Exciton and carrier dynamics of binary layered Dion-Jacobson perovskites

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ABSTRACT

Two-dimensional hybrid halide perovskites have attracted considerable attention for their favorable excitonic properties and high structural tunability. A series of Dion-Jacobson (DJ) perovskites, 3AMP $(MA)_{n-1}Pb_nI_{3n+1}$ (3AMP = 3-(aminomethyl) piperidinium, MA = methylammonium, and n = 1, 2, 3, etc.), constituting a single dimensionality, n, have been investigated in recent years. However, little is known about the photophysics of DJ perovskites with binary inorganic thickness. Here we study the exciton and carrier dynamics of layered 3AMP PbI_4 / 3AMP(MA) Pb_2I_7 thin films and exfoliated flakes. A new absorption feature (n = 1.5) is associated with this binary-composite DJ perovskite and is observed between the n = 1 and n = 2 neat film transitions. Ultrafast transient reflection measurements reveal this intermediate feature is exitonic in nature. Above bandgap pumping in exfoliated samples show the n = 1 resonance can be selectively pumped without populating n = 1.5. This behavior is distinct from non-layered binary perovskite mixtures where an intermediate state is not present and lower energy transitions, i.e. n = 2, have time dependent interconversion with n = 1. These results demonstrate the increased tunability of exciton resonance for DJ perovskites through layer engineering and optical control. Integration of these layers in device architecture may significantly improve functionality by further controlling allowed transitions, which serves to benefit the future of optoelectronics.

Keywords: perovskites, excitons, tunneling, superlattice, carrier dynamics, ultrafast spectroscopy, defects

1. INTRODUCTION

Dion-Jacobson (DJ) perovskites, a family of semiconducting hybrid materials, has been investigated for their potential use in photovoltaics[1]. DJ perovskites, $A'A_{n-1}X_nB_{3n+1}$, consist of cations, A_{n-1}, caged by inorganic octahedra, X_nB_{3n+1}, and separated by divalent spacers, A', where n is the inorganic layer thickness. These materials are electronically two-dimensional and offer greater stability than their 3D counterparts. Hydrophobic organic interlayers protect the metal halide octahedral nanosheets which undergo rapid deterioration from light, moisture and oxygen[2]. The structure of these materials can be represented by quantum wells where the spacers confine charged carriers to the inorganic plane[3,4]. Because the thickness of the organic interlayer is < 1 nm, tunneling is likely to occur and bound states can be envisioned as a series of finite potential wells[5] as shown in Figure 1b.

Multiple quantum well (MQW) perovskites possess electronic 2D wells of varying thicknesses and have high photoluminescent quantum efficiency[6]. Energy transfer in perovskite MQWs is relatively quick and migration occurs from the higher bandgap phase (small n) to the lower bandgap (large n)[7]. The interface of the phases can form type I or type II heterojunctions where both staggered bandgap orientations can lengthen the charge recombination duration[3,11,12].

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Alternatively, mixtures of n=1 and n=2 inorganic sheets exhibit a randomized configuration of the two dimensionalities and form defective grain boundaries between n phases. After excitation and formation of electron-hole pairs, charge separation is facilitated at these boundaries and transfer is possible to neighboring grains[8,9]. The response of this behavior may be observed as Förster resonance energy transfer (FRET), a pathway for excitons to migrate through organic layers[10].

Here we demonstrate the dynamics of a binary layered DJ perovskite superlattice with grain boundaries, where periodically layered 3AMP PbI_4 and 3AMP(MA) Pb_2I_7 results in the formation of an intermediate transition between n=1 and n=2. Exciton dynamics are taken over multiple spatial positions across the crystal surface and ratio changes of the inorganic phases are observed as pump-probe amplitude differences.

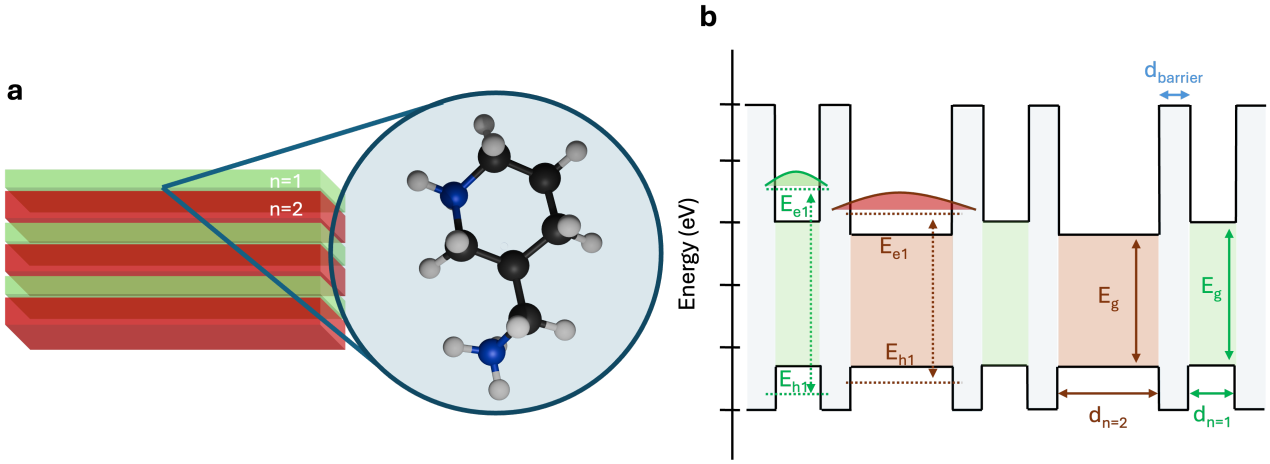

Figure 1. Configuration of the binary layered DJ perovskite. **a.** Binary layering of the n=1 and n=2 perovskite with a 3AMP interlayer. **b.** Finite quantum well depiction of the superlattice where the thin barrier enables tunneling of carriers to adjacent wells.

2. EXPERIMENTAL METHODS

2.1 Absorption

Absorption measurements were conducted using a broadband light source with a focused 50 μm beam. The transmitted spectrum was collected with a spectrometer (Andor Kymera 328i) and CCD (Andor iDus 416).

2.2 Photoluminescence

Photoluminescence (PL) measurements were performed using a lab-built confocal microscopy system. The sample was photoexcited using a supercontinuum pulsed laser (repetition rate 78 MHz, temporal width ~ 50 ps, NKT Photonics) spectrally selected at 480 nm.

2.3 Transient Reflection Spectroscopy

Ultrafast, broadband transient reflection spectroscopy measurements were performed with a Yb:KGW laser, operating at 90 kHz. The supercontinuum white-light probe spanned 500 to 1000 nm. The sample was mounted in vacuum (Montana Instruments Cyrostation, s50) where a 590 nm pump was focused onto the sample. A 0.45 NA, 50x microscope objective (Nikon) focused the pump to 14 μm. The reflected probe beam intensity was measured with a fast line-scan camera (Teledyne e2V Octoplus USB) operating with a burst modulation scheme[13]. The pump and probe beams were linear and cross-polarized.

3. DATA AND RESULTS

Absorption measurements were conducted to confirm the phases present in the binary layered heterostructure. The absorption has a signature with three energies: 2.23 eV, 2.10 eV and 1.75 eV, which correspond to the n=1 exciton, an intermediate transition (n=1.5) and defect states respectively. The n=1 phase dominated the absorption spectrum, and the defects were relatively weak in comparison. Carrier transport through the n=1 and n=2 phases of the material can be probed by PL spectroscopy. Two emission peaks were present in the PL: a 2.02 eV peak, which corresponds to the PL of n=2, and emission from defects at 1.72 eV. Carriers tunnel from the n=1 regions to the smaller bandgap inorganic layers of the material, which is indicated by the lack of an n=1 PL emission peak[3]. This transport is expected in the stacking direction given the 3AMP organic layer is relatively thin in the superlattice.

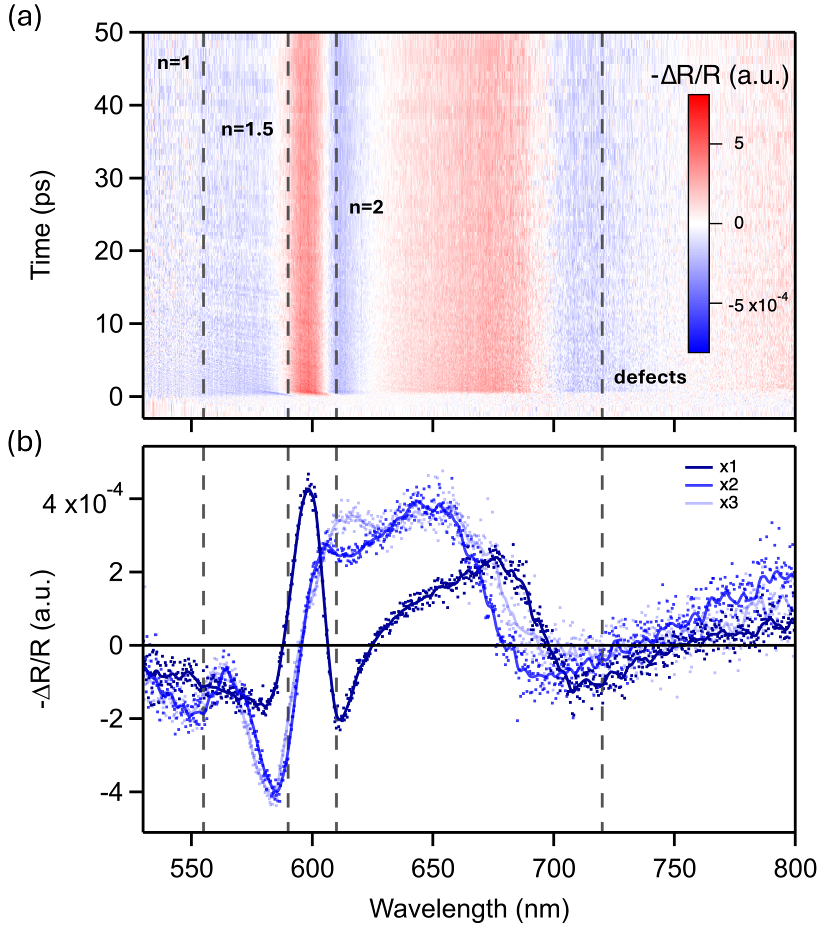

Figure 2. Transient reflection of layered 3AMP n=1 and n=2. **a.** Differential signal after 590 nm pump excitation taken at 0.93 µJ/cm^2. The dashed lines represent the bandgaps of n=1 and n=1.5 and the PL for n=2 and defect states. **b.** Transient spectra taken at three positions on the crystal. Spectra was taken at 0.8 ps after photoexcitation.

Figure 2a shows the transient response of the sample resonantly excited at 590 nm (2.10 eV) at 0.93 µJ/cm^2. Four radiative spectral regions are present, including the ground state bleach (GSB) for n=1, n=1.5 and 1.75 eV as well as PL from n=2. A common source of defective emission in Ruddlesden-Popper perovskites is attributed to “edge” states, or structural defects that facilitate exciton dissociation[8,14]. Broadened emission peaks can evolve from self-trapped excitons and defects in DJ perovskites, but the latter is dependent on long carrier diffusion lengths[15,16]. Transient reflection measurements were taken in two other regions > 10 µm from one another. Figure 2b shows spectral profiles of the differential reflection taken at 0.8 ps. Positions x2 and x3 have similar spectra with minor differences in excited state absorption, whereas the x1 spectrum shows a decrease in the populations of the n=1 and n=1.5 phases with an increase in the n=2 emission. There is a corresponding redshift in the defect emission which can indicate changes in the defect type in different regions of the superlattice[17]. This shift is likely due to the relationship between the grain boundaries of the layered perovskite and the ratio difference between the n=1 and n=2 phases. The dominating phase may change the defects that are the present at the boundaries, appearing energetically shifted in the transient data.

4. CONCLUSIONS

In conclusion, we observed the influence of binary layering DJ perovskites on excitonic transitions and defects. Utilizing transient reflection spectroscopy, we demonstrate a relationship between the ratio of n=1 and n=2 phases and the energetic landscape of edge defects. The difference in defect amplitude was trivial despite the ratio in dimensionality. We also note that a blue-shifted defect emission has a strong correlation to a higher n=1.5 oscillator strength and smaller n=2 emission. Grain boundaries in a superlattice perovskite structure may further the lifetime of hot carriers. By controlling the phase population of these superlattices, the strength of the intermediate state and the defect energy can be tuned.

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