

Supporting Information for

Dynamically Disordered Lattice in a Layered Pb-I-SCN Perovskite Thin Film Probed by 2D IR Spectroscopy

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I. UV-Visible Spectrum of the Pb-I-SCN Layered Perovskite

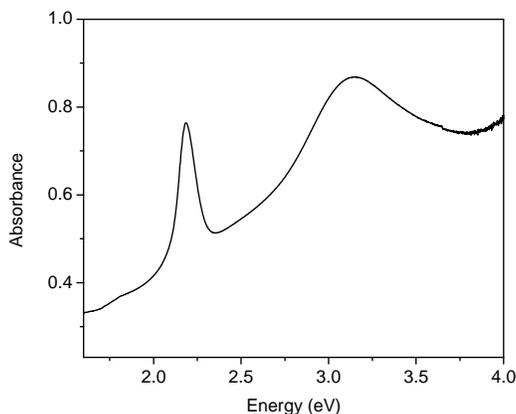


Figure S1. UV-Visible spectrum of the layered perovskite prepared in the manner discussed in the main text. The peak positions and features agree well with the one reported by Umeyama, Lin, and Karunadasa.^{S1} The film visibly appears red. The absorbance is lower compared with the reported spectrum, likely due to the thinner film formed. See Section III and IV for detailed discussion on the thickness and its dependence on the preparation procedure.

II. Photoluminescence Spectrum of the Pb-I-SCN Layered Perovskite

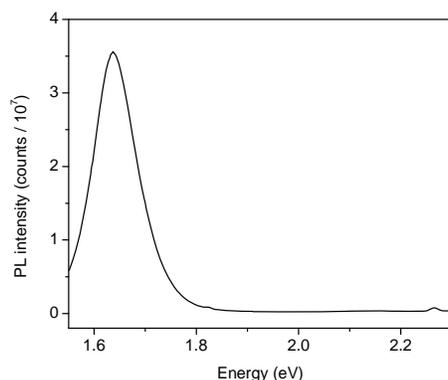


Figure S2. Photoluminescence emission spectrum of the Pb-I-SCN layered perovskite prepared in the manner discussed in the main text. The excitation wavelength is 500 nm. The peak position agrees well with the reported spectrum.^{S1}

III. Powder X-ray Diffraction Pattern (PXRD) of the Pb-I-SCN Layered Perovskite

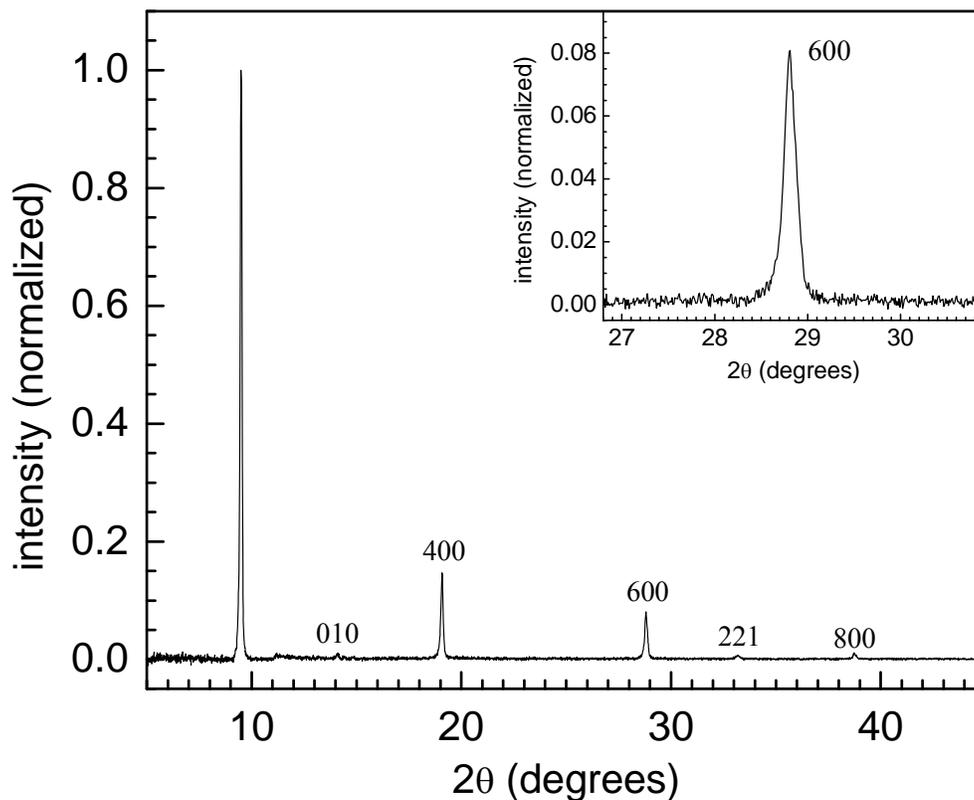


Figure S3. PXRD pattern of the Pb-I-SCN layered perovskite prepared by the identical procedure used to make the final 2D IR and vibrational lifetime measurements. The solid reagents used for the precursor solutions (MAI and $\text{Pb}(\text{SCN})_2$) were vacuum pumped in addition to the drying to remove possible residual traces of water in the reagents. The peaks from the perovskite are as reported previously by Umeyama, Lin, Karunadasa^{S1} except for a very small peak at 14.1° (010), see discussion. The Miller indices for the peaks are given.

In addition to the peaks shown previously by Umeyama, Lin, Karunadasa,^{S1} there is a very small peak at $\sim 14.1^\circ$. This peak has a Miller index of 010; it is large in the PXRD spectrum of a powder sample.^{S1} The 010 peak is caused by slight variations in the orientations of the crystallites that make of the thin film. A peak at this angle can also be caused by water induced MAPbI₃ contamination. However, such contamination produces two additional peaks in the PXDR at 28.3° and 28.5° that are about 30% larger in amplitude than the 14.1° peak.^{S1} The inset shows a blow up of the region around 28° . Peaks at 28.3° and 28.5° are not present, confirming that the peak at 14.1° is not caused by water induced MAPbI₃ contamination.

IV. The Thickness of the Film

Due to the high susceptibility of the sample to the atmospheric humidity, we could not determine the thickness of the film using standard techniques such as atomic force microscopy (AFM) or ellipsometry. Instead, using the transition dipole moment of the CN stretch mode of SCN⁻ anion, which was estimated by the SCN⁻ anion dissolved in DMSO as a solution, we roughly estimated the thickness of the layer by FTIR absorption spectroscopy.

For 0.0565M DMSO solution of NaSCN, the absorption peak area was $\sim 7400 \text{ mOD}\cdot\text{cm}^{-1}$ when the path length was set to $80 \mu\text{m}$. The S¹²CN peak in the Pb-I-SCN perovskite discussed in the main text yielded the area of $\sim 30 \text{ mOD}\cdot\text{cm}^{-1}$, while the concentration of the SCN⁻ within the perovskite structure was estimated to be 8.82M based on the X-ray structure reported by Daub and Hillebrecht.^{S3} By the simple comparison between the concentration and taking into account that S¹²CN only accounts for 5% of the entire SCN⁻ anions in the structure, the thickness was estimated to be on the order of $\sim 40 \text{ nm}$ for the sample discussed in the main text.

Note that the SCN anion in the layered perovskite may have a different transition dipole moment than the one in DMSO solution. This is partially evident in the slight overestimation of the coupling constant as discussed in the main text. Also, we are not taking the orientation of the SCN⁻ anion in the film into account. These factors could affect the estimated thickness of the film.

References

- S1. Umeyama, D.; Lin, Y.; Karunadasa, H. I. *Chem. Mater.* **2016**, *28*, 3241.
- S2. Nishida, J.; Yan, C.; Fayer, M. D. *J. Chem. Phys.* **2017**, *146*, 094201.

S3. Daub, M.; Hillebrecht, H. *Angew. Chem. Int. Ed.* **2015**, *54*, 11016.