Molecular behavior of zero-dimensional perovskites

Jun Yin, Partha Maity, Michele De Bastiani, Ibrahim Dursun, Osman M. Bakr, Jean-Luc Brédas, Omar F. Mohammed

Low-dimensional perovskites offer a rare opportunity to investigate lattice dynamics and charge carrier behavior in bulk quantum-confined solids, in addition to them being the leading materials in optoelectronic applications. In particular, zero-dimensional (0D) inorganic perovskites of the CsPbX₄ (X = Cl, Br, or I) kind have crystal structures with isolated lead halide octahedra (PbX₆)⁴⁻ surrounded by Cs⁺ cations, allowing the 0D crystals to exhibit the intrinsic properties of an individual octahedron. Using both experimental and theoretical approaches, we studied the electronic and optical properties of the prototypical 0D perovskite Cs₄PbBr₆. Our results underline that this 0D perovskite behaves akin to a molecule, demonstrating low electrical conductivity and mobility as well as large polaron binding energy. Density functional theory calculations and transient absorption measurements of Cs₄PbBr₆ perovskite films reveal the polaron band absorption and strong polaron localization features of the material. A short polaron lifetime of ~2 ps is observed in femtosecond transient absorption experiments, which can be attributed to the fast lattice relaxation of the octahedra and the weak interactions among them.

INTRODUCTION

All-inorganic metal-halide perovskites have attracted a great deal of attention over the last few years owing to their tunable band gap (1, 2), high photoluminescence quantum yield (3), and narrow emission linewidth, enabling promising optoelectronic applications, such as light-emitting diodes (4), low-threshold lasers (5, 6), and photodetectors (7). Among these perovskite materials, three-dimensional (3D) inorganic perovskites with the general formula APbX₃ (A = Cs⁺ or Rb⁺ and X = Cl, Br, or I) have been extensively explored (8–13). Three-dimensional perovskites are composed of an extended network of corner-sharing [PbX₆]⁴⁻ octahedra with A residing in the cavities of this network. However, under operating conditions, these 3D perovskites suffer from phase transformation and instability, including surface hydration and ion migration; thus, their reduced-dimensionality counterparts are being increasingly investigated, especially for optoelectronic applications (14, 15). Under Cs⁺-rich synthesis conditions, the 0D phase of Cs₄PbX₄ (X = Cl, Br, or I) can be obtained. This phase exhibits a crystal structure with isolated octahedra [PbX₆]⁴⁻ separated by Cs⁺ ions (16). It should be noted that the 0D perovskites defined here are different from the morphological 0D nanoparticles or quantum dots obtained from 3D perovskites. This specific structure of 0D perovskites is expected to give rise to interesting electronic and optical properties that largely remain to be characterized (17).

Early work on 0D perovskites focused mainly on their fundamental optical absorption and photoluminescence properties and attempted to distinguish their emission properties from those of 3D-like compounds (18–24). These studies have demonstrated that, unlike 3D and other low-dimensional perovskites, the optical characteristics of 0D Cs₄PbX₄ are determined by transitions between electronic states of the Pb²⁺ ions, and their photoluminescence results from the radiative decay of Frenkel-type excitons at Pb²⁺ sites (19). Thus, the separated [PbX₆]⁴⁻ octahedra in 0D perovskites prevent significant interactions among Pb²⁺ ions, leading to the generation of optical properties similar to those of individual octahedra. Recently, the intriguing crystal phase and optical properties of 0D perovskites motivated many experimental groups to fabricate pure single crystals and nanocrystals. For example, the nanocrystals of 0D Cs₄PbBr₆ perovskites have been obtained with controlled sizes by using solution-processed synthesis (25–28).

The complete isolation of the octahedra is expected to lead to strong quantum confinement and electron-phonon interactions that can cause exciton localization and self-trapping (29), as well as small polaron formation upon charging. Thus, these 0D perovskites represent ideal platforms for fundamental photophysical studies of photogenerated excitons, polarons, and charge carriers. Here, we show that Cs₄PbBr₆ exhibits molecular behavior in terms of charge carrier transport and large polaron binding energies. The calculated positive/negative polaron absorption bands of charged 0D units are consistent with experimental broadband photoinduced absorption (PIA) data in the same spectral region indicating a short lifetime of 2 ps. Such a polaron lifetime is reproduced via an analysis of the decay of charge populations for polaronic states, using nonadiabatic molecular dynamics (NAMD) simulations.

RESULTS AND DISCUSSIONS

To better understand the zero-dimensionality effects on the structural and electronic properties of Cs₄PbBr₆, we also include results on the 3D CsPbBr₃ perovskite, which contains the same elements. As shown in Fig. 1 (A and B), CsPbBr₃ has the orthorhombic phase (Pnam) with corner-sharing PbBr₆ octahedra, whereas Cs₄PbBr₆ shows the rhombohedral phase (R3c), which can be described as isolated [PbBr₆]⁴⁻ octahedra bridged by Cs⁺ cations with an average distance of ~10 Å. Starting from the experimental lattice parameters of CsPbBr₃ (a = 8.24 Å, b = 11.74 Å, and c = 8.20 Å) and Cs₄PbBr₆ (a = b = 13.72 Å and c = 17.30 Å), we further optimized their crystal structures at the density functional theory (DFT) generalized gradient approximation (GGA)/Perdew-Burke-Ernzerhof (PBE) level; the resulting lattice constants for CsPbBr₃ are, a = 8.54 Å, b = 11.91 Å, and c = 8.21 Å; and for Cs₄PbBr₆, a = b = 14.08 Å and c = 17.56 Å. The calculated electronic bands and projected density of states are shown in Fig. 1 (C and D). We first compare the band gaps calculated at the GGA/PBE level (this method has been shown to reproduce the band gaps of 3D perovskites well, although this is related to error cancellations) (30). CsPbBr₃ is calculated to exhibit a direct band gap (E_g = 2.13 eV) at the Γ point,
which is slightly smaller than the experimental optical band gap of 2.25 eV (31). Cs₄PbBr₆ also displays a direct band gap at the G point but with a much larger value (E₉ = 3.88 eV). This latter result agrees well with both the recently reported experimental band gap of 3.95 eV (20, 25) and the value of 3.99 eV calculated at the GGA/PBE level (25). The valence and conduction bands are seen to flatten considerably when switching from the 3D to the 0D perovskite, which is consistent with the band gap increase upon decreasing structural dimensionality (29). We note that, when spin-orbit coupling (SOC) effects are included in the electronic band structure calculations, the valence band curvatures are almost unchanged but with increased conduction band degeneracies and largely reduced band gaps; for Cs₄PbBr₆ in particular, several conduction bands appear at approximately 3.2 eV, which are ~0.8 eV below the other conduction bands. In analogy to CsPbBr₃, the conduction band minimum (CBM) of Cs₄PbBr₆ is mainly composed of Pb-6p and Br-4p states, whereas the valence band maximum (VBM) consists of both Pb-6s and Br-4p states. However, these Pb-6s, 6p, and Br-4p atomic orbitals are disconnected between octahedra because of the isolation of the [PbBr₆]⁶⁻ octahedra in the electronic zero dimensionality of the structure, which is also fundamentally responsible for the large band gaps of 0D perovskites.

The different dispersive features in the conduction and valence bands of the 3D CsPbBr₃ and 0D Cs₄PbBr₆ have important implications regarding carrier effective masses. On the basis of the VBM and CBM around the Γ point, for CsPbBr₃, the calculated hole effective mass is mₓ = 0.131 m₀ along the Γ→Y (−0.5, 0.0, 0.0) direction and mₓ = 0.135 m₀ along Γ→Z (0.0, 0.0, 0.5); the electron effective mass is slightly larger, with mₑ = 0.149 m₀ (Γ→Y) and mₑ = 0.142 m₀ (Γ→Z), which agrees well with earlier theoretical results (32). In contrast, Cs₄PbBr₆ shows nearly nondispersive transport along all directions in the electronic bands, which results in heavy charge carriers. In addition, Cs₄PbBr₆ shows 8.68 × 10⁻⁸ S/m electrical conductivity (σ) in the absence of light irradiation, almost one order of magnitude smaller than CsPbBr₃ (7.71 × 10⁻⁷ S/m) (fig. S1A), which agrees well with calculated values of σ/t for both holes and electrons [Cs₄PbBr₆, 2 × 10¹⁸ to 5 × 10¹⁸ (ohms·ms)⁻¹ versus CsPbBr₃, 3 × 10¹⁹ to 6 × 10¹⁹ (ohms·ms)⁻¹] under the same charge carrier concentration of 10²¹ cm⁻³ (see fig. S1B). This is also consistent with the ultralow photocurrent observed in recent experimental work (28), and shows that ion transport has little contribution to the electrical conductivity in 0D perovskites; thus, the low electrical conductivity of Cs₄PbBr₆ is dominated by electrons and/or holes. Overall, the intrinsic large band gap, heavy charge carriers, and low electrical conductivity of 0D perovskites limit their application in photovoltaic devices.

The differences in crystal phases and band structures of CsPbBr₃ and Cs₄PbBr₆ also generate different absorption spectra and exciton wave function features. Figure 1 (E and F) compares the optical absorption spectra of CsPbBr₃ and Cs₄PbBr₆ calculated at the PBE/SOC level with and without electron-hole interactions [details can be found in Fig. 1].
in the DFT calculations section and in the study of Yin et al. (33). In both cases, the main interband electronic transitions related to Pb$^{2+}$ $(6s)\text{Br}^- (4p)\rightarrow \text{Pb}^{2+} (6p)$ at the $\Gamma$ point contribute to the higher-energy absorption continuum. Once electron-hole pair interactions are included, in the case of Cs$_4$PbBr$_6$, the excitonic absorption is weak and the exciton wave function is delocalized over several crystal lattices, which is consistent with its small exciton binding energy (19 to 62 meV) (34, 35). For Cs$_8$PbBr$_6$, the electronic zero dimensionality results in strong quantum confinement, which increases electron-hole interactions and leads to a strong excitonic peak at 3.3 eV and exciton localization on a single [PbBr$_6$]$^{4-}$ octahedron (Fig. 1F). This excitonic peak has been observed in previous experimental absorption measurements at low temperatures (22).

The idea that the weak interactions between neighboring octahedra in 0D crystals cause their properties to be similar to those of individual units is confirmed by time-dependent DFT (TDDFT) calculations on a single Cs$_8$PbBr$_6$ unit. These calculations can reproduce the experimental absorption and capture the absorption features of the Cs$_8$PbBr$_6$ crystal (see Fig. 2A), with a main absorption peak at 320 nm and continuous absorption below 300 nm. Thus, this confirms that a single [PbBr$_6$]$^{4-}$ octahedron reflects the electronic and optical properties of the 0D crystals. In addition, a single unit is an ideal model to study the “molecular” behavior of 0D perovskites, for instance, with regard to the polaronic properties. Upon addition of a charge to highly polar crystals, such as perovskites (36, 37), the strong Coulomb interactions between the excess charge and the lattice ions enhance the electron-vibration couplings (38). When the excess charges are spatially confined to a volume of approximately one unit cell or less, they are referred to as small polarons, which have been observed in many conjugated polymers upon photo-, electro-, or chemically induced doping (39–41). As shown in Fig. 2B, once an electron is removed from a single Cs$_8$PbBr$_6$ unit, the Pb–Br bond length greatly shortens (from 3.10 to 2.69 Å), and the hole spin density localizes on the Pb atom and the surrounding six Br atoms, indicating the formation of a positively charged polaron (Pb$^{2+}$). The addition of electrons to the single unit leads to a strongly localized spin density around Pb$^{2+}$ and large repulsive interactions between Pb and two Br atoms, which markedly elongates these two Pb–Br bonds (from 3.10 to 5.34 Å). Adding an electron to the continuous absorption band below 400 nm, these positive/negative polaronic states (see Fig. 2, B and C) present a new broad absorption feature in the spectral range of 450 to 800 nm, which can thus be assigned to polaron absorption.

To further confirm the presence of polarons in 0D perovskites, we performed femtosecond transient absorption (TA) measurements on Cs$_8$PbBr$_6$ and Cs$_4$PbBr$_6$ thin films. The TA spectra of the Cs$_8$PbBr$_6$ and Cs$_4$PbBr$_6$ films under identical experimental conditions at different time delays are shown in Fig. 3 (A and B). Here, negative features in the TA spectra correspond to ground-state bleaching (GSB), and broad positive features correspond to PIA, mainly because of the formation of polarons. Similar to the TA spectrum of Cs$_8$PbBr$_6$, following the excitation wavelength at 310 nm (that is, above the band gap of both samples), the negative band at approximately 515 nm can be attributed to the GSB of the films owing to the depletion of the ground-state carriers to excited states. A new positive broadband appears above 530 nm in the spectrum of the Cs$_8$PbBr$_6$ film owing to polaron absorption, which is completely absent in the Cs$_4$PbBr$_3$ film. In a 3D perovskite, the excitons can immediately dissociate into free charge carriers because of the small exciton binding energy, which leaves no time for polaron formation. On the other hand, in a way similar to crystalline inorganic materials, adding a charge onto the 3D lattice does not significantly change the surroundings because of the rigid inorganic framework. In this case, a large polaron (Fröhlich polaron) forms because of strong electron-optical phonon coupling, which has optical signatures in a terahertz frequency range (42, 43). However, because a 0D perovskite has a larger exciton binding energy, excitons can hardly dissociate into free charge carriers. Therefore, in a way similar to a polymer system, a 0D perovskite is “soft” (that is, the individual octahedra are easily perturbed by the photoexcitation), which leads to polarons as a new feature present in low-dimensional perovskites. As shown in Fig. 3C, the corresponding kinetics of the polaron absorption band probed at 600 nm shows a lifetime of ~2 ps. This is consistent with the lifetime of polarons observed in pristine polymers (44). Here, the polarons are highly localized on [PbBr$_6$]$^{4-}$ octahedra, and they are likely not to escape but to recombine geminately over a short time.

To mimic the experimental pump-probe measurements and elucidate the charge carrier (polaron) relaxation processes in the 0D perovskite, we performed ab initio NAMD simulations on a single Cs$_8$PbBr$_6$ unit by describing the spontaneous transitions among different electronic states (for details, see the “MD calculations” section). As illustrated in Fig. 3D, we assumed that the photogenerated electron could be pumped into unoccupied energy levels through polaronic transitions PS1 and PS2, following an excitation energy of 4 eV. Starting from these two polaronic states in the 0D system, the charge population decays to 10% within a relaxation time of 1.5 ps, which agrees well with the experimental polaron lifetime of ~2 ps. This fast recombination is due to the similar charge distribution features of molecular orbitals involved in the excited electron relaxations (see the insets of Fig. 3D).

Thus, in contrast to the rigid structure of Cs$_8$PbBr$_6$, the individual [PbBr$_6$]$^{4-}$ octahedra in the 0D crystal can be easily perturbed by photoexcitation processes, leading to polaronic states through structural
deformation potentials (local molecular arrangements). Moreover, the discontinuous character of the 0D crystal significantly increases the charge carrier effective masses and strengthens electron-phonon coupling, facilitating small polaron generation, and providing an important optical fingerprint for the polaron band absorption in molecular 0D perovskites.

The single-unit model also allows us to characterize the actual distortions induced by the presence of small polarons. Here, we have evaluated the polaron binding energy ($E_{\text{polaron}}$) and charge carrier mobility based on molecular Cs$_4$PbBr$_6$ dimers. The positive/negative polaron binding energies ($E_{\text{polaron}}$) are calculated as 785/943 meV, which are values that are much larger than those in typical $p$-conjugated systems (45) but smaller than those in some 3D and 2D hybrid perovskites (33, 46). Because the average distance between neighboring [PbBr$_6$]$^{4-}$ octahedra is quite large (~10 Å), a band-like transport mechanism is not suitable for describing the charge carrier mobility of 0D perovskites. Thus, we applied Marcus theory to derive the charge carrier mobilities by describing the charge hopping between neighboring units in molecular dimers. As shown in Fig. 4A, three possible charge hopping paths in the 0D crystal were considered, while the resulting hole mobility of Cs$_4$PbBr$_6$ is calculated to be $1.4 \times 10^{-9}$ cm$^2$/V · s, whereas the electron mobility is $2.2 \times 10^{-11}$ cm$^2$/V · s. These low hole/electron mobilities are due to the huge reorganization energies for both holes (1.70 eV) and electrons (2.90 eV), as well as the weak electronic couplings between neighboring units (see table S1). The significantly larger negative polaron binding and reorganization energies of molecular Cs$_4$PbBr$_6$ are related to strong structural deformations (47). As illustrated in Fig. 2, the positive polaronic state preserves the symmetric geometry of the neutral state, while the negative polaronic state leads to extreme elongation of two Pb–Br bonds, breaking the symmetry of the negatively charged [PbBr$_6$]$^{4-}$ octahedron. These calculated values are orders of magnitude smaller than those of the 3D CsPbBr$_3$ perovskite, which has a hole mobility of 52 cm$^2$/ V·s and an electron mobility of 11 cm$^2$/V · s (48), and are even lower than those in typical conjugated polymers (for example, P3HT, $\sim 10^{-4}$ cm$^2$/V · s). Low charge carrier mobilities become another electronic feature of molecular 0D perovskites, again limiting their applications in optoelectronic devices.

To examine the small polaron features in bulk Cs$_4$PbBr$_6$ perovskites, following the same computational strategy as in our previous work on 2D hybrid perovskites (33), we exerted local perturbations on 2×2×2 Cs$_4$PbBr$_6$ supercells, where the selected Pb–Br bond lengths of the central [PbBr$_6$]$^{4-}$ unit were shortened or enlarged to create local structural deformations. Figure 4B illustrates the resulting electronic charge densities at the VBM and CBM after local structural perturbations. In the unperturbed systems, the charge densities of the VBM and CBM are highly delocalized in all octahedra (see fig. S2). Once...
the Pb–Br bonds of the central [PbBr$_6$]$^{4-}$ unit are shortened, the hole charge density (blue area) localizes at the central site, leading to the formation of Pb$^{3+}$ centers coupled with the lattice deformation. Similarly, in the case of enlarged Pb–Br bonds, the electron charge density (red area) is also localized at the central [PbBr$_6$]$^{4-}$. As we already demonstrated in the model for the polaronic state of a single unit, the strong interaction between charge carriers and phonons yields the formation of both self-trapped electron and hole states in the 0D crystal, which is in good agreement with previous experimental observations in low-dimensional lead halides (49–51).

On the basis of the perturbed supercell model for describing polaron localization in the 0D crystal, we further performed ab initio MD calculations to study local structural changes and the evolution of the charge density at a central [PbBr$_6$]$^{4-}$ octahedron. As shown in Fig. 4C and fig. S3, upon release from the initial state (for example, polaronic state with the longest Pb–Br bonds), the average Pb–Br bond length decreased, and the CBM energy level increased within the first 1 ps. During this time, the CBM charge density is still localized at the central octahedron, and the Pb–Br bond lengths and CBM energy undergo thermal fluctuations at room temperature. After 1.2 ps, the central octahedron recovers to the neutral state. Therefore, after photoexcitation, the structure deformation of single octahedra leads to the formation of localized polarons with short lifetime and limited transport in the 0D crystal. In addition, although the positive and negative polarons have similar absorption features (Fig. 2), the lifetime of a positive polaron could be even shorter than the negative one because of the faster recovery (within 0.1 ps) of Pb–Br bonds and corresponding VBM energy (fig. S3).

In summary, we studied the molecular behavior of the 0D Cs$_8$PbBr$_6$ perovskite by combining DFT calculations and femtosecond transition absorption measurements. Unlike 3D CsPbBr$_3$, 0D Cs$_8$PbBr$_6$ displays a large band gap, as well as low electrical conductivity and charge carrier mobility. A clear spectral feature for polarons with a short lifetime of ~2 ps is observed in the femtosecond-TA experiments, confirming the generation of small polarons with large binding energies and tight localization at individual [PbBr$_6$]$^{4-}$ octahedra. These findings provide a better understanding of the fundamental photophysical properties of 0D perovskites and open up new avenues for the rational design of low-dimensional perovskites in optoelectronic devices.

**MATERIALS AND METHODS**

**DFT calculations**

DFT calculations were performed to optimize the crystal structures of CsPbBr$_3$ and Cs$_8$PbBr$_6$ using the PWSCF code, as implemented in the Quantum ESPRESSO (QE) package (52). The PBE exchange-correlation functional with ultrasoft pseudopotentials was used with and without consideration of SOC. Plane-wave basis set cutoffs for the wave functions and charge density were set at 50 and 300 rydberg (Ry), respectively. The crystal structures were fully relaxed until the total force on each atom was less than 0.01 eV/Å. A uniform grid of 6 × 6 × 6 k-mesh in the Brillouin zone was used to obtain the electronic band structures and projected density of states for both crystals. A dense k-mesh (24 × 24 × 24) was used to obtain the electrical transport coefficients with the BoltzTraP package (53). On the basis of the electronic wave functions of the ground state obtained by the QE code, the optical transitions of CsPbBr$_3$ and Cs$_8$PbBr$_6$ were calculated using both the random-phase approximation and the Bethe-Salpeter equation approach implemented in the YAMBO code (54). In this case, PBE calculations were performed by using norm-conserving pseudopotentials including SOC effects and plane-wave basis set cutoffs of 80 Ry (400 Ry) for the wave function (charge density) (33).

For the single Cs$_8$PbBr$_6$ unit, the neutral and charged geometries were optimized with the hybrid range-corrected functional CAM-B3LYP using the Gaussian 09 code. The LANL2DZ basis set was used for Cs and Pb atoms, and the 6-31G** basis set was used to describe Br. On the basis of the optimized geometries in both the ground and polaronic states, the PBE0 hybrid functional was used to obtain the
optical absorption spectra using the TDDFT method. A total of 200 singlet states were considered in describing the possible optical transitions.

The charge transfer rates between neighboring octahedra were described by Marcus theory (55, 56) following the equation 
\[
V_{i,i+1} = \frac{V_{\text{exc}}}{k} \sqrt{\frac{\pi}{\ln(a_k T)}} e^{-\frac{h}{k T}},
\]
where \( T \) is the temperature, \( k_B \) and \( h \) refer to the Boltzmann and Planck constants, \( V_{\text{exc}} \) is the electronic coupling between the HOMO or LUMO levels of neighboring octahedra in the \( \text{Cs}_4\text{PbBr}_6 \) dimers, and \( \lambda_{h/e} \) is the hole or electron reorganization energy calculated via the adiabatic potential energy surfaces. \( V_{ij} \) is the electronic coupling, defined as \( \langle \Psi_i | F | \Psi_j \rangle \), which can be calculated by projecting the Fock matrix of the dimer onto the molecular orbitals of the respective donor (\( \Psi_i \)) and acceptor (\( \Psi_j \)) units with subsequent symmetric orthogonalization, where \( F \) is the Kohn-Sham Fock operator for the dimer system. The hole or electron mobility was then described by the Einstein relation \( \mu = \frac{\Delta \phi}{k_B T} \), where \( \epsilon \) is the electron charge and \( D \) is the charge diffusion coefficient of charge carriers, which can be approximately described as \( D = \frac{1}{4} \sum_i r_i^2 k_i \), where \( k_i \) and \( r_i \) are the charge-transfer rate and the neighboring distance for the dimer and \( P_i \) represents the probability for hole/electron hopping in the \( i \)th pathway.

**MD calculations**

Adiabatic ab initio MD calculations were also performed using the QE code with the PBE functional and ultrasoft pseudopotential. The optimized crystal structure of the \( 2 \times 2 \times 2 \) \( \text{Cs}_4\text{PbBr}_6 \) supercell was used as the starting point for the adiabatic MD calculations, where a 5-ps trajectory of the system was obtained with 1-fs time steps. The Andersen thermostat was used to control the temperature of the system.

NAMD calculations on a single \( \text{Cs}_4\text{PbBr}_6 \) unit were performed using the PYXAID code (58, 59) developed by Akimov and Prezhdo. In this code, fewest-switches surface hopping (60) implemented within TDDFT was used to study the hybrid perovskite system (61–63), starting from the time-dependent Schrödinger equation 
\[
i \hbar \frac{\partial}{\partial t} \Psi(t) = H(t) \Psi(t) + \sum_i \Psi_i(t) \Psi_i(t),
\]
and the Kohn-Sham orbitals \( \Psi_i(t) \) and density functional theory (DFT) results. From the solutions of these equations, the probability of transition between adiabatic states \( i \) and \( j \) can be calculated using the wave function expansion coefficients and coupling, defined as \( \langle \Psi_i | F | \Psi_j \rangle \). The detailed descriptions of this NAMD theory can be found in the study of Akimov and Prezhdo (58, 59). Here, we used the real-time TDDFT/NAMD method with decoherence effects on a single \( \text{Cs}_4\text{PbBr}_6 \) unit. A total of 1000 geometries were randomly selected from the adiabatic trajectories and used as initial conditions in the NAMD calculations.

**Preparation of 2D and 3D perovskite films**

Three-dimensional \( \text{CsPbBr}_3 \) and 2D \( \text{CsPbBr}_6 \) thin films were deposited on glass substrates precleaned with acetone/isopropanol. \( \text{CsPbBr}_3 \) was deposited by spin-coating a 0.25 M solution of \( \text{CsBr} \) and \( \text{PbBr}_2 \) in dimethyl sulfoxide, dripped with toluene, and followed by thermal annealing at 100 °C for 10 min. The \( \text{CsPbBr}_6 \) thin film was deposited through the vacuum thermal evaporation (1 × 10^{-6} mbar) of \( \text{CsPbBr}_6 \) powder (16), with a final thickness of 100 nm. The samples were fabricated and stored in a nitrogen-filled glove box. The materials and solvents were provided by Sigma-Aldrich and used without further purification. The experimental x-ray diffraction patterns of \( \text{CsPbBr}_3 \) and \( \text{CsPbBr}_6 \) thin films are shown in fig. S4.

**Electrical conductivity measurements**

The electrical conductivity was determined by investigating the dark current/voltage characteristics of \( \text{CsPbBr}_3 \) and \( \text{CsPbBr}_6 \) thin films on commercial interdigitated substrates with a channel width-to-length ratio of 2000 μm/2.5 μm (Fraunhofer Institute for Photonic Microsystems).

**Femtosecond TA spectroscopy**

The time-resolved experiments were conducted on Exciplex pump-probe spectrometers (CDP), in which the fundamental output came from a Ti:sapphire femtosecond regenerative amplifier operating at 800 nm with 35-fs pulses and a 1-KHz repetition rate. Pump pulses at 310 nm were generated after passing through a fraction of the 800-nm beam into a spectrally tunable (240 to 2600 nm) optical parametric amplifier (TOPAS Prime, Spectra-Physics) and a frequency mixer (NIRUVs, Light Conversion). To generate the probe pulses (ultraviolet-visible and near-infrared wavelength continuum, white light), another fraction of 800-nm–amplified pulses was focused onto 2-mm-thick calcium fluoride (CaF$_2$) crystal. To achieve better signal-to-noise ratios, the resulting white light was split into two channels, denoted the probe and reference, and focused on the different two fiber optics. The pump pulses were overlapped on the sample with the probe pulses after passing through a synchronized chopper (500 Hz), which blocked alternative pump pulses. Finally, the change in absorption (ΔA) of the excited state was calculated by subtracting the absorptions of the excited and unexcited samples.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/12/e1701793/DC1
fig. S1. Experimental and calculated electrical conductivity of \( \text{CsPbBr}_3 \) and \( \text{CsPbBr}_6 \).
fig. S2. Charge density descriptions of \( \text{CsPbBr}_3 \) supercell.
fig. S3. Average Pb–Br bond length and orbital energy evolution.
fig. S4. X-ray diffraction patterns of \( \text{CsPbBr}_3 \) and \( \text{CsPbBr}_6 \) thin films.
table S1. Calculated charge transfer parameters and mobility of the \( \text{Cs}_4\text{PbBr}_6 \) crystal.

**REFERENCES AND NOTES**


Acknowledgments: J.Y., J.-L.B., and O.F.M. acknowledge the IT Research Computing Team and Supercomputing Laboratory at KAUST for their computational and storage resources, as well as their assistance. Funding: This work was supported by the King Abdullah University of Science and Technology (KAUST). The work at Georgia tech was funded by the Office of Naval Research, Award NO. N00014-17-1-2208. Author contributions: J.Y. generated the idea and designed the simulation work. O.M.B. and O.F.M. crafted the experimental plan and directed the research. J.Y. performed all the ab initio calculations. J.Y., J.-L.B., and O.F.M. analyzed the theoretical results. M.D.B. and I.D. prepared the thin film samples and measured the electrical conductivity. P.M. and O.F.M. planned and performed the TA spectrum measurements and analyzed the data. J.Y., J.-L.B., and O.F.M. wrote the manuscript. All authors discussed and commented on the manuscript.

Competing interests: The authors declare that they have no competing interests.

Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 29 May 2017
Accepted 13 November 2017
Published 15 December 2017

10.1126/sciadv.1701793

Molecular behavior of zero-dimensional perovskites
Jun Yin, Partha Maity, Michele De Bastiani, Ibrahim Dursun, Osman M. Bakr, Jean-Luc Brédas and Omar F. Mohammed

Sci Adv 3 (12), e1701793.
DOI: 10.1126/sciadv.1701793

ARTICLE TOOLS
http://advances.sciencemag.org/content/3/12/e1701793

SUPPLEMENTARY MATERIALS
http://advances.sciencemag.org/content/suppl/2017/12/11/3.12.e1701793.DC1

REFERENCES
This article cites 62 articles, 5 of which you can access for free
http://advances.sciencemag.org/content/3/12/e1701793#BIBL

PERMISSIONS
http://www.sciencemag.org/help/reprints-and-permissions

Use of this article is subject to the Terms of Service