Balancing Crystal Size in Small Molecule Non-Fullerene Solar Cells through Fine-Tuning the Film-Forming Kinetics to Fabricate Interpenetrating Network

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**Han Jie and Liang Qiuju contributed equally to this work

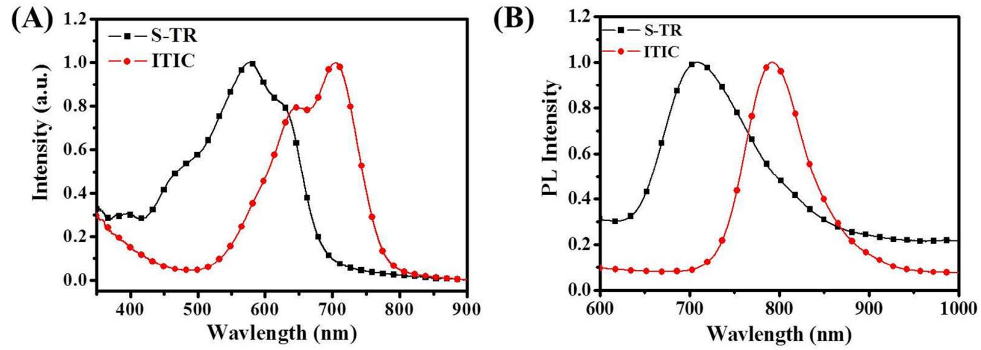

Figure S1. (A) UV-vis absorption spectra of S-TR and ITIC film. (B) Photoluminescence spectra of S-TR, ITIC, and S-TR/ITIC blend film.

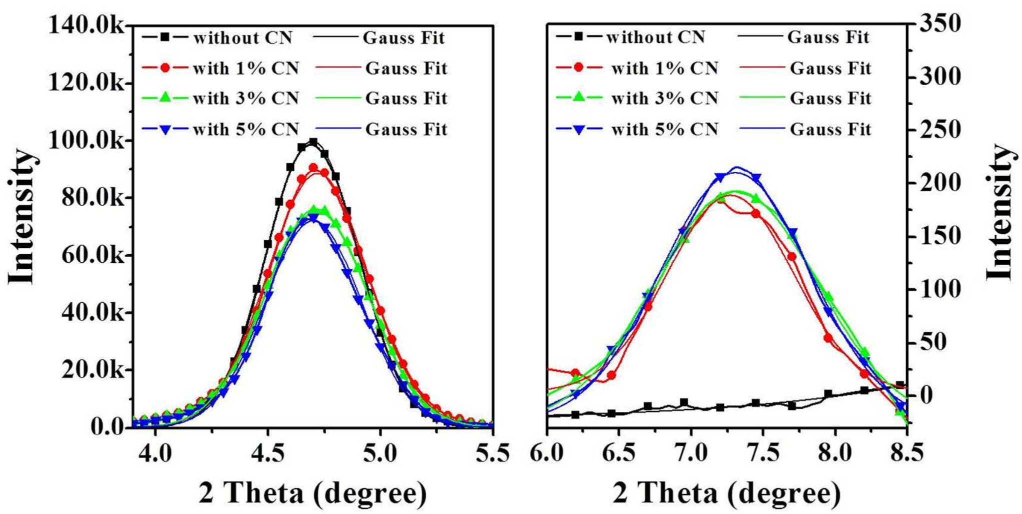

Figure S2. GIXD profiles for blend films with different contents of CN. (Left) the diffraction signal of S-TR; (Right) the diffraction signal of ITIC. The coherent length of the donor and acceptor can be estimated using Scherrer's relation.

$$L = \frac{0.9\lambda}{\Delta_{2\theta} \cos\theta}$$

Where $\Delta_{2\theta}$ is the full width at half maximum of the peak, and it was calculated from Gaussian fitting of the corresponding diffraction peaks.[1, 2]

[1] Zhang, S.; Zuo, L.; Chen, J.; Zhang, Z.; Mai, J.; Lau, T.; Lu, X.; Shi M.; Chen, H. *J. Mater. Chem. A*, **2016**, *4*, 1702–1707.

[2] Rogers, J.; Schmidt, K.; Toney, M.; Bazan, G.; Kramer, E. *J. Am. Chem.Soc.* **2012**, *134*, 2884–2887.

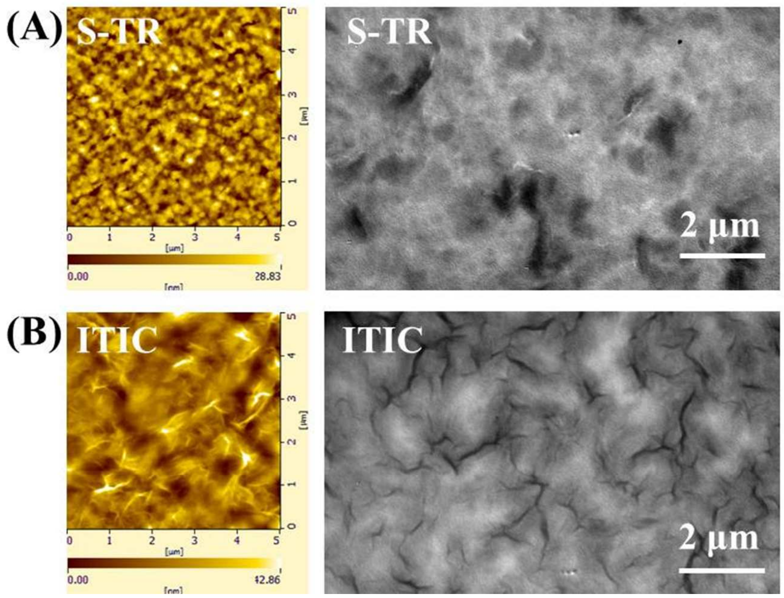

Figure S3. Tapping mode AFM height images and TEM images of neat S-TR film (A) and neat ITIC film (B).

The so-called single carrier devices were also fabricated to investigate the effect of CN on carrier transport. **Figure S4** (A) reveals the dark *J-V* characteristics of the hole-only devices, having a structure of ITO/PEDOT:PSS/S-TR:ITIC/MoO_3/Al with the S-TR:ITIC films without and with different contents of CN, respectively. In addition, the electron-only devices involving a structure of Al/S-TR:ITIC/Ca/Al were also fabricated and the dark *J-V* characteristics are shown in Figure S5(B)

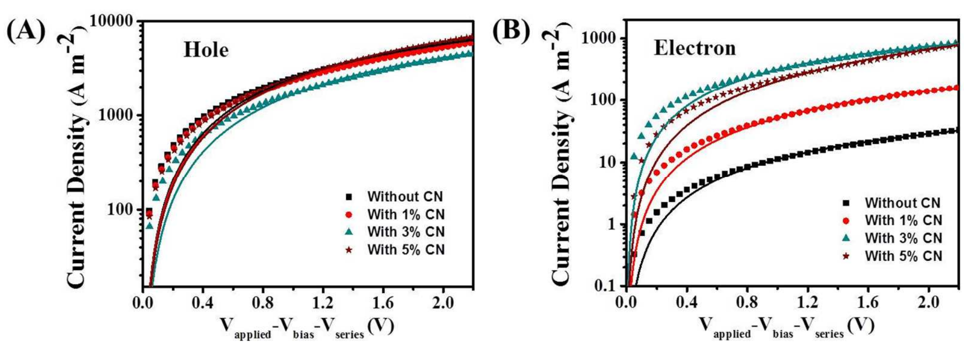

Figure S4. *J-V* curves of hole-only devices (A) and electron-only devices (B) based on the S-TR:ITIC films without and with different contents of CN.

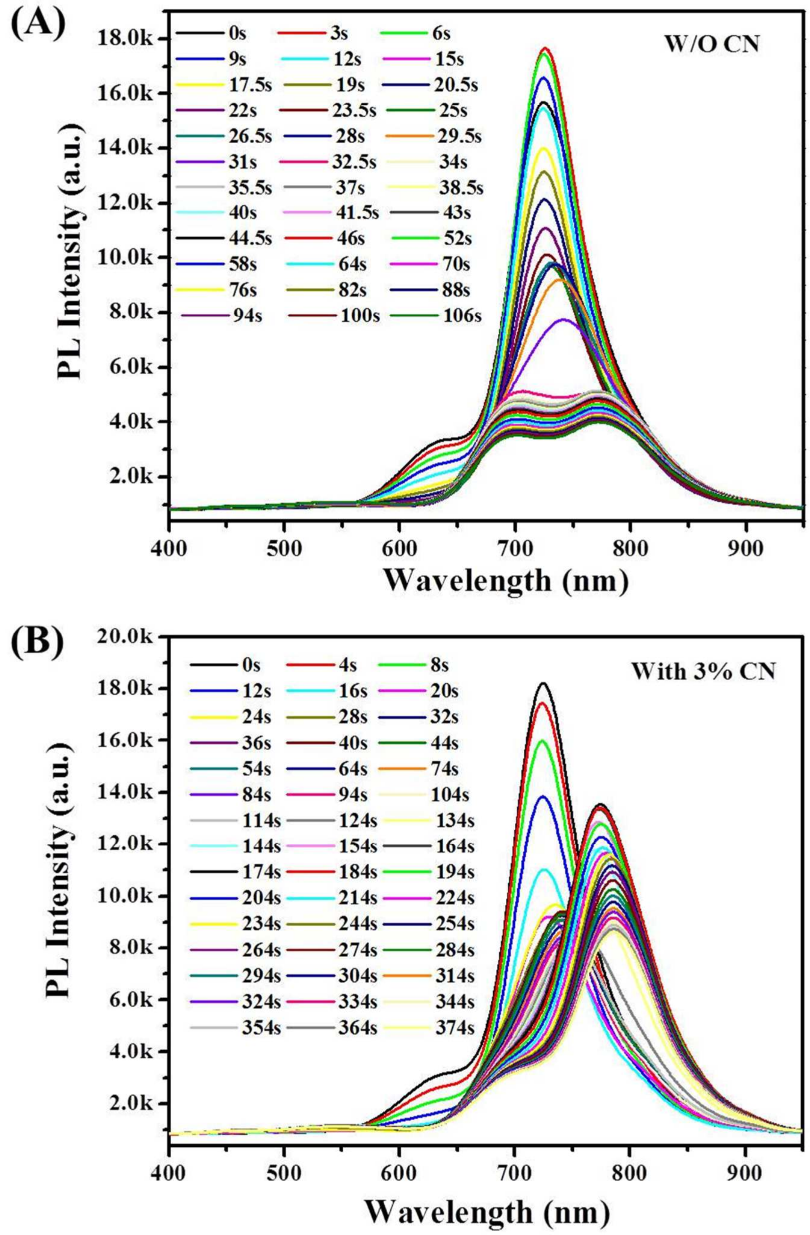

Figure S5. In-situ PL spectra of S-TR/ITIC blend films processed without CN (A) and with 3% CN (B).

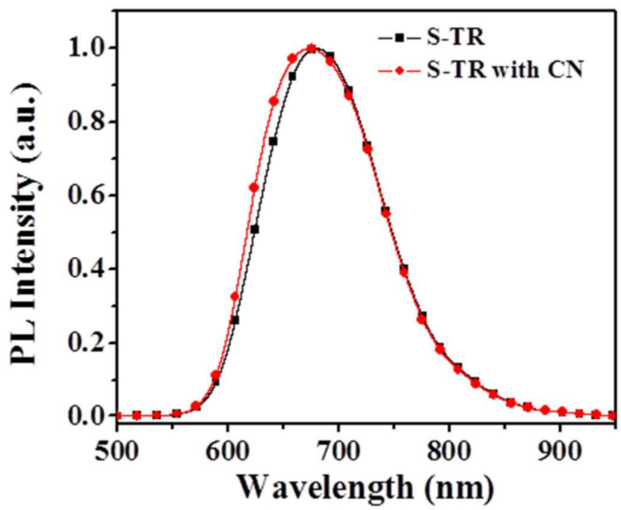

Figure S6. PL spectrum of S-TR solution without and with 3% CN.

As shown in Figure S7, the measurements of *V*oc as a function of light intensity were recorded. As well known, when bimolecular recombination is dominant, the slope of the *V*oc versus light intensity should be equal to kT/*q* (where q represents the elementary charge and k represents the Boltzmann constant). When the slope would be greater than kT/q, it implied the extra interfacial trap-assisted Shockley−Read−Hall recombination is dominant.

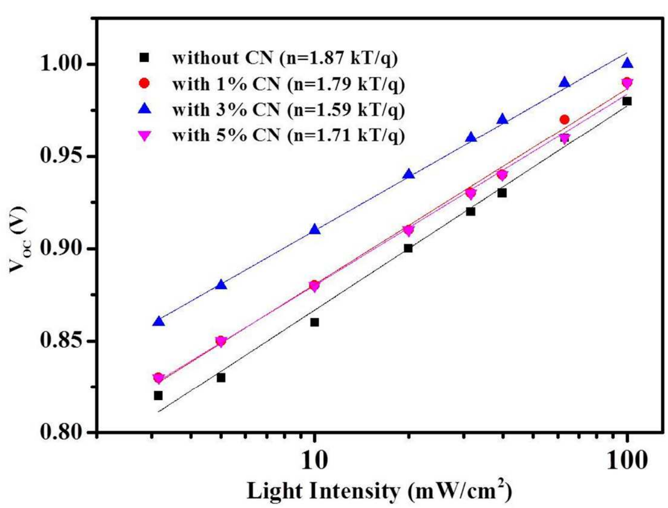

Figure S7. *V*oc of devices processed without and with CN as a function of light intensity.

	b.p. (˚C)	v.p. (kPa)	ITIC (mg/ml)	S-TR (mg/ml)
CB	131.7	1.17	> 60	< 8
CN	260.0	7.13 E-9	> 100	> 18

Table S1. The relative parameters of solvent, additive, donor and acceptor.