation of an injection barrier and potential drop across the semiconductor-electrode interface, as a result of the misalignment of the work function of the injecting electrodes to the semiconductor HOMO (or LUMO) level.²⁵³ Here we chose

Figure 4.4 — Optical probing signals at the DPPT-TT FET electrode edge. (A, B) Electro-absorption in-phase (A) and quadrature phase (B) signals of 1.49 eV probing photon energy acquired in 2nd harmonics. (C, D) CMS in-phase (C) and quadrature phase (D) signals of 1.49 eV probing photon energy acquired in 1st harmonics. Measurements are performed with grounded drain and source, and 50 KHz modulation frequency to modulate gate bias.

probing photon energy of 1.49 eV and record the first (1ω) and second harmonic (2ω) of the change in transmission signal at the electrode edge as a function of gate bias (Figure 4.4). When probing the photon energy of 1.49 eV, EA and charge-induced bleaching features can contribute to the 1ω signal,¹⁷⁵ while the 2ω signal is solely due to EA. When acquiring these signals with a phase-sensitive lock-in amplifier, the 1ω and 2ω of the change in transmission signals are detected in phase and in quadrature, respectively. From ~ -35 V to 20 V, the 1ω signal (Figure 4.4C) monotonically depends on V_{gs} , while two minima at $V_{gs} = 20$ V and $V_{gs} = -35$ V are observed in the 2ω signal (Figure 4.4B). The monotonic dependence of the 1ω signal can be attributed to the superposition of charge-induced bleaching features and EA, where the latter is the one observed in the 2ω signal measurement. When V_{gs} is either higher than 20 V or lower than -35 V, the EA input drops, as evidenced by the reduction of negative 2ω signal in Figure 4.4B. This is also supported by the decrease of 1ω signal (Figure 4.4C) in the same range. This observation suggests that EA signal increases due to trapping of accumulated carriers at the electrode as a result of the injection barrier, and eventually decreases as it is screened by the injected charge carriers for gate biases higher than threshold voltages of holes or electrons. This is also supported by the observed 2ω signal minima at $V_{gs} = 20$ V and $V_{gs} = -35$ V, which correspond roughly to the minima in n- and p-type FET transfer characteristics ($V_{gs} \sim 20$ V and $V_{gs} \sim -40$ V in Figure 4.1C). There are no easy paths for defining the threshold voltages of holes and electrons in an ambipolar FET, as either carriers are hardly totally depleted at the same time. In this case, the EA signal can be a means to study carrier injection. The 2ω signal minima at $V_{gs} = 20$ V and $V_{gs} = -35$ V represent the minimum required voltages for electrons and holes to overcome the respective injection barriers and form an accumulation layer at the semiconductor-dielectric interface.

Nevertheless, the non-zero 2ω in-phase (Figure 4.4A) and 1ω quadrature phase (Figure 4.4D) signals are still observable at the highest modulation frequency of 50 kHz allowed by the bandwidth of the lock-in amplifier. In FETs, the internal electric field does not necessarily depend linearly on applied V_{gs} and V_{ds} . Indeed, interfacial dipoles can be formed upon bias induced charge trapping at the metal-semiconductor interface, screening the applied bias. Besides, the internal field can be screened by injected charges when carriers overcame the respective threshold voltages. As mentioned, full depletion conditions, where signals can be undoubtedly attributed to EA, are hardly achievable in ambipolar transport materials since there is always injection of holes or electrons. This might explain the observed non-zero 2ω in-phase signals (Figure 4.4A). For quadrature phase at 1ω (Figure 4.4D), the signal might be due to the non-linear response from long lived species in the semiconductor.¹⁸⁰

4.4. Carrier distribution in ambipolar field-effect transistor

The analysis in section 4.2 enables us to differentiate the EA and polaronic charge-induced absorption features. Therefore, it is safe to use infrared probing photon energy of 1.13 eV to perform CMM to record the distribution of polarons in ambipolar DPPT-TT FET. CMM is quasi-static measurement technique where carrier density distributions are recorded across the FET active channel.^{175, 176, 180} Previously, carrier mapping of an ambipolar FET was demonstrated using a static FTIR charge modulation technique; however, the limited spatial resolution (20 μm) of the mid-infrared probe¹⁷⁸ is not suitable for CMM studies of organic FETs with typical channel lengths (5- 20 μm). Here we utilize the high spatial resolution of confocal microscopy to map the hole and electron distributions in unipolar and ambipolar regimes of an ambipolar FET, probing at shorter wavelengths.

Figure 4.5A and Figure 4.5B show the charge carrier maps and profiles of the

Figure 4.5 — Distribution of charge carriers along FET channel in e^- and h^- accumulation regimes. (A, B) CMM maps (A) and profiles (B) of DPPT-TT FET in e^- accumulation mode ($V_{gs} = 30 \text{ V} \pm 20 \text{ V}$) at different V_{ds} . (C) Local CMS spectra collected within the FET channel, with $V_{gs} = 30 \text{ V} \pm 20 \text{ V}$ and $V_{ds} = 90 \text{ V}$, at probing spot $\sim 3 \mu\text{m}$ away from drain (black curve) and source (red curve) electrode edges as denoted by the black and red arrows in (B), respectively. (D, E) CMM maps (D) and profiles (E) of DPPT-TT FET in h^- accumulation mode ($V_{gs} = -50 \text{ V} \pm 20 \text{ V}$) at different V_{ds} . (F) Local CMS spectra collected within the FET channel, with $V_{gs} = -50 \text{ V} \pm 20 \text{ V}$ and $V_{ds} = -80 \text{ V}$, at probing spot $\sim 3 \mu\text{m}$ away from drain (black curve) and source (red curve) electrode edges as denoted by the black and red arrows in (E), respectively. Probing photon energy of 1.13 eV was used to acquire CMM.

ambipolar FET in e^- -accumulation mode, for different applied V_{ds} . When $V_{ds} = 0 \text{ V}$,

charge carriers are evenly distributed across the FET channel, while local variation of carrier concentration is known to correlate with the local microstructure and the morphology of the polymers at the semiconductor-dielectric interface.¹⁷⁶ When V_{ds} is applied, the local drain potential decreases, resulting in a relative drop of carrier density close to the drain electrode in comparison to the region next to source.^{175, 179} A further increase of V_{ds} from 40 V to 90 V makes the charge density vanish next to the drain, as expected from unipolar operation of a typical FET and eventually a signal of opposite sign increases at higher V_{ds} bias. The opposite sign is a signature of opposite charge carrier injection, *i.e.* hole injection, as the local drain potential exceeds the hole injection threshold, driving the FET from unipolar into ambipolar injection regime.¹³⁴ To check the spectroscopic signatures of accumulated holes and electrons in the active channel within the ambipolar injection regime ($V_{ds} = 90$ V), we collected local CMS spectra ~ 3 μm away from each of the injecting source and drain electrodes. The acquired spectra are very similar to the local CMS spectra collected at the center of the FET channel (Figure 4.2B).

In h -accumulation mode (Figure 4.5D and Figure 4.5E) carrier distributions are slightly different from those observed in e -accumulation mode (Figure 4.5A and Figure 4.5B). This can be associated to the different field distribution and accumulated charge density at different gate biases ($V_{gs} = -50$ V for holes and 30 V for electrons). Similar to e -accumulation mode, charge carriers are evenly distributed at low V_{ds} (0 V to -30V). However, a substantial drop of carrier concentration across the FET channel is observed when V_{ds} is -40 V. To minimize the shift in threshold voltage by gate bias stress, we alternately acquired maps in e - and h -accumulation. The effect of gate bias stress mainly affects the mapping in h -accumulation, as it is found that higher gate bias ($V_{gs} = -50$ V) is needed to operate in full accumulation, compared to e -accumulation ($V_{gs} = 30$ V), as measurements progress. Besides, the weakened charge injection and a different field

distribution in h -accumulation might also induce device instability at large biases. Despite these little complications, we were still able to extract reliable maps of the carrier distributions in the ambipolar injection regime. Applying higher V_{ds} pinches the FET channel in unipolar saturation regime ($V_{ds} = -60$ V) and subsequently drives the FET into ambipolar injection regime ($V_{ds} = -80$ V). The local CMS spectra collected close (within the FET channel, ~ 3 μm away) to the source and drain electrodes in ambipolar injection regime (Figure 4.5F) are different from those collected at the FET channel center (Figure 4.2B). This shows that spurious EA signal interferes with polaronic features up to ~ 3 μm away from the electrode edge. Here, we show that high resolution maps of carrier distributions in e^- and h -accumulation helps understanding the device operation of FETs in unipolar, saturation, and ambipolar regimes, as well as providing the information on extend of electric field into the channel of FETs.

4.5. Conclusions

To summarize, we utilized CMS and CMM to study the charge transport characteristics of ambipolar DPPT-TT co-polymer FET in both unipolar and ambipolar regimes. We found that profound EA features from the electrode edges, originating from the polarization field experienced by DPPT-TT sandwiched between the top gate and the source/drain electrode, overlaps with polaronic absorption and bleaching features from the center of the FET channel. This has profound effect on interpreting the spectroscopic signatures from macroscopic CMS spectra collected from the entire FET device area, which is a superposition of both polaronic and EA features. We found that CMS spectra in hole- and electron-accumulation modes, collected from the FET channel center, are reminiscent of photo-induced absorption spectra, indicating that spurious effect from EA may play a part in the previous assignment of inter-chain cofacial dimer polaron signatures.^{9,}

^{54, 191} We further performed a sub-micron resolution mapping in the EA-free near

infrared spectral region to obtain the correct carrier distribution in unipolar and ambipolar operating regimes of DPPT-TT FET. This allows the determination of accurate transport parameters in unipolar and saturation regimes, and poses the basis for future ambipolar polymer FET modeling and optimization.

In this chapter, CMS was successfully utilized to address the origin of ambipolar charge transport in DPPT-TT as well as to reveal carrier distribution of an ambipolar FET. These information that provided by CMS were enabled by the unique unipolar excitation or accumulation in FET. Ambipolar transport, meaning the capability of effective transporting hole and electron, is an essential criterion to achieve efficient emission from the light emissive materials, such as hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. In the next Chapter, we utilize CMS to study another ambipolar material with efficient light emission properties, hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$, in which its' nature of charge transport is still debatable.^{264, 265}

Chapter 5

Light-emitting field-effect transistors

As mentioned in Chapter 4, effective transport of hole and electron is critical to have efficient emission from a light emissive ambipolar material, such as organometallic hybrid perovskites. Organometallic hybrid perovskites have been widely adopted in solar cells and light-emitting diodes due to the cheap and easy fabrication methods enabled by their solubility in common solvents.⁵⁹ However, the extraction of their intrinsic charge transport parameters is complicated by the variability of morphology depending on preparation techniques, as well as preconditioning of the devices related to ionic screening effects. In this chapter, we show that lowering the FET operating temperature is an effective way to reduce the ionic screening effects. Below 200 K, the field-effect mobilities of holes and electrons increase by close to two orders of magnitude. In the ambipolar injection regime, we have also observed bright electroluminescence from the FET channel, where the corresponding temperature-dependent spectra reveal a structural phase transition. To the best of our knowledge, this is the first demonstration of solution-processable hybrid perovskite light-emitting FET (LE-FET). The transport parameters extracted from FET measurement are very useful to guide thin film optimization for solar cell and light-emitting diode applications, as well as to develop gated light-emitting devices such as solution-processable electrically-pumped lasers. To shine some light on the nature of charge carrier species in hybrid

perovskites, we have also performed preliminary CMS and PIA studies in the mid-infrared spectral region to examine recent theories on the “large polaron”²⁶⁵ and the “small polaron”¹¹⁹ transports in hybrid perovskites.

5.1. Hybrid perovskite thin film characterization

The charge transport properties of hybrid perovskites are largely dependent on the morphology of the thin film, which typically differs depending on deposition method.²⁶⁶ To obtain a compact and uniform $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite thin film (~150 nm thick) on top of $\text{SiO}_2/(\text{p}^{++})\text{Si}$ substrate (Figure 5.1A), we adopted the solvent engineering deposition method developed for solar cell fabrication.²⁶⁷ As shown in the top view scanning electron microscope (SEM) image (Figure 5.1B), the resulting high quality thin film of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is made of closely-packed, large

Figure 5.1 — Hybrid perovskite thin film characterization and FET device structure. (A, B) Scanning electron microscope (SEM) images of cross sectional (A) and top view (B) of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film. Scale bars: 1 μm . (C) X-ray diffraction (XRD) spectrum of spincoated $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film on $\text{SiO}_2/\text{Si}(\text{p}^{++})$ substrate. The data confirms the tetragonal (space group I4/mcm) structure of the deposited thin film. (D) Schematic of the fabricated LE-FET.

domains with grain size up to 200 nm. X-ray diffraction (XRD) measurements (Figure 5.1C) further reveal that the film possesses a perfect tetragonal crystalline structure. The roughness R_{RMS} of the thin film, assessed by atomic force microscopy (AFM), is determined to be 10.8 nm (Figure 5.2). High quality films minimize the influence of metal contacts and charge carrier scattering across the film, allowing extraction of intrinsic FET transport parameters. A bottom-gate bottom-contact FET configuration (Figure 5.1D) is adopted to allow deposition of hybrid perovskite thin film to be the last step of the fabrication, an approach to avoid possible overheating of thin film from the metal electrode deposition process as well as to minimize the exposure to moisture in ambient environment.

Figure 5.2 — $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film morphology. The atomic force microscopy (AFM) surface image of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film spincoated on $\text{SiO}_2/\text{Si}(\text{p}^{++})$ substrate. The measured root-mean-squared roughness is $R_{\text{RMS}} = 10.8$ nm.

5.2. Reduction of hysteresis in current-voltage characteristics

So far the extraction of intrinsic transport parameters of hybrid perovskites has been hindered by strong hysteresis in the electrical response,^{92, 93, 268} especially for flat-junction $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells.²⁶⁴ Previously, this anomalous hysteretic transport characteristic was accredited to capacitive and ferroelectricity effects from the spontaneous polarization induced by the polar methylammonium cation and the lattice distortions, excess ion diffusions, and the charge trapping/de-trapping at the interface.^{92, 93, 264, 268} Elimination of photocurrent hysteresis in $\text{CH}_3\text{NH}_3\text{PbI}_3$ planar

heterojunction solar cells can be achieved by fullerene passivation of the trap states found on the surface and grain boundaries of the perovskite materials.²⁶⁸ Hysteresis-free photovoltaic devices with well reproducible power conversion efficiency were also demonstrated by using single crystals^{82, 83} and millimeter-scale grain size thin films.²⁶⁹ A reversible switching of the ferroelectric domains in hybrid perovskites has been observed by piezoelectric microscopy.²⁷⁰ However, demonstration of field-switchable photovoltaic effect in hybrid perovskites implied that the formation of p-i-n structures, as observed by electron beam-induced current measurement (EBIC) and Kelvin probe force microscopy (KPFM),^{77, 78} is induced by the ion drift under the electric field in the perovskite layer.⁹⁴ This effect is weakened at low temperature and does not depend on the spacing between the lateral electrodes, indicating that ferroelectric photovoltaic effect is not playing a major role in the observed field-switchable photovoltaic behavior.⁹⁴ Besides, the low formation energies of charged Pb, I, and methylammonium vacancies, as revealed by theoretical calculations,^{75, 271, 272} suggesting that the p- and n-type self-doping may be due the high ionicity nature of the materials.²⁷³

In our case, lowering the operating temperature is found to be an effective method to reduce the hysteretic current-voltage characteristics due to ionic transport/screening (Figure 5.3 and Figure 5.4). This allows studying and exploiting the ambipolar transport characteristics in hybrid perovskites (Figure 5.4, $T = 78$ K). Figure 5.3 and Figure 5.4 show the complete temperature evolution of ambipolar FET characteristics from 298 K to 78 K. The output characteristics display a weak or no gate dependence when temperature is above 198 K (Figure 5.3), while “textbook” n-type output characteristics are observed at 198 K or lower temperatures (Figure 5.3 and Figure 5.4). For p-type measurement, typical output characteristics are only observed at 98 K or lower temperatures. From room temperature down to 258 K, both p- and n-type transfer characteristics are

independent of gate bias, as reflected by the open, large hysteresis loops. Below 258 K (Figure 5.3 and Figure 5.4), transfer characteristics with a closed hysteresis loop and distinct hole- and electron-dominated transport, depending on the applied gate voltage, are observed. The hysteresis behavior in p- and n-type transfer characteristics is considerably reduced at temperatures below 98 K and 198 K,

Figure 5.3 — FET characteristics at 298 K, 278 K, 258 K, 238 K, 218 K, and 198 K. (A) Output characteristics of FET. The n- and p-type output characteristics are shown in right and left columns, respectively. (B) Transfer characteristics of FET. The n- and p-type transfer characteristics are shown in right and left columns, respectively. Solid and dashed lines denote the forward and backward sweeping, respectively.

respectively, as also observed in the output characteristics. Standard FET analysis yields an induced carrier density of $\sim 3.8 \times 10^{16} \text{ cm}^{-2}$, maximum $I_{\text{on}} / I_{\text{off}}$ of $\sim 10^5$, and current density of $\sim 830 \text{ A cm}^{-2}$ (estimated with a $\sim 2 \text{ nm}$ induced charge accumulation thickness) at 198 K. These values are similar to previously reported 2D hybrid perovskite FETs measured at room temperature.^{97, 98} Our low

Figure 5.4 — FET characteristics at 178 K, 158 K, 138 K, 118 K, 98 K, and 78 K. (A) Output characteristics. The n- and p-type output characteristics are shown in right and left columns, respectively. (B) Transfer characteristics. The n- and p-type transfer characteristics are shown in the right and left columns, respectively. Solid and dashed lines denote forward and backward sweeping, respectively.

temperature FET measurement verifies the ambipolar nature of $\text{CH}_3\text{NH}_3\text{PbI}_3$ hybrid perovskite, which can otherwise show preferential p-type or n-type transport characteristics with carrier concentration varying by up to six orders of magnitudes, depending on the ratio of methylammonium halide and lead iodine precursors and thermal annealing conditions.²⁷³

In our study we measured four different FET devices and the temperature dependent electron and hole mobilities (Figure 5.5A) were extracted from the forward sweeping of the transfer characteristics at $V_{\text{ds}} = 20$ V and -20 V, respectively, using the linear regime equation of the gradual channel approximation method.¹³⁴ To avoid misleading results caused by the large hysteresis, we did not calculate mobilities from the backward sweeping of the transfer characteristics. Besides, we also chose not to extract mobilities from transfer characteristics measurement at high V_{ds} (*i.e.* in the saturation regime), since identification of the linear and saturation regimes is somehow arbitrary. Although the extracted electron and hole mobilities vary across different devices, consistent trends of the temperature dependence as well as the relative mobility magnitude are observed.

Figure 5.5 — Experimental and calculated temperature dependent field-effect mobilities. (A, B) Experimental (A) and calculated (B) mobilities of holes and electrons in $\text{CH}_3\text{NH}_3\text{PbI}_3$. The electron (filled symbols) and hole (empty symbols) mobilities are extracted from the forward sweeping of the transfer characteristics at $V_{\text{ds}} = 20$ V and $V_{\text{ds}} = -20$ V, respectively, by using the linear regime FET equation of the gradual channel approximation method. Square, circle, up triangle, down triangle represent 4 different FET devices.

When lowering the temperature from 298 K to 198 K, both electron and hole mobilities are improved by a factor of ~ 100 . Below 198 K, electron mobility shows no significant enhancement while a nearly tenfold increase is obtained for the hole mobility. The improved mobility when lowering the operating temperature can be attributed to the removal of screening effects arising from the ionic transport of methylammonium cations. Previously, combination of DFT and Raman studies estimated the phonon energy of methylammonium cation to be ~ 14.7 meV.²⁷⁴ The observed weak improvement of field-effect mobilities below 198 K ($E_{\text{thermal}} = 16.7$ meV) is therefore consistent with the quenching of phonon interactions associated with organic cations. This also agrees with the observation of a weakened field-switchable photovoltaic effects at low temperature,⁹⁴ strongly suggesting that phonon scattering plays a significant role in limiting field-effect transport at room temperature. Despite of the improved field-effect mobilities, a notable hysteresis is still present at the lowest temperature investigated. This might be due to untreated SiO_2 interface, which affects semiconductor thin film morphology, trap states and surface dipoles density, especially in organic FET devices.¹³⁴ The stability of photovoltaic devices is significantly enhanced by the reduction of trap density in single crystal^{82, 83} and larger grain size thin films.²⁶⁹ Therefore, a reduced hysteresis in FETs is also expected when improving bulk crystallinity and controlling the morphology of hybrid perovskite thin film at the semiconductor-dielectric interface. At 78 K, the extracted hole and electron mobilities in the linear regime ($V_{\text{ds}} = \pm 20$ V) are slightly lower than those from the saturation regime ($V_{\text{ds}} = \pm 80$ V): $\mu_{\text{e,linear}} / \mu_{\text{e,saturation}} = 6.7 \times 10^{-2} / 7.2 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_{\text{h,linear}} / \mu_{\text{h,saturation}} = 6.6 \times 10^{-3} / 2.1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, as extracted from transfer characteristics at 78 K shown in Figure 5.4. Previously, 1 to 2 orders of magnitude suppression of the linear regime mobility compared to the mobility in the saturation regime of spin-coated hybrid perovskite FETs, has been associated to a

large concentration of traps from grain boundary.⁹⁸ Hence, the reported linear regime mobilities could be considered as a lower bound for electron and hole mobilities of $\text{CH}_3\text{NH}_3\text{PbI}_3$.

To better our understanding of the experimental data, we compared the experimental mobilities to the values from theoretical calculations (Figure 5.5B) obtained by using semi-classical Boltzmann transport theory.²⁷⁵ Prior to that, we also deduce the charge carrier effective masses, as summarized in Table 5.1, for both tetragonal and orthorhombic crystallographic phases obtained by quadratic fitting of the band structure dispersion (Figure 5.6A and Figure 5.6B); Table 5.2 lists the fitting values required to calculate the theoretical mobilities. Similar to previous studies,^{276, 277} we found that in both crystallographic phases the effective mass of electrons (tetragonal: $0.197 m_0$, orthorhombic: $0.239 m_0$) is smaller than that of holes (tetragonal: $0.340 m_0$, orthorhombic: $0.357 m_0$). Similar to our experimental results, the calculated mobilities (Figure 5.5B) increase when operating temperature decreases, according to the Boltzmann activation energy (see calculation details in ref. 278). In comparison to experimental mobilities (Figure 5.5A), the calculated values (Figure 5.5B) are larger by several orders of magnitude. However, the relative magnitude between calculated hole and electron mobilities,

Figure 5.6 — Band structure of hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. (A, B) Band structures of tetragonal (A) and orthorhombic (B) crystal structures of hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$.

and their temperature-dependence in both crystallographic phases are in very good agreement with the experimental results. We find that the calculated mobilities of electrons are consistently higher than the one of holes in the investigated temperature range. Both mobilities also increase by close to a factor of 10 in the lower temperature phase. Here we attribute the small experimental mobility values to the increase in effective masses upon scattering effects due to elastic carrier - phonon interactions originating from defects and disorder induced by the organic components in the real crystals, as well as carrier-carrier interactions at high current density of holes and electrons.²⁷⁹ Besides, the discrepancy between the experimental and theoretical values might also be explained by the “large polaron” theory, where a larger effective mass of polarons is proposed to account for difference in calculated and measured carrier mobilities.²⁶⁵ The observation of giant

Phase		m_e^*	m_h^*	Reduced Masses
Tetragonal	Γ -X	0.178	0.261	0.106
	Γ -Z	0.284	0.474	0.177
	Γ -M	0.129	0.284	0.089
	Average	0.197	0.340	0.124
Orthorhombic	Γ -X	0.289	0.344	0.157
	Γ -Z	0.189	0.370	0.125
	Average	0.239	0.357	0.143

Table 5.1 — Calculated effective masses of charge carriers. Estimated effective masses of electron and hole of $\text{CH}_3\text{NH}_3\text{PbI}_3$ from calculated band structure that incorporated spin-orbital coupling effect.

	Tetragonal		Orthorhombic	
	Electron	Hole	Electron	Hole
m_b^*	0.197	0.340	0.239	0.357
m_l^*	0.157	0.290	0.163	0.288
m^*	0.166	0.304	0.173	0.291
Ξ (eV)	7.2	8.4	6.8	7.4
B (GPa)	2.6	2.6	3.3	3.3

Table 5.2 — Required parameters for calculating mobilities. Band (m_b^*), conductivity (m_l^*) and density of state (m^*) effective mass, electron (hole)-phonon coupling (Ξ), and bulk modulus (B).

photoinduced modulation of the dielectric constant in $\text{CH}_3\text{NH}_3\text{PbI}_3$, as attributed to localized polaron with relatively small activation energy,¹¹² could also support to this theory. Moreover, the ferroelectric methylammonium cations might induce different segregation pathways for hole and electron transport, resulting in a longer carrier drifting path that lowers the carrier mobilities.²⁸⁰ The carrier transport can also be weakened by the polycrystalline nature of the solution-processed $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films (Figure 5.1A and Figure 5.1B), where hopping of carriers is required to transport charge along and across domain boundaries as a result of the smaller electronic coupling between grains. Recent report revealed that field-effect transport of $\text{CH}_3\text{NH}_3\text{PbI}_3$ FET with little current-voltage hysteresis is possible at room temperature, where ion migration due to point defects associated with grain boundaries, disorder induced by polarization of the MA^+ cations, and thermal vibrations originated from lead halide inorganic cages have also been identified to limit the charge transport in different operating temperature regime.²⁸¹

5.3. Ambipolar injection and electroluminescence

The remarkable ambipolar transport characteristics of $\text{CH}_3\text{NH}_3\text{PbI}_3$ FET at low temperature are boosting the realization of LE-FET operating under balanced carrier injection.^{64-66, 68-71} Particularly, manipulation of ambipolar transport in the two-dimensional confined active layer at the semiconductor-dielectric interface was previously demonstrated to be an effective method to obtain bright and fast-switching electroluminescence as well as to control the spatial position of the emission zone in organic LE-FET.¹⁴⁹ In LE-FET, proper drain-source and gate biasing allow the simultaneous formation of ambipolar channels and injection of holes and electrons from opposite electrodes. Under balance injection conditions, holes and electrons recombine in the middle of the FET channel, forming a narrow radiative emission zone as illustrated in Figure 5.1D. The spatial position as well as the brightness of the emission zone can be controlled by gate and drain-source

biases.¹³⁴ In comparison to conventional LED devices, LE-FET is proven to increase the efficiency of light emission materials owing to the achievable large injection and high carrier density, and the possibility to obtain balanced charge carrier recombination.^{153, 282-285} Moreover, LE-FET can be possibly integrated as nanoscale light source in photonic and optoelectronic devices, allowing potential applications in optical communication systems, solid-state lighting, and electrically pumped lasers.^{134, 282}

At low temperature (78-178 K), $\text{CH}_3\text{NH}_3\text{PbI}_3$ FETs emit light when biased into the ambipolar regime. Electroluminescence (EL) spectra from 78 K to 178 K are

Figure 5.7 — Low temperature electroluminescence from $\text{CH}_3\text{NH}_3\text{PbI}_3$ LE-FET. (A) Electroluminescence spectra acquired at different indicated temperature with $V_{\text{ds}} = 100$ V and $V_{\text{gs}} = 100$ V. The spectra are normalized to respective maximum peak. Three superimposed Gaussian function (solid lines) is used to fit the normalized spectra. Dashed lines that jointed the blue triangles, red circles, and black squares denote the shift in peak position of 750 nm (Peak 1), 780 nm (Peak 2), and 800 nm (Peak 3), respectively. (B, C) The peak position (B) and the full-width-at-half-maximum (FWHM, C) of the Peak 1, Peak 2, and Peak 3 as a function of temperature.

reported in Figure 5.7A. Note that $\text{CH}_3\text{NH}_3\text{PbI}_3$ FETs do not show any light emission above 198 K, which might be caused by the ion drift/screening effects mentioned in the previous section, so operating in low temperature is still essential at this stage. Work is currently ongoing to raise the operating temperature of perovskite LE-FETs to room temperature; for instance, thin films with higher crystallinity are likely to reduce ionic screening,^{82, 83} and could potentially push the hybrid perovskite LE-FET operating temperature to room temperature. The EL spectra acquired from LE-FET are consistent with radiative recombination of injected holes and electrons in hybrid perovskite active layer. At 78 K, EL spectrum can be deconvoluted into three distinct peaks centered at 750 nm (Peak 1), 780 nm (Peak 2) and 800 nm (Peak 3). The spectral position of these peaks varies with temperature (Figure 5.7B). While Peak 2 is dominant particularly at higher temperature, Peak 1 and Peak 3 are only observable below 158 K, similar to temperature dependent photoluminescence studies of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films and single crystals.^{72, 286} This is attributed to the structural transition from a low-temperature orthorhombic phase to a high-temperature tetragonal phase occurring around 162 K.⁷³ Density functional theory studies also predicted the occurrence of the phase transition,^{287, 288} which was experimentally verified by absorption studies.⁷³ Therefore the temperature dependent features of spectral peak position suggest that Peak 2 has distinct origin from Peaks 1 and 3. Peaks 1 and 3 were previously attributed to bound excitons in the orthorhombic phase, while Peak 2 was ascribed to free excitons in the tetragonal phase.⁷² The origin of these peaks cannot be unambiguously assigned from our electroluminescence data, however it should be noted that a previous study has also attributed Peak 1 and Peak 3 to triplet excitons in the low temperature orthorhombic phase, consistent with their photoluminescence decay dynamics of 5 μs accompanied by saturation at high excitation power⁷² and Peak 2 to spontaneous band-to-band radiative transitions.⁷³ The EL spectra are deconvoluted with a three superimposed Gaussian functions to

quantify the relative intensity and spectral energy of the three emission peaks at different operating temperatures (Figure 5.7B and Figure 5.7C). At the lowest temperature Peak 1 shows the anticipated red shift, despite of complicated temperature dependence from 118 K to 178 K (Figure 5.7B). For Peak 2, the peak position only slightly blue shifts over the investigated temperature range (78-178 K). Meanwhile, the spectral peak of Peak 3 significantly red-shifts from 138 K to 78 K. Their corresponding Gaussian FWHM (full-width-at-half-maximum) are reported in Figure 5.7C. FWHM of Peak 1 reduces with decreasing temperature while an opposite trend is observed for FWHM of Peak 2 and Peak 3, similar to previous low temperature photoluminescence studies.^{72, 286} We show that LE-FET can also be utilized as a complementary tool to photoluminescence study for elucidating the nature of spectral shift and broadening of luminescence peaks.

5.4. Spatial control of electroluminescence

As mentioned in Chapter 1, simultaneous injection of holes and electrons in ambipolar FET is only allowed when the local gate potential at drain and source electrodes are higher than the threshold voltage of either of the charge carrier (*i.e.* $|V_{gd}| > |V_{th,h}|$ and $V_{gs} > V_{th,e}$, or $V_{gd} > V_{th,e}$ and $|V_{gs}| > |V_{th,h}|$).¹³⁴ In the ambipolar injection regime, the density of injected holes and electrons as well the spatial position and intensity of the emission zone are tuned by controlling the drain-source and gate biases.¹³⁴ Figure 5.8 shows optical images of light emitted from $\text{CH}_3\text{NH}_3\text{PbI}_3$ LE-FET at 158 K under different biasing condition. The spatial position of EL can be easily recognized from the images, despite of the grainy light emission pattern, which is due to the polycrystalline nature of the thin film (Figure 5.1B). For gate bias fixed at 100 V (Figure 5.8A to Figure 5.8C), the emission area is mainly located close to the drain electrode when small V_{ds} is applied (Figure 5.8A). This is due to the limited hole injection from drain electrode as a result of the relative low $|V_{gd}|$. By applying a higher V_{ds} , $|V_{gd}|$ increases, allowing a higher

Figure 5.8 — Optical images of light emission from $\text{CH}_3\text{NH}_3\text{PbI}_3$ LE-FET at $T = 158$ K. (A, B, C) Frame images of the FET taken from a video recorded while sweeping V_{ds} from 0 to 100 V at fixed $V_{\text{gs}} = 100$ V. Respective V_{ds} values are indicated in each panels. (D, E, F) Frame images of FET taken from a video recorded while sweeping V_{gs} from 0 to 100 V at fixed $V_{\text{ds}} = 100$ V. Respective V_{gs} values are indicated in each panels. Weak illumination was used to improve the image contrast. Scale bars: 200 μm .

injection density of holes into the active channel, increasing EL emission intensity (Figure 5.8B). The emission area is extended to the center of the channel when hole injection is further increased (Figure 5.8C), further enhancing the emission intensity. On the other hand, the injected current densities of holes and electrons can no longer be controlled independently when a fixed $V_{\text{ds}} = 100$ V is applied (Figure 5.8D to Figure 5.8F). A bright emission close to the drain electrode, as shown in Figure 5.8D, is due to recombination of high electron and hole current density. A decrease in the gate bias increases $|V_{\text{gd}}|$ and decreases $|V_{\text{gs}}|$, but the overall injection of electrons and holes are lowered. This results in a reduction of EL intensity, and in the shift of the emission zone to the center of the channel (Figure 5.8E). A further decrease in gate bias (Figure 5.8F) further shifts the

emission zone to nearby the source electrode. This is a clear demonstration of carrier injection and recombination in $\text{CH}_3\text{NH}_3\text{PbI}_3$ LE-FET achieved by regulating drain-source and gate biases, an essential footstep for realizing hybrid perovskite active matrix displays and possibly electrical injection lasers.

5.5. Infra-red spectroscopy of hybrid perovskites

The nature of charge carriers in hybrid perovskites has been discussed extensively^{73, 106} to optimize their optoelectronic applications. It was found that free charge carriers are primarily generated upon weak photo-excitation, a characteristics similar to conventional direct bandgap inorganic semiconductors.⁷³ This is also supported by the demonstration of relatively high power conversion efficiency hybrid perovskite photovoltaic cells that do not employ additional transporting layer,¹⁰⁷ indicating that heterojunction interface helps facilitating selective charge extraction but not exciton dissociation.⁷³ However, a higher photo-excitation intensity changes the photoexcited species, from free carriers to predominantly excitons,⁷³ a feature that allows potential applications in optoelectronics such as light emitting diodes and possibly optically pumped lasers.⁷⁰

The high power conversion efficiency of hybrid perovskite solar cell¹ is largely attributed to the long carrier diffusion length and the remarkably low trap density in these materials.⁸⁰⁻⁸³ Despite of the high mobility ($> 1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) predicted by theoretical calculations,^{86, 87} relative modest mobilities ($1\text{-}100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) are experimentally measured.^{84, 109, 289} This does not reconcile with the theoretically calculated and experimentally found small effective masses of charge carriers.⁸⁸⁻⁹¹ Besides, hybrid perovskites also exhibit an inverse temperature-dependent mobility¹⁰⁹⁻¹¹¹, a feature similar to conventional inorganic semiconductors such as GaAs and Si, suggesting that charge transport is limited by phonon scattering rather than by impurity scattering.²⁹⁰ On the other hand, hybrid perovskites exhibit unique photo-induced giant dielectric constant effect,¹¹² which may provide a

dominant long range Coulomb potential as the driving force for polaron formation.¹⁰⁸ The above observations support the “large polaron” model proposed by Zhu *et al.*,²⁶⁵ based on commonly observed polarons in a wide range of polar solids, such as inorganic perovskites, ferroelectric materials, and ionic crystals.¹⁰⁸ Recently, a “small polaron” model was proposed by Cortecchia *et al.* to explain the broadband emission from 2D hybrid perovskites, which is an uncharacteristic feature for excitonic species.¹¹⁹ To provide extra insights into the nature of charge carriers in hybrid perovskites, here we provide some preliminary results from PIA and IR-CMS studies in hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ (Figure 5.9).

In PIA spectra (Figure 5.9B), a bleaching characteristic is observed from 0.14 eV to 0.6 eV, while photo-induced absorption appears below 0.14 eV. Sharp peaks reminiscent of infrared absorption spectra are observed below 0.2 eV, which we attribute to the Fano resonance between overlapping vibrational modes, bleaching and band absorption (Figure 5.9A).²⁹¹ Since the material is ambipolar, CMS spectra (Figure 5.9C) can be acquired either in electron or in hole accumulation mode (blue and magenta curves, respectively). For electron and hole accumulation CMS spectra, charge-induced absorption appears from 0.25 eV to 0.6 eV and 0.22 eV to 0.6 eV, respectively. Similar to PIA, both CMS spectra display bleaching features at low energies. We note that CMS and PIA do not reconcile entirely. This can be due to the different thin film preparation processes, where solvent engineering technique²⁶⁷ was applied for fabricating FETs used for CMS, while drop-casting was utilized to form the thin film on CaF_2 substrate used for PIA. From Figure 5.9, we can estimate that the polaron binding energy is below 0.14 eV from PIA measurement, while binding energy derived for both positive and negative polarons from CMS spectra would be 0.28 eV. With these preliminary data we demonstrate that broadband CMS and PIA can be useful techniques to obtain fundamental charge carrier parameters, such as polaron binding energy, in hybrid

Figure 5.9 — Infrared optical characteristics of $\text{CH}_3\text{NH}_3\text{PbI}_3$ at 78 K. (A, B) Absorption (A) and photo-induced absorption (B) spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film deposited on CaF_2 substrate by drop-casting. (C) Charge modulation spectra in electron (blue) and hole (magenta) FET accumulation regimes.

perovskite materials. A more systematic series of measurements on thin films with different morphologies as well as different composition materials (such as $\text{CH}_3\text{NH}_3\text{PbBr}_3$) are still required to fully understand the role of polaronic effects in hybrid perovskites.

5.6. Conclusions

To summarize, hybrid perovskite FETs were fabricated to obtain intrinsic transport parameters of $\text{CH}_3\text{NH}_3\text{PbI}_3$. We found that charge transport in $\text{CH}_3\text{NH}_3\text{PbI}_3$ is intrinsically ambipolar in nature. By lowering the operating temperature, the ionic drifting/screening effects associated to organic cations can be suppressed, allowing the extraction of electron and hole mobilities at different temperatures. Bright EL

was also obtained upon radiative recombination of electrons and holes within the FET channel under ambipolar injection condition; this first demonstration of a perovskite LE-FET could potentially accelerate the realization of solution-processed light-emitting devices such as perovskite large-area LEDs or active matrix displays. The collected EL spectra also reveal the structural phase transition from high temperature tetragonal phase to low temperature orthorhombic phase. Finally, preliminary results on PIA and CMS revealed that the polaron binding energy of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is below 0.3 eV. At this stage the difference in polaron band energy obtained from PIA and CMS is attributed to different morphologies between the samples, but more work needs to be performed to understand the fundamental nature of charge carriers in this unique class of materials. Here we demonstrated that IR-CMS can also be utilized to probe the polaronic signatures in hybrid perovskites. Interestingly, IR-CMS showed different polaronic signatures in electron- and hole- accumulation acquisition modes, providing complementary information about the photophysics of the materials which cannot be achieved with conventional all-optical PIA, *i.e.* polaronic signatures under unipolar excitation.

Chapter 6

Conclusions and perspectives

In this thesis, we studied various prototypical solution-processable materials belonging to the classes of organic conjugated polymers and hybrid organic-inorganic perovskites for unipolar, ambipolar, and light-emitting FETs. We performed a systematic study of different types of FETs, characterizing the FET transport characteristics as well as performing CMS measurements to study device physics and charge-excitation processes in these materials.

We started by studying unipolar p- and n-channel polymer FETs made with P3HT and P(NDI2OD-T2) as active materials. IR-CMS was employed to study polaronic absorption features and IRAV modes; the latter were also compared with IR and Raman modes, and their spectral features were assigned by DFT calculations. Benefiting from the high oscillator strength of IRAVs and high spatial resolution of a confocal microscope, we quantified the polaron density and mapped the carrier distribution along the active channel of P3HT FETs operating in different regimes. Subsequently, we studied bottom-gated P(NDI2OD-T2) FETs fabricated with different SiO₂ surface treatments. We found that the measured electron and hole mobility increase with surface hydrophobicity. These results are also consistent with the extracted sub-threshold slopes from the linear transfer characteristics, as well as the activation energy determined from temperature-dependent FET measurement. This indicates that the surface treatment reduces both the carrier

traps density and the energetic disorder at the semiconductor-dielectric interface. IR-CMS was then carried out to infer structure-property relationships at the semiconductor-dielectric interface, where we resolved the molecular orientation of the P(NDI2OD-T2) switching from a face-on to an edge-on orientation.

Then, we studied ambipolar FETs with DPPT-TT as active material. We elucidated the spectral contributions from polaronic bleaching/absorption and electroabsorption by analyzing the CMS spectra acquired at different local area and with different probing area. Control experiments with DPPT-TT diodes were carried out to confirm the EA signals, which overlap with polaronic absorption and bleaching features. Subsequently, we chose a probing wavelength from the EA-free spectral region to perform CMM on DPPT-TT FETs. Carrier distributions with nearly diffraction limited spatial resolution were acquired in unipolar linear, saturation, and ambipolar regimes to study carrier injection from electrodes as well as the operating mechanism of ambipolar FETs in electron and hole accumulation.

Lastly, we used the knowledge acquired in the previous studies to develop the first hybrid perovskite light-emitting FETs with ambipolar $\text{CH}_3\text{NH}_3\text{PbI}_3$ as active material. By lowering the operating temperature, the hysteresis in current-voltage characteristics reduces and field-effect mobility increases, allowing the observation of ambipolar FET characteristics in $\text{CH}_3\text{NH}_3\text{PbI}_3$. Under balanced ambipolar injection condition, bright EL can be observed; EL spectra were recorded and correlated with a structural phase transition. After that, we demonstrate the spatial control of EL emission zone from FET by manipulating gate and drain-source biases. Finally, to gain further insights on the predicted polaronic nature of charge carriers in hybrid perovskites, we also obtained preliminary photo-induced absorption and CMS data.

In conclusion, we exploited different charged excitation spectroscopic signatures, including polaronic excited states, electroabsorption, and infra-red active

vibrational modes, to study the carrier injection and charge distribution, as well as to examine the structure-properties relation at the semiconductor-dielectric interface of different unipolar and ambipolar FETs. These spectral features, obtained by performing CMS measurements on FETs, are useful to elucidate the nature of the charge carrier species. We demonstrated that charge modulation spectroscopy of solution-processable FETs is a unique technique for characterizing and understanding charge transport, charge injection, and charge distribution in solution-processable materials to develop proper mathematical and physical models to describe the nature of charge carrier species. This is useful information for designing new molecules and for developing different optoelectronic devices based on these materials.

Given the variety of material systems and their potential applications, there are plenty of perspective works to be completed for improving our current understanding on the charge transport properties of solution processable polymer and perovskite materials, as well as developing new devices for optoelectronic applications. As we demonstrated in Chapter 4, mapping of charge carrier density in a working device provides opportunities to understand structure-properties relationships as well as to study charge transport, injection, generation in organic conjugated polymers and hybrid organic-inorganic perovskites. Besides, we also showed that a probe with higher spatial resolution enabled the discrimination of spurious spectral features, thus allowing the recording of the actual carrier distribution across the channel of FETs. Maps with higher spatial resolution essentially allow recording spectral features stem from inter- and intra-molecular (and crystalline) domains; this allows extracting actual transport parameters for mathematical and physical models describing charge transport in solution materials. Therefore we propose super-resolution CMM with super-oscillatory lens as a continuation research outlook for this thesis.

Carrier distribution mapping with super-oscillatory lens

CMM mapping in the visible and near infra-red spectral regime with spatial resolution of 500 nm has been demonstrated.^{175, 176} However, such spatial resolution, limited by the far-field diffraction limits, only allows observing the modulation of the degree of order between semi-crystalline semiconductor domains.¹⁷⁶ Higher spatial resolution mapping could be achieved by employing a shorter probing wavelength; however, solution processable semiconductors tend to be easily degraded upon exposure to high energy photons. Besides, the possibility of CMM mapping with shorter probing wavelength require specific optical response of the active layer in the UV spectral region, while spectroscopic signatures of interest (polaronic and bleaching features) do not typically exist in this spectral domain (Figure 6.1A). Therefore, subwavelength imaging techniques such as super-resolution by super-oscillation,²⁹²⁻²⁹⁵ stimulated emission depletion spectroscopy,^{296, 297} and scanning near-field optical microscopy²⁹⁸ shall be engaged to achieve higher spatial resolution.

We have done preliminary work to assess viability of super-resolution CMM mapping on OFETs with high mobility n-type conjugated polymer P(NDI2OD-T2) (Figure 6.1B, device structure shown in inset). As discussed previously, the charge transport in P(NDI2OD-T2) has intra-molecular character, meaning inter-molecular polaron delocalization over multiple polymer chains is not necessarily required to achieve high mobility in D-A conjugated polymers.^{206, 257} This is also consistent with a recent report showing that D-A polymers consisting of larger and more planar repeating units promote linear conformation of the molecule and endure side-chain disorder. This allows superior charge transport regardless of the thin film microstructure.^{47, 48} Therefore, it would be of great interest to map the distribution of polarons with intra-molecular spatial resolution to examine the charge transport across molecular domains, and it can be made possible by employing subwavelength

Figure 6.1 — CMS of P(NDI2OD-T2) FET. (A) Charge modulation spectrum of the P(NDI2OD-T2) FET. The spectrum is acquired with $V_{gs} = 40 \text{ V} \pm 10 \text{ V}$ and $V_{ds} = 0 \text{ V}$. The black arrow indicates the maximum peak of the bleaching characteristics. (B) Transfer characteristics of P(NDI2OD-T2) FET. The inset shows the device structure of P(NDI2OD-T2) FET.

imaging technique.

To achieve subwavelength imaging, a super-oscillatory lens (SOL) was incorporated in the CMM measurement setup. SOLs utilize the interference of propagating waves with band-limited wavevectors to form super-resolved hotspot beyond the optical near-field region.²⁹⁹ Theoretically, this is possible since the oscillation of band-limited function can be much faster than its highest constituent frequency component,³⁰⁰ which is typically carried by evanescent fields that only exist in the near-field and quickly decay within few wavelengths. In principle, the spatial resolution of SOL has no physical limitations, but at the cost of energy transferred to side lobes of the superresolution spot, which weakens the light intensity concentrated in the hotspot. We used a binary amplitude mask designed and fabricated by Dr. Guanghui Yuan at the Centre for Disruptive Photonic Technologies²⁹⁹ (Figure 6.2A) to obtain super-oscillatory hotspot at a working wavelength of 690 nm, which is the maximum of the bleaching features in the CMS of P(NDI2OD-T2) (Figure 6.1A, black arrow). Formation of super-oscillatory hotspot can be obtained by illuminating uniform monochromatic laser beam over

the entire SOL mask. The optimization of the mask design is described in ref. 299 and the fabrication was performed by focused ion beam (FIB) milling of a thin (100 nm) gold film on a glass substrate.

Figure 6.2 shows the design, simulation and experimental characterization of the SOL mask. The calculations predict that the super-oscillatory hotspot is located at focal length $z = 30 \mu\text{m}$, with a depth of focus of $6 \mu\text{m}$. From the cross-sectional profile (Figure 6.2B), the spatial resolution of the hotspot can be determined to be 0.4λ ($\approx 276 \text{ nm}$). From $z = 27 \mu\text{m}$ to $33 \mu\text{m}$, the intensity of the super-oscillatory hotspot is the strongest (Figure 6.2D) in comparison to other positions, consistent with the simulation results (Figure 6.2C). From the cross-sectional view at the focal length $z = 30 \mu\text{m}$ (Figure 6.2E and Figure 6.2F), a strong intensity hotspot

Figure 6.2 — Super-oscillation lens for $\lambda = 690 \text{ nm}$. (A) Binary mask design of super-oscillation lens (SOL) for $\lambda = 690 \text{ nm}$. The design is $120 \mu\text{m}$ in diameter. (B) Simulation result of normalized full-width-at-half-maximum (FWHM) of SOL hotspot along the propagation direction z . The result indicates that the size of hotspot is smaller than the diffraction limit around $z = 27 \mu\text{m}$ to $33 \mu\text{m}$. (C, D) Simulation (C) and experimental (D) results of the intensity profiles along the propagation direction z . The super-oscillation needle appears around $z = 27 \mu\text{m}$ to $33 \mu\text{m}$. (E, F) Simulation (E) and experimental (F) results of cross-sectional intensity profile at $z = 30 \mu\text{m}$.

can also be seen at the center, accompanied by the rings of side bands with intensity much lower than the hotspot.

The preliminary results of polarized CMM with SOL are shown in Figure 6.3. When comparing maps with orthogonal polarization direction, the maps do not display the “inverse” intensity image, which is expected from the anisotropic absorption of P(NDI2OD-T2). The results also indicate that the experimental setup has to be further optimized to achieve the desired sub-diffraction spectral resolution, hence extracting useful information such as transition dipole moments and degree of order.¹⁷⁶ In principle, a SOL design with longer focal length (currently 30 μm) will facilitate the incorporation of the SOL into the CMM setup. The current setup requires careful alignment of the SOL, as any tilt between the sample and the SOL can easily result in scratching the surface of the FET. This imposes fabrication challenges as a SOL design with longer focal length will require a larger mask area,

Figure 6.3 — Polarized CMM of P(NDI2OD-T2) FET with super-oscillation lens. The maps are obtained by applying $V_{\text{gs}} = 40 \text{ V} \pm 20 \text{ V}$ and grounded both source and drain electrodes. The polarization directions indicated in the maps are measured with respect to the active channel direction of the FET.

which significantly increases the FIB writing time, but is technically doable.

In short, it is of utmost importance to understand charge carrier distribution in the inter- and intra- semicrystalline domain of (~ 100 nm) conjugated polymer fibrils, which is not possible with conventional optical imaging techniques due to the limited spatial resolution imposed by the optical diffraction limit. In general such technique can also be applied to study different material systems, such as donor-acceptor photovoltaic blends (*e.g.* P3HT: PCBM bulk heterojunction^{301, 302}), hybrid perovskite microcrystals / polycrystalline thin films, etc. For bulk heterojunction systems, the active layers of optimized solar cells typically consisted of interconnected network with domains of ~ 100 nm, due to limited carrier diffusion length from the conjugated polymer absorber component.^{266, 267} In hybrid perovskite photovoltaic system, it was reported that grain boundaries between crystalline domains play a critical role in determining current-voltage hysteresis of photovoltaic devices.³⁰³ In above cases, a super-resolution, subwavelength spatial probe is crucial to study the interesting charge transfer phenomenon across semi- and poly-crystalline domains; a necessary step to optimize performances of photovoltaic cells.

Understanding charge transport in inter- and intra-domain helps the optimization of molecule designs / thin film morphologies as well as charge transport parameters for various optoelectronic applications. This would provide a new platform to establish useful mathematical and physical models to describe charge carrier transport in solution processable materials and beyond, based on direct experimental detection of charge carrier parameters at the macromolecular level.

Appendix A

Experimental methods

A.1. Steady-state photo-induced absorption measurements

Photo-induced absorption (PIA) and reflectance (PIR) spectra are measured by acquiring the normalized change in transmission ($-\Delta T/T$) and reflectance ($-\Delta R/R$). The PIA (and PIR) spectra are obtained by calculating the $-(T_{\text{on}} - T_{\text{off}})/T_{\text{off}}$ (and $-(R_{\text{on}} - R_{\text{off}})/R_{\text{off}}$) where T_{on} (R_{on}) and T_{off} (R_{off}) are spectra acquired with and without photo-excitation. The samples, in the form of thin film deposited on an infrared compatible substrate, are mounted in a vacuum sealed cryostat (Advanced Research Systems, Inc.). A vacuum pump (Pfeiffer HiCube 80 Eco) is used to pump the cryostat to $< 10^{-5}$ mbar. The measurements are taken at low temperature ($T = 78$ K) unless otherwise specified. The samples are excited with Nd-YAG (green, $\lambda = 532$ nm) or HeNe (red, $\lambda = 633$ nm) continuous wave laser, while an FTIR spectrometer (Bruker Vertex 80 v) is used for obtaining the spectra with (T_{on} and R_{on}) and without (T_{off} and R_{off}) photo-excitation. PIA and PIR measurements are performed with a Bruker reflection/transmission accessory (A510/Q-T) to allow a near normal incident angle (11°) probing beam. A custom LabVIEW program is written to read the trigger from the interferometer and to control the on/off of laser with an optical shutter (Thorlabs SC10 and SH05). A phase resolution of 8 times of the spectral resolution is used to obtain the spectra. To minimize the heating effect

Figure A.1 — Schematic of photo-induced absorption and reflectance measurement setup.

from the excitation laser, 5-10 scans of T_{on} and T_{off} (R_{on} and R_{off}) are acquired consecutively in a single on/off cycle and the cycle is repeated for 250-1000 times. A liquid nitrogen cooled mercury cadmium telluride (LN-MCT), indium gallium arsenide (InGaAs), and silicon (Si) detectors are used to perform measurements in mid-IR, near-IR, and visible spectral range, respectively. Intrinsic silicon wafer is used as the long pass filter for mid-IR measurement, while proper long pass filters are used for near-IR and visible range measurements depending on the excitation wavelength.

A.2. Infra-red charge modulation spectroscopy measurement

Similar to PIA measurement, infra-red charge modulation spectroscopy (IR-CMS) spectra are obtained by measuring the normalized change in reflectance ($-\Delta R/R$) with and without charge accumulation in FET. Two Keithley 6487 voltage source/picoammeter are used to perform the FET measurement as well as applying

Figure A.2 — Schematic of infrared charge modulation spectroscopy measurement setup.

drain-source and gate voltage biases for acquiring IR-CMS spectra. The drain and source electrodes are grounded unless otherwise specified, while gate voltage biases are applied to induce (“on”, V_{on}) and to deplete (“off”, V_{off}) the carrier accumulation at the semiconducting active layer. The CMS spectra can be obtained by calculating $-(R_{\text{on}} - R_{\text{off}})/R_{\text{off}}$ where R_{on} and R_{off} are reflectance spectra acquired with and without accumulation. The measurements are performed with a Bruker Vertex 80 v FTIR spectrometer coupled to a Hyperion 1000 confocal microscope. The phase resolution of spectra is 8 times of the spectral resolution. A liquid nitrogen cooled mercury cadmium telluride (LN-MCT), indium antimonide (InSb), and silicon (Si) detectors are used to perform measurements in mid-IR, near-IR, and visible spectral range, respectively. The spectra are averaged to improve the signal-to-noise ratio by acquiring 200 cycles of R_{on} and R_{off} with 10 scans each.

A.3. Charge modulation spectroscopy and electroabsorption measurements

Different than infra-red charge modulation spectroscopy measurements, the charge modulation and electroabsorption spectroscopy measurements described in this section are phase-sensitive technique measurements. A homemade vacuum chamber with electrical feedthroughs is used to perform the measurements on FETs and MIS (metal-insulator-semiconductor) diodes at high vacuum condition ($\sim 10^{-5}$ mbar). The source and drain of FETs and the ITO (indium tin oxide) of the diodes are grounded. Modulated voltage biases ($f = 1137$ Hz), obtained by using a waveform generator (Keithley 3390) and a voltage amplifier (Falco Systems WMA-300), are applied to the gate and Au electrode of FETs and diodes, respectively. A monochromator with a tungsten lamp light source is used to obtain the monochromatic light for the measurements. Transmittance and reflectance modes are adopted for FET and diode, respectively. The monochromatic light is focused on the device (FET or diode) and the transmitted (reflected) light are collected by focusing the light to silicon photodetector (Thorlabs FDS100). A transimpedance

Figure A.3 — Schematic of charge modulation and electroabsorption spectroscopy measurement setup.

amplifier (Femto DHPA-100) is used to amplify the signal before it is registered by a lock-amplifier (Stanford Instrument SR830) to obtain the differential transmission ΔT (or reflectance ΔR). Prior to acquiring ΔT and ΔR , the phase of lock-in amplifier is synchronized to the amplified voltage signal from the voltage amplifier system. With the same phase sensitive measurement principle, intensity of monochromatic light, modulated with an optical chopper (Stanford Instrument SR540, $f = 1137$ Hz), is measured to obtain the transmission T (or reflectance R) signal without applying any voltages to the FET or diode. The CMS and electroabsorption spectra $\Delta T/T$ (or $\Delta R/R$) can be obtained by dividing the first and second harmonic components of ΔT (ΔR) to T (R), respectively.

A.4. Charge modulation microscopy measurements

All charge modulation microscopy measurements are performed on a homemade confocal microscope. Monochromatic probing light in the 475-1100 nm region (line widths between 2 and 5 nm) is obtained by generated white light from the supercontinuum laser (NKT Photonics SuperK Extreme) coupled to an acousto-optic modulator (NKT Photonics SuperK Select). The incident beam on the FET, a linear polarized monochromatic light manipulated by a half-wave plate and a linear polarizer, is focused with a 0.7 N.A. objective (Nikon S Plan Fluor 60 $\times$). The transmitted beam, collected with a 0.75 N.A. objective (Nikon CFI Plan Apochromat VC 20 $\times$), is then focused to a multimode fiber with a 50 μm diameter core, which also acts as a confocal aperture. The intensity of the collected light, recorded by a silicon photodetector (Thorlabs FDS100), is then amplified by a transimpedance amplifier (Femto DHPA-100), before it is delivered to data acquisition board (DAQ, National Instruments) and to a lock-in amplifier (Stanford Research Systems SR830 DSP) for obtaining the transmission signal T and

Figure A.4 — Schematic of charge modulation microscopy measurement setup.

differential transmission signal ΔT , respectively. ΔT , acquired at the first and second harmonic, is divided to T ($\Delta T/T$) to obtain the charge-induced absorption and electroabsorption spectra, respectively.

The interfacing of laser system and 3D piezo stage (Physik Instrumente P-517) is controlled with custom written LabVIEW (National Instruments) program to perform raster scan mapping as well as collecting local spectrum. The FET device is mounted on a homemade chamber with electrical feedthroughs, which was purged with very mild nitrogen flow to minimize the exposure to oxygen and moisture for the entire duration of measurement. The drain-source voltages are applied by using a dual channel source-measure unit (Agilent B2912A). A waveform generator (Keithley 3390) is used to supply voltage modulation ($f = 1137$ Hz, unless otherwise specified), which was amplified by a voltage amplifier (Falco Systems WMA-300), before it is applied to the gate electrode. Prior to every measurement, the phase of lock-in amplifier is matched with the amplified voltage modulation from the voltage amplifier.

A.5. Other characterization methods

Raman Spectroscopy

Renishaw Raman microscope constitutes of a charge coupled device array detector is used to perform Raman spectroscopy measurement. A low power (below 1 μW) green ($\lambda = 532 \text{ nm}$) laser is used for sample excitation, while a Leica 100 $\times$ objective lens (N.A. = 0.85) is used to collect the Raman signals. The Raman spectra are acquired with signal integration time of 20 seconds and frequency resolution of $\sim 0.8 \text{ cm}^{-1}$ (with the use of 2400 line/ mm grating).

X-ray diffraction and scanning electron microscopy characterization

A FEI Helios 650 Nanolab scanning electron microscope (SEM) with 10 kV acceleration voltages is used to obtain SEM images. The morphology of the hybrid perovskite thin film is characterized with Scanning Probe Microscope Digital Instrument Dimension V with atomic force microscope (AFM) tapping mode while the editing and plotting of the AFM data is processed with WSxM software. X-ray diffraction (XRD) structural spectra are acquired with step increment of 0.02° , acquisition time of 1 second, and sample rotation of 5 min^{-1} by using a diffractometer Bruker D8 Advance in Bragg-Brentano geometry.

Temperature dependence FET measurement

A liquid nitrogen cooled Linkam Stage (FTIR 600) with electrical feedthroughs is used to manipulate operating temperature of the FET device from 300 K down to 77 K. FET devices are mounted on the heating/cooling block of Linkam stage while thin copper wires and silver paint are used to make electrical contacts between FET and electrical feedthroughs. FET characteristics measurements are performed with Agilent B2902A Precision Source/Measure Unit in dark environment. The data is processed and analyzed with OriginPro software.

Electroluminescence measurement

The electroluminescence (EL) spectra from the FET are collected with Nikon eclipse LV100 microscope with LU plan 10× objective. Agilent B2902A Precision Source/Measure Unit is used to bias FET while operating temperature control is achieved with Linkam stage. EL spectra are recorded by focusing the EL emission from FET into optic fiber that coupled to USB2000 Ocean Optics with 1 second integration time over 3 averages. Optical images of FET are taken by using Thorlabs DCC1545M High Resolution USB2.0 CMOS Camera with weak illumination to improve the optical contrast.

Appendix B

Sample preparation

B.1. Samples used in Chapter 2

P3HT FETs

A 500 nm thermally-grown silicon dioxide (SiO_2) on heavily n-doped silicon wafer (denoted as $n^{++}\text{-Si}$) was used as substrate. The substrates are treated in ultrasonic bath with acetone and isopropanol for 10 minutes each. 500 nm of PMMA (poly(methyl methacrylate), 950 K, 4 % anisole, Microchem) is then deposited by spincoating at 800 rpm for 120 s with 5 s of acceleration. The substrates are hardbaked at 180 °C for 30 minutes to improve the chemical resistivity for subsequent material deposition.^{229, 230} A metal shadow mask is used to define source-drain electrodes, which 100 nm of silver (Ag) is deposited through thermal evaporation. To improve the electrical contact of the gate electrode, Ag is also deposited on the $n^{++}\text{-Si}$ side of the substrate. Highly regioregular Poly (3-hexylthiophene-2,5-diyl) (P3HT, Rieke Metals, Inc. BASF's Sepiolid P200, molecular weight ~20-40 K) is employed as the prototypical active material for infrared charge modulation spectroscopy study. The active material is used without any further purification. P3HT solution of 8 mg/ml in DCB (1,2-dichlorobenzene, Sigma Aldrich) is then prepared (filtered with 0.2 μm PTFE filter). The active

material is deposited by spincoating at 800 rpm for 120 s. A thermal annealing of the sample, at 150 °C³⁰⁴ for 10 minutes, is then performed to complete the device fabrication. The active layer deposition is entirely processed in inert nitrogen environment to minimize the oxidation on the organic semiconductor.

P(NDI2OD-T2) FETs

Heavily p-doped silicon (p++ Si) with thermally-grown 500 nm silicon dioxide (SiO₂) is used as substrate, functioning as the gate and gate dielectric for the bottom-gate bottom-contact configuration adopted in this study. The substrates are thoroughly cleaned by sonication in acetone and iso-propanol for 10 minutes each. A standard lift-off photolithography process is used to define the interdigitated source and drain electrodes. 3 nm of chromium (Cr) is deposited as adhesion layer for the subsequent 50 nm of gold (Au) deposition through thermal evaporation technique without breaking the vacuum. A lift-off process to obtain the desired Au/Cr interdigitated electrodes is achieved by immersing the substrates in acetone overnight. The substrates are again sonicated in iso-propanol for 10 minutes before dried with N₂ flow.

Prior to the deposition of the active material, the SiO₂ substrates are treated with different self-assemble monolayer (SAM) molecules to obtain different surface energy / hydrophobicity surfaces (see surface treatment section). 3 different SiO₂ surfaces are prepared for this study, *i.e.* non-treated, HMDS-treated, and OTS-treated surface. The active material, P(NDI2OD-T2) (Polyera Ink N2200, poly{ [N, N9 - bis(2 - octyldodecyl) - naphthalene - 1, 4, 5, 8 -bis (dicarboximide) - 2, 6 - diyl] - alt - 5, 59 -(2, 29 - bithiophene) } ,), is used as purchased without further purification. P(NDI2OD-T2) solution in THF (tetrahydrofuran) with concentration of 4 mg/ml is filtered with 0.2 µm PTFE filter prior to the spincoating of active material. A thin active layer (40 - 50 nm) of P(NDI2OD-T2) is spun at 2500 rpm

for 90 s with 5 s of acceleration duration. The substrates are then thermally annealed at 110 °C for 11 hours to remove the residual THF solvent in nitrogen environment. To minimize the oxidation of the active layer, PMMA (poly(methyl methacrylate), Sigma-Aldrich, $M_w = 120$ kg/mol) layer with thickness of 500 nm is deposited by spincoating a 80 mg/ml solution of PMMA in *n*-BA (*n*-butylacetate, filtered with a 0.45 μ m PTFE filter) as an encapsulation layer. An overnight thermal annealing of the substrates is performed to remove the residual *n*-BA solvent in nitrogen environment.

Surface treatment

For HMDS-treated surface, a “dry” vapor exposure method is used to treat the SiO₂ surface. HMDS (hexamethyldisilazane, Sigma Aldrich) is used as purchased. The substrates are mounted on a piece of parafilm that is later to be used to seal a glass beaker, with the SiO₂ surface facing down to the bottom of beaker covered with HMDS. SiO₂ surface is modified with HMDS vapor for 24 hours. The substrates are then rinse in iso-propanol and dried with N₂ flow.

For OTS-treated surface, a “wet” spincoating method is used to modify the SiO₂ surface.²⁴⁴ OTS (octyltrichlorosilane, Sigma Aldrich) is used as purchased. Prior to the spincoating of OTS, the substrates are cleaned with plasma treatment for 60 s. OTS is spun at 3000 rpm for 10 s from a solution of 4mM in TCE (trichloroethylene, sigma Aldrich). The substrates are then treated with ammonia vapor by placing it in a closed glass container with a small vial containing a few milliliter of ammonia solution (28-30% in water). The treatment is left for overnight at room temperature. After the ammonia vapor treatment, the substrates are cleaned with sonication bath in toluene for 10 minutes.

B.2. Samples used in Chapter 3

DPPT-TT FETs

A staggered top-gate bottom-contact FET configuration is adopted for this study. Corning 1737F glass is used as substrate and is thoroughly cleaned by sonication in acetone and iso-propanol. Interdigitated source and drain electrodes are pre-patterned with a standard photolithography process. The channel length and width are 20 μm and 20 mm, respectively. Prior to the deposition of 30 nm Au as electrodes, 1.5 nm thick of Cr are deposited to improve the adhesion of Au on glass substrate. After the deposition of bottom electrodes, a thin PEI (branched polyethylenimine, Sigma Aldrich, $M_w = 25$ kg/mol) layer is deposited to improve the injection of electron.³⁰⁵ The layer is coated by spincoating PEI solution in methoxyethanol (weight concentration of 0.4%). A thermal annealing of 10 minutes at 100 °C is performed to remove the residual solvent in ambient environment. A mild flow of distilled water is applied to the PEI surface for 60 s to improve the smoothness of the deposited layer (~10 nm). The active material, DPPT-TT (poly(N-alkyldiketopyrrolo-pyrrole dithienylthieno[3, 2-b]thiophene), LT-S9118, Lumtec Corp., $M_w > 30$ kg/mol), is used as purchased without further purification. Solution of DPPT-TT in DCB (1,2-dichlorobenzene, Sigma Aldrich) with concentration of 5 mg/ml, filtered with 0.2 μm PTFE filter, is used for spincoating the active semiconducting layer DPPT-TT at 1000 rpm for 60 s with acceleration duration of 1 s. A thermal annealing of 160 °C for 30 minutes is performed to improve the thin film morphology.⁴⁹ The substrates are subsequently thermal-annealed at 130 °C for overnight to remove the residual solvent in nitrogen environment. Gate dielectric layer, PMMA (poly(methyl methacrylate), Sigma-Aldrich, $M_w = 120$ kg/mol), is then deposited by spincoating a solution in *n*-butylacetate (80 mg/ml, filtered with a 0.45 μm PTFE filter). The thickness of

dielectric layer is estimated to be 500 nm after an overnight thermal annealing at 130 °C in inert gas environment. A semi-transparent bilayer gate electrode of Al (8nm) and Au (4nm) is then deposited, allowing measurements of CMS and CMM to be implemented in optical transmission mode. All metal depositions are performed with thermal evaporation technique. Finally, the FET devices are thermally annealed overnight at 130 °C to improve the contact between the gate electrode and dielectric layer in nitrogen environment.

DPPT-TT diodes

A conductive ITO (indium tin oxide) on glass is used as substrate for the MIS (metal-insulator-semiconductor) diode fabrication. The substrates are thoroughly cleaned by sonication bath in acetone and iso-propanol for 10 minutes each. The active layer, DPPT-TT, is deposited with the recipe as mentioned in previous section (see DPPT-TT FETs). A thin PMMA dielectric layer of 120 nm is then deposited from a solution, filtered with 0.2 µm PTFE filter, of 20 mg/ml in *n*-butylacetate by spincoating at 2000 rpm for 60 s with acceleration duration of 2 s. Both active and dielectric layers are processed in inert nitrogen environment. Thermal evaporation technique is used to deposit 80 nm of Au electrode to complete the MIS diode. A thermal annealing at 130 °C for 2 hours is performed to remove the residual solvent from the fabricated diode devices in inert gas environment.

B.3. Samples used in Chapter 4

CH₃NH₃I synthesis

10 ml of methylamine solution (CH₃NH₂, 40 % in methanol, TCI) and 14 ml of hydroiodic acid (57 % wt in water, Sigma-Aldrich) are mixed to synthesize the organic precursor methylammonium iodide CH₃NH₃I. The solution is stirred for 2 hours in ice bath to complete the reaction. The solvent is then removed by using

rotary evaporator at 60 mbar for 60 minutes at 60 °C. The product was then purified with 6 repeating washing cycles by dissolution in ethanol and recrystallization with diethylether. A paper filter is then used to filter the solution. Finally, the resulting white powder is obtained by drying in vacuum oven at 60 °C for 24 hours.

Hybrid perovskite deposition

Thin film of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is deposited by spincoating technique. The solvent engineering technique²⁶⁷ is employed to obtain continuous and uniform films. A 20 % (weight percentage) of solution is prepared by mixing 1:1 stoichiometric $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 (99%, Sigma-Aldrich) in a solvent mixture of γ -butyrolactone and dimethylsulfoxide with 7:3 volume ratio. The solution is stirred overnight at 100 °C. The solution is spincoated on SiO_2 substrates with pre-patterned electrodes with 2 ramping steps: 1000 rpm for 10 s, 5000 rpm for 20 s. Toluene is dropped on the substrate during the second ramping step. A thermal annealing is performed with hotplate at 100 °C for 30 minutes to obtain the thin film.

Hybrid perovskite FETs

A pre-cut heavily p-doped Si with 500 nm thermally grown SiO_2 is used as substrate. The substrate is thoroughly cleaned by sonication in acetone and isopropyl alcohol for 20 minutes each. Interdigitated electrodes with channel width of 20 nm and channel length of 80 and 100 μm are patterned by standard photolithography process. 10 nm of nickel and 50 nm of gold are thermally evaporated as source and drain electrodes. Acetone is used to perform the lift-off process. Prior to the perovskite deposition, substrate with interdigitated electrodes are treated with oxygen plasma for 60 seconds to improve the wettability of the surface and to obtain uniform perovskite thin film (see perovskite deposition).

B.4. Photolithography process

Two different processes were used to perform the photolithography. The details are provided in this section.

Process 1

In this recipe, a reverse tone photoresist, AZ5214E (Microchem), is used to perform the patterning of the desired patterns, *i.e.* interdigitated source and drain electrodes. The substrates are first thoroughly washed by sonication in acetone and isopropanol. Photoresist, AZ5214E, is used as purchased without further purification. The photoresist is spun at 4000 rpm for 30 s with acceleration duration of 2 s. The deposited photoresist is baked at 105 °C for 105 s to remove the residual solvent. The thickness of deposited photoresist is estimated to be around 1.2 μm . The substrates are then placed on mask aligner (MJB-3 or MJB-4, Karl Suss) for the first exposure. A soft contact mode is adapted to the contact between negative photomask, *i.e.* the unexposed area being the desired patterns, and substrate. 3 s of first exposure is applied to the sample when the contact is ready. The first exposure is followed by a tone reversal baking at 110 °C for 450 s in a thermal oven. The entire sample is flood-exposed for 25 s after the reverse tone baking process. A mixed solution of AZ developer with deionized water (ratio 1:2) is then used to perform the development process. The developing process typically last around 90 s. The samples are rinsed in deionized water before dried by using N_2 flow. Prior to metal deposition, the sample is treated with oxygen plasma for 120 s with power setting “low” at atmospheric pressure below 250 mtorr. After metal deposition, the samples are immersed in acetone for lift-off process. After obtaining the desired metal structures on the substrate, the samples are then sonicated in acetone and iso-propanol for 5 minutes each to remove the residual photoresist.

Process 2

For this recipe, a bilayer photoresist technique is used to obtain the desired patterns with undercut. The substrates are treated in ultra-sonication bath with deionized water, acetone, and isopropanol for 10 minutes each. Prior to the deposition of LOR (lift-off resist), the substrates are treated with oxygen plasma for 10 minutes to improve the surface wettability. The LOR is spun at 6000 rpm for 60 s with 1 s of acceleration time. Samples are baked at 180 °C for 5 minutes to harden the LOR layer. The process follows with the spincoating of photoresist, S1813 (Microposit), at 6000 rpm for 60 s with acceleration duration of 1 s. Samples are then thermal-annealed at 120 °C for 2 minutes to remove the residual solvent from photoresist. A Karl Suss MJB-3 mask aligner is used to perform the photomask alignment as well as ultraviolet light exposure. The substrate with bilayer resist is then exposed for 9 second with soft contact applied. Upon UV exposure, the substrates are developed with MicroChem MF319 (used as purchased, without further dilution). The samples are then rinsed in deionized water and dried with nitrogen. 1 minute of oxygen plasma is performed to remove the residual organic resist from the developing process. The samples are then loaded to thermal evaporator for metal electrode deposition. 1.5 nm of chromium is deposited as adhesion layer for the subsequent 30 nm of gold deposition. The deposition rates are 0.1 Å/s and 0.2 Å/s for chromium and gold deposition, respectively. N-Methyl-2-pyrrolidone (NMP) is used for lift-off process. The samples are rinsed in NMP overnight. After that, substrates are gently flushed with IPA. The process is followed by sonication with IPA for 5 minutes. The glass substrates are dried with nitrogen.

Appendix C

Contributions

Section 3.1 of Chapter 3

The contents of Section 3.1 are published in the Nature Scientific Reports with manuscript titled “Mapping polarons in polymer FETs by charge modulation microscopy in the mid-infrared”. Within this project, the candidate developed an infra-red CMS setup based on a commercial FTIR system with confocal microscope, performed FET device fabrication, charge transport characterization and analysis. Dr. Wang Zilong helped with initial IR absorption, IR-CMS and mapping measurements of P3HT films. Dr. Yin Jun conducted Raman measurement, DFT calculation, and IRAV mode assignment.

Section 3.2 of Chapter 3

The content of Section 3.2 is the subject of a manuscript titled “Improving charge transport in n-channel polymer transistor by chemical modification of the semiconductor-dielectric interface” that is under preparation. The idea of this project originated from preliminary FET data of Dr. Alessandro Luzio. The candidate proposed to study correlation of CMS and modified FET characteristics. He performed the surface treatment, contact angle measurement, device fabrication, charge transport characterization, IR-CMS measurement and analysis. The IR

absorption and Raman of P(NDI2OD-T2) were obtained by Dr. Wang Zilong and Dr. Yin Jun.

Chapter 4

The content of Chapter 4 is the subject of a manuscript titled “Ambipolar Charge Distribution in Donor-Acceptor Polymer Field-Effect Transistors” that has been submitted to the Journal of Materials Chemistry C. The results described in this Chapter were obtained during the candidate’s research attachment at the Center for Nanoscience and Technology (CNST), Milano, in collaboration with the co-supervisor Dr. Mario Caironi and Dr. Giuseppina Pace. The candidate fabricated the FET devices with the help from Dr. Sadir Bucella and Dr. Alessandro Luzio, collected the charge transport data of FETs, and performed the CMM mapping experiment. Dr. Giuseppina Pace collected the absorption of DPP-DTT, macroscopic CMS and EA spectra of FET and MIS diode.

Chapter 5

The majority of the content of Chapter 5 has been published in a Nature Communications paper titled “Lead iodide perovskite light-emitting field-effect transistor”. The candidate initiated the idea and designed the experiments needed for this project. He fabricated FET devices by photolithography and thermal deposition, performed temperature-dependent FET current-voltage characterization, FET mobility calculations, and CMS measurements. Electroluminescence data were collected with the help of Dr. Stefano Vezzoli and Saleem Umar for instrument setup. Fitting and analysis of the electroluminescence data was performed by Dr. Annalisa Bruno. Synthesis, deposition, and structural analysis of the perovskite films were conducted by Daniele Cortecchia. Dr. Yin Jun performed the DFT modeling and theoretical mobility calculations and Dr. Wang Zilong conducted the PIA measurements.

Chapter 6

The preliminary results for the purposed research outlook, carrier distribution mapping with super-oscillatory lens, were also obtained during the candidate's research attachment at the CNST. The project was conceived based on the original design of super-resolution lenses by Dr. Yuan Guanghui with the aim of demonstrating super-resolution mapping of charge carriers in FET by CMM.

The candidate fabricated and characterized the P(NDI2OD-T2) FETs under the guidance of Dr. Alensandro Luzio. Dr. Giuseppina Pace collected the CMS spectrum of P(NDI2OD-T2) FETs. Dr. Yuan Guanghui designed and fabricated a binary amplitude mask (*i.e.* the super-oscillatory lens). A custom super-oscillatory lens has been designed by the candidate for performing the experiment. The candidate also modified the charge modulation microscopy setup (see section A.4) for performing the super-resolution mapping of charge carriers.

List of publications

Manuscripts in preparation

1. **X.Y. Chin**, A. Luzio, J. Yin, Z. Wang, M. Caironi, C. Soci, Improving charge transport in n-channel polymer transistor by chemical modification of the semiconductor-dielectric interface, in preparation.

Journal publications

1. **X.Y. Chin**, J. Yin, Z. Wang, M. Caironi, C. Soci, Mapping polarons in polymer FETs by charge modulation microscopy in the mid-infrared, Scientific reports, 4 (2014).
2. **X.Y. Chin**, D. Cortecchia, J. Yin, A. Bruno, C. Soci, Lead iodide perovskite light-emitting field-effect transistor, Nature Communication, 6 (2015).
3. **X.Y. Chin**, G. Pace, C. Soci, M. Caironi, Ambipolar Charge Distribution in Donor-Acceptor Polymer Field-Effect Transistors, Journal of Materials Chemistry C, 5 (2017), 754-762.
4. G. Dayal, **X.Y. Chin**, C. Soci, R. Singh, High-Q Whispering-Gallery-Mode-Based Plasmonic Fano Resonances in Coupled Metallic Metasurfaces at Near Infrared Frequencies, Advanced Optical Materials, 4(2016),1295-1301
5. G. Dayal, **X.Y. Chin**, C. Soci, R. Singh, Independent tailoring of super-radiant and sub-radiant modes in high-Q plasmonic Fano resonant metasurfaces, Advanced Optical Materials, 4(2016), 1860-1866
6. G. Dayal, **X.Y. Chin**, C. Soci, R. Singh, High-Q Plasmonic Fano Resonance

for Multiband Surface-Enhanced Infrared Absorption of Molecular Vibrational Sensing, *Advanced Optical Materials*, 5(2017), 1600559

7. W. Dong, M. Krbal, J. Kalikka, **X.Y. Chin**, B. Gholipour, C. Soci, P. Fons, K.V. Mitrofanov, L. Chen, R.E. Simpson, Enhanced Sb₂S₃ crystallisation by E-field induced silver doping, *Thin Solid Films* 616(2016), 80-85

Book chapters

Charge Transport in Organometal Halide Perovskites, F. Maddalena, P. Boix, **X.Y. Chin**, N. Mathews, C. Soci, S. Mhaisalkar, *Organic-Inorganic Halide Perovskite Photovoltaics*, ISBN 978-3-319-35112-4.

Patents and technology disclosures

Lead Iodide Perovskite Light-Emitting Field-Effect Transistor, C. Soci, **X.Y. Chin**, D. Cortecchia, A. Bruno, J. Yin, disclosed to NTU (NTU Ref: PAT/021/15/16/US), US patent application filed (US Patent Application No : 15/199,185).

Conference talk presentations

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3. **X.Y. Chin**, D. Cortecchia, J. Yin, A. Bruno, C. Soci, Perovskite Field-Effect Transistor, in: International Conference on Materials for Advanced Technologies, 2015.
4. **X.Y. Chin**, D. Cortecchia, J. Yin, A. Bruno, C. Soci, Perovskite Light

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