A Universal Halogen-free Solvent System for Highly Efficient Polymer Solar Cells

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Contents of Supporting Information

S1. Physical properties and solubility of polymer (PBDT-TS1) and fullerene in different solvent.

Table S1. Physical properties and solubility of polymer (PBDT-TS1) and fullerene in different solvent.

Solvents		DCB	DIO	*o*-xylene	NMP
Boiling point[a] (℃)		180.0	326	144.5	202.0
Solubility (mg/ml)	PBDT-TS1	4	＜1	1	＜1
	$PC_{71}BM$	203[b]	＜80	66.2[b]	110

[a]Laboratory Solvents and Other Liquid Reagents, in CRC Handbook of Chemistry and Physics, ed. D. R. Lide, CRC Press/Taylor and Francis, Boca Raton, FL, 90th edn, Internet Version 2010. [b]Ref **S1**.

S2. *J-V* characteristics of PBDT-TS1:$PC_{71}BM$ solar cells processed with different concentration NMP and 1-methylnaphthalene (Me-naph)

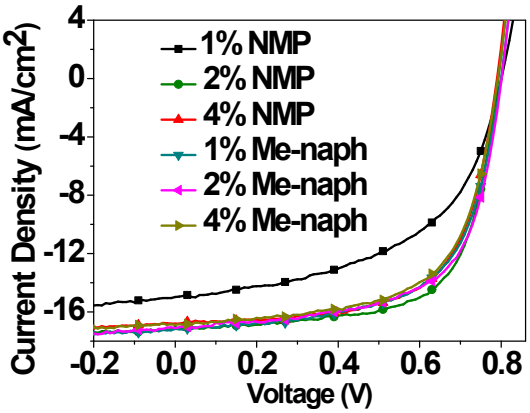

Fig. S1. *J-V* curves of the PSCs based on PBDT-ST1:$PC_{71}BM$ with different volume amount of halogen-free processing additive (NMP) and Me-naph as the processing solvent additive under the illumination of AM 1.5, 100 mW/cm^2, respectively.

Table S2. Photovoltaic device parameters obtained from PSCs fabricated from different concentration of NMP as the processing solvent additive.

Additive	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	PCE_{avg}[a] (%)

	1%	0.80	14.97	52.71	6.31
NMP	2%	0.79	17.02	67.85	9.12
	4%	0.79	16.80	65.03	8.63
	1%	0.80	17.16	62.92	8.64
Me-naph	2%	0.80	17.10	64.33	8.80
	4%	0.79	16.88	63.43	8.46

[a] The average PCE obtained from 10 devices.

S3. *J-V* characteristics of XY/NMP processed PBDT-TS1:$PC_{71}BM$-based device with or without methanol treatment.

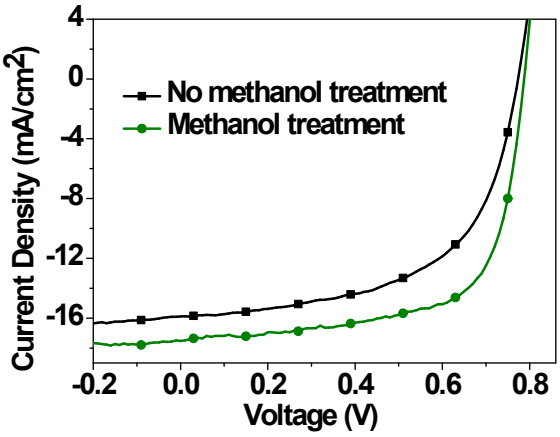

Fig. S2. *J-V* curves of XY/NMP processed PBDT-TS1:$PC_{71}BM$-based device with or without methanol treatment.

Table S3. Photovoltaic device parameters of XY/NMP processed PBDT-TS1:$PC_{71}BM$-based device with or without methanol treatment.

Methanol treatment	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	PCE_{avg} (%)[a]
No	0.77	15.89	57.94	7.09
Yes	0.79	17.24	67.05	9.13

[a] The average PCE obtained from 10 devices.

S4. Hansen parameters of $PC_{71}BM$ and different solvents

Table S4. Hansen solubility parameters for DCB, DIO, XY, NMP and $PC_{71}BM$

solvent	Dispersion (δ_d) ($MPa^{1/2}$)	Polarity (δ_p) ($MPa^{1/2}$)	Hydrogen Bonding (δ_h) ($MPa^{1/2}$)
DCB	19.2	6.3	3.3
DIO	17.6	4.8	4.6
XY	17.8	1.0	3.1
NMP	18.0	12.3	7.2
$PC_{71}BM$	20.2	5.4	4.5

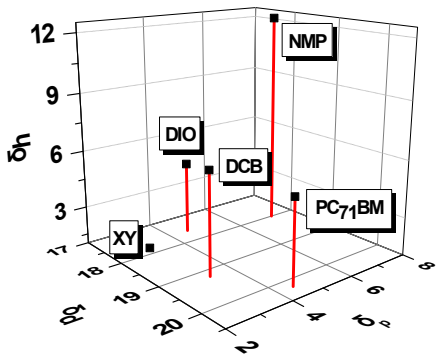

Fig. S3 Hansen solubility parameter (HSP) diagrams of $PC_{71}BM$ and different solvents.

S5. The AFM and TEM images of PBDT-TS1:$PC_{71}BM$ blend films with different processing additive.

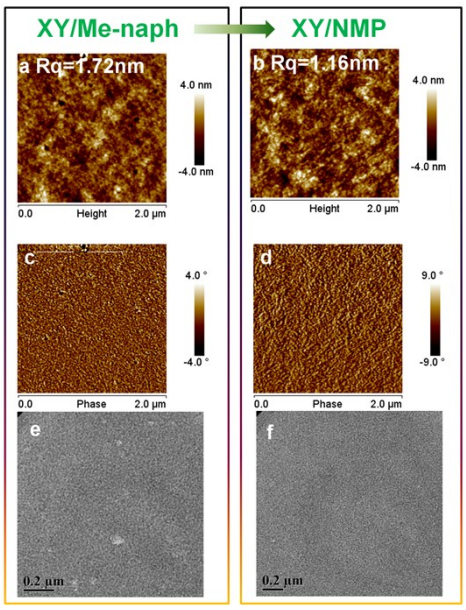

Fig. S4 The AFM height (a, b), phase (c, d) and TEM images (e, f) of PBDT-TS1: $PC_{71}BM$ films cast from XY/Me-naph and XY/NMP, respectively.

S6. *J-V* curves based on PSCs consist of various polymer:$PC_{71}BM$ blends utilizing different solvent as the processing solvent.

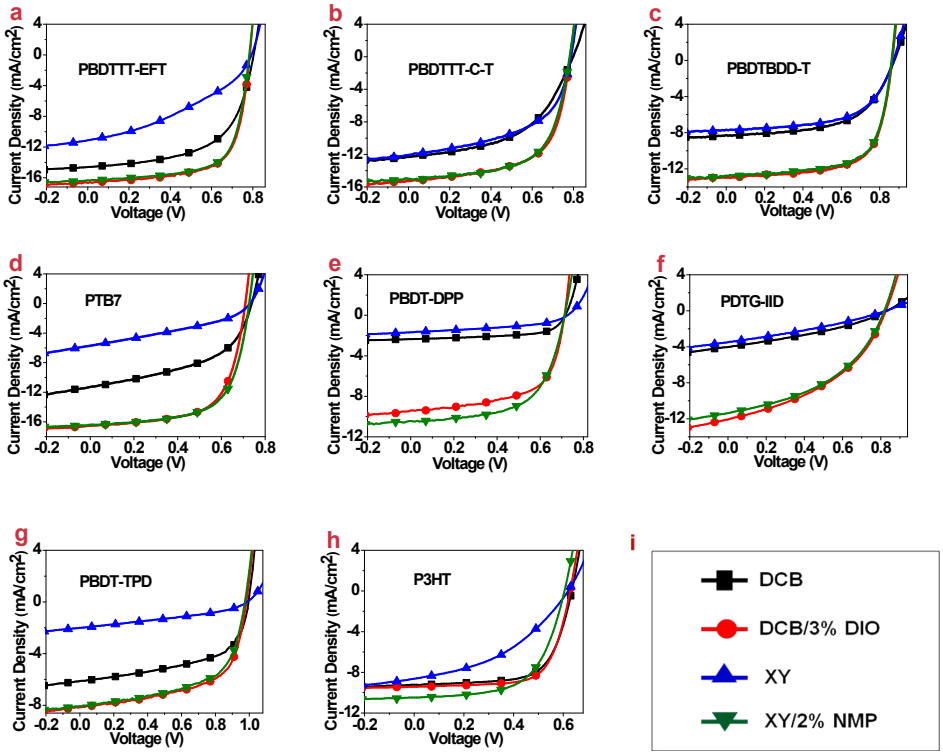

Fig. S5 *J-V* curves based on PSCs consist of various polymer:$PC_{71}BM$ blends (a-h) utilizing different solvent as the processing solvent; (i) The symbols (black, red, blue, green) represented the utilized processing solvents (DCB, DCB/3% DIO, XY, XY/2% NMP), respectively.

S7. The AFM and TEM patterns of eight other polymer:$PC_{71}BM$-blend films cast from solutions of XY and XY/2% NMP

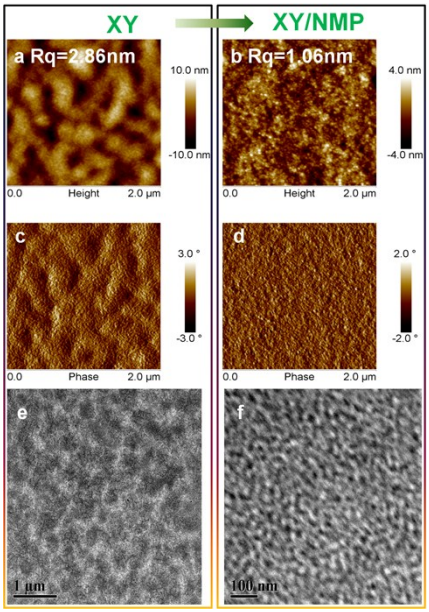

Fig. S6 The AFM height (a, b) and phase (c, d) of PBDTT-EFT: $PC_{71}BM$ films made without using NMP (a, c) and with NMP (b, d) in the XY, TEM images of thin-film PBDTT-EFT:$PC_{71}BM$ blend cast from solutions of (e) XY only (f) 2% NMP in XY.

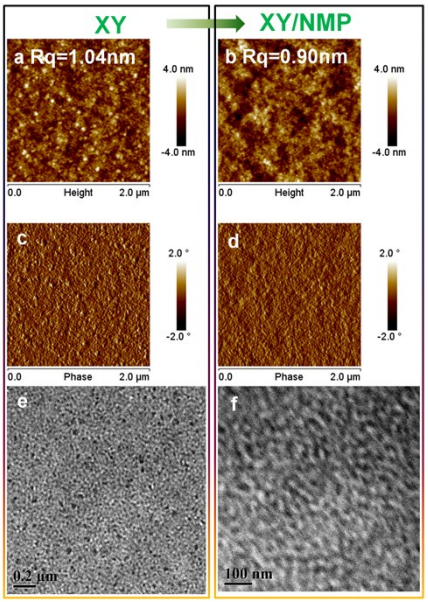

Fig. S7 The AFM height (a, b) and phase (c, d) of PBDTT-C-T: $PC_{71}BM$ films made without using NMP (a, c) and with NMP (b, d) in the XY, TEM images of thin-film PBDTT-C-T:$PC_{71}BM$ blend cast from solutions of (e) XY only (f) 2% NMP in XY.

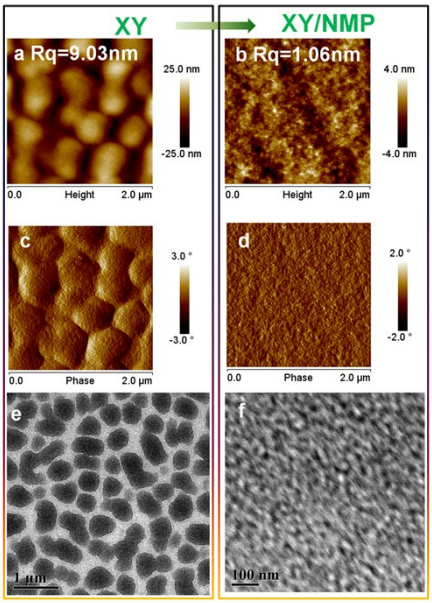

Fig. S8 The AFM height (a, b) and phase (c, d) of PTB7: $PC_{71}BM$ films made without using NMP (a, c) and with NMP (b, d) in the XY, TEM images of thin-film PTB7:$PC_{71}BM$ blend cast from solutions of (e) XY only (f) 2% NMP in XY.

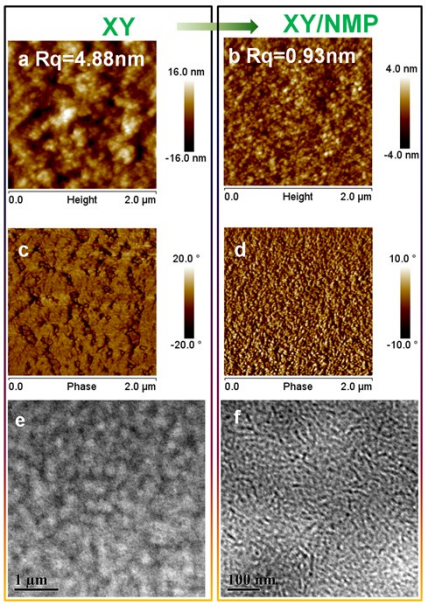

Fig. S9 The AFM height (a, b) and phase (c, d) of PBDTBDD-T: $PC_{71}BM$ films made without using NMP (a, c) and with NMP (b, d) in the XY, TEM images of thin-film PBDTBDD-T:$PC_{71}BM$ blend cast from solutions of (e) XY only (f) 2% NMP in XY.

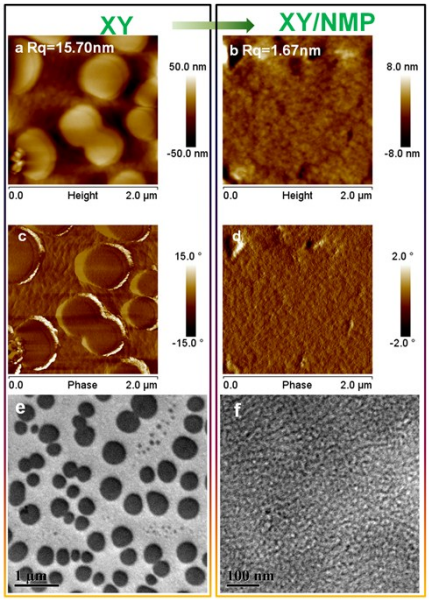

Fig. S10 The AFM height (a, b) and phase (c, d) of PBDT-DPP: $PC_{71}BM$ films made without using NMP (a, c) and with NMP (b, d) in the XY, TEM images of thin-film PBDT-DPP:$PC_{71}BM$ blend cast from solutions of (e) XY only (f) 2% NMP in XY.

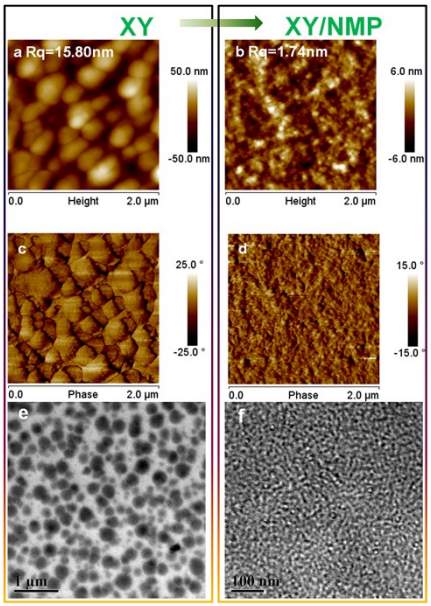

Fig. S11. The AFM height (a, b) and phase(c, d) of PDTG-IID: $PC_{71}BM$ films made without using NMP (a, c) and with NMP (b, d) in the XY, TEM images of thin-film PDTG-IID:$PC_{71}BM$ blend cast from solutions of (e) XY only (f) 2% NMP in XY.

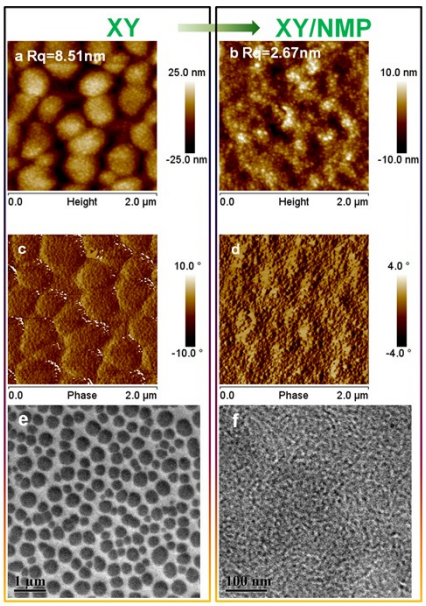

Fig. S12 The AFM height (a, b) and phase(c, d) of PBDT-TPD: $PC_{71}BM$ films made without using NMP (a, c) and with NMP (b, d) in the XY, TEM images of thin-film PBDT-TPD:$PC_{71}BM$ blend cast from solutions of (e) XY only (f) 2% NMP in XY.

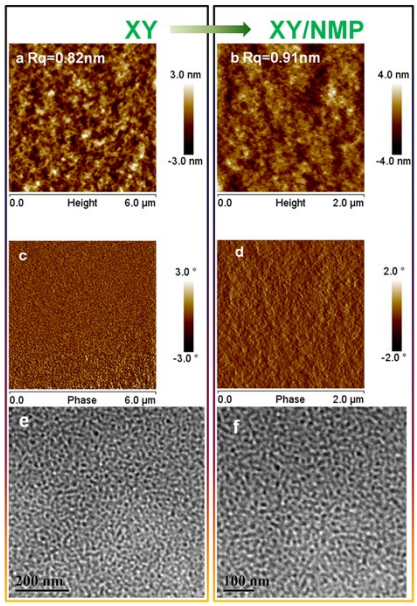

Fig. S13 The AFM height (a, b) and phase (c, d) of P3HT: $PC_{71}BM$ films made without using NMP (a, c) and with NMP (b, d) in the XY, TEM images of thin-film P3HT:$PC_{71}BM$ blend cast from solutions of (e) XY only (f) 2% NMP in XY.

S8. Device fabrication and measurements

For active layers, the fabrication details are listed in the **Table S5** and also obtained from the literatures.[S2-S9] For instance, The PBDTTT-EFT: $PC_{71}BM$ (1:1.5) composite was dissolved in *o*-chlorobenzene (DCB) or *o*-xylene (XY) stirring at 75 °C for 8 h, respectively. The concentration of PBDTTT-EFT and $PC_{71}BM$ in DCB or XY solution is 10 and 15 mg/ml, respectively. 3% DIO (vol) or 2% NMP was added into the blend solution for morphology modulation. Prior to evaporating metal cathodes, methanol treats the BHJ films according to our recent report.[S10] The device fabrication was completed by thermal evaporation of a 20 nm thick Mg and a 80 nm thick Al layer as cathode under vacuum at a base pressure of 1×10^{-4} Pa.

Table S5. The fabrication details of PSCs based on several efficient polymers.

Active layers	D/A ratio	Solvent	*Ref.*	Concentration of Polymer (mg/ml)	Thickness (nm)
PBDTTT-EFT:$PC_{71}BM$	1:1.5	DCB/DIO (97/3)	S2	10	90
		XY/NMP (98/2)			
PBDTTT-C-T:$PC_{71}BM$	1:1.5	DCB/DIO (97/3)	S3	10	95
		XY/NMP (98/2)			
PBDTBDD-T:$PC_{71}BM$	1:1	DCB/DIO (97/3)	S4	12	85
		XY/NMP (98/2)			
PTB7:$PC_{71}BM$	1:1.5	CB/DIO (97/3)	S5	10	90
		XY/NMP (98/2)			
PBDT-DPP:$PC_{71}BM$	1:2	DCB/DIO (99.5/0.5)	S6	6	100
		XY/NMP (98/2)			
PDTG-IID:$PC_{71}BM$	1：1	DCB/DIO (97/3)	S7	10	90

		XY/NMP (98/2)			
PBDT-TPD:$PC_{71}BM$	1:2	DCB/DIO (97/3)	S8	10	100
		XY/NMP (98/2)			
P3HT:$PC_{61}BM$	1:1	DCB/DIO	S9	17	200
		XY/NMP (98/2)			

S9. Morphology and device stability tests of PBDT-TS1:$PC_{71}BM$-based PSCs cast from solutions of DCB/3% DIO and XY/NMP in 8 days.

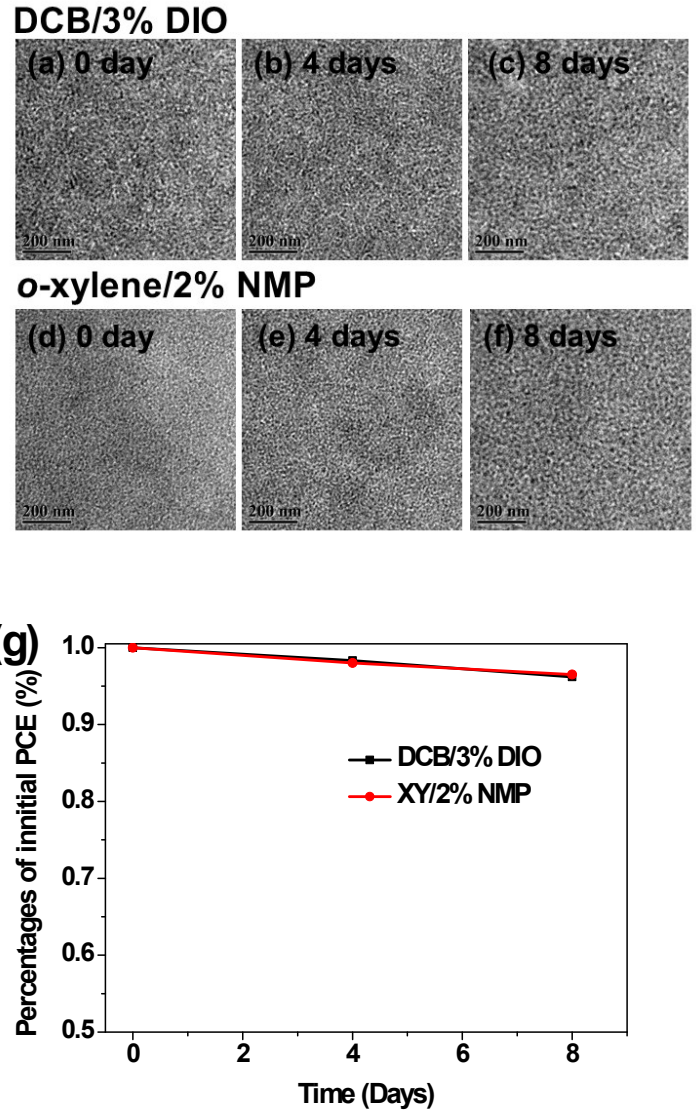

Figure S14. TEM images of thin-film PBDT-TS1:$PC_{71}BM$ blend cast from solutions of DCB/3% DIO (a, b, c) and XY/NMP (d, e, f) every four days, respectively; (g) the corresponding PCE value plots in 8 days.

S10. **Photovoltaic device parameters of XY/NMP processed P3HT: $PC_{71}BM$-based device with different concentration of NMP.**

Table S6. Photovoltaic device parameters of XY/NMP processed P3HT: $PC_{71}BM$-based device with different concentration of NMP.

Additive	Additive Amount	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	*PCE* (%)
	1%	0.61	9.61	59.94	3.51
NMP	2%	0.61	10.47	60.56	3.87
	4%	0.61	9.69	58.40	3.45

References

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