The Nanosecond, Time-Resolved Shift of the Photoluminescence Spectra of Organic, Lead-Halide Perovskites Reveals Structural Features Resulting from Excess Organic Ammonium Halide

Ujjal Bhattacharjee  
*Iowa State University, Ames Laboratory, and IIEST Shibpur*

Long Men  
*Iowa State University and Ames Laboratory*

Han Mai  
*Ames Laboratory*

Daniel Freppon  
*Iowa State University and Ames Laboratory*

Emily A. Smith  
*Iowa State University and Ames Laboratory, esmith1@iastate.edu*

See next page for additional authors

Follow this and additional works at: [https://lib.dr.iastate.edu/chem_pubs](https://lib.dr.iastate.edu/chem_pubs)

Part of the [Materials Chemistry Commons](https://lib.dr.iastate.edu/chem_pubs) and the [Physical Chemistry Commons](https://lib.dr.iastate.edu/chem_pubs)

The complete bibliographic information for this item can be found at [https://lib.dr.iastate.edu/chem_pubs/1183](https://lib.dr.iastate.edu/chem_pubs/1183). For information on how to cite this item, please visit [http://lib.dr.iastate.edu/howtocite.html](http://lib.dr.iastate.edu/howtocite.html).

This Article is brought to you for free and open access by the Chemistry at Iowa State University Digital Repository. It has been accepted for inclusion in Chemistry Publications by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
The Nanosecond, Time-Resolved Shift of the Photoluminescence Spectra of Organic, Lead-Halide Perovskites Reveals Structural Features Resulting from Excess Organic Ammonium Halide

Abstract
The effort to drive solution-based perovskite solar cells towards higher efficiency has been considerable, reaching over 24%. Such progress has been made possible by the low-energy barrier to crystallization. The low-energy barrier in the reverse direction, however, also renders them susceptible to dissociation from heat, moisture, and photoexcitation. Consequently, studies that provide information on the stability of perovskites are of considerable importance. It has been reported that perovskite crystals formed using different stoichiometries of the organic precursors and metal halide are equivalent. Our findings, however, suggest that the difference in reaction pathways affects the quality of the final crystal and that changes in morphology and the production of any defects can lead to differences in behavior under illumination. Here, we present photoluminescence spectra subsequent to nanosecond photoexcitation of perovskites synthesized under various conditions. Our results indicate that the presence of excess precursors (i.e., CH3NH3X, X= I and surfactant) gives rise to an ~20-nanosecond relaxation time with which the photoluminescence spectrum achieves its equilibrium value. This relaxation is absent in bulk, polycrystalline material. This is, to our knowledge, the first report of the ~20-ns relaxation time, which we attribute to cation migration. These structural changes are not detectable subsequent to photoexcitation by x-ray diffraction, nor are they detectable by in situ x-ray diffraction during photoexcitation.

Disciplines
Materials Chemistry | Physical Chemistry

Comments
This document is the unedited Author's version of a Submitted Work that was subsequently accepted for publication in the Journal of Physical Chemistry, copyright © American Chemical Society after peer review. To access the final edited and published work see DOI: 10.1021/acs.jpcc.9b07913. Posted with permission.

Authors
Ujjal Bhattacharjee, Long Men, Han Mai, Daniel Freppon, Emily A. Smith, Javier Vela, and Jacob W. Petrich

This article is available at Iowa State University Digital Repository: https://lib.dr.iastate.edu/chem_pubs/1183
The Nanosecond, Time-Resolved Shift of the Photoluminescence Spectra of Organic, Lead-Halide Perovskites Reveals Structural Features Resulting from Excess Organic Ammonium Halide

Ujjal Bhattacharjee\textsuperscript{1,2,3}, Long Men\textsuperscript{1,2}, Han Mai \textsuperscript{1}, Daniel Freppon \textsuperscript{1,2}, Emily A. Smith \textsuperscript{1,2},

Javier Vela*\textsuperscript{1, 2}, and Jacob W. Petrich*\textsuperscript{1,2}

\textsuperscript{1}Department of Chemistry, Iowa State University, \textsuperscript{2}Ames Laboratory, Ames, Iowa 50011, \textsuperscript{3}Department of Chemistry, IIEST Shibpur, West Bengal, 711103, India

* To whom correspondence should be addressed. email: vela@iastate.edu, jwp@iastate.edu.
ABSTRACT

The effort to drive solution-based perovskite solar cells towards higher efficiency has been considerable, reaching over 24%. Such progress has been made possible by the low-energy barrier to crystallization. The low-energy barrier in the reverse direction, however, also renders them susceptible to dissociation from heat, moisture, and photoexcitation. Consequently, studies that provide information on the stability of perovskites are of considerable importance. It has been reported that perovskite crystals formed using different stoichiometries of the organic precursors and metal halide are equivalent. Our findings, however, suggest that the difference in reaction pathways affects the quality of the final crystal and that changes in morphology and the production of any defects can lead to differences in behavior under illumination. Here, we present photoluminescence spectra subsequent to nanosecond photoexcitation of perovskites synthesized under various conditions. Our results indicate that the presence of excess precursors (i.e., CH$_3$NH$_3$X, X= I and surfactant) gives rise to an ~20-nanosecond relaxation time with which the photoluminescence spectrum achieves its equilibrium value. This relaxation is absent in bulk, polycrystalline material. This is, to our knowledge, the first report of the ~20-ns relaxation time, which we attribute to cation migration. These structural changes are not detectable subsequent to photoexcitation by x-ray diffraction, nor are they detectable by in situ x-ray diffraction during photoexcitation.
INTRODUCTION

Extremely rapid progress\(^1\) in the development of organometal-halide, perovskite solid-state solar cells has provided efficiencies as high as 24%.\(^2\) If the stability of the perovskite-based photovoltaics is improved further, perovskite solar cells have the potential to become a dominant means of obtaining low-cost solar power\(^3\) and to match the capability and capacity of existing technologies.\(^4\)-\(^5\) The most common perovskite solar cells are based on CH\(_3\)NH\(_3\)PbI\(_3\) and spiro-OMeTAD (a hole-transporting medium), producing power conversion efficiency values over 19%;\(^6\)-\(^9\) but others based on organic-inorganic hybrids have been reported.\(^10\)-\(^11\),\(^12\) Though most commonly reported perovskite solar cells employ micro-dimensional, polycrystalline perovskites, the incorporation of nanosized perovskites in the active layer has also been demonstrated in the synthesis of high-performance solar cells,\(^13\)-\(^14\) which primarily results from a relatively higher recombination time of the charge carriers, providing a higher photoluminescence (PL) quantum yield. Greater electron-hole diffusion lengths in perovskites lessen the detrimental effects of crystal boundaries, as the carriers created by photon absorption can easily hop across the grain boundaries from one crystal to another. Thus, in order to study potential nanoperovskite materials with different morphologies, we previously focused on the preparation of nanocrystals of CH\(_3\)NH\(_3\)PbX\(_3\) (X = I, Br) using various solvents and capping ligands (such as, octylammonium halide).\(^15\)

In spite, however, of considerable efforts to achieve higher efficiency and stability, perovskite-based solar cells are not yet ready for commercial adaptation because of lingering issues of instability owing to the low-energy barrier for crystal dissociation.\(^16\) Also, deep electronic-trap states\(^17\)-\(^21\) in addition to more prevalent shallow traps,\(^22\)-\(^23\) and elemental defects\(^23\) in perovskite nanocrystals present challenges and opportunities for further improvement of photovoltaic
performance. To date, such improvements have resulted primarily from better control over thin-film morphology, manipulation of the reaction stoichiometry of the lead-halide and alkylammonium-halide precursors, and the choice of solvent. Several observations have been reported, particularly with respect to the variation of the stoichiometric ratio of metal ion and organic cation. These observations are important for elucidating the wide variation in efficiency of organometallic perovskite-based devices and possible improvements. Recently, excess PbI$_2$ (i.e., a reduced amount of organic precursors) has been shown to be linked to avoiding the photocurrent drop that is otherwise observed in PbI$_2$-deficient samples (i.e., excess organic precursor).\(^{24}\) The drawback in perovskite with excess organic precursor is believed to be due to the accumulation of organic species at the grain boundaries, which has been suggested to give rise to a low charge-carrier mobility.\(^{25}\) On the other hand, the PbI$_2$-deficient compositions present some advantages, which have been attributed partially to higher PL yield and improved crystal quality.\(^{24-25}\) Furthermore, the presence of excess CH$_3$NH$_3$I during perovskite crystallization leads to the formation of layered intermediates and low-dimensional perovskites. Such intermediates give rise to the formation of large, continuous grains in thin films.\(^{26}\) The earlier steps in crystallization, however, involve formation of solvates under stoichiometric precursor concentrations; and this has been correlated with poor surface coverage and needle-like structures in thin films. The activation energy for crystallization with a stoichiometric excess of alkyl ammonium iodide is higher than that with a stoichiometric equivalence of precursors. Excess alkyl ammonium halide involves formation of a solid-state precursor (an iodoplumbate with a varying coordination number) that eventually transforms into perovskite.\(^{16,27-33}\) Similarly, tuning the ratio of CH$_3$NH$_3$Br/PbBr$_2$ precursors and the post-annealing temperature have been reported to be favorable for suppressing the nonradiative defects leading to highly-efficient, green-light-emitting,
perovskite-based diodes. Additionally, in the solution-phase synthesis of perovskite nanocrystals, often an excess of methylammonium halide is required in order to increase the solubility of lead dihalide, which has been thought of forming an adduct.

Here, we report the observation of a nanosecond, time-dependent shift of the PL of CH$_3$NH$_3$PbI$_3$ nanocrystals, prepared with an excess of organic halide precursors: PbI$_2$ : CH$_3$NH$_3$I : CH$_3$(CH$_2$)$_7$NH$_3$I in either 1:3:3 or 1:1.5:1.5 ratios. These are compared to bulk, polycrystalline pervoskites. We argue that the stoichiometry of the synthesis imprints structural characteristics onto the final product that are too subtle to be detected by standard techniques, such as X-ray diffraction. We suggest that the time-dependent shift in the peak position of the PL reports on small structural changes that are facilitated by the higher mobility of the organic cations in the excited state. We further suggest that migration of cations between the crystal lattice and the solution phase can occur and that the alkyl-chain length of the organic ammonium cation in the crystal can alter the band-gap in perovskite crystals (such reversible cation exchanges at room temperature have been reported).

**MATERIALS AND METHODS**

**Materials.** Lead (II) iodide (99%), methylamine solution (33 wt % in absolute ethanol), N, N-dimethylformamide (DMF, anhydrous, 99.8%) and n-octylamine (99%) were purchased from Sigma-Aldrich. Acetonitrile (99.9%) and toluene (99.9%) were from Fisher. All chemicals were used as received unless otherwise specified.

**Synthesis of ammonium halides.** Ammonium halides were prepared by modified literature procedures. Briefly, hydroiodic acid (10 mL, 0.075 mol) was added to a solution of excess methylamine (24 mL, 0.192 mol) in ethanol (100 mL) at 0 °C, and the mixture was stirred for 2 h. The solution was concentrated under vacuum, and the resulting powder was dried under dynamic
vacuum at 60 °C for 12 h, and then recrystallized from ethanol. \(n\)-Octylammonium iodide (CH\(_3(CH_2)_7NH_3\)I) was washed repeatedly with ethyl ether and dried under dynamic vacuum before use.

Polycrystalline (i.e., bulk) CH\(_3\)NH\(_3\)PbI\(_3\) was prepared by adding PbI\(_2\) (3.7 mg, 0.008 mmol) and CH\(_3\)NH\(_3\)I (3.8 mg, 0.024 mmol) to a mixture of acetonitrile (20 mL). 4 mL of the precursor mixture was rapidly mixed with 15 mL of toluene while stirring. Samples were allowed to stand for 24h before isolating the product by centrifugation (10 min at 4000 rpm).

Low-dimensional CH\(_3\)NH\(_3\)PbI\(_3\) with a 1:3:3 lead-halide-to-precursor ratio (Scheme A) was prepared by adding PbI\(_2\) (3.7 mg, 0.008 mmol), CH\(_3\)NH\(_3\)I (3.8 mg, 0.024 mmol), and CH\(_3(CH_2)_7\)NH\(_3\)I (6.2 mg, 0.024 mmol) to acetonitrile (20 mL). 4 mL of this mixture was rapidly combined with 15 mL toluene while stirring. Samples stood for 24h before isolating the product by centrifugation (10 min at 4000 rpm) and washing with toluene (5 mL).

Low-dimensional CH\(_3\)NH\(_3\)PbI\(_3\) with 1:1.5:1.5 lead-halide-to-precursor ratio (Scheme B) was obtained by following the above procedure with a reduced amount of CH\(_3\)NH\(_3\)I (1.9 mg, 0.012 mmol) and CH\(_3(CH_2)_7\)NH\(_3\)I (3.1 mg, 0.012 mmol).

**Structural characterization.** Powder x-ray diffraction (XRD) data were obtained using Cu K\(\alpha\) radiation on a Rigaku Ultima IV diffractometer (40 kV, 44 mA). Samples were prepared by drop-casting from toluene onto a “background free” quartz sample holder. Transmission Electron Microscopy (TEM) was conducted using a FEI Technai G2 F20 field emission TEM operating at up to 200 kV with a point-to-point resolution of less than 0.25 nm and a line-to-line resolution of less than 0.10 nm. Samples were prepared by placing 2 or 3 drops of dilute toluene solutions onto carbon-coated copper grids. Material dimensions were measured manually and with ImageJ. Uncertainties are reported as one standard deviation with respect to the mean.
**Optical characterization.** Steady-state absorption spectra were measured with an Agilent 8453 UV/vis spectrophotometer. Steady-state PL spectra were measured with a Horiba-Jobin Yvon Fluoromax 4 fluorimeter.

Time-resolved PL spectra were measured with a home-made apparatus based upon a Continuum Surelite II laser (5-ns pulsewidth, 20 Hz) providing an excitation wavelength of 532 nm. PL spectra were acquired with an ICCD camera (Andor Technology) synchronized to the laser and coupled to a spectrometer. Samples were dissolved in toluene and kept in a 1-cm path-length cuvette. Absorption and PL intensity were monitored before and after the laser experiment to monitor the integrity of the sample. The transient spectra are used to construct the function:

\[
PL(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \times \frac{\nu(0) - \nu(\infty)}{\nu(t) - \nu(\infty)} \tag{1}
\]

\(\nu(t)\) is the wavenumber of the peak maximum of the PL at time, \(t\); \(\nu(0)\), that at \(t = 0\); and \(\nu(\infty)\), that at times at which the steady-state PL spectrum is collected. The denominator provides a proper normalization of the function and depends on how “zero time” is defined. As the focus of this work is on the slow dynamics, “zero time” is determined by the laser’s 5-ns pulse width. We do not consider earlier-time dynamics, and we do not normalize the shifts. Equation (1) is formally identical to the “solvation correlation function,” \(C(t)\), which has been applied to the dynamic spectral shifts (transient Stokes shifts)\(^{39,40,41}\) of organic fluorophores in polar solvents. We are careful, however, not to abuse this identity as the emission from the perovskites is not fluorescence and as we are interpreting the shift in PL in terms of structural events on the surface of the perovskite rather than of effects of the solvent, which in this case is nonpolar, toluene, and would not be expected to produce a red-shifted emission spectrum. (Toluene is the only solvent in which the perovskites could be conveniently dissolved without inducing sample degradation.)
RESULTS AND DISCUSSION

Composition and structure. The crystal structure of organic, lead-iodide perovskites is tetragonal at room temperature. There is a transition to a cubic geometry above 327 K. Figure 1 presents representative TEM images of polycrystalline perovskites (0.3-2 µm) and perovskite nanocrystals (7 ± 2 nm). The perovskite nanocrystal overall morphology varies with changes in the precursor ratio. Particularly, in the presence of excess precursor, it forms layered intermediates that provide higher coverage in the final thin film. None of the optical properties, however, except the PL quantum yield (which is related to the change in the recombination rate) is significantly affected by the morphology of the crystal. Furthermore, in bulk or low-dimensional perovskites, neither the PL nor the absorption spectra change because of the lack of quantum confinement resulting from the small (2.2-nm) Bohr radius of the iodide perovskites. The PL spectra of the nano-perovskites, however, are broader than those of the micro-perovskites, which suggests a higher degree of inhomogeneous broadening in the former.

The syntheses of the polycrystalline and nanodimensional perovskites differ by the presence or absence of the capping ligand, CH$_3$(CH$_2$)$_7$NH$_3$X, in the precursor solution. This precursor solution, in addition to increasing the PL, also sometimes introduces impurities into the system: the long-chain organic-halide cation can prevent crystal growth in certain directions. Figure 2a presents the XRD of both polycrystalline (bulk) and low-dimensional perovskite materials. The diffraction peaks obtained for all the samples agree with the standard patterns, indicating that the synthetic procedures employed are not introducing any structural anomalies that can be measured within the resolution permitted.

Nanosecond shift of perovskite PL spectra. PL spectra of the various perovskites in toluene were obtained as a function of time subsequent to excitation with 532-nm, 5-ns pulses.
steady-state spectra of the various perovskites were similar (Figure 2b), as noted above, this is not
the case for their time-dependent spectra. Typically, one expects only a gradual decrease in
intensity, determined by the decay of the excited-state, with no shift of the PL spectra. We
observed, however, a time-dependent shift of the PL spectrum for the scheme-A nanoparticles
(Figure 3). The spectrum obtained at “zero-time” with 5-ns pulses is unrelaxed (blue-shifted) with
respect to that of the steady-state spectrum by 18 nm (327 cm\(^{-1}\)). The spectrum relaxes (red shifts)
to the steady-state spectrum in about 20 ns at pulse energies of either 3 mJ or 1 mJ. The extent of
the initial shift from equilibrium, however, depends strongly upon the pulse energy. At 3 mJ it is
327 cm\(^{-1}\) (Figure 3a and 3c); at 1 mJ, 180 cm\(^{-1}\) (Figure 3b and 3d).

The presence of the unrelaxed, “zero-time” spectral feature is dependent upon the type of
sample and its preparation. It is absent in the scheme-B perovskite (Figure 4) and in the bulk,
polycrystalline perovskite (Figure 5). Table 1 provides a summary of these results and the PL
lifetimes of the materials, which are dependent on the pulse energy. For example, the lifetime of
the scheme-A perovskite is 20 ns at 3-mJ and 35 ns at 1-mJ pulse energies. Shortening of the
excited-state lifetimes with excitation fluence has been attributed to higher carrier densities.\(^\text{47}\) The
scheme-B perovskite has a longer excited-state lifetime (83 ns and 43 ns at 1- and 3-mJ pulse
energies, respectively). The longer lifetime for the samples provided by scheme B may result from
a smaller contribution from a recombination channel provided by fast carrier trapping through
surface states.

**Excluding possible alternative explanations.** This spectral shift is distinctly different from what
has been previously observed on femtosecond to picosecond time scales, where it has been
typically attributed to the relaxation dynamics of excitons.\(^\text{1, 25}\) Furthermore, such nanosecond
spectral shifts are not observed in high-quality, vapor-deposited films of CH\(_3\)NH\(_3\)PbI\(_{3-x}\)Cl\(_x\), which
is consistent with our suggestion that the origin of the shift in the scheme-A perovskites is a result of the precursor ratio. Before we discuss the role of the precursor ratio in giving rise to the dynamic spectral shift, we consider two other explanations. The first is heating.

Owing to the large quantum yield of the radiative process in perovskites, laser-induced heating of the nanoparticles is not expected to be significant. Since, however, heat diffusion in nanocrystals can occur on a nanosecond time scale, there is a possibility of transient temperature-dependent changes in the crystal structure; and the effect of laser-induced heating cannot be neglected and should be examined. Organic lead halides are known to undergo a phase transition from tetragonal to cubic above room temperature. Furthermore, it has been reported that in the ranges from 15-80 K and from 150-300 K, there is a blue-shift in the photoluminescence peak with increasing temperature, in contrast to the established Varshini behavior, where the bandgap experiences a redshift with increasing temperature, which has been attributed to the stabilization of the valance-band maximum with better overlap between Pb-6s and I-5p antibonding atomic orbitals. Additionally, temperature-induced electron–phonon coupling induces a slightly enlarged band gap and reduces the electronic relaxation time as the temperature increases.

In order to examine whether heating could generate the observed dynamic PL shifts, we measured spectra as function of temperature. Figure 6 presents the PL of low-dimensional and polycrystalline lead-iodide perovskites in toluene from 20-70°C. For each measurement, the sample was equilibrated for 2-3 min at the given temperature. Only a nominal peak shift in photoluminescence (< 3 nm) was observed. More importantly, the PL quantum yield of the lead–iodide perovskites decreases with increasing temperature, which can be attributed to decreasing ratio of bound excitons to free charges. The reversibility of the spectral intensity and peak position was verified in this temperature range to exclude the possibility of irreversible structural
change or sample damage. In scheme-A nanocrystals, the temperature-induced decrease of the PL intensity is slightly less than that in the scheme-B perovskites. The polycrystalline perovskite is more sensitive to temperature: at 50 °C the PL intensity is too low to be detected, suggesting the roles of a higher ratio of free charges to excitons and of a larger number of recombination centers in reducing the PL quantum yield. Polycrystalline perovskites also exhibit much lower thermal stability. Additionally, we measured the crystal structure with in situ laser illumination (Figure 7). We did not observe any other XRD peaks in the presence of laser illumination. Thus, since the nanosecond shift in PL maximum was observed only in the scheme-A perovskites and not in the scheme-B or polycrystalline material and since the temperature-induced spectral shift was negligible compared to that observed in the photoinduced process, we exclude laser-induced heating as the origin of the nanosecond PL shift.

Secondly, there is the possibility of dynamic solvation in the solid state, which could result in slower dynamics than those typically observed in organic solvents. Since, however, we did not observe such a peak-shift in polycrystalline perovskite particles, we eliminate the possibility of solid-state solvation.

The role of excess precursor. Kamat and coworkers have shown that the means by which the perovskite is formed depends significantly upon the MX$_2$/precursor ratio. In the presence of excess precursor, perovskite formation occurs via a solid-state precursor (SSP). During the transformation from the SSP to the perovskite, excess precursor is expelled from the lattice. This results in changes in band-edge wavelengths, which have been observed in steady-state absorption and in transient absorption measurements. Similar behavior in PL during slow, room-temperature annealing has also been observed. A redshift of the PL peak of low-dimensional CH$_3$NH$_3$PbI$_3$
accompanying sample aging, after preparation, has been observed and discussed.\textsuperscript{58} Red-shifted PL arises from annealing, which occurs via SSP formation, and is associated with cation migration. First, photoinduced cation migration, which can result from metal-to-halide charge transfer, weakens the hydrogen bonding between the organic cation and the halide anion, leading to higher mobility and a possible exchange of the organic cation.\textsuperscript{33, 59} (Such weakening of the hydrogen bond is also responsible for hydration, which eventually degrades perovskite devices.\textsuperscript{59-60}) \textit{Ab initio} calculations also suggest low activation energies for migration of organic cations (0.8 eV \text{MA}^+).\textsuperscript{61} The low activation energy of dissociation, which is unavoidably associated with a low activation energy of formation, facilitates the reverse process of crystallization. Thus a change in organic cation concentration, or exchange or orientation, can be realized in the nanocrystals under illumination. Furthermore, low-dimensionality is achieved by employing a capping ligand, octyl ammonium, which is significantly larger than \text{CH}_3\text{NH}_3^+. Cations that differ in size from \text{CH}_3\text{NH}_3^+ can destabilize the lattice, leading to reverse cation exchange in microscopic equilibrium.\textsuperscript{62} The bandgap of \text{CH}_3\text{NH}_3\text{PbI}_3, characteristic to perovskites, 1.5 eV (820 nm),\textsuperscript{63} decreases with increasing length of the alkyl chain.\textsuperscript{64} Cation exchange with formyl ammonium has led to a decrease in the bandgap and a red-shift of the PL maximum.\textsuperscript{35}

Secondly, in the reverse process of crystal formation \textit{via} SSP,\textsuperscript{44} there is the possibility of the incorporation of excess organic cations in the lattice. This can lead to a transient blue shift of the PL maximum with respect to aged perovskite spectrum similar to a change in band-edge absorption apparent during crystal formation. Also the independence of the PL red shift and its time constant on the irradiance (3- and 1- mJ pulse energies) suggests that they are characteristic of cation migration in a particular crystal sample. Results of 2-dimensional infrared spectra have suggested the existence of much more rapid motions occurring on time scales of 300 fs and 3 ps,
which have been attributed, by means of *ab initio* calculations, to “wobbling” and “jump-like” motions, respectively.\(^{65}\) Other calculations also suggest reorientational motion.\(^{36,66}\) Such motions must, however, be distinctly different from those responsible for the nanosecond PL shift we observe; they may, nevertheless, contribute to cation migration.

Kamat and coworkers have shown that in syntheses using a lower concentration of organic precursors, the perovskite does not form *via* SSP\(^{44}\) indicating that ligand exchange cannot happen effectively in scheme-B perovskites. Both scheme-B and scheme A, however, produce crystals whose structures appear to be indistinguishable, at least as determined by x-ray methods. In order to rationalize the observed PL shifts, we suggest that it is probable that the migration or exchange of organic cations occur more effectively in the presence of defects, which are more frequent in the presence of excess precursor as manifested by an increased number of recombination sites and different band-gap transitions. Furthermore, a gradual decrease of spectral width (as the PL spectra approach the steady-state spectrum) suggests that ligand migration is a contribution to the initial inhomogeneous broadening.

Finally and most importantly, the following control experiment was performed to probe the role of excess organic precursor. If the nanosecond relaxation of the PL spectrum in the scheme-A perovskites arises from excess precursor, then addition of precursor to the scheme-B perovskite ought to produce such a dynamic shift. This is indeed what is observed (Figure 8). In the presence of excess precursor, the scheme-B perovskites exhibit a 30-ns PL relaxation time. This change in relaxation time supports the suggestion that the addition of organic precursors (and hence, the conditions under which synthesis takes place) strongly affects the crystal quality, which in turn governs the ligand-migration time. The dynamic behavior of the PL peak in the presence of excess precursor is also manifested in a steady-state laser-assisted PL peak shift.\(^{58}\) In addition
to the shift in the predominant band-edge peak, a higher-energy peak at ~620 nm appears. This higher-energy peak is also apparent in freshly prepared perovskite solution, but disappears as the sample ages. Its origin is unknown, but it is not unreasonable to attribute it to the formation of octylammonium lead perovskites.\textsuperscript{67-68}

**CONCLUSION**

We describe how excess precursors used in the synthesis of organic lead-iodide perovskites can affect their optical properties, namely by inducing a time-dependent shift in the photoluminescence in which the equilibrium spectrum is attained in ~20 ns. In other words, we suggest that in the presence of excess organic-halide precursors, the perovskite nanocrystal is formed through a different path producing particles with different photophysics. This behavior is attributed to reversible ligand migration on a nanosecond time scale subsequent to photoexcitation being facilitated by small-amplitude reorientation of the cations.\textsuperscript{36, 65} Alternative explanations such as temperature-dependent effects and large-scale structural changes have been eliminated by performing temperature-dependent PL measurements and \textit{in situ} laser-XRD experiments.

**ACKNOWLEDGMENTS**

We thank Professor Xueyu Song for stimulating and insightful conversations regarding dynamic Stokes shifts. This research is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences through the Ames Laboratory. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358.
REFERENCES


Table 1
Summary of Relevant PL Properties of Perovskites in Toluene

<table>
<thead>
<tr>
<th>sample type (preparation)</th>
<th>Pulse energy (mJ)</th>
<th>(\tau) (ns)</th>
<th>(\tau_{PL(0)}) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nanocrystal (scheme A)</td>
<td>1</td>
<td>35</td>
<td>20</td>
</tr>
<tr>
<td>nanocrystal (scheme A)</td>
<td>3</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>nanocrystal (scheme B)</td>
<td>1</td>
<td>86</td>
<td>---</td>
</tr>
<tr>
<td>nanocrystal (scheme B)</td>
<td>3</td>
<td>43</td>
<td>---</td>
</tr>
<tr>
<td>bulk, polycrystalline</td>
<td>3</td>
<td>9</td>
<td>---</td>
</tr>
<tr>
<td>nanocrystal (scheme B + excess precursor)</td>
<td>3</td>
<td>18</td>
<td>30</td>
</tr>
</tbody>
</table>

a Scheme A: PbI\(_2\):CH\(_3\)NH\(_3\):CH\(_3\):(CH\(_2\))\(_7\)NH\(_3\):I = 1:3:3; Scheme B: PbI\(_2\):CH\(_3\)NH\(_3\):CH\(_3\):(CH\(_2\))\(_7\)NH\(_3\):I = 1:1.5:1.5. The excess precursors are CH\(_3\)NH\(_3\)I and CH\(_3\):(CH\(_2\))\(_7\)NH\(_3\)I.

b Lifetime of the photoluminescent excited state. The scheme-B perovskite has longer excited-state lifetimes than its scheme-A counterpart. The longer lifetimes might result from a smaller contribution from a recombination channel provided by fast carrier trapping through surface states.

c Single-exponential time constant describing the relaxation time of the spectral shift. The absence of a value indicates that the equilibrium spectrum appeared within the time resolution of the experiment.
Figure 1. TEM images of (a) polycrystalline, (b) low-dimensional, scheme-A perovskites (1:3:3), and (c) low-dimensional, scheme-B perovskites (1:1.5:1.5).
Figure 2. (a) Powder XRD and (b) Steady-state PL spectra of polycrystalline and low-dimensional (1:1.5:1.5 and 1:3:3) lead-halide perovskites.
Figure 3. Time-dependent spectral shifts of the scheme-A perovskite in toluene upon excitation with a 5-ns laser pulse at 532 nm whose pulse energy is (a) 3 mJ and (b) 1 mJ. Panels (c) and (d) present the function, $PL(t) \propto (\%v(t) - \%v(\infty))$ for the data in panels (a) and (b), respectively. The wavenumber-shift vs. time is plotted for 3 mJ (c) and 1 mJ (d). While $PL(t)$ decays in 20 ns for 3-mJ pulses and in 21 ns for 1-mJ pulses, the extent of the shift is 327 cm$^{-1}$ in the former case and 180 cm$^{-1}$ in the latter. The maximum of the steady-state PL is at 747 nm. Within experimental error, the 110-ns spectrum is identical to the steady-state spectrum.
Figure 4. Time-resolved emission spectra of scheme-B perovskite in toluene at pulse energies of (a) 3-mJ and (b) 1-mJ. The “zero-time” spectrum is the same as that of the steady-state spectrum. The spectra were taken at an interval of 20 ns.

Figure 5. Time-resolved emission spectra of bulk, polycrystalline perovskite in toluene. The “zero-time” spectrum is the same as that of the steady-state spectrum. The pulse energy was 3 mJ, the highest energy that could be used without destroying the sample. Spectra were acquired in 10-ns intervals.
Figure 6. Emission spectra of (a) low-dimensional (1:3:3) scheme-A nanocrystals, (b) low-dimensional (1:1.5:1.5) scheme-B nanocrystals, and (c) polycrystalline perovskites as a function of temperature (°C) in toluene.
Figure 7. \textit{In situ} powder XRD in the presence (grey) and absence (blue) of laser excitation of low-dimensional, Scheme-A (1:3:3) lead-halide perovskites. The laser pulse energy is 3 mJ.
Figure 8. Time-dependent PL shift of perovskites prepared by scheme B in toluene with added precursor (a sufficient excess was provided to prepare scheme-A ratios). The inset presents time-resolved emission spectra at intervals of 15 ns.
The Nanosecond Shift of PL in CH$_3$NH$_2$PbI$_3$