

## Efficient ternary organic photovoltaics with two polymer donors by minimizing energy loss

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### Experimental section

**Device Fabrication:** The patterned indium tin oxide (ITO) coated glass substrates (10  $\Omega$  per square) were cleaned via sequential sonication in detergent, de-ionized and ethanol and then blow-dried by high-purity nitrogen. All pre-cleaned ITO substrates were treated by oxygen plasma for 1 minute (min) to improve their work function and clearance. Subsequently, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, purchased from H.C. Starck co. Ltd.) solution was spin-coated on ITO substrates at 5000 round per minute (RPM) for 40 s and dried at 150 °C for 10 min in atmospheric air. Then ITO substrates coated with PEDOT:PSS films were transferred into a high-purity nitrogen-filled glove box. The used materials J71 and Y6 were purchased from Solarmer Materials Inc. The PF2 was synthesized by Thomas Heiser et al. from Université de Strasbourg. The PF2: Y6 and J71: Y6 with 1:1.5 weight ratio were dissolved in chloroform to prepare 18.25 mg mL<sup>-1</sup> binary blend solutions, respectively. The proportions of PF2: J71 are 1:0, 0.9:0.1, 0.8:0.2, 0.7:0.3, 0.6:0.4, 0.5:0.5, 0.3:0.7, 0:1. The mixed solution was spin-coated onto the PEDOT:PSS/ITO substrates at 3000 RPM for 40 s to prepare the active layers. The active layers were up-side down solvent vapor annealed with carbon disulfide for 30 s and thermal annealed at 100 °C for 5 min. PDIN was dissolved in methanol with the addition of 0.25 vol% acetic acid to prepare a 2 mg mL<sup>-1</sup> solution. The prepared PDIN solution was spin-coated onto the active layers at 5000 RPM for 40 s. Finally, aluminum (Al) electrode was deposited by thermal evaporation. For each of the organic photovoltaics (OPVs), the contacts were deposited at the vacuum condition of 10<sup>-4</sup> Pa. The active area is approximately 3.8 mm<sup>2</sup>, which is defined by the overlapping area of ITO anode and Al cathode.

**Device Measurement:** The current density-voltage (*J-V*) curves of all the OPVs were measured by a Keithley 2400 unit in high-purity nitrogen-filled glove box. The AM 1.5G irradiation was provided by an XES-40S2 (SAN-EI ELECTRIC Co., Ltd) solar simulator (AAA grade, 70×70 mm<sup>2</sup> photobeam size) with light intensity of 100 mW cm<sup>-2</sup>. Our simulator was corrected by using a standard monocrystalline silicon reference cell. The external quantum efficiency (EQE) spectra of

OPVs were measured by a Zolix Solar Cell Scan 100. The absorption spectra of films were measured with a Shimadzu UV-3101 PC spectrometer. Transmission electron microscopy (TEM) images of blend films were obtained by a JEOL JEM-1400 transmission electron microscope operated at 80 kV. The reflection spectra measurement of all devices was performed on a commercial QE measurement system (QE-RT3011, Enlitech) by using an integrating sphere. The absorption spectra of active layers in cells were calculated by subtracting the parasitic absorptions ( $1-R_1$ ) from the total absorption in OPVs ( $1-R_2$ ), where  $R_1$  is the reflection spectrum of device ITO/PEDOT:PSS/PMMA/PDIN/Al,  $R_2$  is the reflection spectra of OPVs ITO/PEDOT:PSS/active layers/PDIN/Al. The PMMA layer in the special device is used to simulate the optical path in real OPVs because PMMA has negligible photon harvesting in the whole spectral range.

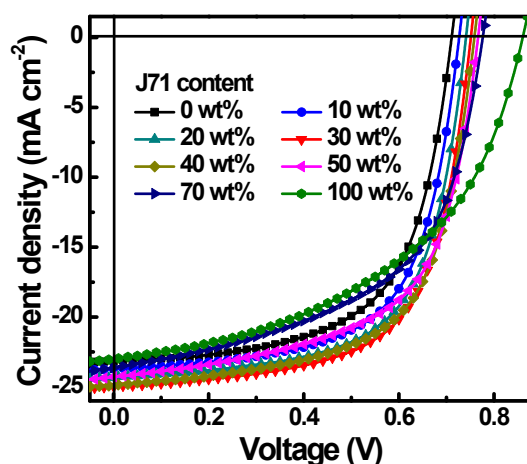


Fig. S1. The  $J$ - $V$  curves of all OPVs with different J71 content.

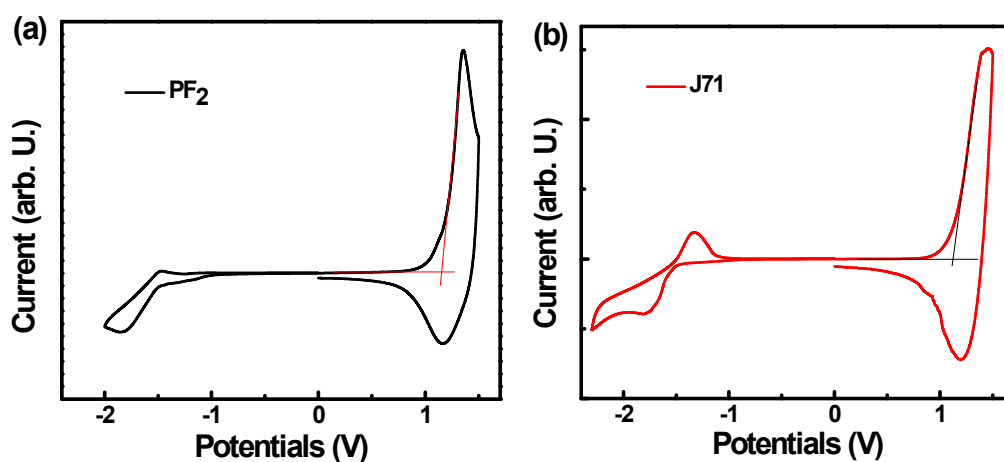


Fig. S2. Cyclic voltammetry (CV) plots of neat PF2 and J71 films.

Cyclic voltammetry (CV) measurement were carried out on a CHI voltammetric analyze at room temperature. The supporting electrolyte is tetrabutyl-lammonium hexafluorophosphate (n-

Bu4NPF6, 0.1 M). The conventional three-electrode configuration consists of a platinum working electrode with 2 mm diameter, platinum wire counter electrode and Ag/AgCl wire reference electrode. Cyclic voltammogram were obtained at a scan rate of 100 mA/s. The potentials were obtained using ferrocene as the reference. The equations of HOMO energy levels is as following.

$$HOMO = - [E_{ox} + (4.80 - E_{Fc})]eV$$

Here,  $E_{OX}$  is the onset of oxidation potential,  $E_{FC}$  represents standard sample of ferrocene. The LUMO energy levels are calculated according to the difference between the  $E_{gap}$  and HOMO energy levels.

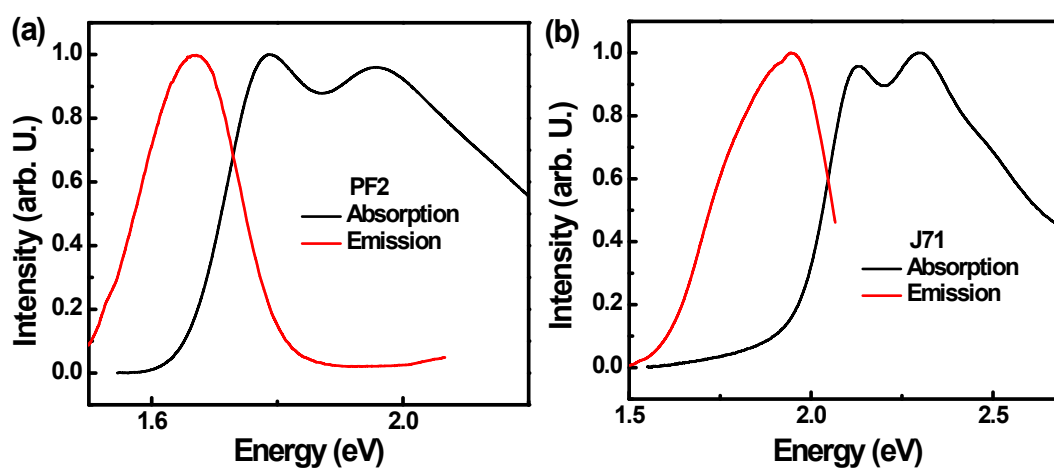


Fig. S3. The normalized absorption and emission spectra of neat PF2 and J71 films.

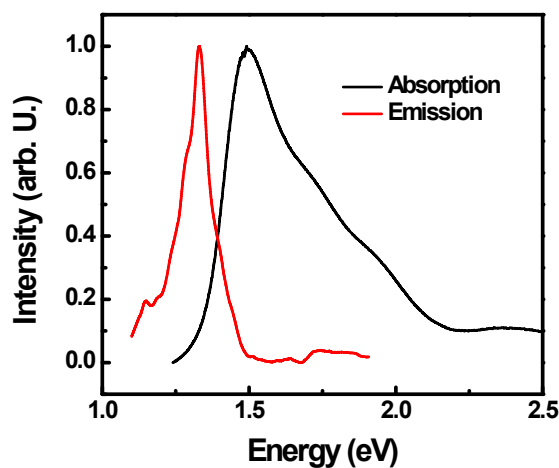
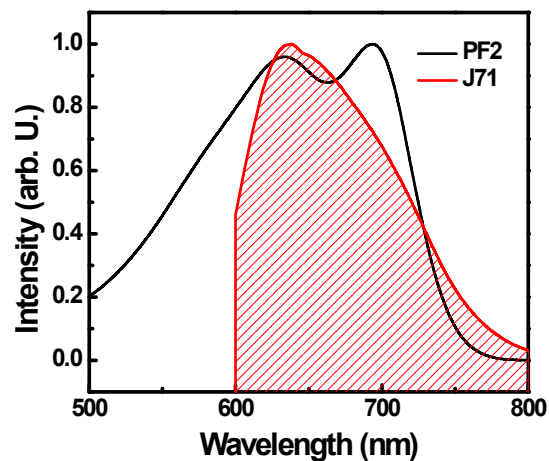


Fig. S4. The normalized absorption and emission spectra of Y6.

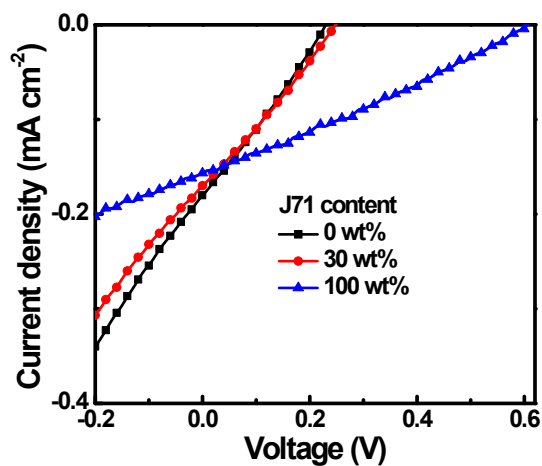


**Fig. S5.** The normalized absorption spectrum of PF2 and emission spectrum of J71.

**Table S1.**  $J_{ph}$  values under short circuit and maximal power output conditions.

J71 content (wt %)	$J_{ph}^a$ (mA cm <sup>-2</sup> )	$J_{ph}^b$ (mA cm <sup>-2</sup> )
0	23.17	18.96
30	24.97	21.27

<sup>a</sup> short-circuit condition, <sup>b</sup> maximal power output condition.



**Fig. S6.**  $J$ - $V$  curves of cells with PF2, J71 and PF2:J71 as active layers

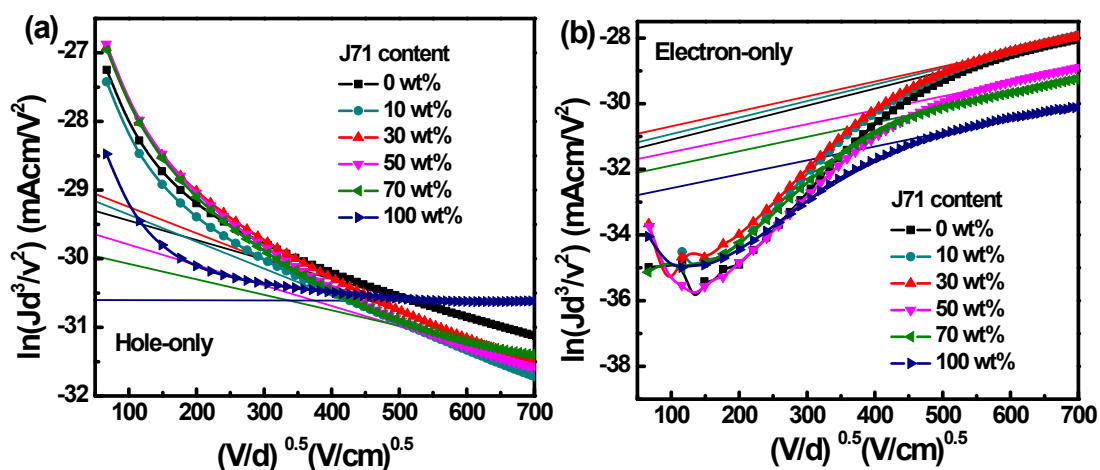


Fig. S7. The plotted  $\ln(Jd^3/V^2)$  versus  $(V/d)^{0.5}$  curves of the devices with different J71 content.

Table S2. The  $\mu_h$ ,  $\mu_e$  and  $\mu_h/\mu_e$  in blend films with different J71 content.

J71 content (wt %)	$\mu_h$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )	$\mu_e$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )	$\mu_h/\mu_e$
0	$6.24 \times 10^{-4}$	$8.04 \times 10^{-5}$	7.76
10	$7.25 \times 10^{-4}$	$9.62 \times 10^{-5}$	7.54
30	$8.10 \times 10^{-4}$	$1.15 \times 10^{-4}$	7.04
50	$4.49 \times 10^{-4}$	$5.66 \times 10^{-5}$	7.93
70	$3.23 \times 10^{-4}$	$3.87 \times 10^{-5}$	8.35
100	$1.72 \times 10^{-4}$	$1.94 \times 10^{-5}$	8.87

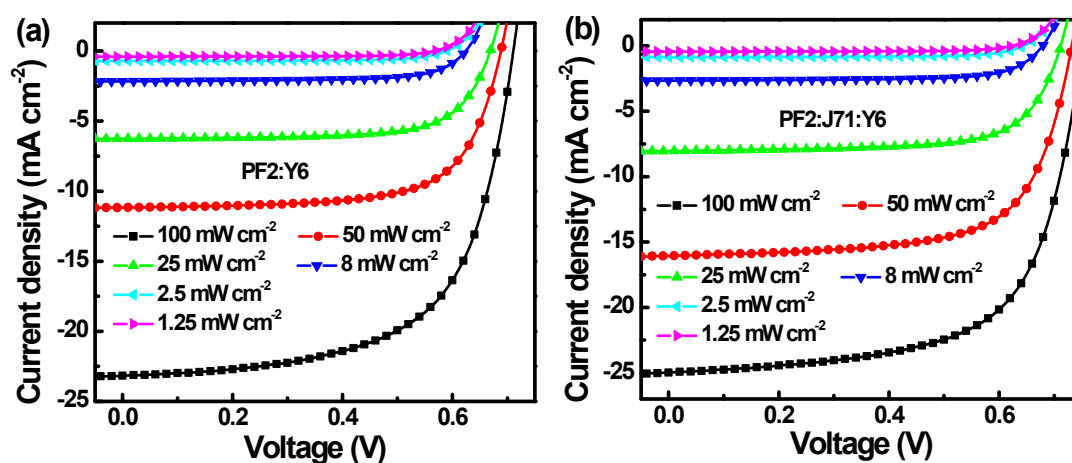


Fig. S8. The  $J$ - $V$  curves of PF2:Y6 based (a) and the optimized ternary (b) OPVs under different light illumination intensity, obtained from standard AM 1.5G ( $100 \text{ mW cm}^{-2}$ ) illumination using a set of neutral optical filters.