#### **Electronic Supplementary Information for:**

## Enhanced performance and stability of p-i-n perovskite solar cells by

### utilizing an AIE-active cathode interlayer

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# 1. NMR spectra











8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 Chemical Shift (ppm)





Fig. S4. <sup>13</sup>C NMR (CDCl<sub>3</sub>) spectrum of M<sub>2</sub>.



3.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 - Chemical Shift (ppm)





Fig. S6. <sup>1</sup>H NMR (DMSO) spectrum of PTN-Br



**Fig. S7.** a) AIE curves of **PTN-Br** (10  $\mu$ M) in Methanol/ether mixtures with different ether fractions ( $f_e$ ). b) PL spectrum of **PTN-Br** at the  $f_e = 90\%$  and in the films.



Fig. S8. CV curve of PTN-Br in the film measured in 0.1 Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN.

CIL	Thickness (nm)	$V_{ m oc}$	$J_{ m sc}$	FF	PCE
		(V)	$(\mathrm{mAcm}^{-2})$	(%)	(%)
w/o <b>PTN-Br</b>	0.0	1.004	20.67	72.93	15.14
$0.2 \text{ mg mL}^{-1} \mathbf{PTN}\text{-}\mathbf{Br}$	4.4	1.016	21.11	75.73	16.24
0.5 mg mL <sup>-1</sup> <b>PTN-Br</b>	5.8	1.023	21.89	77.88	17.44
$1.0 \text{ mg mL}^{-1}$ <b>PTN-Br</b>	8.1	1.023	20.25	75.58	15.66

**Table S1.** Photovoltaic performance parameters of the PVSCs with different concentration of **PTN-Br** CIL under AM 1.5G irradiation.



**Fig. S9.** Steady-state PCE and photocurrent of the reference PVSCs without **PTN-Br** measured at the maximum power point.



Fig. S10. Light intensity dependence of the  $V_{oc}$  of PVSCs with or without PTN-Br.



Fig. S11. AFM images of the films at the concentration of 0.2 a) and 1.0 b) mg mL<sup>-1</sup>, water contact angle of the films at the concentration of 0.2 c) and 1.0 d) mg mL<sup>-1</sup>.



**Fig. S12.** a) Normalized PCE decay of **PTN-Br**-based PVSCs and reference one stored in ambient condition (25 °C, relative humidity = 55%). b) Normalized PCE decay of **PTN-Br**-based PVSCs and reference one in a N<sub>2</sub>-purged glovebox at 50 °C.



Fig. S13. The schematic diagram of the UV stability.