Improved Efficiency and Stability of Outdoor and Indoor Organic Photovoltaics with Suppressed Voltage Loss by Alkoxylation on Dimeric Giant Acceptors Featuring as a Supramolecular Stabilizer

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Material synthesis and characterizations. PM6 was purchased from Volt-Amp Optoelectronics Tech. Co., Ltd, Dongguan, China. All other reagents and chemicals were purchased from Sigma-Aldrich and used without further purification ¹H and ¹³C NMR spectra were obtained with a Bruker AV-400 MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm, δ) ¹H, NMR spectra were referenced to tetramethylsilane (0 ppm) in CDCl₃. Mass spectra were collected on a MALDI Micro MX mass spectrometer, or an API QSTAR XL System.

Optical characterizations. Film UV-Vis absorption spectra were acquired on a Perkin Elmer Lambda 20 UV/VIS Spectrophotometer. All film samples were spin-cast on ITO substrates. UV-Vis absorption spectra were collected from the solution with the concentration of 1.0×10^{-5} M in chloroform. A cuvette with a stopper (Sigma Z600628) was used to avoid volatilization during the measurement. **Note :** The observed 0-0 and 0-1 absorption peaks in the UV–vis spectra correspond to molecular aggregation types: a higher 0-0/0-1 peak ratio suggests a stronger J-aggregation tendency, featuring as a head-to-tail molecular arrangement with a red-shifted and sharp absorption band, whereas a lower ratio indicates an H-aggregation character, associated with a face-to-face stacking and a blue-shifted absorption band.

Electrochemical characterizations. Cyclic voltammetry was carried out on a CHI610E electrochemical workstation with the three electrodes configuration, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the supporting electrolyte. BTP-eC9 and DYO-V were drop-cast onto the glassy carbon electrode from chloroform solutions (5 mg/mL) to form thin films. Potentials were referenced to the ferrocenium/ferrocene couple by using ferrocene as external standards in acetonitrile solutions. The scan rate is 100 mV s^{-1} . The conversion of reduction/oxidation onsets and LUMO/HOMO energy levels can be described as: equation

$$E_{\text{LUMO}} = -[e(E^{\text{red}} - E^{\text{Fc/Fc}^+}) + 4.8]$$
(1)

$$E_{\rm HOMO} = -[e(E^{\rm ox} - E^{\rm Fc/Fc^+}) + 4.8].$$
(2)

Density functional theory (DFT) calculation.

All computations work were performed with the Gaussian 09 program by using DFT. Geometries optimization of BTP-eC9 and DYO-V in neutral state were carried out with B3LYP functional using 6-311G (d,p) level.

Molecular Dynamics simulations and interaction energies estimation. Molecular structures were built and first optimized with deriding force field^[1] with Gasteiger charges^[2] in Materials Studio package and then subjected to quenching MD simulations at high temperature of 500 K for 1 ns. The generated structures were extracted and sorted by energy to select stable interacted molecules. The molecular structures from MD simulations were further optimized at the level of theory of GFN2-xTB.^[3] DFT calculations at B3LYP-D3BJ/def2-SVP were performed in ORCA package to estimate the interaction energies with BSSE correction.^[4–7] Multiwfn and Avogadro were used for input file generation and structure visualization.^[8–10]

Thermogravimetric analysis (TGA) measurements. The TGA thermograms of materials were independently tested on the TA Instruments Q5000 SA Thermogravimetric Analyzer in HKUST. The condition is from room temperature to 800 °C under N₂ atmosphere and the heating rate is 10 °C min⁻¹. Sapphire and Indium were used to calibrate the baseline and temperature.

Differential Scanning Calorimeter (DSC). DSC measurements were performed using the TA Instruments Q1000 Differential Scanning Calorimeter at HKUST. The samples were sealed in aluminium pans with lids, with an empty pan used as the reference. The temperature range was set from room temperature to 350 °C under a nitrogen atmosphere at a flow rate of 50 mL/min, and the heating rate was 10°C/min. The instrument was calibrated for baseline and temperature using standard materials, including indium and sapphire, prior to measurements. Each test included an equilibration step at the starting temperature and one heating cycle from room temperature to 350 °C were performed to obtain the DSC thermograms of BTP-eC9 and DYO-V. Thermograms were recorded to analyze thermal transitions such as the crystallization and melting temperature (T_c , T_m), and enthalpy change of crystallization and melting (ΔH_c , ΔH_m)

Solar cell fabrication and testing. OSCs were fabricated with a device structure of ITO (indium tin oxide) /PEDOT:PSS /PM6:Acceptors/PNDIT-F3N/Ag. The patterned ITO-coated glass was scrubbed by detergent and then cleaned inside an ultrasonic bath by using deionized water, acetone, and isopropyl alcohol sequentially and dried overnight in an oven. Before use, the glass substrates were treated in a UV-Ozone Cleaner for 30 min to improve its work function and clearance. A thin PEDOT: PSS (Heraeus Clevios P VPA 4083) layer with a thickness of about 40 nm was spin-coat onto the ITO substrates at 4000 rmp for 40 s, and then thermal annealing at 150 °C for 15 min in air. The PEDOT:PSS coated ITO substrates were transferred to a nitrogen-filled glove box for further processing. PM6:BTP-eC9 and PM6:DYO-V were prepared in weight ratio of 1:1.2 (donor: acceptor) and the PM6:BTPeC9:DYO-V were prepared in weight ratio of 1:0.8:0.4 (PM6:BTP-eC9:DYO-V). The materials were then dissolved in chloroform with donor concentration of 7 mg mL⁻¹ and with 10 mg/ml TCB as additive. The solution was stirred for 2 hours for intensive mixing in a nitrogen-filled glove box before casting. The active layer blend solution was spin-cast on the top of PEDOT: PSS layer at 2500 rpm for 40 s. Then it was annealed at 100 °C for 5 min to remove the solvent. A thin layer of PNDIT-F3N (~10 nm) was cast onto processed active layer, and Ag layer (~120 nm) was deposited in thermal evaporator under vacuum of 4×10⁻⁵ Pa through a shadow mask. The optimal blend thickness measured on a Bruker Dektak XT stylus profilometer was about 100nm. The current-voltage (J-V) characteristic curves of all packaged devices were measured by using a Keithley 2400 Source Meter in air. Photocurrent was measured under AM 1.5G (100 mW cm⁻²) using a Newport solar simulator in an Air. For stability testing, the optimized device was aged in a glove box under a nitrogen atmosphere at 65°C on a hot plate with LED illumination to assess thermal stability.

Indoor photovoltaic characterization. For indoor testing, the photocurrent was measured under the illumination of an Iwata Tach LED light with adjustable intensity and colour temperature. The optimized device was tested inside a black box, with calibration performed using a lux meter to ensure precise photocurrent measurements. The characterization of indoor

photovoltaic performance follows the methods outlined in our previous work. To ensure accurate evaluation under indoor lighting conditions, anti-reflective-treated masks and blackened testing boxes were used to minimize light scattering and reflections. The integrated current density (J_{cal}) was obtained using equations (3) and (4).

$$J_{\rm SC}(\text{calculated}) = \int EQE(\lambda) * \Phi(\lambda) * q \tag{3}$$

$$H(\lambda) = \Phi(\lambda) * q * E(eV)$$
(4)

where $\Phi(\lambda)$, $H(\lambda)$ are the photon flux and the power density of the indoor light sources.

External Quantum Efficiency (EQE) measurements. EQE spectra were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300 W lamp source.

Fourier-transform photocurrent spectroscopy external quantum efficiency (FTPS-EQE) and (External quantum efficiency of electroluminescence) EL-EQE measurements. FTPS-EQE was measured using an integrated system (PECT-600, Enlitech), where the photocurrent was amplified and modulated by a lock-in instrument. EL-EQE measurements were performed by applying external voltage/current sources through the devices (REPS-Pro, Enlitech). All of the devices were prepared for EL-EQE measurements according to the optimal device fabrication conditions. EL-EQE measurements were carried out from 0 to 1.8 V.

Voltage Loss Analysis. The voltage loss (V_{loss}) in OSCs devices arises due to the difference between the optical bandgap and the open-circuit voltage $V_{\text{OC}} = E_{\text{g}} - V_{\text{loss}}$ and divided into three main components $V_{\text{loss}} = \Delta V_1 + \Delta V_2 + \Delta V_3$ where:

 $\Delta V_1 = \frac{E_g}{q} - V_{\text{OC}}^{\text{SQ}}$: Radiative loss due to the difference between the optical bandgap and the Shockley-Queisser (SQ) limit open-circuit voltage.

 $\Delta V_2 = qV_{\text{OC}}^{\text{SQ}} - qV_{\text{OC}}^{\text{rad}}$: Additional loss due to non-ideal absorptance and sub-gap radiative recombination (it was calculated from EL and EQE-FTPS measurements).

 $\Delta V_3 = q \Delta V_{0C}^{non-rad}$: voltage losses due to non-radiative recombination only. (it was calculated from EL-EQE measurements).

The E_g of the devices are determined from the intersection of normalized EQE and EL, which aligns with the energy transition from the ground state to the lowest singlet excited state (E_{0-0})

Transient photovoltage (TPV) and transient photocurrent (TPC) measurements. In TPV measurements, the devices were placed under background light bias enabled by a focused Quartz Tungsten-Halogen Lamp with an intensity of similar to working devices, i.e., the device voltage matches the open-circuit voltage under solar illumination conditions. Photo-excitations were generated with an 8 ns pulses from a laser system (Oriental Spectra, NLD520). The wavelength for the excitation was tuned to 518 nm with a spectral width of 3 nm. A digital

oscilloscope was used to acquire the TPV signal at the open-circuit condition. TPC signals were measured under short-circuit conditions under the same excitation wavelength without background light bias. The TPV and TPC decay curves were fitted with a single exponential function, and the decay constants were obtained from the fitting.

Space charge limited current (SCLC) Measurements Hole-mobility measurement.

Hole-mobility measurement. The hole mobilities were measured using the space charge limited current (SCLC) method, employing a device architecture of ITO/PEDOT:PSS/blend film/MoO₃/Ag. The mobilities were obtained by taking current–voltage curves and fitting the results to a space charge limited form, where the SCLC is described by equation (5):

$$J = \frac{9\varepsilon_0\varepsilon_r\mu_h \left(V_{appl} - V_{bl} - V_s\right)^2}{8L^3} \tag{5}$$

where ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material (assumed to be 3), μ_h is the hole mobility, *L* is the thickness of the film, V_{appl} is the applied voltage, V_{bi} is the built-in voltage (0.15 V) and V_s is the voltage drop from the substrate's series resistance ($V_s = IR$, *R* was measured to be 10.8 Ω). From the plots of $J^{1/2}$ vs. $V_{appl}-V_{bi}-V_s$, hole mobilities can be deduced.

Electron-mobility measurement.

The electron mobilities were measured using the SCLC method, employing a device architecture of ITO/ZnO/blend film/PNDIT-F3N/Ag. The mobilities were obtained by taking current-voltage curves and fitting the results to a space charge limited form, where the SCLC is described by equation (6):

$$J = \frac{9\varepsilon_0\varepsilon_r\mu_e \left(V_{appl} - V_{bi} - V_s\right)^2}{8L^3} \tag{6}$$

where ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material (assumed to be 3), μ_e is the electron mobility, *L* is the thickness of the film, V_{bi} is the built-in voltage (0.15 V) and V_s is the voltage drop from the substrate's series resistance ($V_s = IR, R$ was measured to be 10.8 Ω). From the plots of $J^{1/2}$ vs. $V_{appl}-V_{bi}-V_s$, electron mobilities can be deduced.

Exciton dissociation probability analysis

Exciton dissociation (P_{diss}) and collection (P_{coll}) efficiencies can be calculated from the relationships between photocurrent (J_{ph}) and effective voltage (V_{eff}). J_{ph} is defined as the difference between the dark current density (J_D) and the current density under illumination (J_L). The definition of V_{eff} is the absolute value of V_0-V_{appl} , where V_0 refers to the voltage value when $J_L = J_D$ and V_{appl} is the applied voltage. At high V_{eff} , almost all excitons are separated and extracted, and J_{ph} reaches saturation (J_{sat}). Accordingly, η_{diss} and η_{coll} can be determined by J_{SC}/J_{sat} and J_{max}/J_{sat} , respectively, in which J_{max} is the current density at the maximal power output point.

Transient absorption spectroscopy (TAS). Measurements were performed using a homebuilt experimental setup with an amplified Ti: sapphire laser (Coherent Legend Elite), with pulse

duration of 120 fs, centered at 800 nm and at a repetition rate of 1000 Hz. The pump pulses were generated using an optical parametric amplifier (Coherent Opera Solo) and then chopped 500 Hz. The probe beam was traversed a mechanical translation stage, enabling a time delay of up to 2 ns between pump and probe pulses, and then was focused on an Yttrium Aluminium Garnet crystal plate. After passing through the photoexcited sample, the probe pulses were spectrally dispersed using grating and then collected with a silicon line CCD (Hamamatsu S8380) (visible components, 500-1000 nm range) or an InGaAs line CCD (Hamamatsu G11620) (IR components, 800-1600 nm range). The differential transmission signals at various delay times were calculated from the sequential probe shots corresponding to the pump on and off cases as $((T_{pump ON} - T_{pump OFF})/T_{pump OFF})$. Measurements were conducted under excitation in fundamental absorption band of the acceptor (800 nm) with an average flux of $\sim 2 \mu J$ cm⁻², which is close to 1-sun illumination. The decomposition of TA spectra was carried out via softmodelling by multivariate curve resolution-alternating least square (MCR-ALS) method with a singular value decomposition parameters as an initial guess. Note : In blend films, we can observe 1) the fast rise of a positive $\Delta T/T$ signal within the fundamental absorption band of the acceptor (800-900 nm for BTP-eC9 and 750-800 nm for DYO-V samples, while in BTPeC9:DYO-V blend the signal in acceptor GSB range is dominated by BTP-eC9 one); 2) the slow rise of $\Delta T/T$ signal in the fundamental absorption range of the donor (580–680 nm), and 3) two photoinduced absorption (PIA) bands located at 900 and 1400 nm respectively.

Time-resolved photoluminescence (**TR-PL**) characterizations. TR-PL measurements were carried out on encapsulated thin films. A 100 fs Ti:Sapphire oscillator (Coherent Mira 900) operating at 76 MHz repetition rate was tuned to 750 nm and focused to excite the sample. The PL was collected and guided into a spectrometer equipped with a silicon single-photon counter to carry out time-correlated single-photon counting (TCSPC), integrating the majority of the PL. The PL spectra were obtained using a Si photodiode array detector.

GIWAXS and GISAXS measurements and fittings. GIWAXS measurements for neat and blend films, and GISAXS measurements for neat films were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300 K detector.7, 8 The incidence angle was 0.15. GISAXS measurements for blend films were conducted at 23A SWAXS beamline at the National Synchrotron Radiation Research Center, Hsinchu, Taiwan, using a 10 keV primary beam, 0.15° incident angle, and Pilatus 1M-F and C9728DK area detector.

AFM analysis. AFM measurements were performed by using a Scanning Probe Microscope Dimension 3100 in tapping mode. All film samples were spin-cast on ITO substrates.

Synthesis



Scheme 1. Synthesis Route for DYO-V

Synthesis of DYO-V

To a mixture of **BTP-OBO-2CHO** (200 mg, 0.14 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (**IC-2F** 27.6 mg, 0.12 mmol) in anhydrous Toluene (30 mL). Subsequently, $BF_3 \cdot OEt_2$ (1.5 mL) and acetic anhydride (1.5 ml) were added, and the reaction mixture was stirred at 0 °C for 15 min and then stir at room temperature for 25 min. Then, the reaction mixture was dropwise into methanol, and the precipitate was collected as a crude product. The residue was purified using column chromatography on silica gel (n-hexane: DCM= 2:1, v/v), yielding a dark green solid **BTP-OBO-IC2F-CHO** (120 mg, 52%).

BTP-OBO-IC2F-CHO (200 mg, 0.172 mmol), **V-DSEE** (44.5 mg, 0.172 mmol), were dissolved in absolute chloroform (10 mL), and pyridine (1.5 mL) were added. The mixture was deoxygenated with nitrogen for 30 min and then refluxed for 6 h. After cooling to room temperature, the mixture was poured into methanol (100 mL) and filtered. The residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:1.5) as eluent, yielding a dark blue solid and recrystallization through MeOH/DCM for two times to obtain **DYO-V** (120 mg, 43%).

DYO-V: ¹H NMR (400 MHz, CDCl₃) δ 9.37 (s, 1H), 9.25 (s, 1H), 8.74 (d, J = 8.2 Hz, 1H), 8.52 (dd, J = 10.0, 6.5 Hz, 1H), 8.07 (s, 1H), 7.88 (d, J = 8.3 Hz, 1H), 7.54 (dd, J = 14.2, 6.7 Hz, 1H), 7.47 (s, 1H), 4.76 (d, J = 6.4 Hz, 4H), 4.72 (d, J = 5.8 Hz, 4H), 2.18 – 2.03 (m, 4H), 1.70 – 0.69 (m, 120H). MALDI-TOF MS: calculated for: C₂₁₈H₂₈₀F₄N₁₆O₈S₁₀ (M⁺), 3649.3; found, 3648.9.



Figure S1. ¹H NMR spectrum of DYO-V (400 MHz, CDCl₃).

MALDI, LZK, 20240717



Figure S2. MS spectrum of DYO-V.



Figure S3. DTF calculations of **DYO-V** (dihedral angles between the end group and the central backbone).



Figure S4. The UV-Vis absorption and photoluminescence spectra of **BTP-eC9** and **DYO-V** for Stokes Shift calculation.



Figure S5. HOMO-1, HOMO, LUMO and LUMO+1 distribution of DYO-V and corresponding energy levels.



Figure S6. Cyclic voltammetry (CV) measurements of DYO-V and BTP-eC9.



Figure S7. Dual fitting of the EQE and EL spectra of PM6:BTP-eC9, PM6:DYO-V and PM6:BTP-eC9:DYO-V.



Figure S8. *J*_{ph}-*V*_{eff} curves of the **PM6:BTP-eC9**, **PM6:DYO-V** and **PM6:BTP-eC9:DYO-V** devices.



Figure S9. Dependence of (a) V_{OC} and (b) J_{SC} on different light intensity (P_{light}) of PM6:BTP-eC9, PM6:DYO-V and PM6:BTP-eC9:DYO-V devices.



Figure 10. $J^{1/2} \sim V$ characteristics of (a) The hole/electron mobility (μ_h/μ_e) of blend films obtained from the SCLC method; (b) hole-only devices and (c) electron-only devices based on the **PM6:BTP-eC9**, **PM6:DYO-V** and **PM6:BTP-eC9:DYO-V**.



Figure S11. AFM images of PM6:BTP-eC9, PM6:DYO-V and PM6:BTP-eC9:DYO-V before and after thermal aging.



Figure S12. TA spectroscopy of neat acceptor films: (a) **BTP-eC9**, (b) **DYO-V**, and (c) **BTP-eC9**:**DYO-V**.



Figure S13. Steady-state UV-Vis absorption of the **BTP-eC9**, **DYO-V** and **BTP-eC9:DYO-V** films.



Figure S14. The spectral (a, b) and time (c, d) component of the local exciton (LE) component in decomposed TA spectra of neat acceptor films.



Figure S15. The spectral (a) and time (b) component of the delocalized exciton (DE) component in decomposed TA spectra of neat acceptor films.



Figure S16. The *J*–*V* characteristic curves of **PM6:DYO-V** in different correlated color temperatures (CCTs): 2600 K, 3000 K, 4000 K, and 6500 K.



Figure S17. 2D GIWAXS plots of the BTP-eC9, DYO-V and BTP-eC9:DYO-V neat acceptors fresh and aged blended films.



Figure S18. 2D GISAXS plots of the PM6:BTP-eC9, PM6:DYO-V and PM6:BTP-eC9:DYO-V fresh and aged blended films.

Materials	Voc	Jsc	FF	PCE	Stability	Condition
	[V]	[mA cm ⁻²]	[%]	[%]		
PM6:BTP-eC9:DYO-V	0.897	28.0	80.4	20.2	<i>T</i> ₉₀ ≈ 2000 hr	65 °C
PM6: L8-BO-D:CH8-4	0.906	27.7	79.6	20.0	$T_{88} \approx 500 \text{ hr}$	65 °C ^[11]
PM6:BTP-eC9:5-IDT	0.863	29.23	0.791	19.96	$T_{93} \approx 200 \text{ hr}$	65 °C ^[12]
PM6: BTP-eC9:6-IDT	0.857	28.79	0.783	19.32	$T_{86} \approx 200 \text{ hr}$	65 °C ^[12]
D18:BTP-eC9:DY-IDT	0.881	29.37	76.93	19.9	/	/ [13]
PM6:L8-BO-X:Tri-V	0.892	27.45	81.1	19.86	$T_{80} \approx 1380 \text{ hr}$	1 sun ^[14]
PM6:DIBP3F-Se:BTP- J17	0.941	26.7	78.01	19.6	$T_{80} \approx 1176 \text{ hr}$	1 sun ^[15]
PM6:CH8-6:L8-BO	0.884	27.46	78.6	19.2	$T_{88} \approx 500 \text{ hr}$	65 °C ^[16]
D18:L8-BO:dBTP- ThC4	0.915	26.3	79.6	19.16	$T_{80} \approx 2200 \text{ hr}$	1 sun ^[17]
PM1:PC6:GDF	0.892	27.03	79.7	19.22	/	/[18]
D18:N3:DOY-TVT	0.856	28.21	79.38	19.20	$T_{90} \approx 865 \text{ hr}$	85 °C ^[19]
PM6:BTP-eC9:DY- P2FH	0.871	27.19	80.61	19.09	$T_{85} \approx 1100 \text{ hr}$	85°C ^[20]
D18:BS3TSe-4F:2Y-	0.847	29.35	0.77	19.13	/	/[21]
PM6:L8-BO:DY-TF	0.905	26.93	78.5	19.13	/	/[22]
D18:N3:DOY-C4	0.853	28.07	0.794	19.01	$T_{85} \approx 800 \text{ hr}$	85 °C ^[23]
D18:N3:DP-BTP	0.87	27.95	78.5	19.07	$T_{80} \approx 4963 \text{ hr}$ $T_{80} \approx 1568 \text{ hr}$	1 sun ^[24]
PM6:BTP-eC9:2Qx-C3	0.861	27.49	79.39	18.79	$T_{80} \approx 1308 \text{ hr}$ $T_{80} \approx 5513 \text{ hr}$	80 °C 85 °C ^[25]
PM6:Y6:dT9TBO	0.88	27.17	77.26	18.41	$T_{98} \approx 1800 \text{ hr}$	65 °C ^[26]
D18:Y6:DYF-TF	0.936	26.55	75.37	18.73	/	/[27]
D18-CI-B:N3:4A-DFIC	0.856	28.35	76.6	18.60	$T_{80} \approx 100 \text{ hr}$	1 sun ^[28]
PM1:BTP-eC9:DT19	0.899	27.8	73.8	18.4	$T_{90} \approx 120 \text{ hr}$	120 °C ^[29]

Table S1. Summary of photovoltaic performance parameters of DGA-based ternary devices

 with PCE over 18%

Device	E _{gap} [eV]	<i>V</i> ос [V]	V _{loss} [V]	V ^{SQ} [V]	ΔV ₁ [V]	V ^{rad} [V]	ΔV ₂ [V]	ΔV3 [V]
PM6:BTP-eC9	1.388	0.852	0.536	1.122	0.259	1.080	0.042	0.235
PM6:DYO-V	1.540	1.005	0.535	1.271	0.271	1.189	0.082	0.182
PM6:BTP-eC9:DYO-V	1.420	0.897	0.523	1.157	0.263	1.113	0.044	0.216

Table S2. Detailed Vloss parameters of the PM6:BTP-eC9, PM6:DYO-V and PM6:BTPeC9:DYO-V

 V_{OC}^{SQ} : Schokley-Queisser limit to V_{OC} . V_{OC}^{rad} : radiative limit to V_{OC} , measured using EQE_{EL}. $\Delta V_{2:} ((qV_{OC}^{SQ} - qV_{OC}^{rad}))$: voltage losses due to non-ideal absorption (it was calculated from EL and EQE-FTPS measurements).

 $\Delta V_3: (q\Delta V_{\rm OC}^{\rm non-rad})$: voltage losses due to non-radiative recombination only.

Table S3. The parameters of hole mobilities and electron mobilities of PM6:BTP-eC9, PM6:DYO-V and PM6:BTP-eC9:DYO-V blends.

Materials	$\mu_{ m h}$	μe	μe/μh
	[10 ⁻⁴ cm ² V ⁻¹ s ⁻¹]	[10 ⁻⁴ cm ² V ⁻¹ s ⁻¹]	
PM6: BTP-eC9	4.9	5.4	1.10
PM6:DYO-V	4.3	5.2	1.21
PM6:BTP-eC9:DYO-V	5.4	5.7	1.06

Table S4. Morphology parameters extracted from the GIWAXS measurements in pristine films.

Sample	π-π stacking	g distance (010)	π - π stacking coherence (010)		
	qz [Å ⁻¹]	<i>d</i> π-π [Å]	FWHM [Å ⁻¹]	CCL [Å]	
BTP-eC9 (Fresh)	1.670	3.760	0.134	46.8	
BTP-eC9 (Aged)	1.692	3.712	0.123	51.2	
DYO-V (Fresh)	1.693	3.710	0.363	17.3	
DYO-V (Aged)	1.679	3.740	0.353	17.8	
BTP-eC9:DYO-V (Fresh)	1.694	3.707	0.403	15.6	
BTP-eC9:DYO-V (Aged)	1.695	3.705	0.396	15.8	

Sample	π-π stacking	g distance (010)	π - π stacking coherence (010)		
	qz [Å ⁻¹]	<i>d</i> π-π [Å]	FWHM [Å ⁻¹]	CCL [Å]	
PM6:BTP-eC9	1.732	3.63	0.227	27.7	
(Fresh)					
PM6:BTP-eC9	1.734	3.63	0.181	34.7	
(Aged)					
PM6:DYO-V	1.671	3.76	0.229	27.4	
(Fresh)					
PM6:DYO-V	1.677	3.75	0.222	28.3	
(Aged)					
PM6:BTP-eC9:DYO-V	1.740	3.61	0.215	29.3	
(Fresh)					
PM6:BTP-eC9:DYO-V	1.740	3.61	0.219	28.7	
(Aged)					

 Table S5. Morphology parameters extracted from the GIWAXS measurements in blend film.

Table S6. Morphology parameters extracted from the GISAXS measurements.

Sample	2 <i>R</i> _{gc} [nm]	Df
PM6:BTP-eC9	35.4	2.72
(Fresh)		
PM6:BTP-eC9	31.9	2.94
(Aged)		
PM6:DYO-V	36.3	3.00
(Fresh)		
PM6:DYO-V	39.0	3.00
(Aged)		
PM6:BTP-eC9:DYO-V	34.0	2.76
(Fresh)		
PM6:BTP-eC9:DYO-V	33.0	2.85
(Aged)		

Table S7. Biexponential fitting parameters of the donor GSB kinetics and DE decay

	Donor G	DE decay(ps)	
Materials	Dissociation	Diffusion	
	lifetime	lifetime	Exciton lifetime
	[7 1]	$[au_2]$	[τ]
PM6: BTP-eC9	0.588	14.54	17.12
PM6:DYO-V	1.384	14.46	41.11
PM6:BTP-eC9:DYO-V	0.493	11.67	18.13
(750nm)			
PM6:BTP-eC9:DYO-V	0.558	13.50	17.62
(790nm)			

Table S8. The photovoltaic parameters of the PM6:DYO-V under 2000 lux LED illumination

Active layer	Colour Temperature [K]	P _{in} [mW cm ⁻²]	Voc [V]	J _{SC} /J _{cal} [μA cm ⁻²]	FF [%]	PCE [%]
PM6:DYO-V	2600	0.637	0.898	265.6 /258.9	75.1	28.1
	3000	0.580	0.894	240.0 /230.2	75.1	27.8
	4000	0.578	0.893	227.9 /222.3	74.9	26.4
	6500	0.612	0.893	234.0 /228.8	74.8	25.5

Table S9. The photovoltaic parameters of the device optimization

Materials	Additives	Voc	J _{SC}	FF	PCE
		[V]	[mA cm ⁻²]	[%]	[%]
PM6:BTP-eC9:DYO-V		0.852	27.9	79.1	18.8
(1:1.2:0) PM6:BTP-eC9:DYO-V		0.873	28.1	79.9	19.6
(1:1.0:0.2) PM6:BTP-eC9:DYO-V	10mg/mL TCB	0.897	28.0	80.4	20.2
(1:0.8:0.4) PM6:BTP-eC9:DYO-V		1.005	22.0	73.6	16.3
(1:0:1.2) PM6:BTP-eC9:DYO-V	0.5% CN	0.898	28.1	79.2	20.0
(1:0.8:0.4)					
PM6:BTP-eC9:DYO-V (1:0.8:0.4)	0.25% DIO	0.900	28.0	78.2	19.7

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