Supporting Information

Distinctive excitonic recombination in solution-processed layered organic-inorganic hybrid two-dimensional perovskites

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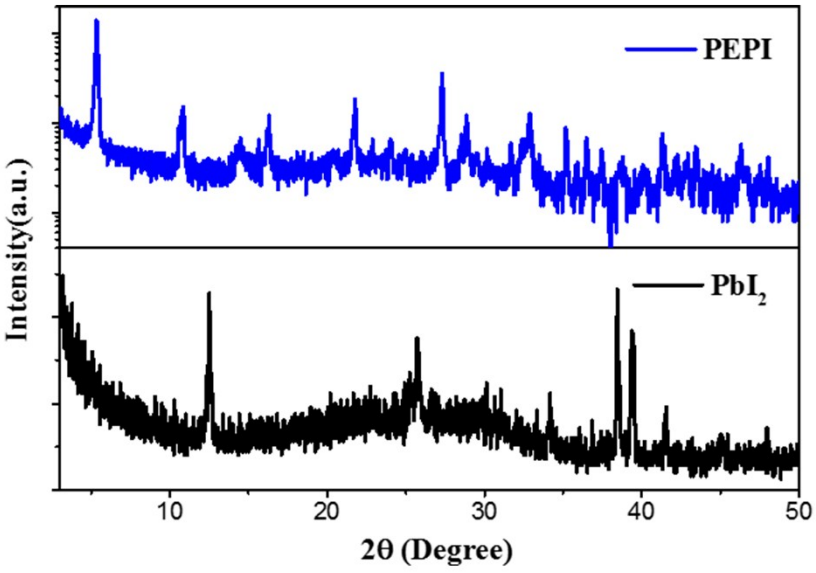

Fig. S1 Powder XRD pattern of PEPI crystals and PbI_2.

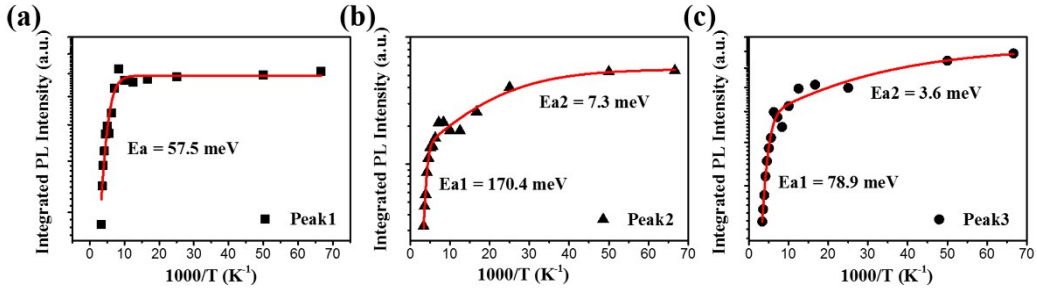

Fig. S2 Integrated PL intensity at different temperatures for peak 1 (a), peak 2 (b), and 3 (c). Peak 1 is fitted with a single exponential Arrhenius equation: $I = \frac{I_0}{1 + \mathrm{a}\exp(-\frac{E_a}{k_B T})}$, where I_0 is the zero-temperature PL intensity, k_B is the Boltzmann constant, a is the ratio between the radiative and the nonradiative decay rates, and E_a is the activation energy. Peak 2 and 3 are fitted with a biexponential Arrhenius equation: $I = \frac{I_0}{1 + \mathrm{a}_1 \exp(-\frac{E_{a1}}{k_B T}) + \mathrm{a}_2 \exp(-\frac{E_{a2}}{k_B T})}$. The obtained activation energy is 57.5 meV for peak 1, 170.4 and 7.3 meV for peak 2, and 78.9 and 3.6 meV for peak 3, respectively.

Quenching behavior of peak 1

The best-refinement of peak 1's quenching behavior gives an E_a of ~51.97 meV (Fig. S2a), far from the exciton binding energy of ~180 meV. Similar phenomenon appears in Gauthron's work[1], in which they performed similar temperature-dependent PL measurements on several PEPI samples prepared at different days, the corresponding E_a was found to significantly vary from sample to sample between 30 and 80 meV. They believed that the decrease of the integrated PL intensity should be related to activation of another carrier recombination channel, which could be a nonradiative mechanism like carrier recombination on impurities inside the barrier, or at the interface between two areas of the inhomogeneous sample. According to their study, we consider that analogous nonradiative mechanism also exists in our case, resulting in the much smaller activation energy.

Determination of activation energy

In determination of E_a, the data of peaks 2 and 3 cannot be well fitted by single-exponential equation, but we need to use biexponential equation. In the biexponential equation, the presence of two E_a is indicative of two competitive nonradiative recombination channels. We note that the activation energies of 7.3 meV (peak 2) and 3.6 meV (peak 3) at low temperature are much smaller than the 13 meV localization energy. Previous study[2] has shown that a low E_a value of a few meV may just result from the temperature-dependent capture cross section of the carriers at the recombination centers, and not from a genuine thermal activation energy.

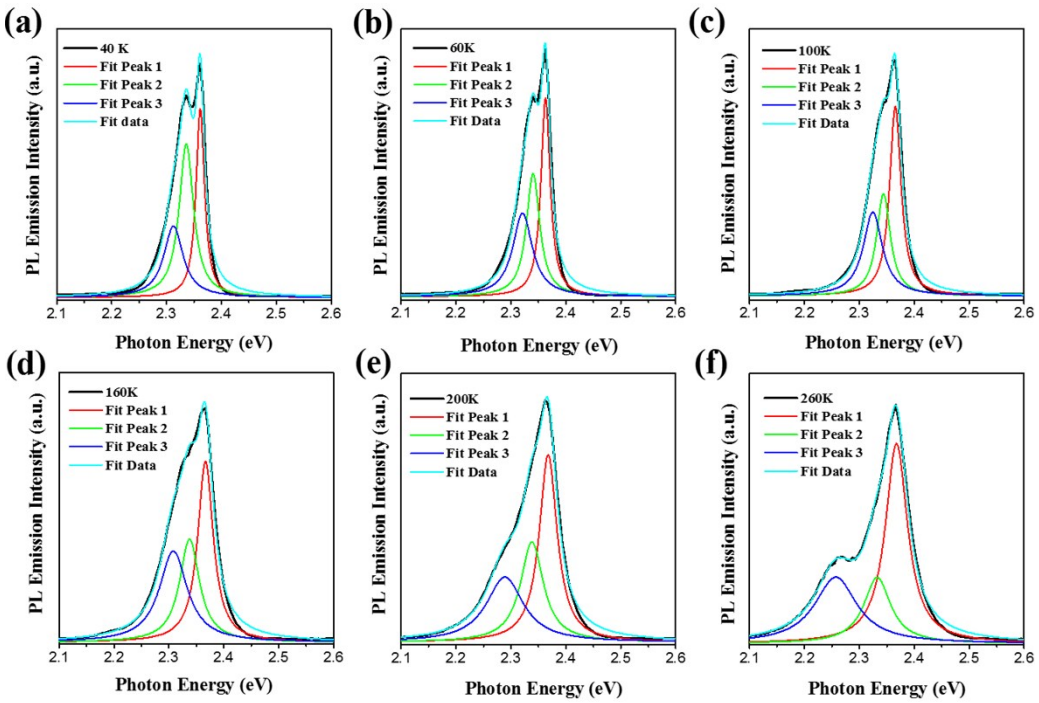

Fig. S3 PL emission spectra with fitting at various temperatures under 405 nm excitation.

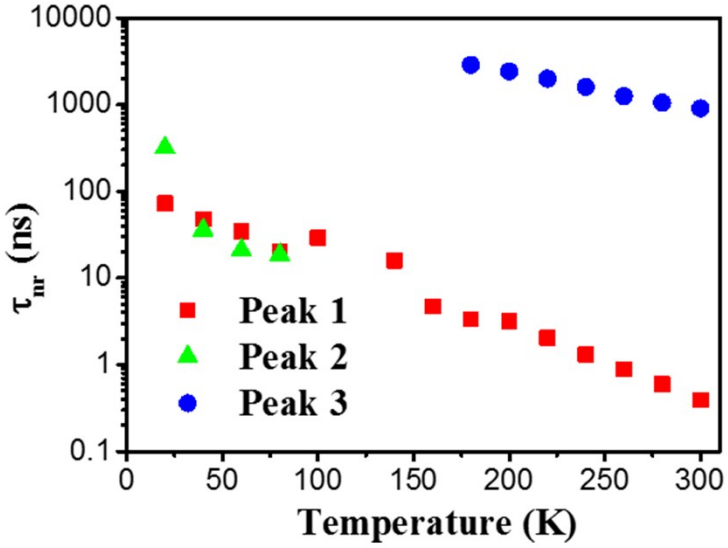

Fig. S4 Temperature dependence of τ_{nr} of peak 1, 2, and 3.

Reference

1. K. Gauthron, J. S. Lauret, L. Doyennette, G. Lanty, A. Al Choueiry, S. J. Zhang, A. Brehier, L. Largeau, O. Mauguin, J. Bloch, and E. Deleporte, *Opt. Express*, 2010, **18**, 5912-5919.
2. J. Krustok, H. Collan, and K. Hjelt, *J. Appl. Phys.*, 1997, **81**, 1442-1445.