Supporting Information

## Gradient band structure: high performance perovskite solar cells using poly(bisphenol A anhydride-*co*-1,3-phenylenediamine)

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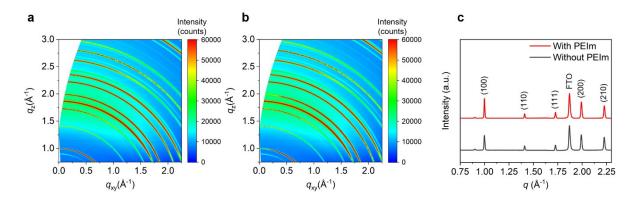


Fig. S1. Crystallinity of the perovskite layer. (a) 2D-WAXS patterns of perovskite layer (a) with and (b) without PEIm. (c) Azimuthally integrated intensity profiles from 2D-WAXS data with and without PEIm. Concentration is 0.25 vol%.

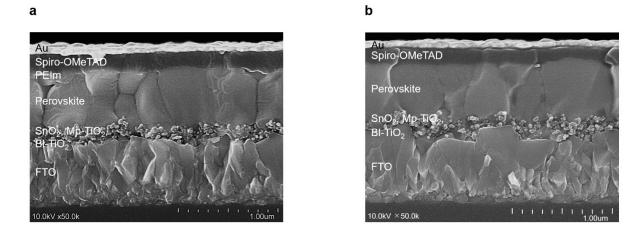


Fig. S2. Cross-sectional scanning electron microscope (SEM) image for perovskite solar cell (a) with and (b) without PEIm. PEIm concentration

were 0.25 and 0.5 vol%.

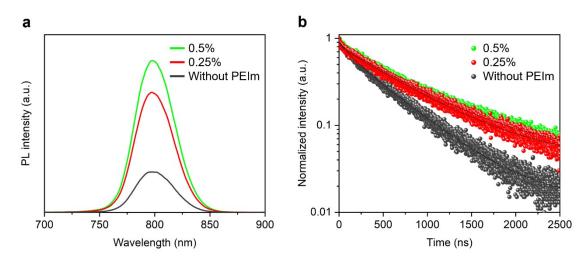


Fig. S3. Photoluminescence spectroscopy of steady-state intensity with and without PEIm concentration. The sample structure is Glass/Perovskite/PEIm. PEIm concentration were 0.25 and 0.5 vol%.

 Table S1. Detailed fitting parameters for the time-resolved photoluminescence measurement. The sample structure was

 Glass/Perovskite/PEIm. PEIm concentration were 0.25 and 0.5 vol%.

_		A <sub>1</sub>	$ au_{a}$ (ns)	A <sub>2</sub>	τ <sub>b</sub> (ns)
-	0.5%	0.101	43.5	0.763	713.2
	0.25%	0.064	31.5	0.733	686.3
	Without PEIm	0.148	98.2	0.730	517.3
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+The equation for the fitting is  $y=y_0+A_1\times exp(-(x-x_0)/\tau_a)+A_2\times exp(-(x-x_0)/\tau_b)$ .

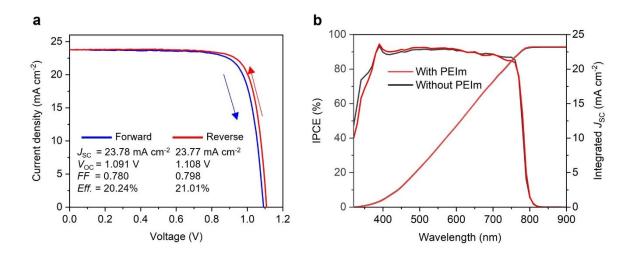


Fig. S4. Device performances of perovskite solar cells. (a) Photovoltaic properties of *I-V* curves for hysteresis. b) IPCE spectra and integrated short circuit current density ( $J_{sc}$ ) with and without PEIm. PEIm concentration is 0.25 vol%.

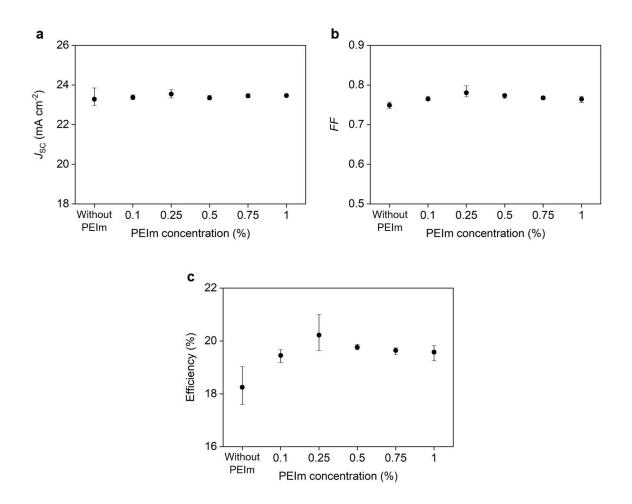


Fig. S5. Photovoltaic property distributions of perovskite solar cells changing PEIm concentration. Distribution of photovoltaic properties for (a)  $J_{sc}$ , (b) fill factor (*FF*), and (c) Photoconversion efficiency as a function of PEIm concentration.

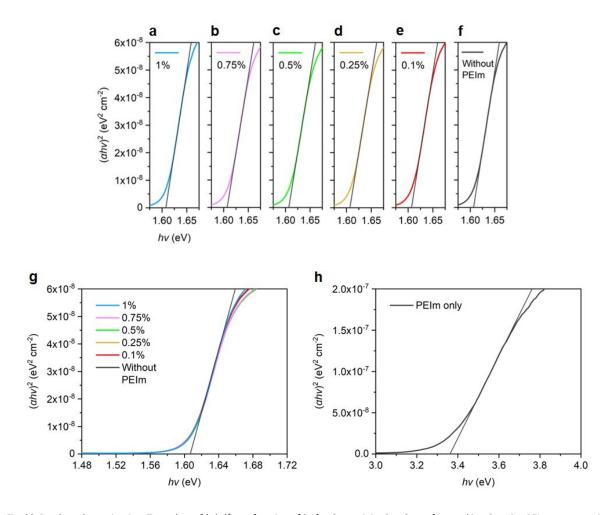


Fig. S6. Bandgap determination. Tauc plots of  $(\alpha h v)^2$  as a function of hv for determining bandgap of perovskite changing PEIm concentration of (a) 1, (b) 0.75, (c) 0.5, (d) 0.25, (e) 0.1, (f) without PEIm and (g) all in one. All of the determined bandgaps were the same as 1.61 eV. (h) Tauc plot only for the PEIm layer (3.36 eV).

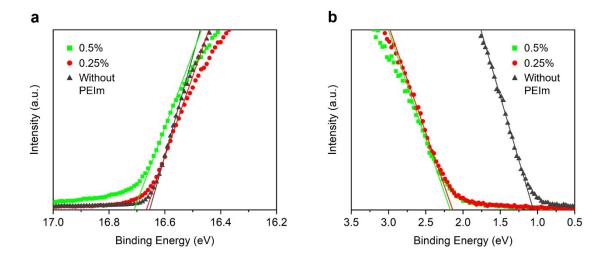


Fig. S7. Measurement of energy band diagram parameters. (a) UPS spectrum edge of work function and (b) valence band edge of perovskite layer with and without PEIm. PEIm concentration were 0.25 and 0.5 vol%.

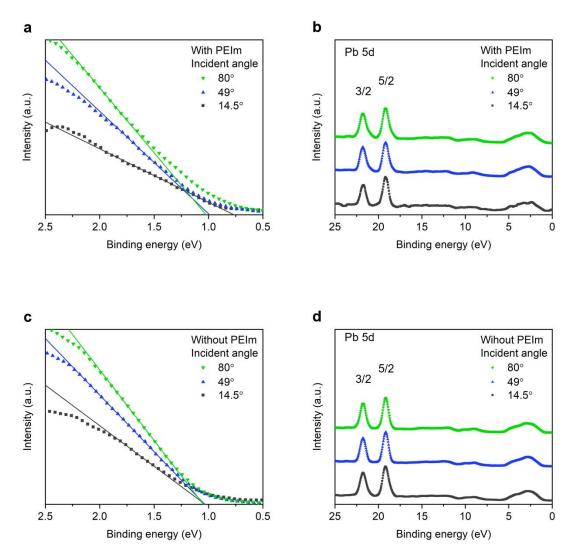


Fig. S8. Measurement of energy band diagram parameter for surface and bulk perovskite. (a) Valence band edge of zoom-in and (b) zoomout of perovskite with PEIm was measured by AD-HAXPES with the photon energy of 7940 eV. (c) Valence band edge of zoom-in and (d) zoom-out of perovskite without PEIm. The incident angle was changed from 14.5 to 80 degrees. PEIm concentration is 0.25 vol%.

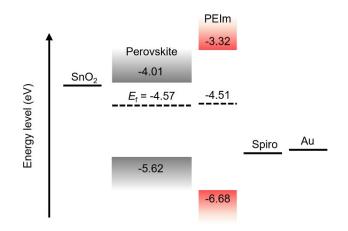


Fig. S9. Energy band diagram for the perovskite solar cells, where each value is from the vacuum level.  $E_{\rm f}$  is assigned to Fermi-Level. PEIm concentration was 0.5 vol%.

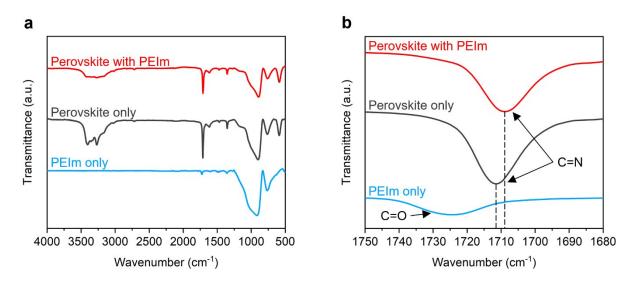


Fig. S10. Infrared transmittance spectra of (a) overview and (b) zoom-up. Samples were structured Glass/Perovskite/PEIm, Grass/Perovskite, and Glass/PEIm. The concentration of PEIm was 0.25vol%.

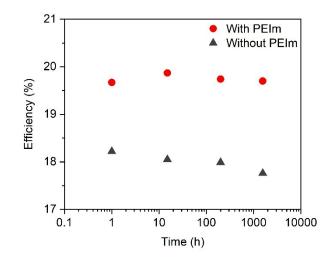


Fig. S11. Stability measurement for perovskite solar cells with and without PEIm. Samples were kept in dark in the air with 10% humidity at 25 °C condition.