Anharmonicity-driven Rashba co-helical excitons break quantum efficiency limitation

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Closed-shell light-emitting diodes (LEDs) suffer from the internal quantum efficiency (IQE) limitation imposed by optically inactive triplet excitons. Here we show an undiscovered emission mechanism of lead-halide perovskites (LHPs) \(\text{APbX}_3\) \((\text{A}=\text{Cs}/\text{FA}; \text{X}=\text{Cl}/\text{Br}/\text{I})\) that circumvents the efficiency limit of closed-shell LEDs. Though efficient emission is prohibited by optically inactive \(J=0\) in inversion symmetric LHPs, the anharmonicity arising from stereochemistry of Pb and resonant orbital-bonding network along the imaginary \(\chi_{\alpha} \cdots \chi_{\beta} (\Gamma_{\alpha} \text{ (TO)})\) transverse optical (TO) modes, breaks the inversion symmetry and introduces disorder and Rashba-Dresselhaus spin-orbit coupling (RD-SOC). This leads to bright co-helical and dark anti-helical excitons. Many-body theory and first-principles calculations affirm that the optically active co-helical exciton is the lowest excited state in organic/inorganic LHPs. Thus, RD-SOC can drive to achieve the ideal 50 % IQE by utilizing anharmonicity, much over the 25 % IQE limitation for closed-shell LEDs.

In recent years, a dossier of studies have reported high photoluminescence (PL) efficiencies using lead halide perovskite (LHP) light emitting diodes (PeLEDs) \(\text{APbX}_3\) \((\text{A}=\text{Cs}/\text{FA}; \text{X}=\text{Cl}/\text{Br}/\text{I})\) that circumvents the efficiency limit of closed-shell LEDs. Though efficient emission is prohibited by optically inactive \(J=0\) in inversion symmetric LHPs, the anharmonicity arising from stereochemistry of Pb and resonant orbital-bonding network along the imaginary \(\chi_{\alpha} \cdots \chi_{\beta} (\Gamma_{\alpha} \text{ (TO)})\) transverse optical (TO) modes, breaks the inversion symmetry and introduces disorder and Rashba-Dresselhaus spin-orbit coupling (RD-SOC). This leads to bright co-helical and dark anti-helical excitons. Many-body theory and first-principles calculations affirm that the optically active co-helical exciton is the lowest excited state in organic/inorganic LHPs. Thus, RD-SOC can drive to achieve the ideal 50 % IQE by utilizing anharmonicity, much over the 25 % IQE limitation for closed-shell LEDs.

In general, the excited state of singlet LEDs emits photons from an optically active singlet \((S = 0)\), while the supplied energy is dissipated through optically inactive triplets \((S = 1)\) non-radiatively (Fig. 1a). In addition, the energy ordering of exciton spin multiplets is usually unfavorable because of the exchange splitting (Fig. 1a). Under the strong SOC by heavy elements, optically active \(J = 1\) and optically inactive \(J = 0\) are formed (Fig. 1b). This is the case for inversion symmetric inorganic LHPs (Fig. 1b). However, the energy ordering is still unfavorable for an efficient PL due to exchange splitting. If the inversion symmetry is violated under strong SOC, the RD-SOC follows by splitting the \(J = 1/2\) band into two helical spin conduction(valence) bands \(\chi_\alpha(V)\). For instance, the Rashba type interactions lead to \(\chi_{\alpha(V)} = +1\) (counter-clockwise) and \(-1\) (clockwise) (Fig. 1c, d). Then, the excited states from the helical RD conduction and valence bands result in either bright co-helical excitons (Exc\(C\)), \(\chi_{\text{cbm}} \cdot \chi_{\text{vbm}} = +1\), or dark anti-helical excitons (Exc\(A\)), \(\chi_{\text{cbm}} \cdot \chi_{\text{vbm}} = -1\). A compelling observation is that an advantageous energy ordering of excitons can be obtained when the spin-pair helicity of CBM and VBM match, forming Exc\(C_{1}\) as the lowest excited states (Fig. 1c and Supplemental Material). Otherwise, Exc\(A\) becomes the source of non-radiative losses as a result of helicity-mismatch (Fig. 1d and Supplemental Material).

The inversion symmetry breaking anharmonicity in LHP originates from the low energy \(\Gamma_{1u}\) TO motion of A-site cation and halide X (Fig. 2a, b) identified by density functional perturbation theory calculations (DFPT) giving \(E_\Gamma (\alpha-\text{CsPbI}_3) = 1.414\) meV, \(E_\Gamma (\alpha-\text{CsPbBr}_3) = 1.09\) meV, \(E_\Gamma (\alpha-\text{FAPbI}_3) = 2.95\) meV (Fig. 2c-f), consistent with the previous studies.\(^{[13, 19]}\)
are opposite (\(s = 1\)) are the lowest excited states. Generally, bright \(s = 0\) relaxes to dark \(s = 1\) via intersystem crossing (zig-zag line).

(b) In lead halide perovskites, the strong SOC splits the triply degenerate p-type conduction bands into \(J = 3/2\) (not shown) and \(J = 1/2\). Still, the optically inactive singlet \(J = 0\) exciton is the lowest excited state. When the inversion symmetry is broken, the RD-SOC introduces co-helical (\(\text{Ex}_2\)) and anti-helical (\(\text{Ex}_1\)) excitons. (c) When the helicities of CBM and VBM match (\(\chi_{\text{cbm}} \chi_{\text{vbm}} = +1\)), the optically active \(\text{Ex}_C\) becomes the lowest excited state, enabling an efficient PL. The energy ordering is \(\text{Ex}_C < \text{Ex}_{A1} < \text{Ex}_{A2} < \text{Ex}_{C2}\) (Supplementary Information). (d) When the \(\chi_{\text{cbm}}\) and \(\chi_{\text{vbm}}\) are opposite (\(\chi_{\text{cbm}} \chi_{\text{vbm}} = -1\)), the optically inactive \(\text{Ex}_{A1}\) is the lowest excited state and becomes a channel for non-radiative energy loss with the energy ordering \(\text{Ex}_{A1} < \text{Ex}_{C1} < \text{Ex}_{C2} < \text{Ex}_{A2}\).

The effective RD-SOC along the TO\(_i\) displacements \(u_{1,2}\) is given by \(\hat{H}_{\text{SOC}} = \lambda \sigma \cdot \{p \times \nabla (u_1, u_2)\}\), where \(\lambda\), \(\sigma\), \(p\) and \(\nabla\) are SOC parameter, spin operator, momentum operator, and the electric field by inversion symmetry breaking, respectively. Depending on the crystal symmetries, the SOC interactions take different forms: Dressehaus SOC, \(H_D \propto \{\mathbf{p}_s^2 - \mathbf{p}_d^2\} \sigma_x + c.p.\) in the zinc-blende crystals or Rashba SOC \(H_R \propto (z \times p) \cdot \sigma\) in the interfacial asymmetry along the \(z\) direction where \(c.p.\) refers to the circular permutations of indices. Because anharmonic TO\(_i\) fluctuations have low energy barrier, TO\(_i\) fluctuates without any loss of energy at room temperature, which is the source of disordered fluctuations.
TO\textsubscript{i} modes u\textsubscript{1,2} (Fig. 3a, c and Supplemental Material) are the dominant source of RD-SOC (Fig. 3b, d and Supplemental Material)\cite{27}. Under a harmonic motion \(u\), one of the split \(J = 1/2\) bands contains the equal contributions of opposite displacements \(+u\) and \(-u\). The opposite displacements lead to the mixing and cancellation of spin eigenstate of RD interactions by

\[
\langle \psi_k^{-u} | \hat{J} | \psi_k^{-u} \rangle = \langle \psi_k^{+u} | \hat{T}^{-1} \hat{I} \hat{T} | \psi_k^{+u} \rangle = \langle \psi_k^{+u} | - \hat{J} | \psi_k^{-u} \rangle,
\]

where \(\hat{I}\) and \(\hat{T}\) are inversion and time-reversal operator\cite{28}. Thus, the subsequent band states remain as two split effective \(J = 1/2\) bands, which lead to an inefficient PL (Fig. 1b).

However, we need to elucidate if the spin of the subsequent exciton state mix into \(J = 1/2\) by TO\textsubscript{i} displacements in average. To make an efficient LED, \(\chi_{cbm}\) and \(\chi_{vbm}\) must be always co-helical \(\chi_{cbm} \cdot \chi_{vbm} = +1\) (protected from the spin mixing) so that the optically bright \(\text{Ex}_C\) is the lowest excited state (Fig. 1c). Although the prediction of spin-pair helicity of CBM and VBM is difficult, there exist some computational results that halide fluctuations contribute to the co-helicity, while Pb motions are related to the anti-helicity\cite{28,29}. We elaborate that the lowest exciton spin state is RD co-helical and is invariant to the TO\textsubscript{i} vibrations for LHPs in the following.

The individual spin helicity of \(\chi_{cbm}\) and \(\chi_{vbm}\) dynamically changes its helicity under TO\textsubscript{i} vibrations\cite{28}, but we find that the non-collinear helical spins of CBM and VBM have the spin-pair helicity of \(\chi_{cbm} \cdot \chi_{vbm} = +1\) under the TO\textsubscript{i} displacements in \(\alpha\)-CsPbI\textsubscript{3} (Fig. 3b). The non-collinear spin states with TO\textsubscript{i} displacements in \(\alpha\)-CsPbBr\textsubscript{3} and \(\alpha\)-CsPbCl\textsubscript{3} demonstrate the consistent co-helicity between CBM and VBM (Supplemental Material) regardless of the halide type in inorganic LHPs. We also find that the non-collinear spins of CBM and VBM in \(\alpha\)-FAPbI\textsubscript{3} (Fig. 3d) are co-helical. The co-helicity of CBM and VBM in \(\alpha\)-FAPbI\textsubscript{3} is invariant to the different FA dipole directions [110] and [111] (Supplemental Material). The results manifest that \(\chi_{cbm} \cdot \chi_{vbm}\) is protected to be co-helical under the anharmonic TO\textsubscript{i} vibrations, irrespective of halide types in \(\alpha\)-CsPbX\textsubscript{3} (Fig. 3b and Supplemental Material) and A-site cation directions in
\(\alpha\)-FAPbI\(_3\) (Fig. 3d and Supplemental Material). Therefore, we expect that the bright \(\text{Ex}_C\) is always the lowest exciton level. On the contrary, \(\langle \chi_{\text{vbm}} \cdot \chi_{\text{vbm}} \rangle\) along the lowest \(T_{1\alpha}\) LO of dominant Cs⋯Pb motion is found to be anti-helical (Supplemental Material).

The optically inactive singlet \(J = 0\) is lower than the optically active triplet \(J = 1\) only at the inversion symmetric \(Pm\overline{3}m\) crystallographic position in inorganic \(\alpha\)-CsPbX\(_3\). Except for this position, the subsequent energy levels of \(\text{Ex}_C\) and \(\text{Ex}_A\) obtained by the Bethe-Salpeter equation (BSE) calculations demonstrate that \(\text{Ex}_C\) is always the lowest excited energy level under the TO\(_i\) fluctuations irrespective of the halide and A-site cation type (Fig. 4 and Supplemental Material). Thus, there exists the intersystem crossing \(|j = 0\rangle \leftrightarrow |\text{Ex}_C\rangle\) around \(q = 0\) for all inorganic LHPs (Fig. 4a-c, e). The energy level splitting between \(\text{Ex}_C\) and \(\text{Ex}_A\) is in the order of \(\text{Cl} < \text{Br} < \text{I}\) (Fig. 4a-c, 4e), which follows the SOC strength of \(\text{Cl} < \text{Br} < \text{I}\). The exchange splitting between \(J = 1\) and \(J = 0\) excitons at \(q_{\text{TO}_i} = 0\) is in the order of \(\text{Cl} < \text{Br} < \text{I}\) (Fig. 4a-c, 4e).

In \(\alpha\)-FAPbI\(_3\), however, the energy crossing between \(\text{Ex}_C\) and \(\text{Ex}_A\) occurs at large displacements of \(\text{TO}_i\), while the \(\text{Ex}_C\) is the lowest energy level at \(q_{\text{TO}_i} = 0\) due to the inversion breaking of FA molecule and the following incommensurate octahedral distortions (Fig. 4d, e). The favorable energy ordering \(\text{Ex}_{C1} < \text{Ex}_{A1}\) is retained regardless of FA dipole direction of [110] and [111] (Supplemental Material), which explicitly manifests the advantage of organic A-site cation by its local inversion symmetry breaking in PeLED.

Our study reveals the undiscovered mechanism of co-helical versus anti-helical excitons in PeLED by the RD-SOC coupled to the anharmonic glassy disorder. This achieves the ideal 50 % IQE by circumventing the 25 % IQE limitation of conventional closed-shell singlet LEDs, paving a way to highly efficient next-generation emitters.

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