

Photophysics at Interfaces between Metal–Halide Semiconductors and Charge–Transport Layers



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Abstract

Metal-halide semiconductors have emerged as promising materials for solar cells, with lead-based perovskites demonstrating remarkable efficiencies in tandem architectures. Yet, their performance still falls short of the theoretical limit, especially for wide-bandgap semiconductors, primarily due to interfacial losses at the semiconductor/charge-transport layer interface. This thesis investigates the photophysics at these interfaces through various spectroscopic techniques, providing insights into the underlying loss mechanisms and guiding mitigating strategies to achieve higher efficiencies.

Unfavourable energy-level alignment at the interface with charge-transport layers results in substantial open-circuit voltage losses. A systematic increase in the valence band maximum of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ with increasing bromide content x from 0 to 1, when interfaced with the commonly employed hole transport layer poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), provides an ideal platform to study photophysical losses arising from energy-level misalignment. The combination of time-resolved photoluminescence and numerical modeling reveals that increasing energy-level misalignment leads to increasing accumulation of holes in PTAA, which then subsequently recombine non-radiatively across the interface via interfacial defects, thereby reducing the open-circuit voltage and overall device efficiency.

Wide-bandgap mixed-halide perovskites often suffer from halide segregation where prolonged illumination drives a spatial separation of the mixed-phase perovskite into both iodide-rich (I-rich) and bromide-rich domains. By using a synchronous multimodal spectroscopy that combines time-resolved photoluminescence, time-resolved microwave conductivity and steady-state photoluminescence spectroscopy, the effect of halide segregation on the interfacial processes at $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ interfaced with commonly used charge-transport layers such as PTAA and SnO_2 is investigated. In neat perovskite films, halide segregation enhances radiative bimolecular recombination as charge-carrier funnelling increases the local carrier density within the narrow bandgap I-rich domains. Nevertheless, the charge-carrier mobility remains largely preserved after segregation. In the presence of charge-transport layers, charge extraction occurs predominantly via the I-rich phase following segregation. Although mobility retention is reduced in these heterostructures, the transport layers facilitate charge back transfer, mitigating the reduction in carrier lifetime at later times. The combined decrease in lifetime owing to enhanced radiative recombination and reduction in mobilities limits the diffusion length and therefore charge-carrier collection efficiency after halide segregation.

Concerns over the lead toxicity and instability of metal-halide perovskites have motivated the development of lead-free, all-inorganic $\text{Cu}_2\text{AgBiI}_6$ within the CuI-AgI-BiI_3 phase space. However, it suffers from lower device efficiencies compared to its lead-perovskite counterparts, primarily due to poor charge-collection efficiency. Optoelectronic studies of coevaporated $\text{Cu}_2\text{AgBiI}_6$ interfaced with various charge-transport layers such as PTAA, CuI , [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and SnO_2 revealed that inorganic transport layers such as CuI and SnO_2 induce the formation of unintended impurity phases within the CuI-AgI-BiI_3 phase space, significantly altering structural and optoelectronic properties. These impurities reduce charge-carrier mobilities and diffusion lengths, thereby limiting its device efficiency.

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List of Abbreviations

BSE	Backscattered electrons
CABI	$\text{Cu}_2\text{AgBiI}_6$
CB	Conduction band
CBM	Conduction band minimum
CCD	Charge-coupled device
c-Si	Crystalline silicon
CTL	Charge-transport layer
CW	Continuous-wave
DFT	Density functional theory
DOS	Density of states
EO	Electro-optic
EQE	External quantum efficiency
ETL	Electron transport layer
E_g	Bandgap
FA	Formamidinium $\text{CH}(\text{NH}_2)_2$
FM	Ferromagnetic
fs	Femtosecond
FWHM	Full width at half maximum
HOMO	Highest occupied molecular orbital
iCCD	Intensified charge-coupled device
IPES	Inverse photoemission spectroscopy
IRF	Instrument response function
J_{SC}	Short-circuit current
LO	Longitudinal optical
LUMO	Lowest unoccupied molecular orbital
MA	Methylammonium CH_3NH_3
MHP	Metal-halide perovskite

MW	Microwave
NM	Non-ferromagnetic
ND	Neutral-density
ns	Nanosecond
OD	Optical density
OPTP	Optical-pump terahertz-probe
P3HT	Poly(3-hexylthiophene-2,5-diyl)
PCBM	[6,6]-Phenyl-C ₆₁ -butyric acid methyl ester
PCE	Power conversion efficiency
PL	Photoluminescence
PLQ	Photoluminescence quenching
PLQY	Photoluminescence quantum yield
PMMA	Poly(methyl methacrylate)
ps	Picosecond
PTAA	Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine]
QFLS	Quasi-Fermi level splitting
$\lambda/4$	Quarter-wave plate
SCXRD	Single-crystal X-ray diffraction
SE	Secondary electrons
SEM	Scanning electron microscopy
SCLC	Space-charge-limited current
SnO ₂	Tin(IV) oxide
SPAD	Single-photon avalanche diode
SQ	Shockley–Queisser
SRH	Shockley–Read–Hall
SRV	Surface recombination velocity
ssPL	Steady-state photoluminescence
TCSPC	Time-correlated single-photon counting
TEM-EDX	Transmission electron microscopy energy-dispersive X-ray spectroscopy
THz	Terahertz
TOF	Time-of-flight

TRMC	Time-resolved microwave conductivity
TRPL	Time-resolved photoluminescence
UPS	Ultraviolet photoemission spectroscopy
VB	Valence band
VBM	Valence band maximum
V_{OC}	Open-circuit voltage
WBP	Wide-bandgap perovskite
XRD	X-ray diffraction

1

Introduction

With the international effort to limit the rise in the global temperature to 1.5 °C,[1] a transition from the extensive use of coal and fossil fuels to renewable energy has become paramount. In particular, direct conversion of solar energy to electricity with photovoltaics is so far the most promising source of renewable energy with significant reduction in the manufacturing cost and increase in the efficiency of crystalline silicon (c-Si) solar cells.[2, 3] However, silicon is not an ideal semiconductor for photovoltaic applications owing to its indirect bandgap at 1.12 eV, which results in weak absorption in the near-infrared region, and enhanced nonradiative Auger recombination.[4–6] Moreover, purification of silicon from silicon oxide requires a tremendous amount of heat (2400 K) in an electric furnace, producing ~ 5 tons CO₂ per ton of Si.[7, 8] In contrast, next-generation solar cells, such as perovskite solar cells introduced later, exhibit a substantially smaller carbon footprint by employing spin-coating methods that only require annealing temperature below 200 °C.[9–11]

In order to circumvent the disadvantages of c-Si solar cells, a type of third-generation solar cell called metal-halide perovskite (MHP) solar cell was developed. As discussed in Chapter 2, MHPs have favourable optoelectronic properties for photovoltaic applications such as high optical absorption coefficients (10^5 cm^{-1}), sharp absorption edges with Urbach energy as small

as 15 meV, high charge-carrier mobilities around tens of $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, bimolecular charge-carrier recombination rates below the Langevin limit for kinetic recombination by at least four orders of magnitude, low exciton binding energy for generation of free charge carriers at room temperature, high defect tolerance and tunability of bandgap in the range of 1.5~2.3 eV.[10, 12–17] These properties contribute to high open-circuit voltages (V_{OC}), long charge-carrier lifetimes and micrometer diffusion lengths, enabling high power conversion efficiencies (PCE). With careful device engineering strategies, the PCE of MHP solar cells has increased from 3.81% in 2009 to 26.95% in 2025, approaching the record PCE of 27.3% for c-Si solar cells.[2] Owing to the bandgap tunability of mixed-halide MHP, further opportunities exist when it is stacked together with c-Si for a tandem solar cell where the narrow bandgap of c-Si is complemented with a wide-bandgap (≥ 1.7 eV) mixed-halide perovskite, reaching the record efficiency of 34.85%, surpassing the thermodynamic limit of a single junction solar cell.[18] However, the present efficiency of c-Si/perovskite tandem solar cells remains well below the theoretical limit of 45.3%. One of the major limitations arises from the suboptimal interface between wide-bandgap perovskites and charge-transport layers (CTLs), which causes V_{OC} to saturate at approximately 1.2 eV for bandgaps above 1.7 eV.[19] Therefore, understanding the loss mechanisms at these interfaces is essential for developing effective mitigation strategies.

In addition, mixed-halide perovskites suffer from halide segregation under illumination where the mixed iodide/bromide phase evolves into separate bromide- and iodide-rich domains. The iodide-rich phase has a lower bandgap compared to mixed phase,[20] compromising V_{OC} and charge-carrier extraction due to the band misalignment with the CTLs, which are typically optimized for the mixed phase.[21, 22]

To address the instability of MHPs under ambient operating conditions and concerns regarding lead toxicity, the research community has explored new classes of materials that overcome these limitations while providing ideal bandgaps for tandem solar cells. Among them, the quaternary compound $\text{Cu}_2\text{AgBiI}_6$ (CABI) in the CuI–AgI–BiI₃ phase space has

attracted considerable attention due to its superior stability arising from its all-inorganic composition,[23] a direct bandgap with high absorption coefficient,[23] and moderate mobility retention of $\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, despite ultrafast localization processes.[24] Despite these favourable optoelectronic properties, the efficiency remains limited to 2.39%, which may in part originate from interfacial losses.

Therefore, this thesis first investigates the photophysics at interfaces between MHPs and CTLs, which represent a critical bottleneck to its efficiency and stability. Particular emphasis is placed on wide-bandgap mixed-halide perovskites, where interfacial losses and halide segregation compromise tandem performance. Moreover, it extends beyond MHPs to examine the promising coevaporated lead-free absorber CABI, where CTLs strongly affect film deposition, inducing impurities and hindering charge-carrier extraction. The overarching aim of this thesis is to elucidate the dominant interfacial loss mechanisms in order to guide the development of future mitigation strategies.

Thesis Overview

Chapter 2 establishes a general understanding of MHPs and CABI, which is essential for interpreting the work presented in this thesis. It begins with an introduction to the structural and optoelectronic properties of MHPs, followed by a discussion of halide segregation and the influence of charge-transport layers on device performance and charge-carrier dynamics. The chapter concludes with an overview of the CuI–AgI–BiI₃ phase space, with particular emphasis on Cu₂AgBiI₆ (CABI), highlighting its structural characteristics and unique charge-carrier localization process.

Chapter 3 introduces and explains experimental techniques and setups used for the studies presented here. These include absorption spectroscopy, photoluminescence spectroscopy, encompassing steady-state (ssPL) and time-resolved (TRPL) measurements, optical-pump

terahertz-probe (OTTP) spectroscopy, time-resolved microwave conductivity (TRMC) spectroscopy, applied as part of synchronous multimodal spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and finally, sample fabrication.

Chapter 4 presents the first experimental results of this thesis, focusing on the charge-carrier dynamics at the interface between $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ (with bromide content x ranging from 0 to 1) and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA). Time-correlated single photon counting (TCSPC), combined with numerical modelling, revealed the charge-carrier dynamics at the interface. Increasing bromide content enhances the energetic offset between the valence band maximum (VBM) of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ and the highest occupied molecular orbital (HOMO) of PTAA, which in turn enhances non-radiative losses owing to reduced hole back-transfer from PTAA and increased across-interface recombination. Therefore, better energetic alignment between $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ and PTAA is critical for minimising the interfacial losses. The numerical modelling further demonstrates the effect of the interfacial processes on the TRPL dynamics and their consequent impact on device performance, particularly on V_{OC} , is discussed.

Wide-bandgap mixed-halide perovskites suffer from halide segregation under prolonged illumination in addition to the interfacial losses discussed in Chapter 4. As an extension, Chapter 5 investigates how halide segregation affects the charge-carrier dynamics at the interface of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ with either the PTAA HTL or the SnO_2 electron transport layer (ETL). Synchronous multimodal spectroscopy combining TRPL, TRMC and ssPL enables decoupling of the charge-selective processes originating either from trap-assisted recombination or interfacial charge transfer from bimolecular radiative recombination while simultaneously tracking the extent of halide segregation with ssPL. The results reveal that charge-carrier funnelling into the I-rich phase enhances radiative recombination while largely preserving carrier mobilities. However, less mobility retention is observed in the presence of charge-transport layers, whereas charge-back transfer alleviates the lifetime reduction caused by

enhanced radiative recombination. The combined effect of reduced lifetime and mobility leads to reduced diffusion lengths, compromising charge-collection efficiency. The adverse effects of halide segregation on device performance are discussed in further detail.

Transitioning to the novel CuI–AgI–BiI₃ phase space, Chapter 6 investigates the influence of commonly used HTLs (PTAA and CuI) and ETLs ([6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and SnO₂) on the composition, crystallinity and morphology of co-evaporated CABI, and assesses how these modifications affect its optoelectronic properties. Owing to the large phase space available for CuI–AgI–BiI₃ compounds, coevaporation of CABI is susceptible to the formation of unintended phases. The combination of XRD and OPTP enables disentanglement of various phases within the CuI–AgI–BiI₃ phase space from CABI. These impurity phases compromise the crystallinity, morphology, and therefore optoelectronic properties of CABI, highlighting the need for improved coevaporated deposition strategies on CTLs to achieve phase-pure CABI and ultimately enhanced device performance.

Chapter 7 summarises the work presented earlier in the thesis, and outline its implication for future research. Additionally, Appendices A, B and C provide supplementary discussions and data for Chapters 4, 5 and 6, respectively.

2

Theory and Background

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This chapter introduces the fundamental properties of metal-halide semiconductors, beginning with metal–halide perovskites (MHPs) and extending to novel CuI–AgI–BiI₃ compounds. Particular emphasis is placed on the interactions with charge–transport layers (CTLs), which form the central theme of the work presented in this thesis.

2.1 Metal-halide Perovskites

2.1.1 Crystal Structure

MHPs belong to the perovskite family, which is derived from the original perovskite mineral CaTiO_3 . MHPs have a general chemical formula ABX_3 , which consists of corner-sharing BX_6 octahedra forming an extended three-dimensional (3D) network with A cation residing in the cuboctahedral spaces formed within the BX_6 octahedra as shown in Figure 2.1.[25]

Typical A monovalent cations in MHPs are CH_3NH_3^+ (MA^+), $\text{HC}(\text{NH}_2)_2^+$ (FA^+), and Cs^+ . Common B divalent cations are Pb^{2+} , and Sn^{2+} . X site anions are I^- , Br^- , and Cl^- . The sum of valence charge of A and B site cations should be equal to X anions to maintain charge neutrality. Various combinations of A, B and X can be used to construct MHPs but the stability of such combination is dependent on the relative sizes of ions. This restriction is expressed by the Goldschmidt tolerance factor, t , which measures the likelihood of A cations to fit in the cavities within the BX_3^{-1} framework:[26]

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (2.1)$$

where r_A is the ionic radius of the A cation, r_B is the ionic radius of the B cation and r_X is the ionic radius of the X halide. The A cation fits perfectly into the the BX_3^{-1} framework if $t = 1$. It has been empirically found that MHPs take a stable perovskite structure if t lies in the range from 0.76 to 1.13.[27] Generally, a cubic structure is likely to be achieved if t lies between 0.89 and 1.0 and tetragonal or orthorhombic structures are likely to form if t is less than that range.[12] Although the Goldschmidt tolerance factor gives insight into the possible combinations of ions, it is not a sufficient condition for the formation of a perovskite structure. In addition, an octahedral factor μ_{oct} , which estimates the preference of BX_6 octahedral formation, is required for an assessment of stability :[27]

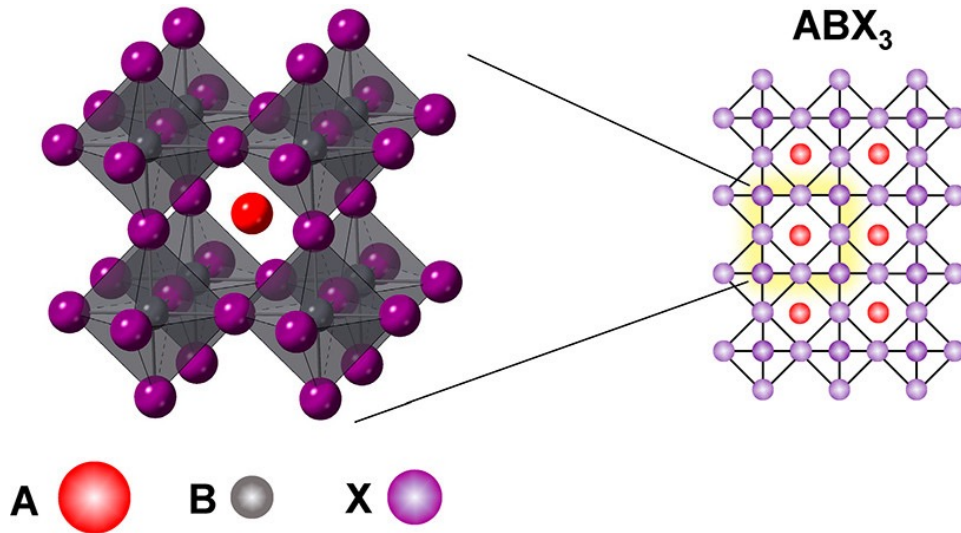


Figure 2.1: 3D crystal structure of metal-halide perovskite (MHP) where A monovalent cations (red spheres) reside with the octahedra formed by B divalent cations (grey spheres) and X halides (purple spheres). Reprinted from Ref [25] with permission. Copyright © 2019, American Chemical Society.

$$\mu_{\text{oct}} = \frac{r_B}{r_X} \quad (2.2)$$

The condition for the stability of the perovskite structure is satisfied for μ_{oct} between 0.414 and 0.732.[27] Although these parameters assume hard-sphere packing and neglect interatomic interactions, they give useful physical intuitions to predict the stability of MHP structures.

The crystal structure of MHPs is also dependent on temperature. For example, MAPbI_3 adopts the cubic phase ($pm\bar{3}m$) at $T > 327\text{ K}$, the tetragonal phase ($I4/mcm$) at $165\text{ K} < T < 327\text{ K}$ and the orthorhombic phase ($pnma$) at $T < 165\text{ K}$. [28] Such transitions are induced by the distortion of BX_6 octahedra as described before. To achieve the favourable cubic structure, MHPs are thermally annealed during the fabrication process.

2.1.2 Bandgap Tunability

The bandgap of MHPs is highly tunable, as different choices of A-site, B-site cations and X-site halide anions in the ABX_3 crystal structure directly modify their electronic structure.[29, 30] Understanding these variations requires a fundamental knowledge of bandgap formation in semiconductors. In a crystalline solid, atoms are arranged periodically, thereby giving rise to a

periodic potential. According to Bloch's theorem, the solutions of the Schrödinger equation in such a potential are Bloch functions.[31–34]

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_{\mathbf{k}}(\mathbf{r}) \quad (2.3)$$

where $\mathbf{r}$ is the position, $\mathbf{k}$ is the crystal momentum and $\mathbf{R}$ is the translation vector. In the tight-binding model, electrons are considered to be bound to atomic nuclei and allowed to move to neighbouring lattice sites through quantum tunnelling. For a one-dimensional chain, the resulting electron wavefunction of the crystal is then constructed as a linear combination of atomic orbitals (LCAO), subject to a normalization condition.[33]

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_j e^{i\mathbf{k} \cdot \mathbf{r}_j} \varphi(\mathbf{r} - \mathbf{r}_j) \quad (2.4)$$

where N is the number of atoms in the chain and φ is the atomic orbital. Solving the Schrödinger equation with this wavefunction yields the following dispersion relation:[31]

$$E(k) = \epsilon_0 - 2t \cos(ka) \quad (2.5)$$

where t is the hopping term and a is the atomic separation. In the limit of a large number of atoms, the discrete levels split into a continuous band of width $4t$.

In semiconductors, multiple atomic orbitals overlap and hybridize to produce distinct bonding and antibonding bands as shown in Figure 2.2. The highest occupied bonding states form the valence band (VB), while the lowest unoccupied states define the conduction band (CB). The bandgap E_g emerges as the energy separation between these bands.[31–35]

Experimentally, photoelectron spectroscopic techniques such as ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPES) are commonly employed to determine the positions of the valence band maximum (VBM) and conduction band minimum (CBM), respectively.[29] In UPS, the VBM is extracted by analyzing the kinetic energy of

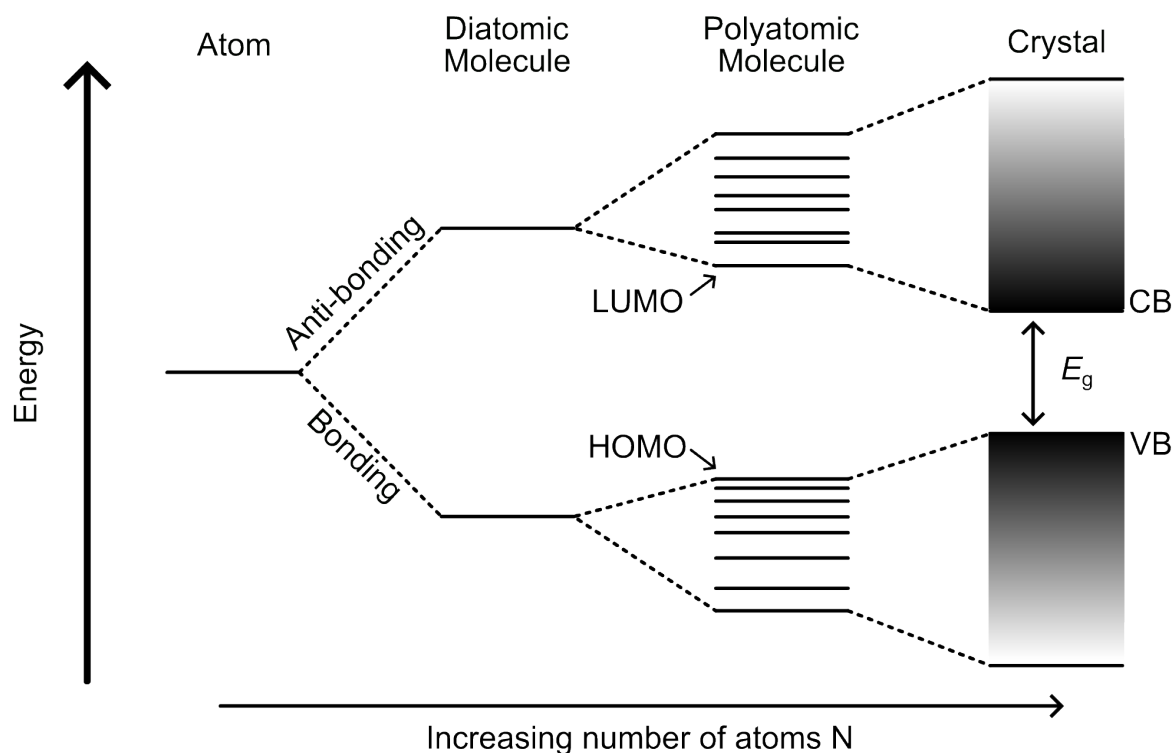


Figure 2.2: A schematic of band formation in a solid. Starting from discrete atomic energy level in an isolated atom, the interaction of orbitals upon bringing multiple atoms together leads to the energy level splitting. For a crystal with N atoms, these level broaden to form the valence band (VB) and conduction band (CB) separated by the bandgap E_g .

photoelectrons emitted upon ionization by incident photons. IPES provides a complementary measurement for CBM: in this case, a collimated electron beam is directed onto the material, and the emitted photons are detected to probe the energies of the unoccupied electronic states. The experimental CBM and VBM positions are typically compared with density functional theory (DFT) calculations, often interpreted through tight-binding analysis, to assign the orbital contributions to the band edges.^[29]

For perovskites with the ABX_3 structure, substituting the halide anion (X) from I to Br to Cl systematically increases the bandgap, as shown in Figure 2.3a. This trend is primarily governed by a downward shift of the VBM.^[30] As the electronegativity of the halide increases, the energy of the X np orbitals decreases, thereby lowering the VBM. At the same time, the increased electronegativity shortens the Pb–X bond length, which enhances electronic confinement on the Pb atom and raises the energy of its 6p orbital, leading to an increase in

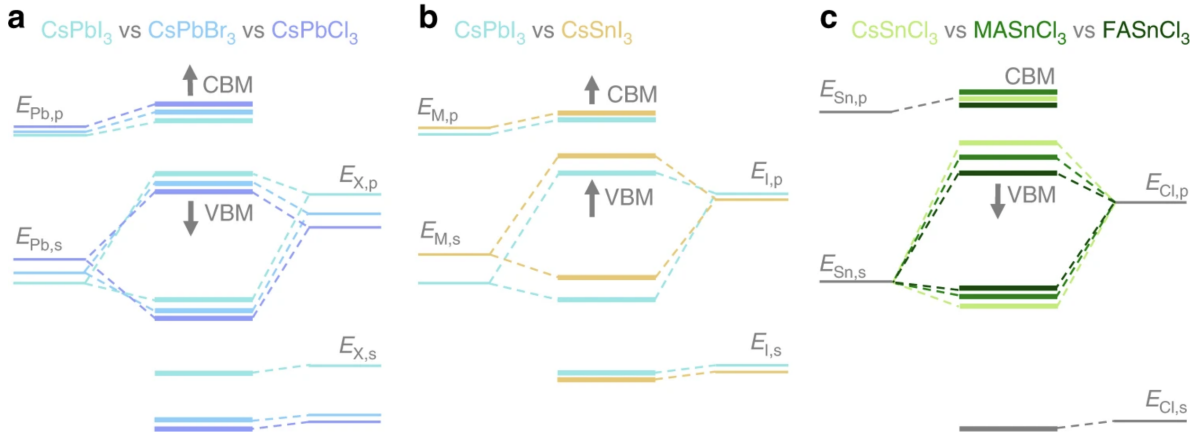


Figure 2.3: Schematic energy levels in ABX_3 perovskites. (a) and (b) represent trends in changing the halide anions X and the metal cations B, respectively, as identified from the tight-binding analysis. (c) is an intuitive illustration of energy-level changes based on structural distortions in tin-based perovskites upon A-site cation substitutions. Arrows indicate the shift in energy levels upon atom or small molecule substitution. Reprinted from Ref [29] with permission. Copyright © 2019, Springer Nature.

its CBM and therefore in the bandgap. However, this confinement also raises the energy of the Pb 6s state, which increases the VBM. Moreover, the Pb 6s/X np hybridization strength increases from I to Br to Cl, shifting the VBM upward. These effects are comparatively minor, leading to an overall increase in E_g . [29]

When Pb is replaced by the smaller and more electronegative Sn at the B-site, both the VBM and CBM shift upwards due to the higher energies of the Sn 5s and 5p orbitals compared to those of Pb. The energy splitting between the s and p states of Sn is smaller than that in Pb, which reduces the bandgap as shown in Figure 2.3b. [29]

The A-site cation do not directly participate in the bonding but it influences the electronic structure indirectly by changing the volume of the AMX_3 crystal or by introducing distortion from the ideal perovskite structure based on Equation 2.1. Such distortions and volume expansion reduce the degree of hybridization and electronic confinement between B-site cation and X-site halides, leading to the downward shift in the VBM as shown in Figure 2.3c. [29]

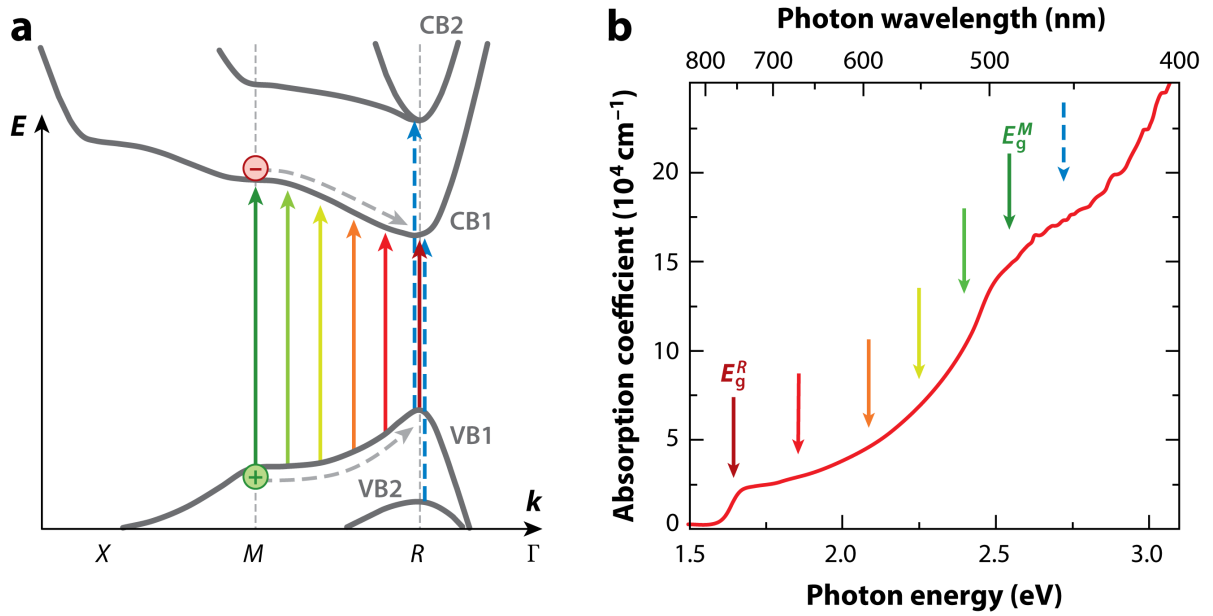


Figure 2.4: (a) Electronic band structure of metal-halide perovskite. The coloured arrows between the valence band (VB) and the conduction band (CB) represent allowed optical transition where the photo-generation of an electron-hole pair is possible. The grey arrows represent the charge-carrier relaxation process to the band edge via thermalization. The blue dashed lines are allowed transitions between different bands. (b) Absorption spectrum of MAPbI₃ with arrows indicating optically allowed transitions shown in (a). Reprinted from Ref [36] with permission. Copyright © 2016, Annual Reviews.

2.1.3 Optoelectronic Properties

2.1.3.1 Absorption

The generation of electron-hole pairs through light absorption is the fundamental process underlying solar cell operation. In an intrinsic semiconductor, the valence band (VB) is fully occupied while the conduction band (CB) is empty, separated by the bandgap energy E_g . When photons with energy greater than or equal to E_g ($\hbar\omega_{\text{photon}} \geq E_g$) are absorbed, electrons are excited into the CB, leaving behind positively charged holes in the VB (see Figure 2.4). Any excess photon energy above E_g may be dissipated through carrier-lattice interactions in a process known as thermalization.[35] The resulting electron and hole populations possess electrochemical potential energy that can be extracted as electrical power when collected at the contacts of the photovoltaic device.[35]

In this regard, MHPs are considered as an excellent active-layer material exhibiting a high

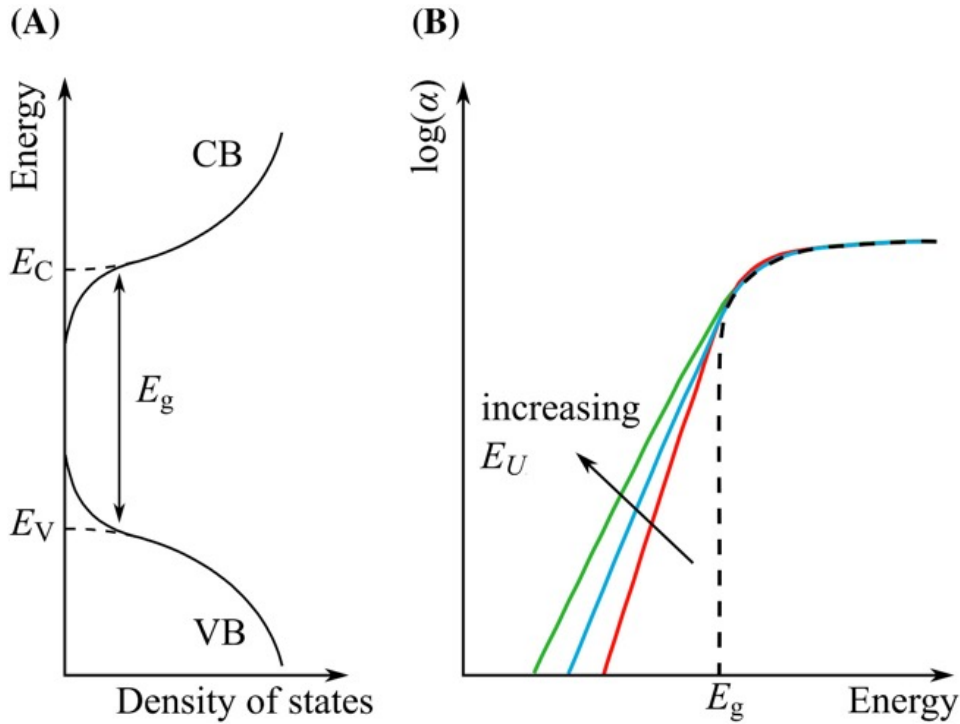


Figure 2.5: (a) In the case of an ideal direct semiconductor, CB and VB band density of states (DOS) do not extend into the bandgap (dashed lines). However, in reality, the DOS may extend exponentially into the bandgap (solid lines). (b) Representative absorption spectra of ideal (dashed lines) and of a real semiconductor (solid lines). As the DOS extends further into the bandgap, the Urbach energy (E_U) increases, giving rise to additional sub-bandgap states that enable optical transitions. The more the DOS extends into the bandgap, the larger the Urbach energy and more sub-bandgap states for transition. Reprinted from Ref [37] with permission. Copyright © 2021, John Wiley & Sons Ltd.

optical absorption coefficient exceeding 10^5 cm^{-1} owing to their direct-bandgap nature.[12]

As a result, thin films, only a few hundred nanometers thick, are sufficient to absorb most of the solar light, in contrast to indirect-bandgap semiconductors such as silicon, which require micrometer-thick active layers to achieve comparable absorption.[5, 10]

The absorption properties of MHPs can be significantly affected by excitonic effects, which give rise to sharp absorption features near the band edge.[38, 39] Excitons are bound electron-hole pairs formed via Coulombic interaction, characterised by a finite exciton binding energy E_b . [38] Although excitons exhibit enhanced oscillator strength at the band edge due to strong electron-hole wavefunction overlap, they can be detrimental to solar cell operation, as they must first dissociate into free charge carriers in order to contribute to the photocurrent.[36] Fortunately, many 3D bulk MHPs possess sufficiently low E_b comparable to the thermal energy

at room temperature ($k_B T \approx 26$ meV), allowing them to dissociate into the free carriers for efficient extraction.[16]

Last but not least, compositional inhomogeneity and defects contribute to sub-bandgap absorption through an exponential extension of the density of states (DOS) into the bandgap. These extended band tails are known as Urbach tails.[37] The presence of such defects compromises solar cell performance by enhancing trap-assisted recombination and hindering charge-carrier transport, as will be discussed in the following sections.[40]

2.1.3.2 Transport

Once electron-hole pairs are generated, they must be able to travel through the whole thickness of the active layer before recombining for efficient extraction. This ability is quantified by the diffusion length L_D , which is defined as:[36]

$$L_D = \sqrt{\frac{\mu k_B T}{e R_T}} \quad (2.6)$$

where μ is the charge-carrier mobility, e is the elementary charge, T is the temperature, k_B is the Boltzmann constant, and R_T is their total charge-carrier recombination rate, which is discussed further in Section 2.1.3.3. A high mobility and long carrier lifetime are therefore both beneficial for achieving a large L_D .

For MHPs, the reported μ values in literature vary by up to two orders of magnitude (2–600 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) depending on the measurement techniques, fabrication methods and compositions of MHP.[14] Measurement techniques can be broadly divided into electrical probes such as space-charge-limited current (SCLC) techniques, Hall effect measurements combined with electrical resistivity measurements, and time-of-flight (TOF) techniques, and non-contact probes such as optical-pump terahertz-probe (OPTP), time-resolved microwave conductivity (TRMC) and photoluminescence quenching (PLQ) techniques. The wide range of μ values might be caused by different spectroscopic techniques probing different spatial regions, where high-frequency

conductivity measurements such as terahertz (THz) probe local charge carrier motions and are therefore less affected by grain boundaries, which can impede charge-carrier motion, than long-range current-extraction or charge-carrier diffusion experiments.[14] For electrical probes, the quality of the electrode contact may also affect the accuracy of measurement.[14]

The charge-carrier mobility is limited by intrinsic and extrinsic factors. Intrinsic limitations arise from the inevitable interaction between charge-carriers and the crystal lattice. Rigorous experimental studies and first-principles calculations have established that Fröhlich interactions are the dominant mechanism limiting the charge-carrier mobilities of MHP at room temperature.[14, 41] These interactions originate from the macroscopic electric field generated by longitudinal optical (LO) phonons coupling to charge carriers in polar semiconductors such as MHPs.[42] Such interactions give rise to quasi-particles known as large polarons, which carry a local polarization field as it moves, thereby reducing its kinetic energy and effective mobility while increasing its effective mass. In contrast, extrinsic limitations to mobility arise from grain boundaries, dopants, and a disordered energy landscape.[14] Despite the presence of such extrinsic effects in solution-processed MHPs, their average charge-carrier mobilities remain on the order of tens of $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ on average.[14] Owing to their high charge-carrier mobilities and long lifetimes, which will be discussed in the next section, MHPs can achieve diffusion lengths over $1\ \mu\text{m}$. [43]

2.1.3.3 Recombination

Considering a 3D bulk MHP film, the charge-carrier recombination dynamics of free charge-carriers can be described by the following generic ABC model:[36]

$$\frac{dn(t)}{dt} = -k_{\text{nonrad}}n - R_{\text{eh}}n^2 - R_{\text{Auger}}n^3 \quad (2.7)$$

where k_{nonrad} , R_{eh} , and R_{Auger} are the rates of monomolecular, bimolecular, and Auger recombination, and n is the density of charge carriers. Upon excitation, an electron in the valence band

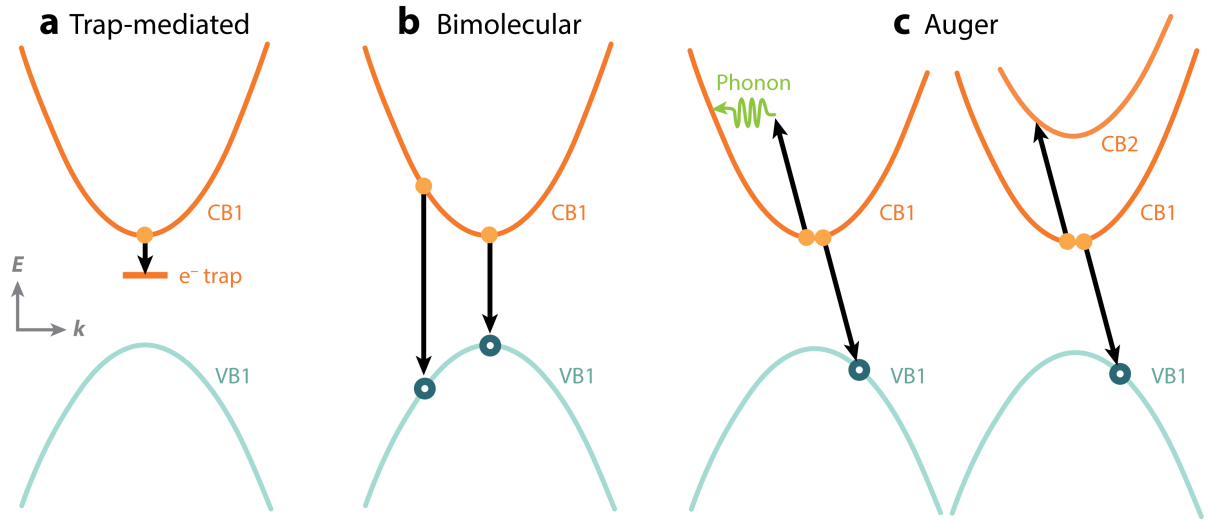


Figure 2.6: Schematic diagram of the main recombination pathways in metal-halide perovskites, including (a) monomolecular trap-mediated via defect states, (b) bimolecular radiative band-to-band recombination, and (c) higher order Auger recombination involving three carriers. Reprinted from Ref [36] with permission. Copyright © 2016, Annual Reviews.

is excited to the conduction band, creating an electron-hole pair. With the low exciton binding energy,[16] charge carriers are likely to exist as free charge carriers at room temperature. The charge carriers then undergo a series of recombination pathways during their lifetime. Firstly, trap-mediated monomolecular recombination, which is also known as Shockley-Read-Hall (SRH) recombination in the limit of deep traps, is a non-radiative process where an electron is captured by a trap located within the bandgap.[35, 36, 44] Secondly, bimolecular recombination is a radiative process, where an electron in the conduction band recombines with a hole in the valence band.[36] Lastly, Auger recombination is a non-radiative many-body process where recombination of electron and hole is accompanied by transfer of energy and momentum to another electron or hole.[36] This process may also involve phonon absorption or emission. The typical values of k_{nonrad} , R_{eh} and R_{Auger} for FA/Cs mixed-halide perovskite thin films, which are extensively studied in this thesis, are on the order of $\sim 10^7 \text{ s}^{-1}$, $\sim 10^{-10} \text{ cm}^3\text{s}^{-1}$ and $\sim 10^{-28} \text{ cm}^6\text{s}^{-1}$ respectively.[45, 46] The processes of monomolecular, bimolecular, and Auger recombinations are shown in Figure 2.6.

As shown in Equation 2.7, the recombination is dependent on the excitation fluence where

$dn(t)/dt \propto n$ for monomolecular recombination, $dn(t)/dt \propto n^2$ for bimolecular recombination and $dn(t)/dt \propto n^3$ for Auger recombination. Therefore, monomolecular recombination dominates at low fluence, while bimolecular and Auger recombinations become more relevant at high fluence. In particular, Auger recombination has a strong dependence on n , and it is typically observed for $n \geq 10^{18} \text{ cm}^{-3}$, which is higher than the excitation density at 1 Sun ($n \approx 10^{15} \text{ cm}^{-3}$).^[47] Thus, in a typical photovoltaic operation condition, Auger recombination can be neglected in Equation 2.7.

The total rate of recombination $R_T(n)$ can be expressed as:

$$R_T(n) = k_{\text{nonrad}} + R_{\text{eh}}n + R_{\text{Auger}}n^2 \quad (2.8)$$

Given that R_{Auger} is not a significant contributor under typical operational conditions, the recombination rate and therefore the diffusion length are dependent on factors affecting k_{nonrad} and R_{eh} . k_{nonrad} is largely dependent on the crystalline quality of MHPs. Grain boundaries and point defects are the main sources of trap states but in MHPs, they are known to be benign with their shallow levels.^[48] Combined with advanced defect passivation strategies, k_{nonrad} can be minimised, enabling long diffusion lengths up to micrometers.^[43] R_{eh} is exceptionally low for MHP as it deviates from the Langevin limit by four orders of magnitudes.^[15] Combination of low k_{nonrad} and R_{eh} enhances the diffusion length and therefore PCE.

The trap-mediated recombination in MHPs does not necessarily follow the first-order recombination in the presence of shallow defects. The SRH recombination rate for one species of singly charged defect is defined as:^[35]

$$R_{\text{SRH}} = \frac{(n_e n_h - n_i^2)}{(n_e + n_{e,1})\tau_{h,\text{SRH}} + (n_h + n_{h,1})\tau_{e,\text{SRH}}} \quad (2.9)$$

where n_e , n_h and n_i denote electron, hole and intrinsic carrier concentrations; $\tau_{p,\text{SRH}}$ and $\tau_{n,\text{SRH}}$ are the SRH lifetimes for hole and electrons; $n_{e,1}$ and $n_{h,1}$ are parameters that introduce the dependency of the recombination rate on the trapping energy level E_T , which are defined as

$$n_{e,1} = N_C \exp\left(\frac{E_T - E_C}{k_B T}\right) \quad (2.10)$$

$$n_{h,1} = N_V \exp\left(\frac{E_V - E_T}{k_B T}\right) \quad (2.11)$$

where N_C and N_V are effective density of states for the conduction and valence bands respectively, and E_V , E_C are the energies of conduction band and valence band edges respectively. Electrons and holes can be captured into traps with characteristic capture times $\tau_{e,SRH}$ and $\tau_{h,SRH}$ respectively, and they can be thermally re-emitted (detrapped) at rates given by $e_n = c_n n_{e,1}$ and $e_p = c_p n_{h,1}$. For deep traps, $n_{e,1}$ and $n_{h,1}$ are exponentially small, so detrapping is negligible and SRH recombination behaves effectively as a first-order recombination. However, MHPs are known to possess shallow defects that preferentially trap electrons.[49] Therefore, $n_{e,1}$ and $n_{h,1}$ are not negligible. Detrapping becomes significant, and the trap-mediated recombination deviate from the first-order recombination.[50]

Such dynamics in MHP can be described by the set of coupled differential rate equations:[51, 52]

$$\frac{dn_e(t)}{dt} = -R_{pop}(N_t - n_t) + k_{detrapp}n_t - R_{eh}n_en_h \quad (2.12)$$

$$\frac{dn_h(t)}{dt} = -R_{depop}N_t n_t - R_{eh}n_en_h \quad (2.13)$$

$$\frac{dn_t(t)}{dt} = R_{pop}(N_t - n_t) - R_{depop}N_t n_t - k_{detrapp}n_t \quad (2.14)$$

where n_e , n_h , n_t and N_t are the electron, hole, trapped electron and total trap densities respectively. The trap population rate R_{pop} governs the rate at which free electrons from the conduction band populate unoccupied trap states of density $(N_t - n_t)$. Once trapped, electrons may detrapp back to the conduction band with a rate $k_{detrapp}$ or depopulate with a rate R_{depop} via nonradiative

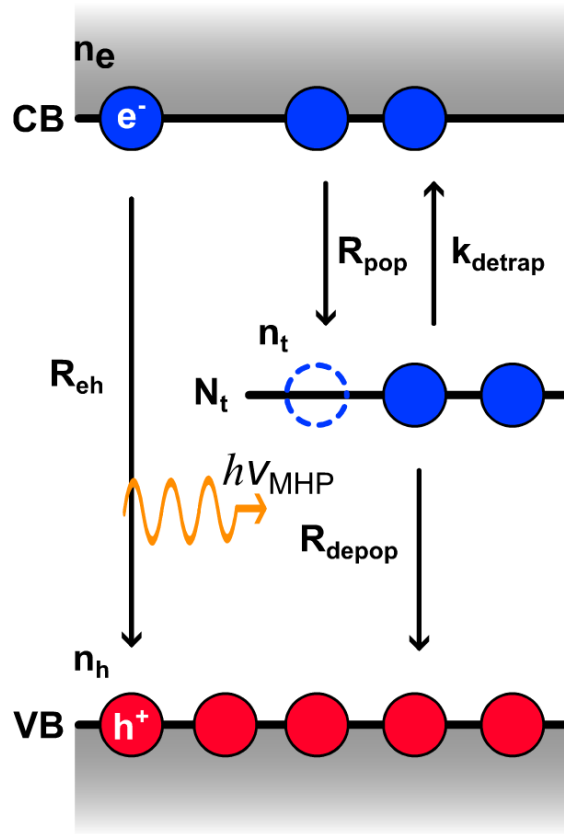


Figure 2.7: Schematic diagram of a trap-mediated charge-carrier recombination model. Free charge-carriers with density n_e in the conduction band (CB) recombine with holes in the valence band (VB) through radiative bimolecular recombination with rate constant R_{eh} . $h\nu_{MHP}$ represent photoluminescence from the radiative recombination. Furthermore, free charge carriers in the CB populate the free trap states with rate constant R_{pop} . Trapped charge carriers with density n_t recombine with holes with density n_h in the VB with a rate constant R_{depop} ; or alternatively, trapped charge carriers detrap with a rate k_{detrap} to return as free charge carriers to the CB. The total trap density is given by N_t .

recombination with a hole in the valence band (This is also equivalent to hole populating the trap). Such recombination processes are summarised in the schematic diagram in Figure 2.7

2.1.4 Halide Segregation

Although halide mixing provides a convenient route to bandgap tunability in MHPs, certain mixed-halide compositions (typically with bromide content greater than 20 %) suffer from halide segregation, where the initially homogeneous mixed phase demixes under external perturbations such as illumination or electric bias to form bromide-rich (Br-rich) and iodide-rich (I-rich) domains with higher and lower bandgaps respectively.[20, 21, 53–58] Such heterogeneous

phase formation can severely compromise device stability under operational conditions and poses a particular challenge for tandem solar cells, where fixed, well-defined bandgap is essential. [22, 58–62]

Halide segregation gives rise to distinctive optoelectronic behaviour where the charge carriers generated from the Br-rich phase funnel into the lower-bandgap I-rich phase, leading to the enhanced, red-shifted photoluminescence (PL).[20, 63] In contrast, only a small fraction of the perovskite ($\sim 1\%$) actually participates in the halide segregation as revealed by the shift in the X-ray diffraction (XRD) peaks or absorption onsets.[20, 22] Importantly, the process is mostly reversible where removing external perturbations allows the material to relax back to its pre-illumination mixed phase, most likely driven by entropic mixing.[56, 57] Notably, both demixing and remixing are facilitated by the low activation barriers for halide migration.[57, 64] These optoelectronic and structural changes are summarised in Figure 2.8

The underlying mechanism of halide segregation remains under debate owing to its complex dependence on multiple factors such as crystallinity, compositional variations, temperature, and surrounding ambient environment.[21] In this section, I introduce and discuss the following three prominent models proposed to explain the phenomenon: trap-mediated charge trapping, polaron, and thermodynamic models.[53–57, 65]

First, numerous studies have shown that mixed-halide perovskites with higher crystallinity (i.e., larger grains with reduced grain boundaries) exhibit increased resistance to halide segregation, often achieved through passivation strategies.[21, 53, 54] This highlights the role of defects and grain boundaries in facilitating halide segregation. Knight et al. proposed that the driving force arises from internal electric fields generated by electrons trapped at defect sites near grain boundaries, and by holes funneled into the I-rich phase.[53] Once charges are separated, they act as a positive feedback loop, building up electric field until it is balanced by back-diffusion governed by the concentration gradient. Moreover, Barker et al. have ascribed halide segregation

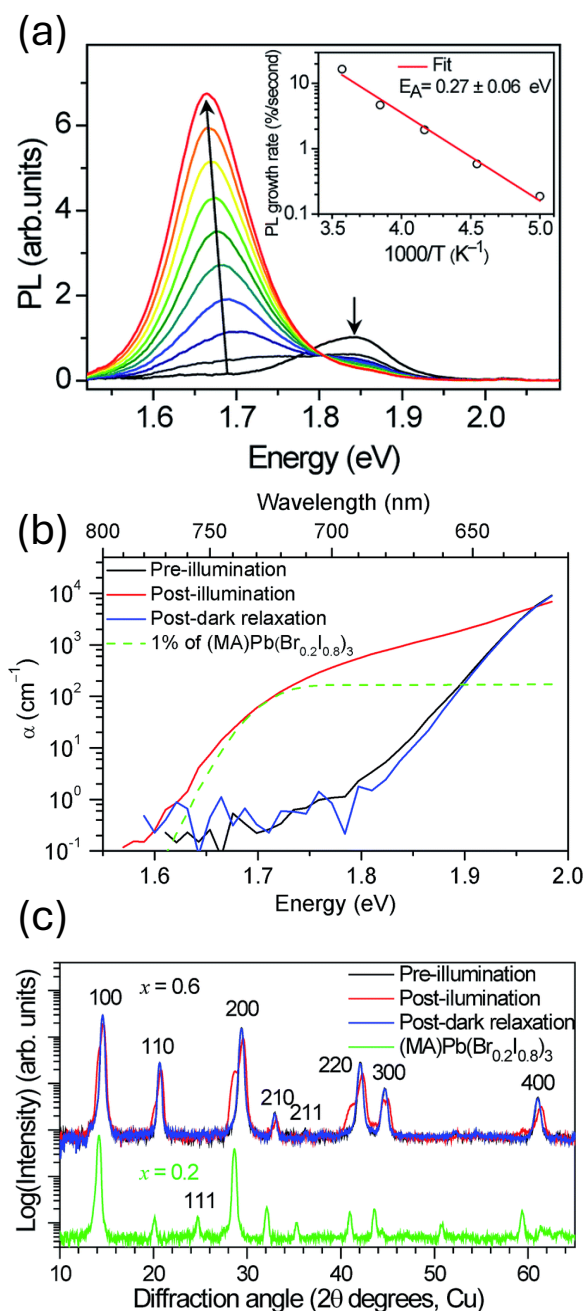


Figure 2.8: (a) Photoluminescence (PL) spectra of a prototypical $\text{MAPb}(\text{I}_{0.6}\text{Br}_{0.4})_{0.3}$ perovskite thin film over 45 s continuous wave excitation at the wavelength of 457 nm and power density of 15 mWcm^{-2} . The inset shows temperature-dependent PL peaks with the activation energy of $0.27 \pm 0.06 \text{ eV}$ obtained from the Arrhenius fit. (b) Absorption spectra of $\text{MAPb}(\text{I}_{0.4}\text{Br}_{0.6})_{0.3}$ film before (black) and after (red) white-light soaking for 5 minutes at the power density of 100 mWcm^{-2} , and after 1 hr in the dark (blue). A scaled absorption spectrum of $\text{MAPb}(\text{I}_{0.8}\text{Br}_{0.2})_{0.3}$ film (dashed green) is shown for comparison. (c) XRD pattern of $\text{MAPb}(\text{I}_{0.4}\text{Br}_{0.6})_{0.3}$ film before (black) and after (red) white-light soaking for 5 minutes at $\sim 50 \text{ mWcm}^{-2}$, and after 2 hr in the dark (blue). An offset is applied for the XRD pattern of $\text{MAPb}(\text{I}_{0.8}\text{Br}_{0.2})_{0.3}$ (green) for better comparison. Reprinted from Ref [20] with permission. Copyright © 2015, The Royal Society of Chemistry.

to the presence of halide-vacancy defects, and demonstrated the suppression of halide segregation by controlling the density of halide defects and more homogeneous carrier-generation profile.[54]

Second, Biskak et al. proposed a polaronic mechanism in which the formation of polarons stabilises I-rich cluster and promote iodide accumulation within them, thereby driving halide segregation until the cluster size is limited by the spatial extent of the polaron-induced lattice deformation.[55] This interpretation was supported by the observation of I-rich clusters preferentially located near grain boundaries, revealed through cathodoluminescence (CL) imaging combined with mean field theory and molecular dynamics simulation. This model accounts for several experimental observations, including the light-intensity dependence of the demixing rate and the stabilising influence of compositional engineering.[10, 66–68]

Lastly, the thermodynamic model predict the stabilisation of the I-rich phase based on the free-energy gained by bandgap difference between the I-rich and mixed phase.[56, 57, 65] Draguta et al. proposed that the valence band offset between the I-rich and Br-rich domains provides an energetic driving force that counterbalances the entropic preference for halide mixing by using DFT calculations.[56] Within this framework, suppression of halide segregation requires reducing the excitation intensity or limiting the carrier diffusion length, since charge carriers must reach the I-rich domains to localize and provide the energetic stabilization. Elmelund et al. further demonstrated through temperature-dependent absorption measurement that halide mixing and demixing are governed by halide-diffusion kinetics, which follow an Arrhenius-type relationship.[57] Their results highlight that both thermodynamic driving forces and kinetic constraints, determined by the activation energy of halide migration, are central to halide segregation.

In summary, halide segregation in mixed-halide perovskites has been rationalized through three main models: (i) trap-mediated carrier effects, where defects and grain boundaries induce local fields that drive halide migration; (ii) polaronic stabilisation, in which lattice distortions

promote iodide accumulation and cluster growth; and (iii) thermodynamic arguments, where free-energy gains and kinetic constraints dictate the balance between mixed and segregated phases. While each framework captures important experimental observations, no single model provides a complete description of the phenomenon, highlighting the fact that halide segregation is a highly complex process sensitive to material quality, composition, and external conditions. Nonetheless, halide segregation remains detrimental to device performance under operational conditions. A detailed understanding of the underlying mechanism is therefore critical for developing effective mitigation strategies, particularly in the context of c-Si/MHP tandem solar cells where their long-term stability is often compromised by wide-bandgap mixed-halide perovskites.

2.1.5 Interfaces between Perovskites and Charge-Transport Layers

2.1.5.1 Impact of Charge-Transport Layers on Device Performance

In addition to halide segregation, wide-bandgap (> 1.7 eV) mixed-halide perovskites typically exhibit substantial V_{OC} losses, primarily due to non-radiative recombination at MHP/charge-transport layer (CTL) interfaces. Suchan et al. correlated the V_{OC} of p-i-n devices employing undoped PTAA and C_{60} CTLs with the reported bandgaps (E_g) of MHP absorbers by performing meta-analysis of 45,000 data from peer-reviewed publications available in the Perovskite Database (<https://www.perovskitedatabase.com>), as shown in Figure 2.9.[19] When E_g exceeds ~ 1.7 eV, the measured V_{OC} begins to plateau despite the increasing E_g , while the Shockley-Queisser (SQ) limit predicts the linear increase in V_{OC} with increasing E_g . [18] This deviation indicates that V_{OC} losses become more pronounced at higher bandgaps.

Three primary mechanisms contribute to V_{OC} losses in mixed-halide perovskites: (i) bulk non-radiative recombination, (ii) interfacial non-radiative recombination associated with CTLs and (iii) phase segregation leading to the formation of narrower-bandgap I-rich domains. Mahesh et al. systematically compared the contributions of the non-radiative V_{OC} losses in wide-bandgap FACs mixed-halide perovskites and revealed that the non-radiative losses (385 mV)

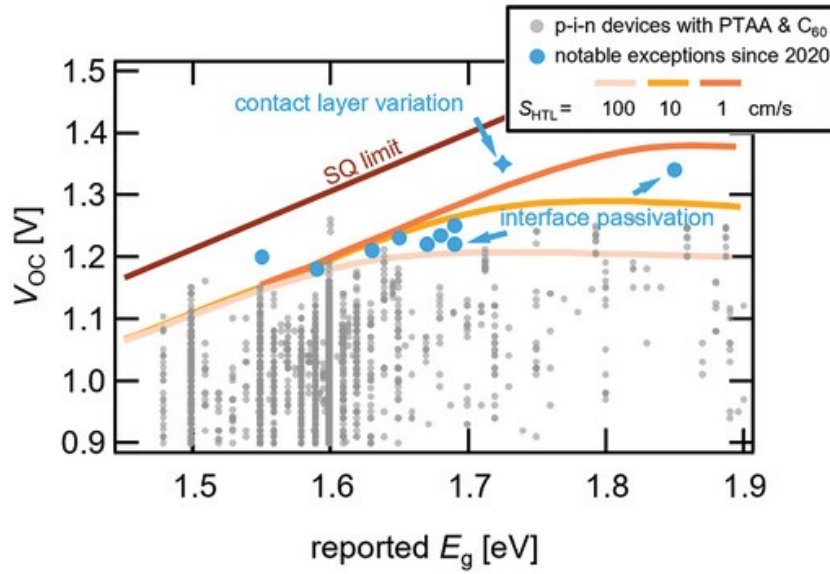


Figure 2.9: Open-circuit voltage (V_{OC}) of p-i-n devices employing undoped PTAA and C_{60} plotted against the reported bandgaps (E_g). Blue symbols indicate notable cases reported since 2020 where interfacial passivation yields exceptional V_{OC} above 1.2 V. The blue star represents an analogous device in which the electron-transport layer was varied. The solid maroon line represents the theoretical V_{OC} based on the Shockley-Queisser (detailed balance) limit, while the orange lines correspond to the drift-diffusion simulations with different surface recombination velocities at the perovskite/hole transport layer interface. Reprinted from Ref [19] with permission. Copyright © 2023, Wiley-VCH GmbH.

dominates over the loss coming from halide segregation (75 mV).[22] Therefore, suppressing trap-mediated recombination in both the bulk and at the interfaces of wide-bandgap mixed-halide is essential for achieving higher V_{OC} values and surpassing the plateau at ~ 1.2 eV commonly reported in literature (Figure 2.9).

The non-radiative recombination leads to the reduction of free charge-carrier density within the band in addition to the intrinsic radiative recombination. The charge-carrier densities in the conduction and valence band of perovskite (n) are directly related to the quasi-Fermi level splitting (QFLS), which represents the chemical potential of free electron-hole pairs $\mu = E_{F,e} - E_{F,h}$ as following:[69]

$$n^2 = N_C N_V \cdot \exp\left(\frac{E_C - E_V}{k_B T}\right) \cdot \exp\left(\frac{E_{F,e} - E_{F,h}}{k_B T}\right) = n_i^2 \exp\left(\frac{QFLS}{k_B T}\right) \quad (2.15)$$

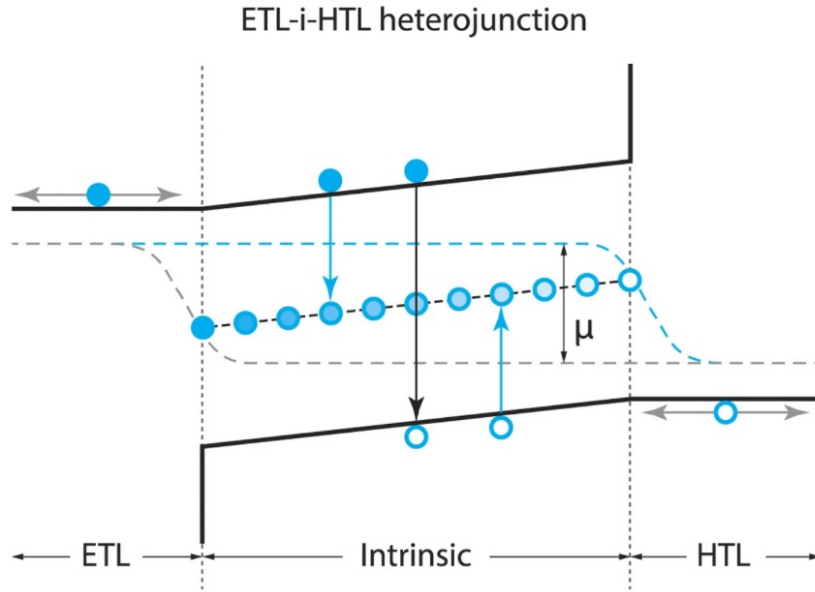


Figure 2.10: Electron transport layer (ETL)–intrinsic perovskite layer (i)–hole transport layer (HTL) heterojunction with the chemical potential of the electron-hole pair $\mu = E_{F,e} - E_{F,h}$, where $E_{F,e}$ and $E_{F,h}$ are the quasi-Fermi levels of electrons and holes. Reprinted from Ref [44] with permission. Copyright © 2017, Springer Nature.

where n_i denotes the intrinsic carrier density; N_C and N_V are the effective densities of states in the conduction and valence bands, respectively; E_C and E_V are the conduction- and valence-band edge energies; and $E_{F,e}$ and $E_{F,h}$ are the quasi-Fermi levels for electrons and holes, respectively. The link between QFLS and measurable optical quantities can be established through Kirchhoff's law of radiation, which expresses the detailed balance between absorption and emission, and its generalization by Würfel to account for non-equilibrium electron and hole populations:[44]

$$J_{PL} = \int a(\omega) \frac{\Omega}{4\pi^3 \hbar^3 c_0^2} \frac{(\hbar\omega)^2}{\exp\left(\frac{\hbar\omega - QFLS}{k_B T}\right) - 1} d(\hbar\omega) \simeq J_{0,rad} \exp\left(\frac{QFLS}{k_B T}\right) \quad (2.16)$$

where J_{PL} is the emitted photon current density, proportional to the external photoluminescence intensity; $a(\omega)$ is the absorptivity; and Ω represents the effective external emission angle. The right-hand side of Equation 2.16 is valid under excitation conditions typical of solar cells, where the carrier distribution can be approximated by the Boltzmann statistics.[44] By rearranging Equation 2.16, the following relationship between QFLS and external photoluminescence

quantum yield (PLQY), which is defined as the ratio between J_{PL} and absorbed excitation photon flux J_{ex} , can be obtained.[44, 69]

$$\text{QFLS} = k_{\text{B}}T \ln\left(\frac{J_{\text{PL}}}{J_{0,\text{rad}}}\right) = k_{\text{B}}T \left[\ln\left(\frac{J_{\text{ex}}}{J_{0,\text{rad}}}\right) + \ln(\text{PLQY}) \right] = \text{QFLS}_{\text{rad}} + kT \ln(\text{PLQY}). \quad (2.17)$$

In a good p-n junction, where the voltage drop outside the junction can be neglected, QFLS is equal to V_{OC} . [70] However, in non-ideal junction where recombination loss predominantly happens at the interface, and QFLS– V_{OC} mismatch occurs.[69, 71]

2.1.5.2 Interfacial Loss Mechanisms

The introduction of charge-transport layers gives rise to additional recombination pathways beyond those occurring in the perovskite absorber alone as shown schematically in Figure 2.11, detrimentally affecting the device performance of solar cells as discussed in Section 2.1.5.1 and 2.1.3.2.

The four additional recombination pathways are :

- (1) **Interface recombination within the perovskite layer**, where both the electrons and holes recombine in perovskite via new surface trap states which are created due to changes in surface stoichiometry or reactions with the C_{60} .
- (2) **Across-interface recombination**, where the electron is extracted to the C_{60} and subsequently recombines with a hole in the perovskite via trap states at the interface.
- (3) **Interface recombination within the C_{60}** , where the electron and hole are extracted to the C_{60} and recombine at the interface via trap states in the C_{60} .
- (4) **Recombination within the bulk of C_{60}** , where electrons and holes are extracted to the C_{60} and recombine via trap states in the C_{60} .

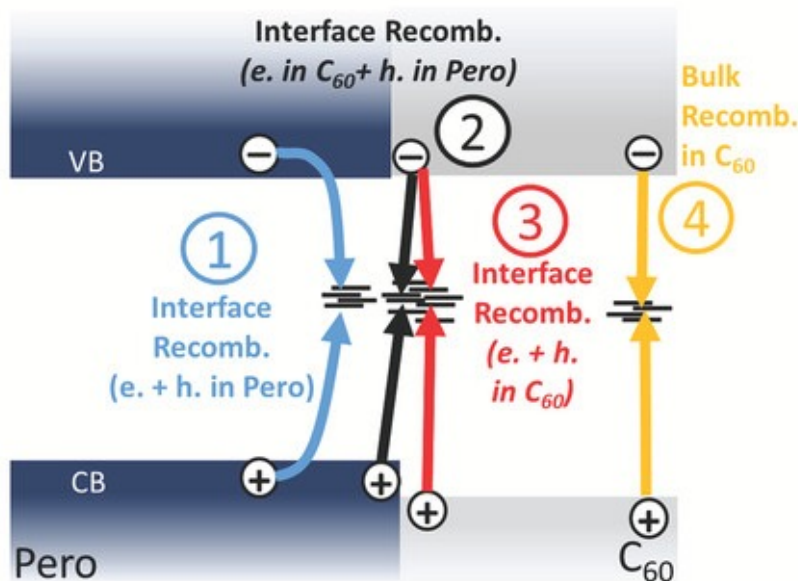


Figure 2.11: Possible recombination pathways at the interface between $(\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ (Perov) and C_{60} : (1) via surface trap states, (2) across-interface recombination, (3) interfacial recombination within C_{60} layer, and (4) C_{60} bulk recombination. Reprinted from Ref [72] with permission. Copyright © 2022, Wiley-VCH GmbH.

The above recombination pathways are not limited to MHP/ C_{60} but can be applied to any MHP/CTL interface. Warby et al. revealed that the recombination losses at the MHP/ C_{60} predominantly originate from across-interface recombination (Mechanism 3) assisted by trap states arising from charge transfer states or DOS broadening at the interface pinning the lowest unoccupied molecular orbital (LUMO) below the CB of the MHP.[72]

An unfavourable band offset at the MHP/CTL interface can also induce non-radiative recombination losses at the interface. Stolterfoht et al. found that the implementation of a majority charge carrier band offset (> 0.2 eV) at the MHP/HTL interface causes considerable upward band bending of the hole quasi-Fermi level $E_{\text{F,h}}$ close to the interface owing to the reduction in the density of majority carriers in perovskite with rapid interfacial recombination.[69, 73] This leads to a QFLS- V_{OC} mismatch given that $E_{\text{F,e}}$ and $E_{\text{F,h}}$ must extend throughout the charge transport layers to the metal contacts in order to produce external V_{OC} as shown in Figure 2.12.

In the presence of CTLs, the effective charge-carrier lifetime τ_{eff} is composed of two

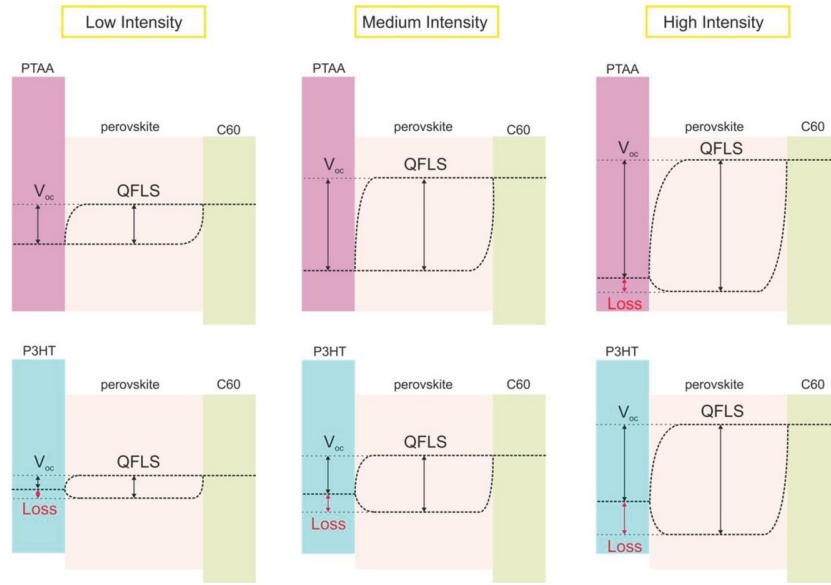


Figure 2.12: Schematic representation of the relationship between quasi-Fermi level splitting (QFLS) and open-circuit voltage (V_{OC}) for different illumination intensities in the solar cells employing poly(3-hexylthiophene-2,5-diyl) (P3HT) and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) as hole transport layer (HTL). The dashed lines in the perovskite layer represent the $E_{F,e}$ and $E_{F,h}$ defining QFLS, whereas the external V_{OC} is given by the respective energy levels at the contacts. The Reprinted from Ref [69] with permission. Copyright © 2019, Wiley-VCH GmbH.

components. One arises from bulk MHP τ_b and another occurring at the CTL τ_s

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{1}{\tau_s} \quad (2.18)$$

By considering the extreme limits (low and high) of surface recombination velocity (SRV) and applying the corresponding boundary conditions at the two surfaces of a thin film, the surface-limited lifetime τ_s can be approximated as:[74]

$$\tau_{s,app} = \frac{d}{2SRV} + \frac{1}{D} \left(\frac{d}{\pi} \right)^2 \quad (2.19)$$

$\tau_{s,app}$ denotes the approximate surface lifetime τ_s ; SRV is the surface recombination velocity; d is the film thickness; and D is the diffusion constant of excess carriers. The first term indicates that the interfacial recombination is governed by inverse of SRV , while the second term shows that the carrier transport to the surface scales quadratically with d and inversely

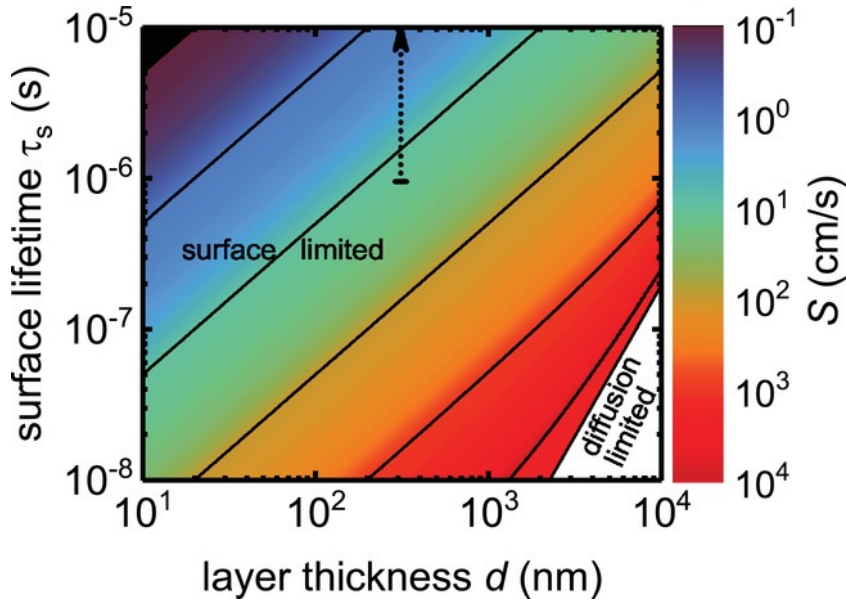


Figure 2.13: Surface recombination velocity (SRV) as a function of the surface lifetime τ_s and the layer thickness d of a MAPbI₃ thin film on glass. The calculation assumes a mobility of $20 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for electrons and holes and equal SRV at the two surfaces of the sample. The blank area in the lower right corner marks the mathematically impossible region where the lifetime is increased by the finite speed of charge-carrier diffusion toward the surfaces. The dotted black line indicates the possible surface lifetimes for the MAPbI₃ thickness of $d = 311 \text{ nm}$. The Reprinted from Ref [75] with permission. Copyright © 2020, Wiley-VCH GmbH.

with D . The simulation in Figure 2.13 visually demonstrates the effect of SRV , d and D on the charge-carrier lifetime at the interface.

2.2 CuI–AgI–BiI₃ Compounds

Despite the rapid progress in power conversion efficiencies, state-of-the-art perovskite solar cells typically employ Pb as the B-site cation (see Section 2.1.1), raising concerns regarding its toxicity and environmental impact.[76, 77] In addition, these devices exhibit limited operational stability due to their sensitivity to ambient environments and illumination.[78, 79] These issues have driven global efforts to develop alternative material classes that not only replicate the exceptional optoelectronic properties of lead-halide perovskites (see Section 2.1.3) but also offer improved resistance to thermal, environmental, and photostability stresses while eliminating lead toxicity.

Recently, increasing attention has been directed towards ternary and quaternary compounds within the CuI–AgI–BiI₃ phase space, which can be obtained by alloying the binary precursors

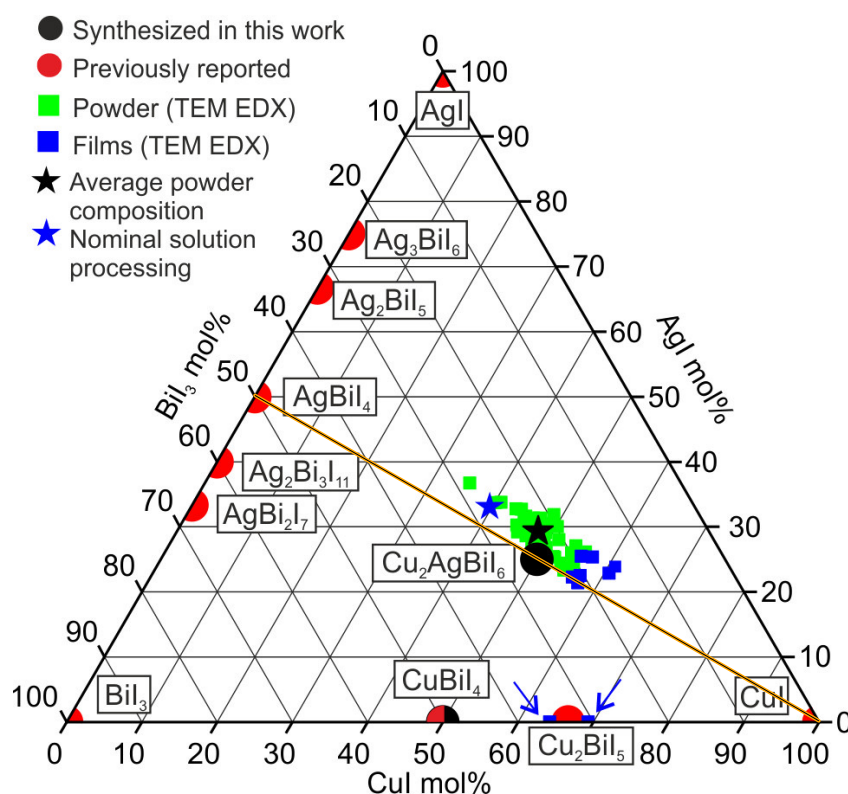


Figure 2.14: Compounds within the CuI–AgI–BiI₃ phase space. Binary and ternary compounds are highlighted in red. The orange line denotes the Cu_{4x}(AgBi)_{1-x}I₄ solid-solution line, along which black, blue, and green symbols indicate powder- and solution-processed compositions with the nominal stoichiometry Cu₂AgBiI₆. The Reprinted from Ref [23] with permission. Copyright © 2021, American Chemical Society.

CuI, AgI, and BiI₃, as illustrated in Figure 2.14.[23, 80] It is important to note that this class of materials is distinct from the perovskite structure discussed in Section 2.1.1. AgI and CuI binary compounds exhibit wide bandgaps of 2.86 and 3.1 eV, respectively, making them unsuitable for solar cell applications.[81, 82] BiI₃, in contrast, has a narrower bandgap of 1.69 eV, but it is indirect in nature and devices based on it have demonstrated only modest power conversion efficiencies (PCEs) of around 1.0%.[83, 84] Among ternary compounds, Ag_{1-3x}Bi_{1+x}I₄ and CuBiI₄ have been reported with bandgaps in the range of 1.64–1.93 eV, which are suitable for tandem solar cells.[83, 85–92] In particular, devices employing Ag₃BiI₆ as the absorber have achieved a moderate PCE of 5.44% upon the introduction of small amounts of sulfur.[93] However, the intrinsically low charge-carrier mobility of Ag₃BiI₆ ($\approx 0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) poses a significant limitation to further performance improvements.[86] Similarly, CuBiI₄ films exhibit

modest PCEs of 1.1% but suffer from poor stability, decomposing at room temperature.[92, 94]

Combining the three binary precursors enables the formation of quaternary compounds along the orange $\text{Cu}_{4x}(\text{AgBi})_{1-x}\text{I}_4$ solid-solution line, as shown in Figure 2.14.[23] Among these, $\text{Cu}_2\text{AgBiI}_6$ has demonstrated promising optoelectronic properties, including a direct bandgap of 2.1 eV, a high absorption coefficient of $\sim 10^5 \text{ cm}^{-1}$, a low exciton binding energy of $\sim 29 \text{ meV}$ comparable to room temperature, and a moderate charge-carrier mobility of $\sim 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ even after charge-carrier localisation.[24] Devices based on $\text{Cu}_2\text{AgBiI}_6$ have so far achieved a maximum PCE of 2.39%,[95] with excellent stability under prolonged illumination of AM1.5 solar spectrum[23] and these favorable properties highlight the potential for further performance improvements through advances in fabrication and interface engineering.

2.2.1 Crystal Structure of $\text{Cu}_2\text{AgBiI}_6$

The crystal structure of $\text{Cu}_2\text{AgBiI}_6$ has been reported in detail by Sansom et al.[23] and is briefly summarized here. $\text{Cu}_2\text{AgBiI}_6$ crystallizes in a small trigonal unit cell with space group $R\bar{3}m$ and lattice parameters $a = 4.2749(3) \text{ \AA}$ and $c = 20.9395(16) \text{ \AA}$, which are metrically cubic within 2σ error (Figure 2.15). The structure exhibits a high degree of heterogeneity and twinning, comprising alternating layers. In the first layer, a cubic close-packed iodide sublattice hosts edge-sharing octahedral sites, with Ag^+ and Bi^{3+} cations adopting a disordered CdCl_2 -type octahedral motif. The atomic occupancies of Ag^+ and Bi^{3+} are 34.7% and 30.6%, respectively. This layer is separated from the next by a vacant octahedral site (Layer 2). The addition of tetrahedral Cu^+ reduces the occupancies of Ag^+ and Bi^{3+} and introduces additional octahedral vacancies to maintain charge balance. Overall, this structure exhibits a far greater degree of cation disorder compared to the conventional corner-sharing octahedral networks typically observed in MHPs (see Section 2.1.1).[36, 96]

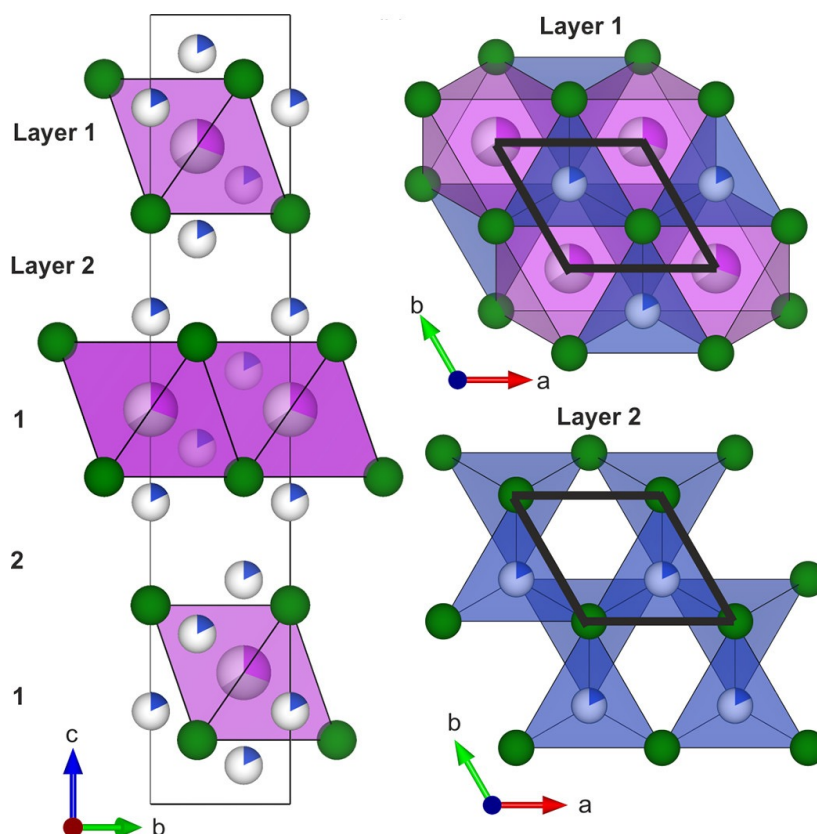


Figure 2.15: Crystal structure of $\text{Cu}_2\text{AgBiI}_6$ determined from 100 K single-crystal X-ray diffraction (SCXRD), with the composition constrained to match the average stoichiometry $\text{Cu}_{2.15(16)}\text{Ag}_{1.04(5)}\text{Bi}_{0.92(7)}\text{I}_{6.00(11)}$ obtained from transmission electron microscopy energy-dispersive X-ray spectroscopy (TEM-EDX). Layer 1 comprises octahedral sites with partial occupancies of 34.6% Ag^+ and 30.6% Bi^{3+} , together with tetrahedral Cu^+ sites. Layer 2 consists of vacant octahedral sites with the tetrahedral Cu^+ sites. The Reprinted from Ref [23] with permission. Copyright © 2021, American Chemical Society.

2.2.2 Charge-Carrier Localisation in $\text{Cu}_2\text{AgBiI}_6$

Ternary $\text{Ag}_{1-3x}\text{Bi}_{1+x}\text{I}_4$ and quaternary $\text{Cu}_{4x}(\text{AgBi})_{1-x}\text{I}_4$ compounds have been demonstrated to undergo ultrafast charge-carrier localisation due to the formation of small polarons.[24, 86, 96, 97] In this section, I focus specifically on the localisation dynamics in $\text{Cu}_2\text{AgBiI}_6$, which are examined in greater detail in Chapter 6. Buizza et al. reported that $\text{Cu}_2\text{AgBiI}_6$ exhibits ultrafast charge-carrier localisation, which they attributed to its low electronic dimensionality (Section 2.2.1), the ease of structural distortion in bismuth-based systems, and the presence of “soft” silver–halide bonds.[97] Evidence for strong electron–phonon coupling was provided by the large Stokes shifts and broad full width at half maximum (FWHM) of the steady-state photo-

luminescence spectra.[24] Furthermore, optical-pump terahertz-probe (OPTP) measurements revealed an ultrafast (~ 1 ps) decay in photoconductivity, followed by a long-lived component exhibiting significantly reduced photoconductivity with lower mobility as shown in Figure 2.16(a).[24] Importantly, the temperature- and fluence-dependent OPTP results indicated that the mobility of the localised state increases with temperature (Figure 2.16(c)), confirming that charge transport is thermally activated in contrast to the case of free carriers.[24] In addition, the rate of the ultrafast localisation process was found to be independent of temperature and fluence (Figure 2.16(d)), reflecting monomolecular-like behaviour and highlighting the almost barrier-free nature of the localisation process.[24] The charge-carrier localisation dynamics in $\text{Cu}_2\text{AgBiI}_6$ are summarised in Figure 2.16(b).

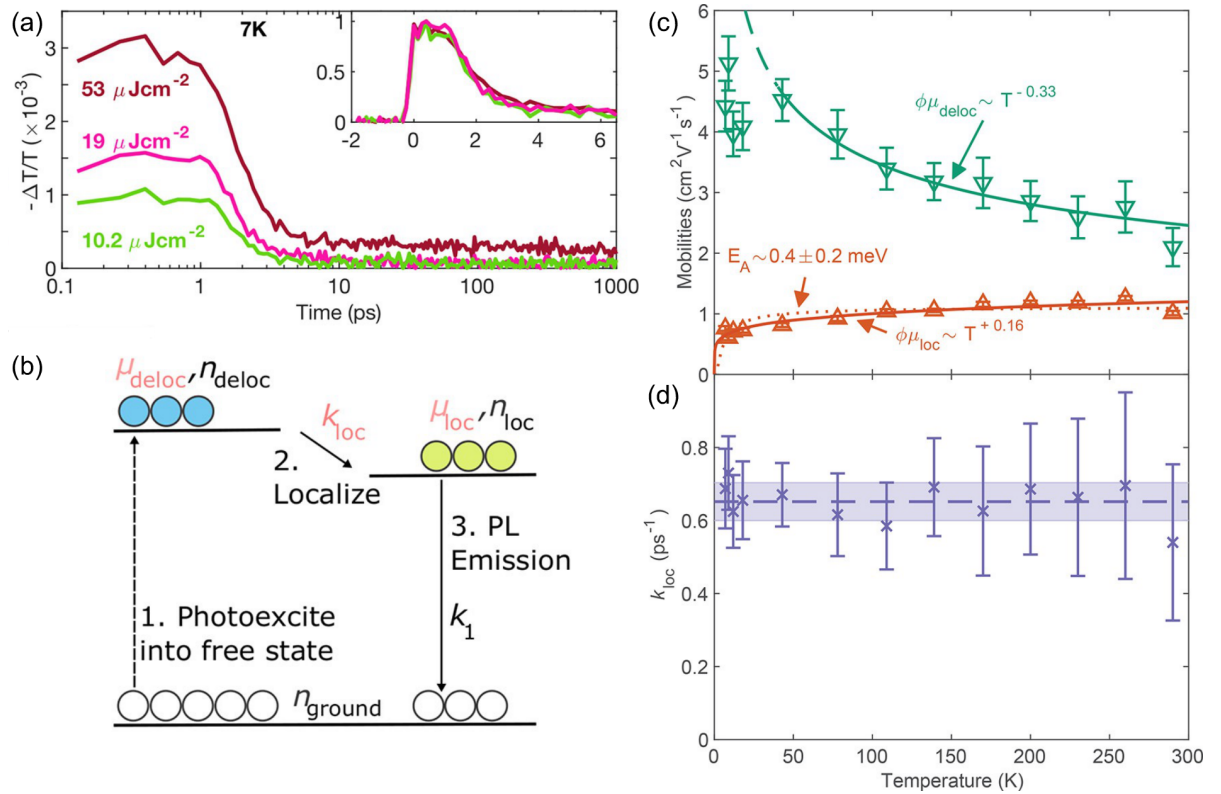


Figure 2.16: (a) Fractional change in the transmitted THz field amplitude ($-\Delta T/T$) of $\text{Cu}_2\text{AgBiI}_6$, proportional to the photoconductivity, measured over a range of excitation fluences at 7 K. The inset shows the normalised transients within the first 6 ps, highlighting the absence of fluence dependence in the charge-carrier dynamics. (b) Schematic illustration of the charge-carrier dynamics in $\text{Cu}_2\text{AgBiI}_6$, showing carrier localisation upon photoexcitation followed by recombination. (c)-(d) Temperature dependence of the effective THz charge-carrier mobilities and localisation rates, respectively. Here, $\phi\mu_{\text{deloc}}$ and $\phi\mu_{\text{loc}}$ represent the effective mobilities of charge-carriers in the delocalised and localised states at THz frequencies, while k_{loc} denotes the rate of the localisation process. The Reprinted from Ref [24] with permission. Copyright © 2021, American Chemical Society.

3

Experimental Theory and Methods

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In this chapter, I explain the details and working principles of the experimental techniques, analysis and sample fabrication carried out for the work presented in this thesis.

3.1 Absorption Spectroscopy

Absorption spectroscopy is a powerful technique for probing the interaction of matter with electromagnetic radiation. By measuring how absorption varies with photon energy, it provides direct insight into the energetic transitions within a material. The amount of light absorption is governed by the likelihood of an electronic transition (or a vibrational transition in the case of low-energy IR photons) occurring at the photon energy of the incident radiation.^[38] This probability is determined by the distribution of available energy levels, the density of states, and the degree of resonance between the photon energy and the transition energy.^[98] Consequently, absorption spectra in the visible-NIR range reveal the fundamental electronic landscape of semiconductors, including the bandgap, exciton binding energy, compositional and structural disorder, and electron-phonon interactions. As such, absorption spectroscopy serves as a fundamental tool for evaluating the intrinsic optoelectronic properties of emerging semiconductor materials studied in this thesis.

3.1.1 Experimental Setup

The reflectance, transmittance, and absorbance of thin films were measured using a Fourier-transform infrared (FTIR) spectrometer (Bruker Vertex 80v) equipped with a reflection–transmission

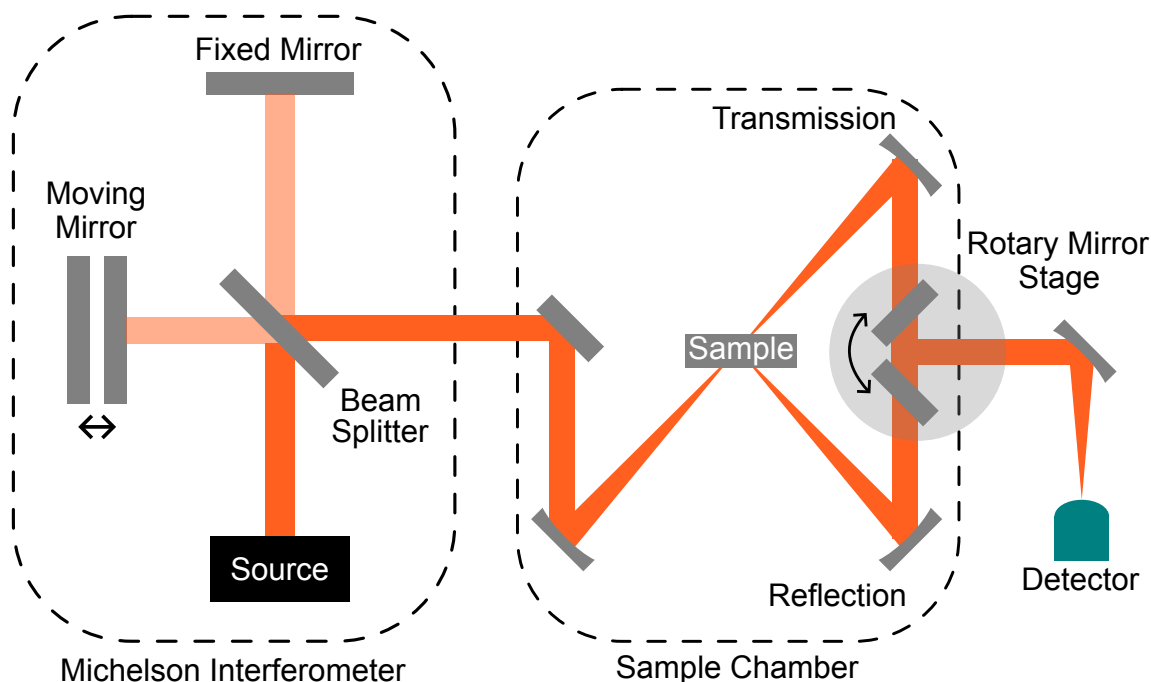


Figure 3.1: Schematic of the Fourier-transform infrared (FTIR) spectroscopy setup. Light from a near-infrared source or tungsten–halogen source is directed onto a CaF_2 beamsplitter, which divides the beam into two paths. One path is reflected by a fixed mirror, while the other is reflected by a movable mirror mounted on a translational stage. Varying the position of the movable mirror changes the optical path length, producing an interference pattern when the two beams are recombined. This interferogram is Fourier transformed to obtain spectral information on the transmitted or reflected light from the sample. Transmission and reflection modes are selected using a mirror turret, and the resulting signals are collected by a silicon photodiode detector.

geometry in the sample chamber (Figure 3.1). The instrument operates on the principle of a Michelson interferometer, in which light from a tungsten–halogen lamp or NIR source is split by a CaF_2 beamsplitter into two arms: one directed towards a stationary mirror and the other towards a motorised mirror that controls the optical path difference. The two beams are then recombined and directed onto the sample, where either transmitted or reflected light is collected by a motorised mirror turret and refocused onto a silicon photodiode detector. A He–Ne laser is employed as a reference for precise calibration of the mirror position and scanning speed. The sample chamber was evacuated to a pressure of ~ 1 mbar in order to minimise signal attenuation from atmospheric absorption and to reduce material degradation during the measurements.

3.1.2 Data Analysis

The absorption coefficient of a material, α , is calculated from the optical density (OD), following Beer-Lambert law, as:

$$\alpha = -\frac{1}{d} \log_{10} \left(\frac{T}{1-R} \right) \quad (3.1)$$

where T and R are the fractional transmittance and reflectance of the sample and d is the film thickness. T and R are obtained using reference measurements that define the 100% transmission and reflection baselines. A silver mirror (for the visible–NIR range) or an aluminium mirror (for the UV range) is used as the reflective reference, while an empty sample holder is used as the transmissive reference. T and R are calculated as follows:

$$T = \frac{T_{\text{Sample}} - T_{\text{Mirror}}}{T_{\text{Blank}} - T_{\text{Mirror}}} \quad (3.2)$$

$$R = \frac{R_{\text{Sample}} - R_{\text{Blank}}}{R_{\text{Mirror}} - R_{\text{Blank}}} \quad (3.3)$$

where T_{Sample} and R_{Sample} denote the transmission and reflection of the sample, respectively; T_{Blank} and R_{Blank} correspond to the measurements with an empty sample holder; and T_{Mirror} and R_{Mirror} represent the measurements taken with the mirrors. Since the setup is limited to transmission and reflection measurements, any diffuse scattering from the sample leads to apparent light loss, which can manifest as artificially enhanced absorption. For further data processing, the absorption spectra were therefore baseline-corrected to zero in this region.

3.1.2.1 Elliott Model

The absorption coefficient spectra were fitted using the Elliott model to obtain the optical bandgap ($E_{\text{g_Elliott}}$), exciton binding energy (E_{b}) and absorption edge broadening parameter (γ_{Abs}).^[38]

The Elliott model represents the total absorption coefficient, $\alpha(E)$ as a linear combination of

the absorption coefficient from bound excitons, $\alpha_{\text{EX}}(E)$, and electron-hole continuum states, $\alpha_{\text{C}}(E)$, for a direct-bandgap semiconductor as shown below:[38, 98, 99]

$$\alpha(E) = \alpha_{\text{EX}}(E) + \alpha_{\text{C}}(E) \quad (3.4)$$

The contribution from $\alpha_{\text{EX}}(E)$ is expressed as:

$$\alpha_{\text{EX}}(E) = \frac{b_0}{E} \sum_{n=1}^{\infty} \frac{4\pi E_b^{3/2}}{n^3} \delta\left(E - \left[E_{\text{g_Elliot}} - \frac{E_b}{n^2}\right]\right) \quad (3.5)$$

where b_0 is a proportionality constant that includes the electric dipole transition matrix element between the valence and conduction bands, $|\langle \Psi_{\text{c}} | P | \Psi_{\text{v}} \rangle|^2$, and n is a positive integer quantum number. Equation 3.5 describes the line series at energies $-E_b/n^2$ below $E_{\text{g_Elliot}}$ and the magnitude are proportional to $1/n^2$.

The contribution from $\alpha_{\text{C}}(E)$ is expressed as:

$$\alpha_{\text{C}}(E) = \frac{b_0}{E} \left[\frac{2\pi \sqrt{\frac{E_b}{E - E_{\text{g_Elliot}}}}}{1 - \exp\left(-2\pi \sqrt{\frac{E_b}{E - E_{\text{g_Elliot}}}}\right)} \right] c_0^{-1} J D o S(E) \quad (3.6)$$

where the joint density of states, $J D o S$ is given by:

$$J D o S(E) = \begin{cases} c_0 \sqrt{E - E_{\text{g_Elliot}}}, & \text{for } E > E_{\text{g_Elliot}} \\ 0, & \text{otherwise} \end{cases} \quad (3.7)$$

and the joint density of states constant c_0 is given by:

$$c_0 = \frac{1}{(2\pi)^2} \left(\frac{2\mu_{\text{red}}}{\hbar^2} \right)^{3/2} \times 2 \quad (3.8)$$

where μ_{red} is the reduced effective mass of the electron-hole system, which is assumed to be $0.15 m_e$ for $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskites in Chpater 4 [100] and $0.375 m_e$ for $\text{Cu}_2\text{AgBiI}_6$ in Chapter 6.[23] The term in the square brackets in Equation 3.6 represents the Coulombic

enhancement factor, which represents the probability of an electron and a hole existing in the same space. The second term $c_0^{-1} J D o S(E)$ represents the absorption coefficient of free electrons and holes in the absence of Coulombic attraction, $\alpha_{\text{Free}}(E)$.

The linear combination of the contributions from the excitonic and continuum states as shown in Equation 3.4 is then convolved with a broadening function, which is written as:

$$g(E) = \frac{1}{\cosh\left(\frac{E - E_b}{\gamma_{\text{Abs}}}\right)} \quad (3.9)$$

where γ_{Abs} is the absorption edge broadening parameter.

3.1.2.2 Tauc Method

For a direct band gap semiconductor, the optical bandgap ($E_{\text{g_Tauc}}$) can be estimated by the following equation: [101]

$$\alpha(E)h\nu \propto (h\nu - E_{\text{g_Tauc}})^{1/2} \quad (3.10)$$

To improve the accuracy of the Tauc method, especially for thin films interfaced with charge transport layers, a linear baseline is fitted to the sub-band gap region. The extracted Tauc bandgap value ($E_{\text{g_Tauc}}$) is the energy where the baseline fit and the linear fit to the square of the absorption coefficient onset meet.

3.1.2.3 Inflection Method

The optical bandgaps were alternatively obtained by using the point of inflection method, which estimates the bandgap from the steepest gradient of the absorption onset. This method has been previous used by Savill et al. and Lal et al. to calculate bandgaps from weak and broadened absorption onset, where the Elliott method fitting can be impractical.[86, 102] To obtain the steepest gradient, the raw absorption onset was fitted with an arbitrary polynomial

function and differentiated using `numpy.diff`. The peak of the first derivative is taken as the optical band gap (E_{g_inf}).

3.2 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a non-contact, non-destructive technique for probing the radiative emission of photons from a photoexcited material. When a sample absorbs photons with energies greater than its band gap, electrons in the valence band are excited to higher-energy states in the conduction band, leaving behind holes (see Section 3.1). As these excited carriers relax back toward equilibrium, they can recombine either radiatively, emitting photons, or through competing non-radiative pathways. Radiative relaxation from the conduction band minimum to the valence band maximum gives rise to photoluminescence, which can be spectrally resolved using steady-state PL (ssPL) spectroscopy or temporally resolved using time-resolved PL (TRPL) spectroscopy. As discussed later in Sections 2.1.3.3 and 2.1.5.2, radiative recombination competes with non-radiative processes such as trap-assisted monomolecular recombination and interfacial recombination in the presence of charge-transport layers. This section introduces both ssPL and TRPL, which are employed in all the work presented in this thesis.

3.2.1 Steady-State Photoluminescence Spectroscopy Setup

Steady-state photoluminescence (ssPL) spectroscopy refers to the measurement of the energy-dependent spectrum of photons emitted from a photoexcited sample that is in equilibrium with an illumination source, such as a continuous-wave (CW) laser. The experimental setup used to measure ssPL consists of a photoexcitation source, collection optics to gather the emitted PL spectrum, and a detector to measure the PL spectrum (see Figure 3.2). A 470 nm wavelength diode laser (PicoQuant, LDH-D-C-470M) (Chapter 4) and a 532 nm wavelength diode laser (Novanta Photonics, Ventus 532) (Chapter 5) operated under CW conditions were used as illumination sources. The laser intensity was adjusted using neutral-density (ND)

filters along the incoming beam path. Apertures and lenses were used to control the beam spot size and shape along the beam path.

The ssPL in Chapter 4 was collected using an intensity charge-coupled device (iCCD) camera with the setup shown in Figure 3.2. Upon excitation of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ thin films with a 470 nm diode laser, the isotropic PL emitted from the sample was collected by a set of collection optics consisting of an achromatic doublet (Thorlabs, AC508-250-A-f=250 mm) to collimate the collected PL, a linear polariser (Thorlabs, LPNIRE200-B) to avoid Wood's anomalies from the diffraction gratings later in the optical path and a 515 nm long pass filter (Comar Optics, 515GY50) to prevent the laser scatter from reaching the detectors.[103] The collimated PL was then focused onto the entrance slit of a grating spectrometer (Princeton Instruments, SP-2558), which then internally re-collimated the light onto a diffraction grating. The diffraction grating separated the light spatially according to its wavelength, and the separated light was then focused onto an iCCD for detection. An iCCD offers an advantage over a conventional CCD in terms of signal-to-noise ratio, as the signal is electronically amplified prior to detection, thereby reducing the impact of readout noise that typically dominates in standard CCDs. In this setup, the samples were mounted in a customised vacuum chamber evacuated to $\sim 10^{-2}$ mbar in order to prevent degradation of the perovskites under illumination, which can be accelerated by exposure to ambient environmental conditions.[78]

In Chapter 5, ssPL was measured with a fibre-coupled portable spectrometer (Ocean Optics, SR6) as part of the synchronous multimodal spectroscopy. Here, the $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ thin film was excited with the 532 nm wavelength CW laser and ssPL was collected with a set of collection optics consisting a 600 nm long pass filter (Thorlabs, FELH0600), a planoconvex lens (Comar Optics, 80PQ25) and through a fibre connected to a fibre coupler (Thorlabs, PAF2A-11B).

The spectral response of the detectors was determined by comparing their measured response to an OL245M irradiance standard tungsten lamp with a known emission spectrum. The

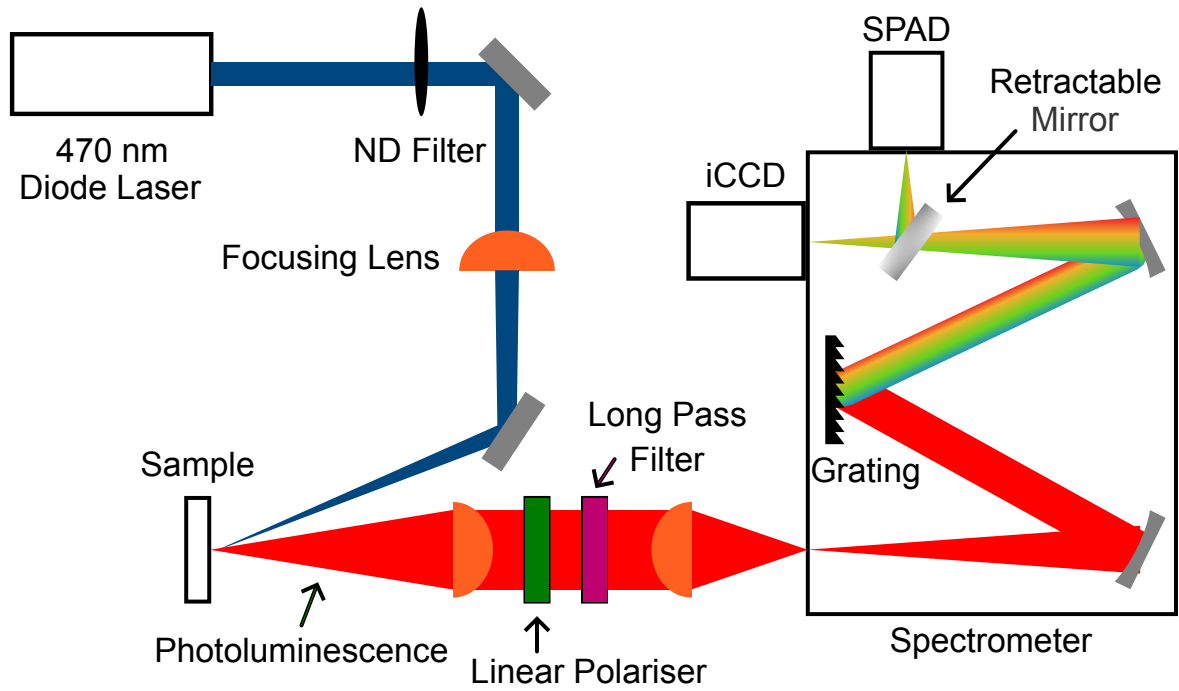


Figure 3.2: Schematic of photoluminescence spectroscopy setup used in Chapter 4. The sample was excited with a 470 nm CW laser with its intensity controlled with the ND filter. The PL was collected by a set of collection optics consisting of lenses, a linear polariser and a long pass filter. The PL was then spectrally separated by the grating and directed onto the intensity charge-coupled device (iCCD) or single photon avalanche diode (SPAD) depending on the position of the retractable mirror.

spectrally corrected spectrum was obtained by applying a wavelength-dependent correction factor to the measured spectrum, as follows:

$$I_{sc}^{PL}(\lambda) = I_m^{PL}(\lambda) \times \frac{I_t^{lamp}(\lambda)}{I_m^{lamp}(\lambda)} \quad (3.11)$$

where I_{sc}^{PL} is the spectrally corrected PL spectrum, I_m^{PL} is the measured PL spectrum, and I_t^{lamp} is the true lamp spectrum.

3.2.2 Time-Resolved Photoluminescence Spectroscopy Setup

Time-resolved photoluminescence (TRPL) spectroscopy is a powerful technique for studying the charge-carrier recombination kinetics of emissive semiconductors by measuring the PL decay on the nanosecond (ns) timescale. The PL decay is sensitive to various non-radiative and radiative processes, and qualitative as well as quantitative analyses of the PL decay data

give a useful insight into the charge-carrier dynamics. TRPL is usually measured by using time-correlated single photon counting (TCSPC) method where a sample is repetitively excited by a pulsed laser and an emitted single photon is measured over time at a target wavelength.[104] This repetitive single photon registration builds a histogram that follows the exponential drop of fluorescence intensity over time.[104] The TCSPC timing is determined by the difference between the start of excitation and detection of single photon by a detector. It is important to note that TCSPC relies on the PL intensity being sufficiently low to ensure that, within each excitation cycle, the probability of detecting more than one photon is negligible. If necessary, this condition can be achieved by attenuating the PL. Consequently, after a large number of excitation cycles, the histogram accurately represents the true temporal photon distribution of the PL signal. If more than one photon were to arrive at the detector per cycle, only the first would be registered and so the histogram would suffer from a bias towards photons with shorter arrival times, which is known as ‘pile-up’.[104] Therefore, the probability of a photon being detected per cycle is usually kept below 1 %.[104]

The excitation and collection beam paths of the TCSPC setup employed in Chapter 4 are identical to those described for the iCCD setup in Section 3.2.1, except that a 470 nm diode laser operated in 1 MHz pulsed mode was used for excitation, and detection was carried out with a photon-counting detector (PDM series Single Photon Avalanche Diode, MPD), whose timing was controlled with a PicoHarp300 TCSPC event timing processor.

In Chapter 5, TRPL was measured with a high-speed free-space Si photodetectors (Thorlabs, DET025A/M) equipped with a 658–694 nm bandpass filter (Edmund optics, #86-988) to detect the higher energy tail of mixed-phase $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ and a 800–850 nm bandpass filter (Edmund optics, #86-957) to detect the lower energy tail of PL emitted from the iodide-rich phase of halide segregated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$. As part of the collection optics, a glass aspheric condensers (Comar Optics, 16AF25) was mounted to focus the PL onto the

detector. The signal was amplified with a broad-band amplifier made in-house and measured with a fast oscilloscope (Tektronix, MSO64).

The timing precision of the TRPL systems was characterized by their instrument response functions (IRFs), which represent the system's temporal response when detecting the laser pulse directly. In an ideal system, this would be infinitely narrow, whereas the deviations from ideality result in a broader IRF.[104] Usually, the main source of IRF broadening is the uncertainty in the photon registration time introduced by the detector as it converts the photon into an electrical pulse, followed by jitter in the synchronisation signal at the excitation source. The PL signal recorded by the TCSPC system is in fact the convolution of the true PL decay with the IRF. Deconvolution can, in principle, recover PL lifetimes down to a tenth of the IRF full-width at half-maximum (FWHM) but is not necessary when analysing decay process that occur on timescales much longer than the IRF.

3.2.3 Data Analysis

3.2.3.1 Linewidth of Steady-State Photoluminescence

The linewidth of ssPL contains a wealth of information about materials ranging from energetic disorder originating from defects or compositional disorder and excitonic effects and phonon interactions.[41, 105] In Chapter 4, the linewidth of ssPL is used to quantify the degree of disorder in MHPs. This is evaluated from the full width at half maximum (FWHM) of the PL spectra, calculated from the standard deviation (σ) obtained by Gaussian fitting.

$$f(x; A, \mu, \sigma) = \frac{A}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x - \mu_{\text{centre}})^2}{2\sigma^2}\right) \quad (3.12)$$

where A is the amplitude, μ_{centre} is the centre. The FWHM is calculated as $2\sigma\sqrt{2\ln 2}$. A larger FWHM reflects greater energetic disorder, particularly when comparing materials within the same class.

3.2.3.2 Extraction of Charge-Carrier Lifetimes

The charge-carrier lifetime can be obtained from the TRPL transients. As discussed in Section 2.1.3.3, the recombination rates can be obtained by solving the complete set of coupled differential equations. Instead, at a low fluence, higher-order recombination can be reduced to:[105]

$$\frac{dn}{dt} = -k_{\text{nonrad}} n \quad (3.13)$$

and its integral leads to the following exponential form:

$$n(t) = n_0 \exp(-k_{\text{nonrad}} t) \quad (3.14)$$

where n_0 is the initial charge-carrier density. Although monomolecular recombination dominates under low-fluence excitation, the observed PL originates from bimolecular radiative recombination, which is geminate in nature ($\text{PL} \propto n(t)^2$). Therefore, the PL intensity $I(t)$ is governed by:

$$I(t) \propto R_{\text{eh}} n_0^2 \exp(-2k_{\text{nonrad}} t) \quad (3.15)$$

Therefore, k_{nonrad} can be obtained by fitting Equation 3.15 to TRPL transient at low fluences. In Chapter 4, this approach is used to estimate k_{nonrad} , which is then fixed in order to obtain a more accurate value of R_{eh} .

In a complex material system, TRPL decay may not necessarily decay monoexponentially owing to the presence of spatial distribution of trap states. Such deviation can be accounted for by a stretched exponential function:[36]

$$n(t) = n_0 \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \quad (3.16)$$

where the time-dependent monomolecular recombination rate can be calculated as:

$$k_{\text{nonrad}}(t) = \beta \tau^{-\beta} t^{\beta-1} \quad (3.17)$$

It is used in Chapter 5 to compare the effective lifetimes of TRPL before and after halide segregation.

3.3 Optical-Pump Terahertz-Probe (OPTP) Spectroscopy

Optical-pump terahertz-probe (OPTP) spectroscopy is a non-invasive, contact-free method that directly probes the time-resolved photoconductivity of free charge carriers on a timescale of picoseconds. Terahertz (THz) radiation lies in the frequency range of 0.1–20 THz, corresponding to photon energies from a few to about 100 meV. In this regime, THz radiation couples strongly to free mobile charge carriers and to lattice phonon modes in semiconductors, enabling the study of phenomena such as charge-carrier recombination processes, polaron and exciton formation. Gaining insight into these processes enables assessment of the suitability of novel materials for photovoltaic applications.

A basic experimental setup of OPTP is shown in Figure 3.3. Firstly, the mode-locked laser such as Ti:sapphire laser followed by an amplifier is used to generate a pulse with less than 100 femtosecond (fs) duration at a wavelength near 800 nm and repetition rate of 5 kHz. The fs laser pulse is split into the excitation beam and additional two beams for THz generation and gate pulse for detection. THz is typically generated by photoconductivity or nonlinear optical processes.[106] The generation of THz with photoconductivity is a resonant process where the charge carriers generated in a semiconductor via photon absorption is accelerated with either an externally applied dc electric field or built-in electric field in the depletion or accumulation region of the semiconductor via doping.[106] The typical semiconductors used for photoconductivity THz generation are highly doped defect-rich semiconductors such as low-temperature grown or ion implanted GaAs and silicon in order to reduce the fall time of the transient current.[106] However, the bandwidth obtained from photoconductivity generation (~ 5 THz) is limited by the finite response time of photoconductivity material rather than the ideal bandwidth of the state-of-the-art mode-locked fs lasers. Instead, nonlinear optical process such

as optical rectification is typically employed because the bandwidth of THz is only limited by the duration of the excitation pulse.[106] Optical rectification is a non-resonant second-order nonlinear process where a DC or low-frequency polarization is evolved when an intense optical excitation beam propagates through a non-centrosymmetric crystal. In the non-linear medium, mixing within the laser pulse of photons with two frequencies, ω_1 and ω_2 occurs to generate a sum-pulse ($\omega_1 + \omega_2$) and a difference-pulse ($\omega_1 - \omega_2$). The difference-pulse generates a low frequency polarization which follows the envelope of the incident laser pulse. When $\omega_1 = \omega_2$, both second harmonic and DC pulses are generated. The typical materials used for THz generation are ZnTe (110), GaAs and GaP.[106] However, the THz bandwidth achievable through optical rectification is limited to $\sim 3\text{--}4$ THz due to strong phonon resonances of such materials at higher frequencies. To extend the accessible spectral range and overcome the limitations of photoconductive emitters, spintronic emitters based on multilayer heterostructures of ferromagnetic (FM) and non-ferromagnetic (NM) metals are employed. When illuminated by fs laser pulses, the majority of electrons in the FM layer have their spins aligned with an externally applied magnetic field. The optical excitation promotes electrons in the heterostructure to states above the Fermi energy, and due to the distinct transport properties of the FM and NM layers, a net spin-polarised current is driven from the FM layer into the NM layer. This spin current is subsequently converted into a transverse charge current via the inverse spin Hall effect, leading to the emission of a broadband THz pulse.[107]

Efficient coupling between the THz emitter and detector is essential for high-quality measurements. Parabolic mirrors are used to guide the radiation in free space from the emitter to the detector. The frequency-doubled optical pump and the THz probe pulses are spatially and temporally overlapped on the sample.3.3.[106]

The transmitted THz electromagnetic transients are detected via the electro-optic (EO) effect, as illustrated in Figure 3.3. When a THz pulse reaches the surface of an EO crystal such as ZnTe (110), its electric field induces birefringence within the crystal. This birefringence is

then measured through the retardation of a gate pulse with pre-aligned polarization. The phase retardation is measured by varying the delay of the excitation pulse relative to the THz probe, while keeping the gate pulse delay fixed. Afterwards, the quarter-wave plate ($\lambda/4$) converts the transmitted gate beam into circularly polarized light, and the Wollaston prism then separates it into orthogonally polarized components, whose relative intensities are modulated by the THz pulse. Subsequently, the balanced differential detector, which is connected to a pre-amplifier and a lock-in amplifier measures the voltage difference, which is proportional to the induced phase retardation and therefore to the electric field strength in the THz pulse. By fixing the THz probe to the peak of its electric field and delaying the excitation beam, the change in the transmission of THz pulse as a function of excitation time can be measured to determine the optoelectronic properties of semiconductors.[106]

3.3.1 Experimental Setup

Our OPTP spectroscopy setup uses a Spectra Physics Mai Tai-Ascend-Spitfire Pro Ti:sapphire regenerative amplifier. The amplifier generates ultrafast laser pulses with 35 fs pulse duration, 800 nm center wavelength and 5 kHz repetition rate. An optical pump excitation wavelength of 530 nm was achieved by using a traveling-wave optical parametric amplifier of superfluorescence (TOPAS) with a sum-frequency generation of the signal pulse. THz probe pulses were generated with a spintronic emitter which consists of 1.9 nm Tungsten/2.0 nm $\text{Co}_{40}\text{Fe}_{40}\text{Be}_{20}$ /1.9 nm platinum coated with antireflectivity and high-reflectivity coatings.[107] The sample stored in an evacuated chamber at pressure less than 10^{-1} mbar was excited with the pump and probed with the THz pulse shortly after. The pump and THz pulses were chopped with optical choppers with frequencies of 1.25 and 2.5 kHz respectively to obtain the THz transmission change ΔT . The sigma of pump and probe beam at the sample positions were measured as 1.75 mm and 0.33 mm, respectively. The power of the pump pulses was tuned by an ND filter wheel. The THz transmission from thin films was detected by an EO sampling in a (110)-ZnTe crystal (1 mm

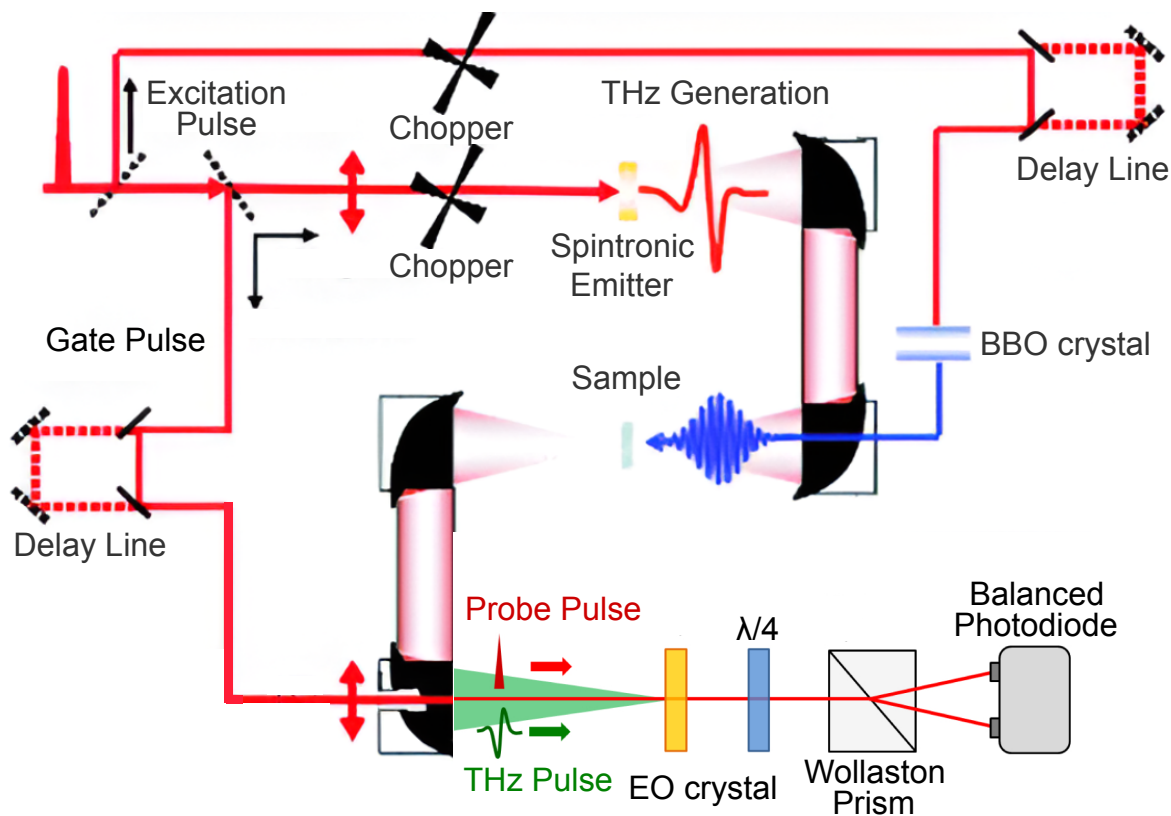


Figure 3.3: Schematic diagram of an optical-pump terahertz-probe (OPTP) setup. A train of fs laser pulses (35 fs, 5kHz, 800 nm) enters the setup from the upper left corner and is split into three beams: the excitation pulse, the THz generation beam (directed to a spintronic emitter), and the gate pulse. Mechanical choppers are placed in both the excitation and Thz beams, operating 1.25 kHz and 2.5 kHz, respectively. The pump pulse is frequency-doubled with a BBO crystal to generate a 400 nm excitation pulse. Two optical delays control the relative arrival times of the three pulses. THz detection is performed by electro-optic (EO) sampling, where the THz field induces a polarization rotation of the gate pulse that is measured with balanced photodiodes. Reproduced from Ref [106, 108] with permission. Copyright © 2011, American Physical Society and Copyright © 2014, Optica Publishing Group.

thickness) with a spatially and temporally overlapping 800 nm gate pulse. The THz transmission was measured at the peak of the THz pulse for different delays of the pump beam, mapping the THz transmission as a function of time after photoexcitation. OPTP decay traces were recorded at different pump–probe delays and excitation fluences to obtain fluence-dependent measurements.

3.3.2 Data Analysis

The gate pulse with a repetition frequency of $f = 5$ kHz is incident on the balanced photodiodes. As described in Section 3.3.1, the THz probe and optical pump beams are mechanically modulated at $f/2$ (2.5 kHz) and $f/4$ (1.25 kHz), respectively. This modulation produces

alternating “THz-On/Off” states at $f/2$ and “Pump-On/Off” states at $f/4$. The fractional change in the transmitted THz signal is then expressed as:

$$\frac{\Delta T}{T} = \frac{(T_{\text{THz_On}}^{\text{Pump_On}} - T_{\text{THz_Off}}^{\text{Pump_On}}) - (T_{\text{THz_On}}^{\text{Pump_Off}} - T_{\text{THz_Off}}^{\text{Pump_Off}})}{T_{\text{THz_On}} - T_{\text{THz_Off}}} \quad (3.18)$$

$\Delta T/T$ is calculated as a function of delay time to obtain the OPTP traces. The signal is acquired and processed using a customised FPGA-based data acquisition board with an appropriate boxcar averaging, and subsequently amplified to maximise the signal-to-noise ratio.

3.3.2.1 Extracting Charge-Carrier Mobility

The sheet photoconductivity ΔS of a thin film between two media of refractive indices n_A and n_B with its thickness much smaller than the THz wavelength can be expressed as :

$$\Delta S = -\epsilon_0 c (n_A + n_B) \left(\frac{\Delta T}{T} \right) \quad (3.19)$$

where ϵ_0 is the vacuum permittivity, c is the speed of light and $\Delta T/T$ is the ratio of photoinduced change in the THz electric field to the transmitted THz electric field in the dark. In this thesis, n_A is the refractive index of a z-cut quartz, which is 2.13 and n_B is the refractive index of air.[15]

Deriving the charge-carrier mobility μ from ΔS requires the knowledge of the number of photo-excited charge-carriers N , which can be calculated as:

$$N = \varphi \frac{E\lambda}{hc} (1 - R_{\text{pump}} - T_{\text{pump}}) \quad (3.20)$$

where φ is the photon-to-charge branching ratio, E is the energy obtained in an optical excitation pulse with wavelength λ , h is the Planck’s constant, R_{pump} , and T_{pump} are the reflected and transmitted fractions of the pump beam. Then, μ can be calculated with:

$$\mu = \frac{\Delta S A_{\text{eff}}}{Ne} \quad (3.21)$$

Here, A_{eff} is the effective area of the overlap of optical pump and THz probe pulse considering the Gaussian beam profiles and e is the elementary charge. As reported by Xia et al.,[109] A_{eff} is defined as $A_{\text{eff}} = 2\pi(\sigma_{\text{Pump}}^2 + \sigma_{\text{THz}}^2)$, where σ_{Pump} and σ_{THz} are the pump and THz beam waists, respectively. To avoid artifacts, the ratio between σ_{Pump} and σ_{THz} is fixed at ~ 6 . [110]

By using the above equations, the effective mobility $\tilde{\mu} = \varphi\mu$ is expressed as:

$$\varphi\mu = -\epsilon_0 c (n_A + n_B) \frac{A_{\text{eff}} h c}{E \lambda e (1 - R_{\text{pump}} - T_{\text{pump}})} \left(\frac{\Delta T}{T} \right) \quad (3.22)$$

Throughout this thesis, φ is assumed to be unity ($\varphi = 1$), given that the exciton binding energies are low and free charge-carriers are mostly generated immediately after excitation. Therefore, $\varphi\mu$ is always underestimated. The charge-carrier mobility obtained here is the sum of electron and hole mobilities and they cannot be separated.

To obtain $\varphi\mu$, $\Delta T/T$ at time zero against E was plotted and a linear function was fitted based on Equation 3.22 across the various fluences where the linearity is conserved. Then, $\varphi\mu$ was obtained from the gradient.

3.3.2.2 Extracting Radiative Recombination Constant

The recombination dynamics in a MHP without a CTL may be governed by first, second and third order processes as shown in the following rate equation as discussed in Section 2.1.3.3:

$$\frac{dn(t)}{dt} = -k_{\text{nonrad}} n(t) - R_{\text{eh}} n(t)^2 - R_{\text{Auger}} n(t)^3 \quad (3.23)$$

Here k_{nonrad} is the first order non-adiative trap-assisted recombination rate, R_{eh} is the second order radiative recombination rate constant and R_{Auger} is the third order Auger recombination rate constant. In Chapter 4, k_{nonrad} is taken from the TCSPC measurements at low fluences using the method illustrated in Section 3.2.3.2. In Chapter 6, k_{nonrad} is fitted together with other variables. For all experimental chapters, R_{Auger} is set as $10^{-29} \text{ cm}^6 \text{ s}^{-1}$ as obtained from literature[46] because the effect of R_{Auger} becomes significant for $n > 10^{18} \text{ cm}^{-3}$. [105]

Equation 3.23 is first solved in terms of the experimentally observed quantity $x(t) = \Delta T/T$, which is the photoinduced change in THz transmission. $n(t)$ is proportional to $x(t)$ with the following relationship:

$$n(t)^i = \phi^{i-1} C^{i-1} x(t)^i \quad (3.24)$$

where i is the recombination order, $C = \tilde{n}_0/x(0)$ is the proportionality factor between the immediate THz response $x(0)$ and the absorbed photon density $\tilde{n}_0$, expressed as:

$$\tilde{n}_0 = \frac{E\lambda}{hcA_{\text{eff}}d} (1 - R_{\text{pump}} - T_{\text{pump}}) \quad (3.25)$$

where d is the thickness of each sample. By substituting Equation 3.24 into Equation 3.23, Equation 3.23 is written as :

$$\frac{dx(t)}{dt} = -k_{\text{nonrad}}x(t) - R_{\text{eh}}\phi C x(t)^2 - R_{\text{Auger}}\phi^2 C^2 x(t)^3 \quad (3.26)$$

The numerical solutions to this ordinary differential equations are fitted globally to the decays using the least squares method across all fluences in order to extract ϕR_{eh} . Given that $0 \leq \phi \leq 1$, the ϕR_{eh} values reported here are underestimated compared to the true intrinsic values.

In order to account for an initially spatially varying charge-carrier density (due to absorption following the Beer-Lambert law), the fitting algorithm takes into account an exponentially decaying charge-carrier density. This is done by dividing the sample into 30 equally thick slices and computing the decay function for each of these individually.

3.3.2.3 Localisation Model

To describe the charge-carrier localization process in $\text{Cu}_2\text{AgBiI}_6$ described in Chapter 6, Buizza et al. and Wright et al. have proposed a two-level mobility model to describe the OPTP photoconductivity transients.[24, 96] In this model, the photoconductivity of the material originates from two different states with different populations and mobilities. An initial

delocalised state ($N_{\text{deloc}}, \mu_{\text{deloc}}$) is populated immediately after the photoexcitation but these charge carriers rapidly transfer to a localised state ($N_{\text{loc}}, \mu_{\text{loc}}$) as a result of the charge-carrier localisation process. Therefore, the resulting sheet photoconductivity (ΔS) can be expressed as:

$$\Delta S = \frac{e}{A_{\text{eff}}} (N_{\text{deloc}} \mu_{\text{deloc}} + N_{\text{loc}} \mu_{\text{loc}}) \quad (3.27)$$

By assuming a predominantly monomolecular charge-carrier recombination regime in the low fluence range, the charge-carrier population of the two states can be described by the following set of coupled rate equations:

$$\begin{cases} \frac{dN_{\text{deloc}}}{dt} = -k_{\text{loc}} N_{\text{deloc}}(t), \\ \frac{dN_{\text{loc}}}{dt} = k_{\text{loc}} N_{\text{deloc}}(t) - k_R N_{\text{loc}}(t). \end{cases} \quad (3.28)$$

where k_{loc} and k_R are the charge-carrier localization and average recombination rates, respectively. The analytical solution to this set of coupled rate equations yields the time-dependent charge-carrier population for the two states. As described previously, the resulting $\Delta T/T$ signal is obtained by combining Equation 3.27 and 3.28.

$$\frac{\Delta T}{T} = -\frac{eN}{\epsilon_0 c (n_A + n_B) A_{\text{eff}}} \left(\left(\mu_{\text{deloc}} - \frac{\mu_{\text{loc}} k_{\text{loc}}}{k_{\text{loc}} - k_R} \right) e^{-k_{\text{loc}} t} + \frac{\mu_{\text{loc}} k_{\text{loc}}}{k_{\text{loc}} - k_R} e^{-k_R t} \right) \quad (3.29)$$

where n_A and n_B are the refractive indices of the optically thick (at THz frequencies) materials interfacing the films, i.e. quartz and air, respectively. For the quartz side, n_A is set as 2.13. For the film/air side, n_B is set as 1.

To account for the instrument response function (IRF) of the OPTP system used here, Equation 3.29 was convolved with a normalised Gaussian pulse with $\sigma_{\text{IRF}} = 0.34$ ps (Refer to Section 3.3.2.4). Accounting for the time zero offset t_0 , the overall analytical expression used to fit the OPTP data was derived as:

$$\begin{aligned} \frac{\Delta T}{T} = & - \frac{eN}{2\epsilon_0 c (n_A + n_B) A_{\text{eff}}} \left[\left(\mu_{\text{deloc}} - \frac{\mu_{\text{loc}} k_{\text{loc}}}{k_{\text{loc}} - k_R} \right) e^{-k_{\text{loc}}(t-t_0) + \frac{k_{\text{loc}}^2 \sigma_{\text{IRF}}^2}{2}} \text{Erfc} \left(\frac{k_{\text{loc}} \sigma_{\text{IRF}}^2 - (t - t_0)}{\sqrt{2} \sigma_{\text{IRF}}} \right) \right. \\ & \left. + \frac{\mu_{\text{loc}} k_{\text{loc}}}{k_{\text{loc}} - k_R} e^{-k_R(t-t_0) + \frac{k_R^2 \sigma_{\text{IRF}}^2}{2}} \text{Erfc} \left(\frac{k_R \sigma_{\text{IRF}}^2 - (t - t_0)}{\sqrt{2} \sigma_{\text{IRF}}} \right) \right]. \end{aligned} \quad (3.30)$$

Here, $\text{Erfc}(x)$ is the complementary error function, defined as:

$$\text{Erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt \quad (3.31)$$

The OPTP transients were globally fitted across all three fluences up to 10 ps, yielding values for μ_{loc} , μ_{deloc} , k_{loc} . k_R was fixed to the value obtained from long-time OPTP fitting (Section 3.3.2.2) to obtain more accurate values for the early time parameters.

3.3.2.4 Instrument Response

The IRF of the THz OPTP spectroscopy system with the 530 nm excitation wavelength used in this thesis was determined by measuring the finely spaced photoconductivity onset of a silicon wafer. The onset was fitted with an error function, which is defined as:

$$F(x) = A (1 - \text{Erf}(B(x - C))) + D \quad (3.32)$$

where A , B , C , D are fitting constants. The $\text{Erf}(x)$ is defined as Equation 3.31. Then, the error function was converted into a Gaussian function to simulate the IRF:

$$G(x) = \alpha \exp \left[- \left(\frac{x - \beta}{\sqrt{2} \sigma_{\text{IRF}}} \right)^2 \right] \quad (3.33)$$

where α is the amplitude, β is the position of the centre of the peak. σ_{IRF} was determined from the fitted value B by $\sigma_{\text{IRF}} = 1/(\sqrt{2}B)$.

From the fit, the σ_{IRF} was determined as 0.34 ps, which is faster than the timescales of the ultrafast localisation process.

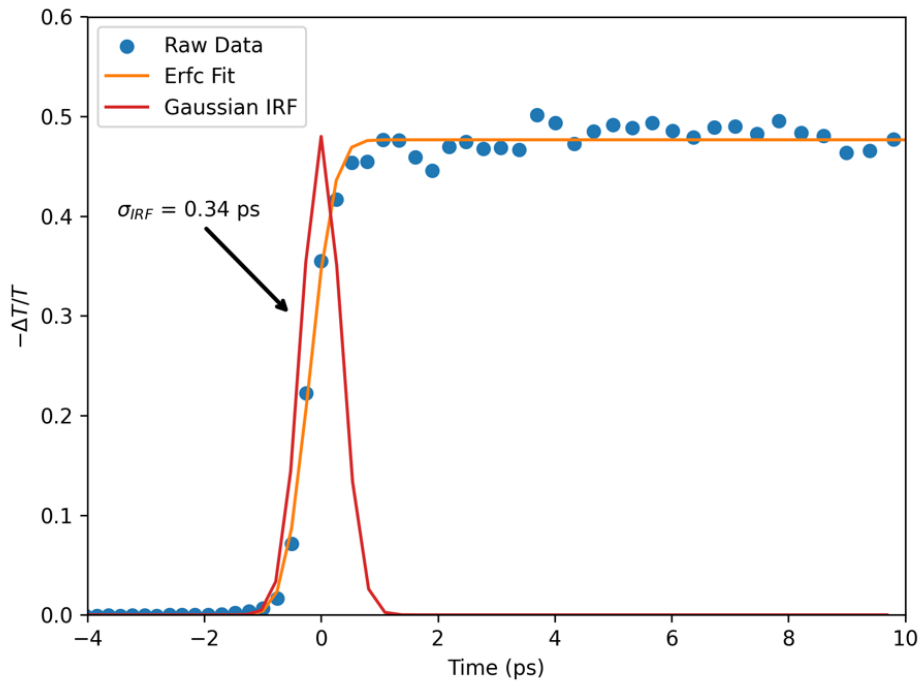


Figure 3.4: OPTP photoconductivity onset of a 2 mm-thick high-resistivity silicon wafer excited at 530 nm wavelength at a fluence of $58.9 \mu\text{Jcm}^{-2}$. The experimental data were fitted with an error function in order to extract the instrument response function (IRF). The resulting Gaussian IRF has a sigma of 0.34 ps, which is much shorter than the ultrafast localisation process discussed in Chapter 6.

3.4 Time-Resolved Microwave Conductivity Spectroscopy

Similar to OPTP, time-resolved microwave conductivity (TRMC) allows us to probe the transient photoconductivity of mobile free charge-carriers but in the GHz-frequency range. Unlike the typical TRMC measurements that measures the relative change of the microwave power reflected from a semiconductor that is caused by a small increase in the conductivity upon excitation in a microwave cavity,[111] TRMC setup here employs a free-space transmission geometry, allowing us to combine TRMC measurements with other complementary techniques such as TRPL and ssPL (see Section 3.2 for further details).

The lower frequencies of TRMC allow us to probe charge-carrier mobilities at longer timescales since the the probed charge transport distance scales with the square root of the inverse probe frequency.[112] Moreover, the TRMC measurements employed here are performed electronically and capture longer timescales, on the order of hundreds of nanoseconds, enabling

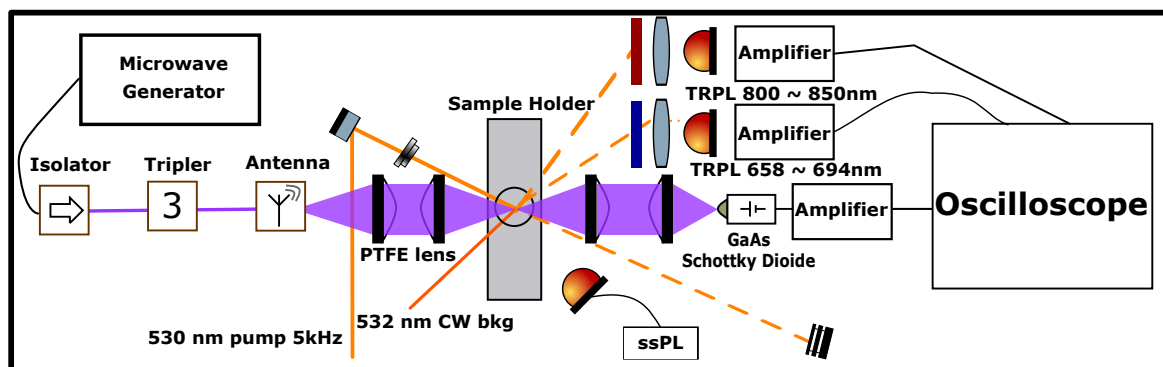


Figure 3.5: Schematic of the synchronous multimodal spectroscopy setup combining TRMC, TRPL, and ssPL. A continuous microwave (MW) probe is directed onto the sample using PTFE lenses, and the transmitted MW signal is detected with a GaAs Schottky diode. The resulting voltage change is amplified, and its temporal evolution recorded with an oscilloscope. The sample is photoexcited using 530 nm femtosecond laser pulses at 5 kHz, while a 532 nm CW laser is simultaneously applied to induce halide segregation (see Chapter 5). TRPL is measured using fast photodiodes, with emission collected in the 658–694 nm and 800–850 nm spectral ranges defined by bandpass filters. Simultaneously, ssPL spectra are acquired using a fibre-coupled spectrometer.

the study of slower electronic processes such as interfacial recombination. This contrasts with OPTP, which is limited to sub-ns resolution constrained by the length of the optical delay stage.

3.4.1 Synchronous multimodal Spectroscopy Setup

The synchronous multimodal spectroscopy that combines TRMC, TRPL (see Section 3.2.2) and ssPL (see Section 3.2.1) is employed in Chapter 5. Microwave radiation at 34 GHz was generated using a signal generator, converted to 102 GHz using a frequency tripler, and launched into free space with a standard gain feed horn antenna. The high-frequency, millimeter-wave microwave radiation was focused onto a sample and re-focused onto a detector with PTFE lenses. The microwave intensity transmitted through the sample was measured with a custom-made GaAs Schottky-diode detector and measured with a fast oscilloscope (Tektronix MSO64). The microwave conductivity system was operated in transmission geometry with most of the incident microwave signal being transmitted through the sample, and the change in transmission directly upon photoexcitation typically amounting to < 5% of the transmitted signal in the absence of photoexcitation, depending on the excitation fluence used. The mixed and I-rich phase

TRPL were measured using 658–694 nm (Edmund Optics, #86–988) and 800–850 nm (Edmund Optics, #86–95) respectively with a fast photodiode detector (Thorlabs, DET025A/M), from which the signal was amplified with a broad-band amplifier made in-house and measured with the same oscilloscope as above. The spectrally resolved photoluminescence was measured using a fibre-coupled spectrometer (Ocean Optics, SR6) with 600 nm long-pass filter (Thorlabs, FELH0600) to filter out the excitation laser peak. The ssPL spectra are spectrally corrected with an OL245M irradiance standard tungsten lamp and background-corrected by a spectrum recorded without laser excitation for the same acquisition time. The samples were photoexcited with pulsed laser light originating from a Ti:Sapphire amplified laser system (Spectra-Physics, MaiTai-Ascend-Spitfire, 35 fs pulse duration), converted to 530 nm central wavelength using an optical parametric amplifier (Light Conversion, TOPAS-C). The 532 nm background CW beam was provided by a Ventus 532 laser.

3.5 X-ray Diffraction

X-ray diffraction (XRD) is commonly employed to identify the crystallographic phases present in a material, assess its overall crystalline quality, and provide information on the orientation and size of the crystallites within the studied phase.[113]

XRD patterns arise from the constructive interference of X-rays scattered by the crystal lattice planes as illustrated in Figure 3.6. Such constructive interference occurs only when the difference in path length between X-rays scattered from successive parallel planes equals an integer multiple of the incident X-ray wavelength. This is described by Bragg's law, which is mathematically expressed as:[31, 113]

$$n\lambda = 2d \sin \theta \quad (3.34)$$

where n is an integer, λ denotes the X-ray wavelength, d is the spacing between lattice planes, and 2θ represents the diffraction angle of the incident X-ray.[31, 113] By analysing the resulting

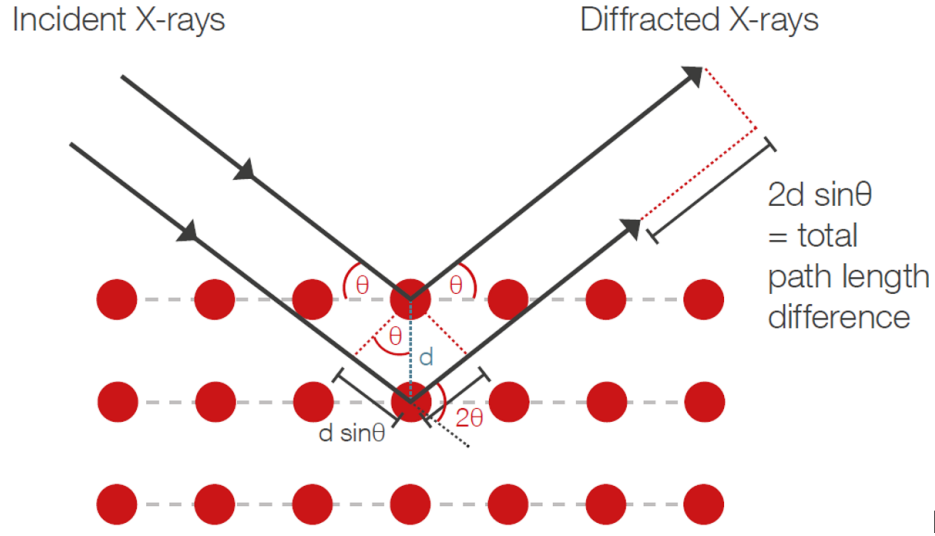


Figure 3.6: Schematic illustration of Bragg diffraction showing X-rays scattering off atoms spaced with distance d (red circles) at the scattering angle 2θ . Figure adapted from Ref [114].

X-ray diffraction patterns, one can evaluate the crystalline quality and crystallographic purity of a material, as well as identify and quantify lattice distortions, expansions, or contractions.[31]

In XRD patterns, each diffraction peak corresponds to a family of lattice planes reflecting a specific periodicity within the crystal lattice, defined by a set of Miller indices (hkl) . [31] These planes are orthogonal to the reciprocal lattice vector $\mathbf{g} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$, where $(\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3)$ are the primitive reciprocal lattice vectors. Equivalently, the (hkl) planes can be described as those intersecting the unit cell axes at a_1/h , a_2/k , and a_3/l , where $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ are the primitive lattice vectors.

3.5.1 Experimental Setup

All X-ray diffraction (XRD) patterns in this thesis were measured in air using a Panalytical Empyrean powder diffractometer with a copper X-ray source (Cu $K\alpha 1$ X-rays with a wavelength of $1.5406 \text{ \AA}$). The scan range was from 10.0° to 45.0° and the scan step size was set as 0.004° . The raw XRD patterns were then corrected for tilt by shifting the 2θ -axis to the z-cut quartz reference peak, which is at $2\theta = 16.433^\circ$. [99]

3.5.2 Pawley Fitting

Pawley fitting is a method in which the diffraction peaks observed in a powder XRD pattern are fitted to 2θ positions determined by the unit cell dimensions and crystal symmetry.[115] The procedure begins by generating a set of expected reflections from an initial unit cell model, after which the lattice parameters are refined to optimise the agreement between calculated and measured peak positions. Once the unit cell is refined, the intensities of individual peaks are adjusted independently, while background, peak shapes, and instrumental correction parameters are simultaneously refined to achieve an accurate representation of the experimental diffraction pattern.[116] Pawley fitting was carried out using HighScore Plus software.

3.6 Scanning Electron Microscopy

[performed by Siyu Yan, Department of Physics, University of Oxford]

Scanning electron microscopy (SEM) is a versatile imaging technique where a focused electron beam is raster-scanned across the surface of a sample to produce high-resolution images, revealing information about surface morphology and composition. The two most commonly employed detection modes are secondary electrons (SE) and backscattered electrons (BSE). SEs primarily provide morphology-based contrast, whereas BSEs carry information on both compositional contrast and, to some extent, surface structure. Because SEs have very low energies, their escape depth is limited to only a few nm from the surface, resulting in a signal that is highly localised to the point of beam interaction. This localisation enables SEM imaging with SE detection to achieve higher spatial resolution compared to BSE detection [117].

For all SEM measurements in this thesis, top-down and cross-sectional SEM images were taken on a FEI Quanta 600 FEG at 5 kV acceleration voltage with current defined by spot size 3.0 using SE.

3.7 Sample Fabrication

3.7.1 $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ Perovskite Thin Films

[performed by Robert D. J. Oliver, Department of Physics, University of Oxford]

3.7.1.1 Details for Chapter 4

The perovskite precursor chemicals were purchased from the following suppliers: lead iodide (PbI_2 , 99.99 %) was purchased from TCI; lead bromide (PbBr_2 , 98 %), cesium iodide (CsI , 99.999 %) and cesium bromide (CsBr , 99.9 %) were purchased from Alfa Aesar; formamidinium iodide (FAI , >99.99 %) and formamidinium bromide (FABr , >99.99 %) were purchased from Greatcell Solar. PTAA (Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine], MW = 13,000 g/mol) was purchased from Flexink. PMMA (Poly(methyl methacrylate), MW = 15,000 g/mol) were purchased from Sigma Aldrich. All solvents in this work were purchased from Sigma Aldrich.

$\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_3$ was formed by weighing CsI , FAI , PbI_2 stoichiometrically in an N_2 filled glovebox. Similarly, $\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbBr}_3$ was formed by weighing CsBr , FABr , PbBr_2 stoichiometrically in an N_2 filled glovebox. To each, an appropriate volume of 4:1 DMF (dimethylformamide) : DMSO (dimethylsulfoxide) was added to achieve a nominal concentration of 0.6 M. Each solution was stirred overnight. To achieve intermediary bromide ratios, appropriate volumes of each of these solutions were mixed.

PTAA and PMMA were dissolved in chlorobenzene at concentrations of 80 mg/mL and 100 mg/mL respectively.

Circular (diameter = 13 mm) z-cut quartz substrates were purchased from UQG optics. Before deposition the following cleaning procedure was undertaken. The substrates were sequentially sonicated for at least 15 minutes in 1 vol % Decon90 in deionised water, acetone and isopropanol. Following the final sonication, the substrates were dried with a N_2 gun. The substrates were then treated with a UV-ozone plasma for 15 minutes before being imme-

Bromide Content (x)	Antisolvent quench time (seconds before end of cycle)
0	5
0.1	5
0.2	5
0.3	6
0.4	6
0.5	7
0.6	8
0.7	8
0.8	11
0.9	11
1.0	15

Table 3.1: Antisolvent quench time in seconds before end of cycle for each bromide content, x

diately transferred into an N₂ filled glovebox where the perovskite thin films and polymer layers were deposited.

To form the perovskite thin films, the following spin-coating procedure was used. 50 μL of perovskite precursor was dynamically deposited onto the substrate spinning at 1000 rpm. After 5 s, the substrate was accelerated at a rate of 800 rpm/s to a final speed of 5000 rpm for 30 s. An antisolvent quench was performed by depositing 50 μL of anisole at optimised times (see below table 3.1) before the end of the spin-coating cycle for each bromide ratio. Following the spin-coating procedure, the perovskite thin films were annealed for 1 hr at 100 °C. After annealing, the samples were allowed to return to ambient temperature (25 °C).

Either polymer layer was applied by depositing 60 μL on a static substrate. The substrate was then accelerated to 2000 rpm for 30s. The samples were then annealed for 5 mins.

3.7.1.2 Details for Chapter 5

Tin(IV) oxide (SnO₂, 15% in H₂O colloidal dispersion) was purchased from Alfa Aesar and diluted to 2% with deionised water. PTAA (Flexink) was dissolved in chlorobenzene (Sigma Aldrich) at a concentration of 2.0 mg mL⁻¹. PMMA (Sigma Aldrich, mean molar weight 97,000 g mol⁻¹) was dissolved in chlorobenzene (Sigma Aldrich) at 150 mg mL⁻¹. The FA_{0.83}Cs_{0.17}Pb

($\text{I}_{0.6}\text{Br}_{0.4}$)₃ perovskite precursor solution was prepared by stoichiometrically weighing FAI (GreatCell Solar), CsI (Alfa Aesar), PbI_2 (TCI), and PbBr_2 (Alfa Aesar) inside a N_2 -filled glovebox. The precursor salts were dissolved in a 4:1 mixture of DMF:DMSO, stirred overnight at room temperature without heating, and used without further processing.

The z-cut quartz substrates were cleaned by sequential sonication in Hellmanex (3% in deionised water), deionised water, acetone, and isopropanol for 15 min each. They were then treated with UV-ozone for 15 min and subsequently transferred into a N_2 -filled glovebox.

The SnO_2 solution was spin-coated in ambient air at 4000 rpm for 30 s and annealed in air at 180 °C for 30 min. Before perovskite deposition, the substrates were treated with UV-ozone for 10 min and transferred into a N_2 -filled glovebox. The PTAA solution was spin-coated by dispensing 50 μL onto quartz substrates spinning at 6000 rpm for 30 s, followed by annealing at 100 °C for 10 min. This layer was subsequently treated with an Al_2O_3 nanoparticle solution (1:150 in isopropanol), spin-coated at 2000 rpm for 20 s, and annealed for 30 s to improve wetting and ensure full film coverage.

For the perovskite layer, 50 μL of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ precursor solution was dynamically dispensed onto substrates spinning at 1000 rpm. After 5 s, the spin speed was increased to 5000 rpm over 5 s and maintained for 30 s. An antisolvent quench was performed by depositing 50 μL of anisole 5 s before the end of the cycle. The films were then annealed at 100 °C for 60 min.

Finally, a PMMA encapsulation layer was applied to minimise atmospheric effects. To form the PMMA film, 40 μL of solution was deposited statically onto the perovskite layer and spin-coated at 2000 rpm for 25 s with an acceleration rate of 1000 rpm s^{-1} . The films were annealed at 100 °C for 3 min to remove residual solvent.

3.7.2 Coevaporation of $\text{Cu}_2\text{AgBiI}_6$ Thin Films

[performed by Benjamin W. J. Putland, Department of Physics, University of Oxford]

3.7.2.1 Fabrication of Quartz/Cu₂AgBiI₆

Prior to the vapor-phase deposition of Cu₂AgBiI₆ (CABI), a tooling factor for each precursor was calculated to correct the divergence between the true evaporation rate and the rate measured by the QCM. For this purpose, 100 nm (as measured on the SQC-310 controller) of each precursor was deposited on 30 × 30 mm glass substrates (Lumtec, product number LT-G000) and the thickness was measured using a Veeco Dektak 150 profilometer. A new tooling factor was calculated using Equation

$$\text{tooling factor} = \text{default tooling factor} \times \frac{\text{thickness (Dektak)}}{\text{thickness (QCM)}} \quad (3.35)$$

The thickness was later verified by using the cross-sectional SEM images as shown in Table 3.2. Detailed CABI vapor-phase deposition parameters are provided together with the information on the fabrication of the various half-stack samples below. Putland et al. have previously shown that for identical vapor-phase deposition protocols for CABI, subsequent annealing of the CABI films led to the formation of additional CuI peaks in the XRD patterns and poor morphology with smaller grains and increased pinhole density.[118] For this reason, CABI thin films were unannealed for this study, in order to minimize the amount of impurity phases included.

Thin films used for characterization were evaporated onto z-cut quartz substrates (UQG, 13 mm diameter × 2 mm thickness) that were first prepared by sequentially sonicating the substrates in 200 mL of Decon90 and DI water (2% concentration) (Milli-Q IQ), 200 mL of DI water (Milli-Q IQ), 200 mL acetone (ACS reagent, ≥99.5%, Sigma-Aldrich), and 200 mL isopropanol (anhydrous, 99.5%, Sigma-Aldrich) for 15 min each, then O₂ plasma cleaned for 10 min (Diener electronics, Model: Pico), and UV–Ozone cleaned for 15 min (Jelight Company Inc., Model: 30-220) prior to deposition of Cu₂AgBiI₆.

Thin films of CABI were fabricated by evaporating under vacuum (BOC Edwards Auto 306) in codeposition bismuth(III) iodide (Alpha Aesar Puratronic, 99.999%), silver(I) iodide

Sample	Thickness (nm)
Q/CABI	240
Q/CABI/PTAA	288
Q/CABI/CuI	416
Q/PCBM/CABI	256
Q/SnO ₂ /CABI	262

Table 3.2: Thicknesses of CABI films determined from cross-sectional SEM, including both CABI and, where present, charge transport layers.

(Alpha Aesar Premion, 99.999%), and copper(I) iodide (Alpha Aesar Puratronic, 99.998%) precursors from three separate, 2.4 cm³ alumina crucibles and thermal sources. The crucibles and sources were custom-made by Moorfield Nanotechnology to fit the dimensions of the evaporation chamber. The precursors were heated to the temperature corresponding to the following evaporation rates: CuI, AgI, BiI₃ = 0.33 Ås⁻¹ (370 °C), 0.18 Ås⁻¹ (475 °C), and 0.50 Ås⁻¹ (230 °C), respectively, and deposited until a CABI film with a thickness of (250 ± 20) nm was reached, as measured by a Veeco Dektak 150 profilometer. The rates were measured using three quartz crystal microbalances (QCM) positioned off center to each source's vapor cone and an Inficon SQC-310 deposition controller.

All depositions were carried out under vacuum ($\sim 2 \times 10^{-6}$ mbar). The substrates were protected during the heating and cooling process by a mechanical shutter, and the substrates were rotated during deposition to improve surface coverage. No intentional substrate heating was applied. However, the substrates reached a maximum temperature of approximately 60 °C during codeposition due to heat transfer from the sources. The temperature of the substrates was measured using RS Electronics PRO nonreversible temperature sensitive labels (RS Stock No.: 779–9779).

3.7.2.2 Fabrication of Quartz/Cu₂AgBiI₆/PTAA

CABI was deposited on quartz as above. PTAA (99.99%, Flexink) was prepared by mixing PTAA in toluene (anhydrous, 99.8%, Sigma–Aldrich) (10 mg/mL). Prior to deposition, the

PTAA solution was filtered using a 0.22 μm PTFE filter (13 mm diameter, Gilson Scientific Ltd.). To deposit the layer, 150 μL was statically spin coated in ambient air at 4000 rpm spin speed, 2000 rpm s^{-1} ramp rate, for 30 s. PTAA films were not annealed. The ambient air temperature and humidity were not measured for each deposition, but the cleanroom where it was carried out ranges in temperature between 18 and 25 $^{\circ}\text{C}$ with a relative humidity between 20 and 50%.

3.7.2.3 Fabrication of Quartz/ $\text{Cu}_2\text{AgBiI}_6$ /CuI

To fabricate Quartz/CABI/CuI thin films, CABI was deposited on quartz as described above. Copper(I) iodide (Alpha Aesar Puratronic, 99.998%) was subsequently deposited in the same chamber, using the same CuI source, and during the same deposition. To do this, after CABI was deposited, the substrate shutter was closed, and the BiI_3 and AgI sources were cooled to room temperature. The temperature of the CuI source was initially held at approximately 100 $^{\circ}\text{C}$ (corresponding to a CuI evaporation rate of 0 $\text{\AA}\text{s}^{-1}$) until the chamber pressure decreased to 10^{-6} mbar. Subsequently, the temperature was increased, and once a stable CuI deposition rate of 0.5 $\text{\AA}\text{s}^{-1}$ was achieved, the shutter was opened, and a nominal CuI thickness of 200 nm was deposited on the CABI film. Films were not annealed postdeposition.

3.7.2.4 Fabrication of Quartz/PCBM/ $\text{Cu}_2\text{AgBiI}_6$

To fabricate quartz/PCBM/CABI samples, [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM) was prepared by dissolving 20 mg/mL in a 3:1 chlorobenzene/dichlorobenzene mixture and stirred for 15 min at room temperature inside a N_2 glovebox (O_2 and H_2O < 5 ppm). Prior to deposition, the solution was filtered using a 0.22 μm PTFE filter (13 mm diameter, Gilson Scientific Ltd.). The PCBM solution was then deposited on the quartz substrates inside an N_2 glovebox (O_2 and H_2O < 5 ppm) by dynamically spin coating 50 μL at 2000 rpm for 30 s followed by annealing at 100 $^{\circ}\text{C}$ for 1 min. After the deposition of PCBM, the samples were transferred to the evaporation chamber and CABI was deposited as described above. The samples were not annealed postdeposition.

3.7.2.5 Fabrication of Quartz/SnO₂/Cu₂AgBiI₆

SnO₂ was deposited onto z-cut quartz substrates by first following the same substrate cleaning procedure as previously described for quartz/CABI films, with the exception that the substrates underwent UV-ozone cleaning for 30 min instead of 15 min. Upon finishing the cleaning procedure, planar SnO₂ was immediately deposited by spin coating 200 μ L of a 2% mixture of SnO₂ nanoparticles (Fisher Scientific, 15% colloidal dispersion in H₂O) in ultrapure water (Cayman Chemical, item no. 400000) in air at 4000 rpm spin speed, 2000 rpm s⁻¹ ramp rate, for 30 s, followed by immediate annealing in air at 150 °C for 30 min before quenching to room temperature. CABI was then fabricated as described above. Films were not annealed postdeposition.

4

Unraveling Loss Mechanisms Arising from Energy-Level Misalignment between Metal Halide Perovskites and Hole Transport Layers

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Jae Eun Lee performed all the experiments and data analysis except sample fabrication and SEM, and wrote the manuscript. Silvia G. Motti and Laura M. Herz supervised. Robert D.J. Oliver fabricated the samples. Siyu Yan conducted SEM. All authors discussed the results and reviewed the manuscript.

4.1 Broader Context

Metal-halide perovskites (MHPs) are promising light absorbers for multijunction photovoltaic applications because of their remarkable bandgap tunability, achieved through compositional mixing on the halide site. However, poor energy-level alignment at the interface between wide-bandgap mixed-halide perovskites and charge-extraction layers (CTLs) still causes significant losses in solar-cell performance. In this chapter, the origin of such losses is investigated, focusing on the energy-level misalignment between the valence band maximum and the highest occupied molecular orbital (HOMO) for a commonly employed combination, $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ with bromide content x ranging from 0 to 1, and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA). A combination of time-resolved photoluminescence spectroscopy and numerical modeling of charge-carrier dynamics reveals that open-circuit voltage (V_{OC}) losses associated with a rising energy-level misalignment derive from increasing accumulation of holes in the HOMO of PTAA, which then subsequently recombine non-radiatively across the interface via interfacial defects. Simulations assuming an ideal choice of hole-transport material to pair with $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ show that such V_{OC} losses originating from energy-level misalignment can be reduced by up to 70 mV. These findings highlight the urgent need for tailored charge-extraction materials exhibiting improved energy-level alignment with wide-bandgap mixed-halide perovskites to enable solar cells with improved power conversion efficiencies.

4.2 Introduction

MHPs have been in the limelight as light-harvesting materials in next-generation “perovskite” solar cells that have demonstrated an unprecedentedly rapid improvement. Their certified power conversion efficiencies (PCE) have risen to 26.95 % over the past decade, approaching the record efficiency of crystalline silicon (c-Si).^[2] Such success derives from their excellent optoelectronic properties including high optical absorption coefficients near 10^5 cm^{-1} ,^[119] sharp absorption edges with Urbach energies as small as 15 meV,^[13] low exciton binding energies similar to thermal energy at ambient temperature,^[16] sufficiently slow electron-hole recombination rates of $\approx 10^{-10} \text{ cm}^3 \text{ s}^{-1}$,^[15] relatively low defect densities even for materials processed with simple solution or evaporation methods,^[120] and long charge-carrier diffusion lengths of a few μm .^[43] In addition, the ease of bandgap tunability of lead mixed-halide perovskites from ≈ 1.5 –2.3 eV through simple adjustment of the ratio between iodide and bromide on the X site of the ABX_3 crystal makes them particularly appealing for use in multijunction solar cells.^[10] For example, c-Si:MHP tandem solar cells are theoretically capable of achieving a PCE of 45.3 %, ^[61, 121] significantly surpassing the thermodynamic limit of a single-junction solar cell.^[18] However, the actual record PCE reported for state-of-the-art c-Si:MHP tandem solar cells is currently only 36.85 %, ^[2] highlighting that significant losses persist.

One of the main challenges of two-terminal tandem solar cells is to ensure current-matching between the subcells while maximizing V_{OC} of each subcell in order to optimize overall PCE.^[61, 121] Such current matching requires careful choice of the bandgaps of the constituent semiconductors. Since the bandgap of c-Si in the bottom cell is fixed, this necessitates tuning of the perovskite top cell in order to achieve a wide-bandgap perovskite (WBP) with a bandgap greater than 1.7 eV. However, it has been widely observed that the average V_{OC} losses increase with increasing bandgap when identical transport layers are used.^[19, 22, 61, 121, 122] Identifying the cause of such loss mechanisms in WBPs has therefore emerged

as a prominent challenge toward the goal of achieving high-performance silicon-perovskite tandem solar cells. Several key factors affecting V_{OC} losses in WBPs have been identified, including bulk non-radiative losses, interfacial losses, and halide segregation under illumination or electric bias, during which the initial mixed iodide and bromide phases segregate to form iodide-rich and bromide-rich phases.[19, 20, 22, 53, 58–61, 63, 121–124] Initially, halide segregation was suspected to be the main source of V_{OC} losses because the formation of the iodide-rich phases with a narrower bandgap,[20, 53, 58–60, 63, 123, 124] and channeling of charge carriers into these phases,[20, 53, 58–60, 63, 123, 124] would ultimately limit the quasi-fermi level splitting (QFLS) to a lower value than that achievable in the original mixed-halide material. However, recent research instead stipulated that non-radiative losses occurring at the interface between the MHP and transport layers are a far more prominent source of losses than those arising from halide segregation.[19, 22, 61, 121, 122] Through the development of novel transport layers with better energy-level alignment, surface passivation techniques, and fabrication process methods, a state-of-the-art ~ 1.7 eV WBP has recently managed to achieve a V_{OC} of just over ~ 1.3 V, corresponding to ~ 80 mV of V_{OC} loss with respect to the Shockley-Queisser limit.[125–132] Notably, this substantial increase in V_{OC} was realized through a treatment based on 1,3-propane-diammonium iodide, which significantly reduces V_{OC} losses originating from the WBP:C60 interface.[125–132] In this case, the losses occurring at the WBP:HTL interface becomes the limiting factor on which further improvement must focus.[19, 22, 73, 122, 133] Importantly, such losses at WBP:HTL interfaces will become even more significant for a 2 eV bandgap WBP, which offers an ideal bandgap for the top cell in perovskite/perovskite/c-Si triple junction solar cells.[19, 22, 122, 134] Therefore, in order for WBPs and the associated tandem solar cells to reach their full potential, an understanding and mitigation of the interfacial losses at the WBP:HTL interface will be critical. However, the extent of interfacial losses with increasing energy-level misalignment and their link with charge-

carrier dynamics as well as the resulting loss mechanisms have not been fully understood.[11, 19, 20, 22, 53, 58–60, 63, 73, 122–124, 133, 135, 136]

In this work, I investigate the photophysical origin of losses at the interfaces between films of the prototypical WBP $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ with bromide content varying $0 \leq x \leq 1$ and the frequently implemented PTAA used as a HTL. I explore how such interfacial losses depend on the varying energy-level misalignment between the valence band maxima (VBM) of the WBPs and the HOMO of PTAA by applying a global kinetic model based on experimentally recorded time-resolved photoluminescence (TRPL) decays. $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ thin films were coated with either PTAA, or poly(methyl methacrylate) (PMMA) as an inert reference, and characterized through X-ray diffraction, optical absorption, photoluminescence, and THz conductivity probes, to ascertain that representative high-quality MHPs had been fabricated across the different bromide contents. A combination of steady-state PL and TRPL shows that the presence of a PTAA hole-extraction layer introduces additional non-radiative recombination processes which become more significant with increasing energy-level misalignment with the WBP. A kinetic model was developed to incorporate a range of dynamical charge-carrier processes occurring at the MHP:PTAA interface, such as hole transfer, hole back transfer, and across-interfacial recombination. Through a correlation of such global modeling with experimental TRPL traces, I reveal that the combination of an increasing degree of hole accumulation, which is defined as the ratio of hole transfer rate to hole back transfer rate, and subsequent across-interfacial recombination significantly enhance non-radiative losses with increasing energy-level misalignment. I show that while the early TRPL dynamics are mainly influenced by hole transfer to the HOMO of PTAA, the later TRPL dynamics are determined by across-interfacial recombination with the amplitude of the late TRPL dynamics determined by the degree of hole accumulation. I further quantitatively assess the extent to which defect-assisted recombination contributes to the dynamics. Based on such complete mapping of individual dynamic processes followed by charge carriers in time, I identify that for the scenario of an

ideally matched HTL, elimination of such loss processes could recover V_{OC} losses by 41 and 70 mV for 1.7 and 2.0 eV MHPs, respectively. These findings provide essential fundamental understanding of the dominant non-radiative losses currently occurring at the interface of WBP with hole extraction layers and pave the way for the design and development of more suitable HTLs with ideal energy-level alignment.

4.3 Results and Discussion

4.3.1 Optoelectronic Properties of $FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$

Thin films of $FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$ with bromide content x ranging from 0 to 1 with an increment of 0.1 were fabricated through a solution-casting method and subsequently coated with a film of either PMMA or PTAA as described in Section 3.7.1.1. **The samples were fabricated by Robert D. J. Oliver, Department of Physics, University of Oxford.** While PMMA acts as an electronically inert encapsulating layer preventing accelerated degradation, e.g. induced by moisture or air under illumination,[20, 53, 58–60, 63, 78, 123, 124] PTAA acts as a HTL, which has proven to work well across the full compositional range investigated.[11, 19, 20, 22, 53, 58–60, 63, 122–124, 135, 136, 138] The structure of such “half stack” architectures is schematically shown in the inset of Figure 4.1a. To illustrate the electronic alignment at the MHP:PTAA interfaces, Figure 4.1a shows the band edge energies for $FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$ together with the HOMO of PTAA, illustrating that with increasing x , the valence band maximum (VBM) of $FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$ deepens with respect to the vacuum level while the conduction band minimum (CBM) changes relatively little. Thus, increasing x leads to a greater energetic offset between the HOMO of PTAA and the VBM of $FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$,[137] which allows a systematic examination of the effect of such band offsets for an unaltered chemical structure of the molecular HTL. Such trends have been well established for lead iodide-bromide perovskites across both theoretical and experimental literature reports.[29, 137–141] The position of the VBM has been shown to be influenced by the hybridization between the 6s state of Pb and np

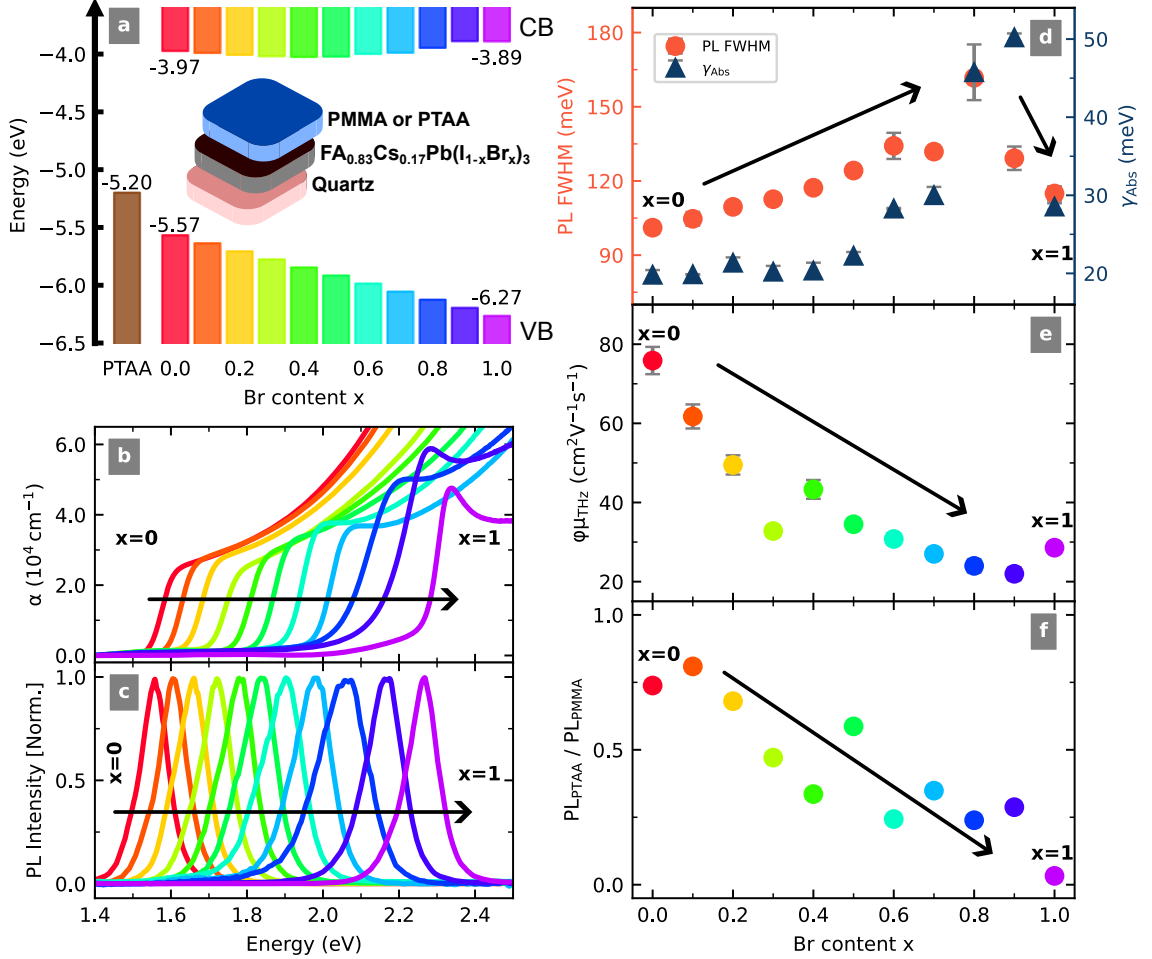


Figure 4.1: Bulk optoelectronic properties of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ for a range of bromide contents x ranging from 0 (red) to 1 (purple). (a) Schematic energy-level diagram for the MHP:PTAA interface, showing the range of valence band maxima (VBM) and conduction band minima (CBM) energies for $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ and the HOMO level of PTAA (brown). Energy values for the VBM of MHPs were obtained by extrapolating the ultraviolet photoelectron spectroscopy (UPS) measurements obtained from Prathapani et al.[137] (See Figure 4.2b) with the CBM obtained through addition of the bandgap energies to VBMs for each Br content. The HOMO of PTAA is taken as the value reported by Endres et al.[138] The inset shows the bilayer structure of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ thin films coated with either PMMA or PTAA. (b) Absorption coefficients (α) of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ coated with PMMA across Br contents x . (c) Normalized steady-state PL of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ coated with PMMA across Br contents x . (d) Corresponding full width at half maximum of the PL spectra (PL FWHM) and absorption edge broadening parameter (γ_{Abs}). (e) Effective THz electron-hole sum mobility ($\phi\mu_{\text{THz}}$) where ϕ is the photon-to-charge branching ratio and μ_{THz} is the sum mobility for the PMMA-coated MHP films with different Br contents x . (f) Ratio of the spectrally integrated PL emerging from the PTAA-coated MHP films to that emerging from the PMMA-coated MHP films, determined as a function of Br contents x .

state of the halides with a dominant contribution from the np states of the halides.[29, 138–141] When I is substituted with Br, the np state shifts downwards with increasing electronegativity deepening the VBM relative to the vacuum level. In contrast, the CBM is dominantly influenced by the 6p state of Pb, and changes in halide content thus have minimal effect on the CBM.[29, 138–141] A more detailed discussion is provided in Section 2.1.2. With general consensus across literature reports for such mixed-halide perovskites,[29, 137–141] I here utilize values for the VBM reported previously from ultraviolet photoelectron spectroscopy (UPS) measurements by Prathapani et al.[137] for the specific compositional range investigated here as shown in Figure 4.2. Values shown for the CBM were determined by adding the optical bandgap energies calculated from Elliot fits to the absorption coefficient spectra. The HOMO energy level of PTAA is taken from previously reported UPS measurements by Endres et al.[138]

I further characterized the basic structural and optoelectronic properties of the $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ films, confirming that these are indeed high-quality representatives and that the intended x has been incorporated for each thin film. Gradual blue shifts in the absorption edges and PL spectra, as shown in Figure 4.1b and c respectively, indicate that the expected increasing bromide content has been incorporated.[10, 137, 143] X-ray diffraction (XRD) patterns display the relevant XRD peaks, together with those of typical impurities, which do not affect our analysis significantly (See Figure 4.3). The perovskite diffraction peaks show a gradual increase in 2θ with increasing x , indicating lattice contraction induced by the replacement of larger iodide ions by smaller bromide ions.[10, 137] I further examine optoelectronic quality across the perovskite series with increasing bromide content. I find that both the full width at half maximum of the photoluminescence (PL FWHM) and the absorption edge broadening parameter (γ_{Abs}) as illustrated in Figure 4.1d increase with increasing x . In addition, the effective electron-hole sum mobilities at THz frequencies ($\phi\mu_{\text{THz}}$) as shown in Figure 4.1e decrease with increasing bromide content. While such trends may partly be influenced by an increase in electron-phonon coupling with increasing bromide content, driven by the increasingly polar lead-halide bond,[143] they

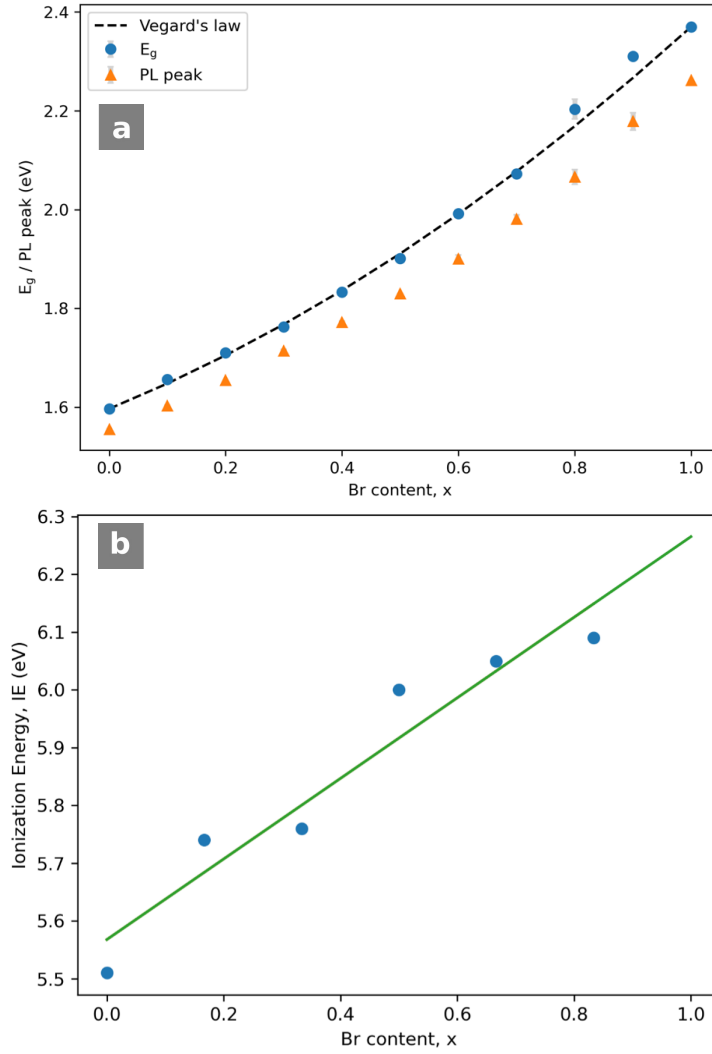


Figure 4.2: (a) Average optical bandgaps (E_g) of the PMMA- and PTAA-coated lead halide perovskite films obtained from the Elliott fit and steady state photoluminescence (PL) peaks plotted against Br content x . E_g is fitted with the modified Vegard's law,[142] which is expressed as $E_g = xE_{g_{Br}} + (1 - x)E_{g_I} - bx(1 - x)$ where $E_{g_{Br}}$ is the bandgap of $x = 1$ perovskite, E_{g_I} is the bandgap of $x = 0$ sample and b is the bowing parameter. From the fit, b is extracted as 0.29 ± 0.1 eV. (b) Linear fit to the ionization energy of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ against x extracted by Prathapani et al. from UPS measurements and reproduced and extrapolated here.[137]

may also be significantly influenced by extrinsic factors, such as scattering deriving from disorder, defects, and other imperfection that increase toward the high-bromide content MHPs, similar to previous reports.[46, 137] The additional XRD, PL, and absorption data of all composition ranges for PMMA- and PTAA-coated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ films can be found in Appendix A

To investigate the impact of the HTL on the overall optoelectronic quality of the half-stack architectures, Figure 4.1f shows the ratio between the spectrally integrated steady-state

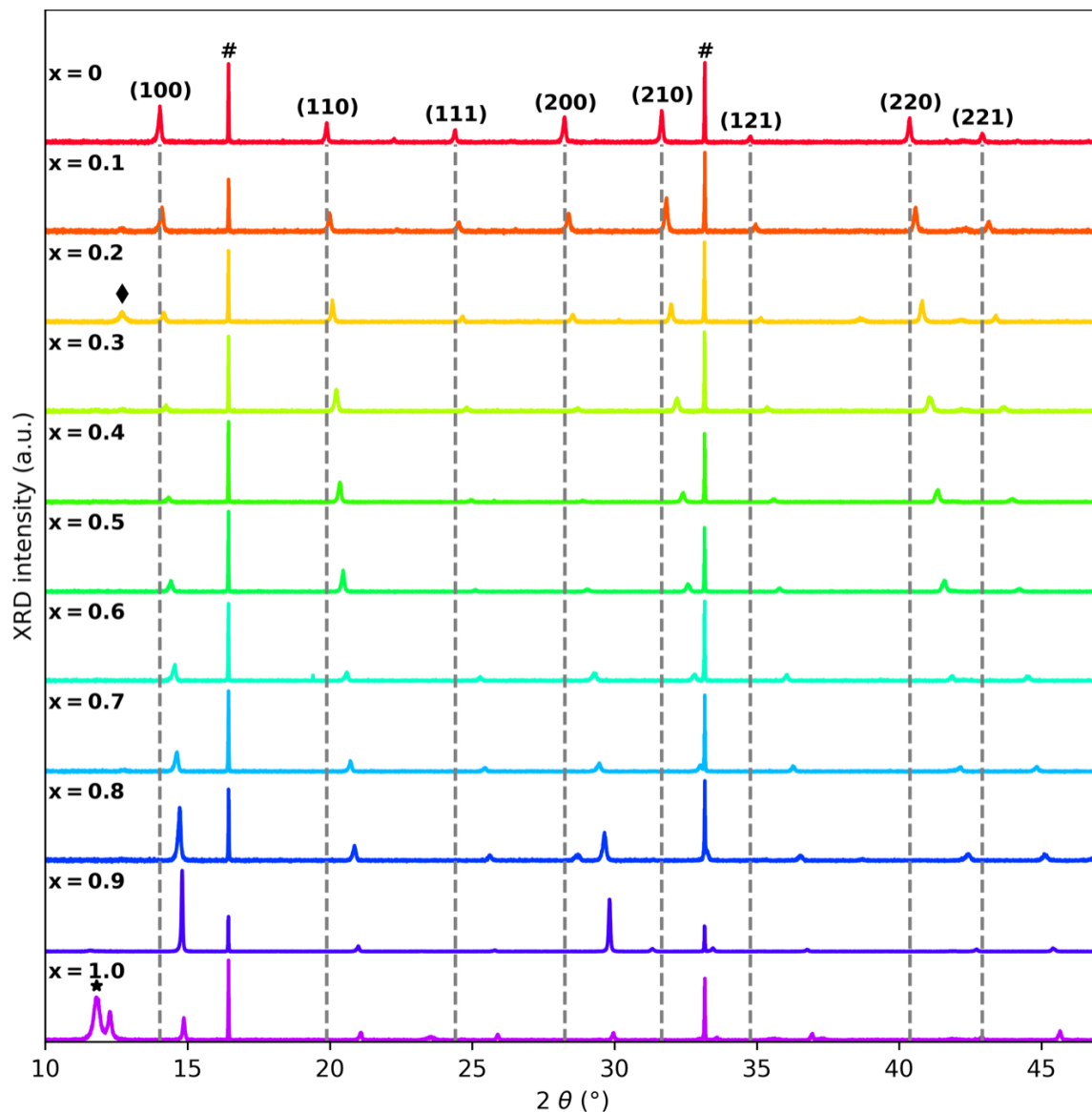


Figure 4.3: XRD spectra of the PMMA-coated perovskites with increasing Br content, x . Relevant pseudo-cubic $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ XRD peaks are labelled with the Miller indices, and they are identical with literature values.[137] The z-cut quartz reference peaks at $2\theta = 16.433^\circ$ and 33.172° are labelled as #.[99] The PbI_2 peak at $2\theta = 12.703^\circ$ is labelled as $\blacklozenge$. [99] The CsPb_2Br_5 peak at $2\theta = 11.801^\circ$ is labelled as $\star$. [144] The grey dotted lines are drawn to visually assist XRD peak shifts to higher 2θ with increasing x .

PL intensity recorded for the PTAA-coated MHP and that for the inert PMMA-coated MHP (PL_{PTAA}/PL_{PMMA}). The observed decrease in PL_{PTAA}/PL_{PMMA} with increasing bromide content x indicates that PTAA introduces significant additional non-radiative losses, compared to the PMMA-coated thin films, that grow markedly with increasing bromide content. According to detailed-balance theory,[145] such additional non-radiative losses introduced by PTAA will detrimentally lower the V_{OC} with respect to the MHP bandgap. To understand the role of the MHP:PTAA interface in such non-radiative losses and the reasons for their growth with increasing bromide content, I examine the charge-carrier dynamics occurring at such interfaces, assessing a complete set of dynamic processes.

4.3.2 Charge-Carrier Dynamics of $FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$

I recorded the time-resolved photoluminescence transients for both PMMA- and PTAA-coated MHP films across the full bromide content range, using the time-correlated single photon counting (TCSPC) technique. Pulsed excitation was carried out at a wavelength of 470 nm to prevent parasitic absorption and charge generation in the PMMA or PTAA layers,[138] which would further complicate the analysis of charge-carrier dynamics. An excitation pulse fluence of 76 nJcm^{-2} was chosen, which is roughly equivalent to 1-sun intensity, injecting an initial charge-carrier density of $\approx 10^{15} \text{ cm}^{-3}$. I ascertained that halide segregation effects, which iodide-bromide perovskites with mid- to high-bromide content are liable to exhibit,[21, 54, 55, 146] had an insignificant effect on those transients, under these excitation conditions with TRPL acquisition time limited to 1 minute (see Figure 4.4 for the PMMA-coated thin films and see Appendix Figure A.4 for the PTAA-coated thin films).

Representative TRPL decay dynamics are shown in Figure 4.5 for the thin films of the $FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$ with bromide content of $x = 0, 0.2$, and 1. I observe that the MHP films coated with the inert PMMA layers exhibit mostly monoexponential PL decays (orange circles), which is in agreement with charge-carrier recombination dominated by defect-assisted

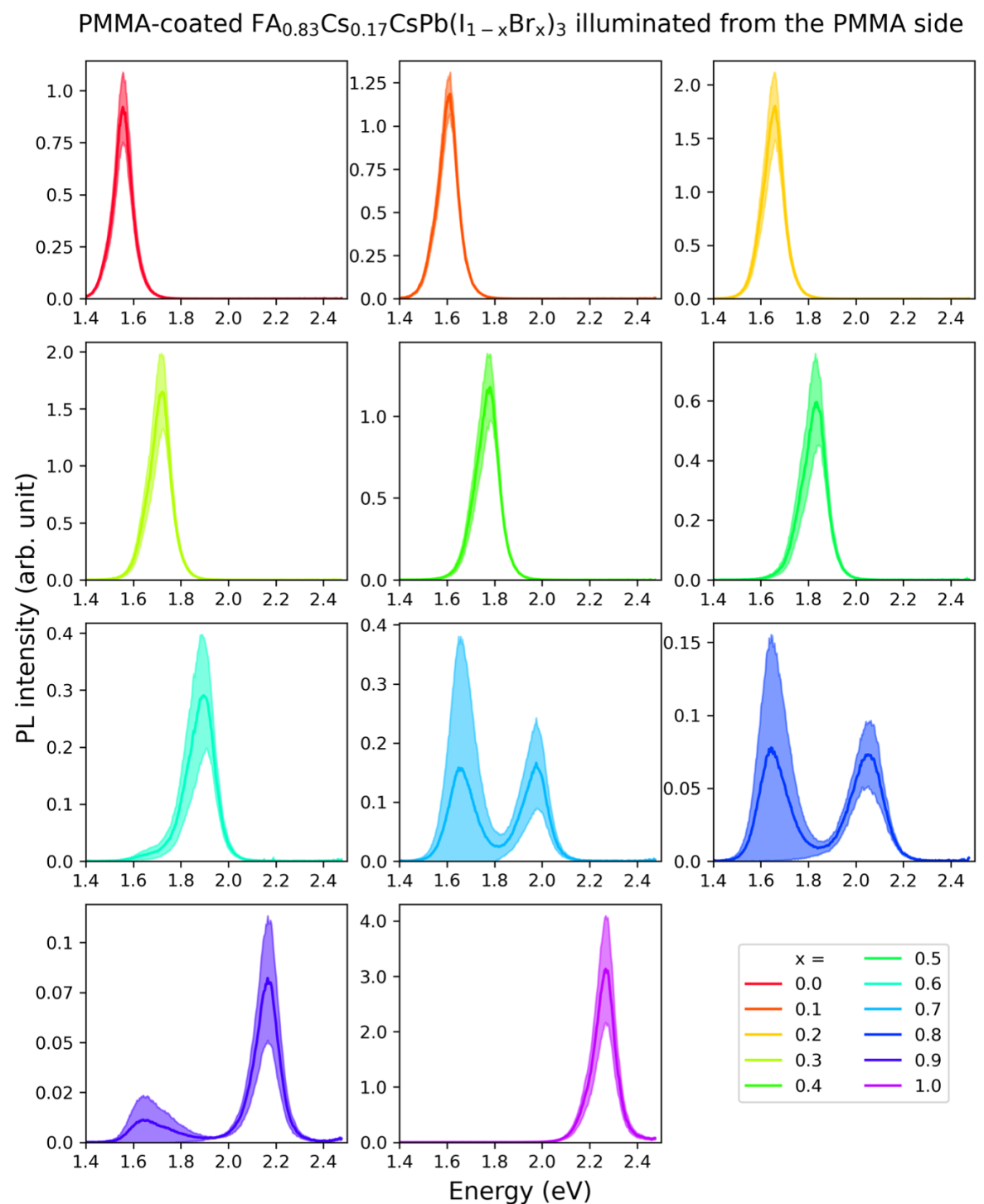


Figure 4.4: Averaged steady-state photoluminescence of 3 different spots in the PMMA-coated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskite films illuminated at a fluence of 76 nJcm^{-2} from the PMMA side before and after each 1-minute transient PL acquisition. The shaded regions represent the standard deviation of the mean.

pathways at sufficiently low charge-carrier densities.[36] However, PTAA-coated MHP films exhibit two distinct regimes in the PL transients (blue triangles), where an initial fast decay occurring within the first 100 ns is followed by a late slow decay occurring over the hundreds of ns. The sufficiently different shapes of the transients recorded for PMMA- and PTAA-coated MHP films lead to a “crossover point” between the two transients for most MHP compositions, as indicated in Figure 4.5 by the black-edged white crosses.

The distinct shape of the transients recorded for MHP films in the presence of the PTAA HTL layers, and its deviation from simple monoexponential decay suggest that in the presence of PTAA, extra dynamic pathways are introduced in addition to the simple bulk defect-assisted recombination present in the PMMA-coated MHP. As Figure 4.5 shows, an increase in bromide content of the PTAA-coated MHP from $x = 0$ to $x = 0.2$ accelerates the early fast decay and delays the “crossover point” from 82 ns to 342 ns. As I show through detailed modeling later, such early-time fast decays are influenced by hole transfer to the PTAA layer and non-radiative recombination. When the bromide content is increased further from $x = 0.2$ to $x = 1$, both early and late decays become even more dominant, leading to an absence of the “crossover point”. I note that such shortening of both early and late PL decays with increasing bromide content is congruent with the decrease in the PL ratios (PL_{PTAA}/PL_{PMMA}) shown in Figure 4.1f, demonstrating that the MHP:PTAA interface introduces additional non-radiative loss channels that become more prominent with increasing bromide content in the MHP. As such, the “crossover point” between transients recorded for the MHP:PTAA interface and those recorded for the interface with electronically inert PMMA can therefore serve as an intuitive figure of merit to quantify the degree of additional non-radiative losses arising from the PTAA interface. As I show through detailed modeling below, holes transferred from the MHP to PTAA may ultimately slowly return to the MHP, leading to the delayed luminescence decay rates observed for MHP:PTAA architectures at long times after excitation. However, if such a return of holes is prevented by an energetic barrier and excessive non-radiative recombination

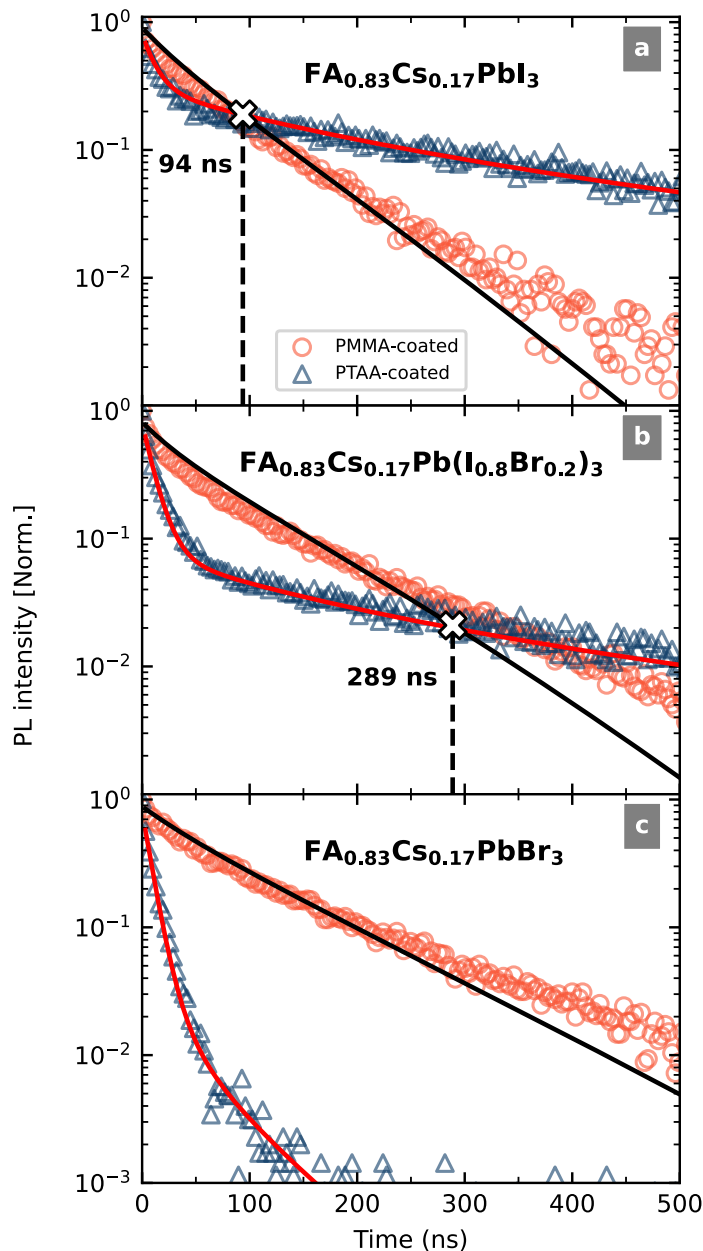


Figure 4.5: Time-resolved photoluminescence, measured with the time-correlated single photon counting (TCSPC) method, for $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ with bromide content of (a) $x = 0$, (b) $x = 0.2$ and (c) $x = 1$, coated with either a PMMA (orange circles) or a PTAA (blue triangles) film. PL transients were recorded following excitation with a pulse fluence of 76 nJcm^{-2} and a wavelength of 470 nm, originating from a diode laser with a repetition rate of 1 MHz. Best fits of the kinetic model described in the text are plotted together in black and red solid lines for the PMMA- and PTAA-coated thin films respectively. The “crossover point” is indicated with a black-edged white cross and label stating its intersection time.

losses across the interface, delayed PL in the MHP will be inhibited and the two curves will no longer cross. As such, the absence of “crossover points” is therefore a clear indicator of detrimental and dominant non-radiative recombination across the interface, unraveled in detail in the model described below.

4.3.3 Modelling TCSPC Decays

In order to understand the losses introduced at the MHP:PTAA interface, I consider a comprehensive set of photophysical processes that contribute to the charge-carrier dynamics in such half stacks, as illustrated schematically in Figure 4.6. Upon photoexcitation, an equal number of electrons and holes are generated in the conduction band (CB) and valence band (VB) of the MHP, and quickly thermalize to their respective band edges. The resulting density of excited electrons in the CB (n_e) undergoes various recombination processes, including (i) band-to-band radiative bimolecular recombination with the holes in the VB, (ii) capture into defect states located either in the bulk or at the surface of MHP, (iii) recombination across the MHP:PTAA with the holes that had previously been transferred to the HOMO of PTAA. Auger recombination is not included here because it is only significant at charge-carrier densities $\approx 10^{18} \text{ cm}^{-3}$, much higher than those present under solar illumination and those injected under the fluences implemented here.[36] Charge-carrier traps may potentially be filled at high excitation densities, which is counteracted by trapped charge carriers, such as electrons shown here, recombining with holes in the VB. These trapped electrons may subsequently return to the CB. In addition, photogenerated holes in the VB of the MHP (n_h) may transfer to the HOMO of PTAA, a portion of which may gradually return back to the VB of the MHP. In this model, I neglect the effect of band bending at the MHP:PTAA interface in the dark as a first approximation, given that the Fermi levels of $\text{PL}_{\text{PTAA}}/\text{PL}_{\text{PMMA}}$ across x are fairly well aligned with those of PTAA.[29, 137–141] In addition, I note that electron transfer to the LUMO of PTAA is considered to be highly unlikely owing to the high energetic barrier $\approx 2.2 \text{ eV}$ and

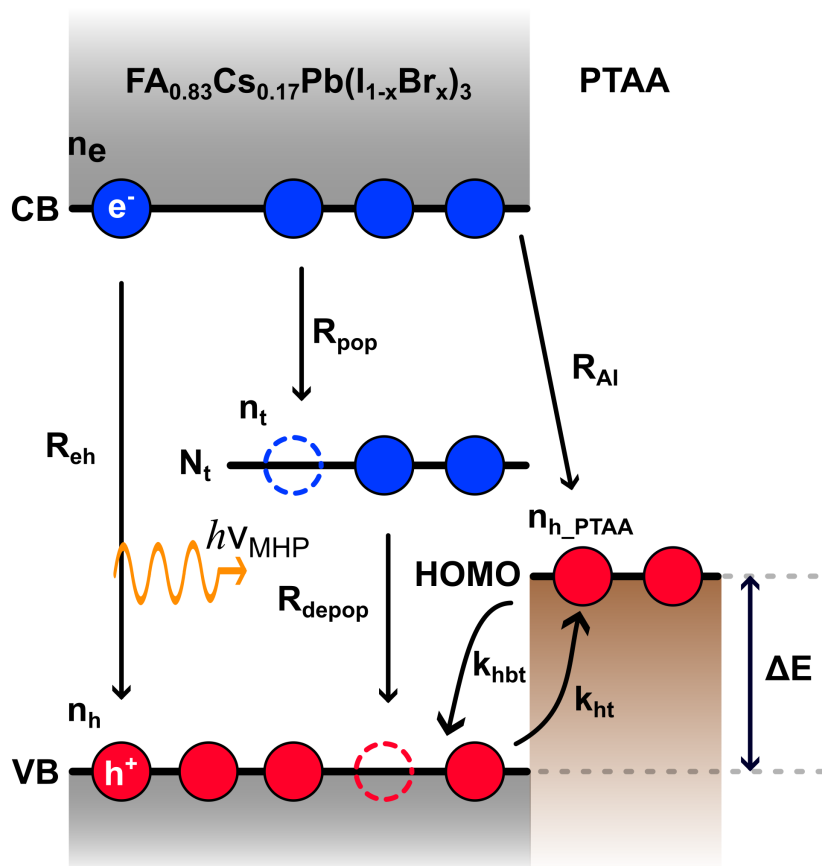


Figure 4.6: Schematic diagram illustrating the dynamical processes occurring in a bilayer stack of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ and PTAA, described by the kinetic model. Upon excitation, electrons (blue solid circles) with density n_e are generated in the conduction band (CB) and an equal number of holes (red solid circles) are generated with density n_h in the valence band (VB). Electrons and holes may undergo band-to-band radiative bimolecular recombination with a rate constant R_{eh} . Alternatively, electrons in the CB may be trapped in the available defect states (dotted empty blue circles) with a rate constant R_{pop} and subsequently recombine with holes in the VB with a rate constant R_{depop} . The total density of defects is N_t , and that of electrons occupying defects is n_t . Trapped electrons may return to the CB with a rate constant k_{detrap} . A fraction of holes in the VB may be transferred to the HOMO of the PTAA layer with a rate k_{ht} , some of which may subsequently return to the VB of the MHP, with a rate k_{hbt} , or recombine with electrons in the CB of the MHP with a rate constant R_{Al} . The density of holes in the HOMO of the PTAA is described by n_{h_PTAA} . ΔE is the energy offset between the VBM of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ and the HOMO of PTAA ($\Delta E = E_{HOMO} - E_{VBM}$). $h\nu_{MHP}$ represents photoluminescence from the MHP and is explicitly shown to indicate that the only radiative recombination results from band-to-band transitions within the MHP.

therefore not included in the model.[138, 147] While the explanation above is limited to the specific case of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$:PTAA bilayers, the mechanisms described generally occur at any MHP interfaced with a charge transport layer.[47, 72]

In past literature reports, various approaches have been employed to describe the dynamics

of charge-carrier recombination at the interface between MHPs and charge transport layers (CTL). As a simple approach, the charge-carrier loss at the interface has been quantified as surface recombination velocity (SRV) by comparing the average recombination lifetimes of a passivated MHP without and with a CTL present.[148] SRV is a useful figure of merit for a quick quantification of the surface recombination introduced by an interface, but it is unable to distinguish and disentangle the various charge-carrier recombination processes mentioned above.[11, 74, 135, 136, 148] On the other hand, such losses can be quantified within a more detailed drift-diffusion model, including transport and Poisson equations.[149–151] Such models have been successfully used to describe and quantify the origin of V_{OC} losses at an interface, but they tend to be too complex and multi-parameterized to allow the extraction of reliable parameters from fits to the TRPL decays. As a compromise, Hutter et al. have successfully used coupled differential equations to quantify and decouple individual charge-carrier dynamics in the bulk as well as the interface of MHPs.[152] I believe that the level of complexity provided by such rate equation models is suitable for the analysis here, given that charge diffusion and Poisson effects are minimal for the excitation fluences under which experiments were carried out here owing to the relative lack of fluence dependent TRPL decays as shown in Figure 4.8.

Therefore, a comprehensive description of the charge-carrier processes in a MHP:PTAA bilayer is provided by applying the following set of couple differential equations, whose solutions are fit to the experimental PL transients in order to decouple and quantify each process:

$$\frac{dn_e(t)}{dt} = -R_{eh} n_e(t) n_h(t) - R_{pop} (N_t - n_t(t)) n_e(t) - R_{AI} n_e(t) n_{h_PTAA}(t) + k_{detrap} n_t(t) \quad (4.1)$$

$$\frac{dn_h(t)}{dt} = -R_{eh} n_e(t) n_h(t) - R_{depop} n_t(t) n_h(t) - k_{ht} n_h(t) + k_{hbt} n_{h_PTAA}(t) \quad (4.2)$$

$$\frac{dn_t(t)}{dt} = R_{\text{pop}}(N_t - n_t(t))n_e(t) - R_{\text{depop}}n_t(t)n_h(t) - k_{\text{detrapp}}n_t(t) \quad (4.3)$$

$$\frac{dn_{h_PTAA}(t)}{dt} = k_{ht}n_h(t) - k_{hbt}n_{h_PTAA}(t) - R_{AI}n_e(t)n_{h_PTAA}(t) \quad (4.4)$$

$$PL(t) = R_{eh}n_e(t)n_h(t) \quad (4.5)$$

Here, $n_e(t)$, $n_h(t)$, $n_t(t)$ and $n_{h_PTAA}(t)$ are the time-dependent densities of electrons in the CB or in defect states of the MHP, the densities of holes in the VB of the MHP, or in the HOMO of PTAA respectively. N_t is the total density of defects (filled or unfilled) in the MHP, R_{pop} is the rate at which these defects are being populated with electrons and R_{depop} is the rate with which they are being depopulated through recombination with holes in the VB of the MHP. k_{detrapp} is the rate of trapped electrons returning to the CB of the MHP. k_{ht} is the rate of hole transfer from MHP to PTAA, while k_{hbt} is the rate with which these holes transfer back from PTAA into the MHP. R_{AI} describes the rate with which holes in PTAA recombine non-radiatively across the interface with electrons in the CB of the MHP.

I solve Equations (4.1), (4.2), (4.3) and (4.4) in order to obtain $n_e(t)$, $n_h(t)$, $n_t(t)$ and $n_{h_PTAA}(t)$ respectively. Model TRPL decays are derived from these quantities through Equation (4.5). Optimised output parameters are then obtained from fits of Equations (4.1), (4.2), (4.3) and (4.4), and (4.5) to TRPL decays globally across a range of fluences. I note that the bimolecular electron-hole recombination rate constant R_{eh} is obtained and fixed prior to this through global fits to fluence-dependent optical-pump terahertz-probe (OPTP) photoconductivity transients which are able to record this second-order effect more accurately owing to higher pulsed excitation fluences using the rate equations illustrated in Section 3.3.2.2.[14, 15, 41] (See Figure 4.9 for the PMMA-coated thin films illuminated from the PMMA side and see Figure A.5 for the

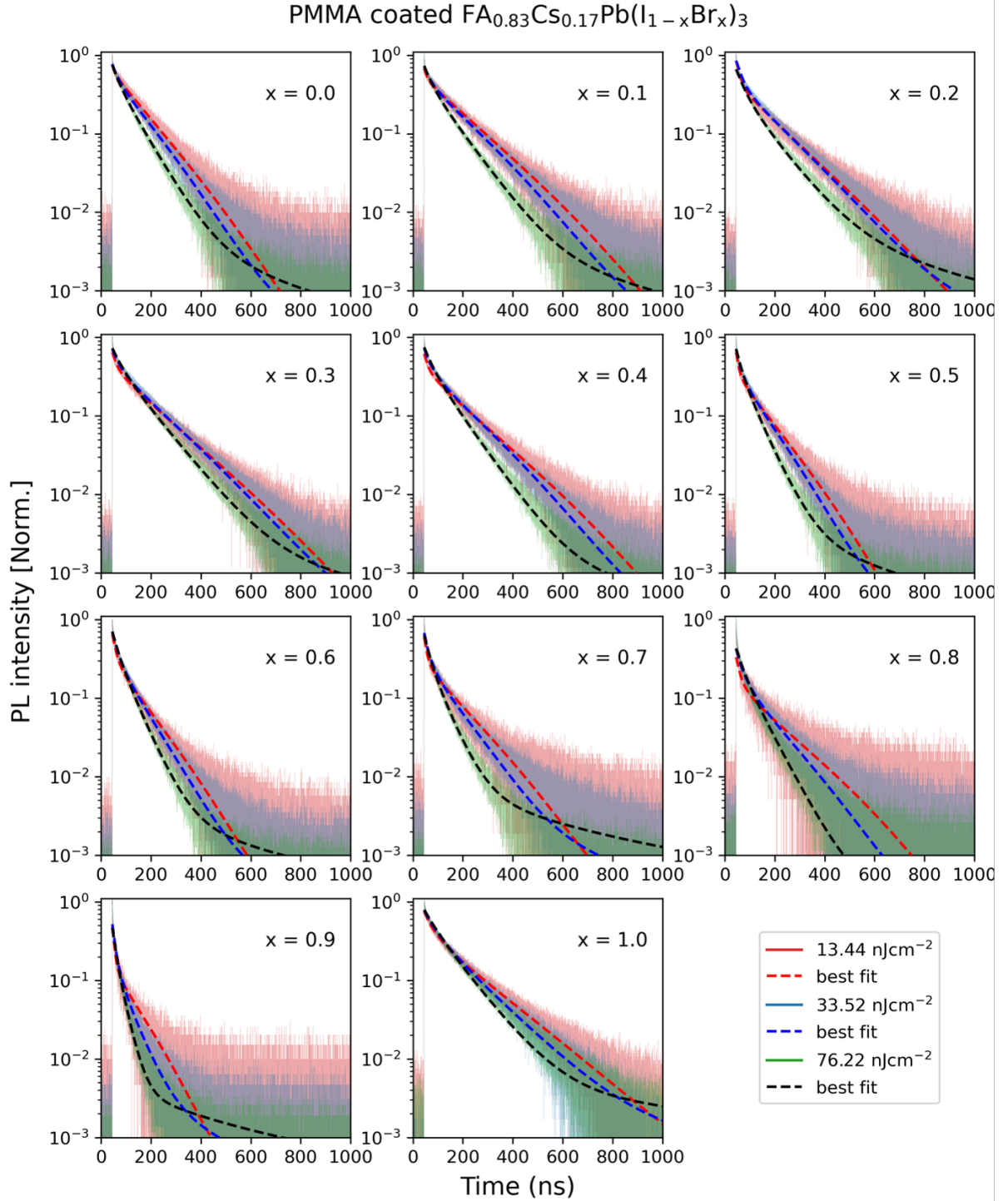


Figure 4.7: TCSPC dynamics of the PMMA-coated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ films across Br contents (x) with the best global fit of the kinetic model across the three excitation fluences; 13.44, 33.52, 76.22 nJcm⁻²

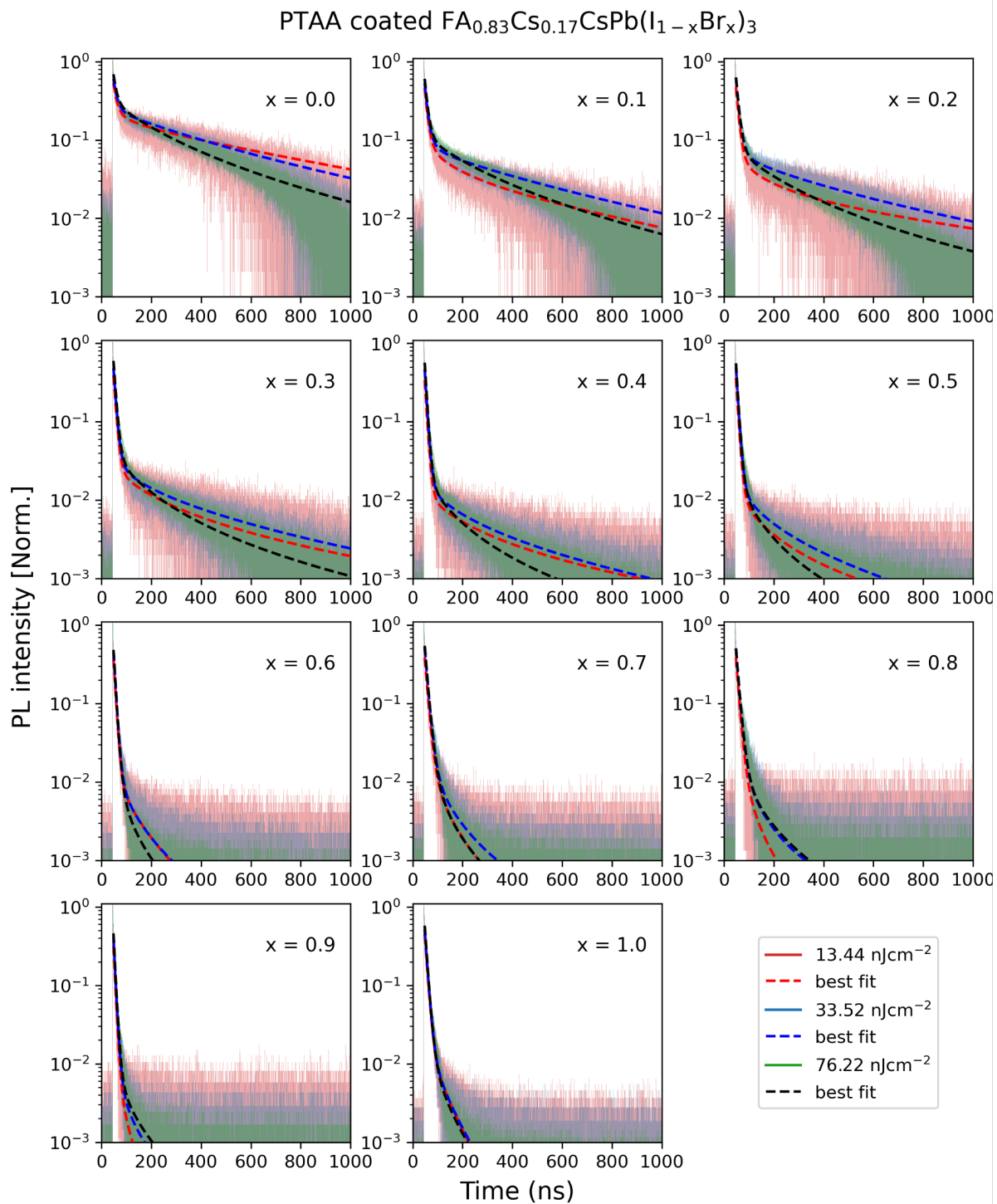


Figure 4.8: TCSPC dynamics of the PTAA-coated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ films across Br contents (x) with the best global fit of the kinetic model across the three excitation fluences; 13.44, 33.52, 76.22 nJcm⁻²

PTAA-coated thin films illuminated from the PTAA side) To achieve high accuracy of resulting output parameters, I follow a two-step process, first determining a subset of parameters for the MHP coated with the electronically inert layer PMMA to determine MHP-specific processes, then using these as inputs to describe the MHP:PTAA bilayer. Specifically, for TRPL transients recorded for the PMMA-coated MHP films, k_{ht} , k_{hbt} and R_{AI} are set to zero and R_{pop} , R_{depop} , k_{detrap} and N_t are obtained from the model. Subsequently, transients for the PTAA-coated MHP films are fitted by fixing R_{pop} , R_{depop} and k_{detrap} to the values obtained from the PMMA-coated MHP films for each bromide content. Thus, I assume that the nature of the electron defects in the MHP is similar for both PMMA and PTAA-coated MHP films, which is a fair assumption given that these MHP films are coated through the same process and their bulk optoelectronic properties appear identical at the same bromide content (see Figure 4.1, 4.3, A.1 and A.2). However, the exact density of defects present in the MHP may differ somewhat owing to different polymer interfaces and N_t is thus allowed to be varied. Moreover, for fits to transients recorded for MHP:PTAA films, k_{ht} , k_{hbt} and R_{AI} are also set as free parameters, given that these processes are significant in this case.

The model reproduces the experimental data with excellent accuracy as seen by the superimposed fits plotted as solid lines in Figure 4.5, 4.7 and 4.8. From the modeled dynamics, I extract important rate constants summarized in Figure 4.10, which shows these parameters either as a function of increasing bromide content, or versus the corresponding increase in band offset between the VBM of the MHP and the HOMO of PTAA ($\Delta E = E_{HOMO} - E_{VBM}$).

Figure 4.10a shows that an increase in Br content x leads to a higher density of defects N_t in the PTAA-coated $FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$ films, both for the PMMA- and PTAA-coated films. This finding is consistent with the characterization of bulk optoelectronic properties described above in Section 4.3.1 and with previous literature reports.[10, 46, 137] It is worth noting that while N_t describes the density of defects in the MHP, it does not discriminate whether these are located in the bulk or at the surface or grain boundaries of the MHP.

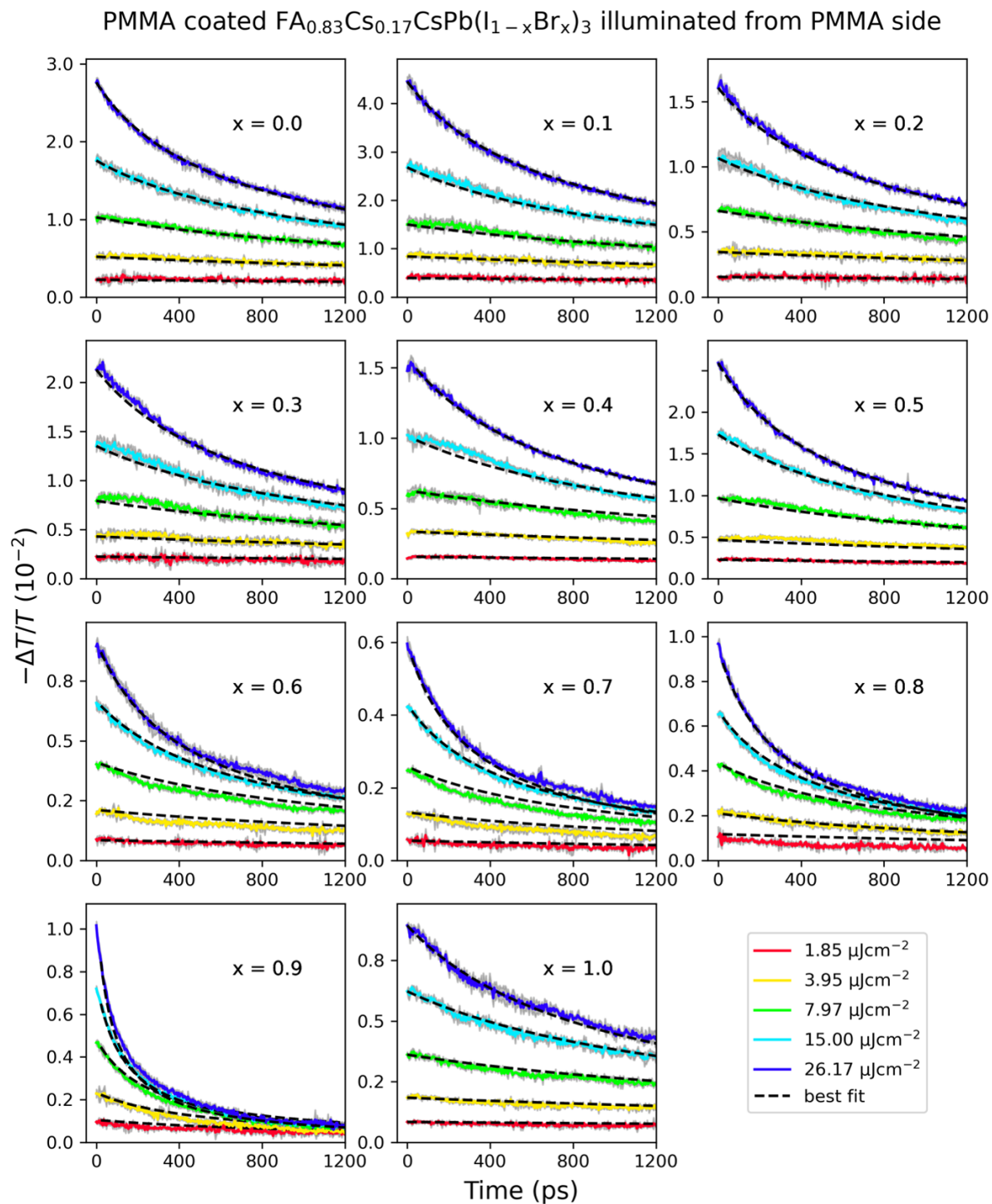


Figure 4.9: Global fit of the OPTP transients across five different excitation fluences recorded for the PMMA-coated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskite films illuminated from the PMMA side

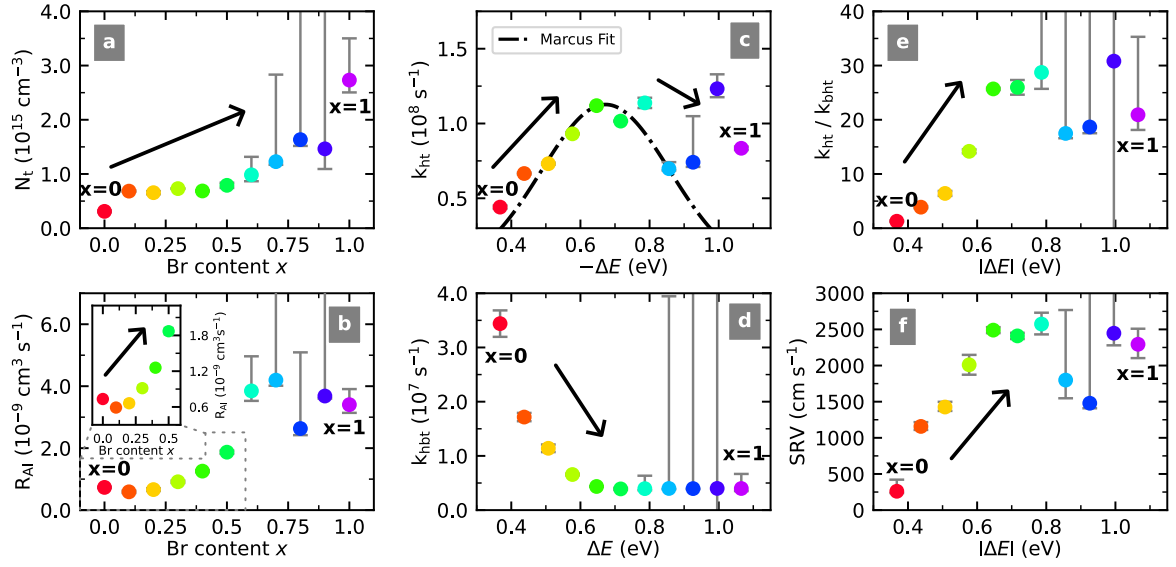


Figure 4.10: (a–d) Parameters obtained from global fits of the kinetic model to experimentally recorded TRPL transients for $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ films coated with PTAA for a range of Br contents x ; (a) total defect density (N_t), (b) across-interfacial recombination rate constant (R_{AI}), (c) hole transfer rate (k_{ht}) from the MHP to PTAA and (d) hole back transfer rate (k_{hbt}) from PTAA to the MHP. The inset in (b) shows the zoomed-in region between $x = 0$ and $x = 0.5$. (e) Ratio of k_{ht} to k_{hbt} representing the degree of hole accumulation with increasing x . (f) Surface recombination velocity (SRV) with increasing x . For (a), (b), and (d)–(f), the large error bars indicate the region of bromide content from which the initial TRPL signal decay becomes so prominent that the fits to the late, slow dynamics dominated by hole back transfer and across-interface recombination are determined with lower accuracy. (c)–(f) are plotted against energy level offset ($\Delta E = E_{\text{HOMO}} - E_{\text{VBM}}$) to explicitly illustrate the impact of ΔE . $-\Delta E$ in (c) indicates energetically favorable energy offset for hole transfer. ΔE in (d) indicates energetically unfavourable energy offset for hole back transfer. $|\Delta E|$ in (e) and (f) represents the absolute energy offset. The arrows are guides to illustrate trends in the data.

I further examine the dependence of the across-interfacial recombination rate constant R_{AI} , which describes the non-radiative recombination of electrons at the CBM of the MHP with holes transferred to the HOMO of PTAA. Figure 4.10b shows that R_{AI} generally increases with increasing bromide content x up to $x = 0.6$. I note that the values of R_{AI} for $x \geq 0.6$ are difficult to interpret because for these compositions, the late decay (> 100 ns) only makes a relatively small contribution to the PL amplitude within the acquisition time, which is limited to 1 minute to avoid halide segregation as shown in Figure 4.4 and A.4. Given that the energy offset bridged by this recombination step is not ΔE but rather the difference between the CBM of the MHP and the HOMO of PTAA which remain relatively unchanged with bromide content

(see schematic in Figure 4.1a), from energetic concerns alone, a relatively constant R_{AI} would be expected. However, R_{AI} extracted from the model shows a clear increasing trend with increasing x , meaning that R_{AI} involves factors other than energetic considerations. I instead propose that such across-interfacial recombination may instead originate from an increase in defect density near the MHP:PTAA interface with increasing x . The propensity for across-interfacial recombination thus seems to correlate well with that of general trap-mediated recombination observed for the MHP layer alone (Figure 4.10a) suggesting that a generally defective MHP will also translate into more defective interface with PTAA. Such presence of defect-mediated across-interfacial recombination has been also proposed for MHPs with different electron transport layers.[47, 72, 153] An accurate quantification of buried defects at the interface is an extremely difficult task and therefore beyond the scope of this research. However, I stipulate that defects in the MHP of MHP:PTAA bilayers may have a tendency to form more prominently near surfaces and grain boundaries, which will offer particularly effective recombination channels to opposite charge carriers located in a charge-extraction layer in close proximity.

I continue by examining the rates of hole transfer rate k_{ht} , hole back transfer rate k_{hbt} and their ratio. Since these parameters likely depend sensitively on the band offset ΔE between the VBM of the MHP and the HOMO of PTAA, they are shown in Figure 4.10c, d, and e as a function of ΔE rather than bromide content x in the MHP. The values of k_{ht} shown in Figure 4.10c are comparable in magnitude to charge transfer rates obtained for a range of MHPs from other spectroscopic techniques such as transient microwave conductivity, surface photovoltage, and absorption spectroscopy.[152, 154, 155] As expected, with increasing energy level offset, hole transfer initially becomes energetically favorable, leading to a faster hole transfer rate with increasing bromide content up to $x = 0.6$ (Figure 4.10c). However, for higher bromide content increasing beyond $x \geq 0.6$, surprisingly, k_{ht} does not seem to increase as expected, showing that any further increase in the energy level offset can no longer enhance hole transfer further. This phenomenon appears analogous to the Marcus inverted region for which a large $-\Delta E$ that might

intuitively expect to be energetically favourable actually leads to a decrease in charge transfer rates.[156, 157] It is worth noting that k_{ht} only contributes to the early TRPL dynamics and therefore it is less affected by low PL amplitudes of later dynamics even for high bromide content MHPs. This is reflected by the error bars for extracted parameters shown in Figure 4.10: while errors for parameters such as N_t , k_{hbt} and R_{AI} that depend critically on the PL at later times after excitation become very large for high bromide content, those for that k_{ht} , which depends largely on the initial PL decay, are smaller, even for high bromide content. However, it is noteworthy that k_{ht} deviates from the Marcus fit at at larger values of $-\Delta E$ where the Marcus fit is given by:

$$k_{ht} = \frac{V^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp \left[-\frac{(\lambda + \Delta E)^2}{4\lambda k_B T} \right] \quad (4.6)$$

where V is the electronic coupling between the perovskite and PTAA, $\hbar$ is the reduced Planck constant, λ is the reorganisation energy, k_B is the Boltzmann constant, and T is the temperature, fixed at room temperature (298.15 K). Such deviation from the classical Marcus theory has been observed in many other systems such as molecules and quantum dots, and other models such as Marcus-Jortner-Levich[157, 158] and Auger-assisted electron transfer[159, 160] models have been proposed to explain such deviation. Although semi-classical Marcus models have been widely used in organic semiconductors or quantum dots where charge transport is assisted via a hopping mechanism,[156, 161, 162] a direct application of the Marcus theory to the interface between a 3D MHP and an organic charge-transport layer has not, to our knowledge, been reported yet. While MHPs are generally assumed to exhibit band-like transport, polymeric semiconductors are likely to display hopping transport of small polarons,[24, 96] opening the question of whether such hopping hole transfer mechanism has relevance at the interface between MHPs and organic transport layers. Given these observations, I propose that, in this scenario, hole transfer at the MHP:PTAA interface may happen via a hopping mechanism with the interface causing a discontinuity of bandlike transport.

As a reverse process of k_{ht} , [157, 158] the hole back transfer rate k_{hbt} extracted from the model decreases with increasing energetic barrier ΔE as shown in Figure 4.10d (I note that beyond $x = 0.6$, errors of determination increase because general non-radiative recombination becomes so strong that different processes can no longer be reliably disentangled at long times after excitation). An increase in k_{ht} and decrease in k_{hbt} with an increasing energy level offset $|\Delta E|$ and bromide content x ultimately means that more holes are being accumulated in the HOMO of PTAA with increasing $|\Delta E|$. The degree of hole accumulation can be quantified as the ratio of k_{ht} and k_{hbt} as shown in Figure 4.10e. I note that I have excluded a discussion of band bending at the interface because I believe that at such low fluence, the effect of electric field owing to hole accumulation is minimal, as shown by a negligible dependence of the TRPL decays on the excitation fluence for the PTAA-coated perovskite films, even as band offsets increase as shown in Figure 4.8.

I further calculate corresponding values for the surface-recombination velocity (SRV) based on the rate constants extracted from the model as a simple measure quantifying the degree of non-radiative dynamics at the MHP:PTAA interface. [47, 72, 74, 148] In the case of MHP:PTAA interface, the SRV can be calculated as:

$$SRV = R_{AI} N_t + (k_{ht} - k_{hbt}) \quad (4.7)$$

Figure 4.10f illustrates how the SRV captures losses at the heterojunction interface arising from hole accumulation and across-interfacial recombination, both of which increase with increasing bromide content up to $x = 0.6$ where the PL amplitude can still be resolved. The determined SRV values are comparable to those in literature reports for interfaces with similar respective band offsets. [11, 19, 22, 122, 135, 136, 148] Therefore, the kinetic model presented here accurately reflects the observation of increasing SRV with increasing band offsets reported across the literature, [11, 135, 136, 148] while disentangling the contributions from different dynamic processes that lead to this effect.

4.3.4 Implications of Recombination Processes at the Interface on Charge-Carrier Dynamics

Having modeled such experimentally acquired curves across the series of mixed-halide perovskites, I am now in an ideal position to predict and understand the effect of increasing bromide content and therefore energy-level misalignment on the total defect densities, across-interfacial recombination, hole transfer, and hole back transfer. I thus proceed by simulating changes in each of these parameters separately, allowing clear guidelines to be established for interpreting such transients. For this purpose, Figure 4.11a–d show simulated TRPL dynamics for a PTAA-coated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ ($x = 0.2$) film, for which only one parameter has been varied, while all other parameters have been fixed to the values obtained from the fit to the real experimental transient, shown also again in Figure 4.11a–d as the black line for comparison. The $x = 0.2$ MHP composition was chosen here specifically as it is known to have an ideal bandgap for two-terminal c-Si:MHP tandem solar cells.[61, 121, 163]

First, I note the effect of change in defect-mediated recombination. As Figure 4.11a shows, an increase in the defect density (N_t) associated with the MHP results in accelerated decay of the transients, shortening both the early and late TRPL dynamics and demonstrating that defect-assisted recombination happens throughout the lifetime of charge carriers. In contrast, Figure 4.11b demonstrates that an increase in across-interfacial recombination rate constant R_{AI} dominantly affects the late dynamics. This is evident, as across-interfacial recombination may only become dominant once sufficient holes have been transferred to the HOMO of PTAA.

Second, I examine the parameters affecting hole transfer, out and back, across the MHP:PTAA interface. Figure 4.11c reveals the effect of an increase in hole transfer rate k_{ht} on the TRPL dynamics. As mentioned before, an increase in the energy level offset between the VBM of the MHP and the HOMO of PTAA energetically favors hole transfer. Hole transfer depletes the density of holes in the VBM of the MHP. When k_{ht} increases, a suppressed density of holes is present in the VBM of the MHP for the given time, leading to reduced chances of band-to-band

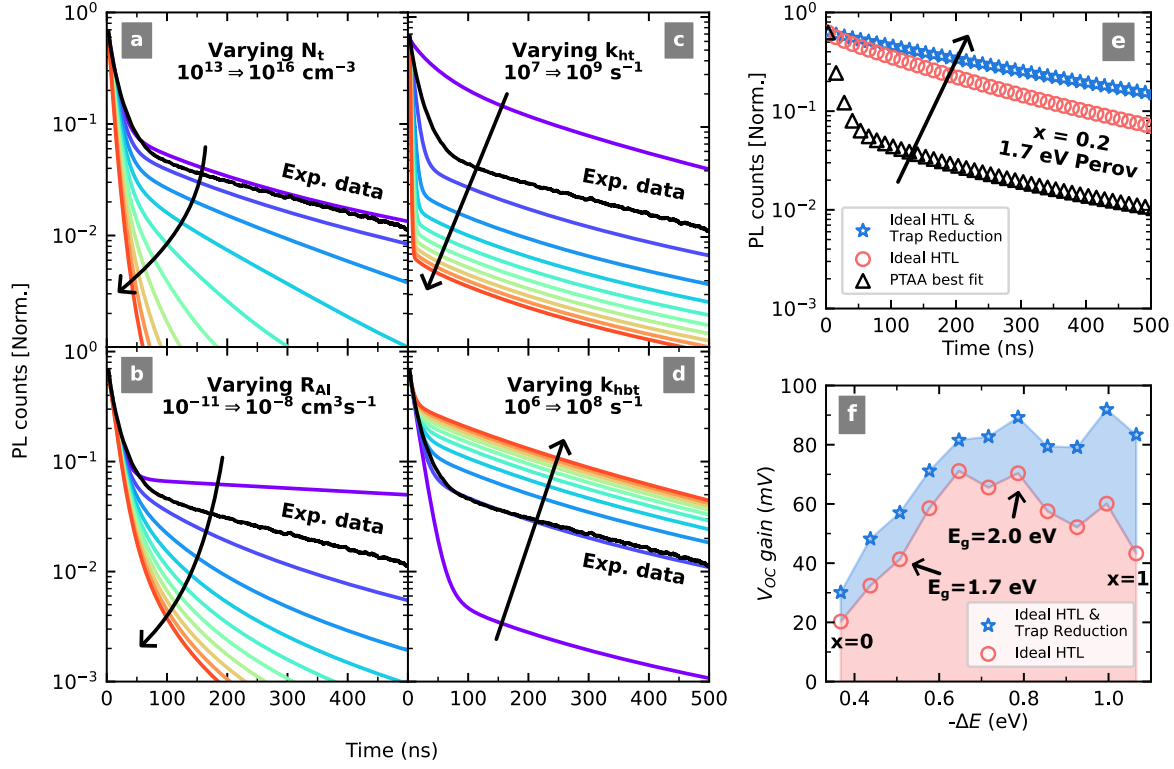


Figure 4.11: TRPL transients simulated through the dynamical model, assuming (a) bulk trap densities (N_t) varying from 10^{13} to 10^{16} cm^{-3} in 10 evenly spaced logarithmic increments, (b) across-interface recombination rate constant (R_{AI}) varying from 10^{-11} to $10^{-8} \text{ cm}^3 \text{ s}^{-1}$ in 10 evenly spaced logarithmic increments, (c) hole transfer rate (k_{ht}) varying from 10^7 to 10^9 s^{-1} in 10 evenly spaced logarithmic increments and (d) hole back transfer rate (k_{hbt}) varying from 10^6 to 10^8 s^{-1} in 10 evenly spaced logarithmic increments. The gradual increase in each parameter is illustrated by the color gradient from purple to red aided by an arrow. All other parameters are fixed at those extracted from fits to the experimental TRPL transients for the film of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ ($x = 0.2$) coated with PTAA measured at a fluence of 76 nJcm^{-2} , also plotted in black for comparison. The experimental data was refined by using a moving average of 200 points. (e) Comparison between the best fit to the experimentally recorded TRPL transients at a fluence of 76 nJcm^{-2} for $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ coated with PTAA (black triangles) and the corresponding modeled transient for an optimized hypothetical HTL (orange circles) which has an ideal energy level offset of $|\Delta E| = 0.33 \pm 0.14 \text{ eV}$ and zero interfacial defects, i.e., assuming an absence of across-interfacial recombination ($R_{AI} = 0 \text{ cm}^3 \text{ s}^{-1}$) and value of $k_{ht} = k_{hbt} = 4.45 \times 10^7 \text{ s}^{-1}$, meaning that hole accumulation in the ideal HTL is eliminated ($k_{ht} - k_{hbt} = 0 \text{ s}^{-1}$). The blue stars represent a modeled transient for an optimized hypothetical HTL combined with a trap reduction to $N_t = 10^{14} \text{ cm}^{-3}$. (f) Open-circuit voltage (V_{OC}) gain calculated from the expected increase in radiative efficiency for an optimized hypothetical HTL (orange circles) and an optimized hypothetical HTL with reduced defect density (blue stars).

radiative bimolecular recombination with electrons in the CBM of the MHP. This results in faster early dynamics with increasing k_{ht} . Finally, Figure 4.11d illustrates the effect of change in the hole back transfer rate k_{hbt} . As expected, increased hole back transfer causes somewhat opposite trends to those of hole transfer, such as an increase in the amplitude of the later-time dynamics. However, it does not alter the lifetime of either the early or the late dynamics, because it is not a loss mechanism and only modulates the density of hole accumulation in the HOMO of PTAA. The intensity of the PL emerging from the PTAA-coated MHP is predominantly affected by the degree of hole accumulation in the HOMO of PTAA, because any holes present in the PTAA are highly likely to suffer from non-radiative recombination across the MHP:PTAA interface. Therefore, hole back transfer and across-interfacial recombination are two competing processes once holes are transferred to the HOMO of PTAA, with the former boosting PL from the MHP and the latter diminishing it. Therefore, importantly, if the energy level offset is small, the hole back transfer may be sufficiently fast to minimize across-interfacial recombination and maximize PL efficiency. On the other hand, if the energy level offset is substantial, the hole back transfer is hindered by the energy barrier and accumulated holes will eventually recombine non-radiatively via across-interfacial recombination. These considerations thus highlight that optimization of the energy offset is key to enhancing PL quantum efficiency. As an aside, I note that hole back transfer is only a lossless process in open-circuit conditions for which all charge carriers ultimately must recombine, rather than being extracted. Under short circuit conditions, an increase in hole back transfer might also lead to reduced charge-carrier collection. However, I note that PL measurements on such half-stacks are always conducted under open-circuit conditions, and these closely mimic the impact on V_{OC} which is an important photovoltaic device parameter.

Overall, these simulations highlight how the TRPL dynamics of MHP:HTL bilayers are determined by a complex interplay between hole transfer, hole back transfer, and across-interfacial recombination, as well as significant trap-mediated recombination in the MHP. The early dynamics are strongly influenced by hole transfer (k_{ht}) while the late dynamics are

mostly governed by across-interfacial recombination (R_{AI}). The amplitude of the late decay is determined by the interplay between out- and back-hole transfer (k_{ht} and k_{hbt}), which reflects the degree of hole accumulation. It is worth noting that while radiative electron-hole recombination (R_{eh}) does not have a significant influence on the TRPL dynamics for the low charge-carrier densities generated in this work such effects may become more significant at higher charge-carrier densities ($> 10^{16} \text{ cm}^{-3}$) or very low trap-mediated recombination rates.[36]

Finally, I note that the relatively simple attribution of the early TRPL dynamics for MHP:HTL bilayers to solely hole transfer,[11, 73, 133, 135, 136, 154, 155, 164–168] and late TRPL dynamic to just across-interfacial recombination[11, 135, 136, 164–168] can sometimes be misleading, in particular for high defect density N_t . As shown in Figure 4.11a, a significant increase in defect density will lead to defect-assisted recombination within the MHP becoming the dominant recombination process, which will prohibit efforts to extract reliable information about hole transfer, hole back transfer, and across-interfacial recombination through the more straightforward surface recombination velocity and differential lifetime methods previously implemented.[11, 74, 135, 136, 148–151] Therefore, our model presented here provides a powerful alternative tool to analyze multi-exponential TRPL dynamics, capable of disentangling such effects and providing an overall picture of multiple processes occurring in multilayer systems comprising MHPs and their charge extraction layers.

4.3.5 Implications of Recombination Processes at the Interface on Device Performance

I further demonstrate how tuning of the energy-level alignment can potentially improve photovoltaic device performance by modeling charge-carrier processes for an ideally energetically matched MHP:HTL interface. Above, I established that a combination of hole accumulation and across-interfacial recombination causes non-radiative recombination at the MHP:PTAA interface. Such processes will ultimately limit the quasi-Fermi level splitting (QFLS) and consequently the qV_{OC} inside a full photovoltaic device.[47, 69, 72, 145] The QFLS can be

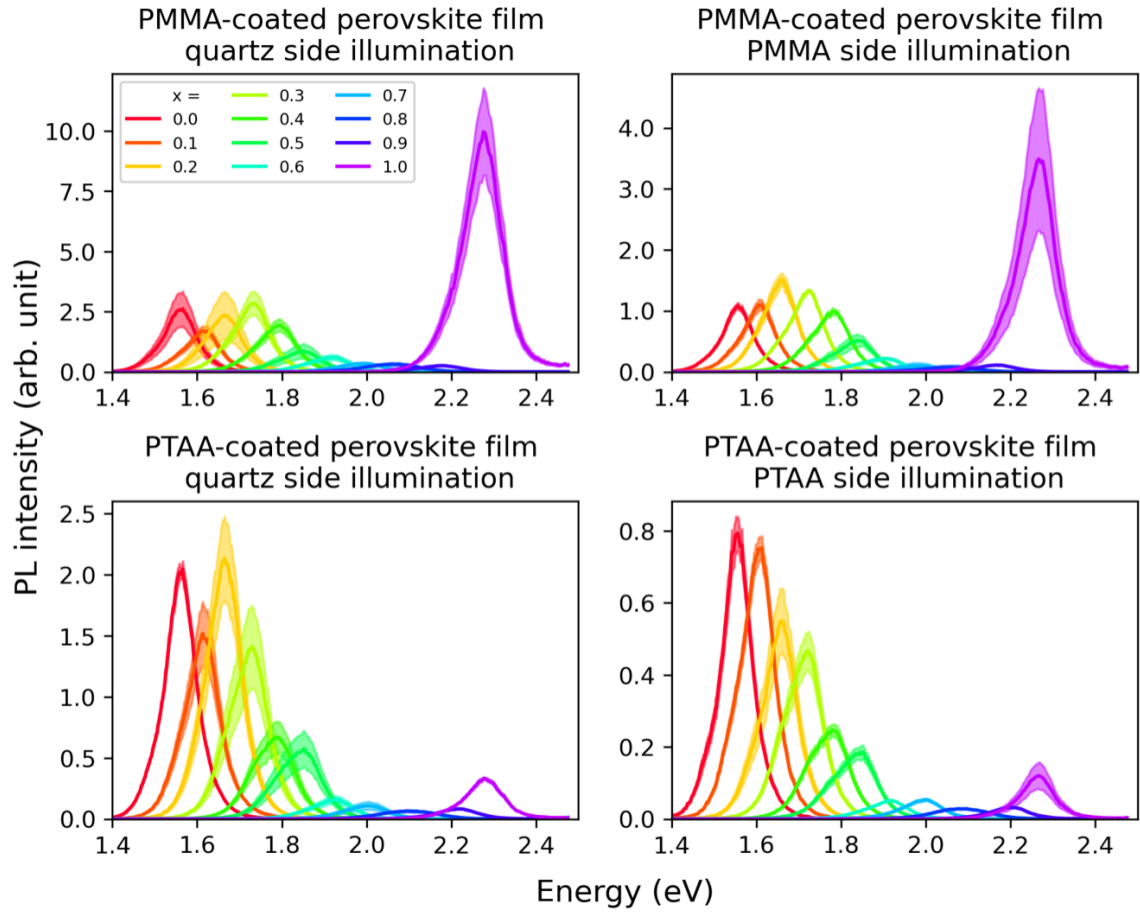


Figure 4.12: Steady-state photoluminescence spectra of the PMMA- or PTAA-coated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskite films excited with the 470 nm diode laser with 1 MHz repetition rate at a fluence of 76.22 nJcm^{-2} illuminated from either the quartz or PMMA/PTAA side. x represents the Br content in the perovskite

extracted from experiments by recording of the photoluminescence quantum yield (PLQY) based on the principle of detailed balance.[19, 22, 47, 58, 69, 72, 73, 122, 133, 145, 149–151, 169–172] For the particular case of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ ($x = 0.2$) examined here, the simulations shown in Figure 4.11e demonstrate that the TRPL lifetime can be significantly improved by replacing PTAA with such an idealized HTL, and further improvement can be realized through passivation strategies that reduce the density of traps. By using the known relationship between PLQY and QFLS, and therefore qV_{OC} , where q is the electron charge, a corresponding increase in qV_{OC} can be calculated from $(k_b T/q) \times \ln(\text{PLQY}_{\text{improved}}/\text{PLQY}_{\text{pristine}})$. Here, the ratio of $\text{PLQY}_{\text{improved}}$ and $\text{PLQY}_{\text{pristine}}$ was obtained from the area under TRPL decays, which provides a

good estimate of the steady-state PL since it follows the same compositional trend as the integral under pulsed excitation (see Figure 4.7, 4.8 and 4.12). The values calculated for qV_{oc} through this approach are presented in Figure 4.11f. The orange-shaded region represents the V_{oc} gain expected from simply replacing PTAA with an ideal HTL having an ideal energy-level alignment of $|\Delta E| = 0.33 \pm 0.14$ eV ($k_{ht} - k_{hbt} = 0$ s⁻¹) and zero interfacial defects ($R_{AI} = 0$ cm³s⁻¹) (see Figure 4.13). The blue shaded region highlights the additional qV_{oc} gain that may be achieved by a reduction in trap density to $N_t = 10^{14}$ cm⁻³, e.g. through suitable passivation approaches. These trends clearly show that as $-\Delta E$ increases, the V_{oc} loss mainly originates from the interface between the perovskite and the PTAA interface. However, for $x > 0.6$, the V_{oc} loss from the interface declines owing to a slight decrease in the value of k_{ht} , while V_{oc} losses arising from defects become more significant with increasing defect densities at higher bromide content x . I note that the compositions of $x = 0.2$ and $x = 0.6$, in particular, possess bandgaps ideal for silicon-perovskite tandem solar cells and perovskite triple junction top cells respectively.[61, 62, 163] Our calculations suggest that simple optimization of the energy alignment to the HTL layer, can result in a V_{oc} improvement by 41 and 70 mV, while additional defect passivation or reduction will increase these values to 57 and 89 mV, respectively, for these compositions. Overall, our comprehensive model encompassing all dynamical processes occurring at the interface between an MHP layer and a charge transport layer thus shows that decreasing band offsets induces a significant reduction in V_{oc} losses at perovskite/HTL interfaces, but defect elimination or passivation may also be crucial, especially for higher bromide contents.

One might expect the scenario of $k_{ht} - k_{hbt} \gg 0$ s⁻¹ to be ideal for efficient charge extraction of holes, but I note that it will also lead to a significant decrease in PL intensity, as shown in Figure 4.10c, owing to hole accumulation in the HOMO of PTAA. $k_{ht} - k_{hbt} \ll 0$ s⁻¹ is not an ideal condition either, despite a slight increase in radiative efficiency, because dominant hole back transfer opposes the external electric field in short-circuit conditions. (see Figure 4.13a). By extrapolating k_{ht} and k_{hbt} in Figure 4.10c,d, I found that an ideal ΔE leading to

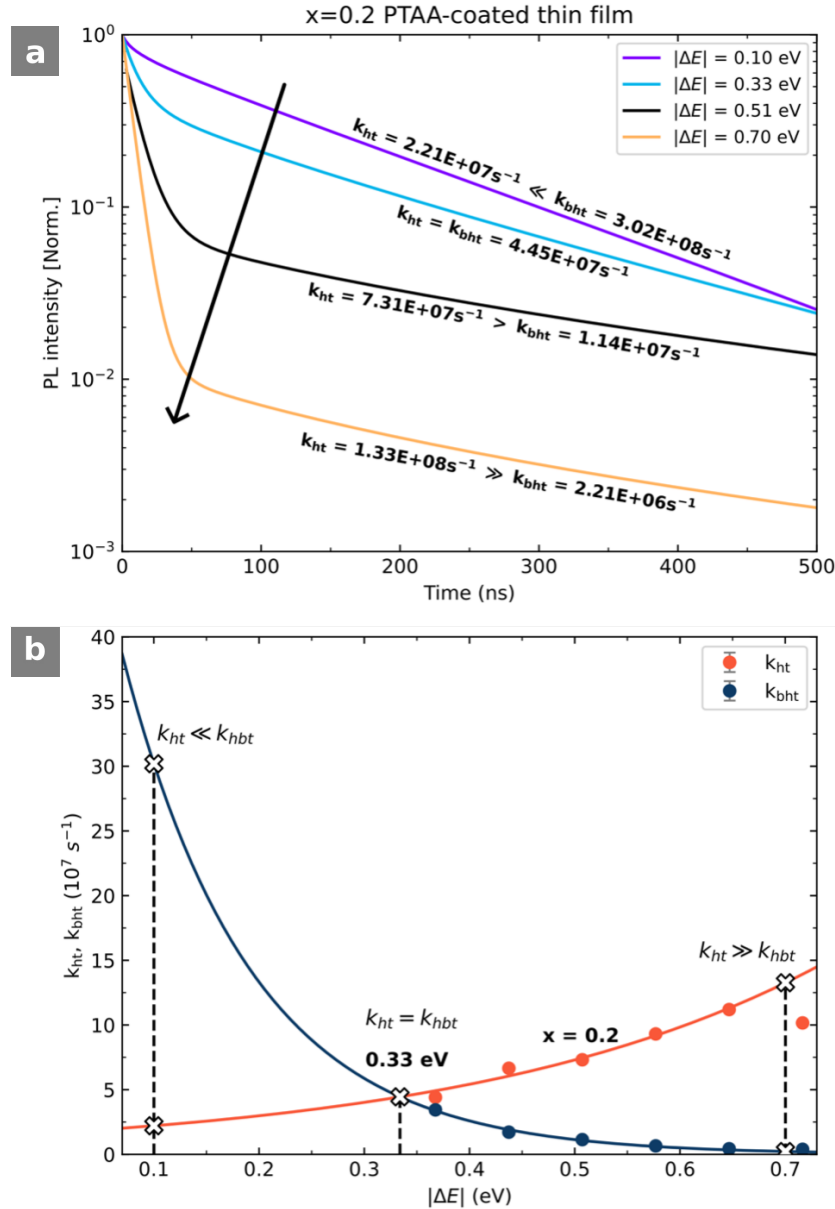


Figure 4.13: (a) Simulated TRPL decays of $x = 0.2$ PTAA-coated thin films at various ratios of hole transfer rates k_{ht} and hole back transfer rates k_{hbt} . The k_{ht} and k_{hbt} values at certain band offset ΔE were taken from exponential fits to the experimentally determined k_{ht} and k_{hbt} values as shown in Figure 4.13b, (b) Hole transfer rates k_{ht} and hole back transfer rates k_{hbt} plotted as a function of energy offset $-\Delta E$. The k_{ht} and k_{hbt} rates at $|\Delta E| = 0.1, 0.33$ and 0.7 eV are marked with crosses.

$k_{\text{ht}} - k_{\text{hbt}} = 0 \text{ s}^{-1}$ is $0.33 \pm 0.14 \text{ eV}$ (see Figure 4.13b). I would like to point out that the ideal ΔE is specific to this set of MHP:PTAA bilayers studied here because under semiclassical consideration, the transfer rates will also depend on the effective density of states (DOS) and electronic coupling,[156–158, 161, 173] which may differ depending on the materials. However, for the general case where the effective DOS of the HOMO of the organic HTL is higher than that of the VB of MHP, I suggest that a slight band offset is beneficial for the device performance, so that V_{OC} can be maximized without compromising short-circuit current.

The new insights gained by the analyses above reveal that an improvement of energy-level alignment and the quality of the MHP:HTL interface is crucial for achieving higher V_{OC} for solar cells incorporating wide-bandgap mixed-halide MHPs. Recent studies illustrated that the replacement of PTAA with self-assembled monolayers (SAMs) can minimize the V_{OC} losses associated with the MHP:HTL interface by 63 mV for devices based on for 1.6 and 1.8 eV-bandgap perovskites.[19, 22, 73, 122, 125, 126, 128–133] This improvement can be attributed to better energetic alignment and fewer defects being present at the MHP:HTL interface. However, the HOMOs of such SAMs are currently still better optimized for the 1.6 eV bandgap perovskites,[73, 133] equivalent to $x = 0$ bromide content for the series of MHPs examined here. Therefore, I conclude that an improvement in the V_{OC} of wide-bandgap perovskites would require the development of novel HTLs with HOMO levels better matching the VBM of respective MHPs. I note that other than such energetic considerations, novel HTLs should have minimal interfacial defects (e.g., offered by SAMs molecules) and wide bandgaps to minimize parasitic absorption while also efficiently blocking electron transfer.[73, 133]

4.4 Conclusion

In conclusion, I have identified and quantified the non-radiative loss mechanisms associated with the interface formed between mixed-halide perovskites and hole extraction layers, through application of a full dynamical model to time-resolved photoluminescence transients. By

tuning the energetic alignment between the valence band maximum of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ metal halide perovskite (MHP) and the highest occupied molecular orbital (HOMO) of the commonly implemented hole extraction material PTAA through changes in bromide content (x) between $x = 0$ to $x = 1$, I have been able to assign and disentangle all relevant processes affecting charge-carrier dynamics in such half-stacks. Comparison of such dynamics with those recorded for corresponding MHPs coated with an inert PMMA layer further allowed the identification of the processes directly arising from the electronically active MHP:PTAA interface. I show that interfacial losses increase with increasing energy-level misalignment primarily because of hole accumulation in the HOMO of the PTAA, followed by subsequent across-interfacial recombination. With an increasing energetic barrier, holes in the HOMO of PTAA are unable to return to the VBM of the MHP, ultimately leading to substantial across-interfacial recombination between the electrons in the conduction band of the MHP with holes accumulated in the HOMO of the PTAA.

I further showed that the assignment of “early” and “late” components in such commonly examined TRPL traces can be too simplistic under certain circumstances. For example, the dynamical model revealed that while the early TRPL lifetime can be dominated by hole transfer and the late TRPL lifetime by across-interfacial recombination, such assignments may no longer be valid when the total density of defects becomes too high. In this case of high defect density, both early and late TRPL dynamics would ultimately be dominated by the defect-assisted non-radiative recombination within MHP itself rather than non-radiative losses at the MHP:HTL interface. I further established that the amplitude of the late TRPL dynamic is usually determined by the amount of hole accumulation in the HOMO of PTAA.

Finally, I examined the extent to which a hypothetical HTL exhibiting ideal energy-level alignment that minimizes hole accumulation and low recombination at the MHP:HTL interface could improve the performance of photovoltaic devices incorporating the wide-bandgap MHPs. I show that V_{OC} loss mainly originates from the interface between the perovskite and the PTAA

and its magnitude increases with increasing energy-level misalignment. For $x > 0.6$, the V_{oc} loss from defects starts to become more significant while V_{oc} loss caused by the interface is still the dominant factor. I, therefore, conclude by stressing the importance of the development of new HTLs specifically designed for wide-bandgap perovskites that are critical to the success of high-efficiency tandem perovskite solar cells. In addition, they should introduce minimal interfacial defects and possess wide bandgaps to minimize parasitic absorption while also efficiently blocking electron transfer. If HTLs can be implemented according to these design criteria, ultra-high efficiency multi-junction perovskite solar cells will make an important leap toward becoming a renewable technology.

5

Impact of Halide Segregation on Interfacial Charge Transfer in Mixed-Halide Perovskites

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The work presented in this chapter is in preparation for publication.

5.1 Broader Context

Mixed-halide perovskites offer ideal bandgaps for tandem solar cells, but they suffer from light-induced halide segregation, which compromises their operational stability. Here, the

impact of halide segregation on charge-carrier dynamics at the interface between a mixed-halide perovskite and charge transport layers is directly probed by using a free-space synchronous multimodal spectroscopy approach, combining time-resolved microwave conductivity, time-resolved photoluminescence and steady-state PL. Halide segregation creates I-rich phases that capture charge carriers within sub-nanoseconds, yet their mobilities remain relatively well preserved in neat perovskites (81%), but become less retained in the presence of charge transport layers (50 ~ 72%). I reveal that charge extraction from such I-rich domains is still surprisingly feasible, but competes with enhanced radiative recombination resulting from higher charge concentrations caused by funnelling into these minority phases. The combination of moderate mobility reduction and accelerated electron-hole recombination upon halide segregation reduces diffusion lengths, and underpins the widely observed reduction in open-circuit voltages and short-circuit currents in solar cells under operational conditions. The findings underscore the urgency of developing strategies to mitigate the adverse impact of halide segregation and guide pathways toward improved device performance.

5.2 Introduction

Recent advances in photovoltaics research have been strongly driven by the remarkable rise in the performance of metal-halide perovskite/silicon tandem solar cells, which have now achieved a record power conversion efficiency (PCE) of 34.58%,[\[2, 174\]](#) surpassing the detailed balance limit of single-junction solar cells.[\[18\]](#) In general, two-terminal tandem solar cells require a combination of a wide bandgap semiconductor (> 1.7 eV) and a narrow bandgap semiconductor (< 1.4 eV) to reduce thermalisation losses while maintaining the current-matching condition.[\[61, 62, 163\]](#) Lead iodide-bromide perovskites are typically employed as the wide bandgap absorber because their bandgaps can be readily tuned by varying the iodide-bromide ratio,[\[10, 29\]](#) offering tailored wide bandgaps to complement the bandgap of the narrow bandgap subcell to achieve an optimal tandem PCE.

However, such mixed-halide perovskites typically suffer from halide segregation where prolonged exposure to light or electric bias drives the spatial separation of the mixed-phase perovskite into both an iodide-rich (I-rich) and a bromide-rich phase.[20, 21, 53, 123] Various models have been proposed to explain the mechanism of halide segregation, ranging from thermodynamic driving forces to polaronic and defect-mediated models.[53–57, 65, 67, 175, 176] However, a comprehensive theory explaining the underlying mechanism of halide segregation remains elusive, owing to the complex interplay of ionic movement with external perturbations as well as morphology, strain, crystallinity and composition of the perovskite thin film.[11, 66, 123, 177–181] Nevertheless, halide segregation is known to adversely affect the optoelectronic properties of metal-halide perovskites for tandem applications: the formation of I-rich domains of lower bandgap induces photoexcited charge carriers to funnel into these domains, red-shifting the targeted wide bandgap, and ultimately compromising the overall device performance by reducing both open-circuit voltage (V_{OC}) and short-circuit current (J_{SC}).[22, 60, 68, 181, 182] Motti et al. have revealed that such charge-carrier funnelling occurs on the timescale of tens of picoseconds, enhancing the effective radiative recombination owing to the increased charge-carrier density in the I-rich domains.[63] However, mitigating device performance losses following halide segregation urgently requires a comprehensive understanding of charge-carrier dynamics associated with the interface between mixed-halide perovskites and charge transport layers. In such half-stack architectures, a range of additional processes occur, including charge transfer across and non-radiative recombination at the heterojunction interface, which are known to be critical to the performance of wide-bandgap mixed-halide perovskite photovoltaics.[19, 22, 105, 122] Such processes in turn may be affected by halide segregation in a variety of ways, which remains largely unexplored.

Here, I reveal how halide segregation moderates the charge-carrier dynamics associated with the interface of the prototypical wide bandgap perovskite $FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})_3$ with

commonly used charge transport layers, either the hole transport layer (HTL) poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) or the electron transport layer (ETL) SnO_2 . I utilise a synchronous multimodal spectroscopy approach, combining time-resolved microwave photoconductivity (TRMC), time-resolved photoluminescence (TRPL), and steady-state photoluminescence (ssPL) to monitor and evaluate the impact of halide segregation. This combinatorial approach allows disentanglement of contributions arising from either intrinsic radiative electron-hole recombination or charge-selective extraction by PTAA or SnO_2 layers. I show that halide segregation leads to funnelling of charge carriers into I-rich domains on a sub-nanosecond timescale where most of their mobilities are retained even at microwave frequencies in neat perovskite. However, the presence of charge transport layers leads to a more pronounced mobility reduction. I further demonstrate that charge-carrier extraction subsequently occurs through the I-rich phase, and remains remarkably effective. However, such extraction competes with enhanced radiative recombination driven by the enhanced charge-carrier density in these domains but the lifetime reduction at later time is alleviated by charge back transfer from the transport layers. Together with reduction in mobility, charge carrier diffusion lengths, and consequently the charge-collection efficiency are compromised. I further evaluate the impact of such effects on predicted solar cell performance parameters.

5.2.1 Synchronous Multimodal Time-Resolved Conductivity and Photoluminescence Approach

To address the complex charge-carrier dynamics arising from halide segregation, a synchronous multimodal spectroscopy approach is employed as illustrated in Figure 5.1a. TRMC, TRPL and ssPL are simultaneously recorded for the same thin-film location under identical excitation conditions, enabling the probing of charge-carrier funnelling as well as the competition between enhanced radiative loss and charge-carrier extraction originating from halide segregation. To investigate the impact of halide segregation on such dynamics, films were exposed to 532 nm continuous wave (CW) illumination at a power density of 150 mWcm^{-2} for the duration of 6 hours

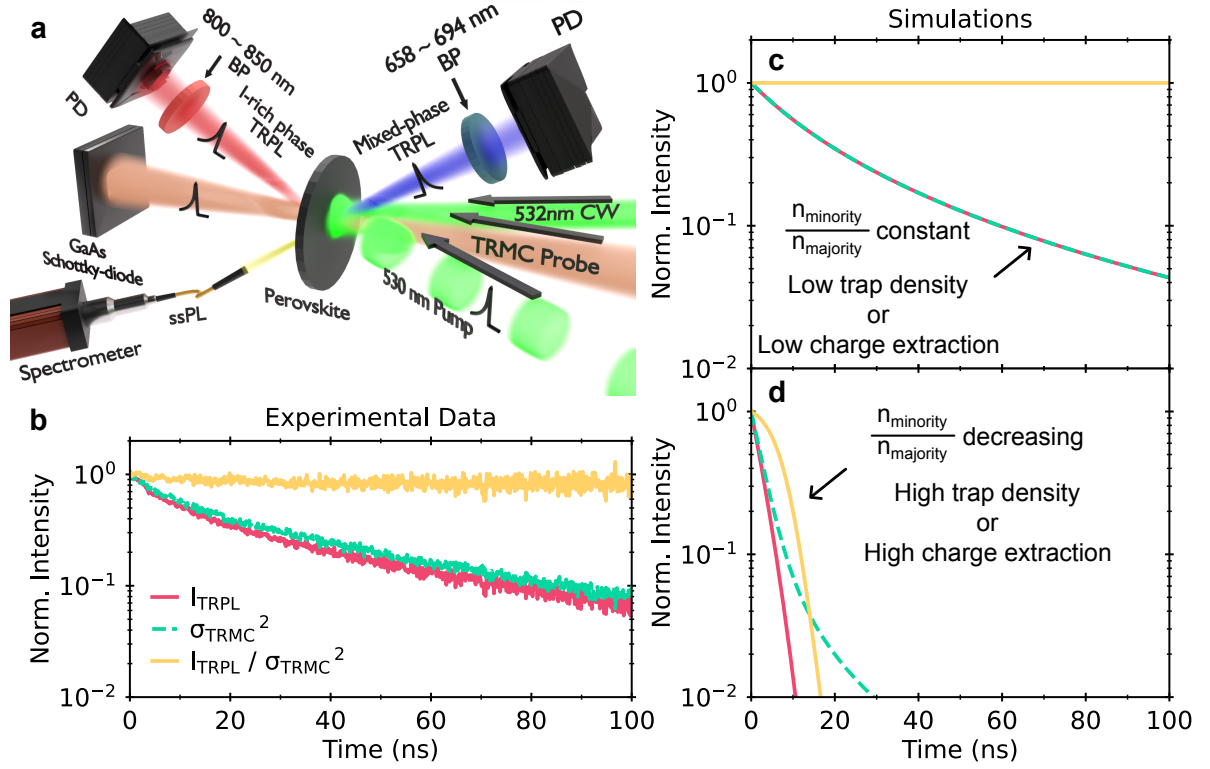


Figure 5.1: (a) Synchronous multimodal spectroscopy system, enabling simultaneous acquisition of time-resolved photoluminescence (TRPL), time-resolved microwave conductivity (TRMC), and steady-state photoluminescence (ssPL). TRPL is filtered into two spectral windows, one to isolate the mixed phase (658–694 nm bandpass (BP) filter) and another the I-rich phase (800–850 nm BP filter), and detected with fast photodiode detectors (PD). TRMC is detected with a GaAs Schottky diode in transmission geometry. ssPL is detected with a fibre-coupled spectrometer. (b) Representative transients measured for a Quartz/FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃/PMMA thin-film stack photoexcited with a 530 nm pulsed laser at a fluence of 3.6 μJcm^{-2} . I_{TRPL} denotes the TRPL intensity transient, σ_{TRMC}^2 the square of the TRMC transient and $I_{\text{TRPL}} / \sigma_{\text{TRMC}}^2$ the ratio between I_{TRPL} and σ_{TRMC}^2 . (c) Simulated transients for the case of low trap density or low charge extraction. (d) Simulated transients for the case of high trap density or high charge extraction. Panels (b), (c) and (d) share the same legend.

(see Figure 5.1a.) to drive significant halide segregation, given that FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃ is a relatively phase stable material undergoing minimal halide segregation even after prolonged pulsed excitation (Figure 5.2).[53, 63] I note that the instantaneous charge-carrier density generated by such long-term background CW illumination is orders of magnitude lower than that of the 530 nm pulsed excitation employed here to record TRPL and TRMC and therefore does not significantly affect the analysis of the recombination dynamics.[63] Moreover, the pulsed excitation and CW illumination wavelengths lie below the bandgap of the transport layers, thereby preventing parasitic absorption and ensuring selective excitation of perovskite.[138, 183]

To enable the multimodal approach, the TRMC signal is recorded in a free-space transmission geometry, and based on a high-frequency (102 GHz) microwave probe[52] to solely detect photoconductivity arising from free charge carriers and limit any contributions from slow ionic motion.[184] To simultaneously probe PL dynamics arising from either the mixed phase or the I-rich phase, TRPL is detected by two fast photodiodes across two separate spectral windows, selected with bandpass (BP) filters at 658–694 nm and 800–850 nm, respectively. These windows capture the higher-energy tail of the mixed-phase PL and the lower-energy tail of the I-rich phase PL which achieves sufficiently wide spectral separation for the two signals not to overlap. A fibre-coupled ssPL probe monitors time-integrated emission spectra as a proxy for the extent and evolution of halide segregation. Further details of the experiment can be found in Section 3.4.1.

The multimodal TRMC and TRPL approach was chosen because it allows for direct distinction between charge-carrier dynamics dominated by either majority or minority carriers. Through judicious analysis, these combined non-contact probes[52, 185] can reveal whether charge-carrier dynamics are dominated by intrinsic radiative electron-hole recombination, or rather by charge-carrier selective processes such as charge extraction at collection layers or electron/hole-specific trapping. This distinction is enabled by TRMC and TRPL reflecting different semiconductor properties: TRMC measures the time-resolved change in photoconductivity (σ_{TRMC}), which is defined as the mobility-weighted sum of the photoexcited charge-carrier densities,

$$\sigma_{\text{TRMC}} = e (\mu_e n_e + \mu_h n_h) \quad (5.1)$$

where e is the elementary charge, n_e and n_h are photoexcited densities of electrons and holes, and μ_e and μ_h are the respective mobilities. In contrast, the TRPL intensity (I_{TRPL}) originates from radiative bimolecular recombination and is proportional to the product of the electron and hole densities,

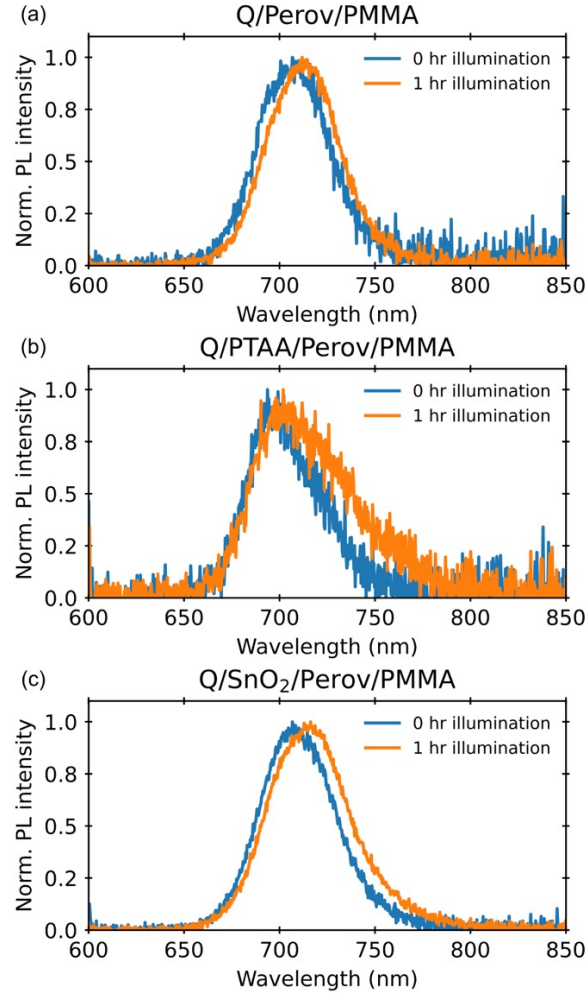


Figure 5.2: Normalised time-integrated photoluminescence of (a) Quartz(Q)/FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃ (Perov)/PMMA, (b) Q/PTAA/Perov/PMMA and (c) Q/SnO₂/Perov/PMMA after 1 hr of continuous exposure to the 530 nm pulsed excitation.

$$I_{\text{TRPL}} \propto R_{\text{ch}} n_{\text{e}} n_{\text{h}} \quad (5.2)$$

where R_{ch} is the radiative recombination rate constant

The imbalances that may occur between electrons and holes over time can be directly visualised by the ratio of I_{TRPL} and σ_{TRMC}^2 transients. According to the above equations, this ratio is given by:

Parameter	Value
n_e (cm ⁻³)	2.42×10^{17}
n_h (cm ⁻³)	2.42×10^{17}
n_t (cm ⁻³)	0
μ (cm ² V ⁻¹ s ⁻¹)	24.5
R_{eh} (cm ³ s ⁻¹)	1.54×10^{-10}
N_t (cm ⁻³)	1.7×10^{15}
R_{pop} (cm ³ s ⁻¹)	9.5×10^{-9}
R_{depop} (cm ³ s ⁻¹)	1.42×10^{-9}
k_{detrap} (s ⁻¹)	5.6×10^4

Table 5.1: List of parameters and values used for the numerical simulation for Figure 5.1c and d based on the rate equation model presented in Section 2.1.3.3.

$$\frac{I_{TRPL}}{\sigma_{TRMC}^2} \propto \frac{R_{eh}n_en_h}{e^2(\mu_en_e + \mu_hn_h)^2} = \begin{cases} \frac{R_{eh}n_e}{e^2\mu_h^2n_h} & \text{if } n_e \ll n_h \quad (\text{case 1}) \\ \frac{R_{eh}n_h}{e^2\mu_e^2n_e} & \text{if } n_h \ll n_e \quad (\text{case 2}) \\ \frac{R_{eh}}{e^2(\mu_e + \mu_h)^2} & \text{if } n_e = n_h \quad (\text{case 3}) \end{cases} \quad (5.3)$$

Here, case 1 and 2 represent scenarios of strong charge-carrier imbalance, e.g. following selective extraction or trapping of electrons (case 1) or holes (case 2), for which the remaining hole or electron conductivities dominate. As Equation 5.3 reveals, under this scenario, I_{TRPL}/σ_{TRMC}^2 evolves with the ratio of the densities associated with minority and majority charge carriers ($n_{minority}/n_{majority}$), which will decline over time as further charge trapping or extraction occurs. In contrast, if no charge-carrier imbalances occur (case 3), I_{TRPL}/σ_{TRMC}^2 is a constant over time, indicating that electrons and holes recombine concurrently, typically through bimolecular radiative recombination. Therefore, any decay in the ratio I_{TRPL}/σ_{TRMC}^2 can visualise directly the presence of charge-carrier selective extraction from the perovskites layer into a charge transport layer, given that these typically exhibits low charge-carrier mobility and so do not contribute significantly to the conductivity.[186, 187]

To visualise how such analysis reveals transient charge imbalances, I conducted numerical simulations that involve non-radiative and radiative recombination based on the rate equation model discussed in Section 2.1.3.3 with the parameters shown in Table 5.1. Figure 5.1c and d

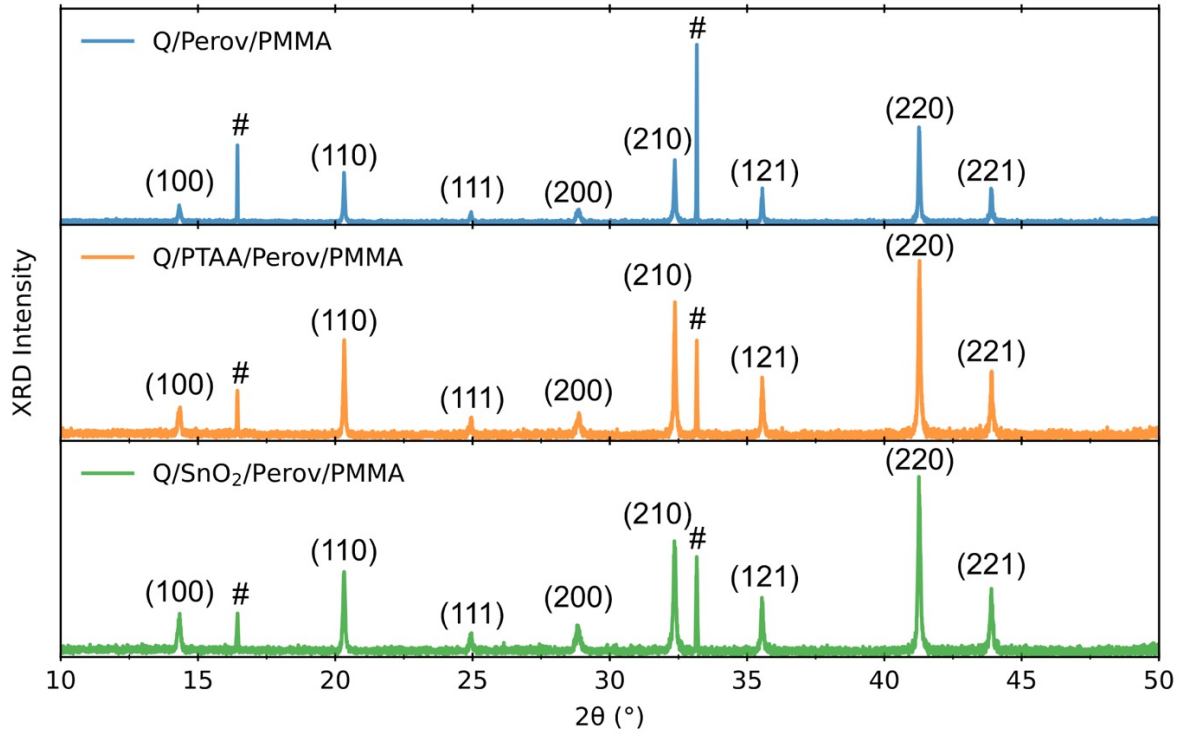


Figure 5.3: XRD spectra of Quartz(Q)/FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃(Perov)/PMMA (blue), Q/PTAA/Perov/PMMA (orange) and Q/SnO₂/Perov/PMMA (green). Relevant pseudo-cubic peaks are labelled with the Miller indices and they are identical to the literature values.[105] The z-cut quartz reference peaks at $2\theta = 16.433^\circ$ and 33.172° are labelled as #.[99]

display the implications of a charge-carrier selective process on I_{TRPL} and σ_{TRMC}^2 and therefore $I_{\text{TRPL}}/\sigma_{\text{TRMC}}^2$. When charge extraction or trapping is low (Figure 5.2c), I_{TRPL} and σ_{TRMC}^2 decay at the same rate, dominated by radiative electron-hole recombination and $I_{\text{TRPL}}/\sigma_{\text{TRMC}}^2$ is constant over time. However, in the case of strong charge extraction or high trap density (Figure 5.1d) the I_{TRPL} and σ_{TRMC}^2 transients diverge because suppression of one species significantly quenches TRPL while TRMC retains longer-lived component originating from the conductivity of the remaining majority carriers. Such divergence between minority and majority charge-carrier densities leads to the simulated drop in $I_{\text{TRPL}}/\sigma_{\text{TRMC}}^2$ over time.

Figure 5.1b shows how measured transients and the derived ratio $I_{\text{TRPL}}/\sigma_{\text{TRMC}}^2$ evolve over time for a FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃ film. The film was deposited on a quartz (Q) substrate and a polymethylmethacrylate (PMMA) top layer served as an inert encapsulating layer to minimize degradation and any influence of the ambient atmosphere.[53] The samples were fabricated by

Robert D. J. Oliver, with details provided in Section 3.7.1.2. Further optoelectronic and structural characterisation, presented in Figures 5.3 and 5.4, confirm the successful synthesis of the nominal composition $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$. This Q/Perov/PMMA stack does not support charge extraction and measurements were carried out under 530 nm pulsed excitation without significant halide segregation occurring. I find that the temporal evolution of I_{TRPL} and σ_{TRMC}^2 is indeed very similar, showing that trap-mediated recombination is minimal with at most minor contributions from shallow traps[50] (see Section B.4 for further details) and recombination is largely governed by radiative bimolecular recombination, as would be expected for excitation densities near 10^{17} cm^{-3} given reported trap densities of $\sim 10^{15} \text{ cm}^{-3}$ for typical lead halide perovskites.[51, 105] The calculated ratio $I_{\text{TRPL}}/\sigma_{\text{TRMC}}^2$ is nearly constant, directly visualising the minimal charge imbalance in the high-quality perovskite film when no extraction layers are present.

5.2.2 Effect of Halide Segregation on Charge-Carrier Mobility and Recombination

I proceed by first establishing how light-induced halide segregation affects charge-carrier dynamics, after which its influence on charge extraction is assessed in the next section. Halide segregation substantially alters the optoelectronic properties of mixed-halide perovskite even though the I-rich domains comprise only a small volume fraction,[20, 22] because charge-carriers generated in the mixed phase rapidly funnel into I-rich phase owing to its lower bandgap.[20] As a result, the evolution of halide segregation is often monitored by red-shifts in photoluminescence spectra. As Figure 5.4a shows, continued illumination of a $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ film (Q/Perov/PMMA) over 6 hours indeed results in a gradual redshift of the original ssPL emission peak associated with the mixed-halide phase to a spectrum reflecting I-rich domains (see Figures B.1, B.2 and B.3 for the ssPL of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ film coated with PTAA and SnO_2). Similarly, Figure 5.4b compares the film's absorption coefficient before (α_B) and after segregation (α_A), evidencing a broadening of the absorption, i.e. a decrease in α near the onset (reduction of original mixed phase) accompanied by an increase in α within the band-tail region (emergence

of I-rich domains). The inset reveals the change in the absorption onset ($\Delta\alpha = \alpha_A - \alpha_B$) during illumination. The corresponding spectral integral ($\int_{E_1}^{E_2} \Delta\alpha dE / \int_{E_1}^{E_2} \frac{\alpha_A + \alpha_B}{2} dE = 0.003$) is very low over the energy range from $E_1 = 1.5 \text{ eV}$ to $E_2 = 2.1 \text{ eV}$. Therefore, little change in overall absorption strength occurs, suggesting negligible degradation or material loss during phase segregation (see Figures B.4, B.5 for the absorption spectra of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ film coated with PTAA and SnO_2).

I next examine how halide segregation affects the charge-carrier mobility and recombination by concurrently recording TRPL transients for mixed-phase ($I_{\text{TRPL}}^{\text{Mixed}}$) and I-rich phase ($I_{\text{TRPL}}^{\text{I-rich}}$) emission, as well as the TRMC conductivity dynamics (σ_{TRMC}). Figures 5.4c and d show how the initial PL intensity recorded immediately following photoexcitation ($t = 0 \text{ ns}$) evolves for $I_{\text{TRPL}}^{\text{Mixed}}$ and $I_{\text{TRPL}}^{\text{I-rich}}$. The initial amplitude of $I_{\text{TRPL}}^{\text{Mixed}}$ ($t = 0 \text{ ns}$) declines rapidly with halide segregation, while that of $I_{\text{TRPL}}^{\text{I-rich}}$ ($t = 0 \text{ ns}$) is initially negligible but increases significantly (Figure 5.4f), mirroring the red-shift observed in the ssPL (Figure 5.4a). Moreover, the charge-carrier dynamics change substantially following halide segregation. For the mixed phase, segregation accelerates the decay of $I_{\text{TRPL}}^{\text{Mixed}}$ substantially (Figure 5.4c) over the 6 hours of illumination, until it is limited by the instrument time resolution ($< 1 \text{ ns}$, see Figure 5.5), consistent with a previous report of charge-carrier funnelling happening within tens of ps.[63] The TRMC (σ_{TRMC}) transients (Figure 5.4e) on the other hand, reflect the dynamics of charge carriers irrespective of whether they are located in the mixed or I-rich phase. Following segregation, σ_{TRMC} exhibits an accelerated decay, caused by funnelling of charge-carriers into I-rich domains, discussed further below. Notably, the initial value of σ_{TRMC} at $t = 0 \text{ ns}$ remains nearly constant throughout the 6 hr CW illumination as shown in Figure 5.4f, suggesting that the effective charge-carrier mobility of $\sum \phi\mu = 24.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ of Q/Perov/PMMA thin film is largely maintained (81 %) even in the I-rich phase (Table 5.2). A similar preservation of charge-carrier mobilities after halide segregation has been reported at THz frequencies,[63] but here I find the excellent mobility retention even at microwave frequencies. Given that the

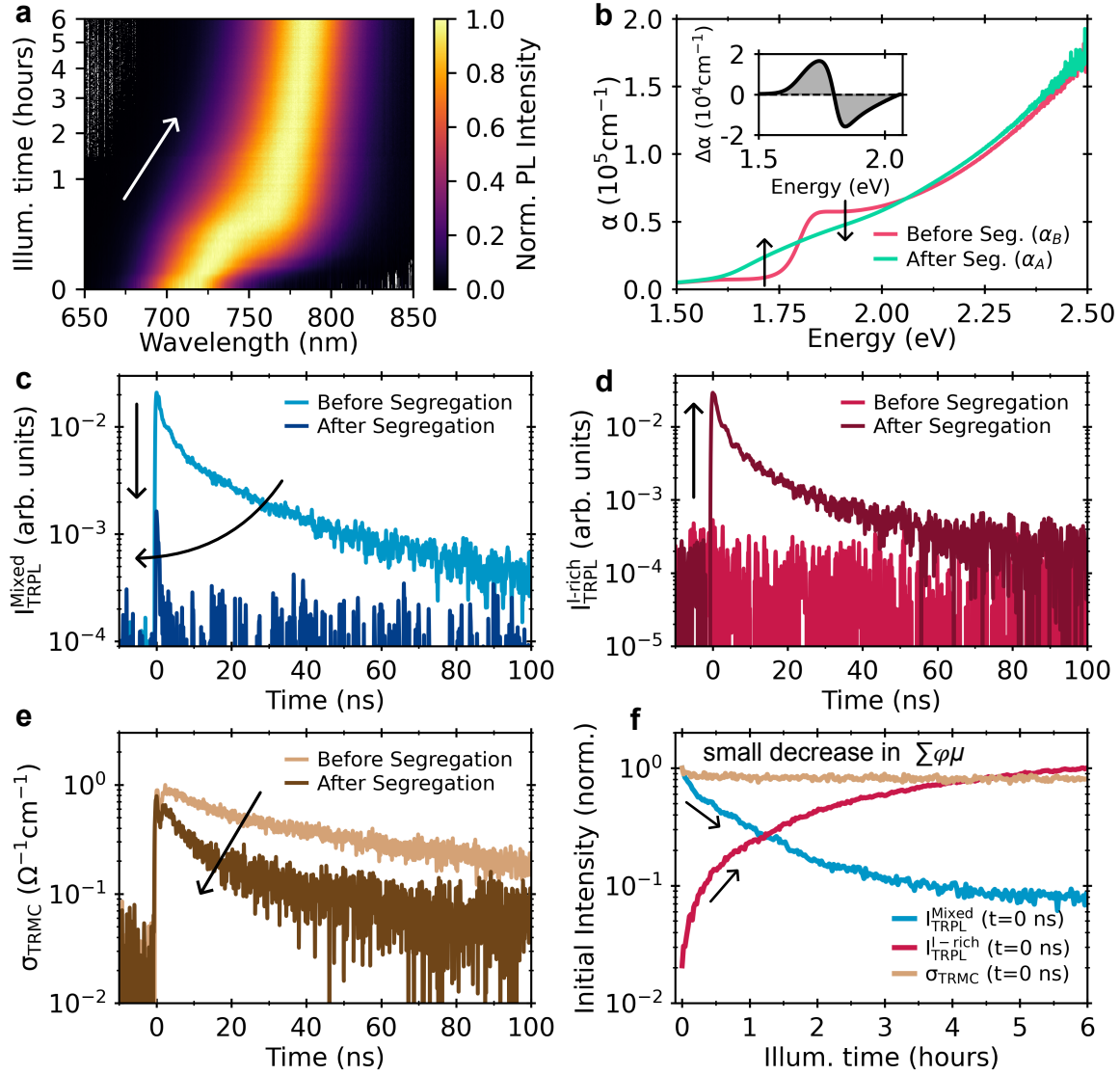


Figure 5.4: (a) Normalised steady-state PL contour map recorded during 6 hours of continuous-wave illumination with 532 nm light at a power density 150 mWcm^{-2} driving halide segregation. The illumination time is plotted on a square-root scale to highlight the early-time PL evolution. The relative increase in the PL intensity upon halide segregation is shown in Figure B.1 (b) Absorption spectra for Quartz(Q)/FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃(perov)/PMMA before (α_B) and after halide segregation (α_A). The inset shows the change in the absorption spectra ($\Delta\alpha = \alpha_A - \alpha_B$ near the absorption edge). (c) Mixed-phase TRPL ($I_{\text{TRPL}}^{\text{Mixed}}$, 658–694 nm) and (d) I-rich phase TRPL ($I_{\text{TRPL}}^{\text{I-rich}}$, 800–850 nm) transients for Q/Perov/PMMA before and after halide segregation. (e) TRMC transients (σ_{TRMC}) for Q/Perov/PMMA before and after halide segregation. (f) Initial intensity value of transients, recorded at $t = 0 \text{ ns}$ after excitation, and plotted as a function of illumination time over 6 hr. $I_{\text{TRPL}}^{\text{Mixed}}(t = 0 \text{ ns})$ and $\sigma_{\text{TRMC}}(t = 0 \text{ ns})$ are normalised with respect to the value recorded when CW illumination commences (Illum. time = 0 hr). $I_{\text{TRPL}}^{\text{I-rich}}(t = 0 \text{ ns})$ values are normalised with respect to the value at 6 hr illumination time. For panels (b)-(e), the label “before halide segregation” corresponds to 0 hours hr of illumination, while “after segregation” corresponds to 6 hours hr of illumination. For panels (c)-(f), Q/Perov/PMMA transients were recorded through pulsed excitation with a 530 nm laser at a pulse fluence of $3.6 \mu\text{Jcm}^{-2}$. Arrows are included as visual guides to illustrate the evolution of relevant features during halide segregation. For Q/PTAA/Perov/PMMA and Q/SnO₂/Perov/PMMA, the ssPL and absorption changes during halide segregation are shown in Appendix B.

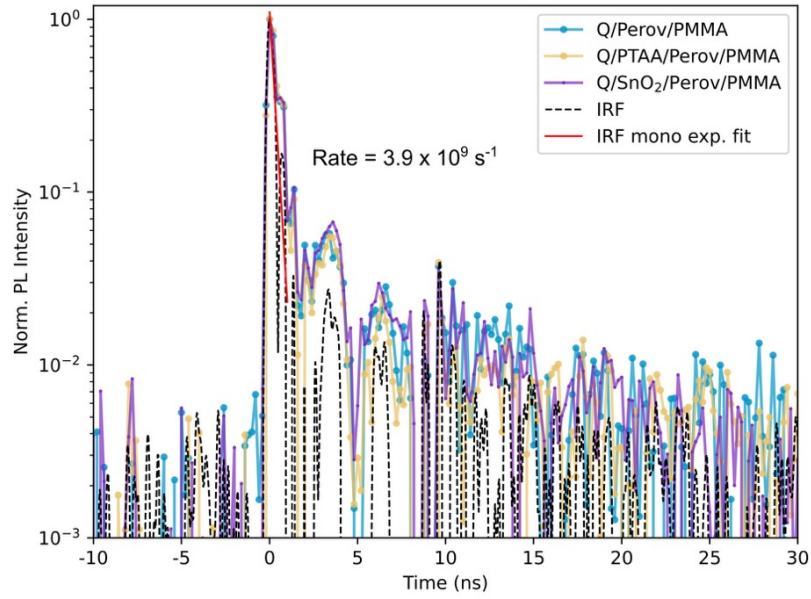


Figure 5.5: Normalised TRPL transients probing the high energy tail (658–694 nm) of the mixed-phase PL after halide segregation together with the instrument response function (IRF). For $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ thin films with and without charge-transport layers (PTAA and SnO_2), the TRPL decay is limited by IRF, indicating that the charge-carrier funnelling from the mixed-phase to the I-rich phase occurs on sub-nanosecond timescales.

probed charge transport distance scales with the square root of the inverse probe frequency,[112] the 102 GHz probe employed here has increased sensitivity to long-range defects and grain boundaries where halide segregation is known to dominantly occur.[53, 55, 178, 188, 189] These results suggest that despite the charge-carrier funnelling, I-rich domains are relatively large, sufficiently spanning grains and grain boundaries to permit relatively free charge-carrier motion within these domains.[55, 63, 178, 181, 189]

Compared to the neat perovskite film, the degree of mobility preservation upon halide segregation decreases in the presence of charge transport layers, yielding 72 % and 50 % mobility retention for Q/PTAA/Perov/PMMA and Q/ SnO_2 /Perov/PMMA respectively (see Table 5.2 for the mobility ratio values and Figures B.6 and B.7 for the TRPL and TRMC transients of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ film coated with PTAA and SnO_2). This additional reduction in mobility likely originates from external factors associated with perovskite/charge transport layer interface, as halide segregation without transport layers preserves greater mobility.

5.2.3 Effect of Halide Segregation on Charge-Carrier Extraction to Transport Layers

I further unravel how halide segregation affects charge extraction by investigating the effects on charge-carrier dynamics in half-stacks comprising $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ with commonly used charge transport materials. For this purpose, films of the perovskite are deposited on films of either the hole transport layer (HTL) poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) or the electron transport layer (ETL) SnO_2 , on quartz substrates. The samples were fabricated by Robert D. J. Oliver, with details provided in Section 3.7.1.2. Steady-state PL, XRD and absorption measurements confirm the formation of the intended nominal composition of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ on these layers (see Appendix B). Figure 5.6 reveals the effect of halide segregation on charge-carrier dynamics in such half-stacks, with the three columns representing Q/Perovskite/PMMA, Q/PTAA/Perovskite /PMMA and Q/ SnO_2 /Perovskite/PMMA architectures, and the three rows the TRPL transients, squared TRMC transients and their ratio. I note that to examine the effect of halide segregation on PL transients, the TRPL of the original mixed phase ($I_{\text{TRPL}}^{\text{Mixed}}$) before segregation with that of the I-rich phase ($I_{\text{TRPL}}^{\text{I-rich}}$) after segregation are compared, because, as discussed above, funnelling is so rapid that recombination predominantly occurs in these two different phases before and after segregation, respectively (see Figure 5.5). Importantly, regardless of whether or not an extraction layer is present, both TRPL and squared TRMC (σ_{TRMC}^2) transients clearly show that halide segregation causes an accelerated decay of the charge-carrier density. This effect is caused by enhanced radiative electron-hole recombination owing to an increase in charge-carrier density following funnelling into the I-rich domains which only cover a fraction of perovskite film volume.[20]

I further probe the effect of halide segregation on charge extraction at the interface of the perovskite with PTAA or SnO_2 . To isolate the effects of charge-selective processes occurring at the perovskite interface from those caused by accelerated radiative recombination, the transient ratios of $I_{\text{TRPL}}/\sigma_{\text{TRMC}}^2$ were calculated and are presented in the bottom row of Figure 5.6. These

ratios reveal any evolving imbalance between electron and hole densities. While electrons and holes are initially photogenerated in equal numbers, transfer or trapping of either only electrons or only holes is expected to lead to a decay of $I_{\text{TRPL}}/\sigma_{\text{TRMC}}^2$ over time. This method thus allows us to qualitatively discuss the effect of such charge selective processes without having to solve multi-parameterised coupled differential equations or computationally expensive drift-diffusion model on charge-carrier dynamics before and after halide segregation.[51, 149, 151, 152, 154, 190] This simplification is particularly valuable because halide segregation likely induces a distribution of I-rich phases rather than a simple two-phase system employed in other studies,[63] further complicating such models.

The $I_{\text{TRPL}}/\sigma_{\text{TRMC}}^2$ transients (bottom row, Figure 5.6) indeed reveal clear evidence for charge extraction in the presence of either PTAA or SnO_2 extraction layers. In the absence of such extraction layers (Q/Perov/PMMA reference stack, Figure 5.6g) the $I_{\text{TRPL}}/\sigma_{\text{TRMC}}^2$ ratio is mostly decays slowly, both before and after halide segregation, indicating little effect of charge-selective shallow trapping, consistent with high-quality film material and interfaces (see Section B.4). I note that halide segregation causes little change to these transients because any acceleration of bimolecular electron-hole recombination owing to increase in the charge-carrier density is cancelled out in the division of I_{TRPL} and σ_{TRMC}^2 transients (Case 3 in Equation 5.3). In contrast, when charge transport layers are introduced (Figure 5.6h and i), $I_{\text{TRPL}}/\sigma_{\text{TRMC}}^2$ transients exhibit an accelerated initial decay within 10 ns followed by a slow component, evidencing charge-selective processes associated with these new interfaces. Given that similar dynamics are observed irrespective of the type of charge transport layer, I attribute the fast early decay to charge extraction rather than enhanced charge-carrier trapping. Importantly, following halide segregation, these $I_{\text{TRPL}}/\sigma_{\text{TRMC}}^2$ still exhibiting the fast decline associated with charge extraction. Given that the PL and conductivity in this case originate from charge carriers located in the I-rich phase, these transients clearly show that charge-extraction is still eminently feasible even after charge carriers have been funnelled into these domains.

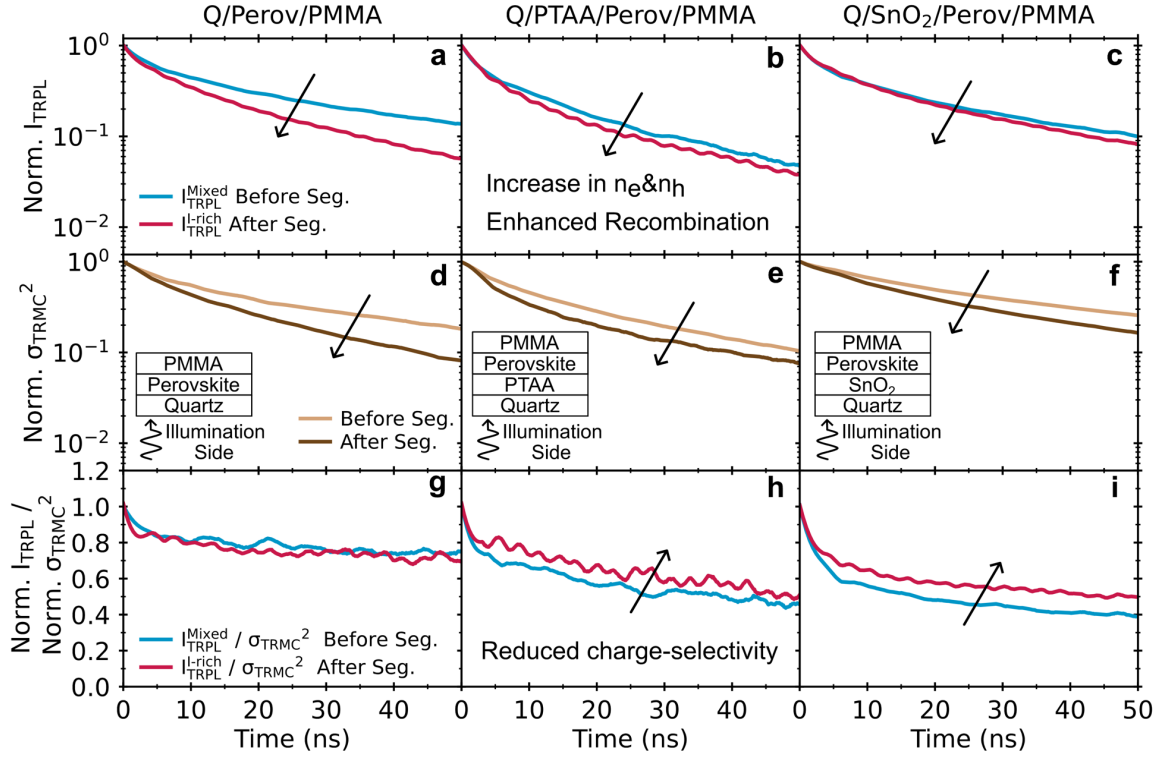


Figure 5.6: (a)-(c) Normalised mixed-phase TRPL transients ($I_{\text{TRPL}}^{\text{Mixed}}$) before halide segregation had commenced (blue) compared with I-rich phase TRPL transients ($I_{\text{TRPL}}^{\text{I-rich}}$) after 6 hours of halide segregation (red), shown for (a) Quartz(Q)/FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃(Perov)/PMMA, (b) Q/PTAA/Perov/PMMA, and (c) Q/SnO₂/Perov/PMMA. (d)-(f) Normalised squared TRMC photoconductivity transients (σ_{TRMC}^2) before (light brown) and after halide segregation for 6 hr (dark brown) for the same device stacks as in (a)-(c). The insets show the thin-film architectures and the illumination direction (arrow) from the quartz substrate near the charge transport layers. A 530 nm pulsed excitation at the fluence of $3.6 \mu\text{Jcm}^{-2}$ was used for transients while 532 nm CW illumination at a power density of 150 mWcm^{-2} was employed to induce halide segregation, both illuminated from the quartz side.. (g)-(i) Ratio of normalised mixed phase TRPL transient to the square of the normalised TRMC photoconductivity ($I_{\text{TRPL}}/\sigma_{\text{TRMC}}^2$) before (blue) and after (red) halide segregation. Legends are shared horizontally across panels (a)-(c), (d)-(f) and (g)-(i).

However, at later times, the charge-carrier imbalance is less pronounced for Q/PTAA/Perov/PMMA and Q/SnO₂/Perov/PMMA, as evidenced by the increased amplitude of late-time value of the ratio of $I_{\text{TRPL}}^{\text{I-rich}}/\sigma_{\text{TRMC}}^2$ shown in Figure 5.6h and i respectively. this behaviour can be attributed to enhanced charge-carrier back transfer from charge transport layer to the I-rich phase. The back transfer injects minority charge carriers into the I-rich phase, resulting in a larger increase in $I_{\text{TRPL}}^{\text{I-rich}}$ than in σ_{TRMC}^2 . Photoluminescence scales with the product of majority and minority carrier densities (Equation 5.2) and is therefore more sensitive to the minority carrier

Sample	$\mu_{\text{after}}/\mu_{\text{before}}$	$\tau_{\text{after}}/\tau_{\text{before}}$ (from I_{TRPL})	$\tau_{\text{after}}/\tau_{\text{before}}$ (from σ_{TRMC})	$L_{D,\text{after}}/L_{D,\text{before}}$
Q/Perov/PMMA	0.81	0.55	0.53	0.662 ± 0.004
Q/PTAA/Perov/PMMA	0.50	0.80	0.69	0.61 ± 0.02
Q/SnO ₂ /Perov/PMMA	0.72	0.87	0.65	0.74 ± 0.05

Table 5.2: Summary of the ratios of mobility (μ), lifetime (τ), and diffusion length (L_D) before and after halide segregation. The diffusion length is calculated as calculated as $L_D = \sqrt{\mu\tau}$, where τ is taken as the average of τ obtained from I_{TRPL} and σ_{TRMC} .

population, whereas σ_{TRMC} reflects the sum of both carrier contributions and weights them equally (Equation 5.1). The asymmetric influence of minority-carrier injection results in less pronounced reduction in I_{TRPL} compared to σ_{TRMC}^2 (Table 5.2), thereby reducing the divergence between I_{TRPL} and σ_{TRMC}^2 and increasing the ratio of $I_{\text{TRPL}}/\sigma_{\text{TRMC}}^2$. This is analogous to case 1 and case 2 described in Equation 5.3, where increase in minority charge carriers (numerator) leads to increase in the ratio of I_{TRPL} and σ_{TRMC}^2 . This agrees well with our previous study that FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃ with higher iodide content exhibit stronger hole back transfer from PTAA owing to a more favourable energy-level alignment.[105] However, such increase in the late-time values of I_{TRPL} and σ_{TRMC}^2 still competes with enhanced radiative recombination, resulting in overall decrease in lifetime after segregation, but to a lesser extent than in neat perovskite. These findings thus indicate that despite extensive phase segregation occurring in the perovskite films, surprisingly effective percolation pathways are maintained towards the charge-extraction layers. Moreover, enhanced charge-carrier back transfer facilitated by more favourable energetic alignment between the transport layer and I-rich domains alleviates the lifetime reduction otherwise caused by enhanced bimolecular radiative recombination owing to charge-carrier funnelling.

5.2.4 Projected Impact of Halide Segregation on Photovoltaic Performance

Figure 5.7 summarises the changes occurring in the dynamical processes following halide segregation for the three half-stack configurations. In the absence of charge extraction layers (Q/Perov/PMMA) and prior to any segregation (Figure 5.7a), charge carriers recombine in

accordance with a typical rate equation model involving radiative electron-hole recombination (R_{eh}) and through population (R_{pop}), depopulation (R_{depop}) and release from (k_{detrap}) traps (see Section 2.1.3.3). However, halide segregation (Figure 5.7b) bypasses these processes by rapid funnelling of charge carriers into the I-rich phase, which only occupies a smaller sub-volume of the film.[20] This funnelling thus leads to a local increase in charge-carrier density, causing accelerated radiative emission (Equation 4.2). Once charge-extraction layers are introduced (Figure 5.7c and e) additional dynamic processes associated with the interface occur, such as charge transfer, back transfer and interfacial recombination.[105] However, following halide segregation (Figure 5.7d and f), charge-carrier funnelling to the I-rich phase occurs much more rapidly than charge extraction from the mixed phase. Therefore, any transfer into either PTAA or SnO_2 must now be accomplished from the I-rich phase and it is still surprisingly effective.

The impact of the mobility and lifetime of charge-carriers on the short-circuit current density J_{SC} is captured through diffusion length, whereas the $I_{\text{TRPL}}/\sigma_{\text{TRMC}}^2$ ratio reflects the change in the ratio of minority to majority carriers and only serves as a metric to confirm the presence of charge-selective processes such as charge extraction without providing quantitative information. Diffusion length (L_{D}) is defined square root of product of total recombination lifetime (τ) taken as the average of lifetime obtained from I_{TRPL} and σ_{TRMC} , and charge-carrier mobility (μ), and the ratio of the diffusion lengths before and after halide segregation ($L_{\text{D_after}}/L_{\text{D_before}}$) allows discussion of the extent to which J_{SC} is affected after halide segregation. By using the mobility changes obtained from initial σ_{TRMC} intensity and lifetime of charge-carrier dynamics for transients shown in Figure 5.6, Q/Perov/PMMA, Q/PTAA/Perov/PMMA and Q/ SnO_2 /Perov/PMMA show $L_{\text{D_after}}/L_{\text{D_before}}$ of 0.66, 0.61 and 0.74 respectively (Table 5.2). For Q/Perov/PMMA, the reduction in L_{D} is mainly driven by reduction in lifetime owing to enhanced radiative recombination, whereas in the presence of charge transport layers, the reduction in L_{D} is driven by the balance between the decrease in μ and τ , which are affected by increase in interfacial defects and charge-carrier back transfer respectively. Such accelerated

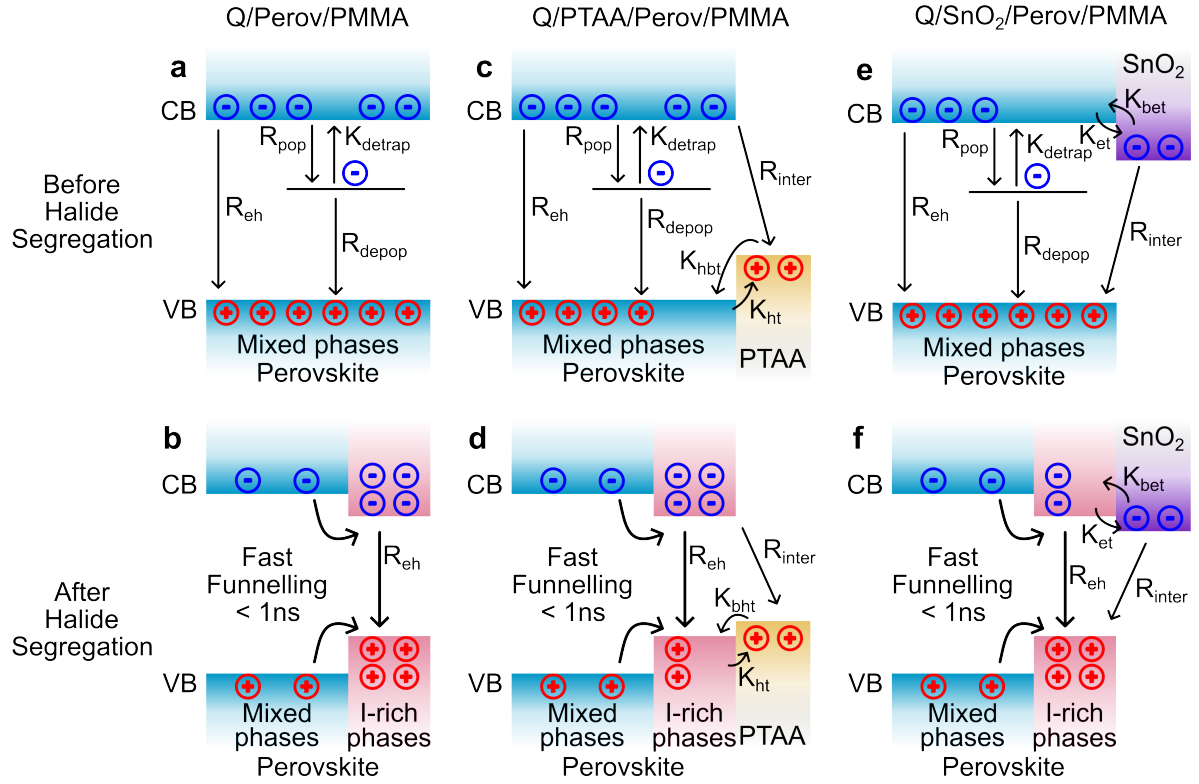


Figure 5.7: (a)-(b) Schematic illustration of charge-carrier dynamics in Quartz(Q)/FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃(perov)/PMMA before and after halide segregation respectively, showing radiative bimolecular recombination (R_{eh}) and the non-radiative trap-mediated recombination processes, which are trap population (R_{pop}), detrapping (k_{detrap}) and depopulation (R_{depop}). The blue region represents conduction band (CB) and valence (VB) of the mixed phase with blue minus and red plus symbols corresponding to electrons and holes respectively. (c)-(d) Schematics of charge-carrier dynamics in the presence of PTAA before and after halide segregation respectively, including additional interfacial processes such as hole transfer (k_{ht}), hole back transfer (k_{bht}) and interfacial recombination (R_{inter}). The yellow region indicates the highest occupying molecular orbital (HOMO) of PTAA. (e)-(f) Schematic illustration of charge-carrier dynamics in the presence of SnO₂ before and after halide segregation respectively with electron transfer (k_{et}) and back transfer (k_{bet}) and R_{inter} . The purple region represents the CB of SnO₂.

radiative recombination and slight reduction in mobility suppress absolute number of charge carriers transferred to the transport layer, which ultimately governs the absolute value of J_{SC} .^[35] These values correlate well with the recent study by Guo et al. reporting a $\sim 35\%$ reduction in J_{SC} upon halide segregation for solar cells based on FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃.^[181] I note that under full device operation, the charge-collection efficiency might be influenced by additional factors such as mobile ion-induced field screening.^[191] However, the results clearly demonstrate that the balance of enhanced radiative recombination and reduction in mobility is the main factor limiting charge-carrier collection efficiency upon halide segregation.

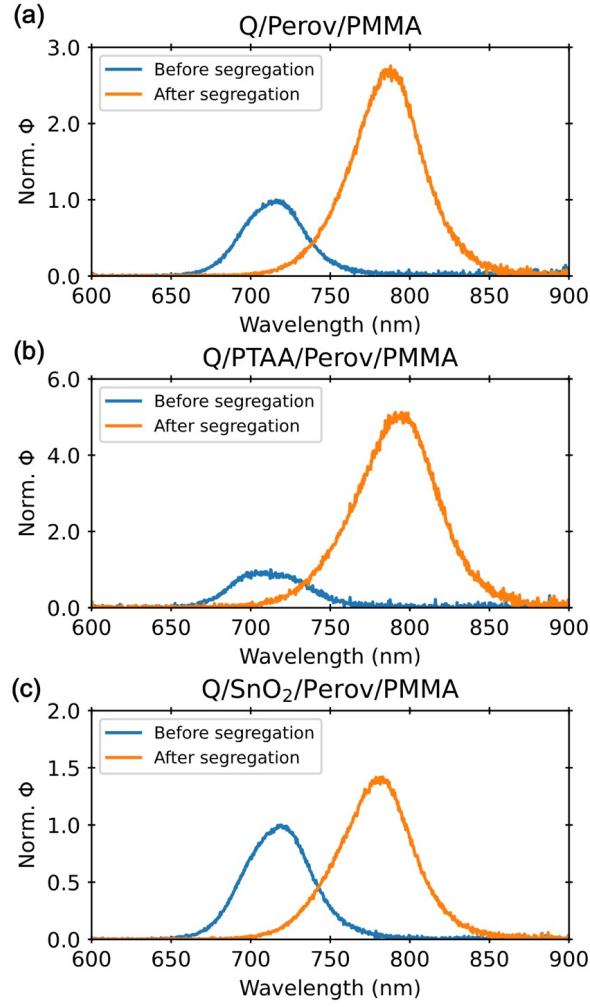


Figure 5.8: Normalised photon flux for (a) Q/FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃ (Perov)/PMMA, (b) Q/PTAA/Perov/PMMA and (c) Q/SnO₂/Perov/PMMA before and after halide segregation

In addition, I consider changes occurring in the open-circuit voltage V_{OC} following halide segregation. In a simple approximation of two phases, charge-carrier funneling from the mixed-halide perovskite FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃ bandgap (see peak emission energy shift in Figure 5.2) should result in a 0.2 eV loss of V_{OC} . However, it could be argued that the increase in photoluminescence quantum yield (PLQY) resulting from accelerated radiative recombination might partly compensate for such losses, since V_{OC} is closely tied to the quasi-Fermi level splitting (QFLS):[69]

$$\Delta QFLS = \frac{k_B T}{q} \ln \left(\frac{PLQY_{After}}{PLQY_{Before}} \right) \quad (5.4)$$

where $PLQY_{After}/PLQY_{Before}$ denote the ratio of the PLQY values before and after halide segregation. Inserting the experimentally determined rise in emitted photon efficiency into Equation 5.4 yields an expected increase in QFLS of only 24.8, 52.2 and 11.9 meV for Q/Perov/PMMA, Q/PTAA/Perov/PMMA and Q/SnO₂/Perov/PMMA respectively (See Figure 5.8), far lower than the 200 meV loss that will be incurred from the bandedge shifts. Interestingly, when PLQY is already near unity, segregation provides negligible V_{OC} compensation, imposing an intrinsic limit to the bandedge shifts. However, such detrimental effect may not be observed in the real devices since highly-performing devices with advanced passivation methods tend to largely suppress halide segregation in the first place.[21, 192] Overall, these considerations explain why halide segregation may lead to widely reported losses in either V_{OC} , J_{SC} or both quantities,[22, 60, 68, 181, 182] and so an overall decline in power conversion efficiency of the solar cell.

5.3 Conclusions

In conclusion, I have demonstrated how halide segregation fundamentally alters charge-carrier dynamics in wide-bandgap mixed-halide perovskites interfaced with charge-transport layers. Using the synchronous multimodal spectroscopy that combines TRMC, TRPL and ssPL, it was shown that halide segregation drives sub-nanosecond funnelling of charge-carriers into the I-rich domains, where enhanced radiative recombination directly competes with charge extraction. In neat perovskite (Q/Perov/PMMA), charge-carrier mobility remains well-preserved after segregation (81%) whereas the carrier lifetime decreases more significantly owing to enhanced radiative bimolecular recombination resulting from charge-carrier funnelling. In the presence of transport layers, charge-carrier mobility retention is reduced while the reduction in the carrier lifetime from enhanced radiative recombination is alleviated by enhanced charge-carrier back transfer that is facilitate by more favourable energy-level alignment between transport layer and

the I-rich phase. Importantly, the free-space multimodal approach employed here provides a powerful diagnostic to disentangle radiative and interfacial processes, which cannot be resolved by TRMC or TRPL alone. These insights establish a direct link between halide segregation and the widely observed V_{OC} and J_{SC} losses in wide-bandgap perovskite solar cells. Overall, the study presented here highlights the need for strategies that either suppress halide segregation or mitigate the adverse effect of charge-carrier funnelling to enable efficient integration of stable wide-bandgap mixed-halide perovskites into multijunction solar cells.

6

Impact of Charge Transport Layers on the Structural and Optoelectronic Properties of Coevaporated $\text{Cu}_2\text{AgBiI}_6$

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Jae Eun Lee performed all the experiments and data analysis, and wrote the manuscript. Marcello Righetto and Laura M. Herz supervised. Benjamin W.J. Putland and Heon Jin fabricated the samples. Siyu Yan measured SEM. Joshua R. S. Lilly and Snigdha Lal helped with OPTP measurement. All authors discussed the results and reviewed the manuscript.

6.1 Broader Context

The copper-silver-bismuth-iodide compound $\text{Cu}_2\text{AgBiI}_6$ has emerged as a promising lead-free and environmentally friendly alternative to wide-bandgap lead-halide perovskites for applications in multijunction solar cells. Despite its promising optoelectronic properties, the efficiency of $\text{Cu}_2\text{AgBiI}_6$ is still severely limited by poor charge collection. Here, I investigate the impact of commonly used charge transport layers (CTLs), including poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), CuI, [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), and SnO_2 , on the structural and optoelectronic properties of coevaporated $\text{Cu}_2\text{AgBiI}_6$ thin films. I reveal that while organic transport layers, such as PTAA and PCBM, form a relatively benign interface, inorganic transport layers, such as CuI and SnO_2 , induce the formation of unintended impurity phases within the CuI-AgI-BiI_3 solid solution space, significantly influencing structural and optoelectronic properties. I demonstrate that identification of these impurity phases requires careful cross-validation combining absorption, X-ray diffraction and THz photoconductivity spectroscopy because their structural and optoelectronic properties are very similar to those of $\text{Cu}_2\text{AgBiI}_6$. The results highlight the critical role of CTLs in determining the structural and optoelectronic properties of coevaporated copper-silver-bismuth-iodide thin films and underscore the need for advanced interface engineering to optimize device efficiency and reproducibility.

6.2 Introduction

Multijunction solar cells based on lead halide perovskites have recently achieved remarkable power conversion efficiencies (PCEs) exceeding 34 % for silicon-perovskite architectures.[2] However, their commercialization remains contingent upon the fabrication of high-quality and stable wide-bandgap perovskites (from ≈ 1.7 eV for perovskite-silicon to ≈ 2 eV for triple-junction cells).[62, 163] The well-known operational instability[78, 79] of wide-bandgap perovskite solar absorbers, together with long-standing concerns regarding the toxicity of Pb^{2+} cations,[76] has fuelled considerable interest in all-inorganic lead-free alternatives. The substitution of Pb^{2+} with the isoelectronic pair $\text{Ag}^+/\text{Bi}^{3+}$ has emerged as a highly promising strategy, capable of achieving the desired wider bandgaps without introducing unstable multiple-halide alloys,[23, 80, 83, 86, 97] and leading to the development of double perovskites, such as $\text{Cs}_2\text{AgBiBr}_6$. [193–196] Silver–bismuth double perovskites exhibit excellent stability,[194, 195] moderate charge-carrier mobility around $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, [96] and long charge-carrier lifetimes,[197] resulting in promising PCEs of up to 6.37 % [194] to date. However, the indirect bandgap nature of $\text{Cs}_2\text{AgBiBr}_6$ around 2 eV, arising from the alternate Ag–Bi occupation of octahedral sites,[95, 194, 196] and the recently discovered ultrafast charge-carrier localization process[96] pose significant limitations on its maximum achievable PCE.

Such limitations have led to the exploration of a broader compositional range, focusing on the CuI–AgI–BiI_3 phase space. Importantly, introducing Cu^+ ions has the 2-fold aim of gaining an extra degree of chemical tunability, and increasing electronic density at the top of the valence band, thus aiming for a direct bandgap character.[23, 97] Among these, the most extensively studied Cu–Bi–I ternary compound CuBiI_4 [90–92] exists as a metastable phase, decomposing back into CuI and BiI_3 precursors at room temperature.[23] However, ternary Ag–Bi–I compounds such as AgBi_2I_7 , AgBiI_4 , Ag_2BiI_5 , and Ag_3BiI_6 are structurally more stable and widely studied.[83, 85, 93, 198, 199] In particular, Ag_3BiI_6 achieved a moderate

record PCE of 5.56 % through bandgap engineering via sulfide additives,[198] but a low reported charge-carrier mobility ($\approx 0.03 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) poses significant limitations.[86] The quaternary compound $\text{Cu}_2\text{AgBiI}_6$ (CABI) has emerged from this compositional space as one of the most promising candidates for multijunction solar cell applications owing to its desirable optoelectronic properties with improved stability.[23, 200] CABI features a direct bandgap of $\approx 2 \text{ eV}$ with a high absorption coefficient exceeding 10^5 cm^{-1} ,[23, 24, 97] an exciton binding energy comparable to thermal energy at room temperature,[97] moderate charge-carrier mobilities ($\approx 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) comparable to those of $\text{Cs}_2\text{AgBiBr}_6$,[24] and extended lifetimes up to hundreds of nanoseconds.[95, 201] These properties position CABI as a strong candidate for lead-free, all inorganic top cell absorbers for tandem solar cells. Pai et al. have fabricated CABI solar cells with a modest record PCE of 2.39 % by improving the film morphology using the hot-casting assisted spin-coating method on a mesoporous TiO_2 scaffold.[95] However, such photovoltaic device efficiency values seem surprisingly low given CABI's favorable optoelectronic properties, raising questions on the underlying factors.

In this context, CABI-based solar cells have been recently found to suffer from limited charge transport and low current density. [23, 95, 118, 201] Buizza et al. have reported the presence of intrinsic charge-carrier localization processes in CABI occurring on a picosecond time scale.[24] However, they noted that despite this process, which intrinsically lowers charge-carrier mobility, CABI still subsequently retains a decent mobility around $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ owing to the low energetic barriers involved in the localization process.[24] Moreover, such ultrafast localization phenomena have also been observed in $\text{Cs}_2\text{AgBiBr}_6$ and Ag–Bi–I compounds as well,[86, 96] suggesting that the low efficiency of the state-of-the-art CABI solar cells may be attributed to extrinsic rather than intrinsic factors, potentially arising only once the material is incorporated into a device structure.

The low solubility of binary iodide precursors in the commonly used solvents (e.g., DMSO/DMF) is detrimental to the quality of solution-processed CABI thin films,[95, 200] and hence

requires further optimization steps (e.g., thermal, antisolvent, additive treatments).[95, 202] Physical vapor deposition techniques have therefore been recently proposed as a promising synthetic route that enables control over thickness, uniform coating and ease of scale-up. Putland et al. deposited CABI thin films using a vapor phase coevaporation method for the first time, yet the reported PCE of the champion device only reached a modest value of 0.43 %.[118] Interestingly, the associated external quantum efficiency (EQE) measurements revealed negligible and imbalanced charge extraction. Given the comparable effective electron and hole masses of CABI (1.0 and 0.6 m_0 respectively),[23] such imbalanced and inefficient charge extraction has raised concerns about the quality of the interfaces between CABI and charge transport layers. The quality of the interfaces plays a critical role in the improvement of charge extraction from solar cells. For instance, wide-bandgap perovskites, typically employed as the top (sun facing) absorber layer in tandem solar cells, have yielded large short-circuit current density (J_{sc}) values in single-junction cells when ionic additives at the charge transport layer/absorber interface had been incorporated,[11, 128] or when novel self-assembled molecular monolayers had been utilized which may enable conformal coverage and better energy-level alignment at the interface.[133] It is therefore clear that for CABI, a similar in-depth understanding and engineering of interfaces with charge transport layers is urgently needed to unleash the potential of this promising solar absorber.[122, 128, 129]

In this chapter, I systematically investigate the impact of popular hole transport layers (HTLs), including poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) and CuI, and electron transport layers (ETLs), including [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and SnO_2 , on the composition, crystallinity and morphology of coevaporated CABI and examine how these changes influence its optoelectronic properties. By using a combination of X-ray diffraction (XRD) and optical-pump terahertz-probe (OPTP) spectroscopy, I obtain comprehensive insight on CABI/charge transport layer interfaces, which are generally concealed in the conventional UV-vis absorption characterization. Notably, I reveal that while the deposition of the organic

charge transport layers (i.e., PTAA, PCBM) has a minor impact on the CABI layer, inorganic charge transport layers (i.e., CuI and SnO₂) drive the formation of impurity phases, significantly affecting the structural and optoelectronic properties of the CABI layer. Taken together, the results provide insight into the causes of underperforming coevaporated CABI solar cells and identify CABI/charge transport layer interfaces as a crucial area of development for this promising solar absorber.

6.3 Results and Discussion

6.3.1 Impact of Charge-Transport Layers on the Optical Properties of Cu₂AgBiI₆

I start by exploring how the electronic states in CABI are affected by the deposition of charge transport layers. In this work, I focused on CABI and solar cell “half stacks” for the best performing n–i–p solar cell configurations[95] (i.e., CABI is evaporated on top of ETLs and HTLs are deposited on CABI without any electrodes). The full details of CABI evaporation and HTL/ETL deposition parameters are provided in Section 3.7.2 *The samples were fabricated by Benjamin W. J. Putland, Department of Physics, University of Oxford.* I first measured the UV-vis absorption spectra of quartz(Q)/CABI, Q/CABI/HTL (see Figure 6.1a), and Q/ETL/CABI (see Figure 6.1b) thin films. By comparing the normalized absorption coefficient spectra of Q/CABI with their half-stack counterparts, it is evident that the absorption onsets of Q/CABI/CuI and Q/SnO₂/CABI exhibit a red shift, while those of Q/CABI/PTAA and Q/PCBM/CABI remain relatively consistent with that of Q/CABI. A wide range of bandgaps has been reported for CABI, spanning from 1.89 to 2.13 eV.[23, 24, 95, 97, 118, 201, 202] In principle, such a significant difference may stem either from variations in the composition and structure of CABI, or from different approaches for extracting bandgap values. To rule out the discrepancies arising from different data analysis techniques, I have extracted the bandgaps for Q/CABI using three widely adopted methods: the Elliott fit, inflection and Tauc methods, as shown in Figure 6.1c–e. The

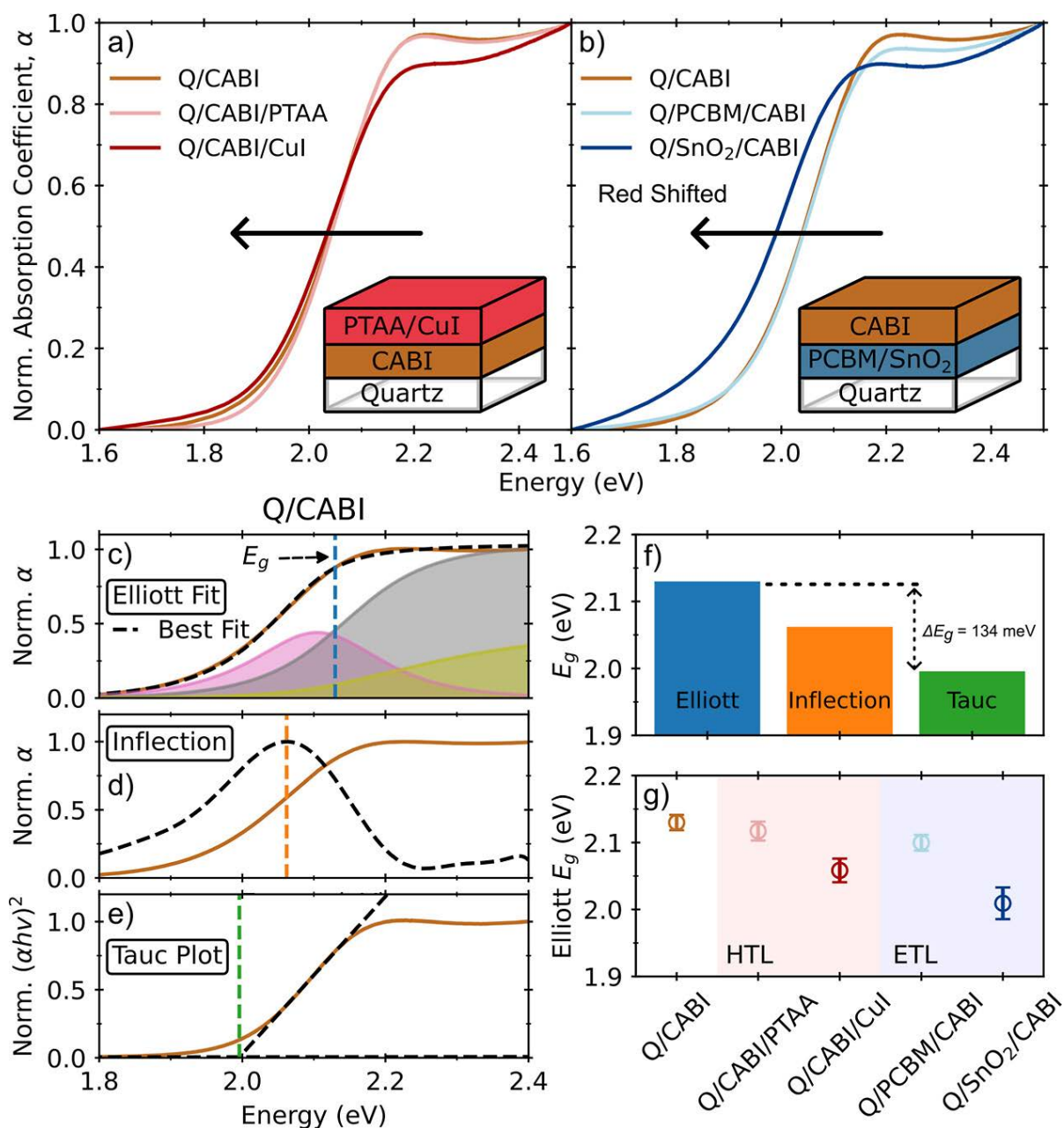


Figure 6.1: (a)-(b) Absorption spectra of CABI and CABI interfaced with charge transport layers. The brown solid line represents quartz(Q)/CABI. The light red and dark red lines represent Q/CABI/PTAA and Q/CABI/CuI respectively. The light and dark blue lines represent Q/PCBM/CABI and Q/SnO₂/CABI respectively. The insets show the half-stack architectures. (c)–(e) Bandgaps obtained from Elliott fit, inflection method and Tauc plot, respectively. The black dashed lines show the best fit of each method, and the vertical dashed lines represent the bandgaps obtained from each method. (f) Bandgap values obtained from each method for Q/CABI. (g) The bandgaps obtained from the Elliott fits for all thin films.

Sample	$E_{g_Elliott}$ (eV)	E_b (eV)	γ_{Abs} (eV)	E_{inf} (eV)	E_{Tauc} (eV)
Q/CABI	2.13	0.036	0.076	2.06	2.00
Q/CABI/PTAA	2.12	0.031	0.069	2.06	2.00
Q/CABI/CuI	2.06	0.016	0.073	2.05	1.97
Q/PCBM/CABI	2.10	0.026	0.072	2.06	1.99
Q/SnO ₂ /CABI	2.01	0.016	0.082	2.01	1.92

Table 6.1: Summary of the extracted absorption parameters of CABI thin film and CABI thin films with transport layers, all on quartz substrates. $E_{g_Elliott}$, E_{inf} , and E_{Tauc} are the bandgaps obtained from the Elliott fit, inflection and Tauc methods respectively. E_b and γ_{Abs} are the exciton binding energy and broadening parameter obtained from the Elliott fit.

Elliott fit method generally yields higher bandgap values (see Figure 6.1f), followed by those determined through the inflection and Tauc methods. I attribute this to Tauc and inflection methods underestimating the bandgap values because they neglect the presence of excitonic effects and are highly sensitive to sub-bandgap defects and scattering contributions.[101] Such contributions are crucial in CABI, whose absorption gradually onsets from around 1.8 to 2.2 eV, which is significantly broader than that of typical lead-halide perovskites.[10] Therefore, the bandgaps extracted from Elliott fits were chosen as a more reliable metric to compare the different CABI half-stack thin films.[38] Note that the >200 meV spread in the bandgaps reported in the literature is significantly larger than the error arising from the use of differing bandgap extraction methods (i.e., 134 meV, see Figure 6.1f), thus suggesting that compositional or structural changes in the bulk CABI thin film could also play a significant role. Nonetheless, the optical bandgap of 2.13 eV obtained from the Elliott fit for Q/CABI here agrees well with the bandgap of coevaporated CABI thin films reported previously, also extracted from Elliott fits to absorption onsets.[118] Overall, these observations thus highlight the importance of considering both deposition methods and fitting techniques when determining the bandgaps.

Figure 6.1g provides a quantitative comparison of the CABI bandgaps across the half-stack architectures, revealing a minor redshift in the bandgaps of Q/CABI/PTAA and Q/PCBM/CABI with respect to those of plain Q/CABI, and more pronounced redshifts for Q/CABI/CuI and Q/SnO₂/CABI. Such shifts suggest the presence of non-CABI phases or structural changes in

these thin films, which is further confirmed by corresponding additional absorption peaks at around 3 eV (see Figure C.1), which has been recently shown to be related to the presence of CuI and AgI-rich phases.[118, 203] Furthermore, Q/SnO₂/CABI exhibits a higher broadening parameter (γ_{Abs}) associated with the absorption edge, corroborating the presence of additional energetic disorder (see Table 6.1). Such disorder is likely to originate from sub-bandgap defect states or lattice disorder induced by the impurities. It is worth noting that a nonuniform distribution of bandgaps related to impurity phases has the potential to impair charge-carrier transport and thus disrupt charge collection efficiency.

6.3.2 Impact of Charge-Transport Layers on the Structural Properties of $\text{Cu}_2\text{AgBiI}_6$

To further investigate the structural and compositional changes of the deposited thin films, I carried out XRD measurements and performed an accurate phase identification and unit cell analysis by using the Pawley fitting method.[115] The XRD pattern of Q/CABI in Figure 6.2 shows distinct peaks corresponding to the (003), (012), (006), and (009) crystallographic planes of the single $R\bar{3}m$ space group associated with CABI (highlighted in the figure by gray vertical dashed lines), as well as a small BiI_3 peak (marked with ○). The relative XRD peak intensities indicate that the coevaporated CABI thin film favors out-of-plane growth along the [003] direction, consistent with a previous report.[118] The lattice parameter was obtained as $a = b = 4.3167(3) \text{ \AA}$, $c = 20.797(2) \text{ \AA}$, which is similar to the reported lattice parameter of the coevaporated CABI thin film ($a = b = 4.3206(8) \text{ \AA}$, $c = 20.888(8) \text{ \AA}$).[118] Interestingly, interfacing the CABI film with PTAA or PCBM charge transport layers enhances the contribution of the BiI_3 peaks, and the overlap of the BiI_3 peak with the (003) and (009) peaks of CABI leads to the latter apparently shifting to higher diffraction angles (see Figures C.7 and C.8). As expected, the Q/CABI/CuI half stack shows additional CuI peaks, marked as □, one of which dominantly overlaps with the CABI (012) peak, leading to its apparent shift to a higher diffraction angle compared to that in Q/CABI. Moreover, an additional peak related to an extra

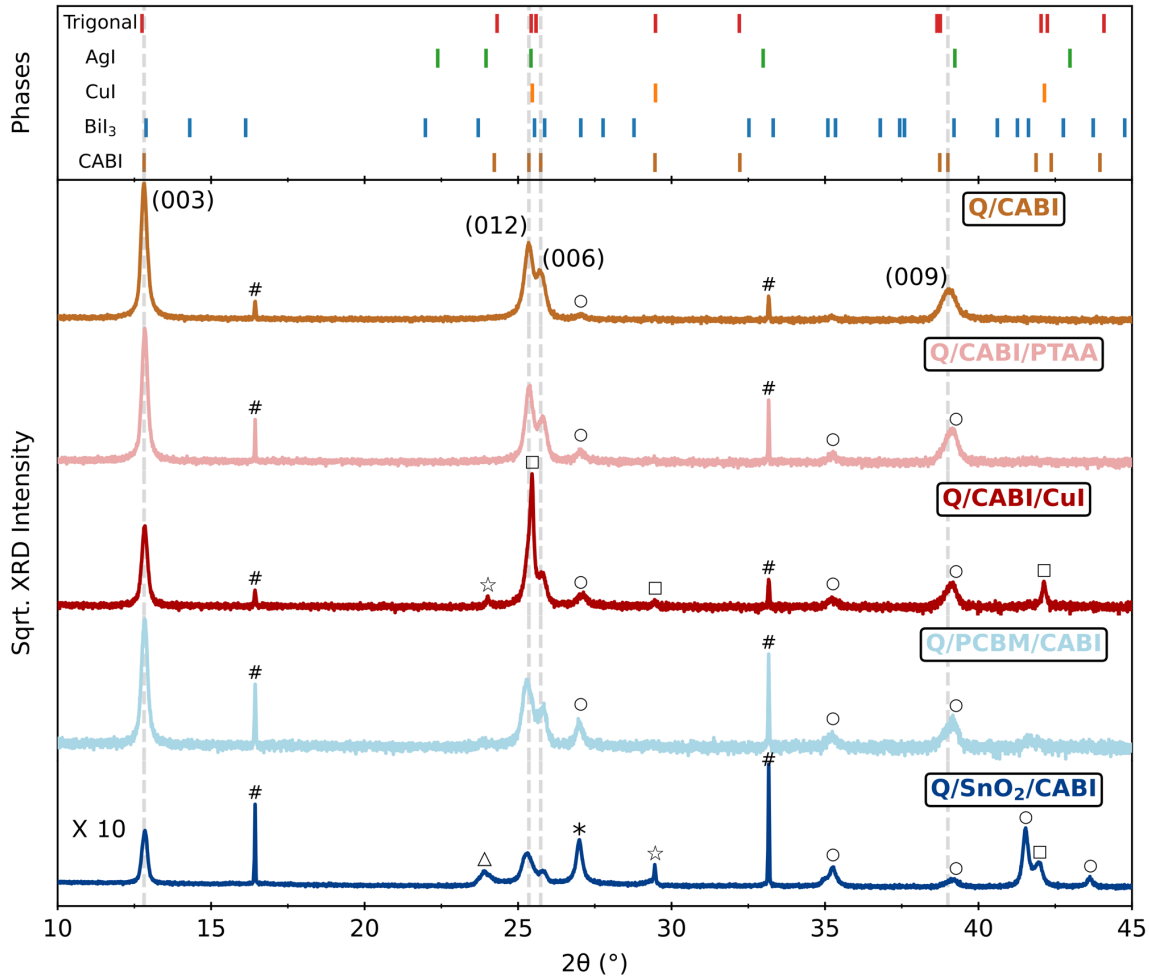


Figure 6.2: X-ray diffraction patterns (Cu $K\alpha_1$ radiation source) of CABI films deposited on a z-cut quartz substrate (Q/CABI) and those of CABI interfaced with HTLs (PTAA and CuI) or ETLs (PCBM and SnO_2). The XRD pattern of Q/ SnO_2 /CABI was measured over a ten times longer period to obtain a comparable signal-to-noise ratio. The vertical ticks above represent the XRD peaks belonging to the additional (unassigned) trigonal phase, binary phases, and trigonal CABI phase. The gray dashed vertical lines are guides to the angular positions of (003), (012), (006), and (009) XRD peaks of the CABI phase. The symbols #, *, O, □, △, ☆ indicate XRD peaks belonging to quartz (#), SnO_2 (*), BiI_3 (O), CuI (□), AgI (△), and additional ternary phases (☆) respectively.

trigonal phase ($R\bar{3}m$) compound is present (marked as ☆). As I discuss later, the assignment of the additional trigonal phase to a specific compound within the CuI–AgI– BiI_3 phase space remains ambiguous because several ternary and quaternary compounds within this phase space share the $R\bar{3}m$ space group and exhibit similar lattice parameters. The Q/ SnO_2 /CABI half stack exhibits surprisingly low XRD intensities (requiring ten times longer acquisition times to achieve a comparable signal-to-noise ratio), thus suggesting that CABI is less crystalline when deposited

on SnO_2 . Moreover, peaks belonging to the binary precursors BiI_3 , CuI , and AgI (marked as $\triangle$), and an additional trigonal phase are clearly observed. The observed XRD pattern suggests that the deposition of CABI on SnO_2 leads to the incomplete formation of CABI, leaving unreacted binary halide precursors in the film, and causing unintentional formation of other trigonal ternary and quaternary phases. Such poor film formation were reproduced and confirmed by undertaking several rounds of CABI deposition on SnO_2 (see Figure C.9) with similar results.

6.3.3 Comparisons of Compositions Across the CuI-AgI-BiI_3 Phase Space

Having identified the emergence of additional phases in nominal CABI films upon the presence of charge transport layers, I propose that the red shifts in the absorption onsets observed for the CABI half stacks (Figure 6.1f) derive from contributions to the absorption by these additional phases. To identify the phases responsible for this phenomenon with greater clarity, I have compiled literature information on the structure, optical bandgaps and charge-carrier mobilities at THz frequencies reported for the isolated binary, ternary and quaternary phases, as summarized in Table 6.2. First, I can rule out a direct influence of the AgI and CuI precursors on the lower-energy absorption onset of the half stacks because the bandgaps of AgI and CuI (2.86 and 3.1 eV respectively) are significantly higher than that of CABI. BiI_3 has an optical bandgap slightly lower than CABI (1.77 eV vs 1.89 eV from the direct Tauc method and 2.00 eV vs 2.06 eV from the Elliott fitting). In general, the binary precursors exhibit structural properties that are clearly distinct from those of CABI, and, apart from BiI_3 , these are not dominant in the measured XRD patterns of nominal CABI films, suggesting the slightly red-shifted bandgaps for Q/CABI/PTAA and Q/PCBM/CABI are likely caused by the contribution from BiI_3 . More challenging, on the other hand, is a distinction of the CABI phase from other ternary and quaternary phases based on the XRD patterns and bandgaps, because they all share similar structures and optical bandgaps. I note that most of the ternary and quaternary phases in the CuI-AgI-BiI_3 phase space share a trigonal unit cell with $R\bar{3}m$ space group and their XRD peaks

System	Compound	Unit cell	Space group	Lattice parameters (Å)	Direct bandgap (eV)		Indirect bandgap (eV)	Elliott bandgap (eV)	Infection bandgap (eV)	THz mobility (cm ² V ⁻¹ s ⁻¹)	
										$\phi\mu_{\text{rubic}}$	$\phi\mu_{\text{loc}}$
Binary	AgI	Hexagonal[204]	$P6_3mc$	$a/b = 4.59$, $c = 7.52$	2.86[81]	–	–	–	–	11[86]	–
Binary	BiI ₃	Trigonal[205]	$R\bar{3}$	$a/b = 7.52$ $c = 20.72$	N/A[86]	1.69[86]	2.00[86]	1.92[86]	1.4[86]	0.19[86]	–
Binary	CuI	Cubic[206]	$F\bar{4}3m$	$a/b/c = 6.1$	2.6[207], 3.0[208], 3.1[82]	N/A[82]	–	–	3.06 ~ 3.11[209]	16[118]	–
Ternary	AgBi ₂ I ₇	Cubic[85]	$Fd\bar{3}m$ (3D)	$a/b/c = 12.223$	1.87[85]	1.66[85]	2.09[86]	2.06[86]	0.49[86]	0.01[86]	–
Ternary	Ag ₂ Bi ₃ I ₁₁	Cubic[87]	$Fd\bar{3}m$ (3D)	$a/b/c = 12.1814$	1.81[87]	1.69[87]	–	–	–	–	–
Ternary	AgBiI ₄	Cubic[83]	$Fd\bar{3}m$ (3D)	$a/b/c = 12.108$	–	–	–	–	–	–	–
Ternary	AgBiI ₄	Trigonal[83]	$R\bar{3}m$ (3D)	$a/b = 4.319$ $c = 20.600$	1.73 ~ 1.80[83]	1.63 ~ 1.75[83]	2.11[86]	2.03[86]	0.46[86], 0.7[86]	0.02[86], 0.07[86]	–
Ternary	Ag ₂ BiI ₅	Trigonal[210]	$R\bar{3}m$ (3D)	$a/b = 4.350$ $c = 20.820$	1.85[88]	1.62[88]	2.11[86]	2.02[86]	0.49[86]	0.03[86]	–
Ternary	Ag ₃ BiI ₆	Trigonal[211]	$R\bar{3}m$ (3D)	$a/b = 4.5537$ $c = 20.810$	1.89[89]	1.83[89]	2.15[86]	1.99[86]	0.41[86]	0.02[86]	–
Ternary	CuBiI ₄	Cubic[90]	$Fd\bar{3}m$ (3D)	$a/b/c = 12.166$	–	–	–	–	–	–	–
Ternary	CuBiI ₄	Trigonal[80]	$R\bar{3}m$ (3D)	$a/b = 4.299$ $c = 21.060$	1.79,[90] 1.84,[91] 2.67[92]	–	–	–	–	–	–
Ternary	Cu ₂ BiI ₅	Trigonal[212]	$R\bar{3}m$ (3D)	$a/b = 4.42$ $c = 20.82$	1.53 ~ 1.74[212]	–	–	–	–	–	–
Quaternary	Cu _{0.4} AgBiI _{4.4}	Trigonal[97]	$R\bar{3}m$ (3D)	$a/b = 4.553$ $c = 20.791$	–	N/A[97]	2.05[97]	–	0.6 ~ 1.3[97]	0.06 ~ 0.32[97]	–
Quaternary	Cu _{0.8} AgBiI ₅	Trigonal[80]	$R\bar{3}m$ (3D)	$a/b = 8.634$ $c = 21.140$	1.94[95]	N/A[95]	2.06[97]	2.02[80]	0.9 ~ 1.6[97]	0.13 ~ 0.84[97]	–
Quaternary	Cu _{0.2} AgBiI ₆	Trigonal[83]	$R\bar{3}m$ (2D)	$a/b = 4.274$ $c = 20.940$	1.89[95]	N/A[23]	2.03,[97] 2.06,[76] 2.13[118]	–	2.0,[118] 3.3 ~ 4.6[97]	1.5,[118] 0.99 ~ 1.73[97]	–
Quaternary	Cu _{0.6} AgBiI ₁₀	Trigonal[97]	$R\bar{3}m$ (3D)	$a/b = 4.307$ $c = 21.171$	1.72[213]	N/A[97]	2.11[97]	–	7.41 ~ 9.77[97]	1.09 ~ 2.40[97]	–

Table 6.2: Summary of structural information, bandgaps, and THz electron–hole sum mobilities of commonly studied compounds in the Cu–Ag–Bi–I phase space. $\phi\mu_{\text{deloc}}$ and $\phi\mu_{\text{loc}}$ denote THz mobilities of delocalized charge carriers upon initial excitation and localized charge carriers formed on a picosecond time scale. N/A represents not application and – indicates that values have not yet been reported. For the quaternary phases, THz mobilities obtained from photoexcitation with energies below 3 eV are listed to rule out contributions from CuI or AgI-rich domains.[118, 203]

could therefore overlap within the line width. Similarly, Table 6.2 shows that the bandgaps of the ternary and quaternary phases fall into a similar range just below the CABI absorption onset. However, determining bandgaps with a variety of methods introduces inconsistencies, obfuscating their net contribution to the observed onset. For example, the bandgap of AgBiI_4 obtained from the direct Tauc method (1.73 eV) is lower than that of CABI (1.89 eV). However, the bandgap obtained from the Elliott fitting is larger for AgBiI_4 (2.11 eV) than for CABI (2.06 eV). This discrepancy complicates the efforts to identify and quantify the extent to which impurity phases affect the optoelectronic properties of CABI.

Interestingly, the literature values listed in Table 6.2 suggest that the charge-carrier mobilities (measured by THz spectroscopy) of ternary compounds and other quaternary phases differ significantly from that of CABI. Crucially, THz mobility is measured on ultrafast time scales and reflects local length-scales, thus making these measurement less sensitive to any presence of long-range grain boundaries. Therefore, I find that THz mobilities are a valuable metric for distinguishing and cross-referencing between different phases present in nominal CABI films. For example, the trigonal Ag–Bi–I ternary phases exhibit THz mobilities that are at least four times lower than those of CABI (≈ 0.5 vs $\approx 2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). Although the THz mobilities of CuBiI_4 and Cu_2BiI_5 have not been measured yet, the reported Hall mobility of $110 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for CuBiI_4 suggests that its THz mobilities may also be significantly higher than that of CABI.[92] As recently demonstrated by Buizza et al., THz mobilities of the quaternary phases $\text{Cu}_{4x}(\text{AgBi})_{1-x}\text{I}_4$ increase with increasing Cu content.[97] This trend has been attributed to the substantial contributions from the enhanced curvature of the valence band maximum of the Cu-d electronic states.[23] As a result, a significant difference in the THz charge-carrier mobilities facilitates the distinction of the lower Cu-content $\text{Cu}_{0.4}\text{AgBiI}_{4.4}$ and the higher Cu-content $\text{Cu}_6\text{AgBiI}_{10}$ from CABI. CuAgBiI_5 has similar bandgap and THz charge-carrier mobility to those of CABI, but it can be distinguished from the XRD patterns since it has significantly different lattice parameters associated with a large trigonal unit cell.[80] Overall, the identification of the

CABI phase can therefore be accomplished with greater confidence when supported by THz mobility measurements as an additional metric.

6.3.4 Impact of Charge-Transport Layers on the Optoelectronic Properties of $\text{Cu}_2\text{AgBiI}_6$

Having established that the THz mobilities offer useful complementary information about different phases within the CuI-AgI-BiI_3 phase space, I extract the THz mobilities of charge carriers within the nominal CABI films in our half stacks from fluence-dependent OPTP measurements. OPTP measures the differential change in the transmitted THz electric field amplitude before and after photoexcitation ($-\Delta T/T$), which is proportional to the transient photoconductivity of the material, with subpicosecond temporal resolution (see Section 3.3 for the further details). I note that the half stacks were excited at a wavelength of 530 nm (2.34 eV photon energy) in order to selectively excite the CABI solar absorber layer[82, 105, 118] rather than the HTLs or ETLs. The photoconductivity transients of CABI on quartz (Figure 6.3a) exhibit a fluence-independent ultrafast decay within a couple of picoseconds, followed by a slower, long-lived fluence-dependent decay (see Figures C.10–C.13 for OPTP transients for all half stacks). To describe such dynamics, the early time photoconductivity transients from -2 to 10 ps were fitted with a two-level mobility model previously employed to describe the ultrafast localization processes in $\text{Cs}_2\text{AgBiBr}_6$, $\text{Cu}_{4x}(\text{AgBi})_{1-x}\text{I}_4$, $(\text{AgI})_x(\text{BiI}_3)_y$ and other silver-bismuth based materials.[86, 96, 97, 214] As indicated by the schematic in Figure 6.3b, this model assumes that charge carriers are initially photoexcited forming a delocalized, large-polaron state with mobility μ_{deloc} and population n_{deloc} . Within about a picosecond after photoexcitation, however, charge carriers localize into a small-polaron state with reduced mobility μ_{loc} and population n_{loc} with localization rate given by k_{loc} . Lastly, the localized electrons and holes recombine back to the ground state with the recombination rate k_{R} . By solving the coupled ordinary differential equations governing the two states and globally fitting solutions to the fluence-dependent OPTP transients, the mobilities associated with each state can

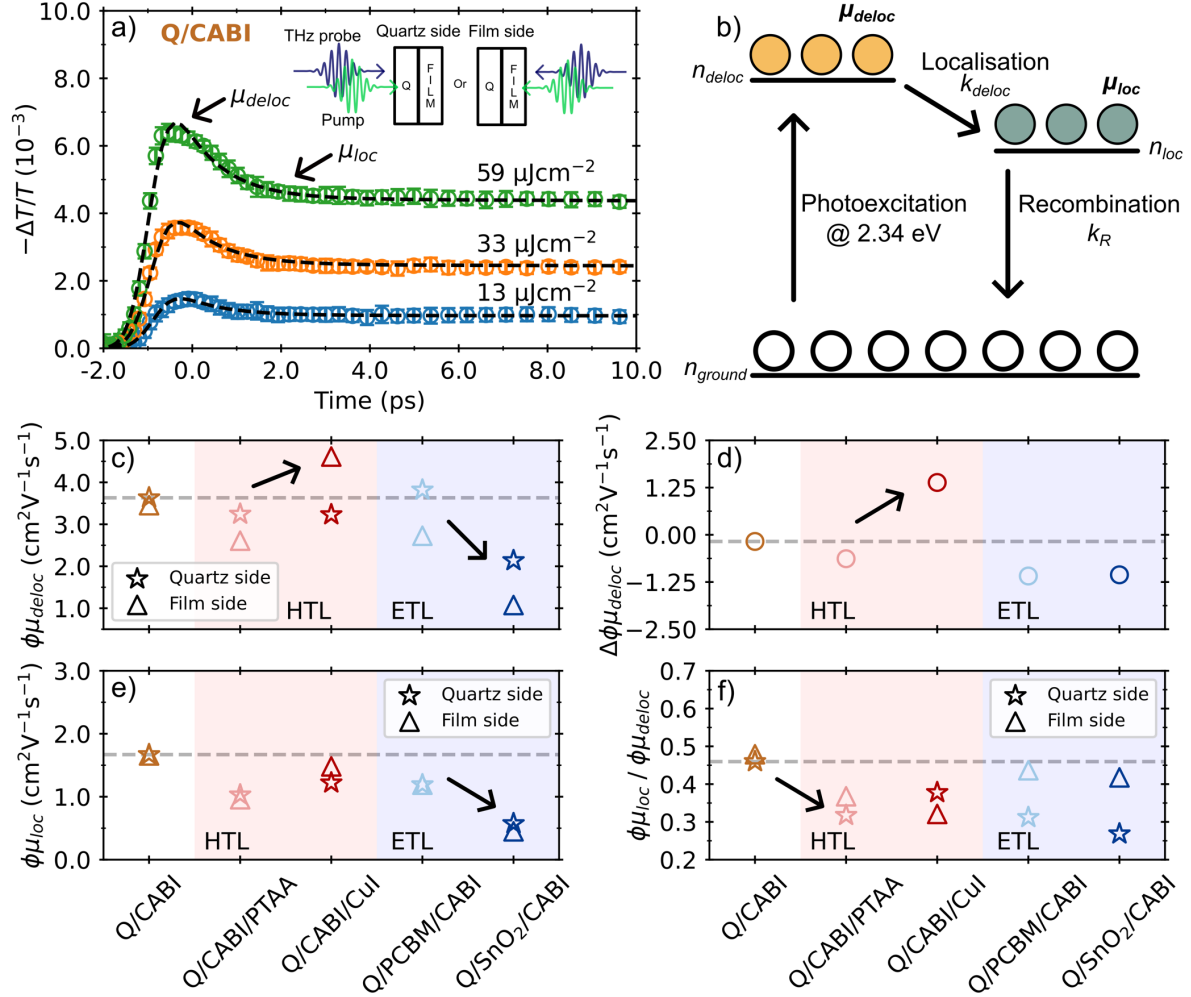


Figure 6.3: (a) OPTP photoconductivity transient of quartz(Q)/CABI excited from the quartz-substrate side with the three excitation fluences of 13, 33, and 59 μJcm^{-2} . The black dashed lines show the best fits of the two-level mobility model. The inset shows the two different excitation conditions, i.e. either from the side of the quartz substrate (left, “Quartz side”) or from the side containing the CABI and potentially ETL or HTL films (right, “Film side”). (b) Schematic diagram illustrating the two-level mobility model. (c) Effective delocalized electron-hole sum mobilities ($\phi\mu_{\text{deloc}}$) at THz frequencies determined following quartz-side and film-side illuminations. (d) Difference between the delocalized mobility values determined for film-side and quartz-side illumination ($\Delta\phi\mu_{\text{deloc}} = \phi\mu_{\text{deloc}}@ \text{film side} - \phi\mu_{\text{deloc}} @ \text{quartz side}$). (e) Effective localized electron-hole sum mobilities ($\phi\mu_{\text{loc}}$) at THz frequencies, determined following quartz-side and film-side illumination. (f) Ratio of localized THz mobilities to delocalized THz mobilities ($R = \mu_{\text{loc}}/\mu_{\text{deloc}}$). For (c)-(f), values for CABI thin films coated with HTLs are colored with a light red background and those deposited on ETLs are colored with a light blue background. The gray dashed horizontal lines are guides to the eye allowing comparison of mobilities with the value for Q/CABI. The error bars are contained within the extent of the data markers and reported in Table 6.3

Sample	Illumination side	$\phi\mu_{\text{deloc}}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	$\phi\mu_{\text{loc}}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	k_{loc} (10^{12}s^{-1})	k_{nonrad} (10^8s^{-1})	R_{eh} ($10^{-11}\text{cm}^3\text{s}^{-1}$)
Q/CABI	Film	3.46(3)	1.655(4)	1.06(3)	7.6(5)	2.12(7)
	Quartz	3.63(7)	1.669(7)	1.31(6)	8.4(3)	2.46(8)
Q/CABI/PTAA	Film	2.61(4)	0.960(4)	1.28(4)	6.9(5)	3.3(1)
	Quartz	3.24(8)	1.029(5)	1.77(8)	16.2(6)	3.5(1)
Q/CABI/CuI	Film	4.61(5)	1.481(5)	1.20(2)	9.9(4)	3.89(8)
	Quartz	3.23(5)	1.220(5)	1.35(5)	7.6(4)	2.55(4)
Q/PCBM/CABI	Film	2.73(7)	1.191(7)	1.21(7)	1.0(3)	3.28(9)
	Quartz	3.8(2)	1.190(7)	2.2(2)	7.3(4)	4.4(1)
Q/SnO ₂ /CABI	Film	1.08(2)	0.450(3)	1.18(6)	0.0(8)	1.17(7)
	Quartz	2.14(8)	0.573(5)	1.7(1)	0.9(6)	3.54(8)

Table 6.3: THz mobilities and recombination rate constants obtained from the localization and rate equation model (see Section 3.3.2.3 and 3.3.2.2 respectively) for the Cu₂AgBiI₆ thin film deposited on a quartz substrate and those interfaced with charge transport layers excited either from the film or quartz side. The total recombination rate k_{R} is calculated as $k_{\text{nonrad}} + R_{\text{eh}}n_{\text{loc}}$.

be independently calculated. A detailed mathematical description of the model can be found in Section 3.3.2.3. To improve the accuracy of extracted parameters governing the early dynamics, k_{R} is fixed to the values obtained from the conventional model describing trap-mediated k_{nonrad} and radiative recombination R_{eh} (see Section 3.3.2.2 for the further details), fitted to the long decay after 10 ps across the range of excitation fluences and their values are reported in Table 6.3 (see Figure C.12 and C.13 for the fits). As shown in Figure 6.3a, the excellent agreement of the best fit (black dashed lines) with the experimentally determined photoconductivity suggests that the two-level mobility model describes the charge-carrier dynamics of CABI well.

THz mobilities at the CABI/charge transport layer interface can be selectively probed by side-dependent illumination, either from the quartz substrate side or from the side of the deposited films. Because the penetration depth at the 2.34 eV excitation energy is very short (≈ 80 nm compared to the ≈ 250 nm thickness of CABI), such side-selective excitation thus enables the determination of charge-carrier mobilities in CABI either far from or close to the buried interface, and deduction of possible compositional and morphological variations along the depth profile.

The extracted THz mobility of delocalized charge carriers ($\phi\mu_{\text{deloc}}$), obtained from the initial THz photoconductivity ($-\Delta T/T = 0$ ps), of Q/CABI is $\approx 3.5\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is in a good

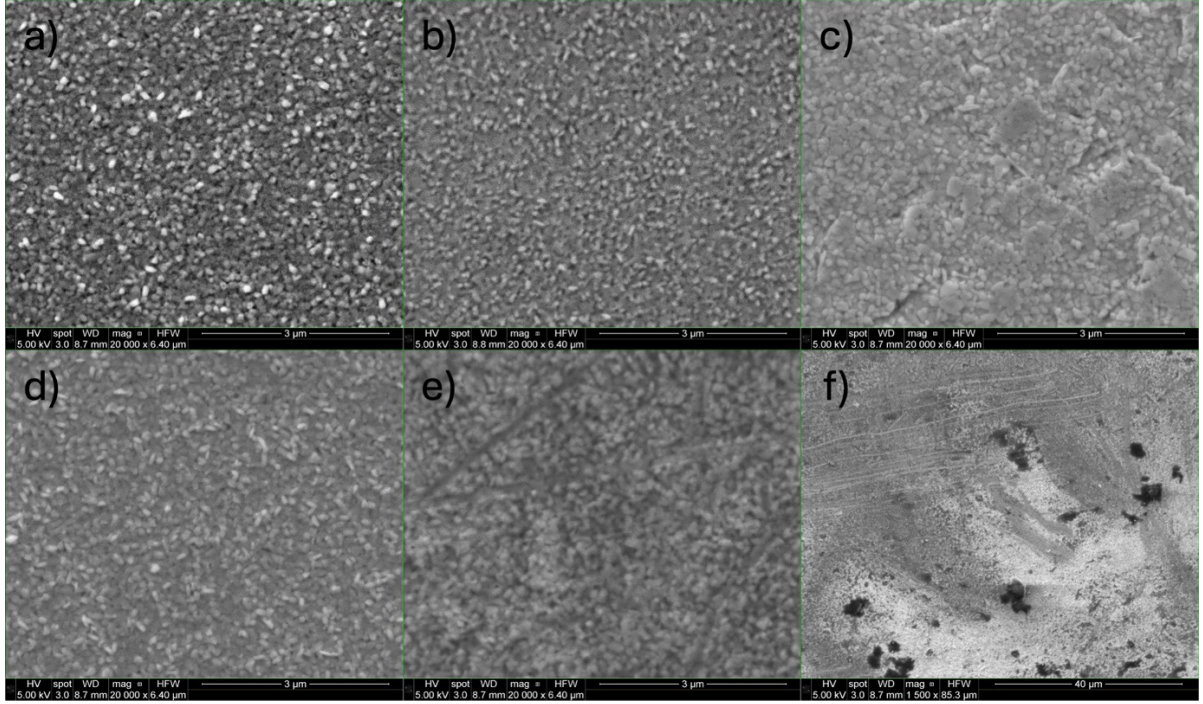


Figure 6.4: Top-view SEM images of (a) Q/CABI, (b) Q/CABI/PTAA, (c) Q/CABI/CuI, (d) Q/PCBM/CABI, (e) Q/SnO₂/CABI, and (f) Q/SnO₂/CABI with lower magnification

agreement with the literature value in Table 6.2. While THz mobilities probe local lengths scales and are therefore dominantly affected by intrinsic effects such as electron-phonon interactions, they may also be influenced by extrinsic factors such as extended disorder, poor morphology and crystallinity caused by the impurity phases.[14] For Q/CABI, I observe similar $\phi\mu_{\text{deloc}}$ values following quartz-side and film-side illumination, which suggests that the composition, crystallinity and morphology of CABI near both interfaces are similar.

For the half stacks, on the other hand, Figure 6.3c reveals significant differences between quartz-side and film-side excitation, arising from differences in CABI film quality near the interface with the HTL or ETL. For Q/CABI/PTAA, Q/PCBM/CABI, and Q/CABI/CuI, illumination from the quartz side reveals delocalized charge-carrier mobilities that are comparable to or slightly lower than that of Q/CABI, suggesting that the impact of the minor BiI₃, CuI, and trigonal impurity phases identified from the XRD patterns is minor on the quartz side. However, for illumination from the film side, Q/CABI/PTAA and Q/PCBM/CABI exhibit $\phi\mu_{\text{deloc}}$ values that are noticeably lower than that of Q/CABI. This trend correlates well with the enhanced

BiI₃ impurity peaks present in XRD patterns and the red-shifted absorption onsets, while changes in the morphologies are not apparent from the scanning electron microscopy (SEM) images as shown in Figure 6.4 (Measured by Siyu Yan, Department of Physics, University of Oxford). I postulate that BiI₃ impurities located near the top interface of CABI decrease the value of $\phi\mu_{\text{deloc}}$ because they may act as scattering sites with enhanced disorder and defects. For Q/CABI/CuI on the other hand, a higher value of $\phi\mu_{\text{deloc}}$ is recorded, in particular for excitation from the “film side” which leads to generation of charge carriers near the CABI/CuI interface, indicating that the deposition of CuI significantly influences the optoelectronic properties near this interface. Although the observed increase in the delocalized mobility may be attributed to passivation effects leading to improved interfacial quality, distinct changes in the XRD pattern of Q/CABI/CuI and non-uniform surface observed from SEM suggest that the composition of CABI is altered upon the deposition of CuI. By considering the XRD patterns and the observed bandgap redshift, which are compatible with trigonal Cu₆AgBiI₁₀, [213] I propose that the observed increase in $\phi\mu_{\text{deloc}}$ arises from the formation of a Cu-rich Cu_{4x}(AgBi)_{1-x}I₄ phase near the CABI/CuI interface, which is known to exhibit comparatively higher mobilities (see Table 6.2). The effect of CuI is further highlighted in Figure 6.3d where the difference in $\phi\mu_{\text{deloc}}$ extracted from film-side and quartz-side measurements ($\Delta\phi\mu_{\text{deloc}}$) is presented. I find that this difference only has a positive value for the Q/CABI/CuI half stack, suggesting that deposition of CuI can be an effective optimization strategy to increase charge-carrier mobility at the expense of modifying the stoichiometry of CABI near such interfaces. Finally, for Q/SnO₂/CABI half stacks I observe $\Delta\phi\mu_{\text{deloc}}$ values significantly lower than those for Q/CABI, most likely linked with the presence of binary and additional ternary phases in CABI evaporated on SnO₂, as evidenced from XRD. While the wide-bandgap binary phases (AgI and CuI) cannot be excited by the excitation pulses employed here, the observed poor mobility values can in principle originate from BiI₃, other low-mobility trigonal phases, or poor film morphology. Overall, these results strongly suggest that the presence of an SnO₂ layer induces an incomplete reaction of the precursors which

severely lowers the charge-carrier mobility associated with the CABI layer in the Q/ SnO_2 /CABI half stacks. The SEM image recorded for this half stack further confirms the poor morphology of the CABI layers evaporated on SnO_2 , showing discontinued and incomplete grains over a long range. Similar to the case of Q/PCBM/CABI, the excitation-side dependence of the extracted mobility value (Figure 6.3c) suggests that the growth of CABI films on SnO_2 particularly favours the formation of impurity phases at the top interface. Therefore, such imperfect morphology of CABI on SnO_2 appears not to dissipate with increasing film evolution and growth.

Finally, I observe that charge-carrier mobilities determined for small polarons formed after the initial localization step ($\phi\mu_{\text{loc}}$, obtained from the THz photoconductivity after ≈ 2 ps), generally follow a similar trend to that discussed above for the initial large-polaron mobilities as shown in Figure 6.3e. Therefore, the changes in composition, morphology and crystallinity clearly affect the delocalized state as well as the localized state that dominates during charge-carrier diffusion and extraction.

Interestingly, the difference in the values of $\phi\mu_{\text{loc}}$ determined for quartz-side and film-side illuminations is not as pronounced as it is for the $\phi\mu_{\text{deloc}}$. This effect is unlikely to derive from electron- or hole-transfer from CABI to ETL or HTL layers because the low recorded mobilities prevent significant charge-carrier diffusion to the interface within the first few picoseconds. I note that in principle, small-polaron transport is more susceptible to disorder owing to its thermally activated nature.[215] However, the observed mobility values arise from an ensemble of phases (i.e., CABI and additional binary/ternary phases), some of which are not being photoexcited (e.g., binary AgI, CuI) and others exhibiting higher degree of localization, thus making contributions difficult to disentangle. To quantify such effect, the ratio of $\phi\mu_{\text{loc}}$ and $\phi\mu_{\text{deloc}}$ ($R = \mu_{\text{loc}}/\mu_{\text{deloc}}$) provides a measure of the overall impact of localization on the mobility retention considering the effect of the impurity phases. For example, the case of $R = 1$ denotes full retention of the initial large-polaron mobility, while $R = 0$ represents full mobility loss ($\phi\mu_{\text{loc}} = 0$) after the first few picoseconds. As presented in Figure 6.3f, CABI on quartz shows $R \approx 0.48$, i.e. it retains about

half of its mobility after localization. However, when CABI is interfaced with charge transport layers, significantly less mobility is retained after localization, i.e. lower R values are observed (Figure 6.3f). Such effects may derive from the presence of impurity phases which have been reported to exhibit greater degree of localization (lower R values), such as BiI_3 ($R \approx 0.13$), $(\text{AgI})_x(\text{BiI}_3)_y$ ($R \approx 0.06$), and Cu-rich $\text{Cu}_6\text{AgBiI}_{10}$ ($R \approx 0.14$).^[86] As a result, $\phi\mu_{\text{loc}}$ values are lower for all half stacks compared to Q/CABI. Such reduction in mobility retention is particularly detrimental for photovoltaic device performance, given that the charge-carrier mobility $\phi\mu_{\text{loc}}$ recorded after the picosecond localization process ultimately determines the charge-carrier diffusion length for a given charge-carrier lifetime, and therefore the feasibility of extraction.

Overall, based on multiple complementary experimental approaches, I reveal that coevaporation of CABI onto an inorganic electron transport layer (i.e., SnO_2) is far more challenging, leading to degraded optoelectronic and transport properties, compared to deposition on organic electron transport layers (i.e., PCBM). Similar challenges have been observed in the more advanced field of coevaporated lead halide perovskites. Patel et al. have observed the formation of amorphous MAPbI_3 following evaporating on compact TiO_2 caused by a lattice mismatch at the interface, leading to poor charge collection efficiency and extensive charge recombination, while high-quality crystalline MAPbI_3 films were formed with PCBM.^[216] In a similar way, CABI growth may be impeded on inorganic transport layers owing to the lattice mismatch between tetragonal SnO_2 and trigonal CABI.^[23, 217] This mismatch likely promotes island growth and therefore facilitates nonuniform grain growth, ultimately leading to incomplete precursor reaction.^[218] In addition, the large CuI–AgI– BiI_3 phase space available makes quaternary CABI more prone than ternary MAPbI_3 to the formation of unwanted secondary phases. Similarly, the deposition of hole transport layers (i.e., PTAA and CuI) onto CABI induces the formation of impurity phases such as BiI_3 and Cu-rich $\text{Cu}_{4x}(\text{AgBi})_{1-x}\text{I}_4$ phases, which somewhat impedes transport in CABI, though this effect seems to be less severe. Crucially, these observations may explain the origin of the poor charge extraction and low reproducibility

reported for solar cells incorporating coevaporated CABI absorber layers.[118] Therefore, these results highlight the urgent need for the development of advanced interface engineering approaches enabling optimized CABI crystal growth on inorganic surfaces and facilitating the deposition of hole transport layers without disrupting CABI. For instance, Yan et al. have recently addressed analogous issues for coevaporated $\text{FA}_{0.9}\text{Cs}_{0.1}\text{PbI}_{3-x}\text{Cl}_x$ growth by introducing an ultrathin templating layer at the charge transport layer/perovskite interface prior to the deposition of the active layer.[219] Furthermore, the optimization of solvents for spin-coated charge transport layers[220, 221] and deposition of thin buffer layers[222, 223] may help to prevent the interaction of charge transport layers with CABI.

6.4 Conclusions

In conclusion, I have systematically identified the compositional, structural and morphological changes that occur when CABI is interfaced with charge transport layers and have investigated the resulting impact on its optoelectronic properties. The presence of charge transport layers is found to induce the unintentional formation of impurities within the CuI-AgI-BiI_3 phase space, which in turn significantly affect the overall optoelectronic properties of CABI layers within such half stacks. Organic transport layers such as PTAA and PCBM induce minor BiI_3 impurity phases, leading to small red shifts in the absorption edge and reduction in the THz electron-hole mobilities. On the other hand, deposition of CuI leads to the formation of a Cu-rich $\text{Cu}_{4x}(\text{AgBi})_{1-x}\text{I}_4$ phase near the CABI/CuI interface, associated with an increase in the initial THz mobility, which is however not sustained after picosecond charge-carrier localization. Additionally, controlling the CABI phase at an interface with CuI may be challenging, opening the door to decreased reproducibility. The deposition of CABI on SnO_2 , on the other hand, is associated with an incomplete reaction of the binary phase precursors and formation of other trigonal phases within the CuI-AgI-BiI_3 phase space, causing a significant decrease in the THz mobility. This finding may thus explain the previously reported poor reproducibility and

low charge collection efficiency of photovoltaic n–i–p devices based on CABI coevaporated on SnO_2 as the electron transport layer.[118] Borrowing wisdom from the extensive field of lead halide perovskites, I predict that such inorganic interfaces can however be improved with the development of tailored interface engineering approaches, unleashing the full potential of CABI-based solar cells. Overall, the results highlight phase control at the charge–extraction interface as a crucial area for the development of CABI solar absorbers.

7

Conclusion and Outlook

This thesis has examined the underlying loss mechanisms at the interfaces between metal-halide semiconductors and charge-transport layers, with particular emphasis on the loss mechanisms that limit the performance of wide-bandgap metal-halide perovskite solar cells and emerging lead-free absorbers. Combining various spectroscopic techniques and numerical modelling, the studies presented here provide a comprehensive understanding of how interfacial energetics, compositional instability, and structural incompatibilities influence device performances.

In Chapter 4, the impact of energy-level misalignment at the perovskite/HTL interface was systematically investigated by using $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ interfaced with PTAA. Increasing bromide content x deepens the VBM of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ with respect to the vacuum level and this increases the band offset gradually with respect to the HOMO of PTAA. Time-resolved photoluminescence combined with numerical modelling revealed that greater energy-level misalignment drives hole accumulation in PTAA, which subsequently recombines non-radiatively with electrons in the CBM of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ via defect-mediated across-interfacial recombination. Such non-radiative losses lead to a substantial reduction in V_{OC} of up to 70 meV. Using the relationship between PLQY and V_{OC} based on the detailed balance theory, numerical simulations revealed that having well-matched band offset between

FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)₃/HTL leads to V_{OC} improvement by 41 and 70 mV for 1.7 and 2 eV perovskites respectively. These findings establish energy-level misalignment as a key origin of voltage and efficiency losses in wide-bandgap perovskite solar cells and underscore the importance of rational band-level engineering of charge-transport materials.

Wide-bandgap mixed-halide perovskites are prone to halide segregation under prolonged illumination, during which an initially homogeneous mixed-phase domain separates into distinct iodide-rich and bromide-rich domains. Chapter 5 examined the impact of halide segregation on interfacial charge transfer in FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃ when interfaced with the commonly used HTL PTAA and ETL SnO₂. Synchronous multimodal spectroscopy combining TRPL, TRMC and ssPL provides a powerful approach to probe charge-carrier dynamics while concurrently monitoring the extent of halide segregation. The ratio between TRPL and squared TRMC transients provides insight into the temporal evolution of charge-selective processes arising from carrier extraction at charge-transport layer interfaces. Halide segregation accelerated the charge-carrier recombination owing to the enhanced radiative bimolecular recombination driven by increase in charge-carrier density in the I-rich phase upon carrier funnelling, as evidenced by the increase in the intensity of the red-shifted ssPL. Surprisingly, carrier confinement in the I-rich phase preserves most of the initial mobility in the case of neat perovskites (81%), whereas further reductions were observed when charge transport layers are present (50 – 72%). The combination of shortened lifetime and reduction in mobility decreased the carrier diffusion length and compromised charge-collection efficiency. Together, these findings elucidate the underlying mechanisms through which halide segregation contributes to long-term instability in device performance.

As a potential alternative to address the lead toxicity and instability of lead-halide perovskites, chapter 6 explored the lead-free all-inorganic absorber Cu₂AgBiI₆ (CABI). However, the solar cells based on CABI currently suffers from sub-optimal device performance compared to its lead-halide perovskite counterparts. Optoelectronic and structural characterisation of coevaporated

CABI films interfaced with common CTLs revealed that inorganic layers such as CuI and SnO₂ promote the formation of unintended impurity phases within the CuI–AgI–BiI₃ phase space. Identifying impurity phases within the CuI–AgI–BiI₃ phase space is particularly challenging because of their structural and optoelectronic similarity to CABI. Through the combined application of absorption spectroscopy, XRD, and OTP, these phases were successfully distinguished, enabling clearer insight into their impact on device performance. These impurity phases degraded crystallinity, morphology, mobility, and ultimately compromised the charge-collection efficiency. These findings highlight the importance of optimising coevaporation on inorganic charge-transport layers to achieve higher efficiencies.

Taken together, these studies demonstrate that the interfacial losses ranging from energy-level misalignment and defect-mediated recombination to segregation-driven instabilities and CTL-induced impurity formation are central to the efficiency limitations of solar-cell devices based on both wide-bandgap mixed-halide perovskites and CABI. Addressing these challenges will require holistic strategies that integrate band-level engineering, defect passivation, stabilisation against segregation, and improved deposition protocols for phase-pure films on transport layers. Looking ahead, several promising directions emerge: the rational selection and molecular design of charge-transport materials with tailored energy levels to mitigate misalignment losses and enhance voltage output; compositional and microstructural engineering to suppress halide segregation and secure long-term tandem stability; and, for lead-free absorbers such as CABI, refined coevaporation methods, interface passivation strategies, and alternative CTLs to unlock their potential as sustainable alternatives. By elucidating the fundamental photophysical pathways that govern interfacial losses, this thesis contributes to advancing metal-halide semiconductors toward their theoretical efficiency limits and accelerating their commercialisation in sustainable photovoltaic technologies.

Appendices



Supplementary Analysis for Chapter 4

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A.1 XRD Data

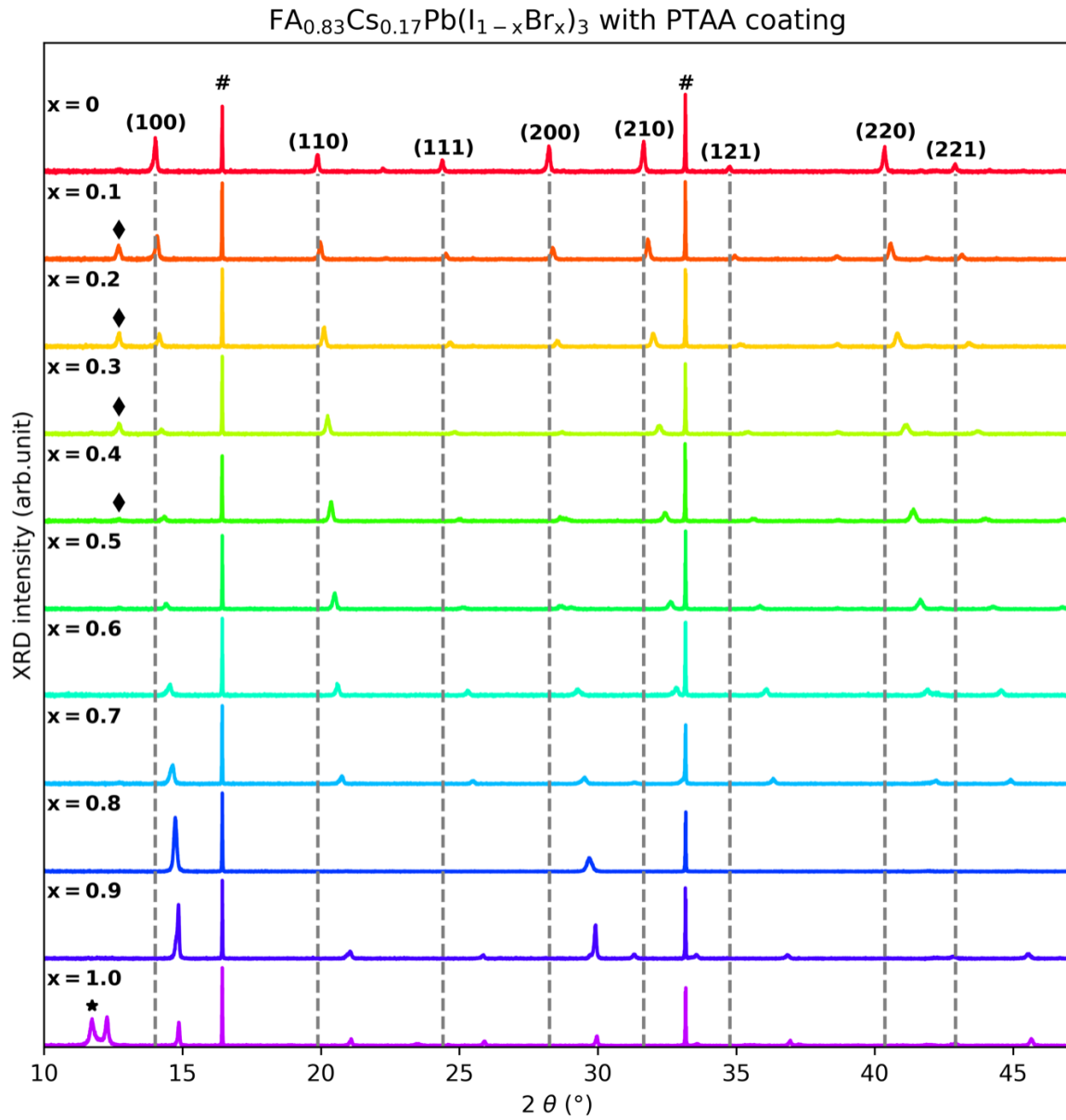


Figure A.1: XRD spectra of the PTAA-coated perovskites with increasing Br content, x . Relevant pseudo-cubic $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ XRD peaks are labelled with the Miller indices, and they are identical with literature values.[137] The z-cut quartz reference peaks at $2\theta = 16.433^\circ$ and 33.172° are labelled as #.[99] The PbI_2 peak at $2\theta = 12.703^\circ$ is labelled as ◆.[99] The CsPb_2Br_5 peak at $2\theta = 11.801^\circ$ is labelled as ★.[144] The grey dotted lines are drawn to visually assist XRD peak shifts to higher 2θ with increasing x .

A.2 Absorption Data

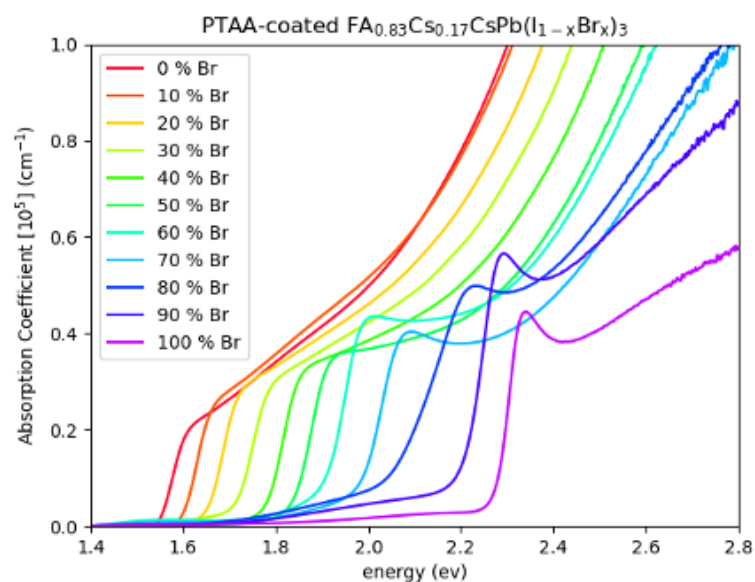


Figure A.2: Absorption coefficient spectra of the PTAA-coated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskites with increasing Br^- content from $x = 0$ (red) to $x = 1$ (purple).

A.3 Steady-state PL Data

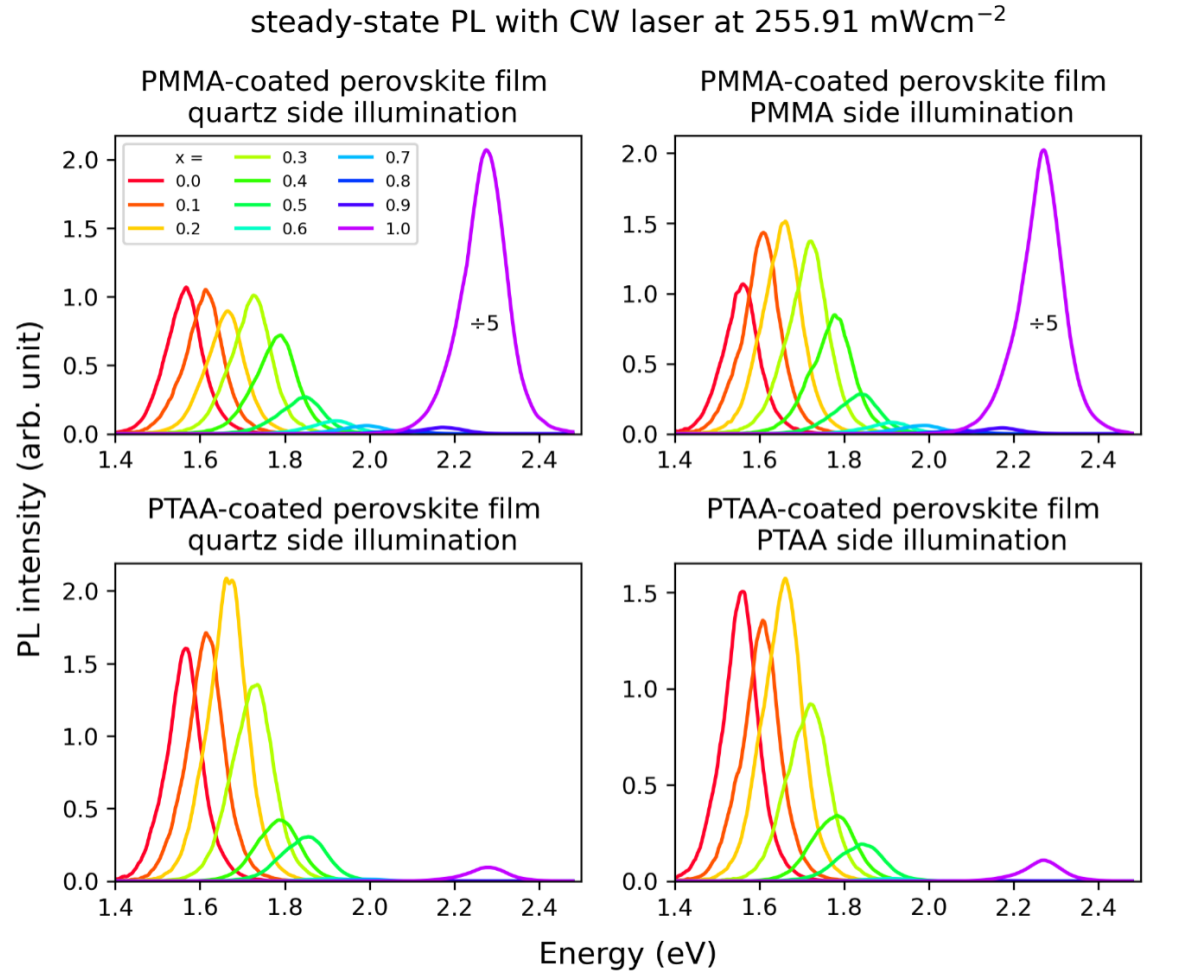


Figure A.3: Steady-state photoluminescence spectra of the PMMA- or PTAA-coated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskite films with the continuous-wave 470 nm diode laser at a power density of 255.91 mWcm^{-2} illuminated from either quartz or PMMA/PTAA side. The PL intensity of the $x = 1$ PMMA-coated perovskites were divided by 5 for comparison. x represents the Br content in perovskite.

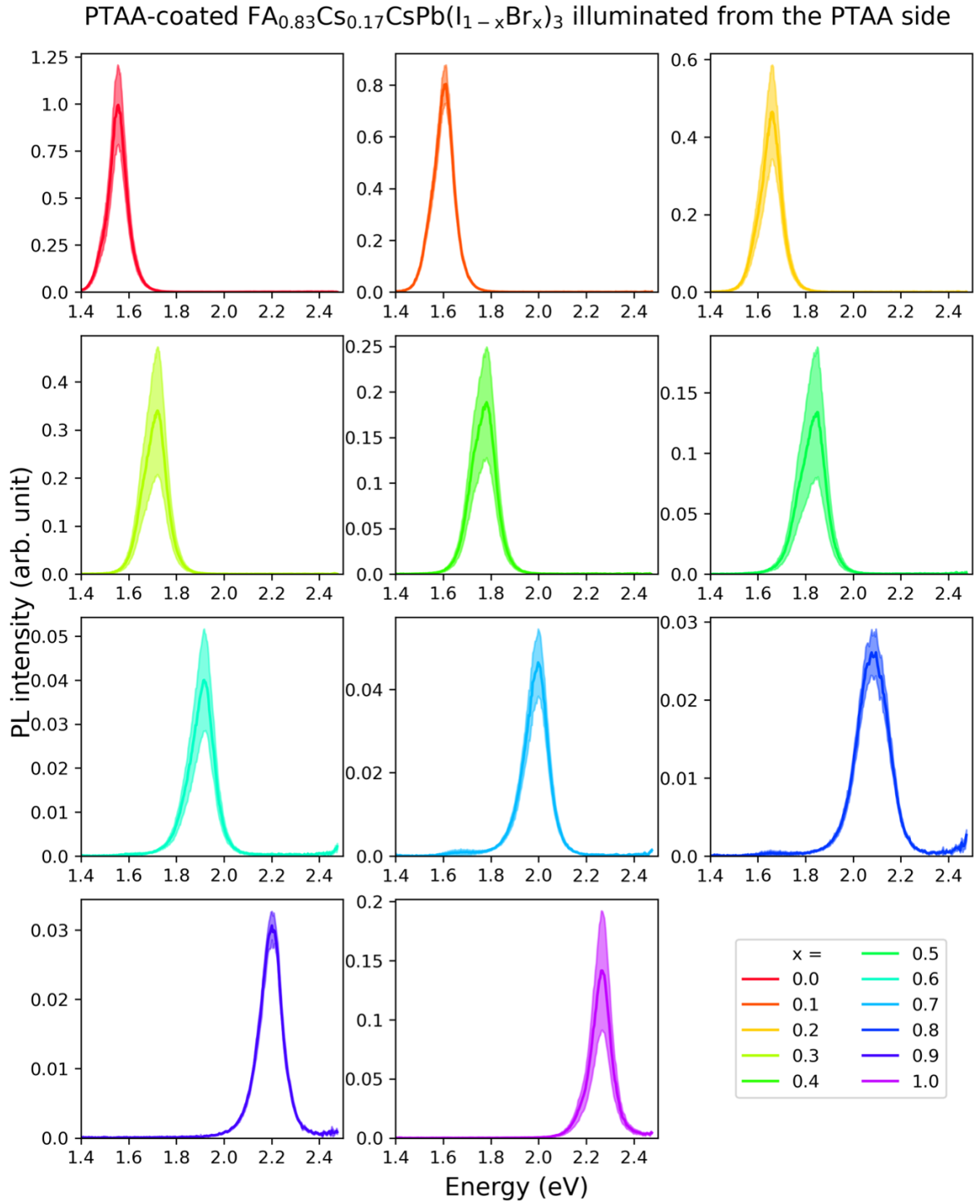


Figure A.4: Averaged steady-state photoluminescence of 3 different spots in the PTAA-coated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskite films illuminated at a fluence of 76.22 nJcm^{-2} from the PTAA side before and after each 1-minute transient PL acquisition. The shaded regions represent the standard deviation of the mean.

A.4 OPTP Data

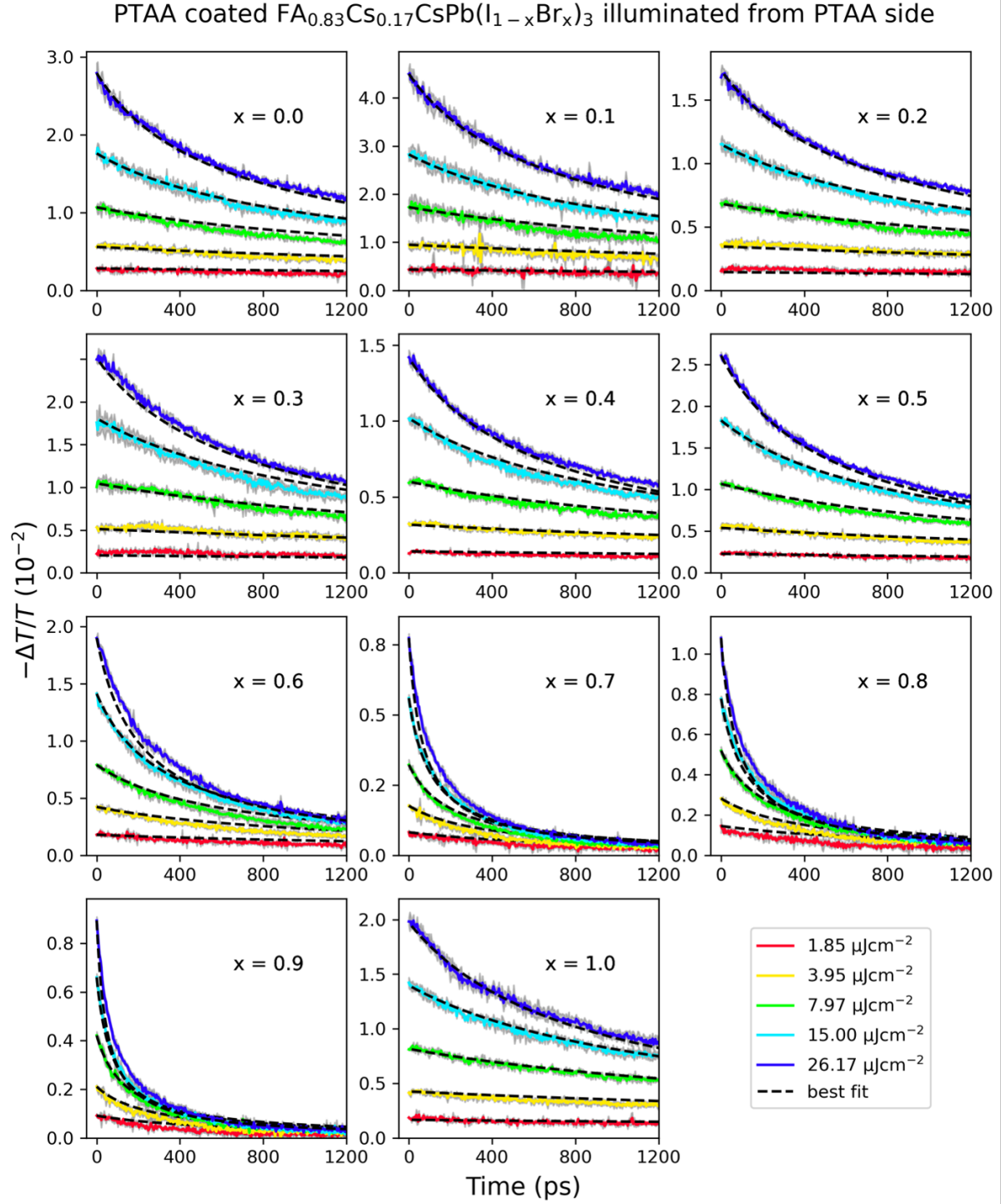


Figure A.5: Global fit of OPTP transients across five different excitation fluences recorded for the PTAA-coated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskite films illuminated from the PTAA side

B

Supplementary Analysis for Chapter 5

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B.4	Effect of Shallow Traps on the Divergence of I_{TRPL} and σ_{TRMC}^2	169

B.1 PL Data

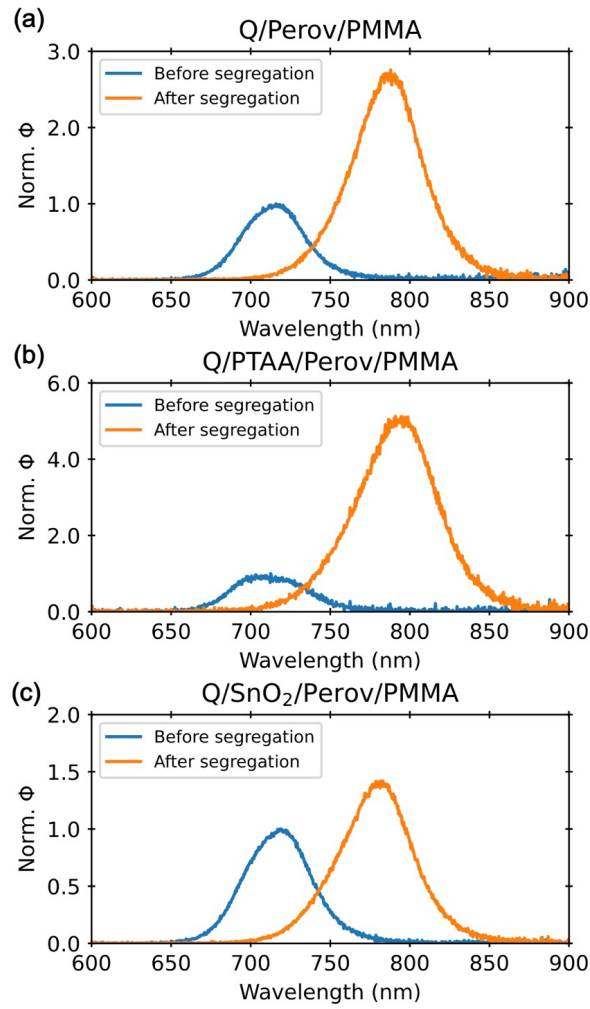


Figure B.1: Normalised photon flux for (a) Q/FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃(Perov)/PMMA, (b) Q/PTAA/Perov/PMMA and (c) Q/SnO₂/Perov/PMMA before and after halide segregation.

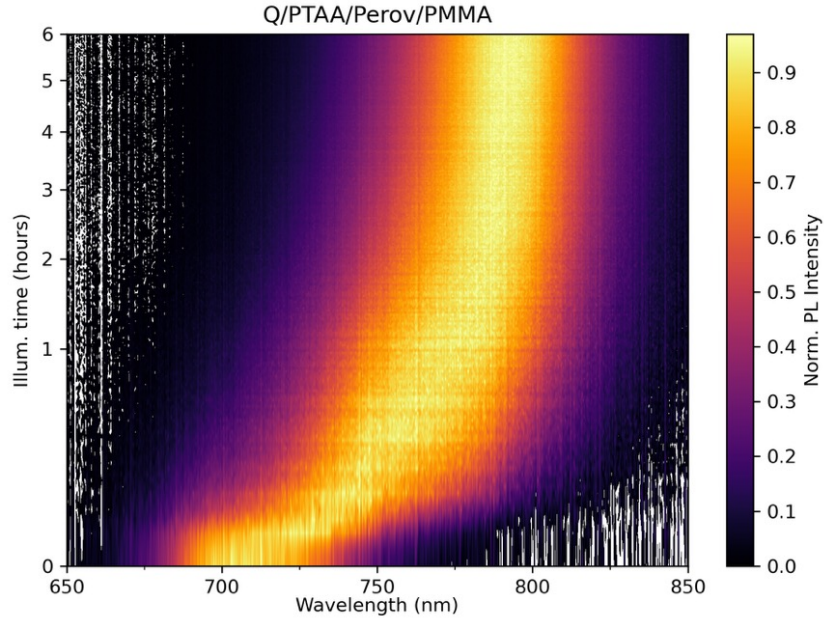


Figure B.2: Normalised steady-state PL contour map of Quartz(Q)/PTAA/FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃ (Perov)/PMMA recorded during 6 hours of CW illumination at the power density of 150 mWcm⁻². The illumination time is plotted on a square-root scale to highlight the early-time PL evolution.

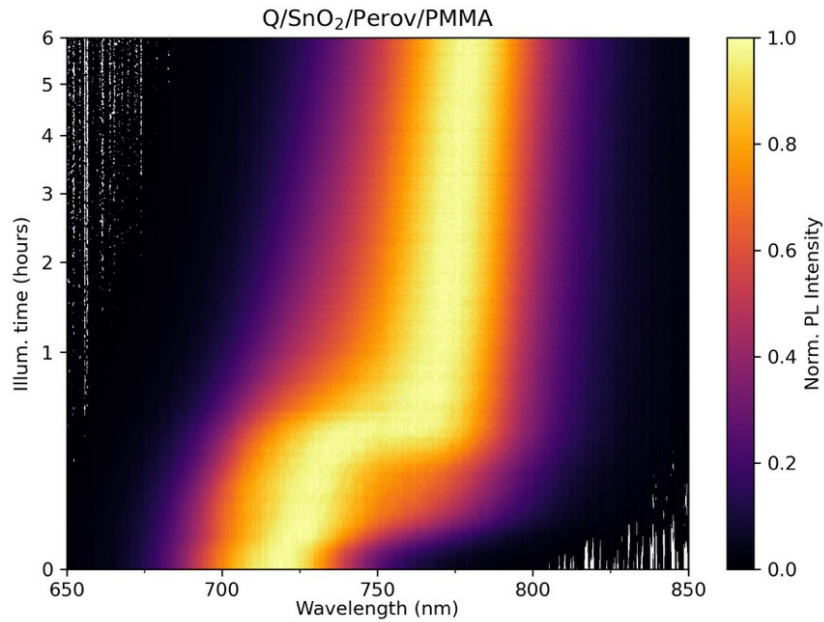


Figure B.3: Normalised steady-state PL contour map of Quartz(Q)/SnO₂/FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃ (Perov)/PMMA recorded during 6 hours of CW illumination at the power density of 150 mWcm⁻². The illumination time is plotted on a square-root scale to highlight the early-time PL evolution.

B.2 Absorption Data

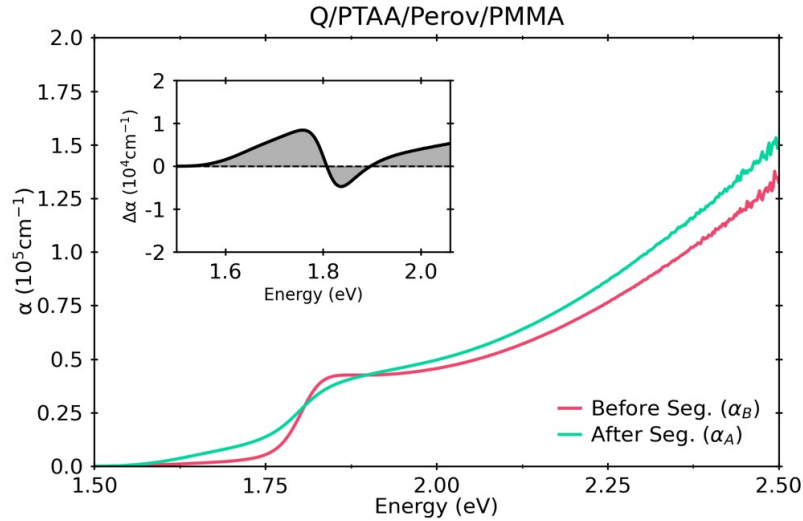


Figure B.4: Absorption spectra of Quartz(Q)/PTAA/FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃ (Perov)/PMMA before (α_B) and after halide segregation (α_A). The inset shows change in absorption spectra at ($\Delta\alpha = \alpha_A - \alpha_B$) at the absorption edge.

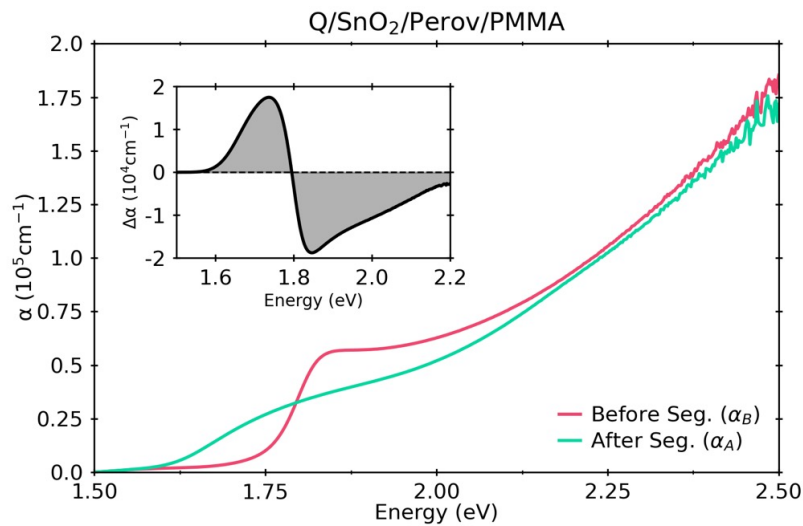


Figure B.5: Absorption spectra of Quartz(Q)/SnO₂/FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃ (Perov)/PMMA before (α_B) and after halide segregation (α_A). The inset shows change in absorption spectra at ($\Delta\alpha = \alpha_A - \alpha_B$) at the absorption edge.

B.3 TRPL and TRMC Transients

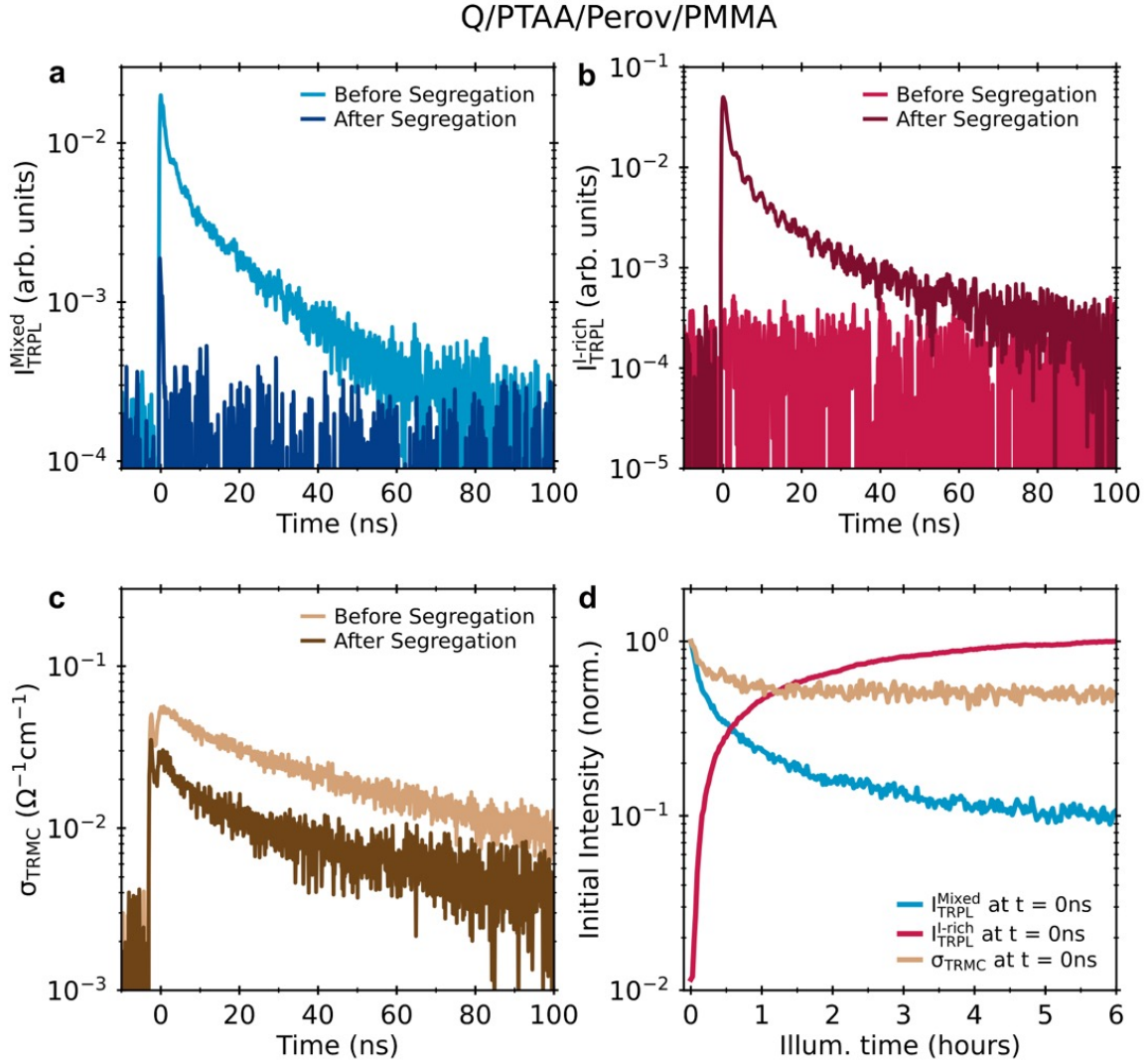


Figure B.6: Comparisons of Q/PTAA/Perov/PMMA transients. (a) Mixed-phase time-resolved photoluminescence (TRPL) $I_{\text{TRPL}}^{\text{Mixed}}$ (658–694 nm) transient before and after halide segregation. (b) I-rich phase TRPL $I_{\text{TRPL}}^{\text{I-rich}}$ (800–850 nm) transient before and after halide segregation. (c) Time-resolved microwave conductivity (σ_{TRMC}) transient before and after halide segregation. (d) Initial intensities of $I_{\text{TRPL}}^{\text{Mixed}}$, $I_{\text{TRPL}}^{\text{I-rich}}$ and σ_{TRMC} at $t = 0$ ns as a function of illumination time.

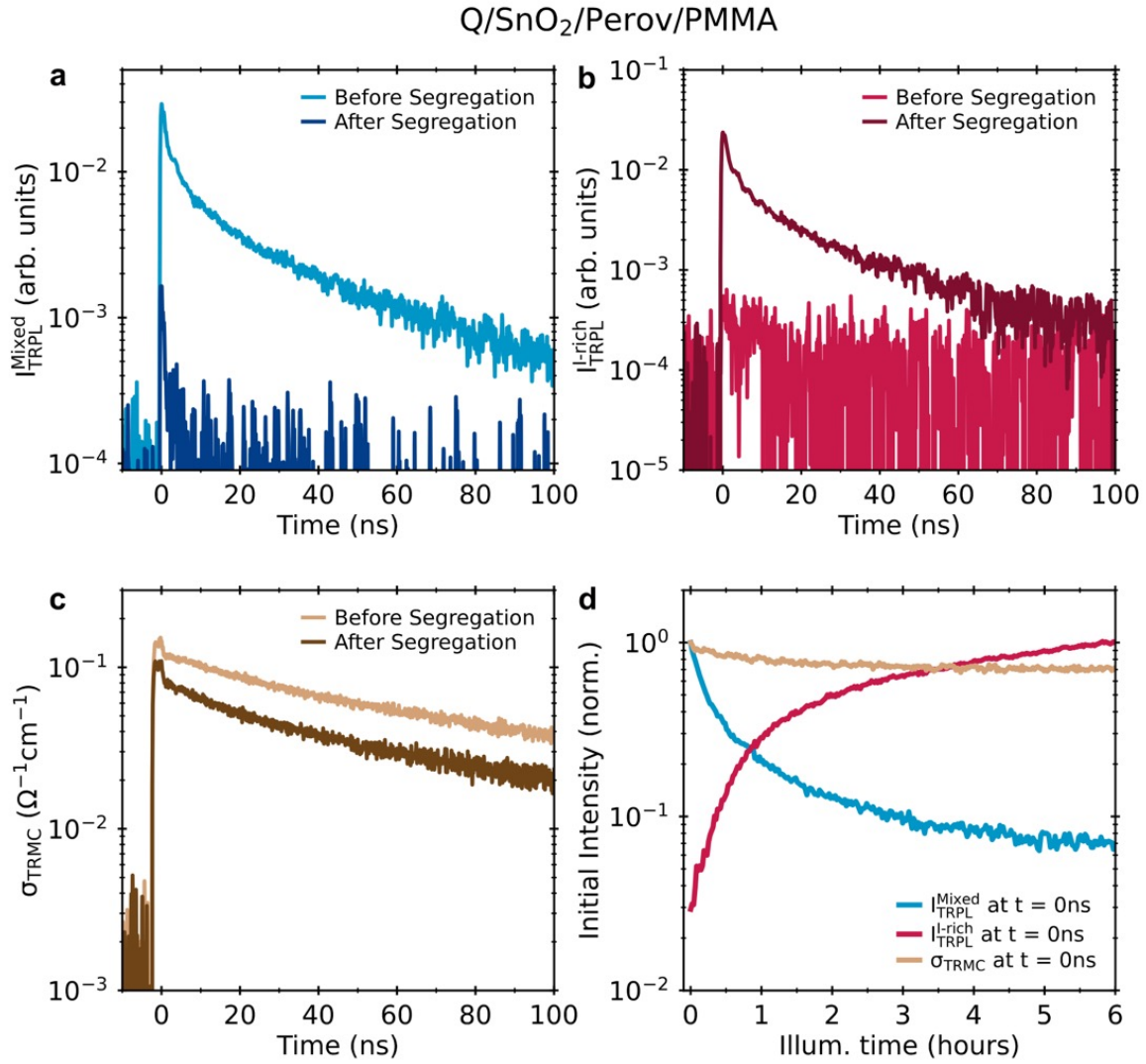


Figure B.7: Comparisons of Q/SnO₂/Perov/PMMA transients. (a) Mixed-phase time-resolved photoluminescence (TRPL) $I_{\text{TRPL}}^{\text{Mixed}}$ (658–694 nm) transient before and after halide segregation. (b) I-rich phase TRPL $I_{\text{TRPL}}^{\text{I-rich}}$ (800–850 nm) transient before and after halide segregation. (c) Time-resolved microwave conductivity (σ_{TRMC}) transient before and after halide segregation. (d) Initial intensities of $I_{\text{TRPL}}^{\text{Mixed}}$, $I_{\text{TRPL}}^{\text{I-rich}}$ and σ_{TRMC} at $t = 0$ ns as a function of illumination time.

B.4 Effect of Shallow Traps on the Divergence of I_{TRPL} and σ_{TRMC}^2

The experimental I_{TRPL} and σ_{TRMC}^2 transients shown in Figure 5.1b in Chapter B show a slight divergence while maintaining sufficiently long lifetime, suggesting that the simple model presented in Section 2.1.3.3 cannot fully capture the complex recombination pathways present in metal-halide perovskite.

The existence of multiple shallow traps is recently demonstrated by Yuan et al.[50] By combining photoluminescence measurements and drift-diffusion modelling, they have shown that the metal halide perovskite exhibit multiple high density ($\sim 10^{18} \text{ cm}^{-3}$) of electron and hole shallow traps. Therefore, the treatment of trap-assisted recombination may be more complicated than simple approximation of electron only traps as reported previously.

Therefore, I simulate the TRPL and TRMC transients by employing a set of coupled differential equations that take shallow trapping of both electron and hole into account as follow:

$$\begin{aligned} \frac{dn_e(t)}{dt} = & -R_{\text{eh}}n_e(t)n_h(t) - R_{\text{pop_e}}(N_{\text{t_e}} - n_{\text{t_e}}(t))n_e(t) + k_{\text{detrap_e}}n_{\text{t_e}}(t) \\ & - R_{\text{depop_h}}n_{\text{t_h}}(t)n_e(t) \end{aligned} \quad (\text{B.1})$$

$$\begin{aligned} \frac{dn_h(t)}{dt} = & -R_{\text{eh}}n_e(t)n_h(t) - R_{\text{depop_h}}n_{\text{t_e}}(t)n_h(t) - R_{\text{pop_h}}(N_{\text{t_h}} - n_{\text{t_h}}(t))n_h(t) \\ & + k_{\text{detrap_h}}n_{\text{t_h}}(t) \end{aligned} \quad (\text{B.2})$$

$$\frac{dn_{\text{t_e}}(t)}{dt} = R_{\text{pop_e}}(N_{\text{t_e}} - n_{\text{t_e}}(t))n_e(t) - R_{\text{depop_e}}n_{\text{t_e}}(t)n_h(t) - k_{\text{detrap_e}}n_{\text{t_e}}(t) \quad (\text{B.3})$$

$$\frac{dn_{\text{t_h}}(t)}{dt} = R_{\text{pop_h}}(N_{\text{t_h}} - n_{\text{t_h}}(t))n_h(t) - R_{\text{depop_h}}n_{\text{t_h}}(t)n_e(t) - k_{\text{detrap_h}}n_{\text{t_h}}(t) \quad (\text{B.4})$$

where $n_{\text{t_e}}(t)$, $n_{\text{t_h}}(t)$, $N_{\text{t_e}}$, $N_{\text{t_h}}$ are the trapped electron density, trapped hole density, total electron trap density and total hole trap density respectively. $R_{\text{pop_e}}$, $R_{\text{pop_h}}$, $R_{\text{depop_e}}$, $R_{\text{depop_h}}$,

Parameter	Value	Reference
n_e (cm ⁻³)	2.42×10^{17}	—
n_h (cm ⁻³)	2.42×10^{17}	—
n_t (cm ⁻³)	0	—
μ (cm ² V ⁻¹ s ⁻¹)	24.5	—
R_{eh} (cm ³ s ⁻¹)	1.54×10^{-10}	—
N_{t_e} (cm ⁻³)	1.64×10^{17}	Simulation
R_{pop_e} (cm ³ s ⁻¹)	1.51×10^{-10}	Simulation
R_{depop_e} (cm ⁻³ s ⁻¹)	1.0×10^{-12}	Simulation
k_{detrapp_e} (s ⁻¹)	7.9×10^7	Simulation
N_{t_h} (cm ⁻³)	6.96×10^{15}	Simulation
R_{pop_h} (cm ³ s ⁻¹)	9.5×10^{-9}	[105]
R_{depop_h} (cm ⁻³ s ⁻¹)	1.42×10^{-9}	[105]
k_{detrapp_h} (s ⁻¹)	5.6×10^4	[105]

Table B.1: Parameters used for simulating I_{TRPL} and σ_{TRMC}^2 transients by using the model discussed in Section B.4.

k_{detrapp_e} , k_{detrapp_h} are the trap population, depopulation and detrapping rate constants for electrons and holes respectively. $(N_t - n_t(t))$ denote the unoccupied trap density. Here, we assume that traps are not filled yet initially ($n_t(t = 0) = 0$).

Equation B.1, B.2, B.3 and B.4 were solved numerically to obtain $n_e(t)$, $n_h(t)$, $n_{t_e}(t)$ and $n_{t_h}(t)$. Then, I_{TRPL} and σ_{TRMC}^2 transients were obtained with Equation 5.1 and 5.2. The following parameters in Table B.1 is used for simulation.

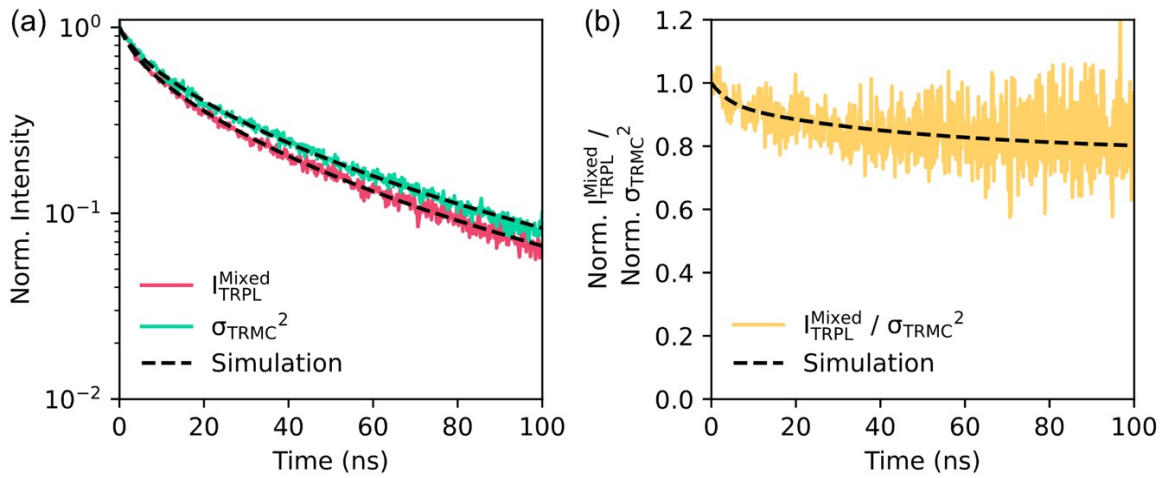


Figure B.8: (a) Mixed-phase TRPL ($I_{\text{TRPL}}^{\text{Mixed}}$) and square of the microwave photoconductivity (σ_{TRMC}^2) transients of Q/FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃/PMMA excited with 530 nm wavelength at the fluence of 3.6 μJcm^{-2} with simulated transients obtained from the model discussed in Section B.4. (b) The ratio of $I_{\text{TRPL}}^{\text{Mixed}}$ and σ_{TRMC}^2 with the simulation.

Inclusion of the extra shallow traps allows us to describe the long-lived charge-carrier dynamics with the slight divergence in the transient originating from trapping. The early decay in the $I_{\text{TRPL}}^{\text{Mixed}}/\sigma_{\text{TRMC}}^2$ ratio arise from the initial charge-carrier trapping, but it is quickly compensated by fast detrapping, mitigating the charge selectivity induced by trapping.

C

Supplementary Analysis for Chapter 6

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C.1 Absorption Data

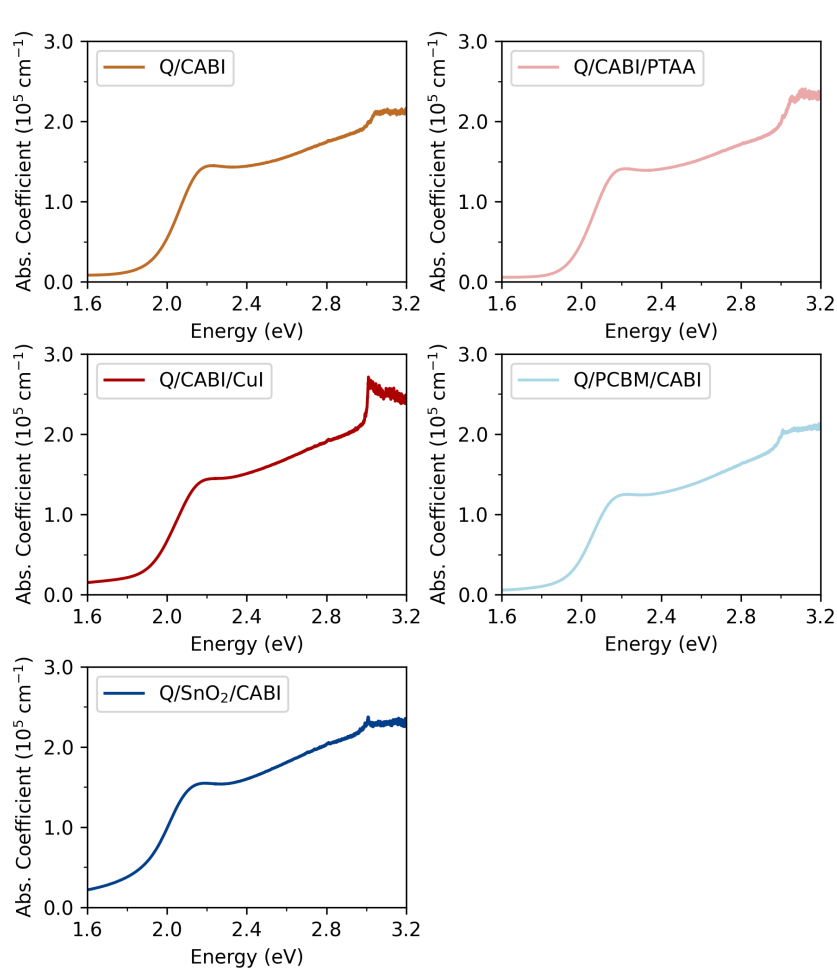


Figure C.1: Absorption coefficient spectra of the CABI thin films with and without charge transport layers, on quartz substrates, covering a wider range of photon energies.

C.2 XRD Data

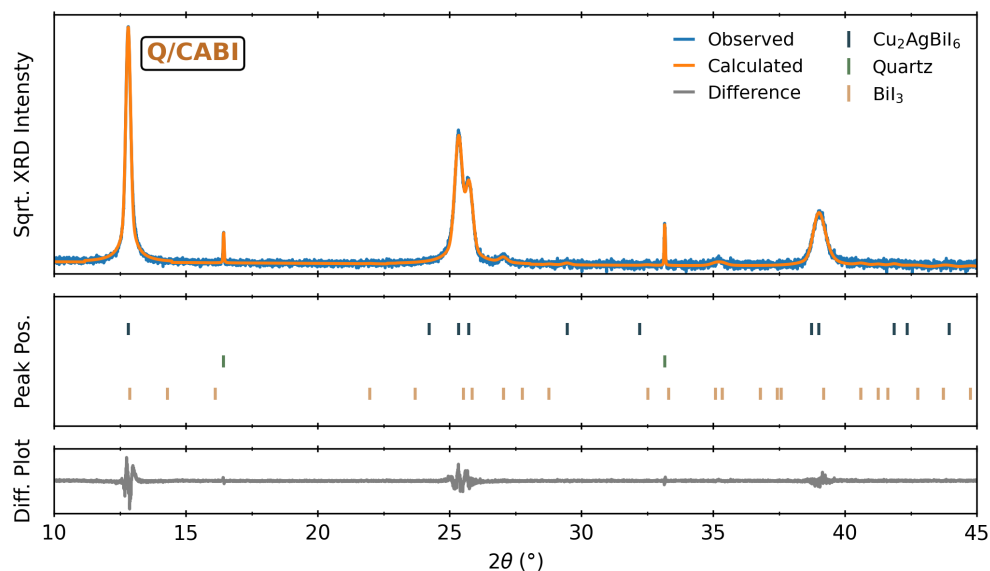


Figure C.2: Pawley fits to the XRD patterns for the Quartz/CABI sample. The calculated pattern is overlaid on the experimental pattern in the upper panel and the difference between the two is shown in the bottom panel in grey. The contribution to the calculated pattern from each phase is shown with vertical markers in the middle panel. The XRD intensity is presented on a square-root scale.

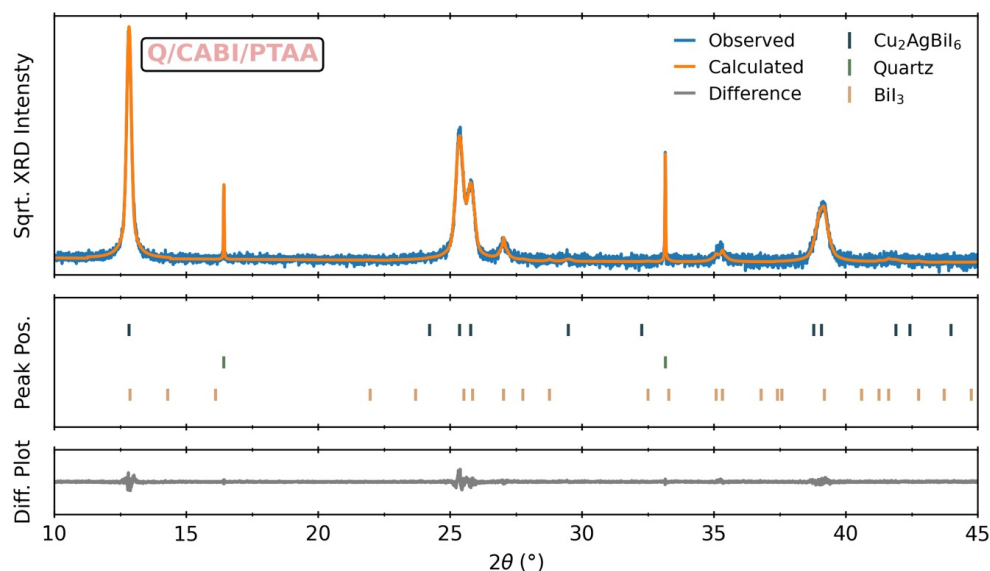


Figure C.3: Pawley fits to the XRD patterns for the Quartz/CABI/PTAA sample. The calculated pattern is overlaid on the experimental pattern in the upper panel and the difference between the two is shown in the bottom panel in grey. The contribution to the calculated pattern from each phase is shown with vertical markers in the middle panel. The XRD intensity is presented on a square-root scale.

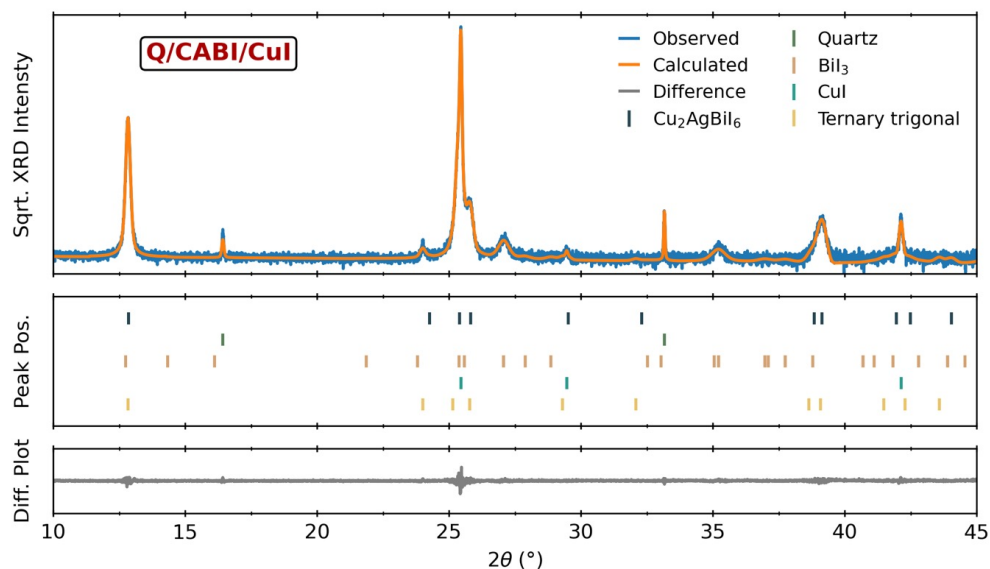


Figure C.4: Pawley fits to the XRD patterns for the Quartz/CABI/CuI sample. The calculated pattern is overlaid on the experimental pattern in the upper panel and the difference between the two is shown in the bottom panel in grey. The contribution to the calculated pattern from each phase is shown with vertical markers in the middle panel. The XRD intensity is presented on a square-root scale.

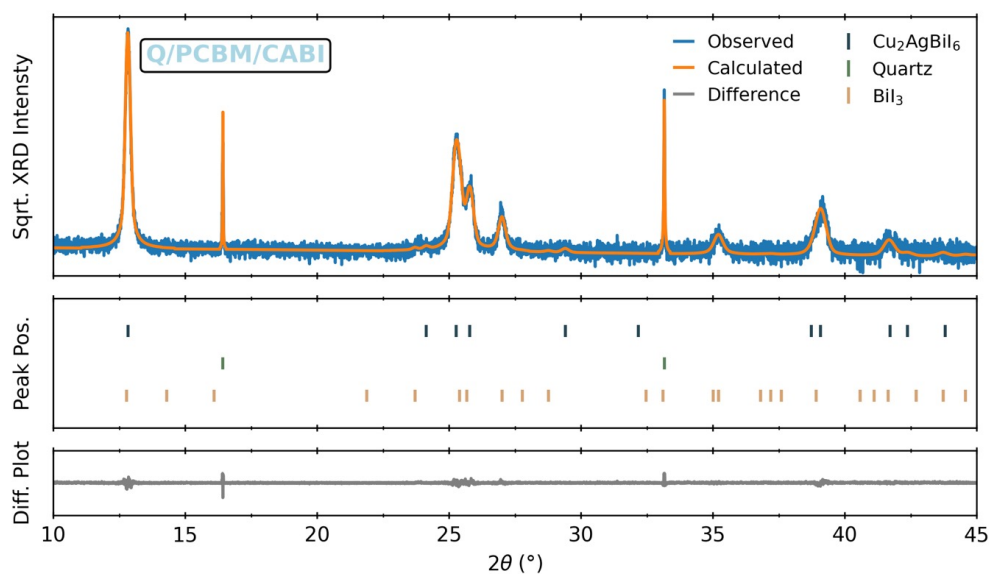


Figure C.5: Pawley fits to the XRD patterns for the Quartz/PCBM/CABI sample. The calculated pattern is overlaid on the experimental pattern in the upper panel and the difference between the two is shown in the bottom panel in grey. The contribution to the calculated pattern from each phase is shown with vertical markers in the middle panel. The XRD intensity is presented on a square-root scale.

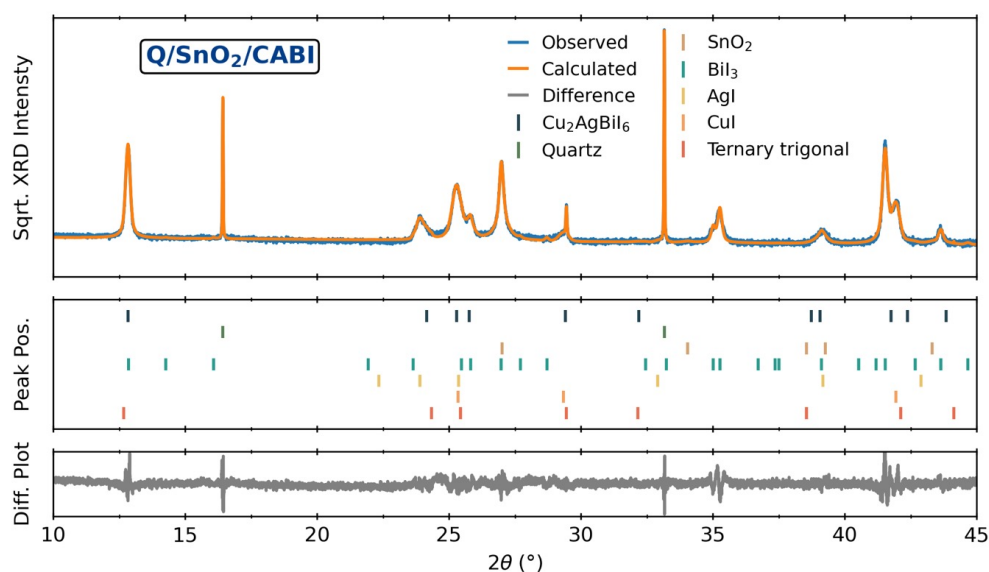


Figure C.6: Pawley fits to the XRD patterns for the Quartz/SnO₂/CABI sample. The calculated pattern is overlaid on the experimental pattern in the upper panel and the difference between the two is shown in the bottom panel in grey. The contribution to the calculated pattern from each phase is shown with vertical markers in the middle panel. The XRD intensity is presented on a square-root scale.

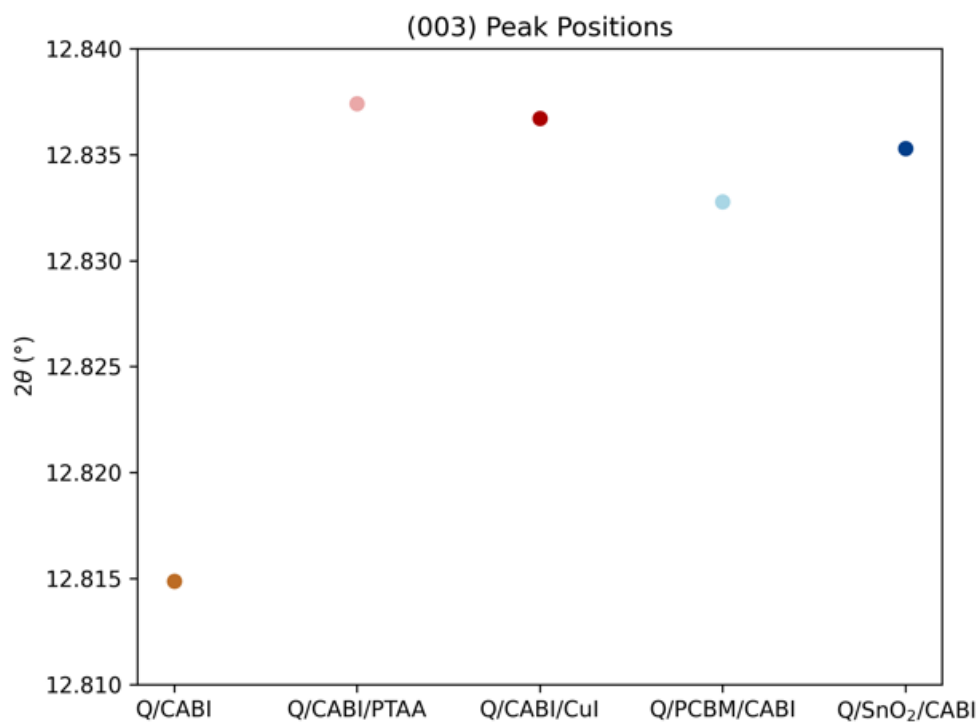


Figure C.7: Extracted peak positions in XRD spectra for the (003) diffraction peak of CABI films and CABI half stacks with charge transport layers, on quartz.

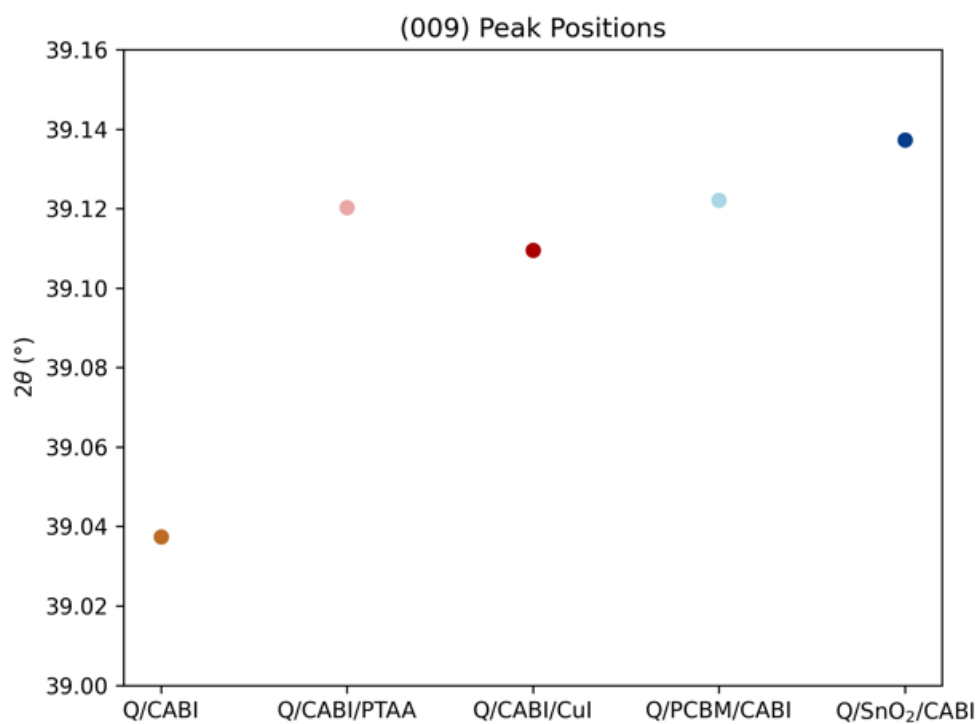


Figure C.8: Extracted peak positions in XRD spectra for the (009) diffraction peak of CABI films and CABI half stacks with charge transport layers, on quartz.

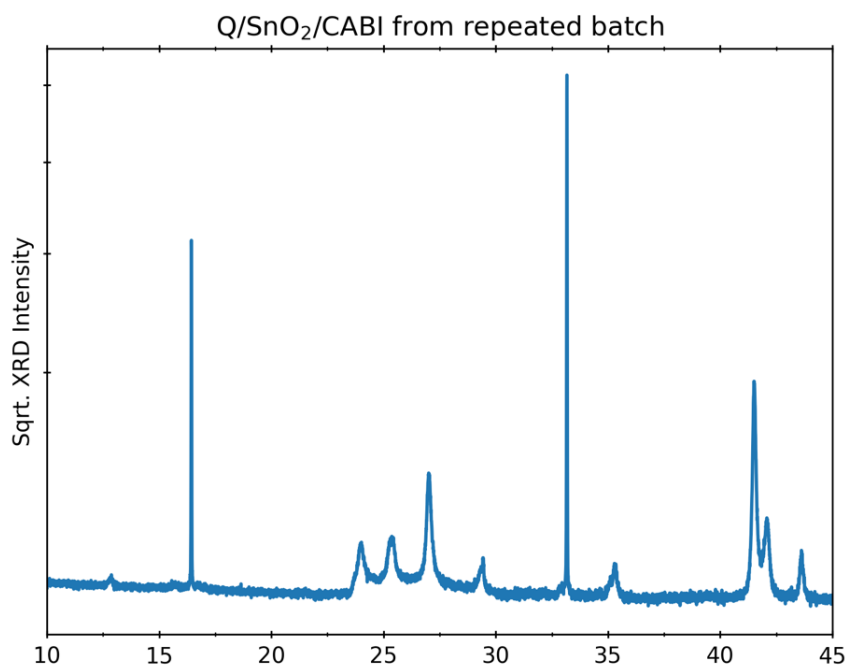


Figure C.9: XRD pattern of a Q/SnO₂/CABI sample from a repeated coevaporated batch.

C.3 OPTP Data

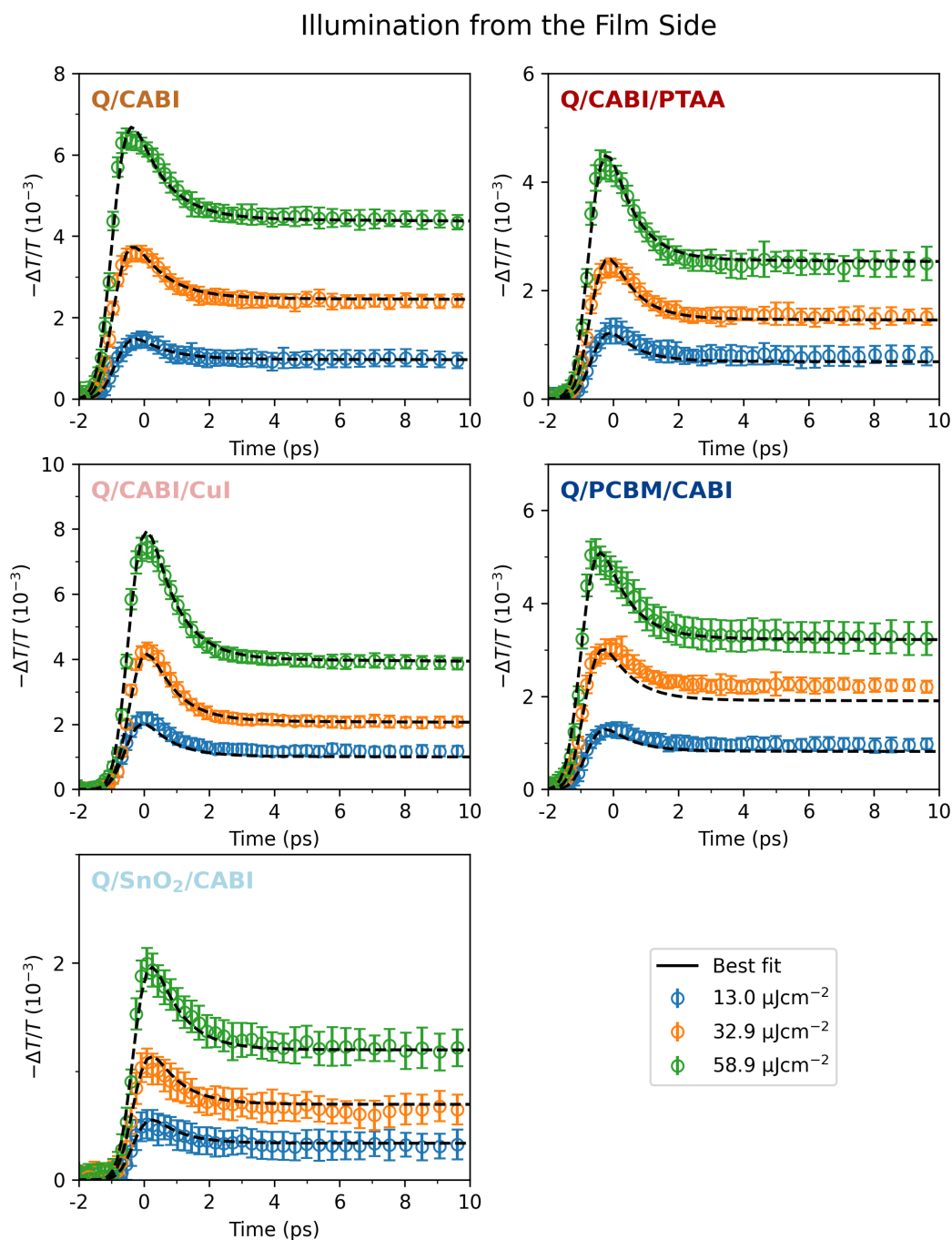


Figure C.10: OPTPS photoconductivity transients shown for times between -2 and 10 ps after excitation for $\text{Cu}_2\text{AgBiI}_6$ thin films and half stacks with hole transport layers (PTAA and CuI) and electron transport layers (PCBM and SnO_2), deposited on a quartz substrate. Samples were illuminated from the film side (i.e. the side opposite the quartz substrate) with excitation pump fluences of 13.0 , 32.9 and $58.9 \mu\text{Jcm}^{-2}$. The dotted black lines are global fits to the fluence-dependent OPTPS transients using the localization model described in Section 3.3.2.3

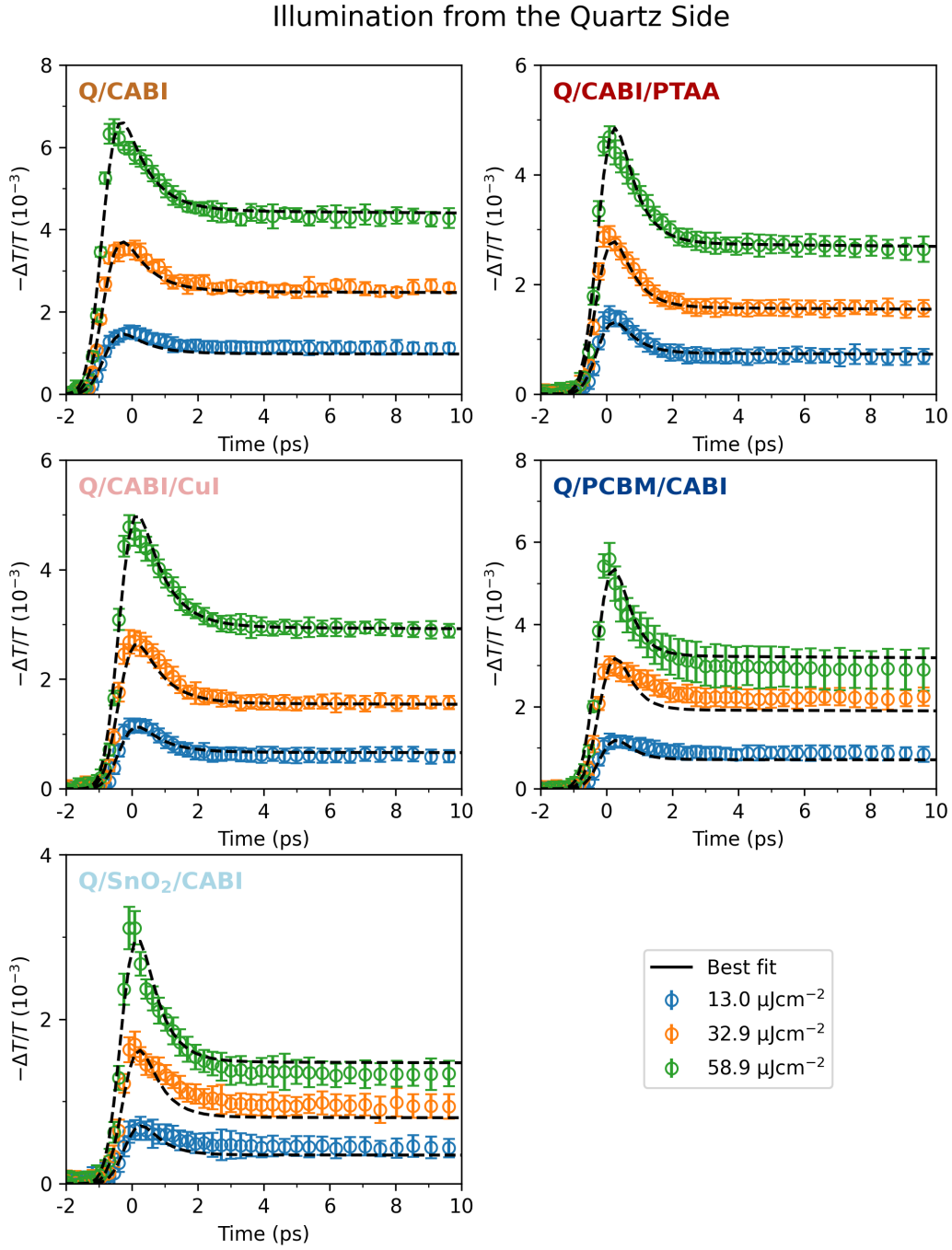


Figure C.11: OPTPS photoconductivity transients shown for times between -2 and 10 ps after excitation for $\text{Cu}_2\text{AgBiI}_6$ thin films and half stacks with hole transport layers (PTAA and CuI) and electron transport layers (PCBM and SnO_2), deposited on a quartz substrate. Samples were illuminated from the quartz side with excitation pump fluences of 13.0 , 32.9 and $58.9 \mu\text{Jcm}^{-2}$. The dotted black lines are global fits to the fluence-dependent OPTPS transients using the localization model described in Section 3.3.2.3

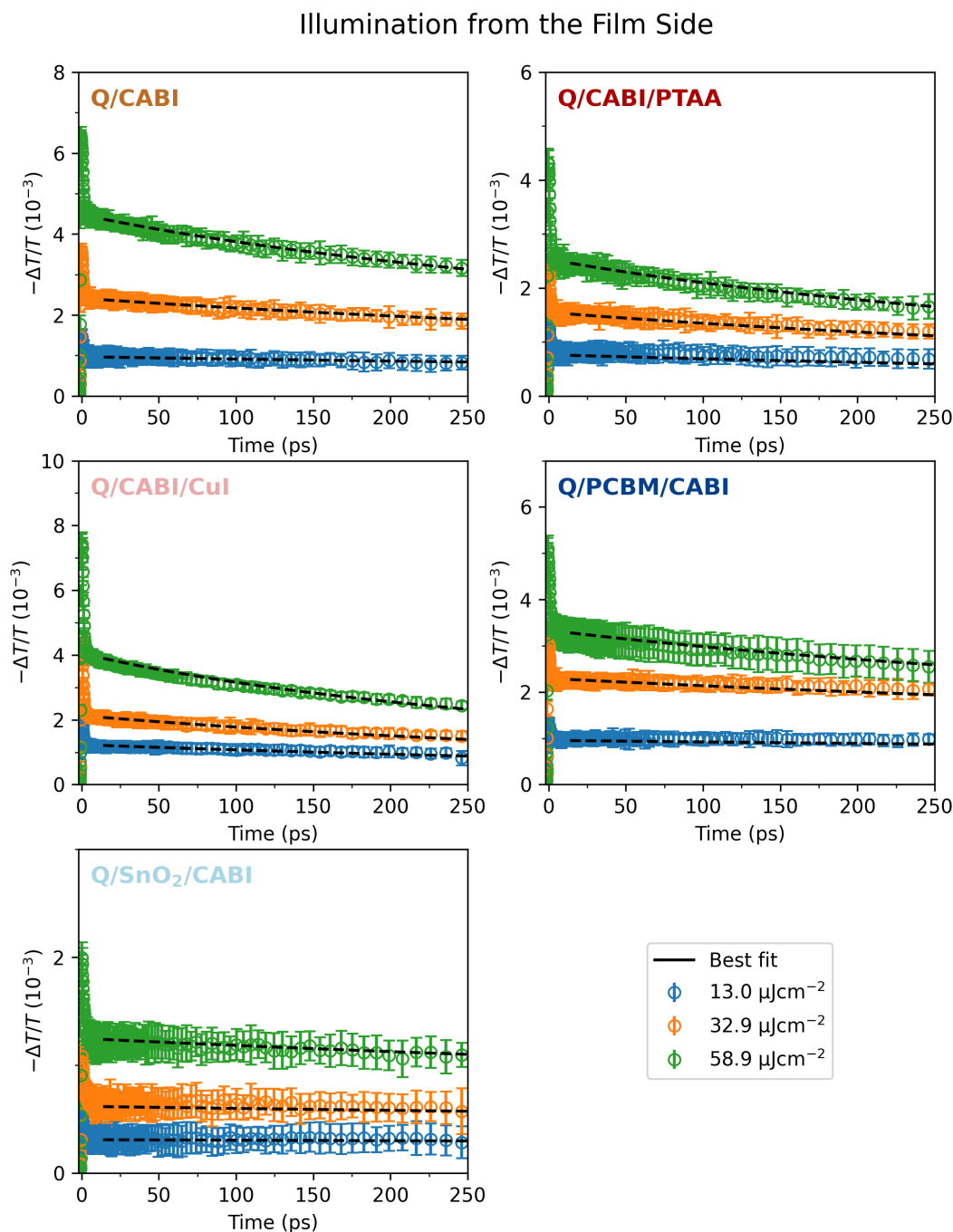


Figure C.12: OPTPS photoconductivity transients for time up to 250 ps after photoexcitation for $\text{Cu}_2\text{AgBiI}_6$ thin films and half stacks with hole transport layers (PTAA and CuI) and electron transport layers (PCBM and SnO_2), deposited on a quartz substrate. Samples were illuminated from the film side (i.e. the side opposite the quartz substrate) with excitation pump fluences of 13.0 , 32.9 and $58.9 \mu\text{Jcm}^{-2}$. The dotted black lines are global fits to the OPTPS transients of the subsequent slow decays using the k_1 - k_2 model described in Section 3.3.2.3

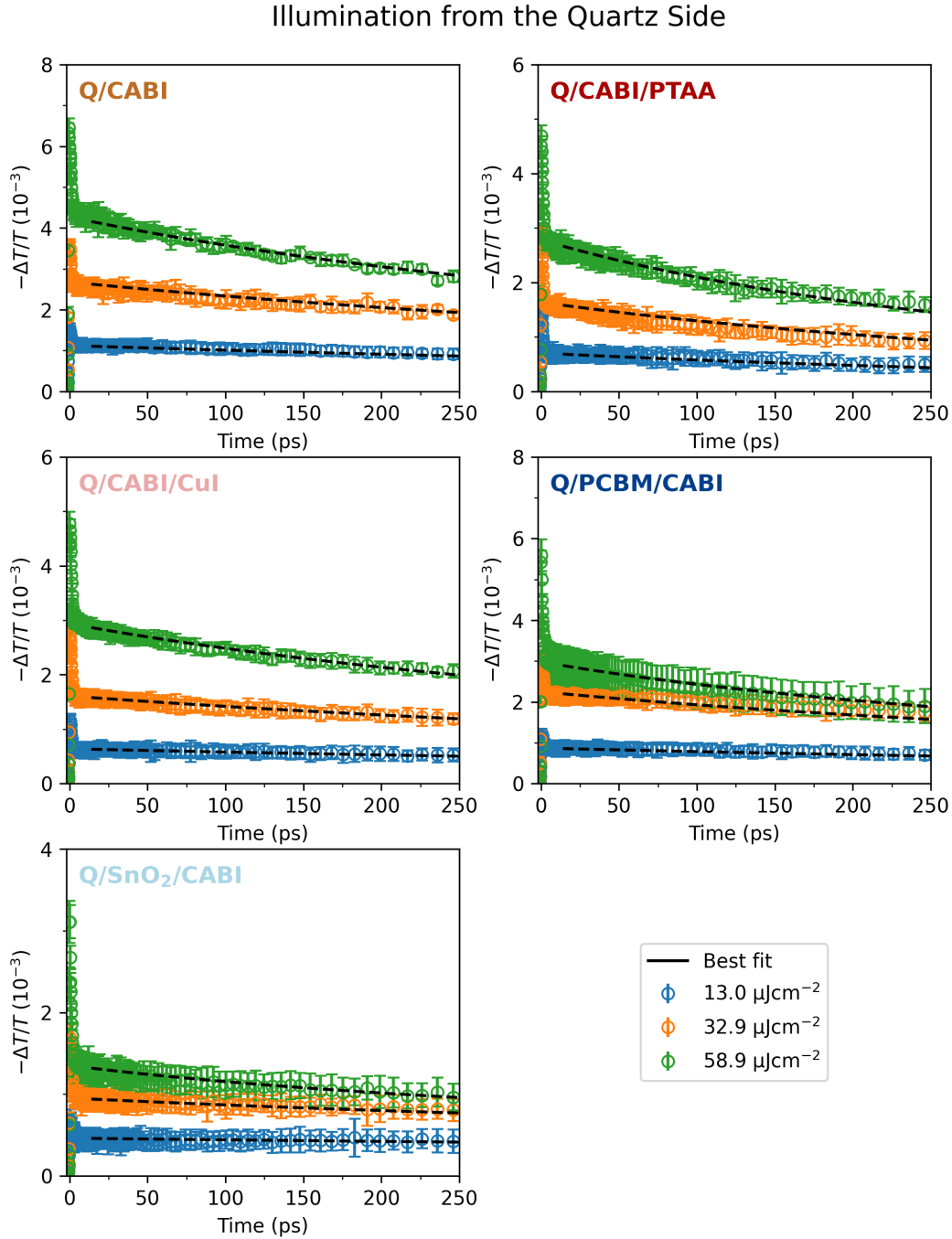


Figure C.13: OPTPS photoconductivity transients for times up to 250 ps after photoexcitation for $\text{Cu}_2\text{AgBiI}_6$ thin films and half stacks with hole transport layers (PTAA and CuI) and electron transport layers (PCBM and SnO_2), deposited on a quartz substrate. Samples were illuminated from the film side with excitation pump fluences of 13.0, 32.9 and $58.9 \mu\text{Jcm}^{-2}$. The dotted black lines are global fits to the OPTPS transients of the subsequent slow decays using the k_1 - k_2 model described in Section 3.3.2.2

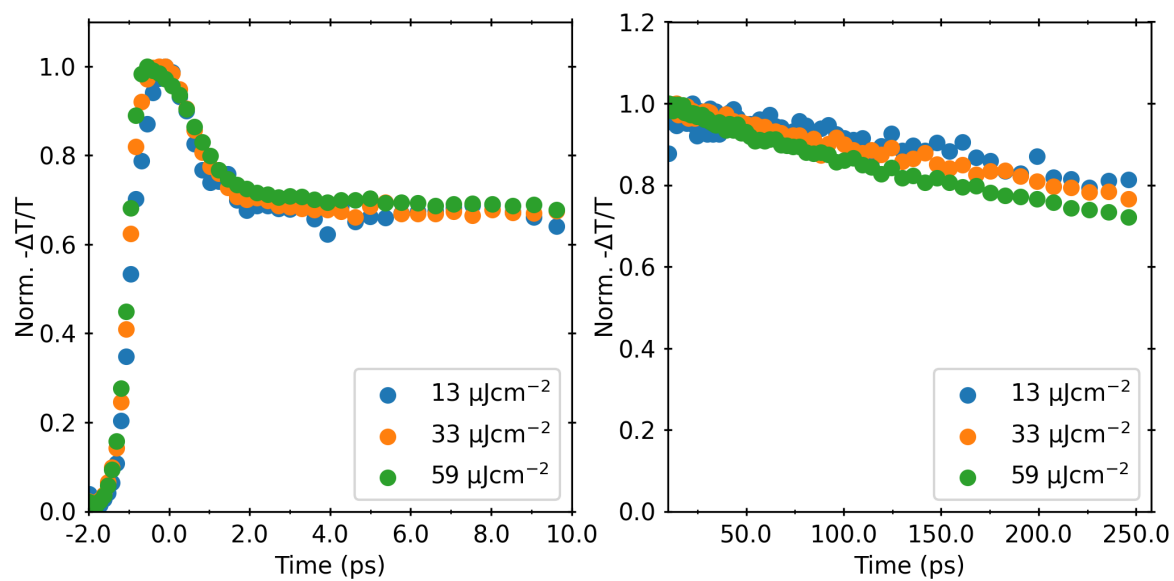


Figure C.14: Normalised OPTPS early-time dynamics (from -2 ps to 10 ps) and late dynamics (from 10 ps to 250 ps) for the Q/CABI sample illuminated from the film side.

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- [1] UNFCCC. *The Paris Agreement*. Publication. 2018.
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