Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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Supporting Information

Towards efficient NFA-based selective near-infrared organic photodetectors: impact of thermal annealing of polymer blends

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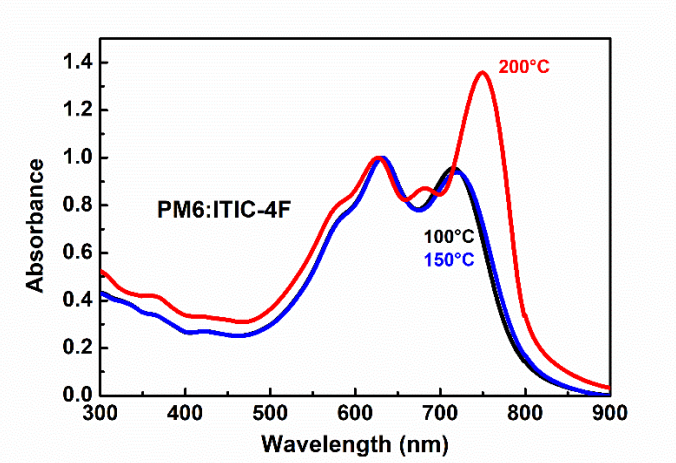

Figure S1. Normalized absorption spectra of PM6:ITIC-4F (1:2 w/w ratio) blend layers as function of thermal annealing temperature.

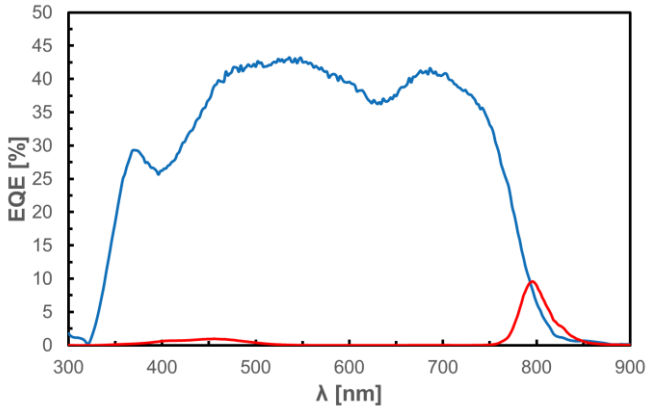

Figure S2. External quantum efficiency (EQE) spectra of photodiode devices in normal structure as ITO/PEDOT:PSS/PM6:ITIC-4F/ZnO/Al. PM6:ITIC-4F blends: 1:1 w/w ratio, annealed at 100°C and 200 nm thick (large band in blue) or > 2 µm thick (narrowband in red). EQE realized under a bias of 0 V.

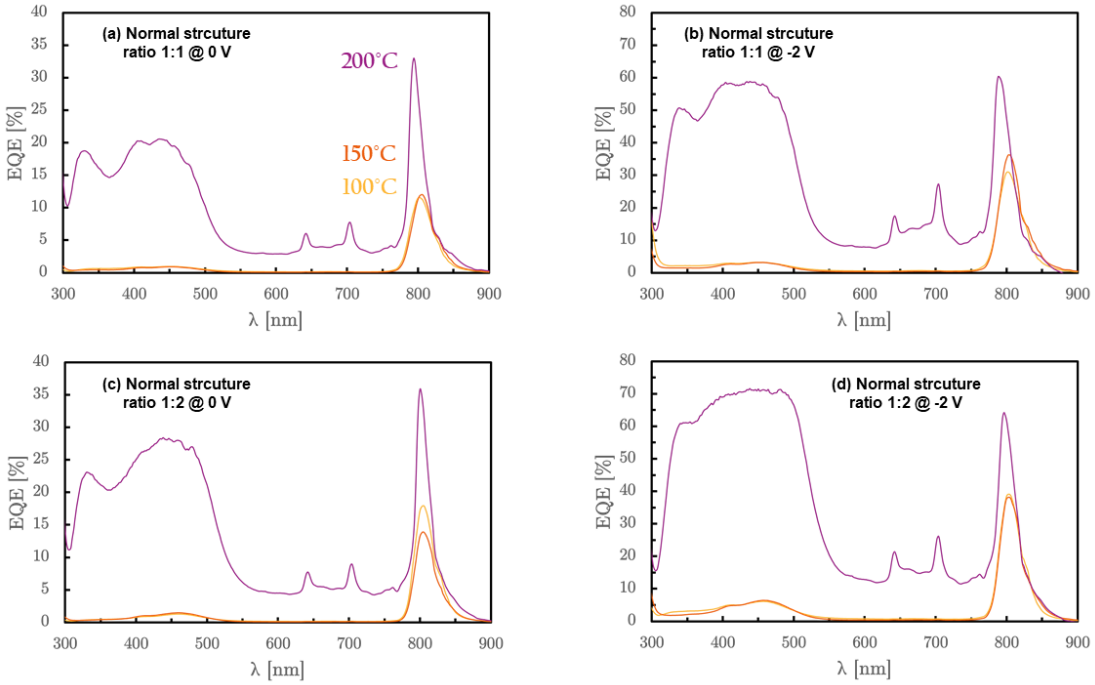

Figure S3. External quantum efficiency (EQE) spectra of OPDs in normal structure as ITO/PEDOT:PSS/PM6:ITIC-4F/ZnO/Al by varying the thermal annealing temperature of the active layers from 100 to 200°C under a bias of 0 V and -2 V. PM6:ITIC-4F blends: 1:1 or 1:2 w/w ratio, > 2 µm thick.

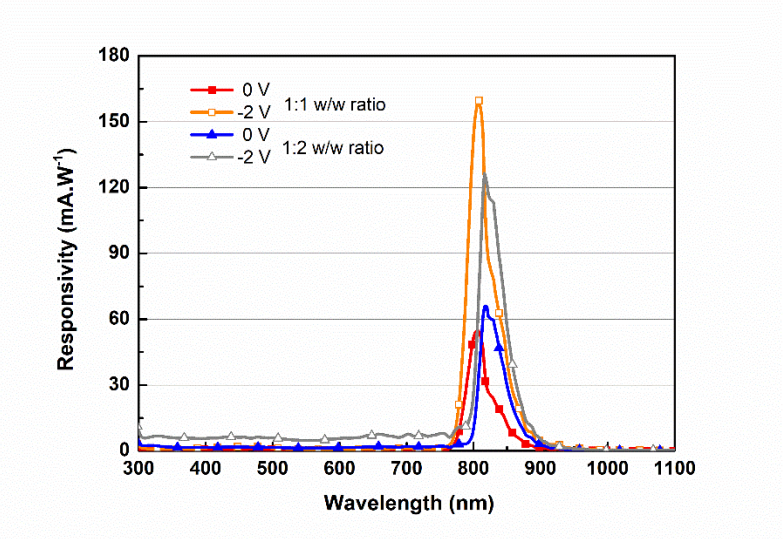

Figure S4. Calculated responsivity spectra of OPDs from the EQE measurement. OPDs in inverted structure as ITO/ZnO/PM6:ITIC-4F/MoO_3/Ag under biases 0 V and -2 V. PM6:ITIC-4F blends: 1:1 or 1:2 w/w ratio, annealed at 200°C, > 2 µm thick.

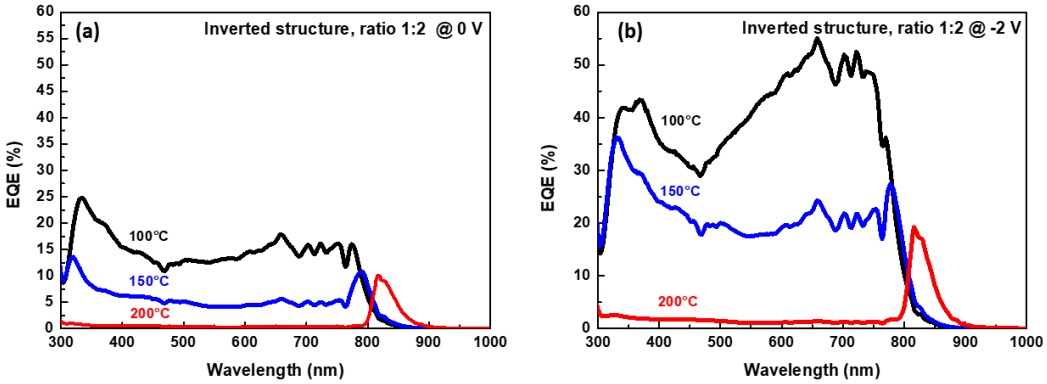

Figure S5. External quantum efficiency (EQE) spectra of OPDs in inverted structure as ITO/ZnO/PM6:ITIC-4F(1:2 w/w ratio, > 2 µm thick)/MoO_3/Ag and by varying the thermal annealing of the active layers from 100 to 200°C under different biases (a) 0 V and -2 V (b).

Table S1. Thickness and OPD parameters of devices in normal and inverted structures at 0 V and -2 V biases for 1:1 and 1:2 w/w ratio.

			1:1 ratio									
			0 V					-2 V				
		d (μm)	λ_{EQEmax} (nm)	EQE[3] (%)	$\Re_{max}$[4] (mA.W^{-1})	FWHM (nm)	SRR[5]	λ_{EQEmax} (nm)	EQE[3] (%)	$\Re_{max}$[4] (mA.W^{-1})	FWHM (nm)	SRR[5]
100°C	I[1]	2.52	782	11.0	69.3	30	6.6	777	24.5	153.3	40	3.4
	N[2]	2.05	802	11.6	74.9	38	21.3	802	31.0	200.2	40	17.1
150°C	I[1]	2.52	796	10.9	69.8	30	31.3	800	28.8	185.5	41	22.5
	N[2]	2.37	806	12.1	78.5	41	23.7	804	36.3	235.5	38	20.4
200°C	I[1]	2.74	806	8.45	54.8	**44**	**74.2**	807	24.5	159.6	**42**	**80.5**
	N[2]	2.02	794	33.0	211	22	2.9[6]	788	60.4	383.3	35	1.8[6]
			1:2 ratio									
			0 V					**-2 V**				
		d (μm)	λ_{EQEmax} (nm)	EQE[3] (%)	$\Re_{max}$[4] (mA.W^{-1})	FWHM (nm)	SRR[5]	λ_{EQEmax} (nm)	EQE[3] (%)	$\Re_{max}$[4] (mA.W^{-1})	FWHM (nm)	SRR[5]
100°C	I[1]	2.23	-[6]	-[6]	-[6]	-[6]	-[6]	-[6]	-[6]	-[6]	-[6]	-[6]
	N[2]	2.27	804	17.9	115.9	38	24.9	802	39.0	251.9	41	11.2
150°C	I[1]	2.36	-[6]	-[6]	-[6]	-[6]	-[6]	-[6]	-[6]	-[6]	-[6]	-[6]
	N[2]	2.32	804	13.9	90	38	16.6	804	38.2	247.3	38	10.4
200°C	I[1]	2.27	818	10	65.8	41	38.1	816	19.2	126.2	43	20.5
	N[2]	2.37	800	35.9	231	22	2.2[6]	796	64.2	411.6	32	1.5[6]

(1) Inverted structure
(2) Normal structure
(3) EQE at λ_{EQEmax}
(4) Responsivity $\Re_{max}$ = EQE x (λq/hc) calculated with EQE at λ_{EQEmax}
(5) SRR: spectral rejection ratio (Responsivity $\Re$ ratio of highest value to that at 460 nm)
(6) No CCN-type OPDs identified from EQE spectra or from SRR value (<3).

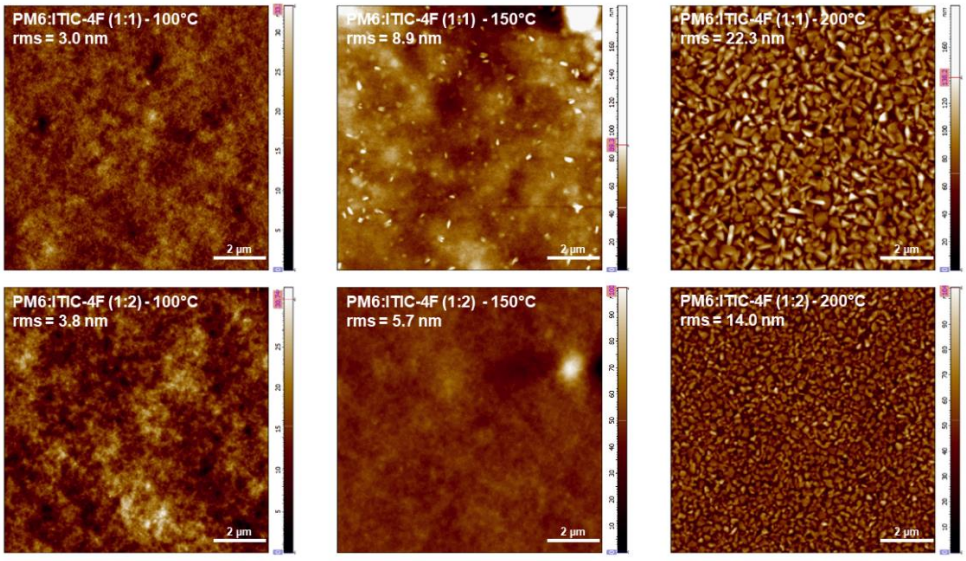

Figure S6. Atomic force microscopy (AFM) height images of PM6:ITIC-4F bulk heterojunction blends (1:1 w/w ratio on top and 1:2 w/w ratio on bottom) annealed at 100°C, 150°C and 200°C. Scale: 10×10 μm^2.

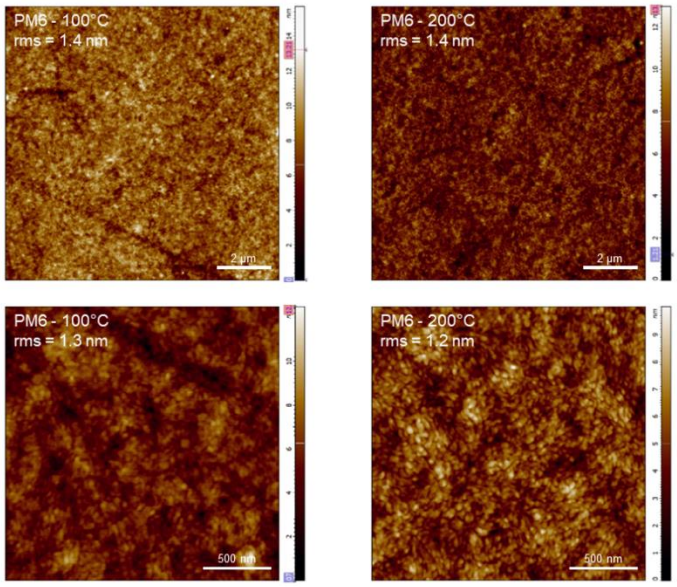

Figure S7. Atomic force microscopy (AFM) height images of neat PM6 layers annealed at 100°C and 200°C. Scales: on top 10×10 µm^2 and on bottom 2×2 µm^2.

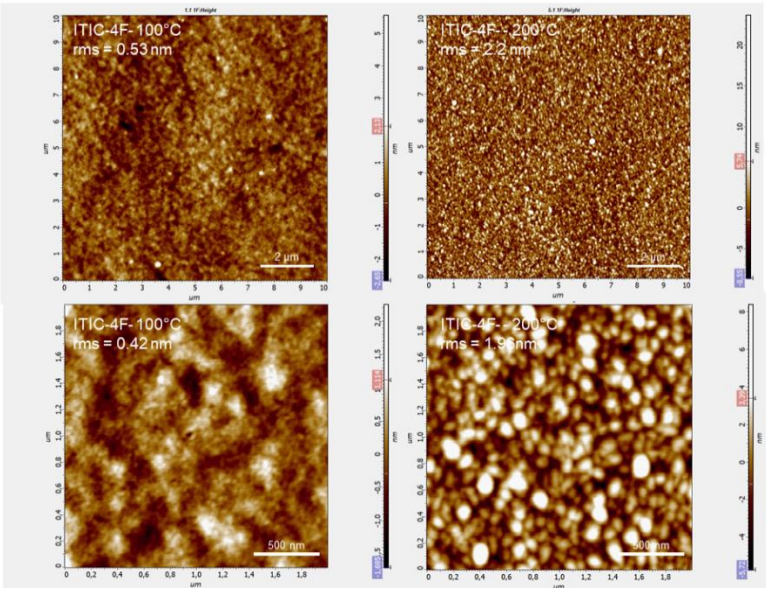

Figure S8. Atomic force microscopy (AFM) height images of neat ITIC-4F layers annealed at 100°C and 200°C. Scales: on top 10×10 µm^2 and on bottom 2×2 µm^2.

Table S2. Root mean square (rms) roughness and water contact angle (WCA) data of neat films (PM6 and ITIC-4F) and PM6:ITIC-4F blends in 1:1 and 1:2 w/w ratio.

Material	Temperature (°C)	rms roughness[(1)] (nm)	**Average WCA (°)**	Min. WCA (°)	Max. WCA (°)	Stan. Dev. (°)
PM6	100	1.3	**101**	100.81	101.19	0.14
	200	1.2	**100.5**	100.38	100.76	0.18
ITIC-4F	100	0.42	**93.6**	91.97	94.77	1.07
	200	1.96	**92.7**	91.09	93.85	1.09
PM6:ITIC-4F (ratio 1:1)	100	2.1	**102.7**	101.64	103.81	0.79
	150	3.8	**105.3**	104.41	106.02	0.58
	200	21.8	**108.0**	107.56	108.27	0.30
PM6:ITIC-4F (ratio 1:2)	100	2.5	**101.1**	100.91	101.30	0.17
	150	2.3	**100.5**	100.40	100.67	0.12
	200	11.3	**107.4**	106.14	108.50	0.90

[(1)] From AFM pictures with a scale 2×2 μm^2.

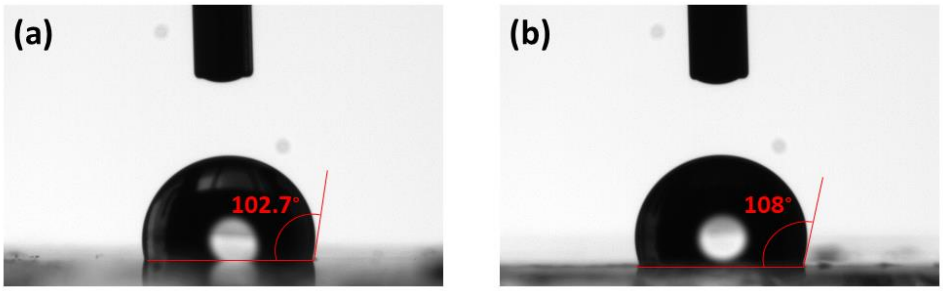

Figure S9. Water contact angle (WCA) images of PM6:ITIC-4F blends in 1:1 w/w ratio at 100°C (a) and 200°C (b)

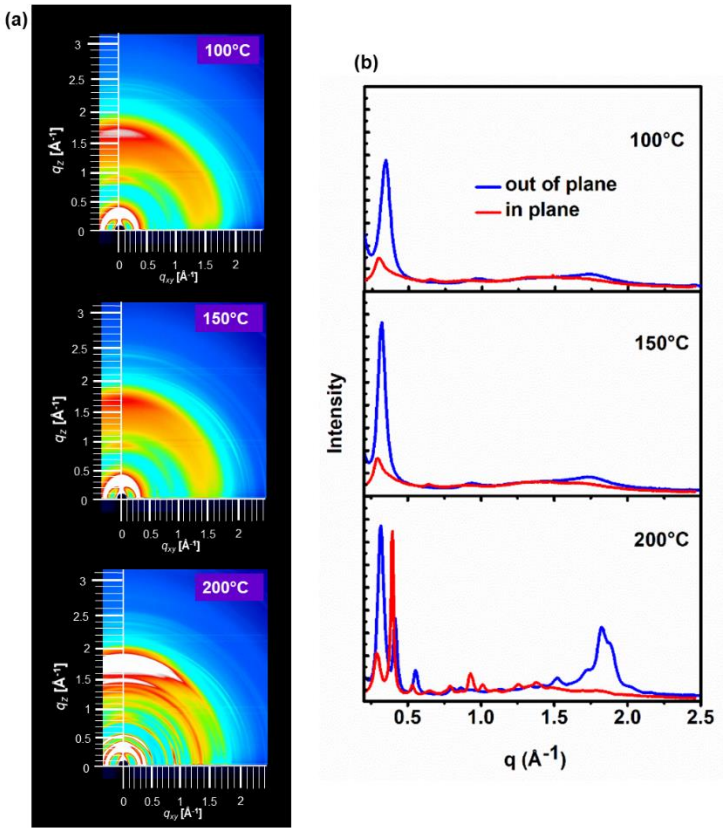

Figure S10. 2D-GIXRD patterns (a) and corresponding in plane and out of plane profiles (b) of PM6:ITIC-4F (1:2 w/w ratio) films deposited on ZnO buffer layer as function of thermal annealing temperature.

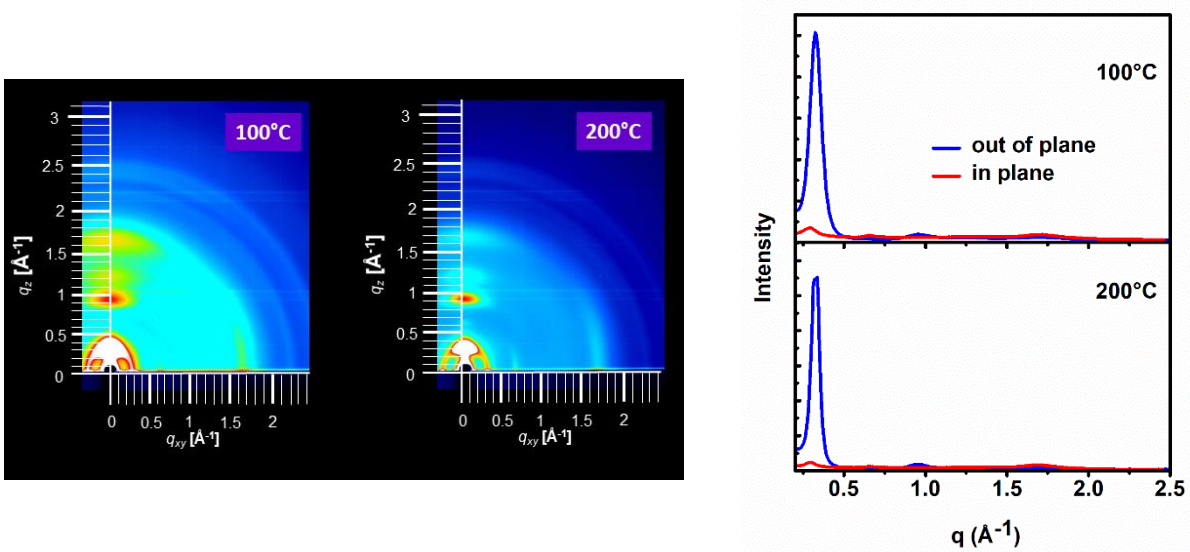

Figure S11. 2D-GIXRD patterns and corresponding profiles (in plane and out of plane) of PM6 thin films deposited on ZnO buffer layer as function of thermal annealing temperature.

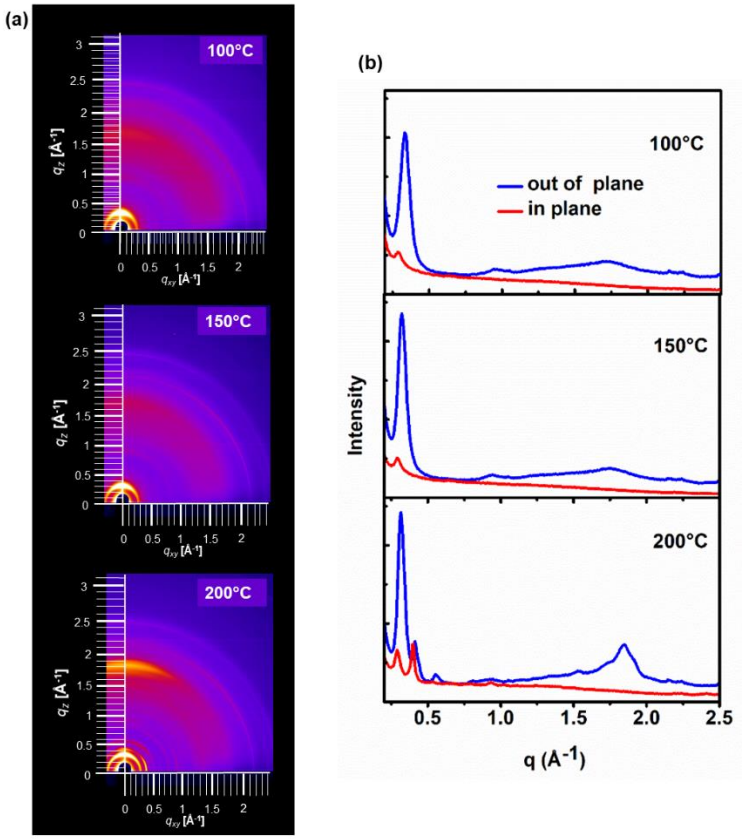

Figure S12. 2D-GIXRD patterns (a) and corresponding in plane and out of plane profiles (b) of PM6:ITIC-4F (1:1 w/w ratio) films deposited on PEDOT:PSS buffer layer as function of thermal annealing temperature.

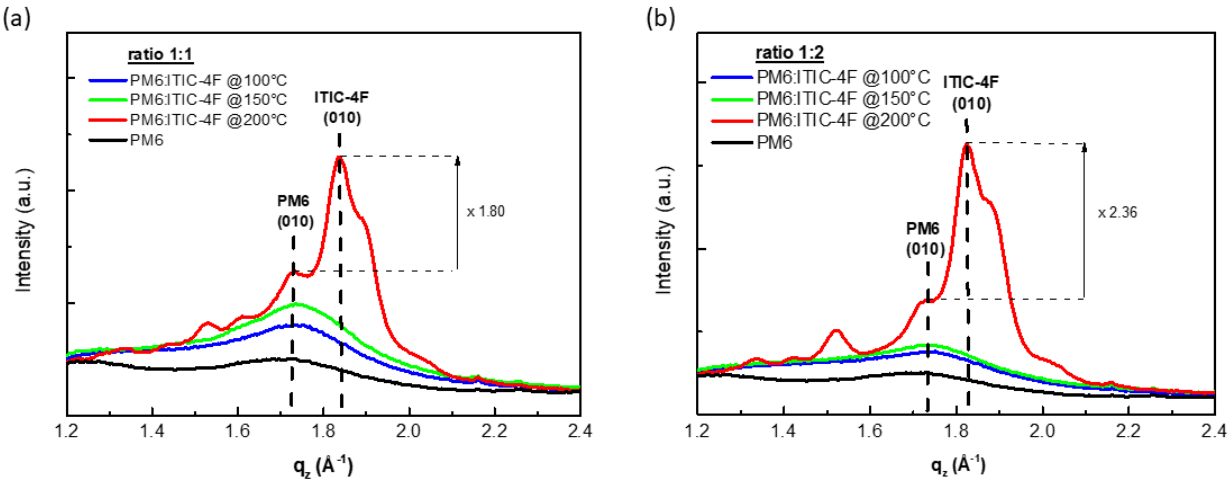

Figure S13. Zoom in OOP profiles of neat PM6 and PM6:ITIC-4F films deposited on ZnO buffer layer as function of thermal annealing temperature in (a) 1:1 and (b) 1:2 w/w ratio.

Table S3. XRD data of PM6:ITIC-4F (1:1 and 1:2 w/w ratio) blend layers deposited on ZnO buffer layer as function of thermal annealing temperature (100°C, 150°C and 200°C). Additionally, data of blend at 200°C deposited on PEDOT:PSS are given for comparison.

Ratio	T (°C)		q_z (Å^{-1}) (100) peak	Peak area[1]	Peak area in %[2]	FMHW[3]	d[4] (nm)	CCL[5] (nm)
1:1	100	PM6	0.337	30571.7	98.3	0.07987	1.86	1.12
		ITIC-4F	0.421	520.6	1.7	0.04001	1.50	2.25
	150	PM6	0.323	32935	90.8	0.06214	1.94	1.45
		ITIC-4F	0.403	3328	9.2	0.05204	1.55	1.73
	200	PM6	0.318	23981.4	80.7	0.05399	1.97	1.66
		ITIC-4F	0.405	5731.3	19.3	0.04169	1.54	2.16
	200[6]	PM6	0.318	4979.9	87.7	0.05087	1.97	1.77
		ITIC-4F	0.414	693.7	12.3	0.04082	1.51	2.2
1:2	100	PM6	0.341	16374.8	98.3	0.07052	1.84	1.27
		ITIC-4F	0.409	270.8	1.7	0.03398	1.53	2.65
	150	PM6	0.322	19019.1	94	0.05677	1.94	1.58
		ITIC-4F	0.408	1206.4	6	0.04234	1.54	2.12
	200	PM6	0.317	17650.1	78.1	0.05021	1.97	1.80
		ITIC-4F	0.414	4938.2	21.9	0.03393	1.51	2.65
PM6	100		0.327			0.08185	1.92	1.10
	200		0.325			0.05666	1.93	1.58

(1) peak area after deconvolution
(2) contribution to the area of the cumulative fit peak
(3) FMHW = full width at half maximum
(4) $d = 2\pi/q$
(5) CCL for crystal coherence length
(6) Blend on PEDOT:PSS

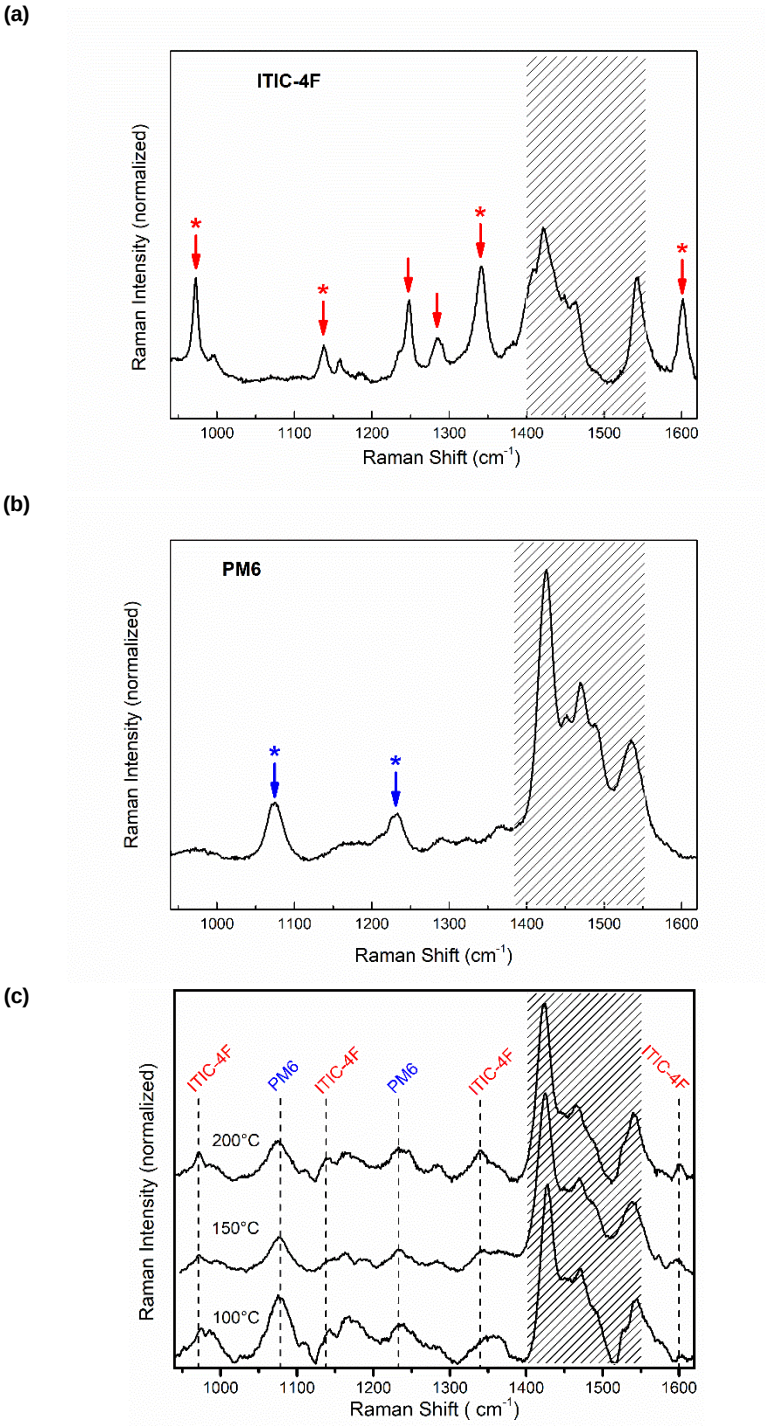

Figure S14. Raman spectra of neat ITIC-4F (a) and PM6 (b) layers annealed at 200°C. (c) Raman spectra from the back side of PM6:ITIC-4F blends with 1:1 w/w ratio annealed at 100°C, 150°C and 200°C. Thickness: ~ 100 nm for (a) and (b), > 2 μm for (c).

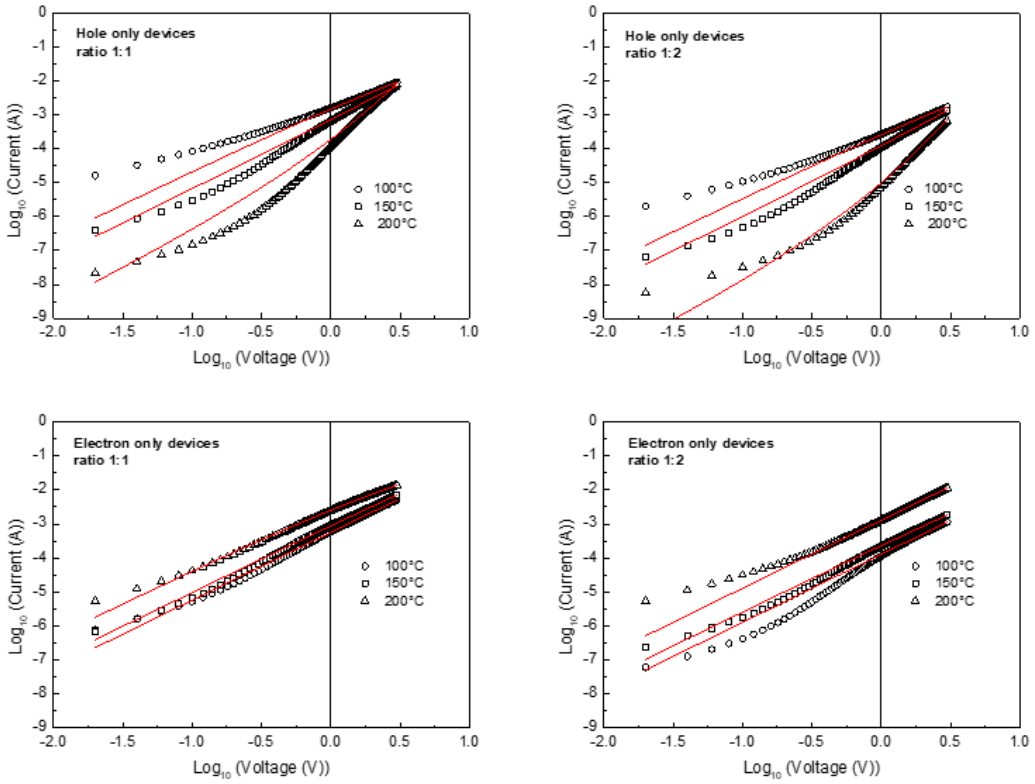

Figure S15. Current *vs.* voltage for holes and electron only devices based on PM6:ITIC-4F blends with 1:1 and 1:2 w/w ratio. The charges carrier mobility values of PM6:ITIC-4F blends were determined following the single-carrier devices SCLC model.

Table S4. Thickness (d), hole (μ_h) and electron (μ_e) mobility values obtained by SCLC of PM6:ITIC-4F bulk heterojunction layers as function of blend ratio, thermal annealing temperature and thickness. Standard deviations are indicated in brackets, from measurements on 6 devices.

ratio	Thermal annealing temperature	Hole only devices		Electron only devices		
		thickness d (nm)	μ_h ($cm^2/V.s$)	thickness d (nm)	μ_e ($cm^2/V.s$)	μ_e/μ_h
1:1	100°C	149 (± 2.5)	$2.46x10^{-4}$ (± $1.9x10^{-5}$)	129 (± 22)	$3.27x10^{-5}$ (± $4.05x10^{-6}$)	0.13
	150°C	146 (± 4.5)	$6.31x10^{-5}$ (± $6.4x10^{-6}$)	140 (± 9)	$7.9x10^{-5}$ (± $7.65x10^{-6}$)	1.25
	200°C	146 (± 10)	$1.79x10^{-6}$ (± $3.6x10^{-7}$)	136 (± 6.5)	$3.68x10^{-4}$ (± $1.8x10^{-5}$)	205
	100°C	1257 (± 15)	$1.66x10^{-5}$ (± $0.5x10^{-5}$)	1818 (± 40)	nd(1)	nd(1)
	200°C	1270 (± 35)	$4.05x10^{-6}$ (± $4.2x10^{-6}$)	1821 (± 70)	$5.9x10^{-4}$ (± $1.5x10^{-5}$)	145
1:2	100°C	236 (± 15.5)	$1.32x10^{-4}$ (± $5.5x10^{-6}$)	271 (± 10)	$8.21x10^{-5}$ (± $6.7x10^{-6}$)	39
	150°C	243 (± 12)	$3.71x10^{-5}$ (± $2.4x10^{-6}$)	276 (± 12.5)	$1.72x10^{-4}$ (± $1.65x10^{-5}$)	4.6
	200°C	228 (± 13.5)	$1.98x10^{-7}$ (± $5.1x10^{-8}$)	266 (± 12)	$6.71x10^{-4}$ (± $9x10^{-6}$)	3388

(1) Not determined: SCLC protocol could not be applied to the curves resulting from the measurement. To apply SCLC protocol, I-V data should include two or three complete sweep cycles from zero volt to positive voltage, then to negative voltage and finally to the point of origin. These sweeps should be free of hysteresis.[1]

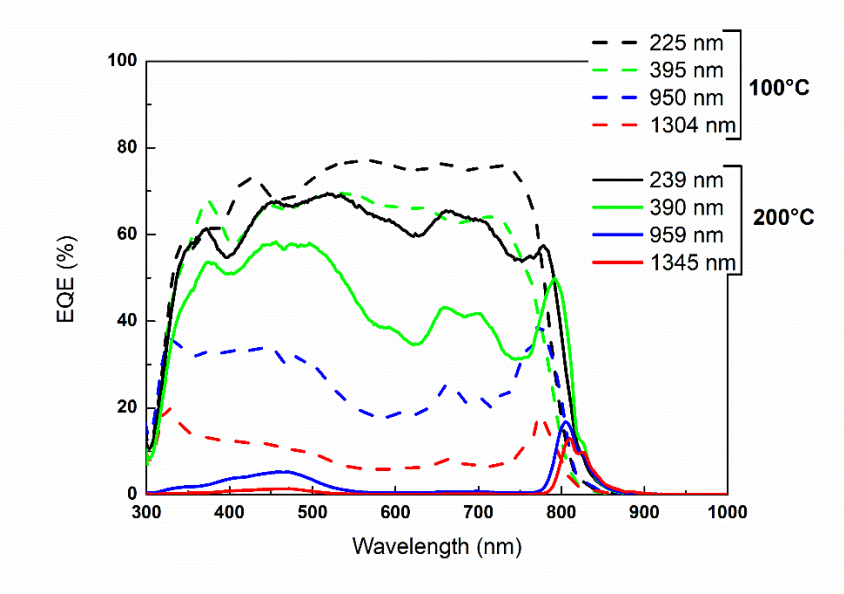

Figure S16. External quantum efficiency (EQE) spectra of OPDs in inverted structure ITO/ZnO/PM6:ITIC-4F(1:1 w/w ratio)/MoO_3/Ag as function of PM6:ITIC-4F thickness and post-annealing temperature.

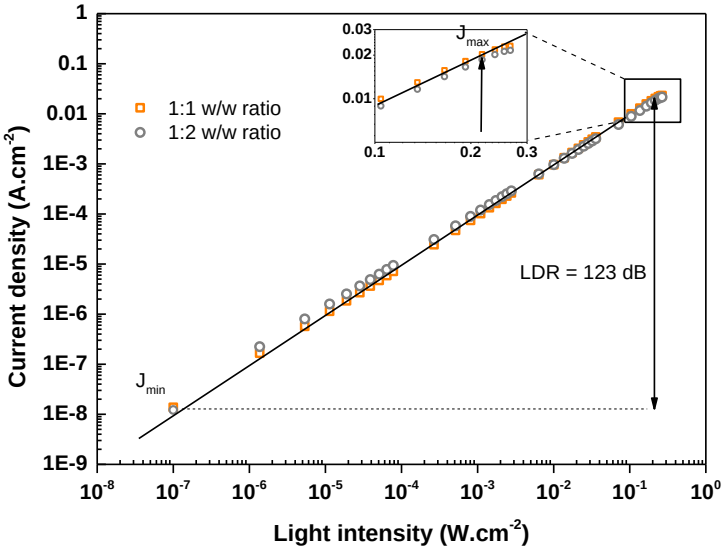

Figure S17. Linear dynamic range (LDR) for the OPD measured at -2 V (pump wavelength ~810 nm).

[1] S. Ben Dkhil, P. Perkhun, C. Luo, D. Müller, R. Alkarsifi, E. Barulina, Y. A. Avalos Quiroz, O. Margeat, S. T. Dubas, T. Koganezawa, D. Kuzuhara, N. Yoshimoto, C. Caddeo, A. Mattoni, B. Zimmermann, U. Würfel, M. Pfannmöller, S. Bals, J. Ackermann and C. Videlot-Ackermann, *ACS Appl. Mater. Interfaces,* 2020, **12**, 28404.