Supplementary Materials

## Improving the Photostability of Small-Molecule-Based Organic Photovoltaics by Providing a Charge Percolation Pathway of Crystalline Conjugated Polymer

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**Figure S1.** Thermal stability of SM-OPV devices. All the devices were subjected to thermal stress at 80°C for 1000h.



**Figure S2.** 2D images of GIXRD as prepared (a) Binary, (b) Ternary-F and (c) Ternary-CN films and light soaked (d) Binary, (e) Ternary-F and (f) Ternary-CN films.

**Table S1.** In-plain  $\pi$ - $\pi$  stack peak information of Binary, Ternary-F and Ternary-CN films before and after light soaking.

Direction	Material	(010) π-π stack		
		Scattering vector(q) [Å <sup>-1</sup> ]	d-spacing [Å]	FWHM
In-plane	Binary	1.689	3.720	0.116
	Binary(L)	1.664	3.775	0.107
	Ternary-F	1.677	3.747	0.088
	Ternary-F(L)	1.630	3.855	0.107
	Ternary-CN	1.622	3.874	0.155
	Ternary-CN(L)	1.634	3.845	0.159

Direction	Material	(200) Lamellar stack			
		Scattering vector(q) [Å-1]	d-spacing [Å]	FWHM	
Out - of plane	Binary(D)	0.425	14.783	0.0349	
	Binary(L)	0.423	14.861	0.0391	
	Ternary-F(D)	0.427	14.706	0.0320	
	Ternary-F(L)	0.425	14.783	0.0307	
	Ternary-CN(D)	0.427	14.706	0.0568	
	Ternary-CN(L)	0.427	14.706	0.0693	

**Table S2.** Out-of-plain lamellar stack peak information of Binary, Ternary-F and Ternary-CN films before and after light soaking.



**Figure S3.** Plots of log (*J*sc) versus log (*I*) for all the devices.

	S value	Standard deviation
Binary	1.04	0.025
Binary(L)	1.02	0.037
Ternary-F	0.96	0.009
Ternary-F(L)	0.98	0.008
Ternary-CN	0.97	0.009
Ternary-CN(L)	0.98	0.018

**Table S3.** The *S* values of all devices before and after light soaking.