Supporting Information for

Selective Stabilization and Photophysical Properties of Metastable Perovskite Polymorphs of CsPbI₃ in Thin Films

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Supporting Figures and Tables



Figure S1. EDS mapping of a stabilized $CsPbI_3$ film using 4-fluorophenylethylammonium as the additive, which shows uniform distribution of the ligand in the sample. We note that the asprepared film was less stable than the PEA-stabilized film



Figure S2. PXRD patterns of the as-deposited CsPbI₃ films with the additives of acetic acid (HAc, molar ratio CsPbI₃ to HAc = 1:2, blue curve), oleylamine (molar ratio CsPbI₃ to oleylamine = 1:1, red curve), and mixed oleylamine and HAc (molar ratio CsPbI₃ to oleylamine to HAc = 1:1:2) with the photos of the corresponding thin films shown as insets. We note that the addition of only oleylamine can partially stabilize the perovskite structure for a short time, but the film convert into the yellow γ -CsPbI₃ phase within 1 day. The recipe of CsPbI₃+HAc could produce the black phase after spin coating, but quickly transformed to the non-perovskite phase upon annealing.



Figure S3. The relative PL quantum yield of the PEA-stabilized CsPbI₃ film under different injected carrier density.



Figure S4. (a) Cross-section SEM image of the PEA-stabilized CsPbI₃ thin film used for the TRPL and PL quenching experiments; (b) Absorption coefficient of the PEA-stabilized CsPbI₃ thin film. The absorption coefficient at 639 nm is 2.0×10^4 cm⁻¹. Inset is the cross-section SEM image of the PEA-stabilized CsPbI₃ thin film sample with a thickness of 75 nm used to collect the absorption spectrum.



Figure S5. TRPL spectra of the neat CsPbI₃, CsPbI₃/PCBM, and CsPbI₃/spiro-OMeTAD films under the same injected carrier density of 2.9×10^{15} cm⁻³, along with the stretched exponential fit for the neat CsPbI₃ film, the fits to one-dimensional diffusion model for CsPbI₃/PCBM and CsPbI₃/spiro-OMeTAD films, and the IRF.



Figure S6. Histograms of the fitting values of β and $1/k_{neat}$ for the neat CsPbI₃ sample, and electron and hole diffusion coefficient for the quenched samples. The statistical distributions of these values give rise to the standard deviations reported in Table S1.

	Average value	Standard deviation
$1/k_{\text{neat}}$ (ns)	45	9
β	0.67	0.07
D _{spiro} (cm ² /s)	0.0013	0.0006
$D_{\rm PCBM}~({\rm cm}^2/{\rm s})$	0.027	0.003
L _{spiro} (nm)	80	20
L _{PCBM} (nm)	350	40

Table S1. Fitting results of the TRPL quenching experiments.