

# Supporting Information

## Optimization of PbI<sub>2</sub>/MAPbI<sub>3</sub> 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<sup>2</sup> 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<sup>1</sup> or a bi-exponential decay function,<sup>2,3</sup>

For a stretch exponential decay function

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

For a bi-exponential decay function

$$I(t) = A_1 e^{-(t/\tau_1)} + A_2 e^{-(t/\tau_2)} \quad (\text{S2})$$

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

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,  $\tau_{PL}$  are determined by bi-exponential decay function.<sup>1-3</sup> The fitting parameters ( $\tau_1, \alpha_1, \tau_2, \alpha_2$ ) and corresponding errors ( $\chi^2$ ) 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,<sup>4-6</sup>

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

where  $n(x,t)$  is charge carrier density,  $D$  is the charge carrier diffusion coefficient,  $k(t)$  is the PL decay rate without quencher.<sup>4</sup> The total decay rate,  $k = k_r + k_{nr} = \beta\tau_s^{-1}\tau_p^{-1}$ , 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:

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

where  $\alpha$  is the absorption coefficient.

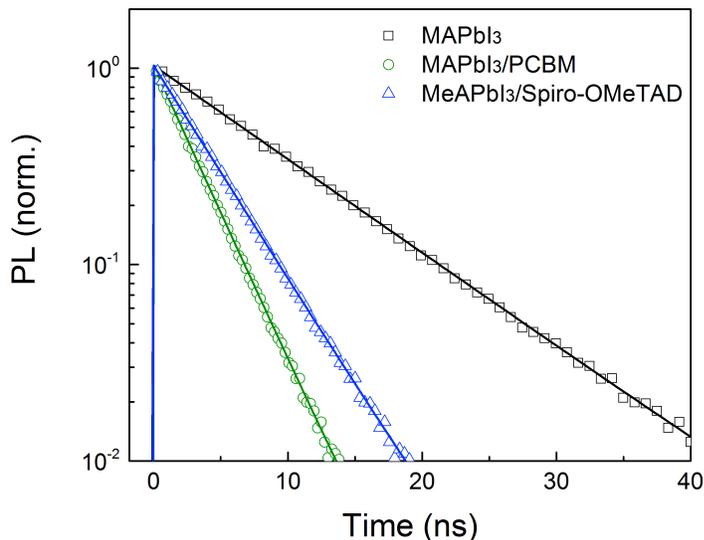
The boundary condition  $n(L,t) = 0$ , where  $x = 0$  at the glass/perovskite interface and  $L$  is the perovskite film thickness, can be obtained by assuming that all charge carriers that reach the interface are quenched. From the initial distribution of photoexcitations and boundary conditions, time-dependent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

$$N(t) = \frac{2n_0L}{\pi} \exp(-kt) \sum_{m=0}^{\infty} \left( \exp\left(-\frac{\pi^2 D}{L^2} (m+0.5)^2 t\right) \frac{\exp(-\alpha L)\pi(m+0.5) + (-1)^m \alpha L}{((\alpha L)^2 + \pi^2(m+0.5)^2)(m+0.5)} \right) \quad (S6)$$

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:

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

where  $\tau_{PL}$  is the lifetime in the absence of quenchers.



**Figure S-1.** Time-resolved photoluminescence measured at 770 nm for MAPbI<sub>3</sub> (black), MAPbI<sub>3</sub>/PCBM (red), MeNH<sub>3</sub>PbI<sub>3</sub>/Spiro-OMeTAD (blue) films after excitation at 485 nm. The solid lines here are the stretch exponential fits of the photoluminescence decay.

**Table S1.** Photoluminescence decay times ( $\tau_s$  and  $\tau_{PL}$ ) and corresponding parameters of PbI<sub>2</sub>/MAPbI<sub>3</sub> composite perovskite films containing 0.0, 1.0, 2.5, 5.0, 7.5, 10 and 15 wt % of excess PbI<sub>2</sub>.

Perovskite	$\tau_1/\text{ns}$ ( $\alpha_1$ )	$\tau_2/\text{ns}$ ( $\alpha_2$ )	$\tau_{PL}^a/\text{ns}$	$\chi^2$	$\tau_s/\text{ns}$	$\beta$
0 % PbI <sub>2</sub> /MeNH <sub>3</sub> PbI <sub>3</sub>	9.1 (100%)	–	9.1 ± 0.1	1.02	8.8 ± 0.2	1.00 ± 0.02
1 % PbI <sub>2</sub> /MeNH <sub>3</sub> PbI <sub>3</sub>	7.9 (18%)	108.9 (82%)	90.7 ± 0.2	1.21	88.5 ± 0.6	0.78 ± 0.03
2.5 % PbI <sub>2</sub> /MeNH <sub>3</sub> PbI <sub>3</sub>	9.0 (17%)	122.7 (83%)	103.3 ± 0.2	1.25	97.5 ± 0.8	0.83 ± 0.04
5.0 % PbI <sub>2</sub> /MeNH <sub>3</sub> PbI <sub>3</sub>	7.3 (18%)	101.6 (82%)	84.6 ± 0.1	1.18	82.6 ± 0.5	0.77 ± 0.03
7.5% PbI <sub>2</sub> /MeNH <sub>3</sub> PbI <sub>3</sub>	6.2 (19%)	86.7 (81%)	71.3 ± 0.2	1.16	68.7 ± 0.3	0.76 ± 0.03
10 % PbI <sub>2</sub> /MeNH <sub>3</sub> PbI <sub>3</sub>	8.2 (100%)	–	8.2 ± 0.1	1.03	7.8 ± 0.2	1.00 ± 0.02
15 % PbI <sub>2</sub> /MeNH <sub>3</sub> PbI <sub>3</sub>	4.4 (100%)	–	4.4 ± 0.1	1.03	4.1 ± 0.2	1.00 ± 0.02

<sup>a</sup>  $\tau_{PL} = \langle \tau \rangle = \sum_i \alpha_i \tau_i$ ; the two amplitudes,  $\alpha_1$  and  $\alpha_2$ , in the photoluminescence decay of 0%, 10%, 15% PbI<sub>2</sub>/MAPbI<sub>3</sub> films were the same, which demonstrated that they are belong to single-exponential decay.

## References

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