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A novel azo dye molecule enables defect passivation and crystallization toward efficient perovskite solar cells

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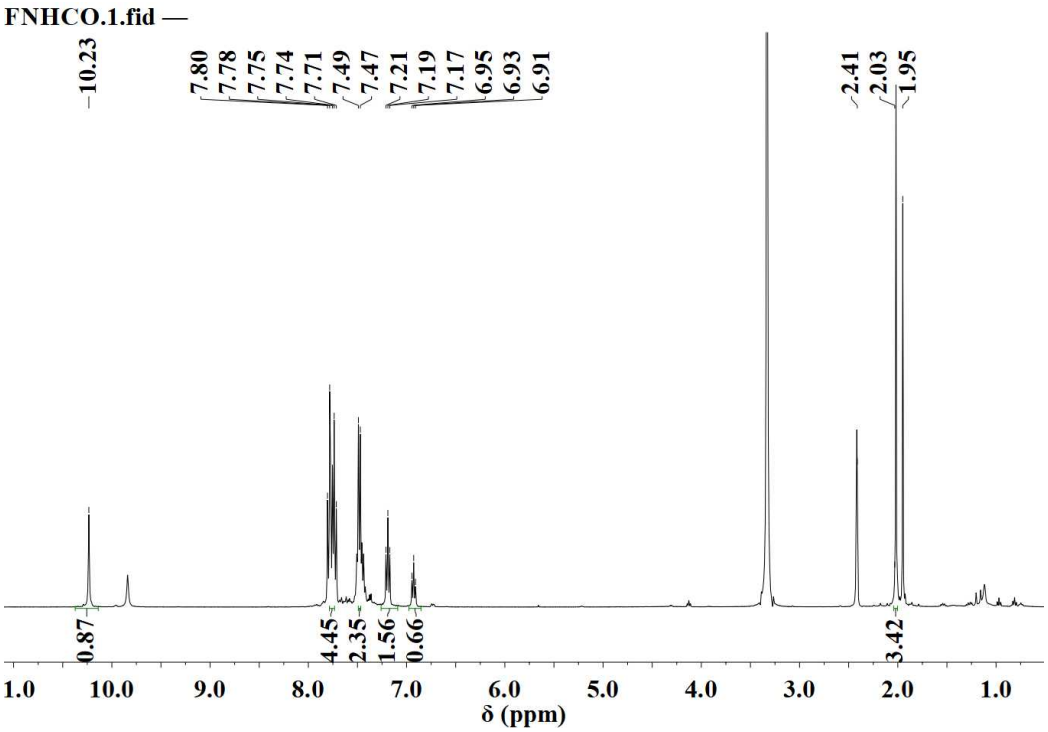


Figure S1. The ^{1}H nuclear magnetic resonance (NMR) spectra of Ph-azo-PhAmi in DMSO-d6.

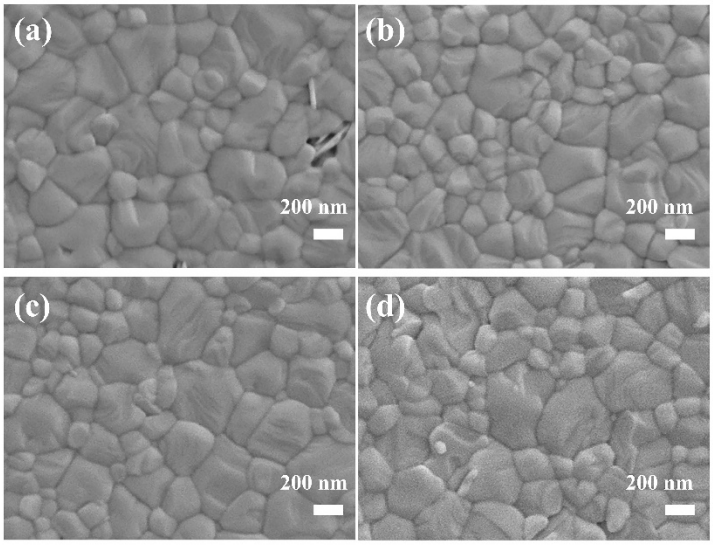


Figure S2. The SEM surface images of the perovskite film with (a) 0, (b) 0.05, (c) 0.1 and (d) 0.2 mg/mL Ph-azo-PhAmi.

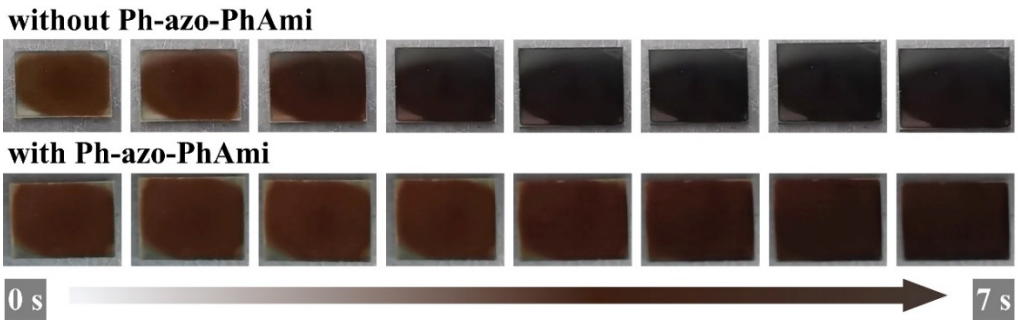


Figure S3. The morphological changes of perovskite films during annealing.

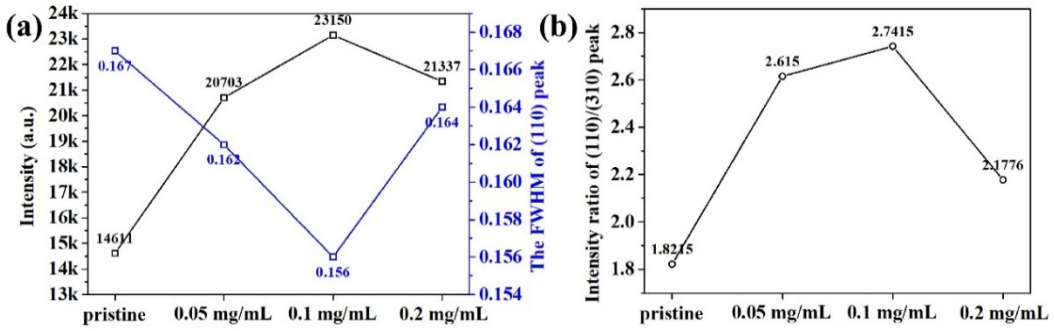


Figure S4. (a) The intensity and peak width at half height for the (110) peak of the perovskite. (b) The intensity ratio of (110)/(310) peak of the perovskite with different concentration of Ph-azo-PhAmi (0, 0.05, 0.1, 0.2 mg/mL).

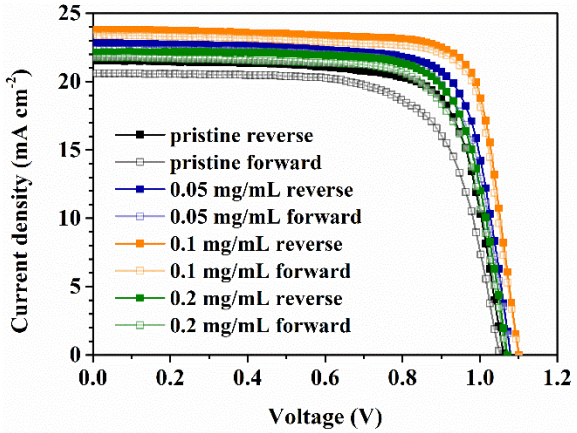


Figure S5. The J-V curves of the PSCs with different concentration of Ph-azo-PhAmi (0, 0.05, 0.1, 0.2 mg/mL).

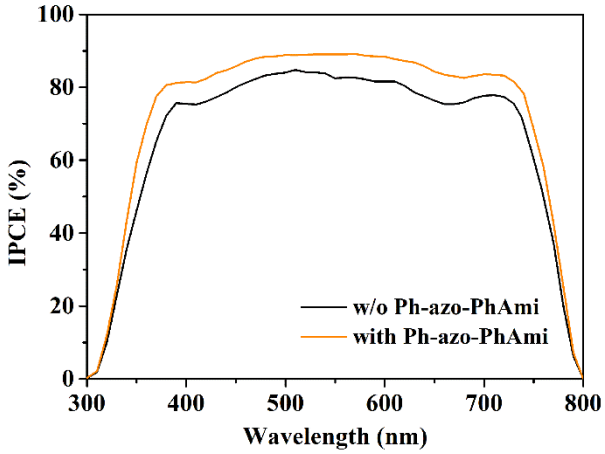


Figure S6. The IPCE spectra of the PSCs without and with 0.1 mg/mL Ph-azo-PhAmi.

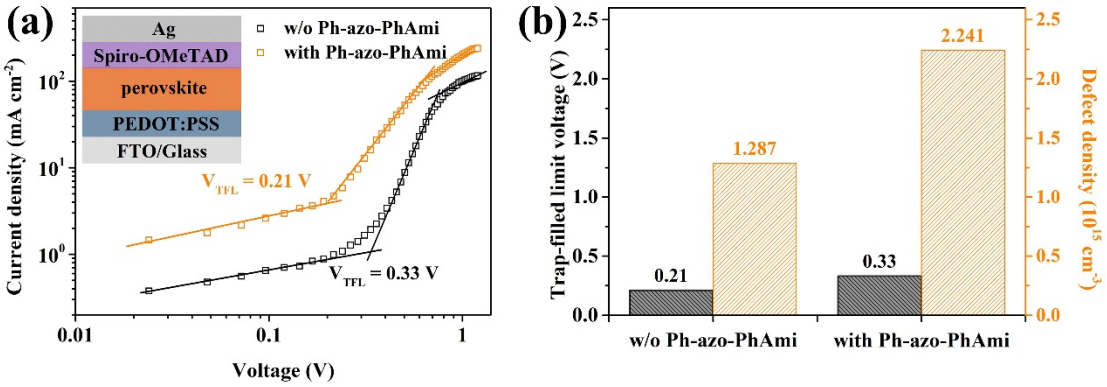


Figure S7. (a) The SCLC curves of electron-only PSCs (without and with Ph-azo-PhAmi) with the structure of FTO/PEDOT:PSS/$MAPbI_3$/spiro-OMeTAD/Ag.

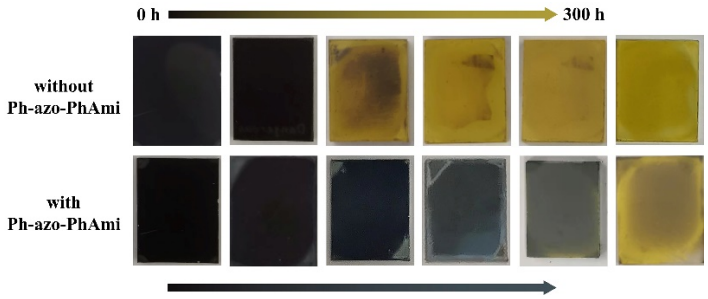


Figure S8. The morphology photographs for the perovskite films without and with Ph-azo-PhAmi under dark and humid air condition (in room temperature and RH: 65-75%) for 300 h without stress.

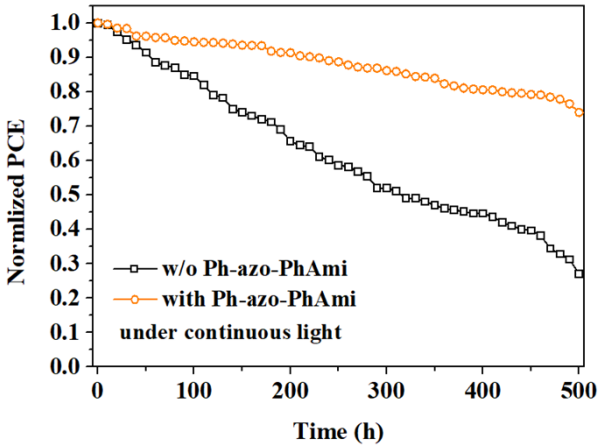
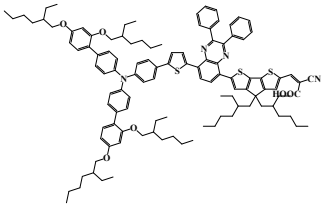
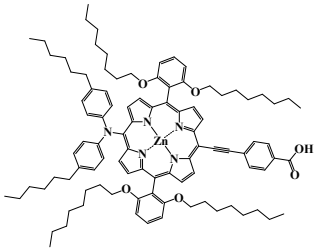
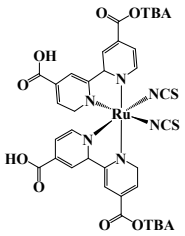
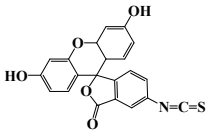
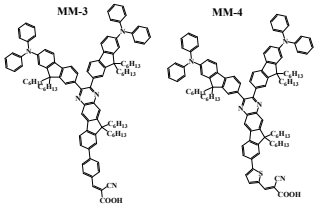
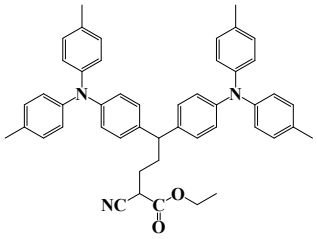
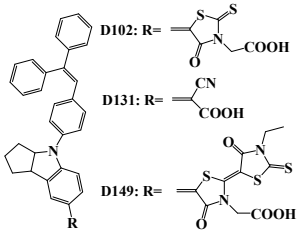
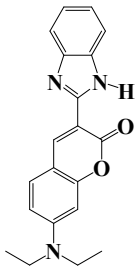
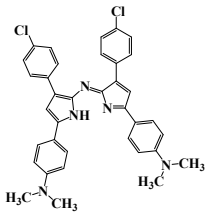
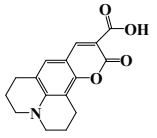
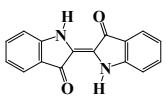


Figure S9. The light stability of devices without and with Ph-azo-PhAmi under continuous light soaking 100 mW/cm^2 for 500 h at room temperature (RH: 30±5%).

Table S1. Summary of PSCs fabricated in open air with different dye additives in literature.

Additives	**Categories**	**Structures**	**Perovskite**	**Anchor**	**PCE (%)**	**Ref**
AQ310	organic dye		FAMA perovskite	-COOH	19.43	1
YD2-o-C8	zinc porphyrin dye		CsFAMA perovskite	-C=O	20.5	2
N719	organic dye		FAMA perovskite	-C=O	19.6	3

FITC	organic dye		$CsPbI_{1.5}Br_{1.5}$	-SCN	14.05	4
MM-3 MM-4	organic dyes		CsFAMA perovskite	-COOH	20.31	5
MC1	merocyanine dye		CsFAMA perovskite	-CN -C=O	20.31	6
D102 D131 D149	indoline dyes		$Cs_2AgBiBr_6$	-C=O	3.97 2.57 4.23	7
8GFF	fluorescent dye		$MAPbI_3$	-C=O	19.16	8
Aza-DIPY	organic dye		$MAPbI_3$	pyrrole, benzene ring and Cl	19.71	9
Coumarin 343	organic dye		FACs perovskite	-C=O	20.9	10
Indigo	organic dye		CsFAMA perovskite	-C=O -N-H	23.22	11

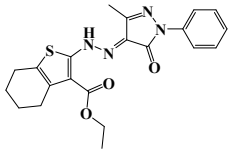
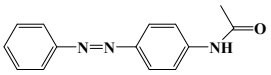
Th-azi-Pyr	hydrazone dye		$MAPbI_3$	-C=O -N-H S atom	19.27	12
Ph-azo-PhAmi	azo dye		$MAPbI_3$	-N-H -C=O	20.85	This work

Table S2. The fitting results of the TRPL and EIS measurements of perovskite films with and without Ph-azo-Ph.

Samples	A_1 (cnts)	τ_1 (ns)	A_2 (cnts)	τ_2 (ns)	τ_{ave}	R_s	R_{ct}
without Ph-azo-PhAmi	437.83	4.63	292.44	67.716	61.85	2.04	4130
with Ph-azo-PhAmi	337.77	141.28	237.03	6.32	137.22	0.36	6460

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