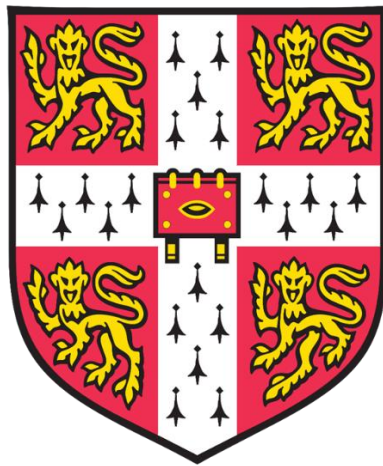

All Inorganic Colloidal Perovskite Nanocrystals for Optoelectronic Applications



Junzhi Ye

Churchill College

Cavendish Laboratory, Department of Physics

University of Cambridge

This thesis is submitted for the degree of

Doctor of Philosophy

November 2022

Declaration of Originality

I declare that the contents of this thesis are the result of my own work, except where specific reference is made to the work of others. This thesis has not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other university. This dissertation contains fewer than 60,000 words including appendices, bibliography, footnotes, tables and equations.

Junzhi Ye

November 2022

All Inorganic Colloidal Perovskite Nanocrystals for Optoelectronic Applications

Junzhi Ye

This dissertation focuses on the optoelectronic properties and device performance of colloidal all-inorganic metal-halide perovskite nanocrystals (CsPbX_3 NCs, where $\text{X}=\text{Br}$ or I). These types of materials have shown promising performance in applications including photovoltaics (PVs) and light-emitting diodes (LEDs) due to their excellent optoelectronic properties, such as high photoluminescence quantum yields (PLQYs), high carrier mobility, long diffusion lengths, low Urbach energies and tuneable bandgaps across the visible and near-infrared wavelength ranges.

In this thesis, I investigate how the surface chemistry of $\text{CsPbBr}_x\text{I}_{3-x}$ NC systems is affected by the polarity of the antisolvent used during purification. I find that higher polarity antisolvents result in an increase in the selective etching of surface iodides, resulting in a decrease in PLQYs and blue-shift in the optical bandgap. Through detailed ^1H nuclear magnetic resonance (NMR), X-ray photoemission spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and transmission electron microscopy (TEM) measurements, I show that the cause for these effects is that higher-polarity antisolvents favour condensation reactions between the oleylamine and oleate ligands, resulting in their detachment, and the removal of surface iodides hydrogen bonded to these ligands. I show how the resulting increase in halide vacancies leads to not only increased non-radiative recombination, but also faster red-shifts in the electroluminescence (EL) peak from LEDs, due to faster ion migration. This work therefore identifies antisolvent polarity, particularly the use of low polarity antisolvents, as a critical parameter for controlling the surface chemistry of halide perovskite NCs.

In the next Chapter, I investigate the effect of surface traps on hot carrier cooling kinetics, making use of polar antisolvents to intentionally introduce surface traps in inorganic $\text{CsPbBr}_x\text{I}_3$.

x NCs. Through energy-dependent PLQY measurements, I observe the increased tendency of the hot carriers to localise in the trap states as their excess energy is increased, especially for Br-based and mixed Br/I NCs. I extract the hot carrier cooling lifetimes for NCs with different composition and defect densities through pump-probe and pump-push-probe transient absorption spectroscopy measurements. These results, together with density function theory calculations, suggest that the defect tolerance found in band-edge charge-carriers can be extended to hot carriers. That is, the relaxation kinetics of hot carriers in materials with shallower defect states, such as I-based NCs, tend to be less influenced by the traps. This new understanding is important in the future design of systems that can extract hot carriers, and the ultimate realisation of hot carrier solar cells.

In the final Chapter, I achieve the synthesis of CsPbI₃ nanoplatelets with colour-pure emission. By developing a solution-based route to self-assemble these nanoplatelets and therefore control the isotropy of the transition dipole moment, I achieve the first demonstration of directly-generated linearly polarised electroluminescence (EL) from perovskite nanoplatelet systems. PbI₂ precursors are used to passivate surface I-vacancies to reduce trap-assisted recombination and exciton-exciton annihilation. As a result, I achieve CsPbI₃ light-emitting diodes (LEDs) with 2.7% external quantum efficiency (EQE; the highest reported for a strongly-confined perovskite nanoplatelet system). This enabled the demonstration of perovskite LEDs with a high degree of optical polarisation (DOP) of 74.4%. By comparing the polarised emission with weakly confined NCs and bulk films, I find that the degree of polarisation is also related to the exciton fine structure splitting energy which can be governed by exciton binding energy.

Through these investigations, I offer new insights into how the surface defect chemistry of metal-halide perovskite NCs can be controlled, and how this influences hot-carrier cooling, which is important for ultimately realising hot carrier solar cells. This work opens up the possibility of developing linearly polarised light emitters that could be achievable across the entire visible and near-infrared wavelength ranges, which can be used for 3D displays and optical communication.

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Chapter 1: Introduction

Population growth has exerted enormous pressure on energy sectors. It is reported that the global population will increase from 7.3 billion in 2015 to 9.2 billion in 2050 ^{1,2}. Population growth will directly lead to an increase in electricity consumption, and from 2016-2018, this has been growing at an annual compound growth rate of 10%. As an indication of energy consumption, the amount of CO₂ emission is one of the key standards^{1,3}. According to the Global Climate Change Impacts in the United States report from the U.S. Global Change Research Program (USGCRP), global annual average temperature (as measured over both land and oceans) has increased by more than 1.5 °F (0.8 °C) since 1880 (through 2012) ⁴. As shown in Figure 1, the red bars show temperatures above the long-term average, and blue bars indicate temperatures below the long-term average. The black line shows atmospheric carbon dioxide (CO₂) concentration in parts per million (ppm). The empirical data demonstrates that there is a clear long-term global warming trend with an increase amount of CO₂ concentration.

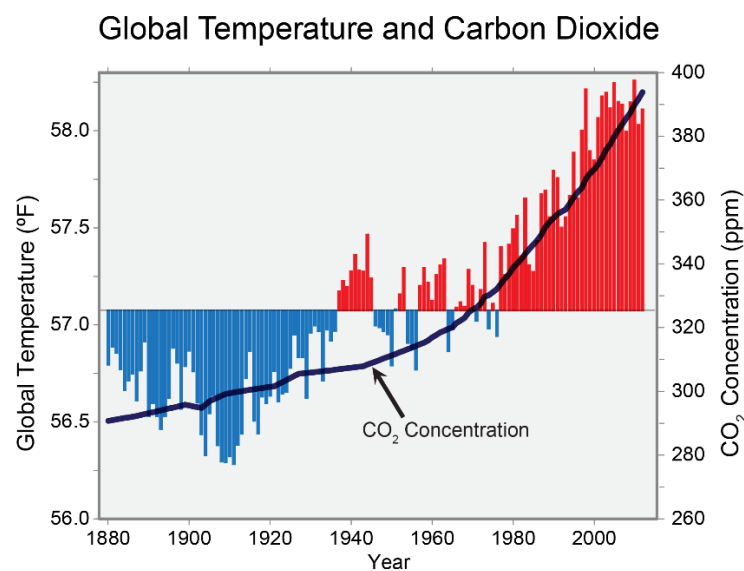


Figure 1. 1 Global Temperature and carbon dioxide (average carbon dioxide concentration). Figure is from reference ⁴.

The increasing in global temperature could directly exhibit physical impact on local areas⁵. Woetzel *et al.* provide a case study in India that the heat and humidity will increase in India, causing about 160 to 200 million people could live in regions with an average 5% annual probability of experiencing a heat wave that exceeds the survivability threshold for a healthy human being absent an adaptation response based on a CO₂ concentration pathway of 8.5 scenario ⁵. Another very recent example is the extremely hot summer in England in 2022, which is a milestone of reaching the highest temperature in the United Kingdom (40.7 °C) Based on the analysis released by the UK Health Security Agency, from 17 to 20 July, when temperatures were at their highest, there were an estimated 1,012 excess deaths in those aged over 65. Additionally, the heat-period in the summer of 2022 with the highest excess mortality overall was from 8 to 17 August, which saw an estimated 1,458 excess deaths (excluding COVID-19) in those over the age of 65 ⁶.

Apart from the sustainable development requirement on energy supply sectors, global pandemic and geopolitical conflicts such as the Russia-Ukraine conflict also adversely affect the global energy supply⁷⁻¹¹. These facts clearly suggested that a dramatic change in the global energy supply sector is required urgently, moving from the traditional fossil fuel based fire-power plant to sustainable and renewable energy source including photovoltaics, bio-fuel, hydro-power and so on.

In addition to the energy harvesting and generation, improving the efficiency of the use of electricity should be another focus. For example, according to the U.S. Energy Information Administration (EIA) in the Annual Energy Outlook 2022 that in 2021, the U.S. residential and commercial sectors combined used about 211 billion kilowatt-hours (kWh) of electricity for lighting. This was about 8% of total electricity consumption by both of these sectors and about 5% of total U.S. electricity consumption by all sectors ¹². Replacing traditional incandescent and halogen light bulbs to more efficient lighting technologies such as light-emitting diodes (LEDs) would certainly

reduce the lighting energy consumption¹³. The LED market analysis performed by LED inside highlighted in its “2017 Global Lighting Market Outlook” that LED lighting market to worth US \$29.6 billion in 2016 and is rise to the US \$ 33.1 billion as of 2017. The global Flex LED Strip Lights market size is projected to reach USD 5172.2 million by 2026, from USD 2201.4 million in 2020, at a CAGR of 15.3% during 2021-2026.¹⁴ Therefore, there is a strong economic and environmental motivation to investigate highly efficient LED devices for ultra-high-definition display.

Colloidally-synthesised metal-halide perovskite nanocrystals (NCs) represent a new class of low thermal-budget materials with highly desirable optoelectronic properties. These materials could lead to efficient light-emission sources, as well as efficient light harvesters. By reducing the dimensionality from a bulk 3D compound to a 2D nanoplatelet, the excitonic, optical and charge-carrier recombination properties can be finely tuned, leading to new opportunities, such as the possibility of polarised light sources if the transition dipole moment could be controlled by controlling the orientation of nanoplatelets. This represents, together with the curiosity of understanding fundamental physical processes of the materials, the main driver for my work summarised in this PhD thesis.

In Chapter 2, I will firstly review the basic concepts about developing efficient perovskite-based optoelectronic devices, including its fundamental semiconducting material properties, material synthesis and the current progress on device development. Chapter 3 will then provide an overview of the methods used in the studies of this PhD thesis, focusing mainly on synthesis and structural and optical characterisation.

In Chapter 4, a study on elucidating the role of antisolvents on the surface chemistry and optoelectronic properties of mixed halide metal-perovskite nanocrystals. It provides insights on understanding the origin of surface defects during the purification process, and how this could influence the material optical properties such as carrier lifetime and photoluminescence quantum yield. Also, it provides design guideline for

mitigating the instability of red LEDs due to the halide segregation issue.

In Chapter 5, I will continue the study on how the surface defects would influence the hot carrier relaxation process, which is an crucial process to further improving the power conversion efficiency of perovskite-based solar cells. By utilising transient absorption spectroscopies, I found the ability to tolerant the surface defects would vary upon the change in halide composition. Hence, it provides fundamental understandings about the defect-tolerance nature of perovskite to the hot carriers, which is helpful to harvesting the energy more efficiently from these hot carriers.

Chapter 6 summarised the development of the world-first CsPbI₃ nanoplatelet-based LEDs with high degree of linearly polarised (DOP=74.4%) electroluminescence directly from the materials. I investigated the originality of the high degree of linear polarisation, including the ability to align the transition dipole moment through self-assembly, high photoluminescence quantum yield dominated by excitonic radiative recombination and large exciton fine-structure splitting due to the strong size and dielectric confinement.

Finally, in Chapter 7, I will summarise these results and provides outlooks for solving the current obstacles for colloidal perovskite nanocrystal devices.

Chapter 2 Theoretical Background

2.1 Semiconductor Theory Background

2.1.1 Band Theory

In a solid crystalline semiconductor, the approximation of the electronic properties of a solid with non-interacting electrons can be found by solving Schrödinger's equation. For example, a hydrogen atom energy is shown in eq. 2.1. For a more complex system with electron-electron interactions, the Hamiltonian will change based on the effects of the neighbouring Coulomb wells, which will not be discussed here.

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\varphi(r) = E\varphi(r) \quad (2.1)$$

Where $-\frac{\hbar^2}{2m}\nabla^2$ is the kinetic energy of electrons in solids and $V(r)$ is the atomic potential energy. In a crystalline material, the atomic potential energy is arranged on an infinite periodic lattice. The periodicity of the lattice means that the probability distribution of the electrons is repeatable periodically. Bloch wavefunction is used to describe the electrons with periodicity, which contains a periodic factor $u_{ik}(r)$ and a plane wave $e^{ik \cdot r}$ (eq. 2.2).

$$\varphi(k, r) = u_{ik}(r)e^{ik \cdot r} \quad (2.2)$$

The Bloch wavefunction can be characterised by a crystal band i and a wavevector (crystal momentum) k . As the direct lattice is periodic in real space, its reciprocal lattice used in momentum space should be also periodic.

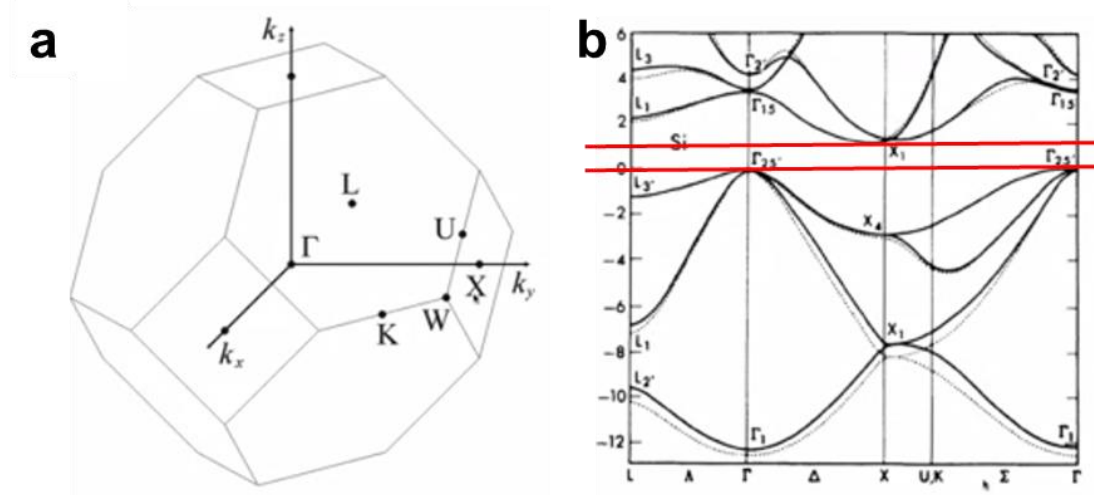


Figure 2. 1 a. Material shown in reciprocal space. b.: Band structure of silicon

As an example, Figure 2.1a demonstrates the reciprocal lattice of a unit cell (known as a Brillouin zone). The map of energies, E , against wavevector, k , is known as the band structure. For example, Γ is the center of the Brillouin zone ($k=0$), and X , K and L are at the Brillouin zone boundaries along the $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$ directions. By plotting the energies of bands in the solid with respect to different k values, a band structure diagram can be constructed, as shown in Figure 2.1b (using Si as an example). The region with no allowed energy states in any chosen direction is the forbidden band gap (shown between the two red lines).

Conduction Band: The conduction band is immediately above the forbidden band gap, with the conduction band minimum (CBM) occurring at a certain k -vector (X_1 in the case of Si, Figure 2.1b). The energy of the state about conduction band minimum can be approximated by (eq. 2.3):

$$E(k) = E_{c0} + \frac{\hbar^2 |k - k_{oc}|^2}{2m_c^*} \quad (2.3)$$

Where $E_{c0} = E_c(k_0)$, the conduction band minimum can be found at the wavevector where has the lowest energy, in figure 2.1b, it is at point X . m_c^* is the electron effective mass, larger effective mass means that the conduction electrons are strongly influenced

by atomic potentials. The electron velocity (v) and momentum (p) can be calculated by the following equations (eq. 2.4):

$$v = \frac{\hbar(k - k_{0c})}{m_c^*}, \quad p = \hbar(k - k_{0c}) \quad (2.4)$$

Valence Band: In comparison, the valence band is immediately below the band gap. The energy of the hole near the valence band maximum can be approximated by (eq. 2.5):

$$E(k) = E_{v0} + \frac{\hbar^2 |k - k_{vc}|^2}{2m_v^*} \quad (2.5)$$

Where $E_{v0} = E_v(k_0)$ (assuming the maximum is at $k=0$ direction), m_v^* is the hole effective mass. The hole velocity (v) and momentum (p) can be calculated by the following equations (eq. 2.6):

$$v = \frac{\hbar(k - k_{v0})}{m_v^*}, \quad p = -\hbar(k - k_{v0}) \quad (2.6)$$

The minimum amount of energy needed to promote an electron from the valence band into conduction band is equal to the fundamental band gap (E_g). If the conduction band minimum and valence band maximum occur at the same value of k , then a photon of energy E_g is sufficient to create an electron-hole pair. This type of semiconductor is called a direct band gap material. If the conduction band minimum and valence band maximum occur at different values of k , then, to excite an electron from valence band to conduction band, a photon of energy E_g is not sufficient, a change in momentum is also required. In a crystal, as the momentum is conserved and a photon does not possess momentum, the change in momentum can be supplied by phonons (a lattice vibration). The photon can be only absorbed when there is enough momentum can be provided, such a material is called indirect band gap material, which normally has lower absorption than direct band gap material.

2.1.2 Charge-Carrier Dynamics: Photogeneration, Thermalisation, Relaxation and Recombination

In this section, different charge-carrier dynamics will be discussed when a single photon with energy above the bandgap is being absorbed. The process of photogeneration, thermalisation, relaxation and recombination will be introduced.

Photogeneration is an electronic excitation event which increases the number of free carriers available to carry charge. It requires an input of energy such as photon absorption. Usually, generation would be the promotion of an electron from valence to conduction band, which generates an electron-hole pair. It also could be from valence band into a localised state in the band gap, or localised state to conduction band.

Thermalisation: After the carriers are excited to the energy states above the bandgap, the excited hot electrons (or hot holes) share the same energy matching the absorbed photon energy, forming a non-thermal equilibrium state (undefined) in the conduction band (or valence band) (Figure 2.2a, process 1-2). These hot electrons (or hot holes) undergo carrier-carrier collisions and intervalley scattering to form a Fermi-Dirac distribution (quasi-Boltzmann distribution). The two Boltzmann distributions of electrons and holes may refer to different electron or hole temperatures showing the respective distributions of the kinetic energy of electrons and holes (Figure 2.2a, process 3). This charge-carrier thermalisation occurs very rapidly with a time scale of less than 100 fs¹⁵.

Relaxation: After thermalisation, Boltzmann distributions are established among the carriers, but the carriers are still not yet in equilibrium with the lattice. hot carriers interact with the lattice primarily through longitudinal-optical (LO) phonon emission on a sub-picosecond timescale. This leads to the cooling of carriers and heating of the crystal lattice, transforming kinetic energy into heat. Finally, the whole system reaches

thermal equilibrium, with charge-carrier distributions sharing the same temperature as the lattice temperature, and electrons and holes are cooled to the edges of the conduction band and the valence band ((Figure 2.2a, process 4), and then undergo recombination processes, the recombination process can also happen before the entire population has cooled to the band edges.

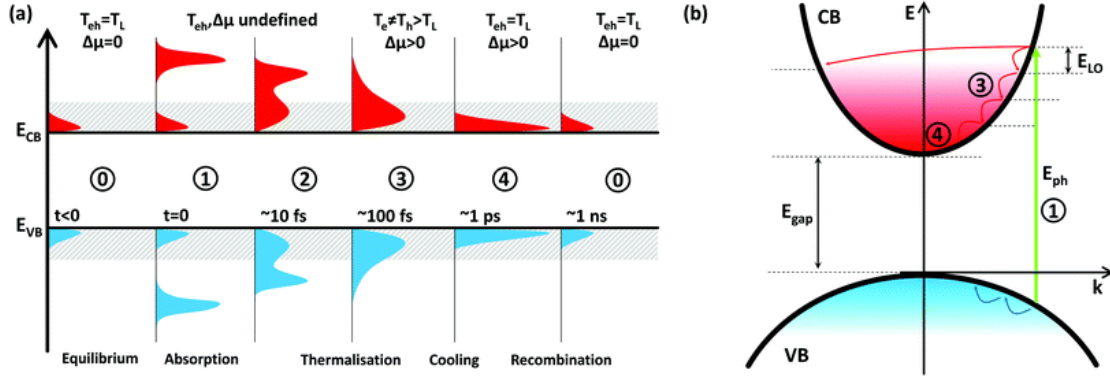


Figure 2. 2 Schematic of the charge carrier distribution in the valence (VB) and conduction band (CB) of an arbitrary semiconductor with a narrow band gap (a). When in equilibrium (0), charge carriers are thermally excited into the bands and have the same temperature as the lattice. Photoexcitation promotes an excess amount of electrons into the CB and holes into the VB (1). Ultrafast elastic carrier-carrier scattering will set in (2) and transform the non-equilibrium carrier distribution to a thermal distribution of hot carriers in the CB/VB (3). Carrier cooling (4) will equilibrate the temperatures before eventual carrier recombination. The schematic in (b) displays the cooling for electrons and holes in parabolic bands of unequal curvature (thus different carrier effective masses). In polar materials, the initial energy loss predominantly occurs through the emission of longitudinal optical phonons (E_{LO}) and many classical materials exhibit slow cooling only for hot electrons. Reproduced with permission under Creative Commons Attribution-Non Commercial 3.0 Unported Licence from Ref. ¹⁵

Recombination is an electronic relaxation event of the electrons and/or holes that results in the annihilation of the photogenerated charge-carriers. Recombination can involve energy transitions from band-to-band, or involve energy transitions via defect

trap states. The energy released can in the form a photon (radiative recombination), or as heat through phonon emission (defect-assisted non-radiative recombination) or as kinetic energy to another free carrier (Auger Recombination) (Figure 2.3).

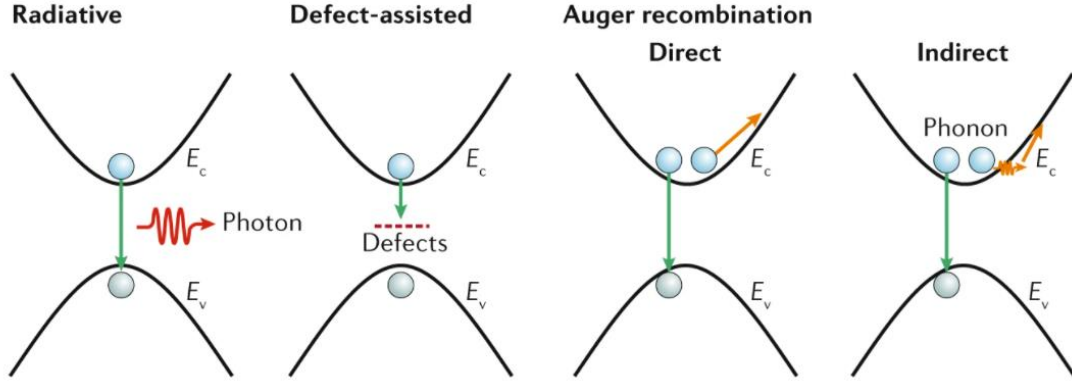


Figure 2. 3 Charge Carrier Recombination Process. Radiative recombination is when charge-carrier recombine and emit photons. Defect-assisted recombination is when charge-carrier recombine in traps and do not emit photons. Auger recombination is when more than two charge carriers, e.g. two electrons and a hole, or two holes and a electrons, collide. For direct Auger process, the energy would be given to the carrier with the same polarity and promote it to higher kinetic energy. For indirect Auger process, the excess energy would be given up as heat or phonons. Reprint with permission from Ref.¹⁶ Copyright © 2019, Springer Nature Limited

Radiative recombination can be classified into unavoidable recombination processes due to optical generation, spontaneous and stimulated emission. For photovoltaics, radiative recombination occurs when the photogenerated electrons in conduction band relax and recombine with the holes in valence band to emit photons. The rate of radiative recombination rate can be simplified by the following equation (eq. 2.7):

$$U_{rad} = B_{rad}(np - n_i^2) \quad (2.7)$$

where U_{rad} is the rate of radiative recombination, B_{rad} or k_2 is the radiative recombination coefficient that is carrier density independent (it is a temperature dependent material property), n and p are the free electron and hole concentration and

n_i is the intrinsic carrier concentration. In other words, radiation recombination is an unavoidable process. A semiconductor with a higher absorption coefficient will have a higher population of photogenerated charge-carriers (large np product), which leads to a higher radiative recombination rate.

Trap-assisted Recombination: In comparison with unavoidable radiative recombination, Trap-assisted (Shockley Read Hall) recombination occurs via trap states, and so could, in principle, be avoided in a semiconductor if all trap states within the band gap could be eliminated. In a band diagram, trap states are represented as a horizontal line to show that these are localised states with no dispersion, and charge-carriers reaching these states are localised spatially, unless they can be energetically promoted to a band state through light absorption or thermal activation. But if the trap captures a charge-carrier of the opposite polarity before the first carrier is released, then annihilation occurs. The term *traps* is usually used to refer to states which capture one type of charge-carrier. If the trap can capture both types of charge-carrier, it is called a recombination center. The following equation defines the rate of trap-assisted (k_1) recombination (U_{SRH}) for a semiconductor with one trap state (eq. 2.8):

$$U_{SRH} = \frac{np - n_i^2}{\tau_{n,SRH}(p + p_t) + \tau_{p,SRH}(n + n_t)} \quad (2.8)$$

where $\tau_{n,SRH} = \frac{1}{N_t \sigma_{t,e} v_{th,e}}$ and $\tau_{p,SRH} = \frac{1}{N_t \sigma_{t,h} v_{th,h}}$, they are the lifetime of the carriers captured by the trap (the lifetime is inversely proportional to trap density, N_t , carrier mean thermal velocity, $v_{th,e}$ (*electron*) and $v_{th,h}$ (*hole*) and trap capture cross section, $\sigma_{t,e}$ (*electron*) and $\sigma_{t,h}$ (*hole*)), n_t and p_t are the carrier density when the Fermi level is equal to the trap level, $n_t = n_i \exp\left(\frac{E_t - E_i}{kT}\right)$ and $p_t = n_i \exp\left(\frac{E_t - E_i}{kT}\right)$, the density of carriers are related to the trap energy position, E_t . For doped materials, this equation can be further simplified into: $U_{SRH} \approx \frac{n - n_0}{\tau_{n,SRH}}$ (for p-type material), $U_{SRH} \approx \frac{p - p_0}{\tau_{p,SRH}}$ (for n-type material), where n_0 and p_0 are thermal equilibrium carrier concentrations.

Auger recombination occurs when a collision occurs between two similar carriers, causing the excitation of one carrier to higher kinetic energy, and the recombination of the other across the band gap with a carrier of opposite polarity. For direct Auger recombination, the recombination releases the kinetic energy to the other carrier and excite it to higher energy state. For indirect Auger recombination, the energy which is released through recombination is given up as heat or phonon energy to the other carrier. If the Auger recombination is band-to-band with an electron and two holes or a hole and two electrons, the rate of recombination is proportional to the densities of all three carriers (e.q. 2.9):

$$U_{Aug} = A_n(n^2p - n_0^2p_0), \quad U_{Aug} = A_p(p^2n - p_0^2n_0) \quad (2.9)$$

Where U_{Aug} or k is the rate of Auger recombination, A is the recombination coefficient for carriers in n-type or p-type materials, n_0 and p_0 are thermal equilibrium carrier concentrations.

Overall recombination rate for free carrier dominant systems. The trap-assisted recombination rate is related to either electron density or hole density based the type of doping material if the doping density is significantly higher than the major carriers and the product of minor carrier lifetime and doping density is higher than the lifetime of major carrier lifetime and minor carrier density. In other word, U_{SRH} is proportional to only the excess carrier density (first order). In contrast, U_{rad} is related to both n and p , i.e. it is a second order term with respect to carrier density. U_{Aug} involves two similar carriers and one carrier with opposite polarity, i.e. it is a third order term. Hence, the overall rate of recombination can be expressed as (eq. 2.10):

$$\frac{dn}{dt} = -k_1n(t) - k_2n(t)^2 - k_3n(t)^3 \quad (2.10)$$

where k_1, k_2 and k_3 are the first order, second order and third order rate constants associated with defect-assisted (Shockley Read Hall), radiative (bimolecular) and

Auger (three body) recombination respectively, and n refers to photo-generated carrier density.

2.1.3 Excitons

The Coulombic attraction between a negatively charged electron, e.g. excited in the conduction band, and the positively charged hole, for example the vacancy left in the valence band upon excitation, causes the electron and hole motion to be correlated. The resulting electron-hole pair is called an exciton and the total energy of the system is thus reduced compared to the separate electron and hole energies.

Here, I discussed two types of excitons depending on the strength of electron-hole interaction, *Frenkel* exciton and *Wannier-Mott* exciton. In the limit of a *Frenkel* exciton, the electron-hole pair is highly localised to within one or two unit cells of an ionic crystal, or a single molecule. In contrast, *Wannier-Mott* excitons have weakly bound electron-hole pair, such that electrons and holes are delocalised over a large number of crystalline unit cells. This usually requires large dielectric constants in the medium enabling effective charge screening. The exciton binding energy E_b can be calculated by eq. 2.11:

$$E_b = -\frac{\mu^* R_H}{m_0 \epsilon_r^2 n^2} \quad (2.11)$$

Where μ^* is the reduced effective mass, R_H is the hydrogen atom Rydberg constant (13.6 meV), m_0 is the electron rest mass (9.11×10^{-31} kg), ϵ is the dielectric constant of the material and the integer principal quantum number n . The Bohr radius of the exciton can be estimated based on eq. 2.12 similar to hydrogen atom Bohr radius (a_H):

$$a_X = \frac{m_0 \epsilon_r n^2 a_H}{\mu^*} \quad (2.12)$$

In practice, the binding energy can be estimated based on the steady-state absorption measurement using Elliott model. To extract exciton binding energy (E_b), the absorption spectra can be fitted to include both lowest-energy 1s excitonic transition states (α_b) and unbound continuum absorption states (α_c) based on Elliott model (e.q. 2.13)

$$\alpha(\hbar\omega) = A \cdot \Theta(\hbar\omega - E_g) \cdot D_{CV} \cdot \left(\frac{\pi e^{\pi x}}{\sinh \pi x} \right) + A \cdot E_b \sum_{n=1}^{\infty} \frac{4\pi}{n^3} \delta \left(\hbar\omega - E_g + \frac{E_b}{n^2} \right) \quad (2.13)$$

Where $\alpha(\hbar\omega)$ is absorption, E_g is the bandgap, E_b is the exciton binding energy n is positive integer associated with order of exciton electronic states, δ is a Dirac delta function. The first term related to the exciton-related absorption, and the second term is the contribution from the continuum states.

Overall recombination rate for exciton dominant systems. For exciton dominant system such as 2D materials, the rate equation is shown in eq. 2.14:

$$-\frac{dn_{ex}}{dt} = k_{rad}n_{ex}(t) + \frac{1}{2}k_{ann}n_{ex}(t)^2 \quad (2.14)$$

where n_{ex} is the density of photo-generated excitons, k_{rad} is the total monomolecular recombination rate including monomolecular trap-assisted recombination and radiative recombination. k_{ann} is the exciton-exciton annihilation rate, analogous to Auger recombination. The formation of the exciton and the free carrier equilibrium can be studied by Saha equation, which will be discussed later in section 2.3.2 about perovskite LED device.

2.2 Material Background

2.2.1 Semiconductor Quantum Dots

Compared with bulk semiconductors with infinite number of unit cells with long range crystalline order, semiconductor quantum dots have limited number of unit cells. The long-range ordered unit cell lattice is usually cut-off by the surroundings organic ligands. As a result, the actual optical bandgap of the quantum dots (QDs) are also governed by the size and dielectric mismatch between the lattice and ligands, i.e. size confinement and dielectric confinement effect. Figure 2.4 demonstrates quantised energy diagram and emissions from CdSe QDs with different sizes.

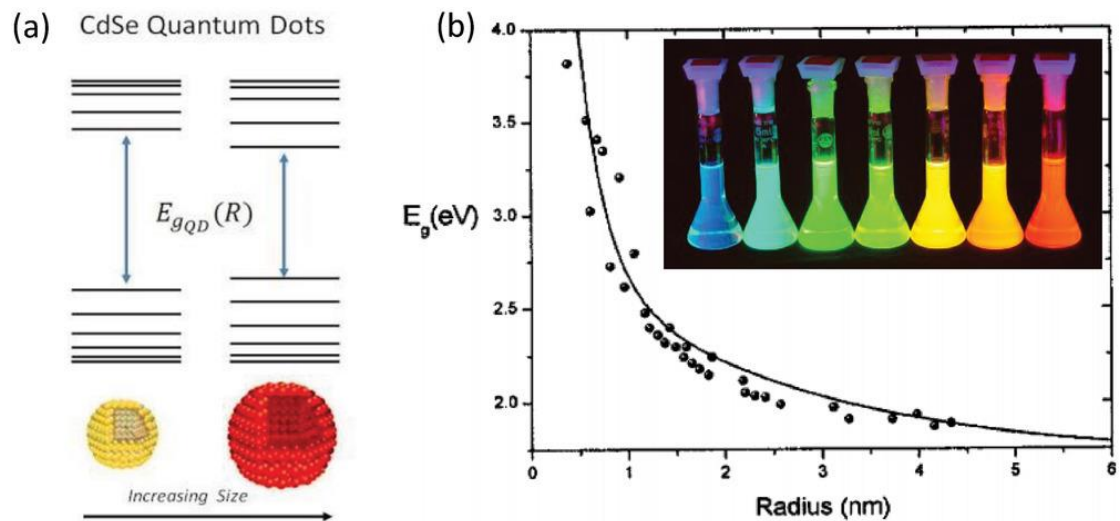


Figure 2. 4 a) Schematic illustration of the band structure of CdSe QDs of two different sizes. b) Energy bandgap dependence on the radius of CdSe QDs, here dots are the experimental data and the solid line is the calculated data .The inset shows photograph of core/shell CdSe/ZnS QDs of different sizes (synthesised at University of Hamburg in 2001) emitting all over the visible spectral range. Reproduced with permission.¹⁷ Copyright 2006, American Institute of Physics.

For **quantum size confinement**, we consider the ‘particle-in-a-sphere model’. The model has been successfully employed for the description of nanocrystals in the early pioneering work by Efros¹⁸ and Brus¹⁹:

We consider a particle of mass m_0 inside a spherical potential of radius a , $V(r) = 0$, when $r < a$; and $V(r) = \infty$, when $r > a$. The possible particle energy can be calculated by equation 2.15:

$$E_{n,l} = \frac{\hbar^2 k_{n,l}^2}{2m_0} = \frac{\hbar^2 a_{n,l}^2}{2m_0 a^2} \quad (2.15)$$

Where $k_{n,l}$ is the wavevector, n (1, 2, 3 ...) and l ($s, p, d \dots$) are quantum number. $E_{n,l}$ is the energy associated with the specific quantum states inside the quantum dots, $\hbar$ is the Planck constant and m_0 is the mass of electrons. It shows that electrons in confined space have quantised energies. The energies are identical to that of the kinetic energy of a free particle, but quantised by the boundary condition set by the potential well in discrete values of the wavevector $k_{n,l}$.

In order to apply this model to semiconductor nanocrystals, we assume bulk isotropic valence(v) and conduction (c) bands that can be described by the ‘effective mass approximation’. Where the energy of the valence band can be approximated as $E_k^v = -\frac{\hbar^2 k_{n,l}^2}{2m_{eff}^v}$, and the energy of the conduction band can be approximated as $E_k^c = \frac{\hbar^2 k_{n,l}^2}{2m_{eff}^c} + E_g$, where the carriers are described as free particles with effective mass $m_{eff}^{v,c}$.

Therefore, taking account the bulk bandgap energy (E_g) and Coulomb energy correction (E_C), the confinement leads to an exciton energy with lowest pair states $n=1$ and $l=s$ shown in equation 2.16:

$$E_{EX} = E_g + \frac{\hbar^2}{2m_0 a^2} \left(\frac{a_{1,s}^2}{m_{eff}^v} + \frac{a_{1,s}^2}{m_{eff}^c} \right) - E_C \quad (2.16)$$

For dielectric confinement, the localization of charge carriers in QD is strongly affected by the polarizability of the surrounding polar lattice. These self-energy contributions are enhanced in nanostructures by dielectric inhomogeneities. Hence, it will influence the electron-hole interactions, as the wavefunction of the carriers would be screened by the surrounding materials. For QDs or 2D layered materials with organic spacers or ligands, the dielectric confinement effect occurs when the dielectric constant of the inorganic layer is larger than the dielectric constants of the neighbouring organic layer. In the inorganic layer, the electrostatic forces between electrons and holes are increased because the electric field lines between the charges extend into the organic layers, where they are less effectively screened, resulting in stronger attraction between the carriers. Larger differences in dielectric constant result in increased exciton binding energy, as well as increases in the electronic band gap owing to larger changes in the energy levels as the electrostatic forces change²⁰.

To quantify the effect of confinement, Bohr radius (a_B) would be a useful parameter to compare with the size of the particles. $a_B = \varepsilon \frac{m_0}{m^*} a_0$, where ε is the material's dielectric constant, m_0 is the electron rest mass, m^* is the particle's effective mass, and a_0 is the hydrogen atom Bohr radius. Generally, three different limits can be considered, depending on the individual system's dominating optical properties:

1. The strong confinement regime: If the nanocrystal radius a is much smaller than the electron, hole, or exciton Bohr radius, the electron and hole are strongly spatially confined within the material object's boundaries.
2. The weak confinement regime: When a is larger than the individual Bohr radii of the electron and hole, but smaller than that of the exciton, only the exciton's centre of mass motion will be confined.

3. The intermediate confinement regime: Here, a is in between the electron's and hole's Bohr radius, thus only one type of charge carrier, e.g. the hole, is strongly confined while the other is not.

2.2.2 Metal-Halide Perovskite Quantum Dots

The earliest work on metal halide perovskites (MHPs) was conducted in the late 1800s by Wells,²¹ while the detailed structural characterisation was carried out by Weber in the 1900s.²²⁻²⁴ Their potential applications in electronic and optical devices have attracted attention in the late 1990s and the early 2000s, long before captivating the broad scientific community.^{25,26} In 2009, Kojima *et al.*²⁷ demonstrated the use of lead halide perovskites (LHPs) as visible-light sensitisers in solar cells, but it took another three years to fully grasp their potential for highly efficient photovoltaics.^{28,29} Since then, the number of researchers working on MHPs has been increasing significantly over the years, accompanied by a substantial increase in research output in this area. The high efficiency of LHP photovoltaic cells is attributed to long charge carrier diffusion lengths along with low Urbach energies, high photoluminescence quantum yields and high absorption coefficients.^{30,31} These significant features are of interest not only for the device communities, but also for the chemistry, physics and materials research communities. Over the last decade, numerous advances have been made towards the fundamental understanding as well as potential applications of MHPs. The certified power conversion efficiency (PCE) of single-junction perovskite-based solar cells has surpassed 25% in a short span of time, demonstrating an order of magnitude higher rate of improvement compared to other photovoltaic technologies.³² MHPs have recently emerged at the forefront of materials research not only because of their impressive photovoltaic performance but also due to their attractive optical and electronic properties.^{30,31,33-50} Over the years, they have already shown great promise in a wide range of technological applications encompassing photovoltaics (PVs), light-emitting diodes (LEDs), lasers, transistors, photodetectors and photocatalysts.^{47,51-66}

The optical and electronic properties of MHPs were shown to be strongly dependent on their dimensionality (both structural and morphological).^{26,34,36,38,42,50,67-70}

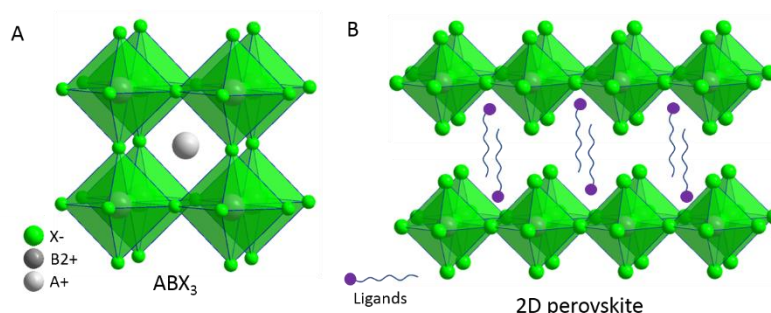


Figure 2. 5 Illustrations of cubic crystal structure of a, 3D perovskites, b, 2D layered perovskites. Reprint with permission under Creative Common Licence from Ref.⁷¹ Copyright © 2021 American Chemical Society

Three-dimensional (3D) MHPs refer to a class of crystalline compounds adopting the generic chemical formula ABX₃, where the cation “B” has six nearest-neighbour anions “X”, while the cation “A” sits in a cavity formed by eight corner-shared BX₆ octahedra.^{30,72,73} MHPs are generally classified into either organic-inorganic hybrid (OIH) or inorganic perovskites depending on whether the A-site cation is organic or inorganic. OIH perovskites generally have methylammonium (MA) or formamidinium (FA)) as the monovalent A-site cation, lead, tin, or germanium as the divalent B cation, chlorine, bromine, iodine, or their combinations as the halide ion (X). On the other hand, inorganic perovskites have cesium (Cs) or rubidium (Rb) as the A cation. The ideal structure of the perovskite, which is illustrated in Figure 2.5a, is based on a cubic lattice. However, the deviation from the ideal perovskite structure in ABX₃ materials can be predicted through the Goldschmidt tolerance factor t ($t = (r_A + r_X)/[\sqrt{2}(r_B + r_X)]$), where r_A , r_B and r_X are the ionic radii of the corresponding ions, t is defined as the ratio of the distance A-X to the distance B-X). Unlike classical semiconductors (such as Ge, Si, GaAs, CdS, CdSe, InP), high-quality MHPs can be prepared by simply mixing the corresponding precursor solutions at room temperature (RT) under ambient conditions

due to their inherent ionic character.^{49,74,75} The optical properties of MHPs are easily tunable across the visible spectrum of light by simply varying the halide composition.^{50,76-78} While the bulk properties of MHP are significant, decreasing the size of the crystals to the nanoscale reveals their size-dependent optical and electronic properties. For instance, nanosized crystals (nanocrystals, NCs) of MHP exhibit quantum confinement effects that can be exploited to tune the optical properties,^{34,36,39,42} much like in other semiconductors.^{79,80} The structural dimensionality of MHPs is easily tunable from 3D to 2D using long-chain alkylammonium cations in their synthesis (Figure 2.5b). The emission wavelength and exciton binding energies of these layered perovskites are controllable by the number of octahedral layers between the long-chain organic layers ($n = 1$ to ∞).^{69,81,82} The tunable emission wavelength, narrow emission, and low nonradiative losses of MHPs make them potential candidates for LEDs. In addition, the long charge carrier diffusion lengths in MHPs facilitate efficient recombination of electrically injected charge carriers. Bulk perovskites suffer from low photoluminescence quantum yields (PLQYs) due to inherent defects, particularly those present at grain boundaries, surfaces and interfaces.^{35,83,84} On the other hand, MHP NCs emerged as extremely efficient light emitters with near-unity PLQY. Typical MHP NC solution under illumination can be shown in Figure 2.6.



Figure 2. 6 Photograph of the colloidal dispersions of CsPbX₃ NCs with different halide (X=Cl, Br, and I) Reprint with permission under Creative Common Licence from Ref. ⁷¹ Copyright © 2021 American Chemical Society

Apart from the compositional control to the colour, controlling the size of the NCs can also tune the emission wavelength. The optical and electronic properties of halide perovskites are also tunable by accessing quantum confinement effects in these materials, which can be achieved by reducing the size of at least one dimension below the Bohr diameter (~ 7 nm for CsPbBr₃).^{34,71,85} Among all, 2D and quasi-2D nanoplatelets (NPLs) have been receiving special attention owing to their thickness-dependent optical properties caused by the 1D spatial confinement of charge carriers.^{36,67,81,86,87} Halide perovskite NPLs generally exhibit narrow absorption and emission (fwhm ~ 10 -15 nm) features with small Stokes shift (< 10 meV), regardless of their lateral dimensions, meaning that the emission wavelength is mainly dependent on the thickness of the NPLs, while it is less dependent on their lateral dimensions.^{36,38,81,86-88} Thus 2D NPLs exhibit blue-shifted emission compared to their bulk counterparts, and the extent of the blue-shift depends on their thickness. As the NPLs get thinner, they no longer possess an ABX₃ chemical composition, instead, they can be represented with the composition L₂[ABX₃]_{n-1}BX₄, where L is a ligand (long-chain alkylammonium cation), and n is the number of octahedral monolayers (MLs).⁸⁶ The monolayer (ML) refers to the 2D layer of PbX₆⁴⁻ octahedra, as illustrated in Figure 2.7a and b.

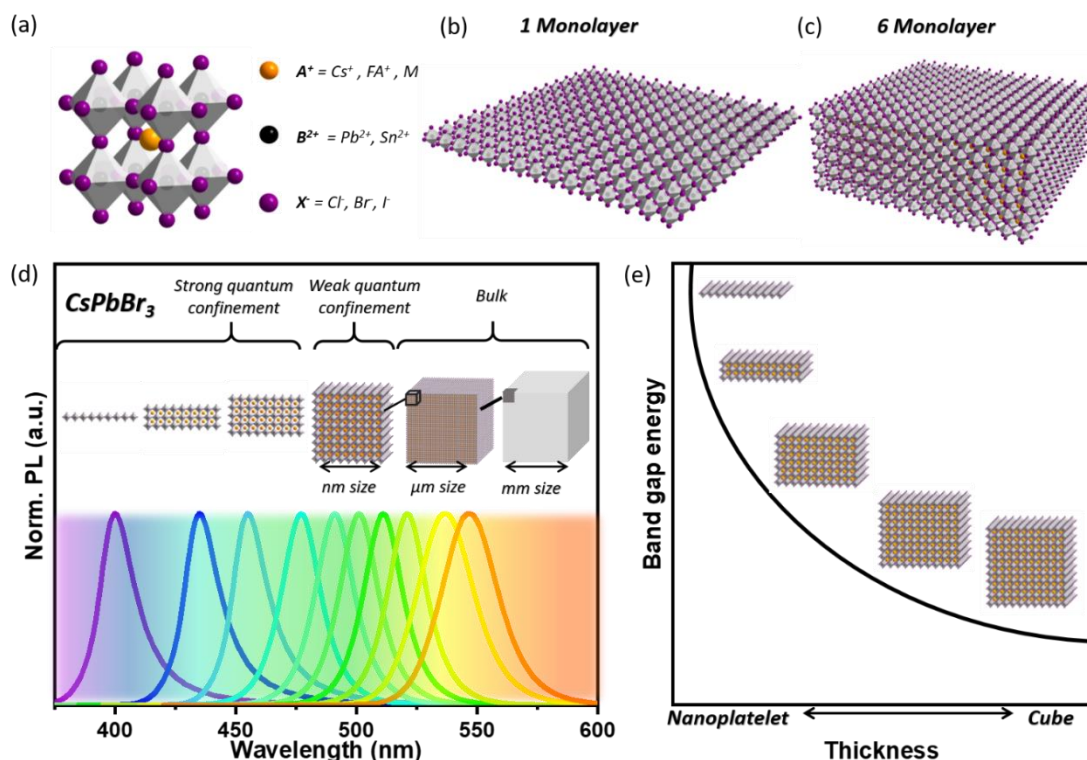


Figure 2. 7 (a) Typical cubic crystal structure of ABX_3 perovskites (A =methylammonium (MA) or formamidinium (FA) or cesium (Cs) cation, B =lead (Pb) or Tin (Sn) divalent cation, X =chloride, bromide or iodide). (b & c) Schematic illustration of a monolayer and a six-layer perovskite NPLs. (d) Spectral illustration of the approximate PL spectra for bulk, weakly-confined nanocubes and nanoplatelets of $CsPbBr_3$. All spectra are manually drawn based on the literature reports. (e) Schematic representation of the thickness-dependent emission energy of lead halide perovskite NPLs. Reproduced with permission from Ref.⁸⁹ © 2022 The Authors. Advanced Materials published by Wiley-VCH GmbH

The thickness of colloidal perovskite NPLs is precisely controllable from a strongly quantum-confined monolayer (Figure 2.7b) to weakly quantum-confined few monolayers (Figure 2.7c).^{36,86-88,90} Figure 2.7d illustrates the expected photoluminescence (PL) spectra for bulk, weakly-confined nanocubes, and nanoplatelets of $CsPbBr_3$.^{38,50,81,87,90} According to literature survey, bulk single-crystals (millimeter and micron size) and polycrystalline thin films of $CsPbBr_3$ exhibit weak PL in the range of $\sim 530-560$ nm,⁹¹⁻⁹⁵ while the corresponding nanocubes ($\sim 8-12$ nm)

exhibit a strong PL peak in the range of ~510-520 nm.^{34,50,81} The PL peak of nanocubes compared to bulk single crystals suggest that the nanocubes are weakly quantum-confined. On the other hand, the CsPbBr₃ NPLs exhibit further blue-shifted emission compared to nanocubes and their PL peak varies between ~400-500 nm depending on their thickness (Figure 2.7d).^{38,81,87} For instance, monolayer CsPbBr₃ NPLs exhibit PL ~400 nm, which is significantly blue-shifted compared to nanocubes, suggesting strong quantum confinement.⁹⁰ Figure 2.7e illustrates the thickness-dependent emission energy trend for lead halide perovskite NPLs. As the thickness of the NPL decreases, the emission energy nonlinearly increases due to the strong quantum confinement of thinner NPLs.⁸¹ Similarly, the emission wavelength for CsPbI₃ NPLs is tunable from ~525-700 nm by controlling their thickness.³⁸ Thus, the emission color is tunable across the visible wavelength range by controlling the thickness of bromide and iodide-based lead halide perovskite NPLs.³⁸ The detailed studies on CsPbI₃ NPLs will be discussed in Chapter 6 .

2.2.3 Surface Chemistry and Defects

Surface chemistry plays a critical role on the optical, electronic properties and stability of MHPs. Therefore, the surface chemistry of LHPs has been heavily investigated, but is still not fully understood.⁹⁶⁻¹⁰⁰ During the perovskite thin-film crystallization process, its surface can terminate either with PbX₂, AX or both depending on the film processing conditions.⁹⁷ The electronic band structure of the surface could be different from that of bulk and the type of surface termination can significantly influence the band alignment with other molecular systems.^{97,101,102} Although AX termination is thermodynamically stable, it can be changed to PbX₂ when organic-inorganic hybrid perovskite films are exposed to moisture due to the differences in interaction with water molecules. This is because the AX termination can undergo fast hydration as compared to PbX₂ termination because of the stronger, more covalent Pb-X bond.

However, the presence of higher humidity can lead to complete hydration of the surface regardless of the type of surface termination. In order to improve the stability of MHP films by increasing the surface resistance to moisture, long-chain alkylammonium halide molecules have been incorporated into perovskite films giving rise to 2D halide perovskites.¹⁰³ These molecules can also passivate the surface defects in MHP films. Like in classical semiconductors, two of the main classes of defects are point defects (atomic-scale) and structural defects. Compared with a perfect lattice (Figure 2.8 a i), point defects (native defects) include vacancies (atoms absence from their lattice sites; Figure 2.8 a,ii-iv), interstitial defects (atoms located between lattice sites; Figure 2.8 a,v-vii) and anti-site defects (atoms occupying another species' lattice site; Figure 2.8 a,ix-xiv). Structural defects (extended defects) include dislocations (Figure 2.8 a,xv) and GBs (Figure 2.8 a,xvi). In addition, defect complexes can occur. These include Schottky defects (pair of anion and cation vacancies; Figure 2.8 a, xvii) and Frenkel defects (a pair of an interstitial and a vacancy created from the same ion; Figure 2.8 a, xviii). Beyond these intrinsic defects, extrinsic impurities can also occur (Figure a, viii,2.8 xix). Unlike conventional semiconductors such as Si, CdTe or GaAs, which require low defect concentrations to mitigate the deleterious effects of their deep traps, the common point defects in perovskites (A- and X-site vacancies) are usually shallow level defects (at least for Br- or I-based perovskites) and are not detrimental to their device performance. Point defects with deep traps state such as interstitial or anti-site defects are almost absent in perovskites since they have high formation energies.⁴³ Therefore, the types of defect which we should consider during synthesis and passivation would more likely to be uncoordinated Pb^{2+} ions and surface charged defects.

On the other hand, the surface chemistry of colloidal perovskite NCs is more complex in the presence of capping ligands on the surface (Figure 2.8b).^{97-100,104} Most often, long-chain amines in combination with a long chain acid have been used as ligands in the synthesis of colloidal perovskite NCs. One of the most commonly used amine-acid

pair is oleylamine and oleic acid. In this base-acid pair, the proton is exchanged from acid to amine, leading to the formation of an ammonium cation ($R-NH_3^+$), which then occupies the A site positions on the NC surface (Figure 2.8b). Theoretical studies suggest that ammonium cation ligands replace 50% of the ‘A’ cations on the NC surface and these ligands help to maintain the colloidal stability of perovskite NCs in nonpolar solvents.¹⁰⁵ Furthermore, it was shown experimentally through X-ray photoelectron spectroscopy (XPS) and ^1H nuclear magnetic resonance (NMR) measurements that the ($R-NH_3^+$) binds to the surface of $CsPbBr_3$ NCs by replacing most of the Cs^+ cations and forming hydrogen bonds with Br^- anions.¹⁰⁰ However, interestingly, it was argued that the $R-COO^-$ ions do not bind to the NC surface, but plays an important role in the colloidal stability of $CsPbBr_3$ NCs by forming an equilibrium with surface-bound $R-NH_3^+$ ions and maintains charge neutrality.¹⁰⁰ In contrast, the quantitative ^1H NMR studies by Smock *et al.* suggest that both the oleylamine and oleic acid ligands bind to the surface of $CsPbBr_3$ NCs.⁹⁸ Similarly, De Roo *et al.*, using ^1H NMR spectroscopy, showed that oleic acid binds to the NC surface in the form of oleylammonium oleate only when excess oleylamine was added to the purified NC solution and this helps to improve the PLQY.⁹⁶ Another hypothesis is that the long-chain carboxylic acid molecules replace some of the surface halides to complete the octahedral coordination of lead, and thus passivates the mid-gap traps (figure 2.8b).⁹⁹ Amine-free synthesis methods were also reported, in which the nanocrystals were solely capped by oleic acid,^{106,107} this results in colloidal $CsPbBr_3$ NCs with only oleate-terminated surfaces. Although the role of oleic acid in the colloidal stability of perovskite NCs is being debated, it is widely accepted that alkylammonium cation ligands bind to the surface of perovskite NCs. However, the ligand binding to perovskite NC surface is highly dynamic and therefore the surface is properly passivated only in the presence of excess free ligands in the solution. Because they are labile, surface ligands often desorb from the perovskite NC surface upon ageing, dilution or purification by washing and these processes lead to the formation of surface defects, and thus a reduction in PLQY (Figure

2.9a).⁹⁶ It is worth mentioning that a small amount of additional ligands need to be added during the purification for maintaining the colloidal stability and high PLQY of perovskite NCs.⁹⁶ To overcome these difficulties, various ligands such as quaternary alkylammonium cations, alkyl phosphonates, and zwitterionic molecules have been tested as alternatives to the oleylamine/oleic acid pair (Figures 2.8b, Figure 2.9b).¹⁰⁸⁻¹¹⁵ It is well-established that the stability and PLQY of perovskite NCs strongly depend on the capping ligands binding affinity. Recent studies suggest that the ligands with multiple functional groups with opposite charges (e.g. zwitterionic molecules such as 3-(*N,N*-dimethyl-octadecylammonio)-propanesulfonate) tightly binds to perovskite NC surface and thus significantly improves their stability. It was hypothesised that the ammonium cation of the zwitterionic molecules occupies A-site position, while the carboxylate or sulfonate group simultaneously bind to uncoordinated Pb to complete its octahedral coordination (Figure 2.8b). In this regard, Krieg *et al* demonstrated that the CsPbBr₃ NCs capped with zwitterionic molecules could be washed multiple times without hampering the PLQY and chemical stability, suggesting that these type of ligands bind strongly to perovskite NC surface.¹¹⁴ In principle, perovskite NCs also exhibit similar types of defects as in bulk thin films shown in Figure 2.8a. Additionally, perovskite NCs exhibit surface vacancies caused by the desorption of ligand molecules (Figure 2.8b). The origin of the surface defect formation is then studied in chapter 4.

The defects in both thin films and NCs can cause either shallow or deep states in the electronic band structure. Defects in a specific material is generally studied by calculation of their formation energies in different charge states. It has been said that the vacancies (A, Pb and X point defects) in perovskites form shallow traps due to their low formation energy^{116,117}. The common types of defects which act as non-radiative recombination centres observed in perovskite films include Pb vacancies and metallic Pb₀ interstitials¹¹⁸, halide vacancies and interstitials¹¹⁹. All of these defects would quench the PL^{120,121}.

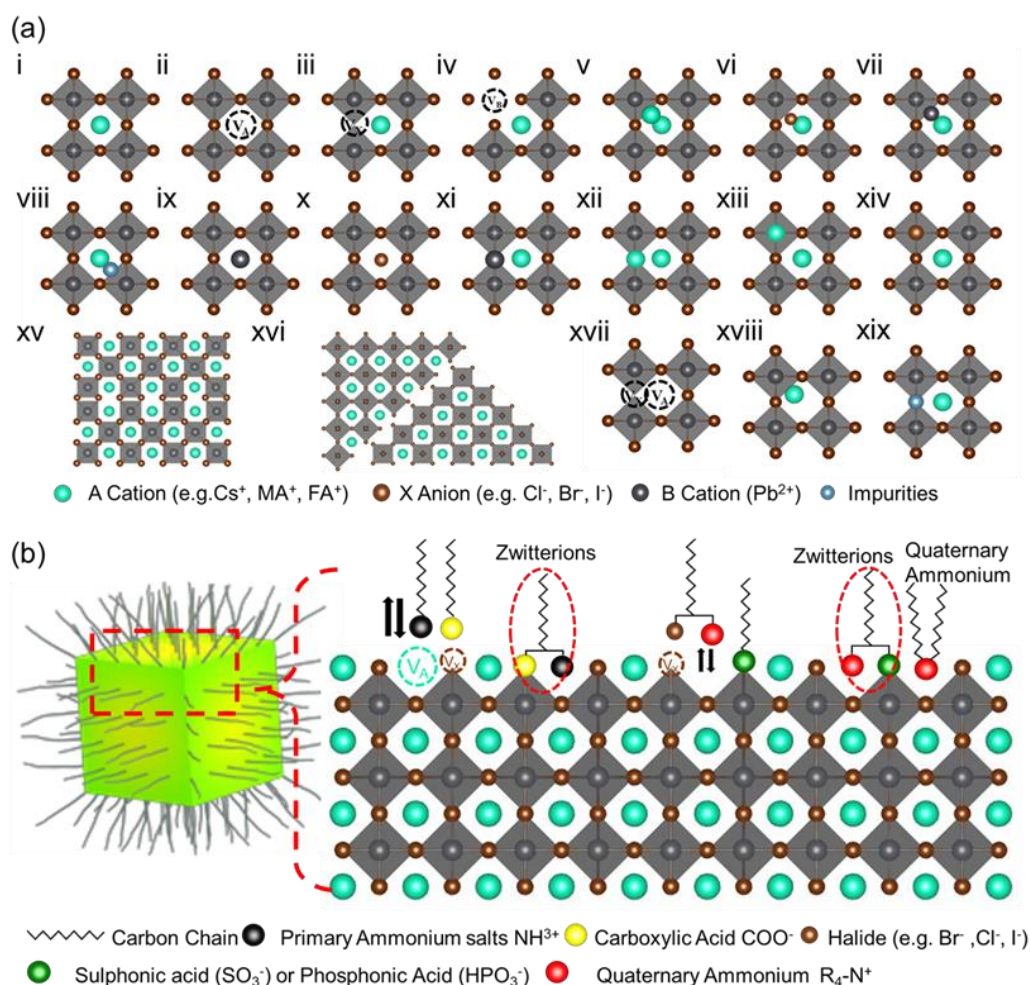


Figure 2. 8 Defects in lead-halide perovskites. (a) Types of defects in lead-halide perovskites, (i) perfect crystals (ii) A-site vacancy (iii) X-site vacancy (iv) B-site vacancy (v) A-site interstitial (vi) X-site interstitial (vii) B-site interstitial (viii) impurity interstitial (ix) AB anti-sites (x) AX anti-sites (xi) XB anti-sites (xii) XA anti-sites (xiii) BA anti-sites (xiv) Bx anti-sites (xv) lattice dislocations (xvi) grain boundary defects (xvii) Schottky defect (anion and cation vacancies occurring together) (xviii) Frenkel defect (interstitial and vacancy created from the same ion) (xix) impurity substitution b) Schematic illustration of the ligand capped LHP nanocrystal and its zoom-in view of the nanocrystal surface with defects and different types of surface ligands used for stabilization of NCs, including alkylammonium, carboxylic acid, and zwitterions such as amino acids. Reprint with permission under Creative Commons CC BY license from Ref. ¹²²

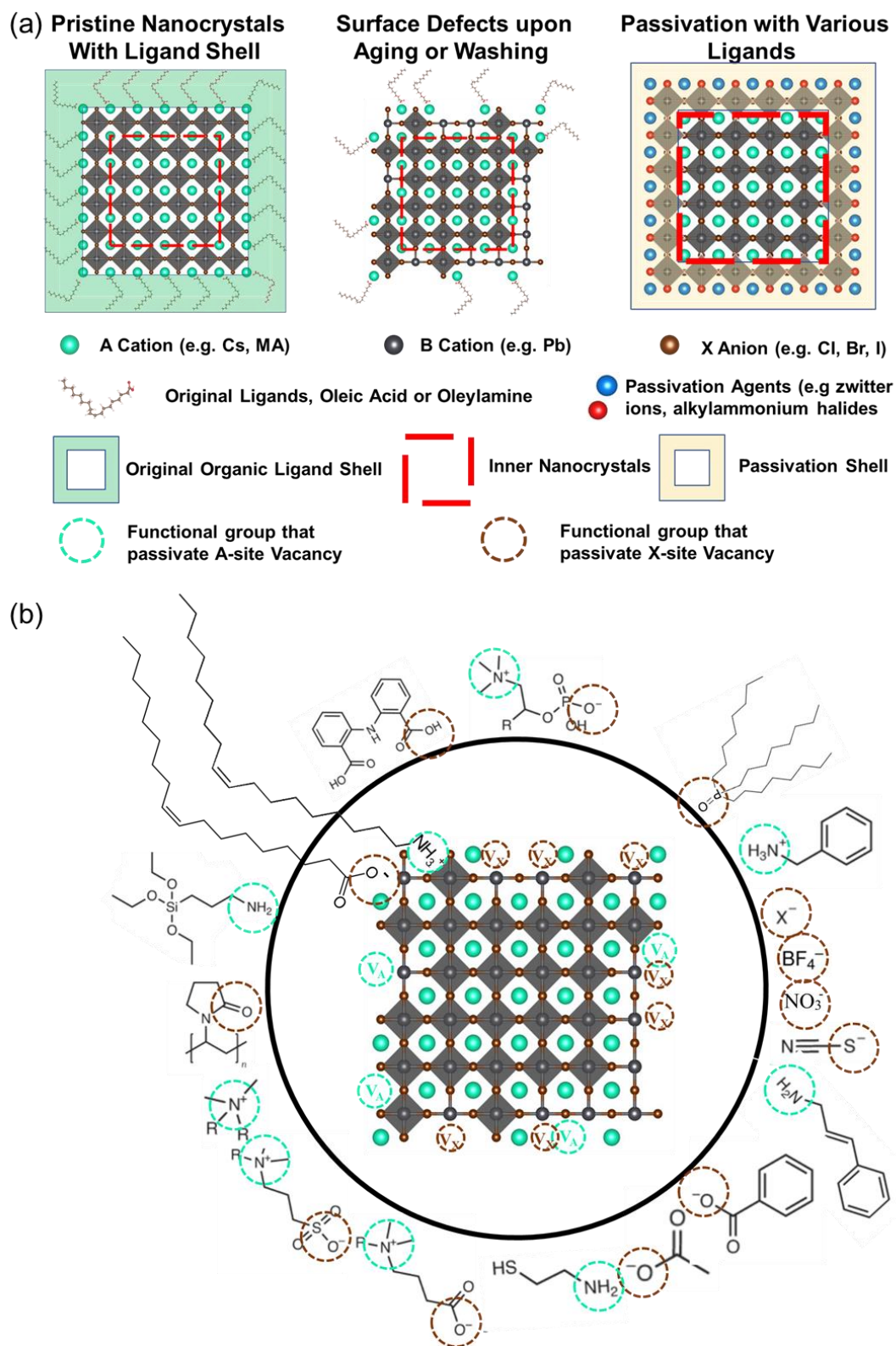


Figure 2. 9 Perovskite nanocrystal surface chemistry and defect passivation (a) Illustration of surface defects formation from pristine nanocrystals with well-capped organic ligands, aging

or washing process will lead to ligand detachment and surface defects, surface passivation agents are used to reform the protective shell. (b) Types of passivation ligands used in perovskite nanocrystal systems. The figure is inspired by Ref. ¹²³ and Ref. ¹²⁴ Reprint with permission under Creative Commons CC BY license from Ref. ¹²² © 2021 The Authors. Angewandte Chemie International Edition published by Wiley-VCH GmbH

Defect Tolerance. A key enabling feature of lead-halide perovskites is their defect tolerance, in which low non-radiative recombination rates are achieved despite high densities of defects.^{104,125,126} Owing to their defect tolerance, lead-halide perovskite thin films and nanocrystals that have several orders of magnitude higher defect densities than silicon or GaAs could still realise efficient solar cells and light-emitting diodes.^{43,127} This is because the trap levels from these defects are shallow and have low capture cross-sections, and can be understood from the classic equation for trap-assisted (U_{SRH}) recombination (e.q. 2.8),¹⁰⁴ Based on Equation (2.8), there are three ways to limit U_{SRH} : First, by having a low trap density (N_t); secondly, by having low carrier capture cross-sections ($\sigma_{t,h}$ and $\sigma_{t,e}$); thirdly, by having the defect energy levels (E_t) far away from the map-gap energy level (*i.e.*, close to the band-edge), giving rise to a larger n_t or p_t . In the third case, having a trap close to one band-edge would allow it to be highly occupied by one of the carriers (hence high n_t or p_t) but it would be difficult for the other carrier to reach that trap state because of the large energy difference. Thus, non-radiative recombination is reduced. Traditionally, materials growers have opted for the first option of minimizing N_t . Defect tolerance focuses on designing materials that have low capture cross-sections and shallow defects, enabling low U_{SRH} values despite high N_t values. Defect tolerance in the lead-halide perovskite family was originally identified in methylammonium lead iodide (MAPbI₃),¹²⁸ and rationalized based on the electronic structure.^{104,129} The Pb 6s and I 5p orbitals hybridise to form a pair of bonding and antibonding states in the upper valence band, while the Pb 6p orbital hybridises with the I 5p orbital to form a bonding state in the upper valence band and an antibonding state in the band minimum.¹⁰⁴ As a result, the original atomic orbitals are

close to the band-edges rather than inside the band gap (as shown in Figure 2.10 right). To a first approximation, defect states form close to the original atomic orbitals, and the electronic structure of MAPbI₃ makes it more likely that these states are resonant within the bands or shallow within the band gap. This contrasts to the electronic structure of traditional semiconductors (*e.g.*, silicon) (as shown in Figure 2.10, left), in which the bonding-antibonding states form across the band gap, and the original atomic orbitals are within the band gap, making deep traps more likely to form. Furthermore, the presence of heavy elements in MAPbI₃ leads to strong spin-orbit coupling, which reduces the band gap, making it more likely that trap states are shallow.^{104,129} The shallow trap energy in perovskite is usually less than 0.5 eV below the conduction band, which is about 19 times of the room temperature thermal activation energy (26 meV). Meanwhile, the high polarizability of the Pb²⁺ cation also leads to a high dielectric constant, which favors lower capture cross-sections of charged defects.^{104,130} The combination of shallowness in the trap energy levels and low capture cross-sections leads to low trap-assisted recombination rates despite high defect densities. However, the defect tolerance of MAPbI₃ has not been found to be generalizable across the entire lead-halide perovskite family, the study of the defect tolerance on different halide composition to band-edge and hot carriers will be discussed in Chapter 5.

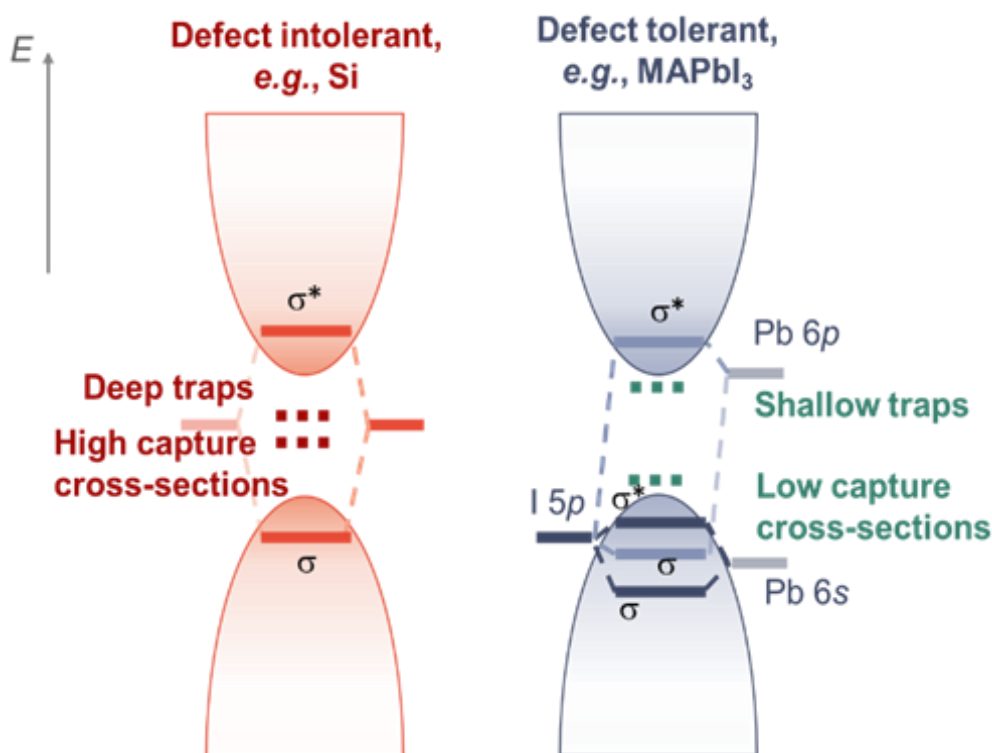


Figure 2. 10 Illustration of how the electronic structure can enable defect tolerance. The electronic structure of defect intolerant materials (e.g., silicon) is shown on the left, in which traps primarily form deep within the band gap and have high capture cross-sections. On the right is the electronic structure of defect tolerant materials (e.g., MAPbI₃), which primarily forms shallow traps with low capture cross-sections. Reprint with permission under Creative Commons CC BY license from Ref.¹²² © 2021 The Authors. *Angewandte Chemie International Edition* published by Wiley-VCH GmbH

2.2.4 Exciton Fine Structure and Polarisation

Excitons are the central emitting species in the semiconductor nanostructures that appear as additional (sometimes sharp) optical transitions at the optical band edge.¹³¹⁻¹³³ The degeneracies of the lowest exciton states can be broken by several factors, including strong exchange interactions, spin-orbit coupling, intrinsic crystal field; nanostructures shape anisotropy, thus giving rise to the multiple splitting of the lowest

exciton states known as exciton fine structure.^{132,134-137} The strength of the fine structure splitting energy is directly proportional to the strength of the electron-hole exchange interactions, J , and the crystal field parameter, $\mathcal{E}$, which is governed by the crystallinity of the unit cell, i.e. determined by whether the unit cell is cubic, tetragonal or orthorhombic for perovskite⁸⁵. In almost all bulk III-V semiconductor hetero-structures, II-VI core-shell colloidal nanostructures, the lowest available exciton states are found to be optically inactive known as dark exciton.¹³⁸⁻¹⁴⁰ In case of bulk semiconductor the splitting between the bright (optically active) and the dark (optically inactive) exciton is very small, generally less than the thermal energy even at cryogenic temperature. Hence, the photoluminescence decay is not strongly affected by temperature.^{131,132} Nevertheless, the energy separation between them is increased up to tens of meV in case of semiconductor nanostructures where the photoluminescence decay is prolonged at low temperature due to acoustic phonon mediated relaxation of the bright exciton to the dark exciton states.^{138,140-142}

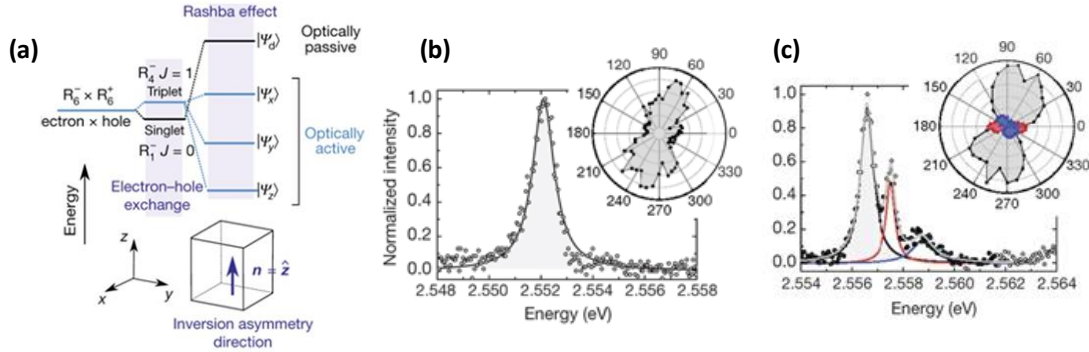


Figure 2. 11 (a) Fine structure of the band-edge exciton considering short-range electron–hole exchange (middle) and then including the Rashba effect (right) under orthorhombic symmetry. The latter splits the exciton into three bright states with transition dipoles oriented along the orthorhombic symmetry axes (labelled x , y and z) and a higher-energy dark state (labelled ‘ d ’). The energetic order of the three lowest sublevels is determined by the orthorhombic distortion. Photoluminescence spectra from individual NCs showing (b) one and (c) three

photoluminescence peaks. Adapted with permission from reference ¹⁴³. Copyright © 2018 Macmillan Publishers Limited, part of Springer Nature. All rights reserved

In almost all MHPs, it is observed that the photoluminescence decay becomes faster at low temperature where the photoluminescence quantum yield increases when the temperature is decreasing.^{143,144} The explanation of the high radiative recombination in Pb^{2+} halide perovskites at low temperature was proposed by Becker *et al.*¹⁴³ They claimed the lowest exciton state as the bright triplet state for CsPbX_3 ($\text{X}=\text{Br}, \text{Cl}, \text{I}$) crystals structure arising due to combination of strong spin-orbit coupling with Rashba-effect.¹³⁵ According to them,¹⁴³ if only short-range electron-hole exchange interaction is taken into account then the singlet state lies below the triplet state, making the lowest available exciton state dark (Figure 2.11a). They showed that the inclusion of the Rashba effect leads to the alteration of the bright and dark exciton levels in CsPbX_3 NCs. Rashba effect is a momentum-dependent splitting of spin bands in bulk crystals, it can be influenced by both spin-orbit interaction and asymmetry of the crystal potential. If the effective Rashba field is parallel to one of the orthorhombic symmetry axes of the CsPbX_3 NCs the bright triplet exciton states split into three linearly polarised sub-levels (Figure 2.11b-c).¹⁴³ In a detailed study by Sercel *et al.* they demonstrated that the ground state of the perovskite nanostructure is indeed optically inactive (dark) like any other classical semiconductor quantum dots, if only exchange interaction has been considered.¹³⁵ However, the experimentally observed bright exciton level order in tetragonal CsPbBr_3 NCs can be explained including the contribution of the Rashba effect, which supports the theory by Becker *et al.*¹⁴³ Moreover, it was shown that the bright-dark state positions could be reversed in low dimensional nanostructures, which, consequently, possess a dark exciton ground state.¹³⁵ Opposite experimental observations were found in case of CsPbBr_3 , FAPbBr_3 and FAPbI_3 nanocrystals.¹⁴⁵⁻¹⁴⁷

Early studies also show that the transition from these exciton fine structure energy levels gives linearly polarised emission, especially for the single-particle with asymmetric shape, such as NPLs. Huo *et al.*¹⁴⁸ measured the PL spectra from multiple single nanoplatelets at 5 K. They

showed that the CsPbBr_3 NPIs have multiple PL peakss as illustrated in Figure 2.12 (a)-(c). Some showed one peak, while some show two or three peaks. The energy differences are labelled as ΔE , ΔE_1 and ΔE_2 , with numerical values of 0.71 meV, 0.57 meV and 1.84 meV, respectively. Figure 2.12 (d)–(f) illustrates the polar plots of the polarization dependence of the intensity of each peak present in the corresponding spectra in Figure 2.12 (a)-(c). The lateral anisotropic morphology induced an almost 80% polarization of the single peak emission in Figure 2.12 (a). This angle-dependent polarization is also reported in perovskite nanostructures including NPIs.⁷¹ In the cases of nanoplatelets exhibiting multiple emission peaks (Figure 2.12(b) and c), the polarizations of the two lower energy peaks (shaded in red and blue in Figure 2.12(b) and (c)) are almost orthogonal to each other (Figure 2.12(f), whereas the higher energy peak is almost co-polarised as the lower energy peak. The observed polarization dependence of the emission peaks strongly indicates that they arise from the exciton fine structure.¹⁴⁸ These findings provide an extra degree of freedom to manipulate the electronic and optical properties of perovskite NPI-based materials and devices, it will be studied in Chapter 6.

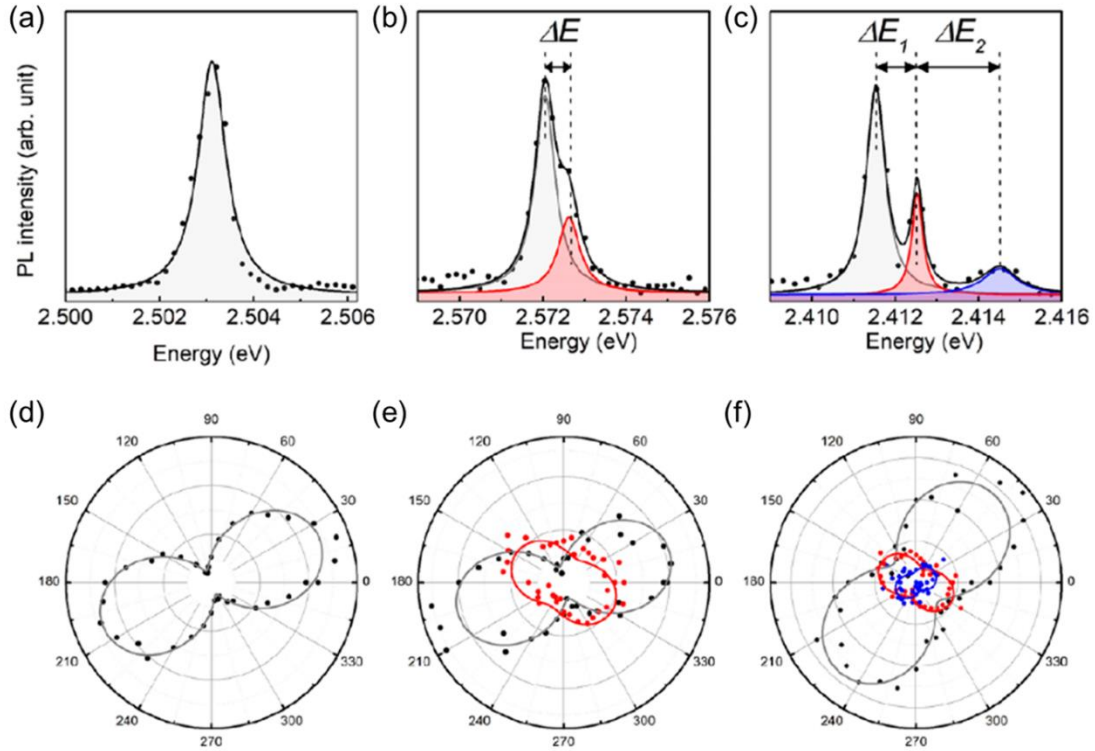


Figure 2. 12 Excitonic fine structure of the CsPbBr₃ nanoplatelets. PL spectra of the single nanoplatelets with one peak (a), two peaks (b), and three peaks (c) as well as the corresponding linear polarization properties (d–f). In (b) and (c), the splittings are labeled ΔE , ΔE_1 , and ΔE_2 and are deduced from the fittings to be 0.71, 0.57, and 1.84 meV, respectively. (g) The relative abundance of the single CsPbBr₃ nanoplatelet with one, two, and three emission peaks. Reproduced with permission from Ref. ¹⁴⁸ Copyright © 2020 American Chemical Society

2.3 Device Background

2.3.1 Solar Cells

Silicon solar cells are commonly based on a p - n junction diode, which is created by doping different regions of the same semiconductor differently, so there is an abrupt interface between p type and n type layers of the same material. The work function of p type semiconductor is higher than the n type semiconductor for the same material ($\phi_{m2} (p - \text{type}) > \phi_{m1} (n - \text{type})$), where ϕ_{m1} and ϕ_{m2} are the work function of the two materials. The Fermi energy level of p type semiconductor (E_{f2}) is closer to the valance band maximum (E_{v2}), while the fermi energy level of n type semiconductor (E_{f1}) is closer to the conduction band minimum (E_{c1}) before putting them into contact. After putting them into contact, there is an electric field established around the junction region due to the difference in work function. As a result, the photogenerated electrons from p type semiconductors will drift to n side, and holes from n type semiconductors will drift to p side, leading to a charge separation. The junction region is depleted of both electrons and holes, and acts as a barrier to majority carriers to avoid charge recombination. The electrons from p side will be further transported due to the diffusion gradient after reaching n side and get extracted from electrode. Similarly diffusion occurs for holes after reaching p side. (Figure 2.13a) For perovskite, it is hard to create the n -type of p -type perovskite to make the p - n junction solar cell through homogenise doping. Hence, people typically use positive-intrinsic-negative (p - i - n) (Figure 2.13b) or negative-intrinsic-positive (n - i - p) (Figure 2.13c) device structures for perovskite solar cells.

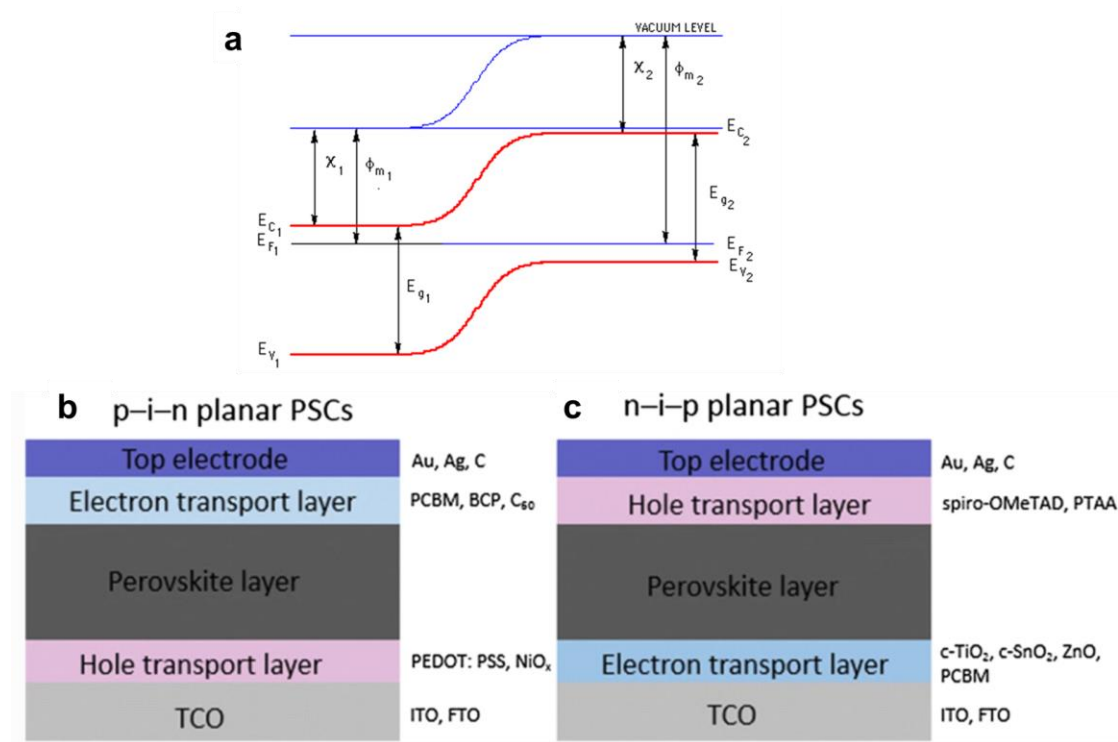


Figure 2. 13 Solar cell working principle and device structure. a. The energy band diagram of the p-n junction. b. perovskite p-i-n device structure. c. perovskite n-i-p device structure.

2.3.2 Light-Emitting Diodes

LEDs are also diode, but they operate in an inverse fashion to solar cells, in that electrons and holes are injected by the application of an electric field, and these recombine within the active layer to emit photons of a particular energy. The energy of photon is governed by the band gap energy of the semiconductors, and the region in which radiative recombination takes place. Efficient light emission occurs when injected or photoexcited charges to interact strongly in forms of recombination arises from free charge carriers or excitonic states.

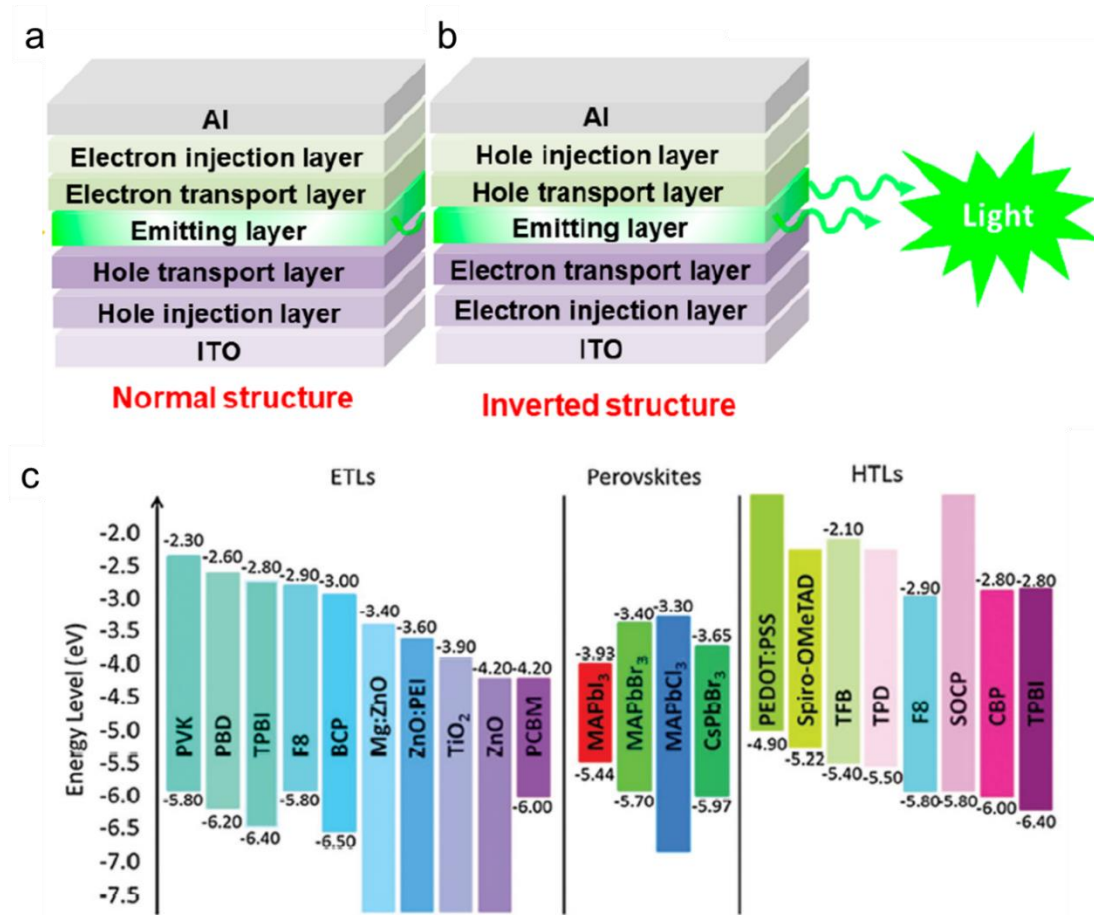


Figure 2. 14 Device structures of perovskite LEDs. (a) Normal structure; (b) Inverted structure. Reprinted with permission under Creative Commons Attribution License from reference ¹⁴⁹ (c) Energy level alignment of various materials used as perovskites, ETLs, and HTLs in the reported HPLEDs. Reproduced with permission from reference ¹⁵⁰. Copyright © 2017 Elsevier.

In general, the emissive layer (EML) of an LED device made by different semiconducting materials such as organic semiconductors, all-inorganic perovskites and cadmium-based quantum dots etc., can be sandwiched by electrons and holes transport layers (ETL and HTL). The charge carriers (electrons and holes) are supplied to the system when the electrons and holes injection layers (EIL and HIL) are connected to an external field via cathodes and anodes. Under operation, charge carriers enter the two terminals of the LED devices and recombine radiatively in the emitting layers which lead to electroluminescence. A successful electroluminescence can be achieved

by carefully alignment of the energy levels of each stacked layer in the devices (Figure 2.14) .

Compositional and Dimensional Engineering: Perovskite-based light-emitting diodes (PeLEDs) have gained tremendous attention since they were first reported by Tan *et al.* in 2014.⁵¹ Although green and near-infrared PeLEDs have achieved external quantum efficiencies (EQEs) higher than 20%,¹⁵¹⁻¹⁵³ there are still challenges with fabricating spectrally-stable and highly efficient pure red and blue PeLEDs, particularly for devices that emit with Commission Internationale de l'éclairage (CIE) coordinates approaching the Rec. 2020 specified red (0.708, 0.292) and blue (0.131, 0.046) colors that are required for ultra-high-definition displays (in addition to the green emitters that are easier to achieve).¹⁵⁴ In this section, different methods of preparing pure red and blue perovskite emitters will be discussed, with particular emphasis on utilizing perovskite NPLs as a route to achieving high PLQY and spectrally-stable LEDs. These are compared to bulk 3D perovskite thin films and perovskite nanocubes.

Compositional engineering with bulk 3D and weakly Confined Nanocrystals: One method to fabricate pure-red and blue perovskite emitters is through compositional engineering, by mixing bromide and iodide together for red emitters,^{151,155,156} or bromide and chloride for blue emitters.¹⁵⁶⁻¹⁵⁸ Bulk 3D perovskite blue emitters with a mix of Br and Cl were first achieved by Kumawat *et al.* in 2015.¹⁵⁷ They successfully fabricated MAPbBr_{3-x}Cl_x based blue PeLEDs with an emission peak center at 482 nm, a brightness of 2 cd m⁻² and a low EQE of 0.0001% when the Cl to Br atomic ratio was 1.92:1.08. One of the challenges of producing high-performance bulk Br-Cl mixed perovskite blue emitters is the high levels of non-radiative recombination. The reported efficiencies in other early works on blue PeLEDs based on bulk 3D perovskite were also low. For example, Yuan *et al.* reported 2.01% EQE for sky-blue emitters in 2017 and Wang *et al.* reported 0.062% for pure-blue emitters in 2019.¹⁵⁹⁻¹⁶¹ Many efforts have been made to improve bulk blue PeLEDs, such as through doping or defect

passivation.^{158,162,163} ¹⁶⁴ Often defect passivation, particularly of surfaces, is achieved using long-chain organic ligands. Similarly, in LHP NCs, the surfaces are effectively passivated with coordinating ligands, as well as through many other strategies, as discussed in the synthesis section. As a result, LHP NCs have achieved near-unity PLQY, making them highly promising for PeLED applications.¹⁶⁵⁻¹⁶⁷ For example, Takayuki *et al.* illustrated that by mixing bromide and iodide anions, a red PeLED emitting at 649 nm can be achieved with an EQE of 21.3% and CIE coordinates of (0.72, 0.28).¹⁵¹

However, the almost unavoidable drawback of blue-shifting the emission of perovskites by mixing halides is the spectral instability associated with halide migration under the application of an electric field. A redshift in the position of PL or electroluminescence (EL) peak and a broadening of the peak FWHM are commonly observed under illumination or bias.¹⁶⁸ For instance, Li *et al.* observed a redshift in the EL spectrum of red CsPbBr_{0.75}I_{2.25} and blue CsPbBr_{1.5}Cl_{1.5} NC PeLEDs over time at a constant operating voltage of 3.5 V.¹⁵⁶ The origin of the spectral instability is attributed to anion segregation in the mixed halide perovskite emitters.^{155,169} The halide segregation is highly dependent on factors such as chemical potential gradient, thermal gradient, applied electric field, and the photon flux and frequency of the incident light. Three well-established models have been put forward in the literature to account for phase-separation: 1) a thermodynamic model that is related to surface halide defect density; 2) a model in which polaron-induced lattice strain provides the driving force for halide anion migration; 3) a model in which charge-carrier gradients and localised electric fields trigger the movement of halides.¹⁷⁰ Knight *et al.*¹⁶⁹ reviewed methods to mediate the anion segregation effect in halide perovskite films, such as stoichiometric A-site and B-site engineering, halide defects and distribution management and crystallinity control.¹⁶⁹ Although compositional engineering was the initial strategy to blue-shift the bandgap and emission wavelength of perovskite emitters, it also led to higher densities of deep defect states, which compromise the PLQY of the film, and ultimately device

performance and stability. Whilst many groups have worked on addressing these limitations by controlling defect density, an alternative approach is starting to use dimensional engineering for controlling the band gap.

Dimensional Engineering: Quasi-2D vs. Colloidal Nanoplatelets: In contrast to compositional engineering, low dimensional perovskites provide an alternative route to achieve spectrally-stable devices with desirable color emission coordinates. As discussed in earlier sections, low-dimensional perovskites include quasi-2D perovskites,¹⁷¹⁻¹⁷⁵ strongly quantum confined quantum dots,¹⁷⁶ and colloidal perovskite NPLs. The key difference between quasi-2D and colloidal perovskite NPLs is the types of insulating layers used, i.e., spacers or ligands. Whilst spacers separate inorganic layers or lead-halide octahedra (thus determining the n -values of quasi-2D perovskites), ligands passivate surfaces and determine the size of NPLs, i.e., thickness and lateral dimensions. Therefore, the adequate use of different organic compounds during synthesis will give the desired optical properties for colloidal perovskite NPLs. The progress of quasi-2D perovskites in PeLEDs can be found in other reviews.^{177,178} Despite the advantages of using large organic molecules, such as improving PLQY and stability, quasi-2D perovskites have several disadvantages. For example, as discussed in Section 3, charge transport in quasi-2D perovskite films becomes anisotropic and highly restricted in the out-of-plane direction, due to the insulating nature of the large organic cation spacers. Changes in the spacer would lead to changes in the optical properties, such as bandgaps and exciton binding energies. Also, the spacer cations tend to decompose under high applied biases or long operation times in PeLEDs, which is detrimental to the device stability.¹⁷⁹ On the other hand, colloidal perovskite NPLs contain well-defined ligands on the surface, in which charge transport properties can be controlled by tuning the length of the ligands without compromising on the size of the NPLs.¹⁸⁰⁻¹⁸³

Since NPLs can achieve blue or red emission with a single halide composition, they do not suffer from the phase separation issue faced by mixed halide perovskites, this is conducive towards achieving spectrally-stable emission that does not broaden or red-shift over time, several challenges need to be overcome first.^{112,184-187} For example, Wang *et al.* observed that CsPbBr₃ NPLs aggregate to form a bulk phase under exposure from low UV irradiation (20 mW cm⁻²).¹⁸⁴ The merging of NPLs under UV-irradiation leads to a red-shift in the emission spectrum, from 436 nm (3 monolayers) to, 466 nm (6 monolayers), 484 nm (9 monolayers) and 521 nm (bulk) gradually. The trigger of the merging is attributed to the desorption of liable surface ligands and hence leading to self-assembly of the NPLs like a lamellar stacking.^{184,185} Apart from photon-induced phase transformation, NPLs can undergo rapid aggregation when excess thermal energy is supplied.¹⁸⁶ Dang *et al.*¹⁸⁶ reported that colloidal CsPbBr₃ NPLs would first undergo surface ligand detachment and merge to form nanobelts, then the nanobelts would join with the neighboring nanobelts to form extended nanosheets, resulting in the PL red-shifting over time (22 days) from 460 nm to 515 nm. This merging process can accelerate if external thermal energy is supplied. For example, the time taken for the PL to red-shift to 515 nm is only 40 mins at 110 °C.¹⁸⁶ Joule heating would be present during LED device operation, and this can therefore accelerate NPL agglomeration. To mitigate photon-induced and thermally-induced aggregation, ligands that can be tightly bound to the surface of the NPLs can be used. For example, Shamsi *et al.* replaced the OLA ligands with short hexylphosphonate ligands (C₆H₁₅O₃P) which are more tightly bound to the surface.¹¹² As a result, the NPLs can be preserved for months with the same PL peak position. Therefore, exploring alternative ligands would be a possible method to further improve the PL/EL stability for NPLs based LEDs.

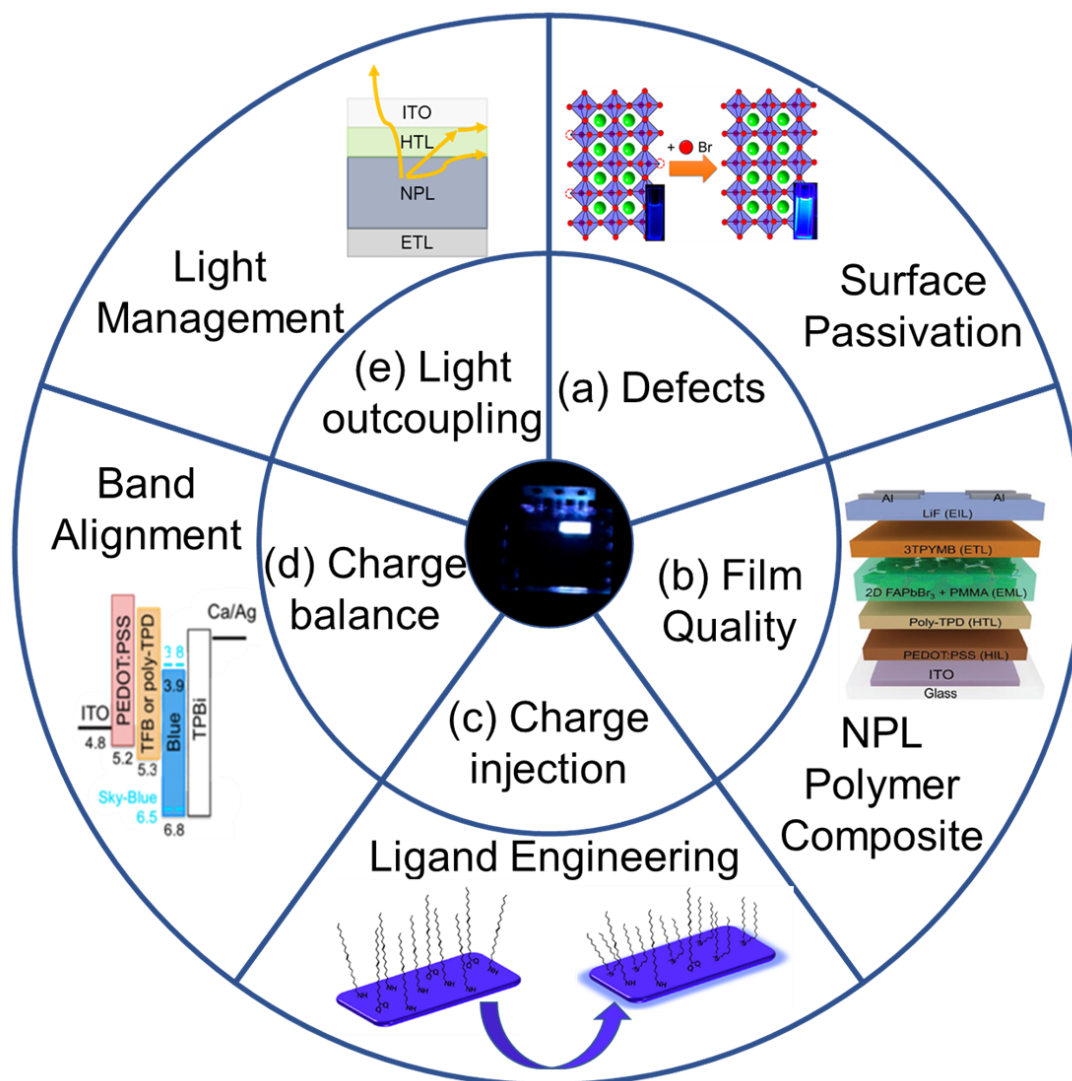


Figure 2. 15 *Factors limiting PeLED performance and strategies for overcoming these factors in NPLs PeLEDs. (a) Defect passivation method: Reproduced from Ref.¹⁸⁸ Copyright © 2018 American Chemical Society (b) Film Morphology Modification: Improve film morphology by making 2D FAPbBr₃ perovskite-PMMA composite film. Reproduced from Ref.¹⁸⁹ Copyright © 2017 American Chemical Society (c) Ligand Exchange Method: Insert Schematic illustration of the post-synthetic surface ligand exchange treatment of CsPbBr₃ NPLs. Reproduced from¹⁹⁰. Copyright © 2019 American Chemical Society (d) Band-Alignment and interfacial engineering Method: Band structure of perovskite LED devices with blue or sky-blue emitters (left) without or (right) with a polymer interlayer. Reproduced under CC-BY license from Ref.¹⁹¹ Copyright © 2019 American Chemical Society (e) Maximizing light outcoupling efficiency. Reprint with*

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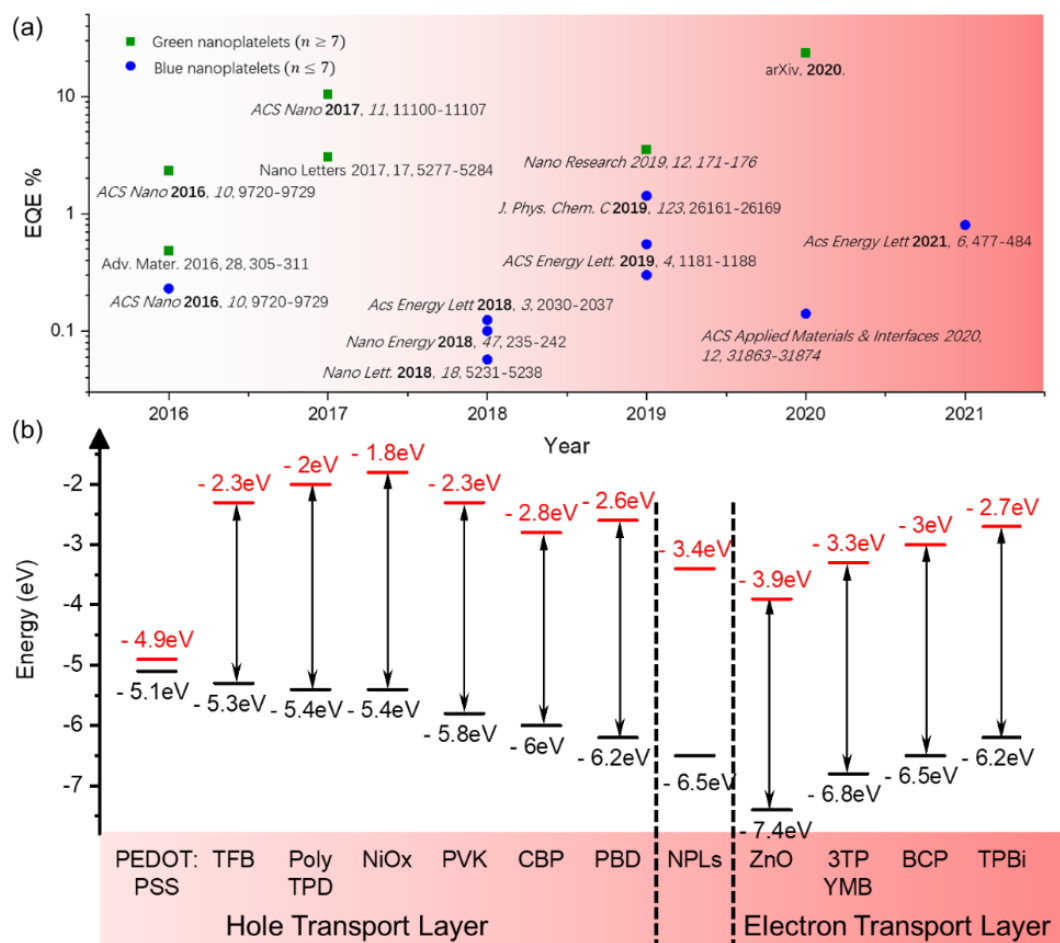


Figure 2. 16 Perovskite Nanoplatelet (NPL) Light-Emitting Diodes (LEDs). (a) Development of Perovskite NPL LEDs over time. (b) Valence and conduction band extrema (or LUMO and HOMO levels for organic materials) of the reported hole and electron transport layer in perovskite nanoplatelet LEDs. Band positions of transport layers¹⁹² and perovskite NPLs (-3.4 eV to -6.5 eV)¹⁹³ obtained from the literature. The NPLs band position depends on the number of monolayers, the graphic value is based on the monolayer of Br-based NPLs.

Strategies to Improve Colloidal Perovskite Nanoplatelets LED Performance: The progress of colloidal perovskite NPL LEDs is illustrated in and Figure 2.16a. The EQE

of pure-green-emitting bromide-based perovskite NPIs (with >7 monolayers) has increased from 0.48% in 2016¹⁹⁴ to 23.6% in 2020.¹⁹⁵ For blue PeLEDs (465 nm - 485nm emission wavelength), the efficiency has improved from <0.1%⁸¹ to 1.42%.¹⁹⁰ So far, the most commonly-used structure for perovskite NPI LEDs is ITO/PEDOT:PSS/NPI/TPBi/Electrodes. Figure 2.15 provides insights into the strategies for improving NPI PeLED performance. The EQE of LED devices is influenced by four main factors: 1) the percentage of radiative recombination among all recombination processes in the emitter layer (PLQY); 2) the probability of balanced charge injection (f_{balance}); 3) the chance of effective electron-hole coupling ($f_{\text{e-h}}$); and 4) the fraction of photons generated that are emitted out of the device ($f_{\text{outcoupling}}$).¹⁹⁶ The influence of each factor on the performance of NPI PeLEDs is discussed below.

Internal Quantum Efficiency: One of the most important parameters for LEDs is the internal quantum efficiency or PLQY of the emitter film. It is well-accepted that in a strongly quantum-confined nanoplatelet system, the PLQY depends on the competition between first-order exciton radiative recombination (k_{exciton}) and the first-order exciton trap-assisted recombination (k_{trap}) at low fluence (when carrier density, N , is small enough, usually below 10^{16} cm^{-3} or low current density, for example below 10 mA cm^{-2}) (Equation 2.17).^{167,192,197,198}

$$PLQY = \frac{k_{\text{exciton}} + N \cdot k_2}{k_{\text{exciton}} + k_{\text{trap}} + N \cdot k_2 + N^2 \cdot k_3} \quad (2.17)$$

Therefore, under the normal LED operating regime (carrier density 10^{10} - 10^{16} cm^{-3}),¹⁹⁹ the trap-assisted exciton recombination rate, k_{trap} , is the factor that needs to be minimised to improve PLQY. Previous works have highlighted the influence of defect passivation on PeLED device performance.^{165,167,188,200,201} Primary and quaternary amine, phosphonic and sulfonic acid, zwitterions and inorganic salts have been found to be effective for passivating surface defects in perovskite nanocrystals.^{71,114,167,202,203}

For nanoplatelets, it is useful to identify the dominant type of surface traps and passivate them with appropriate ligands. To identify the surface traps present, Bertolotti *et al.* investigated the surface termination of CsPbBr₃ NPLs using X-ray total scattering techniques, based on the Debye scattering equation (DSE) approach.²⁰⁴ The DSE model is considered as one of the most accurate expressions to model the diffraction pattern from nanoparticle systems. The method illustrates a comprehensive characterization of the nanosized materials and full XRD pattern reconstruction, both in terms of Bragg peaks and diffuse scattering, which intrinsically arise from the detailed atomistic model definition of NPLs, developed in the real space.²⁰⁵ (Equation 2.18)

$$I(Q) = \sum_{i=1}^N \sum_{j=1}^N f_i(Q) f_j^*(Q) \frac{\sin(Qr_{ij})}{Qr_{ij}} \quad (2.18)$$

Where $Q = 4\pi \sin(\Theta)/\lambda$, the wavevector transfer modulus (Θ is half the scattering angle and λ the radiation wavelength), f the atomic scattering factor and r_{ij} the magnitude of the distance between any two of the N atoms composing an atomistic aggregate.²⁰⁶ Based on DSE analysis of 6 monolayer CsPbBr₃ NPLs (one monolayer being ca. 0.59 nm thick), Bertolotti *et al.* claimed that the NPLs exhibit an orthorhombic structure with (100) pseudocubic facets, which correspond to two (010) and four (101) planes of the orthorhombic CsPbBr₃ lattice ($Pnma$ space group). The basal facets of the N are of the (101) family, whereas two remaining (101) planes and both (010) planes make for side NPLs facets. Hence, it is suggested that CsBr-terminated surfaces are preferentially exposed, with almost half Cs sites and a half Br sites vacant.²⁰⁴ It indicates that vacancy defects would be one of the dominant non-radiative recombination pathways which reduce the PLQY.

Previous theoretical calculations have shown that the formation energy required to create vacancies in CsPbBr₃ nanocrystals are in the range of 1.4–2.3 eV, depending on the position of the vacancy in the lattice for the perovskite nanocrystal system.²⁰⁷ Brinick *et al.* found from computations that the defect formation energy for a charged

or neutral Br vacancy tends to be lower than the defect formation energy for a Cs vacancy or a Pb vacancy (calculated defect formation energies in CsPbBr₃ NCs can be found in Figure 2.17).²⁰⁷ Br vacancies are therefore more common. Hence, the passivation of Br-based NPLs has focused on eliminating or minimizing halide vacancies to improve their performance in PeLEDs.^{81,188} For example, Wu *et al.* proposed an *in-situ* passivation method by adding excess Br⁻ (HBr) to form an interconnected Pb-Br octahedral framework before nucleation which could significantly reduce the density of bromide vacancies in the NPLs (Figure 2.15a).¹⁸⁸ As a result, the PLQY of the NPLs increased from 18% (pristine NPLs) to 96% (passivated NPLs), and the average carrier lifetime measured by transient absorption increased from 3.96 ns to 6.46 ns with a pump intensity of 1.25 $\mu\text{J cm}^{-2}$ (2s.f.).

Apart from passivating the bulk material, passivating defects at interfaces between the perovskite layers and charge-injecting layers is also important. For example, Hoyer *et al.* reported by adding an extra poly-TPD layer between the conventional PEDOT:PSS hole-injection layer and CsPbBr₃ NPLs emitter, the EQE of the blue PeLED could be improved from 0.007% to 0.3% (shown in Figure 2.15d).¹⁹¹ poly-TPD was shown through PLQY and time-resolved photoluminescence measurements to reduce non-radiative recombination at the hole-injecting interface. Other organic passivating layers and strategies that have been effective in perovskite solar cells (*e.g.*, PTAA) could also be applied to NPL LEDs.^{208,209} For instance, an emerging idea in the perovskite photovoltaics scene that could also be translated to the PeLED field is to use self-assembled monolayers (SAMs) to passivate the bottom interface beneath the solution-processed emitter.²¹⁰

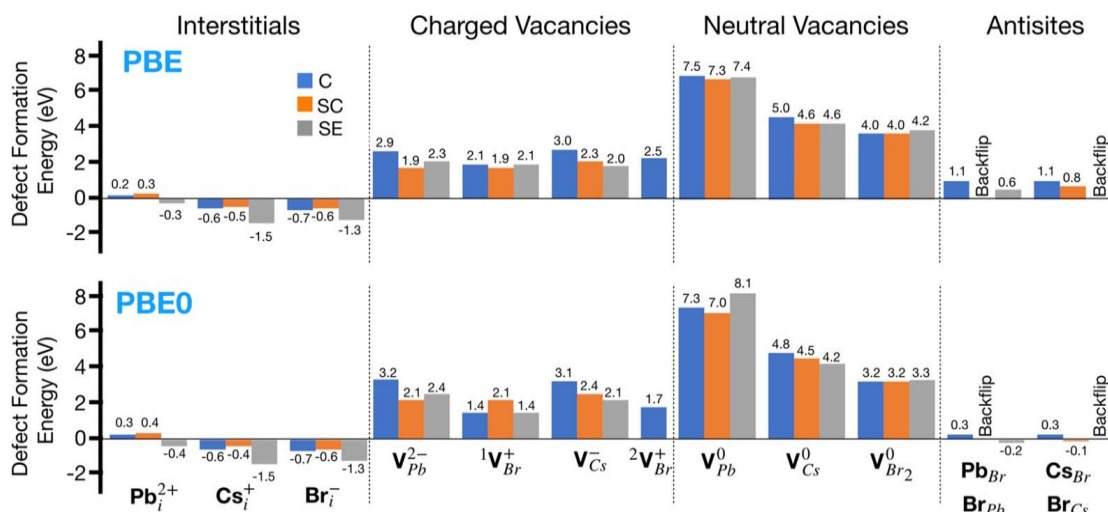


Figure 2. 17 Defect formation energies (DFEs) associated with interstitial, charged, neutral vacancies, and antisite substitutions listed in electronvolts. The DFEs are computed following geometry optimizations carried out at the DFT/PBE0 level of theory. Backflip means that the antisite displacement goes back to its initial non-defective configuration. Note that here we report only the defect name without the counterion. C, SC and SE are defects at core/surface, surface-center/surface and surface-edge/surface, respectively. Reproduced with permission under CC-BY-NC-ND license from Ref. ²⁰⁷. Copyright © 2019 American Chemical Society.

Apart from suppressing trap-assisted recombination through defect passivation, reducing Auger recombination during device operation is another important factor that needs to be considered. When the injected current density is large (typically larger than 1-10 mA cm⁻² or carrier density is larger than 10¹⁶ cm⁻³), LEDs will suffer from significant efficiency roll-off when the injected charge carrier density is high (Figure 2.18). The origin of the efficiency roll-off in colloidal NPLs systems has not yet been studied. For quantum-confined systems, such as quasi-2D perovskite thin films (Figure 2.18 a and b) and 2D NPLs (Figure 2.18c), an explanation that has been put forward is Auger recombination, which is also a three-body non-radiative recombination pathway that lowers the PLQY.^{198 211,212} Another cause would be exciton-exciton annihilation, as discussed earlier in the carrier dynamics section. When increasing the excitation carrier density, radiative bimolecular recombination gradually dominates over the

monomolecular process, so the PLQY would increase initially with the current density as shown in Figure 2.18b for a quasi-2D system. At higher carrier densities, three-body Auger recombination becomes dominant, resulting in decreases in PLQY (Figure 2.18a). It is also noticed that in a quasi-2D or colloidal 2D system, the $k_{exciton}$ is proportional to the exciton binding energy E_b in quantum wells.¹⁹⁸ For instance, Philbin *et al.* illustrated that Auger recombination lifetimes depend nearly linearly on the lateral area and somewhat more strongly on the thickness of the nanoplatelets.²¹³ Therefore, developing a facile approach to manage Auger recombination would be critical to reducing efficiency roll-off in 2D perovskite LEDs.

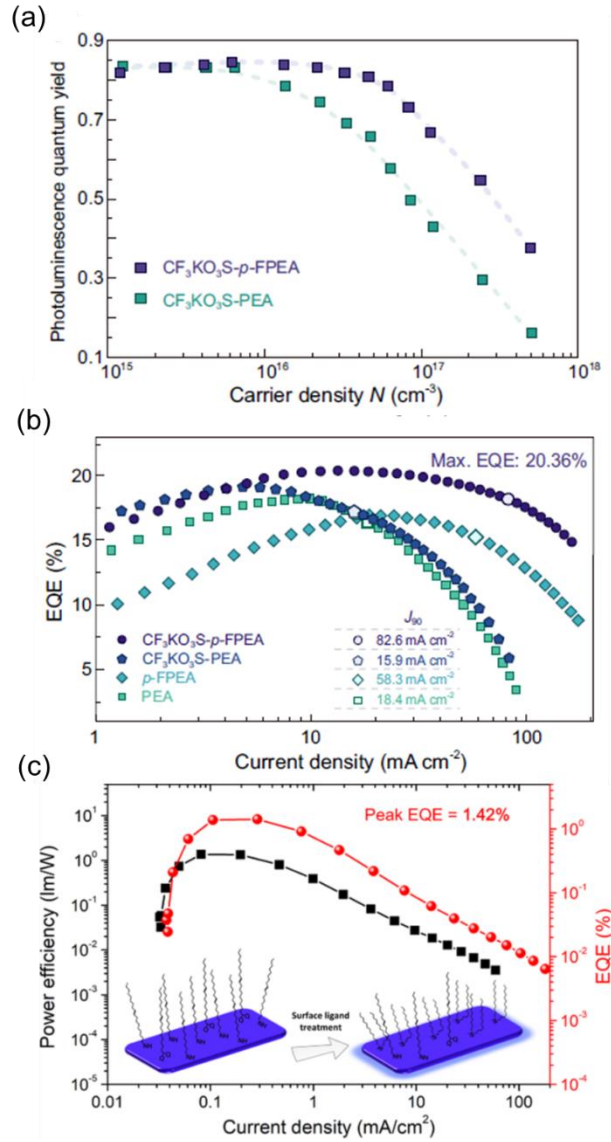


Figure 2. 18 Demonstration of efficiency roll-off in blue PeLEDs. (a) Film's PLQYs as a function of carrier density for CF3KO3S-PEA and CF3KO3S-p-FPEA quasi-2D films. (b) Current density-dependent EQE curve for different quasi-2D PeLEDs. Reproduced under Creative Commons CC BY license from ref.¹⁹⁸ Copyright © 2021, The Author(s) (c) External quantum efficiency–current density curve of the treated CsPbBr₃ NPL-based LED. Reproduced from¹⁹⁰ Copyright © 2019 American Chemical Society

Charge injection and charge balance: Charge injection and charge balance are also critical factors for device performance. It strongly depends on the film quality of the NPL emissive layer. Incomplete film coverage (pinholes) would lead to current leakage, charge imbalance and carrier quenching at interfaces.²¹⁴ Kumar *et al.* mixed FAPbBr₃ NPLs with PMMA solution to improve the film quality.¹⁸⁹ By adding PMMA, the emitting film became more uniform, and the root-mean-square roughness decreased from 7.91 nm to 0.63 nm. Furthermore, the presence of PMMA molecules around the FAPbBr₃ NPLs altered the surrounding dielectric constant, leading to an increase in the exciton binding energy (increased from 149.3 meV to 161.3 meV) through dielectric confinement.²¹⁵ The increase in exciton binding energy led to an increase in the PLQY (from 88% (solution) to 92% (composite film)) because the more tightly bonded excitons could undergo monomolecular radiative recombination rather than dissociating into free carriers which are more easily trapped by defects. As the result of improved film coverage and PLQY, the device EQE increased from 1.14% (0 wt% PMMA) to 3.04% (8 wt% PMMA).¹⁸⁹

Another challenge for effective and balanced charge injection in NPL PeLEDs arises from the long-chain ligands (usually oleylamine and oleic acid) that are present at the surface of NPLs. These long-chain ligands are needed in order to control the growth of the nanoplatelets, prevent agglomeration and passivate surfaces. On the other hand, these ligands limit charge injection. An appropriate ligand management method is needed to balance the need for high PLQY vs. efficient charge injection.^{183,216} Kumar

et al. demonstrated that by replacing long-chain ligands (16 carbons, hexadecylamine) with shorter ligands (6 carbons, hexylamine) during the synthesis, the current density under the same injection voltage and carrier lifetime increased.¹⁸³ This indicated that a shorter chain ligand can improve charge injection, the turn-on voltage at an operating current density of 1 mA cm^{-2} decreased from 4.32 V with hexadecylamine to 3 V with hexylamine. As a result, the luminance (in cd m^{-2}) of the PeLED increased when using shorter chain ligands, for instance, the luminance increased from 2.46 cd m^{-2} for hexadecylamine (16 carbons), to 3322 cd m^{-2} for decylamine (10 carbons) and 9555 cd m^{-2} for hexylamine (6 carbons). Zhang *et al.* performed post-synthesis ligand engineering by exchanging long-chain OLA and OA ligands with shorter dimethylammonium bromide (DDAB) ligands (Figure 15c).¹⁹⁰ After ligand treatment, the CsPbBr_3 NPL PLQY increased from 45.1% to 69.4%, as the DDAB ligands not only partially replaced the original ligands but also passivated surface defects. The shorter DDA^+ ligands also decreased NPLs spacing and led to a more delocalised wave function, contributing to decreased turn-on voltages from 6.4V to 3.6V, since the better balanced charges can be more easily injected into the NPLs, leading to the EQE increasing from 0.02% to 0.56%.¹⁹⁰ Developing suitable and exchangeable ligands is still quite challenging for perovskite NPLs.^{71,180} Chen *et al.* reviewed feasible ligands that can exchange with the liable ligands for perovskite nanocrystals, including short-chain acid and amine ligands, and complex ligands such as perylene diimide.¹⁸⁰ However, no studies yet have been done on how the ligand exchange process would affect the size, shape and optical properties of the NPLs.

Interfacial engineering is another important area to improve charge injection and balance, as well as reducing interfacial PL quenching.¹⁹¹⁻²¹⁷ For a commonly used PeLED structure (ITO/PEDOT:PSS/NPLs/TPBi/LiF/Al), the energy discrepancy between the work function of the anode (usually LiF/Al, -2.9eV) and the LUMO of the electron injecting layer (TPBi, -2.7eV) (Figure 2.16b) is negligible. There is almost no energy barrier for electron injection from the cathode into the conduction band

minimum (CBM) of the perovskite NPIs (around -3eV). However, on the anode side, there is a significant energy barrier between the transparent ITO (work function -4.7eV) and the perovskite valence band maximum (VBM) (around -6 to -7 eV). The large energy difference makes it more difficult for hole injection, resulting in higher electron current densities, with electrons accumulating at the hole injection interface with the emitter. One solution would be to introduce a multi-layer HTL with cascade-type energy levels. For blue PeLEDs, researchers now tend to use the first hole transport layer that has high hole mobility and can form a quasi-Ohmic contact with the ITOs, such as NiO_x and PEDOT:PSS. Then a second hole transport layer with deeper HOMO is used to form cascade-type energy levels to improve hole injection and charge balance, for example, poly-TPDs (Poly[N,N'-bis(4-butylphenyl) -N,N'-bis(phenyl)-benzidine]), TFB (Poly(9,9-dioctylfluorene-alt-N-(4-sec-butylphenyl)-diphenylamine)) and PVK (Poly(9-vinylcarbazole)).^{218,219} However, the role of these layers is still unclear, whether they form an energy cascade to facilitate charge injection or passivating interfacial defects to reduce PL quenching, or that they improve the surface roughness and uniformity of the top perovskite layers.

Formation of Electron-Hole Pairs (Excitons): Electroluminescence is generated when injected electrons and holes are effectively correlated to each other and radiatively recombine, such as through the formation of excitons.^{167,220} The exciton binding energy (E_b) then becomes an important parameter to determine the equilibrium population of excitons (n_x) and unbounded carriers (holes (n_h) and electrons (n_e)).²²⁰ The formation of excitons from free electrons and holes, and the reverse process (i.e., dissociation into free charges), can be seen as a chemical reaction between these three species. The equilibrium populations of these species depend on their overall concentration. With increased optical (or electrical) excitation, the pairing of electrons and holes to form bound neutral states becomes more favored and excitons thus become the dominant species. Conversely, at low injection levels, unbound electrons and holes are unlikely

to meet and to give rise to excitons, which therefore are the minority species. The Saha equation (Equation 2.19) is normally used to describe the equilibrium between free electrons/holes and excitons:

$$n_e n_h = n_x n_{\text{equilibrium}} \quad (2.19)$$

$$n_{\text{equilibrium}} = \left(\frac{\mu_x k_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}} e^{-\frac{E_b}{k_B T}} \quad (2.20)$$

In Equations 2.19 and 2.20, n_x , n_h and n_e are the exciton, hole and electron populations, respectively, $n_{\text{equilibrium}}$ is the equilibrium constant, which is determined by temperature (T) and the exciton binding energy (E_b), μ_x is the reduced exciton mass. $n_{\text{equilibrium}}$ is typically on the order of 10^{17} , 10^{16} and 10^{16} cm^{-3} for bulk MAPbI₃, MAPbBr₃ and MAPbCl₃, respectively.²²⁰ Typically, for a 2D exciton-dominant system, the emitted light intensity should have a linear relationship with moderate carrier injection intensity (injected carrier density 10^{16} - 10^{19} cm^{-3}) since the exciton is the dominant species for light emission in NPLs.²²¹ However, there is still a lack of fundamental studies about how excitons and free carriers are generated during the operation of NPL-based LED devices.

Outcoupling : Typically, the perovskite layers have a much larger refractive index (n , typically 2.1-2.6) than the surrounding materials, for example, the glass substrate ($n = 1.5$), ITO ($n = 1.8$), commonly used organic transport layers (*e.g.*, TPBi) ($n = 1.73$) and air ($n = 1$).^{192,222} Light will only propagate from a higher-refractive-index material (*i.e.* perovskites) to a lower-refractive-index material (*i.e.* air) when the incident angle is larger than the critical angle. As a result, the majority of electroluminescence from PeLEDs would undergo Fresnel reflection and waveguiding within the glass substrate. The light loss mechanisms include parasitic absorption by adjacent layers, longitudinal oscillation of electrons at metal interfaces (surface plasmon polariton), waveguide mode which traps the light between ETL, HTL layers and ITO glasses.²²² Zhang *et al.*

conducted a detailed review on light outcoupling management in PeLEDs,²²² here I would like to discuss the intrinsic light outcoupling in perovskite NPLs.

The large discrepancy between the intrinsic perovskite light outcoupling efficiency and the organic counterparts is due to the random orientation of the transition dipole moments (TDMs) in perovskite NPLs.²²³ Currently, there is a lack of methods to align the TDMs in perovskites, in contrast to organic emitters. In organic emitters, the alignment of TDMs can be tailored by designing the molecular structure, which can influence the intermolecular interactions, including *van der Waals* (vdW) and electrostatic forces, and thermodynamically determine the molecular configuration and conformation of the emitters. The orientation of the molecules can also be tuned through the processing.²²⁴ However, these methods are far more difficult to apply with perovskite emitters. It is worth noting that the TDMs that are horizontally-aligned with respect to the electrode interface are favored for light outcoupling while the vertically-aligned TDMs largely contribute to energy losses due to waveguiding.²²⁵ Therefore, to increase outcoupling, maximizing the horizontally oriented TDMs is preferred. Jurow *et al.* reported a method to change the orientation of the average TDMs by reducing the dimensions of the nanocrystals and depositing them face down onto a substrate by spin coating at 1500 rpm in toluene on glass substrates to create a monolayer of NPLs.²²³ The percentage of horizontal TDMs can be measured in the setup shown in Figure 2.19a. Recently, Cui *et al.*²²⁶ and Kumar *et al.*²²⁷ illustrated that self-assembled 2D perovskite NPLs could exhibit a higher outcoupling efficiency as the orientation of TDMs are well aligned in the spin-coated NPLs films. For example, Cui *et al.* estimated the ratio of horizontal TDMs, Θ_H , in their anisotropic NPLs films is 84% based on the angle-dependent PL measurement, which provides an ensemble measurement of the intensity of p-polarised emission against the detection angle.²²⁶ The Θ_H value in NPLs film (84%) is larger than the Θ_H value in isotropic emitters (67%), and it leads to an increase in simulated device outcoupling efficiency from 23.4% (isotropic emitters) to 31.1% (anisotropic emitters). As a result, they achieved a green PeLED with an EQE of 23.6%.

Similar results were also achieved by Kumar's group, with a Θ_H value of 72% (Figure 2.19b) in the optimised mixed cation NPLs, and a device efficiency of 24.2%.²²⁷ These pioneering works provide excellent guidance for measuring and orienting the TDMs in low dimensional halide perovskites.

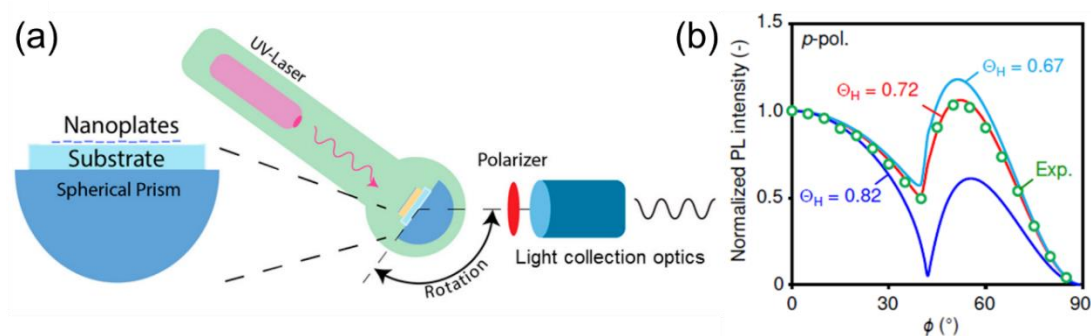


Figure 2. 19 *Quantifying the horizontal transition dipole moments in perovskite films. (a) Schematic of a film of perovskite nanoplates on a spherical prism to analyze the emitted light and calculate the average orientation factor (Θ_H) of the material at each wavelength. Reproduced from reference²²³ Copyright © 2019, American Chemical Society (b) Experimental and calculated thin-film p-polarised PL intensity as a function of viewing angle ϕ , using the thin-film horizontal dipole ratio Θ_H as the control parameter. Reproduced under Attribution 4.0 International (CC BY 4.0) license from reference²²⁷ 2021*

Chapter 3: Methodology

3.1 Material Synthesis

3.1.1 Nanocubes

Materials: Cesium carbonate (Cs_2CO_3 , 99,9%, Sigma Aldrich), formamidine acetate salt ($\text{CH}_4\text{N}_2\cdot\text{C}_2\text{H}_4\text{O}_2$, 99%, Sigma Aldrich), methylammonium bromide ($\text{CH}_3\text{NH}_3\text{Br}$, >99%, anhydrous, Sigma Aldrich), lead (II) bromide (PbBr_2 , >98%, Sigma Aldrich), lead (II) iodide (PbI_2 , 99%, Sigma Aldrich), 1-octadecene (ODE, $\text{C}_{18}\text{H}_{36}$, 90%, Sigma Aldrich) oleic acid (OA, $\text{C}_{18}\text{H}_{34}\text{O}_2$, 90%, Sigma Aldrich) and oleylamine (OLA, $\text{C}_{18}\text{H}_{37}\text{N}$, 70%, Sigma Aldrich) were purchased from Merck. Methyl acetate ($\text{CH}_3\text{COOCH}_3$, 99%) and toluene (C_7H_8 , <99.8%) was supplied by Alfa Aesar. All chemicals were used without further purification.

Preparation of a stock of cesium-oleate (Cs-OL): In a typical synthesis, 407 mg of Cs_2CO_3 (1.25 mmol) and 1.25 mL of oleic acid (3.5 mmol) were added to 20 mL of 1-octadecene in a 50 mL sample vial. The resulting mixture was heated at 150 °C under stirring until the salt is completely dissolved. The Cs-oleate complex generally precipitates at room temperature, however, it can be easily dissolved again by continuous stirring at 120 °C.

Preparation of a stock of different lead halides (PbX_2): In a typical synthesis, the lead halide salt 345 mg of PbBr_2 (0.94 mmol) or 433 mg of PbI_2 (0.94 mmol) was added to a mixture of 2.5 mL of OLA (5.3 mmol), 2.5 mL of oleic acid (7.0 mmol) and 25 mL of 1-octadecene in a 50 mL sample vial. The resulting mixture was heated at 150 °C under continuous stirring until the salt completely dissolves.

Preparation of oleylammonium iodide solution for halide exchange: 0.1844 g of PbI_2 (0.4 mmol), hexane (10 mL), oleylamine (0.4 mL) and oleic acid (0.4 mL) were combined in a 20 mL vial. The resulting mixture was heated at 50 °C under continuous stirring overnight to completely dissolve the salt.

Synthesis of CsPbBr₃, CsPbI₃, and CsPbBrI₃ perovskite NCs: In a typical synthesis, 6 mL of the corresponding PbX₂ precursor solution in a 20 mL glass vial was heated on a hot-plate until the temperature of the precursor solution reaches 175 °C in the case of CsPbBr₃ and 150 °C for CsPbI₃, and then, 400 µL of the pre-heated Cs-OL stock solution was swiftly injected into it under vigorous stirring (1,000 rpm). After 5 s, the vial cooled in an ice-water bath to quench the reaction. Subsequently, the thus obtained colloidal dispersion was purified by centrifugation at 8000 rpm for 10 min. Then, the supernatant was discarded to remove the unreacted precursors and ligands and the pellet was redispersed in 5 mL of toluene. The colloidal dispersion was centrifuged again at 5,000 rpm for 8 min to remove largest particles in the sediment.

Synthesis of CsPb(Br,I)₃ perovskite NCs: Firstly, lead iodide solutions were prepared by dissolving 0.2 mmol of PbI₂ powder in a mixture of 10 mL toluene, 0.2 mL oleylamine and 0.2 mL oleic acid at 100 °C under continuous stirring until the precursor dissolves. Then, the appropriate amount of PbI₂-ligand solution was added to the parent CsPbBr₃ NC colloidal solution to initiate halide ion exchange. The mixed halide ratio between Br and I is aimed to be 3:7 after the reaction. The reaction mixtures were stirred at 800 rpm for 30-40 min at 40 °C.

Purification process for preparing NCs with different antisolvents: The washing process was performed with the antisolvents of butanol, acetone or methyl acetate. 1 mL antisolvent was added to 1 mL of the as-prepared solution and purified by centrifugation at 8000 rpm for 15 min. The supernatant was immediately discarded and the precipitated NCs were redispersed in 1 mL hexane for characterization.

Purification process for preparing NCs with different defect densities: 1 mL of synthesised NCs solution (denoted as 0th wash) was added into centrifuge tube, mixing with 0.5 mL of methyl acetate. Then the mixture was centrifuged at 8000 rpm for 10 mins. The precipitates were collected and redispersed in 1 mL hexane (denoted as 1st wash). Then, the same process was repeated again to prepare the most defective NCs samples (denoted as 2nd wash). The 0th, 1st, and 2nd samples were then used for compositional and optical characterization.

3.1.2 Nanoplatelets

Materials: CH₃COOCs (cesium acetate, 99.9% trace metal basis), PbI₂ (lead(II) iodide 99%), oleic acid (technical grade 90%), oleylamine (technical grade 70%), toluene (Anhydrous, >99.8%), heptane (HPLC, grade ≥99.0%, GC), were purchased from Sigma-Aldrich. All chemicals were used as received.

Synthesis: The synthesis method is modified based on a previous reported method.⁷⁵ Cesium-oleate (Cs-oleate) precursor was prepared by dissolving 0.5mmol cesium acetate in 10 mL of oleic acid (concentration: 0.05 mol/L) under stirring at 60 °C for 1 hour. PbI₂ precursor solution was prepared by dissolving 0.1 mmol PbI₂ powder (46.1 mg) in a mixture of 100 μL of oleic acid, 100 μL oleylamine and 10 mL toluene (concentration: ~0.01 mol/L) at 80 °C under continuous stirring. Then both precursor solutions are cooled down to room temperature. In a typical nanoplatelets synthesis, 10 mL of PbI₂ precursor solution is taken to a glass vial with stir bar, then the glass vial is placed in an ice-water-bath and stirred for 2 mins. Finally, 250 μL of cesium-oleate was added into 10 mL of PbI₂ precursor (prepared in toluene) solution under vigorous stirring in the ice-water bath. After 2 mins of stirring, the solution was poured into a centrifuge tube and centrifuged at 14000 rpm for 10 mins and the precipitate was redispersed in 2 mL of hexane (edge-up), cyclohexane (mixture of edge-up and face-down) and heptane (face-down).

3.2 Material Characterization

3.2.1 Structural and Chemical Property Characterization

3.2.1.1 Proton Nuclear Magnetic Resonance (¹H-NMR)

Room temperature liquid-state ¹H-NMR (500.2 MHz) spectra were recorded on a Bruker Avance III HD 11.7 T spectrometer equipped with a BBO Smart Probe. ¹H

chemical shifts were referenced using the residual CH₃ signal of toluene-d₆ (2.51 ppm) as a secondary reference. All NMR samples were prepared by adding 5 μ L of test samples (including original NC solution, different antisolvent washed NC solution and corresponding supernatants, oleic acid, oleylamine and different antisolvents) into 5 mL of toluene-d₆.

3.2.1.2 X-ray Diffraction (XRD)

The crystalline structure of the perovskite films was investigated with an *X-ray diffractometer* (Bruker D8 Advance powder X-ray diffractometer) equipped with a Cu-K α X-ray tube, using glass/perovskite as samples measured with an air-free sample holder.

3.2.1.3 X-ray Photoemission Spectroscopy (XPS)

XPS data was acquired using a Kratos Axis SUPRA using monochromated Al K α (1486.69 eV) X-rays at 12 mA emission and 15 kV HT (180 W), with an analysis area of 700 $\times$ 300 μ m². The instrument was calibrated to the gold metal Au 4f core level (83.95 eV) and dispersion adjusted give a binding energy (BE) of 932.6 eV for the Cu 2p_{3/2} line of metallic copper. Ag 3d_{5/2} line FWHM at 10 eV pass energy was 0.544 eV. Source resolution for monochromatic Al K α X-rays is $\sim$ 0.3 eV. The instrumental resolution was determined to be 0.29 eV at 10 eV pass energy using the Fermi edge of the valence band for metallic silver. Resolution with charge compensation system on <1.33 eV FWHM on PTFE. High resolution spectra were obtained using a pass energy of 20 eV, step size of 0.1 eV and sweep time of 60 s, resulting in a line width of 0.696 eV for Au 4f_{7/2}. Survey spectra were obtained using a pass energy of 160 eV. Charge neutralization was achieved using an electron flood gun with filament current = 0.38 A, charge balance = 2 V, filament bias = 4.2 V. Successful neutralization was adjudged by analyzing the C 1s region wherein a sharp peak with no lower BE structure was obtained.

The spectra were charge corrected to the main line of the carbon 1s spectrum (adventitious carbon) set to 284.8 eV. All data was recorded at a base pressure of below 9×10^{-9} Torr and at room temperature (294 K). Data was analyzed using the software CasaXPS v2.3.19PR1.0.

3.2.1.4 Grazing-incidence Wide-angle X-ray Scattering (GIWAXS)

Grazing-incidence wide-angle X-ray scattering (GIWAXS): The 2d GIWAXS data was taken at German synchrotron DESY in Hamburg, Petra III, at the P03 MiNaXS beamline.²²⁸ A Lambda9M detector from X-spectrum was used with a wavelength of 1.05 Å. Processing of the 2d data was done using the software INSIGHT.²²⁹ This includes transformation to q-space, flatfield correction, masking, intensity corrections for detector absorption, solid angle, photon polarization and path attenuation and obtaining pseudo-XRD cuts.

3.2.1.5 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) in Chapter 4 was measured using Transmission IR spectroscopy (Shimadzu IRTracer 100). The samples were prepared by spin-coating the perovskite NCs solutions washed by different antisolvents with similar concentration (15 mg/mL) at 1500 rpm for 30 s on CaF₂ substrates (Knight Optical), and referenced to the transmission of IR in air. The spectrum was acquired in air with Happ-Genzel apodization, a resolution of 4 cm⁻¹, and 15 scans.

3.2.1.6 Transmission electron microscopy (TEM) and energy dispersive X-ray spectrometry (EDX)

Transmission electron microscopy (TEM) in Chapter 4 and energy dispersive X-ray spectrometry (EDX) measurements were taken in STEM mode (200 kV acceleration voltage) using a FIB-TEM Helios Nanolab 450S in SAE Technologies Development (Dongguan) Co.,

Ltd, Guangdong Province, China. The TEM samples were prepared inside a glovebox by dropping 5 μL of NC solution with a concentration of 10 mg mL^{-1} onto a copper TEM grid and dried inside the glovebox for 20 mins. A GATAN 648 vacuum transfer holder was used to eliminate the exposure to the ambient atmosphere to avoid degrading the NCs between the glovebox and TEM vacuum chamber.

TEM for Chapter 6 NPI samples were prepared by putting a small drop of nanoparticle solution onto the carbon-coated copper grid in a glovebox. Transmission electron microscopy images were recorded using a FEI Tecnai F20 (120 kV). A GATAN 648 vacuum transfer holder was used to eliminate the exposure to the ambient atmosphere to avoid modification of the nanoparticles between the glove box and the TEM vacuum.

3.2.2 Optical Property Characterization

3.2.2.1 Transient Absorption Spectroscopy (TAS)

Transient absorption spectroscopy (TAS) was used to reveal the carrier dynamics of the colloidal perovskite nanocrystals upon photoexcitation. Here, I mainly used short-time TA (less than 2 ns) to probe the early carrier kinetics including the influence of NC surface traps on carrier relaxation and recombination. In this section, the working principle of the short-time transient absorption spectroscopy and its instrument set-up with detailed implementation method would be introduced.

Working Principles:

In TAS set-up, a sample would be initially excited with the first laser pulse, so-called the “pump” laser, then a second laser pulse will arrived at the sample with a controlled time delay (t), so-called the “probe” laser. The second pulse laser (the probe) is a broad-band white light that covers the wavelength that can be absorbed by the samples. The change of absorption (ΔA), or in our set-up, the transmittance (ΔT) to the probe is

monitored at different time after the arrival of the first pulse laser (the pump). The final TA signal is recorded as $\Delta T/T$, which can be calculated by the following equation (3.1):

$$\frac{\Delta T}{T} = \frac{T_{pump\ on} - T_{pump\ off}}{T_{pump\ off}} \quad (3.1)$$

where ‘pump on’ and ‘pump off’ correspond to transmittance measurements of the probe light with and without the presence of the pump on the samples. The simplified set-up illustration can be found in Figure 3.1a.

The final TA spectra consists of both positive signal and negative signal (shown in Figure 3.1c). The positive signal can be further classified into ground state bleach (GSB) and stimulated emission (SE). GSB is the carrier depopulation process from the ground state (or valence band, VB) due to the pump excitation. As a result, it reduces the amount of absorption of the probe light at the corresponding wavelength. Therefore, the transmittance of the probe when the pump is on becomes larger than the transmittance of the probe when the pump is off. Therefore, GSB will introduce a positive $\Delta T/T$ signal. On the other hand, when the probe pulse pass through the excited carriers generated by the pump pulse, it increases the photon intensity in the detector due to the induced photoluminescence. Therefore, the pump-on signal is higher than the pump-off signal and leads to a positive $\Delta T/T$ signal (Figure 3.1b).

The negative signal is caused by photo-induced absorption (PIA). It can be explained by either the sub-band or intra-band state absorption such as the presence of self-trap states (STEs) (this is also known as product absorption (PA), as the pump excited carriers in these trap states and lead to an increase in probe absorption upon pump excitation) or the excited states absorption (ESA). Also, the process of bandgap renormalization (BGR) can lead to a negative $\Delta T/T$ signal. In summary, by analysing the resulted overall TA spectra from both positive and negative signals, a change of signal intensity overtime at different wavelength can be obtained which reflects the

change of carrier densities overtime due to different carrier loss pathways such as charge-carrier recombination, charge transferring and *etc.*

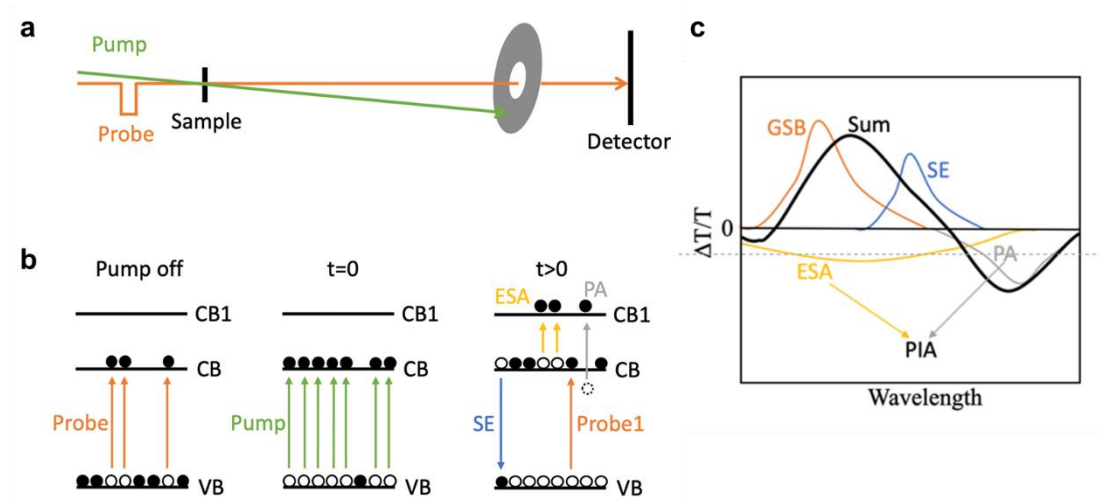


Figure 3. 1 Illustration of the transient absorption spectroscopy working principles. *a.* Schematic diagram of the transient absorption spectroscopy. *b.* Carrier excitation processes during the TA measurement. *c.* Example of the contributed component of the TA signal (TA spectra), including GSB (ground state bleach), SE (stimulated emission), ESA (excited state absorption), PA (product absorption), PIA (photoinduced absorption). The graph is modified based on Ref.²³⁰

TA Implementations: we used both Pump-Probe Transient Absorption Spectroscopy (PP-TAS) (Chapter 5-6) and Pump-Push-Probe Transient Absorption Spectroscopy (PPP-TAS) (Chapter 5) for the work described in this thesis. The details about the equipment set-up are shown below.

Pump-Probe Transient Absorption Spectroscopy (PP-TAS): The output of a Ti:sapphire amplifier system (Spectra Physics Solstice Ace) operating at 1 kHz and generating ~ 100 fs pulses (fundamental, 800 nm) is split into pump pulses and probe pulses. The 400 nm pump pulses are created by sending the 800 nm fundamental beam of the Solstice Ace through a second harmonic generating beta barium borate (BBO) crystal (Eksma Optics). The pump is blocked by a chopper wheel rotating at 500 Hz.

The broadband probe (330-700 nm) is generated by focusing the 800 nm fundamental beam onto a CaF₂ crystal (Eksma Optics, 5 mm) connected to a digital motion controller (Mercury C-863 DC Motor Controller). The pump-probe delay (100 fs to 2 ns) is controlled by a mechanical delay stage (Thorlabs DDS300-E/M). The transmitted pulses are collected with a monochrome line scan camera (JAI SW-4000M-PMCL, spectrograph: Andor Shamrock SR-163). The spectrum is taken with liquid samples inside a 1 mm thick cuvette. Concentrations of samples are adjusted to an absorbance of 1 OD at 400 nm.

Pump-Push-Probe Transient Absorption Spectroscopy (PPP-TAS): The PPP-TA experiments are based on extended modification of commercially available Helios transient absorption spectroscopic setup (Ultrafast systems). Fundamental 800 nm (1 kHz, <100 fs pulse duration) fs-laser pulses, which were generated from a Ti:sapphire regenerative amplifier (Solstice, Spectra Physics, Newport Corp.) divided three portions to derive pump, push and probe pulses. The first portion of it is directed to a β -barium borate (BBO) crystal to generate second-harmonic output (400 nm) which acts as pump. The second portion of the 800 nm is directed towards an optical parametric amplifier (TOPAS Prime, Spectra-Physics) and a frequency mixer (Niruvix, Light Conversion) to generate NIR push pulse (1300 nm). The remaining 800 nm pulses are used and focused into a sapphire or a YAG crystal to generate broadband visible probe (450 – 750 nm) and NIR probe (900 – 1400 nm), respectively.

In the present setup, the push beam is adjusted by varying the optical path length to arrive 10 ps later than the pump, while the probe beams are delayed w.r.t. pump by automated mechanical delay stages. The three beams are focused onto the sample surface at the same spot (diameter $\sim$ 0.5 mm), and the transmitted probe is collected by a CCD spectrometer. To mitigate shot-to-shot noise, we use another CCD spectrometer to measure fluctuations in a reference beam that is split off from the probe before it hits the sample. A mechanical chopper is in place in the pump beam path to modulate at

500 Hz to block every other pulse and relay the TA signal. Under same experimental condition, we record the pump-probe signal when push beam is blocked and open to obtain PP and PPP spectral/dynamical features, respectively.

3.2.2.2 Transient Photoluminescence Spectroscopy (TRPL)

Similar to transient absorption spectroscopy, transient photoluminescence spectroscopy is another power techniques to study the carrier dynamics, especially for the carriers that are undergoing radiative recombination. It allows us to study the change of PL intensity as a function of time and wavelength. Based on the requirement of the probing time window, we used two methods in the relevant experiment performed in this thesis. They are time-correlated single photon counting (TCSPC) and intensified charge-coupled devices (iCCD) with an electronically controlled shutter. In this section, the working principles and instrument set-up will be introduced.

Time-Correlated Single Photon Counting (TCSPC)

The working principle of TSCPS is to measure the time delay between emission of a pump pulse and arrival of the first PL photon from the emitting sample. The so acquired time-of-flights are then sorted in a histogram format, which after many repetitions, the histogram plots will eventually reflect the decay dynamics of the emitting sample, as the time counting resolution is precisely controlled by the laser repetition rate²³¹.

The TCSPC measurement is conducted as follow: The PL decay curve is obtained by exciting the samples (NC films for chapter 4 and NPI solution and films for chapter 6) with a Pico Quant LDH407 laser diode at 407 nm with a repetition rate of 2.5 MHz at different fluences. The emission signal was selected with a monochromator to obtain the desired emission wavelength and detected by a Hamamastu R3809U-50 photomultiplier detector. Color filters (longpass filter) were utilised to remove the scattered photons from the excitation laser.

Intensified Charge-Coupled Devices (iCCD)

iCCDs are charge-coupled device (CCD) cameras with an intensifier unit in front of them that multiplies the number of incoming photons and allows an electronic gating of the signal at the same time. Firstly, the incoming photons pass through an electronically controlled mechanic shutter, which has the fastest response (i.e. smallest measurement resolution around 4 ns). Then the photons are converted to photoelectrons through a photocathode. The photoelectrons would then be strongly intensified by a microchannel plate with high voltage acceleration and ionising the channel wall to increase the overall number of photoelectrons. Finally, the intensified photoelectrons will be absorbed by a phosphor coating layer to re-convert into photons and entering the CCD camera to obtain spectral information at different shutter time delay.

The set-up used in Chapter 6 can be described as below: the iCCD camera system Andor iStarDH740 CCI-010 connected to a grating spectrometer (Andor SR303i). Excitation was realised through femtosecond laser pulses generated in a homebuilt setup by second harmonic generation (SHG) in a BBO crystal from the fundamental output (pulse energy 1.55 eV, pulse length 80 fs) of a Ti:Sapphire laser system (Spectra Physics Solstice). The laser pulses had an energy of 3.1 eV. Temporal resolution of the PL emission was obtained by measuring the PL from the sample and stepping the iCCD gate delay for different delays with respect to the excitation. The best achievable time resolution of our iCCD is about 4 ns as determined via measuring the instrument response of the iCCD to a 100 fs laser pulse.

3.2.2.3 Photothermal Deflection Spectroscopy (PDS)

PDS is an ultrasensitive absorption measurement technique that detects heating of the sample due to the nonradiative relaxation of absorbed light and is insensitive to reflection and scattering. PDS enables the detection of absorbance signals with 5-6 orders of magnitude weaker than the band edge absorption. For the measurements in

Chapter 4, the sample (film on quartz substrate) was illuminated with a monochromatic pump beam. Light absorption leads to a thermal gradient near the sample surface via non-radiative relaxation induced heating. This results in a refractive index gradient in the area surrounding the sample surface. This refractive index gradient is further enhanced by immersing the sample in an inert liquid FC-72 Fluorinert[®] (3M Company) which has a high refractive index change per unit change in temperature. A fixed wavelength cw laser probe beam was passed through this refractive index gradient, producing a deflection proportional to the absorbed light at that particular wavelength, which is detected by a photodiode and lock-in amplifier combination. Scanning through different wavelengths gives us the complete absorption spectra. Because this technique makes use of the non-radiative relaxation processes in the sample, it is immune to optical effects like interference and scattering.

3.2.2.4 Photoluminescence Quantum Yield (PLQY)

The power-density dependent PLQY measurement in Chapter 5 was measured using a commercial setup from Ocean Optics with excitation from a 405 nm wavelength continuous wave (CW) diode laser.

The energy-dependent PLQY measurement in Chapter 5 was by UV-NIR absolute PLQY spectrometer (HAMAMATSU, Quantaaurus-QY plus; with excitation wavelength 375 nm to 575 nm). The optical density of the 0th wash (less defect sample) and 2nd wash (more defect sample) samples were tuned to be the same (< 0.1) with hexane dilution.

3.2.2.5 k-space Fourier Microscopy

k-Space Fourier Microscopy measurement in Chapter 6 is conducted as follow: Perpendicular excitation of the perovskite film is performed by focusing a 448 nm cw laser on the centre of the back aperture of an oil-immersion objective (Nikon, Apo TIRF,

100x, NA 1.49). The reemitted photoluminescence at $< 79^\circ$ is collected through the same objective and the emission pattern is determined using the light intensity distribution in the back focal plane of the objective. The back focal plane image is demagnified by 3 times before being imaged on the entrance slit (100 μm wide) of a spectrometer, where a narrow slice of the scattering pattern near $k_x/k_0=0$ is filtered and dispersed by a grating (150 lines/mm) and collected using an EMCCD.

3.3 Device Fabrication and Characterization

Device Fabrication: ITO/glass substrates (Colorado Concept Coatings LLC) were cleaned by ultrasonication in acetone and isopropanol for 15 min each and dried in the oven. The substrates were subsequently O_2 -plasma treated for 10 min at 250 W forward power (0 W reverse power), using a radio-frequency plasma source. For bipolar devices, poly(3,4- ethylene dioxythiophene) polystyrene sulfonate (PEDOT: PSS; Heraeus Clevis P Al.4083) was subsequently deposited at 3500 rpm for 30 s (1000 rpm s^{-1} acceleration), then annealed at 145 $^\circ\text{C}$ for 15 min. Poly(N,N'-bis(4- butyl phenyl)-N,N'-bis-phenyl benzidine) (poly-TPD; 1-Material) were dissolved in chlorobenzene (anhydrous 99.8%, Sigma Aldrich) with a concentration of 8 mg mL^{-1} . These polymer layers were spin-cast over the PEDOT: PSS at 2000 rpm for 30 s inside a nitrogen-filled glovebox and annealed at 120 $^\circ\text{C}$ for 10 min. The NCs/NPIs were subsequently deposited at 1500 rpm for 30 s inside an N_2 -filled glovebox. For NC LEDs in Chapter 4, 35 nm of 2,2',2''-(1,3,5-benzinetriyl)- tris(1-phenyl-1-H-benzimidazole) (TPBi; Ossila) was thermally evaporated over the NCs under a base pressure of 1×10^{-6} mbar, followed by 1 nm LiF and 100 nm Al. The devices were measured in a glovebox. For NPI LEDs in Chapter 6, 20 nm of 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP; Ossila) was thermally evaporated over the NPIs under a base pressure of 1×10^{-6} mbar, followed by 100 nm Ag. The devices were measured in ambient.

LED device characterisation:

For NC LEDs in Chapter 4, the EL spectra are measured with commercialised system (XPQY-EQE-350-1100, Guangzhou Xi Pu Optoelectronics Technology Co., Ltd) that was equipped with an integrating sphere (GPS-4P-SL, Labsphere) and a photodetector array (S7031-1006, Hamamatsu Photonics). All devices are measured in N₂-filled glovebox.

For NPI LEDs in Chapter 6, the Current density–voltage (J–V) characteristics were measured using a Keithley 2400 source-meter unit. The photon flux was measured simultaneously using calibrated silicon photodiodes centred over the LED. The radiance (in W sr⁻¹ m⁻²) of the devices was calculated based on the emission function of the PPBH LED and on the known spectral response of the silicon photodiode, and the EQEs were calculated assuming a Lambertian profile. The electroluminescence spectra of the devices were measured using a calibrated iCCD camera system (AndoriStar DH740 CCI-010) connected to a grating spectrometer (Andor SR303i). The accuracy of the spectral data was cross-checked against a Labsphere CDS-610 spectrometer.

3.4 Density Function Theory Calculation (DFT) and Modelling

Details about the DFT calculation in Chapter 4 is described as the following: The first-principles calculations were carried out based on DFT with the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional as implemented in the Vienna ab initio Simulation Package (VASP). The all-electron projector-augmented wave (PAW) method was adopted. All the density functional theory (DFT) calculations were performed under periodic boundary conditions using the Vienna ab simulation package (VASP). The projector-augmented-wave (PAW) method with a plane-wave basis set was used. The plane-wave energy cutoff is set to 600 eV for CsPbBr_{0.6}I_{2.4} unit cell. A Monkhorst–Pack Brillouin zone sampling grid with a resolution of $2\pi \times 0.03 \text{ \AA}^{-1}$ is adopted to ensure that all the enthalpy calculations are well converged with an

error less than 1 meV/atom. After the unit cell fully relaxed, a $2 \times 2 \times 2$ supercell was adopted to simulate the atomic position in a $\text{CsPbBr}_{0.6}\text{I}_{2.4}$ unit cell.

The energy barriers of halide ion migrations in these perovskites were studied by the nudged elastic band (NEB) method. To simulate the halide ion migration, a $2 \times 2 \times 2$ supercell was used to calculate the vacancy formation energy and optimise the minimum energy pathway of halide ion migration. Five images (excluding initial and final states) are linearly interpolated between the initial and final states during the mitigation process.

Details about the DFT calculation in Chapter 5 is described as the following: Structural relaxations and electronic properties calculations were performed based on density-functional theory as implemented in the Vienna Ab initio Simulation Package (vasp)²³². The exchange and correlation functional were described using the Perdew-Burke-Ernzerhof generalised gradient approximation (GGA)²³³. The all-electron projector augmented wave (PAW) method was adopted to describe the electron-ion interactions²³⁴, treating 5s25p66s1, 6s26p2, 4s24p5 and 5s25p5 as valence electrons for Cs, Pb, Br and I atoms, respectively. To ensure that all enthalpy calculations were well converged to the level of 1 meV per atom, the plane-wave energy cutoff was set at 500 eV, and Monkhorst-Pack k-point grids with a reciprocal space resolution of $2\pi \times 0.03 \text{ \AA}^{-1}$ in the Brillouin zone were chosen²³⁵. Structural relaxations were performed with forces converged to less than $0.001 \text{ eV \AA}^{-1}$. The defect structure of CsPbX_3 was constructed by removing a halogen atom from the $2 \times 1 \times 1$ supercell.

The optical simulation Chapter 6 was performed based on the Green's function formalism which is described below: The electric field (E) generated at position r due to a dipole source at r_0 is calculated via the electric Green's function $G(r, r_0)$ in free space, given by $E(r) = \omega^2 \mu_0 G(r, r_0) \mu$, where μ_0 is the vacuum permeability. In the case of a dipole placed within a multilayer structure, Green's function for the system can be separated into two parts – the free space part and the reflected part. The reflected

part contains the $k_{||}$ dependent Fresnel reflection coefficients for different polarizations. We use this stratified system Green's function to estimate the electric field from a dipole source inside the multilayer structure to infinite half spaces (super/ substrate). To obtain the radiation patterns, we use the far field approximation to the Green's function. This involves a transformation from Cartesian to spherical coordinates. Thus, using the asymptotic electric field, we calculate the radiated power per unit solid angle by integrating the time averaged Poynting vector which gives the radiation pattern.

Chapter 4: Elucidating the Role of Antisolvents on the Surface Chemistry and Optoelectronic Properties of CsPbBr_xI_{3-x} Perovskite Nanocrystals

Junzhi Ye, Robert L.Z. Hoyer conceived the projects. Zhenchao Li, Ziming Chen and Hin-Lap Yip performed TEM measurements and host Junzhi during the pandemic in 2020. Dominik J. Kubicki and Clare P. Grey performed the H-NMR measurements. Yunwei Zhang Performed DFT calculations. Junzhi Ye, Clara Otero-Martinez, Kavya Reddy Dudipala synthesised the materials. Manuel A. Reus and Peter Muller-Buschbaum performed GIWAXS measurements. Zahra Andaji-Garmaroudi performed PDS measurements. This chapter is based on Ref.²³⁶

4.1 Introduction

Cesium lead halide perovskite nanocrystals (NCs) have drawn significant attention due to their superior optoelectronic properties, which include their efficient luminescence and narrow emission peak that is spectrally tunable over the entire visible wavelength range.^{34,41,78,156,237-240} Since Kovalenko and co-authors established a simple hot injection synthesis method for CsPbX₃ (X = Cl, Br, or I) NCs in 2015,³⁴ these all-inorganic perovskite NCs have emerged as an appealing class of materials for ultrahigh-definition display (*via* light-emitting diodes, LEDs),^{238,240-244} lasing,^{238,245} and photovoltaic applications.^{238,241,246,247} For all of these applications, it is important to be able to fine-tune the optical bandgap, and this is commonly achieved by mixing species in the halide site, such as Br/Cl for blue-emitters or Br/I for red-emitters according to the Rec. 2020 standard.^{151,203,219,248-252}

One of the essential steps to obtain low polydispersity NCs for LED devices is purification. This step is needed to remove impurities, such as unreacted precursors or ligands, which can significantly affect film formation and device performance. The solubility of perovskites in different solvents is related to its relative polarity (which is correlated to the dielectric constant, ϵ_r), in which more polar solvents have a stronger dipole moment, and therefore a greater ability to dissociate bonded species to cause dissolution. The as-synthesised NCs are usually capped with long-chain alkyl ligands (namely oleic acid, OA; or oleylamine, OAm) and dissolved in “good” solvents, such as toluene ($\epsilon_r = 2.24$; relative polarity = 0.099), which are typically non-polar and have low dielectric constants. During purification, “poor” solvents (*i.e.*, antisolvents, which are polar, with high dielectric-constants), such as alcohols, are added to precipitate the NCs from “good” solvents, leaving behind impurities in the original solution (the supernatant). However, several groups have observed that the optoelectronic properties of the resulting NCs depend on the antisolvent used.²⁵³⁻²⁵⁵ For example, Hoshi *et al.* observed that the photoluminescence quantum yield (PLQY) of CsPbBr₃ NCs decreased when washing with polar solvents, such as acetonitrile, acetone and methanol.²⁵⁵ Similarly, for mixed-halide perovskite NCs, such as CsPbBr_xI_{3-x} NCs, selective etching was observed when the NCs were purified with acetone. That is, iodides were removed during the purification process, while bromides were retained in the NCs.²⁵⁶ As a result, the photoluminescence (PL) peak blue-shifted and the PLQY decreased after purification. These indicate that an increase in the bandgap occurred due to changes in mixed halide composition caused by a partial removal of iodide from the NC surface.^{219,256-258} However, the cause of the decrease in PLQY, removal of surface halides after washing, and relationship between the selective etching of iodides and the properties of the antisolvents used during washing remains unclear. Hints on how the surface chemistry of these NCs are influenced during washing can be found by looking to the work on single-halide perovskite NCs.^{96,257,259} These include the work by Grisorio *et al.*,²⁵⁷ who proposed that there are interactions between polar antisolvents, and the OA and OAm ligands that cause surface ligand detachment. However, detailed studies into the mixed-halide systems are needed

to understand how the synergistic effects between the surface ligands and antisolvent cause the selective etching of the surface halides, and how this can be mitigated. It is also critical to understand how these factors influence the optoelectronic properties of the NCs through their surface chemistry, and how the purification process can be designed to maximise the PLQYs and photostability after washing.

To address these critical questions, we studied the mixed-halide system CsPbBr_xI_{3-x}, which in itself is an important composition for a variety of applications, such as pure-red emitters, as well as the top-cell for tandem photovoltaics with silicon.^{242,260,261} We investigated antisolvents with different polarity (relative polarity to water shown in brackets): methyl acetate (0.253), acetone (0.355) and 1-butanol (0.552), which are all commonly used for perovskite NC purification. Our studies indicate that the degree of PL blue-shift, and therefore the change in surface I to Br ratio, is correlated to the relative polarity of the antisolvents. This work aims to investigate the effect of antisolvent polarity on the surface iodide and hence the properties of NCs. We integrate detailed proton Nuclear Magnetic Resonance (¹H-NMR), Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD) and X-ray Photoemission Spectroscopy (XPS) analysis to understand the surface chemistry of the system. We identified that the increasing blue-shift in bandgap with the polarity of the antisolvent is due to the more polar antisolvents triggering a reaction between the OA and OAm ligands, causing the removal of surface iodides. We show that these effects can be suppressed by reducing the polarity of the antisolvent. The detailed understanding of the NC purification mechanism put forward in this work could facilitate the fabrication of more stable and high-performance NCs for applications like LEDs and photovoltaics.

4.2 Results

4.2.1 Influence of Antisolvent Polarity on NC Optoelectronic Properties.

The mixed I-Br halide perovskite nanocrystals (CsPbBr_xI_{3-x} NCs) were synthesised by tip-ultrasonication, followed by anion exchange, as previously reported by Tong *et al.*^{50,262} The synthesis scheme is shown in Figure 4.1(a), with the Scanning Transmission Electron Microscopy (STEM) image of the NCs shown in Figure 4.1(b) and Figure 4.2. The as-prepared NCs were washed in different antisolvents to remove unreacted precursors (Figure 4.1(a), step 3). The obtained NCs were re-dispersed in hexane and spin-coated onto glass substrates for characterization. Based on the photothermal deflection spectroscopy and UV-Vis absorption spectroscopy measurements (Figure 4.1(d) and Figure 4.3(a)), the absorption of the original NC thin films is blue-shifted after washing with more polar antisolvents, from methyl acetate, to acetone, to butanol. The original as-prepared CsPbBr_xI_{3-x} NCs had an absorption onset at c. 630 nm and additional absorption peak at 560 nm (Figure 4.3(a)). The dual absorption peak in the crude original solution may originate from unreacted precursors. After washing with different antisolvents (acetone, 1-butanol or methyl acetate), the absorption peak at 560 nm disappeared, likely due to the removal of these excess precursors. XRD and EDX measurements showed that the NCs remained as perovskites after purification. This is because the diffraction peaks after washing matched those of the cubic perovskite phase (Figure 4.1d). Also, no significant differences in the elements present and their distribution across the NCs were observed in the elemental mapping measurements, which showed that all NCs after washing still retained Cs, Pb, I and Br (Figure 4.4). However, by washing with different antisolvents, we observed a shift in the absorption onset in the PDS spectra (Figure 4.1(d)), along with a concomitant shift in PL peak position (Figure 4.1e). With no solvent used during washing (*i.e.*, by centrifuging only), the PL peak of the resulting NCs was centered at 653 nm. With the use

of methyl acetate, acetone or butanol during purification, the PL peak blue-shifted to 638 nm, 599 nm and 538 nm, respectively (Figure 4.1(h) and Table 4.1). Comparing the PDS and UV-Vis absorption results shown in Figure 4.1(d) and Figure 4.3(b) in logarithmic scale, the same trend of absorption blue-shift is observed upon washing. However, there is a slight difference in the amount of shifting when washing with the same antisolvents. This might be due to the batch-to-batch synthesis variation. The starting composition and concentration of the unwashed NCs would be slightly different, so that the exact bandgap of the NCs after washing would also have differences, but the overall trend is preserved. Furthermore, the absorption onset and the sub-bandgap absorption were less clear in Figure 4.3(b) for normal UV-Vis absorption spectra measurement comparing to PDS.

In addition to these changes in the bandgap, the PLQY and PL lifetime (measured from spin-coated films of NCs) also decreased after washing (Table 4.1). We observed that these decreases were larger when more polar antisolvents were used. To understand these observations, we firstly determined whether quantum confinement effects could have played a role (i.e. if the NC size reduced after washing). We analyzed the distribution in the sizes of the NCs measured by TEM before and after washing with different antisolvents (Figure 4.2), and found there to be no significant changes (Figure 4.3(c)). An example can be found in Figures 4.1(b) and (c), which compares the original NCs and NCs after washing with methyl acetate. Furthermore, the median size of the NCs in all cases were close to 8 nm (Figure 4.3(c)). These results therefore rule out the possibility of the size-induced changes in PL emission wavelength. However, the size analysis based on TEM images only revealed the face-up orientation when the NCs lying vertically to the substrates. We did observed that the shape of NCs became more irregular due to merging after washing (Figure 4.2 (k) and (l)). Therefore, the reduction of surface halide may have slightly change the NC sizes, but it is hard to directly observe from TEM measurements.

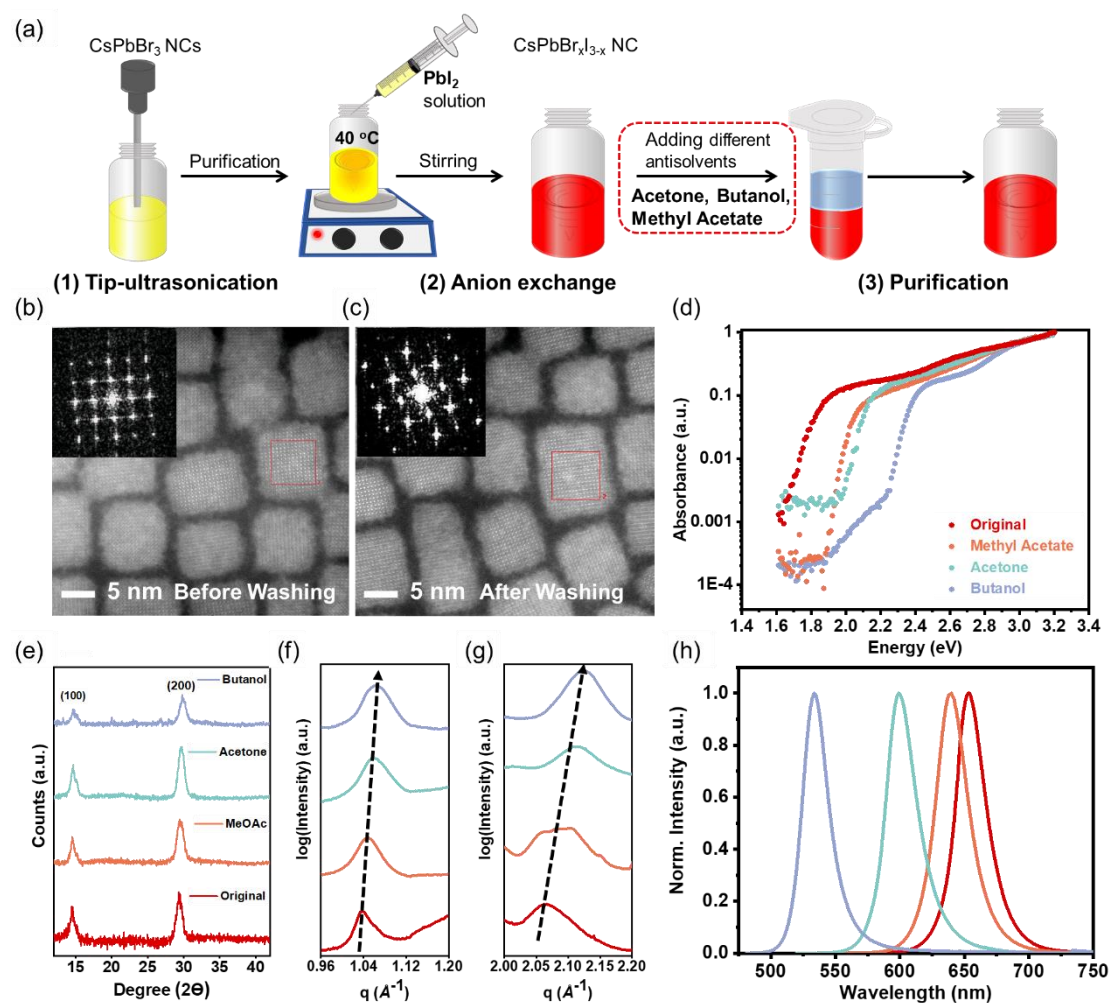


Figure 4. 1 (a) Schematic illustration of the synthesis of mixed bromide-iodide inorganic perovskite nanocrystals (NCs) through halide exchange on CsPbBr₃ NCs, which were grown a tip-sonication approach. The anion exchange reaction replaces bromides with iodides to obtain red-emitting CsPbBr_xI_{3-x} NCs, which are purified by adding different antisolvents, including methyl acetate, acetone, and *n*-butanol. (b, c) Scanning Transmission Electron Microscopy (STEM) of the as-synthesised (left) and acetone-washed CsPbBr_xI_{3-x} NCs (right). The inserts are the Fast Fourier Transform images of the NCs in the selected red region. (d) Photothermal deflection spectra of the pristine and washed NC films. (e) X-ray diffraction patterns of pristine and purified NC thin films on glass substrates. (f) GIWAXS line cut plots for (100) face in *q* space. (g) (200) face in *q* space. (h) Photoluminescence spectra of CsPbBr_xI_{3-x} NC thin films

after purification with different antisolvents: (red) no antisolvent (dissolved in hexane only), (yellow) methyl acetate (MeOAc) (1:1, v/v); (green) acetone ((1:1, v/v) ;(blue) butanol (1:1, v/v). All graphs in this Chapter are reprinted with permission under Attribution 4.0 International (CC BY 4.0) from Ref. ²³⁶ Copyright © 2022 The Authors. Published by American Chemical Society

Table 4. 1 Properties of antisolvents and their influence on the optoelectronic properties of CsPbBr₃I_{3-x} NCs. The PLQY was measured using a 405 nm cw laser under different power densities. DN= Gutmann donor number, AN = Gutmann acceptor number. Dielectric constant is the average dielectric constant of the antisolvents. Solvent polarity is the relative polarity to water.

Washing Solvent	Solvent Polarity	Dielectric Constant (298 K)	Solvent DN/AN	PL Peak (nm)	FWHM (nm)	PLQY (125 μW cm ⁻²)	I composition from TEM EDS(XPS)
Hexane	0.009	1.9	0/0	653	35	81.9%	82 at%
MeOAc	0.253	6.7	16.5/10.7	637	35	62.9%	55 (44) at%
Acetone	0.355	20.7	17.0/12.5	599	32	32.1%	37 (18) at%
Butanol	0.552	17.3	19.5/36.8	533	34	10.1%	25 (14) at%

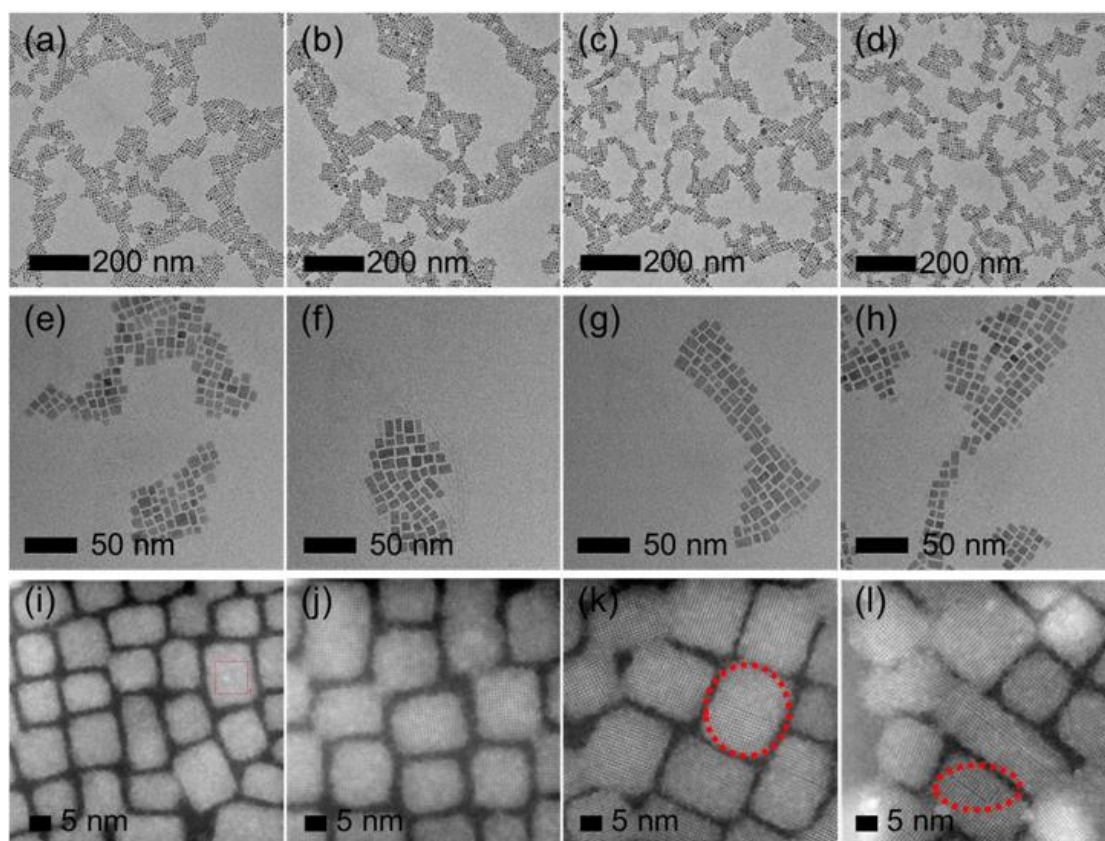


Figure 4. 2 (a)-(h) TEM images. (i)-(l) STEM images. Image (a), (e) and (i) are original NCs. Image (b), (f) and (j) are NCs washed with methyl acetate. Image (c), (g) and (k) are NCs washed with acetone. Image (d), (h) and (l) are NCs washed with butanol.

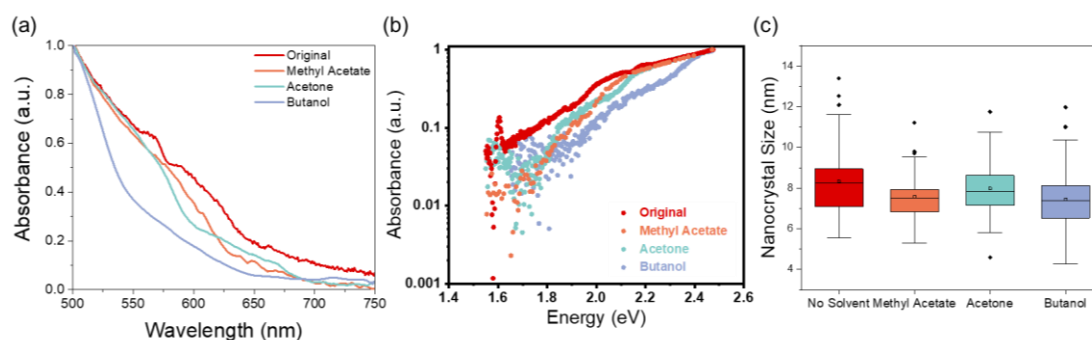


Figure 4. 3 (a) UV-Vis absorption spectra of washed NC films prepared by spin-coating (linear scale). (b) UV-Vis absorption spectra of washed NC films prepared by spin-coating (logarithmic scale) (c) Box plots of the nanocrystal size distribution.

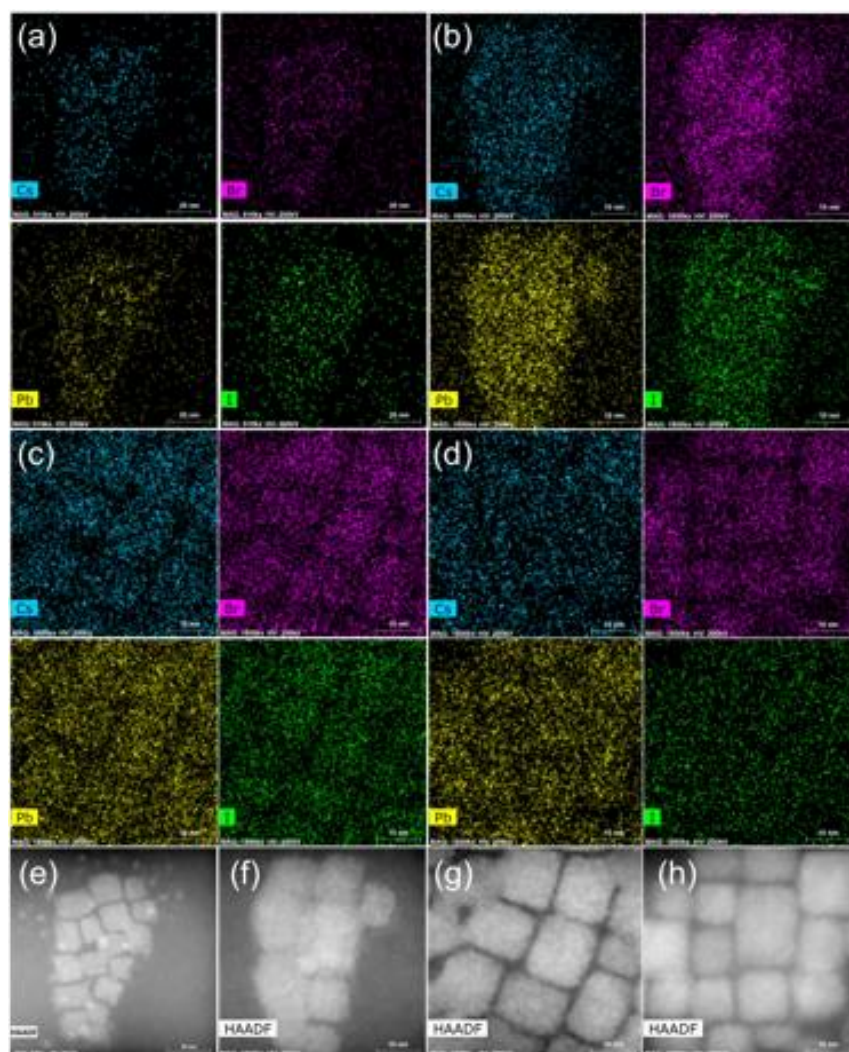


Figure 4. 4 TEM EDX Elemental Mapping a) No solvent, b)Methyl Acetate c) Acetone d) Butanol. (e)-(h) are their corresponding HAADF TEM images where the EDX elemental mapping is recorded.

On the other hand, TEM-EDX and XPS results showed that the NC chemical composition in both the bulk and surface became more bromide-rich after washing (Table 4.2), especially with the use of more polar antisolvents. This relationship between antisolvent polarity, Br/I composition and PL properties is shown in Figure 4.5. Figure 4.5(a) demonstrated a clear inverse relationship between the antisolvent polarity and the I/Br ratio. Washing with more polar antisolvents tends to reduce the I/Br ratio more as the surface I was removed. This is also

observed in I 3d core level XPS spectrum shown in Figure 4.6(a), in which the I 3d XPS peak intensity decreased more after washing with butanol than methyl acetate or acetone. In addition, XRD measurements showed that the (100) and (200) peaks of the NCs shifted towards higher 2θ values as the antisolvent polarity was increased (Figure 4.1(e)), showing that the lattice parameter was reduced, which correlates with the removal of the larger I⁻ anions. The calculated lattice constants are shown in Table 4.3. The calculated lattice constant decreased from 6.11 Å (original) to 6.08 Å (methyl acetate washed), to 6.03 Å (acetone washed) and 6.02 Å (butanol washed). The calculated value is in between 6.02 Å (cubic CsPbBr₃) and 6.41 Å (cubic CsPbI₃).²⁶³ The change in d-spacing is also observed in our GIWAXS line cut plot. (Figure 4.1(f) and (g)). Figure 4.1(f) and (g) show that the q value increased for the (100) and (200) planes as the NCs were washed with more polar solvents, which is consistent with the 1D XRD θ - 2θ line scan results shown in Figure 4.1(e). Overall, these observations suggest that increasing the polarity of the antisolvent led to the preferential removal of I, which in turn leads to an increase in the density of non-radiative recombination centers that reduce the PLQY. This is also confirmed by PDS measurements (Figure 4.1(c)), which show an increase in the sub-bandgap absorption of the colloidal NC solution after washing with the most polar antisolvents (acetone or butanol). In addition, the absorption onset became less steep after washing with more polar antisolvents, indicating an increase in disorder (see Figure 4.7 and Table 4.4). The methyl acetate washed NC has the steepest slope which indicates it has less disorder as the methyl acetate washed NCs have the unreacted ligands and precursors removed without creating too many surface defects. The increased disorder (acetone and butanol washed NCs) may arise as a consequence of the selective removal of iodide species from different parts of the NCs during purification.

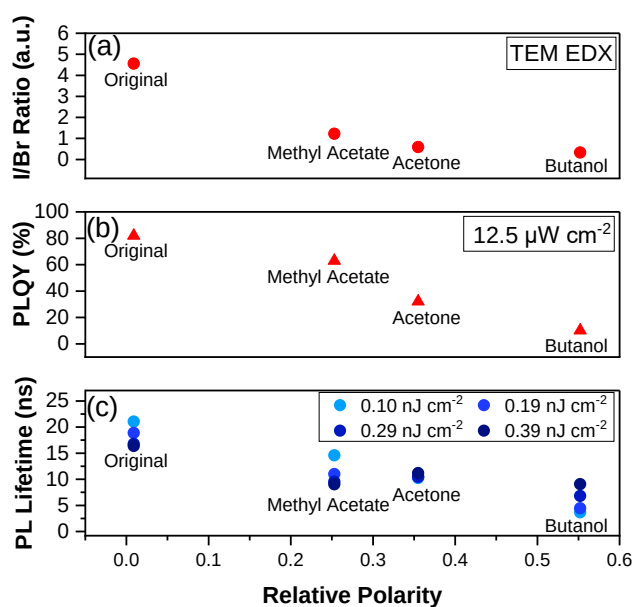


Figure 4. 5 Influence of the relative polarity of the antisolvent on the (a) I/Br ratio, (b) PLQY and (c) PL lifetime of the washed NCs, as compared to the NCs precipitated without the use of any antisolvents (denoted as a relative polarity of 0).

Table 4. 2 Composition study. TEM-EDX and XPS results for NC washed with and without solvents.

TEM EDX		Atomic Percentage (%)			Ratio (%)
Antisolvents	Cs	Pb	Br	I	I/(Br+I)
Original	14.44	10.54	13.39	61.63	82.15
Methyl Acetate	15.37	25.97	28.73	29.93	51.02
Acetone	18.03	23.39	37.22	21.37	36.47
Butanol	13.29	23.08	47.65	15.98	25.11
XPS		Atomic Percentage (%)			Ratio (%)
Antisolvents	Cs	Pb	Br	I	I/(Br+I)

Original	Covered by ligands (Atomic % cannot be resolved)				
Methyl Acetate	13.57	27.64	32.80	25.99	44.21
Acetone	12.91	29.36	47.52	10.21	17.69
Butanol	11.68	27.00	52.46	8.85	14.43

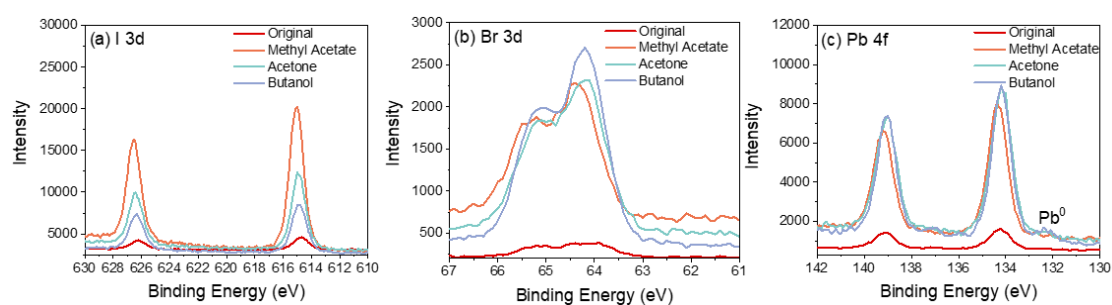


Figure 4. 6 XPS spectra of (a) I 3d, (b) Br 3d and (c) Pb 4f core level.

Table 4. 3 XRD analysis to calculate lattice constant. X-ray wavelength is 1.5406 Å.

Antisolvent	Miller Indices			Bragg's Angle		d-spacing	Lattice Constant (Å)	Average
S				2θ	θ	$d_{hkl} = \lambda / (2 \sin \theta)$	$a = d_{hkl} * \sqrt{h^2 + k^2 + l^2}$	a
	h	k	l					(Å)
Butanol	1	0	0	14.69	7.34	6.03	6.03	6.02
	2	0	0	29.71	14.86	3.00	6.01	
Acetone	1	0	0	14.67	7.34	6.03	6.03	6.03
	2	0	0	29.64	14.82	3.01	6.02	
	1	0	0	14.50	7.25	6.10	6.10	6.08

Methyl	2	0	0	29.44	14.72	3.03	6.06
Acetate							
Original	1	0	0	14.44	7.22	6.13	6.11
	2	0	0	29.32	14.66	3.04	6.09

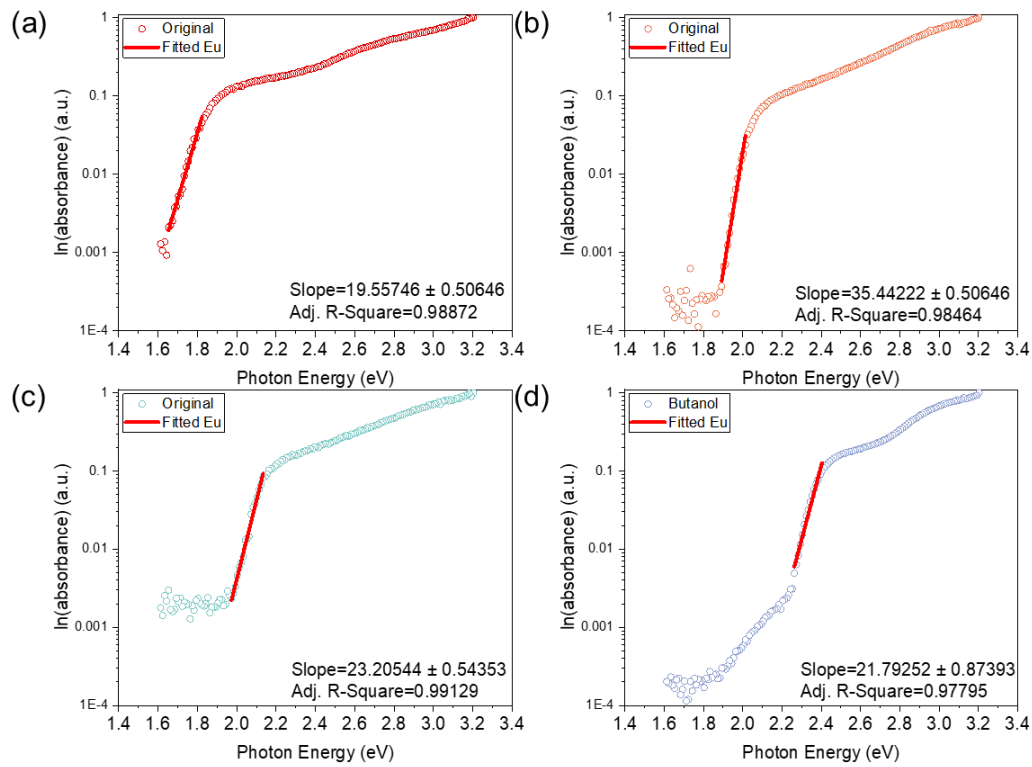


Figure 4. 7 Fitted PDS data to extract Urbach Energy. (a) original NC films. (b) methyl acetate washed NCs.(c) acetone washed NCs. (d) butanol washed NCs.

Table 4. 4 Fitted Urbach energy of NC thin films. The value is fitted based on the following equation $\alpha = \alpha_0 + e^{\frac{E}{E_u}}$ (1), $E_u = \frac{\log(\alpha - \alpha_0)}{E} = \frac{1}{slope}$ (2), where α is the absorption coefficient, E is the energy of the light absorbed, and E_u the Urbach energy. We note that in fitting the model given in equation to the PDS data in Figure 4.8, we are assuming that there is

Urbach absorption in the energy range considered. However, this region is convoluted with the excitonic peak superimposed over the rise in the absorption continuum. The Urbach energies obtained and shown in Table 4.4 are therefore approximate values. Regardless, we can see from Figure 4.8 that the NCs treated with methyl acetate had steeper absorption onsets than NCs purified with acetone or butanol, which is either due to lower Urbach energies or narrower excitonic peaks, with can both arise due to reduced disorder in the NCs.

Samples	Slope	Eu (meV) (1/slope)
Original	19.6	51.0
Methyl Acetate	35.4	28.2
Acetone	23.2	43.1
Butanol	21.8	45.9

To understand the influence of these defects introduced after washing on the PL lifetime, TCSPC was measured on the spin-coated NC films. The data is fitted with a numerical three component exponential decay function shown in Table 4.5. We note that whilst this model is not necessarily physically-relevant, it provides a numerical description of the PL decay curves that is not reliant on knowing the recombination mechanism a priori or fitting a large number of variables to each PL decay curve, which may lead to inaccurate local minima fittings. Figure 4.5(c) and Table 4.5, show the fitted average time constants from our model at different fluences from 0.009 nJ cm⁻² pulse⁻¹ to 0.39 nJ cm⁻² pulse⁻¹. At low fluence (0.009 nJ cm⁻² pulse⁻¹), the PL lifetime decreased from 21.05 ns (original) to 14.58 ns (methyl acetate), 10.25 ns (acetone) and 3.67 ns (butanol), as shown in Figure 4.8(a). The decrease in PL lifetime after washing with more polar solvents (Figure 4.5(c)) is consistent with the presence of a high density of recombination centers. This trend of decreasing in PL lifetime shown in Figure 4.8(a) also

matches the decreasing trend of PLQYs as shown in Figure 4.5(b). However, as we increased the fluence, the PL lifetime decreased for the original NCs and the NCs washed with methyl acetate (Figure 4.8(e-f)). Since the measurement fluence is in the $\text{nJ cm}^{-2} \text{ pulse}^{-1}$ range, Auger recombination is unlikely to have occurred. The current density at 0.1 nJ cm^{-2} would generate carrier densities around 10^{12} cm^{-3} ($N < 0.001$) following the method of estimating carrier density^{264,265}. In low defect-density systems, (i.e., the original NCs and methyl acetate washed NCs), the decrease in PL lifetime when increasing the measurement fluence could be explained by an increasing proportion of radiative recombination (bimolecular), as opposed to Shockley-Read-Hall recombination. In contrast, the PL lifetime increased with fluence for the acetone- and butanol-washed NCs (Figure 4.8(g-h)). The increase in PL lifetime is likely due to the trap-filling effect as fluence increased.²⁶⁶ These washing-induced defects can be atomically resolved with HAADF-STEM images, and are visualised in Figure 4.9. The HR-TEM images of the NCs (Figure 4.9) provides several pieces of evidence for structural defects in the purified NCs. Figure 4.9(a) and (b) shows a single acetone-washed NC, in which the bottom half of the NC is maintained as cubic-phase perovskite, but the top half has been changed to the Ruddlesden-Popper (RP) phase. In RP phases, all the [001]-projected cation atom columns are composed of Cs-Pb-Br columns (Figure 4.9 (a) and (b)).⁴¹ This matches with the previous study by Yu et al., in which they also observed the co-existence of cubic and RP phase perovskites in CsPbBr₃ nanosheets.²⁶⁷ The boundary between the two phases may be a site for non-radiative recombination to quench the PL. Another form of defects observed in the washed NCs are line defects, as shown in Figures 4.9(c)-(e). There are clear line cuts on the same NCs which separate the perovskite into two regions with about 1/2 lattice offset (shown by the region surrounded by the red dotted lines in Figures 4.9(d) and (e)). We believe that this is a typical antiphase boundary, and it is regarded as a translation boundary defect in the perovskite phase.^{267,268} Lastly, Figure 4.9 (f) shows a change in brightness on the same NCs after washing, indicating that there is either a change in the thickness, or a change in the surface termination in these dark and bright regions.²⁶⁷ All of these atomic-level structural defects could act as non-radiative

recombination centers that influence charge-carrier dynamics. As these traps occurring at these structural defects were increasingly filled at higher fluences, fewer were available for trap-mediated recombination, leading to an increase in the PL lifetime as shown in Figure 4.8 (g) and (h).

Table 4. 5 Fitted Fluence dependent TCSPC from 0.1 nJ/cm²/pulse to 0.39 nJ/cm²/pulse.

The fitting is based on the following equation (3) and (4): $y = y_0 + A_1 e^{-(x-x_0)/t_1} + A_2 e^{-(x-x_0)/t_2} + A_3 e^{-(x-x_0)/t_3}$ (3), $\tau_{average} = \frac{A_1 \times t_1^2 + A_2 \times t_2^2 + A_3 \times t_3^2}{A_1 \times t_1 + A_2 \times t_2 + A_3 \times t_3}$ (4).

Sample 0.39 nJ/cm ²	$t_{average}$	t_1	A_1	t_2	A_2	t_3	A_3
Original	16.40	1.72	0.23	7.81	0.50	24.10	0.21
Methyl Acetate	9.03	0.80	0.37	4.52	0.47	14.30	0.16
Acetone	11.17	0.84	0.13	5.48	0.51	14.60	0.33
Butanol	9.07	0.83	0.42	4.29	0.37	14.90	0.12
Sample 0.29 nJ/cm ²	$t_{average}$	t_1	A_1	t_2	A_2	t_3	A_3
Original	16.79	1.37	0.22	7.09	0.53	23.80	0.24
Methyl Acetate	9.55	0.72	0.49	4.60	0.57	14.40	0.23
Acetone	10.51	1.02	0.13	5.26	0.52	13.80	0.34
Butanol	6.82	0.41	0.89	3.03	0.52	10.60	0.20
Sample 0.19 nJ/cm ²	$t_{average}$	t_1	A_1	t_2	A_2	t_3	A_3
Original	18.87	23.50	0.22	6.76	0.29	1.35	0.01

Methyl Acetate	10.99	0.93	0.34	5.58	0.59	16.10	0.26
Acetone	10.44	0.71	0.23	4.97	0.53	13.70	0.36
Butanol	4.45	3.92	0.46	0.67	3.48	12.70	0.09

Sample 0.10 nJ/cm ²	t _{average}	t ₁	A ₁	t ₂	A ₂	t ₃	A ₃
Original	21.05	7.11	0.12	24.10	0.16	1.61	0.00
Methyl Acetate	14.58	2.13	0.20	8.88	0.60	22.40	0.20
Acetone	10.25	1.14	0.18	5.91	0.56	14.80	0.24
Butanol	3.67	2.95	0.43	0.45	5.71	10.40	0.13

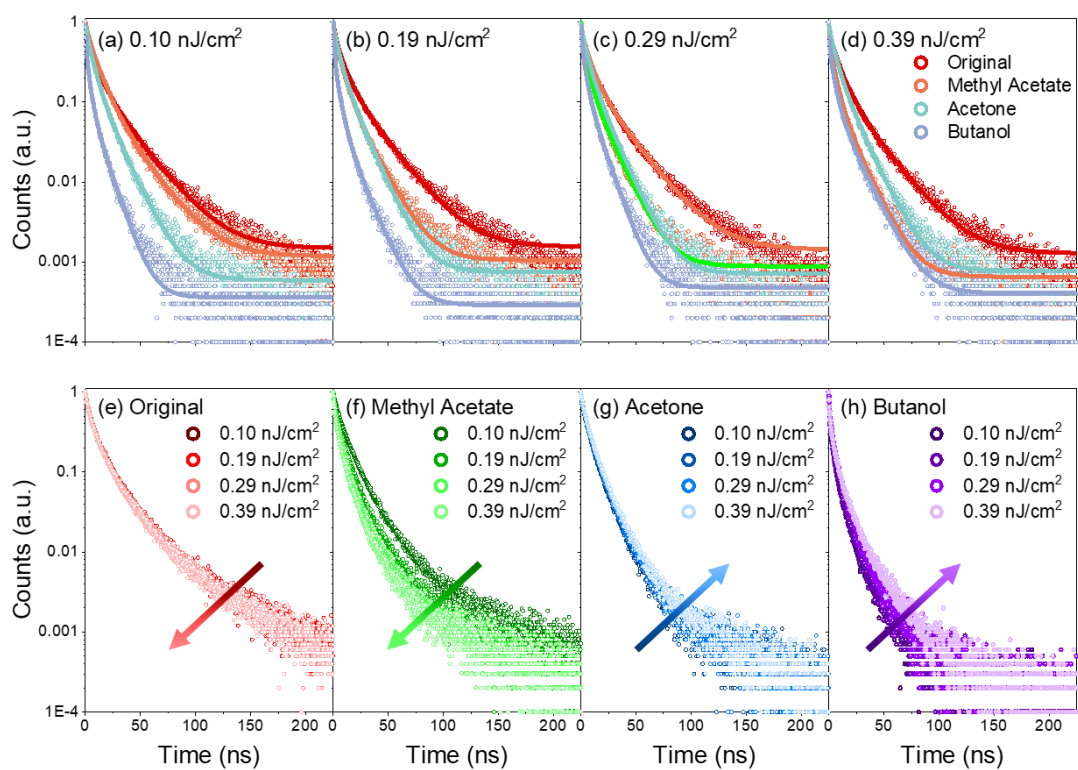


Figure 4. 8 TCSPC. (a)-(d) Fitted TCSPC at different fluences. (e)-(h) Fluence Dependent TCSPC. Excited with 400 nm pulse laser.

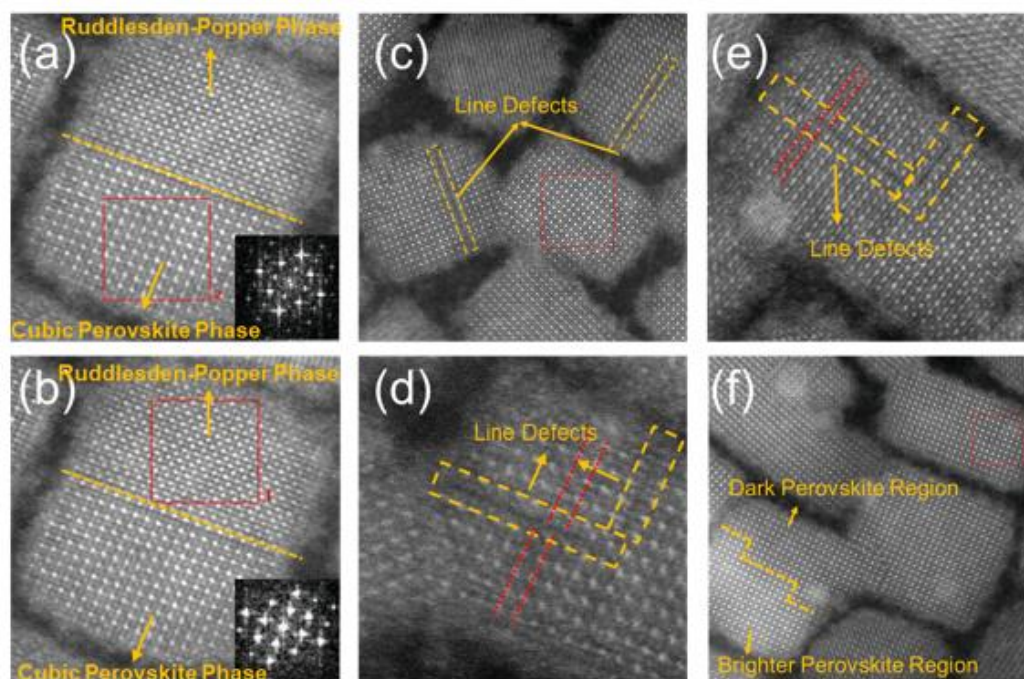


Figure 4. 9 STEM mode of High-Angle Annular Dark-Field imaging (HAADF) to reveal the structural defects in purified NCs. (a,b) HAADF images of acetone-washed NCs, with the fast Fourier transform (FFT) of the area shown in the red square shown inset. These data show that after washing with acetone, there is a possibility of introducing Ruddlesden-Popper phase into the cubic phase perovskite NCs (top-half of the NC imaged). (c), (d) and (e) focus on the line defects introduced after washing the NCs with (c) methyl acetate, (d) acetone, and (e) butanol. (f) STEM image of washed NCs which show regions with different brightness on the same NC, which could indicate a change in the NC surface termination, or a change in the thickness after washing.

4.2.2 Mechanistic study into antisolvent polarity-induced changes in the surface chemistry of LHP NCs.

To explain the cause of the dependence of the composition and optoelectronic properties of CsPbBr_xI_{3-x} perovskite NCs on the polarity of the antisolvent during purification, we propose two potential mechanisms, as illustrated in Figure 4.10. Herein, we will first detail these two mechanisms, before providing experimental evidence for or against them.

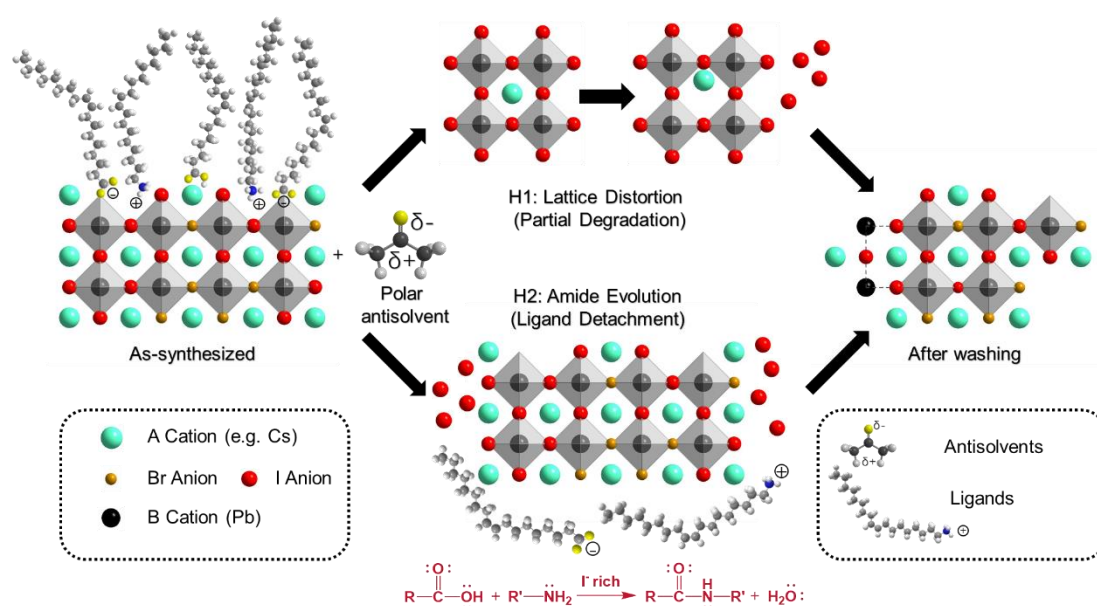


Figure 4. 10 Proposed mechanisms for the antisolvent-dependent selective etching of the mixed I-Br perovskite NCs. Hypothesis one (H1): Solvent induced lattice distortion, which leads to nanocrystal degradation and the formation of PbI₂. Hypothesis two (H2): Polar solvent induced amide evolution, which leads to surface ligand and iodide detachment.

Our first hypothesis is antisolvent-induced lattice distortion. Antisolvents with different polarities could impose different lattice distortions on the NCs during washing. When more polar antisolvent molecules (e.g., acetone) attach to the iodine-rich NCs (original NCs have a Br/I ratio of approximately 18%:82%), the strong dipole present causes a distortion in the [PbI₆]⁴⁻ octahedra on the surface. Sun et al. previously found from density function theory (DFT)

calculations that when polar ethanol molecules are chemisorbed onto the surface of CsPbI₃ NC surfaces, the polar molecule can induce a shift in electron cloud of the Cs⁺ cations, thus breaking the symmetry of the surrounding [PbI₆]⁴⁻ octahedra, and inducing polarization in CsPbI₃.²⁶⁹ The distortion could lead to perovskite NCs degrading into PbI₂ during centrifugation, which could then cause an overall loss in iodide content and defect formation at the surface of the NCs. However, the proposed mechanism requires the antisolvent to be in direct contact with the NC surface. By contrast, there is strong evidence that the NC surface is entirely capped by organic ligands. XPS measurements (Figure 4.6(a)) support this because the intensity of the I 3d core level of the original NCs are very low compared to the purified NCs, despite the original NCs having higher I content, as found from TEM EDX. By having a high ligand density, the I signal in XPS is obscured by the long carbon-based chains. Additionally, our DFT calculations show that the oleylammonium ions bind with surface halides through hydrogen bonding. Meanwhile oleate ions balance the NC surface charge without forming bonds (Figure 4.11). This result is consistent with previous solid-state NMR analysis by Chen et al.²⁵⁹ Since the NCs are capped with the ligands, they will protect the NCs from substantial contact with the antisolvents. The antisolvent molecules are likely to be sterically hindered from interacting with the NC surface due to the presence of ligands. Furthermore, we found that adding excess PbI₂ to all colloidal solutions of purified NCs resulted in the PL peak red-shifting and stabilizing at a wavelength of 680 nm (Figure 4.12). One possible explanation would be that the excess PbI₂ can reconstruct the damaged lattice and restore it to its state before purification (i.e., the I ratio increased and PL peak red-shifted). However, we cannot rule out other possibilities such as the PbI₂ added triggering further halide exchange between the exposed surface Br after purification with the added iodides. To further test the validity of hypothesis 1 (H1 – lattice distortion), we investigated the surface composition of the washed NCs with XPS (Figure 4.6). We found that the intensity of the Pb 4f core level spectrum remained almost the same for NCs washed by different antisolvents, whereas there was an obvious reduction in the I 3d core peak intensity after washing with more polar antisolvents, indicating that perovskite degradation to PbI₂ is

unlikely, as only the I content changed while the Pb content remained almost the same. We also examined the elemental composition of the supernatants following washing using SEM-EDX (Figure 4.13 (b)-(d)). The ratio of I/Br in the supernatants showed the opposite trend to that found in NCs measured by TEM-EDX. In the supernatants, the I ratio increased with antisolvent polarity, indicating that more I was removed from the NCs (Figure 4.13(a)). Similarly, the Pb ratio in the supernatants remained approximately constant (~29%; Figure 4.13(a)), which was consistent with the XPS results (Figure 4.6). Therefore, we believe that perovskite degradation is unlikely to be the primary reason for iodide removal when washing with polar antisolvents, since only the I content changed significantly. The addition of excess PbI₂ would repair the halide vacancies induced during the washing process, or undergo halide exchange to re-introduce extra I to the surface of the NCs.

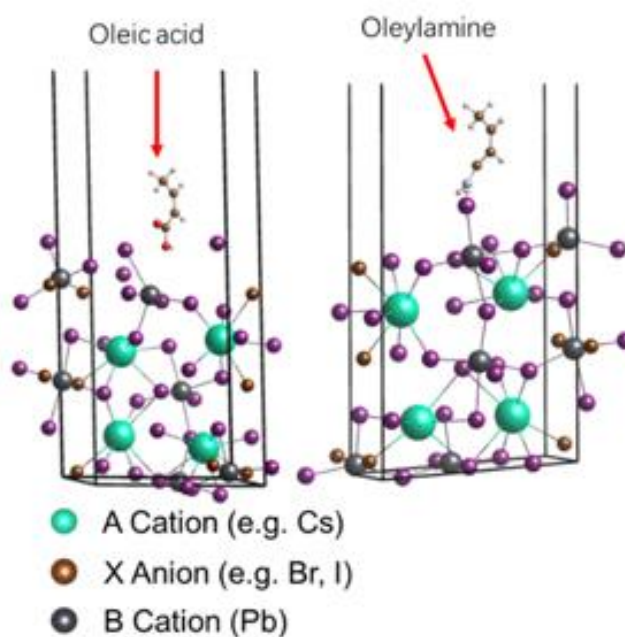


Figure 4. 11 DFT calculations. The NC is bound to oleylammonium ligand through hydrogen bonding from the amine group to the halide. The oleic acid or oleate ions are also attached closely to NC surface by balancing the surface charge of the NCs, mostly Pb²⁺ states. Calculations are performed by Dr. Yunwei Zhang, and the method is stated in Chapter 3.

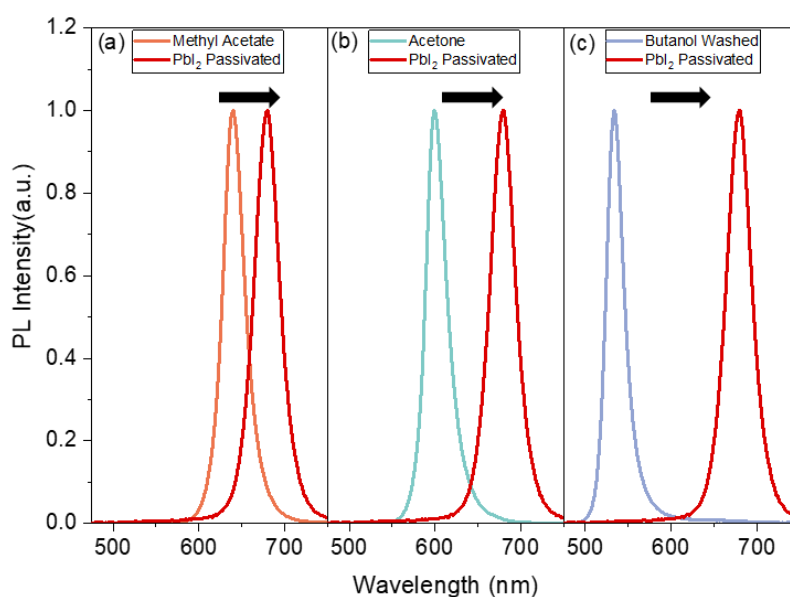


Figure 4. 12 PL spectra for NCs re-passivate with PbI_2 precursors. (a) Methyl acetate, (b) acetone and (c) Butanol.

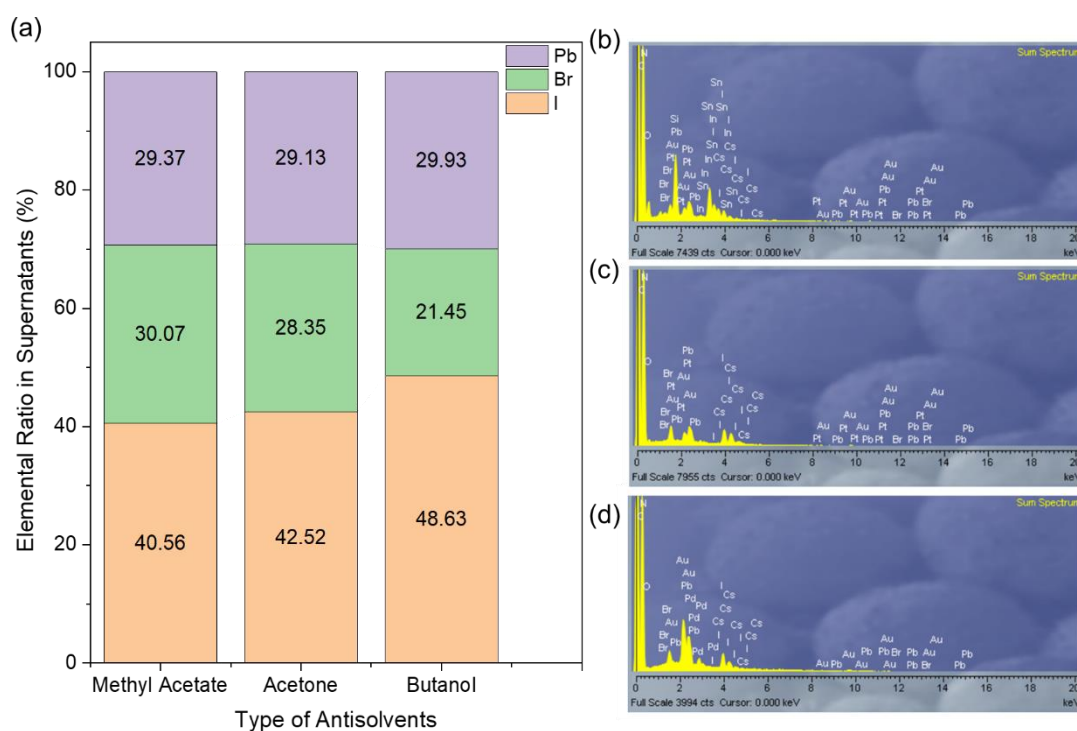


Figure 4. 13 SEM-EDX of the drop cast supernatants obtained from colloidal NCs washed by different antisolvents. The SEM used is LEO 1530 VP instrument and the EDX detector is from

Oxford Instruments. (a) Atomic ratio of Pb, I and Br on drop-casted supernatants prepared by washing the NCs with butanol, acetone and methyl acetate. Screen shot of the SEM-EDX of supernatants obtained following NC purification using (b) methyl acetate, (c) acetone, and (d) and butanol. The samples were prepared by dropping 100 μ L of supernatant solution onto ITO/glass substrates.

Our second hypothesis is antisolvent-induced amide evolution that leads to the detachment of surface ligands and iodides. Initially, NCs are stabilised in their original colloidal solution with unreacted precursors, including PbI₂-ligand, Cs- or Pb-Oleate, ammonium-halide (R-NH₃⁺-Br⁻/I⁻) and unbound ligands (R-COOH and R-NH₂). The initial NC surface is iodine-rich and capped by oleic acid (R-COO⁻) and oleylammonium (R-NH₃⁺) ligands. During the washing process, the addition of the polar solvents destroys the original charge balance of ligands bound to the surface of the NCs, triggering condensation reactions between the amine groups from the oleylammonium ligands and carboxylic acid groups from oleate ligands to form amide groups on an I-rich NC surface. The formation of amides will lead to a passivation failure where the amine and carboxylic acid groups can no longer bind with the NC surface to protect the NCs from the surroundings. This is consistent with the decrease in FTIR absorption intensity (at 3300-2500 cm⁻¹) of the signature peak for oleic acid ligands (Figure 4.14(c)). As the ligands are removed, the NCs are exposed to the surrounding polar molecules. The polar solvents may easily attach to the surface of the NCs and strip away the surface iodine through this amide evolution reaction. As a result, the Br/I ratio will be changed until a new chemical equilibrium is re-established when the Cs surface or uncoordinated Pb atoms are re-passivated by the ligands in solution. XPS measurements (Figure 4.6(b,c)) show the Br 3d and Pb 4f core level peaks are not significantly influenced by washing with different antisolvents. It is only the I 3d core peaks that decrease in intensity after washing. These results suggest that it is primarily the I species that are influenced by the polar solvents, which is in good agreement with the TEM-EDX (Table 4.2) measurements of the bulk composition of the NCs. We believe that the reason for the Br species to not be as strongly influenced by the polar solvents is that the mixed halide

NCs we studied in this work were prepared through halide exchange from CsPbBr₃ as the starting material. The diffusion-driven halide exchange process will exchange the outer Br with I first.²⁷⁰ As a result, the outside of the NCs during washing would be iodine rich, and also as I is a larger atom than Br, it is unlikely for I to diffuse to the inner core of the NCs.²⁵⁷ Therefore, the Br, present in high concentrations in the inner part of the NCs, are not as significantly affected as the I during the purification process, which this possibly explains the unchanged Br 3d core level spectra in Figure 4.6(b).

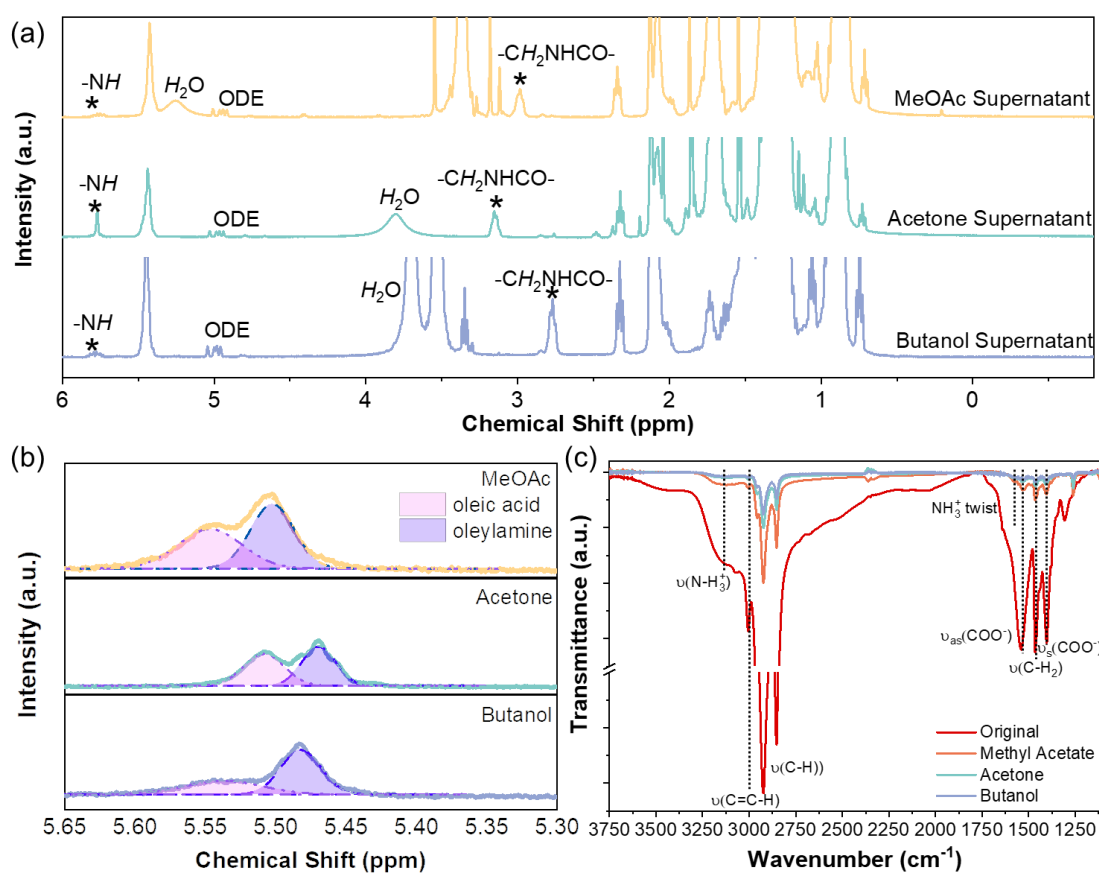


Figure 4. 14 (a) ¹H-NMR spectra of the supernatant solutions after NC purification. (b) Close up of the C=C double bond section of the ¹H-NMR spectra for oleate and oleylammonium ligands on washed NCs. (c) FTIR transmittance spectra of spin-coated NC films on CaF₂ substrates.

To further understand the effect of antisolvents on the selective etching of surface halides relevant to the initial surface halide composition, we examined the PL of two new systems in contrast to the results described above on CsPbI_{3-x}Br_x NCs prepared by diffusing I into CsPbBr₃. The first system is mixed-halide NCs prepared by diffusing Br into CsPbI₃ NCs (i.e., PbBr₂ was added to CsPbI₃ NCs solutions to trigger the Br halide exchange, as shown in (Figure 4.15(a) and (b)). Interestingly, the PL peak was still blue-shifted after purifying these CsPbBr_xI_{3-x} NCs. Figure 4.15 (b) showed that with different amount of PbBr₂ added to CsPbI₃ NCs, the PL peak positions of the unwashed NCs can be tuned to represent different initial Br/I compositions (e.g. 605 nm (high I content), 575 nm (moderate I content) and 537 nm (low I content)), we found the amount of blue-shifting in PL after washing is related to the initial Br/I ratio (more blue-shift is observed if the initial I content is higher, Figure 4.15(b)). Similarly, the extent of blue-shift is smaller than found from mixed-halide NCs obtained by diffusing I into CsPbBr₃ (Figure 4.1(h, table 4.1 and table 4.6)), which is likely due to the less effective removal of I ions due to the Br-rich surface. The results suggest that the antisolvents etch the I ions more effectively compared to Br ions even though we have halide exchange from I-rich surface to Br-rich surface. The second system examined is CsPbBr₃ NCs, i.e., where the surface halide is purely Br. A similar phenomenon was observed by washing the CsPbBr₃ NCs with antisolvents of different polarity, The PLQY decreased from 55.0% for the original CsPbBr₃ NCs, to 32.2% for NCs washed with methyl acetate, 28.0% for NCs washed with acetone, and 19.1% for NCs washed with butanol, as shown in Figure 4.15(c). This time there was no change in PL peak position since there was only one halide species (Figure 4.15(c), inset). But XPS measurements of the CsPbBr₃ NCs showed a reduction in the ratio of Br:Pb after washing with methyl acetate (Figure 4.15(d)). The relative ratio of surface Br decreased from 42% to 39%, while the ratio of surface Pb increased from 58% to 61%. This is consistent with a removal of surface Br, which correlates with the decrease in PLQY found. Therefore, these results show that it is the surface halides that are primarily affected by the removal of the ligands, and that the selective etching of I occurs more easily than Br removal.

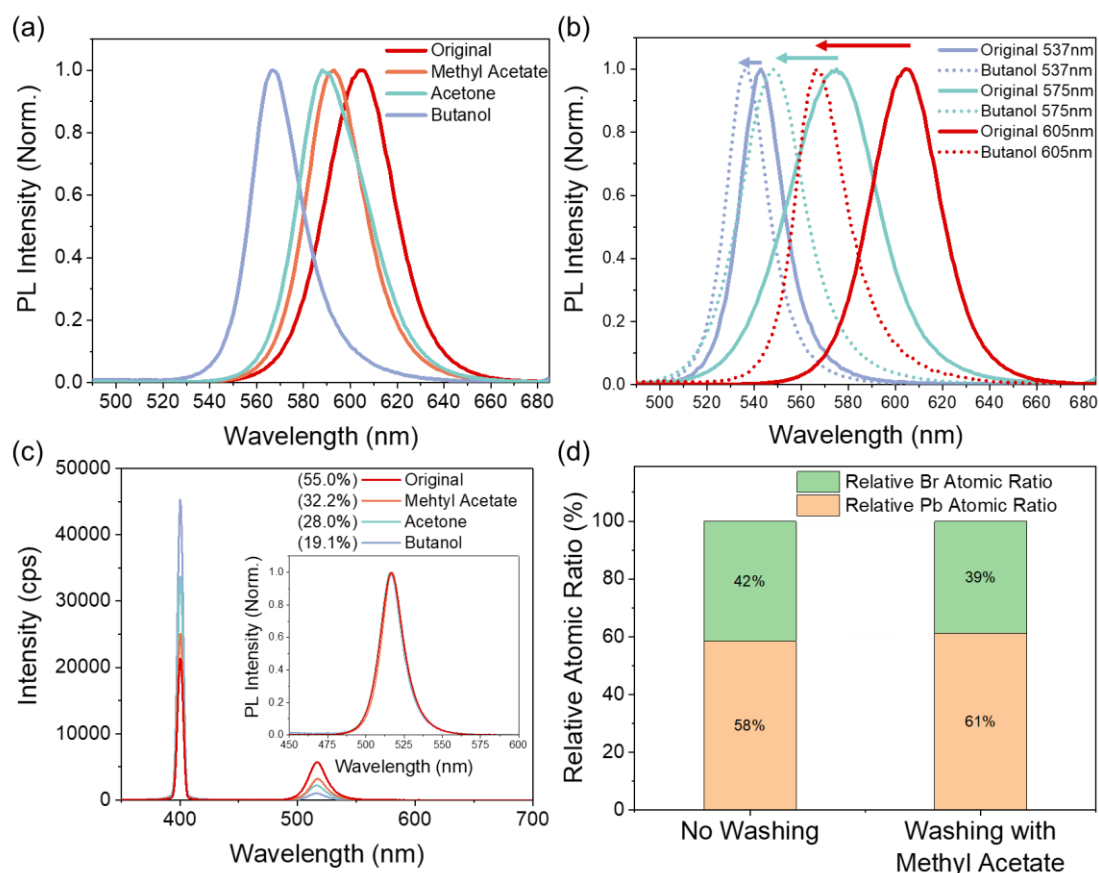


Figure 4. 15 Washing study on CsPbBr_xI_{3-x} NCs prepared by Br exchange starting from CsPbI₃ and pure CsPbBr₃ NCs. (a) PL spectra of CsPbBr_xI_{3-x} NCs prepared by Br exchange starting from CsPbI₃ and purified with methyl acetate, acetone and butanol antisolvents (b) PL spectra of CsPbBr_xI_{3-x} NCs with different Br/I ratio prepared by Br exchange starting from CsPbI₃ and purified with butanol antisolvents (c) PL spectra and PLQYs of CsPbBr₃ NCs purified with methyl acetate, acetone and butanol antisolvents, compared to purification without antisolvents ("Original"). The PLQYs obtained from these measurements are shown in the brackets in the labels. (d) Surface Br and Pb atomic ratio of the original NCs and methyl acetate washed NCs obtained based on XPS results.

Table 4. 6 PL shift of washed CsPbBr_xI_{3-x} NCs prepared through Br halide exchange from CsPbI₃ NCs

Washing Solvent	Solvent Polarity	PL Peak (nm)
Hexane	0.009	605
Methyl acetate	0.253	593
Acetone	0.355	588
Butanol	0.552	565

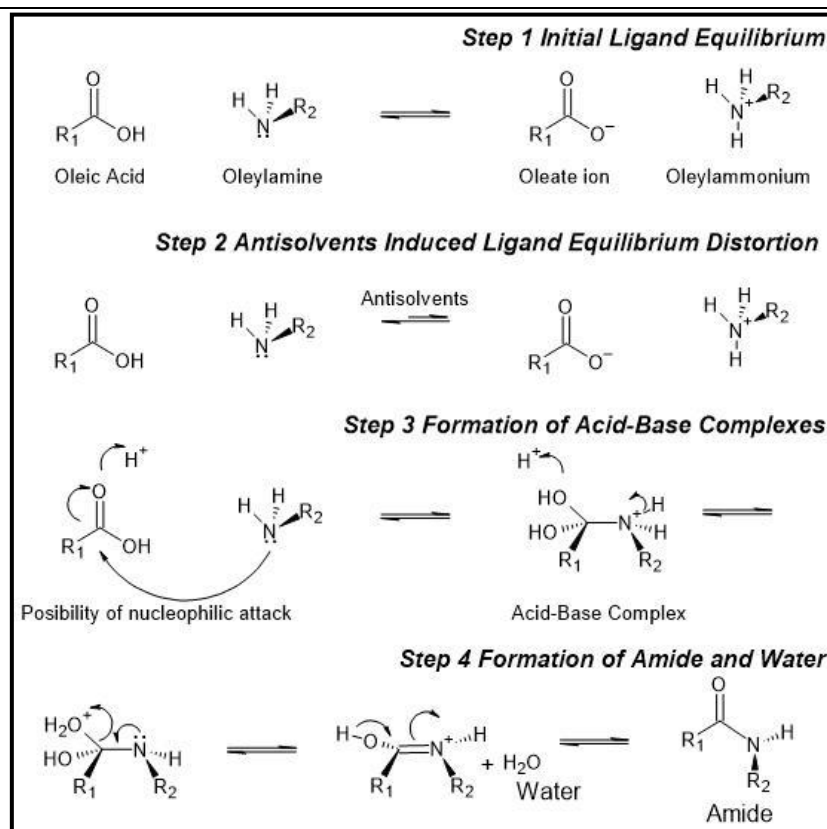


Figure 4. 16 Mechanism of amide formation for Hypothesis 2 from the reactions between oleylammonium and oleate ligands on the surface of the NCs

The proposed mechanism of amide formation is summarised in Figure 4.16. In the original NC solution, the oleic acid and oleylamine ligands achieve a dynamic equilibrium with their ionic forms: oleate and oleylammonium ions (Figure 4.16 step 1). When antisolvents are introduced into the solution, the polar antisolvent molecules would distort the original equilibrium (Figure 4.16, step 2). The presence of polar antisolvent molecules triggers the amine-carboxylic acid condensation reaction at the surface of the NCs.^{257,271} The interactions between the acidic ions and polar antisolvents allow the attack of the lone pair electrons, and transfer from the nitrogen nucleophile in the amine group to the carbon in the carboxylic acid group (Figure 4.16, step 3). Intermediates are then formed through deprotonation and protonation of the carbonyl group to form an acid-base complex (Figure 4.16, step 3). The direct proton transfer to the hydroxyl group in the intermediates allows the formation of charged $-OH^{2+}$ groups, which are subsequently removed from the complexes as a neutral water molecule by-product (Figure 4.16, step 4). Lastly, as the water molecule is removed, amides are formed as the final products (Figure 4.16, step 4). Once the amide group is generated, the ligands lose the ability to bind to the surface as both the ammonium and carboxylic acid groups are consumed to form amide groups. As the ligands are detached, the iodides that were previously bound to the ammonium groups are also removed. Typically, amide formation requires heating at above 100 °C.²⁷² However, herein, we believe that the condensation reaction can occur at room temperature in the presence of polar antisolvents because the perovskite NCs could act as catalysts. Based on the available evidence in the literature,^{257,273} the catalytic effect of the perovskite NCs is likely achieved by 1) the close proximity of the amine and acid groups from ligands bound to the surface of the NCs, and 2) the release of oleylammonium ligands resulting in excess protons being introduced to the NC surface, which can interact with the carboxylic acid groups from the oleic acid ligands, rendering them more amenable to attacking the amine groups (see Figure 4.16, especially steps 2 and 3).⁴⁷ Similarly, it has previously been shown that amides can form at room temperature when appropriate catalysts are added, such as boronic acids or SO₂F₂.^{274,275}

Amine-acid ligand reactions have also been observed in NaYF₄ nanoparticles with oleic acid and octadecylamine ligands at room temperature.²⁷¹

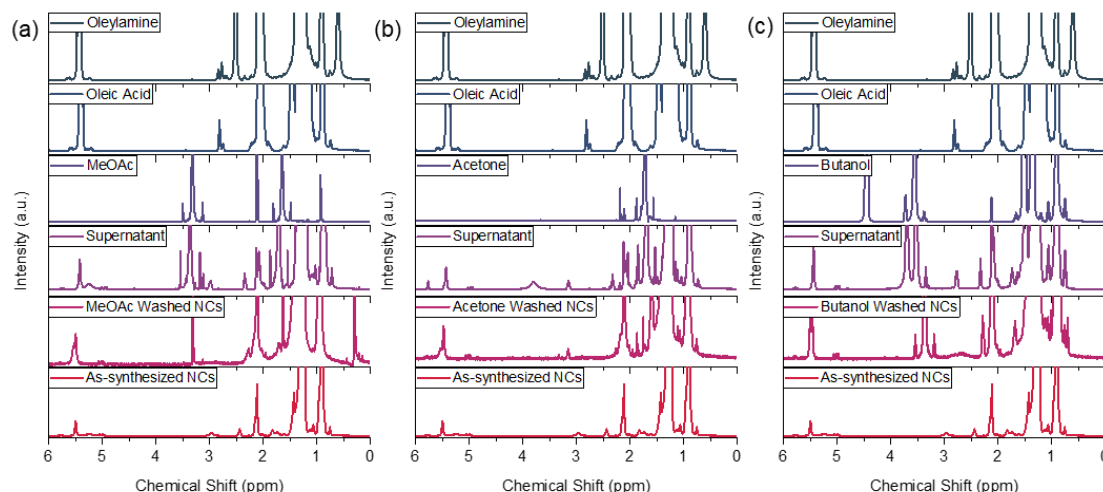


Figure 4. 17 ^1H -NMR spectra of antisolvents, ligands, original NCs, washed NCs and its supernatant solution. (a) Methyl acetate series. (b) Acetone series (c) Butanol series.

To determine the validity of this second hypothesis, ^1H -NMR measurements were performed on both the colloidal solutions of the washed NCs, as well as the supernatant solutions (Figure 4.17). Here, the NMR samples were prepared by adding 5 μL of pure oleic acid, oleylamine, antisolvents, the as-synthesised and purified NCs and their corresponding supernatants solutions individually into 5 mL of deuterated toluene ($\text{C}_6\text{D}_5\text{CD}_3$). By comparing the known ^1H -NMR peaks from the pure oleic acid and oleylamine with those found from the supernatant solution, we identified some new species, including peaks at $\delta=2.98$ ppm and $\delta = 5.25$ ppm for methyl acetate washed NCs, $\delta = 3.15$ ppm; $\delta = 3.80$ ppm for acetone washed NCs, and $\delta = 2.76$ ppm and a significant increase for the peak at $\delta = 3.72$ ppm for butanol washed NCs (shown in Figure 4.14(a)). The peaks at $\delta = 2.98$ ppm, 3.15 ppm, and 2.76 ppm can be assigned to the hydrogen atoms (*italic*) in the $-\text{CH}_2\text{NHCO}-$ group.²⁵⁷ The peaks at $\delta = 5.9$ ppm is likely to be the signal from $-\text{NH}$ protons in the amide. The broad peaks at $\delta = 5.25$ ppm, 3.80 ppm and 3.72 ppm are attributed to protons in the OH group, which can be due to water molecules (Figure 4.14a). The NMR spectra are normalized to the aromatic signals of the

residual protonated toluene (Figure 4.18). The toluene here is referred to as residual because the solvent is nearly fully deuterated. Since each sample examined by NMR was comprised of the same amount of solvent and test sample (i.e., 5 mL d₆-toluene + 5 μ L supernatant), and the way of obtaining the NCs and their supernatants were also identical, it is reasonable to compare the relative peak intensities by normalizing the signals to the reference aromatic signals at 7.11-7.09 ppm (Figure 4.18). The results show that there are indeed more amides being produced if we washed with higher polarity antisolvents as the peak intensity for the $-CH_2NHCO-$ group is the highest in the supernatants obtained after butanol washing and lowest in the supernatants obtained after methyl acetate washing. We note that chemical shifts can be strongly affected by the solvent. We therefore attribute the differences in chemical shifts of these peaks to differences in polarity of the solvents. Overall, the peak positions show good agreement with the results from Grisorio's work.²⁵⁷

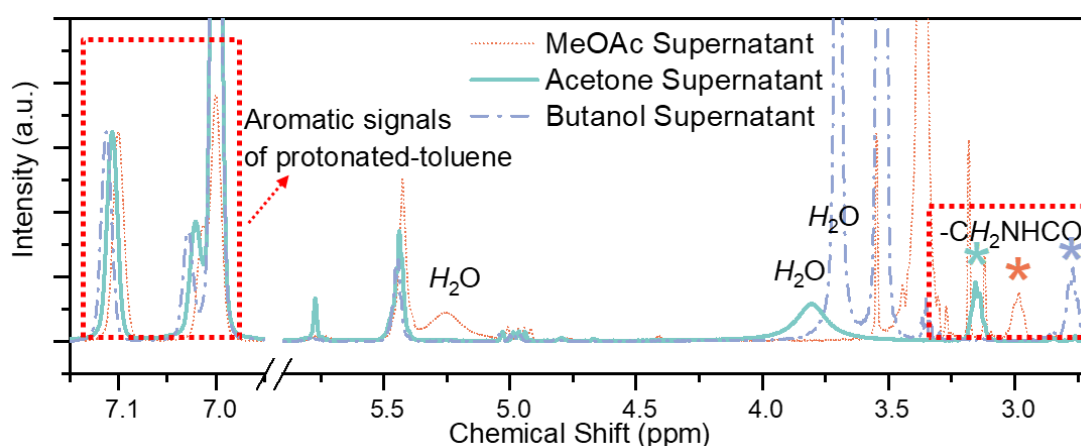


Figure 4. 18 ^1H -NMR spectrum of the supernatants (Normalised to the aromatic signal of residual protonated toluene in the d-6 toluene). The H -species characterised in the NMR peak is italicised.

Apart from the formation of amide and water, another observation that supports the second hypothesis is that the change in the ratio of the surface ligands (oleate and oleylammonium) after washing is antisolvent-dependent, as shown in the ^1H -NMR (Figure 4.14b) and FTIR spectra (Figure 4.14c). From the NMR spectra, the peaks at $\delta = 5.55$, 5.51 and 5.54 ppm are

associated with vinyl groups (C=C) in oleate ions, while $\delta = 5.51, 5.47$ and 5.48 ppm are associated with vinyl groups in oleylammonium ions for NCs washed with methyl acetate, acetone and butanol respectively.²⁵⁷ These are ligands remaining on the surface of NCs after purification (Figure 4.14b), and we found that the ratio of OA to OAm surface ligands was highest when using the low polarity methyl acetate, and lowest ratios when using the most polar butanol. When using acetone, this ratio remained fairly similar to the NCs washed with methyl acetate. From the amide evolution hypothesis, OA and OAm should be lost in equal amounts. However, we can see that there were slightly more OAm than OA. It is therefore possible that with butanol washing, a sufficiently large quantity of OA and OAm was removed that the NMR trace was dominated by the residual excess OAm. Indeed, from FTIR (Figure 4.14c), the signature peak (O-H stretch) for the carboxylic acid group in the oleic acid ligands ($3300\text{--}2500\text{ cm}^{-1}$) reduced more as the antisolvent polarity increased. Similarly, the stretching mode of N-H₃⁺ from $3250\text{--}3100\text{ cm}^{-1}$ and the twisting mode of N-H₃⁺ at 1580 cm^{-1} in oleylammonium ions in Figure 4.14(c) demonstrated the same trend, indicating that more oleylammonium ligands are removed as antisolvent polarity is increased. These results support the second hypothesis by showing that more surface ligands take part into the amide formation reaction when using more polar antisolvents and fewer ligands are maintained on the surface of the NCs after washing. As a result, more surface iodide anions bound to the ligands are removed when using acetone and butanol. We note here that whilst the data more strongly supports the second hypothesis, we cannot rule out the possibility that the first proposed mechanism occurs after the ligands are removed during the condensation reaction. Therefore, the loss of iodides may be due both amide evolution and polar solvent induced NC degradation after some of the surface ligands are detached.

4.2.3 The impact of antisolvents on the stability in emission wavelength from NCs under the application of an electric field

So far, we have discussed the influence of the antisolvents used during purification on the NC surface chemistry and optical properties. Having shown the impact of the antisolvent polarity on the density of iodide vacancies in the NCs, we investigate the implications on the stability of the emission wavelength. It is well known that halide vacancies in perovskites act as enablers for ion migration, and this can accentuate the phase segregation of mixed-halide perovskites. For LEDs, phase segregation can occur when an applied bias is used, which can cause the electroluminescence (EL) peak to red-shift to the lowest bandgap species formed. Having understood how to control the iodide vacancy concentration after purification, we elucidated the impact on EL stability. Our LED test structures had the following architecture: glass/ITO/PEDOT:PSS/Poly-TPD/Perovskite NC/TPBi/LiF/Al. The fabrication procedures can be found in the Supporting Information. Figure 4.19 and Figure 4.20, demonstrated the change in EL spectra over time for devices made by NCs washed with different antisolvents and current injection levels.

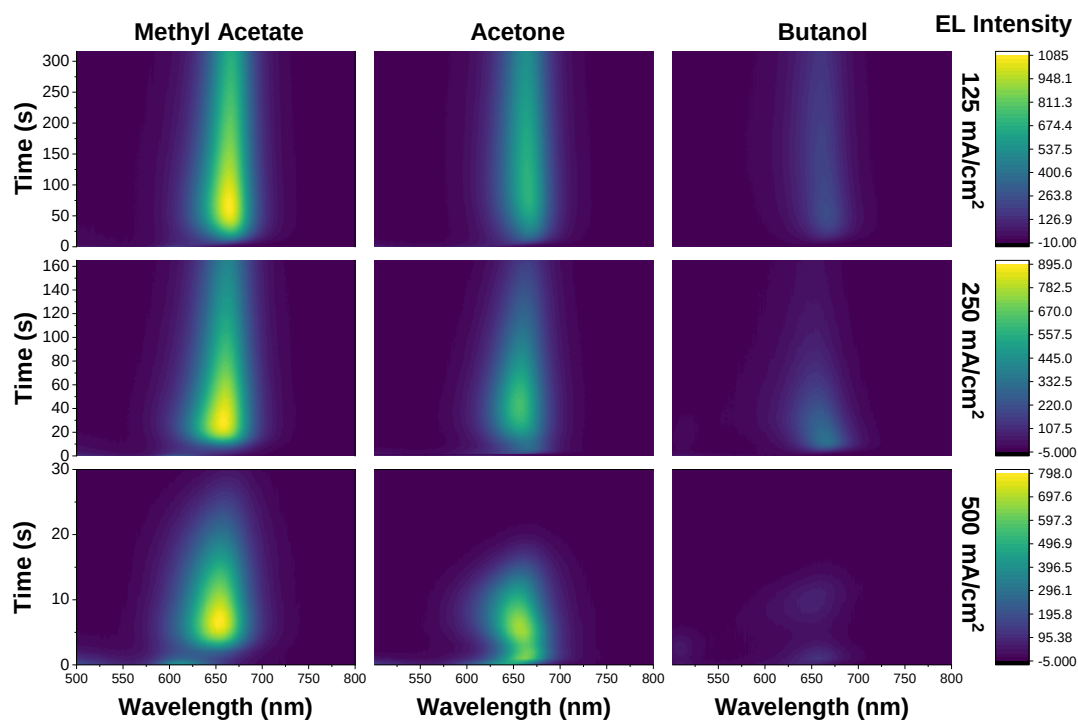


Figure 4. 19 Electroluminescence stability of purified NC-based LEDs, in which the CsPbBr₃I_{3-x} NCs were purified using methyl acetate, acetone and butanol antisolvents

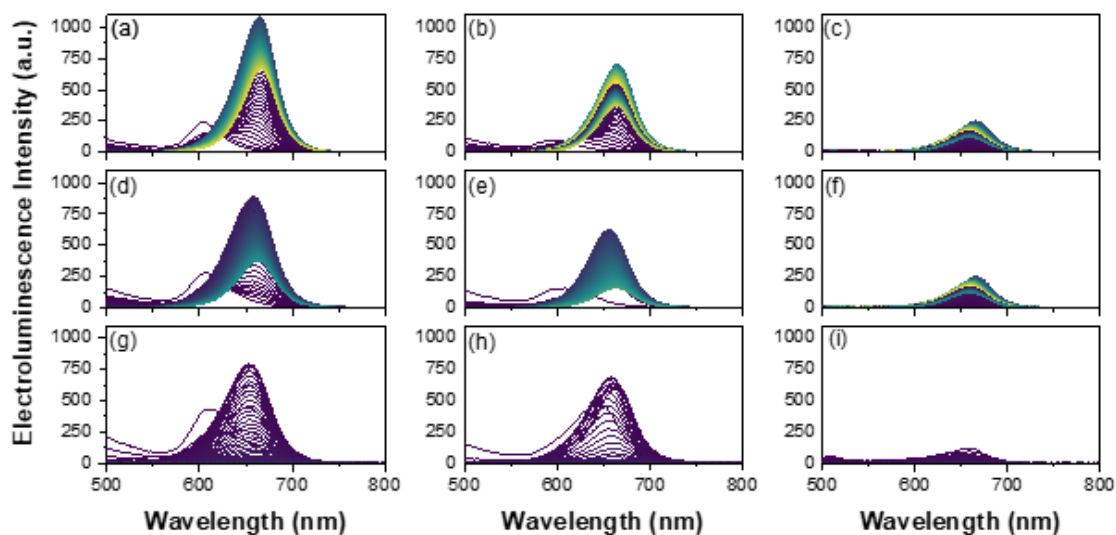


Figure 4. 20 Electroluminescence Spectra. (a),(d) and (g) are NCs washed by methyl acetate. (b), (e) and (h) are NCs washed by acetone and (c), (f) and (i) are NCs washed by butanol. (a)-

(c) are measured at 125 mA cm⁻². (d)-(f) are measured at 250 125 mA cm⁻². (g)-(i) are measured at 500 125 mA cm⁻².

It is clear that devices made from NCs washed using low polarity antisolvents produced brighter EL that did not decay as quickly over time (Figures 4.19 and 4.21(a-c)). This is consistent with the PLQY and PL lifetime data reported in Figure 4.5. The expulsion of iodides during washing has influence on both device efficiency (EL intensity) and operational stability (EL decay speed). Furthermore, Figures 4.21(d) and (e) show the effect on EL spectral stability at different injection levels. In both cases, the EL is gradually red shifted and stabilised at around 664 nm. The differences between the PL emission and the EL emission (red-shift) is well observed and studied in many previous works.²⁷⁶⁻²⁷⁸ When an external voltage is applied to the NC films, the iodide ions tend to migrate and form a I-rich and Br-rich region on the film. The injected carriers will eventually radiatively recombine at places with lower bandgaps, i.e. the I-rich regions, causing the EL shifts to a lower energy position (Figure 4.21(d) and (e)). However, at 250 mA cm⁻², methyl acetate washed NC device clearly show a slower red shift compared to the NCs washed by higher polarity solvents. We believe the speed of ion migration is related to the initial halide vacancies present in the NC films. This is supported by our DFT calculations, shown in Figure 4.22. The Climbing Image Nudged Elastic Band method was used to calculate the energy needed for iodide ions to move from one spot to adjacent vacancies at different initial halide vacancy concentration (Figure 4.22(a)). The results show that for lower initial vacancy concentrations, the ions need to overcome a 2.80 eV energy barrier to migrate. This situation corresponds to the case of NCs washed by lower polarity anti-solvents, such as methyl acetate. In contrast, for higher initial vacancy concentrations, the energy barrier reduced to 2.49 eV. This corresponds to the case for NCs washed by higher polarity antisolvents, such as acetone and butanol. Herein, we would like to emphasis that the activation energy estimated here is based on the simple model of taking small amount of halide away from a $2 \times 2 \times 2$ supercell. The values are much larger (> 100 times) than the thermal activation energy (26 meV) at room temperature (The actual barriers energy might not be exactly the same as the calculated one

shown in Figure 4.22.). The ions are unlikely to migrate at room temperature, so the NCs are stable in ambient at room temperature. We only observed the luminescent spectra change when there is an external bias applied to the NC films during the device operation, which the electrical bias provide enough energy to overcome the barriers. Since the EL peak center for methyl acetate washed NC device red-shifts slower than for the two other solvents (Figure 4.21(e)), we believe that the NCs washed with lower polarity antisolvents could induce a lower concentration of defects, and hence improve device EL stability. An important direction for future work is to explore and develop antisolvents that induce lower surface damage to the NCs. A marginal reduction in the antisolvent relative polarity from methyl acetate (relative polarity = 0.253) by using ethyl acetate (relative polarity = 0.228) was insufficient to reduce the blue-shift in PL after purification (Figure 4.23), and alternative routes will need to be explored.

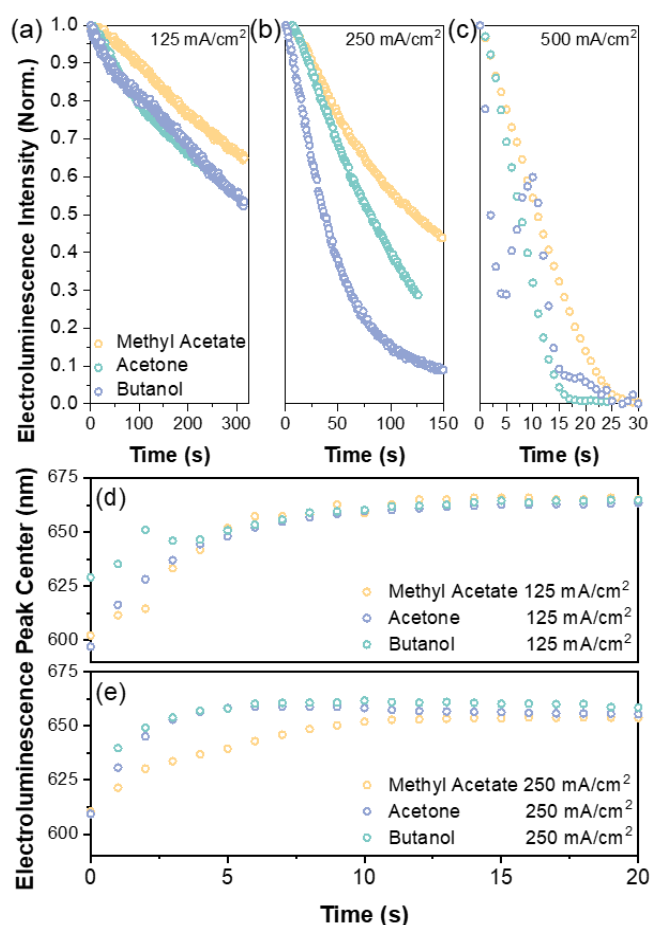


Figure 4. 21 LED device stability. (a)-(c) Electroluminescence intensity over time at different current injection densities (125, 250, and 500 mA cm⁻²). (d)-(e) The change in the electroluminescence spectra peak center over time at 125 mA cm⁻² and 250 mA cm⁻².

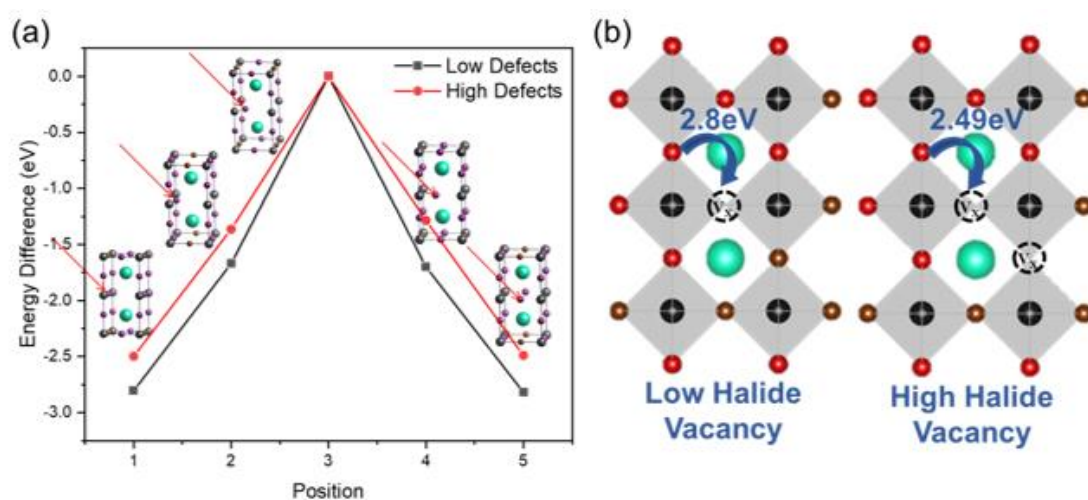


Figure 4. 22 DFT calculation to explain the halide phase segregation during device operation. (a) Climbing Image Nudged Elastic Band method to calculate the energy needed for iodide to move from one spot to adjacent vacancies at different initial halide vacancy concentration. (b) Schematic diagram to show the energy needed for halide to migrate with different initial V_x

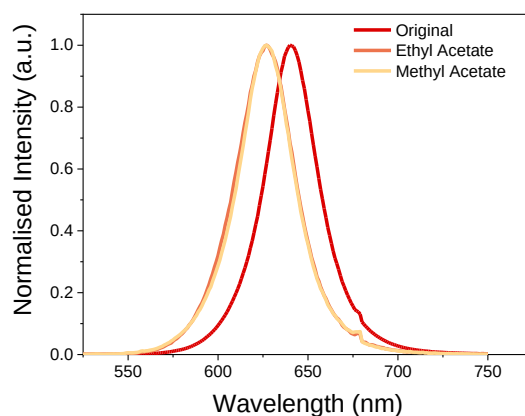


Figure 4. 23 Photoluminescence of the original NCs and NCs washed by methyl acetate and ethyl acetate.

4.3 Conclusion

In conclusion, this study aimed to unravel how the surface chemistry of all-inorganic mixed-halide (Br/I) perovskite NCs was influenced by the antisolvent during the purification process, which is a crucial step for preparing high-performance optoelectronic devices, such as light-emitting diodes and solar cells. Higher-polarity antisolvents led to increased selective etching of the surface halides (in this case iodides), resulting in increased sub-bandgap trap density and consequent reductions in PLQY and PL lifetimes. We put forward and examined two possible mechanisms to explain these effects. Based on the NMR, XPS and FTIR studies, along with the DFT calculations, we believe that the second hypothesis – amide evolution – to be the most likely. That is, we believe that the presence of polar antisolvents promotes the condensation reaction between the ligands to form amides that are no longer capable of binding to the surface of the NCs, which then leads to the removal of the surface halides that were bound to these ligands. Antisolvents with higher relative polarity tend to favor the shift in the OA-OAm equilibrium towards their acid/amine forms, thus promoting amide formation, and increasing the removal of surface ligands and iodides. Minimizing these effects through the use of lower-polarity antisolvents led to brighter and more operationally-stable LEDs. By providing new fundamental insights into how antisolvents influence the surface chemistry of mixed-halide perovskite NCs, this work will guide the future design of NC synthesis routes, not only for halide perovskites, but also for other NC systems. In particular, this work shows that achieving purified NCs with higher PLQY that lead to more efficient and stable LEDs not only can be achieved by using lower-polarity antisolvents, but could also be realised through careful tuning of ligand-ligand and surface-ligand interactions to change the surface reactions that occur following the introduction of polar antisolvents.

Chapter 5: Extending the Defect Tolerance of Perovskite Nanocrystals to Hot Carrier Cooling Dynamics

Junzhi Ye, Robert L.Z. Hoyer conceived the projects. Navendu Mondal performed pump-push-probe TA measurements Yunwei Zhang and Zhiqiang Cui performed DFT calculations. Junzhi Ye, Clara Otero-Martinez synthesised the materials. Junzhi Ye and Linjie Dai performed pump-probe TA measurements. Ben Carwithen conducted the modelling. Junzhi Ye and Xiangbin Fan performed energy dependent PLQY measurements. Mark Isaac performed the XPS measurements.

5.1 Introduction

The power conversion efficiency (PCE) of LHP PVs has now reached a certified value of 25.7% under 1-sun illumination²⁷⁹, which is rapidly approaching but still falls short of the radiative limit of ~30%^{280,281}. A large fraction of the remaining energy losses in these devices arise from the inefficient management of heat dissipation, especially for charge-carriers excited above the bandgap (i.e. hot carriers, HCs)²⁸²⁻²⁸⁶. Theoretically, the thermodynamic solar conversion efficiency for an ideal single-junction hot carrier solar cell (i.e., assuming no loss of excess energies above threshold) can be as high as $\approx 67\%$ ^{287,288} which is beyond the SQ limit, and approaching the efficiency limit of an infinite tandem cell under 1 sun irradiation²⁸⁸. However, practically, the excess energy of the HCs can not be fully utilised and extracted efficiently because the HC cooling process is much faster than the charge-carrier extraction process at the interface of perovskite layer and carrier extraction contact layers²⁸⁸⁻²⁹⁰. Therefore, understanding the origin of the fast-cooling process of halide perovskites with different bandgaps and compositions is crucial for slowing down the hot carrier cooling process and further improving the performance of perovskite solar cells.

One of the key enabling, but unusual, properties of LHPs is defect tolerance, which can be defined as the free charge-carrier lifetime and mobility not being affected by the presence of defects²⁹¹⁻²⁹⁴. Typically, it is point defects that are considered in models for defect tolerance, such as vacancies, interstitials and anti-sites²⁹¹⁻²⁹⁴. The critical implication of defect tolerance is that long diffusion lengths can be achieved in thin films processed using low-temperature, facile fabrication methods, enabling efficient, cost-effective optoelectronic devices. This contrasts to traditional semiconductors, such as silicon or gallium arsenide, which have relied on minimising defect densities, often through capital-intensive fabrication processes, to operate efficiently in electronic devices^{295,296}. Defect tolerance in LHPs arises due to the dominant point defects forming shallow transition levels, such that low Shockley-Read-Hall recombination rates can be achieved despite high trap densities^{128,292}. This was proposed to arise due to the unusual electronic structure of LHPs, in which the upper valence band is comprised of bonding and antibonding states from the hybridisation between Pb 6s orbitals and halide valence p orbitals. This, in addition to the strong spin-orbit coupling present in LHPs, lead to more disperse bands and a smaller bandgap, increasing the likelihood of shallow trap formation²⁹². However, the defect tolerance of the LHPs is not preserved across the entire halide composition series. Nenon *et al.* showed experimentally that whilst the photoluminescence quantum yield (PLQY) of CsPbI₃ was maintained despite the intentional introduction of defect states, the PLQY CsPbBr₃ was more sensitive to defect introduction, and the luminescent properties of CsPbCl₃ were severely deteriorated in the presence of defects²⁹⁷. These effects were due to the increased ionicity and smaller lattice constants as lighter halides were used, leading to increased likelihoods of deep traps forming^{297,298}.

A critical unanswered question is how the traps in LHPs influence HC cooling. Although several works have illustrated how defects can have a direct influence on the HC cooling lifetime^{289,299,300}, it remains unclear whether the defect tolerance of LHPs can be extended to HCs as well. PLQY and time-resolved PL, which have commonly been used to study defect tolerance in LHPs, only reveal the effects of band-edge charge-carriers. In this chapter, we refer the hot carrier cooling lifetime as the combination effect of both hot carrier relaxation and hot

carrier trapping process. Understanding the relationship between HC cooling lifetime and defect densities in compositional tuneable perovskites would be beneficial to improve the development of wide-gap and narrow-gap perovskite absorption layers for single-junction and tandem solar cells^{301,302}.

Pump-probe (PP) and pump-push-probe (PPP) transient absorption (TA) spectroscopy are commonly used to investigate the hot carrier cooling dynamics, such as hot phonon bottleneck effect^{264,303}, Auger heating^{290,304}, size- or cation- effects³⁰⁵ and hot-cold carrier interactions^{306,307}. Here, we utilised both PP and PPP TA techniques to investigate the effect of surface defect densities on hot carrier cooling dynamics of CsPbBr₃, CsPbBr_xI_{3-x} and CsPbI₃ NCs. The defect densities are controlled by number of purification processes with antisolvents, and it is monitored by the change of Pb-halide surface composition (measured by X-ray Photoemission spectroscopy) and PLQY²³⁶. Then, the hot carrier cooling lifetime is extracted from the PP and PPP TA measurements as a function of excitation fluence. The results from both sets of TA measurements indicated that the hot carrier lifetime decreased upon increasing in defect densities for CsPbBr₃ and CsPbBr_xI_{3-x} NCs. However, the HC cooling lifetime was relatively unaffected for CsPbI₃ NCs when defect densities increased. First-principles density function theory (DFT) and theoretical carrier dynamics modelling were performed to explain these experimental phenomena. We believe that hot carrier cooling can be influenced by trap density (number of times NCs were treated with polar antisolvents), trap occupation density (excitation fluence) and trap energies relative to the nearest band-edge (lead-halide ionicity). These insights provide design guidelines that can pave the way for efforts to develop hot carrier solar cells.

5.2 Results

5.2.1 Characterisation of band-edge carriers

I synthesised ambient condition stable CsPbX_3 ($X = \text{Br}$, and I) NCs using hot-injection methods based on our previous studies^{236,308}. The as-synthesised CsPbBr_3 , $\text{CsPbBr}_x\text{I}_{3-x}$ and CsPbI_3 NCs were purified by adding methyl acetate antisolvent with volume ratio of 1:2 (see Chapter 3 for details on synthesis and purification of NCs). The purification process is essential before using these NCs for device fabrications to remove unreacted precursors^{122,236}. However, the added polar antisolvents would partially remove some surface ligands and halides due to the ligand-ligand interactions, shown in Figure 5.1 a and b²³⁶. These halide vacancies can act as non-radiative recombination centre which deteriorates the device performance. The relative changes of the surface Pb to halide composition after washing two times with methyl acetate were shown in Figure 5.2 a-c. It demonstrated that the halide ratio, Br and I, decreased as the number of washing time increased from 0th to 2nd for pure Br and I NCs, while the Pb ratio increased (Figure 5.2 a and c). For the mixed halide cases, our previous studies showed that surface iodides are more easily removed than Br²³⁶, so we still observed a decrease in overall halide composition on the surface of NCs for $\text{CsPbBr}_x\text{I}_{3-x}$ NCs (Supplementary Figure 5.1b). As the surface halide decreased upon multiple washing, the halide vacancy defect densities increased. This could also be supported by the PLQY measurements shown in Figure 5.1c. For higher bandgap NCs, i.e. CsPbBr_3 and $\text{CsPbBr}_x\text{I}_{3-x}$, the PLQY dropped with the number of washing. On the other hand, the PLQY of CsPbI_3 NCs stayed relatively constant. This phenomenon is related to the relative defect position within the band due to the removal of halides and the dangling bonds from the Pb. The band-edge carriers can be easily undergoing trapping and de-trapping (return to band-edge and undergo radiative recombination) process from the shallower traps, i.e. I-based NCs, so the trap-assisted recombination rate is lower^{122,297,309}. The PL and absorbance of the different NC solutions were shown in Figure 5.1 d-f. For pure Br- and I based NCs, the change in PL was negligible, indicating the bandgap remained almost constant after

washing. However, a large blue-shift in PL was observed for mixed halide NCs after washing which was attributed to the Br/I composition change after washing ²³⁶. Figure 5.1c demonstrated the defect tolerance of the band-edge carriers especially for CsPbI₃ NCs.

To further understanding the influence of the trap to how carriers, excitation energy-dependent PLQY was performance on colloidal NCs that were unwashed (centrifuge without adding antisolvents) vs. washed twice. The concentration of all solution samples were tuned to have the optical density below 0.2 to minimise the concentration effect ^{297,299}, and the results are shown in Figure 5.1 h-g. Previously, Righetto *et al.* demonstrated that the PLQY of the NCs would be lower when excited with higher energy light ²⁹⁹. For less defective samples (0th washing), the PLQY remained relatively constant when exciting with higher energy light. For more defective samples, i.e. 2nd washing, the PLQY decreased when pumping with higher energy light, especially for CsPbBr₃ and CsPbBr_xI_{3-x} NCs, as more carriers tend to be trapped when they had higher excess energy, which indicates that the trap-assisted recombination became more dominant compared with radiative recombination. However, the change of PLQY against the pump energy was not obvious for CsPbI₃ NCs, indicating the hot carriers were less influenced by the traps, so that most of the carriers can thermalise to band-edge and undergo radiative recombination rather than recombine non-radiatively in the trap. .

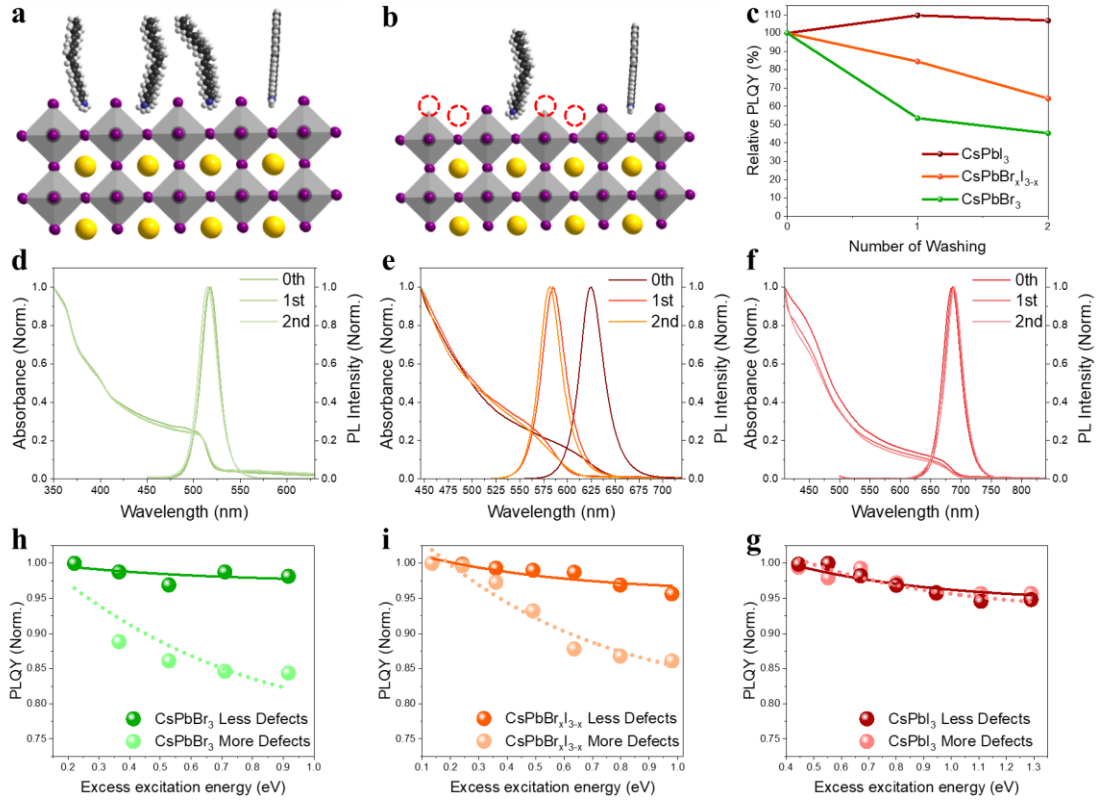


Figure 5. 1 Steady State Optical Properties. *a.* Schematic illustration of 0th washed NCs with less surface defects. *b.* Schematic illustration of washed NCs (1st or 2nd) with more surface defects. *c.* PLQY against the number of washing. *d.* PL and absorbance of 0th, 1st and 2nd washed CsPbBr₃ NCs. *e.* PL and absorbance of 0th, 1st and 2nd washed CsPbBr_xI_{3-x} NCs. *f.* PL and absorbance of 0th, 1st and 2nd washed CsPbI₃ NCs. *h-f* Excitation dependent PLQY for 0th and 2nd washed CsPbBr₃, CsPbBr_xI_{3-x}, and CsPbI₃ NCs respectively.

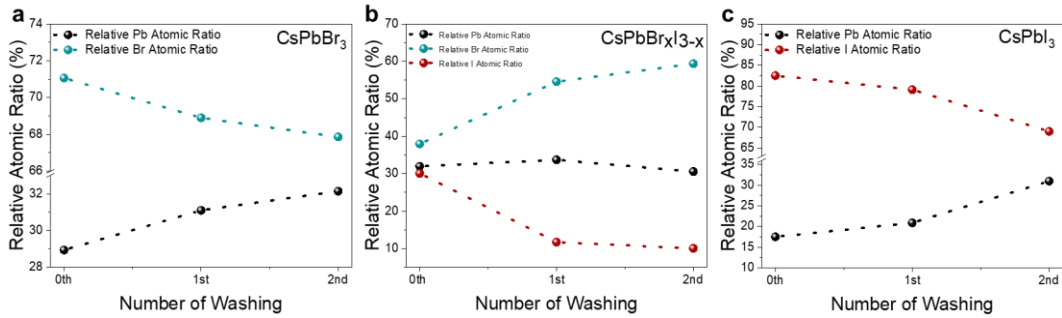


Figure 5. 2 Compositional analysis based on X-ray photoemission spectroscopy. *a.* Relative Pb/Br ratio for CsPbBr₃ NCs after washing. *b.* Relative Pb/Br and I ratio for CsPbBr_xI_{3-x} NCs after washing. *c.* Relative Pb/I ratio for CsPbI₃ NCs after washing.

5.2.2 Influence of the traps on hot carrier cooling lifetime probed by two-pulse and three-pulse transient absorption spectroscopy

Even though aforementioned time-averaged spectroscopic data hints towards existence of hot-carrier trapping, dynamical perspective of hot carrier cooling under various defect densities can only be obtained through time-resolved spectroscopic measurements. For this, we have performed pump-probe (two-pulse) and pump-push-probe (three-pulse) transient absorption spectroscopic measurements. Figure 5.3 demonstrated the PP TA results for CsPbBr₃ NCs. The NC solution was pumping with photon energy significantly higher than the bandgap ($\hbar\omega_{\text{pump}} = 3.1$ eV, $\lambda_{\text{pump}} = 400$ nm). The TA maps and TA spectra (0.5-30 ps, at $116.58 \mu\text{J cm}^{-2}$) are presented in Figure 5.3. It shows spectral signatures like broad PIA (blue-side of the bleach) and GSB featuring similar decay dynamics, indicating depopulation of band-edge carriers, consistent with literature. While below band-gap short-lived PIA (red-side of the bleach) often ascribed to biexciton like effect to band-gap renormalization. Decay dynamics of this red-side PIA signal (which disappears during band-edge excitation) and formation of GSB (due to state-filling process) often been used as a marker to interpret hot carrier cooling dynamics in semiconductors including perovskites. Figure 5.3d-f showed that the ground state bleach (GSB) signal becomes narrower when increasing the number of purification steps. The cooling kinetics can be extracted from the high energy tail of the TA spectra based on the Maxwell–Boltzmann distribution function assuming the hot carriers have Fermi-Dirac distribution^{264,290} (Eq. 5.1):

$$-\frac{\Delta T}{T}(E) = T_0(E)e^{-\frac{E}{k_B T_e}} \quad (5.1)$$

where $\frac{\Delta T}{T}(E)$ is the transient transmittance obtained from the TA measurement, T_e is the carrier temperature. The high energy tail of the GSB became narrower over the delay time indicating the high energy carriers gradually cooled to the band-edge.

Figure 5.3 h-g showed the extracted carrier temperature as a function of time for different initial carrier densities or fluences, with biexponential fitting parameters listed in Table 5.1. For low fluence, the carrier temperatures can be fit by single exponential decay, corresponding to rapid carrier cooling via the Fröhlich interaction where carrier-LO-phonon scattering has been confirmed as the dominant effect for hybrid halide perovskites at room temperature²⁹⁰. With pump fluence increased to $194.32 \mu\text{J cm}^{-2}$, another slow cooling process appeared after the initial sub-ps decay. This reduced relaxation rate of hot carrier temperature under high-level carrier injection results from the hot phonon bottleneck effect^{303,304}, where a non-equilibrium phonon population increases the probability of carriers reabsorbing the phonon energy³⁰³. Apart from phonon heating, enhanced carrier-carrier interaction at high carrier concentrations could also contribute to the reduced cooling rate by a non-radiative Auger heating process³⁰⁴. However, this second cooling component at high fluence became less obvious after the 1st washing, and even more less obvious after the 2nd washing, the fitted hot carrier cooling lifetime reduced from 3.47 ± 0.34 ps for 0th washed sample, to 2.54 ± 0.41 ps for 1st washed sample, and to 1.11 ± 0.07 ps for the 2nd washed sample at $194.32 \mu\text{J cm}^{-2}$ (Table 5.1). This indicated that the presence more defects speed up the cooling process by reducing the effect of hot phonon bottleneck and Auger reheating effect as the carrier density reduced significantly due to the presence of the defects. The same results were shown in Figure 5.4 for $\text{CsPbBr}_x\text{I}_{3-x}$ NCs, where the second component appeared clearly for the fluence at $178.18 \mu\text{J cm}^{-2}$ or higher, and almost disappeared for the 1st washing and 2nd washing samples. The cooling lifetime decreased from 6.49 ± 0.05 ps for the unwashed sample to 2.49 ± 0.18 ps for the 1st washed sample and stabilised around 2.56 ± 0.04 ps for the 2nd washed sample (Table 5.2). However, for the CsPbI_3 NCs, the change of the spectra, map and extracted carrier cooling kinetics did not vary much when the number of washing increased (Figure 5.5). The observation of hot phonon bottleneck effect occurred at much lower pump fluence ($30.14 \mu\text{J cm}^{-2}$), and the cooling lifetime was similar between the washed and unwashed samples (around 12 ps at $30.14 \mu\text{J cm}^{-2}$, shown in Table 5.3).

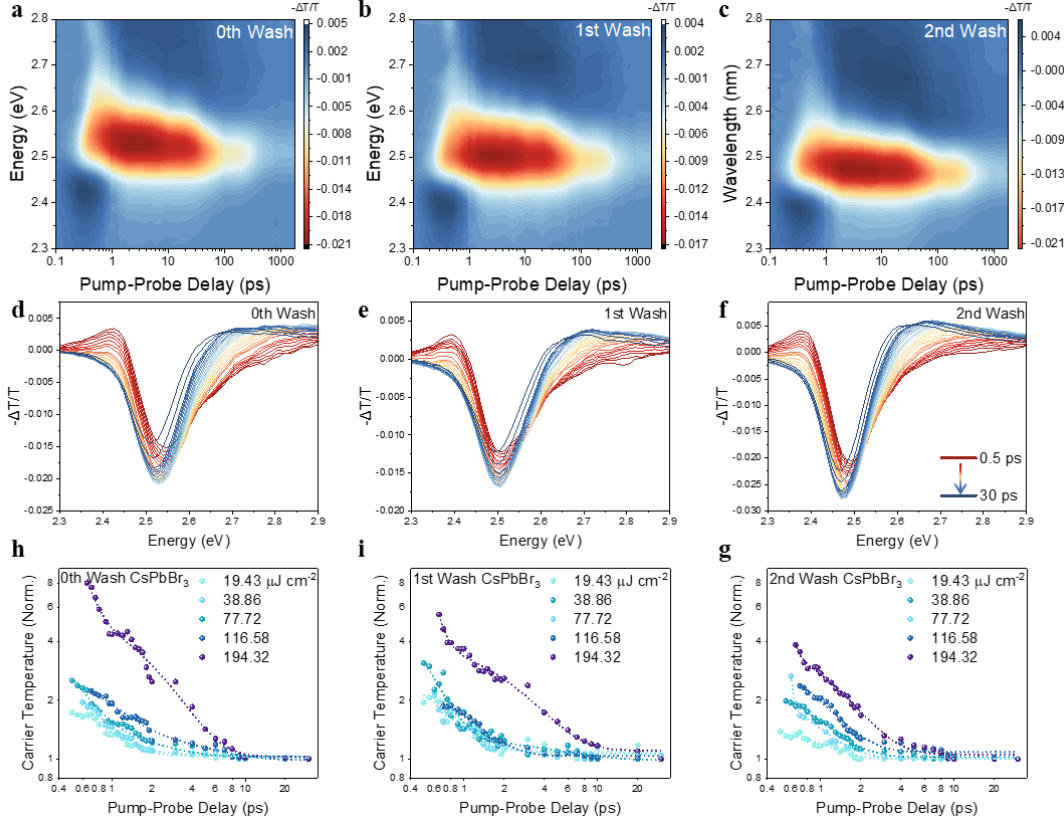


Figure 5. 3 Hot carrier cooling kinetics based on pump -probe transient absorption spectroscopy for CsPbBr₃ NCs. a-c. TA map of 0th, 1st and 2nd washed CsPbBr₃ NCs samples at 194.32 μJ cm⁻². d-f. TA spectra of 0th, 1st and 2nd washed CsPbBr₃ NCs samples from 0.5 ps to 30 ps at 194.32 μJ cm⁻². h-g. Extracted carrier temperature against the pump-probe delay time of 0th, 1st and 2nd washed CsPbBr₃ NCs samples with different pump fluences.

Table 5. 1 Fitted Cooling Kinetics for CsPbBr₃ NCs.

0th Washing								
Fluence $\mu\text{J cm}^{-2}$	t_{average}	Err	t_1	Err	A_1	t_2	Err	A_2
19.43	0.51	0.06	0.51	0.06	0.72	0.08	0.07	0.00
38.86	1.28	0.09	0.30	0.07	1.28	1.79	0.13	0.42
77.72	2.18	0.05	0.44	0.05	0.83	4.02	0.05	0.09
116.58	3.44	0.22	0.61	0.19	0.82	4.22	0.26	0.43
194.32	3.47	0.34	0.65	0.24	4.76	4.56	0.47	1.74
1st Washing								
Fluence $\mu\text{J cm}^{-2}$	t_{average}	Err	t_1	Err	A_1	t_2	Err	A_2
19.43	0.49	0.10	0.49	0.10	1.27	0.03	0.06	0.00
38.86	0.60	0.08	0.02	0.04	1.82	0.63	0.12	0.78
77.72	0.90	0.18	0.25	0.09	1.87	1.50	0.31	0.34
116.58	1.41	0.27	0.51	0.27	0.65	1.99	0.27	0.26
194.32	2.54	0.41	0.61	0.08	7.21	3.45	0.54	2.70
2nd Washing								
Fluence $\mu\text{J cm}^{-2}$	t_{average}	Err	t_1	Err	A_1	t_2	Err	A_2
19.43	0.41	0.18	0.41	0.18	0.75	0.40	0.18	0.00
38.86	0.57	0.06	0.03	0.01	1.58	0.61	0.07	0.85
77.72	0.66	0.08	0.12	0.02	1.55	0.70	0.08	3.61
116.58	0.75	0.12	0.75	0.11	0.78	0.75	0.13	0.60
194.32	1.11	0.07	0.05	0.02	0.76	1.13	0.07	2.31

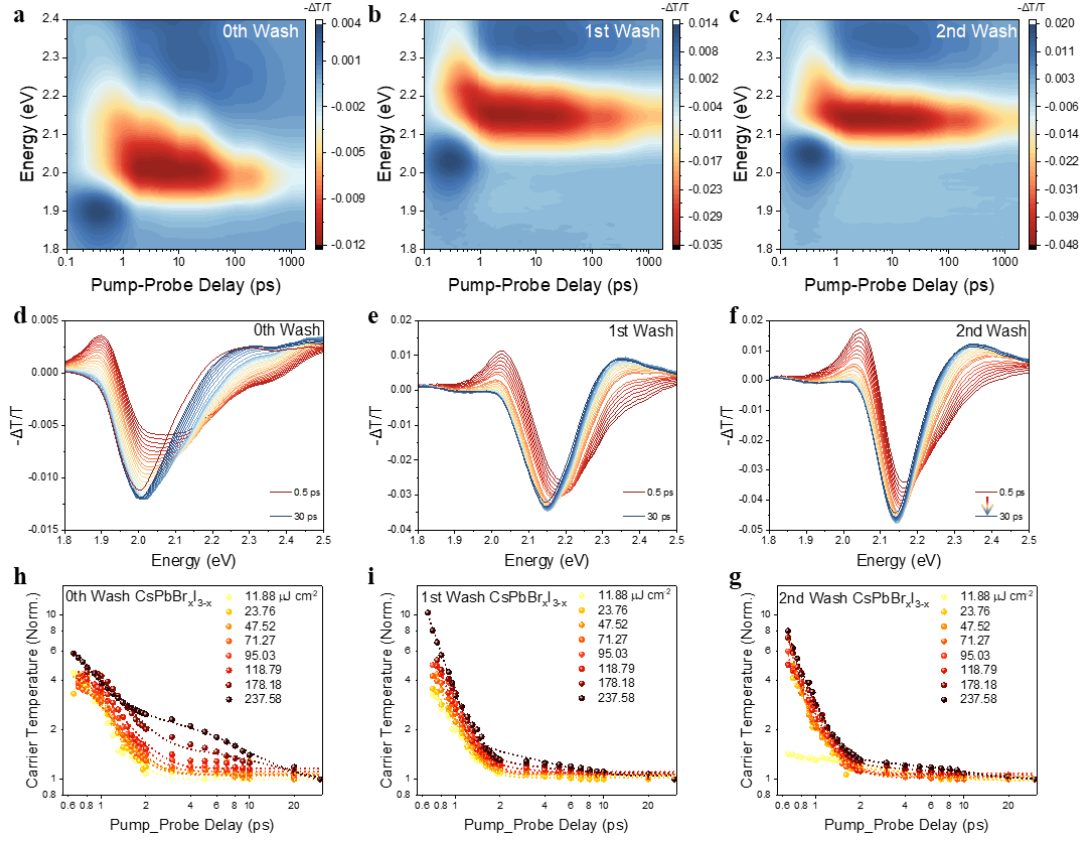


Figure 5. 4 Hot carrier cooling kinetics based on pump -probe transient absorption spectroscopy for $\text{CsPbBr}_x\text{I}_{3-x}$ NCs. a-c. TA map of 0^{th} , 1^{st} and 2^{nd} washed $\text{CsPbBr}_x\text{I}_{3-x}$ NCs samples at $237.58 \mu\text{J cm}^{-2}$. d-f. TA spectra of 0^{th} , 1^{st} and 2^{nd} washed $\text{CsPbBr}_x\text{I}_{3-x}$ NCs samples from 0.5 ps to 30 ps at $237.58 \mu\text{J cm}^{-2}$. h-g. Extracted carrier temperature against the pump-probe delay time of 0^{th} , 1^{st} and 2^{nd} washed $\text{CsPbBr}_x\text{I}_{3-x}$ NCs samples with different pump fluences.

Table 5. 2 Fitted Cooling Kinetics for $\text{CsPbBr}_x\text{I}_{3-x}$ NCs.

0th Washing								
Fluence $\mu\text{J cm}^{-2}$	t_{average}	Err	t_1	Err	A_1	t_2	Err	A_2
11.88	0.46	0.06	0.46	0.06	2.12	0.46	0.07	1.94
23.76	0.55	0.07	0.55	0.07	1.39	0.55	0.07	1.32
47.52	0.48	0.22	0.48	0.05	1.12	0.48	0.24	2.29

71.27	0.61	0.06	0.61	0.06	1.49	0.61	0.05	1.39
95.03	0.64	0.10	0.64	0.10	1.58	0.64	0.11	1.49
118.79	0.69	0.07	0.69	0.02	0.96	0.69	0.07	2.30
178.18	1.17	0.07	1.17	0.08	2.17	1.17	0.02	0.79
237.58	6.49	0.05	0.39	0.01	4.06	7.27	0.06	1.70
1st Washing								
Fluence $\mu\text{J cm}^{-2}$	t_{average}	Err	t_1	Err	A_1	t_2	Err	A_2
11.88	0.32	0.01	0.32	0.01	2.69	0.00	0.00	0.00
23.76	0.33	0.07	0.33	0.07	3.11	0.14	0.17	0.01
47.52	0.34	0.01	0.36	0.01	2.76	0.05	0.01	1.79
71.27	0.37	0.02	0.37	0.02	2.86	0.04	0.03	0.00
95.03	0.41	0.08	0.41	0.08	3.17	0.41	0.09	1.84
118.79	0.68	0.06	0.42	0.01	3.51	1.68	0.13	0.23
178.18	1.32	0.08	0.28	0.02	3.61	2.51	0.15	0.35
237.58	2.49	0.18	0.21	0.00	14.18	5.33	0.24	0.44
2nd Washing								
Fluence $\mu\text{J cm}^{-2}$	t_{average}	Err	t_1	Err	A_1	t_2	Err	A_2
11.88	0.11	0.07	0.11	0.07	0.76	2.42	0.00	0.00
23.76	0.24	0.23	0.06	0.01	32.14	0.54	0.31	2.23
47.52	0.26	0.10	0.10	0.07	1.56	0.29	0.11	2.24
71.27	0.27	0.06	0.17	0.05	6.63	0.48	0.07	1.14
95.03	0.34	0.14	0.15	0.22	1.17	0.36	0.10	4.56
118.79	0.41	0.23	0.20	0.14	2.73	0.51	0.29	2.36

178.18	0.61	0.04	0.23	0.02	5.97	1.17	0.08	0.78
237.58	2.56	0.04	0.24	0.01	9.41	4.89	0.12	0.45

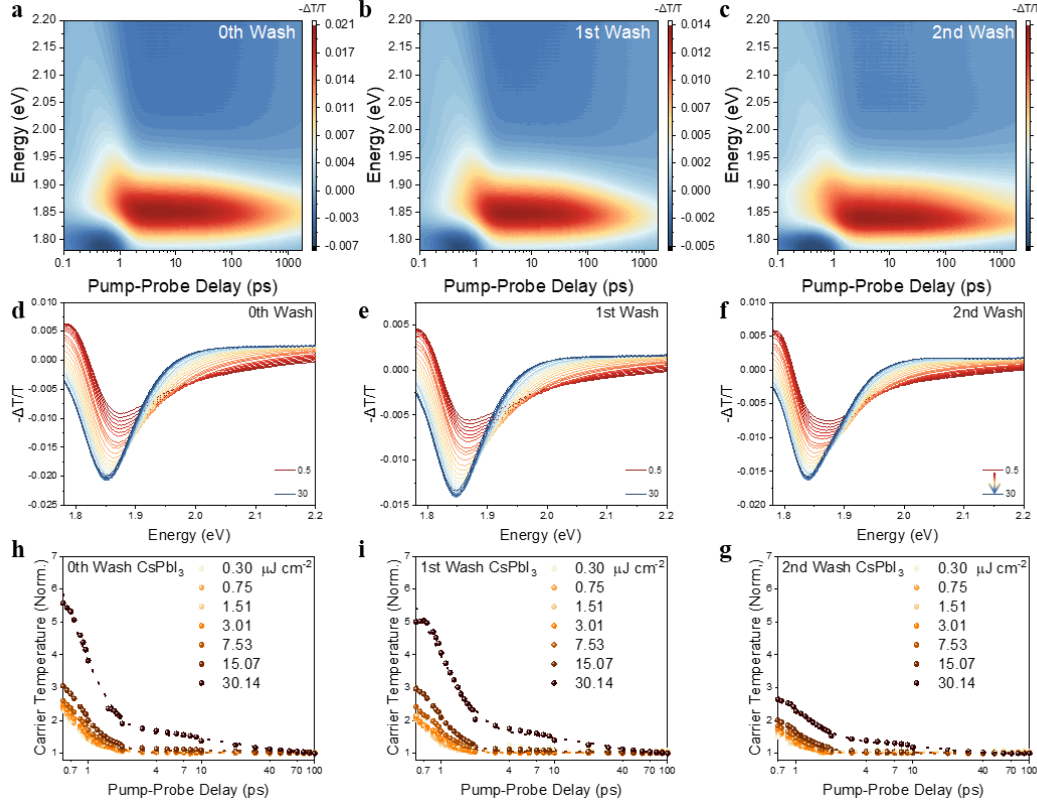


Figure 5. 5 Hot carrier cooling kinetics based on pump-probe transient absorption spectroscopy for CsPbI₃ NCs. a-c. TA map of 0th, 1st and 2nd washed CsPbI₃ NCs samples at 30.14 μJ cm⁻². d-f. TA spectra of 0th, 1st and 2nd washed CsPbI₃ NCs samples from 0.5 ps to 30 ps at 30.14 μJ cm⁻². h-g. Extracted carrier temperature against the pump-probe delay time of 0th, 1st and 2nd washed CsPbI₃ NCs samples with different pump fluences.

Table 5. 3 Fitted Cooling Kinetics for CsPbI₃ NCs.

0th Washing								
Fluence μJ cm ⁻²	t _{average}	Err	t ₁	Err	A ₁	t ₂	Err	A ₂
0.30	0.26	0.07	0.86	0.15	4.41	0.26	0.07	6809.22
0.75	0.35	0.28	0.33	0.46	0.25	0.36	0.10	1.21
1.51	0.40	0.16	0.40	0.12	0.85	0.41	0.20	0.53

3.01	0.41	0.14	0.46	0.15	1.15	0.35	0.14	1.09
7.53	0.50	0.16	0.50	0.17	1.36	0.50	0.14	0.16
15.07	0.55	0.35	0.55	0.41	1.66	0.55	0.20	1.24
30.14	12.19	1.43	0.60	0.04	5.32	15.68	1.68	0.68
1st Washing								
Fluence $\mu\text{J cm}^{-2}$	t_{average}	Err	t_1	Err	A_1	t_2	Err	A_2
0.30	0.28	0.07	0.05	0.11	0.02	0.28	0.07	0.80
0.75	0.31	0.20	0.31	0.20	0.51	0.31	0.20	0.51
1.51	0.40	0.37	0.40	0.33	0.93	0.40	0.42	0.71
3.01	0.46	0.28	0.46	0.28	0.96	0.46	0.24	0.00
7.53	0.55	0.29	0.55	0.25	1.11	0.55	0.33	0.86
15.07	0.61	0.30	0.61	0.35	1.49	0.61	0.12	1.16
30.14	12.12	1.59	0.79	0.07	3.83	15.24	1.89	0.72
2nd Washing								
Fluence $\mu\text{J cm}^{-2}$	t_{average}	Err	t_1	Err	A_1	t_2	Err	A_2
0.30	0.28	0.12	0.79	0.14	0.40	0.22	0.12	11.22
0.75	0.35	0.29	0.35	0.28	0.69	0.35	0.30	0.64
1.51	0.37	0.23	0.37	0.22	0.74	0.37	0.23	0.69
3.01	0.41	0.19	0.41	0.18	0.71	0.41	0.21	0.62
7.53	0.51	0.17	0.51	0.15	0.68	0.51	0.19	0.53
15.07	0.53	0.29	0.42	0.25	0.76	0.62	0.33	0.60
30.14	12.62	3.36	0.78	0.05	1.41	14.63	3.51	0.44

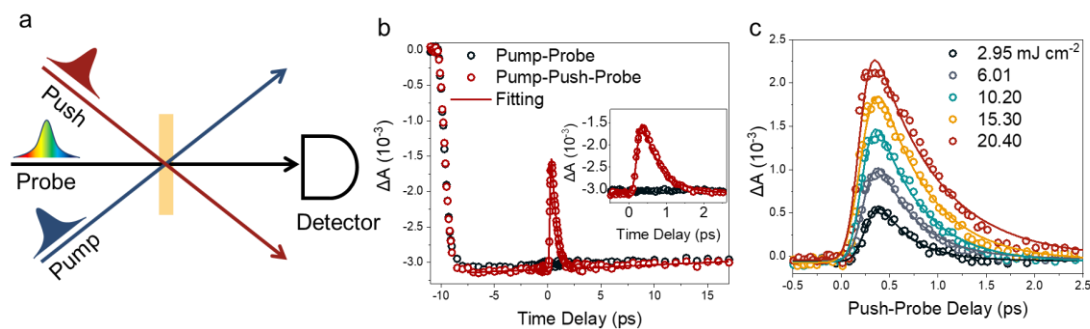


Figure 5. 6 Hot carrier cooling kinetics based on pump-push-probe transient absorption spectroscopy. a. Schematic diagram of a pump-push-probe TA setup. b. The PP and PPP ground state bleach decay kinetics with a pump-push delay of 10 ps. Inset shows the zoomed-in area of the push-induced decay curve. c. Push-fluence dependent GSB decay curves.

The changes in the HC cooling lifetime and excitation fluences at which HC cooling dynamics being to slow down among the perovskites of different compositions are difficult to interpret because the excess excitation energy (for 400 nm pump) with respect to the bandgap is different from pure-Br to pure-I systems. Therefore, to enhance our understanding, we use a three-pulse based pump-push-probe spectroscopic approach in which an additional narrowband IR-push pulse is being introduced to optically re-excite the band-edge carriers to a higher energy level (hot state). Details of the PPP-TA set up is described in experimental methods. As the IR-push pulse is meant to create intra-band transients, we first make an attempt to identify what push-energy could be relevant to induce maximum/strong intra-band transitions for CsPbX_3 NCs. Typical TA measurements with a broadband probe in near-IR allows us to choose 1300 nm wavelength as the push source to employ in our study for all the samples we investigated. To ensure push-pulse exclusively acts on band-edge carriers as well as the excess energy dumped by the push-pulse remains same for all the systems (irrespective of the bandgaps), we introduce the push beam 10-ps after excitation with the 400 nm wavelength pump-beam (Figure 5.6a,b). Unlike conventional PP, this PPP offers additional control on the sub-population of hot carriers (by push fluence) w.r.t. the cold-

carriers (by pump fluence), which would unravel to discern the role of carrier-carrier interactions from carrier-phonon interactions in HC cooling dynamics.

To verify our hypothesis of push-pulse exclusively creating transient hot-state, in first instance, we measured the effect of near-IR push on the broadband visible TA signals of representative CsPbBr₃ NCs case. As can be seen from Figure 5.7, notable differences in all TA signals (e.g. emergence of an additional bleaching feature in blue-side photo-induced absorption (PIA), reduction in GSB signal amplitude and reappearance of red-side PIA features) observed during the interaction of push-pulse. All these Push-induced TA features recover back to their original pump-probe background within-ps timescale. When push-laser optically reheats the pump-generated band-edge charge carriers to the higher energy levels, it basically reduces the band-edge population transiently and increases subsequently to the hot-state. This reflects as a reduction in blue-side PIA and GSB signals and increase in red-side PIA signal and all of them ideally should represent the same dynamical event which is hot-carrier cooling to the band-edge state. Subtracting the push-induced kinetics from the pump-probe kinetics indeed results identical decay process (same decay time-constant) for both PAs- and GSB-signals. Though the push-induced effect on any one of the TA signals can be used as a marker to extract the hot carrier cooling dynamics, we relied only on GSB features throughout this work as this carries an order of larger magnitude of signal compared to the PIAs.

As can be seen (Fig 5.6c) in representative case for CsPbBr_xI_{3-x} NCs, increasing the push fluence creates more hot charge carriers and that reflects as more reduction in GSB feature. Following the same subtraction procedure one can extract the time-constant of the hot carrier cooling process as a function of hot-carrier density (push fluence) for all the systems under investigation. The subtracted push-induced kinetics can only be best fitted monoexponential decay function with gaussian convolution. The fitting

parameters are plotted against the push fluence for all the three different halide compositions-based samples including their respective washed samples (Fig. 5.8d-f).

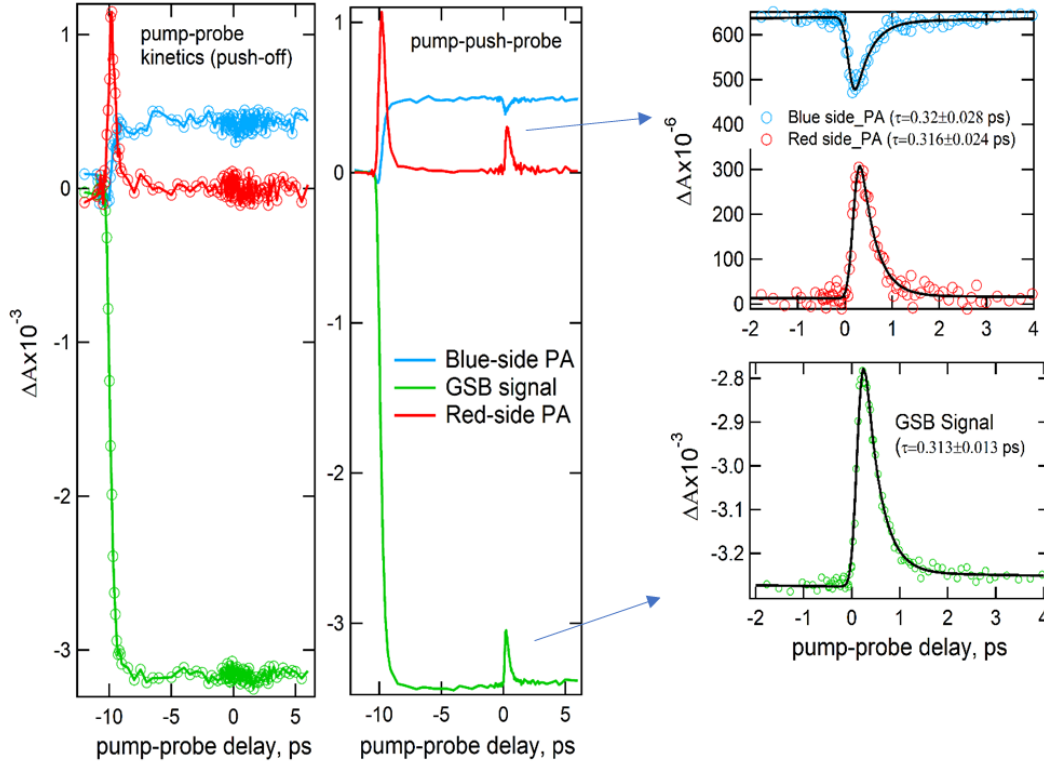


Figure 5. 7 Kinetics of GSB and PAs for the representative case of CsPbBr_3 under PP and PPP-TA measurements. All samples are solution samples and are measured inside a 1 mm thick cuvette. The NIR push beam has an energy of 0.954 eV. The pump laser is a 400 nm pulse laser at $2 \mu\text{J cm}^{-2}$.

Fig. 5.8 summarises the fitted hot carrier cooling lifetime (τ_{cool}) estimated from both PP TA and PPP TA based spectroscopic measurements. The cooling lifetime obtained from PPP TA follows similar trend as the PP TA results. In all cases, generally the τ_{cool} increased with the pump/push fluence due to the increasing carrier densities perhaps due to hot phonon bottleneck effect. However, in the PPP TA, we have restricted our pump fluence within $\mu\text{J cm}^{-2}$ (corresponds to $\langle N \rangle \ll 1$, the carrier density per nanocrystal) to rule out any contribution from nonlinear Auger processes related to cold carrier-cold carrier interactions. At the same time, through the fluence of the push beam,

I could selectively control the hot-carrier density. Therefore, the observed slowing down of hot-carriers at high density of hot carriers in PPP measurements is solely due to hot-phonon bottleneck effect. On the contrary, in PP measurements, higher pump fluence increases both the hot and cold carriers' density, so prevalence of both hot phonon bottleneck and Auger heating induced slowing down of hot carriers is obvious. This is consistent with the contrasting difference observed in hot carrier lifetime estimated from PP to PPP measurements. The second slower cooling time-component ($\sim$ few-ps) observed in PP measurements perhaps arises due to the Auger heating process that kicks in under high density of carriers. Albeit the general trend of increase of hot carrier lifetime with increase in hot carrier density remain same for all the perovskites under study, subtle differences can be found among the pristine to defective samples. We rationalise this observation as follows. It is clearly evident from Figure 5.8, that the intrinsic cooling lifetime for the defective samples is shorter than their respective pristine samples except for the CsPbI_3 case in which lifetime remain invariant. This points to halide-vacancy related defects in CsPbBr_3 and $\text{CsPbBr}_x\text{I}_{3-x}$ systems introducing a competing channel for the intra-band relaxation process leading to faster dynamics. Interestingly, under a high density of hot-carriers, the cooling lifetime of the defective samples tend to approach to the cooling time of their respective pristine samples. We believe that this possibly arises due to the trade-off between hot-phonon bottleneck and trap-state saturation under high density of hot carriers. When all the vacant trap-sites are filled by the carriers, the competing pathway for the intra-band relaxation process is blocked and therefore all the defective samples tend to return to their pristine values. Also, the push beam energy is only about 0.954 eV which is much lower than the bandgaps, so only carriers at trap states and band-edge that have not yet recombined can be re-excited. Therefore, the resulting carrier densities would be low after push beam arrived. However, we still observed that the cooling lifetime decreased with the increase in number of washings for CsPbBr_3 and $\text{CsPbBr}_x\text{I}_{3-x}$ NCs, and

relatively constant cooling lifetime for CsPbI₃ NCs with and without washing despite the 2nd washed CsPbI₃ NCs became unstable.

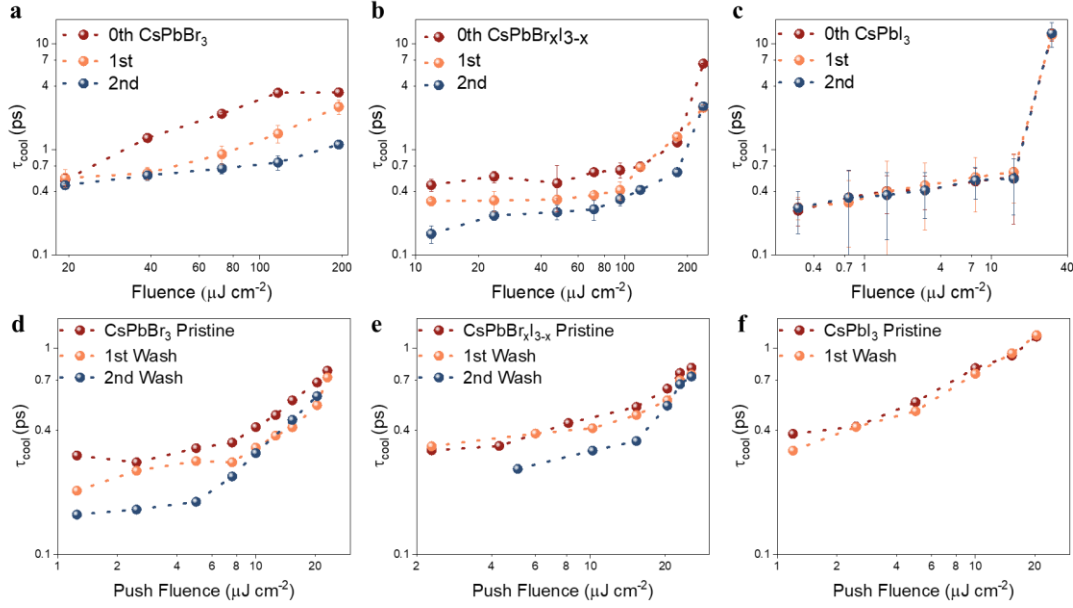


Figure 5.8 Hot carrier cooling lifetime from PP and PPP TA. a-c. Cooling lifetime fitted from PP TA data for CsPbBr₃, CsPbBr_xI_{3-x}, and CsPbI₃ NCs respectively. d-f. Cooling lifetime fitted from PPP TA for CsPbBr₃, CsPbBr_xI_{3-x}, and CsPbI₃ NCs respectively.

To test our proposed hypothesis, various routes of interactions especially the carrier-defect scatterings (trapping) to and carrier-phonon related interactions were considered to develop a simple kinetic model. Figure 5.8 shows the fitted hot carrier cooling lifetime (τ_{cool}) from both PP TA and PPP TA. As discussed previously, the cooling lifetime obtained from PPP TA showed similar trend as the PP TA results. In all cases, the τ_{cool} increased with the push fluence due to the increasing in carrier densities and phonon bottleneck effect. However, in the PPP TA, the decay curve can be explained well with a one-component exponential decay function. We did not observe the second slower cooling component. This might be due to the push fluence was not high enough to re-excited carrier densities above 10^{17} to 10^{18} cm⁻³, so that no hot phonon bottleneck and Auger reheating effect occurred. Also, the push beam energy is only about 0.954 eV which is much lower than the bandgaps, so only carriers at trap states and band-

edge that have not yet recombine can be re-excited, therefore the resulted carrier densities would be low. However, we still observed that the cooling lifetime decreased with the increase in number of washings for CsPbBr₃ and CsPbBr_xI_{3-x} NCs, and relatively constant cooling lifetime for CsPbI₃ NCs with and without washing despite the 2nd washed CsPbI₃ NCs became unstable.

To explain these observations on the trap densities related hot carrier cooling kinetics, we modelling the hot carrier population kinetics based on Eq.5.2-5:

$$\frac{dn_{hot}}{dt} = \tilde{I}n_{cold} - \alpha n_{cold}n_{hot} - \beta n_{ph}n_{hot} - \gamma(N_t - n_t)n_{hot} \quad (5.2)$$

$$\frac{dn_{cold}}{dt} = -\tilde{I}n_{cold} + \alpha n_{cold}n_{hot} + \beta n_{ph}n_{hot} - k_r n_{cold} \quad (5.3)$$

$$\frac{dn_{ph}}{dt} = -\beta n_{ph}n_{hot} + \nu(N_{ph} - n_{ph}) \quad (5.4)$$

$$\frac{dn_t}{dt} = \gamma(N_t - n_t)n_{hot} - k_t n_t \quad (5.5)$$

where n_{hot} is hot carrier density, n_{cold} is cold carrier density, n_{ph} is *vacant* phonon density, n_t is *occupied* trap density, N_{ph} is total phonon density, and N_t is total trap density. For the coefficient, $\tilde{I}$ is push Gaussian envelope, α is hot-cold carrier cooling, β is hot carrier-phonon cooling, γ is hot carrier trapping, k_r is cold carrier recombination, ν = occupied phonon freeing, and k_t is trap recombination. The fitted results can be found in Figure 5.9 The fitted cooling lifetime against the hot carrier densities or fluences matched well with our experimental results. In the modelling, the N_t is mainly governed by the number of washings, as N_t increases, the cooling lifetime would reduce or curve down. The effect of defect densities on hot carrier cooling can be also influenced by pump or push fluence due to the trap filling effect when the fluence increases, i.e. the occupied trap densities n_t would reduce. Both N_t and n_t influence the total free carrier densities which is the key for phonon bottleneck and reheating effect, and ultimately achieving slower cooling. This

explained well for the observed up-curvature for the 1st and 2nd washed defect samples for CsPbBr₃ and CsPbBr_xI_{3-x} NCs. The upper curvature indicated the trap filling effect when fluence increases, thus higher free carrier densities and longer cooling lifetime (Figure. 5.8 a-b, d-e). The model pattern compares very satisfactorily with salient qualitative trends observed in experimental Figure 5.8d-f giving further credence to the idea that the hot carrier trapping can accelerate the cooling process as well as the interplay of hot-phonon bottleneck and saturation of the trap-states could lead to attain longer cooling lifetime for the defective samples. This illustration should not, however, be misconstrued for a frame-work to fit the experimental data with few kinetic parameters, which would instead require a detailed understanding of the density-dependent relaxation processes.

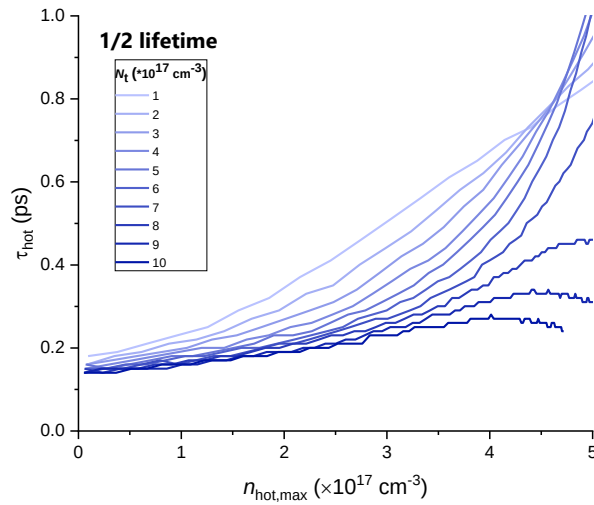


Figure 5. 9 Modelling of the hot carrier cooling kinetics.

Another key observation from Figure 5.8 was that the differences in cooling lifetime upon washing became smaller as the composition changed from Br to I. For example, for pure Br NCs in Figure 5.8a, the vertical gap between 0th and 2nd was large, it became smaller when adding some I, and became almost zero for pure I NCs (Figure 5.8c and f). We think this is due to the change of γ , (i.e. hot carrier trapping constant, which

describes the tendencies of the hot carriers that could be trapped), which we have discussed previously based on the energy dependent PLQY, which confirmed that the hot carriers can be directly trapped. The magnitude of γ or the trap-carrier electronic coupling is governed by compositions. The change in halide composition could influence the bandgap and also the defect position relevant to the conduction band-edge.

To confirm our hypothesis, we used DFT calculations to determine the band structures, density of states and trap-positions relative to the conduction band minimum. The results are shown in Figure 5.10. Figure 5.10 a-c show the band structure and projected density of states (PDOS) of the perfect lattice, i.e. no halide vacancy. The results match well with previous literatures that the conduction band DOS is mainly come from Pb and halide orbitals. Figure 5.10 d-f show the defective lattice by partially removing bonded halides. Here, we did not obtained isolated trap states in the bandgap with a flat band structure as previously reported by *Li et al.*³¹⁰. This might be due to the large local distortion and geometry breaking of the cubic unit cell when removing the high ratio of bonded halides in a relatively smaller supercells to represent the case of NCs which contain a finite number of unit cells (unit cell diagrams shown in Figure 5.10 a-f insets). As a result, the high local halide vacancies densities and dangling bonds from Pb atoms can extend the trap band partially into the conduction band which make the band structures more complicated. Similar band calculation is reported by *Zhou et al.*²⁸⁹. Based on our calculations, the trap position for CsPbBr₃ is 0.666 eV, for CsPbBr_xI_{3-x} is 0.513 eV and for CsPbI₃ is only 0.278 eV. When the trap position is more closed to the CB minimum, the carrier trap coupling would be smaller and the carriers can be easily escaped from the trap states so that the free carrier densities can be well maintained for Auger reheating or hot phonon bottleneck effect to occur, hence leads to a slower cooling lifetime.

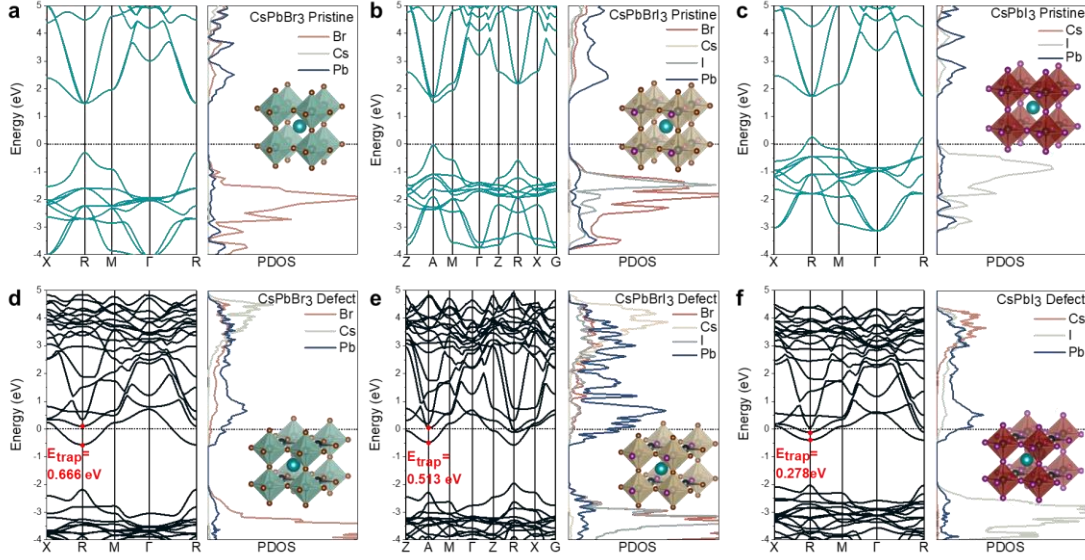


Figure 5. 10 Density function theory calculation for band structures. a-c. Band structures and projected density of states of pristine (no defect) CsPbBr_3 , $\text{CsPbBr}_3\text{I}_{3-x}$, and CsPbI_3 NCs respectively. d-f. Band structures and projected density of states of defective (illustrate the washed NCs) CsPbBr_3 , $\text{CsPbBr}_3\text{I}_{3-x}$, and CsPbI_3 NCs respectively. The calculation method can be found in Chapter 3.

5.3 Conclusion

In conclusion, we investigated the influence of trap states on the rate of hot carrier cooling, revealing the defect tolerance exhibited by band-edge charge-carriers extends also to hot carriers. We confirmed firstly with the PLQY analysis that the carriers with more excess energy (hotter carriers) tend to be trapped more easily to increase the trap-assisted non-radiative recombination, especially for Br-based NCs. Hot carriers in pure I-based NCs suffer less from the defect trapping. Based on our PP and PPP TA analysis of the hot carrier cooling lifetime, we also observed more obvious defect tolerance nature for narrower gap perovskites compared with wide gap perovskites. This indicates that wide gap solar cells suffer more problems for managing the carrier cooling through defects. For NC-based solar cells, the surface ligand density is an important factor, although low ligand densities would be beneficial for charge transportation between

NCs, but the ensuing higher defect densities are detrimental for the recombination of both band-edge and hot carriers. It elucidates the influence of defect densities on hot carrier cooling lifetime, which is important for developing hot carrier solar cells. Our studies also provide guidelines for the effect of defect densities on different composition of perovskites. The defect densities of NC-based solar cells with different requirement of the bandgap, I-rich for narrow gap or Br-rich for wide gap, can be optimised individually to achieving better balance between carrier trapping and carrier transportation or extraction.

Chapter 6: Direct Emission of Linearly-Polarised Electroluminescence from CsPbI₃ Perovskite Nanoplatelets

Junzhi Ye, Linjie Dai and Robert L.Z. Hoyer conceived the projects. Junzhi Ye performed the material synthesis and optimisation. Junzhi Ye and Aobo Ren optimised devices. Tomi Baikie performed the polarisation measurements. Renjun Guo, Manuel A Reus and Peter Müller-Buschbaum performed the GIWAXS measurement and analysis. Debapriya Pal, Gianluca Grimaldi and A. Femius Koenderink constructed the optical simulation model. Junzhi Ye and Sebastian Gorgon performed low temperature PL measurement.. Junyang Huang, Rakesh Arul and Jeremy J. Baumberg performed and analyse the k-space Fourier microscopy measurement. Yuqi Sun supplied the FAPbI₃ LEDs. Linjie Dai. and Kaiwen Zhang performed the TEM measurements. Junzhi Ye performed TA and TRPL measurements and analysis.

6.1 Introduction

Linearly-polarised light has a wide range of applications, including radiometric analysis, bio-imaging, detecting counterfeit items, liquid crystal displays, and emerging 3D display technologies³¹¹⁻³¹⁸. Conventionally, linear polarisation is obtained by passing unpolarised light through a linear polariser, which is typically constructed from highly-oriented long-chain molecules or wire grids with photonic structures. However, this approach results in a significant reduction in intensity due to optical absorption losses^{311,318}. Organic molecules with aligned transition dipole moments, as well as anisotropic inorganic nanorods and nanoplatelets have demonstrated direct linearly polarised emission following photoexcitation or electrical-injection (Table 6.1). However, the degree of polarization (DOP) of EL from thin film LEDs is usually below 30%, due to a lack of effective control over the alignment of the transition dipole

moment in colloidal quantum dots or molecular systems. For example, OLEDs can only achieve DOP values of 10–30% in thin film form³¹⁹⁻³²¹. Photonic structures, such as Ag nanogratings, are needed to generate higher DOPs³²². Meanwhile, for anisotropic nanostructured inorganic materials, such as cadmium selenide nanorods, indium phosphide nanowires or lead-halide perovskite nanowires, high DOPs (>70%) have only been achieved at the single particle level, or on substrates with pre-patterned photonic structures^{89,223,311,312,323-329}. DOP values significantly decrease when making them into films because the quantum dots would then have a random orientation, which limits the ability to transfer the polarised emission from single particles to the device level^{311,327,330}. Therefore, approaches need to be developed to finely control the orientation of the anisotropic nanostructures in order to achieve high DOPs at the device level.

Table 6. 1 Materials for linearly polarised emission.

Materials	Emission Peak (nm)	Degree of Linear Polarization (%)	Ref.
Lead-halide perovskites			
MAPbBr ₃ NW arrays/AAO	540	84 (PL)	327
Individual (BA) ₂ PbI ₄ NW	518	73 (PL)	331
Individual MAPbI ₃ NW	760	70 (PL)	332
CsPbBr ₃ NW Arrays/mica	515	78 (PL)	333
CsPbBr ₃ NWs-PLMA polymer	517	44 (PL)	334
CsPbBr ₃ NWs/PU fiber	490	30 (PL)	335
MAPbBr ₃ QD/PVA fiber	525	53 (PL)	336
CsPbI ₃ QD film	693	40 (PL)	337
MAPbBr ₃ QD/PVDF	528	33 (PL)	338
MAPbI ₃ QD solution	711	28 (PL)	339
(MBA) ₂ PbI ₄ microplates	510	17.6 (PL)	340
Rubbed CsPbBr ₃ NWs film	519	50 (PL)	330
Self-Assembled CsPbI₃ NPLs with no photonic structure	620	74.4 (EL)	This work
Organics			
F(MB)5	412	11.8 (EL)	319

F(Pr)5F(MB)2	420	14.7 (EL)	320
F(MB)7F(DMO)2	448	31.2 (EL)	320
Doped OF-8	560	25.6 (EL)	321
mCP: Ir(ppy)3 (Nanograting)	530	87 (EL)	322
Other Semiconductors			
Individual CdSe quantum rods	590	86 (PL)	323
Individual InP nanowires	850	91 (PL)	324
CdSe NPL films	517	41 (PL)	341

Colloidal perovskite nanocrystals have potential as an alternative class of materials for achieving polarised light emission⁷¹. Beyond the advantages stated in Chapter 2.2 in terms of the bulk properties and processability, perovskites can also be fabricated as anisotropic nanostructures, such as nanoplatelets and nanowires, which in other materials systems have led to a high degree of polarisation to be achieved^{143,331,332}. Becker *et al.* showed that the presence of the exciton fine structure in cesium lead halide nanocrystals leads to distinct bright triplet states which yield strong linearly polarised light^{143,342}. However, the relationship between the fine structure splitting, alignment of dipoles and the DOP has not been studied experimentally. Seminal works on controlling the transition dipole moment (TDM) alignment in weakly-confined CsPbBr₃ nanoplatelets (9±2 nm thickness, >10 monolayers) have recently appeared^{343,344}. But as far as the authors are aware, there is no report on the orientation-controlled self-assembly of strongly-confined perovskite NPLs (*i.e.*, with < 4 monolayers), and no demonstration of direct emission of linearly-polarised EL. Indeed, strongly-confined NPLs have so far demonstrated limited external quantum efficiencies (EQEs) in LEDs, with highest reported EQE value of 2% for pure blue-emitting CsPbBr₃ NPLs^{89,345}. Furthermore, whilst progress has been made with green- and blue-emitting CsPbBr₃ NPLs, there has been no report of EL from red-emitting CsPbI₃ NPLs, due to the instability nature of the I-based nanocrystals upon the purification process (as discussed in Chapter 4). Addressing these gaps in the literature, from demonstrating linearly polarised EL through to pure-red nanoplatelet LEDs, will be critical for achieving

advanced ultrahigh definition displays that fulfil the Rec.2020 standard, as well as technologies relying on polarised light emission.

In this chapter, I aim to address these pressing challenges by devising a solution-based route to synthesising CsPbI₃ NPLs with a uniform thickness that can give pure red emission, and with a high degree of confinement to give strong exciton fine structure splitting. To directly achieve linearly-polarised EL, we focus on addressing three critical factors. The first is achieving the self assembly of these CsPbI₃ NPLs to achieve the alignment of transition dipole moments, and we investigate making use of solvents with different evaporation rates. The second factor is achieving high photoluminescence quantum yields (PLQYs) in the strongly-confined systems, and we investigate the use of PbI₂-ligand passivation. The third factor is that the exciton fine structure splitting needs to be large enough so that the aligned dipole can generate a high DOP when an external bias is applied during device operation. We utilise structural (transmission electron microscopy, TEM; grazing-incidence wide-angle X-ray scattering, GIWAXS), optical (K-space fourier microscopy) and first-principles analyses to understand the self-assembly properties and dipole alignment of the films. Additionally, we probe the effects of defect passivation on charge-carrier kinetics using time-resolved photoluminescence (TRPL) and transient absorption spectroscopy (TAS). Lastly, we measure the PL spectra at 5.2 K to compare the fine structure splitting energy for the strongly confined NPL system against a weakly confined nanocube and a bulk system. We demonstrate efficient pure-red CsPbI₃ LEDs, with EQEs up to 2.7% EQE, and an EL DOP of 74.4%, which, to our knowledge, is the highest EL DOP for any organic and inorganic emitter reported thus far (Supplementary Table 1), as well as the most efficient pure-red perovskite nanoplatelet LED.

6.2 Results

6.2.1 Uniform, strongly-confined CsPbI₃ nanoplatelets with colour-pure photoluminescence

CsPbI₃ NPLs were synthesised by the spontaneous crystallization method using a nonpolar toluene solvent for PbI₂ precursors and oleic acid for Cs-acetate precursors (see Methods)³⁴⁶. The NPL solution was obtained by reacting 50 μ L Cs-precursors into 2 mL PbI₂ precursors. The PL spectra and TEM images of the synthesised NPLs are shown in Figure 6.1 and Figure 6.2, with details on the optimisation in Figure 6.3a-c. The single PL peak was obtained when using Cs-acetate precursors and dual peaks were obtained when using Cs-carbonate precursors. The multiple peaks are due to the different NPL thicknesses (shown in Figure 6.3a). When mixing Cs-carbonate with oleic acid, water is usually a by-product for the reaction between the carbonates with acids. The present of polar water molecules usually leads to removal of the surface ligands²³⁶, and cause merging of the nanocrystals to create thicker NPLs. Thicker NPLs can also be grown when the reaction temperature is high³⁴⁶. Figure 6.3b demonstrated that by reducing the reaction temperature from room temperature to ice-water bath, we could eliminate the dual peaks in the PL spectra. Additionally, by monitoring the amount of Cs-acetate precursor used during injection into the PbI₂ precursors, we can tune the emission peak center from 598 nm (NPLs $n=3$) to 700 nm (NCs) (Figure 6.3c). Monodisperse NPLs with relatively single size distribution is important for self-assembly. A size distribution analysis from TEM measurements confirmed that the NPLs have a length of 22 ± 2 nm, a width of 22 ± 3 nm and a thickness of 2.6 ± 0.5 nm (Figure 6.3d). The thickness of the NPLs is much smaller than the Bohr radius of CsPbI₃ (~ 12 nm)³⁴, and therefore a strong excitonic peak was observed in the absorption spectra (Figure 6.1b-d). The good size distribution for $n=3$ NPLs are governed by the competition nucleation between PbI₂ atoms and the binding ligands³⁴⁷. After nucleation,

the growth rate is governed by the temperature, PbI₂ and ligands concentrations. When the growth rate giving ligands enough time to form compact layers on the two broader parallel facets to form the ligand covered layers, then the crystal grows as an NPLs³⁴⁷.

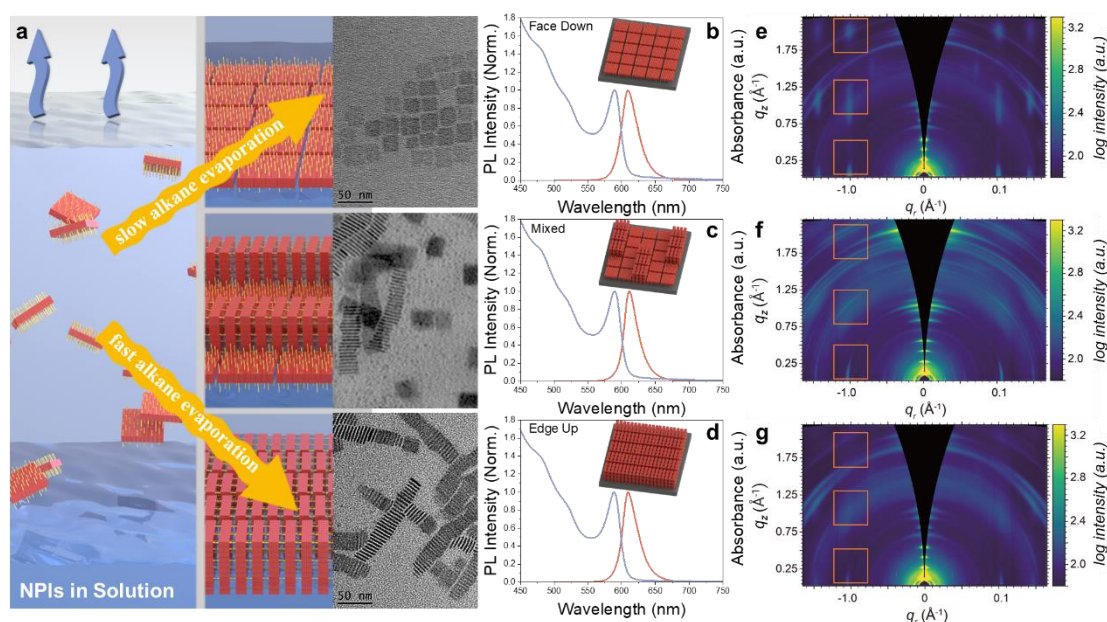


Figure 6. 1 Achieving orientation control in self-assembled CsPbI₃ nanoplatelets. a, Schematic illustrating how the orientation of the NPLs could be controlled by adjusting the solvent evaporation rate. The insets show TEM images of the face-down (top), mixed (middle) and edge-up (bottom) NPLs. b-d, Steady state PL and UV-Vis spectra of face-down, mixed face-down and edge-up and edge-up NPL films, respectively. GIWAXS patterns of e, face-down, f, mixed and g, edge-up NPL films.

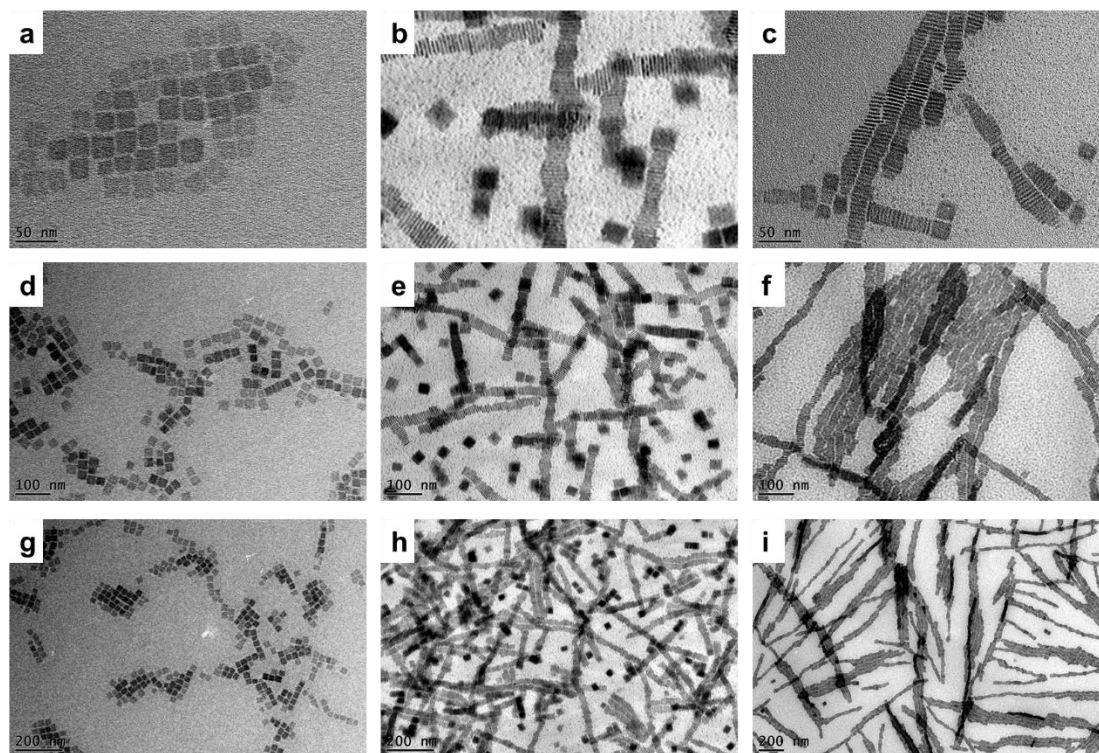


Figure 6. 2 Transmission Electron Microscopy images of nanoplatelets with different orientation. a-c, NPLs with different orientation (face-down, mixture of face-down and edge-up, and edge-up) with 50 nm scale bar. d-f. NPLs with different orientation with 100 nm scale bar. g-i, NPLs with different orientation with 200 nm scale bar.

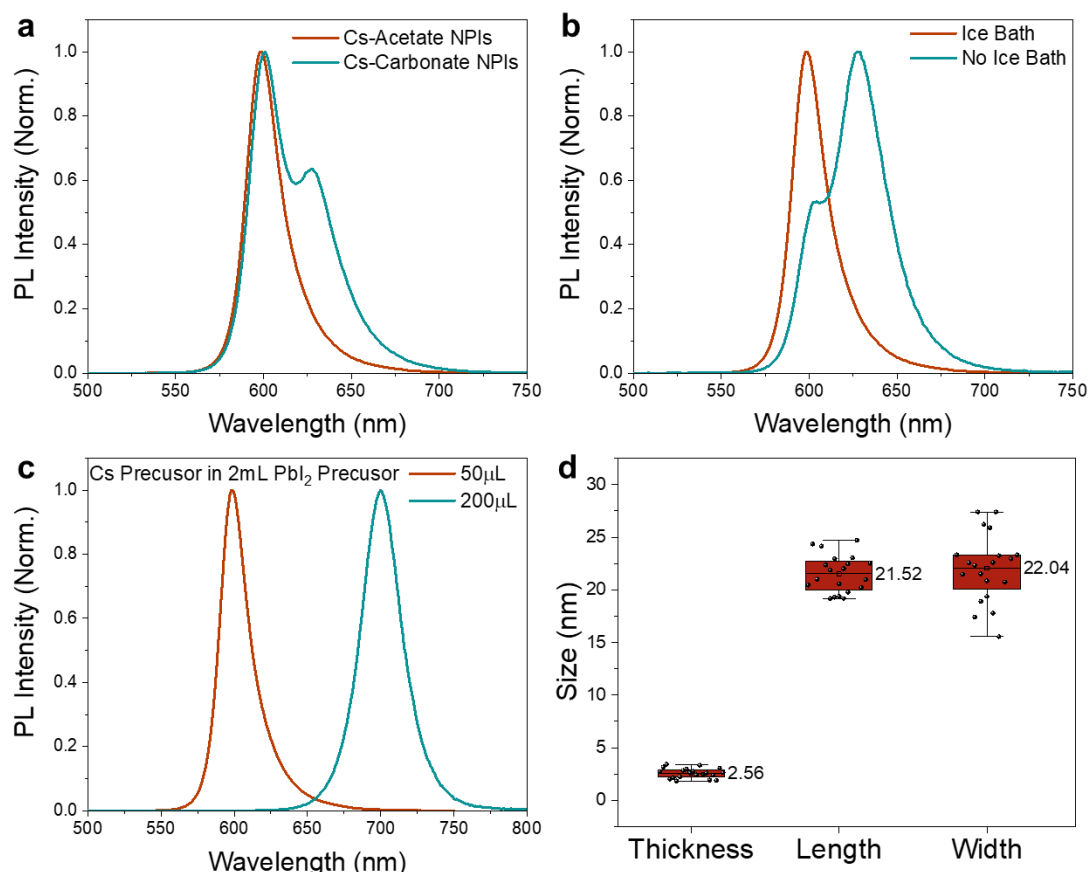


Figure 6. 3 Synthesis Optimization to achieve mono-dispersed NPLs. *a*, Cs precursor effect on photoluminescence. *b*, Reaction temperature effect on photoluminescence. *c*, Cs precursor to PbI₂ precursor volume ratio effect on photoluminescence. *d*, Size distribution of the NPLs.

6.2.2 Controlling the orientation of CsPbI₃ nanoplatelets through self-assembly

To control the self-assembly of the NPLs, we developed a strategy based on precipitating out the NPLs at different rates based on the evaporation rate of the solvent³⁴⁸. After centrifuging the crude solution at 14 000 rpm for 10 min, the precipitated NPLs were dispersed in solvents with different boiling points (Bp) and vapour pressures (P_v): hexane (Bp = 69 °C, P_v = 20.49 kPa), cyclohexane (Bp = 80.75 °C, P_v = 13.01 kPa), and heptane (Bp = 98.42 °C, P_v = 6.08 kPa). The use of solvents with different Bp and

P_v changes the evaporation rate of the solvents during spin-coating. As a result, the NPLs can be trapped kinetically on the substrate to form films with different orientations without changing their size, thus maintain their absorption and PL profiles (Figure 6.1b-d). For a slowly evaporating solvent, such as heptane, the NPLs adopted a face-down orientation (Figure 6.1b), as they have efficient time to form isolated NPLs and lying flat on the substrates when the solvents are evaporated away slowly; using a fast-evaporating solvent, such as hexane, resulted in an edge-up orientation (Figure 6.1d), the stacked NPLs will be trapped quickly onto the substrates as the solvents go away much faster. Further TEM images showing NPLs with different orientations can be found in Figure 6.2.

The change in NPL orientation was corroborated by GIWAXS measurements (Figure 6.1 e-g). Films with face-down NPLs (Figure 6.1e) showed strongly observable peaks associated with (100), (101) and (102) planes (highlighted in the orange boxes from bottom to top, respectively), which became weaker and non-existent in the mixed (Figure 6.1f) and edge-up films, respectively (Figure 6.1g) ³⁴⁹. In addition, there was a spread in the scattering of X-rays perpendicular to the diffraction rings (see orange boxes in Figure 6.1e), which is consistent with the layer-by-layer stacking of NPLs in the face-up orientation. The more obvious vertical periodic signal in the GIWAXS plots indicates that there is more periodic stacking of face-down NPLs lying horizontally on the substrates as the solvent partial pressure decreases.

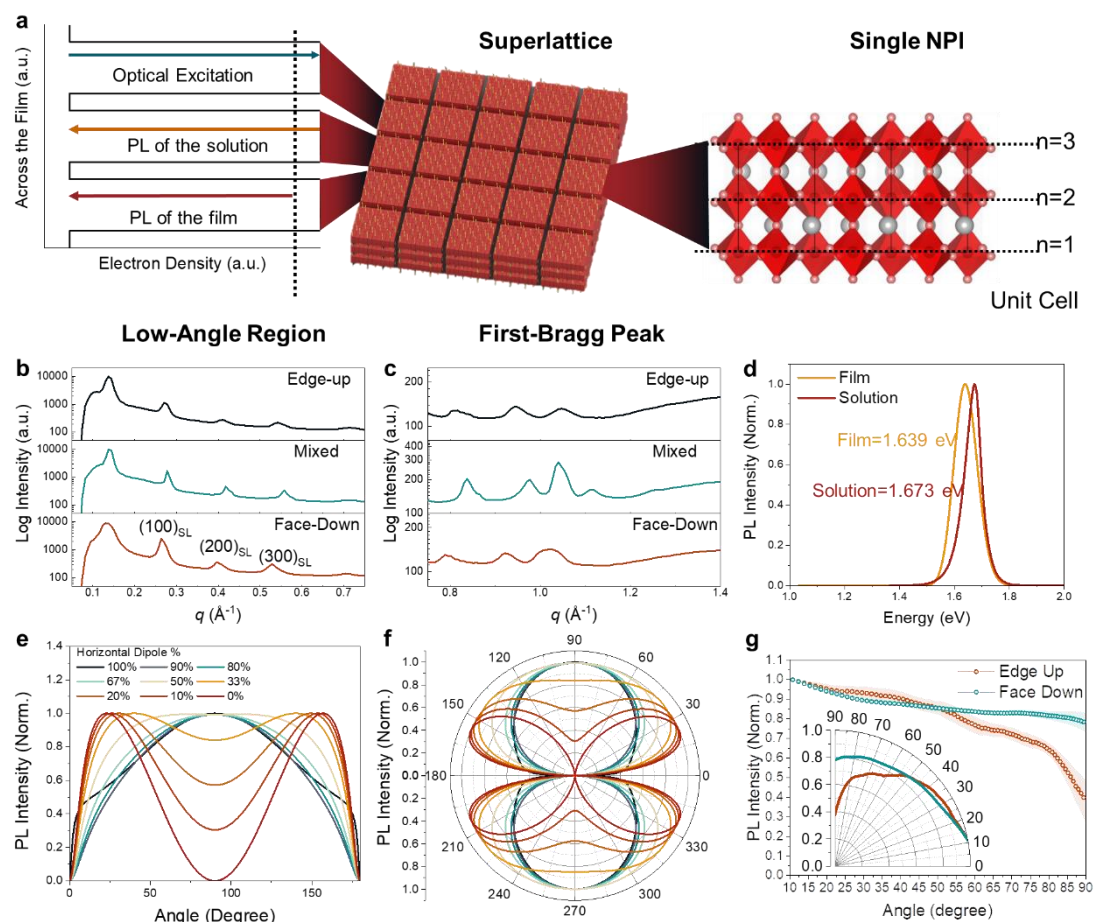


Figure 6. 4 Structural and optical characterisation of self-assembled NPI films. *a*, Illustration of superlattices formed from the stacking of multiple NPIs, and how the electron density changes between inorganic perovskites and organic ligands. The black dotted line indicates a lower energy states when the dipole orientation is aligned in the film due to NPI self-assembled superlattice. *b*, GIWAXS line cut spectra of the low angle region. *c*, GIWAXS line cut spectra of the first Bragg peak region. *d*, The PL of the NPIs in solution and films. The red shift in PL from solution to film could be the emission from self-assembled structures. *e-f*, Film light-outcoupling. Simulated light outcoupling of the thin films with different percentage of horizontal transition dipole moment (100% ideal face-down, 90%, 80%, 67%, 50%, 37%, 20%, 10% and 0% ideal edge-up) to represent different NPI configurations. *e*, Planar scale. *f*, Polar scale. *g*, Angle dependent PL obtained from K-space Fourier Microscopy. The details about the data collection and analysis can be found in Supplementary Figure6. 0 degree is where the

collection is parallel to the substrate and 90 degree is where the collection is perpendicular to the substrate.

Careful analysis of the GIWAXS line-cut results reveal that the high degree of NPl orientation is related to the self-assembly of the NPls during film formation. A schematic of a NPl superlattice is shown in Figure 6.4a. The regular variation in electron density across the cross-section of the superlattice between the inorganic sublattice (high electron density) and organic ligands (low electron density; Figure 6.4a) results in peaks in the low-angle scattering region from the GIWAXS scans (Figure 6.4b)^{343,349}. The formation of superstructures and alignment of transition dipole moments in the strongly confined NPls could lead to lower energy states that result in the film PL shifting to lower energies, as shown in Figure 6.4d, and illustrated in Figure 6.4a^{350,351}. This red-shift in PL between NPls in solution to NPls in superlattice in the films is approximately 34 meV, which matches with previous reports of PL red-shifts in superlattices of CsPbBr₃ and CsPb(Br_{0.72}I_{0.28})₃ nanocrystals (12-96 meV).^{350,351}

Apart from structural evidence for self-assembly, optical analysis also shows there to be strong NPl orientation. Optical simulations of light emission from the films with different transition dipole alignments are shown in Figure 6.4e and f. These simulations show that when the dipole is aligned out-of-plane (i.e. edge-up NPls), the vertical emission profile comes mainly from the out-of-plane dipole (i.e. along the confined or thickness direction), thus the PL intensity would be lower in the normal position compared to the horizontal direction. In contrast, when the NPls were face-down, the emission normal to the plane mainly comes from the horizontal dipole. Controlling the NPl orientation from edge-up to face-down would therefore increase the percentage of the horizontal transition dipole moments contributing towards the emission in the normal direction.^{223,343,344,352}

To validate the simulation results, angle-resolved PL was extracted from K-space Fourier Microscopy measurements (Figure 6.4g; details in Figure 6.5). In Figure 6.4g,

90° is where the collection is perpendicular to the substrates and 0° is where the collection is parallel to the substrates. The PL spectra at 90° and 11° can be found in Figure 6.5b and c. By integrating the PL spectra at each collection angle, we found that the edge-up NPl film has higher PL intensities at low collection angles, which then decreased markedly as the collection angle increased. By contrast, the PL intensity for the face-down NPl films remained relatively constant over the range of collection angles (Figure 6.4g and Figure 6.5c). These trends in angle-resolved PL match the simulation results shown in Figure 6.4a and b. However, it is difficult to estimate the percentage of in-plane transition dipole moments using the current data, as the collection solid angle covers the signal within a few degrees, and the data obtained therefore averages over the signal from adjacent NPls. By measuring 5 sample points across the films to eliminate random error, the same trends shown in Figure 6.4g were maintained. Collectively, these data suggest that the face-down NPl films have higher vertical outcoupling in a planar film structure compared to the edge-up NPl film. The change in light outcoupling in turn indicates that there is a substantial degree of dipole alignment in the films, which is beneficial for generating polarised emission²²³. A further advantage of controlling the transition dipole moment in these self-assembled NPls is that they can be used to increase the outcoupling in planar thin film LEDs, thus overcoming a key challenge in perovskite LEDs (see later sections on LEDs)^{223,343,344}.

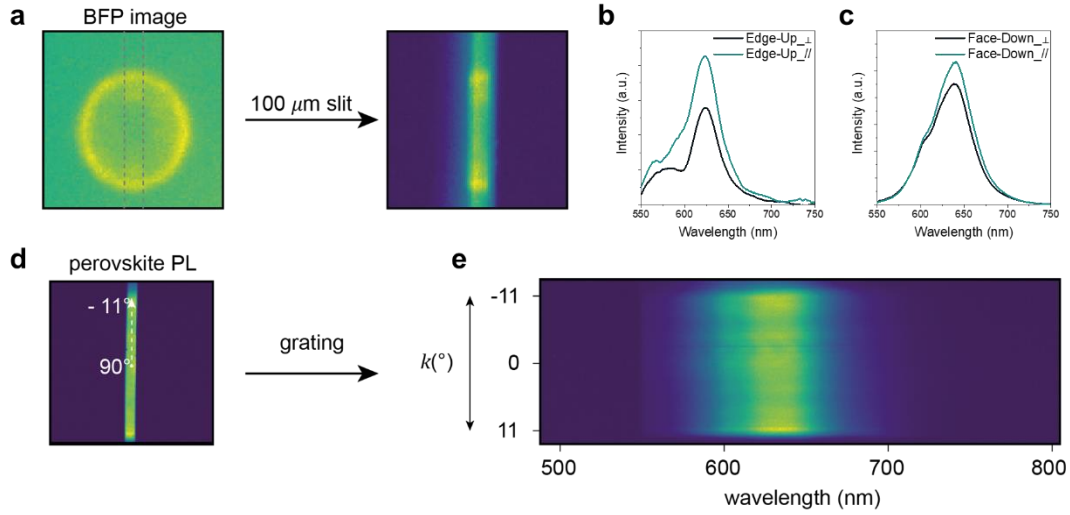


Figure 6.5 k-Space Fourier Microscopy. *a*, Intensity distribution in the back focal plane (BFP) of the objective imaged on an EMCCD before and after applying a 100 μm wide entrance slit. *b*, PL spectra of the Edge-Up films collected at 90° (⊥) and 11° (//). *c*, PL spectra of the Face-Down films collected at 90° (⊥) and 11° (//). *d-e*, Energy-momentum spectrum of face-down perovskite photoluminescence captured by filtering a wavevector range of the BFP image near $k_x/k_0=0$ and dispersed by a grating, this explains how we obtained the PL spectra for *b* and *c* at each angle from 90° to 11° degrees using K-Space Fourier Microscopy. Perpendicular excitation of the perovskite film is performed by focusing a 448 nm cw laser on the centre of the back aperture of an oil-immersion objective (Nikon, Apo TIRF, 100x, NA 1.49). The reemitted photoluminescence at < 79° is collected through the same objective and the emission pattern is determined using the light intensity distribution in the back focal plane of the objective. The back focal plane image is demagnified by 3 times before being imaged on the entrance slit (100 μm wide) of a spectrometer, where a narrow slice of the scattering pattern near $k_x/k_0=0$ is filtered and dispersed by a grating (150 lines/mm) and collected using an EMCCD. Radial intensity profile in Figure 6.5 is calculated by integrating the PL intensity from 610 nm to 650 nm at different emission angles. Standard deviation is evaluated from 5 different sample locations.

6.2.3 Reducing non-radiative recombination and exciton-exciton annihilation rates in CsPbI₃ nanoplatelets through surface passivation

Apart from controlling the alignment of the transition dipole moment, improving PLQYs through surface defect passivation is also essential for fabricating efficient linearly polarised LEDs²³⁶. Possible defects that can be present on the nanocrystal surface, and ways in which they can be passivated are summarised in Figure 6.6a. From XPS measurements of the perovskite NPL films, it was found that the surface was terminated primarily with Pb and I, with negligible quantities of Cs (Figure 6.6b and Figure 6.7). In particular, we found significant quantities of metallic Pb (Pb⁰) on the surface (Figure 6.6b), which would act as sites of non-radiative recombination. We found that we could reduce the fraction of surface Pb⁰ by passivating with PbI₂-ligand (Figure 6.6b). In addition, there was an increase in the I content on the surface (Figure 6.7), which is consistent the passivation of I vacancies on the NPL surface. Both factors led to an increase in the PLQY from 48±2% to 66±1% at low power density after passivation (Figure 6.6d).

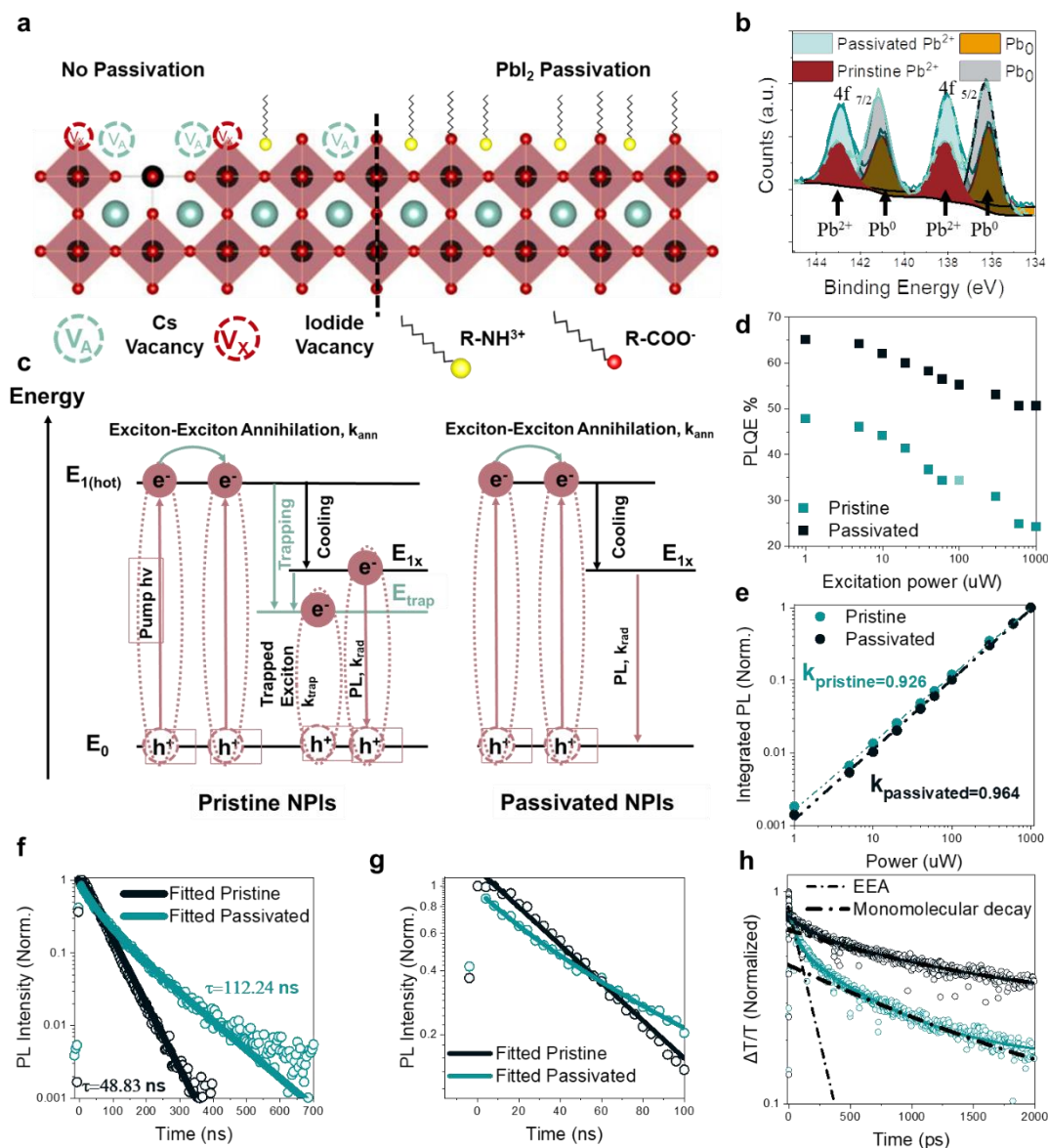


Figure 6. 6 Carrier dynamics of pristine and passivated NPLs. (a) Illustration of typical point defects present in lead-halide perovskites, and PbI_2 passivation strategies. (b) Fitted XPS Pb 4f core level spectra. (c) Energy diagram of exciton dynamics in pristine and passivated NPLs. (d) Power dependent PLQY (405 nm CW laser). (e) Power dependent carrier density against PL plots. (f) Long time scale of the time-resolved PL decay (0-700 ns). (g) Short time scale the time-resolved PL decay (0-100 ns). (Excited with 400 nm pulse laser at $0.25 \mu J cm^{-2}$) (h) Short-time scale transient absorption decay. (0-2 ns) (Excited with 400 nm laser at $301.5 \mu J cm^{-2}$). All samples are solution samples, measured in 1 mm thick cuvette.

PL spectroscopy and transient absorption spectroscopy were used to further understand the mechanism of the passivation and the defect-related carrier kinetics for the strongly confined NPL systems. Figure 6.6c illustrates possible recombination pathways for the excitons present in the NPLs. Owing to the strong quantum and dielectric confinement in the perovskite NPLs^{353,354}, the large exciton binding energy makes the recombination processes dominated by excitons rather than free carriers. This was confirmed by the linear increase in PL intensity with excitation power density for both the pristine and passivated NPL films (Figure 6.6e). The monomolecular radiative recombination of excitons (with rate k_{rad}) would be competing with monomolecular exciton trapping (k_{trap}) and a bimolecular exciton-exciton annihilation during cooling or at band-edge or traps (k_{ann}). When defects are passivated, the k_{trap} term would be smaller indicating less carriers will be trapped at surfaces of NPLs. The rate equation for the above-described processes are described by Equations 1 and 2:

$$-\frac{dn_{ex}}{dt} = k_{PL}n_{ex}(t) + \frac{1}{2}k_{ann}n_{ex}(t)^2 \quad (1)$$

$$n_{ex}(t) = \frac{n_{ex}(0)}{1+k_{ann}n_{ex}(0)t} = \frac{n_{ex}(0).e^{-\frac{t}{\tau}}}{1+k_{ann}\tau.n_{ex}(0).(1-e^{-\frac{t}{\tau}})} \quad (2)$$

where n_{ex} is the density of photo-generated excitons, k_{PL} is the total monomolecular recombination rate ($k_{PL} = \frac{1}{\tau} = k_{rad} + k_{trap}$, with τ is the exciton lifetime at low fluence where exciton-exciton annihilation is negligible), and $n_{ex}(0)$ is the initial exciton density immediately after photo-excitation. The strong exciton binding energy leads to a high exciton population density, even at low power densities. Therefore, exciton-exciton annihilation begins to dominate at low power densities, leading to decreases in PLQY (Figure 6.6d). Figure 6.6f and g show the TRPL decay at long time scale and short time scale, respectively. At low fluence ($0.25 \mu\text{J cm}^{-2} \text{ pulse}^{-1}$), the passivated sample has a shorter lifetime and exhibits a linear decay curve compared to the pristine sample (Figure 6.6f). This longer lifetime in the pristine sample

is attributed to the exciton trapping and de-trapping. The nearly monoexponential PL decay curve (Figure 6.6f) indicates that recombination is dominated by monomolecular trap-mediated recombination, since the PLQY of the pristine sample falls below that of the passivated sample. The non-monoexponential PL decay curve from the pristine sample highlights that additional contributions occur, likely from bimolecular recombination as trapped excitons lead to Auger or exciton-exciton interactions ($k_{\text{ann}}=0.019 \text{ cm}^2 \text{ s}^{-1}$, Table 6.2).

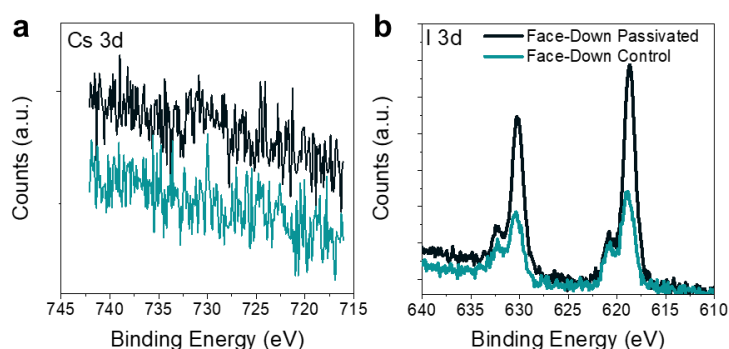


Figure 6. 7 XPS core level spectra of NPLs. a, Cs 3d. b, I 3d core level spectra of pristine and passivated sample. XPS data was acquired using a Kratos Axis SUPRA using monochromated Al K α (1486.69 eV) X-rays at 12 mA emission and 15 kV HT (180 W), with an analysis area of $700 \times 300 \mu\text{m}^2$. High resolution spectra were obtained using a pass energy of 20 eV, step size of 0.1 eV and sweep time of 60 s, resulting in a line width of 0.696 eV for Au 4f_{7/2}. The penetration depth for the XPS is about 5-50 Å.

The intersection of the pristine and passivated PL decay curves can be observed in Figure 6.6f. For convenience, the data has been plotted for a narrow time window to highlight the short time scale in Figure 6.6g. Here we see that at early stage ($t < 100 \text{ ns}$, where there is surface trap-dominated regime and no de-trapping process is considered), the lifetime of passivated sample (159.94 ns) is longer than the pristine sample (61.18 ns). The shorter lifetime of the pristine sample is due to a fast trapping process of free excitons. Based on this low fluence lifetime and PLQY where k_{ann} for both samples where small, we estimated the exciton recombination rate (k_{PL}) as 0.017 ns^{-1} for the

pristine and 0.006 ns⁻¹ for the passivated sample. Notably, the exciton trapping rate (k_{trap}) decreased from 0.009 ns⁻¹ to 0.002 ns⁻¹. Values of the fitting are reproduced in Table 6.2 and fitted decay curves and TA maps are given in Figure 6.8.

To get obtain a more accurate estimation of the exciton-exciton annihilation (EEA, k_{ann}) rate, short time (0-2 ns) fluence-dependent transient absorption spectra were measured for both pristine and passivated samples (Figure 6.8c, d, g, h). The fitted EEA rate was approximately 0.382 cm² s⁻¹ for the pristine sample, and 0.282 cm² s⁻¹ for the passivated sample at fluences between 15 and 361 $\mu\text{J cm}^{-2}$. These values are similar to previously-reported values of 0.24 cm² s⁻¹ for 2D perovskites and 0.134 cm² s⁻¹ for monolayer WS₂.^{355,356} The reduction of the EEA, k_{ann} rate indicated that there were fewer excitons contributed to EEA process as less were held in trap states after passivation. Similarly, we observed fewer changes or slower decays of the $\Delta T/T$ signal when the fluence increased for the passivated sample than the pristine sample (Figure 6.8b and f, and Figure 6.9).

Table 6. 2 Fitted carrier kinetics parameters based on the time-resolved PL and transient absorption using equation 1 and 2.

Measurement	Sample	k_{ann}	τ	k_{PL}	PLQY	k_{rad}	k_{trap}
Type	(solution)	(cm ² s ⁻¹)	(ns)	(ns ⁻¹)	(%)	(ns ⁻¹)	(ns ⁻¹)
TRPL [#]	Pristine	0.019	61.18	0.017	47.83%	0.008	0.009
(0.25 $\mu\text{J cm}^{-2}$)	Passivated	0.000	159.94	0.006	65.13%	0.004	0.002
TA*	Pristine	0.382					
(15-361 $\mu\text{J cm}^{-2}$)	Passivated	0.282					

For the TRPL fitting, we assumed that the measurement fluence is low enough so that we assume no or minimum EEA takes place. *For the TA fitting, we assumed that there is no radiative recombination occurred yet in the fitting time window (0-100 ps).

The fitted short-time TA for the face-down film is shown in Figure 6.6h. The dotted line indicates the mono-exponential decay of the passivated films. When superpositioning the fitted EEA and monomolecular decay of the passivated sample to the pristine sample, there is a clear mismatch of the fit to the experimental data, confirming trap-induced carrier losses at early times without passivation.

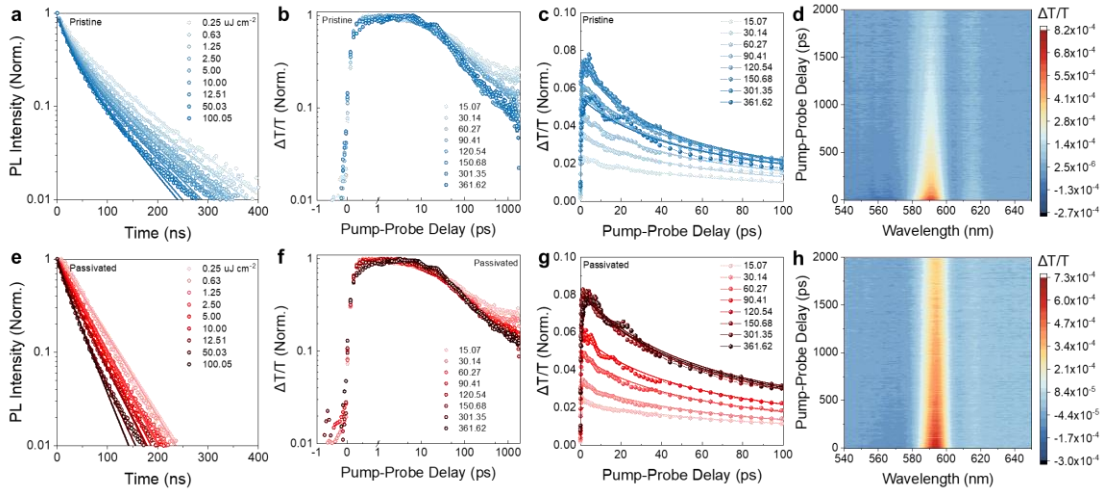


Figure 6. 8 Carrier Kinetic Parameter fitting. a, Fluence dependent TRPL of pristine sample. b, Fluence dependent TA of pristine sample (0-2000 ps). c, Fluence dependent TA of pristine sample (0-100 ps). d, TA map of pristine sample at $5 \mu\text{J cm}^{-2}$. e, Fluence dependent TRPL of passivated sample. f, Fluence dependent TA of passivated sample (0-2000 ps). g, Fluence dependent TA of passivated sample (0-100 ps). h, TA map of passivated sample at $5 \mu\text{J cm}^{-2}$.

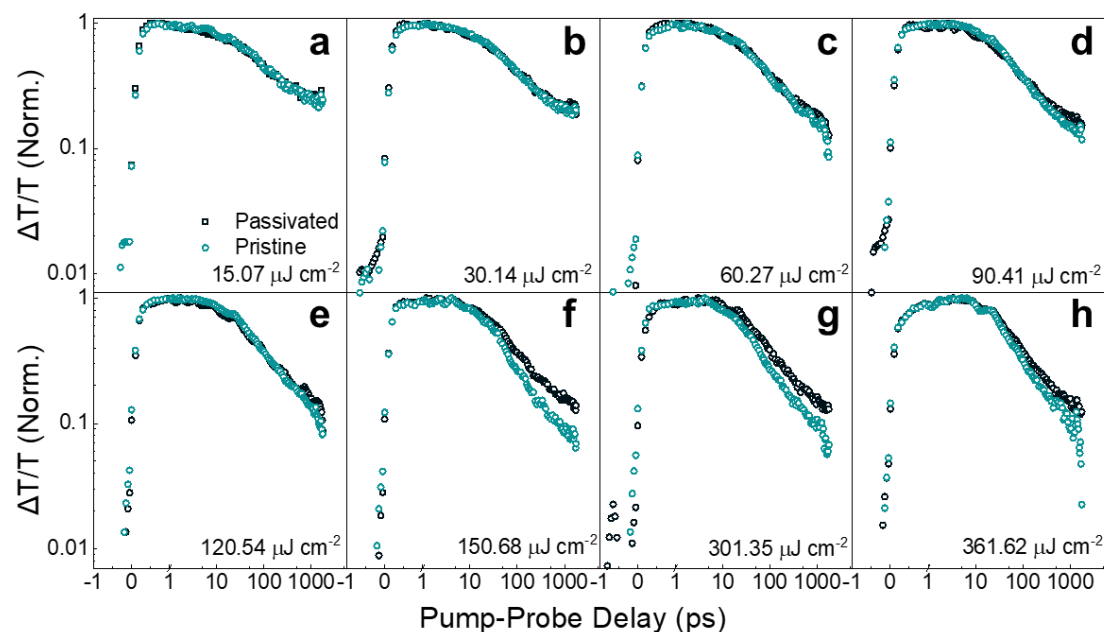


Figure 6. 9 Fluence Dependent Short Time Transient Absorption. a-h, Short time (0-2000 ps) transient absorption ground state bleach with fluence at 15.07, 30.14, 60.27, 90.41, 120.54, 150.68, 301.35, 361.62 mJ cm⁻² respective.

6.2.4 Linearly polarised LEDs with orientation controlled CsPbI₃ nanoplatelets fulfilling Rec. 2020

Edge-up and face-down NPI films were fabricated into LED devices using the following structure: ITO/PEDOT:PSS/poly-TPD/NPIs/BCP/Ag (Figure 6.10c). The electroluminescence spectra at different voltages (3.5-7 V) are shown in Figure 6.10a. A stable red emission with CIE coordinates (0.661, 0.338) was achieved, which is close to the Rec. 2020 standard for pure red emission (Figure 6.11a and inset). Unlike the mixed Br-I perovskite systems, the composition purity of CsPbI₃ NPIs in the halide site enables the devices to avoid halide segregation even at high applied biases (7 V).^{219,236} There is negligible change in the colour coordinates when increasing the voltage from 3 V to 7 V, from (0.661, 0.338) to (0.658, 0.341), due to the heat-induced merging of NPIs at higher operation voltages. By combining the effects of surface passivation (improving PLQY) and NPI orientation control (improving outcoupling),

we increased the average EQE of the pristine devices (control) from 1.12% to 1.22% when changing the NPI orientation from edge-up to face-down. After surface passivation using PbI₂, the average EQE increased from 1.12% to 1.67% (edge-up), and from 1.22% to 2.38% (face-down) (Figure 6.11b). The current injection is improved after passivation, especially for the face-down configuration devices (Figure 6.11c). The champion NPI device (face-down configuration after passivation) achieved 2.7% EQE with a maximum luminance of 408 cd m⁻² at 7 V (Figure 6.10b and Figure 6.11d).

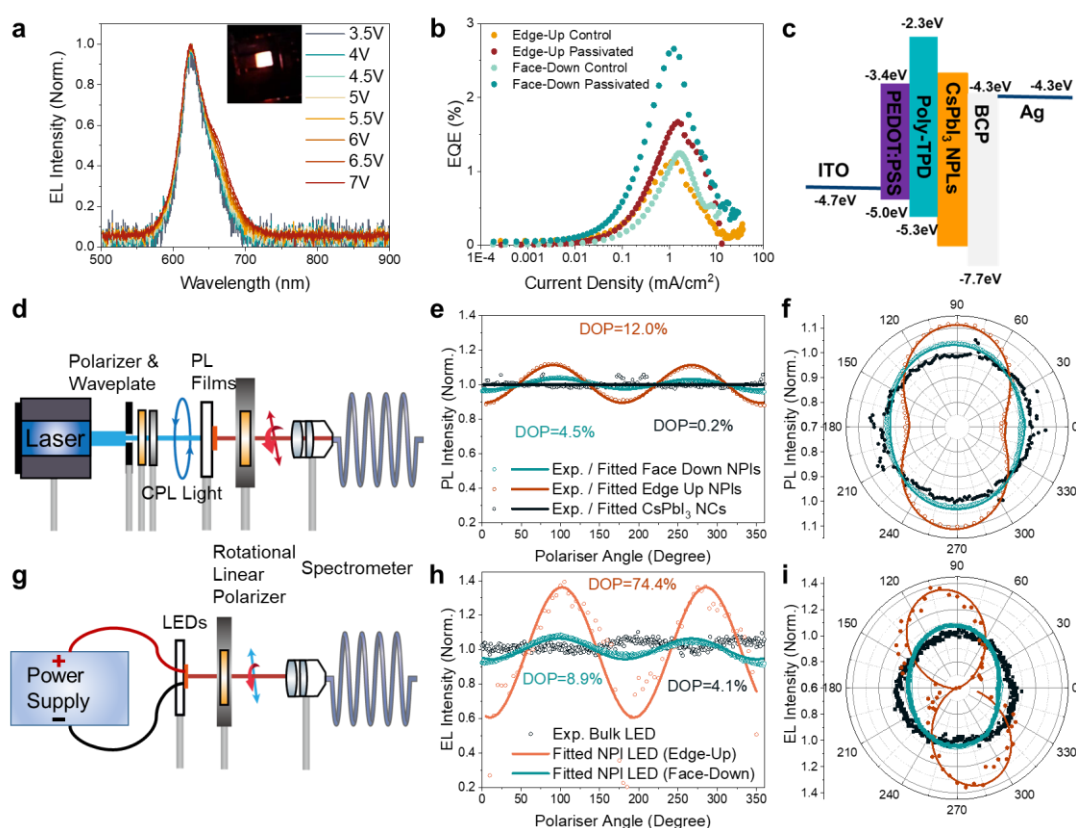


Figure 6. 10 Linearly polarised emission from CsPbI₃ NPI films and devices. a, Electroluminescence Spectra of optimised NPI LEDs from 3.5 V to 7 V. Inset shows the LED under operation (pixel area 0.16 cm²). b, Current density against EQE for pristine and passivated edge-up and face-down NPI LEDs. c, the optimised LED device structure: ITO/PEDOT:PSS/poly-TPD/NPIs/BCP/Ag. d, Scheme of producing and testing the polarised

photoluminescence. *e*, Polarization dependence of the PL for face-down, edge-up and bulk FAPbI₃ films at a fixed detection angle of 0° with respect to the substrate normal. *f*, Polar plots of the polarised PL. *g*, Scheme of producing and testing the polarised electroluminescence. *h*, Polarization dependence of the EL for edge-up and bulk FAPbI₃ LEDs at a fixed detection angle of 0° with respect to the substrate normal. *i*, Polar plots of the polarised EL. The degree of polarisation, DOP, was calculated from: $DOP = (I_{max} - I_{min}) / (I_{max} + I_{min})$

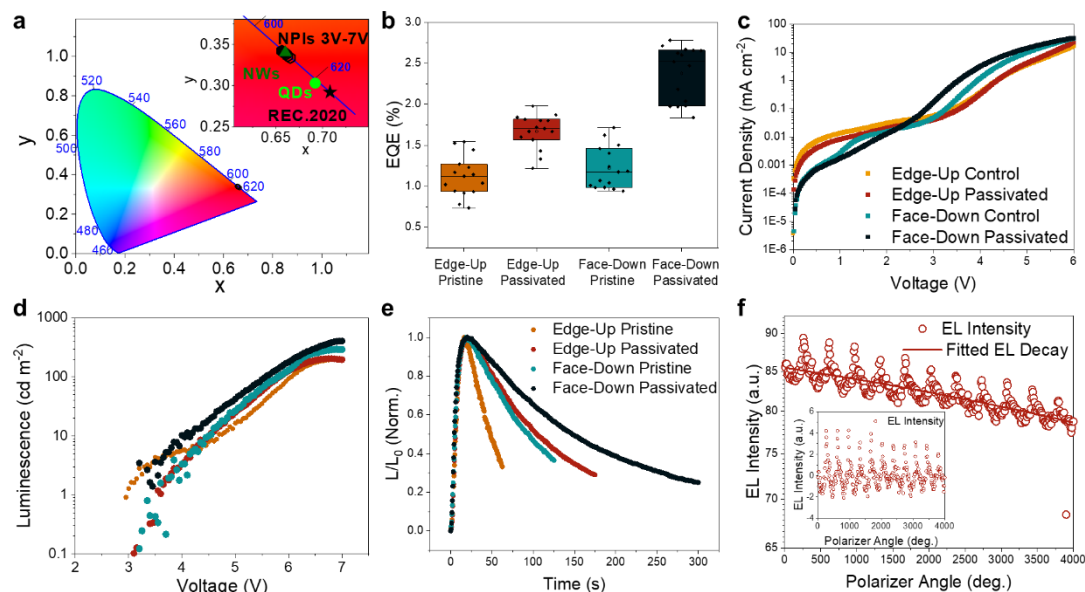


Figure 6. 11 LED device characterization. *a*, CIE colour coordinates of the electroluminescence at different voltage. Inset shows the zoomed in area of the red emission for different perovskite materials (NW=nanowires, NPLs=nanoplatelets, QDs=quantum dots, the star=the REC.2020 standard). *b*, Box plot of EQEs of the face-down and edge-up NPL LEDs with and without passivation. *c*, J-V curve. *d*, Luminance -voltage curve. *e*, LED stability at 5V. *f*, EL intensity against the polariser angle overtime. Inset shows the decay corrected EL intensity after taking account of the device degradation. .

The self-assembly of strongly-confined, and highly oriented NPLs leads to strongly linearly polarised EL from the LEDs, as shown in Figure 6.10. Circularly polarised light (CPL) was generated by passing unpolarised light from the laser LEDs into a linear polariser and a waveplate. The emission of the sample was then passed through a linear polariser mounted on

an electrically driven rotation stage and coupled into a spectrometer. (Figure 6.10d) The electroluminescence was recorded in the same way (Figure 6.10g), the decay of the LEDs during the measurement is back corrected based on the LED stability test of the EL decay (see Figure 6.11e and f). Both PL and EL show clear polarised emission relative to more isotropic emitters, such as weakly confined CsPbI₃ nanocubes films and bulk FAPbI₃ thin film LEDs. The edge-up configuration (DOP=12%) demonstrated a stronger degree of polarization than the face-down NPLs (DOP=4.5%), which matched with the reported phenomenon of self-assembled CdSe NPLs³⁴⁸ and theory prediction³⁴² (Figure 6.10e and f). The CsPbI₃ NCs showed 0.4% degree of polarization which acted as a control experiment. For the edge-up LEDs, a DOP of 74.4% was achieved (Figure 6.10h and i), which is the highest reported direct linearly polarised LEDs without using any photonic grating (Table 6.1 and Supplementary Figure 6.12a)

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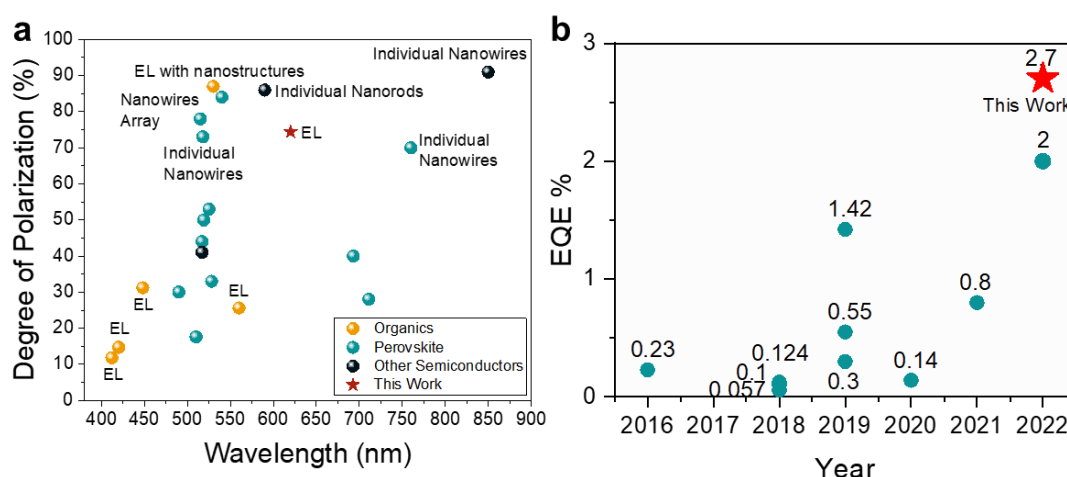


Figure 6. 12 Comparing the polarised emission and EQE with other literatures. a, Degree of polarization of different materials. b, Summary of the device EQE of strongly confined NPL LEDs.

To understand the origin of the high DOP in the NPL films and devices, we measured the PL of the face-down and edge-up CsPbI₃ NPL films, and compared with weakly-confined CsPbI₃ NC films and FAPbI₃ bulk thin films at 5.2 K (Figure 6.13). The origin of linearly polarised PL can be explained by band-edge excitons and its fine-structure splitting (FSS)^{312,342}. In perovskites,

a reverse band ordering is observed for the band-edge states compared to more conventional II–VI semiconductors, such as CdSe. The lowest energy excitons should be the bound states, pairing an upper valence band (VB) hole. In contrast the electron from the lowest split-off conduction band would give rise to four excitonic states. The FSS is the result of the interplay of crystal field and the electron–hole (e–h) exchange interaction. The latter effect splits the four exciton states in one optically inactive state (dark state, singlets) with total angular momentum $j = 0$, and three optically active states (bright states, optically active, triplets) having $j = 1$, which is related to the spatial dipole arrangement based on the unit cell crystal symmetry^{143,312,358,359}. Figure 6.13a and b illustrate a typical tetragonal phase CsPbI₃ unit cell with a size-effect induced FSS, in which the z-direction is the confinement direction. Previous theory calculation has proven that the FSS will be enhanced by the size and dielectric confinement (i.e., FSS energy is inversely proportional to the NPL thickness), particularly strong in NPLs with a thickness of the order of few atomic layers, as the confinement would enhance the short range and long range electron-hole exchange interactions, which ultimately enhances the FSS energy^{342,359-361}. Previous works have reported the observation of FSS of single CsPbBr₃ NPLs, i.e., the PL spectra split into multiple peaks (1-3) at cryogenic temperature^{329,362}. These FSS are more difficult to observe at the film level when the NPLs or NCs are randomly distributed. However, in our case, we can still observe PL splitting at 5.2 K at the film level (Figure 6.13c and d), possibly due to the uniform orientation of the TDMs of the NPLs through self-assembly. A FSS energy of 19.77 meV (edge-up) and 11.38 meV (face-down) can be calculated by fitting the PL spectra. These values are significantly larger than the FSS energy of the reported isolated cuboidal NC (~1 meV)^{143,329}. Since our NPLs are strongly confined in the z-direction, the aspect ratio (thickness to length/width ratio) is very small (~0.13), the FSS value for such small aspect ratio NPLs match well with the calculations from theory papers (~20 meV)³⁴². Compared with the strongly oriented NPL films we achieve here, no obvious FSS-induced PL splitting or polarised light emission was observed in weakly-confined NCs or bulk thin films (Figure 6.13e).

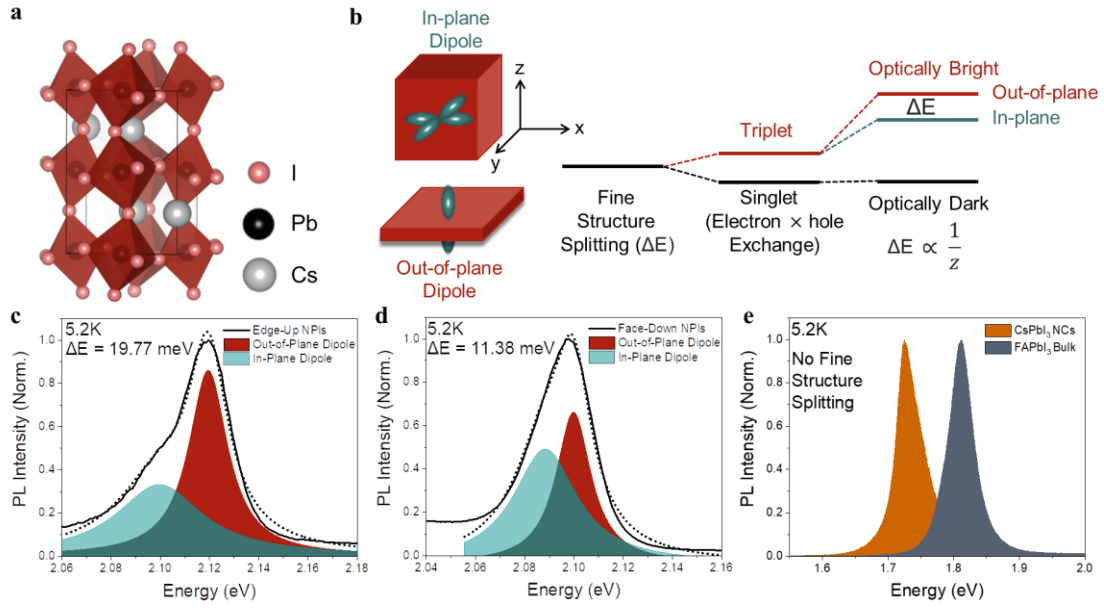


Figure 6. 13 Origin of linearly polarised emission. *a*, Tetragonal crystal structure of the CsPbI₃. *b*, Schematic diagram to illustrate the confinement effect on the fine structure splitting. The axis shows the dimension of the colloidal nanocrystals, which z-direction is the confined direction, i.e. the thickness of the NPLs, *z*. *c*, Low temperature (5.2 K) PL spectra of the edge-up NPL films, the fitted peaks represents the emission from fine-structures, and the detector angle is perpendicular to the film. *d*, Low temperature (5.2 K) PL spectra of the face-down NPL films. *e*, Low temperature (5.2 K) PL spectra of the CsPbI₃ nanocubes and bulk FAPbI₃ thin films, no splitting is observed.

For the NPL cases (Figure 6.13c and d), We believe that the higher energy PL peak is raised by the out-of-plane dipole relative to the NPL plane (*z*-direction), while the lower energy PL comes from the carrier recombination from the in-plane dipole (*x* or *y* direction) induced fine structure energy level. The emission from each fine-structure exhibits single polarization, with *x*- and *y* direction polarization being orthogonal to each other. Since we have similar sizes in the *x*- and *y* directions, the splitting between these two non-degenerate states in tetragonal phase CsPbI₃ would be negligible, and the emission from this state should have negligible polarization as they cancel each other out. So, the main polarization of the NPLs comes from the emission from the higher energy states (*z*-direction dipole or out-of-plane dipole). It is clear that the edge-up

film PL consists of more emission from the higher energy states while the face-down film PL have more closed ratio between the emission from different fine structures energy levels. This could explain why the edge-up film has higher DOP than the face-down films. However, the total DOP and PL splitting should be influenced by a combination of depolarization within the FSS manifold due to energy transfer^{342,363}, the detection geometry relevant to crystal plane³⁶² and the local field effect³⁶⁴. The DOP in EL (74.4%) was significantly increased over the DOP for PL (12.0%), and this could be explained by further increases in the dipole alignment by the applied electric field during LED operation that leads to most of the injected carriers recombining at one particular energy level with minimise energy transfer to other triplet states. This observation matches well with previous studies on GaAs quantum dots, in which an increase in the DOP was also observed after increase in the applied electrical field³⁶⁵.

6.3 Conclusion

In conclusion, we have made the first demonstration of the direct emission of linearly polarised light from halide perovskites, through use of strongly-confined and highly oriented CsPbI₃ nanoplatelets. These nanoplatelet LEDs fulfil Rec. 2020 and have 2.7% EQE, which is not only the highest for CsPbI₃ nanoplatelet LEDs, but also the highest reported for strongly-confined NPL LEDs (Supplementary Figure 6.14b)⁸⁹. The orientation of the NPLs, and hence the percentage of in-plane/out-of-plane transition dipole moments, can be manipulated through the evaporation rate of the solvent for the deposited NPL colloidal solution. NPLs in hexane would allow us to prepare films with more edge-up NPLs, and NPLs in heptane would allow us to prepare films with more face-down NPLs. PbI₂ with oleic acid ligands would passivate the surface halide vacancies and reduce the monomolecular trap-assisted recombination and the bimolecular exciton-exciton annihilation to the overall recombination rate. Importantly, we demonstrated a high degree of linear polarisation (74.4%) in the EL from pure-red LED devices, which is attributed towards three key factors: (1) high degree of orientation in the NPLs, (2) high PLQYs, such that the emission is strongly governed by

the band edge excitons, and (3) large exciton fine structure splitting due to strong quantum confinement and nanoplatelet alignment. This opens a new frontier in enabling applications for displays and optical communications with more efficient linearly polarised LEDs.

Chapter 7: Conclusions and Outlook

In this thesis, I have created new understanding new understanding on the surface defect chemistry of perovskite nanocrystals, and how they can be controlled during purification (Chapter 4), and how these trap states in turn influence hot carrier cooling (Chapter 5). In Chapter 6, I devised an approach to passivate surface defects in strongly-confined CsPbI₃ nanoplatelets, and how to self-assemble them to control the transition dipole moment, and thereby achieved linearly polarised electroluminescence in LEDs.

7.1 Conclusion

In the first study, I investigated the origin of the surface traps in CsPbBr_xI_{3-x} NC system, which is an important composition for producing red emitter meet the requirement of REC 2020 standard for display technology. I focused on the purification step with the use of different antisolvents of the NC synthesis, as it is the critical procedure to remove unreacted insulate ligands and precursors. I found that the PL peak position and halide composition especially the iodide composition change dramatically with the relative polarity of the antisolvents. I then utilised multiple spectroscopy techniques including photothermal deflection spectroscopy (PDS), transient photoluminescence spectroscopy (TSCPS) and photoluminescence quantum yield measurement to correlate how the change of antisolvent polarities would influence its optical properties. I performed detailed NMR and FTIR studies to reveal the cause of these changes is due to the condensation reaction between the oleic acid ligands and oleylamine ligands at the surface of NCs, which forms amides and lead to repulsion of surface halides. Furthermore, I demonstrated this antisolvent induced halide removal would have detrimental effect on device stability by measuring the electroluminescence peak change of the LEDs. I found that using methyl acetate to wash the NCs would create the least amount of halide vacancies and better optical properties and device stability. The first study provides understandings about the formation of the surface trap during the purification, it offers us two possible solutions in the future to mitigate the formation of defects and improve device stability.

Firstly, finding suitable antisolvent that has smaller relative polarity than methyl acetate so that it can create even less amount of defects. Secondly, adding ligand-anchoring or halide anchoring chemicals during the washing step to reduce the formation of amides, so that less halide would be removed with the ligands.

My second study focused on how these washing induced defects would affect the hot carrier cooling process of the nanocrystal with different halide composition. Or in other word, are the hot carriers generated in perovskite nanocrystals upon excitation tolerant to defects? Through the pump-probe and pump-push-probe transient absorption spectroscopy studies, I found that the hot carriers generated in I-based NCs have high tolerance to defects than the Br-based NCs, since the cooling lifetime stays almost constant by varying the surface defect densities. While the cooling lifetime decreases significantly for Br-based and Br/I mixed NCs with an increase in surface defect densities. Through the modelling and DFT calculation, I found that the hot carrier cooling lifetime is significantly influenced by the carrier densities during the cooling process, maintaining high carrier densities would increase the cooling lifetime due the phonon bottleneck or hot phonon bottleneck effect. The carrier densities in NCs are relevant to the relative position of the trap states to the conduction bandedge. I-based NCs have the traps that are close to the conduction bandedge so that the carrier can be easily depopulated from the traps to maintain high bandedge carrier densities and hence constant cooling lifetime. In the future, based on this investigation, the amount of ligands and surface traps can be optimised to balance the non-radiative losses with the inter-particle charge transportation. It would be valuable if I can also correlate the surface defect densities to the conductivity of NC films so that the NC-based device efficiency can be further improved.

Apart from mixed halide NCs, I also offered a new solution for making pure red LEDs with direct linearly polarised electroluminescence in my third work. The highlights of this work include (a) The degree of linear polarization (DOP) from the device is 74.4%, which is the highest reported DOP from direct emission without any use of photonic structures or patterned substrates. (b) It is the first reported CsPbI₃ red NPI LEDs with 2.7% EQE (highest reported

EQE for strongly confined ($n \leq 3$ monolayer) perovskite colloidal nanoplatelets. (c) It achieved the control of transition dipole moments at film level through self-assembled superstructures (supported with structural (GIWAXS) and optical analysis (simulation and experiment)). (d) I provide experimental study on the origin of the linear polarization, which I believe is from the large exciton fine structure. In the future, the efficiency of the 2D NPL-based LEDs can be improved by improving the charge injection efficiency. Currently, the current densities at the highest EQE position are only around 1 mA cm^{-2} , which is much lower than the weakly confined NCs and bulk counterparts (ca reach $10\text{-}1000 \text{ mA cm}^{-2}$). Developing efficient and stable washing protocols for the strongly confined NPLs and overcoming the high exciton-exciton annihilation rate due to the high binding energy would be the future direction of improving NPL-based devices including LEDs and solar cells.

7.2 Outlook

Based on my study in Chapter 4, we elucidate the role of antisolvents and their influence on creating surface halide defects during the purification. Developing new facile purification methods would be one of the future directions to synthesise high quality NCs. Since the detachment of surface halides and ligands is due to the polar antisolvent induced ligand interactions, we can mitigate the issue by focusing on 1) the antisolvents, and 2) on the ligands. Finding antisolvents with lower polarity, or mapping out the influence of antisolvent polarity, volume ratio, centrifuge time and speed would be valuable for the field. Since, we know the stronger polarity antisolvents would generate more surface defects, we can mitigate this by lowering its volume used during purification, reduce centrifuge speed or time. Also, we can discover lower polarity antisolvents than the methyl acetate. On the other hand, I found the ligand chemistry during the purification is influential on the surface chemistry of perovskite NCs. Reducing the amide formation between amine based ligands and carboxylic based ligands during the purification would be another future direction to make better NCs and devices. Anchoring ligands with additives, using ligands with binary functional groups, developing amine free ligand synthesis and adding buffer ligands during the purification process would be

reasonable future works in the field to reduce the surface defect formation on the surface during the washing process.

For Chapter 5, we understand that the mid-gap trap states can speed up the cooling process and this effect is only negligible when the trap state position is very shallow or close to the band edge. However, we do not fully understand if the formation of halide vacancies will also generate defects above the band edge. It would be scientifically interesting if we could run the pump-push-probe TA using different push beam energy, so that we can map out the energy level of defects states. Secondly, finding suitable passivation agents to reduce the effect of traps for wide-gap absorbers would be novel. Identifying the role of other types of point defects such as anti-sites on the cooling kinetic experimentally would be beneficial for material designing and synthesis. Damping ligands such as 3-aminopropyltriethoxysilane (APTES) has been proved useful in slowing down the hot carrier cooling process³⁰⁰. These ligands or other passivation salts can be tried to further extend the carrier cooling lifetime. Additionally, finding suitable coupling ligands or transporting layers to extract the carriers when it is still “hot” would be another future direction for developing practical feasible hot carrier solar cell devices. This would require good understanding about the energy level above the bandgap with the presence of imperfect perovskite lattice.

In Chapter 6, I highlighted that one of the key limitations for the 2D NPI LED efficiency comparing with the counter parts bulk or weakly confined NC systems is the difficulty of charge injection. Currently, there is no facile approach to crash out the NPIs with antisolvents, it only relies on high centrifuge speed. Therefore, the relevant ligand coverage on the NPI surface is still high, which hinders the conductivity and charge injection. Using the antisolvent for CsPbI₃ NPI purification would lead to detachment of ligands and the shape of NPIs cannot be hold, and this leads to quick degradation. Additionally, the high binding energy of the NPIs would lead to higher exciton-exciton annihilation rate which also limit the amount of carriers that undergo useful radiative recombination in LED devices. Therefore, one of the future directions would be focusing on improving the charge injection of the NPI-based LEDs. Secondly, the

fundamental understanding of exciton fine structure splitting and polarisation emission is still required. The polarisation dephasing process in the shape or thickness control perovskite NCs or NPIs would be worth to explore for developing good single photon emission source.

In conclusion, I have investigated the state-of-art NC and NPI based devices and their carrier dynamics including both bandedge carriers and hot carriers. I correlated the surface chemistry of these colloidal metal-halide perovskite nanocrystals with their optoelectronic properties and device performance. The research presented in this thesis will hopefully provide useful guidelines and stimulate the progress of the future investigation on designing novel MHP NCs and fabricating more stable and efficient MHP NC-based devices to mitigate the climate change and achieve a sustainable energy future.

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