Supporting Information

Optimization of PbI_2/$MAPbI_3$ Perovskite Composites by Scanning Electrochemical Microscopy

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Experimental Section

Time-resolved Photoluminescence. Steady-state and time-resolved photoluminescence (PL) measurements were made using the FluoroLog Time Correlated Single Photon Counting (TCSPC) Spectrofluorometer. The PL decay time for perovskite films was monitored at 770 nm with a 485 nm pulsed LED laser (Horiba Scientific) with a pulse duration < 200 ps (instrument response function ~ 300 ps) and the fluence of ~30nJ/cm^2 on the spectrofluorometer. The instrument response function was obtained at 485 nm using glass slides. The photoluminescence decay kinetics was fitted to a stretch exponential decay function[1] or a bi-exponential decay function,[2,3]

For a stretch exponential decay function

$$I(t) = I_0 \exp(-(t/\tau_s)^{\beta^s}) \quad \text{(S1)}$$

For a bi-exponential decay function

$$I(t) = A_1 e^{-(t/\tau 1)} + A_2 e^{-(t/\tau 2)} \quad \text{(S2)}$$

$$\tau_{PL} = <\tau> = \alpha_1 \tau_1 + \alpha_2 \tau_2 \quad \text{(S3)}$$

Where $\alpha_1 = A_1/(A_1+A_2)$ and $\alpha_2 = A_2/(A_1+A_2)$,

In order to easily compare lifetimes of all perovskite films, τ_{PL} are determined by bi-exponential decay function.[1-3] The fitting parameters (τ_1, α_1, τ_2, α_2) and corresponding errors (χ^2) of photoluminescence decay are listed in Table S1.

Diffusion modeling. The diffusion coefficient of electrons and holes can be estimated by the number and distribution of excitations in the bilayer system by means of the 1-D diffusion equation,[4-6]

$$\frac{\partial n(x,t)}{\partial t} = D\frac{\partial^2 n(x,t)}{\partial x^2} - k(t)n(x,t) \quad \text{(S4)}$$

where n(x,t) is charge carrier density, D is the charge carrier diffusion coefficient, $k(t)$ is the PL decay rate without quencher.[4] The total decay rate, $k = k_r + k_{nr} = \beta\tau_s^{-\beta}\tau^{\beta-1}$, was estimated by using a stretched exponential function to fit photoluminescence decay curves of perovskite films without quenchers. And x is the vertical distance of a point in the perovskite layer from the interface of the substrate/perovskite layer. Under the photoexcitation, the initial distribution of photoexcitations was given by:

$$n(x,0) = n_0 \exp(-\alpha x) \quad \text{(S5)}$$

where α is the absorption coefficient.

The boundary condition n(L,t) = 0, where x = 0 at the glass/perovskite interface and L is the perovskite film thickness, can be obtained by assuming that all charge carriers that reach the interface are quenched. From the initial distribution of photoexcitations and boundary conditions, time-dependent of total carrier number, $N(t)$, can be derived in Equation S4, which is in line with the previous report.[7]

$$N(t) = \frac{2n_0 L}{\pi}\exp(-kt)\sum_{m=0}^{\infty}\left(\exp\left(-\frac{\pi^2 D}{L^2}(m+0.5)^2 t\right)\frac{\exp(-\alpha L)\pi(m+0.5)+(-1)^m\alpha L}{((\alpha L)^2+\pi^2(m+0.5)^2)(m+0.5)}\right) \quad \text{(S6)}$$

The diffusion coefficient, D, can then be estimated by fitting the measured photoluminescence decay with Equation S6. The carrier diffusion length, L_D, was then determined from Equation S7:

$$L_D = (D \cdot \tau_{PL})^{1/2} \quad \text{(S7)}$$

where τ_{PL} is the lifetime in the absence of quenchers.

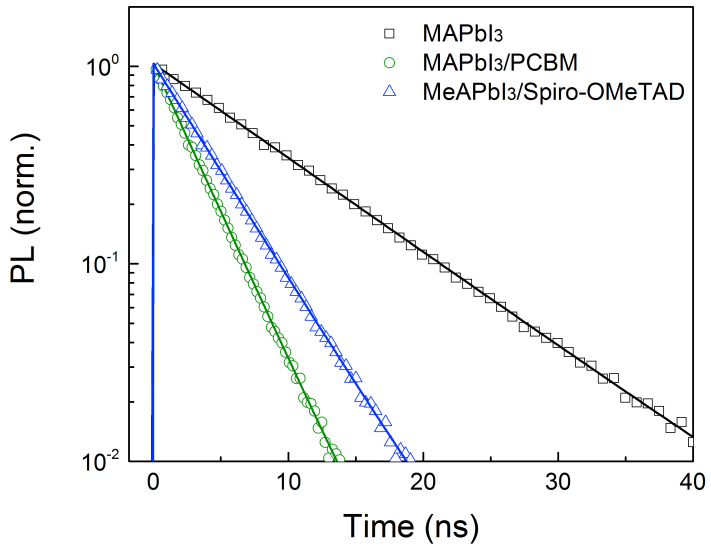

Figure S-1. Time-resolved photoluminescence measured at 770 nm for $MAPbI_3$ (black), $MAPbI_3$/PCBM (red), $MeNH_3PbI_3$/Spiro-OMeTAD (blue) films after excitation at 485 nm. The solid lines here are the stretch exponential fits of the photoluminescence decay.

Table S1. Photoluminescene decay times (τ_s and τ_{PL}) and corresponding parameters of $PbI_2/MAPbI_3$ composite perovskite films containing 0.0, 1.0, 2.5, 5.0, 7.5, 10 and 15 wt % of excess PbI_2.

Perovskite	τ_1/ns (α_1)	τ_2/ns (α_2)	τ_{PL}[a]/ns	χ^2	τ_s/ns	β
0 % $PbI_2/MeNH_3PbI_3$	9.1 (100%)	–	9.1 ± 0.1	1.02	8.8 ± 0.2	1.00 ± 0.02
1 % $PbI_2/MeNH_3PbI_3$	7.9 (18%)	108.9 (82%)	90.7 ± 0.2	1.21	88.5 ± 0.6	0.78 ± 0.03
2.5 % $PbI_2/MeNH_3PbI_3$	9.0 (17%)	122.7 (83%)	103.3 ± 0.2	1.25	97.5 ± 0.8	0.83 ± 0.04
5.0 % $PbI_2/MeNH_3PbI_3$	7.3 (18%)	101.6 (82%)	84.6 ± 0.1	1.18	82.6 ± 0.5	0.77 ± 0.03
7.5% $PbI_2/MeNH_3PbI_3$	6.2 (19%)	86.7 (81%)	71.3 ± 0.2	1.16	68.7 ± 0.3	0.76 ± 0.03
10 % $PbI_2/MeNH_3PbI_3$	8.2 (100%)	–	8.2 ± 0.1	1.03	7.8 ± 0.2	1.00 ± 0.02
15 % $PbI_2/MeNH_3PbI_3$	4.4 (100%)	–	4.4 ± 0.1	1.03	4.1 ± 0.2	1.00 ± 0.02

[a] $\tau_{PL} = <\tau> = \Sigma_i \alpha_i \tau_i$; the two amplitudes, α_1 and α_2, in the photoluminescence decay of 0%, 10%, 15% $PbI_2/MAPbI_3$ films were the same, which demonstrated that they are belong to single-exponential decay.

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