

### Supporting Information

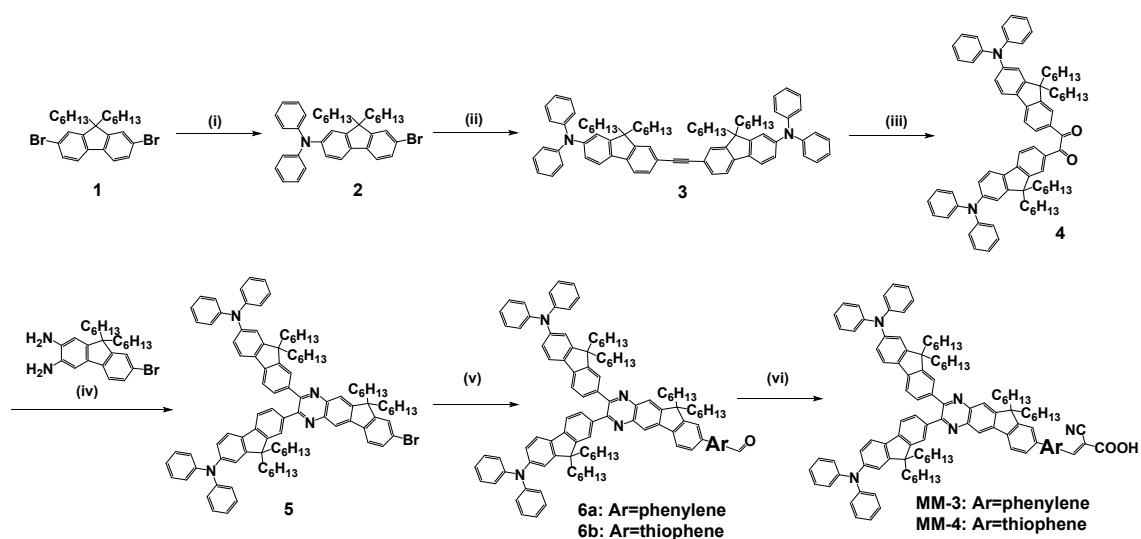
## D-A- $\pi$ -A Organic Sensitizers Surface Passivation for Efficient and Stable Perovskite Solar Cells

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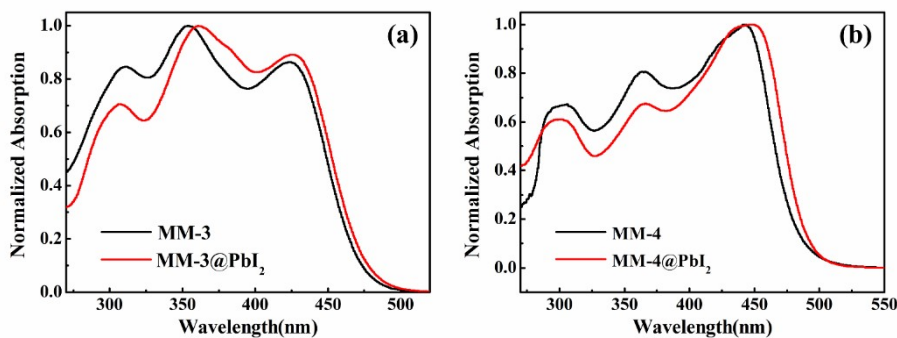
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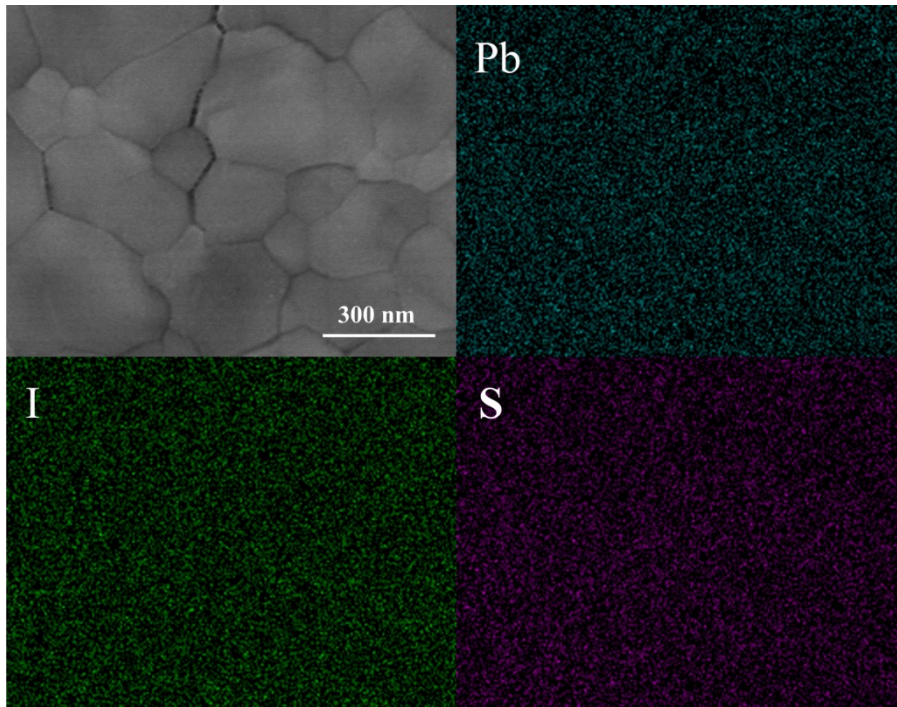
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**Scheme S1** Synthesis condition of organic dye sensitizer: (i)  $\text{Pd}_2(\text{dba})_3$ , dppf, Sodium *tert*-butoxide, toluene, 110 °C; (ii) Acetylenedicarboxylic acid, dppb, DBU,  $\text{PdCl}_2(\text{PPh}_3)_2$ , DMSO (iii)  $\text{KMnO}_4$ ,  $\text{NaHCO}_3$ , Aliquat 336,  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ ; (iv)  $\text{CH}_3\text{COOH}$ , 110 °C; (v) (4-(1,3-dioxolan-2-yl)phenyl)tributylstannane/(5-(1,3-dioxolan-2-yl)thiophen-2-yl)tributylstannane,  $\text{PdCl}_2(\text{PPh}_3)_2$ , DMF, 100 °C; then THF/HCl, rt.; (vi)  $\text{CNCH}_2\text{COOH}$ , piperidine, chloroform, reflux.



**Fig. S1** UV-vis absorption spectra of (a) MM-3, MM-3@ $\text{PbI}_2$ , and (b) MM-4, MM-4@ $\text{PbI}_2$  in the DMF solution.



**Fig. S2** SEM-EDS elemental maps of perovskite film passivated by MM-4.

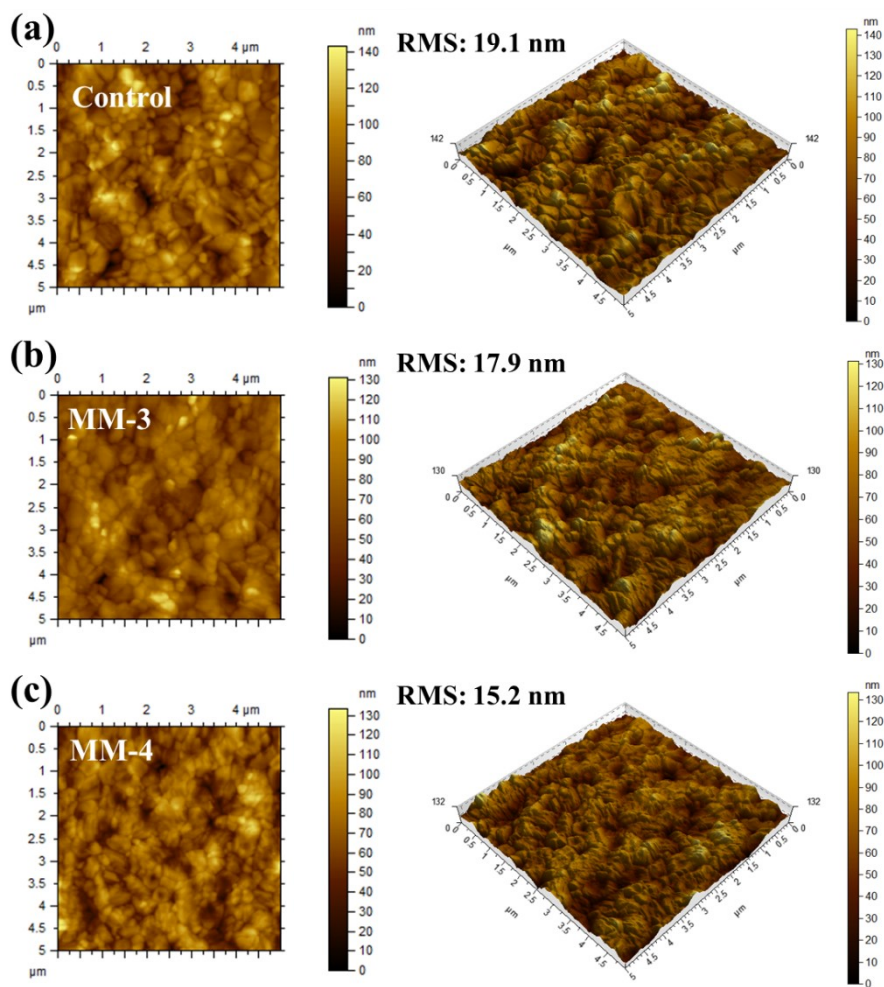


Fig. S3 AFM images of the perovskite films of (a) control, and passivated by (b) MM-3, and (c) MM-4.

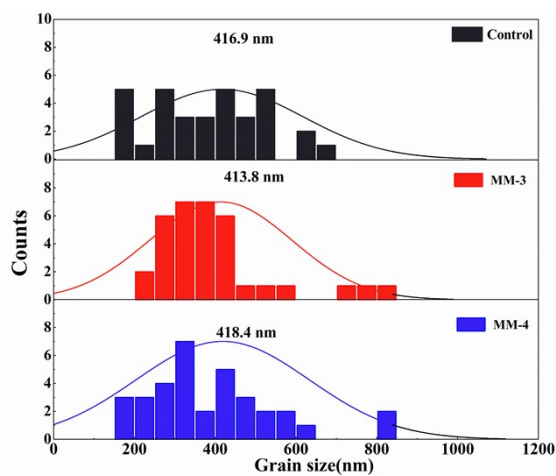
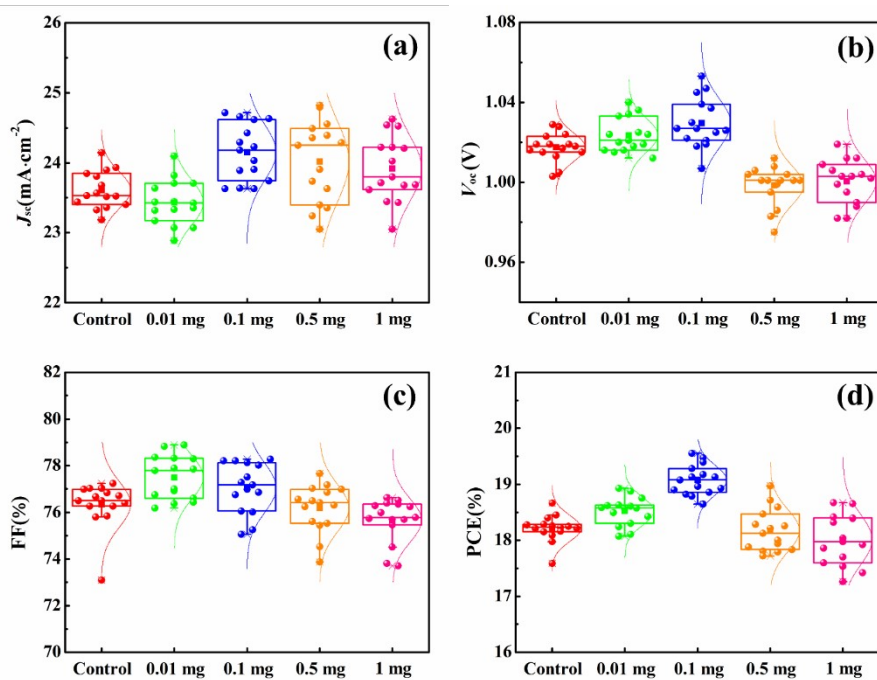
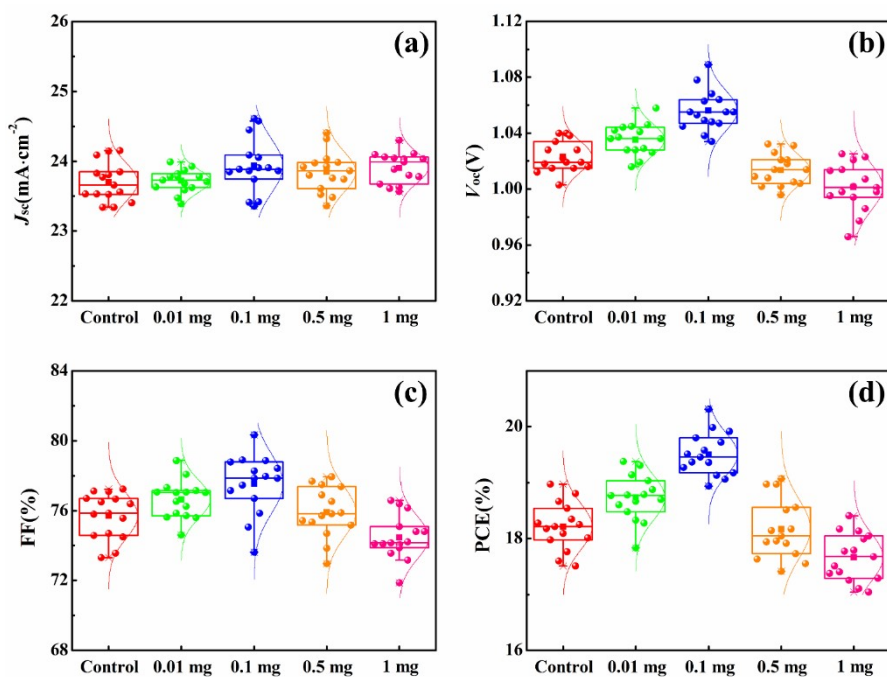


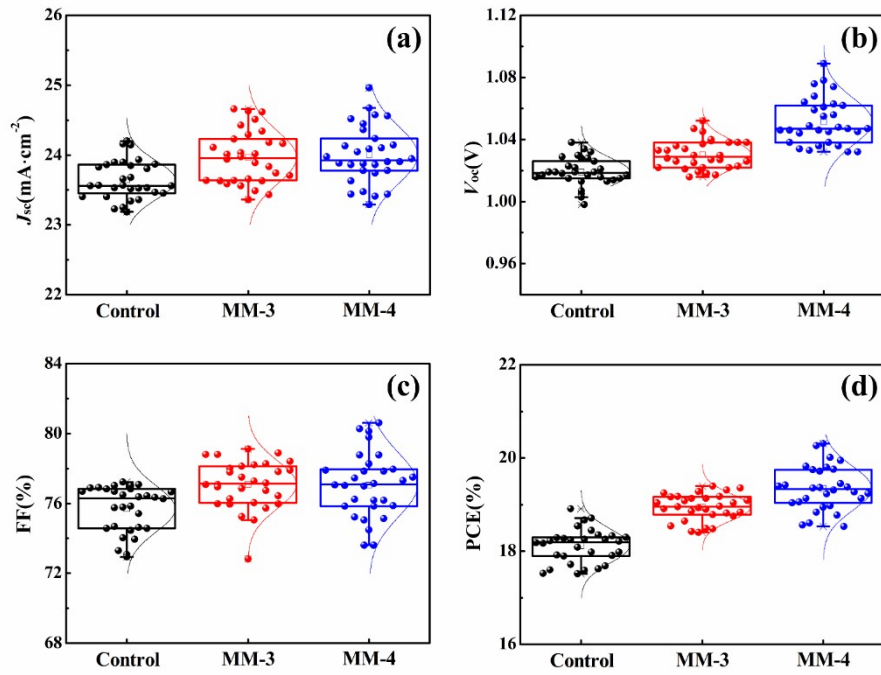
Fig. S4 The statistical distribution histograms of perovskite grain sizes without and with MM-3 or MM-4 passivation obtained from the top-view SEM images.



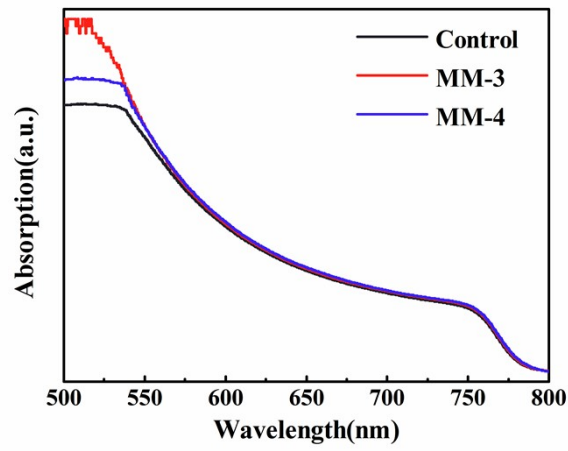
**Fig. S5** Statistical distribution of photovoltaic parameters of (a)  $J_{sc}$ , (b)  $V_{oc}$ , (c) FF, and (d) PCE, obtained by  $J$ - $V$  measurements of PSCs passivated by MM-3 with different concentrations.



**Fig. S6** Statistical distribution of photovoltaic parameters of (a)  $J_{sc}$ , (b)  $V_{oc}$ , (c) FF, and (d) PCE, obtained by  $J$ - $V$  measurements of PSCs passivated by MM-4 with different concentrations.



**Fig. S7** Statistical distribution of photovoltaic parameters of (a)  $J_{sc}$ , (b)  $V_{oc}$ , (c) FF, and (d) PCE, obtained by  $J$ - $V$  measurements of PSCs without and with different sensitizers passivation.



**Fig. S8** UV-vis absorption spectra of the perovskite films without and with different sensitizers passivation.

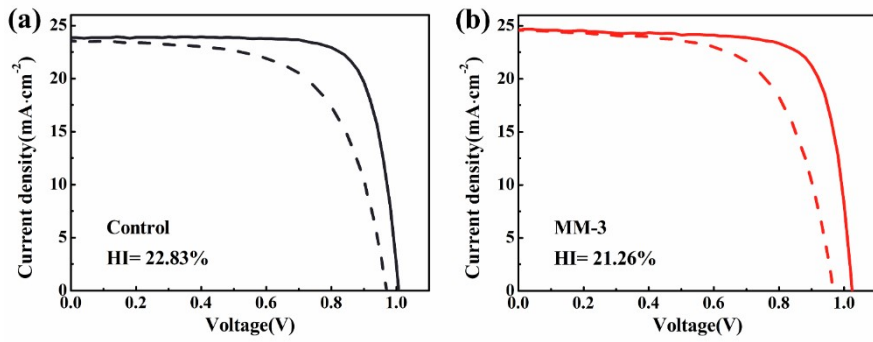


Fig. S9 *J-V* curves of the PSCs (a) without, and with (b) MM-3 at reverse and forward scans.

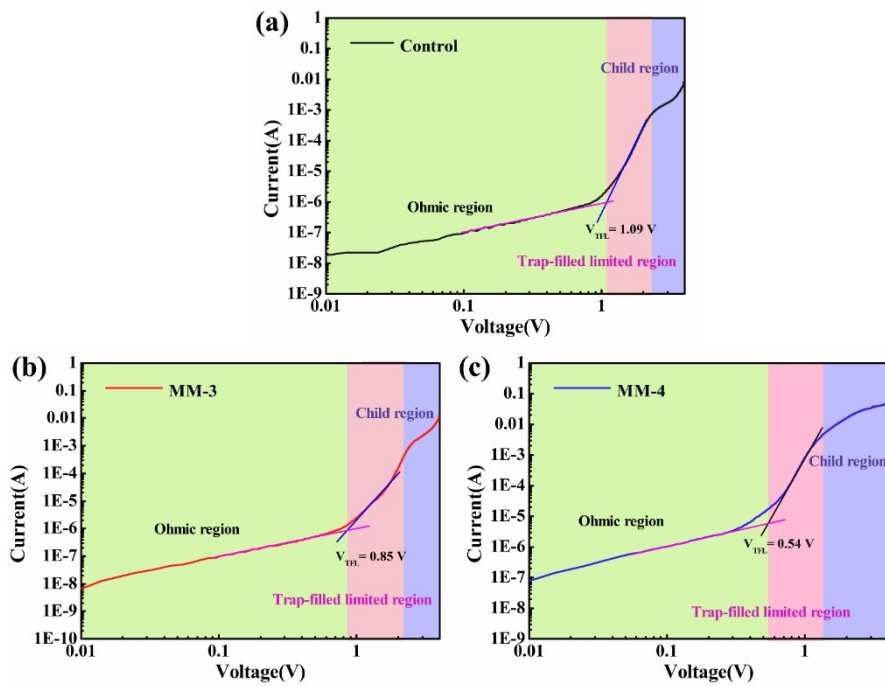
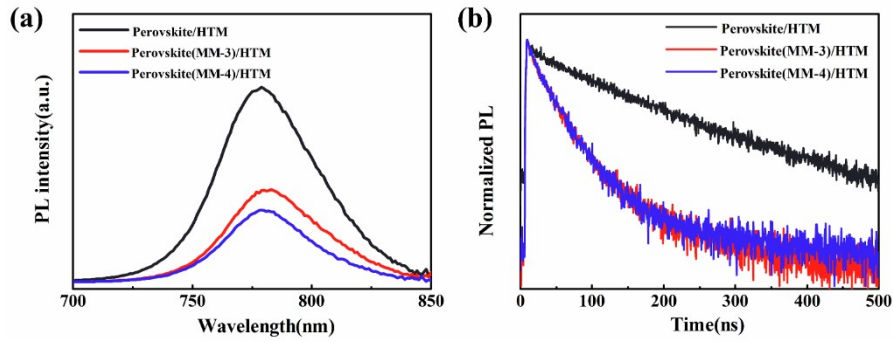
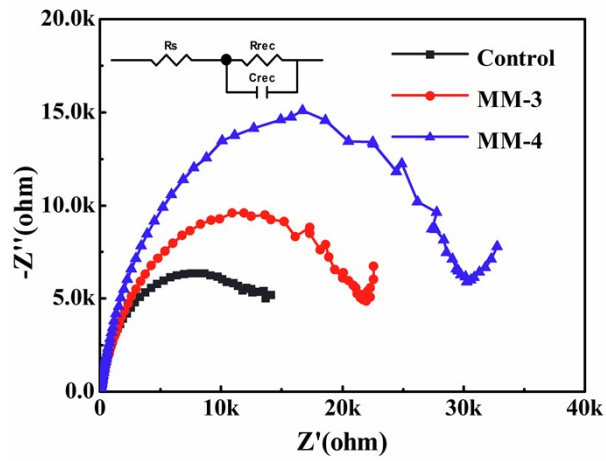


Fig. S10 Dark *I-V* curves of the electron-only device structure of FTO/TiO<sub>2</sub>/perovskite/PCBM/Au, (a) control, (b) MM-3, and (c) MM-4.



**Fig. S11** The PL spectra and TR-PL spectra of perovskite films without and with sensitizers passivation based on the structure of glass/perovskite/HTM.



**Fig. S12** Nyquist plots of PSCs without and with different sensitizers passivation under the dark condition at bias.



**Table S1** Photovoltaic parameters of champion PSCs of the control device and with the passivation of MM-3 and MM-4 at reverse and forward scans.

Sample	Scan direction	$J_{SC}/\text{mA cm}^{-2}$	$V_{OC}/\text{V}$	FF/%	PCE/%	HI <sup>[a]</sup> /%
Control	Reverse	23.83	1.01	77.92	18.66	22.83
	Forward	23.54	0.97	63.24	14.40	
MM-3	Reverse	24.63	1.02	76.75	19.28	21.26
	Forward	24.56	0.97	64.20	15.18	
MM-4	Reverse	24.96	1.08	76.19	20.26	6.12
	Forward	24.92	1.06	72.85	19.02	

$$HI_{[a]} = \frac{PCE_{Reverse} - PCE_{Forward}}{PCE_{Reverse}}$$

**Table S2** Fitted data for TRPL decay based on the structure of glass/perovskite without and with sensitizers passivation.

Sample	$A_1(\%)$	$\tau_1(\text{ns})$	$A_2(\%)$	$\tau_2(\text{ns})$	$\tau_{ave}^{[b]}(\text{ns})$
Control	3.13	38.14	96.87	326.91	325.83
MM-3	1.10	20.1	98.90	448.85	448.64
MM-4	4.14	82.21	95.86	625.36	622.30

$$\tau_{ave}^{[b]} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$$

**Table S3** Fitted data for TRPL decay based on the structure of glass/perovskite/HTM without and with sensitizers passivation.

Sample	$A_1(\%)$	$\tau_1(\text{ns})$	$A_2(\%)$	$\tau_2(\text{ns})$	$\tau_{\text{ave}}^{[b]}(\text{ns})$
Control	0.88	11.35	99.12	178.18	178.09
MM-3	9.67	14.6	90.33	51.28	50.20
MM-4	4.59	9.23	95.41	46.51	46.16

**Table S4** EIS parameters of PSCs without and with different dye molecules passivation under the dark condition at bias.

Sample	$R_s/\Omega$	$R_{\text{rec}}/\Omega$
Control	10.7	14883
MM-3	10.4	24721
MM-4	11.4	34900