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Supporting Information for

Nature of Different Emissive States and Strong Carrier-Phonon Couplings in Quasi-Two-Dimensional Perovskites Derived from Phase-Modulated Two-Photon Micro-Photoluminescence Spectroscopy

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Author Contributions

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Material Synthesis

Chemicals

Lead bromide ($PbBr_2$, 99%, Sigma), cesium bromide (CsBr, 99%, Alfa), methylammonium bromide (MABr, GreatCell Solar), hexylammonium bromide (HexBr, GreatCell Solar), chlorobenzene (Merck) dimethylformamide (DMF, Sigma), and dimethyl sulfoxide (DMSO, Sigma) were purchased and used as-is without any further purification. All the salts were stored in a glove box under N_2 atmosphere to prevent moisture and oxidation.

Synthesis of quasi-2D perovskite nanoparticles

The quasi-2.5-dimensional perovskite precursors were prepared by solubilizing specific stoichiometric quantities of $PbBr_2$, MABr (or CsBr), and HexBr in DMSO following the procedure reported by Wei *et al.*[S1] Ruddlesden Popper perovskite with a chemical formula of $(CH_3(CH_2)_3NH_3)_2A_{n-1}Pb_nBr_{3n+1}$ (where A is either Cs or CH_3NH_3) and n = 3 have been targeted with a $PbBr_2$:MABr (or CsBr):HexBr molar ratio of 3:2:2x for x = 0.5. For example, quasi-$MAPbBr_3$ or $CsPbBr_3$ (qMPB or qCPB) were synthesized by dissolving 0.3 mmol $PbBr_2$ (110.1 mg), 0.2 mmol MABr (22.4 mg), and 0.1 mmol HexBr (18.2 mg) in 2 ml DMSO solution followed by stirring for 2 hr at 800 rpm. Then, 50 µl of this stock precursor solution was added dropwise into 10 ml chlorobenzene under vigorous stirring overnight. The particles were centrifuged and the precipice was dispersed in hexane for further use. Since we employed a $PbBr_2$:MABr (or CsBr):HexBr molar ratio of 3:2:2x, where x = 0.5, the as-prepared particles are in between n = 2 and 3.[S1, S2]

Material Characterization

For the optical and structural measurements, the particles dispersed in hexane were drop-casted on a cover slide followed by drying at room temperature to form a thin film. Grazing incident XRD was acquired using a Bruker D8 machine to observe low-angle X-ray scattering peaks. We have investigated the morphology of these particles by using FEI-FluoSEM (Si wafer substrate, 20 kV).

Quantification of exciton (monomolecular) and free carrier (bimolecular) recombination contributions from the phase-modulated two-photon photoluminescence (2PPL) signals

Details of the 2PPL methodology are given in ref. S3. Here, we emphasize the main arguments in the derivation of the expressions. If we assume that the difference in the frequency between the two phase-modulated beams is ϕ_a, then the intensity of the output beam from a balanced Mach-Zehnder interferometer is given by $I(t) \propto 1+ \cos(\phi_a t)$. The population of electrons (n_e) and holes (n_h) excited by two-photon excitation using the

intensity modulated beam is proportional to $I^2(t)$ and is therefore given by $n_e = n_h \propto 3 + 4\cos(\phi_a t) + \cos(2\phi_a t)$. The amplitude of the modulations at ϕ_a and $2\phi_a$ have a ratio of 4:1.[S3] This ratio can be observed in the photoluminescence if it arises from a monomolecular recombination process. The ratio will differ from this if the transfer function of the detector is not flat over the relevant frequency range. The data should be calibrated by the transfer function in such cases. In any case, a monomolecular recombination does not produce modulations at higher modulation frequencies. The 2PPL signals at $3\phi_a$ and $4\phi_a$ are clear indications of bimolecular recombination processes since here the product $n_e n_h$ has to be considered.

References

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