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Influence of π -conjugated cations and halogen substitution on the optoelectronic and excitonic properties of layered hybrid perovskites

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Low-cost chemical engineering of two-dimensional layered hybrid halide perovskite structures allows for the design of hybrid semiconductor quantum wells with tailored room temperature excitonic optical absorption, emission, and charge carriers transport properties. Here density functional theory and the Bethe-Salpeter equation are used to predict the electronic structure and optical response of layered perovskites with two representative single-ring conjugated organic spacers, ammonium-propyl-imidazole (API) and 2-phenethylammonium (PEA). The inorganic perovskite quantum well properties are further tuned by analyzing the effect of halogen (X=I, Br, Cl) substitution. We found that visible light absorption occurs primarily within the perovskite layer and that UV light absorption induces partial electron-hole separation between layers. In addition, a strong exciton binding energy and influence on absorption spectrum is found by solving the Bethe-Salpeter equation. Our results suggest that further engineering is necessary beyond the single-ring limit, by introducing more conjugated rings and/or heavier nuclei into the organic spacer. This is a promising future direction to achieve photo-induced charge separation and more generally hybrid heterostructures with attractive optoelectronic properties.

I. INTRODUCTION

Three-dimensional (3D) hybrid organic-inorganic perovskites (HOPs) have rapidly emerged as some of the most promising thin-film photovoltaic materials.¹⁻³ Their allure comes from a combination of high photo-conversion efficiency (PCE), low device processing cost due to low-temperature solution processing, and composition from earth-abundant and readily available materials. In particular, hybrid lead-halide perovskite (e.g. methylammonium lead iodide, MAPbI₃, and formamidinium lead iodide, FAPbI₃) solar cells have undergone a PCE increase from 3.5 % to over 20 % in about 5 years.⁴⁻⁶ These devices have currently exceeded the certified record efficiency of multicrystalline Si cells.⁷ Beyond photovoltaic applications, HOPs show potential in many other fields including hydrogen generation,⁸ X-ray and Gamma-ray detection,⁹⁻¹² light emitting diodes (LEDs),¹³ spintronics,^{14,15} and sensors.¹⁶ Setting aside the issue of lead toxicity,¹⁷⁻²² the main impediment to industry deployment of perovskite devices is their instability to air, moisture,²³ and light exposure.^{24,25}

Recently, *layered* HOPs (LHOPs) have re-emerged as promising alternatives to their 3D counterparts. They have been suggested to be used as highly efficient white LEDs²⁶ and tunable optical detectors.²⁷ In these, quantum confinement effects within perovskite layers can be engineered and tailored to specific applications.²⁸⁻³¹ In particular, they are able to overcome some of the above-mentioned limitations,³²⁻³⁴ by offering much improved stability and decent photo-conversion performance: Tsai *et al.* reported that non-encapsulated single crystals of *n*-butylammonium-methylammonium lead-iodine with *n*=3 and 4 layers resists

moisture-driven chemical degradation. They also showed that encapsulation of the crystals resulted in no chemical degradation under highly illuminated conditions, and built solar cells with a PCE of 12.5 with *n*=3 and *n*=4 layers.³² The broad applications and variability of LHOPs have opened a field of research that is just beginning to produce deeply insightful and practically applicable results.

The LHOPs studied in this work fall into the Ruddlesden-Popper crystal class³⁵ and their characteristic structure consists of 2D layers of *n* corner-sharing metal-halide octahedra separated by, and ionically bonded to, large charged polyatomic cations (see Fig. 1). The inorganic perovskite layer can be tuned to a specific width of *n* octahedra or even cleaved along various planes, linking the octahedra in linear or zig-zag corrugated patterns.³⁶⁻³⁸ Opportunities to engineer LHOPs not only originate from changing the inorganic perovskite stoichiometry, but also by choosing one or more of many complex large organic cations to separate the layers.^{26,36-39} Promising organic cations range from simple carbon chains with ammonium caps to large chromophore complexes.⁴⁰⁻⁴² These degrees of freedom allow for the exploration of a wide variety of electronic properties and to tune optical response.

In this context, optically activated charge separation between the organic and inorganic layers of LHOPs has been long sought to reduce the overlap between electron and hole wave functions and, thus, allow utilization of separated electron-hole channels for highly efficient charge transport. The advent of organic solar cells has proven that π -conjugated polymers are fully capable of producing and transporting bound electron-hole pairs (excitons) under illumination.^{43,44} It has further been suggested that inter-chain charge separation of bound electron-hole pairs is possible in these

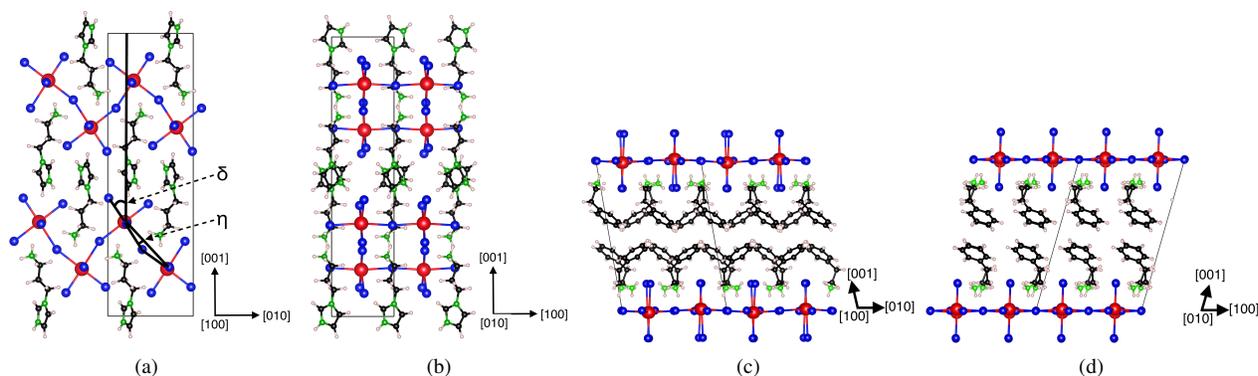


FIG. 1. (Color online.) The atomic structure of ammonium-propyl-imidazole (API)-PbBr₄ projected along the (a) [100] direction and (b) [010] direction and 2-phenethylammonium (PEA₂)-PbBr₄ projected along the (c) [100] and (d) [010] axis. The stacking direction is [001]. Atomic color coding: Pb (red), Br (blue), C (black), N (green), and H (pink). Tilting angle δ and bond angle η are indicated (see text).

76 systems.⁴⁵ Furthermore, charge transfer between semicon- 115
 77 ductor CdSe quantum dots and poly[2-methoxy-5-(2-ethyl- 116
 78 hexyloxy-p-phenylenevinylene)] bonded functional coatings 117
 79 has been observed.⁴⁶ This raises an interesting question 118
 80 whether organic layers in LHOPs with π -conjugated organic 119
 81 cations could similarly carry photo-current under illumination
 82 if optical absorption excites electrons and holes that are lo-
 83 calized in parallel layers of the LHOP system. If so, exten-
 84 sive chemical degrees of freedom in LHOPs could allow for
 85 engineering a layered organic-inorganic compound material
 86 that are capable of efficiently separating electrons and holes.
 87 These layers may provide separate conduction channels for
 88 electrons and holes, potentially reducing detrimental recombi-
 89 nation. However, it is unknown how active the π -conjugated
 90 organic compounds in LHOPs are under UV-VIS absorption,
 91 in particular in the stoichiometric limit of $n=1$ perovskite lay-
 92 ers between each organic layer.

93 To address this, Li *et al.* conclude from a large Stokes 120
 94 shift in the photoluminescence emission spectrum that charge 121
 95 separation occurs between the organic ammonium-propyl- 122
 96 imidazole (API) layer and inorganic PbBr₄ perovskite layer 123
 97 of [110] oriented API lead-bromide ($n=1$).⁴⁷ They also per- 124
 98 formed density functional theory (DFT) calculations and re- 125
 99 port an isolated carbon- π^* state in the fundamental band 126
 100 gap, to which they attribute the carrier separation and re- 127
 101 sulting massive Stokes shift. However, this material has not 128
 102 been studied by modern first-principles approaches that in- 129
 103 clude the effects of spin-orbit coupling (SOC) and electron- 130
 104 hole interaction on the optical-absorption spectrum. In par- 131
 105 ticular, SOC has shown to be very important in determin- 132
 106 ing the correct electronic band structure in Pb-containing hy- 133
 107 brid perovskite materials.^{14,15,29,48} Furthermore, several rea- 134
 108 sons for a large Stokes shift are debated and no conclusion 135
 109 has been reached: It has been suggested recently that it ori- 136
 110 ginates from strongly bound small-polaron states that form in 137
 111 the perovskite layer, lowering the emission energy of electron- 138
 112 hole pairs.^{49,50} While the extent of octahedral tilting in and 139
 113 out of the perovskite plane has also been correlated with the 140
 114 magnitude of the Stokes shift,^{51,52} Du *et al.* found no such

115 correlation from their analysis of the optical absorption and
 116 emission character of layered Pb(I,Br,Cl)₄ perovskites with
 117 acene alkylamine organic cation layers.⁵³ Hence, the debate
 118 to what extent π -conjugated organic layers participate in the
 119 optical absorption and emission of LHOPs is still open.

120 In the present study, we report first-principles calculations,
 121 for single π -conjugated LHOPs to determine the organic and
 122 inorganic layer contributions to electronic structure and op-
 123 tical absorption. We also clarify at what energies this be-
 124 comes a significant contributor to the total optical response.
 125 The materials of interest are the $\langle 110 \rangle$ API-PbX₄ class (X=I,
 126 Br, Cl) of layered perovskites, motivated by the work of Li *et*
 127 *al.*⁴⁷ and the single π -conjugated organic cation perovskites 2-
 128 phenyl-ethylammonium (PEA) PEA₂-PbX₄ (X=I, Br, Cl) due
 129 to their readily available experimental atomic geometries and
 130 single π -conjugated (benzene) group per organic ion (see Fig.
 131 1). We compute the ion-projected electronic structure and
 132 single-particle optical response using density functional the-
 133 ory (DFT), including spin-orbit coupling (SOC) and band gap
 134 corrections determined by HSE06 hybrid-functional calcula-
 135 tions. The PBE+SOC+ Δ_{HSE06} calculations reported in this
 136 work are an approximation of the full single-particle exci-
 137 tation energy calculations within the *GW*+SOC many-body
 138 perturbation theory formalism.⁵⁴ The two-particle optical re-
 139 sponse, which includes the effect of exciton formation, is
 140 calculated from the solution of the Bethe-Salpeter equation
 141 (BSE). Our results clarify energetic alignment of the bands
 142 associated with organic and perovskite components in both
 143 materials and provide detailed analysis of essential electronic
 144 wavefunctions and individual contributions to optical absorp-
 145 tion spectra. This allows us to answer the question whether
 146 optical excitations occur within individual layers of single
 147 π -conjugated LHOPs or whether optical excitations partially
 148 separate electrons and holes between layers.

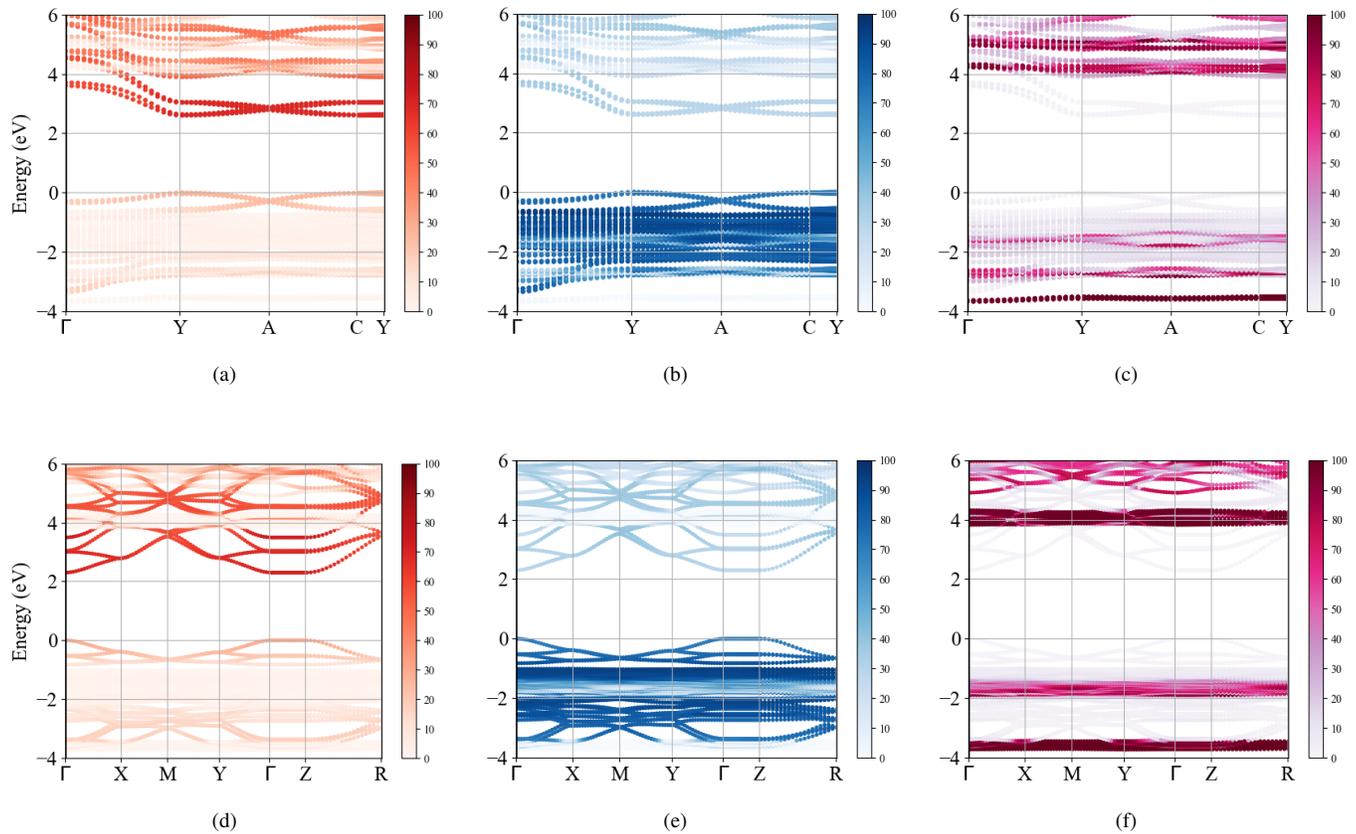


FIG. 2. (Color online.) The ion-projected band structures, computed using PBE+SOC+ Δ_{HSE06} , of API-PbBr₄ (a-c) and PEA₂-PbBr₄ (d-f). The color bar indicates the contribution of Pb (red), Br (blue), and API/PEA (magenta) to each state as a percentage.

149

RESULTS

Atomic Structure: The structure of single-layer $\langle 110 \rangle$ API-PbX₄ compounds resembles that of the $\langle 100 \rangle$ class of layered perovskites: The major difference is the corrugation of the perovskite layer with a zig-zag type octahedral linking in the $\langle 110 \rangle$ compounds and a linear-type linking in the $\langle 100 \rangle$ compounds. Figure 1 shows the [100] and [010] projections of both API-PbBr₄ and PEA₂-PbBr₄. PEA₂-PbX₄ experimental structures are used in our study.^{55–57} Since experimental data is available only for API-PbBr₄,⁴⁷ we fully relax all API-PbX₄ atomic geometries in the $P2_1/c$ symmetry space group. The resulting lattice parameters and vector angles, unit-cell volumes, octahedron tilting angles, and Pb–X–Pb bond length ranges are reported in supplemental information (SI) Table S1 for all systems. The relaxed API-PbBr₄ atomic structure is in excellent agreement with the experimental structure determined by Li *et al.*,⁴⁷ with errors of under 1% for lattice parameters, 0.2% for unit-cell volume, 1% for lattice vector angles, 2.5% for out-of-plane tilting, and 15% for in-plane tilting angles. The out-of-plane tilting angles δ_1 and δ_2 in the corrugated $\langle 110 \rangle$ API-PbX₄ systems should be 45°, if no tilting is present. For the relaxed API-PbX₄ structures we find

two distinct δ_1 and δ_2 in the range between 33.7° and 33.8° and 51.4° and 53.9°, respectively.

In the linearly-linked PEA₂-PbX₄ systems, $\delta=0^\circ$ under no tilting and indeed in the experimental structures, the out-of-plane tilting angles remain small, in the range of 1° to 3°. The in-plane-tilting angles, ranging between $\eta=12.2^\circ$ and $\eta=14.5^\circ$, are larger compared to those found in the API-PbX₄ systems, ranging from $\eta=8.5^\circ$ to $\eta=10.5^\circ$. This in-plane tilting is very similar to the octahedron tilting in orthorhombic MAPbX₃ 3D HOPs.⁵⁸

Electronic Structure: The band structures of API-PbX₄ and PEA₂-PbX₄ reveal dispersive band frontiers attributed to states localized on the perovskite as well as flat, non-dispersive bands, situated more than 1 eV away from the band frontiers, that are attributed to the organic π and π^* states (see Fig. 2). Throughout the remainder of the paper, the label PBE+SOC+ Δ_{HSE06} refers to the PBE+SOC band structure with conduction bands rigidly shifted to higher energy to match the HSE06+SOC band gap, and HSE06+SOC refers to fully non-collinear HSE06 hybrid-functional calculations that take SOC into account. Table I reports relevant calculated and experimentally determined energy gaps of these materials.

Ion-projected PBE+SOC+ Δ_{HSE06} band structures are plot-

TABLE I. Energy gaps (in eV) computed using different levels of theory. PBE+SOC+ Δ_{HSE06} refers to the PBE+SOC electronic structure with the band gap rigidly shifted to the HSE06+SOC band gap value (see text).

Level of theory	API-PbI ₄	API-PbBr ₄	API-PbCl ₄
PBE+SOC	1.44	1.94	2.41
HSE06+SOC	2.10	2.74	3.32
$\pi - \pi^*$ gap (PBE+SOC+ Δ_{HSE06})	5.87	5.88	5.7
BSE Optical gap	1.74	2.23	2.68
Exp. Optical gap ⁴⁷	–	3.18	–
	PEA ₂ -PbI ₄	PEA ₂ -PbBr ₄	PEA ₂ -PbCl ₄
PBE+SOC	1.33	1.75	2.12
HSE06+SOC	1.95	2.45	2.95
$\pi - \pi^*$ gap (PBE+SOC+ Δ_{HSE06})	5.39	5.82	5.53
Exp. optical gap ⁵³	2.45	3.0	3.6

ted for API-PbBr₄ in Fig. 2(a)-(c). Similar data for the other API and PEA LHOPs considered in this work can be found in SI Figs. S2 and S3. Due to the $P2_1/c$ symmetry, the API-PbX₄ materials exhibit direct gaps of 2.10 eV, 2.74 eV, and 3.32 eV for API-Pb(I, Br, and Cl), respectively, at the Y point of the Brillouin zone (BZ). The Y point folds back to the Γ point when a 2×2 conventional cell is considered as demonstrated by Pedesseau *et al.*²⁹ The band gap we computed for API-PbBr₄ using the HSE06 exchange-correlation functional with spin-orbit coupling underestimates the gap of 3.18 eV measured from the optical onset by Li *et al.*⁴⁷ This can be attributed to the fact that HSE06, albeit it improves over the DFT-PBE description, does not fully capture quasiparticle effects for the systems studied here. More sophisticated, but computationally more expensive methods, such as many-body perturbation theory, could mitigate these shortcomings.⁵⁹ Additionally, in this comparison the electron-hole interaction was neglected and, thus, the calculated electronic gap differs from the measured optical gap by the exciton binding energy. This will be discussed in the results for optical response. Differences between our relaxed structure and the experimental structure of API-PbBr₄ are expected to result in only small changes of the band gap, within 0.2 eV, based on the effects of in- and out-of-plane angles on gap values explored by Pedesseau *et al.*²⁹ Figure 2 clearly shows that the band dispersion of API-PbBr₄ along the $Y - \Gamma$ direction is free-electron like, with a parabolic curvature near the Y point. Along the $Y - A$ direction, the dispersion has a lower curvature, indicating a higher electron effective mass. Finally, along the $Y - C$ direction the bands are effectively flat due to the layered and reduced periodicity of the LHOP crystals along the [001] direction. We observe the same trend for API-PbI₄ and API-PbCl₄.

In contrast, band structures of the PEA₂-PbX₄ LHOPs, with space groups $P2_1/c$, $P\bar{1}$, and $P\bar{1}$ for I, Br, and Cl, respectively, exhibit direct gaps of 1.95 eV, 2.45 eV, and 2.95 eV at the Γ -point. The difference between the space groups of PEA₂-PbI₄ and PEA₂-Pb(Br,Cl)₄ is due to the bis-phenylethylammonium conformation of the chosen PEA₂-PbI₄ structure.⁵³ The general PEA₂ conformation explored by Du *et al.* assumed the same $P\bar{1}$ space group as the PEA₂-PbBr₄ and PEA₂-PbCl₄

systems. The band structure of PEA₂-PbBr₄, illustrated in Fig. 2(d)-(f), exhibits highly dispersive, free-electron like band frontiers along the $\Gamma - X$ and $\Gamma - Y$ directions, as well as flat, non-dispersive band frontiers in the $\Gamma - Z$ direction. Unlike the API-PbX₄ corrugated perovskites, the PEA₂-PbX₄ perovskites explored in this work are not corrugated in either in-plane direction. Thus, they have a higher periodicity in both in-plane lattice directions which manifests itself in highly dispersive band frontiers along two reciprocal-lattice directions. As a consequence, corrugated API-PbX₄ shows low effective-mass band frontiers only along $\Gamma - Y$, whereas PEA₂-PbX₄ shows low effective masses along both $\Gamma - X$ and $\Gamma - Y$.

In traditional 3D HOPs such as MAPbX₃, valence and conduction band frontiers are comprised of X: p +Pb: $6s$ and Pb: $6p$ states, respectively.⁶⁰ While in principle, in the layered systems with conjugated organic cations explored in this work, API and PEA π and π^* states could contribute in the near-gap region, we find from the ion-projected band structure that the valence and conduction band frontiers are comprised of X: p +Pb: $6s$ and Pb: $6p$ states, respectively. This is very similar to the 3D MAPbX₃ HOPs. However, unlike 3D MAPbX₃ HOPs that have organic states far below (about 6 eV) and above the band frontiers,⁶⁰ API-PbX₄ and PEA₂-PbX₄ have flat, non-dispersive bands attributed to API and PEA₂ π and π^* orbitals within 1.0 to 2.0 eV of the band frontiers, as shown in Fig. 2.

Furthermore, due to the strong contributions of Pb-derived states to the band frontiers in API-PbX₄ and PEA₂-PbX₄, the spin-orbit interaction lowers the energy of conduction-band minimum states (see Fig. S5). This energy reduction of Pb: p conduction-band states is well known in Pb- and Sn-containing HOP and LHOP systems^{14,15,29,48} and attributed to the large mass of Pb atoms. Hence, SOC-related energy contributions are critical for correctly predicting the energetic ordering of states near the band-extrema and, in particular, to *qualitatively* explain the relative energy position of organic π and π^* states. In Fig. 2 (as well as Figs. S4 (a) and (b) and S5 (a) in the SI) we clearly show that once SOC is taken into account, the ion-resolved band ordering at the Γ -point conduction band minimum changes: The Pb: p states are lowered in energy relative to the API π^* states which remain unaffected by the spin-orbit interaction. As a result, we observe Pb: p character for all \mathbf{k} points throughout the BZ. In contrast, without the inclusion of SOC, a band inversion occurs at the Γ -point and the conduction band minimum would be attributed to mostly API π^* states. Hence, if SOC is neglected, electronic-structure calculations could, depending on transition matrix element amplitude, incorrectly predict that excitations from the Γ -point band frontiers result in charge separation between perovskite and API layers. This behavior is different from what has been observed for 3D MAPbX₃ HOPs, for which ion projection of the band frontiers remain the same, with X+Pb and Pb attributed to the valence and conduction band frontiers, respectively,⁶⁰ whether or not SOC is included. Finally, we note that the difference between HSE06+SOC and the PBE+SOC+ Δ_{HSE06} approach is minimal, and PBE+SOC+ Δ_{HSE06} calculations are a good basis for

293 optical response calculations. To this end we show in detail
 294 in the SI that for optical excitations energies below 5 eV, only
 295 small errors of under 0.5 eV are expected for spectral features.

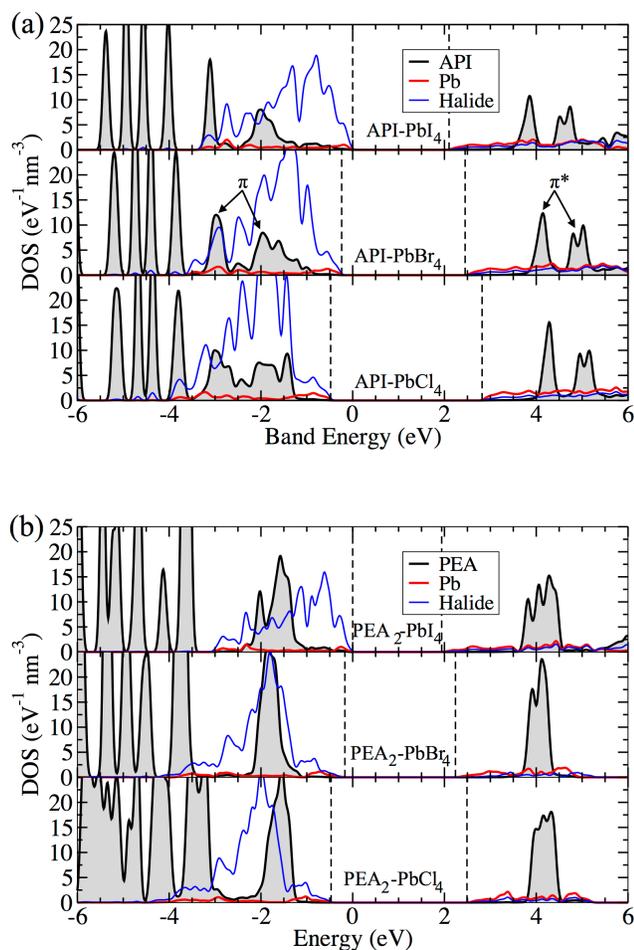


FIG. 3. (Color online.) The PBE+SOC+ Δ_{HSE06} ion-projected DOS of (a) API-PbI₄, API-PbBr₄, API-PbCl₄ and (b) PEA₂-PbI₄, PEA₂-PbBr₄, and PEA₂-PbCl₄. The energies of the Pb 5*d* states at -15.3 eV are used for alignment, and the valence band maxima of API-PbI₄ and PEA₂-PbI₄ are used as energy zero. Dashed lines mark the band extrema. Color coding: Pb (red), halide (blue), organic layer (shaded brown).

296 The ion-resolved density of states (DOS) in Fig. 3 illus-
 297 trates that in all six perovskite systems, the valence- and
 298 conduction-band frontiers are attributed to halide and Pb
 299 states, respectively. For this analysis, we aligned the Pb 5*d*
 300 states at -15.3 eV across the different materials. Importantly,
 301 Fig. 3 shows a reduction of the valence-band maximum in energy
 302 with decreasing halide mass: The valence band maxima
 303 of API-PbX₄ shift from 0.0, to -0.24 , and -0.48 eV for X
 304 = I, Br, and Cl, respectively. The same trend of the valence
 305 band maximum located at 0.0, -0.17 , and -0.47 eV occurs
 306 for the PEA₂-PbX₄ systems for X = I, Br, and Cl, respec-
 307 tively. This decrease can be understood by examining stan-

308 dard atomic ionization energies of halide atoms, with I, Br,
 309 and Cl having ionization energies of 10.45, 11.81, and 12.96
 310 eV (from the NIST Atomic Spectra Database Ionization Energ-
 311 ies Form).⁶¹ Since the valence-band maximum of each per-
 312 ovskite material in this work is attributed to halide *p*-states,
 313 our findings are commensurate with trends of these atomic
 314 ionization energies.

315 At the same time, this figure shows that organic π and π^*
 316 states are not affected by the changing halide mass and remain
 317 approximately aligned in both systems. The API π states ap-
 318 pear as broad peaks at -2.00 , -1.78 , and -1.40 eV for I, Br,
 319 and Cl, respectively. This broadening is due to static molec-
 320 ular disorder and coupling between organic molecular states.
 321 The lowest energy π^* states appears as sharp peaks centered
 322 around 3.87, 4.10, and 4.30 eV for I, Br, and Cl, respectively.
 323 The resulting $\pi - \pi^*$ gaps, defined as the energy differences
 324 of these peaks, are 5.87, 5.88, and 5.70 eV and show a width
 325 of about 0.5 eV from the broadening of the π^* state. The
 326 PEA₂-PbX₄ systems display a highest occupied π state peak
 327 spanning the range between -1.3 and -2.1 eV. A single low-
 328 est unoccupied π^* peak is located between 3.84 and 4.10 eV
 329 for all PEA₂-PbX₄ materials. This leads to $\pi - \pi^*$ gaps of
 330 5.39, 5.82, and 5.53 eV for I, Br, and Cl, respectively, with a
 331 width of about 1.0 eV. The variations in the $\pi - \pi^*$ gaps in the
 332 PEA₂-PbX₄ systems are attributed to differences in the exper-
 333 imental X-ray atomic structures of the organic layers used in
 334 the unit cells of this study. As we chose to relax the API-
 335 PbX₄ structures (due to the similarities of the relaxed and
 336 experimental API-PbBr₄ structures and the lack of available
 337 experimental data for API-Pb(I,Cl)₄) the $\pi - \pi^*$ gaps are uni-
 338 form across the choice of halide. We note that quasiparticle
 339 corrections computed within HSE06+SOC also produce an
 340 energy-dependent band dilation, not reproduced by the scissor
 341 approach. This increases the $\pi - \pi^*$ gaps of the API and PEA
 342 systems to about 6.1–6.3 eV, suggesting that $\pi - \pi^*$ optical
 343 transitions will occur well in the UV photon energy range.
 344 The PBE+SOC+ Δ_{HSE06} approximation captures the UV re-
 345 sponse of the intra-organic transitions, albeit at slightly lower
 346 energies compared to HSE06+SOC, and therefore provides a
 347 reasonable approximation for optical response calculations. It
 348 should be mentioned that, in reality, the absorption onset of
 349 such molecules is at lower energies due to large exchange en-
 350 ergy contributions. For example, benzene in an alcohol solu-
 351 tion has an absorption onset of about 4.8 eV.⁶² However, this
 352 is still in the UV energy range.

353 Figure 3 also shows that, due to a lower cation charge of
 354 +1 on PEA compared to +2 in API, the ratio of organic to
 355 inorganic density of states is higher in the PEA₂-PbX₄ struc-
 356 tures. This implies that, if organic-perovskite optical transi-
 357 tions are allowed, the PEA₂-PbX₄ systems have more possible
 358 charge-separation pathways under optical excitation. In ex-
 359 amining the ion-resolved density of states of API-PbX₄, it can
 360 be seen that the optical response below the 5.7 eV $\pi - \pi^*$ gap
 361 contains mostly transitions between perovskite-derived states.
 362 Only small contributions due to transitions from perovskite-
 363 to API-derived states are expected between the optical onset
 364 and 5.7 eV. This changes in the PEA₂-PbX₄ systems, where
 365 the PEA density of states amplitude in the valence and is about

equal to or greater than the perovskite density of states at the PEA π -state energy. Consequently, the optical response could have a large contribution from perovskite to PEA transitions at lower energies than the $\pi - \pi^*$ gap. This implies that if transitions between perovskite and PEA are optically allowed, the PEA₂-PbX₄ systems have more possible charge separation states available.

Finally, in the context of achieving charge separation between organic and perovskite layers upon optical excitation, we find that PEA₂-PbCl₄ is a particularly promising candidate. The ion-resolved DOS in Fig. 3 shows a pronounced peak associated with the organic molecule that is centered near 1.5 eV below the valence-band maximum. Not only is this peak higher in energy than another peak at -2 eV that is attributed to Cl ions, but it also is of the same magnitude, as discussed above. This energetic positioning of states suggests the strong potential for partial charge separation, generating holes in the PEA₂ π state and electrons in the conduction-band Pb:6*p* state. The actual probability of charge separation between layers, however, depends again on the dipole matrix elements for the corresponding optical transitions between these organic and perovskite states. This will be discussed next.

Optical Response: The ion-projected dielectric function $\epsilon_2(\omega)$ is illustrated in Fig. 4 for all considered materials. Here we distinguish between transitions among perovskite ions ('inorganic') and organic cations ('organic') by bundling them into the inorganic-inorganic, organic-organic, organic-inorganic and inorganic-organic subcategories. The first two correspond to intra-layer transitions and the latter two to inter-layer transitions. If the two sub-layers were to act as separate optically active materials, the amplitude of inter-layer $\epsilon_2(\omega)$ is vanishing. In the case of intra-layer optical excitation, these projections are finite.

By ion-resolving the imaginary dielectric function of API-PbX₄, we show that optical excitations below 4 eV are entirely dominated by intra-perovskite transitions, whereas inter-layer transitions contribute significantly to the optical response above 4 eV. As discussed above, this is because states in the vicinity of the gap are attributed entirely to perovskite states (Fig. 3). Absorption between API-derived states, with an onset around the $\pi - \pi^*$ gap, contributes weakly to the overall optical response even in the UV energy range due to a low relative API- π density of states compared the halide density of states in the valence band. Figure 4 also shows that transitions from PbX₄ to API states are responsible for a significant portion of the optical response in the UV energy range, and thus partial electron and hole separation occurs between the API and PbX₄ layers. However, this partial separation has little utility for optoelectronic applications requiring charge separation for visible light energy excitations.

The PEA₂-PbX₄ systems demonstrate a much stronger intra-organic optical response within the PEA layers, along with significant inter-layer absorption in the UV energy range. As with API-PbX₄, the near-gap and visible energy range of the spectra is governed by intra-perovskite optical response. Around the $\pi - \pi^*$ gap, a large peak appears in the imaginary dielectric function which is attributed to the intra-PEA optical transitions and transitions from PbX₄ to PEA states. Transi-

tions from PbX₄ to PEA states appear at higher energies at lower halide masses, corresponding to the increased VBM- π^* gap by the decrease in the valence band energy. In PEA₂-PbI₄, strong transitions are observed from PbI₄ to PEA states at lower energies than those between PEA states, leading to the same partial charge separating activity seen in API-PbX₄ above 4 eV. In PEA₄-PbBr₄, the contributions due to transitions from PbBr₄ to PEA and PEA to PbBr₄ are roughly equal in the 4 to 5 eV photon range, leading to a cancellation in partial charge separation character due to hybridization. PEA₂-PbCl₄ shows a change in behavior: The optical response between 3.5 and 4 eV largely arises from intra-perovskite transitions and contributions from PEA to PbCl₄ states, partially separating holes to the PEA layer and electrons to the PbCl₄ layer. This behavior is due to the proximity of the PEA π states to the PbCl₄ attributed valence band maximum, leading to inter-layer transitions closer to the absorption onset. However, overall, in PEA₂-PbX₄, where the organic optical activity is more significant compared to API-PbX₄, partial charge separation only occurs in the UV energy range.

In all three LHOP API-PbX₄ compounds, excitonic effects are expected to be stronger compared to their 3D HOP MAPbX₃ counterparts owing to quantum and dielectric confinement effects.³⁰ This increased binding energy was first explained by the works of Rytova and Keldysh, who separately established the theory of quantum confinement of charge carriers and the Coulomb interaction in low dimensional systems.^{63,64} This was further explored in layered semiconductors by Hanamura and layered perovskites by Ishihara and Koutselas.⁶⁵⁻⁶⁸ In 3D HOPs such as MAPbI₃, MAPbBr₃, and MAPbCl₃, the high-frequency dielectric constants ϵ_∞ are about 4-7.^{48,69-71} MAPbX₄ also has highly dispersive band frontiers, leading to a low reduced electron-hole mass of about 0.1*m*₀.⁷² Using a simple Wannier-Mott model, the exciton binding energy is in the range of 25 to 85 meV. As determined in experiments and predicted by theory, the low-frequency dielectric constants are also large ($\epsilon_s > 20$), which enhances the screening of the electron-hole Coulomb potential.^{29,72-75} Given the API-PbBr₄ electronic structure determined in this work, the high-frequency dielectric constant is determined to be 3.94 by density-functional perturbation theory (DFPT) and the reduced electron-hole mass at the band frontiers is approximately 0.610*m*₀, based on an averaged parabolic fit to the dispersive, in-plane, $Y \rightarrow G$ and $Y \rightarrow A$ directions. This leads to a Wannier-Mott binding energy of 525 meV, which is an order of magnitude higher compared to the 3D counterparts. The lower high-frequency dielectric constants predicted by DFPT range from 3.47 to 4.76 for the LHOP systems (see Tab. S2) and originate from the alternating low and high values of ϵ_∞ between layers averaged over the unit cell volume.⁷⁶ This leads to an average dielectric constant that is lower than those typically measured and calculated for 3D HOPs.^{29,30}

The excitation energies of lone API molecules in air are calculated in the Gaussian suite⁷⁷ to determine if the organic optical response will comprise a significant portion of the optical response near the perovskite absorption edge. The HSE, B3LYP, and CAM-B3LYP functionals are used to calculate the homo-lumo gaps of 5.60, 5.84, and 8.05 eV respec-

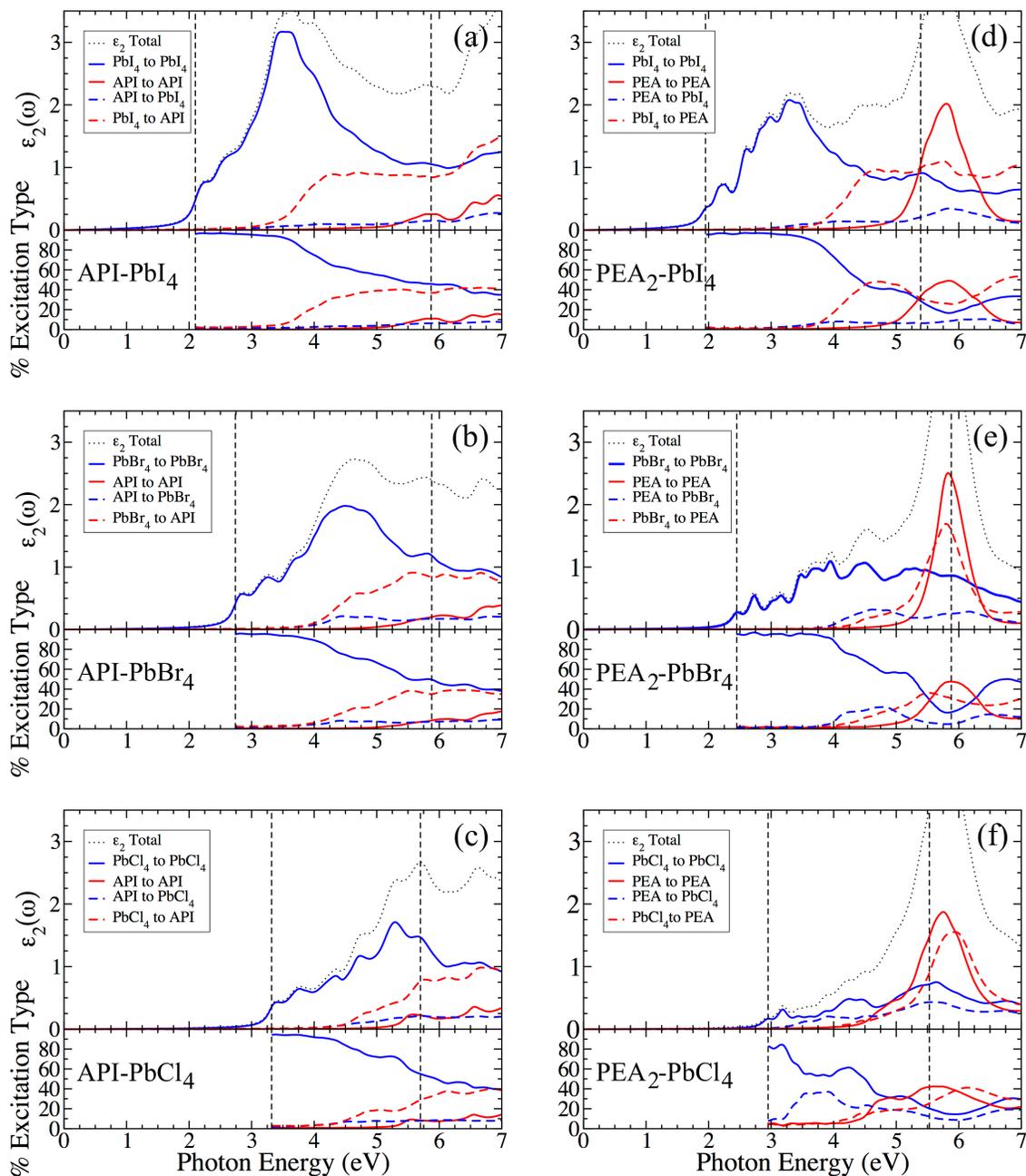


FIG. 4. (Color online.) The ion-resolved imaginary dielectric functions of (a) API-PbI₄, (b) API-PbBr₄, (c) API-PbCl₄, (d) PEA₂-PbI₄, (e) PEA₂-PbBr₄, and (f) PEA₂-PbCl₄. The color coding indicates the resolution of ϵ_2 along specific ion-to-ion transitions, which are (in valence ions \rightarrow conduction ions notation) perovskite \rightarrow perovskite (blue, solid), organic \rightarrow organic (red, solid), organic \rightarrow perovskite (blue, dashed), perovskite \rightarrow organic (red, dashed), and all (black, dotted). The bottom panels show the percent that each type of transitions contributes to the total ϵ_2 as a function of photon energy.

482 tively in the singlet-relaxed geometry. The HSE and B3LYP
 483 agree very well with the π - π^* gap found in API-PbX₄ at the
 484 PBE+SOC+ Δ_{HSE06} level of theory. Excitation energies are
 485 calculated using time-dependent DFT and are found to be
 486 5.42, 5.23, and 5.75 eV within the HSE, B3LYP, and CAM-
 487 B3LYP functionals, respectively. These results suggest that
 488 the excitonic absorption onset of the API spacer will not oc-

489 cur near the perovskite excitonic absorption edge.

490 Strong excitonic effects and, hence, large exciton bind-
 491 ing energies are predicted for the API-PbX₄ materials from
 492 first principles, with values comparable to available experi-
 493 mental data for LHOP systems. For API-PbX₄, we show in
 494 Fig. 5 that excitonic effects significantly influence the optical-
 495 absorption spectra. The gradual absorption onset observed in

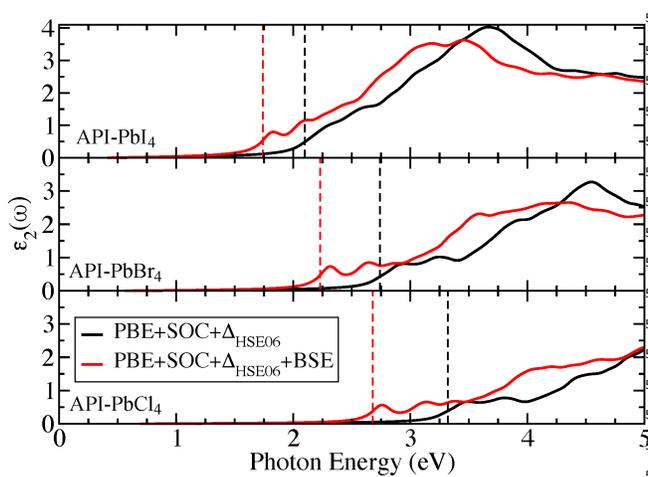


FIG. 5. (Color online.) Imaginary part of the dielectric function of API-PbI₄ (top), API-PbBr₄ (middle), and API-PbCl₄ (bottom) with (red lines) and without (black lines) excitonic effects. The PBE+SOC Kohn-Sham energies and states are used as input to the BSE and the single-particle band gap is shifted to the HSE06+SOC value. That band gap and the lowest excitation from the BSE are marked by vertical black and red dashed lines, respectively.

the single-particle dielectric function becomes a pronounced excitonic peak, red-shifted to lower energy, that is associated with the lowest-energy electron-hole bound state. In addition, there is also a significant red shift of broad high-energy peak structures between 3.5 eV and 4.5 eV, resulting in strongly increased absorption at lower energies. In our calculations, the energy difference of the onsets of single-particle and BSE spectrum correspond to the binding energy of the lowest electron-hole pair. The high computational cost of the BSE calculations in this work, due to large unit cells and inclusion of spin-orbit coupling, does not allow a dense enough multiple \mathbf{k} -point sampling⁷⁸ to provide fully converged results for this quantity. Given the choice of \mathbf{k} -point mesh, we estimate that our numbers are within 100 meV of the converged result (see SI figure S6). From our data we extract ≈ 357 meV (see Fig. 5) for the exciton-binding energy of API-PbI₄, which is the smallest value for the three API-PbX₄ compounds studied in this work. API-PbBr₄ shows a stronger exciton binding energy due to the lower dielectric constant compared to API-PbI₄, and consequently a stronger red shift of the onset by ≈ 505 meV. Finally, the strongest excitonic red shift in the optical spectrum of ≈ 638 meV is predicted for API-PbCl₄, with the lowest high-frequency dielectric constant. High-frequency dielectric constants are slightly overestimated as they are calculated at the PBE+SOC level of theory. However, from test calculations we estimate that increasing the band gap to the experimental value would decrease the dielectric constant by less than 15%. Since we do not have accurate band gap data to compare with for the API-PbX₄ materials, we use the PBE+SOC high-frequency dielectric constant as a good ap-

proximation.

The predicted exciton binding energies and relative positions of spectral peaks are in good agreement with available experimental data of layered perovskite systems.⁴⁷ Wang *et al.* measured exciton binding energies of 218 meV in hexadecammonium-lead bromide (HA)₂PbBr₄,⁷⁹ Blancon *et al.* measured binding energies of 380, 270, and 220 meV in $n = 1$, $n = 2$, and $n > 2$ -layered (BA)₂(MA)_{*n*}Pb_{*n*}I_{3*n*+1},³⁹ and Ishihara *et al.* calculated a binding energy of 320 meV in $n=1$ layered PbI₄ octahedra with no organic spacer.⁶⁶ As a model function relying on a single, material-averaged, dielectric constant is used to compute the screened Coulomb interaction between electrons and holes, we do not account for the local field effects arising from the high spatial variability of the dielectric constant in LHOPs.^{29,30} More precise techniques such as including the full inverse dielectric tensor $\epsilon_{G,G'}(q)^{-1}$ or semi-classical and semi-empirical methods that describe dielectric constant fluctuations can be used for a higher degree of accuracy.^{29,80–82} These high binding energies are also potentially detrimental to solar cell applications, which rely on splitting of electron-hole pairs. Investigations by Smith *et al.* have shown that the introduction of halogens by I₂ intercalation into the organic layer strongly reduces binding energy and the dielectric confinement of the layered perovskite systems,⁸³ potentially lowering the exciton binding energy of LHOPs which is preferable for photo-voltaic application.

II. CONCLUSIONS AND FUTURE DIRECTION

This computational study predicts that the optical response of single-layered lead-halide perovskites with single- π -conjugated organic layers API and PEA₂ is dominated by intra-perovskite optical excitations in the visible energy range. A partial charge separation between the organic perovskite states can only be achieved at UV energies. Given these results, we conclude that single-layered PbX₄ LHOP systems with π -organic cation spacing layers composed of moieties with single aromatic rings act as one optically active perovskite material. Transitions involving both layers only occur at UV photon energies. Importantly, the lack of π and π^* states near the band extrema causes transitions in the visible energy range to be contained within the perovskite layer, meaning all electron-hole generation for optoelectronic applications in this energy range will be localized to the PbX₄ octahedral layers. At UV energies, significant electronic delocalization and charge separation is allowed, however the corresponding excitation energies are close to or above the ionization energy of perovskite systems.

The natural follow-up question is: How can charge separation be further achieved in layered hybrid perovskite systems? The first item that must be addressed is the $\pi - \pi^*$ gap of the conjugated groups. As discussed above, the absorption onset of single aromatic ring moieties occurs well below the homolumo gap due to large exciton binding energies on the order of electron volts.⁸⁴ Benzene, with an optical onset of 4.8 eV experimentally and between 4.7 and 6.9 eV theoretically by PBE0+BSE and GW+BSE calculations,^{62,85} has a predicted

581 homo-lumo gap in solution of between 4.5 and 6 eV.⁸⁶ Like-
 582 wise, imidazole has a range of predicted excitation energies
 583 between 5.61 and 6.96 eV.⁸⁵ Thus, the interplay between the
 584 homo-lumo gap and the optical gap should be carefully con-
 585 sidered in further engineering of layered perovskites for inter-
 586 layer charge separation application. Ideally, the homo-lumo
 587 gap can be lowered by adding more conjugated groups such
 588 as aromatic rings to the system. For example, layered per-
 589 ovskites with naphthalene groups have been investigated ex-
 590 perimentally and have shown signs of exciton energy trans-
 591 fer between perovskite and organic layers.^{41,42} Secondly, the
 592 orbital overlap between the layers must be improved to in-
 593 crease the amplitude of the inter-layer transition dipole ma-
 594 trix elements. Larger overlap could be achieved by includ-
 595 ing heavier elements, such as chlorine, in the organic layer
 596 which has been recently explored experimentally.^{36,38,87} Our
 597 future studies of such compounds will include organic-PbX₄
 598 ion-projected band structures and densities of states to map
 599 the effects of decreased homo-lumo organic gap and organic
 600 halogenation.

601 Currently, $n = 1$ LHOPs with single conjugated rings face
 602 challenges as effective solar cell materials but show promise
 603 in a wide range of optoelectronic application. Quantum con-
 604 finement of the perovskite layer increases the gap relative to
 605 the 3D HOPs and thus reduces the absorption range of the ma-
 606 terial in the visible optical spectrum. LHOPs with $n > 1$ help
 607 to decrease the gap,³² but at the cost of reducing the density of
 608 states of, and degree of optical coupling to, the organic lattice.
 609 Secondly, minimal π -stacking is observed in these systems,
 610 leading to highly localized electron and hole states in the or-
 611 ganic layer. This in turn results in a high effective mass, low
 612 mobility in the form of incoherent hopping, and large bind-
 613 ing energies of electron-hole pairs. Improving π -stacking of
 614 the organic conjugated layer in LHOPs is a promising future
 615 research direction, to achieve improvements.⁸⁸ Recent inves-
 616 tigations have also shown that interfacing 2D LHOPs with
 617 3D HOPs can lead to increased photovoltaic efficiency in Sn-
 618 based systems, opening the intriguing question of whether this
 619 can be done with Pb-based systems as well.⁸⁹ Besides appli-
 620 cations as solar cells, $n = 1$ layered perovskites have shown
 621 promise as light emitters.⁹⁰ Resonant coupling between the
 622 organic and perovskite layered of $n = 1$ systems opens the
 623 possibility of engineering the emission wavelength and inten-
 624 sity as a function of LHOP stoichiometry.^{42,91}

625 It is important to note that everything studied in this
 626 manuscript is related purely to absorption in the singlet spin
 627 state. Thus, nothing is said about relaxation in the excited
 628 state or emission in the explored LHOP systems. Both triplet
 629 and singlet energy levels and their post-optical absorption dy-
 630 namics are fundamental to understanding how organic com-
 631 pounds behave in the excited state. The interplay between
 632 perovskite band energies and the organic singlet and triplet
 633 states must be understood to determine excited state charge
 634 transport, ion dynamics, and recombination in LHOPs with
 635 conjugated organic layers. The combination of methods in
 636 this work for determining optical absorption properties and
 637 methods such as time-dependent density functional theory and
 638 molecular dynamics can be used to predict and disentangle

639 the full optical excitation and relaxation process of conjugated
 640 LHOP materials.

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664 COMPUTATIONAL DETAILS

665 DFT calculations, using the projector-augmented wave method, are
 666 performed with the Vienna *Ab-Initio* Simulation Package (VASP).⁹²⁻⁹⁵
 667 The generalized-gradient approximation of Perdew, Burke, and Ernzerhof
 668 (PBE)⁹⁶ is used to describe exchange and correlation (XC). Kohn-Sham wave
 669 functions are expanded into a plane-wave basis with an energy cutoff of 500
 670 eV and the Brillouin zone (BZ) is sampled using a Γ -centered $4 \times 4 \times 2$ \mathbf{k} -
 671 point mesh. With this setup, total energies of the API-PbX₄ structures are
 672 converged to within 5 meV per formula unit. Equilibrium positions of all
 673 atoms, cell volumes, and unit cell parameters are optimized by minimizing the
 674 external pressure and Hellman-Feynman forces to below a threshold of 10^{-2}
 675 eV/Å using the PBEsol XC functional⁹⁷ and an increased plane-wave cutoff
 676 of 900 eV. The use of PBEsol is based on previous studies where lattice pa-
 677 rameters of hybrid perovskite materials are predicted to high accuracy.⁵⁸ The
 678 symmetries of the experimentally determined unit cell are preserved in the
 679 first-principles atomic position and cell geometry relaxation. Band structures,
 680 ion-resolved densities of states (DOS), and ion-resolved optical-absorption
 681 spectra are calculated, taking spin-orbit coupling (SOC) into account.⁹⁸ The
 682 high-frequency dielectric constant ϵ_∞ is calculated using density functional
 683 perturbation theory on a $5 \times 5 \times 2$ Γ -centered \mathbf{k} -point mesh for API-PbX₄
 684 (see supplemental material Fig. S1). Band gaps are determined using the
 685 Heyd-Scuseria-Ernzerhof (HSE06) hybrid XC functional⁹⁹ with a fraction of
 686 $\alpha=0.25$ exact exchange. Due to the high computational cost of including
 687 SOC in hybrid functional calculations, these are performed using a $2 \times 2 \times 2$
 688 Γ -centered \mathbf{k} -point mesh.

689 Linear optical response, described by the components of the complex
 690 frequency-dependent dielectric tensor $\epsilon_2^{\alpha\beta}(\omega)$, where α and β are Cartesian
 691 coordinates, is computed using the Ehrenreich-Cohen formula:^{76,100}

$$692 \epsilon_2^{\alpha\beta}(\omega) = \frac{8\pi^2 e^2}{\Omega} \sum_{c\nu k} \frac{\langle \phi_{c\nu} | \hat{p}_\alpha | \phi_{\nu k} \rangle \langle \phi_{\nu k} | \hat{p}_\beta | \phi_{c\nu} \rangle^*}{(\epsilon_{c\nu} - \epsilon_{\nu k})^2} \delta(\epsilon_{c\nu} - \epsilon_{\nu k} - \hbar\omega) \quad (1)$$

692 Here, ϵ_{ck} and ϵ_{vk} are the conduction and valence band energies of the single-
693 particle states at electronic wave vector \mathbf{k} , along with their respective Kohn-
694 Sham wave functions ϕ_{ck} and ϕ_{vk} . \hat{p}_β is the Cartesian component of the mo-
695 mentum operator and Ω is the volume of the unit cell. We use PBE+SOC
696 Kohn-Sham energies and wave functions and a scissor shift to adjust the en-
697 ergies of the conduction bands to the HSE06+SOC band gap (referred to as
698 PBE+SOC+ Δ_{HSE06}). The transition-matrix elements in Eq. (1) are computed
699 using the VASP code.⁷⁶

700 We also compute the ion- and angular-momentum resolved optical re-
701 sponse by weighting the transition-matrix element for a given transition using
702 the projection P_{lmnk}^N of the wave function ϕ_{nk} on a spherical harmonic Y_{lm} for
703 a given ion N , with m and l being the magnetic and orbital quantum number,
704 respectively.¹⁰¹ The sum of P_{lmnk}^N over all N , l , and m equals to one for each
705 wave function ϕ_{nk} . This turns Eq. (1) into:

$$\epsilon_2^{\alpha\beta}(\omega) = \frac{8\pi^2 e^2}{\Omega} \sum_{cvk} \left(\sum_{N,l,m} P_{lmnk}^N \right) \frac{\langle \phi_{ck} | \hat{p}_\alpha | \phi_{vk} \rangle \langle \phi_{vk} | \hat{p}_\beta | \phi_{ck} \rangle^*}{(\epsilon_{ck} - \epsilon_{vk})^2} \delta(\epsilon_{ck} - \epsilon_{vk} - \hbar\omega) \quad (2)$$

706 Restricting the sum in parentheses to certain ions, angular-momentum com-
707 ponents, or bands (e.g. n being v or c when resolving valence or conduction
708 states), allows us to compute ion- and angular-momentum resolved optical
709 response.

710 In addition, we study excitonic effects on the dielectric functions of API-
711 PbX₄ from the solution of the Bethe-Salpeter equation (BSE)^{78,102,103} for
712 the optical polarization function. The large computational cost of this ap-
713 proach requires us to restrict these calculations to a $4 \times 4 \times 2$ \mathbf{k} -point grid. A
714 small random shift of this grid lifts degeneracies and, on DFT level, allows us
715 to reproduce dielectric functions calculated on a well-converged Γ -centered
716 $8 \times 8 \times 2$ \mathbf{k} -point grid (see supplemental information, Fig. S6). The absorp-
717 tion edges from shifted and well-converged Γ -centered \mathbf{k} -point grids disagree
718 by about 100 meV. Converging exciton-binding energies, defined as the dif-
719 ference between the lowest optical and the lowest single-particle excitation
720 energies, to high accuracy requires much denser \mathbf{k} -point sampling near the
721 band extrema,⁷⁸ which is beyond the scope of this study. Hence, estimates
722 for exciton-binding energies reported here have error bars of about 100 meV.

723 The screened electron-hole Coulomb interaction W in the BSE kernel is

724 calculated using the model dielectric function proposed by Cappellini *et al.*¹⁰⁴
725 The dielectric constant used in the model dielectric function is the average
726 of the diagonal components of the high-frequency dielectric tensor $\epsilon_\infty^{\alpha\beta}$ cal-
727 culated by density functional perturbation theory (DFPT) (see supplemental
728 information Tab. S1), representing the average dielectric response of the layer-
729 ed material. It has been extensively shown that the organic and perovskite
730 layers of LHOPs have spatially resolved dielectric constants of ≈ 2.5 and 5
731 respectively,^{29,30} and thus this work will use the spatially averaged dielec-
732 tric constant determined by DFPT as an approximate value.⁷⁶ Other methods
733 are available in the literature to handle this spatial variability of the dielec-
734 tric constant.^{29,80,81} In this work, the BSE is solved as an eigenvalue problem
735 in the Bloch basis^{78,103} of the excitonic Hamiltonian, and using the Tam-
736 Dancoff approximation:

$$H_{cvk}^{c'v'k'} = (\epsilon_{ck} - \epsilon_{vk}) \delta(cc') \delta(vv') \delta(kk') - W_{cvk}^{c'v'k'} + 2\bar{V}_{cvk}^{c'v'k'} \quad (3)$$

737 Here, band energies ϵ_{ck} and ϵ_{vk} from the PBE+SOC+ Δ_{HSE06} level of the-
738 ory are used. Non-interacting electron-hole pairs with energies up to 5 eV
739 (applied to the PBE+SOC band structure) are used to compute the excitonic
740 Hamiltonian. These include, in (nv,nc,nk) format: API-PbI₄ (112,48,32),
741 API-PbBr₄ (110,40,32), and API-PbCl₄ (104,32,32). Matrix elements $W_{cvk}^{c'v'k'}$
742 of the attractive electron-hole Coulomb potential and $\bar{V}_{cvk}^{c'v'k'}$ of the local repul-
743 sive Coulomb potential are computed using spin-polarized Kohn-Sham
744 wave functions. The eigenvalues E^λ of $H_{cvk}^{c'v'k'}$ describe optical λ th excita-
745 tion energies, with excitonic states A_{cvk}^λ being the eigenvectors, and they can
746 be determined by solving the eigenvalue equation for $H_{cvk}^{c'v'k'}$. Dielectric func-
747 tions, including excitonic effects, are calculated from the excitonic Hamil-
748 tonian in Eq. (3) using a time-propagation technique.^{105,106} The rigid band
749 gap shift is added to the diagonal of the excitonic Hamiltonian, increasing
750 the energy window of the excitonic Hamiltonian from 5 eV to $5 + \Delta_{\text{HSE06}}$ eV.
751 For the above-mentioned energy window of 5 eV, 5594 time steps of 0.0022
752 per eV are required. The lowest excitation energies are found by applying a
753 conjugate-gradient scheme to iteratively compute the lowest eigenvalues. All
754 these calculations are carried out using the BSE implementation discussed in
755 Refs. 78 and 107.

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