Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Effects of the diphenyl ether additive in halogen-free processed non-fullerene acceptor organic solar cell

Supplementary Information

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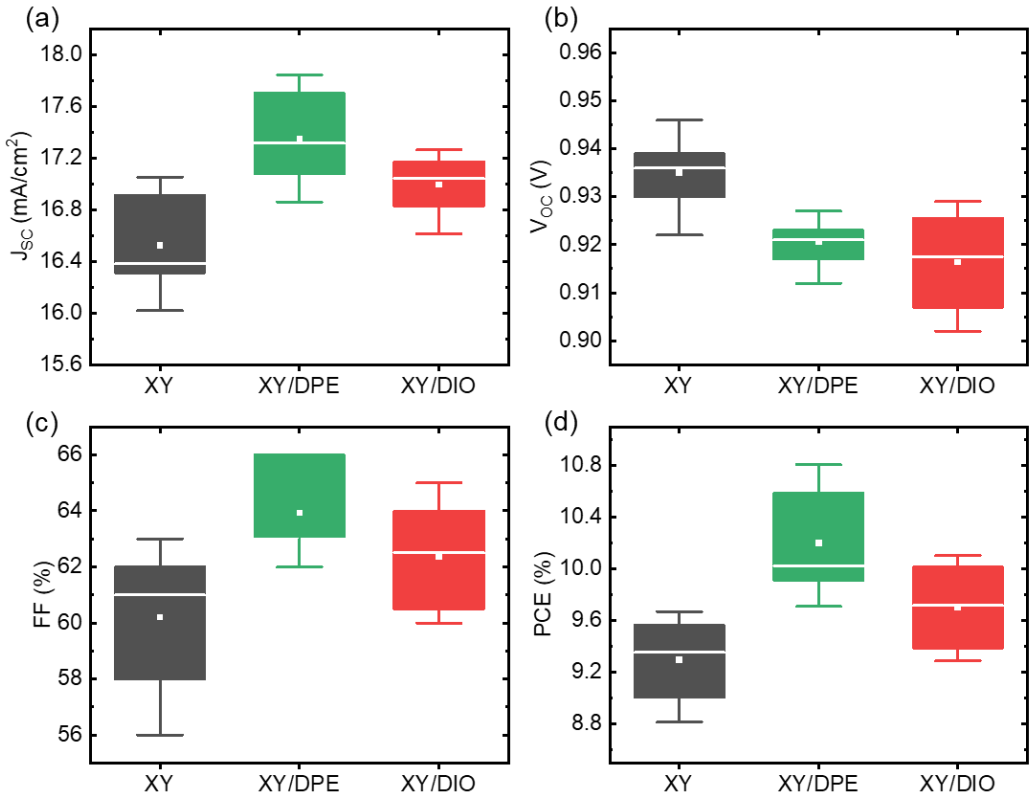

Figure S1 Box charts of the photovoltaic parameter distributions for devices fabricated spin coating the blend solution without additive, with DPE and with DIO. Values from 15 devices for each condition. The active area of the devices is 10 mm^2.

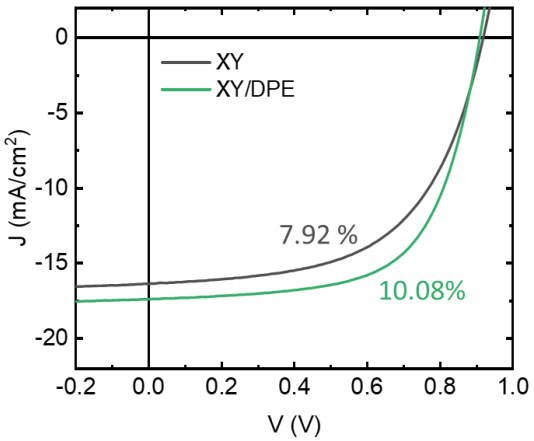

Figure S2 J-V curves under illumination (AM 1.5, 100 mW cm^{-2}) of TPD-3F:IT-4F devices fabricated depositing the active layer by blade coating, from a solution without additive and with 3 wt% of DPE. Numbers indicate the PCE obtained for each device.

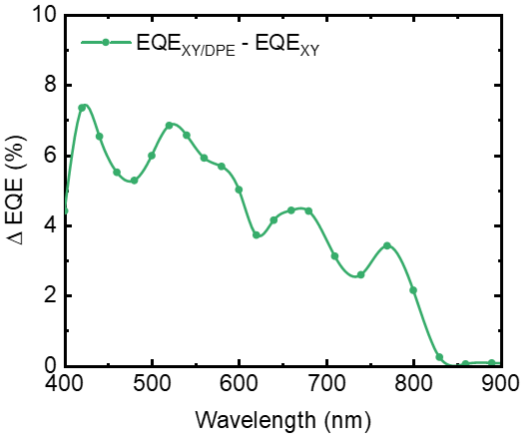

Figure S3 Difference of external quantum efficiency (ΔEQE) between TPD-3F:IT-4F devices fabricated with DPE and devices fabricated without additive.

Table S1 Components of the equivalent circuit as extracted by fitting the Nyquist plot data for TPD-3F:IT-4F devices fabricated with and without the use of DPE.

Solution	R_s (ohm)	L (μH)	Rp (kohm)	CPE (nF)	CPE-P	τ (μs)
XY	54.02	2.493	3.831	12.66	0.918	48.50
XY/DPE	22.20	2.524	1.786	29.49	0.887	52.67

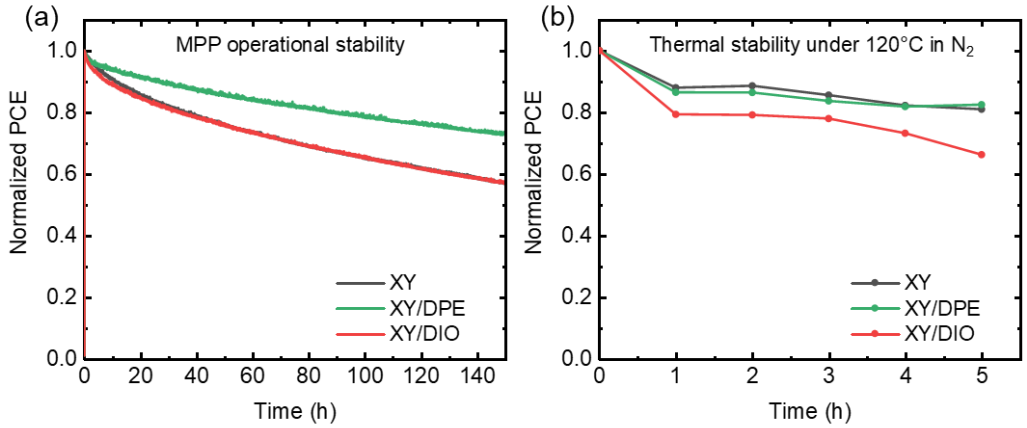

Figure S4 Stability of TPD-3F:IT-4F solar cells fabricated casting the blend film from a solution without additive, with DPE and with DIO: (a) stability in operation at maximum power point (MPP), under continuous illumination (AM 1.5, 100 mW cm^{-2}); (b) thermal stability, annealing solar cells at 120 °C in N_2 atmosphere.

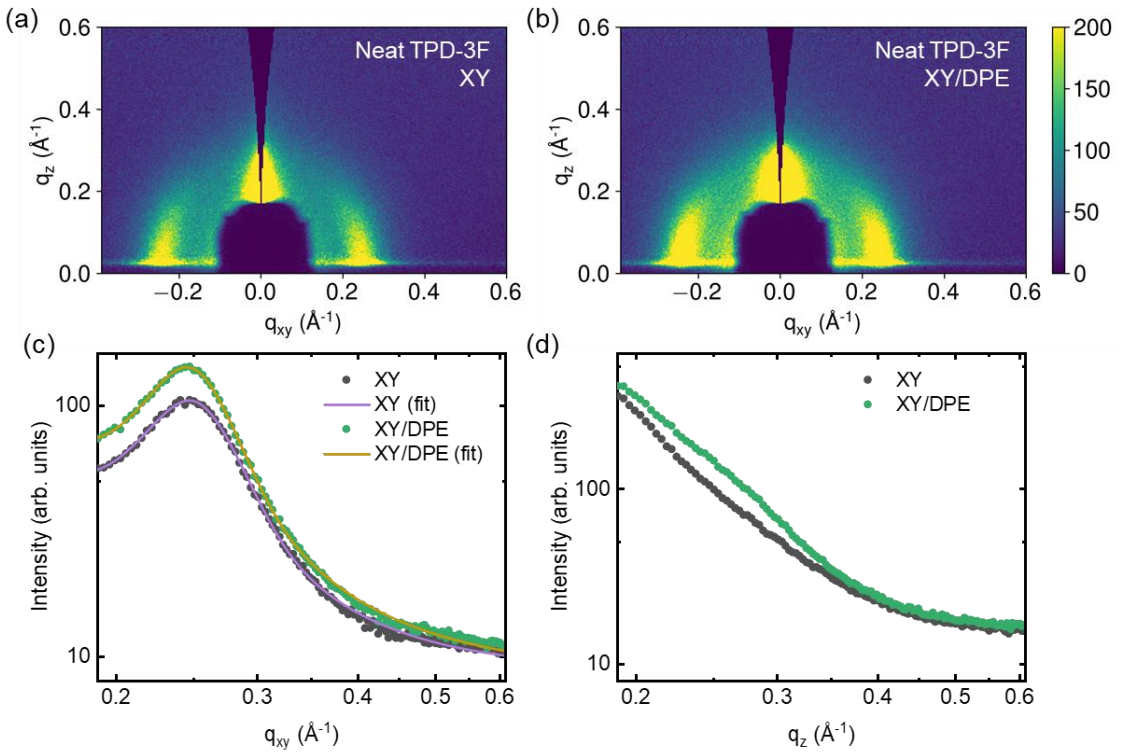

Figure S5 2D GIWAXS data and cuts of measurements on films of pure TPD-3F donor cast with and without the use of DPE in solution: 2D false-color maps for a film without additive (a) and with additive (b); corresponding in-plane (c) and out-of-plane (d) line cuts.

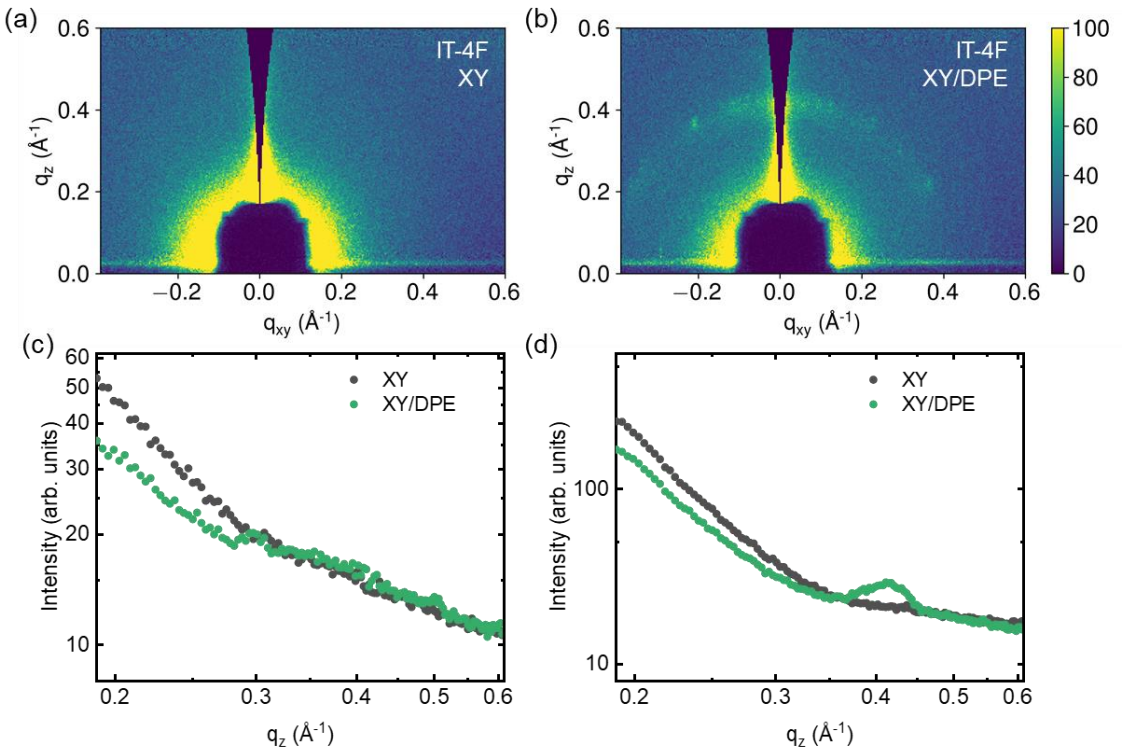

Figure S6 2D GIWAXS data and cuts of measurements on films of neat IT-4F acceptor cast with and without the use of DPE in solution: 2D false-color maps for a film without additive (a) and with additive (b); corresponding in-plane (c) and out-of-plane (d) line cuts.

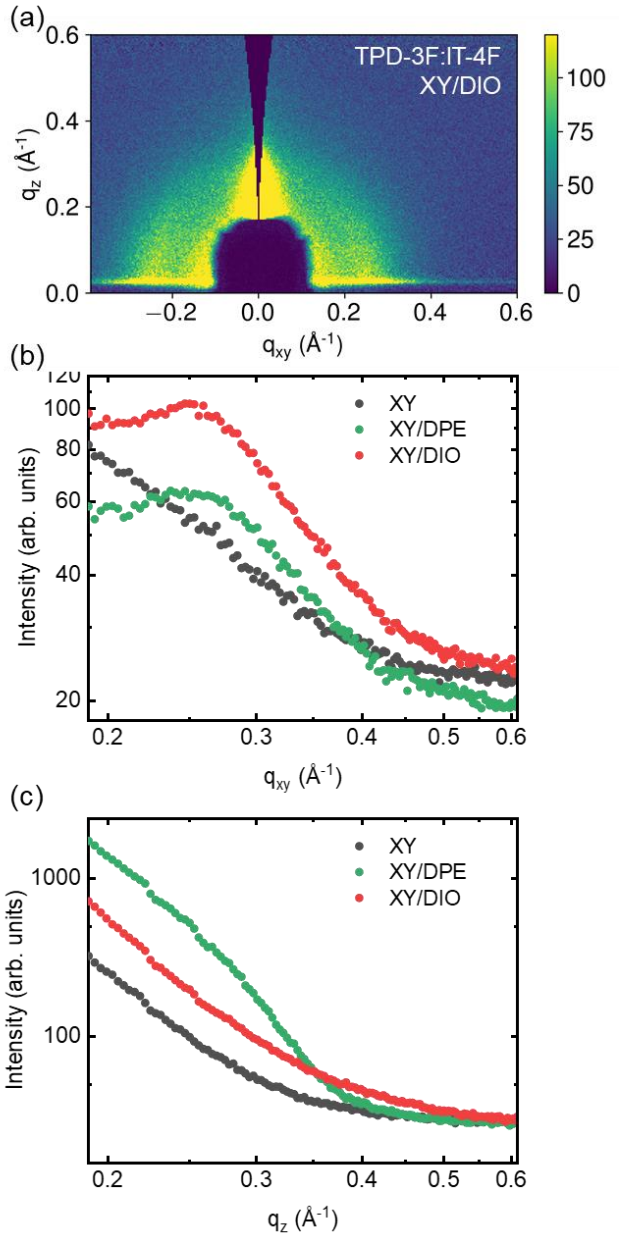

Figure S7 2D GIWAXS data and cuts of measurements on TPD-3F:IT-4F blend films cast with the use of DIO in solution: 2D false-color maps (a) and corresponding in-plane (b) and out-of-plane (c) line cuts.

Table S2 Fitting parameters for the time-resolved PL decays and calculated average lifetimes.

Solution	A_1	τ_1 (ps)	A_2	τ_2 (ps)	A_3	τ_3 (ps)	τ_{avg} (ps)
XY	0.59	4.5	0.25	15.5	0.03	68.3	24.6
XY/DPE	0.71	5.2	0.20	16.7	0.01	64.2	16.4

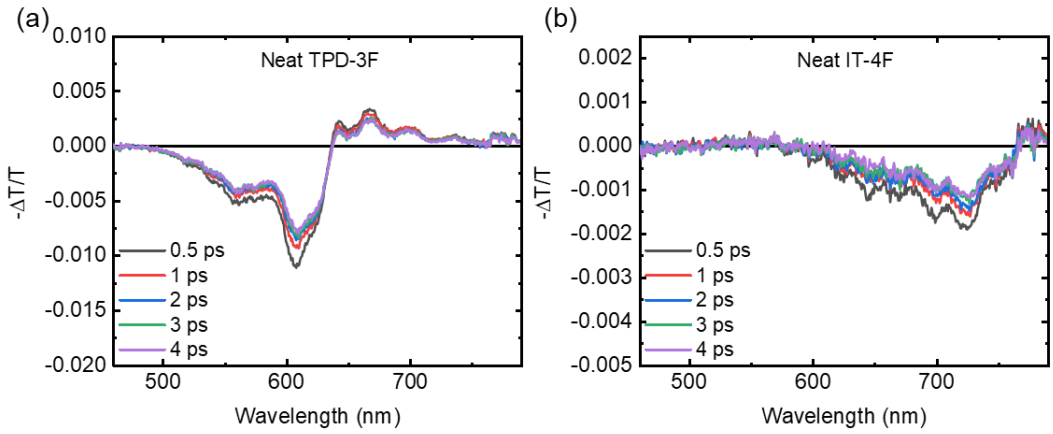

Figure S8 Transient transmission spectra acquired at different time delays for the films of pure TPD-3F donor (a) and of pure IT-4F acceptor. Excitation wavelength 360 nm. Films cast without using any additive.

Table S3 Photovoltaic parameters of solar cells fabricated casting the blend film from a solution without additive and with DPE in different concentrations.

Solution	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
XY	0.921	16.49	51.59	7.83
XY/1% DPE	0.931	15.19	60.10	8.50
XY/3% DPE	0.915	16.88	62.27	9.62
XY/5% DPE	0.911	17.14	60.23	9.41

From the results of the characterizations reported in the manuscript for the concentration of 3% in comparison with the sample without additive, it is reasonable to expect differences in the nanostructure with a different concentration of DPE. This indeed, it is expected to affect the solar cell performance. The concentration of 1% is not enough to achieve a sufficient phase separation of the two blend components, with the result of a not optimal charge carrier collection (as supported by the low short circuit current of the solar cells). On the other hand, a concentration of 5% leads to an excessive segregation of the two components, with big domain size and, thus, with increased non-radiative recombination (as supported by the low open circuit voltage and fill factor of the solar cells).