Supplementary Information

Eco-Friendly Non-Volatile Solid Additives for High-Efficiency Sustainable Organic Photovoltaic Cells

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Experimental method

Device fabrication:

Eco-friendly OPVs were fabricated with the structure ITO/Br-2EPSe/photoactive layer/PDINN/Ag. The ITO substrates were cleaned with acetone and isopropanol (IPA) using ultrasonication and then dried in an oven at 100°C for 1 hour. The dried ITO substrates were treated with UV for 1 hour. Br-2EPSe was coated onto the UV-treated ITO substrate by spin-coating at 5000 rpm, followed by annealing at 100°C for 10 minutes. The Br-2EPSe-coated ITO substrates were then transferred to a glovebox under a N_2 atmosphere to deposit the photoactive layer. PM6:L8-BO (1:1.2, w/w) blend solutions in o-xylene (20 mg ml^{-1}) with eco-friendly solid additives of DBP (70%), DMBP (70%), and DM (30%) were stirred for 3 hours. The concentration of the eco-friendly solid additives was adjusted based on the donor amount. The blend solution was spin-coated onto the Br-2EPSe film and annealed at 130°C for 10 minutes. The PDINN layer was spin-coated onto the photoactive layer from a solution with a concentration of 1 mg ml^{-1} in methanol at 5000 rpm. The Ag electrode was deposited by thermal evaporation to a thickness of 100 nm under a vacuum pressure of $<10^{-6}$ Torr.

Device characterization:

The current density-voltage (*J-V*) characteristics of the OPVs were obtained using a Keithley 2401 source measurement unit under AM 1.5G simulated illumination (100 mW cm^{-2}). The intensity of simulated sunlight was calibrated using a standard Si photodiode detector with a KG-3 filter (Newport Co., Oriel). Device stability was measured over 1000 hours after storage in a N_2 atmosphere. The external quantum efficiency (EQE) spectra of the OPVs were measured using the IQE-200B (Newport Co., Oriel). The surface morphologies of the photoactive layer, depending on the additives, were analyzed by atomic force microscopy (AFM, Nanocute, SII Nano Technology Inc.). The charge carrier mobilities of PM6:L8-BO

with and without DBP, DMBP, and DM were measured using the space charge limited current (SCLC) method. The structures of the hole-only and electron-only devices were ITO/PEDOT:PSS/active layer/MoO_3/Ag and ITO/ZnO/active layer/Phen-NaDPO/Ag, respectively. The *J-V* curves were measured using a Keithley 2401 source meter under dark conditions.

Fourier-transform infrared (FTIR) spectra were obtained using a Bruker INVENIO-R spectrometer. FTIR-EQE was measured in an in-house FTPS setup consisting of an INVENIO-R spectrometer equipped with a quartz beam splitter. The photocurrent produced by the PSC under illumination was amplified using an SR570 low-noise preamplifier (Stanford Research System) and fed back into the external detector port of the FTIR. The electroluminescence (EL) spectra were obtained using a MAYA2000 PRO spectrophotometer (Ocean Optics). The electroluminescence external quantum efficiency (EQE_{EL}) was calculated from the ratio of injected current to emitted photon flux of the OSCs. The injected current was recorded using a Keithley 2401 source meter.

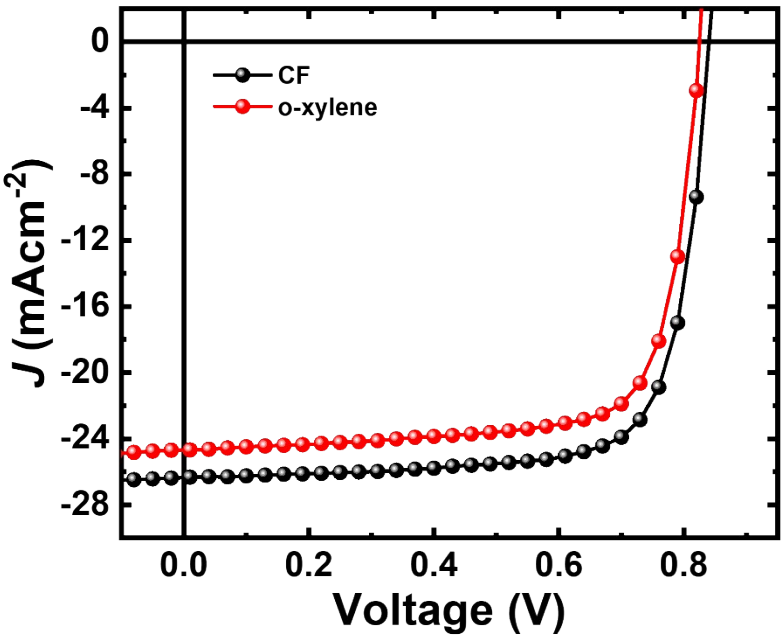

Fig. S1. *J-V* characteristics curves of the device based on PM6:L8-BO with CN.

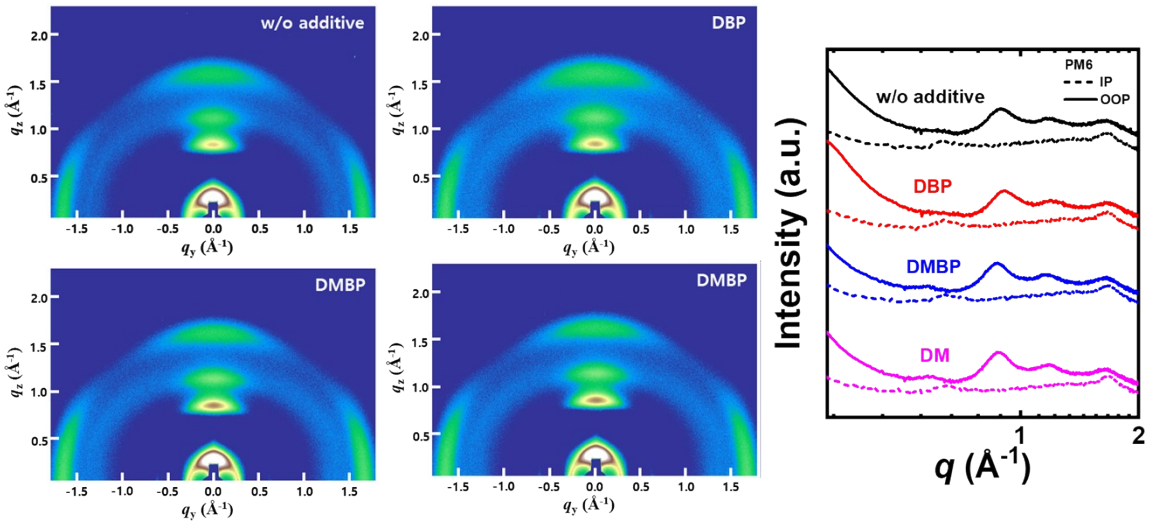

Fig. S2. 2D GIWAXS scattering patterns and the corresponding line-cut profiles of PM6 films without additives, and with DBP, DMBP, and DM.

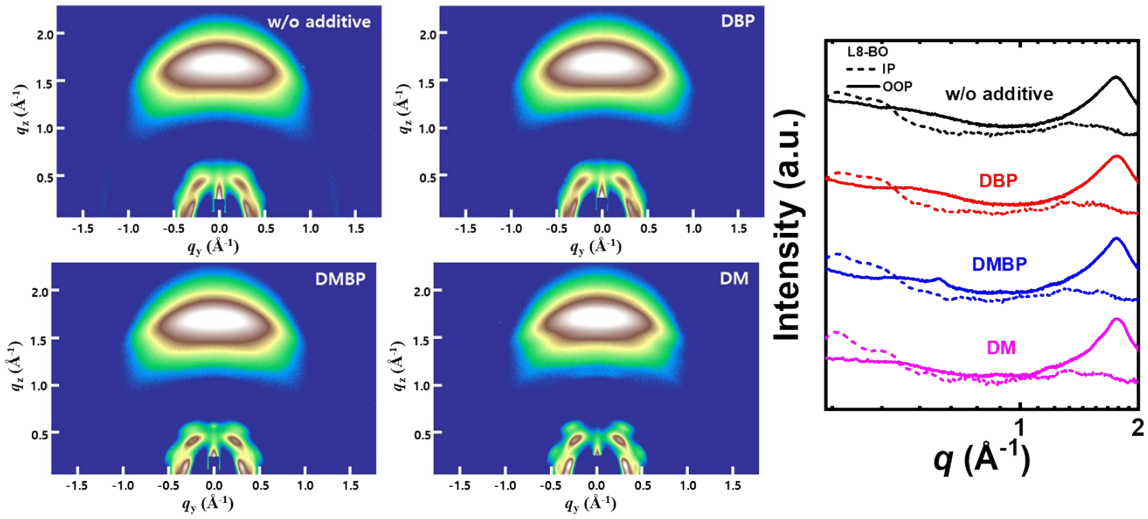

Fig. S3. 2D GIWAXS scattering patterns and the corresponding line-cut profiles of L8-BO films without additives, and with DBP, DMBP, and DM.

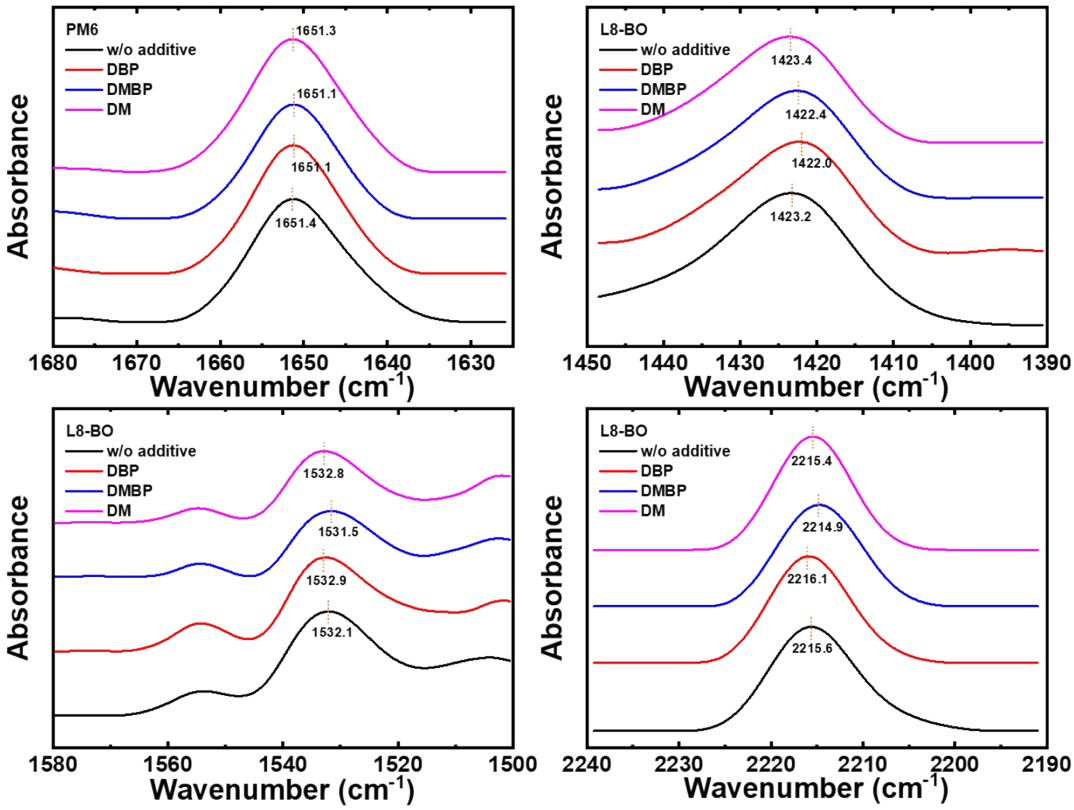

Fig. S4. FTIR spectra of PM6 and L8-BO films without additive and with DBP, DMBP, and DM.

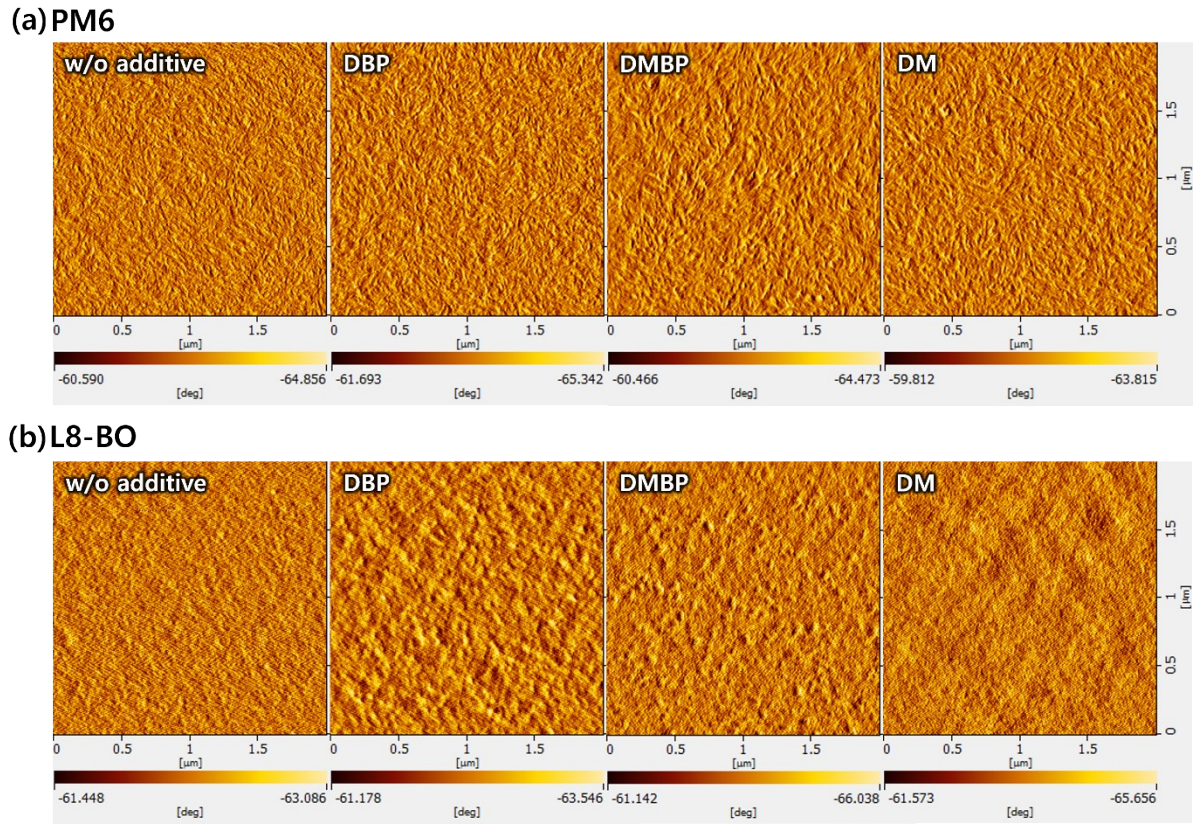

Fig. S5. (a) AFM phase images of PM6 and (b) L8-BO films without additives and with DBP, DMBP, and DM.

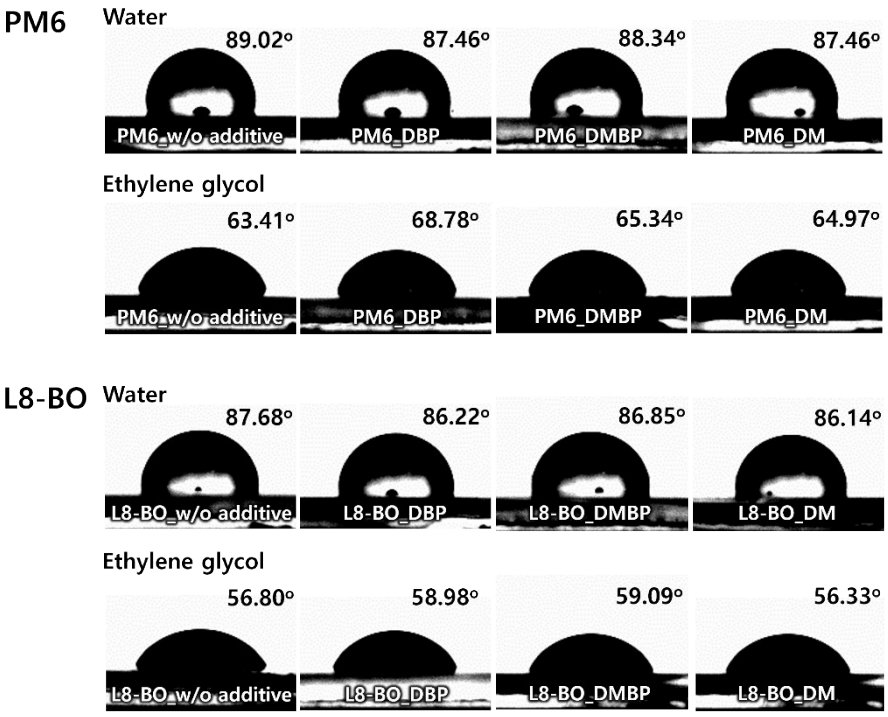

Fig. S6. Contact angles of PM6 and L8-BO films measured using deionized water and ethylene glycol.

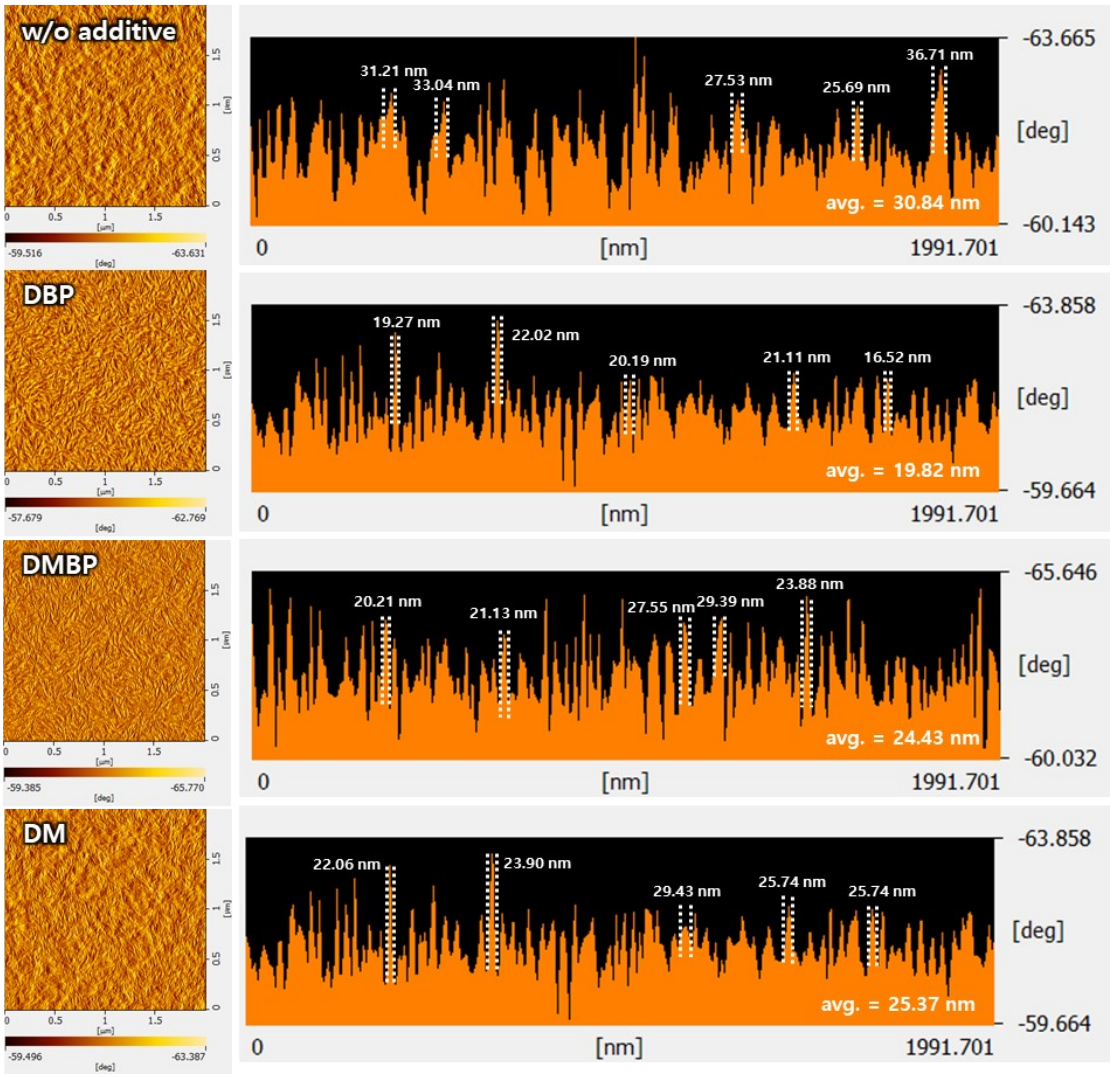

Fig. S7. AFM phase images and corresponding line profiles of PM6:L8-BO blend films without additives and with DBP, DMBP, and DM.

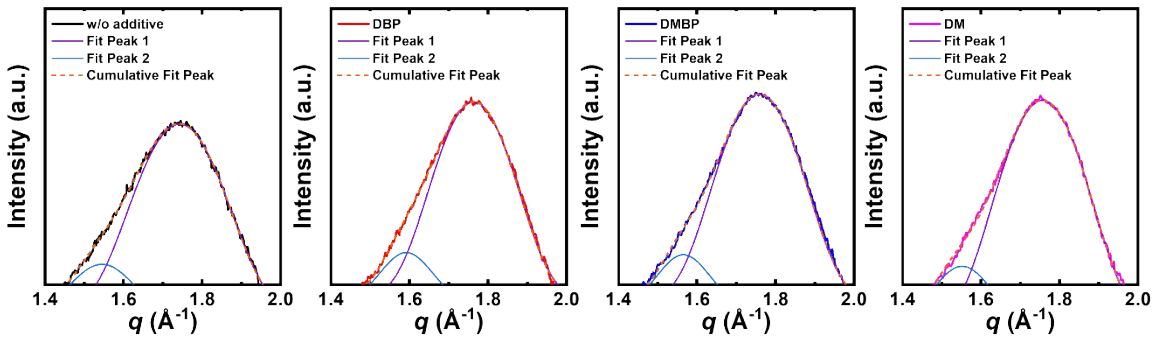

Fig. S8. Fitted out-of-plane (OOP) profiles of PM6:L8-BO blend films without additives and with DBP, DMBP, and DM.

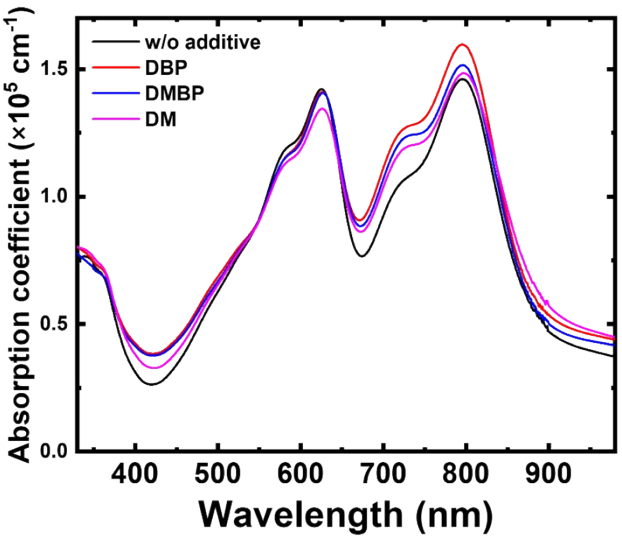

Fig. S9. Absorption coefficient of PM6:L8-BO blend films without additives and with DBP, DMBP, and DM.

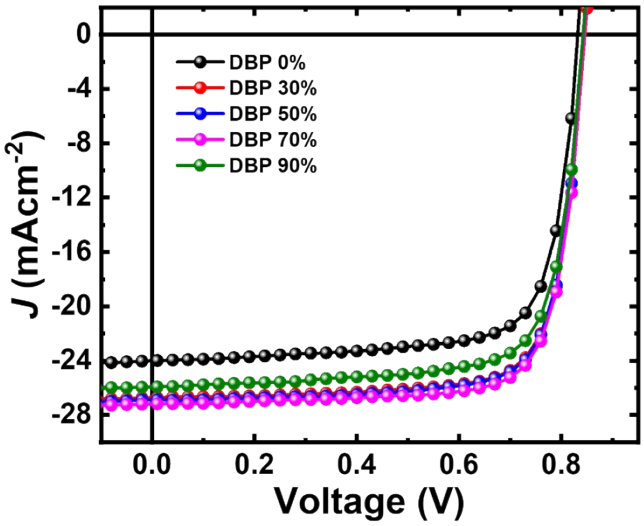

Fig. S10. *J-V* characteristic curves of devices based on PM6:L8-BO with varying concentrations of DBP.

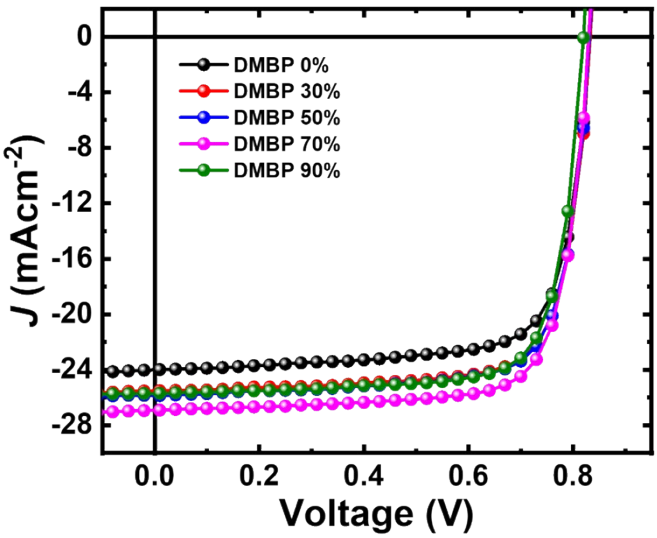

Fig. S11. *J-V* characteristic curves of devices based on PM6:L8-BO with varying concentrations of DMBP.

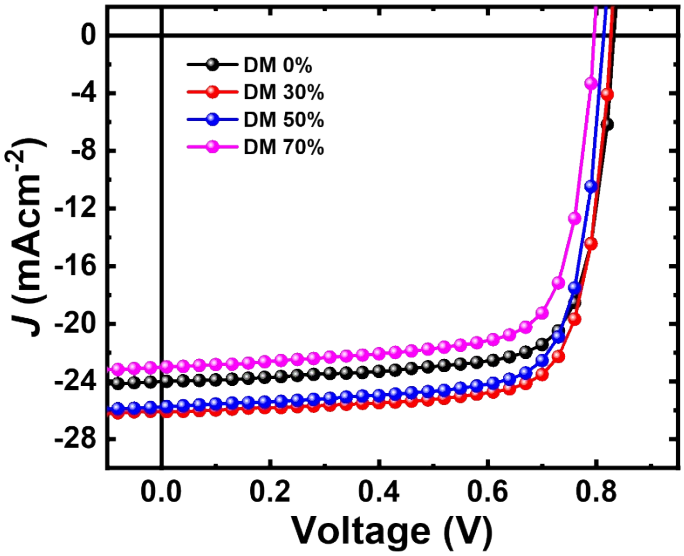

Fig. S12. *J-V* characteristic curves of devices based on PM6:L8-BO with varying concentrations of DM.

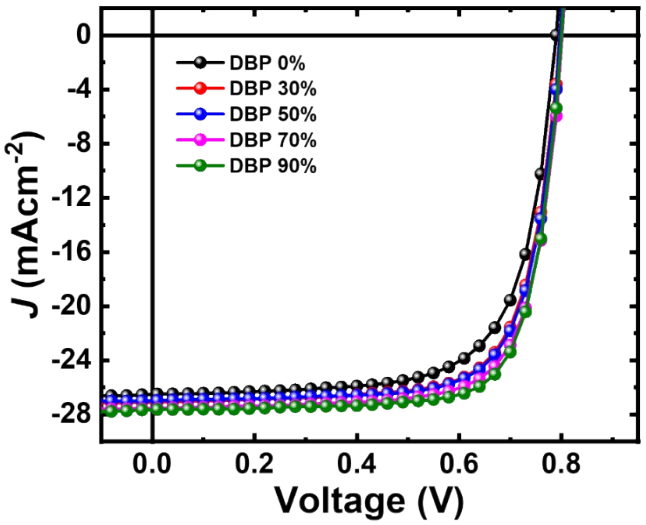

Fig. S13. *J-V* characteristic curves of devices based on PM6:BTP-eC9 with varying concentrations of DBP.

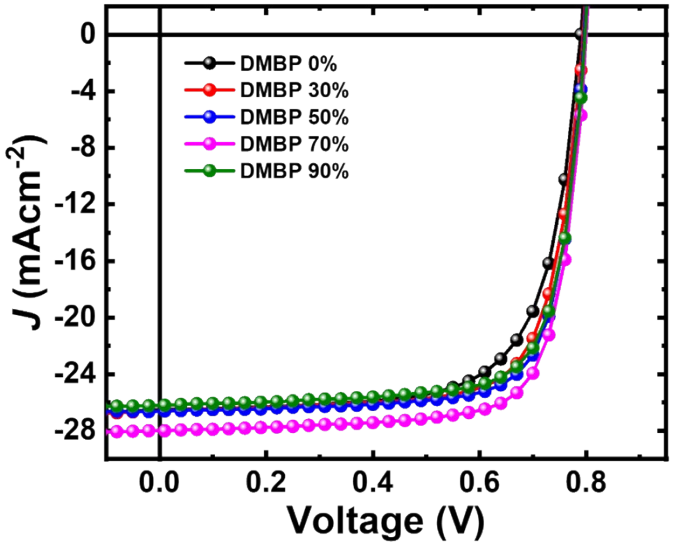

Fig. S14 *J-V* characteristic curves of devices based on PM6:BTP-eC9 with varying concentrations of DMBP.

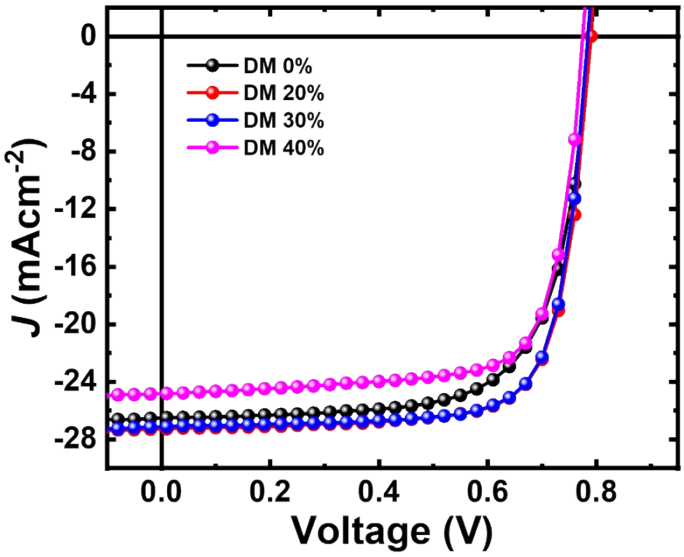

Fig. S15. *J-V* characteristic curves of devices based on PM6:BTP-eC9 with varying concentrations of DM.

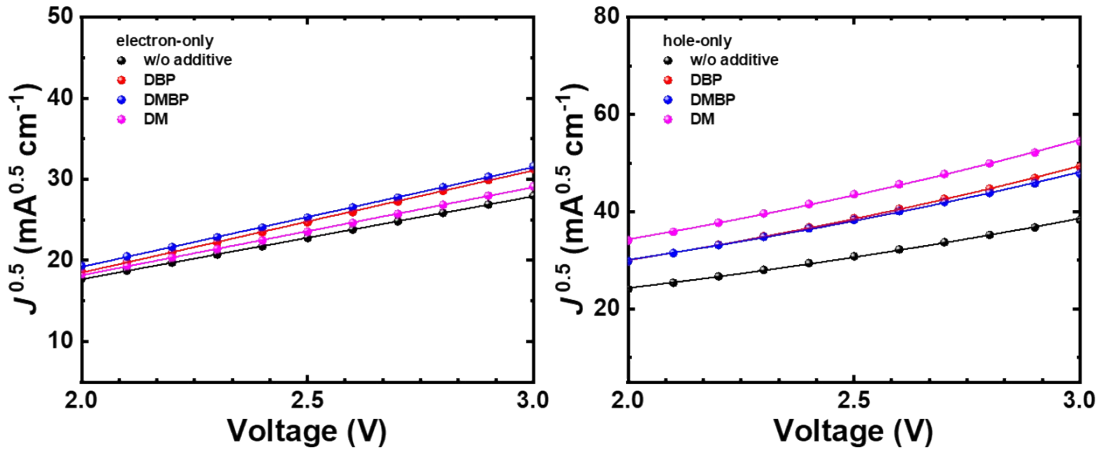

Fig. S16. Space charge limited current (SCLC) characteristics of electron-only and hole-only devices.

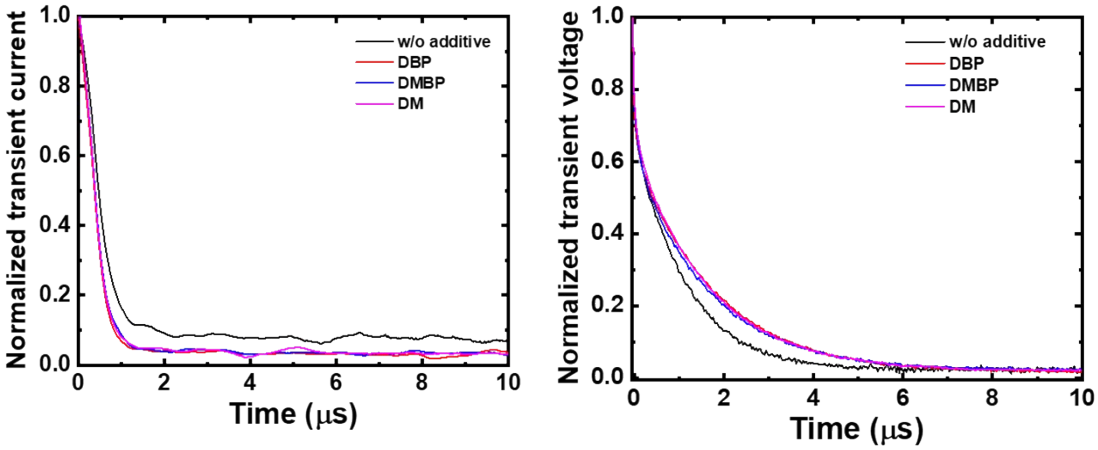

Fig. S17. Normalized transient current (TPC) and normalized transient voltage (TPV) of OPVs without additives and with DBP, DMBP, and DM.

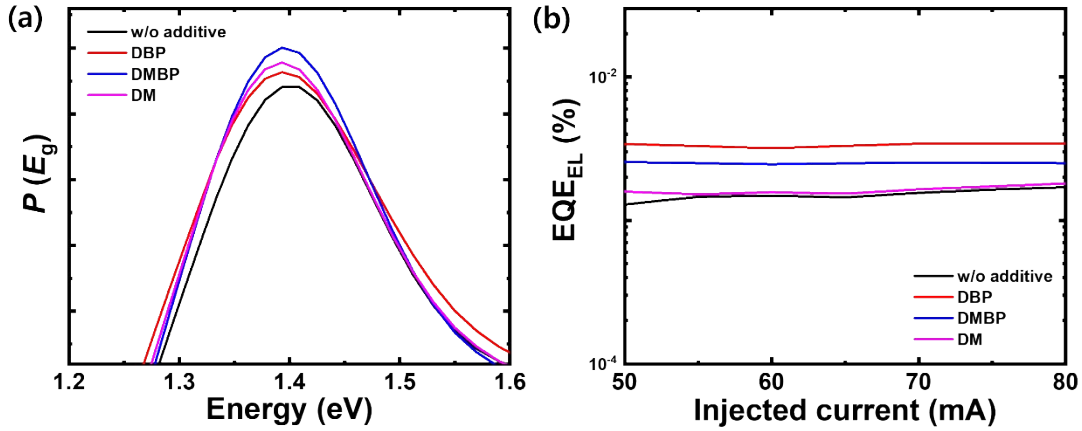

Fig. S18. Bandgap distributions and EQE_{EL} of PM6:L8-BO without additives and with DBP, DMBP, and DM.

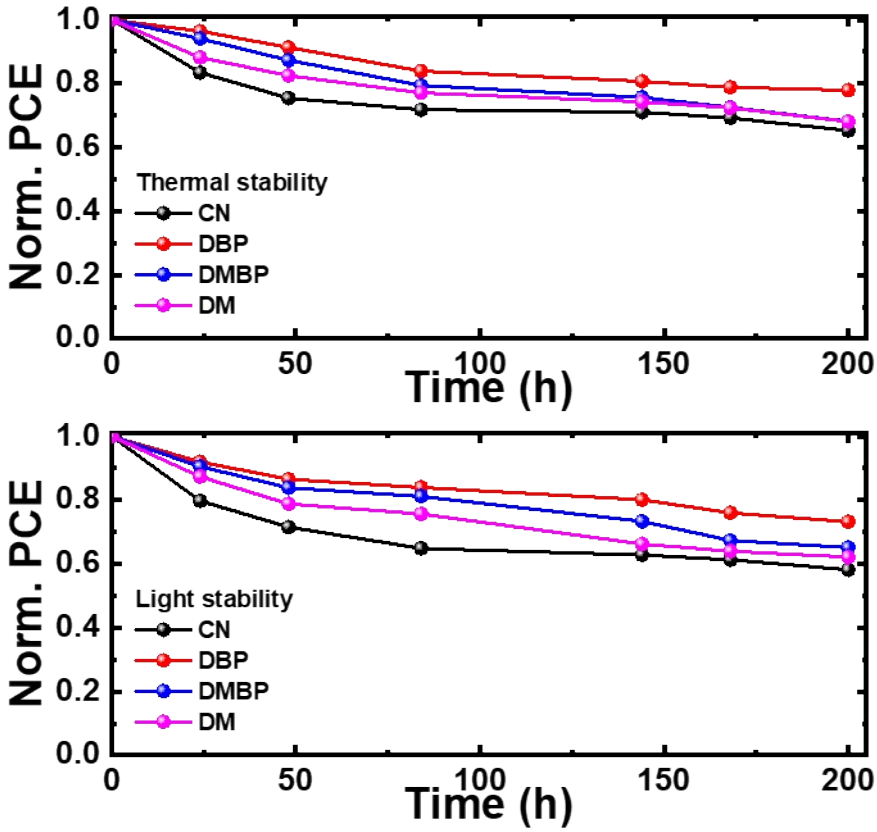

Fig. S19. Thermal (at 70°C under dark condition) and photo-stability (with the irradiation intensity of 100 mW cm^{-2} white LED in ambient air condition) of OPVs based PM6:L8-BO with CN, DBP, DMBP, and DM.

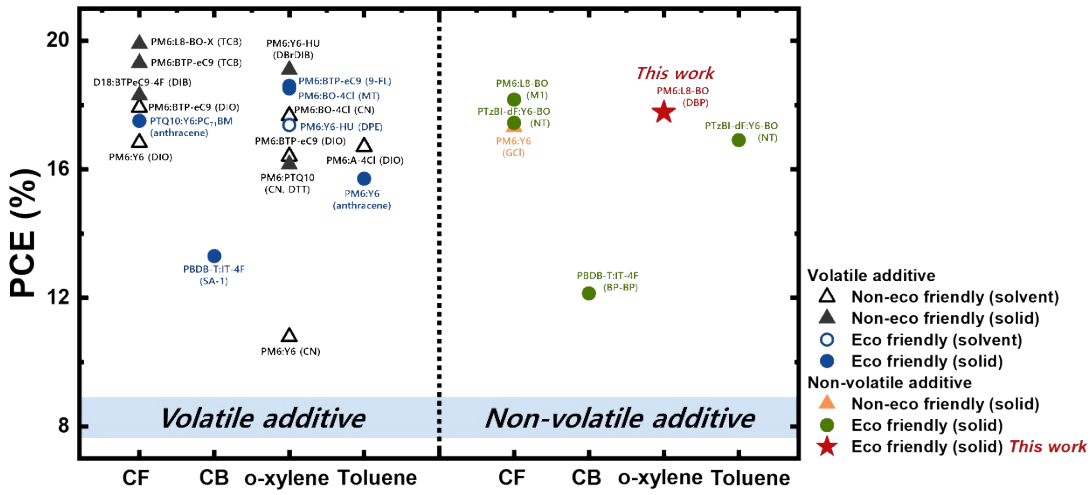

Fig. S20. Comparison of PCEs for OPVs with volatile or non-volatile additives in various solvents from the literature and this work. Detailed information on the devices used in this figure is listed in **Table S14**.

Table S1. Detailed photovoltaic parameters of devices based on PM6:L8-BO with CN.

Solvent	J_{SC} [mA cm^{-2}]	V_{OC} [V]	*FF* [%]	PCE [%]
CF	26.34	0.840	75.61	16.74
o-xylene	24.68	0.825	75.29	15.33

Table S2. Summarized GIWAXS parameters of PM6 films without additives and with DBP, DMBP, and DM.

PM6	π-π spacing from (010) in the OOP direction	
Additive	q [Å^{-1}]	d [Å]
w/o additive	1.660	3.785
DBP	1.666	3.771
DMBP	1.661	3.783
DM	1.660	3.785

Table S3. Summarized GIWAXS parameters of L8-BO films without additives and with DBP, DMBP, and DM.

L8-BO	π-π spacing from (010) in the OOP direction	
Additive	q [Å^{-1}]	d [Å]
w/o additive	1.751	3.588
DBP	1.772	3.545
DMBP	1.758	3.574
DM	1.757	3.576

Table S4. Summarized contact angles and Flory-Huggins interaction parameters (χ) of PM6 and L8-BO films without additives and with DBP, DMBP, and DM.

Additive	Film	Contact angle [º]		Surface energy γ [mN m^{-1}]	$\chi_{donor-acceptor}$
		Water	Ethylene glycol		
w/o additive	PM6	89.02	63.41	19.37	$0.0426K$
	L8-BO	87.68	56.80	21.33	
DBP	PM6	87.46	68.78	19.87	$0.0235K$
	L8-BO	86.22	58.98	21.26	
DMBP	PM6	88.34	65.34	19.44	$0.0293K$
	L8-BO	86.85	59.09	20.98	
DM	PM6	87.46	64.97	19.94	$0.0410K$
	L8-BO	86.14	56.33	21.79	

Table S5. Summarized GIWAXS parameters of PM6:L8-BO blend films without additives and with DBP, DMBP, and DM.

PM6:L8-BO	π-π spacing from (010) in the OOP direction			
Additive	q [Å^{-1}]	d [Å]	FWHM [Å^{-1}]	L_C [Å]
w/o additive	1.742	3.607	0.224	25.24
DBP	1.763	3.564	0.204	27.72
DMBP	1.759	3.572	0.207	27.32
DM	1.757	3.576	0.210	26.93

Table S6. Detailed photovoltaic parameters of devices based on PM6:L8-BO with varying concentrations of DBP.

PM6:L8-BO	J_{SC} [mA cm^{-2}]	V_{OC} [V]	*FF* [%]	PCE [%]
DBP 0%	24.00	0.832	75.16	15.01
DBP 30%	26.72	0.846	76.79	17.35
DBP 50%	26.88	0.842	77.13	17.47
DBP 70%	27.18	0.845	77.43	17.78
DBP 90%	25.93	0.842	75.28	16.45

Table S7. Detailed photovoltaic parameters of devices based on PM6:L8-BO with varying concentrations of DMBP.

PM6:L8-BO	J_{SC} [mA cm^{-2}]	V_{OC} [V]	*FF* [%]	PCE [%]
DMBP 0%	24.00	0.832	75.16	15.01
DMBP 30%	25.51	0.832	76.58	16.26
DMBP 50%	25.84	0.831	76.15	16.36
DMBP 70%	26.91	0.830	76.74	17.13
DMBP 90%	25.69	0.820	76.89	16.21

Table S8. Detailed photovoltaic parameters of devices based on PM6:L8-BO with varying concentrations of DM.

PM6:L8-BO	J_{SC} [mA cm^{-2}]	V_{OC} [V]	*FF* [%]	PCE [%]
DM 0%	24.00	0.832	75.16	15.01
DM 30%	26.07	0.826	76.38	16.46
DM 50%	25.76	0.813	75.33	15.78
DM 70%	23.00	0.796	74.05	13.55

Table S9. Detailed photovoltaic parameters of devices based on PM6:BTP-eC9 with varying concentrations of DBP.

PM6:BTP-eC9	J_{SC} [mA cm^{-2}]	V_{OC} [V]	*FF* [%]	PCE [%]
DBP 0%	26.51	0.789	70.08	14.67
DBP 30%	27.07	0.797	72.81	15.71
DBP 50%	26.97	0.797	73.53	15.81
DBP 70%	27.55	0.801	74.24	16.38
DBP 90%	27.63	0.800	75.83	16.77

Table S10. Detailed photovoltaic parameters of devices based on PM6:BTP-eC9 with varying concentrations of DMBP.

PM6:BTP-eC9	J_{SC} [mA cm^{-2}]	V_{OC} [V]	*FF* [%]	PCE [%]
DMBP 0%	26.51	0.789	70.08	14.67
DMBP 30%	26.59	0.794	73.79	15.58
DMBP 50%	26.62	0.796	75.89	16.08
DMBP 70%	27.99	0.799	75.78	16.96
DMBP 90%	26.21	0.797	75.22	15.72

Table S11. Detailed photovoltaic parameters of devices based on PM6:BTP-eC9 with varying concentrations of DM.

PM6:BTP-eC9	J_{SC} [mA cm^{-2}]	V_{OC} [V]	*FF* [%]	PCE [%]
DM 0%	26.51	0.789	70.08	14.67
DM 20%	27.27	0.789	75.19	16.20
DM 30%	27.12	0.784	76.03	16.17
DM 40%	24.82	0.775	74.30	14.29

Table S12. Summarized electron and hole mobilities.

Additive	μ_e [$cm^2V^{-1}s^{-1}$]	μ_h [$cm^2V^{-1}s^{-1}$]	μ_e/μ_h
w/o additive	3.61×10^{-4}	3.84×10^{-4}	0.942
DBP	4.13×10^{-4}	4.22×10^{-4}	0.978
DMBP	3.91×10^{-4}	4.08×10^{-4}	0.959
DM	3.72×10^{-4}	3.89×10^{-4}	0.955

Table S13. Summary of charge extraction time (τ_t) and charge carrier lifetime (τ_r) of OPVs without additives and with DBP, DMBP, and DM.

Additive	τ_t [μs]	τ_r [μs]
w/o additive	0.405	1.13
DBP	0.293	1.76
DMBP	0.322	1.63
DM	0.314	1.65

Table S14. Summary of literature references for OPVs with volatile and non-volatile additives used in **Figure S20**.

Additive type		Additive	Solvent	Active layer	PCE [%]	Ref.
Volatile	Non-eco friendly (solvent)	1,8-diiodooctane (DIO)	chloroform	PM6:Y6	16.83%	[1]
Volatile	Non-eco friendly (solvent)	1,8-diiodooctane (DIO)	chloroform	PM6:BTP-eC9	17.93%	[1]
Volatile	Non-eco friendly (solid)	DIB	chloroform	D18:BTPeC9-4F	18.31%	[2]
Volatile	Non-eco friendly (solid)	1,3,5-trichlorobenzene (TCB)	chloroform	PM6:L8-BO-X	19.91%	[3]
Volatile	Non-eco friendly (solid)	1,3,5-trichlorobenzene (TCB)	chloroform	PM6:BTP-eC9	19.31%	[1]
Volatile	Eco friendly (solid)	anthracene	chloroform	PTQ10:Y6:$PC_{71}BM$	17.51%	[4]
Volatile	Eco friendly (solid)	SA-1	chlorobenzene	PBDB-TF:IT-4F	13.30%	[5]
Volatile	Non-eco friendly (solvent)	1-chloronaphthalene (CN)	o-xylene	PM6:BO-4Cl	17.67%	[6]
Volatile	Non-eco friendly (solvent)	1,8-diiodooctane (DIO)	o-xylene	PM6:BTP-eC9	16.41%	[7]
Volatile	Non-eco friendly (solvent)	1-chloronaphthalene (CN)	o-xylene	PM6:Y6	10.79%	[4]
Volatile	Non-eco friendly (solid)	1-chloronaphthalene (CN)+DTT	o-xylene	PM6:PTQ10	16.16%	[8]
Volatile	Non-eco friendly (solid)	1,4-dibromo-2,5-diiodobenzene (DBrDIB)	o-xylene	PM6:Y6-HU	19.10%	[9]
Volatile	Eco friendly (solvent)	diphenyl ether (DPE)	o-xylene	PM6:Y6-HU	17.38%	[10]
Volatile	Eco friendly (solid)	9-fluorenone (9-FL)	o-xylene	PM6:BTP-eC9	18.6%	[11]
Volatile	Eco friendly (solid)	Menthol (MT)	o-xylene	PM6:BO-4Cl	18.52%	[12]
Volatile	Non-eco friendly (solvent)	1,8-diiodooctane (DIO)	toluene	PM6:A-4Cl	16.71%	[13]

Volatile	Non-eco friendly (solid)	anthracene	toluene	PM6:Y6	15.71%	[4]
Non-volatile	Non-eco friendly (solid)	chlorine-functionalized graphdiyne (GCl)	chloroform	PM6:Y6	17.32%	[14]
Non-volatile	Eco friendly (solid)	naphtho[1,2-c:5,6-c′]bis[1,2,5] thiadiazole (NT)	chloroform	PTzBI-dF:Y6-BO	17.45%	[15]
Non-volatile	Eco friendly (solid)	3,6-di(thiophen-2-yl)pyridazine (M1)	chloroform	PM6:L8-BO	18.17%	[16]
Non-volatile	Eco friendly (solid)	Bifunctional bis-benzophenone (BP-BP)	chlorobenzene	PBDB-T:ITIC	12.14%	[17]
Non-volatile	Eco friendly (solid)	naphtho[1,2-c:5,6-c′]bis[1,2,5] thiadiazole (NT)	toluene	PTzBI-dF:Y6-BO	16.91%	[15]

References

1 J. Fu, P. W. K. Fong, H. Liu, C. S. Huang, X. Lu, S. Lu, M. Abdelsamie, T. Kodalle, C. M. Sutter-Fella, Y. Yang, G. Li, *Nat. Commun.*, 2023, **14**, 1760.

2 X. Jiang, X. Wang, Y. Wang, G. Ran, W. Liu, H. Lu, H. Li, N. Wei, Z. Wei, Y. Lin, Z. Ma, Y. Liu, W. Zhang, X. Xu, Z. Bo, *Adv. Funct. Mater.*, 2024, **34**, 2406744.

3 Y. Wang, K. Sun, C. Li, C. Zhao, C. Gao, L. Zhu, Q. Bai, C. Xie, P. You, J. Lv, X. Sun, H. Hu, Z. Wang, H. Hu, Z. Tang, B. He, M. Qiu, S. Li, G. Zhang, *Adv. Mater.*, 2024, **36**, 2411957.

4 H. Fan, H. Yang, Y. Wu, O. Yildiz, X. Zhu, T. Marszalek, P. W. M. Blom, C. Cui, Y. Li, *Adv. Funct. Mater.*, 2021, **31**, 2103944.

5 R. Yu, H. Yao, L. Hong, Y. Qin, J. Zhu, Y. Cui, S. Li, J. Hou, *Nat. Commun.*, 2018, **9**, 4645.

6 D. Wang, G. Zhou, Y. Li, K. Yan, L. Zhan, H. Zhu, X. Lu, H. Chen, C. Z. Li, *Adv. Funct. Mater.*, 2022, **32**, 2107827.

7 Y. Zhang, K. Liu, J. Huang, X. Xia, J. Cao, G. Zhao, P. W. K. Fong, Y. Zhu, F. Yan, Y. Yang, X. Lu, G. Li, *Nat. Commun.*, 2021, **12**, 4815.

8 S. Bao, H. Yang, H. Fan, J. Zhang, Z. Wei, C. Cui, Y. Li, *Adv. Mater.*, 2021, **33**, 2105301.

9 M. Haris, Z. Ullah, S. Lee, D. H. Ryu, S. U. Ryu, B. J. Kang, N. J. Jeon, B. J. Kim, T. Park, W. S. Shin, C. E. Song, *Adv. Energy Mater.*, 2024, **14**, 2401597.

10 S. Rasool, J. W. Kim, H. W. Cho, Y. Kim, D. C. Lee, C. B. Park, W. Lee, O. Kwon, S. Cho, J. Y. Kim, *Adv. Energy Mater.*, 2023, **13**, 2203452.

11 L. Xu, Y. Xiong, S. Li, W. Zhao, J. Zhang, C. Miao, Y. Zhang, T. Zhang, J. Wu, S. Zhang, Q. Peng, Z. Wang, L. Ye, J. Hou, J. Wang, *Adv. Funct. Mater.*, 2024, **34**, 2314178.

12 Z. Jia, J. Pan, X. Chen, Y. Li, T. Liu, H. Zhu, J. Yao, B. Yan, Y. Yang, *Energy Environ. Sci.*, 2024, **17**, 3908-3916.

13 D. Wang, H. Liu, Y. Li, G. Zhou, L. Zhan, H. Zhu, X. Lu, H. Chen, C. -Z. Li, *Joule*, 2021, **5**, 945-957.

14 L. Liu, Y. Kan, K. Gao, J. Wang, M. Zhao, H. Chen, C. Zhao, T. Jiu, A.-Y. Jen, Y. Li, *Adv. Mater.*, 2020, **32**, 1907604.

15 D. Zhang, Y. Li, M. Li, W. Zhong, T. Heumüller, N. Li, L. Ying, C. J. Brabec, F. Huang, *Adv. Funct. Mater.*, 2022, **32**, 2205338.

16 Y. Miao, Y. Sun, W. Zou, X. Zhang, Y. Kan, W. Zhang, X. Jiang, X. Wang, R. Yang, X. Hao, L. Geng, H. Xu, K. Gao, *Adv. Mater.*, 2024, **36**, 2406623.

17 P. Fan, W. Sun, X. Zhang, Y. Wu, Q. Hu, Q. Zhang, J. Yu, T. P. Russell, *Adv. Funct. Mater.*, 2021, **31**, 2008699.