Supplementary Information (SI) for Sustainable Energy & Fuels.

Enhancing the efficiency of non-fullerene organic solar cells by using a volatilizable solid additive system

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1. Experimental Section

1.1 Materials

Chloroform (CF), molybdenum oxide (MoO_3), 2-methoxyethanol ($CH_3OCH_2CH_2OH$, 1-chloronaphthalene (CN), 1,4-diiodobenzene (DIB), zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, > 99.0 %) and ethanolamine ($NH_2CH_2CH_2OH$, > 99.5 %) were purchased from Sigma-Aldrich, Gallium(III) nitrate hydrate were purchased from Sigma Aldrich . ITO Glass substrates (12 × 12 mm) were obtained from Lumtec. 1-materials provided the PM6, Y6, PTB7-Th, and IEICO-4F were used as supplied.

1.2 UV-Vis-NIR absorption, and FTIR measurements

Ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectra were taken on a Perkin Elmer-Lambda 1050 UV-Vis-NIR Spectrophotometer. Fourier transform infrared (FTIR) spectroscopy was performed on a Thermo Fisher Nicolet iS50 FT-IR/Raman Spectrometer.

1.3 J-V and EQE measurements

The organic solar cells (OSCs) were stored in a nitrogen (N_2) glovebox and afterward evaluated in ambient air within a two-day timeframe following their fabrication. The utilization of this methodology was implemented in order to mitigate the influence of device degradation on the acquired outcomes. The *J-V* measurements were performed using a solar cell *I-V* tester provided by PV Measurements, Inc., which utilized a Keithley 2400 source metre. The measurements were conducted using a solar simulator with an illumination output of 100 mW/cm^2, namely the AM 1.5G solar simulator. The calibration of the light intensity of the solar simulator was performed utilising a silicon solar cell as a reference. In order to mitigate the potential overestimation of short-circuit current density (*J*sc) values resulting from lateral charge transfer, a metal shadow mask was utilized to standardize the device area at 0.12 cm^2 for each device type featuring different electron transport layers (ETLs). The measurements for all the devices were conducted under ambient temperature conditions. The EQE measurements were carried out using a QEX10 spectral response equipment provided by PV measurements.

1.4 AFM and SEM measurements

The investigation of the film's surface morphology was carried out with atomic force microscopy (AFM) employing a Bruker Dimension ICON scanning probe microscope (SPM). The surface topography image was acquired utilising the FEI Nova Nano SEM 230, a scanning electron microscope (SEM) equipped with a field emission electron source.

1.5 XPS and UPS measurements

The X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements were conducted in an ultra-high-vacuum environment using a device called ESCALAB 250Xi from the British firm Thermo Scientific (Cramlington, UK). The Al K radiation source was used to conduct the XPS and He I (energy 21.2eV) was used to conduct UPS measurements respectively. This investigation made use of Thermo ScientificTM Avantage Software (v5.9925).

1.6 Fabrication and Characterization of Organic Solar Cells

ITO (indium tin oxide) transparent conductive glass substrates were placed on substrate holders. Afterward, a consecutive ultrasonic cleaning procedure was carried out utilizing deionized water, acetone, and isopropanol solutions. Each step of the cleaning process lasted for a duration of 10 minutes. Following the cleaning procedure, the glass substrates were dried using N_2 gas blown upon them. A 20-minute UV ozone system was utilized to clean the substrates.

Methoxyethanol was used as the solvent for the fabrication of the electron transport layer. Zinc acetate was used as the solute, and ethanolamine was used as a catalyst to aid in the development of ZnO. The mass ratio of solute to solvent was estimated at 109.3 mg/mL, whereas the ratio of additive to solvent was set at 32 µL/mL. For the modified ZnO electron transport layer gallium(III) nitrate hydrate was added with ZnO with different concentrations

(2%, 4%, 6%, 8%, and 10%). The quantities of zinc acetate and gallium nitrate were measured in glass vials, followed by a gradual introduction of a pipette, methoxy ethanol, and ethanolamine. Afterward, the solution was tightly closed once a magnetic stir bar was added and placed on a magnetic stirrer at room temperature for at least 5 hours. The substrates that had been prepared were placed onto a spin coater. Then, a volume of 45 µL of the ZnO solution was applied onto each substrate while the spin coater was spinning at a speed of 4000 RPM.

The deposited films underwent annealing at a temperature of 170 °C for 45 minutes to achieve a stable transport layer of thin films.

For the preparation of the photoactive layer, the PM6:Y6 (donor:acceptor) ratio was 1.0:1.2. Chloroform was employed as the solvent, with a specific solute-solvent concentration ratio of 22 mg/mL and 7.3 vol% of CN additive. In the case of the modified active layer, 12mg/mL 1,4 diiodobenzene (DIB) was added with PM6:Y6 solution. The solution was kept in the glovebox and stirred at room temperature for a whole night. For three hours at 60 ◦C, the PM6:Y6 solution was agitated before being spun into a coating. Spin coating at 5000 RPM for 60 s was used to deposit the annealed PM6:Y6 film and dry it inside the glovebox at room temperature and for the annealed film annealing temperature of 90 ◦C for 10 min was used to dry the PM6:Y6 film.

The hole transport layer and metal anode were fabricated using a high-vacuum thermal evaporation equipment. The evaporation process of MoO_3 began when the vacuum gauge reading reached 10^{-5} Pa, and the deposition of MoO_3 ended when the thickness monitor measured a layer thickness of 10 nm. Following a short time of cooling, the process of depositing Ag electrodes took place at a rate of ~2 Å/s, ultimately resulting in a final thickness of 100 nm.

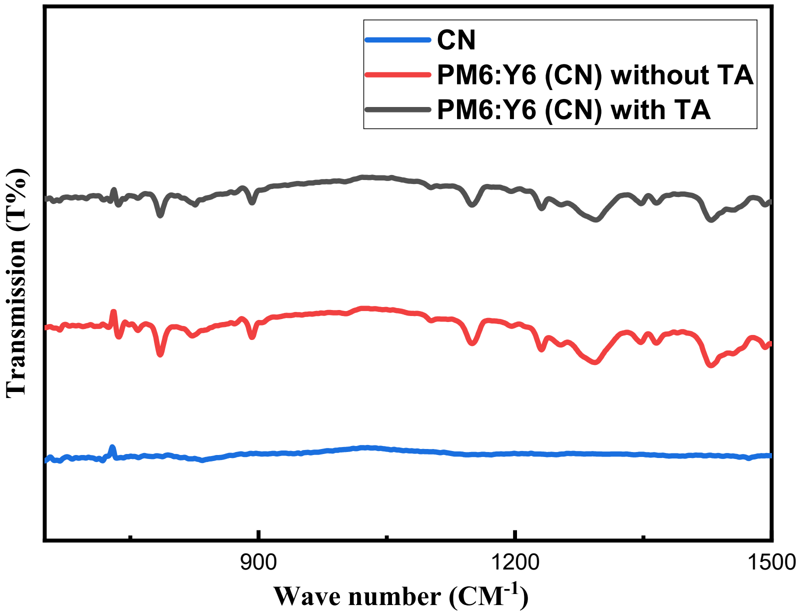

Figure S1: Fourier transform infrared spectroscopy (FTIR) transmission spectra of CN with and without thermal annealing.

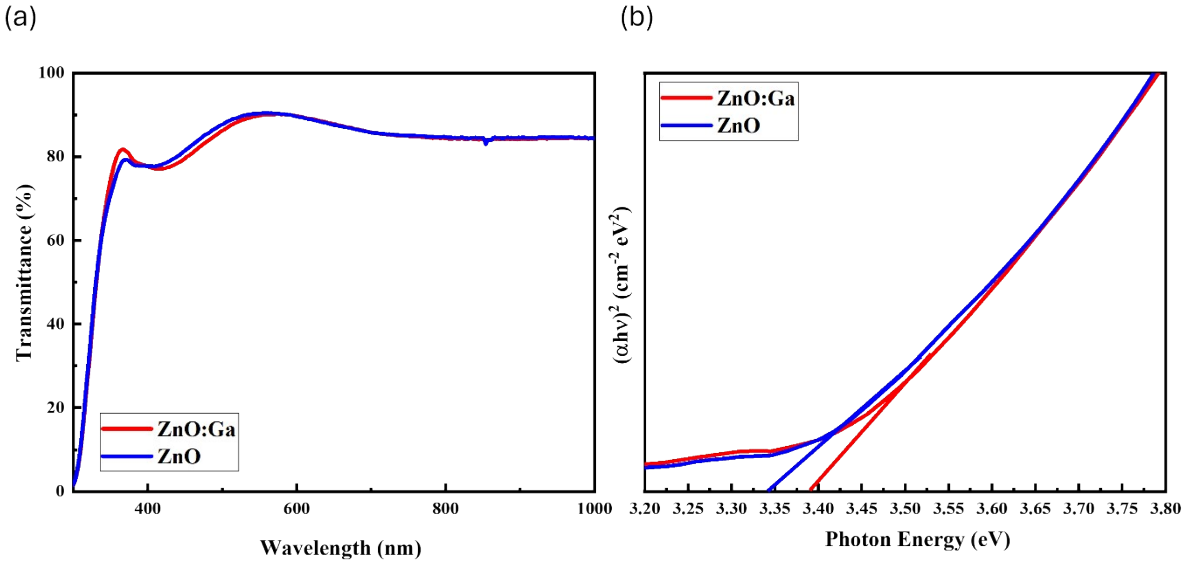

Figure S2: (a) Transmission spectra of pure ZnO and Ga-doped ZnO layer. (b) Bandgap of pure ZnO and Ga-doped ZnO layer.

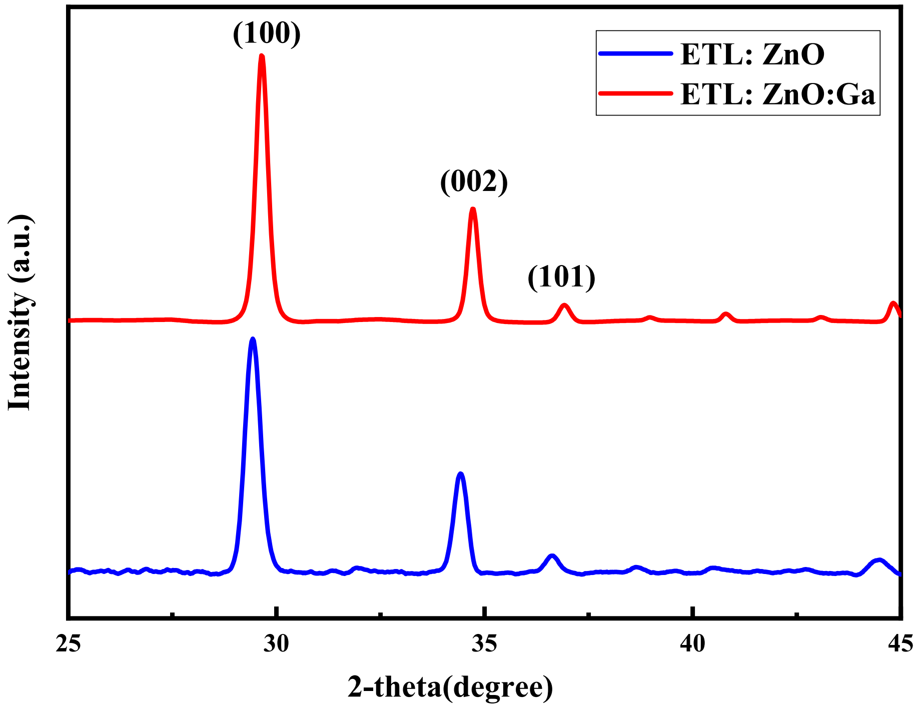

Figure S3: (a) X-ray diffraction pattern of pure ZnO and Ga-doped ZnO layer.

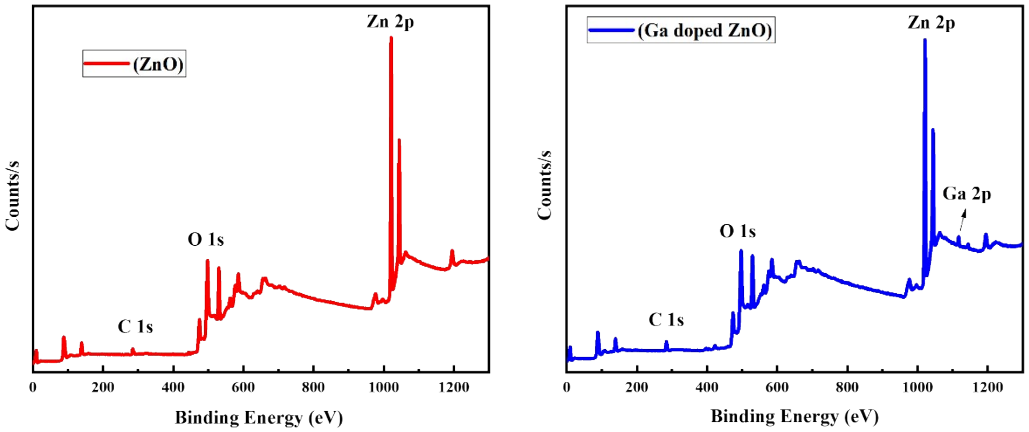

Figure S4: X-ray photoelectron spectroscopy (XPS) spectra of ZnO, and Ga-doped ZnO ETL.

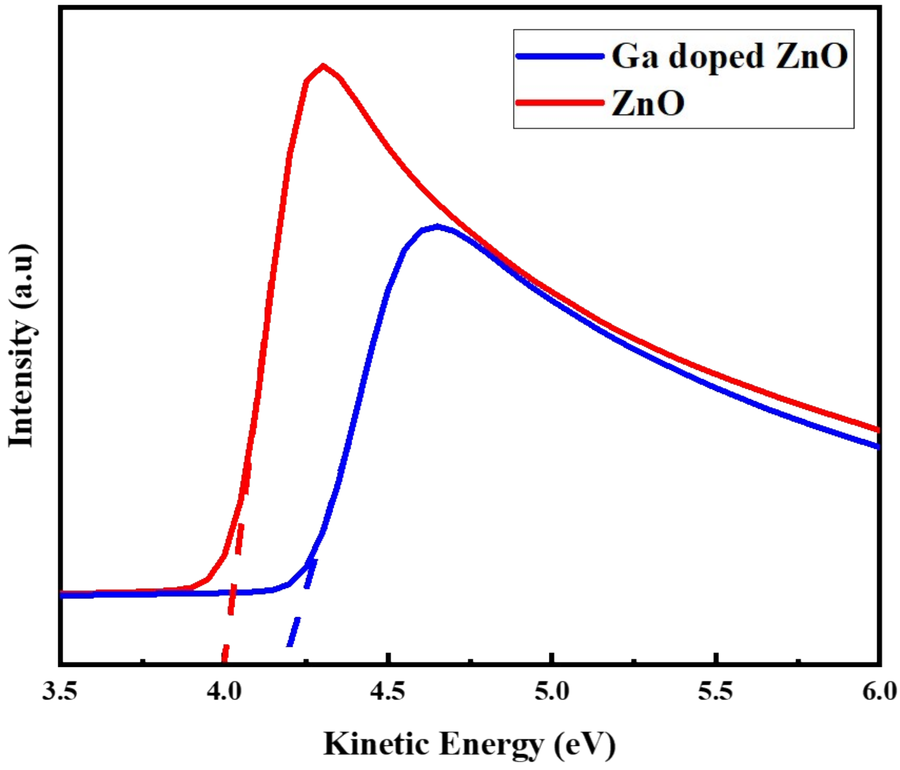

Figure S5: UV photoemission spectroscopy (UPS) spectrum of ZnO and Ga-doped ZnO ETLs.

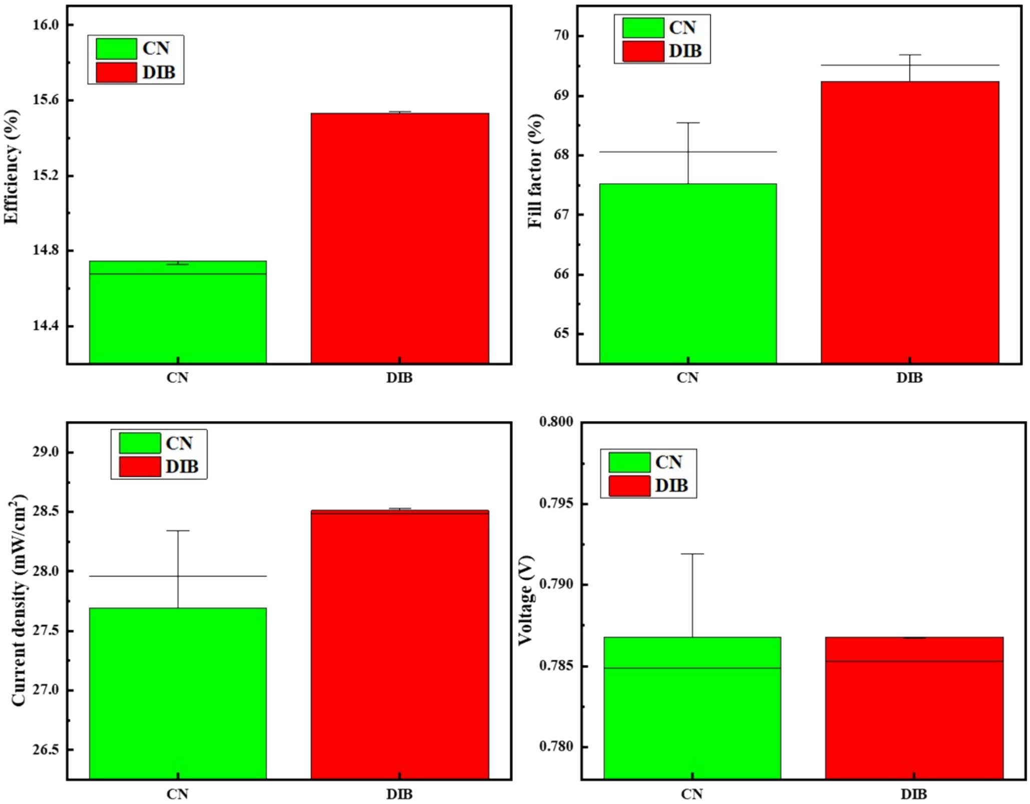

Figure S6: Statistical distribution of V_{OC}, J_{SC}, FF, and PCE of CN and DIB-based devices.

Table S1: Electrical parameters extracted from Nyquist plot for CN and ZnO DIB-based devices

Device	Parameters	CN	DIB	Unit
PM6:Y6	Series resistance, R_s	80.06	75.06	Ω

	Transport resistance, R_t	838.2	947.8	Ω
	Recombination resistance, R_{rec}	3.05	6.87	KΩ
	Bulk capacitance, C_g	5.11	6.48	nF
	Chemical capacitance, C_μ	10.98	2.95	nF

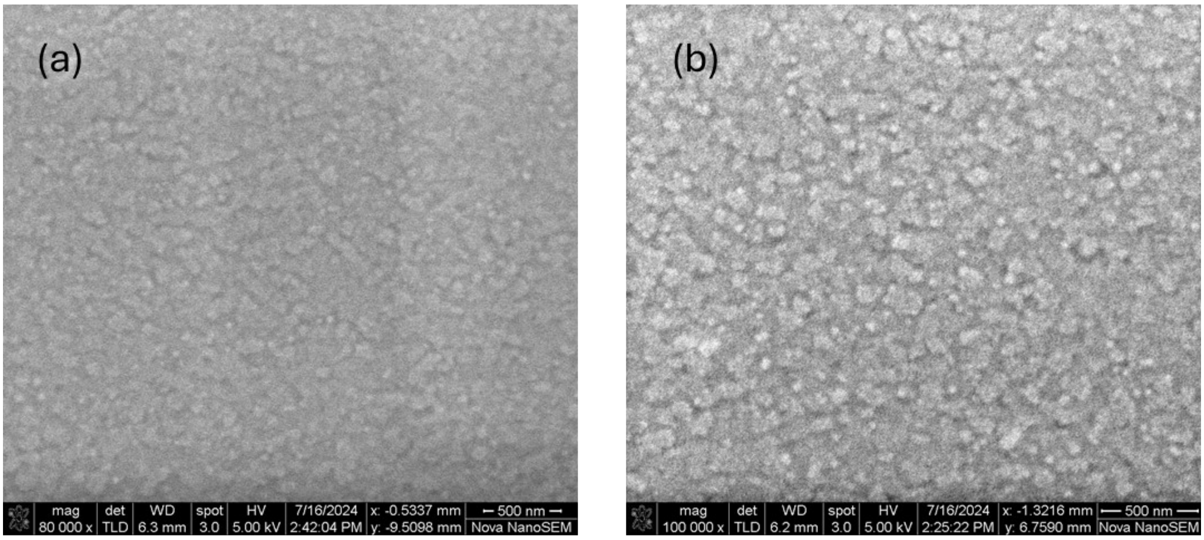

Figure S7: Scanning electron microscopy images of pure ZnO and Ga-doped ZnO layer.

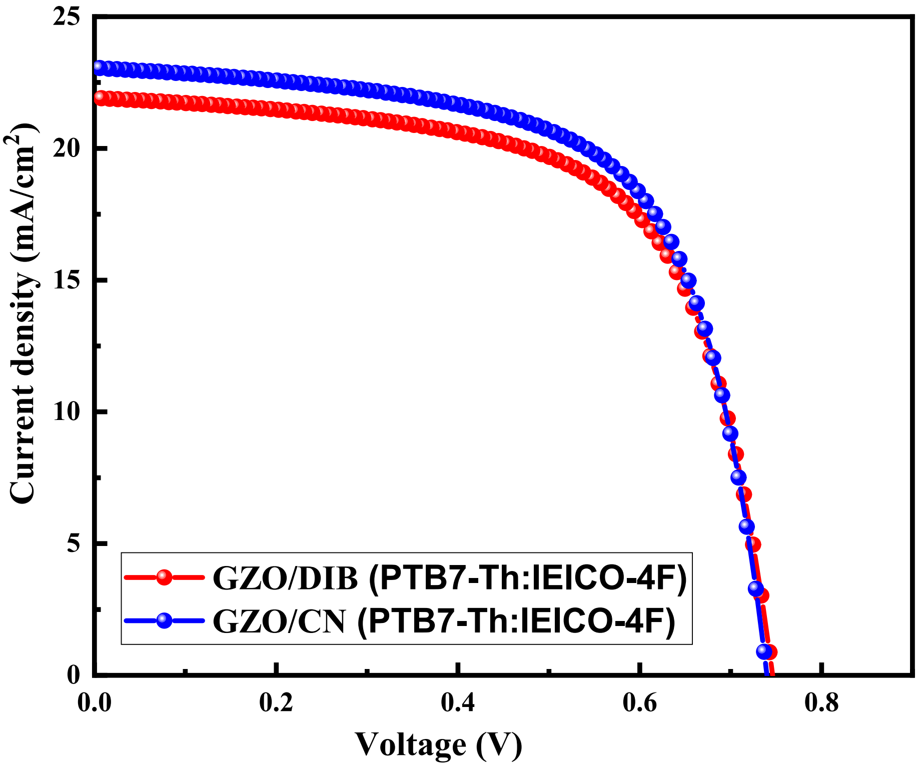

Figure S8: Current density versus voltage (*J–V*) characteristics of the best-performed devices based on PTB7-Th:IEICO-4F active layer with solvent additive CN and solid additive DIB.

Table S2: The PTB7-Th:IEICO-4F-based devices parameters are presented in Table S2.

Devices	PCE (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)
Ga:ZnO/ PTB7-Th:IEICO-4F (CN)	10.48	0.746	21.91	64.12
Ga:ZnO/ PTB7-Th:IEICO-4F (DIB)	11.03	0.74	23.056	64.67

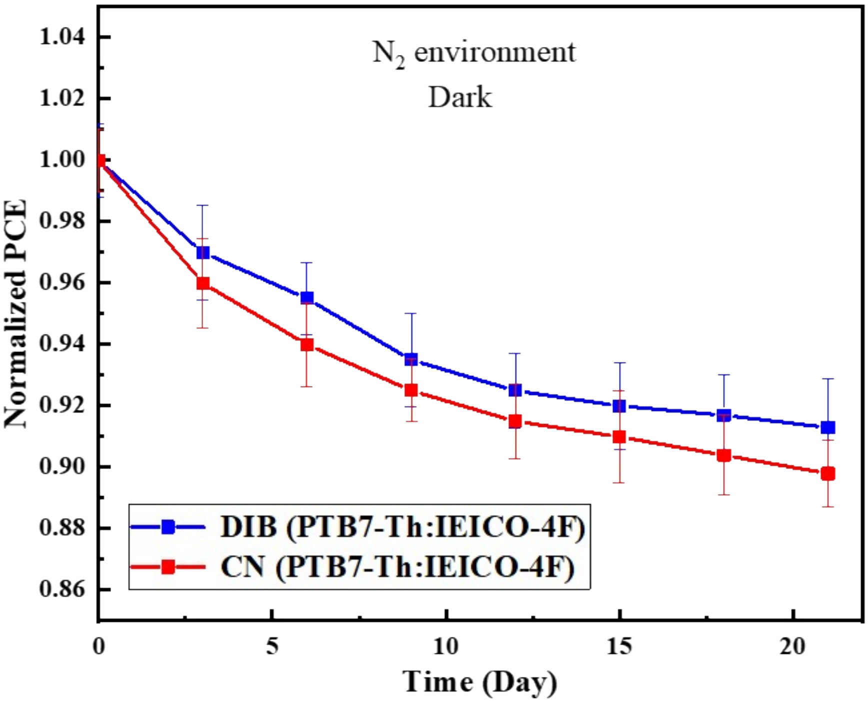

Figure S9: Normalised PCE for CN and DIB-based devices with Ga-doped ZnO ETL with time.