Electronic Supplementary Information for:

**A non-fullerene electron acceptor modified by thiophene-2-carbonitrile for solution-processed organic solar cells**

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**Instrument**

$^1$H NMR and $^{13}$C NMR spectra were obtained on a Bruker Advance III 400 (400 MHz) nuclear magnetic resonance spectroscope. UV-vis absorption spectra were taken on a Shimadzu UV-2450 spectrophotometer. MALDI-TOF MS spectra were measured on a Walters Maldi Q-TOF Premier mass spectrometry. Thermogravimetric analysis (TGA) was carried out on a WCT-2 thermal balance under protection of nitrogen at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was recorded on a Pekin-Elmer Pyris 1 differential scanning calorimeter. Cyclic voltammetry (CV) was done on a CHI600A electrochemical workstation with Pt disk, Pt plate, and standard calomel electrode (SCE) as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate ($\text{Bu}_4\text{NPF}_6$) $\text{CH}_2\text{Cl}_2$ solution. The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene-ferrocenium ($\text{Fc/Fc}^+$) redox couple (4.8 eV below the vacuum level). Topographic images of the films were obtained on a Veeco MultiMode atomic force microscopy (AFM) in the tapping mode using an etched silicon cantilever at a nominal load of ~2 nN, and the scanning rate for a 10 μm ×10 μm image size was 1.5 Hz.

**Materials**

All reagents and solvents, unless otherwise specified, were purchased from Aladdin, Aldrich and J&K Scientific Ltd. and were used without further purification. P3HT (96% H-T regioregularity, $M_n = 26$ kg/mol, polydispersity = 2.0) was
purchased from Merck Co. Poly [(9,9-bis(3’-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-
(9,9-dioctylfluorene)] (PFN, $M_n = 20.0$ kg/mol, polydispersity = 2.1) was synthesized
in our lab according to the published procedure.\textsuperscript{1}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig_s1.png}
\caption{TGA curve of F8-DPPTCN.}
\end{figure}
Fig. S2  DSC curve of F8-DPPTCN.

Fig. S3  $J$-$V$ curves at different annealing temperatures (Blend ratio: 1:2).
Fig. S4  $J-V$ curves at different weight ratios (annealed at 95 °C).

Fig. S5  $J-V$ curves at different amounts of DIO additives (Blend ratio: 1:3).
Fig. S6  $^1$H NMR spectrum of F8-DPPTCN solution in CDCl$_3$.

Fig. S7  $^{13}$C NMR spectrum of F8-DPPTCN solution in CDCl$_3$. 

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**Fig. S8** AFM height images (a, b, c and d) and phase images (e, f, g and h) of 1:2 as-cast (a, e), 1:2 annealed (b, f), 1:3 annealed (c, g) and 1:3 annealed DIO (d, h) films.

**References**