Supporting Information

Non-halogenated Solvent and Layer-by-Layer Blade-coated Organic Solar Cells via Non-halogenated Additive Adjusting Morphology and Crystallization

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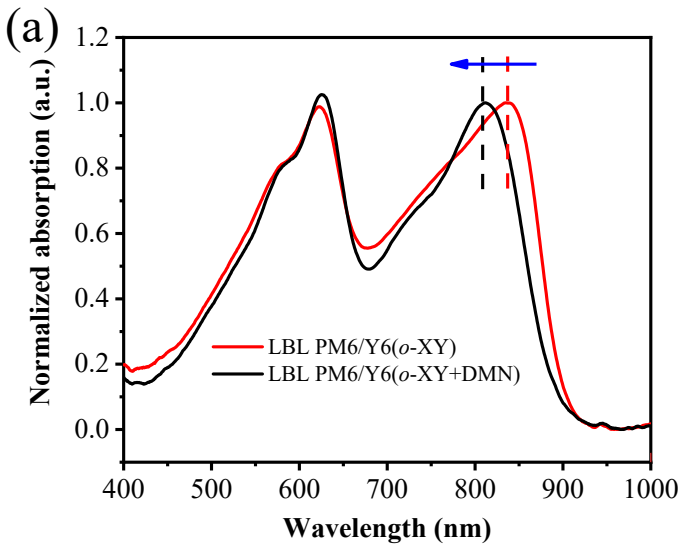

Fig. S1 (a) The normalized absorption spectra of the LBL blade-coated PM6/Y6(*o*-XY) or PM6/Y6(*o*-XY+DMN) films.

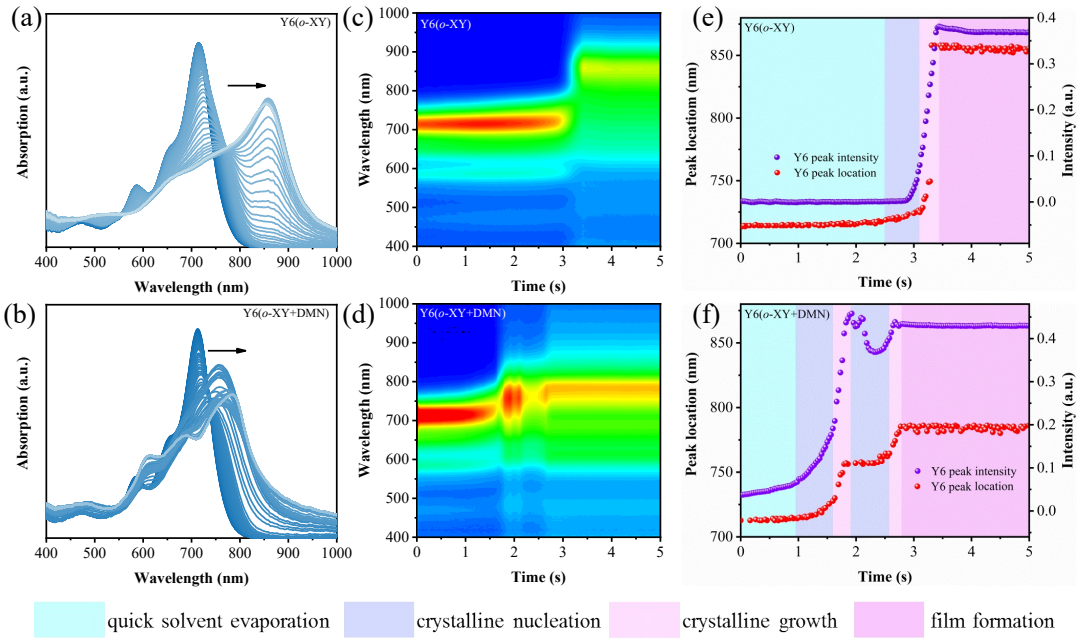

Fig. S2 The *in-situ* UV-vis absorption of the blade-coated Y6 films prepared with *o*-XY and *o*-XY+DMN solvents from the solution to thin film state: (a, b) the changes of line absorption profiles with time, (c, d) time-resolved 2D UV-vis absorption spectra and (e, f) the evolution of the Y6 characteristic absorption peak and peak intensity with time.

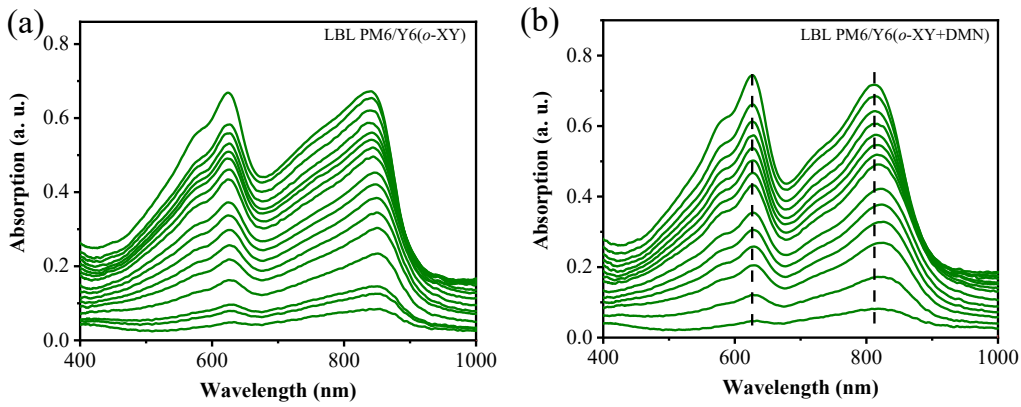

Fig. S3 Film-depth-dependent light absorption spectroscopy of (a) LBL blade-coated PM6/Y6(*o*-XY) and (b) PM6/Y6(*o*-XY+DMN) active layer films with different etching depth.

Table S1 The *d*-spacing and crystal coherence length (CCL) of the (100) peak in the in-plane and the (010) peak in the out-of-plane direction for LBL blade-coated PM6/Y6(*o*-XY) and PM6/Y6(*o*-XY+DMN) films

Coating method	Peak position	*q* (Å^{-1})	*d*-spacing (Å)	FWHM (Å^{-1})	CCL (Å)
LBL PM6/Y6(*o*-XY)	100 (IP)	0.285	22.05	0.099	58.99
LBL PM6/Y6(*o*-XY+DMN)		0.294	21.37	0.046	126.90
LBL PM6/Y6(*o*-XY)	010 (OOP)	1.736	3.62	0.269	21.71
LBL PM6/Y6(*o*-XY+DMN)		1.731	3.63	0.175	33.37

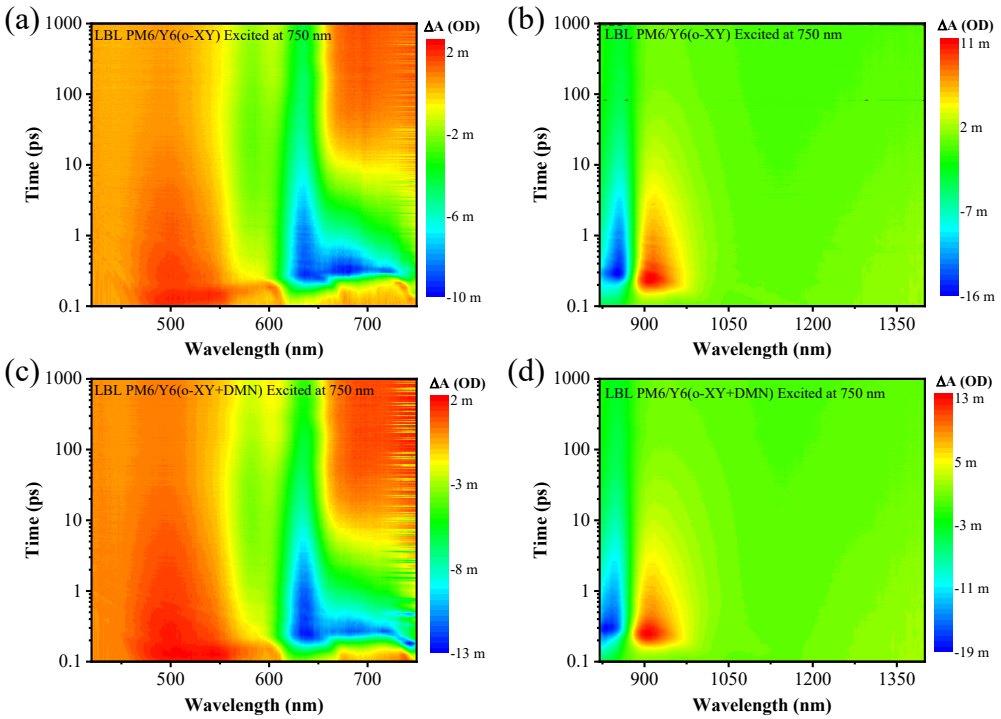

Fig. S4 2D color plot of TA spectra of the LBL blade-coated (a, b) PM6/Y6(*o*-XY) and (c, d) PM6/Y6(*o*-XY+DMN) films excited at 750 nm.

Table S2 The fitted time and relative population of the rising process of PM6 GSB for the LBL blade-coated PM6/Y6(*o*-XY) and PM6/Y6(*o*-XY+DMN) films excited at 750 nm

Coating method	τ_1 (ps)	A_1 (%)	τ_2 (ps)	A_2 (%)
LBL PM6/Y6(*o*-XY)	0.40	79.2	4.02	20.8
LBL PM6/Y6(*o*-XY+DMN)	0.24	76.7	2.07	23.3

(a) ITO/ZnO/Active layer/PFN-Br/Al (b) ITO/PEDOT:PSS/Active layer/MoOx/Ag

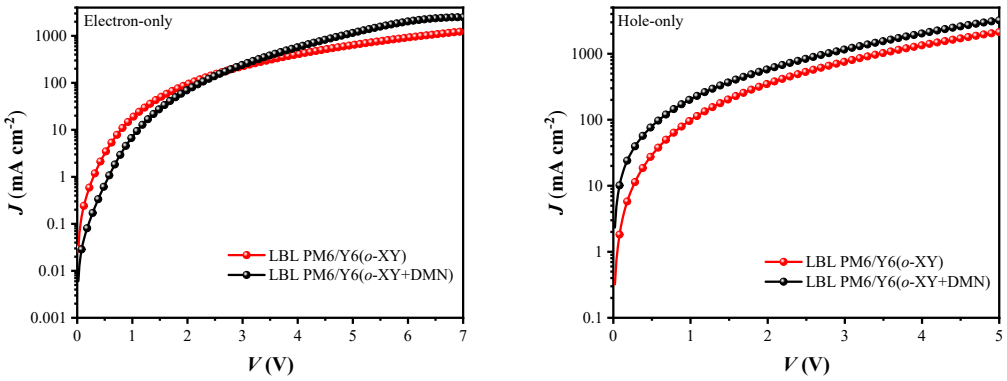

Fig. S5 The dark *J*-*V* characteristics of (a) electron-only and (b) hole-only devices based on LBL blade-coated PM6/Y6(*o*-XY) or PM6/Y6(*o*-XY+DMN) active layer.

Table S3 Electron mobility (μ_e), hole mobility (μ_h) and the ratio of the ratio of μ_h/μ_e for the LBL blade-coated PM6/Y6(*o*-XY) and PM6/Y6(*o*-XY+DMN) active layers

Coating method	μ_h ($cm^2\ V^{-1}\ s^{-1}$)	μ_e ($cm^2\ V^{-1}\ s^{-1}$)	μ_h/μ_e
LBL PM6/Y6(*o*-XY)	2.03×10^{-4}	1.14×10^{-4}	1.78
LBL PM6/Y6(*o*-XY+DMN)	4.31×10^{-4}	3.25×10^{-4}	1.32

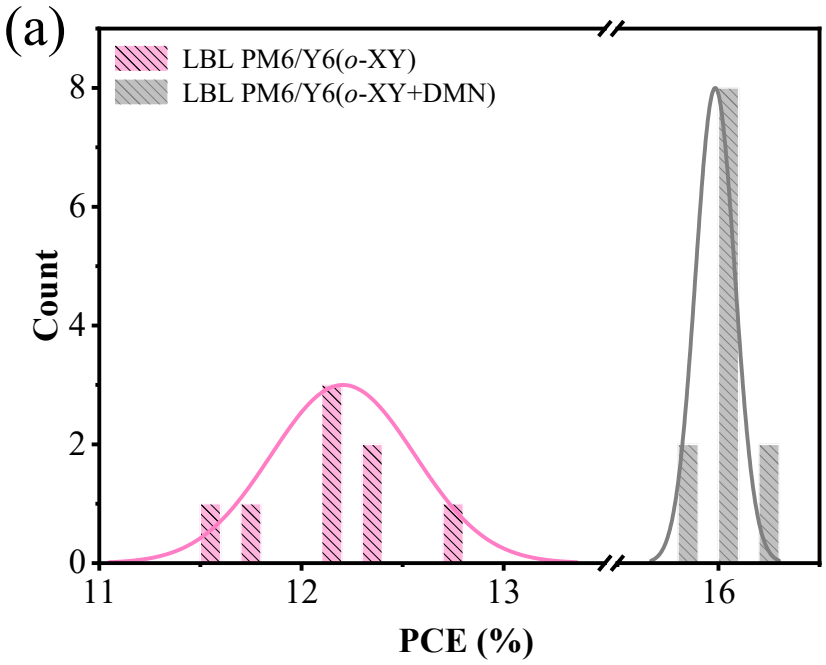

Fig. S6 (a) PCE statistics of the OSCs based on LBL blade-coated PM6/Y6(*o*-XY) and PM6/Y6(*o*-XY+DMN) active layers.

Table S4 Photovoltaic parameters of the PM6/Y6 based OSCs prepared by blade-coating in different solvent systems

	Solvent	Method	PCE_{max}(%)	Ref.
All Halogenated Solvents	CF	LBL	16.26	1
	CF	LBL	16.17	2
	CF	BHJ	15.83	3
	CB	BHJ	12.17	
	CF	LBL	16.35	4
	CF	BHJ	15.37	
Non-halogenated Solvents+Halogenated Additive	*o*-XY+CN	BHJ	15.10	5
All Non-halogenated Solvents	PX	BHJ	11.26	3
	o-XY	BHJ	12.98	6
	o-XY+DMN	BHJ	15.51	
		LBL	16.15	this work

Table S5 E_g, V_{OC} and E_{loss} of the OSCs based on LBL blade-coated PM6/Y6(*o*-XY) and PM6/Y6(*o*-XY+DMN) active layer

Coating method	E_g (eV)	V_{OC} (V)	E_{loss} (eV)
LBL PM6/Y6(*o*-XY)	1.353	0.764	0.589
LBL PM6/Y6(*o*-XY+DMN)	1.364	0.849	0.515

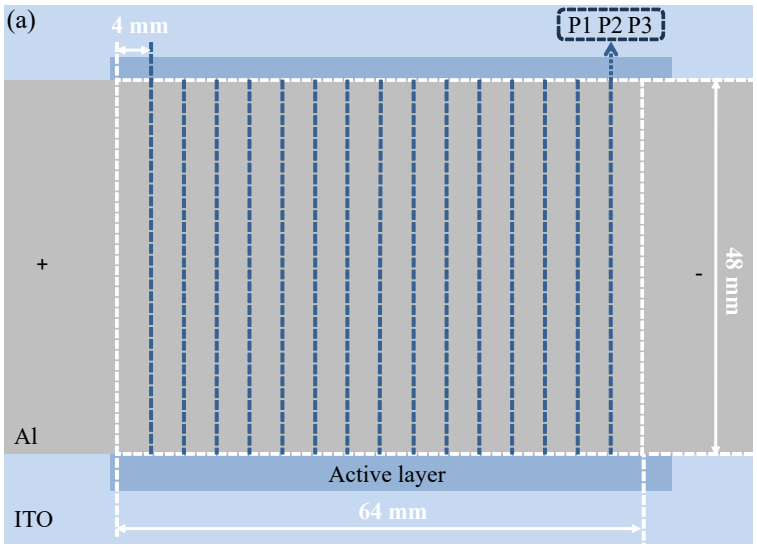

Fig. S7 Schematic of top-view large-area OSCs module.

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