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Interlayer Triplet Energy Transfer in Dion–Jacobson Two-Dimensional Lead Halide Perovskites Containing Naphthalene Diammonium Cations

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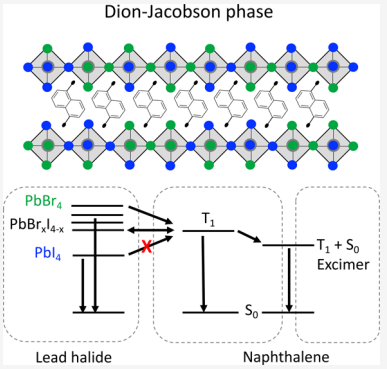
ABSTRACT: Recently, hybrid perovskites have gained attention as sensitizers for molecular triplet generation. Layered, two-dimensional (2D) perovskites are especially well-suited for this purpose because the triplet donor (inorganic framework) and triplet acceptor (organic layer) are self-assembled into adjacent sheets, so that with the appropriate energetics, triplets can be driven across the interface. Here we examine interlayer energy transfer in a series of mixed-halide Dion–Jacobson 2D perovskites containing divalent naphthalene cations. We find that the sensitized phosphorescence in these compounds is dominated by naphthalene triplet excimer emission, but when the inorganic exciton is tuned near resonance with the naphthalene triplet, naphthalene monomer phosphorescence competes with triplet excimer formation. The interlayer energy-transfer process is further revealed by ultrafast transient absorption spectroscopy through kinetic variations in triplet excimer formation times. Ultimately, gaining control over interlayer interactions in 2D perovskites through cation design will help uncover new functions and applications for these materials.



The ability to tune the heterojunction energy level alignment in layered 2D perovskites is well-documented, with both early works and more recent studies reporting interfacial triplet energy transfer in certain pairings of lead halide with small conjugated organic spacer cations.[1−8] Such 2D perovskites are promising systems for sensitized molecular phosphorescence,[9] which has varied applications in optoelectronics, solar energy conversion, and photoredox catalysis.[10−12] However, even for a given organic cation core, variations in the cation structure (e.g., location of the ammonium substituent, length and type of alkyl linker, and valency of the cation) can dramatically alter the organic layer morphology and electronic coupling between the inorganic and organic layers.[13−16]

While interlayer triplet energy transfer has been studied in Ruddlesden–Popper (RP) phase 2D perovskites containing monovalent naphthalene cations,[1,4,6,17] the photophysical properties of their Dion–Jacobson (DJ) analogue, formed with divalent naphthalene cations, have not been reported. There are many structural differences between the RP and DJ perovskite phases with possible relevance to interlayer triplet energy transfer and the fate of the triplet exciton thereafter. Notably, while RP structures contain monovalent organic cations that are electrostatically bound to the inorganic lead halide framework on one end only, resulting in a double layer of cations maintained by van der Waal interactions, DJ phases contain single layers of divalent organic cations that are electrostatically tethered on both ends to the inorganic framework.[14] In principle, these structural differences can impact the rigidity, conformational freedom, and intermolecular interactions between neighboring naphthalene cations within the organic layer. Moreover, the relative orientation of organic cations with respect to the octahedral lead halide network can affect the degree of electronic coupling between the two layers, which dictates the rate of triplet energy transfer through a Dexter electron exchange process.[18]

Triplet energy transfer is energetically favorable ($\Delta E \approx 0.4$ eV) at the interface between lead bromide and naphthalene in an $n = 1$ 2D perovskite structure. Various groups have studied this process in lead bromide RP perovskites incorporating either 1-naphthylmethylammonium[1,4,6] or 1-(2-naphthyl) methanammonium cations.[17] The phenomenon was first described by Era and co-workers in the late 1990s,[1] while Tian and co-workers refined the mechanism of triplet energy transfer in a recent work.[6] Interestingly, at room temperature, following triplet energy transfer, the photoluminescence in these RP compounds is dominated by naphthalene excimer emission. In this case, the excimer is composed of a naphthalene triplet excited state electronically coupled to a nearby molecule in its ground state. Naphthalene is reported to possess stable excimers in both face-to-face and L-shaped arrangements.[19−21] Regardless of the exact configuration of the

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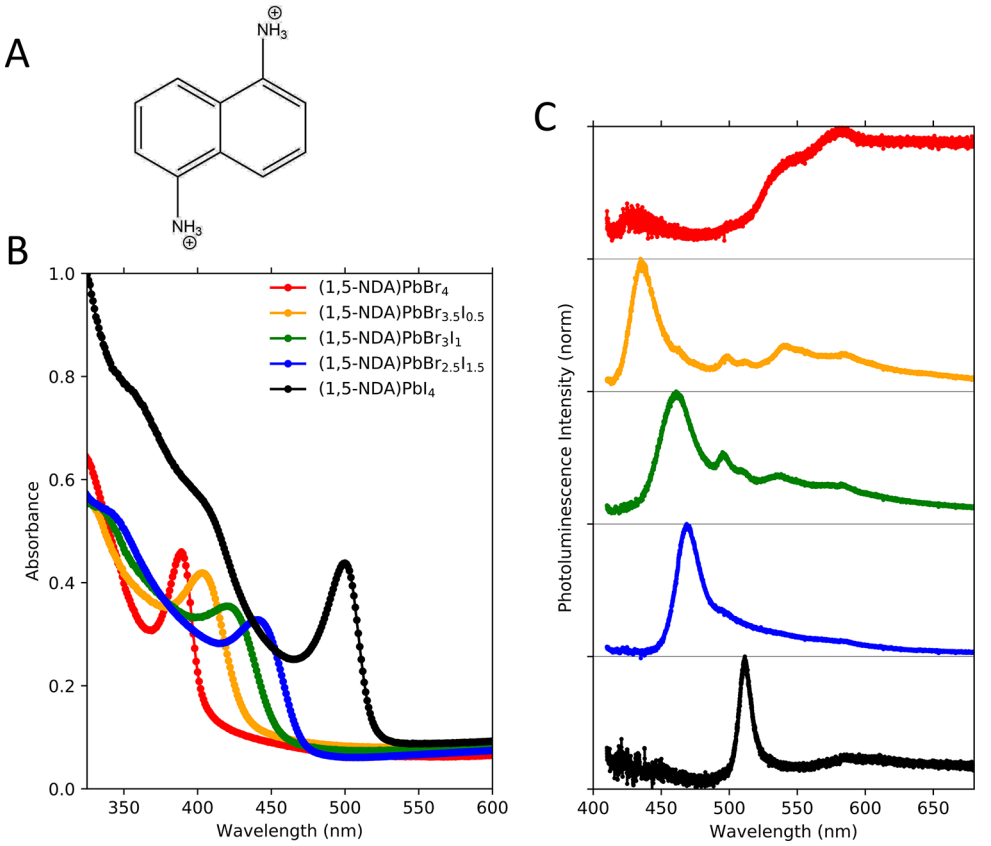

Figure 1. (A) Structure of 1,5-naphthalene diammonium (1,5-NDA). (B) Absorbance spectra of mixed-halide thin films. (C) Photoluminescence spectra of mixed-halide thin films measured at 77 K when excited at 365 nm. Spectra are normalized within each panel, and panels B and C share the same legend.

excimer, it is clear that the optical properties of naphthalene-based 2D perovskites will depend sensitively on the intermolecular juxtaposition within the organic layer. In particular, because interfacial triplet energy transfer in layered 2D perovskites requires that the triplet level of the organic cation lies below that of the inorganic exciton level, an aromatic chromophore with extended π-conjugation is used instead of an aliphatic one. While conjugated organics result in lower-energy transitions, they are also more susceptible to $\pi-\pi$ interactions that foster excimer formation.

Whereas the crystal structure of the DJ lead bromide perovskite is uncharacterized, the known crystal structure of the iodide analogue shows that the naphthalene cations are arranged in a nearly orthogonal fashion with little to no π-orbital overlap between neighboring molecules.[22] Given that excimer formation is highly dependent on the relative orientation of the participating molecules, one might expect the DJ perovskite, with its single layer of relatively rigid and electronically isolated cations, to exhibit weaker excimeric interactions compared to its RP counterparts.

In this work, we investigate the photophysical properties of a series of n = 1 DJ 2D perovskites containing 1,5-naphthalene diammonium (1,5-NDA) cations (Figure 1A), with general formula (1,5-NDA)PbX_4 where X is a halide (either Br or I). Because the inorganic exciton energy is primarily determined by the lead halide framework,[15] we are able to vary the halide compositions from pure bromide to pure iodide in order to access a range of energetic driving forces for triplet energy transfer across the lead halide/naphthalene interface.

The absorbance spectra of the series of (1,5-NDA)PbX_4 thin films are shown in Figure 1B. Typical of layered 2D perovskites, all of the compounds exhibit sharp transitions corresponding to excitons supported in the inorganic lead halide layers via a combination of quantum and dielectric confinement effects.[14,15] The exciton peaks show a continuous progression between the pure bromide to the pure iodide compositions, implying that the halides are homogeneously mixed as opposed to phase-segregated.

Unlike their RP counterparts, which exhibit strong room-temperature photoluminescence that is visible to the naked eye (see SI Figure 1B), the DJ films showed comparatively weaker photoluminescence, and it was necessary to cool the films to 77 K to observe appreciable emission. While the reason for their low luminescence efficiency was not investigated in this work, there may be an underlying structural explanation, as many low-dimensional perovskites exhibit self-trapping of excitons due to structural distortions in the lead halide octahedral lattice.[23,24]

The low-temperature photoluminescence spectra of the DJ films are shown in Figure 1C. The samples were excited with 365 nm photons, ensuring that the initial excitations are localized in the lead halide layers rather than directly populating the singlet state of naphthalene. The observed photoluminescence spectra correlate with the strength of the driving force for interlayer triplet energy transfer: the larger the driving force, the stronger the naphthalene emission compared to the lead halide exciton emission. The (1,5-NDA)$PbBr_4$ composition shows very weak emission from the inorganic exciton centered at 425 nm, and the spectrum is instead

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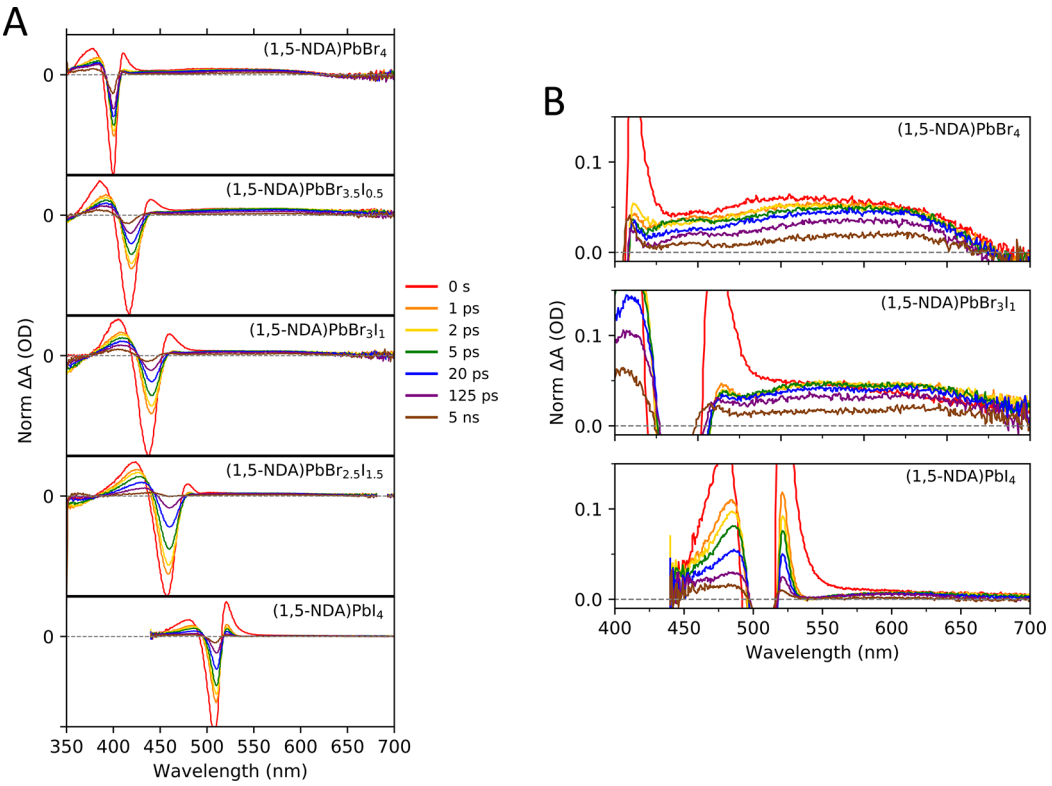

Figure 2. (A) Transient absorption spectroscopy of the DJ perovskite film series showing evolution of the differential absorption (ΔA) spectra at various time points between 0 and 5 ns following excitation with a 340 nm pump pulse. Spectra were collected at 77 K, and traces are normalized to the bleach minimum within each panel. Dashed gray lines are guides for the eye, indicating zero differential absorption. (B) Expanded view of the photoinduced absorption feature beyond the exciton bleach for select compounds. The bromide rich compounds exhibit long-lived broad positive features in this region, whereas the pure iodide compound does not.

dominated by a broad, unstructured low-energy emission that resembles the naphthalene triplet excimer photoluminescence spectrum.[20,21] These observations are consistent with a nearly complete transfer of the exciton energy from the lead bromide layer to naphthalene, made possible by a large driving force of around 0.36 eV. However, as the driving force for triplet transfer is reduced in the mixed halide compositions, the samples exhibit emission from both the inorganic exciton and naphthalene species. Finally, for the (1,5-NDA)PbI_4 composition, triplet transfer is inhibited by an energy barrier of around 0.18 eV, such that the sample exhibits emission almost exclusively from the inorganic exciton centered at 510 nm. Note that while the spectrum in Figure 1C appears to show a broad emission around 550−650 nm, the overall photoluminescence intensity of (1,5-NDA)PbI_4 is relatively weak compared to the bromide-containing compounds (see SI Figure 2), such that this low-energy feature is amplified by normalization. In reality, the actual number of photoluminescence counts is extremely low in this region and not significantly more than the background signal generated by a blank substrate. For this reason, we do not believe this low-intensity feature is attributable to a naphthalene species (which are highly emissive) and is more likely a substrate or material impurity.

Interestingly, for the mixed halide compositions in which the exciton level of the lead halide layer is near-resonant with the triplet level of naphthalene ((1,5-NDA)$PbBr_{3.5}I_{0.5}$ and (1,5-NDA)$PbBr_3I_1$ in Figure 1C), we observe two additional closely spaced peaks in the photoluminescence spectra, located at 495 and 510 nm. The fact that these peaks are sharp and closely spaced suggests their origin is unlikely to stem from the naphthalene excimer (because excimers are able to access unlimited molecular conformations, their emission profiles are broad with no vibrational structure).[25] Moreover, the positions and spacing between these peaks correspond well to vibronic transitions between the triplet and ground-state manifolds of naphthalene monomers in solution.[21] The appearance of these monomeric transitions is consistent with the reduced driving force for triplet energy transfer in these compounds. Because the inorganic exciton level is close in energy to the triplet level of naphthalene, some reversible energy transfer may occur across the interface, providing an additional pathway that competes with naphthalene excimer formation. As a result, direct phosphorescence from the naphthalene monomer triplet is enhanced with respect to excimer formation and emission. In fact, similar behavior was observed by Kawano and co-workers in an RP 2D perovskite containing 1-(2-naphthyl)-methanammonium cations in which the halide composition was tuned to resonance with the triplet level of naphthalene.[17]

We used ultrafast transient absorption spectroscopy to probe the interfacial dynamics in the DJ thin films. The samples were pumped with 340 nm pulses, and the differential absorption was probed by broad band visible pulses at pump−probe time delays up to 5 ns. As with the steady-state photoluminescence measurements, the 340 nm pump wavelength ensures that the initial excitations are localized on the lead halide layers. The spectral traces for all of the mixed-halide compositions at various time points are summarized in Figure 2A. Each of the films exhibits a strong exciton bleach corresponding to depopulation of the lead halide exciton ground states

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immediately after absorbing the pump pulse, which is roughly 170 fs in duration at full width at half-maximum (SI Figure 4). These exciton bleaches are accompanied by small positive modulations on either side of the bleaches, which can be interpreted as a transient Stark effect induced by gradual filling of exciton states with charge-transfer-like character.[26,27]

Notably, in addition to the exciton ground-state bleach, each of the compounds in which interfacial triplet energy transfer is energetically favorable exhibits a broad photoinduced absorption (PIA) feature at longer wavelengths beyond the bleach (approximately 450−650 nm). An expanded view of this wavelength range is shown for select samples in Figure 2B. For each of the bromide-rich compounds, the broad PIA feature is long-lived and does not fully decay within the 5 ns window afforded by the transient absorption setup. However, the transient spectra of the pure iodide compound (1,5-NDA)PbI_4 contains only the exciton bleach and no appreciable PIA at longer wavelengths. At least qualitatively, these patterns suggest that the long-lived PIA may be associated with a naphthalene triplet species. This assignment is consistent with a previous microsecond transient absorption study that was conducted on concentrated, triplet-sensitized solutions of naphthalene, in which the authors observed a broad intermoiety charge-transfer absorption band in the region of 450−650 nm with definitive links to the naphthalene triplet excimer.[28] Similar broad PIA features have also been observed in an RP 2D perovskite containing thieno[3,2-*b*]thiophene-2-methylammonium cations (which are structurally similar to naphthalene) and were assigned to triplet excited-state absorption of the organic molecule.[5] On the basis of our experimental observations and these comparisons with examples in the literature, we believe the broad and long-lived PIA in the 450−650 nm probe range is related to a naphthalene triplet species.

For each of the bromide-rich compounds, the appearance of the broad PIA feature is ultrafast. We monitored the kinetics at a probe wavelength of 550 nm, shown in Figure 3, where each kinetic trace is normalized within the panel to its maximum amplitude. For the pure bromide compound, (1,5-NDA)$PbBr_4$, the maximum PIA amplitude at 550 nm coincides with the arrival of the pump pulse shortly after time zero. Given the large driving force for triplet energy transfer, the triplet excimer states are being populated at subpicosecond time scales, faster than the resolution of the measurement system. However, for the other mixed halide compositions with lower energetic driving force for interfacial triplet transfer, the appearance of the maximum PIA amplitude occurs at a slight delay between 1 and 10 ps after the pump pulse. Again, this is consistent with slower triplet energy transfer (and possible back transfer) between the inorganic and organic layers.

The main features of the photoluminescence and transient absorption spectroscopy data can be understood in terms of the energy level diagram shown in Figure 4. First, an incident photon (365 nm for photoluminescence spectroscopy and 340 nm for transient absorption spectroscopy) generates an exciton localized in the inorganic lead halide layer. The lead halide composition determines the exciton band alignment at the interface with naphthalene such that in the pure bromide compound, the initial exciton undergoes efficient triplet energy transfer to the 1,5-NDA moiety, whereas in the pure iodide compound, this process is thermodynamically unfavorable. In addition, for certain intermediate bromide−iodide compositions, the close alignment between the inorganic exciton band

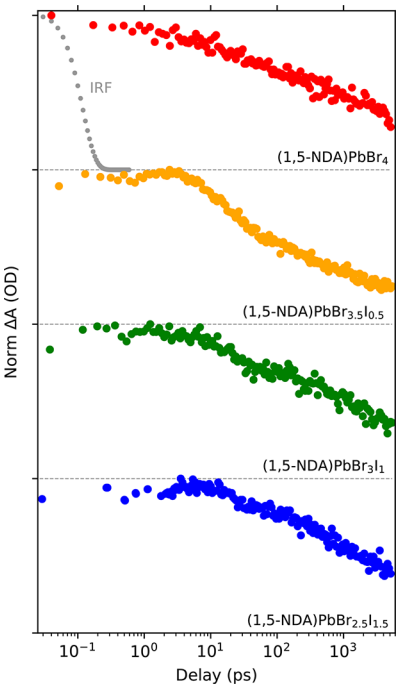

Figure 3. Normalized kinetic traces of the photoinduced absorption from Figure 2A measured at a probe wavelength of 550 nm. A Gaussian fit to the instrument response function (IRF) is shown in gray.

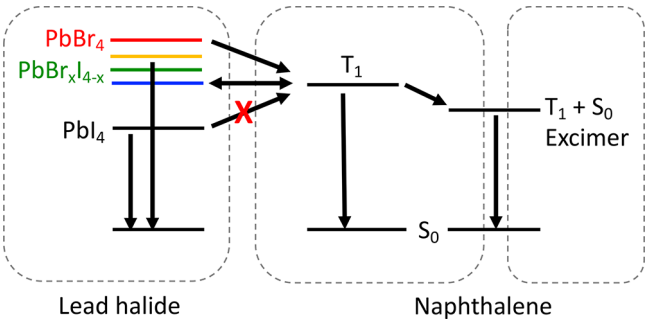

Figure 4. Energy level diagram of the lead halide/1,5-naphthalene diammonium cation interface. Inorganic exciton bands are shown for different lead halide compositions: T_1, triplet excited state; S_0, singlet ground state.

and the naphthalene triplet facilitates reversible triplet energy transfer across the interface. It should be noted that as the bromide:iodide ratio is adjusted to near resonance with the triplet level of naphthalene, it would be more accurate to regard the exciton as a hybridized species, with a wave function composed of both inorganic and organic components, rather than as the distinct levels shown in Figure 4. Following population of the naphthalene triplet, it can either decay directly to the ground state (S_0), emitting light according to its monomer phosphorescence spectrum, or it can couple to a nearby ground-state naphthalene, forming an excimer (T_1 + S_0) and relaxing to the ground state via a broad, unstructured, and red-shifted excimeric emission spectrum.

At this point it is worth revisiting the hypothesis presented earlier that the DJ phase 2D perovskite studied in this work would exhibit reduced excimeric interactions compared to its RP counterparts. This hypothesis was formed based on two assumptions: (1) that the strong electrostatic bonding on both

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ends of the diammonium cation would restrict access to the conformational states required for excimer formation and (2) that face-to-face $\pi-\pi$ interactions would be suppressed by the orthogonal cation geometry that has been reported in the crystal structure of (1,5-NDA)PbI_4.[22] However, our studies suggest that in spite of these predictions, the naphthalene triplet excimer remains the most stable emissive state in these DJ systems. One possible explanation is that while pairs of nearest neighbors in an orthogonal cation geometry have very little $\pi-\pi$ interaction, excimer formation could be occurring between *diagonal* pairs of cations that exist in a slipped-parallel arrangement. However, a more rigorous structural characterization of the bromide compound combined with theoretical studies would be needed to test these possibilities.

In summary, we have observed interlayer triplet-sensitized emission from a series of mixed-halide DJ 2D perovskites containing naphthalene diammonium cations. Like their previously studied RP counterparts, the sensitized molecular emission in these DJ compounds is dominated by naphthalene triplet excimer emission. However, by tuning the inorganic exciton level near the triplet level of naphthalene through halide mixing, we observe enhanced monomer phosphorescence from naphthalene due to competition from reversible energy transfer across the interface. Transient absorption spectroscopy reveals a broad PIA feature at long wavelengths that is correlated with the population of naphthalene triplet species. Finally, by inspecting the kinetics of these broad PIA features, we find that the time scale of naphthalene triplet formation is correlated with the strength of the energetic driving force for interlayer triplet energy transfer. When considered alongside previous studies on naphthalene-containing RP perovskites, our work brings attention to how the structural and compositional versatility of layered 2D perovskites can be leveraged for the fine-tuning of their photophysical properties.

EXPERIMENTAL METHODS

Naphthalene diammonium halide salts were prepared by first dissolving 1,5-diaminonaphthalene in tetrahydrofuran (THF) at 0.5 M concentration and then reacting either HBr (48 wt % in water) or HI (57 wt % in water) with the diamine solution at a 2.2:1 molar ratio while stirring. The precipitates were collected by vacuum suction filtration and rinsed several times using a 3:1 volume mixture of THF:dichloromethane before drying the powders overnight in a vacuum oven at 65 °C.

The perovskite precursor solutions were prepared by dissolving stoichiometric ratios of the naphthalene diammonium halide salt and lead halide at 0.25 M concentration in a 4:1 volume mixture of dimethylformamide/dimethyl sulfoxide. The mixed halide compositions were prepared by combining the bromide and iodide perovskite stock solutions together at their nominal ratios. Thin films were then spun on cleaned quartz substrates at 4000 rpm for 60 s, followed by annealing at 140 °C for 20 min. All solutions and thin films were prepared in a nitrogen glovebox.

Absorption spectroscopy was conducted at room temperature and in ambient air using an Agilent Cary 6000i UV−vis−NIR spectrophotometer with an integrating sphere attachment. A clean quartz substrate served as the reference blank. Low-temperature steady-state photoluminescence experiments were conducted in an Oxford Instruments sample-in-N_2-vapor cryostat. The samples were excited with a 365 nm LED, and the emitted light was fiber coupled to a Princeton Instruments PyLoN spectrometer and CCD array.

For the low-temperature transient absorption spectroscopy experiments, samples were mounted in a Janis Research sample-in-vacuum cryostat. The 340 nm pump beam was generated by a TOPAS-C optical parametric amplifier excited by an 800 nm Coherent Libra Ti:sapphire laser. The supercontinuum probe beams were generated by focusing a portion of the Ti:sapphire laser output on either a CaF_2 crystal (probe = 350−680 nm) or a 1 mm thick sapphire crystal (probe = 440−800 nm). The pump beam intensity was adjusted for each sample to achieve a maximum exciton bleach amplitude of −10 mOD, with pulse energies ranging from 100 to 390 nJ prior to the cryostat window. An Ultrafast Systems Helios transient absorption setup with a multipass delay stage was used to measure differential absorption at pump−probe delays up to 5 ns. Spectra were analyzed using Ultrafast Systems Surface Xplorer software. Chirp of the supercontinuum probe was characterized using the response from a blank glass substrate. All reported spectra were adjusted for time zero, removal of the spectral background, and chirp correction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c01232.

Optical properties of Ruddlesden−Popper compounds and additional PL and TA spectra for Dion−Jacobson compounds (PDF)

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Notes

The authors declare no competing financial interest.

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