Electronic Supplementary Information for:

Non-fullerene Acceptor Alloy Strategy Enabling Stable Ternary Polymer Solar Cells With Efficiency Of 17.74%

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Contents

Experiment Details

Fig. S1 $V_{\rm OC}$ as a function of Y6 weight ratio in the blend films.

Fig. S2 The normalized absorption spectra of binary and ternary films.

Fig. S3 The normalized PL spectra of binary and ternary films.

Fig. S4 The cyclic voltammetry curves of blend films with different Y6 weight ratios.

Fig. S5 Nonencapsulated device stability statistics (J_{SC} , FF) that annealed (a,c) at 80 °C and (b,d) under AM 1.5G radiation (100 mW cm⁻²) in ambient atmosphere.

Table S1. Summary of Estimated Energy Parameters at Different Weight Ratios of Y6

Table S2. Summary of Carrier Mobilities of Solar Cells with Different Blend Films

Table S3. Summary of Primary Current Parameters of Solar Cells with Different Blend

 Films

Experiment Details:

Material Preparation: D18-Cl, N3 are commercially available from EFlexPV Ltd. Y6, PDINN is commercially available from Organtec Ltd. Chloroform is commercially available from konoscience. PEDOT:PSS is commercially available from Xi'an Polymer Light Technology Corp.

Device Fabrication: The devices were fabricated with a conventional structure of ITO/PEDOT:PSS/active layer/PDINN/Ag. The ITO glass was cleaned with sequential ultrasonication in deionized water, ethanol, acetone, and ethanol. The ITO glass was treated in an ultraviolet ozone box for 30 min. Then, the PEDOT:PSS (4083) was spincoated on the ITO substrates at 4000 rpm for 30 s, and the substrates were annealed at 150 °C for 15 min. The substrates were then transferred into a nitrogen-filled glovebox. D18-Cl:Y6, D18-Cl:N3 and D18-Cl:Y6:N3 were dissolved in chloroform to prepare a 15.6 mg/ml blend solution, respectively, and the weight ratio between donor and acceptor was kept at 1:1.6. After stirring overnight, the active layer material mixture was spincoated on the PEDOT:PSS layer at 2800 rpm for 40 s, and then the active layers were upside-down solvent vapor annealed with chloroform for 5 min in a small glass dish. Subsequently, PDINN was spin-coated on the active layer at 3000 rpm for 40 s. Finally, Ag was deposited about 100 nm under the pressure of 5×10^{-4} Pa. The hole-only devices were fabricated with a structure of ITO/PEDOT:PSS/active layer/MoO₃/Au, while the electron-only devices were fabricated with a structure of ITO/ZnO/active layer/PDINN/Ag

Characterization and Measurements: The simulated solar light (100 mW cm⁻² AM 1.5 G) was provided by a Newport Oriel Sol3A solar simulator. The device's basic photovoltaic properties, carrier mobilities, J_{ph} - V_{eff} curves, and the light intensity dependence of J_{SC} and V_{OC} were measured by a Keithley 2400. The UV-vis absorption

spectra were measured on a Hitachi U-3010 UV-vis spectroscopy. The EQE spectra were measured by QTEST HIFINITY5 solar cell IPCE test system. The photoluminescence spectra were measured on a Hitachi F-4600 spectrophotometer. The contact angles of neat films were measured by a Kruss DSA100 drop shape analyzer. The cyclic voltammetry was performed on a CHI600E electrochemical analyzer. The surface morphology of the films was investigated by an FEI Tecnai G2 F20 transmission electron microscope and Bruker Dimension Icon atomic force microscope. The GIXRD was measured on a Bruker D8 ADVANCE diffractometer platform.



Fig. S1 $V_{\rm OC}$ as a function of Y6 weight ratio in the blend films.



Fig. S2 The normalized absorption spectra of binary and ternary films.



Fig. S3 The normalized PL spectra of binary and ternary films.



Fig. S4 The cyclic voltammetry curves of blend films with different Y6 weight ratios.



Fig. S5 Nonencapsulated device stability statistics (J_{SC} , FF) that annealed (a,c) at 80 °C and (b,d) under AM 1.5G radiation (100 mW cm⁻²) in ambient atmosphere.

Table S1. Summary of Estimated Energy Parameters at Different Weight Ratios of Y6

Y6	$V_{\rm OC}({ m V})$	LUMO (eV)	$E_{\rm g}({\rm eV})$	$E_{\rm loss}~({\rm eV})$
0%	0.856	-4.33	1.15	0.294
30%	0.863	-4.26	1.22	0.357
50%	0.866	-4.22	1.26	0.394
100%	0.872	-4.10	1.38	0.508

Table S2. Summary of Carrier Mobilities of Solar Cells with Different Blend Films

Blend films	$\mu_{\rm h} ({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})$	$\mu_{\rm e} ({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})$	$\mu_{ m h}/\mu_{ m e}$
D18-C1:N3	6.40×10 ⁻⁴	3.56×10 ⁻⁴	1.80
D18-Cl:N3:Y6	7.25×10-4	4.87×10-4	1.49
D18-Cl:Y6	6.27×10 ⁻⁴	3.45×10 ⁻⁴	1.82

Table S3. Summary of Primary Current Parameters of Solar Cells with Different BlendFilms

Blend films	$J_{\rm SC}$ (mA cm ⁻²)	$J_{\rm sat}$ (mA cm ⁻²)	$J_{\text{power}} (\text{mA cm}^{-2})$	$\eta_{\rm diss}(\%)$	$\eta_{\rm coll}(\%)$
D18-Cl:N3	26.40	27.75	23.25	95.1	83.8
D18-Cl:N3:Y6	27.53	28.19	24.05	97.7	85.3
D18-Cl:Y6	26.58	27.84	22.91	95.5	82.3