First principles studies of multidimensional hybrid materials

Yin, Jun

2017

Yin, J. (2017). First principles studies of multidimensional hybrid materials. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/69901>

<https://doi.org/10.32657/10356/69901>

FIRST PRINCIPLES STUDIES OF MULTIDIMENSIONAL HYBRID MATERIALS

YIN JUN

**SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES
DIVISION OF PHYSICS AND APPLIED PHYSICS**

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2016

YIN JUN

Acknowledgements

I would like to express my deepest gratitude to everyone who have bestowed their wishes, blessings, and support on me in my life.

First and foremost, I would like to thank my supervisor, Nanyang Assistant Professor Cesare Soci, for his great guidance, support and patience during my four years' PhD study. His immense zeal, great diligence, and steady efforts towards science and research have always been an inspiration to me. I especially appreciate his encouragement to me for exploring unknown research fields. I believe that the interdisciplinary research and collaboration atmosphere of physicists and chemists in our group exert an edifying influence on my whole PhD career. I would also like to thank my co-supervisor, Professor Shen Zexiang for his guidance, mentorship and advice which wasn't just limited to the confines of academics.

I sincerely thank Professor Dmitri B. Migas, from Belarusian State University of Informatics and Radioelectronics, for his great help, motivation, and collaboration in the hybrid III-V/polymer project.

I appreciate all the suggestions from and discussions with Dr. Daniele Fazzi from Max Planck Institut für Kohlenforschung, especially regarding the project of IRAV modes.

I also thank Dr. Giorgio Adamo from the Center for Disruptive Photonic Technologies at NTU for his great suggestions and discussions about the project on plasmonic topologic insulators.

I would like to extend my special thanks to my experimental collaborators: Dr. Chen Shi from PAP in NTU, for the XPS and UPS measurements and extensive discussions on the interfacial energetics of different material systems; Dr. Ma Lin and Professor Gagik G. Gurzadyan previously from PAP in NTU, for the optical measurements of

polymer/quantum dots blends; Dr. Wang Zilong from our group, for photo-induced absorption measurements of polymers; Daniele Cortecchia and Dr. Annalisa Bruno from our group, for their major contributions and many fruitful discussions in the hybrid perovskite projects.

I gratefully acknowledge Soh Hwee Jin from the High Performance Computer Centre in NTU for the continuous technical support.

I am very glad to have been working with all of my colleagues in our group: Xin Yu Chin, Majid Panahandeh-Fard, Manoj Kumar, Anurag Krishna, Paola Lova, and Dai Xing who made my PhD life enjoyable by being great companions not only for research but also for daily life.

Last but not least, I would like to convey my deepest appreciation and gratitude to my parents, my sister's family and my dearest friends, for their endless and unconditional love, encouragement and support. Especially, I would like to thank my beloved wife, Dr. Lei Qiong, for her love in my life.

Table of Contents

Acknowledgements i

Table of Contents iii

List of Abbreviations ix

Abstract 1

Chapter 1 Introduction 3

 1.1 Background and Motivations 3

 1.2 Aims and Implementation 9

Chapter 2 Density Functional Theory 13

 2.1 Introduction 13

 2.2 Basics of Density Functional Theory 15

 2.2.1 The Hartree approximation 15

 2.2.2 The Hartree–Fock approximation 16

 2.2.3 The Hohenberg–Kohn theorems 19

 2.2.4 Kohn–Sham equations 21

 2.2.5 Bloch’s theorem 22

 2.2.6 Self-consistent calculations 23

 2.3 Optical Response 24

2.3.1 Time-dependent density functional theory	24
2.3.2 Bethe–Salpeter equation	27
2.4 Computational Codes	28
Chapter 3 Polymer/III-V Photovoltaic Hybrid Systems.....	30
3.1 Electronic and Vibrational Properties of Model Conjugated Polymer P3HT	32
3.1.1 Electronic Properties of P3HT	32
3.1.2 Vibrational Properties of P3HT	36
3.1.3 Experimental Section	40
3.1.4 Results on Structural, Vibrational and IR/V Modes of P3HT	42
<i>Structural properties of RR and RRa-P3HT</i>	<i>42</i>
<i>Vibrational modes in ground states of RR and RRa-P3HT</i>	<i>44</i>
<i>Vibrational modes in chemically-doped RR and RRa-P3HT</i>	<i>46</i>
<i>Interpretation of IR/V modes of RR and RRa-P3HT</i>	<i>49</i>
3.2 Surface Polarity Effects at Photovoltaic Hybrid Interfaces	54
3.2.1 Hybrid Polymer/Inorganic Semiconductors.....	54
3.2.2 Photophysical Processes in Hybrid Photovoltaics	56
3.2.3 Hybrid Polymer/GaAs Heterointerfaces	59
3.2.4 Experimental Methods	61
3.2.5 Results on the Surface Polarity Effects on the Charge Redistribution and Transfer at P3HT/GaAs Heterointerfaces	63

<i>Interfacial geometric structures of P3HT on GaAs surfaces</i>	63
<i>Electronic coupling of P3HT with GaAs surfaces</i>	66
<i>Charge redistributions in GaAs/P3HT heterointerfaces</i>	69
<i>Energy alignments of GaAs/P3HT bilayers</i>	73
3.3 Electron Transfer in P3HT/InP Quantum Dots	77
3.3.1 Hybrid organic/inorganic nanocrystal system.....	77
3.3.2 Materials and Methods.....	81
3.3.3 Computational Approach	83
3.3.4 Results on Ligand and Small-Size Effects on Electron Transfer in P3HT/InP Quantum Dots	87
<i>Ligand exchange and characterizations of InP QDs</i>	87
<i>Density functional theory calculations of InP QDs</i>	90
<i>Absorption and photoluminescence properties of InP QDs</i>	93
<i>Transient absorption and kinetics measurements of InP QDs</i>	96
<i>Charge transfer and separation rates between InP QDs and P3HT</i>	100
3.4 Summary	105
Chapter 4 Multidimensional Hybrid Perovskites	107
4.1 Background and Motivations	109
4.1.1 3D organic-inorganic perovskites	110
4.1.2 2D organic-inorganic perovskites	112

4.1.3 Organic/perovskite heterointerfaces	113
4.2 Experimental Methods	114
4.3 Results on Three-Dimensional Perovskites	120
4.3.1 Structural and optical properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$	120
4.3.2 Transport properties of crystalline $\text{CH}_3\text{NH}_3\text{PbI}_3$	124
4.4 Results on Two-Dimensional Perovskites.....	127
4.4.1 Electronic properties of (EDBE) PbCl_4 and (EDBE) PbBr_4	128
4.4.2 Self-trapping charge properties of (EDBE) PbCl_4 and (EDBE) PbBr_4	129
4.5 Results on Organic/ Perovskite Hybrid Interfaces	132
4.5.1 Electronic structures of organic molecules on $\text{CH}_3\text{NH}_3\text{PbI}_3$ surfaces	133
4.5.2 Energy alignments of organic molecules on $\text{CH}_3\text{NH}_3\text{PbI}_3$ surfaces	139
4.5.3 Charge redistributions of organic molecules on $\text{CH}_3\text{NH}_3\text{PbI}_3$ surfaces.....	140
4.6 Summary	145
Chapter 5 Plasmonic Topological Insulators	147
5.1 Background and Motivations	148
5.1.1 Chalcogenide topological insulators	149
5.1.2 Electronic properties of TI Materials	150
5.1.3 Plasmonic properties of TI Materials	151
5.2 Computational Methods	154
5.3 Results on Electronic and Optical Properties of Plasmonic Topological Insulators	156

5.3.1 Crystal and electronic structures of BSTS Compounds..... 157

5.3.2 Optical response of TI materials 160

5.3.3 Plasmonic behaviour of TI materials 166

5.4 Summary 171

Chapter 6 Conclusions and Perspectives 172

References 179

Appendixes..... 197

A. Appendix to Chapter 3 197

B. Appendix to Chapter 4..... 205

C. Appendix to Chapter 5..... 209

List of Publications 213

Page intentionally left blank

List of Abbreviations

BLD	Bond length difference
BSE	Bethe–Salpeter equation
CB	Conduction band
CP	Car–Parrinello
DFT	Density functional theory
DOS	Density of states
GGA	Generalized gradient approximation
GSB	Ground state bleaching
GW	Green's function (G) and the screened Coulomb interaction (W)
HF	Hartree–Fock
HOMO	Highest occupied molecular orbital
ICT	Integer charge transfer
IRAV	Infrared active vibrational
KS	Kohn–Sham
LDA	Local density approximation
LUMO	Lowest unoccupied molecular orbital
LR-TDDFT	Linear response time-dependent density functional theory
MBPT	Many-body perturbation theory
MLJ	Marcus–Levitch–Jortner
P3HT	Poly(3-hexylthiophene)
PCBM	[6,6]-Phenyl-C61-butyric acid methyl ester
PCE	Power conversion efficiency

PDOS	Projected density of states
PIA	Photoinduced absorption
PV	Photovoltaic
PWscf	Plane-Wave Self-Consistent Field
QDs	Quantum dots
QL	Quintuple layer
RR-P3HT	Regioregular poly(3-hexylthiophene)
RRa-P3HT	Regiorandom poly(3-hexylthiophene)
SOC	Spin-orbit coupling
SOS	Sum-over-states
SPP	Surface plasmon polariton
TDDFT	Time-dependent density functional theory
TI	Topological insulator
UPS	Ultraviolet photoelectron spectroscopy
UV	Ultra-violet
VB	Valence band
vdW-DF	Van der Waals density functional
WF	Work function
XPS	X-ray photoelectron spectroscopy

Abstract

Multidimensional hybrid systems play a major role in most applications of modern materials science, including relevant research areas of energy conversion and storage (solar cells, batteries), chemical and biochemical processes (photocatalysis, drug delivery, sensors), nanoelectronics (LEDs, FETs), and nanophotonics (light sources and amplifiers, plasmonic waveguides and modulators). By taking advantage of two or more components with distinctly different physical and electronic properties, for instance organic and inorganic constituents, hybridization at the atomic level and exploitation of dimensionality effects allow designing nanostructured material with properties “on demand”. From the theoretical standpoint, the in-depth understanding of structure-property relationships of such inhomogeneous systems poses new challenges: methods that proved successful for describing homogeneous components may not be applicable to the hybrid systems, and are likely to fail to capture the physics of abrupt heterointerfaces.

In this thesis, we consolidated a theoretical framework to study hybrid nanostructured materials by a combination of computational strategies and first-principle approaches, including density functional theory (DFT), time-dependent DFT and many-body perturbation theory. Within this framework, we studied the structural, vibrational, electronic and photophysical properties of model material systems with different

dimensionality and functions, including polymer/fullerene blends, polymer/III-V heterointerfaces, organic-inorganic perovskites for photovoltaic applications, and metallic/dielectric topological insulators for active plasmonics.

Our main findings are the following: *i*) a complete description of the vibrational fingerprints of polaronic and excitonic states in conjugated polymers; *ii*) the quantification of dimensionality and surface polarity effects on charge transfer and separation in hybrid polymer/III-V (film and quantum dots) photovoltaic systems; *iii*) the demonstration of dimensionality and self-trapping effects on charge transport and photoluminescence of multidimensional organic-inorganic perovskites for photovoltaic and light-emission applications; *iv*) the determination of composition-dependent dielectric and metallic optical properties of topological insulator crystals for low-loss plasmonic devices operating in the visible part of the spectrum.

Our predictions compare favorably with structural and spectroscopic data of the actual hybrid material systems, demonstrating the flexibility and potential of first principle calculations for the computational discovery of novel material systems, and their optimization for real-life applications.

Chapter 1

Introduction

1.1 Background and Motivations

Rapid advances in material science, such as organic chemical synthesis and inorganic nanostructure fabrication techniques, have led to a boost in design and manufacturing of novel nanostructured material systems that exhibit unique and unforeseen properties with improved electronic, optical, and plasmonic functions and performance. For example, conjugated polymers,¹⁻² inorganic colloidal quantum dots,³⁻⁴ hybrid organic-inorganic perovskites,⁵⁻⁶ and topological insulators are some of the most studied and promising optoelectronic active-layer materials of recent times. One of the greatest advantages of these materials is the ability to control their properties by tuning the composition, dimensionality, surface terminations, and interfacial structures. This tenability, together with a relatively low fabrication cost, allows exploiting these nanostructured materials as the main building blocks for the next generation of photovoltaic and plasmonic technologies of the future. Meanwhile, the new physical and chemical phenomena arising at the hybrid nanostructured interfaces must be deeply understood before rational designs and new concepts for the nanostructured hybrid materials could be developed.

Many difficulties arise from the controlled design of desired nanostructures to the

conversion of properties initiating at the nanoscale to the mesoscale and macroscale.

Once the novel nanostructures are constructed based on the materials' building blocks, new properties may appear due to quantum effects, which cannot be simply predicted by scaling with size. Besides the practical issues of controlling material morphology and manipulation, and interface engineering of such nanoscale structures, there are needs for understanding the basic physical mechanisms behind these optoelectronic devices that govern the performance of hybrid material systems.

Special experimental and theoretical attention is required for designing multidimensional hybrid nanostructures, which generally contain two main components (e.g. organic and inorganic materials) with distinctly different properties. Sometimes organic materials alone will not give satisfactory optoelectronic performance due to their low carrier mobility and ease of recombination of photoexcited excitons (electron-hole pairs). On the other side, inorganic semiconductors are attractive because of their low electron-hole binding energies and high charge carrier mobilities, but lack of tunability of electronic properties. Thus, hybrid nanostructured system utilizing these organic and inorganic materials allow not only to integrate both advantages, but also to go beyond the individual features of their constituents. Since new features and phenomena appearing at the interface that will be inactive in either of the building blocks, the rich physics behind hybrid system is worth being deeply investigated.

To provide accurate insights and predictions on interfacial phenomena and properties, and to understand their electronic, atomic, and molecular interactions and dynamics,⁷ developing advanced theory and simulation methods is needed. Thanks to the theories and computational tools developed over the past few decades in both condensed matter physics and quantum chemistry communities, nowadays first-principles theory is crucial for understanding the structure-property relationships of a given material, predicting the properties of unknown materials, and greatly accelerating materials design and discovery at the fundamental atomic level. Specifically, density functional theory (DFT)⁸⁻⁹ has become the most popular first-principle method for studying classes of material system with nanostructures.¹⁰ DFT calculations can help predicting qualitative behaviors, understand experimental observations, design new optoelectronic materials, and engineer hybrid interfaces with precisely tailored properties. This success is largely due to the computational accuracy, applicability and efficiency of DFT method,¹¹ such as:

- i)* convenient conversion of physical problem to a computable atomistic model;
- ii)* accurate description of the electronic and optical properties of different states;
- iii)* direct validation of the theoretical results by comparison with experimental data.

A computational DFT strategy to hybrid systems can be represented as a stepwise problem, whereby one needs to accurately simulate the individual components, then move to the relevant heterointerfaces. The fundamental information required on

individual compounds are: *i)* frontier molecular orbital energies, vibrational modes and optical absorption spectra of small molecules or polymers; *ii)* band structure of inorganic compounds and their density of states of slab models. These information constitute the basis for the screening and design of new organic materials and inorganic nanostructures. For interacting hybrid interfaces, one needs to know in addition: *i)* interfacial structures; *ii)* energy alignments and electronic distributions; and *iii)* charge redistributions. A complete DFT description of inhomogeneous systems poses new challenges: methods that proved successful for describing the individual components may not be applicable to the hybrid system as a whole, and are likely to fail to capture the physics of abrupt heterointerfaces. Therefore, various DFT strategies are provided to treat different material systems and obtain their properties using electronic wave functions and densities as the starting point. Combining DFT, time-dependent DFT (TDDFT) and many-body perturbation theory (MBPT), we construct a powerful theoretical framework to obtain the desired properties of most hybrid materials and their interfaces based on the following:¹²

1. ***Crystal Structures.*** For inorganic crystals, the gradient-corrected exchange-correlation functionals have been successfully applied in accurately predicting lattice parameters. On the other hand, the calculations of organic crystals are performed by fixing the lattice parameters, demonstrating remarkably good internal geometries and capturing both strong intramolecular bonds and weak

intermolecular interactions. Moreover, including van der Waals functionals¹³ can provide rather reliable cohesive structural properties of π -conjugated polymers.

2. ***Vibrational Spectroscopy.*** The calculations of vibrational frequencies and infrared and Raman scattering intensities of molecular and crystalline systems are performed either by direct force-constant methods¹⁴ or a linear response route.
3. ***Optical Excitations.*** TDDFT has been most favorable for molecular systems, its success for extended systems is pretty limited to metals or other systems where excitonic effects are very weak. Bethe–Salpeter equation (BSE) is the method of choice for studying optical excitations,¹⁵ which can capture the features of strongly bound electron-hole pairs in core-level excitations and molecular materials, as well as the Wannier-type excitons in inorganic semiconductors.
4. ***Charge Transport.*** DFT calculations of charge transport in nanostructured materials has advanced considerably through ad-hoc approaches for different material systems and applications. For inorganic semiconductors, the combination of DFT with Boltzmann-type transport equations has been proven successful to obtain bulk transport coefficients (effective mass, electron-phonon coupling etc.).¹⁶ For organic molecular systems, the flow of current can be described as quantum transport using the Landauer-Büttiker theory. For purely organic single crystals, the two most widely used concepts are the Holstein type models and electron-hopping Marcus theory.

These methods allow for quantitative calculations of charge carrier mobility, including their temperature dependence.

5. ***Surfaces and Interfaces.*** Bringing organic and inorganic materials together, strong covalent bonding or weakly molecular interactions are formed, increasing complexity of the description of surface and interfacial structures. Therefore, accurate calculations of surface and interfacial geometries and energies are regarded as an important prerequisite to determine and understand the interfacial properties. For instance, the pronounced orientation and anisotropy of organic molecule-inorganic substrate interactions should be considered in the DFT calculations.¹⁷

6. ***Dynamics.*** Car–Parrinello molecular dynamics allows investigating hybrid systems at finite temperature.¹⁸ Recently, an advanced DFT strategy was developed by dealing with non-adiabatic couplings among different electronic states, based on first-principles molecular dynamic calculations to study the timescale of photoinduced electron transfer. This method takes the dynamical effects of both nuclei and electrons within the frameworks of molecular dynamics and TDDFT.¹⁹

Although there are a number of successful examples to predict the properties of new materials or explaining the experimental observations using DFT calculations, it is important to point out that DFT calculations still have flaws. The Kohn–Sham

single-particle states from DFT calculations are usually good approximations to the quasi-particle states, but a major concern is that the shift of single-particle energies leads to the underestimation of band gaps if standard approximations to electron correlation and exchange effects are employed. Another general issue is the inclusion of relativistic effects by considering the spin-orbit coupling contributions in heavy element-containing systems. Thus, for any specific system, it is necessary to gauge the level of accuracy achievable in calculations of a given property, and to validate the DFT results by direct comparison with the available experimental data.

1.2 Aims and Implementation

In this thesis, we develop theoretical approaches/models in the DFT framework for a broad range of material systems and chiefly deal with three main computational issues: *i*) developing a theoretical method to describe the vibrational modes of singlet excited states for polymers, which will help us uncover the experimental infrared-active vibrational modes beyond the conventional phenomenological assumptions. To achieve this, we implement the TDDFT method in vibrational calculations through a careful treatment of polymer structure; *ii*) building a computational model for treating the large hybrid organic/inorganic interfacial structures. According to this, we build a robust “organic monolayer/inorganic slab” model for obtaining their electronic properties across hybrid interfaces and determining the surface polarization effects of inorganic/hybrid

semiconductors on their interfacial charge transfer and redistribution in combination with organic molecules; *iii*) getting physical insights into DFT results to explain the experimental phenomena. We extract a number of useful physical parameters that cannot be obtained directly from experimental measurements by dealing with electronic bands and complex coupling matrix, such as implementing the quantum chemistry results in Marcus theory to predict charge transfer rates between polymer and nanocrystals and integrating molecular dynamics and electronic density mapping to demonstrate self-trapping charges of hybrid organic-inorganic crystals.

Specifically, Figure 1.1 shows our integrated computational and experimental study of several novel material systems as well as interfacial charge/energy transfer processes in the complex organic/inorganic hybrid systems at the atomic level using *i*) quantum chemistry calculations to deal with the molecular structural and vibrational modes of polymer and charge transfer rate between polymer and nanocrystals; *ii*) solid state physics calculations to treat different hybrid organic/inorganic system, including the interfacial structures and their electronic properties and charge redistributions; and *iii*) many-body perturbation theory calculations to obtain the optical permittivity of plasmonic topological insulators.

Figure 1.1. Model material systems showed in this thesis and properties of interest.

Our discussions are mainly focused on the structural, electronic, and optical properties of these systems, namely the molecular and crystal structure, vibrational modes, interfacial charge transfer rates, electronic band structures, projected density of states, charge redistribution and optical response. Our DFT results tries to address questions like: How do correlations between molecules and interfacial interactions rule properties of oriented hybrid organic/inorganic nanostructures? How do physical chemical properties and photophysical processes change when molecules are in contact with inorganic surfaces? What are the effects of reduced dimensionality on the charge localization and transport of hybrid organic-inorganic semiconductors? How can the optical response of inhomogeneous systems be simulated by DFT calculations? How can all these properties be harnessed to design or discover new functional optoelectronic materials?

Based on the type of different material systems, this thesis is organized as follows: in Chapter 2, we briefly introduce density functional theory, optical response theory of solids and computational codes used in this thesis. Chapter 3 focuses on the polymer/III-V hybrid system for the photovoltaic applications, including the electronic and vibrational properties of conjugated polymer, surface polarity effects on charge redistribution at GaAs/P3HT heterointerfaces, and ligand and size effects on electron and energy transfer in InP quantum dots/P3HT blends. Chapter 4 deals with the three- and two-dimensional organic-inorganic perovskites, including the electronic, transport and self-trapping charge properties, as well as interfacial charge transfer anisotropy between lead iodide perovskite and hole- (electron-) transporting materials. In Chapter 5, we discuss the results on topological insulators treated as hybrid metal/dielectric materials and we investigate their electronic and optical properties with particular emphasis on their plasmonic behavior emerging from the conducting surface.

This thesis presents both computational and experimental results. The author conducted all the simulation work and experiments on and IR, Raman, absorption and photoluminescence spectroscopy of polymers (Chapter 3.1) and polymer/InP QDs system as well as the ligand exchange of InP QDs (Chapter 3.3). The rest of the experimental work was done by the coauthors named in List of Publications.

Chapter 2

Density Functional Theory

In this chapter, we present the theoretical foundations of the methods and calculations that are employed in this thesis. The first section deals with a brief historical introduction of Density Functional Theory (DFT). The next section of this chapter gives the basic principles of time-dependent DFT and Bethe–Salpeter equation for optical response calculations. The last section is a summary of the main computational codes used in this thesis. Note that we give a brief description of the basic principles in this chapter without the detailed mathematical subtleties, since the theory itself is not the objective of the thesis, rather how it can be exploited for studying the electronic and plasmonic properties for the particular material system.

2.1 Introduction

Modern computational modelling, which relies on the quantum mechanical description of the atomic nuclei and electrons interactions, has given a marked impact on chemistry, physics and materials science, paving the way for understanding structural and optoelectronic properties of novel materials and for designing new materials for future technologies and applications.¹¹ To accurately describe the chemical bonding between atomic nuclei and physical interactions between molecules, simulations of materials are

performed to obtain energies and acting forces by solving Schrödinger equations based on the atomic constituents and coordinates as inputs. However, Schrödinger equations for complex systems are not analytically fully solvable, so a variety of theoretical and computational approaches were developed. A breakthrough in these theoretical efforts was achieved in 1964 when Pierre Hohenberg, Lu Jeu Sham and Walter Kohn developed DFT with two published manuscripts in *Physical Review*, titled “Inhomogeneous electron gas”⁸ and “Self-Consistent Equations Including Exchange and Correlation Effects”⁹. The essential idea behind DFT is involving the electron density instead of dealing with complex many-body Schrödinger equations. This method is strongly relevant to independent particle approaches, including the electron interactions and correlations. Since many-body wavefunctions cannot be explicitly defined, the proper Hartree and Hartree-Fock approximations are needed to develop the suitable single-particle equations. Understanding the properties of electron density and approximate functionals was the key to develop reliable and advanced *ab-initio* models. Since then, DFT became an almost universal method for studying a wide variety of material systems, including organic molecules, inorganic solids and nanostructures, surfaces and hybrid interfaces, from organic chemistry to condensed matter physics domains.

To investigate the properties of materials at the atomic scale, we need to acknowledge that they consist of interacting atomic nuclei and electrons. As the nuclei are much

heavier than electrons, atomic nuclei can be treated as point charges, the so called *Born-Oppenheimer approximation*. This assumes that electrons are dynamic while nuclei are frozen, significantly simplifying the problem of all interacting particles to the interacting electrons moving in the field generated by atomic nuclei. So the molecular electronic Hamiltonian can be expressed as:

$$H = K_e + V_{ee} + V_{en} + V_{nn}, (2.1)$$

where K_e is the quantum kinetic energy of electrons: $K_e = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2$;

V_{ee} is the electron-electron interaction potential: $V_{ee} = -\frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$;

V_{en} is the potential due to electrostatic interactions between electrons and ions: $V_{en} =$

$$-\sum_{il} \frac{Z_l e^2}{|\mathbf{r}_i - \mathbf{R}_l|};$$

and V_{nn} is the potential due to electrostatic nucleus-nucleus repulsion interactions.

2.2 Basics of Density Functional Theory

2.2.1 The Hartree approximation

In the independent electron approximation, the effective potential for the motion of each electron consists of the sum of a term accounting for attraction from all nuclei, and a term that accounts for the repulsive interaction between one electron and the average distribution of all the other electrons. The many-body wavefunctions could be appropriately expressed as the product of all single orbitals if the electrons were treated as non-interacting particles:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2) \dots \varphi_n(\mathbf{r}_n). \quad (2.2)$$

The wavefunctions $\varphi_i(\mathbf{r}_i)$ are single-particle states under a realistic approximation and the total energy ($E_{Hartree}$) of many-body system can be expressed as follows using the Hartree approximation:

$$E_{Hartree} = \langle \Psi | \mathcal{H} | \Psi \rangle = \sum_{i=1}^Z \int d^3\mathbf{r}_i \varphi_i^*(\mathbf{r}_i) \left(-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) \varphi_i(\mathbf{r}_i) + \frac{e^2}{4\pi\epsilon_0} \sum_{i>j} \sum_j \frac{|\varphi_i(\mathbf{r}_i)|^2 |\varphi_j^*(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (2.3)$$

Using a variational argument, we can then obtain the single-particle Hartree equations:

$$\left[-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} + \frac{e^2}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3\mathbf{r}_j \frac{|\varphi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \varphi_i(\mathbf{r}_i) = \epsilon_i \varphi_i(\mathbf{r}_i). \quad (2.4)$$

From this equation, each orbital $\varphi_i(\mathbf{r}_i)$ could obtained by solving the single-particle Schrödinger equation if knowing all the other $\varphi_j(\mathbf{r}_j)$, $i \neq j$. The problem of self-consistency can be iteratively solved with the equation of one φ_i , which depends on all the other φ_j 's. First of all, a new set of φ_i 's is chosen to build the single-particle Hamiltonian to solve the equations for these new φ_i ; then the results of φ_i 's equations are compared with the original ones; finally, the original wavefunctions are substituted with the new estimated φ_i 's. This cycle of steps is repeated until input φ_i 's and output φ_i 's coincide within the desired total energy difference δ_{tot} (self-consistency).

2.2.2 The Hartree–Fock approximation

Because electrons are fermions, the wave function must change sign if two electrons change places with each other, which is known as the anti-symmetry principle.

Exchanging two electrons does not change the sign of the Hartree product, which is a serious drawback. We can obtain a better approximation to the wave function by using a Slater determinant. In a Slater determinant, the N-electron wave function is formed by combining one-electron wave functions in a way that satisfies the antisymmetry principle as follows:

$$\Psi(\mathbf{r}_i) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \cdots & \varphi_1(\mathbf{r}_N) \\ \vdots & \ddots & \vdots \\ \varphi_N(\mathbf{r}_1) & \cdots & \varphi_N(\mathbf{r}_N) \end{vmatrix}, \quad (2.5)$$

where n is the total number of electrons. The Slater determinant has the anticipated property that interchanging the spatial coordinates of two electrons leads to the same effect through interchanging their columns in the determinant. This will also change its sign.

Applying the theorem that the value of a determinant is unchanged by any non-singular linear transformation, we may choose the φ to be an orthonormal set. We now introduce a Lagrange multiplier ϵ_i to impose the condition that the φ are normalised, and minimise with respect to the φ :

$$\frac{\delta}{\delta \varphi} [\langle \hat{H} \rangle - \sum_j \epsilon_j \int |\varphi_j|^2 d\mathbf{r}] = 0 \quad (2.6)$$

An enormous simplification of the expressions for the orbitals φ results. They reduce to a set of one-electron equations of the form

$$\frac{-\hbar^2 \nabla^2}{2m_e} \varphi_i(\mathbf{r}) + V_{ion}(\mathbf{r}) \varphi_i(\mathbf{r}) + U(\mathbf{r}) \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}) \quad (2.7)$$

where $U(\mathbf{r})$ is a non-local potential and the local ionic potential is denoted by $V_{ion}(\mathbf{r})$.

The one-electron equations resemble single-particle Schrödinger equations.

The full Hartree-Fock equations are given by

$$\left[\frac{-\hbar^2 \nabla^2}{2m_e} + V_{ion}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) + \sum_j \int d\mathbf{r}' \frac{|\varphi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \varphi_i(\mathbf{r}) - \sum_j \delta_{\sigma_i \sigma_j} \int d\mathbf{r}' \frac{\varphi_j^*(\mathbf{r}') \varphi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}). \quad (2.8)$$

There is one extra term in this equation, which includes an unphysical self-interaction of electrons when $j=i$ called the “exchange” term, as compared with the Hartree equation.

The exchange term results from our inclusion of the Pauli principle and the assumed determinantal form of the wavefunction.

Then it is instructive to try to put this term in such a form, by multiplying and dividing by the proper factors. First of all, we can write the Hartree term in a different way, where single-particle and total densities become:

$$\rho_i(\mathbf{r}) = |\varphi_i(\mathbf{r})|^2; \text{ and } \rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r}); \quad (2.9)$$

the Hartree potential follows the form

$$V_i^H(\mathbf{r}) = e^2 \sum_{i \neq j} \frac{\rho_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' = e^2 \int \frac{\rho(\mathbf{r}') - \rho_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}', \quad (2.10)$$

and the single particle exchange density is constructed as

$$\rho_i^X(\mathbf{r}, \mathbf{r}') = \sum_{i \neq j} \frac{\varphi_i(\mathbf{r}') \varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}')}{\varphi_i(\mathbf{r}) \varphi_i^*(\mathbf{r})}. \quad (2.11)$$

Then the single-particle Hartree-Fock equation becomes

$$\left[\frac{-\hbar^2 \nabla^2}{2m_e} + V_{ion}(\mathbf{r}) + V_i^H(\mathbf{r}) + V_i^X(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}), \quad (2.12)$$

with the exchange potential as follows

$$V_i^X(\mathbf{r}) = -e^2 \int \frac{\rho_i^X(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (2.13)$$

In the HF approximation, the potential for electron-electron interaction has the following form, by considering Hartree and exchange potentials:

$$V_i^X(\mathbf{r}) = e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - e^2 \int \frac{\rho_i(\mathbf{r}') + \rho_i^X(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (2.14)$$

which can be expressed using the HF density

$$\rho_i^{HF}(\mathbf{r}, \mathbf{r}') = \sum_j \frac{\varphi_i(\mathbf{r}') \varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}')}{\varphi_i(\mathbf{r}) \varphi_i^*(\mathbf{r})}. \quad (2.15)$$

Finally, the following equation gives the total electron-electron interaction potential with the first term of total Coulomb repulsion potential for all the electrons and second term of the fermionic exchange effect:

$$V_i^{HF}(\mathbf{r}) = e^2 \int \frac{\rho(\mathbf{r}') - \rho_i^{HF}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (2.16)$$

2.2.3 The Hohenberg–Kohn theorems

It is arduous to directly solve the Schrodinger's equation of the Hamiltonian. The approach of Hohenberg and Kohn is to express density functional theory as an exact many-body system theory. This formulation can be applied to any system of interacting particles moving under an external potential $V_{ext}(\mathbf{r}_i)$ created by atomic nuclei:

For such system, the Hamiltonian can be expressed as

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i V_{ext}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (2.17)$$

Hohenberg and Kohn summarized two important theorems of DFT as follows:

Theorem I: “For any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$ in any system, the potential $V_{ext}(\mathbf{r}_i)$ is determined uniquely, except for a constant, by the ground state particle density $n_0(\mathbf{r})$.”

Corollary I: Since the number of electrons in the system is fully determined by $n_0(\mathbf{r})$, it follows that all electronic properties of the system are completely determined by the ground state density $n_0(\mathbf{r})$.

Theorem II: “A universal functional for the energy $E[\mathbf{n}]$ in terms of the density $n(\mathbf{r})$ can be defined, valid for any external potential $V_{ext}(\mathbf{r})$. For any particular $V_{ext}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(\mathbf{r})$ that minimizes the functional is the exact ground state density $n_0(\mathbf{r})$.”

$$E[\mathbf{n}] = \int d\mathbf{r} n(\mathbf{r}) V_{ext}(\mathbf{r}) + F[n]. \quad (2.18)$$

Corollary II: The functional $E[\mathbf{n}]$ alone is sufficient to determine the exact ground state energy and density. In general, excited states of the electrons must be determined by other means.

2.2.4 Kohn–Sham equations

A many-electron interacting system could be onto a fictitious system of non-interacting "electrons", but enforce that the two systems have identical ground state electron density. The non-interacting system can be described by single-particle equations and the ground state solution is the corresponding Slater determinant. Following this idea, we can derive the Kohn-Sham equations,⁹ which are the basis of Kohn-Sham density functional theory to describe the realistic solid systems. Given a single-particle description, we can first write out the energy functional Eq. 2.17 explicitly:

$$E[n(\mathbf{r})] = \frac{-\hbar^2}{2m_e} \sum_i \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \frac{e^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[n(\mathbf{r})] + \int d\mathbf{r} n(\mathbf{r}) V_{ion}(\mathbf{r}), \quad (2.19)$$

where the electron density of the non-interacting system can be written as:

$$n(\mathbf{r}) = \sum_i |\varphi_i(\mathbf{r})|^2, \quad (2.20)$$

where i is single-particle states and the sum is over all the occupied states. $E_{xc}[n(\mathbf{r})]$ is exchange-correlation functional.

To find the ground-state density $n(\mathbf{r})$ for this non-interacting system, we can simply solve the one-electron Schrödinger equations:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{KS} \right) \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}), \quad (2.21)$$

where $V_{KS}(\mathbf{r})$ is composed of the Hartree potential and the local ionic potential:

$$V_{KS}(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + V_{ion}(\mathbf{r}) + V_{xc}(\mathbf{r}). \quad (2.22)$$

The last term is the exchange-correlation potential defined as:

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (2.23)$$

Once the equations are solved self-consistently, the ground state electron density is obtained:

$$n_0(\mathbf{r}) = \sum_i |\tilde{\varphi}_i(\mathbf{r})|^2; \quad (2.24)$$

and the total ground state energy can be written as:

$$E_0 = \frac{\hbar^2}{2m_e} \sum_i \langle \tilde{\varphi}_i | \nabla^2 | \tilde{\varphi}_i \rangle + \frac{e^2}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[n(\mathbf{r})] + \int d\mathbf{r} n_0(\mathbf{r}) V_{ion}(\mathbf{r}). \quad (2.25)$$

Note that ion-ion interaction $E_{ion-ion}$ was not included in the total energy, because $E_{ion-ion}$ is a constant by summing over Coulombic pair repulsions. But the term $E_{ion-ion}$ should be considered when the ions are moved to calculate the energy and the forces acting on them.

2.2.5 Bloch's theorem

For periodic material systems, such as semiconductor slab models, the atomic nuclei can be arranged in a regular periodic array, which is invariant under translation by the Bravais lattice vectors. The potential of this system is also translationally periodic:

$$V^{SP}(\mathbf{r} + \mathbf{R}) = V^{SP}(\mathbf{r}), \quad (2.26)$$

so that the single-particle wavefunctions can be expressed plus a phase factor:

$$\varphi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \varphi_{\mathbf{k}}(\mathbf{r}). \quad (2.27)$$

As an alternative formulation of Bloch's theorem, the single-particle wavefunctions can

also be written as:

$$\varphi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} u_{\mathbf{k}}(\mathbf{r}), \quad u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{\mathbf{k}}(\mathbf{r}), \quad (2.28)$$

where the wavefunctions $\varphi_{\mathbf{k}}(\mathbf{r})$ can be written as the product of the functions $u_{\mathbf{k}}(\mathbf{r})$ multiplied by the phase factor $e^{i\mathbf{k} \cdot \mathbf{R}}$. These functions have the full translational periodicity of the Bravais lattice. Note that these two formulations of Bloch's theorem are equivalent.

2.2.6 Self-consistent calculations

To get the accurate electronic density of whole material system, a simple and useful approximation is to construct the first guess for the electron density by adding up the densities of each atom. As illustrated in Figure 2.1, the initial estimates of the Hartree and exchange and correlation potentials ($V_{\text{H}} + V_{\text{xc}}$) can then be built, before proceeding with the numerical solution of the Kohn–Sham equations. By solving the Kohn–Sham equations, one can then obtain a new set of wavefunctions, which are used to construct a better estimate of the density (n) and the total potential (V_{tot}). This process is repeated until the new density agrees well with the old density, within a desired tolerance, and self-consistency is achieved.

Figure 2.1. Schematic flow-chart for finding self-consistent solution of the Kohn–Sham equations.

2.3 Optical Response

2.3.1 Time-dependent density functional theory

To predict the optical properties of molecules and inorganic crystals, time-dependent density functional theory (TDDFT) has been widely used.²⁰ Specifically, for the linear response TDDFT (LR-TDDFT), the density response of a system is studied within an external time dependent perturbation:

$$\rho(\mathbf{r}, t) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r}, t). \quad (2.29)$$

The basic term of LR-TDDFT is the density-density response function:

$$\chi(\mathbf{r}, t, \mathbf{r}', t') = \left. \frac{\delta\rho(\mathbf{r}, t)}{\delta v_{ext}(\mathbf{r}', t')} \right|_{v_0}, \quad (2.30)$$

which relates the first order density response $\delta\rho(\mathbf{r}, t)$ to the applied perturbation

$\delta v(\mathbf{r}, t)$

$$\delta\rho(\mathbf{r}, t) = \int_{t_0}^t dt' \int d\mathbf{r}' \delta v(\mathbf{r}', t') \chi(\mathbf{r}, t, \mathbf{r}', t'). \quad (2.31)$$

Here the total external potential, $v_{ext}(\mathbf{r}, t)$, can be expressed by summing up the static ground state Kohn–Sham potential $v_0(\mathbf{r})$, and the external potential $\delta v(\mathbf{r}, t)$.

The response function is relevant to the non-interacting Kohn–Sham response function by using Dyson-like equation:

$$\chi(\mathbf{r}, t, \mathbf{r}', t') = \chi_s(\mathbf{r}, t, \mathbf{r}', t') + \int d^3\mathbf{r}_1 dt_1 \int d^3\mathbf{r}_2 dt_2 \chi_s(\mathbf{r}, t, \mathbf{r}_1, t_1) \left(\frac{\delta(t_1 - t_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{\delta v_{xc}(\mathbf{r}_1, t_1)}{\delta\rho(\mathbf{r}_2, t_2)} \right) \chi(\mathbf{r}_2, t_2, \mathbf{r}', t'). \quad (2.32)$$

where $\chi_s(\mathbf{r}, t, \mathbf{r}', t')$ is the “non interacting” density response

$$\chi_s(\mathbf{r}, t, \mathbf{r}', t') = \sum_{k,j} (f_k - f_j) \frac{\psi_k^*(\mathbf{r}) \psi_j(\mathbf{r}) \psi_j(\mathbf{r}') \psi_k^*(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_k) + i\eta}. \quad (2.33)$$

The relationship between the exact density response function and the Kohn–Sham response function, can be compactly written in term of the inverse of their corresponding

Fourier transform the time:

$$\chi^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \chi_s^{-1}(\mathbf{r}, \mathbf{r}', \omega) - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - f_{xc}(\mathbf{r}_1, \mathbf{r}_2, \omega). \quad (2.34)$$

The problem of finding excitation energies of the interacting system has been simplified

as the search of the poles of the response function. In fact, $\chi(\omega)$ has poles at the true excitation energies ω_I , while the non-interacting response, $\chi_S(\omega)$, has poles at the Kohn–Sham orbital energy differences.

The calculation of the dynamic dipole polarizability, $\alpha(\omega)$, is of particular interest in molecular spectroscopy. The response function that relates the external potential to the change in the dipole can be expressed as:

$$\mu_x(\omega) = \mu_x + \int_{-\infty}^{\infty} dt' \alpha_{xz}(t - t') \varepsilon_z(t') + \dots \quad (2.35)$$

Then using the convolution theorem

$$f(\omega) = \int_{-\infty}^{\infty} dt' g(t - t') h(t') \Rightarrow f(\omega) = g(\omega) h(\omega). \quad (2.36)$$

The Fourier transform of the dynamic dipole polarizability is written as:

$$\delta\mu_x(\omega) = \alpha_{xz}(\omega) \varepsilon_z(\omega), \quad (2.37)$$

where $\alpha_{xz}(\omega) = -\sum_{ij,kl} x_{ij} \chi_{ij,kl}(\omega) z_{kl}$, and $x_{ij} = \langle \psi_i | \hat{x} | \psi_j \rangle$.

Applying the sum-over-states (SOS) relation

$$\bar{\alpha}(\omega) = \sum_I \frac{f_I}{\omega_I^2 - \omega^2}, \quad (2.38)$$

and considering that

$$f_I = \frac{2}{3} \omega_I (|\langle \psi_0 | \hat{x} | \psi_I \rangle|^2 + |\langle \psi_0 | \hat{y} | \psi_I \rangle|^2 + |\langle \psi_0 | \hat{z} | \psi_I \rangle|^2). \quad (2.39)$$

So the poles of the dynamic polarizability can determine the excitation energies, ω_I ; and the residues, f_I , can determine the corresponding oscillator strengths. The absorption spectra can be determined by these oscillator strengths through Gaussian broadening.

2.3.2 Bethe–Salpeter equation

In organic and inorganic crystals, optical excitations, the interaction between excited electrons and empty hole state, can be described within the framework of many-body perturbation theory using the Bethe–Salpeter equation (BSE).²¹ This method accounts for the lowest-order screened direct and bare exchange electron-hole interaction terms, and yields results for the optical absorption spectra.

The optical response performed by BSE method can be expressed as:²²⁻²³

$$(E_{c\mathbf{k}} - E_{v\mathbf{k}})A_{vc\mathbf{k}}^S + \sum_{\mathbf{k}'v'c'} \langle vc\mathbf{k} | K_{eh} | \mathbf{k}'v'c' \rangle A_{\mathbf{k}'v'c'}^S = \Omega^S A_{vc\mathbf{k}}^S, \quad (2.40)$$

where $E_{c\mathbf{k}}$ and $E_{v\mathbf{k}}$ are the quasiparticle energies of the conduction and valence states, respectively. $A_{vc\mathbf{k}}^S$ are the expansion coefficients of the excitons, and Ω^S are the eigenenergies.

The imaginary part of the permittivity could be calculated by evaluating direct electronic transitions between occupied and higher-energy unoccupied electronic states as obtained from

$$\varepsilon''(\omega) \propto \sum_S \left| \sum_{cv\mathbf{k}} A_{vc\mathbf{k}}^S \frac{\langle c\mathbf{k} | p_i | v\mathbf{k} \rangle}{\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}}} \right| \delta(\Omega^S - \hbar\omega - \Gamma), \quad (2.41)$$

where $\langle c\mathbf{k} | p_i | v\mathbf{k} \rangle$ are the dipole matrix elements for electronic transitions from valence to conduction states.

The real part can then be calculated via the Kramers-Kronig relation:

$$\varepsilon'(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon''(\omega') \omega' d\omega'}{\omega'^2 - \omega^2}. \quad (2.42)$$

2.4 Computational Codes

In this thesis, different computational codes were used to treat different material systems: Quantum ESPRESSO (QE) package was used to study the electronic band and charge distributions of hybrid polymer/inorganic and perovskites systems containing the periodic structures. Gaussian package was employed to study the molecular orbitals and charge transfer rates of polymers and nanocrystals. In addition, the Yambo code was applied to calculate the optical properties of topological insulators based on the electronic wavefunctions obtained from QE calculations. Our generated pseudopotential for heavy atoms (Bi, Te and Sb) and code for calculating charge transfer integrals have been shared with the scientific community. (<https://github.com/oson>)

Quantum ESPRESSO package,²⁴ ESPRESSO stands for *Open Source Package for Research in Electronic Structure, Simulation, and Optimization*. It has the core packages Plane-Wave Self-Consistent Field (PWscf) and Car-Parrinello (CP) for calculating electronic-structure properties and dynamics processes within the framework of Density-Functional Theory (DFT) using a plane-wave basis set and pseudopotentials. The package includes more specialized calculations such as atomic relaxation and self-consistent calculations, post-processing calculations, atomic-projection, phonon calculations and Wannier. The QE codes can be performed on different types of Unix/Linux systems and machines, including parallel techniques using both MPI and

GPU accelerations.

Gaussian package, a quantum chemistry program for predicting the molecular and reactions properties, including molecular structures, energies and orbitals, multipole moments, atomic charges, excited states, and vibrational frequencies of small molecules and polymers.

Yambo code,²² within the framework of many-body perturbation theory and time-dependent density functional theory, Yambo code is for obtaining the quasiparticle energies and optical properties of many-body systems. It has been applied to a large range of physical systems, especially is suited for the periodic bulk systems. Quasiparticle energies are evaluated by the GW approximation; and optical properties are calculated either using adiabatic local density approximation or by solving the BSE.

Chapter 3

Polymer/III-V Photovoltaic Hybrid Systems

To relive today's energy crisis, harvesting the solar energy and transforming it into electrical energy efficiently and economically is the most challenging and promising way to obtain clean and renewable energy. This problem has stimulated a great quantity of experimental²⁵⁻²⁸ and theoretical studies²⁹⁻³¹ in order to find novel materials with the ability of either converting solar energy into electricity (photovoltaics)^{3, 25, 32-33} or produce desired chemical reactions, like hydrogen production or water oxidation (photocatalysis)³⁴⁻³⁷. The dominant photovoltaic technologies used today are based on inorganic materials, such as large-grain silicon crystals. These materials are expensive and short-lived, limiting their wide applications in our daily life.³⁸ So reducing material and manufacturing costs and archiving high power conversion efficiencies are of crucial importance to improve photovoltaic competitiveness over other energy technologies. Especially, hybrid polymer/inorganic system have attracted great attention in developing the low-cost and robust photovoltaic technologies.

According to the three computational issues we proposed in the section 1.2, in this chapter, we chose the model conjugated polymer P3HT as electron donor and III-V

semiconductors as electron acceptor materials and mainly focus on dimensionality effects on the charge redistribution and transfer at these heterointerfaces. This chapter is divided into three sections. In the first section, we introduce the conjugated polymer P3HT and study its electronic and vibrational properties. The original part of this work, in which we assign and reproduce quantitatively the transition energies and intensities of vibrational normal modes in the ground and excited electronic states of P3HT, was published in "A First Principles Study of the Nuclear Dynamics of Doped Conjugated Polymers" (*J. Phys. Chem. C*, 2016, 120, 1994). Then we move on to investigate the interactions between P3HT and III-V semiconductor with different dimensionalities, namely GaAs/P3HT bilayer systems and InP quantum dots/P3HT blends. In GaAs/P3HT, we show that the electronic orbitals and charge redistribution are highly affected by GaAs surface polarity. This part of the work was earlier published in "Charge Redistribution at GaAs/P3HT Heterointerfaces with Different Surface Polarity" (*J. Phys. Chem. Lett.*, 2013, 4, 3303). As a last section of this chapter, we discuss the charge transfer dynamics at InP QDs/P3HT heterointerfaces as a function of core size and length of the surface ligands, a recently published in "Small-Size Effects on Electron Transfer in P3HT/InP Quantum Dots" (*J. Phys. Chem. C.*, 2015, 119, 26783).

3.1 Electronic and Vibrational Properties of Model Conjugated Polymer P3HT

Knowledge of ground and excited state electronic structure and related photogenerated species (exciton and polaron) of conjugated polymers is an essential prerequisite to study and understand the photophysical properties of hybrid polymer/inorganic systems. In this section, we start with the brief introduction of electronic and vibrational features of conjugated polymers followed by a review of previous experimental and theoretical work on infrared-active vibrational modes for the doping polymers. Then we give the computational methods to describe the nuclear dynamics of polymers in details, especially the way to obtain the vibrational modes of singlet excited state of polymers. Finally, we present the main results and discussions on structural, vibrational and IRAV modes of regioregular and regiorandom P3HT.

3.1.1 Electronic Properties of P3HT

Conjugated polymers have been widely investigated in both experiment and theoretical modelling due to their potential applications in organic optoelectronic devices.³⁹⁻⁴² Among these polymers, poly(3-hexylthiophene) (P3HT) is one of the most widely studied semiconducting polymers for organic electronic devices due to its excellent thermal and

environmental stability, solubility, good processability, and high charge carrier mobility. To date P3HT and its derivatives have been used in a variety of applications including organic field effect transistors and bulk heterojunction solar cells. The current highest power conversion efficiency of P3HT-based photovoltaic device is over 5%⁴³ since its first application in solar cell device with PCE of 0.2% in 2003.⁴⁴ The good photovoltaic performance of P3HT is mainly due to the broad absorption in the entire visible region, and its large Stokes-shift (see Figure 3.1.1). For RR-P3HT model, the electronic cloud distribution of highest occupied molecular orbital (HOMO) shows π -bonding character and lowest unoccupied molecular orbital (LUMO) shows π^* -antibonding character, and both spread over the whole eight repeated units, increasing the intermolecular couplings.

Figure 3.1.1. Molecular structure of regioregular (RR-) and regiorandom (RRa-) P3HT and their absorption (solid line) and normalized photoluminescence spectra (dashed line) together with the electronic cloud distribution of RR-P3HT model calculated by B3LYP/6-31(d,p) functional.

Excitons are electron-hole pairs that form when light is absorbed by conjugated polymers. Exciton energetics and transport are central to solar energy processes. The separation of the exciton into a free electron and free hole is the source of usable electrical energy in a polymer heterojunction photovoltaic. The diffusion of excitons to an engineered interface that can subsequently split them into electrons and holes remains a central challenge in many photovoltaic studies. Excitons can be categorized into three types according to their radius and binding energy: *i) Frenkel type excitons* are strongly bounded with small radius, residing on a single molecular site or monomer; *ii) Wannier-Mott excitons* have large radius and low binding energies; *iii) charge-transfer excitons* are an intermediate type, for which electron and hole stay in neighboring sites or molecules. In conjugated polymers P3HT, both Frenkel excitons and Wannier-Mott excitons exist in this quasi-one dimensional intra-molecular chains. The exciton diffusion length of P3HT is ~8.5 nm determined by time-resolved fluorescence measurements.⁴⁵

Polarons are quasi particles formed by strong coupling of charge carriers and phonons (also referred as localized lattice distortion), which can be regarded as charge carriers self-trapped within potential wells in the lattice. They are usually found in polar and ionic solids, molecular crystals, and polymers due to the strong electron-phonon interaction. Polaron absorption in conjugated polymers is a nonlinear response to light: photogeneration of polarons modifies the energy bands of the polymer inducing two new

intra-bandgap energy levels, the P1 and P2 states (see Figure 3.1.2a). Photoinduced absorption (PIA) spectroscopy requires two beams to detect the polaron states: one beam is used for light excitation, while the second broadband beam is used to probe the transitions between polaron states, HOMO and LUMO. For positive polarons (radical cations), the P1 state is singly occupied and the P2 state is empty with total spin $1/2$, while for negative polarons (radical anions), the P1 state is doubly occupied and the P2 state singly occupied with total spin $1/2$. For P3HT, interchain interactions strongly modify the electronic properties. Polarons are no longer localized inside the polymer chain, but rather they become delocalized over the neighboring polymer chains. Both experimentally and theoretically it has been shown that the increase of interchain coupling leads to a splitting of energy levels from that of one dimensional localized polaron; as a result, new photoinduced polaronic transitions appear with red shifted polaron absorption peak in the low energy region (mid-IR) and blue shifted in the near infrared (NIR) spectral region.

Figure 3.1.2. (a) schematic representations of localized and delocalized polaron (hole) states with P1, P2, DP1, DP2, denoting the dipole allowed polaronic transitions; (b) photoinduced absorption and IR/V modes in doped P3HT (ref⁵⁴).

Figure 3.1.2 also shows the typical photoinduced absorption spectra of P3HT and allowed infrared polaron transitions. With the same transition energies between HOMO to P1 state in positive polaron and P2 state to LUMO in negative polaron, one cannot distinguish between positive and negative polarons simply by photoinduced absorption spectra. Since the new transitions that appear upon photoexcitation are also subjected to dipole transition and selection rules, the transitions of HOMO to P2 and P1 to LUMO are symmetry forbidden.

3.1.2 Vibrational Properties of P3HT

Due to the large electron-phonon coupling, changes in the electronic structure of π -conjugated polymers lead to significant variations in the nuclear structure and

dynamics.⁴⁶⁻⁵¹ Thus, vibrational (IR and Raman) spectroscopy, which is sensitive to variations of local dipole moments and polarizability with nuclear oscillations, has been the technique of choice to understand electronic and nuclear structures, charge generation, and charge/energy transfer mechanisms in these systems.⁵²⁻⁵⁶

Figure 3.1.3. Previous studies of IRAV modes in conjugated polymers: (a) the first experimental observation of IRAV modes in doped polyacetylene (ref ⁶⁰); (b) IRAV modes in doped conjugated polymers (ref ⁵⁴); and (c) assignment of the IRAV modes of P3HT by phenomenological amplitude mode model (ref ⁶³).

In π -electron conjugated polymers with symmetric structure, collective oscillations in which the bond length alternation varies in phase⁴⁶ are Raman active normal modes (i.e. g symmetry), but IR silent.⁵⁷⁻⁵⁹ These oscillations are particularly sensitive to the electronic structure and conjugation length of the systems: the higher the electron delocalization, the lower the energy of the vibrational transition associated to the collective oscillation, and the higher the Raman intensity.⁶⁰⁻⁶¹ These Raman active modes may be turned into infrared-active vibrational (IRAV) modes once charge carriers are injected onto the

polymer chain and self-localize, breaking the local spatial symmetry of the backbone.^{62,63}

IRAV modes are arguably the most specific optical probe for charged excitation density⁶⁴ and dynamics⁶⁵⁻⁶⁶ in π -electron conjugated polymers upon photo-, electro- or chemical-induced doping.⁶⁷⁻⁶⁹ After the first experimental observation of IR-active modes in chemically doped polyacetylene by Fincher and coworkers (see Figure 3.1.3a),⁷⁰ similar modes were also observed upon photoexcitation of polyacetylene, and attributed to charged solitons.⁷¹ In non-degenerate ground state polymers, IRAV modes are directly related to charged polarons.^{64, 72} Thanks to their specificity and sensitivity, over the past two decades IRAV modes have been largely employed as a direct probe of polaron density in pristine polymers,^{67, 69, 73} charge transfer processes and polaron dynamics in donor-acceptor blends,^{64, 72, 74-75} structure-charge relationships in polymers,^{67, 76-77} polaron spatial distribution within the active region of working devices⁷⁸⁻⁷⁹ and, most recently, coupling of polarons to surface plasmons in infrared nanoantennas.⁸⁰

From the theoretical standpoint, substantial work was done to understand and rationalize the description of IRAV modes. The first successful model capable of reproducing the key properties (frequency, relative intensities, and their one-to-one match with Raman modes) of the IRAV modes was developed by Horovitz *et al.* considering the pinning potential of the polymer skeleton chain.⁸¹⁻⁸² Later on, Zerbi *et al.* developed a theory based on the effective conjugation coordinate (ECC) to explain and interpret the

activation of IRAV modes and the phonon dispersion curves of π -electron conjugated systems.⁸³ IRAV spectral signatures have also been described within the framework of the amplitude mode model in Peierls organic semiconductors and their lineshapes have been well reproduced by Fano-type antiresonances between the discrete IRAV modes and the low-energy broad polaron band (see Figure 3.1.3c).^{73, 84}

Despite the significant advances of these theoretical models for the IRAV modes in organic semiconductors, so far most descriptions have been based on phenomenological assumptions. Up to date, some fundamental aspects of vibrational modes in photo- or chemical- induced absorption spectra, such as their dependence on spatial delocalization of excited states and the quantitative assignment of vibrational modes to specific photoexcitations, remain unclear. In this part of the thesis work, we combined *first principles* response calculations, infrared and Raman spectroscopy to study the vibrational properties of RR- and RRa-P3HT, a model polymer system to understand the influence of structural order on photoconductive properties. By combining density functional theory (DFT) and time-dependent DFT (TDDFT) calculations,⁸⁵⁻⁸⁶ we reproduce and distinguish frequencies and relative intensities of ground, charged, and singlet excited state vibrational normal modes, and specifically assign their spectroscopic fingerprints. Besides *conventional* IRAV modes due to local symmetry breaking, we identify excitonic fingerprints in the photoexcitation spectrum, due to the strengthening

of specific bonds upon generation of singlet excitons. Furthermore, we relate the splitting of the C=C Raman and excited state absorption bands, and the C—S stretching peaks, to the polymer regioregularity, providing a new indicator of the degree of structural order of polymeric chains.

3.1.3 Experimental Section

DFT calculations were performed to study the singlet geometries of neutral (P3HT), radical cation (P3HT^+ , i.e. polaron) and radical dication (P3HT^{++} , i.e. bipolaron) electronic states and corresponding vibrational modes by adopting restricted and unrestricted B3LYP functional, with 6-31G(d) basis set. The choice of a rather low basis set (i.e. 6-31G(d)) was based on the evaluation of both equilibrium geometries and vibrational force fields of long oligomers in the ground, charged (+1 and +2) and excited electronic states. The P3HT was represented by finite length oligomers (eight repeat units) to mimic the properties of the corresponding polymer;⁸⁷ side hexyl chains were replaced by methyl groups and both RR- and RRa- substitutions were taken into account. The geometries and vibrational force fields of the lowest (dipole active) excited state (S_1 , labeled as $^1\text{P3HT}^*$) were obtained through TDDFT calculations (TD-B3LYP/6-31G(d)) for both RR-P3HT and RRa-P3HT oligomers, without any symmetry constrain. The theoretical model by implementing the TDDFT in vibrational calculations was developed to obtain the vibrational signature of singlet excited states. All calculations were

performed using the Gaussian09 program (revision D.01).

Infra-red absorption spectra were obtained in a Fourier Transform Infra-red (FTIR) spectrometer (Bruker Vertex 80v) equipped with room temperature DTGS detector. Spectral and phase resolution used during Fourier transformation were 4 and 32 cm^{-1} , respectively. Photo-Induced absorption (PIA) spectra were recorded at low temperature ($T=78\text{ K}$) by photoexciting the samples with continuous wave green laser ($\lambda_{\text{ex}}=532\text{ nm}$) and probing the induced change in transmission ($-\Delta T/T$) by an FTIR spectrometer equipped with an MCT detector. Thick ($\sim 3\text{ }\mu\text{m}$) RR-P3HT and RRa-P3HT films were drop-cast on CaF_2 substrates for IR-PIA measurements in transmission mode measurements in near-normal back scattering geometry. The differential signal of over 5000 consecutive scans with pump light on and off was averaged to increase the signal to noise ratio. Raman spectra were obtained in a Renishaw Raman microscope configured with a charge coupled device array detector. A green ($\lambda_{\text{ex}}=532\text{ nm}$) laser line was used for excitation with power below 1 mW. Raman signals were collected by a Leica 1003 objective lens ($\text{NA}=50.85$) and dispersed by 2400 line/mm gratings with frequency resolution of 0.8 cm^{-1} . The integration time was 20 s.

3.1.4 Results on Structural, Vibrational and IR/V Modes of P3HT

Structural properties of RR and RRa-P3HT

Figure 3.1.4. (a) Schematic molecular structures of ground, polaron, bipolaron and excited state of RR-P3HT; (b and c) bond length difference (BLD) for polaron, bipolaron, and excited state (i.e. S_1) RR- (b) and RRa- (c) oligomers, computed with respect to their ground state structure.

Figure 3.1.4 shows the main skeletal molecular structures and bond length variations for RR-P3HT and RRa-P3HT evolving from the ground state to the *i*) polaron, *ii*) bipolaron and *iii*) first dipole allowed excited state (S_1). The structural variations induced by the different excitations *i-iii*), are mainly localized in the central part of the chain, and differ only in terms of *extension* and *amplitude* due to the different local molecular order and regioregularity of RR- vs RRa-P3HT. Polymer regioregularity affects the *amplitude* of the structural defects (e.g. bond lengths and torsional variations), with RRa-P3HT showing higher structural reorganizations than RR-P3HT, for each excitation. For the

polaron (Figure 3.1.4b, c) the maximum bond length deformation (BLD) is ~ 0.02 Å for RR- and ~ 0.04 Å for RRa-P3HT, while the bipolaron (Figure 3.1.4b, c) the structural changes are larger, with a maximum BLD of ~ 0.04 Å for RR- and ~ 0.06 Å for RRa-P3HT. The first excited state equilibrium structure features a maximum BLD of ~ 0.03 Å for RR- and ~ 0.04 Å for RRa-P3HT. Different structural relaxations imply different electron-phonon coupling factors, which would in turn affect the vibrational properties (IR, Raman and IRAV modes). Starting from a non-planar ground state, with an average angle of $\sim 16^\circ$ for RR- and $\sim 48^\circ$ for RRa-P3HT, we find that all excitations (*i-iii*) induce a quinoidal-like, planar molecular structure in both RR and RRa cases (see Figure A.1 of Appendix A).⁸⁸⁻⁸⁹ The *defect extensions* (i.e. the length for which BLDs are > 0.015 Å) for polaron, bipolaron and S_1 are 18.2, 28.8 and 14.3 Å for RR-P3HT, and 19.6, 27.3 and 15.7 Å for RRa-P3HT. In both cases, the bipolaron results to be the most extended defect. Note that the computed defect amplitudes and extensions may be affected by the choice of the exchange-correlation DFT functional. B3LYP is known to over-delocalize the extension of the defect,⁹⁰⁻⁹¹ a tendency corrected by introducing range-separated functionals (e.g. CAM-B3LYP, ω B97XD or BNL, see ref⁹²). Nevertheless, we decided to use this functional because of its documented reliability in predicting force constants and vibrational spectra for both neutral and charged/excited states.⁹³⁻⁹⁴

Vibrational modes in ground states of RR and RRa-P3HT

Figure 3.1.5. Experimental and calculated IR and Raman spectra of (a) RR- and (b) RRa-P3HT. The experimental IR and Raman spectra were measured in the thick film of RR- and RRa-P3HT on CaF_2 substrates.

Figure 3.1.5 compares the experimental and calculated IR absorption spectrum of neutral RR- and RRa-P3HT in the range $500\text{--}1700\text{ cm}^{-1}$ (the frequency values associated with the main experimental IR and Raman peaks are also reported in the figure; the corresponding eigenvectors can be found in Figures A.3-A.5 of Appendix A). To compare the DFT results with experimental spectra, the calculated frequencies were scaled by the standard scaling factor of 0.9594 for the B3LYP functional.⁹⁵

The calculated IR spectrum of the neutral species reproduces well the main experimental features, similar to previous results for polythiophene⁹⁶ and derivatives.⁹⁷⁻⁹⁹

In both RR- and RRa-P3HT, the most relevant backbone modes are the following:

- 1) the 820 (RR-) and 827 (RRa-) cm^{-1} (calculated: 814 and 812 cm^{-1}) bands, due to the $\text{C}_\beta\text{—H}$ out-of plane deformations⁹⁶;
- 2) the two bands in the 1420-1520 cm^{-1} spectral region, due to the carbon-carbon bonds stretching vibrations of the thiophene rings.

The broad band around 1460 (RR-) and 1462 (RRa-) cm^{-1} (calculated: 1426 and 1442 cm^{-1}) is associated to symmetric $\text{C}_\alpha=\text{C}_\beta$ bonds stretching vibrations, while the peaks at 1512 (RR-) and 1516 (RRa-) cm^{-1} (calculated: 1499 and 1510 cm^{-1}) are related to antisymmetric $\text{C}_\alpha=\text{C}_\beta$ bonds stretching vibrations. Moreover, the vibrational fingerprints of hexyl side chains are observed at 725 and 1377 cm^{-1} for RR-P3HT, and 727 and 1375 cm^{-1} for RRa-P3HT, which can be assigned to the rocking vibration of methyl substituent and deformation of terminal methyl groups.

The simulations of Raman spectra are also in good agreement with experiments: when increasing the number of thiophene rings from 2 to 8, the computed spectrum red shifts (by about 12 cm^{-1}) and the peak energies approach the experimental values (refer to Figure A.3 in Appendix A). Among the few Raman active modes in the 500-1700 cm^{-1} spectral region, the two in-plane ring skeleton modes at 1382 and 1450 cm^{-1} for RR-P3HT, and 1375 and 1458 cm^{-1} for RRa-P3HT, due to the C—C and C=C stretching modes, are most sensitive to π -electron delocalization; the ratio of single to double carbon bond stretching mode intensity is a good indicator of the conjugation length ($I_{\text{C—C}}/I_{\text{C=C}}$)⁹⁷:

here we obtain $I_{C-C}/I_{C=C}$ of 0.24 and 0.14 for RR- and RRa-P3HT, respectively.

Noticeably, the computed peak at 1443 cm^{-1} splits into two peaks in the case of RRa-P3HT, as also reflected in photoinduced absorption spectra (see later discussion).

The two peaks are assigned to symmetric $C=C/C-C$ stretching/shrinking modes localized on different segments of the long oligomer chain.

Vibrational modes in chemically-doped RR and RRa-P3HT

Figure 3.1.6. Experimental and calculated IR and Raman spectra of charge states of (a) RR-P3HT and (b) RRa-P3HT. The experimental IR and Raman spectra were measured in the thick film of FeCl_3 -doping RR- and RRa-P3HT on CaF_2 substrates.

After reproducing the vibrational properties of the polymers in the ground state, we calculated the vibrational properties of the polymers in the polaronic states. The results can be directly compared with the IR and Raman spectra of chemically doped polymers,

where polarons and bipolarons are permanently induced. Figure 3.1.6 shows the experimental IR and Raman spectra of FeCl₃ doped RR- and RRa-P3HT, together with DFT calculated spectra for polarons and bipolarons. Due to the overlap between the broad polaron “P₀ band” and the sharp vibrational resonances,^{73, 84} the vibrational modes appear as Fano anti-resonances (spectral dips) in the IR transmittance spectra of chemically-doped P3HT. For both RR- and RRa-P3HT, the experimental spectra are broadened and red-shifted compared to the undoped polymers. The calculated IR spectra of polaron and bipolaron agree well with the trend of the experimental IR spectra of doped RR- and RRa-P3HT. When polarons or bipolarons are formed, the thiophene ring in the polymer repeat unit assumes a quinoid-like structure, with characteristic vibrational signatures in the region of 1200-1400 cm⁻¹. Specifically, the bands around 1324 cm⁻¹ (RR-) and 1326 cm⁻¹ (RRa-) (calc.: 1326 and 1334 cm⁻¹) are due to C_α=C_α bonds stretching between neighboring thiophene rings. Other bands at 1386 cm⁻¹ (RR-) and 1388 cm⁻¹ (RRa-) (calc.: 1376 and 1378 cm⁻¹) are ascribed to the inter-ring C_α—C_β symmetric stretching. The experimental IR transmittance band at 1216 cm⁻¹ (RR-) and 1218 cm⁻¹ (RRa-) (calc.: 1191 and 1196 cm⁻¹), assigned to C_β—H bending vibrations of thiophene ring, become stronger compared to the same mode in the ground state.

Figure 3.1.6 also reports the theoretical Raman spectra of doped P3HT. In this case, the slight red shift of the experimental resonant Raman spectra compared to the calculated

data may be due to a more equalized bond-length pattern than the one predicted.¹⁰⁰ Three main Raman bands for the doped samples at 1380, 1448, and 1510 cm^{-1} for RR-P3HT, and at 1377, 1460, and 1517 cm^{-1} for RRa-P3HT, similar to those of undoped P3HT, arise from the C—C/C=C stretching modes delocalized over the entire oligomer. The calculated (non-resonant) Raman spectra of charged states of P3HT also show two main peaks at 1432 cm^{-1} (RR-) and 1412 cm^{-1} (RRa-) for polarons, and at 1372 cm^{-1} (RR-) and 1338 cm^{-1} (RRa-) for bipolarons. However the computed spectra are more structured than the experimental ones, and this may be due to the fact that calculations do not include resonance effects, which may enhance the peak intensity of some Raman active modes.^{47,}

¹⁰¹ Since $C_\alpha=C_\alpha$ and $C_\beta=C_\beta$ modes coexist in the quinoid structure of the doped polymer, some of the normal Raman modes can be attributed to totally symmetric stretching of $C_\alpha=C_\alpha$ bonds, as previously reported by Casado *et al.* for doped oligothiophenes.¹⁰²

Overall, the comparative analysis of IR and Raman spectra of chemical doped-P3HT clearly indicate the transition from benzenoid to quinoid structure due to polaron and/or bipolaron formation.

Interpretation of IRAV modes of RR and RRa-P3HT

Figure 3.1.7. Photo- and chemically-induced absorption spectra of (a) RR- and (b) RRa-P3HT, and the corresponding calculated IR spectra of polaron, bipolaron, excited (singlet), and ground states of (c) RR- and (d) RRa-P3HT. The red asterisks show the newly identified excitonic mode.

Figure 3.1.7 shows the comparison between experimental photo-induced absorption, chemically-induced absorption, and Raman spectra of RR- and RRa-P3HT in the

500-1700 cm^{-1} spectral region, and the computed polaron, singlet-excited and ground state IR modes. For both cases the photo-induced absorption (PIA) spectra were obtained by photoexciting the samples with continuous wave green laser ($\lambda=532\text{ nm}$) and probing the induced change in transmission ($-\Delta T/T$); conversely, the chemically-induced spectra were derived from the change of IR spectra of undoped and doped samples. Table A.1 summarizes the main modes and their assignment. The IRAV modes of both samples can be attributed, on the basis of DFT and TDDFT calculations, to peaks present in the IR spectra of polaron (P3HT^+), bipolaron (P3HT^{++}) or excited state ($^1\text{P3HT}^*$) species, and Raman spectra of the neutral species. RR- and RRa-P3HT show five principal negative photoinduced absorption (PIA) bands around 730, 800, 1360, 1450 and 1510 cm^{-1} . In the following, we will focus our discussion on the differences induced by conformational disorder in *conventional* IRAV modes (i.e. those corresponding to Raman modes) in RR- and RRa-P3HT, and on the origin of the mode around 800 cm^{-1} , which does not have a Raman counterpart.

The *conventional* IRAV modes, i.e. 730, 1360, 1450 and 1510 cm^{-1} can be associated to the active Raman modes of anti-symmetric $\text{C}_\alpha\text{—S—C}_\alpha$ deformation (727 and 731 cm^{-1} for RR and Ra, respectively), symmetric $\text{C}_\beta\text{—C}_\beta$ stretching (1382 and 1375 cm^{-1} for RR and Ra, respectively), symmetric $\text{C}_\alpha\text{=C}_\beta$ stretching (1450 and 1458 cm^{-1} for RR and Ra, respectively), and antisymmetric $\text{C}_\alpha\text{=C}_\beta$ stretching (1512 and 1522 cm^{-1} for RR and Ra,

respectively) vibrations of ground state P3HT. PIA spectra of RR- and RRa-P3HT show significant differences in the 1300-1600 cm^{-1} region, specifically: *i*) different intensity ratio between the $\sim 1450 \text{ cm}^{-1}$ and the $\sim 1360 \text{ cm}^{-1}$ bands: $I_{1450/1360} (\text{RRa-}) < I_{1450/1360} (\text{RR-})$; and *ii*) $\sim 1450 \text{ cm}^{-1}$ band splitting in the case of RRa-P3HT – this is a direct consequence of the reduction of intensity and splitting of the 1443 cm^{-1} C=C stretching Raman mode discussed earlier for RRa-P3HT in the ground state. The PIA band of RR-P3HT around 1360 cm^{-1} can be interpreted as a superposition of the calculated IR spectra for polaron, bipolaron and excited state species. In this region are collocated the quinoid $\text{C}_\beta=\text{C}_\beta$ symmetric bonds stretching modes at 1324 (polaron), 1325 (bipolaron) and 1330-1400 (excited state) cm^{-1} , and the interrering $\text{C}_\alpha=\text{C}_\alpha$ anti-symmetric bonds stretching at 1384 (polaron), 1385 (bipolaron) and 1401 (excited state) cm^{-1} . Thus, the activity of these modes in the PIA spectra cannot be uniquely attributed to the IR and Raman spectra computed for the neutral species, rather to a *photoexcited* structure resembling that of exciton and/or polaronic species. In the case of RRa-P3HT, the 1360 cm^{-1} PIA band is also well reproduced by the computed IR spectra of polaron, bipolaron and excited states, but it is more intense than in RR-P3HT. Thus, a thorough comparison between the PIA spectra and first principles calculations can provide fine details on the degree of disorder of the polymeric chains.

The intense and specific PIA mode around 800 cm^{-1} cannot be ascribed to Raman mode

conversion induced by charged excitations. This IR active mode is due to the $C_{\alpha}-S$ stretching of the thiophene rings in the singlet excited state, whereas in the ground state normal modes in this spectral region are assigned to $C_{\beta}-H$ out-of-plane deformation.¹⁰³⁻¹⁰⁴ Since this IR active band has a large cross section in the excited state, the corresponding IRAV mode can be regarded as a signature of long lived photoexcited excitonic species ($^1P3HT^*$). Similar to carbon-carbon stretching modes, the intra-molecular $C_{\alpha}-S$ stretching mode is very sensitive to the local chain conformations/distortions. Thus, the intensity ratio I_{817}/I_{730} , can be used as a spectroscopic marker of the polymer chain structure. Indeed, this ratio decreases from RR- to RRA-P3HT because of their different local intra- and inter-chain structure. To the authors' knowledge, this is the first observation of a vibrational signature of singlet excited states in the PIA spectra of P3HT, which provides a new probe for structural deformations induced by photo-excitations.

The two points discussed are crucial to draw proper structural-functional relationships of general validity for polymeric chains. RRA- chains are characterized by a larger ground state structural distortion than RR-, leading to higher relaxations and favoring self-localization and charge trapping processes after the photoexcitation. Exciton, polaron and bipolaron are generated at different time scales (from fs to ns), leading to localization processes and structural relaxation¹⁰⁵⁻¹⁰⁶ with spectroscopic signatures sensitive to the

local molecular conformations and order. Therefore, as results from our IRAV analysis, RRa- chains trap charges and localized the excitations more efficiently than RR-chains, leading to more structured IRAV spectral pattern (e.g. see intensity ratios $1450/1360\text{ cm}^{-1}$, and $817/730\text{ cm}^{-1}$ bands, Figure 3.1.7).

3.2 Surface Polarity Effects at Photovoltaic Hybrid Interfaces

After studying the electronic and vibrational properties of conjugated polymers in the previous section, here we will use a “organic monolayer/inorganic slab” model to deal with the large hybrid polymer/inorganic interfacial structure. This section begins with a brief introduction of hybrid polymer/inorganic system for photovoltaic applications, and is followed by the description of photophysical processes in hybrid photovoltaics and the motivation of studying particular polymer/GaAs systems. The results of surface polarity effects on the charge redistribution and transfer at hybrid GaAs/P3HT heterointerfaces are then presented by a joint experimental and theoretical analysis of photoelectronic spectroscopy on polymer/GaAs bilayers and DFT calculations on our proposed model.

3.2.1 Hybrid Polymer/Inorganic Semiconductors

Organic/inorganic hybrid solar cells based on organic polymers and inorganic nanocrystallites (nanoparticles, nanorods or quantum dots) have attracted great attention in developing the low-cost, scalable and robust photovoltaic technologies.^{4, 107} Combining the organic materials (high absorption coefficients and flexibility) with inorganic semiconductors (high electron mobilities, and superior stability) to form

various nanostructures, hybrid solar cells can achieve unique functionalities that cannot be achieved by the individual components alone, such as interfacial hybrid state for promoting charge transfer. The performance of hybrid photovoltaics is strongly influenced by the competition between interfacial charge separation and charge recombination.¹⁰⁸⁻¹⁰⁹ Typically, the energetic offsets between conjugated polymers and inorganic nanocrystals promote dissociation of the photogenerated excitons and prevent charge recombination.¹¹⁰ Recently, significant research efforts were directed toward hybrid photovoltaics using different inorganic nanostructure composites of group IV (Si¹¹¹ and Ge¹¹²), group IV-VI (PbS¹¹³ and PbSe¹¹⁴), group II-VI (CdSe¹¹⁵⁻¹¹⁶ and CdS¹¹⁷) and metal oxides (TiO₂⁴ and ZnO¹¹⁸⁻¹¹⁹). The mainstream III-V semiconductors (*e.g.* GaAs and InP), with high carrier mobility and direct bandgap absorption well-overlapped with the solar irradiance, are rapidly emerging as exceptional photovoltaic materials for thin film technologies¹²⁰, including bilayer hybrid solar cells.¹²¹⁻¹²⁴ However, despite their tantalizing potentials, the power conversion efficiencies of these hybrid solar cells are still low compared to all organic photovoltaics. Current understanding of the electronic properties leading to charge transfer at organic-inorganic interfaces is limited.¹²⁵⁻¹²⁸ Moreover, the nature of charged photoexcitations at the interface of highly delocalized inorganic crystals and more localized, disordered conjugated systems is of great fundamental interest.¹²⁹⁻¹³³ From this perspective, better understanding of the nature of

primary photoexcitations and fundamental physical processes at polymer/inorganic heterointerfaces from a theoretical stand point is highly desirable. Figure 3.2.1 shows a schematic representation of hybrid P3HT/GaAs bilayer model for studying the electronic properties of localized/delocalized system.

Figure 3.2.1. Schematic of experimental measurements (absorption, photoluminescence, X-ray and ultraviolet photoelectron spectroscopy) and theoretical models on the hybrid organic/inorganic interfaces.

3.2.2 Photophysical Processes in Hybrid Photovoltaics

In the hybrid active layer, the electron-hole binding energy at the heterointerface is efficiently reduced as compared to one in the organic material by taking full advantage of the organic light absorbers and dielectric screening from inorganic components.¹³⁴ This means that excitons created at the interface have Wannier-type character (a radius larger than lattice spacing); while holes are localized in the organic part, electrons can migrate and transfer into the inorganic part. This ultimately facilitates exciton dissociation into free carriers, and effectively enhance transport to their respective electrode. Several key

quantities could be obtained with the help of theoretical descriptions of such systems, including the hybrid interfacial structures and corresponding optoelectronic properties, the nature of photogenerated exciton and diffusion, the transport properties of charge-carrier, and the time scales of charge separation and recombination. Knowing these important parameters through DFT calculations can offer insights into mechanisms and phenomena of hybrid systems.

Figure 3.2.2. Charge transfer processes at organic/organic and organic/inorganic interfaces.

Organic or hybrid solar cells usually comprise two different materials with type-II energy alignment, as represented in Figure 3.2.2. In the photophysical processes of

organic or hybrid solar cells initiated by light irradiation, the first step is light absorption by the active materials, for instance low band-gap polymers, quantum dots, or hybrid perovskites, resulting in photo-generation of an exciton in the donor material. Note that this photo-excitation can be treated as a single photon absorption process. The next step is electron relaxation toward the lowest unoccupied molecular orbital (for organic acceptors, such as fullerenes) or conduction band minimum (for inorganic acceptors). For organic materials, the hole and electron are usually tightly bounded with large exciton binding energy (a few hundred meV), due to the strong attraction between the hole and the electron in the active layer; therefore, the large spatial electronic overlap of hole and electron will lead to a high chance of charge recombination, provided that such electronic transitions are not symmetry-forbidden. However, in bulk inorganic materials the exciton binding energy is relatively small (just a few meV), and comparable to the thermal energy. The exciton can then be dissociated into free carriers, which are transported independently and in opposite directions through the active layer toward the metal electrodes. Charge transport is primarily limited by the charge carrier mobility and by the extraction and collection efficiency of charge carriers by their corresponding electrodes. Among these physical processes, the (desirable) charge separation and (undesirable) charge recombination compete with each other, ultimately determining the final power conversion efficiency.

Experimentally, it is difficult to probe charge separation processes since only indirect interfacial electronic structures can be obtained. In this respect, DFT calculations can provide strong direct theoretical support in understanding the electronic properties and photophysical processes via accurate descriptions of hybrid structures at the organic/organic or organic/inorganic interfaces.

3.2.3 Hybrid Polymer/GaAs Heterointerfaces

GaAs, a typical III-V semiconductor material with large carrier mobility ($\mu \sim 8500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and absorption spectra well-overlap with solar irradiance, outstands as photovoltaic compound in thin film technologies.¹³⁵ Early demonstration of a quaterthiophene/GaAs bilayer PV gave 1.7% PCE;¹²¹ while recently GaAs nanowire/P3HT (poly(3-hexylthiophene-2,5-diyl)) bulk heterojunctions showed $\sim 2.37\%$ PCE,¹²² and GaAs/polymer bilayers performed the PCE of 1.4-4.2%,¹³⁶ especially, GaAs (111)B/P3HT can achieve 4.2% PCE.¹³⁷ In spite of the attractive device performances, current understanding of the electronic properties of organic-inorganic interfaces, such as GaAs/P3HT, and their influences on the charge transfer, is relatively limited.¹³⁸ For instance, the surface polarity effects on the interfacial electronic properties and the photophysical processes between delocalized band states of inorganic crystals and discrete molecular orbitals of the polymer are still unknown. In this part of the thesis, we describe the structural and electronic properties of the hybrid interfaces formed by P3HT

thin layers with polar GaAs (111)B and nonpolar GaAs (110) substrates (see Figure 3.2.3). The most stable interfacial configurations are determined by studying the preferred orientation and position of P3HT molecules on the different GaAs surfaces from total energy calculations. Overlapping of projected density of states and redistribution of interfacial charges suggest that hybrid states are formed at the GaAs/P3HT interfaces upon photoexcitation. The energy alignment and electronic coupling properties of GaAs/P3HT interfaces obtained from density functional theory calculations agree well with the experimental results from ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) measurements. Lastly, the effect of ground-state charge transfer on surface polarities are identified, indicating that electron and hole accumulation layers can be engineered via the control of GaAs crystal orientation to optimize the photovoltaic devices.

Figure 3.2.3. Crystal structures of GaAs (111)B and GaAs (110) slabs cutting from bulk.

3.2.4 Experimental Methods

Computational method: DFT with local density approximation (LDA) functional¹³⁹ calculations are conducted with the QE software package.¹⁴⁰ Description of electron-ion interactions is realized by the ultrasoft (C, S and H atoms) and norm-conserving of (Ga and As atoms) pseudopotentials. The electronic wavefunctions and charge density are expanded with an energy cutoff of 40 and 320 Ry, respectively. Considering the significant additive stabilization effect of dispersion forces on CT systems, the vdW-DF functional¹⁴¹ that accounts for dispersion effects self-consistently is also used for structural and electronic calculations. Regarding the calculations of bulk GaAs, integration over the Brillouin Zone is conducted with a k-points grid of $8 \times 8 \times 8$ while optimizing the crystal cell and calculating the electronic properties. The lattice constant is determined to be 5.543 Å, similar with the experimental value 5.653 Å. Since they are experimentally observed to be stable and both terminated with As atoms in the top layer,¹⁴²⁻¹⁴³ surface orientations of (110) and (111)B are chosen to investigate the effects of GaAs surface polarity. To simulate the GaAs slabs, optimization of the bulk (110) and bulk (111)B crystals is carried out to determine the corresponding in-plane lattice parameters of the two GaAs surfaces. They are represented by periodically repeated 4×2 surface supercells derived from common GaAs (110) (1×1) and GaAs (111)B (2×1) surface reconstructions. Each slab layer consists of 4 bilayers, where atomic positions in

the bottom bilayer are fixed to mimic the bulk GaAs while the others are fully relaxed. A vacuum region of ~ 15 Å is added to avoid interaction between adjacent slabs. For the calculations of crystalline P3HT, the polymer structure was determined from a repeat unit containing two thiophene rings. Our “organic monolayer/inorganic slab” model was built by combining the GaAs surface supercells and the two repeated unit (no interdigitation of alkyl side chain), to treat the large hybrid interfacial structures. The transverse area is found to be 22.17×7.70 Å² for GaAs (110) slab, and 20.37×7.66 Å² for GaAs (111)B slab. A $4 \times 4 \times 1$ k-point grid is used to study both bare GaAs surfaces and GaAs/P3HT heterojunctions. Broyden-Fletcher-Goldfarb-Shanno (BFGS) method is applied for the optimizations of all surface and interface geometries, until all the forces on all atoms are lower than 0.02 eV/Å and the total energy difference between two optimization steps of the minimization procedures is less than 10^{-4} eV. Three-dimensional illustrations of charge density are produced by VMD.¹⁴⁴ The surface energy is defined as $E_{\text{surf}} = (1/2A)[E_{\text{slab}} - nE_{\text{bulk}}]$,¹⁴⁵ where E_{surf} denotes the total energy of the surface, n denotes the total number of atoms in the slab, E_{bulk} denotes the energy per atom of the bulk structure, and A denotes the area of the surface.

XPS and UPS spectroscopy: XPS and UPS are used to study the energy band alignments of two types of GaAs/P3HT heterojunctions. *n*-doped GaAs (110) and (111)B substrates are etched with diluted $\text{H}_2\text{SO}_4:\text{H}_2\text{O} = 1:10$ solution. P3HT is dissolved in

1,2-dichlorobenzene at a concentration of 4 mg/ml and spin-coated onto the GaAs substrates at 3000 rpm for 60 s. The thickness of resulted polymer film is determined to be 5-7 nm using atomic-force microscopy. Upon deposition, samples are thermally annealed at 150°C for 20 min in inert atmosphere of Ar gas. XPS and UPS measurements are carried out under high vacuum with excitations of Al K α ($h\nu = 1486.7$ eV) and He I ($h\nu = 21.2$ eV).

3.2.5 Results on the Surface Polarity Effects on the Charge Redistribution and Transfer at P3HT/GaAs Heterointerfaces

Interfacial geometric structures of P3HT on GaAs surfaces

DFT calculations were performed to optimize the interfacial geometric structures of P3HT absorbed on GaAs surfaces by full relaxing the atomistic coordinates, based on which the electronic couplings and charge density redistribution were determined. From the view of the optimized slabs, the outmost layer alignment of polar GaAs (111)B surface is very stable, whereas strong reorganization is found at the nonpolar GaAs (110) surface as both As and Ga atoms experience outward and inward relaxation, respectively. These structural properties are consistent with previous calculated results.¹⁴⁶⁻¹⁴⁷ As a result of surface relaxation, the Ga-As bonds in GaAs (111)B surface bilayer are elongated from 2.400 to 2.417 Å, while Ga-As bonds in GaAs (110) surface bilayer are shortened to 2.375 Å. Similar to the well-studied case of ZnO/P3HT interface, the

physisorbed P3HT molecules are believed to form a flat layer upon GaAs surfaces due to van der Waals interactions of thiophene π band of side-chain. Dag *et al.* suggested that LDA method can be used to accurately predict ZnO and P3HT interactions although the long-range van der Waals attractive components were not included.¹⁴⁸ Hence, the same method is carried out in our study to model the GaAs/P3HT interfaces, where the outmost bilayer of GaAs slabs is used to demonstrate the original GaAs surface and two repeated molecular units to represent polymer P3HT. This is a common computational strategy for studying the bonding energy of hybrid systems.¹⁴⁸⁻¹⁴⁹

Figure 3.2.4. (a) binding energy of P3HT on GaAs (110) and GaAs (111)B as a function of the interfacial distance along z -axis; (b) bonding energy as a function of the rotation angle (0-30°) between P3HT and GaAs. The optimal rotational angles in the x - y plane are at 0° in both cases.

Figure 3.2.5. Optimized heterointerfacial GaAs/P3HT structures: (a, a') top views of the optimized geometries of P3HT on GaAs (110) and GaAs (111)B; binding energy of P3HT on (b, c) GaAs (110) and (b', c') GaAs (111)B surfaces as a function of its relative position along the x and y axes.

Various energy minimization steps were conducted to obtain the optimized structures.

First of all, the stable interfacial distances are found to be 3.10 and 2.95 Å for GaAs (110)/P3HT and GaAs (111)B/P3HT, respectively, correspond to the minima of the binding energy-distance curves in Figure 3.2.4a. Then the optimal rotational angle in the

x - y plane is determined to be 0° , which corresponds to the minima of the binding energy-rotation angle curves shown in Figure 3.2.4b. Finally, $x=1.5$ Å and $y=2$ Å were determined to be the most stable configuration for GaAs (110) (Figures 3.2.5b and 3.2.5c), and $x=3.5$ Å and $y=0$ Å for GaAs (111B) (Figures 3.2.5b' and 3.2.5c'). Figure 3.2.5a and 3.2.5a' illustrate the resulting most stable P3HT adsorption sites upon GaAs (110) and GaAs (111)B surfaces, respectively. For both GaAs surface orientations, the minimal energy configurations of P3HT molecule are obtained when the S atom overlaps with the beneath As atom on the top of GaAs surface, and the hexyl chain of P3HT inclined to line with the x -axis. Note that all studies presented in the following on electronic properties of GaAs/P3HT are based on these stable bilayer configurations.

Electronic coupling of P3HT with GaAs surfaces

The interfacial electron transfer has an important effect on the charge generation efficiency of GaAs/P3HT PV devices. The efficiency of electron transfer is generally determined by the energy alignment and the electronic couplings cross the hybrid interfaces, as well as the variations in geometric and electronic structure of P3HT caused by thermal fluctuations.¹⁴⁸ Experimentally, as indicated by Cabanillas *et al.*, for GaAs/oligothiophene bilayer system, electrons could transfer toward the GaAs conduction band after exciton diffuses to the hybrid interface.¹⁵⁰ Theoretically, Prezhdov *et al.* provided the detailed studies on the interfacial charge separation and relaxation

processes in hybrid systems by time-domain *ab-initio* modelling.^{19, 151} For alizarin/TiO₂ interface, the adiabatic mechanism is believed to be dominate over nonadiabatic one because of strong electronic coupling across the hybrid interface.¹⁵² For graphene/TiO₂ interface, due to the strong electronic coupling between graphene and TiO₂, the time scale of electron injection is found to be ultrafast, and the delocalized photoexcited states promotes both electron injection and energy transfer.¹⁵³ Additionally, Hertz *et al.* investigated the idealized GaAs (10-10)/P3HT interface using DFT modelling, suggesting that the formed interfacial dipole can lower the HOMO level of the low-bandgap polymer until the whole hybrid system reached equilibrium.¹³⁸

Figure 3.2.6. Density of states and electronic orbital distributions of hybrid GaAs (110)/P3HT and GaAs (111)B/P3HT systems: (a, a') total and projected density of states (the vertical dashed line indicates the Fermi level); electronic distribution of the electron (b, b') and hole (c, c') orbitals.

After charge redistribution, the energy alignment and electronic coupling between polymers and semiconductor substrates could be determined by analyzing the total density of states (DOS) and projected density of states (PDOS).¹⁵⁴ In Figures 3.2.6a and 3.2.6a', the overall DOS of GaAs/P3HT combined system is mostly governed by the PDOS of GaAs whereas the PDOS of P3HT only contributes little to the valence band of the whole system. The characterization of orbital overlap across the interface is realized by the analysis of interactions between frontier orbitals of the P3HT and GaAs substrate. As compared to the small overlap of the HOMO of P3HT and the GaAs valence band, electronic states of the P3HT spread over a broad energy range, resulting in large overlap between the LUMO level of P3HT and conduction band of GaAs. This leads to strong electronic coupling between P3HT main chain and GaAs surface. Figure 3.2.6 also illustrate the spatial electron density distribution of HOMO and LUMO levels of P3HT. For GaAs (110)/P3HT, electrons could be easily transferred to the the GaAs substrate due to the highly overlapped electronic clouds at the interface, implying the formation of hybrid delocalized states. Meanwhile, hole transfer is unfavorable and hole would be confined to GaAs (110) surface, which leads to the poor overlap between the GaAs conduction band and HOMO level of P3HT.

As shown in Figure 3.2.6a', the surface dangling bonds have a severe influence on the DOS of GaAs (111)B surface: both As-4p states on the top surface layer and Ga-4p states

on the bottom layer lie at the Fermi level within the bandgap, which leads to the formation of multiple middle-gap states and narrows the energy bandgap upon lowering the conduction band.¹⁵⁵ This change of GaAs (111)B conduction band has significant effect on the relative overlap between GaAs and P3HT and also changes the corresponding electronic density distribution. Specifically, the valence band of GaAs (111)B can overlap with the HOMO of P3HT, facilitating the hole transfer from GaAs (111)B to P3HT. While electron distribution may be confined to the GaAs (111)B surface, restricting the electron transfer from P3HT to GaAs (111)B as compared to the previous case; but holes delocalize between the thiophene chain and GaAs (111)B surface states and penetrate deeply into the GaAs bulk.

Charge redistributions in GaAs/P3HT heterointerfaces

For the quantification of actual charge transfer and separation processes at the hybrid interfaces, we evaluated the charge density redistribution upon P3HT adsorption on GaAs and estimated induced interfacial dipole moment and work function.¹⁵⁶ At the organic/inorganic hybrid interfaces, adsorption of organic layer onto the inorganic layer is always along with the redistribution of electronic charge density across the interface. Consequently, charges would transfer between the organic molecule and the inorganic substrate, generating a dipole moment that compensates the interfacial potential as well as decreases the energy level mismatch.¹⁵⁷⁻¹⁵⁸ Hence, the innate characters and polarity of

inorganic substrate play an important role in forming interfacial dipoles and in promoting charge separation. Figure 3.2.7 represents the rearrangement of electronic charge after GaAs/P3HT heterojunctions is formed. Quantification of the charge transfer from polymer molecule to inorganic substrate is based on the charge density difference: $\Delta\rho(r) = \rho_{\text{GaAs/P3HT}} - [\rho_{\text{GaAs}} + \rho_{\text{P3HT}}]$, where r denotes the position vector in the computational cell, ρ_{GaAs} , ρ_{P3HT} and $\rho_{\text{GaAs/P3HT}}$ represent the charge densities of GaAs (110) and (111)B slabs, P3HT alone, and GaAs/P3HT bilayer, respectively. In both cases of GaAs (110) and GaAs (111)B/P3HT heterointerfaces, abundant charge transfer is promoted and distinct charge accumulation/depletion layers are formed upon the adsorption of polymer molecules onto the substrates, indicating the significance of electrostatic interactions between the polymer and inorganic substrate.¹⁵⁹⁻¹⁶⁰ In Figures 3.2.7a and 3.2.7a', one-dimensional plane-averaged charge density difference ($\Delta\rho$) along z-direction can quantitatively estimate the accumulation of electron ($\Delta\rho < 0$) and hole ($\Delta\rho > 0$), implying a greater charge rearrangement on the polar GaAs (111)B surface ($\sim 5.3 \times 10^{-3} \text{ e}/\text{\AA}^3$) in comparison with the nonpolar GaAs (110) surface ($\sim 0.8 \times 10^{-3} \text{ e}/\text{\AA}^3$). The major difference of the two surfaces lies in the way that charges accumulate at the interface: for nonpolar GaAs (110) surface, holes would gather at both sides of the GaAs surface; on the other hand, a distinct electron accumulation layer is formed along the top As monolayer of the polar GaAs (111)B surface. The generated electron accumulation layer can not only

reduce electrostatic screening thanks to the great interfacial hole density, but also favor the hole transfer from the substrate to polymer molecule in comparison with the nonpolar GaAs (110).

Figure 3.2.7. Charge redistribution in hybrid GaAs (110)/P3HT and GaAs (111)B/P3HT systems: (a, a') one-dimensional plane-averaged charge density difference upon P3HT adsorption; (b, b') three-dimensional representation of the charge density difference with an isovalue of $\pm 0.005 e/\text{\AA}^3$. In (a, a'), solid lines represent the average positions of the GaAs surface and the P3HT molecular plane, and horizontal dashed lines indicate the interfacial position at which charge depletion converts into charge accumulation.

Both bare GaAs (110) and GaAs (111)B surfaces have distinct polarization properties. In the case of GaAs (110) surface, though it is usually considered to be nonpolar, there is a small intrinsic dipole moment produced by the tendency of surface Ga atoms penetrating towards the GaAs bulk, resulting in an As-terminated surface. Such kind of charge-unbalance generates a negative dipole moment pointing towards the bulk, and resulting surface charge density of is $q_{\text{GaAs}(110)} = 2.2 \times 10^{13} \text{ e/cm}^2$. The intrinsic dipole moment in GaAs (111)B is much larger than GaAs (110) surface due to the alternately stacked As- and Ga-terminated layers, and the surface charge density is determined to be $q_{\text{GaAs}(111)\text{B}} = 7.4 \times 10^{13} \text{ e/cm}^2$.¹⁶¹

Charge rearrangement induced by polymer adsorption can enhance the intrinsic surface dipole moment of GaAs surfaces. To understand the origin of interfacial dipole moment, Löwdin analysis of charge density was carried out in these hybrid systems.¹⁴⁰ By comparing the total Löwdin charges before and after the formation of heterojunctions, total charge transfer (ΔQ) across the interface is determined to be $0.207e$ and $0.209e$ for GaAs (110)/P3HT and GaAs (111)B/P3HT bilayer system, respectively. These values are much smaller than typical metal/organic systems, such as Au (111)/Naphthalocyanine ($\sim 0.7e$) and Cu (110)/Petencene ($\sim 0.8e$),¹⁶²⁻¹⁶³ but they are comparable with metal-oxide/polymer (ZnO/P3HT, $\sim 0.3e$) and metal-oxide/graphene system (ZnO/Graphene, $\sim 0.4e$).¹⁶⁴⁻¹⁶⁵

Energy alignments of GaAs/P3HT bilayers

Figure 3.2.8. UPS spectra of thin P3HT film on GaAs substrates at Fermi-edge regions: (a) HOMO of P3HT on GaAs (110) = 1.10 eV, (b) VBM of GaAs (110) = 0.69 eV, (c) HOMO of P3HT on GaAs (111)B = 0.65 eV, (d) VBM of GaAs (111)B = 0.68 eV.

XPS and UPS measurements are utilized to validate our calculated results on the energy alignment of GaAs/P3HT interfaces. Using the integer charge transfer (ICT) modelling,¹⁶⁶ the energy alignment at organic/inorganic heterojunctions with weak interfacial interactions is obtained based on the change of work function after the organic molecule is adsorbed onto the substrate. Upon the removal of charges from conjugated polymer, significant geometric and electronic relaxation effects can be induced, leading to the formation of localized positive polaronic states (p^+).¹⁶⁷ When the work function of substrate (Φ_{SUB}) is higher than the energy of polaronic states (E_{p^+}), electrons transfer from the organic moiety to the inorganic part would spontaneously occur, while an interfacial dipole that can reduce the vacuum level is created. The interfacial dipole energy (Δ) can be determined as the difference between Φ_{SUB} and E_{p^+} .

Figure 3.2.9. UPS spectra of thin P3HT film on GaAs substrates at cutoff: (a) WF of P3HT on GaAs (110) = 3.78 eV, (b) WF of GaAs (110) = 4.76 eV, (c) WF of P3HT on GaAs (111)B = 4.00 eV, (d) WF of GaAs (111)B = 4.95 eV.

As shown in Figures 3.2.8a and c, the HOMO levels of P3HT coated onto GaAs (110) and GaAs (111)B are 1.10 and 0.64 eV, respectively, lower than the Fermi energy indicated by the Fermi-edge regions of UPS spectra of these two heterojunctions. The work functions of P3HT on substrates ($\Phi_{\text{P3HT/SUB}}$) are determined to be 3.78 and 4.00 eV for GaAs (100)/P3HT and GaAs (111)B/P3HT, respectively, according to the cutoff of the UPS spectra (Figures 3.2.8a and c). In inert argon-gas atmosphere, the surface oxide layer of GaAs substrate is carefully removed via H_2SO_4 solution treatment, followed by P3HT adsorption. Complete removal can be confirmed by the absence of Ga_2O_3 and As_2O_3 peaks in the XPS spectra of substrates. For the determination of the energetics of bare inorganic substrates, the polymer layers are discarded *in-situ* by Ar ion sputtering until clean GaAs surfaces are recovered. GaAs (110) substrate gives a valence band maximum (VBM) of 0.69 eV and a work function of 4.76 eV, while the corresponding value for

GaAs (111)B substrate are 0.68 and 4.95 eV, respectively (shown in Figures 3.2.8b and d, Figures 3.2.9b and d). For P3HT, Summation of the optical gap energy (1.9 eV) and the HOMO is regarded as the LUMO; similarly, for GaAs, the summation of the optical gap energy (1.42 eV) and VBM is the CBM.

Figure 3.2.10. Energy diagrams of hybrid: (a) GaAs (110)/P3HT and (a') GaAs (111)B/P3HT interfaces interpreted from UPS measurements.

Figures 3.2.10a and a' summarize the overall energy alignment of the two different GaAs/P3HT hybrid interfaces on the basis of the above measurements. The energy band alignment at the GaAs (110)/P3HT heterojunction is determined to be the type-I, or straddling gap, whereas that at the GaAs (111)B/P3HT interface is observed to be the type-II, or staggered gap, in accord with our calculation results as shown in Figures 3.2.5a and 4.5a'. Thanks to the barrier between the LUMO of P3HT layer and the CBM of GaAs surface, electron transfer from the organic moiety to the inorganic substrate is

favored in both configurations. Such displacement of negative charge promotes the formation of -0.98 eV interfacial dipole barrier for the bare GaAs (110) surfaces over the corresponding heterojunctions, and -0.95 eV for the bare GaAs (111)B. However, GaAs (111)B provides a larger valence level offset which favors hole transfer into the polymer molecules ($E_{\text{HOMO}}-E_{\text{VBM}}=0.04$ eV), implying that the polymer layer in the current heterojunction can function as ‘hole acceptor’; while in the case of GaAs (110), it is predicted to behave to the contrary. The vacuum level shift caused by the interfacial dipole ($\Delta\Phi$) is obtained by comparing the electrostatic potentials between the inorganic surface and the polymer layer with the Helmholtz equation: $\Delta\Phi = \mu n/\epsilon_0$ ¹⁵⁶, where μ denotes the interface dipole moment, namely the amount of excess charge based on the Löwdin charge analysis multiplied by the interfacial distance, $n = 1/A$, where A denotes the surface area of the interface). The $\Delta\Phi$ of GaAs (110) and GaAs (111)B are found to be 0.868 and 0.769 eV, respectively, slightly lower than the experimental values, as there is only one polymer monolayer taken into consideration in our simulations. Our ultrafast spectroscopy study on the current hybrid bilayers evidences the following predictions: for both GaAs surfaces, electrons transfer rapidly (<100 fs) from the P3HT monolayer into the inorganic crystal upon the photoexcitation of P3HT; hole injection into the polymer monolayer is also observed by means of energy-selective excitation of GaAs.

3.3 Electron Transfer in P3HT/InP Quantum Dots

Following the previous studies on GaAs/P3HT, in this section we deal with another hybrid organic-inorganic system formed by conjugated polymer and quantum dots. We get insights into the photophysical processes by implementing the quantum chemistry results in Marcus theory to obtain the charge transfer rate between polymer and nanocrystal. The discussions and results are mainly focus on the ligands and small size effects on the charge transfer processes between P3HT and InP quantum dots (QDs) through the combination of spectroscopic measurements on InP QDs/P3HT blends and quantum chemistry calculations on the dimer polymer/nanocrystal models.

3.3.1 Hybrid organic/inorganic nanocrystal system

Hybrid organic/inorganic solar cells combining organic conductive polymers and inorganic nanocrystals have been developed in recent years as an alternative to all-organic solar cells.^{4, 168-169} The possibility of replacing fullerene derivatives, commonly used as acceptors in organic solar cells, with nanostructured inorganic semiconductors offers benefits of tunable absorption and emission spectra, particularly in the near infrared spectral range, higher charge carrier mobility,¹⁷⁰ multiple exaction generation¹⁷¹ and better thermal- and photo- stability.¹⁷² Meanwhile, the high dielectric

constant of inorganic nanocrystals assists charge separation and suppresses recombination at the organic/inorganic interfaces.¹⁷³ Various composites based on Si,¹⁷⁴⁻¹⁷⁵ ZnO,¹¹⁸ CdSe¹⁷⁶⁻¹⁷⁸, PbS¹⁷⁹⁻¹⁸¹ and a few other II-VI and III-V nanocrystals are currently studied from both experimental and theoretical standpoints. Nevertheless, the power conversion efficiency of QDs/polymer solar cell remain quite low compared to purely organic counterparts (Si: 1.1%,¹⁷⁴ CdSe: 3.6%,¹⁸² CdSe: ~4%¹⁸³, PbS: 4.23%¹⁸⁴). For these hybrid systems, the choice of QDs size and organic molecules used for coating QDs governs the optical behavior of inorganic cores and influences the performance of QDs-based photovoltaic devices.¹⁸⁵ On one hand, the organic ligands passivating the surface of QDs can exert considerable influence over their photophysical and charge or energy transfer properties when mixed with low bandgap polymers, such as P3HT, poly(3-hexylthiophene-2,5-diyl). For example, the long alkane ligands (*e.g.* trioctylphosphine oxide and oleylamine) required to stabilize the colloid can be replaced with shorter ligands to reduce the distance between QDs and polymer chains.¹⁸⁶ On the other hand, reducing the QDs size allows exploiting quantum confinement effects to adjust energy levels to match with frontier orbital energy of polymers and form type-II hybrid heterojunctions that promote charge separation.¹⁸⁷ For instance, the external quantum efficiency of hybrid solar cells was found to decrease by increasing the core size of PbS QDs blended with conjugated polymer PTB1.¹⁸⁷ In extremely small QDs,

however, charge transfer may be inhibited by unfavorable energy alignment, particularly upon ligand exchange. Thus, quantum size effect, which controls the spread of the wave function outside the QD core, must also be carefully considered to improve the photovoltaic performance of hybrid blends.¹⁸⁸⁻¹⁸⁹

III-V QDs display size-tunable absorption and emission in a wide range of the visible spectrum, and are somehow less toxic than typical II-VI QDs containing Cd or Se elements.¹⁹⁰ In particular, InP QDs are known to exhibit a range of ligand-dependent behavior and provide an ideal system for investigating the underlying photophysical and charge transfer mechanisms. However, partly due to the difficulty in the synthesis of III-V QDs compared to other types of inorganic QDs,¹⁹¹ few works on the organic ligand effects on the electronic band energies and ultrafast charge transfer dynamics between QDs and low bandgap polymers have been reported.¹⁹²⁻¹⁹³ Blackburn *et al.* demonstrated the successful injection of electrons into the conduction band of InP QDs and the relaxation rate of 1P-1S increases with decreasing InP QD size.¹⁹⁴ Hole transfer from photoexcited InP QDs to the hole acceptor TMPD molecule and electron transfer to nanocrystalline TiO₂ films were also examined by time-resolved transient absorption measurements.¹¹⁶ Selmarten *et al.* showed that the polymer and InP QD can form a stable complex and the excited InP QD transfers its hole to the conductive polymer.¹⁹⁵ In theory, quantitative understanding of interfacial charge transfer processes of hybrid molecular

systems have been well described by the Marcus theory based on *ab initio* calculations. Wu *et al.* studied dangling bonds effect on the charge transfer processes in hybrid silicon quantum dots/P3HT system.¹⁹⁶ Wang *et al.* demonstrated that hole transfer from the CdSe/CdS quantum rod to the tethered ferrocene moiety is in the inverted region of Marcus theory.¹⁹⁷

Here we combined a variety of spectroscopy measurements and quantum chemical calculations to examine the combined effects of size and organic ligands on the electronic properties of InP QDs and charge transfer processes in hybrid InP QDs/P3HT thin films. We observed an instantaneous creation of singlet excitons that subsequently dissociate to form polarons on an ultrafast time scale; the yield of polaron formation is significantly enhanced by adding InP QDs as electron acceptors. The enhancement of polaron absorption upon photoexcitation proves that electron injection from P3HT into 4.5 nm, pyridine ligand capped InP QDs is very efficient due to large electronic coupling between the lowest unoccupied molecular orbital (LUMO) level of P3HT and the conduction band (CB) of InP QDs. On the other hand, in 2.5 nm InP QDs/P3HT system, electron injection is rather inefficient and back energy transfer is possible because of the overlap between the emission spectrum of P3HT and the absorption of 2.5 nm InP QDs. These findings supplement our understanding of interfacial charge transfer dynamics between small QDs and organic semiconductors, and can assist the rational design of functional nanocrystals.

3.3.2 Materials and Methods

Materials and sample preparation: regioregular P3HT and InP quantum dots were purchased from Rieke Metals and NN-lab, respectively, and used without further purification. To exchange the oleylamine ligands, the InP QDs were precipitated by addition of methanol and then isolated by centrifugation to obtain a solid pellet. Then a small amount of pyridine was added into the InP pellet and the resulting dispersion was heated gently at 60°C under inert atmosphere overnight. Afterwards, the pyridine modified InP QDs are precipitated with methanol, recovered by centrifugation and then dispersed in solvent of dichlorobenzene:pyridine (9:1 vol. ratio). InP QDs/polymer blend films with weight ratio of 3:1 (InP QDs: 30 mg/ml and P3HT: 10 mg/ml) were spin-coated at 800 rpm under nitrogen atmosphere onto glass substrate for 60 seconds. In absence of device data for III-V QD/polymer solar cells, the weight ratio of 3:1 was chosen based on optimal conditions for II-VI/polymer blends, as they are expected to be similar. Before spin-coating, the glass substrates were cleaned by subsequent ultrasonic treatment in acetone, isopropanol and deionized water for 10 min each step. The images of atomic force microspectra (AFM) measurements of these InP QDs/P3HT thin film samples (in Figure A.6 of Appendix A) show large number of small domains, yielding large interfacial area between InP QDs and P3HT.

Infrared absorption: FTIR absorption spectra were obtained by using Bruker Vertex 80v equipped with RT-DTGS detector. Spectral and phase resolution used during Fourier transformation were 4 and 32 cm^{-1} , respectively.

Steady-state absorption and photoluminescence: Steady-state absorption spectra were obtained by an UV-Vis spectrophotometer (Cary 100Bio, Varian) at 1.0 nm resolution, and the steady state photoluminescence spectra were recorded by a spectrofluorometer (Fluorolog-3, HORIBA Jobin Yvon).

Time-resolved photoluminescence: Fluorescence lifetime measurements were performed by time-correlated single photon counting (TCSPC) and by fluorescence upconversion. TCSPC measurements were conducted on a FluoTime 200 platform from Picoquant GmbH. A titanium-sapphire 100 fs laser (Chameleon, Coherent Inc. 100 fs pulse width, 80 MHz repetition rate) combined with a harmonic generator was used as the excitation source with an excitation wavelength of 400 nm ($I=8.5 \text{ nJ/cm}^2$). The detector was a microchannel plate (MCP) PMT system HAM-R3809U-50 (Hamamatsu) with spectral sensitivity from 200 nm to 850 nm and instrument response function of 30 ps. Fluorescence up-conversion was measured with a FOG100, CDP spectrometer using 400 nm excitation femtosecond laser source (100 fs, 80 MHz). The fluorescence was collected by parabolic mirror and focused into a 0.5 mm BBO crystal (cut angle 38, ooe interaction) together with the fundamental radiation (800 nm). The resulting

sum-frequency radiation after passing through a double monochromator (CDP2022D) was detected by photomultiplier-based photoncounting electronics.

Transient absorption spectroscopy: Transient absorption experiments were carried out using a femtosecond pump-probe setup where the excitation source was generated from the optical parametric amplifier (OPA). The second (400 nm) or third harmonic (267 nm) of the fundamental (800 nm) of a Ti:Sapphire femtosecond laser (repetition rate 1KHz, pulse width of 100 fs and 2 W power) were used as pump, and white light was used as probe for measuring the transient absorption spectrum. The signals were collected and monitored using a monochromator/PMT configuration with lock-in detection. Third order nonlinear effects were minimized by setting the excitation density to a value $15 \mu\text{J}/\text{cm}^2$ per pulse. The entire measurements were performed on samples placed in a cryostat which was brought to pressure of $<10^{-3}$ Pa.

3.3.3 Computational Approach

Similar to the magic-sized $\text{Cd}_{33}\text{Se}_{33}$ structure,¹⁹⁸ the InP QDs were constructed using $\text{In}_{31}\text{P}_{31}$ clusters with diameters of about 1.3 nm characterized with high stability, although magic-sized InP has not been experimentally reported yet. On the other hand, $\text{In}_{31}\text{P}_{31}$ model is large enough to exhibit the characteristic feature of a nanocrystal but are still feasible for ionic relaxation. The initial geometry of the $\text{In}_{31}\text{P}_{31}$ was obtained from the bulk structure using a spherical cutoff. Then the ligands were added to the optimized

In₃₁P₃₁, and geometries of the combined ligand-capped InP systems were optimized. The geometries were optimized using the hybrid B3LYP functional with the LANL2DZ/6-31G* mixed basis set, where the LANL2DZ core pseudopotentials and associated valence basis sets were chosen for heavy In atoms and the 6-31G* all-electron basis set was assigned to other atoms (H, C, N, S and P atoms). The oligomers were considered to represent the low bandgap polymer P3HT (eight repeated units) based on the effective conjugated length of polythiophene as being between 6-12 units. The InP/P3HT interfacial structures were obtained from optimized molecular structures of P3HT and In₃₁P₃₁ and superimposing them to mimic the interfacial structures. The beginning intermolecular distance between P3HT and In₃₁P₃₁ was set to be 3.5 Å. Here we only considered the thiophenes of P3HT faced to InP surface because of the effective interactions between these donor-acceptor systems acquiring relatively larger electronic couplings.

Non-radiative charge transfer rate: The rates of charge transfer between organic and inorganic hybrid systems can be approximately described by Marcus equation¹⁹⁹ by the following equation $k = \frac{2\pi}{\hbar} |V|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{\lambda}{4k_B T}\right)$ in the high-temperature limit, where T is the temperature, k and $\hbar$ refer to the Boltzman and Planck constants, respectively, λ is the electron reorganization energy due to geometric relaxation accompanying charge transfer, and V is the electronic coupling matrix element between

the interesting frontier orbitals of donor and acceptor. In lower temperature, it is appropriate to use the Marcus Levitch Jortner (MLJ) equation formulation of the rate expression containing the effect of the quantum vibrational modes:²⁰⁰

$$k = \frac{2\pi}{\hbar} |V|^2 \frac{1}{\sqrt{4\pi\lambda_{ext}K_B T}} \sum_v \exp(-S^{eff}) \frac{(S^{eff})^v}{v!} \exp\left(-\frac{(\lambda_{ext} + v\hbar\omega^{eff} + \Delta G)^2}{4\lambda_{ext}K_B T}\right)$$

where S^{eff} is the effective Huang-Ryhs factor, ω^{eff} is the frequency of one effective mode that incorporates the effect of all the quantum modes in an average way. ΔG is the Gibbs free energy between the initial and final states. These parameters were extrated from quantum chemistry results to predict charge transfer/recombination rates between polymer and nanocrystals as following:

Internal and external reorganization energy: The reorganization energy (λ) can be separated into the internal reorganization energy (λ_{int}) and external reorganization energy (λ_{ext}). λ_{int} is normally further decomposed into contributions along the various normal frequency modes of the molecule according to $\lambda_{int} = \sum S_i \hbar \omega_i$, where S_i is the Huang-Rhys factor of the corresponding frequency mode, describing the electron-vibration coupling strength in terms of the projection along the normal mode of the displacement between the equilibrium of initial and final geometry. The analysis of the electron transfer rate was greatly simplified by defining effective frequency ω_{eff} and effective Huang-Ryes factor $S_{eff} = \sum_i S_i \hbar \omega_i / \omega_{eff}$. The calculations of the Huang–Rhys factors were carried out with the DUSHIN program.²⁰¹

The λ_{ext} empirical formula can be expressed as:

$$\lambda_{\text{ext}} = \frac{(\Delta q)^2}{2} \left(\frac{1}{\sqrt[3]{(R_x R_y R_z)_D}} + \frac{1}{\sqrt[3]{(R_x R_y R_z)_A}} - \frac{2}{l_{DA}} \right) \left(\frac{1}{\epsilon_{\text{opt}}} - \frac{1}{\epsilon_s} \right),$$

where Δq is the transferred charge, R_i are the semi-axes of the ellipses that separately encompass the donor and acceptor: (7.91, 5.41, 7.88) Å for In₃₁P₃₁ and (14.59, 5.43, 7.84) Å for P3HT. The $l_{DA} = 10.08$ Å is the center-to-center distance between donor and acceptor, and ϵ_{opt} and ϵ_s are the optical and static dielectric constants of the surrounding P3HT matrix²⁰² by using experimental values of $\epsilon_{\text{opt}} = 1.96$ and $\epsilon_s = 3.3$.²⁰³

Electronic couplings: The electronic coupling V_{ij} , which is defined as $\langle \phi_i | \hat{F} | \phi_j \rangle$, between the ϕ_i and ϕ_j orbitals of the isolated donor and acceptor fragments can be calculated by projecting the Fock Matrix of dimer onto molecular orbitals of respective donor and acceptor molecule with the subsequent symmetric orthogonalization, where $\hat{F}$ is the Kohn–Sham Fock operator of the whole system. The electronic coupling in the charge separation process (V_{CS}) is taken to be the coupling between the LUMO of P3HT and In₃₁P₃₁. The electronic coupling in the charge recombination process (V_{CR}) is taken to be the coupling between HOMO of P3HT and LUMO of In₃₁P₃₁.

Gibbs free energy: The Gibbs free energy for charge recombination (ΔG_{CR}) and separation (ΔG_{CS}) can be calculated as the energy changes of isolated donor and acceptor, where the $\Delta G_{\text{CS}} = E_D^+ + E_A^- + E_C - E_D^0 - E_A^0 - E_g^{\text{opt}}$, and $\Delta G_{\text{CR}} = E_D^0 + E_A^0 - E_D^+ -$

$E_A^- - E_C$, where $E_D^{+/0}$ and $E_A^{-/0}$ are ionic/ground state energy of donor and acceptor, E_C is the Coulomb stabilization energy, and E_g^{opt} is the optical gap of the donor.

3.3.4 Results on Ligand and Small-Size Effects on Electron Transfer in P3HT/InP Quantum Dots

Ligand exchange and characterizations of InP QDs

Figure 3.3.1. (a) Transmission electron microscopy (TEM) images of InP QDs encapsulated with oleylamine and pyridine ligands, after the oleylamine to pyridine ligand exchange process shown in the schematics; (b) XPS of In 3d orbitals and (c) FTIR transmittance spectra of InP QDs, capped with oleylamine and pyridine ligands.

Given the extremely large surface to volume ratio, the electronic properties of QDs are strongly dependent on surface functionalization.²⁰⁴⁻²⁰⁵ In this work, the long ligand (oleylamine) used to stabilize colloidal dispersions of InP QDs and prevent their aggregation was replaced by a short ligand (pyridine) to reduce the spacing between InP core and P3HT polymer chains in hybrid photovoltaic blends (Figure 3.3.1a). Different from common ligand-exchange methods for II-VI QDs, here methanol was used to precipitate the InP cores instead of the less-polar hexanes (see experimental section for details on ligand exchange).

Low resolution transmission electron microscopy (LR-TEM) images recorded before and after ligand exchange reveal that the average radii of original InP QDs were 2.5 and 4.5 nm, and that QDs retain almost the same size after ligand exchange (Figure 3.3.1a).²⁰⁶ XPS and FTIR transmittance spectra measurements were used to determine the elemental composition and chemical bonding of InP QDs with different ligands. As shown in Figure 3.3.1b, the In 3d XPS spectrum exhibits two contributions, 3d_{5/2} and 3d_{3/2}, respectively located at 447 and 454 eV, which are subject to a rather small shift (less than 1 eV) due to formation of In-N(pyridine) bonds upon ligand exchange. This suggests that N atoms bind much stronger to In rather than to P atoms, in agreement with previous findings by Dung *et al.*²⁰⁷ Nevertheless, in InP(4.5 nm) the red shift of the 3d_{5/2} and 3d_{3/2} peaks is larger than in InP(2.5 nm), most likely due to the high binding efficiency of pyridine

on the surface. The P 2p spectrum indicates the presence of two chemical environments for the P atoms: the predominant peak, with binding energy below 130 eV, is characteristic of InP; the other peak, located at higher binding energies (133.2-134.1 eV), can be attributed to the phosphorus in an oxidized environment (InPO_x).²⁰⁸ The FTIR spectrum in Figure 3.3.1c shows two bands between 1100 and 1200 cm⁻¹, which can be attributed to the P=O stretching mode corresponding to phosphine oxide.²⁰⁹ The vibrational signatures confirm the success of ligand-exchange with pyridine, with clear signatures of the C=CH out of plane vibration at 869 cm⁻¹, and C=N stretching mode at 1610 cm⁻¹, proving that N in pyridine was successfully bounded to the InP QD surface after ligand exchange. The oleylamine ligands are not fully removed as indicated by the appearances of stretching modes at 962 and 1072 cm⁻¹ (C=C stretching), and 1262 cm⁻¹ (C-N stretching).

Density functional theory calculations of InP QDs

Figure 3.3.2. (a) Calculated energy level (HOMO and LUMO) of InP QDs with and without organic ligands (methylamine represents the oleylamine), for different coverage of In atoms (5%, 50% and 100%); PDOS on In (gray) and P (yellow) atoms with organic ligand (b) amino (purple) and (c) pyridine (green). The Fermi level (vertical dashed line) is chosen to be in the middle of the HOMO-LUMO.

Methylamine (NH_2CH_3) ligand modified $\text{In}_{31}\text{P}_{31}$ is a good reduced model for InP QDs chemically passivated by oleylamine ligand. Although the experimental band gap of InP QDs (2.5 and 4.5 nm) cannot be reproduced using small size InP model, it still allows capturing the effects of different organic ligands and surface coverage on the electronic properties from computable point of view, which can provide guidance to design ligand-InP QDs complexes with proper energy levels. As shown in Figure 3.3.2a, the DFT results demonstrate that both type of organic ligands and surface coverage have significant influence on the HOMO and LUMO energy levels. For both methylamine and pyridine ligands, increasing the ligand coverage can destabilize both HOMO and LUMO levels. The band gap of $\text{In}_{31}\text{P}_{31}$ slightly reduces due to the surface reconstruction and introduction of midgap levels from pyridine segments capped on the surface. Figure 3.3.2a also shows the spatial electronic density distributions of HOMO and LUMO levels of the representative $\text{In}_{31}\text{P}_{31}$ with different organic ligands. It can be clearly seen that the HOMO mainly resides on the surface, representing the p-orbital character oriented to the (111) direction, while the LUMO is localized in the inner regions of $\text{In}_{31}\text{P}_{31}$ QDs, where most of the contributions of LUMO and HOMO stem from InP core atoms obtained from the projected density of state (PDOS, shown in Figure 3.3.2b). The methylamine ligands have little contribution to the density of states at the frontier energy region, but pyridine ligands contribute to the LUMO level of ligand-InP QD complex, where the HOMO is

localized within the InP core and the LUMO is localized on pyridine. Electronic coupling between the pyridine HOMOs and the first state for hole ($1S_h$) of $In_{31}P_{31}$ in the ground state of the complex create hybrid orbitals at the inorganic/organic interface. Such orbitals present a lower potential energy barrier, allowing holes to delocalize into the newly accessible states with mixed QD-surfactant character.¹⁸⁸ Thus, the band gaps of InP QDs, directly affected by both HOMO and LUMO states, could loosely depend on the non-conjugated ligand species binding to the surface, but only on conjugated ligands, such as pyridine used here. The pyridine ligands are not expected to contribute to optical transition near the HOMO-LUMO gap energy, because the overlap of these LUMO wave function with the HOMO is negligible and optical transition into these states are expected to have small transition matrix elements.

As shown in Figure 3.3.3, the photoluminescence of 2.5 nm InP QDs in toluene solvent shows a slightly red-shift after pyridine replacement and enhancement of the emission peak at 700 nm, possibly due to the presence of surface trap states. Conversely, for 4.5 nm QDs, the modest reduction in the average dot size during ligand-exchange becomes dominant, resulting in a slight blue shift of photoluminescence spectra after pyridine exchange.

Figure 3.3.3. Normalized photoluminescence spectra of (a) InP(2.5 nm) and (b) InP(4.5 nm) with ligands of oleylamine and pyridine in toluene solvent.

Absorption and photoluminescence properties of InP QDs

The absorption spectra of P3HT, InP QDs capped with oleylamine and pyridine, and their InP/P3HT blends (weight ratio of 3:1) are shown in Figure 3.3.4a (left curves). The lowest energy absorption offsets, due to the lowest allowed transition ($1S_h-1S_e$), occur from 530 to 640 nm, in accordance with the size of InP QDs obtained by TEM.²⁰⁶ After mixing InP QDs with P3HT (black solid curve), the absorption spectra reflects the superposition of the absorption of individual components (P3HT and InP QDs). The photoluminescence spectra of these blends, obtained by photoexcitation at 500 nm, are also shown in Figure 3.3.4a (right curves; note that emission intensity was normalized with respect to the absorbance at the excitation wavelength). The photoluminescence intensity of InP(4.5 nm)/P3HT is found to be significantly reduced compared to pristine P3HT, especially in the case of py-InP(4.5 nm). It is possible that the oleylamine coating of the InP QDs quenches the photoluminescence as electron transfer occurs over a

relatively small distance (5 to 8 Å). In the case of InP(2.5 nm)/P3HT, the photoluminescence intensity from P3HT is even higher than the pristine polymer, suggesting that electron injection from P3HT to InP(2.5 nm) is inefficient.

Figure 3.3.4. (a) Absorption (left) and photoluminescence (right) spectra of thin films of P3HT (solid black line), InP QDs (dashed lines) and InP QDs/P3HT blends (solid lines); (b) Time-resolved photoluminescence decay of thin films of P3HT and InP QDs/P3HT blends upon pulsed photoexcitation at 400 nm.

To deepen our understanding of exciton dynamics in InP(2.5 nm) and InP(4.5 nm) blended with P3HT, we conducted time-resolved photoluminescence measurements by TCSPC, Figure 3.3.4b. All the samples were excited at 400 nm, and emission was monitored at 650 nm. The photoluminescence decays show a fast and a slow decay component, which were fitted by a double exponential function, $I(t) = a_1 \exp\left(-\frac{t}{\tau_1}\right) + a_2 \exp\left(-\frac{t}{\tau_2}\right)$. The extracted parameters are reported in Table A.2. For pristine P3HT, the fast decay component is 57 ps, while the slow decay component is 337 ps. The slow component agrees well with reported values of singlet exciton annihilation by

monomolecular non-radiative or radiative processes.²¹⁰ Photoluminescence lifetimes are shorter in QD/polymer blends due to effective exciton dissociation at the InP/P3HT heterointerfaces. The interfacial charge transfer efficiency can be estimated from the ratio between the exciton lifetime of QD/P3HT blends and that of pristine P3HT. The resulting efficiencies are 14.2% in py-InP(2.5 nm)/P3HT and 17.8% in py-InP(4.5 nm)/P3HT. In agreement with DFT calculations, the py-InP(4.5 nm) QDs are more effective electron acceptors than the py-InP(2.5 nm) QDs thanks to their proper energy alignment. To elucidate the origin of the fast decay components, we measured the fluorescence lifetime of our samples at $t < 15$ ps by upconversion measurements (see Figure A.7 in Appendix A). Here the fast decay time is strongly sensitive to excitation intensity, and even at the lowest intensity needed to obtain a detectable signal ($I = 8.5 \text{ nJ/cm}^2$), the fluorescence lifetimes are reduced to only few picoseconds. This indicates that the fast fluorescence decays are due to diffusion-limited singlet-singlet annihilation. Similar bimolecular recombination effects were previously observed in PbS QDs/P3HT blends.²¹¹

Transient absorption and kinetics measurements of InP QDs

Figure 3.3.5. Transient absorption spectra of pristine P3HT, (a) InP(2.5 nm) QDs/P3HT and (b) InP(4.5 nm) QDs/P3HT before and after ligand exchange measured at 200 fs, 10 ps, 100 ps and 500 ps after excitation. Excitation: 400 nm, 15 $\mu\text{J}/\text{cm}^2$.

Transient absorption (TA) measurements were further performed to quantify the charge transfer processes in the hybrid InP QDs/P3HT blends following excitation at 400 nm, with a fluence of 15 $\mu\text{J}/\text{cm}^2$. Transient spectra of neat P3HT and InP QDs/P3HT films at different time delays are compared in Figure 3.3.5. At 400 nm, both P3HT and InP QDs absorb, and the spectra were recorded in the differential transmission mode ($\Delta T/T$). Here the positive features in TA spectra correspond to ground state bleaching (GSB), revealing the characteristic vibronic structure of the P3HT film; negative features correspond to photoinduced absorption (PIA) mainly due to polarons arising from exciton dissociation at the hybrid interfaces. The corresponding kinetics of transient absorption signals for GSB and PIA are compared in Figure 3.3.5 and fitting parameters are shown in Table A.3

and A.4. Comparing with pristine P3HT, the GSB kinetics of InP(2.5 nm)/P3HT thin film decays within the first 100 ps, suggesting that the electron transfer from P3HT to InP (2.5 nm) is insufficient, even with pyridine ligands, likely due to trapping states induced by the ligand exchange on the surface of InP QD cores. In the case of InP(4.5 nm)/P3HT, the GSB signal at 600 nm shows slow decay kinetics within 500 ps, which is an evidence for the formation of long-lived charges in this blend. The control sample of py-InP(4.5 nm) was obtained by isolating QDs on the PMMA matrix. Figure 3.3.6 compares the ground state bleaching kinetics of py-InP(4.5 nm) in PMMA matrix and P3HT with same QDs concentration. Expectedly, the observed GSB signal ($\lambda_{\text{probe}}=550$ nm) is very weak control sample, and dominant in InP/P3HT blend; observation of a long-lived GSB in InP/P3HT confirms the efficient electron injection from P3TH to the InP QDs.

Figure 3.3.6. Comparison of kinetics of transient absorption signals for py-InP (4.5 nm) in PMMA matrix and P3HT with probe wavelength of 550 nm.

Figure 3.3.7. Comparison of kinetics of transient absorption signals for ground state bleaching ($\lambda_{\text{probe}}=600 \text{ nm}$) and polaron formation ($\lambda_{\text{probe}}=900 \text{ nm}$) of P3HT and InP QDs/P3HT blends.

The PIA region between 850-1000 nm, known as positive polaron absorption of P3HT, reveals additional differences between the hybrid blends and neat P3HT. In the absence of electron acceptor, excitons generated in the pure P3HT film decay without forming polarons. Addition of InP(4.5 nm) QDs to P3HT rapidly reduces the number of singlet excitons and also reveals a region of enhanced PIA signal. Since no detectable signal could be recorded in this spectral region in the control sample, we deduce that the PIA signal originates from the interaction of InP QDs and P3HT in the blend and conclude that the enhanced PIA features in InP(4.5 nm)/P3HT blend is due to the formation of

P3HT hole polarons, generated by electrons transferred from polymer to the InP QDs. In the InP(2.5 nm)/P3HT blend, this polaron absorption is also present, albeit at a significantly reduced level. From a comparison of the 900 nm PIA signal magnitude in neat P3HT film and hybrid heterojunction, we infer that polaron yield increases by more than a factor of 2 in InP QDs/P3HT heterojunctions. Clearly, there is an ultrafast electron transfer from P3HT to InP(4.5 nm) QDs, a promising electron acceptor for hybrid photovoltaic devices. Finally, we assign the photoinduced absorption in this spectral range (1100-1300 nm) to absorption by singlet excitons, in agreement with previous investigations.²¹² The kinetics probed at 1300 nm (Figure 3.3.8) also suggests that, independently of the choice of ligands, P3HT excitons are efficiently quenched by the InP QDs, in line with the photoluminescence kinetics in Figure 3.3.4. The hybrid films exhibit a long-lived component that is fully absent in the neat polymer. This long-lived PIA is therefore related to the presence of QDs in the blends, which could arise from electronic transitions in the reduced InP QDs after charge transfer or from transitions from states akin to CT states that involve positive polarons on the polymer chains and electrons on the QDs. Although there is a small signal in this 850–1000 nm region in the neat polymer films, its decay dynamics are similar to those of the singlet and polaron bands. Therefore, this neat polymer film signal can be separated from the large and long-lived signal observed in the hybrid films. In addition, both the prompt polymer

bleach (observed at 600–800 nm) and the prompt polaron signal are enhanced in the hybrid blends. This enhancement is due to higher yield of charge carriers (by a factor of 2–3 at 1 ps), comparable to the yield estimated in py-InP(4.5 nm)/P3HT hybrid heterojunctions. This observation and the concomitant increase of polaron absorption when P3HT is combined with InP QDs suggest the dissociation of singlet excitons being a precursor for polaron formation. We therefore conclude that the enhancement of polaron yield in P3HT by adding InP(4.5 nm) is due to an ultrafast electron transfer from P3HT (electron donor) to InP (electron acceptor).

Figure 3.3.8. Comparison of kinetics of transient absorption signals for exciton ($\lambda_{\text{probe}}=1300$ nm) of P3HT and InP QD/P3HT blends.

Charge transfer and separation rates between InP QDs and P3HT

Quantum chemical calculations using a phonon-assisted full quantum treatment are used to elucidate the charge separation and recombination processes in these systems. Similar to the typical organic/organic system (P3HT:PCBM) shown in Figure 3.3.9a, the calculated hole wave function in hybrid QD/polymer blends is localized along the P3HT

molecule. This and other factors such as the presence of the spacer between the QD and the polymer, as well as the absence of actual chemical bonds or hybrid clusters, strongly reduce the possibility of direct charge generation in the InP QDs/P3HT blends. Conversely, the electron wave function is localized both at the InP core and on P3HT. This is indicative of charge transfer occurring at the InP/P3HT interface after photoexcitation.

Figure 3.3.9. Energy level alignment and electronic distribution of HOMO and LUMO of (a) P3HT/PCBM and (b) In₃₁P₃₁/P3HT interface with fully passivated InP with hydrogen. The isosurfaces are plotted with electron densities of 0.02 e/Å³.

Table 3.3.1 summarizes and compares the charge transfer and recombination rates at P3HT:PCBM and ideal In₃₁P₃₁/P3HT interfaces (InP QD is fully passivated with hydrogen) calculated using non-radiative Marcus charge transfer theory. The average electronic coupling for charge separation (V_{CS}) between initial state (LUMO of P3HT)

and final state (LUMO of InP QD) is 15.2 meV, which is larger than that of the reference P3HT:PCBM system. The calculated electron transfer rate is $4.49 \times 10^{11} \text{ s}^{-1}$ for $\text{In}_{31}\text{P}_{31}$, indicating efficient charge separation in InP QDs/P3HT hybrid system. This value is in good agreement with our pump-probe measurements ($<1 \text{ ps}$), demonstrating that the model of $\text{In}_{31}\text{P}_{31}$ /P3HT accurately captures the key features of the charge transfer dynamics. The predicted charge separation rate is larger by 3–4 orders than the charge recombination rate, in accordance with the time scale of electron injection from P3HT to InP QDs. Different from the ideal model (fully passivated InP QD), dangling bond defects or oxidation state on the surface may act as charge recombination centers in hybrid blends, resulting in increased charge recombination rate.

Finally, we propose a mechanism of charge and energy transfer at InP QDs/P3HT heterointerfaces, as shown in Figure 3.3.10. For $\text{InP}(4.5 \text{ nm})/\text{P3HT}$ blend, electrons can be effectively injected from P3HT into InP QDs within 1 ps. This can be attributed to the proper energy alignment and short spacing between InP cores and P3HT by replacing oleylamine ligand with pyridine. Electron injection is inefficient at the $\text{InP}(2.5 \text{ nm})/\text{P3HT}$ hybrid interface, probably due to the unfavorable interfacial energy alignment after ligand exchange. The enhancement of photoluminescence at 724 nm could result from either P3HT or $\text{InP}(2.5 \text{ nm})$ emission. Energy transfer from $\text{InP}(2.5 \text{ nm})$ to P3HT may also

increase the emission intensity of P3HT due to the overlap of P3HT absorption and InP(2.5 nm) photoluminescence spectra, as shown in Figure 3.3.10c.

Table 3.3.1. The calculated parameters for non-radiative charge separation and recombination rates at P3HT/PCBM and In₃₁P₃₁/P3HT interfaces.

System	S_{eff}	$G_{\text{CS}}/G_{\text{CR}}$ (eV)	λ_{ext} (eV)	λ_{int} (eV)	$V_{\text{CS}}/V_{\text{CR}}$ (meV)	$k_{\text{CS}}/k_{\text{CR}}$ (s ⁻¹)
P3HT:PCBM	1.38	-0.96/-1.24	0.26	0.320	13.8/19.6	$5.73 \times 10^{11}/1.96 \times 10^{10}$
In ₃₁ P ₃₁ /P3HT	1.36	-1.19/-1.32	0.12	0.316	15.2/18.4	$4.49 \times 10^{11}/2.28 \times 10^{10}$

Figure 3.3.10. Proposed mechanism of (a) electron injection process between P3HT and py-InP(4.5 nm), and (b) energy transfer process between P3HT and py-InP(2.5 nm), and (c) spectral overlap between absorption of P3HT and photoluminescence of py-InP(2.5 nm).

In polymer/small QDs with short ligands, Dexter transfer is the dominating energy transfer mechanism.²¹³ We evaluated the Dexter energy transfer rate for our systems according to $k_{Dexter} = KJ \exp\left(\frac{-2R_{DA}}{L}\right)$, where J is the normalized spectral overlap integral, R_{DA} is the calculated distance between the InP QD and P3HT, and L is the van der Waals radius of P3HT (evaluated by the Polymorph code) and K is a proportionality factor ($K=2/3$ in the case of polymer/fullerene blends).²¹⁴ For the py-InP(2.5nm) QDs, we obtained $k_{Dexter} = 1.83 \times 10^{13} \text{ s}^{-1}$, which is indeed larger than the charge injection rate ($\sim 4.5 \times 10^{11} \text{ s}^{-1}$).

3.4 Summary

In this chapter, different computational strategies and various experimental spectroscopy measurements were combined to study hybrid polymer/III-V systems for photovoltaic applications. Starting from electronic and vibrational properties of the individual components, we investigated effects of dimensionality in P3HT/GaAs interfaces and P3HT/InP QDs blends.

Experimental IR, Raman and PIA spectroscopy and quantum chemical calculations were combined to study the signatures of polaron, bipolaron and singlet excited states for both RR- and RRa-P3HT. We successfully assigned the IR, Raman, and IRAV modes and correlated them with the local molecular structure of the polymer. Moreover, theoretical models were developed to obtain the vibrational signature of singlet excited states by TDDFT calculations for the first time, which provides a new tool for studying structural deformations induced by photo-excitations. We also attributed the specific IRAV fingerprints (band splitting and intensity patterns) of RR- and RRa- P3HT to their different regioregularity.

For P3HT/GaAs planar heterointerfaces, we provided the monolayer/slab models to mimic the GaAs/P3HT heterojunctions and study their atomic configurations and electronic properties. The surface polarity of GaAs substrates is found to greatly affect the electronic orbital and charge redistribution properties according to the calculated

projected density of states and interfacial dipole moments. For both GaAs orientations, the electron transfer from organic moiety to inorganic moiety is favored; meanwhile, GaAs (111)B surface can promote the hole transfer into the polymer layer and function as 'hole acceptor'. Our theoretical predictions confirmed the ambipolar charge photogeneration and transfer at GaAs/P3HT heterointerfaces.

In InP QDs/P3HT blends, we presented a combined theoretical and experimental study of their charge transfer processes. Various spectroscopic measurements were performed to study the interfacial charge carrier dynamics, showing that InP (4.5 nm) is more favor for charge separation and transfer than InP (2.5 nm). Our DFT calculations on the InP nanocrystals and InP/P3HT dimer model help elucidate this phenomena: the effective charge separation in InP (4.5 nm)/P3HT is due to the large charge transfer rate predicted by Marcus theory, and the inefficient charge transfer in InP (2.5 nm)/P3HT is due to the unfavorable energy alignment and dominant energy transfer.

In short, our calculated results correlate well with experimental observations made by UPS and ultrafast spectroscopy measurements, validating our proposed theoretical DFT framework, and suggesting that it could be applied with confidence to a vast set of organic semiconductors and hybrid organic/inorganic systems to elucidate the degree of disorder of the organic constituents and dimensionality effects of the inorganic parts on the chemical-physical properties occurring upon photoexcitation.

Chapter 4

Multidimensional Hybrid Perovskites

While the field of conjugated polymers and organic semiconductors has somehow reached its maturity, in the past few years, a new class of solution-processable hybrid organic-inorganic perovskite materials has emerged conspicuously as an alternative for photovoltaic and light-emitting applications. The recent advancement in metal-halide perovskite solar cells with extremely high power conversion efficiency has stimulated significant theoretical efforts on the understanding of fundamental mechanism of these structures and compounds.

With the experience gained from studying hybrid organic-inorganic system for photovoltaics, in this Chapter, similar theoretical framework is employed to investigate three- and two-dimensional organic-inorganic perovskites, mainly focusing on their electronic bands, charge transport and self-trapping properties, as well as hybrid interfaces formed by small molecules and perovskites. The calculated transport results were published in “Lead iodide perovskite light-emitting field-effect transistor” (Nat. Commun., 2015, 6, 7383), the results of self-trapping charges in two-dimensional white-light emission perovskites are to be submitted in “White-light emission by polaron

self-localization in 2D hybrid perovskites", and charger transfer properties were published in "Interfacial charge transfer anisotropy in polycrystalline lead iodide perovskite films" (J. Phys. Chem. Lett., 2015, 6, 1396).

4.1 Background and Motivations

Perovskite refers to the mineral CaTiO_3 and any structure adopting the same ABX_3 three-dimensional (3D) structural framework. 3D perovskites have the octahedral form with an extended network by all-corner-connected type. In the case of organic-inorganic perovskites, typically, A cation is organic, while B is a metal and X is a halogen (Cl, Br, or I). As for two-dimensional (2D) perovskite with layered structure, we can imagine that the 3D perovskite is cut into one layer-thick slices and separate them apart. After the substitution by the appropriate organic molecules/ions, the monolayer inorganic perovskite slabs are sandwiched by the organic amine molecules and the corresponding 2D perovskite is produced. This structural flexibility and tunability of the dimensionality provide a rich “playground” for searching for investigating the crystal structures with varying physical properties.

In the following we will give the detail descriptions of 3D and 2D perovskites and organic/perovskite heterointerfaces, and discuss three main issues based on our developed theoretical methods/models as following: *i*) obtaining the electronic structure, optical and transport properties of 3D lead iodine perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) from DFT calculations to investigate the ambipolar nature of charge transport in $\text{CH}_3\text{NH}_3\text{PbI}_3$; *ii*) DFT descriptions of self-trapping charges of 2D lead iodine perovskites (EDBEPbCl_3 and EDBEPbBr_3) to reveal the broad photoluminescence of these 2D perovskites; and *iii*) extending our

interfacial models to study charge transfer and redistribution properties at organic hole- (electron-) transporting materials/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ hybrid interfaces.

4.1.1 3D organic-inorganic perovskites

Figure 4.1. Crystal structure for typical organic-inorganic perovskite hybrid halide.

The combination of solution-processable methylammonium metal halide perovskites, typically lead iodide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$, see Figure 4.1), with organic materials has opened new avenues to high-efficiency, low-cost, third generation photovoltaic devices. These devices operate similarly to solid-state dye-sensitized solar cells, in that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ sensitizer doubles as light absorber and charge carrier transporter.²¹⁵⁻²¹⁶ Since the first demonstration of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in solid dye-sensitized solar cells, the efficiency of lead halide perovskite solar cells has dramatically increased from 3.8% to more than 20%.^{6, 217-220} Such highly efficient conversions can be related mainly to the high optical absorption coefficient, ambipolar properties²²¹ and long carrier diffusion lengths ($\sim 1 \mu\text{m}$) of lead halide perovskites.²²²⁻²²³ The high optical absorption coefficient

($\sim 10^5 \text{ cm}^{-1}$) of perovskites enables improved efficiency but with much thinner absorber layer ($< 500 \text{ nm}$).

In addition to the bulk properties of perovskites, surface passivation, interfacial construction and energy alignment between perovskite and the carrier transporting layers exert a major impact on the efficiency of charge extraction and carrier transport.²²⁴ Recently, research on the electrical potential distribution in mesoporous photovoltaic devices has emphasized the similarity to *p-i-n* type junctions, confirming the significance to optimize charge transfer from perovskite towards both hole and electron transporting materials.²²⁵ The control over crystallization and morphology of perovskite active layers using solvent engineering techniques also plays an important role²²⁰ on photovoltaic performances,²²⁶ by affecting interfacial energetics,²²⁷ optical absorption,²²⁸ charge carrier mobility, and exciton diffusion length.²²⁹ The highest PCE has reached $\sim 19.3\%$ in a planar geometry through careful control of perovskite layer crystallization and prudent choice of charge transporting materials.²¹⁸ Lately, millimeter-scale single crystals have been produced by means of vapor-assisted crystallization and solution-based hot-casting,²³⁰⁻²³¹ leading to low trap state density and long carrier diffusion. From the theoretical point of view, it is interesting to study and understand the unique physical properties of 3D perovskites as a start, such as the crystal and electronic structures, density

of states, optical absorption and ambipolar nature of charge carriers, to unravel the origin of outstanding photovoltaic performance.

4.1.2 2D organic-inorganic perovskites

Similar to the three-dimensional perovskite, 2D perovskites have the formula of A_2MX_4 and BMX_4 , where M is a metal in 2+ oxidation state (e.g. Pb^{2+} , Sn^{2+} , Cu^{2+}), X is a halogen and A and B are respectively mono- and bidentate organic cations, usually ammonium salts $R-NH_3^+$.²³² The basic structure is formed by an alternation of inorganic sheets of corner sharing octahedra $[MX_4]^{2-}$ sandwiched between organic layers, which allows the incorporation of bulky organic cations preserving the stability of the layered structure and multiplying the synthetic combinations and functionalization.²³³⁻²³⁴ The layered configuration is responsible for the formation of a quantum well structure leading to a strong exciton confinements within the inorganic sheets. This would result in sharp excitonic absorption peaks visible at room temperature as well sharp photoluminescence peaks.²³⁵⁻²³⁷ Interestingly, broadband photoluminescence has also been observed in a restricted group of 2D perovskites. For examples, broadband emission was reported in $(C_6H_{11}NH_3)_2PbBr_4$, showing the coexistence of both excitonic and broadband photoluminescence at low temperature and supporting the hypothesis of self-trapped excitons formation.²³⁸ At this stage, the exact mechanism responsible for white light generation and the identification of the emissive species of 2D perovskites remain elusive.

In particular, open questions remain regarding the origin of the large Stoke-shift of the luminescence, such as the identity of emissive traps and their distribution in the material, or the nature of self-trapped excitons and the role played by organic cations in their formation. So a deeper understanding of the processes involved is necessary to guide the design of materials with improved optoelectronic properties.

4.1.3 Organic/perovskite heterointerfaces

Besides the rapid improvement in photovoltaic devices, the deep understanding of the fundamental mechanisms governing the photovoltaic performance of lead halide perovskites has also led to impressive progress. Previous studies based on DFT calculations has successfully unraveled effects of intrinsic optical and transport parameters, interfacial energetics, and crystallographic-electronic structure properties of perovskite materials.²³⁹⁻²⁴³ For example, the long-range ambipolar transport property of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was explained by effective masses of photogenerated electrons and holes including spin-orbit coupling (SOC) effects.²⁴⁴ The absorption spectra of bulk perovskite was well reproduced based on crystal structure by DFT+D2 method.²⁴⁵ The crystal (110) and (001) surfaces of $\text{CH}_3\text{NH}_3\text{PbI}_3$ were found to contribute to the long carrier lifetime, and the shallow surface states on these flat terminations to be efficient intermediates for hole transfer.²⁴³ The electronic structure of hybrid TiO_2 /perovskite interfaces showed that the stronger interaction of $\text{MAPbI}_{3-x}\text{Cl}_x$ with TiO_2 modifies the interface electronic

structure leading to a larger interfacial coupling.²⁴⁶⁻²⁴⁷

The surface orientation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was found to strongly affect hole/electron injection behaviors towards the corresponding charge transfer layer. The calculated interfacial dipoles at the $\text{CH}_3\text{NH}_3\text{PbI}_3$ surfaces were used to quantitatively estimate the charge transfer yield and determine the most favorable surface polarity to each of the charge carriers: electron transfer is enhanced on polar surfaces with PCBM and Spiro-OMeTAD, while hole transfer yield is higher on nonpolar surfaces. The interfacial model and simulations underline the importance of control over the crystallization and surface orientation of perovskite for the design of optimized hybrid perovskite photovoltaic devices, and may be further extended to a broad range of organic/perovskite heterojunctions.

4.2 Experimental Methods

Computational approach: Optimizations on the geometry and electronic structures have been conducted with the GGA method using the QE package.²⁴⁸ Electron-ion interactions are described by ultrasoft pseudopotentials with electrons from H ($1s^1$); O, N and C ($2s^2, 2p^2$); I ($5s^2, 5p^2$); Pb ($5d^{10}, 6s^2, 6p^2$), shells explicitly included in the calculations.²⁴⁹ Single-particle wave functions (charges) are expanded on a plane-wave basis set up to a kinetic energy cutoff of 40 Ry (300 Ry) for unit slabs and 25 Ry (200 Ry) for large interfacial structures to acquire computational modelling of the interface

considering accurate and computational point. The vdW-DF2 functional²⁵⁰⁻²⁵¹ is used for both dispersion effects self-consistently and electronic calculations, considering the significant additive stabilization effect of dispersion forces on the charge transfer systems.^{141, 252} The Monkhorst-Pack type k-meshes is $4 \times 4 \times 2$ for tetragonal phase of bulk $\text{CH}_3\text{NH}_3\text{PbI}_3$. A regular (4×4) grid of k-points is used to sample the 2D Brillouin zone of the slab cell and (2×2) for the hybrid interfaces. Periodically repeated supercells are used for the simulation of all involved systems. The unit cells have a (2×2) lateral periodicity and contain four bilayers of $\text{CH}_3\text{NH}_3\text{PbI}_3$ exposing the (001) and (100) surface. Slab replicas are separated by ~ 15 Å of vacuum. All forces on single atoms of each structure are smaller than 0.02 eV/Å after optimization. The ground state charge transfer occurring in the electronic ground state is taken into consideration in the current study. Car-Parrinello (CP) molecular dynamics¹⁸ is applied to investigate the effect of thermal fluctuations on the ground state charge transfer at the heterojunctions. The fictitious electron mass and time step are fixed as 500 a.u. and 0.121 fs, respectively. The interfacial configuration of Spiro-OMeTAD/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ is firstly optimized to an energy minimum by static relaxation, and then to reach thermal equilibrium by damped dynamics for both ions and electrons within 100 fs and subsequently heated up to 300 K with a 100 fs molecular dynamics run, and then maintained at 300 K for 1000 fs. Lastly, another 1000 fs MD production run is carried out and six selected electronic structures are recorded

during the first 100 fs trajectory. Molecular graphics viewer VDM and VESTA are utilized to plot the molecular structures and wavefunctions.¹⁴⁴

Mobility Calculations: The crystal cell parameters were $a = b = 8.81 \text{ \AA}$, and $c = 12.99 \text{ \AA}$ for tetragonal phase (Pm3m space group); and $a = 8.77 \text{ \AA}$, $b = 8.56 \text{ \AA}$ and $c = 12.97 \text{ \AA}$ for the orthorhombic phase (PNMA space group) of bulk $\text{CH}_3\text{NH}_3\text{PbI}_3$. The effective masses for electron (m_e^*) and hole (m_h^*) were estimated by fitting of the dispersion relation of $m^* = \hbar^2 \left[\frac{\partial^2 \epsilon(k)}{\partial k^2} \right]^{-1}$ from band structures along the directions Γ -X, Γ -Z and Γ -M for tetragonal phase and Γ -X and Γ -Z for orthorhombic phase together with average values in these different routes. The carrier lifetime was evaluated by the semi-classical Boltzmann transport theory.²⁵³ The only contribution of acoustic phonons was considered in evaluating scattering lifetime, where the charge carrier density (n) and mobility (μ) are approximated as²⁵⁴⁻²⁵⁵

$$n = \frac{(2m^*k_B T)^{3/2}}{2\pi^2 \hbar^3} {}_0F_0^{3/2}; \quad \mu = \frac{2\pi \hbar^4 e B}{m_l^* (2m_b^* k_B T)^{3/2} \Xi^2} \frac{{}_3^0 F_{-2}^1}{{}_0F_0^{3/2}},$$

where ${}_n F_l^m = \int_0^\infty \left(-\frac{\partial f}{\partial \zeta} \right) \zeta^n (\zeta + \alpha \zeta^2)^m [(1 + 2\alpha \zeta)^2 + 2]^{l/2} d\zeta;$

$$f = 1/(e^{\zeta - \xi} + 1); \quad \alpha = k_B T / E_g,$$

k_B is the Boltzmann constant, e is the elementary charge, T is the temperature, $\hbar$ is the Planck constant, and ξ is the reduced chemical potential; m^* is the density of state effective mass, m_l^* is the conductivity effective mass, m_b^* is the band effective mass; B is the bulk modulus ($B = \partial^2 E / \partial V^2$), $\Xi_{e-p/h-p}$ is the electron-phonon (or hole-phonon)

coupling energy ($\Xi_{e-p/h-p} = V_0(\Delta E_{CBM/VBM}/\Delta V)$), n , m , and l power integer indices, E_g is the electronic band gap, and ζ the reduced carrier energy. Note that the GGA method including SOC yields largely underestimated values of the band gaps. Detailed estimate of the band gap values would require many-body perturbation theory (GW method).^{49, 50} However since the band structure is not significantly affected by GW correction our calculations of the effective mass and mobility are still reliable.

Self-trapping Charge Calculations: Norm-conserving Troullier-Martins pseudopotentials including full-relativistic effect were used to describe electron-ion interactions with electronic orbitals of H ($1s^1$); O, N and C ($2s^2, 2p^2$); Cl ($3s^2, 3p^5$); Br ($4s^2, 4p^5$) and Pb ($5d^{10}, 6s^2, 6p^2$). Plane-wave basis set cutoffs of the wave functions and the augmented density was set to be 60 and 400 Ry, respectively. The $4 \times 4 \times 4$ and $4 \times 2 \times 4$ Monkhorst–Pack grids were chosen for sampling the Brillouin zone of (EDBE)PbCl₄ and (EDBE)PbBr₄, respectively. Spin polarized calculations were used for mapping the self-trapping hole/electron: one electron was removed or added to the stable neutral structure, and then relaxed to the corresponding charged state. To mimic the thermally induced self-trap holes/electrons, *ab-initio* molecular dynamic calculations were performed to raise the temperature to 300 K with repeated velocity scaling; the charged crystal system was then kept at 300 K for 500 fs. The molecular dynamic production run was performed for another 500 fs with a time-step of 1 fs. At every 25 fs, the

self-trapping hole/electron density was plotted as the charge density difference between charged and natural one ($\rho_{\text{trap}} = \rho_{\text{charge}} - \rho_{\text{netrual}}$).

Sample preparation: Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) was prepared by mixing 15 ml methylamine solution (CH_3NH_2 , 40% in methanol, TCI) with 14 ml hydroiodic acid (57 wt% in water) in ice bath for 2 h. Solvent was then removed by rotary evaporator at 60 °C for 1 h, and the obtained solid was dissolved in ethanol. Recrystallization was conducted with diethylether, followed by 6 times wash and desiccation in vacuum oven at 60 °C for 24 h, to obtain $\text{CH}_3\text{NH}_3\text{I}$ as white powder. Methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) was prepared by mixing 0.395 g $\text{CH}_3\text{NH}_3\text{I}$ with 1.157 g PbI_2 (99%, Sigma-Aldrich) in 2 ml DMF overnight at 60 °C under nitrogen flux. Solvent was removed by rotary evaporator at 80 °C for 2 h and the solid was dried in vacuum oven at 100 °C for 12 h. The obtained $\text{CH}_3\text{NH}_3\text{PbI}_3$ was spin-coated onto p-doped silicon substrate in N_2 atmosphere to form thin film, where the substrates are pre-cleaned by successive sonication in acetone and IPA for 10 minutes and exposure to O_2 plasma for 20 min. To fabricate the organic/perovskite heterojunctions, 49.5 mg $\text{CH}_3\text{NH}_3\text{I}$ and 144.5 mg PbI_2 are firstly dissolved in 1ml γ -butyrolactone and stirred at 60 °C overnight. The solution was spin-coated in three steps: 1000 rpm for 60 s, 2000 rpm for 60 s and 4000 rpm for 60 s; and the films are annealed at 100 °C for 30 min. Then, Spiro-OMeTAD (50

mg/ml in chlorobenzene) and PCBM (10 mg/ml in chlorobenzene) are spin-coated onto the perovskite layer at 4000 rpm for 30 s, respectively.

XRD measurements: Diffractometer BRUKER D8 ADVANCE with Bragg-Brentano geometry was used for the X-ray characterization, using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$), with step increment of 0.02° and acquisition time of 1 s. The Pawley fit was processed with TOPAS 3.0 using the lattice parameter for the tetragonal structure and space group I4/mcm previously reported. Peak profile and background are fitted with a TCHZ Pseudo-Voigt function and a Chebichev polynomial of fifth order with $1/x$ function, respectively. The refined parameters include the scale factor, lattice parameters, zero error, and linear absorption coefficient.

UPS spectroscopy: UPS analysis was used for the investigation of energy alignments within Spiro-OMeTAD/CH₃NH₃PbI₃ and PCBM/CH₃NH₃PbI₃ interfaces. The organic molecules are dissolved in chlorobenzene to a concentration of 50 mg/ml, followed by spin-coating onto the p-doping Si substrates with CH₃NH₃PbI₃ at 2000 rpm for 60 s. The thickness of resulted organic films are ~ 20 nm according to our AFM measurements. Upon deposition, samples are thermally annealed at 150 °C for 20 min protected by nitrogen atmosphere. All UPS measurements are carried out under high vacuum with excitations of Al K α ($h\nu = 1486.7 \text{ eV}$) and He I ($h\nu = 21.2 \text{ eV}$).

4.3 Results on Three-Dimensional Perovskites

The solution-processed lead iodine perovskites ($\text{CH}_3\text{NH}_3\text{PbI}_3$) have a polycrystalline character with tetragonal phase domains at room-temperature and interestingly it becomes the orthorhombic phase at low temperature with increases charged carrier mobility ($<167\text{ K}$). In this part of the thesis work, we study the structural, electronic, and transport properties of bulk lead iodine perovskite in different phases, and also investigate the electronic bands and surface energies of perovskite slabs with different surface orientation.

4.3.1 Structural and optical properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$

Figure 4.2. X-ray diffractogram of $\text{CH}_3\text{NH}_3\text{PbI}_3$ powders synthesized from DMF solution; side- and top-view of bulk $\text{CH}_3\text{NH}_3\text{PbI}_3$ in tetragonal phase.

A commonly used deposition method was adopted for fabricating $\text{CH}_3\text{NH}_3\text{PbI}_3$ films, specifically, PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ precursors are spin-coated in one-step,²²⁶ generating a

polycrystalline thin film with tetragonal phase domains which is similar to the bulk crystal powders (Figure 4.2a). Comparing with the XRD data of $\text{CH}_3\text{NH}_3\text{PbI}_3$ bulk, the thin films show a weak preferential orientation toward the (001) orientations relative to the substrate plane (Figure 4.3b).

Figure 4.3. (a) SEM image of top-view the polycrystalline film; (b) XRD pattern, indicating a single-phase sample with tetragonal phase at room temperature; (c) Side-view of tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$ slabs along the direction (001), (110) and (100); (d) Calculated band structure and measured absorption and photoluminescence spectra (insert: Tauc plot of the absorption spectrum).

To understand the spontaneous formation of polycrystalline domains, the tetragonal crystal structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was optimized based on the experimental cell parameters and coordinates (space group $I4/mcm$, $a=8.87 \text{ \AA}$, $c=12.65 \text{ \AA}$). From the calculating crystal surface energies in Table 4.1, most stable slab geometries were

determined to be (110) ($E_s=4.7\times10^{-3}$ eV/Å²), (100) ($E_s=3.5\times10^{-3}$ eV/Å²), and (001) ($E_s=1.6\times10^{-3}$ eV/Å²). Side-view of the slab structures along these orientations are illustrated in Figure 4.3c.

Table 4.1. Surface energies for CH₃NH₃PbI₃ slabs with different orientation of (001), (100) and (110).

Orientation	Surface Area (Å ²)	Before relaxation (eV/Å ²)	After relaxation (eV/Å ²)
(001)	16.672 × 16.672	0.002495	0.001642
(100)	16.672 × 23.905	0.006564	0.003521
(110)	23.905 × 23.705	0.006133	0.004676

In the optimized bulk crystalline structure, the Pb–I bond lengths were estimated to be 3.278, 3.258 and 3.155 Å, in good agreement with previous results reported by Geng, W. and Torres, A. who also took SOC out of consideration.^{242, 256} After optimizing the geometry with vdW-DF2, a direct band gap energy of $E_g=1.60$ eV was obtained at the Γ point (Figure 4.3d). Although it is slightly higher than the value from the Tauc plot of experimental absorbance ($E_g=1.58$ eV), it nicely parallels earlier predictions.²⁴² Figure 4.4 shows a decrease in band gap energy ($E_g=0.52$ eV) caused by the inclusion of SOC. Due to the big volume of our interfacial structures, many-body perturbation theory (GW method) calculations, cannot be used for correction.²⁵⁷ Therefore, further studies on the electronic properties of the current heterojunctions with vdW-DF2 were carried out

without SOC for heavy atoms (Pb). This allowed us to qualitatively follow the GW-SOC trends, and to capture the long-range dispersive interactions, which have great impact on the understanding of hybrid interfacial structures and physisorption process. In comparison with the bulk, the optimized (001), (100) and (110) $\text{CH}_3\text{NH}_3\text{PbI}_3$ slabs share similar conduction and valence bands, which are basically composed by the 6p orbital of Pb and the 5p orbital of I. As shown in Figure 4.4, only small decrease in the band gaps (~ 0.2 eV) has been observed in spite of excluding SOC. We believe the major reason lies in the existence of surface dangling bonds, considering the less contribution of the projected density of states (PDOS) of the organic part (CH_3NH_3) at the $\text{CH}_3\text{NH}_3\text{PbI}_3$ surface to both valence band top region and conduction band (CB) bottom region for both bulk and slabs.

Figure 4.4. Density of states of tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$ bulk and slabs along the direction (001), (110) and (100) (a) with and (b) without SOC effects.

4.3.2 Transport properties of crystalline $\text{CH}_3\text{NH}_3\text{PbI}_3$

Figure 4.5. Band structures of the tetragonal (a) and orthorhombic (b) phases calculated by DFT-PBE method with (solid blue curves) and without (dotted black curves) spin orbital coupling (SOC); (c) calculated temperature dependence hole (red curves) and electron (black curves) mobility in tetragonal ($T=300\text{--}160\text{ K}$) and orthorhombic ($T=160\text{--}77\text{ K}$) phases of $\text{CH}_3\text{NH}_3\text{PbI}_3$.

The charge carrier transport in organic-inorganic perovskite materials can be theoretically described by coherent band-like model, where carrier mobility has temperature dependence that the mobility was limited by scattering of the charge carriers (electrons or holes) and phonons at room temperature induced by crystal lattice deformations, and increased mobility can be achieved at low temperature. On the other

hand, different from traditional high-mobility inorganic semiconductors, solution-processed organic-inorganic perovskite thin films have polycrystalline domains, which will weaken the electronic coupling and further reduce the effective carrier mobility; charge carrier transport along and across these domain boundaries can be described based on hopping transport model. Thus, from theoretical point of view, it's crucial to build a relationship of charge transport and perovskite crystal structure, *i.e.* inorganic framework and composition of halogen element.

Table 4.2. Estimated effective mass for electron and hole of CH₃NH₃PbI₃ from band structure including spin-orbital coupling effect.

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

We estimated the mobility of CH₃NH₃PbI₃ for both tetragonal and orthorhombic crystallographic phases using semi-classical Boltzmann transport theory,²⁵³ upon deducing charge carrier effective masses and electron (hole)-phonon coupling. The effective masses of electron and hole in Table 4.2 were derived by quadratic fitting of the band structure dispersion (Figures 4.5a and 4.5b). The average effective mass of electrons (tetragonal: 0.197 m_0 , orthorhombic: 0.239 m_0) is consistently smaller than the one of

holes (tetragonal: 0.340 m_0 , orthorhombic: 0.357 m_0), which are in agreement with previous reports.^{258, 259}

The resulting mobilities (Figure 4.5c) increase at lower temperatures due to the Boltzmann activation energy, in agreement with the trend of the experimental data.²⁶⁰⁻²⁶¹ Although the calculated mobilities are substantially larger than the experimental values, calculations reflect fairly well the relative magnitude of electron vs hole mobility, as well as the different mobility of the two crystallographic phases. Within the entire temperature range investigated, electron mobilities exceed hole mobilities by approximately a factor of two, and increase by nearly one order of magnitude below the phase transition temperature ($\mu_e=2577-11249 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $\mu_h=1060-4630 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the orthorhombic phase and $\mu_e=466-2046 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $\mu_h=140-614 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the tetragonal phase).

Table 4.3. Band (m_b^*), conductivity (m_l^*) and density of state (m^*) effective mass, electron (hole)-phonon coupling (Ξ), and bulk modulus (B).

	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

The small experimental values can partly be attributed to the increase of effective masses by elastic carrier-phonon scattering, which is expected in real crystals due to defects and disorder induced by the organic components, as well as carrier-carrier scattering at high electron and hole concentrations.²⁶² Formation of segregation pathways for hole and electron transport due to the ferroelectric methylammonium cation could also elongate the carrier drifting path, hence lower carrier mobilities.²⁶³ In addition, polycrystalline domains typical of solution-processed $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films are likely to weaken the electronic coupling between grains, requiring charge carriers to hop along and across domain boundaries, further reducing the effective carrier mobility. This is consistent with observation of giant photoinduced modulation of the dielectric constant, which was attributed to localized polaron hopping with relatively small activation energy.²⁶⁴

4.4 Results on Two-Dimensional Perovskites

Different from the narrow bandgap and light-emission of 3D perovskites, 2D perovskites usually have the large bandgap and broad photoluminescence. In this part of the thesis work, we studied the mechanisms involved in the white light emission using the perovskite (EDBE) PbX_4 ($\text{X} = \text{Cl}, \text{Br}$) as model material. We develop a theoretical method by a combination of molecular dynamics and charge density mapping obtained to explain the broad emission of these two perovskite compounds. The calculated results

show that electron and hole localization in specific lattice sites resulting in their self-trapping within the inorganic framework of the perovskite.

4.4.1 Electronic properties of (EDBE)PbCl₄ and (EDBE)PbBr₄

The band structures and optical transitions calculated by DFT are used to elucidate the origin of experimental band gap and absorption spectra.²⁶⁵ As shown in Figure 4.6, (EDBE)PbCl₄ demonstrates a direct band gap (3.53 eV) at the Γ point and (EDBE)PbBr₄ shows an indirect band gap (2.52 eV) at A point. Even though the spin-orbital coupling (SOC) effects weren't included for the heavy Pb atoms, the resulting band gap values are still lower than the experimental absorption edges, which are 4.09 eV for (EDBE)PbCl₄ and 3.65 eV for (EDBE)PbBr₄. Including the SOC effects lowers the band gap energy to 2.93 and 1.91 eV, respectively. The projected density of states (PDOS) suggests that the organic compound (EDBE) contributes little to both top region of the valence band and bottom region of the conduction band in both cases, having a similar feature as three-dimensional Pb-based perovskites, like CH₃NH₃PbI₃. From the PDOS, the P-bands can be assigned to the exciton resulting from the interband transition $\text{Pb}^{2+}(6s)\text{Cl}^-(3p) \rightarrow \text{Pb}^{2+}(6p)$ and $\text{Pb}^{2+}(6s)\text{Br}^-(4p) \rightarrow \text{Pb}^{2+}(6p)$,²⁶⁶ similarly to the transitions involved in the parent lead halides PbX_2 .²⁶⁷ Consequently, the optical properties are mainly determined by the inorganic part of the perovskite.

Figure 4.6. Crystal, band structure, and projected density of states of (a) (EDBE)PbCl₄ and (b) (EDBE)PbBr₄.

4.4.2 Self-trapping charge properties of (EDBE)PbCl₄ and (EDBE)PbBr₄

The broad photoluminescence of (EDBE)PbX₄ (X = Cl and Br) can be observed in the whole visible range from 1.6 to 2.8 eV as shown in Figure 4.7a. The inorganic layers present in (EDBE)PbX₄ are closely related to the original lead halide precursors PbX₂ and the broad photoluminescence of the two-dimensional perovskite are mainly affected by the inorganic component. Here we assume that the self-trapping mechanisms can be similar to those involved in PbX₂. To prove this hypothesis, we calculated the charge density mapping at room temperature for holes and electrons in (EDBE)PbCl₄ (Figure 4.7b) and (EDBE)PbBr₄ (Figure 4.7c). We can observe that the charge density is mainly

confined in the inorganic scaffold, suggesting that polaron formation is taking place in the Pb-X framework, while the organic part do not actively contribute to the trapping process. Interestingly, we notice that charges are not selectively trapped at the organic/inorganic interface, excluding the possibility that surface states are acting as main trapping sites, as was previously suggested for similar layered materials like 2D-[Cd₂S₂(*n*-butylamine)].²⁶⁸ The temporal evolution of charge localization is shown independently for holes and electrons for both the perovskite in supporting information (Figures B.1-B.4 of Appendix B). In particular, for both the materials, electrons are selectively localized on lead atoms, consistently with previous observation in lead halides of self-trapped electrons (STEL) sites Pb₂³⁺,²⁶⁹⁻²⁷¹ which are dimers formed when one electron is equivalently localized in two nearest-neighbors Pb²⁺ centers. Alternatively, the electron could also localize on a single lattice point to form Pb⁺, however the existence of this STEL have never been demonstrated.²⁷² In our calculations, we cannot exclude the formation of Pb⁺ STEL, as we do not see a significant change in the nearest-neighbors Pb-Pb distance which would strongly support the formation of the dimer Pb₂³⁺, but this could be due to the rigidity of the inorganic framework. However, we clearly see that electron localization on lead atoms causes the elongation of Pb-Cl (2.841 → 3.074 Å) in apical position of the PbCl₆⁴⁻ octahedra, as expected by the reduced positive charge of the lead center upon electron trapping. On the contrary, holes localize both around lead and

halogen atoms, oscillating in time from one site to the other. This will give rise to two different polarons, the self-trapped holes (STH) Pb^{3+} and X_2^- ,²⁷²⁻²⁷⁵ where $\text{X} = \text{Cl}$ or Br depending on the perovskite type. The last type of self-trapped holes are also known as V_k centers,²⁷⁶⁻²⁷⁷ commonly observed in alkali halides,²⁷⁸ which lead to the formation of the dimer-molecules X_2^- within the crystal lattice, where a pair of halides is more strongly interacting as a consequence of the hole localization.²⁷³ Consistently, from the calculated structure we observe this pairing effect as slight decrease of the X-X distances compared to the neutral structure (e.g. $3.112 \text{ \AA} \rightarrow 3.060 \text{ \AA}$ for Cl-Cl and $3.831 \text{ \AA} \rightarrow 3.821 \text{ \AA}$ for Br-Br).

Figure 4.7. (a) photoluminescence spectra of EDBEPbCl₄ and EDBEPbBr₄ in the temperature range between 78 K and 298 K; charge density differences calculated for (b) EDBEPbCl₄ and (c) EDBEPbBr₄. The charge density mapping shows confinement in the inorganic layers, with preferential localization of electrons on Pb atoms, while holes are distributed between Pb and Cl atoms, both acting as self-trapping sites for polaron formation.

We then propose an original model to explain the white light generation in (EDBE)PbX₄. The electronic excited states undergo relaxation to form polaron intra-band states, which we identify specifically as self-trapped electrons (STEL) Pb₂³⁺ and self-trapped holes (STH) Pb³⁺ and X₂⁻, with relative energies $E_{Pb^{3+}}^{STH} < E_{X_2^-}^{STH} < E_{Pb_2^{3+}}^{STEL}$ as determined from our calculations. Since the charge density maps for holes gives an averaged situation between the two possible trapping sites Pb³⁺ and X₂⁻ and the charge distribution oscillates between these two sites at different time, we can estimate their relative energy by considering two different time in which positive charges are preferentially localized in one of the two trapping sites. As a consequence of different charge-phonon coupling in different trapping sites, the two STH levels will also have different shift in the configuration coordinate. Annihilation of each of these self-trapped states via electron-hole recombination finally results in light emission centered at different wavelengths, which correspond to the three main bands observed in steady state photoluminescence.

4.5 Results on Organic/ Perovskite Hybrid Interfaces

The objective of this part of the thesis work was to understand the effects of surface orientation of perovskite on the electronic properties within organic/polycrystalline CH₃NH₃PbI₃ hybrid systems based on our “organic monolayer/inorganic slab” model. We used a combination of ultraviolet photoelectron spectroscopy (UPS) analysis and

first-principle DFT and molecular dynamics calculations to investigate the ground state electronic properties, charge transfer and redistribution at the hybrid interfaces, namely Spiro-OMeTAD/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ and PCBM/ $\text{CH}_3\text{NH}_3\text{PbI}_3$.

4.5.1 Electronic structures of organic molecules on $\text{CH}_3\text{NH}_3\text{PbI}_3$ surfaces

Given the weak physisorption between perovskite and the organic materials, the interfacial models in the current study are built by simply placing the organic monolayer. Specifically we used Spiro-OMeTAD and PCBM, respectively, over the optimized $\text{CH}_3\text{NH}_3\text{PbI}_3$ slabs with preferred orientations. It should be noted that chemical or covalent bonds are hardly formed at the heterojunctions since the bonding energy between $\text{CH}_3\text{NH}_3\text{PbI}_3$ surface dangling atoms (e.g., Pb and I) and the organic terminal groups is too small.

Figure 4.8. Density of states of the Spiro-OMeTAD molecule on $\text{CH}_3\text{NH}_3\text{PbI}_3$ (a) (001), (b) (100) and (c) (110) surfaces (the vertical dashed line shows the Fermi energy level); three-dimensional representation of VBM, HOMO-1 and HOMO levels of (d) Spiro-OMeTAD/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (001), (e) Spiro-OMeTAD/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (100) and (f) Spiro-OMeTAD/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (110).

The PDOS after charge redistribution can be used to interpret the energy levels and electron distribution of orbital wavefunctions at the heterojunctions. Figures 4.7a-c show

the total PDOS of Spiro-OMeTAD/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ interface with different orientations, where the contributions from Spiro-OMeTAD part have been broke down and shown as the gray shaded areas. In all three cases, the HOMO and HOMO-1 (degenerated energy levels) of the organic molecules are higher than the perovskite valence band maximum (VBM), facilitating hole transfer towards the Spiro-OMeTAD monolayer and thereby increasing the charge separation efficiency across the interface. Meantime, electron flow is restricted due to the higher LUMO of Spiro-OMeTAD. For both (001) and (110) orientations, holes preferentially lay on the top of perovskite surface, partially overlapping with the HOMO electronic clouds localized on the organic branches of Spiro-OMeTAD; whereas holes reside well beneath the top layer of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (100) at the hybrid interface. Consequently, the former two orientations yield stronger electronic cloud overlap across the heterojunction, forming a hybrid interface state near the Fermi energy once holes are transferred. Haruyama *et al.* also conclude $\text{CH}_3\text{NH}_3\text{PbI}_3$ (001) and (110) surfaces as efficient hole transfer intermediates in their recent simulation reports, which agrees well with our findings.²⁴³

Experimentally, charge separation at the Spiro-OMeTAD/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ hybrid interface has been observed at a time scale of 100 fs upon the photoexcitation of perovskite absorber.²⁷⁹ Theoretically, molecular dynamics together with time-dependent DFT are the main tools to address such photoinduced interfacial charge separation and relaxation

processes in heterojunctions.¹⁹ However, it has also been reported that pure molecular-dynamic method can sufficiently describe the photophysics of hybrid systems, such as dye-TiO₂, where adiabatic mechanisms are preferred over nonadiabatic ones as a result of the strong electronic coupling at the heterojunction.¹⁵² In light of this, Car-Parrinello molecular dynamic simulations were utilized in the current study to investigate the ground-state charge transfer process caused by thermal fluctuations at room temperature. As illustrated in Figure 4.9, the Spiro-OMeTAD molecule on top of CH₃NH₃PbI₃ (001) surface starts to accumulate holes at 30 fs after relaxing the initial ground state owing to the fluctuation of perovskite VB energy edge and the orbital overlap with Spiro-OMeTAD HOMO. This observation agrees well with the high efficiency of hole transfer towards Spiro-OMeTAD which is estimated by hybridizing the s-p states of Pb atoms in perovskite with the HOMO orbitals at the hybrid interface (Figure 4.8a).²⁴⁶ Namely, the photoexcited charge transfer in current hybrid interface is enhanced by the surface-delocalized hole states of CH₃NH₃PbI₃ as shown in Figure 4.8d. Conversely, the overlap between Spiro-OMeTAD HOMO and the VB energy edge of CH₃NH₃PbI₃ (100) is weak (Figure 4.8e), suggesting hindered hole transfer resulted by the highly localized electronic distribution within the perovskite bulk. Therefore, (001) and (110) orientations of CH₃NH₃PbI₃ surface are determined to be more preferable in

promoting hole transfer towards the hole extracting material in hybrid photovoltaic devices based on $\text{CH}_3\text{NH}_3\text{PbI}_3$.

Figure 4.9. Car-Parrinello molecular dynamics simulation of Spiro-OMeTAD on $\text{CH}_3\text{NH}_3\text{PbI}_3$ (001) surface within the first 80 fs from the beginning of ground-state relaxation. Hole wavefunction distributions are plotted at different time intervals.

Orientations of $\text{CH}_3\text{NH}_3\text{PbI}_3$ surface also play an important role in defining the electronic and charge transfer properties of the PCBM/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ heterojunctions, where PCBM functions as electron-acceptor. As presented in Figure 4.10a, our calculated LUMO of PCBM lies higher than CBM of $\text{CH}_3\text{NH}_3\text{PbI}_3$, facilitating the electron transfer from perovskite towards the PCBM layer while blocking holes. Despite the well-known underestimation in band gap energies, DFT calculation can accurately predict the electron distributions. The CBM electronic cloud distributions of the nonpolar $\text{CH}_3\text{NH}_3\text{PbI}_3$ (001) and (110) both localize beneath the top layer, generating a weak overlap with LUMO of PCBM (Figure 4.10d and 4.10f). On the other hand, surface charges of the polar $\text{CH}_3\text{NH}_3\text{PbI}_3$ (100) at the VBM exhibit enough electronic delocalization that can afford

efficient overlap with localized charges at the PCBM LUMO (Figure 4.10e), promoting the electron migration from perovskite towards PCBM.

Figure 4.10. Density of states of the PCBM molecule on $\text{CH}_3\text{NH}_3\text{PbI}_3$ (a) (001), (b) (100) and (c) (110) surfaces (the vertical dashed line shows the Fermi energy level); three-dimensional representation of CBM and LUMO levels of (d) PCBM/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (001), (e) PCBM/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (100) and (f) PCBM/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (110).

4.5.2 Energy alignments of organic molecules on CH₃NH₃PbI₃ surfaces

Figure 4.11. UPS spectra of thin Spiro-OMeTAD and PCBM film on perovskite CH₃NH₃PbI₃ substrates at Fermi-edge regions.

Despite the anticipated dependency of hole/electron transfer on the electronic charge distribution of VBM and CBM of CH₃NH₃PbI₃, our calculated energy band alignments obtained by the PDOS analysis are found to be considerably similar among those stable surface orientations, facilitating the comparison of calculated results to experimental data obtained from UPS measurements and thereby providing an ensemble average over all the possible orientations. As shown in Figure 4.11, VBM and WF of organic and CH₃NH₃PbI₃ films can be obtained from the VB onset in UPS spectra after baseline subtraction around the Fermi level, and the results agree well with previous observations.^{219, 280-281} Figure 4.12 summarizes the general interfacial energy alignments within CH₃NH₃PbI₃/Spiro-OMeTAD and CH₃NH₃PbI₃/PCBM hybrid interfaces based on

the UPS and optical data. Specifically, UPS results confirm our DFT predictions on the formation of type-II heterojunctions, which can promote charge transfer from perovskite to the organic layers. It should be noted that the experimental discontinuities of valence (Δ_h) and conduction (Δ_c) levels in our ~ 20 nm thick organic films indicate flat-band energy levels of the bulk,²²⁷ and are consistently smaller than interfacial discontinuities predicted from simulations of a single organic monolayer used to build the interfacial model (Figures 4.5 and 4.7).

Figure 4.12. Energy alignments of (a) Spiro-OMeTAD and (b) PCBM on $\text{CH}_3\text{NH}_3\text{PbI}_3$ film obtained from UPS measurements.

4.5.3 Charge redistributions of organic molecules on $\text{CH}_3\text{NH}_3\text{PbI}_3$ surfaces

For the quantification and comparison of actual charge transfer across the hybrid interfaces, charge redistribution density and corresponding electrostatic potential were evaluated after the organic layers were adsorbed on different perovskite surfaces, and the resulted interfacial dipoles are also estimated.²⁸²

Figure 4.13. One-dimensional plane-averaged charge density differences (ρ_{diff}) and induced electrostatic potential (green lines) of (a) Spiro-OMeTAD/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (001); (b) Spiro-OMeTAD/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (100); (c) PCBM/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (001) and (d) PCBM/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (100) interfaces.

Figures 4.13 shows the plane-averaged charge density differences ($\Delta\rho$) and corresponding electrostatic potential along the vertical direction, as a quantitative

description of the electron ($\Delta\rho<0$) and hole ($\Delta\rho>0$) accumulation behavior. Upon organic layer deposition, the major difference of charge redistribution between perovskite polar (100) and nonpolar (001) (110) surfaces, lies in that the former attract more electrons at the PCBM/CH₃NH₃PbI₃ heterojunction while the latter collect more holes above the top layer when interacting with Spiro-OMeTAD. Both kinds of charge accumulation would reduce the electrostatic screening and therefore favor the charge exchange across the hybrid interfaces.

To quantitatively compare the charge density above different CH₃NH₃PbI₃ surfaces, integration of the surface components of $\Delta\rho$ (shaded areas in Figure 4.13) was carried out, where a total surface-accumulated positive charge density of $2.99\times10^{13} \text{ e/cm}^2$ is obtained for Spiro-OMeTAD/CH₃NH₃PbI₃ (001) and $9.20\times10^{11} \text{ e/cm}^2$ for Spiro-OMeTAD/CH₃NH₃PbI₃ (100). Obviously, there is more significant hole accumulation in the case of (001) orientation, thanks to the large charge displacement between surface Pb atoms and the methoxybenzene group (CH₃OC₆H₅). On the other hand, similar charge displacement is gained at the PCBM/CH₃NH₃PbI₃ (100) heterojunction, and its negative charge density above perovskite top layer is determined to be $-3.25\times10^{12} \text{ e/cm}^2$, while it is only $-1.27\times10^{12} \text{ e/cm}^2$ for (001) surface.

Figure 4.14. One-dimensional plane-averaged charge density differences and induced electrostatic potential at (a) Spiro-OMeTAD/CH₃NH₃PbI₃ (110) and (b) PCBM/CH₃NH₃PbI₃ (110) interfaces.

As indicated by the solid green line in Figure 4.13, the electrostatic potential provide additional information regarding the effect of organic charge transporting materials on the local charge redistribution once hybrid interfaces are formed. For Spiro-OMeTAD/CH₃NH₃PbI₃, the large potential leads to significant hole accumulation, promoting interfacial electron-hole pair dissociation. While in the case of PCBM/CH₃NH₃PbI₃, especially in (100) surface, the potential drops attracting more electrons than holes. According to Berger and coworkers' real-space analysis, the electrical potential barrier formed upon accumulation of excess holes may be a serious bottleneck to improving device efficiency.²²⁵ Our experimental UPS analysis has confirmed the formation of interfacial dipole barriers, whose values are 0.43 eV for Spiro-OMeTAD/CH₃NH₃PbI₃ and 0.19 eV for PCBM/CH₃NH₃PbI₃, due to the flow of positive charge from perovskite towards Spiro-OMeTAD and negative charge from

perovskite towards PCBM, respectively. The vacuum level shift caused by interfacial dipole can be obtained by comparing the interfacial electrostatic potential ($\Delta\Phi$) between perovskite surface and the organic molecular plane with Helmholtz equation $\Delta\Phi = \mu n/\epsilon_0$, where μ denotes interface dipole moment, namely the amount of excess charge obtained from integrating $\Delta\rho$ from the origin to the point where charge depletion switches to charge accumulation, $n = 1/A$, and A denotes the surface area of the interface.²⁸³ Theoretical interfacial dipole barriers are calculated to be ~ 0.09 and ~ 0.04 eV for Spiro-OMeTAD/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ and PCBM/ $\text{CH}_3\text{NH}_3\text{PbI}_3$, respectively. Although they are lower than the experimental values due to the organic monolayer used in our simulation, the relative magnitude of electron and hole interfacial dipoles are well reproduced. Hence, we believe the proposed hybrid interfacial model could be applied for the search of novel charge transporting materials, as an effort to surmount the charge extraction bottleneck in hybrid photovoltaic devices based on hybrid perovskite.

4.6 Summary

Here we presented our studies on electronic and transport properties of hybrid 2D and 3D organic-inorganic perovskites, an emerging design of materials for photovoltaic and light-emitting applications.

We discussed the electronic and optical properties of 3D perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) for both tetragonal and orthorhombic phases and their slabs with different surface orientations. In addition, we deduced the charge carrier effective masses and electron (hole)-phonon couplings of two phases $\text{CH}_3\text{NH}_3\text{PbI}_3$ from electronic band structures and estimated their mobility using semi-classical Boltzmann transport theory. We found the calculated mobilities increase from room to lower temperatures, in agreement with the trend of experimental results, confirming the ambipolar nature of charge transport in $\text{CH}_3\text{NH}_3\text{PbI}_3$.

We then studied the electronic bands and self-trapping charge properties of white-light emission 2D perovskites (EDBEPbCl_4 and EDBEPbCl_4). The optical transitions were mainly determined by the inorganic framework and strongly influenced by excitonic confinement in the layered hybrid structure and the corresponding emissive species were self-trapped electrons and holes. We successfully correlated these chromophores to the formation of polarons strongly confined in the inorganic lattice from simulated time-resolved charge density mapping.

Finally, we investigated the energy alignment and charge transfer properties within hybrid interfaces formed by different $\text{CH}_3\text{NH}_3\text{PbI}_3$ surfaces and organic charge transporting materials. Our theoretical predictions show that the nonpolar perovskite (001) and (110) surfaces tend to favor the hole injection towards Spiro-OMeTAD, whereas the polar perovskite (100) surface is likely to promote the electron transfer towards PCBM owing to largely delocalized surface states and orbital coupling. Hole/electron are predicted to accumulate above the top layers of $\text{CH}_3\text{NH}_3\text{PbI}_3$ with different orientations, leading to the formation of large interfacial dipole moments at the hybrid interfaces.

Our findings point out the significance of the crystallization and surface orientation of perovskite in optimizing not only transport parameters but also charge transfer properties of perovskite-based solar cells. We believe that tuning the dimensionality of organic-inorganic perovskites can provide additional solutions to increase the charge carrier mobility and enlarge the intrinsic interfacial dipole moments and optimize the performance of hybrid perovskite photovoltaic devices.

Chapter 5

Plasmonic Topological Insulators

As a final part of the thesis work, we extended our studies to a different and very interesting class of multidimensional hybrid material system - topological insulators (TI). TIs can be viewed as hybrid dielectric/metallic systems, where the different phases are protected by topological effects. In particular, our interest, motivated by recent experimental results, was in understanding the nature of TI plasmonic response and its dependence on TI crystal composition, which have profound plasmonic response up to the visible part of the spectrum. DFT and MBPT calculations were combined to obtain electronic bands and optical permittivity of dichalcogenides compounds and to isolate the optical response of conducting surfaces of these TI materials. Our results show the potential of first-principle calculations to identify low-loss plasmonic topological insulators and design the next-generation broadband metamaterials, that could be ultimately tuned by injection of free carriers or by manipulating the spin degree of freedom. This work will be reported in "Plasmonic Topological Insulators" (manuscript under submission).

5.1 Background and Motivations

Topological insulators (TIs) represent a new quantum phase of matter originating from the topological character of the bulk electronic bands in certain materials and compounds. Different from other electronic states of condensed matter, topological insulating phases were first proposed theoretically and then observed experimentally.²⁸⁴⁻²⁸⁵ These phases can appear due to strong spin-orbit interactions, as described in band theory. Topological surface states form Kramer pairs with linear dispersion, have a helical spin texture, and are topologically protected as long as time-reversal symmetry is preserved. The surface conduction electrons also exhibit unusual spin-momentum locking features (carrier spin lies in-plane, locked at right angles to the carrier momentum).²⁸⁶ These effects on a TI surface coupled with magnetic layers are relevant to potential applications in designing new quantum computing,²⁸⁷ THz detectors,²⁸⁸ and spintronic devices²⁸⁹. Recent experimental demonstrations of TI plasmonic behaviour from THz²⁹⁰ to visible²⁹¹ spectral region have also opened novel opportunities to realize broadband metamaterials and induce topologically protected surface plasmon polariton. However, detailed studies of plasmonic features in the visible region of chalcogenide TI materials are still missing, and isolating the contribution of conducting surface layers to the optical response of TI thin films is a big challenge.

5.1.1 Chalcogenide topological insulators

Figure 5.1. (a) crystal structure of Bi_2Se_3 with three lattice vectors; (b) top view of Bi_2Se_3 crystal along the z-direction; (c) side view of the quintuple layer structure. (*Nature Physics*, 2009, 438)

The most widely studied 3D TIs are the Bi chalcogenides Bi_2X_3 ($\text{X} = \text{Se}, \text{Te}$). Their crystal structures are rhombohedral with the space group D_{3d}^5 ($\text{R}\bar{3}\text{m}$) and with five atoms in the trigonal unit cell. This structure can be also simply visualized in terms of a layer structure and a hexagonal unit cell as shown in Figure 5.1a. Take an example of Bi_2Se_3 , the five individual atomic layers are formed as the quintuple layer with the sequence $\text{Se}(1)\text{--Bi--Se}(2)\text{--Bi--Se}(1)$, where $\text{Se}(1)$ and $\text{Se}(2)$ denote the two different types

of selenium atom in the crystal. The intra-layer interaction within the quintuple layer shows the covalent or ionic character, whereas inter-layer interaction is weak van der Waals.

5.1.2 Electronic properties of TI Materials

Figure 5.2. Energy-band structure and spin orientation in normal and helical metals. a) in a normal metal, electrons occupy energy levels up to a maximum level, the Fermi level; b) in a helical metal, the energy levels form two cone-shaped bands that meet at their tips, and for a given k there is only one spin orientation. (*Nature*, 2010, 323)

In topological insulators, the spin-orbit interaction is so strong that the insulating energy gap is inverted—the states that should have been at high energy above the gap appear below the gap. This twist in the order of electronic states cannot be “unwound” (this accounts for the topological nature of the new class of insulators). As a result, highly conducting metallic states appear on the surface, unlike ordinary insulators. Moreover, it was experimentally demonstrated that these surface states predicted in theory have electrical properties which are fundamentally different from other two-dimensional

conducting states. Underlying the novel properties of these topological surface states are their unusual spin texture and their light-like (Dirac) energy-momentum relation. The prediction and confirmation of these novel electronic states have led to an explosion of activity in this area. Specifically, Bi_2X_3 surfaces present a single nondegenerate Dirac cone around the Brillouin zone center. The electrons populating the topological surface states, although free to move parallel to the surface, are mainly confined within the two surface most Qs, forming a two-dimensional massless Dirac Fermion gas with a well-defined spin helicity. Therefore, surfaces and nanostructures of Bi chalcogenides are ideal candidates to realize the predicted exotic plasmonic phenomena.

5.1.3 Plasmonic properties of TI Materials

Surface plasmons, defined as electromagnetic waves arising from collective oscillations of electrons at hybrid metal/dielectric interfaces, can support highly localized oscillation and either confine light into subwavelength volumes or propagate along the surface.²⁹² Surface plasmons in the visible spectral region are an appealing research topic due to their application in photovoltaics,²⁹³ waveguides,²⁹⁴ and sensing.²⁹⁵ On the other hand, the fields of metamaterials and plasmonics have seen in recent years an extraordinary evolution, from the initial demonstrations of unusual phenomena,²⁹⁶⁻²⁹⁷ towards a more general paradigm enabling optical (meta)devices with various functionalities that can be engineered and obtained on demand.²⁹⁸⁻³⁰⁰ Typical plasmonic

materials such as gold or silver have high carrier concentration with the large optical loss in the UV-visible region. There are needs to find the new low-loss plasmonic materials that can be operated at the UV-visible region. Generally, there are two approaches to achieve plasmonic behavior at optical frequencies. One is to heavily dope semiconductors to increase their charge carrier concentration, but this approach has been successful only up to near-IR regime; the other is to mix metals with non-metals or other metals. Nevertheless, the UV-visible spectrum region remains an extremely challenging for plasmonics using these doped semiconductors or intermetallic.

Some two-dimensional plasmonic materials, such as TIs have attracted recent attentions as plasmonic materials. TIs behave as insulator in their interior but possess a conducting surface, where electrons can form a metallic 2DEG at the surface and only move parallel to the surface. These surface states are protected by time-reversal symmetry, and cannot be destroyed or gapped by scattering processes. The plasmonic behavior of several TI materials was previously observed, in particular: *i*) Dirac plasmon excitations were observed at terahertz frequencies in the Bi_2Se_3 thin film;²⁹⁰ *ii*) Bi_2Se_3 microrings were shown to have bonding and antibonding plasmon modes by tuning their frequency in the THz region;³⁰¹ *iii*) $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.8}\text{Se}_{1.2}$ was proved be a good plasmonic material in the visible part of the spectrum due to a combination of bulk charge carrier response and topological surface charge carriers;²⁹¹ and very recently *iv*) solution-synthesized

hexagonal Bi_2Te_3 nanoplates showed multiple plasmon modes covering the entire visible range.³⁰²

Topological insulators are particularly interesting because they exhibit a wide tunability of their optical properties, which means that their plasmonic response can be improved and optical losses lowered via the engineering of the electronic band structure by varying their elemental composition. Typically, the optical permittivity of plasmonic media is obtained by optical measurements and theoretically described through the phenomenological Drude-Lorentz models. These approaches, however, are not capable of capturing permittivity variations that depend on elemental composition or dimension, especially within a few atomic layers. Theoretical techniques like DFT are best suited to predict the optical properties of “on-demand” plasmonic materials, and have already proven effective in screening out many potentially good plasmonic materials such as alkali-noble intermetallics,³⁰³ and gallium-doped zinc oxide.³⁰⁴ At the same time, DFT is immensely beneficial for examining the optical response of thin-films, leading to a parameter-free bottom-up design of plasmonic materials for photonic device applications.

In this chapter, we employ first-principles DFT to study the influence of elemental composition on the electronic band structure, optical properties and plasmonic behaviour of seven different topological insulator compounds of the $\text{Bi}_x\text{Sb}_{1-x}\text{Te}_y\text{Se}_{1-y}$ (BSTS) family, both in bulk and thin-film samples. Optical permittivities determined from interband

transitions of bulk TI materials are calculated based on many-body theory and compared. The contribution of surface carriers to the plasmonic response of the optical permittivity is also determined by extracting effective mass, surface carrier concentration and in-plane permittivity of slab models with the (111) orientation. Our results elucidate the interplay of bulk and surface contributions to the short-wavelength plasmonic response of these families of topological insulators, enabling the design of a new class of low-loss plasmonic materials operating at optical frequencies.

5.2 Computational Methods

DFT calculations were used to study the electronic structure and optical response of TI materials employing the local density approximation (LDA), using the QE package.²⁴ Experimental lattice parameters of bulk TI materials³⁰⁵⁻³⁰⁶ were used as the initial structure, and ground states geometries of the TI systems were obtained by the total energy minimization method upon relaxing their crystal framework and atomic coordinates. Electron-ion interactions (plane waves and core electrons) were generated by norm-conserving non-relativistic and relativistic pseudopotentials with electrons for Bi (6s 2, 6p 3, 5d 10); Sb (5s 2, 5p 3); Se (4s 2, 4p 2); Te (5s 2, 5p 2, 4d 10). The relativistic effects and spin-orbital coupling (SOC) have significant effects on the band structure due to heavy elements, such as Bi, Sb, and Te. Figure C.1 shows the small energy differences (<0.005 Ry) between all-electron and our generated pseudopotentials, confirming the

good transferability properties of these pseudopotentials. Single-particle wave functions were expanded on a plane-wave basis set up to a kinetic energy cutoff of 40 Ry for both TI bulk and slabs. The bulk and thin film layers were relaxed until forces on the atoms were lower than 0.01 eV/Å. The k-space grid of 6×6×6 in the Brillouin zone, and 32 q-points for the calculation of the dynamical matrix.

The optical response calculations were performed by the Bethe–Salpeter equations (BSE) method with the YAMBO code, using ground state wavefunctions from Quantum ESPRESSO.²²⁻²³

$$(E_{c\mathbf{k}} - E_{v\mathbf{k}})A_{v\mathbf{c}\mathbf{k}}^S + \sum_{\mathbf{k}'v'c'} \langle v\mathbf{c}\mathbf{k} | K_{eh} | v'\mathbf{c}'\mathbf{k}' \rangle A_{v'\mathbf{c}'\mathbf{k}'}^S = \Omega^S A_{v\mathbf{c}\mathbf{k}}^S,$$

where $E_{c\mathbf{k}}$ and $E_{v\mathbf{k}}$ are the quasiparticle energies of the conduction and valence states, respectively; $A_{v\mathbf{c}\mathbf{k}}^S$ are the expansion coefficients of the excitons, and Ω^S are the eigenenergies. The imaginary part of the permittivity was calculated by evaluating direct electronic transitions between occupied and higher-energy unoccupied electronic states as obtained from

$$\varepsilon'(\omega) \propto \sum_S \left| \sum_{c\nu\mathbf{k}} A_{v\mathbf{c}\mathbf{k}}^S \frac{\langle c\mathbf{k} | p_i | v\mathbf{k} \rangle}{\varepsilon_{c\mathbf{k}} - \varepsilon_{v\mathbf{k}}} \right| \delta(\Omega^S - \hbar\omega - \Gamma),$$

where $\langle c\mathbf{k} | p_i | v\mathbf{k} \rangle$ are the dipole matrix elements for electronic transitions from valence to conduction states. The real part can then be calculated via the Kramers-Kronig relation $\varepsilon'(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon''(\omega') \omega' d\omega'}{\omega'^2 - \omega^2}$. SOC interactions and the spinor wave functions were included as input for the electronic and optical calculations on the level of many-body

perturbation theory. Previously this approach has been used to successfully study the optical properties of systems with strong spin-orbital interaction.³⁰⁷ For optical permittivity calculations a k-point grid corresponding to $12 \times 12 \times 12$, both for bulk and slabs, was chosen to ensure a sufficient description of the optical permittivity.

For the TI slabs, the optical permittivity consists of interband contribution from the bulk and Drude-like free-electron intraband contribution from the metallic surface, which can be described by the Drude model determined by the plasma frequency and phenomenological Drude damping, $\epsilon(\omega) = \epsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma}$, where $\omega_p^2 = \frac{Ne^2}{m^* \epsilon_0}$ is the plasma frequency dependent on the free carrier concentration and effective mass of electrons. ϵ_{∞} is the high-frequency dielectric constant, and Γ is the damping constant of free electron plasma. Giving the accurate description of the interband component of the dielectric response and position of the plasma frequency, by this simple additive method we can accurately describe the optical response of TI slabs.

5.3 Results on Electronic and Optical Properties of Plasmonic Topological Insulators

In this part of the thesis work, we study the influence of elemental composition on the electronic band structure, optical properties and plasmonic behaviour of seven different topological insulators compounds (both bulk and slab models). Optical permittivities determined from interband transitions of bulk TI materials are calculated based on

many-body theory. The contribution of surface carriers to the plasmonic response of the optical permittivity is also studied by extracting the effective mass, surface carrier concentration and in-plane permittivity of slab models with the (111) orientation.

5.3.1 Crystal and electronic structures of BSTS Compounds

To determine the optical properties of topological insulators of the BSTS family from first principles, we first optimized their crystallographic structures. Bi-chalcogenides three dimensional topological insulator compounds maintain the same rhombohedral crystal structure as their binary end members when arranged in the order of Bi(Sb)-Se(Te)-Bi(Sb)-Se(Te), and belong to space group $R\bar{3}m$.³⁰⁶ As shown in Figure 5.2a, the equivalent hexagonal phase has a layered structure with five atomic layers, forming the quintuple layer (QL) unit cell. The intra-layer interaction within a QL has covalent or ionic character, whereas inter-layer interaction is weak van der Waals. The equilibrium lattice constants of the seven BSTS compounds calculated with and without SOC effects are shown in Figure 5.2b and 5.2c, together with available experimental data for comparison. We find that the optimized lattice parameters of bulk TIs by our generated non-realistic and realistic pseudopotentials well reproduce the experimental crystal structures from literature.³⁰⁵⁻³⁰⁶

Figure 5.2. (a) Crystal structure of BSTS TI compounds (rhombohedral and equivalent hexagonal lattice cell); lattice parameters a_{hex} (b) and c_{hex} (c) of the hexagonal lattice cell calculated by LDA and LDA+SOC method.

The LDA method tends to underestimate the experimental lattice parameters, a known consequence of the local density approximation, which nevertheless does not affect accuracy of resulting electronic properties. As the Te content of the quaternary alloys increases relative to Se (e.g. Bi_2Te_3 vs. Bi_2Se_3), both lattice parameters a_{hex} and c_{hex} increase, due to the larger ionic radius of Te. The same trend is obtained with inclusion of SOC corrections, which further validates the accuracy of our generated pseudopotentials.

Figure 5.3. (a) Band Structure of bulk BSTS TI compounds calculated with and without SOC (the dashed lines indicate the Fermi energy levels); (b) 3D Brillouin Zone of the bulk TI compounds and 2D projection of the (111) surface; (c) Direct and indirect electronic band gap energies determined from the band structures.

The calculated band structures of the seven BSTS TI compounds without (black dashed line) and with (solid blue line) SOC effects are shown in Figure 5.2. Without inclusion of SOC effect, all the bulk TI materials show Dirac-like band dispersion with small (<0.5 eV) direct bandgap at the Γ -point. The calculated direct energy gap values for the binary compounds Bi_2Se_3 , Bi_2Te_3 and Sb_2Te_3 are 54 meV, 159 meV, and 123 meV, respectively,

and for the ternary compounds $\text{Bi}_2\text{Se}_2\text{Te}$ and $\text{Bi}_2\text{Te}_2\text{Se}$ are 477 meV and 84 meV. These values are comparable to the results of previous calculations which did not include SOC effects.^{308,309} The characteristic effect of SOC in DFT calculations of the electronic band structure of TIs is to produce band inversion at special time-reversal-invariant momentum points, induced by the atomic band splitting of the heavy atoms and open up the direct band gaps.³¹⁰⁻³¹¹ This can indeed be seen at the Γ -point of the band structures obtained with SOC (blue solid lines in Figure 5.3a), confirming the topological insulator nature of these compounds. Consequently, the conduction band minima and the valence band maxima shift away from the Γ -point along the symmetric Z-F direction, inducing a transformation from minimum direct band gaps to minimum indirect band gaps with energies in the range of 0.10-0.35 eV (refer to the values in Figure 5.3c). Note that the absolute values of band gap energies may be estimated more accurately introducing self-energy corrections in the quasiparticle energy approximation, using many-body perturbation theory (e.g., the GW method);³¹²⁻³¹³ however this would not have noticeable effects on the visible to near-infrared optical properties, which are dominated by higher energy interband transitions.

5.3.2 Optical response of TI materials

To quantify the plasmonic performance of BSTS TI compounds, we separately evaluated the bulk and surface contributions to the dielectric functions. The bulk

contribution to the real (ϵ') and imaginary (ϵ'') parts of the dielectric functions due to interband transitions was obtained from the band structures using the Bethe–Salpeter and Kramers–Kronig equations (see Computational Methods for details), and the results are shown in Figure 5.4. Composition of the BSTS compounds has significant effect on both ϵ' , which describes the strength of the polarization induced by an external electric field, and ϵ'' , which describes the losses encountered in polarizing the material.³¹⁴ The strongest peak of the imaginary part of the dielectric function moves from the near-infrared (0.5–1.5 eV) to the visible spectral region (1.5–2.5 eV) when reducing Te content. This peak originates from interband transitions occurring along the symmetry line near the Γ -point (0, 0.16666, -0.16666). The transition details for the optical permittivity are listed in Table S1 of Supporting Information. Our predicted optical permittivity without SOC effects agree well with the available experimental data, with the prominent peaks of the imaginary part of permittivity appearing around 2 eV for Bi_2Te_3 , Sb_2Te_3 and $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.8}\text{Se}_{1.2}$ (see Figure 5.4b).^{315–316} The amplitude of calculated permittivity peaks for the Bi_2Te_3 , Sb_2Te_3 and $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.8}\text{Se}_{1.2}$ are consistently higher than the experimental ones due to the lack of broadening in our calculations. Once SOC effects are included in the optical response calculations (see Figure C.3 of Appendix C), the main peaks of ϵ'' red-shift to ~ 1.5 eV, and other strong peaks appear at ~ 0.5 eV due to interband transitions around the (0.33333, -0.5, -0.5) point, which are totally absent without

inclusion of SOC effects. This optical transition is expected to become dominant in the nanoscale TI thin films due to the significant surface states, so SOC effects are still included in obtaining the optical permittivity of TI slabs in the following studies.

Figure 5.4. Interband transition contribution to the real (ϵ') and imaginary part (ϵ'') of the permittivity of bulk TI materials: (a) DFT results and (b) experimental data obtained from references.

For the real part of the optical permittivity, the main features are fairly broad peaks cantered around 1.0-2.0 eV, followed by a steep decrease between 1.5 and 3.0 eV, after which ϵ' becomes negative and eventually increases slowly toward zero at higher energies. Minimum values of ϵ' appear in the UV-visible region (between 2.0-3.0 eV). Negative permittivity due to interband transitions has been theoretically predicted for Bi_2Se_3 within

the DFT framework based on full potential linearized augmented plane wave and local orbitals.³¹⁷ Here it is interesting to find that increasing the composition of Te results in larger negative permittivity, especially for Bi_2Te_3 , but at the same time increases the optical losses in the same spectral region.

Figure 5.5. Q-factor for surface plasma polariton (Q_{SPP}) for bulk BSTS compounds, together with the experimental Q-factor of noble metals Au and Ag.

The performance of media for plasmonic devices and metamaterials are usually quantified over a wide frequency band through quality factors (Q-factors), whose definitions vary depending on the applications they are intended for, such as, for example waveguiding, focusing, transformation optics, etc.^{314, 318} Here we use the Q-factor

definition for surface plasmon polaritons (SPP) to evaluate the properties of the bulk TI:

$$Q_{\text{SPP}} = \epsilon'^2/\epsilon'' \text{ (for } |\epsilon'| \gg 1\text{)}.$$

We plot both experimental and calculated Q-factors for bulk TIs compounds in Figure 5.5a and 5.5b, and compare them to the best plasmonic metals in the UV to near-IR spectral region. We observe that all the TI compounds show a plasmonic behaviour in their bulk properties that outperforms classical plasmonic metals, such as gold and silver, in a wide spectral region spanning from ~250 to 550 nm. Interestingly, TIs retain a small negative real part of the permittivity in the UV together with low losses, thus are potentially interesting for transformation optics devices in this wavelength region.

Figure 5.6. Band structure of (a) 3QL and (b) 5QL-slab Bi_2Se_3 with and without SOC effects and corresponding the charge distribution of conducting Dirac surface state; (c) real and (d) image part of dielectric function for Bi_2Se_3 bulk, 3QL and 5QL.

In addition to their negative bulk permittivity, topological insulators show robust, spin-polarized surface states, which are capable of supporting surface plasmons over a very broad wavelength range, far beyond the region where the bulk switches from metal to dielectric: topological insulators are for these reasons appealing candidates for the development of many devices benefiting from a combination of metallo-dielectric materials whose properties can be controlled by optical and electrical stimuli, like reconfigurable metamaterials and plasmonic waveguides. To study the optical response of topological surface states, we performed DFT calculations considering thin slabs of the BSTS compounds presented thus far.

The emergence of topological effects and charge accumulation at surface states in TIs is expected to onset in slabs with thickness greater than three quintuple layers (3QL), since previous theoretical work has predicted a penetration depth of the topological surface states of the order of two quintuple layers (2QL).^{311, 319} This has been confirmed experimentally, since 5QL thick films already show dominant surface states.³²⁰ Based on this, we carried out DFT calculations for (111) TI slabs with 3QL (~3 nm) and 5QL (~5 nm), and looked for the emergence of surface states upon activation of SOC effects. Here we take Bi₂Se₃ slabs as an example and present their electronic structure, charge distribution of the Dirac surface state, and optical permittivity (Figure 5.6). Similar data for the other BSTS compounds are provided in Figure C.3 and Figure C.4 of Appendix C.

Without inclusion of SOC effects, the band structure of the 3QL and 5QL Bi₂Se₃ slabs (black solid lines in Figure 5.6) are rather similar to those obtained for the bulk using fully periodic boundary conditions (Figure 5.3). Increasing the slab thickness from 3QL to 5QL decreases the energy band gap because of the reduction of quantum confinement, with the energy gap approaching the bulk value at about 19QL thickness (see Figure C.2 in Appendix C). Upon including the SOC effects, a single non-degenerate Dirac point appears at the Γ -point. At the Dirac point, the electronic wavefunction distribution is mainly localized at the surface with the penetration depth of 2 or 3 QLs. The optical response of 3QL or 5QL-slab behaviour shows similar spectral features as the bulk. For the imaginary part of the permittivity, the dominant peak appears at 2.5 eV, and a low-energy peak clearly emerges around 0.5 eV. This further improves the agreement with the experimental dispersion curves of TIs shown in Figure 5.3b.

5.3.3 Plasmonic behaviour of TI materials

Knowledge of band structure and surface charge distribution of the TI slabs allows extracting effective mass (m^*) and sheet carrier concentration (n_{2D}) to derive the three-dimensional plasma frequency, $\omega_p = \sqrt{\frac{n_{2D}e^2}{\epsilon_0 dm^*}}$. For the TI 5QL-slabs, the effective mass for electron was estimated by fitting the dispersion curve ($m^* = \hbar^2 \left[\frac{\partial^2 \epsilon(k)}{\partial k^2} \right]^{-1}$) for the lowest conduction band (see Figure C.5a), while the surface carrier concentration was obtained by integrating the two-dimensional surface charge distribution (see Figure C.5b).

As shown by consolidated results in Table 5.1, the quaternary TI materials (BiSbTeSe₂ and BiSbTeSe₂) have higher surface carrier concentration than the binary and ternary compounds. Nonetheless, irrespectively of the actual carrier concentration, the three-dimensional plasma frequencies inferred from DFT calculations all lay in the UV part of the spectrum, within 4 and 6 eV. In particular, the plasma frequency of Bi₂Se₃, $\omega_p = 5.76$ eV, agrees very well with the experimental value determined by electron energy loss spectroscopy measurement probing the surface plasmons.³²¹

Table 5.1. The effective mass (m^*), carrier concentration (n_e) of surface state and three-dimensional plasma frequency (ω_p) of 5QL-TI slabs.

Surface	Effective Mass $m^*(\times m_0 kg)$	Carrier Concentration $n_{2D}(e/cm^3)$	Surface State Thickness (nm)	Plasma Frequency $\omega_p(eV)$
Bi ₂ Se ₃	0.158 (exp: 0.15, ref. ³³)	6.33×10^{14} (exp: 3.0×10^{13} , ref. ²¹)	0.92	7.74
Bi ₂ Se ₂ Te	0.191	2.97×10^{13}	1.27	4.11
Bi ₂ Se ₂ Te	0.191	7.91×10^{13}	1.28	6.68
Bi ₂ Te ₃	0.172	8.74×10^{13}	1.90	6.07
Sb ₂ Te ₃	0.164	5.67×10^{13}	1.79	5.16
BiSbTeSe ₂	0.231	7.74×10^{14}	1.20	6.20
BiSbTe ₂ Se	0.330	9.56×10^{14}	2.05	4.41

Figure 5.7. The real and image part of surface conductivity of topological surface state with a Drude-like dispersion. Exp-Surface are the experimentally determined optical constants from Ref. 11, in which a surface Drude layer was used to fit ellipsometric data of BSTS, with plasma frequency of 7.5 eV and damping factor of 0.05.

To quantify the plasmonic contribution to the optical response of TI slabs, a Drude term was then added to the theoretical model of the optical transitions, using the parameters determined from DFT calculations (Table 5.1). When the Drude term (intra-band) is added to the inter-band contribution (refer to Figure C.6) to the optical response of the TI slabs, the calculated spectra correctly reproduce the dispersion of the optical permittivity

determined experimentally from ellipsometric measurements of BSTS, assuming a multilayer model with a thin surface Drude layer (Figure 5.7).³¹⁵ This confirms that the oscillation of topologically protected surface charge carriers has appreciable contribution to the plasmonic response of metallic-like TI surfaces in the UV-visible part of the spectrum. It also gives us confidence that the proposed TI slab model, in which the contributions of the conducting surface layer and the bulk are treated independently, can adequately describe the optical and plasmonic response of this family of TI materials.

To conclude, we would like to discuss the implications of adopting a 3D rather than a 2D model for the Drude dispersion of the thin surface layers of TI. In these systems, surface plasmons arising from charge carriers on the crystal surface have been previously assimilated to Dirac plasmons in double layer graphene,³⁰ with an effective plasma frequency given by $\omega_{2D} = \frac{1}{2\pi} \sqrt{k} \left(\frac{e^2}{4\pi\epsilon_0\epsilon\hbar} V_F \sqrt{2\pi n_{2D} g_s g_v} \right)^{1/2}$,^{9,29} where k is the wavevector, v_F is the Fermi velocity, n_{2D} is the 2D electron gas density, and g_s and g_v are the spin and the valley degeneracies, respectively. Within this framework, even for the highest surface carrier density and Fermi velocity of our BSTS compounds (refer to Table C.2), the plasma frequency is only of the order of $\omega_{2D}/\sqrt{k} = 2 \times 10^{-5} \text{ eV} \cdot \text{m}^{\frac{1}{2}}$ (g_s and g_v are taken to be both equal to 1). For symmetric nanogratings patterned in TI like in Ref. 11, with typical width of $W=500 \text{ nm}$ and selected wavevector of $k=\pi/W=6.3 \times 10^6 \text{ m}^{-1}$,^{290,}
 323-324 289, 322-323 288, 321-322 287, 320-321 286, 319-320 286, 319-320 285, 318-319 the resulting plasma

frequency would then be located in the mid-infrared region ($\omega_{2D} \sim 0.07 \text{ eV}$). Therefore, recent experimental evidence of the existence of visible plasmons supported by TIs,^{315, 325-326} implies that the conventional 3D Drude model is a far better description of surface plasmons in TI crystals than 2D models for graphene plasmons. Indeed, our DFT calculations and previous reports on the onset of spin-orbit effects in TI slabs^{311, 319-320} indicate a thickness of the surface charge layers of the order of 2 to 3 nm, which is also consistent with thicknesses derived from ellipsometric modelling of the optical constants³¹⁵ and two-channel modelling of the Hall conductivity³²⁷ of $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.8}\text{Se}_{1.2}$. Such large thickness of the surface layer is inconsistent with the description of TI surface electrons as a pure 2D Fermi gas.

5.4 Summary

We presented a systematic study of the optical and plasmonic properties of BSTS topological insulator compounds by DFT and many-body perturbation calculations. We highlighted the dependence of the optical bandgap and permittivity on composition by comparing the calculated dielectric functions of TI films, indicating that plasmonic behaviour of these compounds in the UV-NIR spectral region arises from the interplay between a bulk negative permittivity and a contribution from metallic-like surface states. Figures of merit for propagating surface plasmons confirm that BSTS compounds are better plasmonic materials than conventional noble metals Ag and Au in the UV-visible part of the spectrum, and suggest that increasing Te vs Se content can extend the overall plasmonic response to the NIR region.

We also show that the electronic wavefunction distribution is uniformly spread within 2 to 3 quintuple layers from the surface (~ 2.5 - 3.5 nm), suggesting that a conventional 3D Drude model should be used to describe the optical response of plasmonic surface layers rather than 2D Drude models typical of graphene and other 2D materials with physical thickness of only few Angstroms. Our DFT results demonstrate the potential of DFT calculations to predict not only the electronic but also the optical properties of topological insulators, and will be useful to effectively screen for low-loss TI plasmonic compounds.

Chapter 6

Conclusions and Perspectives

This thesis employed different computational/modelling methods and spectroscopic measurements to investigate vibrational modes, electronic bands, optical response, and charge transfer processes of different optoelectronic material systems, including low band-gap conjugated polymers, polymers/III-V nanocrystals, molecules/hybrid perovskites, and topological insulators. We have *i*) developed a theoretical method by implementing the TDDFT method in vibrational calculations to describe vibrational modes of singlet excited state of polymers; *ii*) built a robust “organic monolayer/inorganic slab” model for studying surface polarization effects; *iii*) involved the quantum chemistry results in Marcus theory to predict charge transfer rates between polymer and nanocrystals; and *iv*) integrated molecular dynamics and electronic density calculations to demonstrate self-trapping charges of hybrid organic-inorganic crystals. Our detailed theoretical and experimental results provided insight into the effects of adsorption of organic molecules or polymers on the inorganic compounds with different dimensionality and orientation on electronic properties and photophysical processes. Additionally, several design strategies were proposed for improving the performance of

photovoltaic devices, such as properly choosing the orientation of two-dimensional III-V semiconductor compounds for bilayer system, the size and organic ligands of III-V nanocrystals for heterojunction system, and the composition of topological insulators for plasmonic system. These computational/modelling methods could be further extended to other hybrid material systems to accelerate the design and screening of new functional materials for photovoltaic and plasmonic applications.

The specific results emerging from our thesis work could be summarized as follows:

- 1) In Chapter 3, we used DFT calculations and spectroscopic measurements to study hybrid polymer/III-V photovoltaic systems. We showed that *i*) for conjugated polymers, the electronic and vibrational properties are strongly influenced by their degree of disorder; *ii*) for P3HT/GaAs planar heterointerfaces, the electronic orbitals and charge redistribution are highly affected by GaAs surface polarity; *iii*) in P3HT/InP quantum dots blends, surface ligand functionalization and core size should be optimized simultaneously for promoting exciton dissociation and charge transfer. Our DFT framework can be applied to understand the influence of disorder on exciton and charge-carrier localization in functional organic systems and the effects of inorganic dimensionality on the interfacial charge transfer in hybrid organic-inorganic systems.

- 2) In Chapter 4, we studied the electronic, optical, and transport properties of three- and two-dimensional perovskite and charge redistribution at the interfaces between different orientations of $\text{CH}_3\text{NH}_3\text{PbI}_3$ surface and typical organic hole acceptor Spiro-OMeTAD or electron acceptor PCBM. We elucidated the origin of ambipolar nature of 3D $\text{CH}_3\text{NH}_3\text{PbI}_3$ and broad photoluminescence of 2D (EDBE) PbCl_4 and (EDBE) PbBr_4 attributing it to the self-trapping of holes and electrons. We also demonstrated that the orientations of $\text{CH}_3\text{NH}_3\text{PbI}_3$ surface have significant influence on both electron and hole interfacial transfer: both (110) and (001) surfaces favor the hole injection into Spiro-OMeTAD, while the (100) surface tends to facilitate the electron transfer towards PCBM. Molecular dynamic simulations suggest that this may be due to the significant orbital interactions under thermal fluctuations at room temperature, implying potential improvements of charge separation and extraction in perovskite-based photovoltaic devices through the control on film crystallization and surface orientation.
- 3) In Chapter 5, we presented an *ab-initio* analysis of the band structures and dielectric functions of the important class of quaternary dichalcogenide compounds that exhibit topological insulator behavior. The calculated results elucidate origin of bulk plasma properties and reveal the contribution of surface electrons to the optical response. We showed that surface plasmonic properties of certain

dichalcogenides are better than that of gold and silver in the visible and near-infrared parts of the spectrum and found that increasing tellurium content tends to extend plasmonic behavior to longer wavelengths. These results will help designing new hybrid electro-optical and plasmonic devices that exploit plasmonic peculiarities of the band structure and topologically protected surface spin dependent response in these compounds.

Overall, the theoretical results obtained in the different model systems we have advanced our understanding of the complicated electronic and photophysical properties of hybrid optoelectronic materials, elucidating some of the complex interactions between different nanostructure components. Despite significant progress in searching for emerging materials, many additional computational effects are needed for further developments, particularly in these three areas:

- 1) Although DFT calculations are proved to be a powerful tool to describe the charge transport properties of organic crystals and the electronic interactions taking place at organic/inorganic interfaces. More theoretical efforts are still needed to estimate the electronic couplings between molecular orbitals and energy bands, and electron-phonon couplings at a high level of theory within acceptable computational cost. Moreover, nonlocal electron-vibration couplings must be included to provide a

full account of phonon dispersion in describing the IRAV modes of conjugated polymers.

- 2) Combining many-body (GW method) calculations and spin-orbital coupling (SOC) effects for heavy atoms (Pb, Sn) or including spin-polarization effects for transition metals (Zn and Cu) should be considered in predicting the electronic properties and optical response of new hybrid perovskites. However, the SOC-GW approach is not suitable for treating the large molecule/perovskite interfaces that contain hundreds of atoms. Thus, improved modelling strategies by combining different computational codes and theoretical techniques are needed to investigate these large-scale hybrid systems.
- 3) Advanced theory/modelling is needed to improve our understanding exciton formation and dissociation and carrier diffusion in hybrid perovskite-based solar cells. Although substantial efforts were made to treat non-adiabatic processes within the *ab-initio* molecular dynamics framework, challenges remain for both theoretical developments and numerical efficiencies. Combining time-dependent density functional theory with nonadiabatic molecular dynamics might be an alternative approach to generate a statistically accurate ensemble of trajectories for investigating the time evolution of the electronic structure. This will allow us studying lifetime of electronic excitations

and the dynamics of electron transfer processes at hybrid polymer/inorganic interfaces.

Regarding the design of new hybrid materials and interfaces, we propose several interesting ideas for the future work.

- 1) Since surface polarization/orientation effect of inorganic or hybrid organic-inorganic materials plays an important role for promoting charge separation and reducing charge recombination at the heterojunctions, this effect should be considered in other low-dimensional semiconductor systems with cleaved surface for improving efficiency of hybrid photoelectronic devices.
- 2) We have argued that the broadband emission of 2D organic-inorganic perovskites stems from self-trapped charge carriers. Further studies in this direction may regard structural design strategies to increase charge-phonon correlations, such as reducing the interlayer distance using short organic cation or hydrostatic pressure. It will also be interesting to identify charge self-trapping effects in 3D perovskites, particularly to achieve white-emitting materials with large mobility in the relevant transport direction. Such studies may ultimately improve performance of perovskite-based white-light emitting diodes.
- 3) We determined the plasmonic behavior of the Bi-chalcogenide family of topological insulator compounds by first principles and screened the most favorable compositions

for topological plasmonic materials. Similar workflow could be applied to other classes of topological insulator compounds, such as SnTe or phase-change GeSbTe (GST). Another very interesting possibility is to include effects of an external magnetic field to DFT calculations to predict the optical response of actively tunable plasmonic devices.

References

1. Li, G.; Zhu, R.; Yang, Y. *Nat. Photonics* **2012**, *6*, 153-161.
2. Forrest, S. R. *Nature* **2004**, *428*, 911-918.
3. Ruhle, S.; Shalom, M.; Zaban, A. *Chemphyschem* **2010**, *11*, 2290-2304.
4. Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425-2427.
5. Green, M. A.; Ho-Baillie, A.; Snaith, H. J. *Nat. Photonics* **2014**, *8*, 506-514.
6. Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. *J. Am. Chem. Soc.* **2009**, *131*, 6050-6051.
7. Draxl, C.; Nabok, D.; Hannewald, K. *Acc. Chem. Res.* **2014**, *47*, 3225-3232.
8. Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, B864-+.
9. Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, 1133-&.
10. Kanai, Y.; Wu, Z. G.; Grossman, J. C. *J. Mater. Chem.* **2010**, *20*, 1053-1061.
11. Hafner, J.; Wolverton, C.; Ceder, G. *MRS Bull.* **2006**, *31*, 659-665.
12. De Angelis, F. *Acc. Chem. Res.* **2014**, *47*, 3349-3360.
13. Dion, M.; Rydberg, H.; Schroder, E.; Langreth, D. C.; Lundqvist, B. I. *Phys. Rev. Lett.* **2004**, *92*.
14. Frank, W.; Elsasser, C.; Fahnle, M. *Phys. Rev. Lett.* **1995**, *74*, 1791-1794.
15. Onida, G.; Reining, L.; Rubio, A. *Rev. Mod. Phys.* **2002**, *74*, 601-659.
16. Nigam, S.; Gupta, S.; Banyai, D.; Pandey, R.; Majumder, C. *PCCP* **2015**, *17*, 6705-6712.
17. Choudhary, D.; Clancy, P.; Shetty, R.; Escobedo, F. *Adv. Funct. Mater.* **2006**, *16*, 1768-1775.
18. Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471-2474.
19. Akimov, A. V.; Neukirch, A. J.; Prezhdo, O. V. *Chem. Rev.* **2013**, *113*, 4496-4565.
20. Runge, E.; Gross, E. K. U. *Phys. Rev. Lett.* **1984**, *52*, 997-1000.
21. Bethe, H. A.; Salpeter, E. E. *Phys. Rev.* **1951**, *82*, 309-310.
22. Marini, A.; Hogan, C.; Gruning, M.; Varsano, D. *Comput. Phys. Commun.* **2009**, *180*,

1392-1403.

23. Rohlfing, M.; Louie, S. G. *Phys. Rev. B* **2000**, *62*, 4927-4944.
24. Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I., *et al.* *J Phys-Condens Mat* **2009**, *21*.
25. Hagfeldt, A.; Boschloo, G.; Sun, L. C.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595-6663.
26. Suntivich, J.; May, K. J.; Gasteiger, H. A.; Goodenough, J. B.; Shao-Horn, Y. *Science* **2011**, *334*, 1383-1385.
27. Nozik, A. J.; Beard, M. C.; Luther, J. M.; Law, M.; Ellingson, R. J.; Johnson, J. C. *Chem. Rev.* **2010**, *110*, 6873-6890.
28. Oregan, B.; Gratzel, M. *Nature* **1991**, *353*, 737-740.
29. Coropceanu, V.; Cornil, J.; da Silva, D. A.; Olivier, Y.; Silbey, R.; Bredas, J. L. *Chem. Rev.* **2007**, *107*, 926-952.
30. Smith, M. B.; Michl, J. *Chem. Rev.* **2010**, *110*, 6891-6936.
31. Labat, F.; Le Bahers, T.; Ciofini, I.; Adamo, C. *Acc. Chem. Res.* **2012**, *45*, 1268-1277.
32. Ardo, S.; Meyer, G. J. *Chem. Soc. Rev.* **2009**, *38*, 115-164.
33. Hagfeldt, A.; Gratzel, M. *Chem. Rev.* **1995**, *95*, 49-68.
34. Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q. X.; Santori, E. A.; Lewis, N. S. *Chem. Rev.* **2010**, *110*, 6446-6473.
35. Maeda, K.; Domen, K. *J. Phys. Chem. Lett.* **2010**, *1*, 2655-2661.
36. Kubacka, A.; Fernandez-Garcia, M.; Colon, G. *Chem. Rev.* **2012**, *112*, 1555-1614.
37. Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37-38.
38. Wadia, C.; Alivisatos, A. P.; Kammen, D. M. *Environmental Science & Technology* **2009**, *43*, 2072-2077.
39. Chiang, C. K.; Fincher, C. R.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gau, S. C.; Macdiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098-1101.
40. Heeger, A. J. *Angew Chem Int Edit* **2001**, *40*, 2591-2611.
41. Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M., *et al.* *Nature* **1999**,

397, 121-128.

42. Bredas, J. L. *J. Chem. Phys.* **1985**, *82*, 3808-3811.

43. Irwin, M. D.; Buchholz, B.; Hains, A. W.; Chang, R. P. H.; Marks, T. J. *PNAS* **2008**, *105*, 2783-2787.

44. Chirvase, D.; Chiguvare, Z.; Knipper, A.; Parisi, J.; Dyakonov, V.; Hummelen, J. C. *Synth. Met.* **2003**, *138*, 299-304.

45. Shaw, P. E.; Ruseckas, A.; Samuel, I. D. W. *Adv. Mater.* **2008**, *20*, 3516-+.

46. Castiglioni, C.; Delzoppo, M.; Zerbi, G. *Journal of Raman Spectroscopy* **1993**, *24*, 485-494.

47. Negri, F.; di Donato, E.; Tommasini, M.; Castiglioni, C.; Zerbi, G.; Mullen, K. *J. Chem. Phys.* **2004**, *120*, 11889-11900.

48. Hernandez, V.; Casado, J.; Ramirez, F. J.; Zotti, G.; Hotta, S.; Navarrete, J. T. L. *J. Chem. Phys.* **1996**, *104*, 9271-9282.

49. Hernandez, V.; Castiglioni, C.; Delzoppo, M.; Zerbi, G. *Phys. Rev. B* **1994**, *50*, 9815-9823.

50. Casado, J.; Ortiz, R. P.; Navarrete, J. T. L. *Chem. Soc. Rev.* **2012**, *41*, 5672-5686.

51. Fazzi, D.; Caironi, M. *PCCP* **2015**, *17*, 8573-8590.

52. Hwang, I.; Scholes, G. D. *Chem. Mater.* **2011**, *23*, 610-620.

53. Banerji, N. *J Mater Chem C* **2013**, *1*, 3052-3066.

54. Di Nuzzo, D.; Fontanesi, C.; Jones, R.; Allard, S.; Dumsch, I.; Scherf, U.; von Hauff, E.; Schumacher, S.; Da Como, E. *Nat Commun* **2015**, *6*.

55. Wang, C.; Angelella, M.; Doyle, S. J.; Lytwak, L. A.; Rossky, P. J.; Holliday, B. J.; Tauber, M. J. *J. Phys. Chem. Lett.* **2015**, *6*, 352-3527.

56. Diesinger, H.; Chan, E. A.; Yin, J.; Soci, C. Ultrafast Charge Carrier Dynamics in Organic (Opto)Electronic Materials. In *Handbook of Organic Materials for Optical and Optoelectronic Devices: Properties and Applications*, Ostroverkhova, O., Ed. Woodhead Publishing Series in Electronic and Optical Materials: 2013.

57. Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra (Dover Books on Chemistry)*. 2001.

58. Cross, P. C.; Wilson, E. B.; Decius, J., J. C. . *Molecular Vibrations: The Theory of*

Infrared and Raman Vibrational Spectra. Dover Books on Chemistry: 1980.

59. Lucotti, A.; Tommasini, M.; Fazzi, D.; Del Zoppo, M.; Chalifoux, W. A.; Ferguson, M. J.; Zerbi, G.; Tykwinski, R. R. *J. Am. Chem. Soc.* **2009**, *131*, 4239-4244.

60. Castiglioni, C.; Tommasini, M.; Zerbi, G. *Philosophical Transactions of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences* **2004**, *362*, 2425-2459.

61. Milani, A.; Tommasini, M.; Del Zoppo, M.; Castiglioni, C.; Zerbi, G. *Phys. Rev. B* **2006**, *74*.

62. Bredas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18*, 309-315.

63. Heeger, A. J. S., N.S.; Namdas, E.B. . *Semiconducting and Metallic Polymers*. Oxford University Press: New York, 2010.

64. Soci, C.; Moses, D.; Xu, Q. H.; Heeger, A. J. *Phys. Rev. B* **2005**, *72*.

65. Galimberti, D.; Milani, A.; Castiglioni, C. *J. Chem. Phys.* **2013**, *139*.

66. Pensack, R. D.; Asbury, J. B. *J. Phys. Chem. Lett.* **2010**, *1*, 2255-2263.

67. Osterbacka, R.; An, C. P.; Jiang, X. M.; Vardeny, Z. V. *Science* **2000**, *287*, 839-842.

68. Li, Z. Q.; Wang, G. M.; Sai, N.; Moses, D.; Martin, M. C.; Di Ventra, M.; Heeger, A. J.; Basov, D. N. *Nano Lett.* **2006**, *6*, 224-228.

69. Kim, Y. H.; Spiegel, D.; Hotta, S.; Heeger, A. J. *Phys. Rev. B* **1988**, *38*, 5490-5495.

70. Fincher, C. R., Jr.; Ozaki, M.; Heeger, A. J.; MacDiarmid, A. G. *Phys Rev B* **1979**, *19*, 4140-4148.

71. Schaffer, H. E.; Friend, R. H.; Heeger, A. J. *Phys Rev B* **1987**, *36*, 7537-7541.

72. Miranda, P. B.; Moses, D.; Heeger, A. J. *Phys. Rev. B* **2001**, *64*.

73. Osterbacka, R.; Jiang, X. M.; An, C. P.; Horovitz, B.; Vardeny, Z. V. *Phys. Rev. Lett.* **2002**, *88*.

74. Lee, K. H.; Janssen, R. A. J.; Sariciftci, N. S.; Heeger, A. J. *Phys. Rev. B* **1994**, *49*, 5781-5784.

75. Sheng, C. X.; Basel, T.; Pandit, B.; Vardeny, Z. V. *Org. Electron.* **2012**, *13*, 1031-1037.

76. Jiang, X. M.; Osterbacka, R.; Korovyanko, O.; An, C. P.; Horovitz, B.; Janssen, R. A. J.; Vardeny, Z. V. *Adv. Funct. Mater.* **2002**, *12*, 587-597.

77. Jiang, X. M.; An, C. P.; Osterbacka, R.; Vardeny, Z. V. *Synth. Met.* **2001**, *116*, 203-206.
78. Chin, X. Y.; Yin, J.; Wang, Z.; Caironi, M.; Soci, C. *Sci Rep-Uk* **2014**, *4*.
79. Khatib, O.; Mueller, A. S.; Stinson, H. T.; Yuen, J. D.; Heeger, A. J.; Basov, D. N. *Phys. Rev. B* **2014**, *90*, 235307.
80. Wang, Z. L.; Zhao, J.; Frank, B.; Ran, Q. D.; Adamo, G.; Giessen, H.; Soci, C. *Nano Lett.* **2015**, *15*, 5382-5387.
81. Horovitz, B. *Solid State Commun* **1982**, *41*, 729-734.
82. Horovitz, B.; Gutfreund, H.; Weger, M. *Phys Rev B* **1978**, *17*, 2796-2799.
83. Zerbi, G. G., M.; Castiglioni, C. *Conjugated Polymers*. Kluwer Academic Publishers: 1991.
84. Horovitz, B.; Osterbacka, R.; Vardeny, Z. V. *Synth. Met.* **2004**, *141*, 179-183.
85. Yildizhan, M. M.; Fazzi, D.; Milani, A.; Brambilla, L.; Del Zoppo, M.; Chalifoux, W. A.; Tykwinski, R. R.; Zerbi, G. *J. Chem. Phys.* **2011**, *134*.
86. Fazzi, D.; Scotognella, F.; Milani, A.; Brida, D.; Manzoni, C.; Cinquanta, E.; Devetta, M.; Ravagnan, L.; Milani, P.; Cataldo, F., *et al.* *PCCP* **2013**, *15*, 9384-9391.
87. Gierschner, J.; Cornil, J.; Egelhaaf, H. J. *Adv. Mater.* **2007**, *19*, 173-191.
88. Casado, J.; Zgierski, M. Z.; Ewbank, P. C.; Burand, M. W.; Janzen, D. E.; Mann, K. R.; Pappenfus, T. M.; Berlin, A.; Perez-Inestrosa, E.; Ortiz, R. P., *et al.* *J. Am. Chem. Soc.* **2006**, *128*, 10134-10144.
89. Casado, J.; Hernandez, V.; Ortiz, R. P.; Delgado, M. C. R.; Navarrete, J. T. L.; Fuhrmann, G.; Bauerle, P. *Journal of Raman Spectroscopy* **2004**, *35*, 592-599.
90. Salzner, U.; Aydin, A. *J. Chem. Theory Comput.* **2011**, *7*, 2568-2583.
91. Fazzi, D.; Caironi, M.; Castiglioni, C. *J. Am. Chem. Soc.* **2011**, *133*, 19056-19059.
92. Kronik, L.; Stein, T.; Refaely-Abramson, S.; Baer, R. *J. Chem. Theory Comput.* **2012**, *8*, 1515-1531.
93. Casado, J.; Hernandez, V.; Kanemitsu, Y.; Navarrete, J. T. L. *Journal of Raman Spectroscopy* **2000**, *31*, 565-570.
94. Malagoli, M.; Coropceanu, V.; da Silva, D. A.; Bredas, J. L. *J. Chem. Phys.* **2004**, *120*, 7490-7496.

95. Irikura, K. K.; Johnson, R. D.; Kacker, R. N. *J. Phys. Chem. A* **2005**, *109*, 8430-8437.
96. Brambilla, L.; Tommasini, M.; Botiz, I.; Rahimi, K.; Agumba, J. O.; Stingelin, N.; Zerbi, G. *Macromolecules* **2014**, *47*, 6730-6739.
97. Tsoi, W. C.; James, D. T.; Kim, J. S.; Nicholson, P. G.; Murphy, C. E.; Bradley, D. D. C.; Nelson, J.; Kim, J. S. *J. Am. Chem. Soc.* **2011**, *133*, 9834-9843.
98. Fei, Z. P.; Boufflet, P.; Wood, S.; Wade, J.; Moriarty, J.; Gann, E.; Ratcliff, E. L.; McNeill, C. R.; Siringhaus, H.; Kim, J. S., *et al.* *J. Am. Chem. Soc.* **2015**, *137*, 6866-6879.
99. Casado, J.; Hernandez, V.; Delgado, M. C. R.; Ortiz, R. P.; Navarrete, J. T. L.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 13364-13372.
100. Singh, R. K.; Kumar, J.; Singh, R.; Kant, R.; Rastogi, R. C.; Chand, S.; Kumar, V. *New J. Phys.* **2006**, *8*.
101. Neugebauer, J.; Hess, B. A. *J. Chem. Phys.* **2004**, *120*, 11564-11577.
102. Casado, J.; Katz, H. E.; Hernandez, V.; Lopez, J. T.; Navarrete, J. T. *J. Phys. Chem. B* **2002**, *106*, 2488-2496.
103. Giussani, E.; Fazzi, D.; Brambilla, L.; Caironi, M.; Castiglioni, C. *Macromolecules* **2013**, *46*, 2658-2670.
104. Giussani, E.; Brambilla, L.; Fazzi, D.; Sommer, M.; Kayunkid, N.; Brinkmann, M.; Castiglioni, C. *J. Phys. Chem. B* **2015**, *119*, 2062-2073.
105. Magyar, R. J.; Tretiak, S. *J. Chem. Theory Comput.* **2007**, *3*, 976-987.
106. Fazzi, D.; Barbatti, M.; Thiel, W. *PCCP* **2015**, *17*, 7787-7799.
107. Yin, Y.; Alivisatos, A. P. *Nature* **2005**, *437*, 664-670.
108. Vaynzof, Y.; Kabra, D.; Zhao, L. H.; Ho, P. K. H.; Wee, A. T. S.; Friend, R. H. *Appl. Phys. Lett.* **2010**, *97*, 033309-033312.
109. Park, H.; Gutierrez, M.; Wu, X.; Kim, W.; Zhu, X. Y. *J. Phys. Chem. C* **2013**, *117*, 10974-10979.
110. Vanlaeke, P.; Swinnen, A.; Haeldermans, I.; Vanhoyland, G.; Aernouts, T.; Cheyns, D.; Deibel, C.; D'Haen, J.; Heremans, P.; Poortmans, J., *et al.* *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 2150-2158.
111. He, L. N.; Rusli; Jiang, C. Y.; Wang, H.; Lai, D. *IEEE Electron Device Lett.* **2011**, *32*, 1406-1408.

112. Du Pasquier, A.; Mastrogiovanni, D. D. T.; Klein, L. A.; Wang, T.; Garfunkel, E. *Appl. Phys. Lett.* **2007**, *91*, 183501.
113. Gunes, S.; Fritz, K. P.; Neugebauer, H.; Sariciftci, N. S.; Kumar, S.; Scholes, G. D. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 420-423.
114. Cui, D.; Xu, J.; Zhu, T.; Paradee, G.; Ashok, S.; Gerhold, M. *Appl. Phys. Lett.* **2006**, *88*, 183111-183111-183113.
115. Zhou, Y.; Riehle, F. S.; Yuan, Y.; Schleiermacher, H.-F.; Niggemann, M.; Urban, G. A.; Kruger, M. *Appl. Phys. Lett.* **2010**, *96*, 013304-013304-013303.
116. Blackburn, J. L.; Selmarten, D. C.; Ellingson, R. J.; Jones, M.; Micic, O.; Nozik, A. *J. J. Phys. Chem. B* **2005**, *109*, 2625-2631.
117. Ren, S.; Chang, L.-Y.; Lim, S.-K.; Zhao, J.; Smith, M.; Zhao, N.; Bulovic, V.; Bawendi, M.; Gradecak, S. *Nano Lett.* **2011**, *11*, 3998-4002.
118. Beek, W. J. E.; Wienk, M. M.; Janssen, R. A. J. *Adv. Funct. Mater.* **2006**, *16*, 1112-1116.
119. Oosterhout, S. D.; Wienk, M. M.; van Bavel, S. S.; Thiedmann, R.; Koster, L. J. A.; Gilot, J.; Loos, J.; Schmidt, V.; Janssen, R. A. J. *Nat. Mater.* **2009**, *8*, 818-824.
120. Yablonovitch, E.; Miller, O. D.; Kurtz, S. R.; Ieee. *The Opto-Electronic Physics That Broke the Efficiency Limit in Solar Cells*. Ieee: New York, 2012; p 1556-1559.
121. Ackermann, J.; Videlot, C.; El Kassmi, A. *Thin Solid Films* **2002**, *403*, 157-161.
122. Ren, S. Q.; Zhao, N.; Crawford, S. C.; Tambe, M.; Bulovic, V.; Gradecak, S. *Nano Lett.* **2011**, *11*, 408-413.
123. Chao, J. J.; Shiu, S. C.; Lin, C. F. *Sol. Energy Mater. Sol. Cells* **2012**, *105*, 40-45.
124. Mariani, G.; Laghumavarapu, R. B.; de Villiers, B. T.; Shapiro, J.; Senanayake, P.; Lin, A.; Schwartz, B. J.; Huffaker, D. L. *Appl. Phys. Lett.* **2010**, *97*, 013107-013109.
125. Yong, C. K.; Noori, K.; Gao, M.; Joyce, H. J.; Tan, H. H.; Jagadish, C.; Giustino, F.; Johnston, M. B.; Herz, L. M. *Nano Lett.* **2012**, *12*, 6293.
126. Park, H.; Gutierrez, M.; Wu, X.; Kim, J. W.; Zhu, X. *J. Phys. Chem. C*, **2013**, *117*, 10974.
127. Cabanillas-Gonzalez, J.; Gambetta, A.; Zavelani-Rossi, M.; Lanzani, G. *Appl. Phys. Lett.* **2007**, *91*, 122113-122113-122113.
128. Cabanillas-Gonzalez, J.; Egelhaaf, H.-J.; Brambilla, A.; Sessi, P.; Duò, L.; Finazzi,

- M.; Ciccacci, F.; Lanzani, G. *Nanotechnology* **2008**, *19*, 424010.
129. Bassani, F.; La Rocca, G. C.; Basko, D. M.; Agranovich, V. M. *Phys. Solid State* **1999**, *41*, 701-703.
130. Blumstengel, S.; Sadofev, S.; Xu, C.; Puls, J.; Henneberger, F. *Phys. Rev. Lett.* **2006**, *97*, 237401-237404.
131. Zhang, Q.; Atay, T.; Tischler, J. R.; Bradley, M. S.; Bulovic, V.; Nurmikko, A. V. *Nat. Nanotechnol.* **2007**, *2*, 555-559.
132. Nizamoglu, S.; Sun, X. W.; Demir, H. V. *Appl. Phys. Lett.* **2010**, *97*, 263106-263108.
133. Yong, C. K.; Joyce, H. J.; Lloyd-Hughes, J.; Gao, Q.; Tan, H. H.; Jagadish, C.; Johnston, M. B.; Herz, L. M. *Small* **2012**, *8*, 1725-1731.
134. Rand, B. P.; Burk, D. P.; Forrest, S. R. *Phys. Rev. B* **2007**, *75*.
135. Yablonovitch, E.; Miller, O. D.; Kurtz, S. R. *2012 38th IEEE Photovoltaic Specialists Conference (PVSC)* **2012**, 1556-1559.
136. Yan, L.; You, W. *Acs Nano* **2013**, *7*, 6619-6626.
137. Yan, L.; You, W. *Org. Electron.* **2015**, *16*, 71-76.
138. Yong, C. K.; Noori, K.; Gao, Q.; Joyce, H. J.; Tan, H. H.; Jagadish, C.; Giustino, F.; Johnston, M. B.; Herz, L. M. *Nano. Lett.* **2012**, *12*, 6293-6301.
139. Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5048-5079.
140. Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I., *et al.* *J. Phys.: Condens. Matter* **2009**, *21*, 395502-395520.
141. Dion, M.; Rydberg, H.; Schroder, E.; Langreth, D. C.; Lundqvist, B. I. *Phys. Rev. Lett.* **2004**, *92*, 246401.
142. Ohtake, A.; Nakamura, J.; Komura, T.; Hanada, T.; Yao, T.; Kuramochi, H.; Ozeki, M. *Phys. Rev. B* **2001**, *64*, 45318-45325.
143. Skeath, P.; Saperstein, W. A.; Pianetta, P.; Lindau, I.; Spicer, W. E.; Mark, P. *J. Vac. Sci. Technol.* **1978**, *15*, 1219-1222.
144. Humphrey, W.; Dalke, A.; Schulten, K. *J. Mol. Graphics Modell* **1996**, *14*, 33-38.
145. D'Amico, N. R.; Cantele, G.; Ninno, D. *J. Phys. Chem. C* **2012**, *116*, 21391-21400.
146. Qian, G. X., Richard, M. M., and Chadi, D. J. . *Phys. Rev. B* **1988**, *37*, 1303-1307.

147. Yi, Z. J.; Ma, Y. C.; Rohlfing, M. *J. Phys. Chem. C* **2011**, *115*, 23455-23462.
148. Dag, S.; Wang, L. W. *Nano. Lett.* **2008**, *8*, 4185-4190.
149. Calzolari, A.; Ruini, A.; Catellani, A. *J. Phys. Chem. C* **2012**, *116*, 17158-17163.
150. Cabanillas-Gonzalez, J.; Gambetta, A.; Zavelani-Rossi, M.; Lanzani, G. *Appl. Phys. Lett.* **2007**, *91*, 122113-122115.
151. Tully, J. C. *J. Chem. Phys.* **1990**, *93*, 1061-1071.
152. Duncan, W. R.; Craig, C. F.; Prezhdo, O. V. *J. Am. Chem. Soc.* **2007**, *129*, 8528-8543.
153. Long, R.; English, N. J.; Prezhdo, O. V. *J. Am. Chem. Soc.* **2012**, *134*, 14238-14248.
154. Nenon, S.; Mereau, R.; Salman, S.; Castet, F. *J. Phys. Chem. Lett.* **2012**, *3*, 58-63.
155. Lin, L.; Robertson, J. *Appl. Phys. Lett.* **2011**, *98*, 082903-082905.
156. Sai, N.; Gearba, R.; Dolocan, A.; Tritsch, J. R.; Chan, W. L.; Chelikowsky, J. R.; Leung, K.; Zhu, X. Y. *J. Phys. Chem. Lett.* **2012**, *3*, 2173-2177.
157. Ishii, H.; Sugiyama, K.; Ito, E.; Seki, K. *Adv. Mater.* **1999**, *11*, 972-972.
158. Crispin, X.; Geskin, V.; Crispin, A.; Cornil, J.; Lazzaroni, R.; Salaneck, W. R.; Bredas, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 8131-8141.
159. Nemec, H.; Rochford, J.; Taratula, O.; Galoppini, E.; Kuzel, P.; Polivka, T.; Yartsev, A.; Sundstrom, V. *Phys. Rev. Lett.* **2010**, *104*, 197401-197404.
160. Monti, O. L. A. *J. Phys. Chem. Lett.* **2012**, *3*, 2342-2351.
161. Bernardini, F.; Fiorentini, V.; Vanderbilt, D. *Phys. Rev. B* **1997**, *56*, 10024-10027.
162. Terentjevs, A.; Steele, M. P.; Blumenfeld, M. L.; Ilyas, N.; Kelly, L. L.; Fabiano, E.; Monti, O. L. A.; Della Sala, F. *J. Phys. Chem. C* **2011**, *115*, 21128-21138.
163. Muller, K.; Seitsonen, A. P.; Brugger, T.; Westover, J.; Greber, T.; Jung, T.; Kara, A. *J. Phys. Chem. C* **2012**, *116*, 23465-23471.
164. Noori, K.; Giustino, F. *Adv. Funct. Mater.* **2012**, *22*, 5089-5095.
165. Geng, W., Z., X. F., Liu, H. X., Yao, X. J. *J. Phys. Chem. C* **2013**, *117*, 10536-10544.
166. Braun, S.; Salaneck, W. R.; Fahlman, M. *Adv. Mater.* **2009**, *21*, 1450-1472.
167. Xu, Z.; Chen, L. M.; Chen, M. H.; Li, G.; Yang, Y. *Appl. Phys. Lett.* **2009**, *95*,

013301-013303.

168. Tang, J.; Kemp, K. W.; Hoogland, S.; Jeong, K. S.; Liu, H.; Levina, L.; Furukawa, M.; Wang, X.; Debnath, R.; Cha, D., *et al. Nat. Mater.* **2011**, *10*, 765-771.
169. McDonald, S. A.; Konstantatos, G.; Zhang, S. G.; Cyr, P. W.; Klem, E. J. D.; Levina, L.; Sargent, E. H. *Nat. Mater.* **2005**, *4*, 138-142.
170. Sandeep, C. S. S.; Ten Cate, S.; Schins, J. M.; Savenije, T. J.; Liu, Y.; Law, M.; Kinge, S.; Houtepen, A. J.; Siebbeles, L. D. A. *Nat Commun* **2013**, *4*, 2360.
171. Schaller, R. D.; Klimov, V. I. *Phys. Rev. Lett.* **2004**, *92*, 186601.
172. Tan, Y. Z.; Jin, S.; Hamers, R. J. *ACS Appl. Mat. Interfaces* **2013**, *5*, 12975-12983.
173. Li, Z.; Gao, F.; Greenham, N. C.; McNeill, C. R. *Adv. Funct. Mater.* **2011**, *21*, 1419-1431.
174. Liu, C. Y.; Holman, Z. C.; Kortshagen, U. R. *Nano Lett.* **2009**, *9*, 449-452.
175. Herrmann, D.; Niesar, S.; Scharsich, C.; Kohler, A.; Stutzmann, M.; Riedle, E. *J. Am. Chem. Soc.* **2011**, *133*, 18220-18233.
176. Greaney, M. J.; Das, S.; Webber, D. H.; Bradforth, S. E.; Brutchey, R. L. *Acs Nano* **2012**, *6*, 4222-4230.
177. Cappel, U. B.; Dowland, S. A.; Reynolds, L. X.; Dimitrov, S.; Haque, S. A. *J. Phys. Chem. Lett.* **2013**, *4*, 4253-4257.
178. Grancini, G.; Biasiucci, M.; Mastria, R.; Scotognella, F.; Tassone, F.; Polli, D.; Gigli, G.; Lanzani, G. *J. Phys. Chem. Lett.* **2012**, *3*, 517-523.
179. Piliago, C.; Manca, M.; Kroon, R.; Yarema, M.; Szendrei, K.; Andersson, M. R.; Heiss, W.; Loi, M. A. *J. Mater. Chem.* **2012**, *22*, 24411-24416.
180. Jarzab, D.; Szendrei, K.; Yarema, M.; Pichler, S.; Heiss, W.; Loi, M. A. *Adv. Funct. Mater.* **2011**, *21*, 1988-1992.
181. Gocalinska, A.; Saba, M.; Quochi, F.; Marceddu, M.; Szendrei, K.; Gao, J.; Loi, M. A.; Yarema, M.; Seyrkammer, R.; Heiss, W., *et al. J. Phys. Chem. Lett.* **2010**, *1*, 1149-1154.
182. Jeltsch, K. F.; Schadel, M.; Bonekamp, J. B.; Niyamakom, P.; Rauscher, F.; Lademann, H. W. A.; Dumsch, I.; Allard, S.; Scherf, U.; Meerholz, K. *Adv. Funct. Mater.* **2012**, *22*, 397-404.
183. Zhou, R. J.; Stalder, R.; Xie, D. P.; Cao, W. R.; Zheng, Y.; Yang, Y. X.; Plaisant, M.;

- Holloway, P. H.; Schanze, K. S.; Reynolds, J. R., *et al. Acs Nano* **2013**, *7*, 4846-4854.
184. Yuan, J. Y.; Gallagher, A.; Liu, Z. K.; Sun, Y. X.; Ma, W. L. *J Mater Chem A* **2015**, *3*, 2572-2579.
185. Rhee, J. H.; Chung, C. C.; Diau, E. W. G. *Npg Asia Mater* **2013**, *5*.
186. Brown, P. R.; Kim, D.; Lunt, R. R.; Zhao, N.; Bawendi, M. G.; Grossman, J. C.; Bulovic, V. *Acs Nano* **2014**, *8*, 5863-5872.
187. Nagaoka, H.; Colbert, A. E.; Strein, E.; Janke, E. M.; Salvador, M.; Schlenker, C. W.; Ginger, D. S. *J. Phys. Chem. C* **2014**, *118*, 5710-5715.
188. Frederick, M. T.; Amin, V. A.; Swenson, N. K.; Ho, A. Y.; Weiss, E. A. *Nano Lett.* **2013**, *13*, 287-292.
189. Frederick, M. T.; Amin, V. A.; Weiss, E. A. *J. Phys. Chem. Lett.* **2013**, *4*, 634-640.
190. Xie, R.; Battaglia, D.; Peng, X. *J. Am. Chem. Soc.* **2007**, *129*, 15432-15433.
191. Harris, D. K.; Bawendi, M. G. *J. Am. Chem. Soc.* **2012**, *134*, 20211-20213.
192. Couderc, E.; Greaney, M. J.; Brutchey, R. L.; Bradforth, S. E. *J. Am. Chem. Soc.* **2013**, *135*, 18418-18426.
193. Strein, E.; deQuilettes, D. W.; Hsieh, S. T.; Colbert, A. E.; Ginger, D. S. *J. Phys. Chem. Lett.* **2014**, *5*, 208-211.
194. Blackburn, J. L.; Ellingson, R. J.; Micic, O. I.; Nozik, A. J. *J. Phys. Chem. B* **2003**, *107*, 102-109.
195. Selmarten, D.; Jones, M.; Rumbles, G.; Yu, P. R.; Nedeljkovic, J.; Shaheen, S. J. *Phys. Chem. B* **2005**, *109*, 15927-15932.
196. Li, H. S.; Wu, Z. G.; Lusk, M. T. *J. Phys. Chem. C* **2014**, *118*, 46-53.
197. Tarafder, K.; Surendranath, Y.; Olshansky, J. H.; Alivisatos, A. P.; Wang, L.-W. *Journal of the American Chemical Society* **2014**, *136*, 5121-5131.
198. Del Ben, M.; Havenith, R. W. A.; Broer, R.; Stener, M. *J. Phys. Chem. C* **2011**, *115*, 16782-16796.
199. Marcus, R. A. *Faraday Discuss.* **1982**, *74*, 7-15.
200. Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148-13168.
201. Reimers, J. R. *J. Chem. Phys.* **2001**, *115*, 9103-9109.

202. Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966-978.
203. Liu, T.; Troisi, A. *J. Phys. Chem. C* **2011**, *115*, 2406-2415.
204. Peterson, M. D.; Cass, L. C.; Harris, R. D.; Edme, K.; Sung, K.; Weiss, E. A. *Annu. Rev. Phys. Chem.* **2014**, *65*, 317-339.
205. Lee, J. R. I.; Whitley, H. D.; Meulenberg, R. W.; Wolcott, A.; Zhang, J. Z.; Prendergast, D.; Lovingood, D. D.; Strouse, G. F.; Ogitsu, T.; Schwegler, E., *et al. Nano Lett.* **2012**, *12*, 2763-2767.
206. Micic, O. I.; Ahrenkiel, S. P.; Nozik, A. J. *Appl. Phys. Lett.* **2001**, *78*, 4022-4024.
207. Dung, M. X.; Mohapatra, P.; Choi, J. K.; Kim, J. H.; Jeong, S.; Jeong, H. D. *Bull. Korean Chem. Soc.* **2012**, *33*, 1491-1504.
208. Virieux, H.; Le Troedec, M.; Cros-Gagneux, A.; Ojo, W. S.; Delpech, F.; Nayral, C.; Martinez, H.; Chaudret, B. *J. Am. Chem. Soc.* **2012**, *134*, 19701-19708.
209. Sharma, S. N.; Vats, T.; Dhenadhayalan, N.; Ramamurthy, P.; Narula, A. K. *Sol. Energy Mater. Sol. Cells* **2012**, *100*, 6-15.
210. Banerji, N.; Cowan, S.; Vauthey, E.; Heeger, A. J. *J. Phys. Chem. C* **2011**, *115*, 9726-9739.
211. Firdaus, Y.; Miranti, R.; Fron, E.; Khetubol, A.; Vandenplas, E.; Cheyins, D.; Borchert, H.; Parisi, J.; Van der Auweraer, M. *J. Appl. Phys.* **2015**, *118*.
212. Tamai, Y.; Matsuura, Y.; Ohkita, H.; Bente, H.; Ito, S. *J. Phys. Chem. Lett.* **2014**, *5*, 399-403.
213. Hoffman, J. B.; Choi, H.; Kamat, P. V. *J. Phys. Chem. C* **2014**, *118*, 18453-18461.
214. Armaroli, N.; Barigelletti, F.; Ceroni, P.; Eckert, J. F.; Nicoud, J. F.; Nierengarten, J. F. *Chem. Commun.* **2000**, 599-600.
215. Hodes, G.; Cahen, D. *Nat. Photonics* **2014**, *8*, 87-88.
216. Snaith, H. J. *J. Phys. Chem. Lett.* **2013**, *4*, 3623-3630.
217. Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J. *Science* **2012**, *338*, 643-647.
218. Zhou, H.; Chen, Q.; Li, G.; Luo, S.; Song, T.-b.; Duan, H.-S.; Hong, Z.; You, J.; Liu, Y.; Yang, Y. *Science* **2014**, *345*, 542-546.
219. Kim, H. S.; Lee, C. R.; Im, J. H.; Lee, K. B.; Moehl, T.; Marchioro, A.; Moon, S. J.;

- Humphry-Baker, R.; Yum, J. H.; Moser, J. E., *et al. Sci Rep-Uk* **2012**, 2, 591.
220. Burschka, J.; Pellet, N.; Moon, S. J.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Gratzel, M. *Nature* **2013**, 499, 316-319.
221. Chin, X. Y.; Cortecchia, D.; Yin, J.; Bruno, A.; Soci, C. **2015**, arXiv:1501.04407.
222. Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J. *Science* **2013**, 342, 341-344.
223. Xing, G. C.; Mathews, N.; Sun, S. Y.; Lim, S. S.; Lam, Y. M.; Gratzel, M.; Mhaisalkar, S.; Sum, T. C. *Science* **2013**, 342, 344-347.
224. Lindblad, R.; Bi, D. Q.; Park, B. W.; Oscarsson, J.; Gorgoi, M.; Siegbahn, H.; Odelius, M.; Johansson, E. M. J.; Rensmo, H. *J. Phys. Chem. Lett.* **2014**, 5, 648-653.
225. Bergmann, V. W.; Weber, S. A. L.; Ramos, F. J.; Nazeeruddin, M. K.; Gratzel, M.; Li, D.; Domanski, A. L.; Lieberwirth, I.; Ahmad, S.; Berger, R. *Nat Commun* **2014**, 5, 5001.
226. Jeon, N. J.; Noh, J. H.; Kim, Y. C.; Yang, W. S.; Ryu, S.; Il Seol, S. *Nat. Mater.* **2014**, 13, 897-903.
227. Schulz, P.; Edri, E.; Kirmayer, S.; Hodes, G.; Cahen, D.; Kahn, A. *Energy Environ. Sci.* **2014**, 7, 1377-1381.
228. Grancini, G.; Marras, S.; Prato, M.; Giannini, C.; Quarti, C.; De Angelis, F.; De Bastiani, M.; Eperon, G. E.; Snaith, H. J.; Manna, L., *et al. J. Phys. Chem. Lett.* **2014**, 5, 3836-3842.
229. Wehrenfennig, C.; Eperon, G. E.; Johnston, M. B.; Snaith, H. J.; Herz, L. M. *Adv. Mater.* **2014**, 26, 1584-1589.
230. Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M. J.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenberger, A.; Katsiev, K., *et al. Science* **2015**, 347, 519-522.
231. Nie, W.; Tsai, H.; Asadpour, R.; Blancon, J. C.; Neukirch, A. J.; Gupta, G.; Crochet, J. J.; Chhowalla, M.; Tretiak, S.; Alam, M. A., *et al. Science* **2015**, 347, 522-525.
232. Cheng, Z.; Lin, J. *CrystEngComm* **2010**, 12, 2646-2662.
233. Mitzi, D. B. Synthesis, Structure, and Properties of Organic-Inorganic Perovskites and Related Materials. In *Prog Inorg Chem*, John Wiley & Sons, Inc.: 2007; pp 1-121.
234. Mitzi, D. B. *Journal of the Chemical Society, Dalton Transactions* **2001**, 1-12.
235. Mitzi, D. B. Hybrid Organic-Inorganic Electronics. In *Functional Hybrid Materials*, Wiley-VCH Verlag GmbH & Co. KGaA: 2005; pp 347-386.

236. Ishihara, T. Optical Properties of Pb-Based Inorganic-Organic Perovskites. In *Optical Properties of Low-Dimensional Materials*, pp 288-339.
237. Muljarov, E. A.; Tikhodeev, S. G.; Gippius, N. A.; Ishihara, T. *Physical Review B* **1995**, *51*, 14370-14378.
238. Yangui, A.; Garrot, D.; Lauret, J. S.; Lusson, A.; Bouchez, G.; Deleporte, E.; Pillet, S.; Bendeif, E. E.; Castro, M.; Triki, S., *et al.* *The Journal of Physical Chemistry C* **2015**, *119*, 23638-23647.
239. Even, J.; Pedesseau, L.; Jancu, J. M.; Katan, C. *J. Phys. Chem. Lett.* **2013**, *4*, 2999-3005.
240. Umari, P.; Mosconi, E.; De Angelis, F. *Scientific Reports* **2014**, *4*, 7.
241. A., E. D.; Leeor, K. *J. Phys. Chem. Lett.* **2014**, *5*, 2733.
242. Geng, W.; Zhang, L.; Zhang, Y. N.; Lau, W. M.; Liu, L. M. *J. Phys. Chem. C* **2014**, *118*, 19565-19571.
243. Haruyama, J.; Sodeyama, K.; Han, L. Y.; Tateyama, Y. *J. Phys. Chem. Lett.* **2014**, *5*, 2903-2909.
244. Giorgi, G.; Fujisawa, J. I.; Segawa, H.; Yamashita, K. *J. Phys. Chem. Lett.* **2013**, *4*, 4213-4216.
245. Feng, J.; Xiao, B. *J. Phys. Chem. Lett.* **2014**, *5*, 1278-1282.
246. Roiati, V.; Mosconi, E.; Listorti, A.; Colella, S.; Gigli, G.; De Angelis, F. *Nano Lett.* **2014**, *14*, 2168-2174.
247. Mosconi, E.; Ronca, E.; De Angelis, F. *J. Phys. Chem. Lett.* **2014**, *5*, 2619-2625.
248. Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I., *et al.* *J. Phys.: Condens. Matter* **2009**, *21*, 395502.
249. Garrity, K. F.; Bennett, J. W.; Rabe, K. M.; Vanderbilt, D. *Comput. Mater. Sci.* **2014**, *81*, 446-452.
250. Roman-Perez, G.; Soler, J. M. *Phys. Rev. Lett.* **2009**, *103*, 096102.
251. Lee, K.; Murray, E. D.; Kong, L. Z.; Lundqvist, B. I.; Langreth, D. C. *Phys. Rev. B* **2010**, *82*, 081101.
252. Thonhauser, T.; Cooper, V. R.; Li, S.; Puzder, A.; Hyldgaard, P.; Langreth, D. C. *Phys. Rev. B* **2007**, *76*, 11.

253. Wang, H.; Pei, Y. Z.; LaLonde, A. D.; Snyder, G. J. *PNAS* **2012**, *109*, 9705-9709.
254. Ravich, Y. I.; Efimova, B. A.; Tamarche, Vi. *Physica Status Solidi B-Basic Research* **1971**, *43*, 11-33.
255. He, Y. P.; Galli, G. *Chemistry of Materials* **2014**, *26*, 5394-5400.
256. Torres, A.; Rego, L. G. C. *J. Phys. Chem. C* **2014**, *118*, 26947-26954.
257. Umari, P.; Mosconi, E.; De Angelis, F. *Sci Rep-Uk* **2014**, *4*, 4467.
258. Amat, A.; Mosconi, E.; Ronca, E.; Quarti, C.; Umari, P.; Nazeeruddin, M. K.; Grätzel, M.; De Angelis, F. *Nano letters* **2014**, *14*, 3608-3616.
259. Umari, P.; Mosconi, E.; De Angelis, F. *Sci. Rep.* **2014**, *4*, 4467.
260. Chin, X. Y.; Cortecchia, D.; Yin, J.; Bruno, A.; Soci, C. *Nat Commun* **2015**, *6*.
261. Brenner, T. M.; Egger, D. A.; Rappe, A. M.; Kronik, L.; Hodes, G.; Cahen, D. J. *Phys. Chem. Lett.* **2015**, *6*, 4754-4757.
262. Ma, J.; Wang, L. W. *Nano Letters* **2014**, *15*, 248-253.
263. Frost, J. M.; Butler, K. T.; Brivio, F.; Hendon, C. H.; van Schilfgaarde, M.; Walsh, A. *Nano Letters* **2014**, *14*, 2584-2590.
264. Juarez-Perez, E. J.; Sanchez, R. S.; Badia, L.; Garcia-Belmonte, G.; Kang, Y. S.; Mora-Sero, I.; Bisquert, J. *The Journal of Physical Chemistry Letters* **2014**, *5*, 2390-2394.
265. Dohner, E. R.; Jaffe, A.; Bradshaw, L. R.; Karunadasa, H. I. *J. Am. Chem. Soc.* **2014**, *136*, 13154-13157.
266. Ishihara, T.; Takahashi, J.; Goto, T. *Physical Review B* **1990**, *42*, 11099-11107.
267. Abreu, R. A. *Physics Letters A* **1984**, *100*, 375-378.
268. Ki, W.; Li, J. *Journal of the American Chemical Society* **2008**, *130*, 8114-8115.
269. Nistor, S. V.; Schoemaker, D. *physica status solidi (b)* **1995**, *190*, 339-346.
270. Iwanaga, M.; Azuma, J.; Shirai, M.; Tanaka, K.; Hayashi, T. *Physical Review B* **2002**, *65*, 214306.
271. Nistor, S. V.; Goovaerts, E.; Schoemaker, D. *Physical Review B* **1993**, *48*, 9575-9580.
272. Iwanaga, M.; Shirai, M.; Tanaka, K.; Hayashi, T. *Physical Review B* **2002**, *66*,

064304.

273. Williams, R. T.; Song, K. S. *Journal of Physics and Chemistry of Solids* **1990**, *51*, 679-716.

274. Iwanaga, M.; Hayashi, T. *Journal of Luminescence* **2003**, *102–103*, 663-668.

275. Kink, R.; Avarmaa, T.; Kisand, V.; Lõhmus, A.; Kink, I.; Martinson, I. *Journal of Physics: Condensed Matter* **1998**, *10*, 693.

276. Känzig, W. *Physical Review* **1955**, *99*, 1890-1891.

277. Castner, T. G.; Känzig, W. *Journal of Physics and Chemistry of Solids* **1957**, *3*, 178-195.

278. Jette, A. N.; Gilbert, T. L.; Das, T. P. *Physical Review* **1969**, *184*, 884-894.

279. Marchioro, A.; Teuscher, J.; Friedrich, D.; Kunst, M.; van de Krol, R.; Moehl, T.; Gratzel, M.; Moser, J. E. *Nat. Photonics* **2014**, *8*, 250-255.

280. Tada, A.; Geng, Y. F.; Wei, Q. S.; Hashimoto, K.; Tajima, K. *Nat. Mater.* **2011**, *10*, 450-455.

281. Wang, Q. K.; Wang, R. B.; Shen, P. F.; Li, C.; Li, Y. Q.; Liu, L. J.; Duhm, S.; Tang, J. X. *Adv. Mater. Interfaces* **2015**, *2*, 1400528.

282. Yin, J.; Migas, D. B.; Panahandeh-Fard, M.; Chen, S.; Wang, Z. L.; Lova, P.; Soci, C. *J. Phys. Chem. Lett.* **2013**, *4*, 3303-3309.

283. Sai, N.; Gearba, R.; Dolocan, A.; Tritsch, J. R.; Chan, W. L.; Chelikowsky, J. R.; Leung, K.; Zhu, X. Y. *J. Phys. Chem. Lett.* **2012**, *3*, 2173-2177.

284. König, M.; Wiedmann, S.; Brune, C.; Roth, A.; Buhmann, H.; Molenkamp, L. W.; Qi, X. L.; Zhang, S. C. *Science* **2007**, *318*, 766-770.

285. Fu, L.; Kane, C. L. *Phys. Rev. B* **2007**, *76*.

286. Hsieh, D.; Qian, D.; Wray, L.; Xia, Y.; Hor, Y. S.; Cava, R. J.; Hasan, M. Z. *Nature* **2008**, *452*, 970-U975.

287. Kitaev, A.; Preskill, J. *Phys. Rev. Lett.* **2006**, *96*.

288. Zhang, X. A.; Wang, J.; Zhang, S. C. *Phys. Rev. B* **2010**, *82*.

289. Chen, Y. L.; Analytis, J. G.; Chu, J. H.; Liu, Z. K.; Mo, S. K.; Qi, X. L.; Zhang, H. J.; Lu, D. H.; Dai, X.; Fang, Z., *et al.* *Science* **2009**, *325*, 178-181.

290. Di Pietro, P.; Ortolani, M.; Limaj, O.; Di Gaspare, A.; Giliberti, V.; Giorgianni, F.;

- Brahlek, M.; Bansal, N.; Koirala, N.; Oh, S., *et al. Nat. Nanotechnol.* **2013**, *8*, 556-560.
291. Ou, J. Y.; So, J. K.; Adamo, G.; Sulaev, A.; Wang, L.; Zheludev, N. I. *Nat Commun* **2014**, *5*.
292. Barnes, W. L.; Dereux, A.; Ebbesen, T. W. *Nature* **2003**, *424*, 824-830.
293. Atwater, H. A.; Polman, A. *Nat. Mater.* **2010**, *9*, 205-213.
294. Liu, L.; Han, Z. H.; He, S. L. *Opt. Express* **2005**, *13*, 6645-6650.
295. Liao, H. W.; Nehl, C. L.; Hafner, J. H. *Nanomedicine-Uk* **2006**, *1*, 201-208.
296. Smith, D. R.; Pendry, J. B.; Wiltshire, M. C. K. *Science* **2004**, *305*, 788-792.
297. Pendry, J. B.; Schurig, D.; Smith, D. R. *Science* **2006**, *312*, 1780-1782.
298. Zheludev, N. I. *Science* **2010**, *328*, 582-583.
299. Zheludev, N. I.; Kivshar, Y. S. *Nat. Mater.* **2012**, *11*, 917-924.
300. Zheludev, N. I. *Science* **2015**, *348*, 973-974.
301. Autore, M.; D'Apuzzo, F.; Gaspare, A. D.; Giliberti, V.; Limaj, O.; Roy, P.; Brahlek, M.; Koirala, N.; Oh, S.; Abajo, F. J. G. d., *et al. Advanced Optical Materials* **2015**.
302. Zhao, M.; Bosman, M.; Danesh, M.; Zeng, M. G.; Song, P.; Darma, Y.; Rusydi, A.; Lin, H.; Qiu, C.-W.; Loh, K. P. *Nano Lett.* **2015**.
303. Blaber, M. G.; Arnold, M. D.; Ford, M. J. *J Phys-Condens Mat* **2010**, *22*.
304. Kim, J.; Naik, G. V.; Gavrilenko, A. V.; Dondapati, K.; Gavrilenko, V. I.; Prokes, S. M.; Glembocki, O. J.; Shalae, V. M.; Boltasseva, A. *Phys Rev X* **2013**, *3*.
305. Madelung, O.; Rössler, U.; Schulz, M. *Non-Tetrahedrally Bonded Elements and Binary Compounds I*. Springer: 1998; p 1-4.
306. Ren, Z.; Taskin, A. A.; Sasaki, S.; Segawa, K.; Ando, Y. *Phys. Rev. B* **2011**, *84*.
307. Minaev, B. F.; Muldakhmetov, Z. M. *Opt. Spektrosk.* **1984**, *56*, 48-52.
308. Yazyev, O. V.; Kioupakis, E.; Moore, J. E.; Louie, S. G. *Phys. Rev. B* **2012**, *85*.
309. Chang, J. W.; Register, L. F.; Banerjee, S. K.; Sahu, B. *Phys. Rev. B* **2011**, *83*.
310. Fu, L.; Kane, C. L.; Mele, E. J. *Phys. Rev. Lett.* **2007**, *98*.
311. Zhang, H. J.; Liu, C. X.; Qi, X. L.; Dai, X.; Fang, Z.; Zhang, S. C. *Nat. Phys.* **2009**, *5*, 438-442.

312. Aguilera, I.; Friedrich, C.; Bihlmayer, G.; Blugel, S. *Phys. Rev. B* **2013**, *88*.
313. Kioupakis, E.; Tiago, M. L.; Louie, S. G. *Phys. Rev. B* **2010**, *82*.
314. West, P. R.; Ishii, S.; Naik, G. V.; Emani, N. K.; Shalaev, V. M.; Boltasseva, A. *Laser Photonics Rev.* **2010**, *4*, 795-808.
315. Ou, J.-Y.; So, J.-K.; Adamo, G.; Sulaev, A.; Wang, L.; Zheludev, N. I. *Nat Commun* **2014**, *5*.
316. Adachi, S. *The Handbook on Optical Constants of Semiconductors: In Tables and Figures*. World Scientific: 2012.
317. Sharma, Y.; Srivastava, P. *Aip Conf Proc* **2010**, *1249*, 183-187.
318. Naik, G. V.; Shalaev, V. M.; Boltasseva, A. *Adv. Mater.* **2013**, *25*, 3264-3294.
319. Zhang, W.; Yu, R.; Zhang, H. J.; Dai, X.; Fang, Z. *New J. Phys.* **2010**, *12*.
320. Zhang, Y.; He, K.; Chang, C. Z.; Song, C. L.; Wang, L. L.; Chen, X.; Jia, J. F.; Fang, Z.; Dai, X.; Shan, W. Y., *et al. Nat. Phys.* **2010**, *6*, 584-588.
321. Liou, S. C.; Chu, M. W.; Sankar, R.; Huang, F. T.; Shu, G. J.; Chou, F. C.; Chen, C. H. *Phys. Rev. B* **2013**, *87*.
322. Bansal, N.; Kim, Y. S.; Brahlek, M.; Edrey, E.; Oh, S. *Phys. Rev. Lett.* **2012**, *109*.
323. Profumo, R. E. V.; Asgari, R.; Polini, M.; MacDonald, A. H. *Phys. Rev. B* **2012**, *85*.
324. Sarma, S. D.; Hwang, E. H. *Phys. Rev. Lett.* **2009**, *102*.
325. Dubrovkin, A. M.; Adamo, G.; Sulaev, A.; Wang, Q. J.; Wang, L.; Zheludev, N. I. Near-Field Detection of Plasmonic Modes in Topological Insulator Nanostructures in the Visible Part of the Spectrum. In *CLEO/Europe - EQEC 2015: Conference Digest*, Munich, 2015.
326. Zhao, M.; Bosman, M.; Danesh, M.; Zeng, M.; Song, P.; Darma, Y.; Rusydi, A.; Lin, H.; Qiu, C. W.; Loh, K. P. *Nano Lett* **2015**, *15*, 8331-8335.
327. Xia, B.; Ren, P.; Sulaev, A.; Liu, P.; Shen, S. Q.; Wang, L. *Phys Rev B* **2013**, *87*.

Appendixes

A. Appendix to Chapter 3

Figure A.1. Optimized molecular structures of ground, charged and first excited states of RR- and RRa-P3HT.

Figure A.2. Calculated Raman spectra of RR-P3HT with repeated units from 2 to 8.

Figure A.3. B3LYP/6-31G* eigenvectors of vibrational modes for ground states of RR- and RRa-P3HT.

Figure A.4. B3LYP/6-31G* eigenvectors of vibrational modes for polaron states (P3HT⁺) of RR- and RRa-P3HT.

Figure A.5. B3LYP/6-31G* eigenvectors of vibrational modes for singlet excited states of RR- and RRa-P3HT.

Table A.1. Main experimental IR, Raman, and PIA vibrational modes of RR- and RRa-P3HT, calculated electronic states and their assignments.

Polymer type (RR-, RRa-)	Mode wavenumber - Experiment (cm ⁻¹)			Mode wavenumber - Theory (cm ⁻¹)				Optical activity
	Photo-doping	IR	Raman	IR-Ground	IR-Polaron (Singlet)	IR-Excited (Singlet)	Raman - Ground	
RR			599					
RR	681		678	686	689	680	696	
RRa	687			684	687	677		
RR	727	725	727	705				
RRa	731	727		712	708	697		
RR	818	820		814		813		
RRa	820	827		812		811		
RR	1216			1191				
RRa	1218			1196				
RR	1324			1326				
RRa	1326			1334				
RR	1386			1376				
RRa	1388			1378				
RR	1375	1369	1382	1386		1354	1349	
RRa	1375	1373	1375	1387		1363		
RR	1450	1464	1450	1426		1446	1430	
RRa	1458	1450, 1470	1458	1442		1448	1444	
RR	1512	1512	1512	1499		1486	1448	
RRa	1522	1516	1522	1510		1500	1483	

Table A.2. Fitting parameters of time-resolved photoluminescence spectra using TCSPC technique.

Sample	a ₁	τ ₁ (ps)	a ₂	τ ₂ (ps)
P3HT	0.58	57	0.42	337
InP(2.5 nm)/P3HT	0.64	62	0.36	322
py-InP(2.5 nm)/P3HT	0.60	56	0.40	289
InP(4.5 nm)/P3HT	0.64	51	0.36	280
py-InP(4.5 nm)/P3HT	0.68	52	0.32	277

Table A.3. Fitting parameters of kinetics for photobleaching at 600 nm.

Sample	a ₁	τ ₁ (ps)	a ₂	τ ₂ (ps)	a ₃	τ ₃ (ps)
P3HT	44%	1.6	31%	28.0	25%	866.8
InP(2.5 nm)/P3HT	51%	1.0	35%	14.3	14%	1015.4
py-InP(2.5 nm)/P3HT	55%	0.9	32%	13.9	13%	1826.6
InP(4.5 nm)/P3HT	24%	2.1	54%	71.8	22%	>10 ns
py-InP(4.5 nm)/P3HT	24%	6.5	38%	93.3	38%	>10 ns

Table A.4. Fitting parameters of kinetics for polaron at 900 nm.

Sample	a ₁	τ ₁ (ps)	a ₂	τ ₂ (ps)	a ₃	τ ₃ (ps)
P3HT	40%	1.1	30%	15.6	30%	376.4
InP(2.5 nm)/P3HT	35%	1.7	43%	17.2	22%	227.7
py-InP(2.5 nm)/P3HT	33%	2.2	35%	16.9	32%	296.5
InP(4.5 nm)/P3HT	28%	2.6	27%	23.5	45%	493.6
py-InP(4.5 nm)/P3HT	22%	2.3	26%	27.8	52%	566.3

Figure A.6. Atomic force microspectra (AFM) images of thin films of pure P3HT and InP QDs/P3HT blends with different ligands (oleylamine and pyridine).

Figure A.7. Time-resolved photoluminescence decay of thin films of P3HT and InP QDs/P3HT blends upon pulsed photoexcitation at 400 nm using fluorescence upconversion technique.

B. Appendix to Chapter 4

Figure B.1. (EDBE)PbCl₄ hole density maps. Time evolution of the hole distribution in the perovskite, showing that holes localize on both lead and halides, oscillating in time between these two sites. This originates the two self-trapped holes (STH) Pb³⁺ and Cl₂[•]. The relative energies of these two species were estimated by evaluating the energy of the system at the time 75 fs and 275 fs, where holes are preferentially localized on lead or chlorine, respectively.

Figure B.2. (EDBE)PbCl₄ electron density maps. Time evolution of the electron distribution in the perovskite, showing strong electron localization on the Pb²⁺ sites, originating the self-trapped electron Pb₂³⁺. The trapped species Pb⁺ may also be formed during the localization process, however their existence have never been demonstrated in lead halides.

Figure B.3. (EDBE)PbBr₄ hole density maps. Time evolution of the hole distribution in the perovskite, showing that holes localize on both lead and halides, oscillating in time between these two sites. This originates the two self-trapped holes (STH) Pb³⁺ and Br₂⁻. The relative energies of these two species were estimated by evaluating the energy of the system at the time 225 fs and 400 fs, where holes are preferentially localized on lead or chlorine, respectively.

Figure B.4. (EDBE)PbBr₄ electron density maps. Time evolution of the electron distribution in the perovskite, showing strong electron localization on the Pb²⁺ sites, originating the self-trapped electron Pb₂³⁺. The trapped species Pb⁺ may also be formed during the localization process, however their existence have never been demonstrated in lead halides.

C. Appendix to Chapter 5

Figure C.1. Comparison of the all-electron wavefunctions with pseudowavefunction of Bi, Sb, Te and Se atom.

Figure C.2. Band gaps of Bi_2Se_3 slabs with 3QL to 19QL.

Figure C.3. Interband transition contribution to the real (ϵ') and imaginary part (ϵ'') of the permittivity of bulk TI materials calculated by the BSE method with SOC effects.

Figure C.4. Band structures of 5QL-slab of TI materials including SOC effects.

Table C.1. Peak position of image part (ϵ'') of Bi_2Se_3 together with the dominant contributions to each peak.

Peak	Energy (eV)	Dominant Transitions	Direct Transition K-point
LDA	2.051	VBM->CBM	(0, 0.16666, -0.16666)
LDA+SOC	1.540	VBM-3->CBM, VBM-2->CBM+1	(0.33333, -0.5, -0.5)
	0.697	VBM-1->CBM, VBM->CBM+1

Figure C.5. (a) Band structure of lowest conduction band of TI slabs; (b) surface charge distribution of TI materials.

Figure C.6. (a) real and (b) image part of dielectric function for TI 5QL-slabs including SOC effects.

Table C.2. The Fermi velocity (m^*), two-dimensional carrier concentration (n_e) of surface state and 2D Dirac plasma frequency (ω_p) of 5QL-TI slabs with $W=500$ nm.

Surface	Fermi Velocity (m/s)	Carrier Concentration $n_e(e/cm^2)$	Plasma Frequency $\omega_p(eV)$
Bi ₂ Se ₃	6.66×10^5	6.33×10^{14}	0.095
Bi ₂ Se ₂ Te	6.35×10^5	2.97×10^{13}	0.077
Bi ₂ Se ₂ Te	7.84×10^5	7.91×10^{13}	0.109
Bi ₂ Te ₃	6.84×10^5	8.74×10^{13}	0.105
Sb ₂ Te ₃	5.04×10^5	5.67×10^{13}	0.081
BiSbTeSe ₂	5.15×10^5	7.74×10^{14}	0.088
BiSbTe ₂ Se	7.22×10^5	9.56×10^{14}	0.110

List of Publications

Journals

1. **J. Yin**, G. Adamo, N. I. Zheludev, C. Soci, Plasmonic Topological Insulators, in preparation.
2. **J. Yin**, Z. L. Wang, D. Fazzi, Z. X. Shen, C. Soci, A First Principles Study of the Nuclear Dynamics of Doped Conjugated Polymers, *J. Phys. Chem. C*, 2016, 120, 1994.
3. **J. Yin**, M. Kumar, Q. Lei, L. Ma, R. S. S. Kumar, G.G. Gurzadyan, and C. Soci, Small-Size Effects on Electron Transfer in P3HT/InP Quantum Dots, *J. Phys. Chem. C*, 2015, 119, 26783.
4. **J. Yin**, D. Cortecchia, A. Krishna, S. Chen, N. Mathews, A.C. Grimsdale, C. Soci, Interfacial charge transfer anisotropy in polycrystalline lead iodide perovskite films, *J. Phys. Chem. Lett.*, 2015, 6, 1396.
5. **J. Yin**, D. B. Migas, M. Panahandeh-Fard, S. Chen, Z. L. Wang, P. Lova, C. Soci, Charge Redistribution at GaAs/P3HT Heterointerfaces with Different Surface Polarity, *J. Phys. Chem. Lett.*, 2013, 4, 3303.
6. R. S. S. Kumar, **J. Yin**, G. Grancini, C. Soci, V. R. Soma, G. Lanzani, L. Giribabu, Femtosecond to Microsecond Dynamics of Soret-Band Excited Corroles, *J. Phys. Chem. C*, 2015, 119, 28691.
7. M. Panahandeh-Fard, **J. Yin**, K. Michael, Z. L. Wang, H. F. Leong, T. C. Sum, C. Soci, Ambipolar Charge Photogeneration and Transfer at GaAs/P3HT Heterointerfaces, *J. Phys. Chem. Lett.*, 2014, 5, 1144.
8. X. Y. Chin, **J. Yin**, Z. L. Wang, M. Caironi, C. Soci, Mapping polarons in polymer FETs by charge modulation microscopy in the mid-infrared, *Scientific Reports*, 2014, 4, 3626.
9. D. Cortecchia, H. A. Dewi, **J. Yin**, A. Bruno, S. Chen, T. Baikie, P. P. Boix, M. Graetzel, S. Mhaisalkar, C. Soci, N. Mathews, Lead-Free $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$ Hybrid Perovskites, *Inorg. Chem.*, 2016, 55, 1044.
10. X. Y. Chin, D. Cortecchia, **J. Yin**, A. Bruno, C. Soci Lead iodide perovskite light-emitting field-effect transistor, *Nat. Commun.*, 2015, 6, 7383.

11. A. Krishna, D. Sabba, **J. Yin**, A. Bruno, P.P. Boix, Y. Gao, H.A. Dewi, G.G. Gurzadyan, C. Soci, S.G. Mhaisalkar, A.C. Grimsdale, Facile synthesis of a furan-arylamine hole transporting material for high efficiency mesoscopic perovskite solar cells, *Chem. Eur. J.*, 2015, 21, 15113.
12. Y. Gao, T. C. He, **J. Yin**, C. Soci, A. C. Grimsdale, H. D. Sun, Rare S2 emission in a carbazole-terpyridine triad and its Zn²⁺ complex: emission mechanism, fluorescence tunability and applicability for sensors, *Dalton. Trans.*, 2016, in revision.
13. A. Krishna, D. Sabba, H. Li, **J. Yin**, P.P. Boix, C. Soci, S. G. Mhaisalkar, A. C. Grimsdale, Novel hole transporting materials based on triptycene core for high efficiency mesoscopic perovskite solar cells, *Chemical Science*, 2014, 5, 2702.

Book Chapter

1. **J. Yin**, M. Kumar, M. Panahandeh-Fard, Z. Wang, F. Scotognella, C. Soci, in: Ultrafast Dynamics in Molecules, Nanostructures and Interfaces, G. G. Gurzadyan, G. Lanzani, C. Soci, T. C. Sum, Ed., 2014, World Scientific Publishing Series in Optics and Photonics, Vol. 8 ISBN: 978-981-4556-91-0.
2. H. Diesinger, E. Chan, **J. Yin**, C. Soci, Handbook of organic materials for optical and optoelectronic devices: Properties and applications, Woodheads Publishing, Cambridge, UK (2013) ISBN-13: 978-0-85709-265-6.

Conferences (as presenter)

1. **J. Yin**, Z. Wang, W. Wu, G. Adamo, N.I. Zheludev, C. Soci, Electronic and plasmonic properties of topological insulator crystals, Conference on Materials for Advanced Technologies (ICMAT), 2015, Singapore. (oral)
2. **J. Yin**, M. Kumar, Q. Lei, G.G. Gurzadyan, C. Soci, Dimensionality effects on charge transfer at polymer/III-V heterointerfaces, Conference on Materials for Advanced Technologies (ICMAT), 2015, Singapore. (oral)
3. **J. Yin**, Z. Wang, W. Wu, G. Adamo, N.I. Zheludev, C. Soci, Electronic and optical properties of plasmonic topological insulators, CLEO Europe, 2015, Munich (Germany). (oral)

4. **J. Yin**, M. Kumar, Q. Lei, L. Ma, R.S.S. Kumar, C. Soci, Ultrafast electron transfer from P3HT to InP quantum dots: ligand and size effects, MRS Spring Meeting, San Francisco (USA). (oral)
5. **J. Yin** and C. Soci, Dimensionality Effects on Charge Transfer at Polymer/III-V Heterointerfaces for Hybrid Photovoltaic Applications, the 9th International Conference on Computational Physics, 2015 Singapore. (oral)
6. **J. Yin**, D. Cortecchia, A. Krishna, S. Chen, N. Mathews, A.C. Grimsdale, C. Soci, Interfacial modelling of lead iodide perovskite and organic charge transporting heterostructures, European Optical Society Annual Meeting (EOSAM) 2014, Berlin (German). (oral)
7. **J. Yin**, M. Kumar, Q. Lei, M. Panahandeh-Fard, D. Cortecchia, Z. L. Wang, R. S. S. Kumar, and C. Soci, Ultrafast Electron Transfer from P3HT to Pyridine-Capped InP Quantum Dots, EMRS Spring 2014, Lille (France). (oral)
8. **J. Yin**, M. Kumar, Q. Lei, M. Panahandeh-Fard, D. Cortecchia, Z. L. Wang, R.S.S. Kumar, and C. Soci, Pyridine-capped InP Quantum Dots as Electron Acceptors for Polymer Photovoltaics, IPS 2014, Singapore. (oral)
9. **J. Yin**, Dmitri B. Migas, Majid Panahandeh-Fard, Zilong Wang, Shi Chen, Cesare Soci, Molecular Dynamics Simulations of Photoexcited Charge Transfer and Recombination Processes at GaAs/P3HT Interfaces, ICMAT 2013, Singapore. (poster)
10. **J. Yin**, M. Panahandeh-Fard, D. B. Migas, Z. L. Wang, S. Chen, C. Soci, P3HT/GaAs Heterointerfaces: a First-Principle Study of Polar GaAs(111)B and Nonpolar GaAs(110) Surfaces, EMRS Spring 2013, Strasbourg (France). (poster)
11. **J. Yin**, Z. L. Wang, X. Y. Chin, Z. X. Shen, C. Soci, A Study of IR/V Modes in Conjugated Polymers by Density Functional Theory: Intra- and Inter-Chain Effects, MRS Fall 2012, Boston (USA). (poster)