**Ferroelectric Alignment of Organic Cations Inhibits Nonradiative Electron–Hole Recombination in Hybrid Perovskites: Ab Initio Nonadiabatic Molecular Dynamics**

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**Supporting Information**

**ABSTRACT:** Hybrid organic–inorganic perovskites show impressive potential for photovoltaic applications and currently give rise to one of the most vibrant research areas in the field. Until recently, the electrostatic interactions between their organic and inorganic components were considered mostly for stabilization of the fragile perovskite structure. We study the effect of local interactions of polar C–N bonds in the organic layer on the nonradiative electron–hole recombination in the recently reported room-temperature ferroelectric hybrid perovskite, (benzylammonium)\(_2\)PbCl\(_4\). Using nonadiabatic molecular dynamics and real-time time-dependent density functional theory, we show that ferroelectric alignment of the polar groups weakens the electron–hole nonradiative coupling and inhibits the nonradiative recombination. The effect is attributed to suppression of contributions of higher frequency phonons to the electron–phonon coupling. The coupling is dominated in the ferroelectric phase by slower collective motions. We also demonstrate the importance of van der Waals interactions for the charge-phonon relaxation in the hybrid perovskite systems. Combined with the long-range charge separation achievable in the ferroelectric phase, the weakened electron–phonon coupling indicates that ferroelectric order in hybrid perovskites can lead to increased excited-state lifetimes and improved solar energy conversion performance.

Because of their numerous outstanding optical and electronic properties, hybrid organic–inorganic perovskites (HOIPs) are currently identified among the most promising materials for photovoltaic applications. In particular, hybrid perovskites stand out with their large light absorption coefficients,\(^4–8\) long and balanced electron and hole diffusion lengths,\(^6,9\) and high dielectric constants.\(^7,9\) Furthermore, the bandgap (BG) in these materials is easily tunable through structural modifications,\(^10–14\) spanning values from ultraviolet to near-infrared and thus allowing for an almost perfect match with the desired optimum absorption range for the solar cells.\(^15,16\) Apart from their excellent photophysical properties, hybrid perovskites attract much attention due to the low cost of their production process.\(^17–19\) All of these features, being systematically improved since the initial recognition of hybrid perovskites as robust photovoltaic media,\(^20,21\) contribute to the unprecedentedly rapid progress in the perovskite-based solar cells efficiency, which has been recently reported to reach 21.1% for a mixed-cation material.\(^22\) The ongoing material research efforts toward the further enhancement of the perovskites performance cover a number of issues, with the doping effects and material durability playing a prominent role.\(^25–30\) Numerous thorough and up-to-date review articles are available on the subject.\(^31–35\)

In addition to the basic requirements usually required for light-harvesting materials, one may consider other features that can enhance the overall photovoltaic performance, such as ferroelectricity of the active medium.\(^36,37\) Macroscopic ferroelectric effects are known to support photoexcited charge-carrier separation and are considered as a possible origin for the observed switchable anomalous photovoltaic effect, in which the photogenerated voltage reaches values far beyond the BG limit.\(^38–39\) Moreover, combining ferroelectricity and photo-triggered electric response opens the possibility for novel material applications, such as memory storage media, field effect transistors, and so on.\(^40–44\) This topic has been widely investigated for the purely inorganic perovskites.\(^45–49\) Merging favorable photovoltaic and synthetic properties of hybrid perovskites with the ferroelectric effects has thus been recognized as a promising direction for future HOIP device development. Liao et al. has recently reported the synthesis of the first hybrid-perovskite room-temperature ferroelectric semiconductor, an important step toward this goal.\(^50\) The observed HOIP ferroelectricity is attributed to the relative orientation of polar C–N bonds in the material’s organic cation component.\(^50,51\)

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Investigations in the field of HOIP materials cover a rich set of topics; however, up to now, electrostatic interactions between the organic and inorganic constituents in hybrid perovskites have been mostly considered in terms of stabilization of the perovskite structure. This stabilization is controlled through matching between the size of the organic linking group and the optimal shape of the inorganic framework. The extent of the organic molecule in the direction perpendicular to the inorganic plane controls the dimensionality of the inorganic subsystem active in the photovoltaic process. Some very recent studies have been devoted to the polar group effects on the basic HOIP photovoltaic properties, such as charge-carrier interaction screening and separation, or possible dynamics changes of the BG character from direct to indirect. The newly observed highly ordered and stable ferroelectric orientation of the polar C–N bonds in HOIPs raises new questions for the possible role and impact of the interlayer interactions on the photovoltaic performance, especially because the C–N moiety acts as an universal linker to the inorganic framework in the hybrid perovskite family (with the formamidinium cation being a notable exception). Some very recent studies have been devoted to the polar group orientation effects on the basic HOIP photovoltaic properties, such as charge-carrier interaction screening and separation, or possible dynamics changes of the BG character from direct to indirect.57 Also, polar group reorientation effects on the thermal transport have been recently analyzed.58 These latest emerging reports set up a new direction in the perovskite properties studies, now placing the issue of organic–inorganic component interactions as one of the possible keys to understanding the preeminent photovoltaic properties of the hybrid perovskite family.

We apply ab initio nonadiabatic molecular dynamics (NAMD) to investigate the effect of the local electric order within the organic HOIP layer on the nonradiative hole–electron recombination rate, which has a strong influence on efficiencies of photovoltaic, photocatalytic, and related devices. We demonstrate that electrostatic interactions between the organic and inorganic subsystems have a strong effect on the electron–phonon nonadiabatic coupling (NAC) and excited-state lifetime. Ferroelectric arrangement of polar organic groups suppresses coupling of the electronic subsystem to higher frequency phonons and inhibits the charge recombination. The suppressed charge–phonon interactions works hand-in-hand with the long-range effects, such as electron–hole separation and improved carrier mobility, which altogether can lead to longer excited-state lifetimes and improved solar cell performance. We also demonstrate the important role of the inclusion of dispersive van der Waals interactions in the studies on HOIP materials structural and electronic properties and electron-vibrational dynamics.

We focus on the room-temperature ferroelectric HOIP material proposed by Liao et al., (benzylammonium)_2PbCl_4, for its proved stable regular orientation of the polar C–N bonds, enabling unambiguous interpretation of the polar order effects. Our analysis starts with choice of model crystal cells to represent the experimentally observed ferro- and paraelectric phases. The ferroelectric phase (Figure 1a,c) has been modeled directly with a single-crystal form, ferro, in which all polar C–N bonds are fully aligned and which was found the most...
energetically stable among other possible isomers. To map the paraelectric phase (Figure 1b,d), we choose two structures: the anti-ferro form with zero net electric dipole moment per crystal cell and mixed form in which the disordered paraelectric phase character is modeled through mixture of aligned and antialigned C–N bonds pairs. These forms were found to be less stable energetically than the ferro form by 0.16 and 0.09 eV, respectively. In all cases, the crystal cell includes two pairs of benzylammonium cations further duplicated according to the base-centered cell type (eight organic units altogether, with Pb$_4$Cl$_{16}$N$_8$C$_{56}$H$_{80}$ total cell composition), thus allowing for characterization of nearest-dipole-neighbor interactions.

Figure 2 illustrates total and atom-projected density of states calculated for the most stable ferro form. The data show that the top of the valence band is dominated by the halogen orbitals (of p character) and contributions from the organic cation (mostly p orbitals of the aromatic carbon atoms); at the same time, the bottom of the conduction band consists predominantly of the Pb s orbital functions. A similar picture, staying in line with typically observed HOIP patterns, has been found for the paraelectric forms: The corresponding figures have been included in the Supporting Information (SI, Figure S1). HOMO and LUMO orbitals calculated at the Γ k-point are shown as inset in Figure 2. The active space for the NAMD simulations consisted of these two orbitals, HOMO and LUMO, as they correspond to the lowest-energy hole states, as they correspond to the lowest-energy hole states, simulations consisted of these two orbitals, HOMO and LUMO, as they correspond to the lowest-energy hole states, respectively. In all cases, the crystal cell includes two pairs of benzylammonium cations further duplicated according to the base-centered cell type (eight organic units altogether, with Pb$_4$Cl$_{16}$N$_8$C$_{56}$H$_{80}$ total cell composition), thus allowing for characterization of nearest-dipole-neighbor interactions.

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After thermal equilibration at room temperature (300 K), the 15 ps long NAMD simulations have been performed. The energy- and time-related results of the simulation are summarized in Table 1. The canonically averaged BG values shown in the first column concentrate around 3.50 eV for all three forms of the perovskite; in particular, the 3.56 eV value for the ferro form matches very well the experimentally measured 3.65 eV BG. The pure-dephasing times indicate ultrafast decoherence effects (≤10 fs) and also remain comparable in all cases. The main quantities of interest, the calculated recombination times (τ), reveal an increasing trend in the anti-ferro → mixed → ferro sequence: Thus structures representing the paraelectric phase, anti-ferro and mixed, exhibit faster electron–hole recombination than the fully ordered ferro structure. This difference in charge recombination dynamics stays in line with a tendency observed for mean electron–phonon NAC. To gain understanding of physical nature of the observed phenomenon, one needs to take a deeper look at the dynamics-related properties of the system, standing behind the NAC value.

In Figure 3 one can see a correlation relation between BG and NAC absolute value, plotted for the all three forms. While the data obtained for anti-ferro and mixed show relatively narrow BG energies distribution with NAC modulus reaching loosely the 3 meV range, the most-ordered ferro form shows higher BG with a long but sparse tail of low-energy values and truncated NAC distribution, limited to 2 meV. A combination of smaller coupling and larger gap observed for ferro favors slower relaxation. On the contrary, thermal fluctuations that decrease the energy gap and simultaneously increase the NAC provide the most important contribution to the nonradiative relaxation pathway, enhancing the relaxation rate in anti-ferro and mixed.

To obtain further insights into the electron–phonon coupling, we report the power spectra (Figure 4) calculated as Fourier transforms of the autocorrelation functions of the BG oscillations. Again, we observe similarity between the paraelectric anti-ferro and mixed forms, which differ from the ferro structure. Specifically, in the ordered ferro case the vibration frequencies having the highest impact on the BG

<table>
<thead>
<tr>
<th>form</th>
<th>bandgap/eV</th>
<th>σBG/meV</th>
<th></th>
<th>NAC]/meV</th>
<th>dephasing/fs</th>
<th>τ/ps</th>
</tr>
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<tbody>
<tr>
<td>ferro</td>
<td>3.56</td>
<td>0.13</td>
<td>0.658</td>
<td>7.5</td>
<td>800</td>
<td></td>
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<tr>
<td>anti-ferro</td>
<td>3.37</td>
<td>0.11</td>
<td>0.849</td>
<td>8.0</td>
<td>559</td>
<td></td>
</tr>
<tr>
<td>mixed</td>
<td>3.41</td>
<td>0.10</td>
<td>0.768</td>
<td>10.0</td>
<td>612</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Canonically Averaged Bandgap and Its Standard Deviation (σBG), Absolute Value of NAC, Pure-Dephasing Time, and Nonradiative Electron-Hole Recombination Time (τ) for Studied Perovskite Forms
energy are concentrated in the lowest energy region: Frequencies below 100 cm$^{-1}$ contribute 72% to the overall integrated spectrum intensity, mostly corresponding to polar C–N group rocking in the direction parallel to the inorganic plane. The high intensity indicates a strong impact of the BG oscillations and is responsible for the observed fast dephasing (see Table 1). At the same time, in the disordered phases, anti-ferro and mixed, we observe smaller intensity of the low-energy peaks (48 and 55% integrated intensity below 100 cm$^{-1}$, respectively), with visible contributions from the higher frequency phonons, explaining the higher mean NAC value observed for the anti-ferro and mixed forms. The explicit relative intensities of peaks lying in the low-energy part of the spectrum are shown in Table S1 in the SI.

It should be also stressed that in the course of our study we witnessed a fundamental role of the van der Waals interactions inclusion for a proper description of the electronic structure response to the nuclei dynamics. Without this correction one arrives with a noticeably different NAMD results, showing much weaker response of the flexible organic component to the inorganic layer vibrations; therefore, the NAC distribution and power spectrum shape are also strongly affected. For comparison, we show the uncorrected results in the SI (Table S2 and Figures S2 and S3).

In summary, we used state-of-the-art ab initio nonadiabatic molecular dynamics simulations to model how local electric order in a ferroelectric HOIP material affects the hole–electron recombination. For our study, we chose the (benzylammonium)$_2$PbCl$_4$ material, for which a room-temperature stable ferroelectric phase was reported recently. We found that the ferroelectric phase exhibits slower electron–hole recombination than the crystal forms representing the paraelectric phase. To understand the reasons, we considered in detail the key electronic structure features and their dynamic characteristics. We established that despite similar BGs and pDOS spectra of all forms, the electron–phonon NAC distributions are notably different. In particular, the higher NAC value tail is missing in the ferroelectric phase. This observation underlines the crucial role of dynamics effects in identification and understanding of the material features that influence the electron–hole recombination process. The difference of the ferroelectric phase from the other structures finds further manifestation in the electron–phonon power spectrum. The ferroelectric order suppresses electronic coupling to higher frequency modes. The suppression is responsible for the lower NAC values and slower recombination dynamics. Finally, in the course of the investigation, we identified the essential role of the inclusion of dispersive van der Waals interactions, not only for the structural and electronic properties of HOIP materials but also for the electron–phonon dynamics. The reported study generates important insights into the fundamental mechanisms responsible for charge recombination and loss of photovoltaic efficiency in hybrid organic–inorganic perovskites. Combined with the long-range charge separation and improved carrier mobilities expected in ferroelectric systems, the suppressed electron–hole recombination acts further to extend excited-state lifetimes and enhance solar energy conversion efficiencies. Although the reported study focuses on a single perovskite system, (benzylammonium)$_2$PbCl$_4$, the uncovered difference between the ordered and disordered phases should be generic due to the universal presence of the polar C–N moiety in the HOIP family of compounds and the general importance of lower frequency collective vibrational motions in ordered ferroelectric systems.

### COMPUTATIONAL METHODS

We employ the plane-wave density functional theory approach, as implemented in Quantum Espresso program package, to describe the electronic properties of the hybrid perovskite system. The crystal structure parameters and initial atomic coordinates have been taken from ref 66; the latter have been further reoptimized. For the optimized structure coordinates, please refer to Tables S2–S4 in the SI. For all electronic calculations we used the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional with ultrasoft pseudopotential including nonlinear-core and scalar-relativistic corrections, the Grimme’s DFT-D2 dispersion correction was also applied. The basis set energy cutoff was set to 60 Ry. For the structural optimization, molecular dynamics, and DOS calculations, a uniform Monkhorst–Pack mesh of $6 \times 6 \times 6$ k-points was used, while in other cases (NAC and NAMD) the calculations comprised the Γ-point only. The chosen approach, despite possible limitations arising from restricted k- (electrons) and q- (phonons) momentum space sampling, has been considered a method of choice for the aimed NAMD analysis due to its affordability and innate capability of explicit treatment of the anharmonic effects, expected to play an important role in the studied system. Following a 500 fs thermalization dynamics at 300 K performed under the Andersen thermostat conditions, 3.1 ps microcanonical trajectories were generated and used to sample initial conditions for the extended 15 ps nonadiabatic dynamics study with a time step set to 1 fs. (The molecular parameters acquired during the 3.1 ps simulation were repeated periodically.) The NAMD calculation was performed using the decoherence-induced surface hopping (DISH) approach, implemented with the PYXIAID code under the classical path approximation. The nonadiabatic effects have been averaged over 1000 trajectories, each of them involving 1000 realizations of the stochastic surface hopping process to achieve high-quality time-scale estimations. The nonadiabatic electron–hole recombination timescales ($\tau$) have been obtained from an exponential fit to the population change, in its short-time approximation: $\exp(-t/\tau) \approx 1 - t/\tau$. The integration of the power spectra covered frequency region up to $815$ cm$^{-1}$. DOI: 10.1021/acs.jpclett.7b00008
500 cm\(^{-1}\). The atomic structure and orbital visualizations have been obtained with XCrysDen software.\(^7\)

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcl.7b00088.

Figure S1: Total density of states and projected DOS calculated for the anti-ferro and mixed forms. Table S1: Power spectrum - comparison of relative peaks' heights within the low-energy spectrum region. Table S2: Canonically averaged bandgap and its standard deviation, absolute value of NAC, pure-dephasing time, and nonradiative electron-hole recombination time for all studied perovskite forms without the dispersion correction. Figure S2: Correlation plot of BG versus NAC absolute value for all studied forms calculated without the dispersion correction. Figure S3: Power spectra and low-energy IR vibrational spectra for all studied forms calculated without the dispersion correction. Table S3: Optimized Cartesian atomic positions of the ferro form. Table S4: Optimized Cartesian atomic positions of the anti-ferro form. Table S5: Optimized Cartesian atomic positions of the mixed form. (PDF)

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#### Notes

The authors declare no competing financial interest.

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### REFERENCES


