Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Eco-friendly volatile additive enabling efficient large-area organic photovoltaic module processed with non-halogenated solvent

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Figure S1. The shape and appearance of MT.

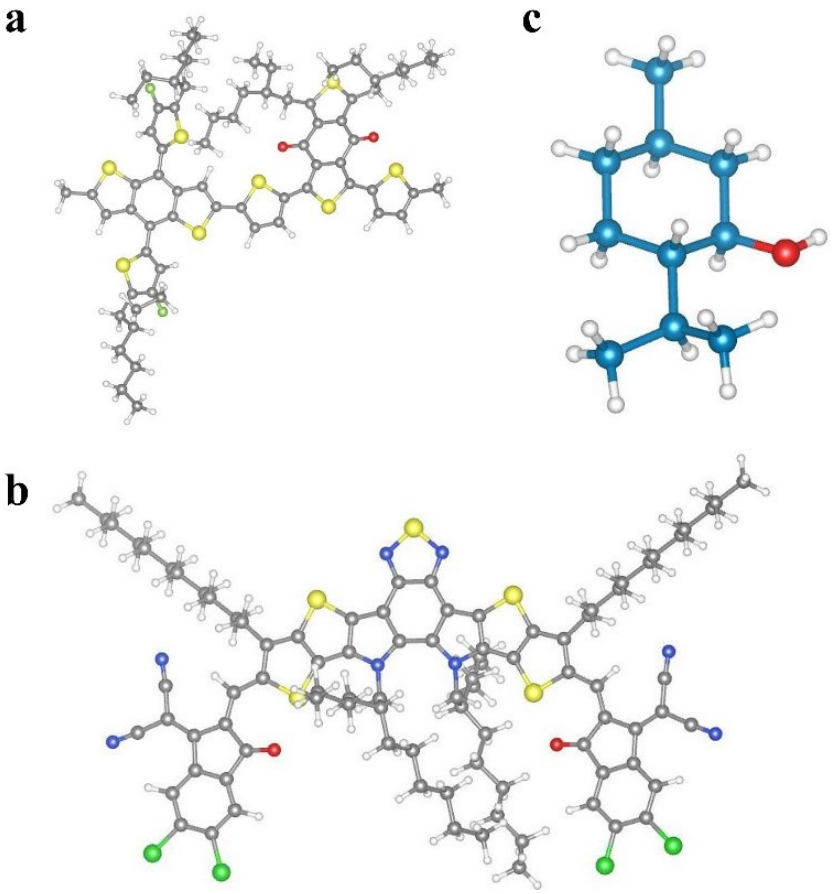


Figure S2. The optimized geometry structures of a) PM6, b) BO-4Cl, and c) MT.

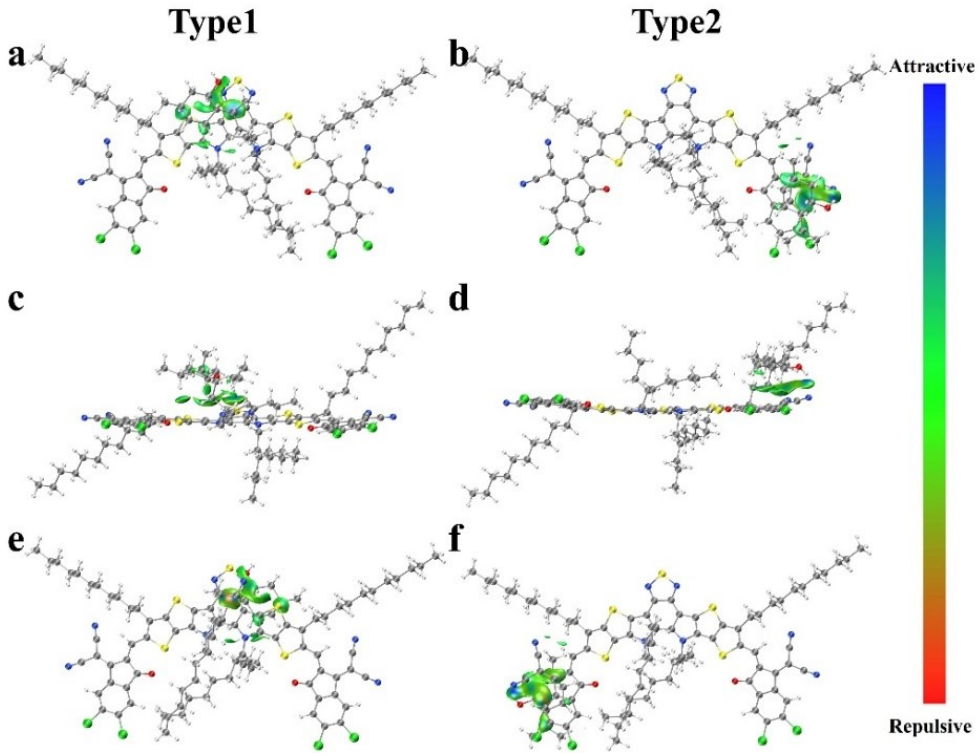


Figure S3. The non-covalent interaction (NCI) graphs by IGM approach for two types of combinations between BO-4Cl and MT from the front view (a, b), bottom view (c, d) and the back view (e, f), respectively.

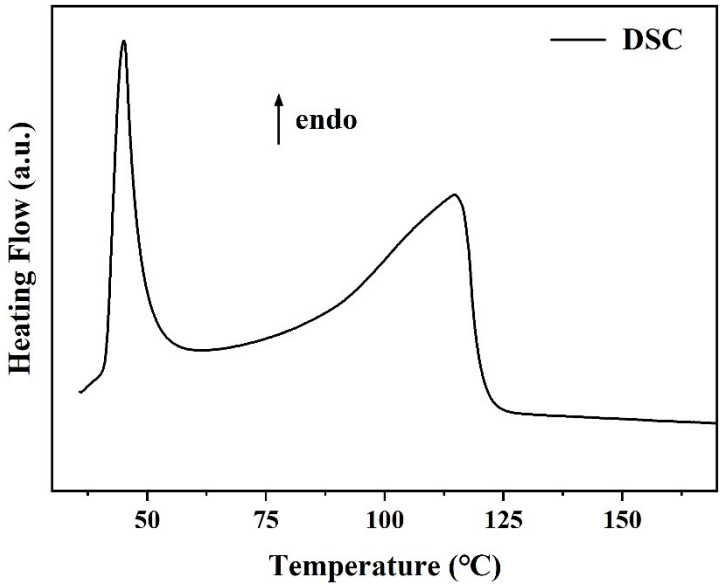


Figure S4. The DSC thermogram of MT under N_2 at a scan rate of 5°C min^{-1}.

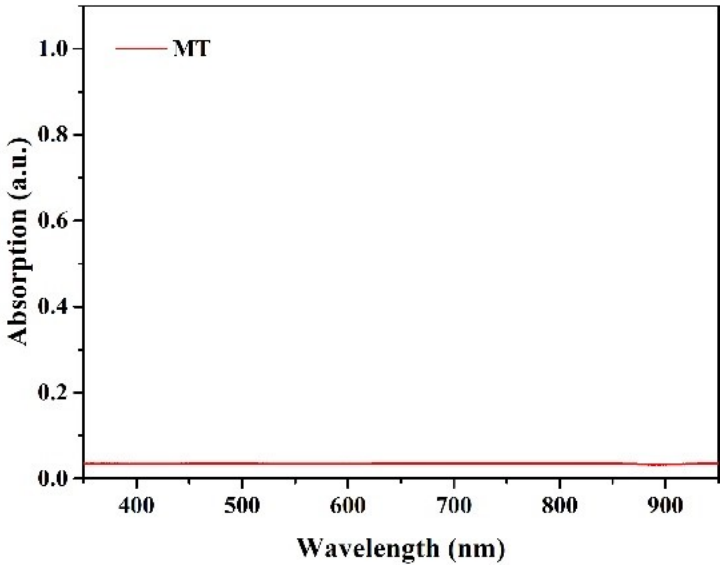


Figure S5. The UV-vis spectrum of MT film.

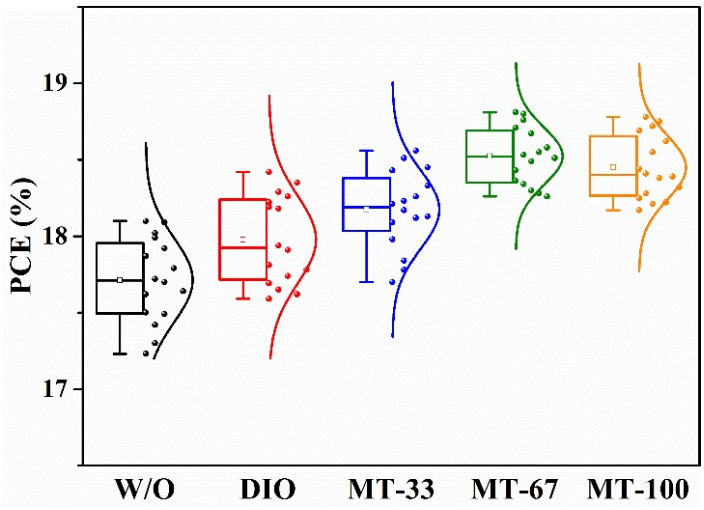


Figure S6. The average PCEs of the devices processed by diverse additives.

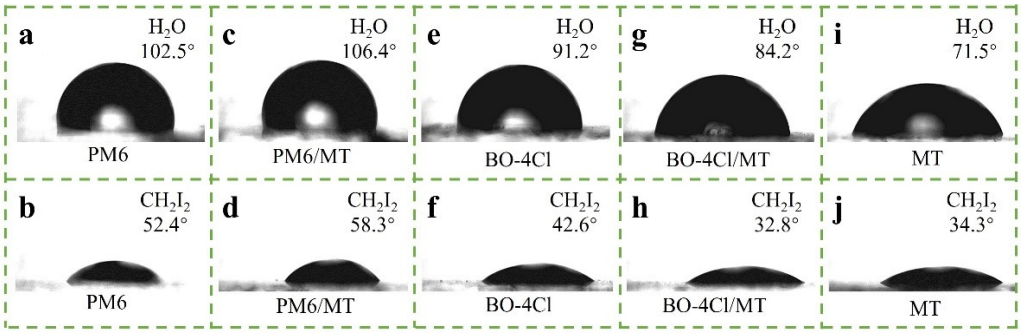


Figure S7. The images of the water and the diiodomethane droplet contact angles on the surfaces of PM6, PM6/MT, BO-4Cl, BO-4Cl/MT, and MT films.

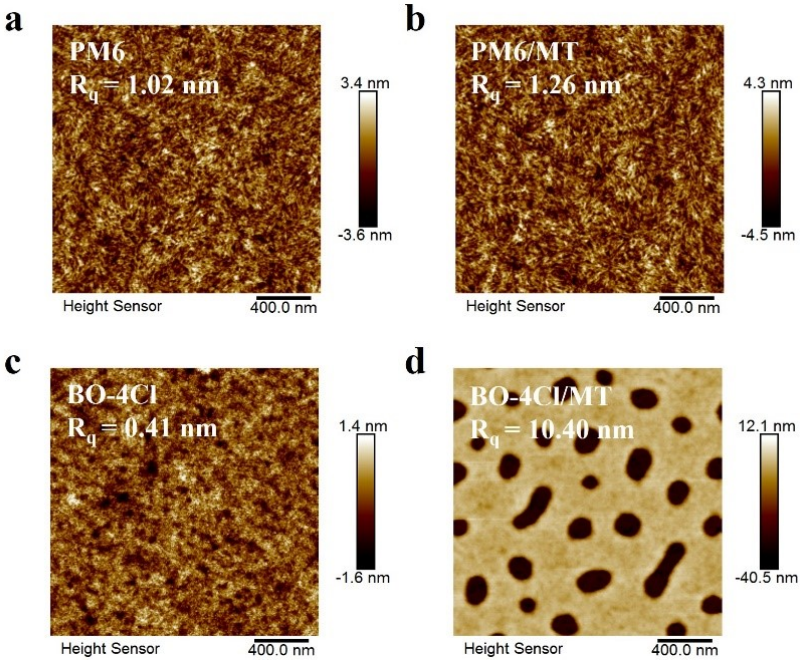


Figure S8. The AFM images (2 μm × 2 μm) and R_q values of a) PM6, b) PM6/MT, c) BO-4Cl, and d) BO-4Cl/MT films.

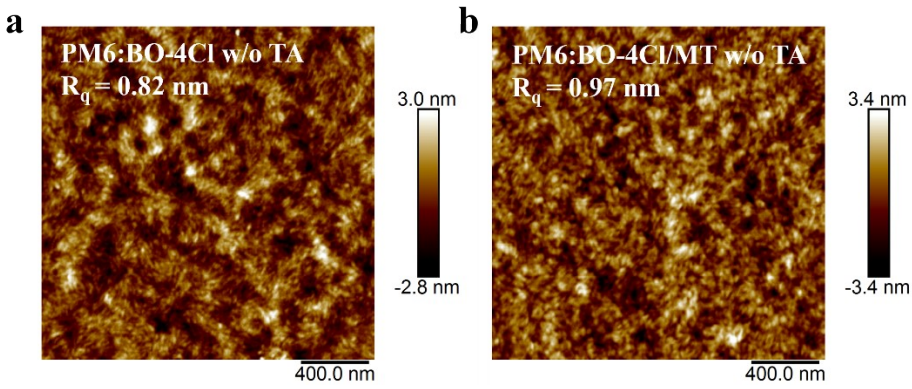
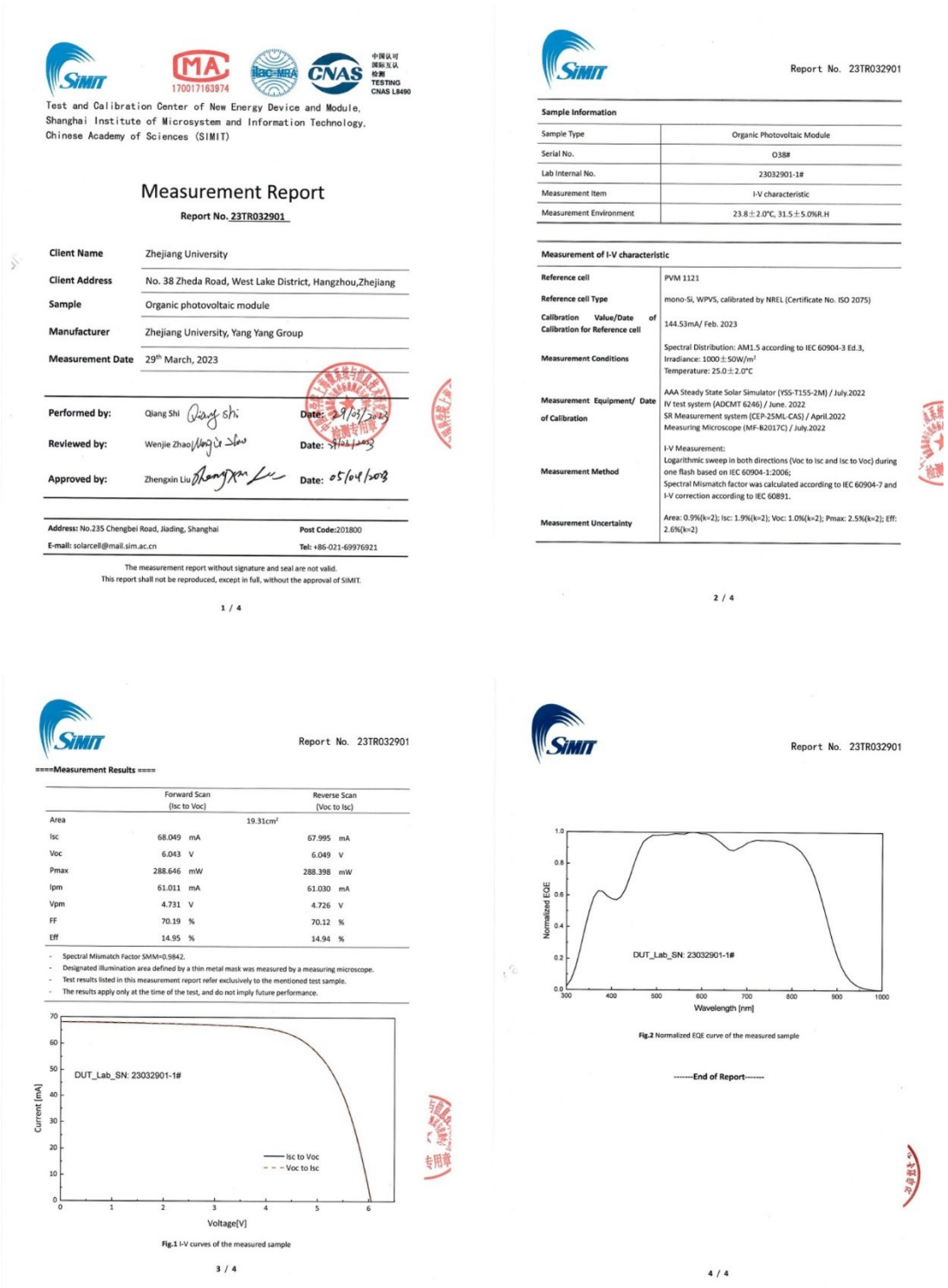


Figure S9. The AFM images (2 μm × 2 μm) and R_q values of a) PM6:BO-4Cl and b) PM6:BO-4Cl/MT films without thermal annealing (TA).



Test and Calibration Center of New Energy Device and Module,
Shanghai Institute of Microsystem and Information Technology,
Chinese Academy of Sciences (SIMIT)

Measurement Report

Report No. 23TR032901

Client Name	Zhejiang University
Client Address	No. 38 Zheda Road, West Lake District, Hangzhou,Zhejiang
Sample	Organic photovoltaic module
Manufacturer	Zhejiang University, Yang Yang Group
Measurement Date	29th March, 2023

Performed by: Qiang Shi Date: 29/03/2023

Reviewed by: Wenjie Zhao Date: 31/03/2023

Approved by: Zhengxin Liu Date: 05/04/2023

Address: No.235 Chengbei Road, Jiading, Shanghai Post Code:201800
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The measurement report without signature and seal are not valid.
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Report No. 23TR032901

Sample Information

Sample Type	Organic Photovoltaic Module
Serial No.	O38#
Lab Internal No.	23032901-1#
Measurement Item	I-V characteristic
Measurement Environment	23.8±2.0℃, 31.5±5.0%R.H

Measurement of I-V characteristic

Reference cell	PVM 1121
Reference cell Type	mono-Si, WPVS, calibrated by NREL (Certificate No. ISO 2075)
Calibration Value/Date of Calibration for Reference cell	144.53mA/ Feb. 2023
Measurement Conditions	Spectral Distribution: AM1.5 according to IEC 60904-3 Ed.3, Irradiance: 1000±50W/m² Temperature: 25.0±2.0℃
Measurement Equipment/ Date of Calibration	AAA Steady State Solar Simulator (YSS-T155-2M) / July.2022 IV test system (ADCMT 6246) / June. 2022 SR Measurement system (CEP-25ML-CAS) / April.2022 Measuring Microscope (MF-B2017C) / July.2022
Measurement Method	I-V Measurement: Logarithmic sweep in both directions (Voc to Isc and Isc to Voc) during one flash based on IEC 60904-1:2006; Spectral Mismatch factor was calculated according to IEC 60904-7 and I-V correction according to IEC 60891.
Measurement Uncertainty	Area: 0.9%(k=2); Isc: 1.9%(k=2); Voc: 1.0%(k=2); Pmax: 2.5%(k=2); Eff: 2.6%(k=2)

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====Measurement Results ====

	Forward Scan (Isc to Voc)	Reverse Scan (Voc to Isc)
Area	19.31cm²	
Isc	68.049 mA	67.995 mA
Voc	6.043 V	6.049 V
Pmax	288.646 mW	288.398 mW
Ipm	61.011 mA	61.030 mA
Vpm	4.731 V	4.726 V
FF	70.19 %	70.12 %
Eff	14.95 %	14.94 %

- Spectral Mismatch Factor SMM=0.9842.
- Designated illumination area defined by a thin metal mask was measured by a measuring microscope.
- Test results listed in this measurement report refer exclusively to the mentioned test sample.
- The results apply only at the time of the test, and do not imply future performance.

Fig.1 I-V curves of the measured sample

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Fig.2 Normalized EQE curve of the measured sample

-------End of Report-------

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Figure S10. Independent certification results of the large-area module (19.31 cm^2) based on the PM6:BO-4Cl device from Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, confirming a high PCE of 14.95% (Certificate No. 23TR032901).

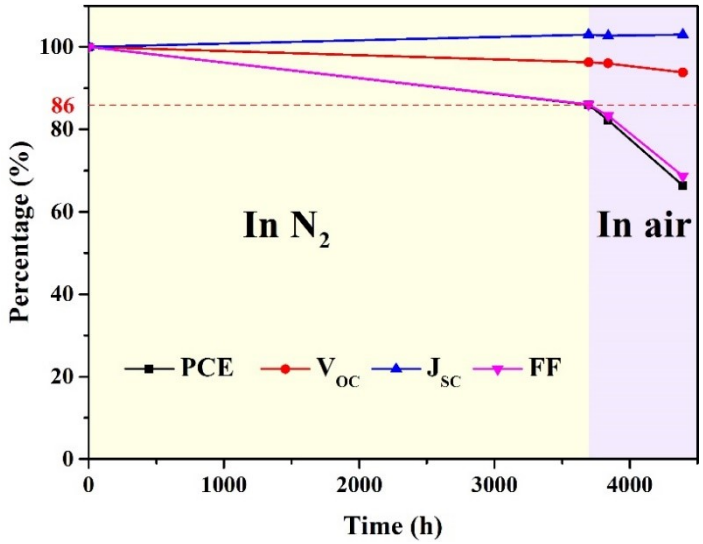

Figure S11. The shelf stability of the encapsulated large-area module processed with o-XY.

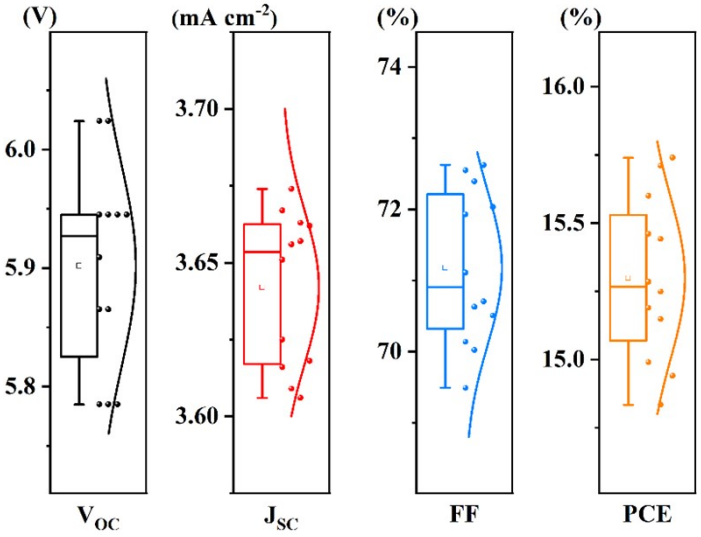

Figure S12. Statistics of the photovoltaic parameters from 12 large-area modules.

Table S1. The calculated results of the binding energy between BO-4Cl and MT.

Condition	E (Hartree)	E (kcal/mol)
E_{BO-4Cl}	-7901.331	\
E_{MT}	-467.481	\
E_{type1}	-8368.840	\
E_{type2}	-8368.842	\
ΔE_{type1}	-0.028	-17.650
ΔE_{type2}	-0.030	-18.788

Table S2. Detailed photovoltaic parameters of devices under different conditions.

Condition	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE_{max} (%)	PCE_{avg}[a] (%)
PM6:BO-4Cl	0.853	27.55	76.95	18.09	17.71±0.28
PM6:BO-4Cl/DIO	0.835	28.06	78.62	18.42	17.98±0.29
PM6:BO-4Cl/MT-33	0.853	28.19	77.17	18.56	18.17±0.26
PM6:BO-4Cl/MT-67	0.853	28.35	77.76	18.81	18.52±0.19
PM6:BO-4Cl/MT-100	0.844	28.55	77.92	18.78	18.45±0.21

[a] Average data were obtained from 16 independent devices.

Table S3. Summary of representative high-performance binary OPVs (PCE > 17%) based on PM6 processed by non-halogenated solvents.

Active layer	Solvent	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	Ref.
PM6:L8-BO	o-XY	0.867	25.37	77.23	17.07	1
PM6:BTP-eC9	o-XY	0.84	26.8	76.3	17.2	2
PM6:BO-4Cl	Tol	0.854	26.1	77.7	17.33	3
PM6: BTP-eC9	o-XY:CS_2	0.85	26.2	78.9	17.6	4
PM6:BO-4Cl	o-XY	0.84	26.7	79.0	17.7	5
PM6:Y6-BO	o-XY	0.832	27.3	78.4	17.8	6
PM6:BO-4Cl	o-XY	0.847	26.86	79.63	18.12	7
PM6:EV-i	o-XY	0.897	26.60	76.56	18.27	8
PM6:L8-Ph	o-XY	0.870	26.40	80.11	18.40	9
PM6:BTP-eC9	o-XY	0.847	27.22	80.31	18.52	7
PM6:BO-4Cl	o-XY	0.853	28.35	77.76	18.81	This Work

Table S4. The photovoltaic parameters calculated from J_{ph}-V_{eff} curves.

Condition	J_{sat} (mA cm^{-2})	J_{ph}[a] (mA cm^{-2})	J_{ph}[b] (mA cm^{-2})	P_{diss} (%)	P_{coll} (%)
PM6:BO-4Cl	27.94	27.26	25.01	97.57	89.51
PM6:BO-4Cl/MT	28.83	28.38	26.02	98.44	90.25

[a] J_{ph} under short circuit conditions.

[b] J_{ph} under maximal power output conditions.

Table S5. The hole and electron mobilities of devices.

Condition	μ_h (10^{-4} cm^2 V^{-1} s^{-1})	μ_e (10^{-4} cm^2 V^{-1} s^{-1})	μ_h/μ_e
PM6:BO-4Cl	5.19	13.30	0.39
PM6:BO-4Cl/MT	5.88	14.20	0.41

Table S6. The calculated surface tensions of the films based on the OWRK model.

Film	γ (mN m^{-1})
PM6	33.12
PM6/MT	29.86
BO-4Cl	38.35
BO-4Cl/MT	43.42
MT	45.85

Table S7. The interaction parameters of the films based on the Flory-Huggins model.

Film	χ
PM6:BO-4Cl	0.192
PM6:MT	1.033
BO-4Cl:MT	0.335
PM6:(BO-4Cl/MT)	0.696
BO-4Cl:(PM6/MT)	0.531

Table S8. Data for GIWAXS measurements.

Condition	Blend	Location (Å^{-1})	d-spacing (Å)	FWHM (Å^{-1})	CCL (Å)
Q_{xy} (100)	PM6:BO-4Cl	0.272	23.100	0.148	38.209
	PM6:BO-4Cl/MT	0.271	23.185	0.079	71.581
Q_z (010)	PM6:BO-4Cl	1.725	3.642	0.267	21.179
	PM6:BO-4Cl/MT	1.732	3.628	0.224	25.245

Table S9. The universal study about MT in other binary systems.

Active layer[a]	Solvent	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE_{max} (%)	PCE_{avg}[b] (%)
PM6:L8-BO	o-XY	0.875	25.50	77.63	17.32	17.06±0.17
PM6:L8-BO/MT	o-XY	0.875	26.23	78.52	18.02	17.68±0.21
PM6:L8-BO	CF	0.901	24.65	73.15	16.25	16.01±0.14
PM6:L8-BO/MT	CF	0.899	25.29	74.81	17.01	16.69±0.19
PM6:BO-4Cl	CF	0.868	26.37	74.36	17.02	16.65±0.24
PM6:BO-4Cl/MT	CF	0.869	27.09	75.35	17.74	17.35±0.27
D18:L8-BO	CF	0.917	25.13	74.47	17.16	16.87±0.15
D18:L8-BO/MT	CF	0.919	25.36	75.97	17.71	17.38±0.22

[a] PM6:L8-BO: 22 mg mL^{-1} in o-XY, 17 mg mL^{-1} in CF; PM6:BO-4Cl: 16 mg mL^{-1} in CF; D18:L8-BO: 11 mg mL^{-1} in CF.

[b] Average data were obtained from 16 independent devices.

Table S10. Summary of the photovoltaic parameters for recently reported large-area organic photovoltaic devices processed by non-halogenated solvents.

Active layer	Solvent	Area (cm^2)	PCE (%)	Ref.
PTQ10:PYF-T-o	o-XY	1	11.24	10
PBSF-D12:IT-4F	Tol	1	11.9	11
PM6:BTP-eC9	o-XY	1	15.5	12
PM6:PYTCl-A	Tol	1.21	14.7	13
PTB7-Th:$PC_{71}BM$	2-mMA	16	7.5	14
PM6:PY-82:PY-DT	o-XY	16.5	13.84	15
PM6:DTY6	o-XY	18	14.4	16
PM6:BTP-eC9	o-XY	25	11.29	12
PM6:CH7	o-XY	25.2	14.42	17
PM6:Y6	o-XY	28.82	12.64	18
PBDB-T-2F(3/4):Y6-HU	THF	31.50	6.26	19
PM6:Y6-HU	o-XY	31.50	12.44	20
PV2300:PV-A3:$PC_{61}BM$	o-XY	32.6	10.3	21
PM6:Y6: BTO:$PC_{71}BM$	p-XY	36	14.26	22
PTB7-Th:EH-IDTBR:T2-OEHRH	Tol	55.5	9.32	23
PF2:$PC_{71}BM$	o-XY	66	6.1	24
PM6:L8-BO:BTP-S8:BTP-S2	Tol	72.25	12.78	25
PM6:BO-4Cl	o-XY	19.31	15.74	This Work

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