Supporting information

Structure-property relationship of D-A type copolymers based on phenanthrene and naphthalene units for organic electronics

Yeong-A Kim[a], Minji Kang[a], Ye-Jin Jeon[a], Kyeongil Hwang[a], Yeon-Ju Kim[a], Soo-young Jang[a,b], In-Bok Kim[c], Gucheol Kwon and Dong-Yu Kim[a,c,*]

[a] School of Materials Science & Engineering, Gwangju Institute of Science and Technology (GIST), 123 Cheomdangwagi-ro, Buk-gu, Gwangju 61002, Republic of Korea

[b] current address : Department of Chemistry and Centre for Plastic Electronics, Imperial College London, Exhibition Rd, London, SW7 2AZ, UK.E-mail: s.jang@imperial.ac.uk

[c] Institute for Solar and Sustainable Energies (RISE), Gwangju Institute of Science and Technology (GIST), 123 Cheomdangwagi-ro, Buk-gu, Gwangju 61002, Republic of Korea

Figure S1. Synthetic Routes to Key Monomers

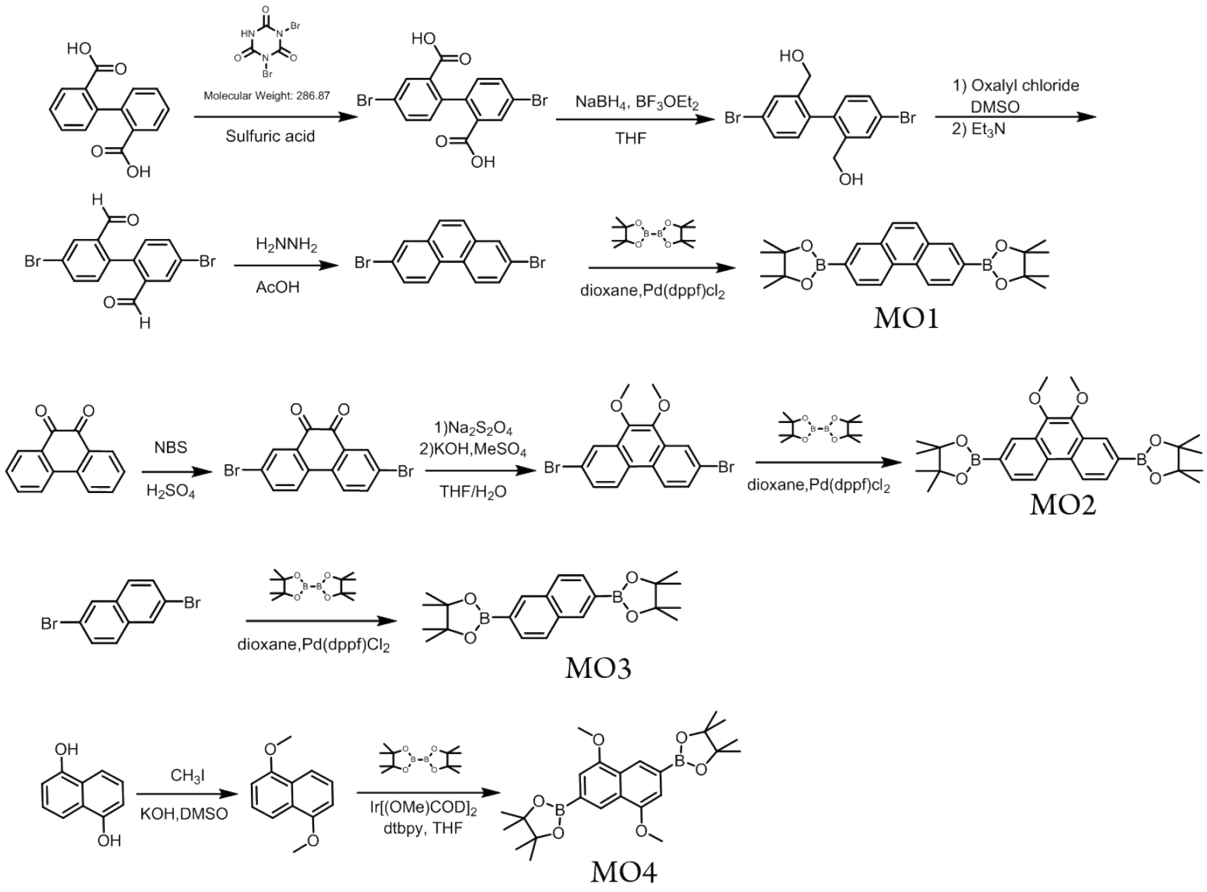

Figure S2. TGA plots of (MeO)PA-based copolymers at a heating rate of 10°C/min under a nitrogen atmosphere.

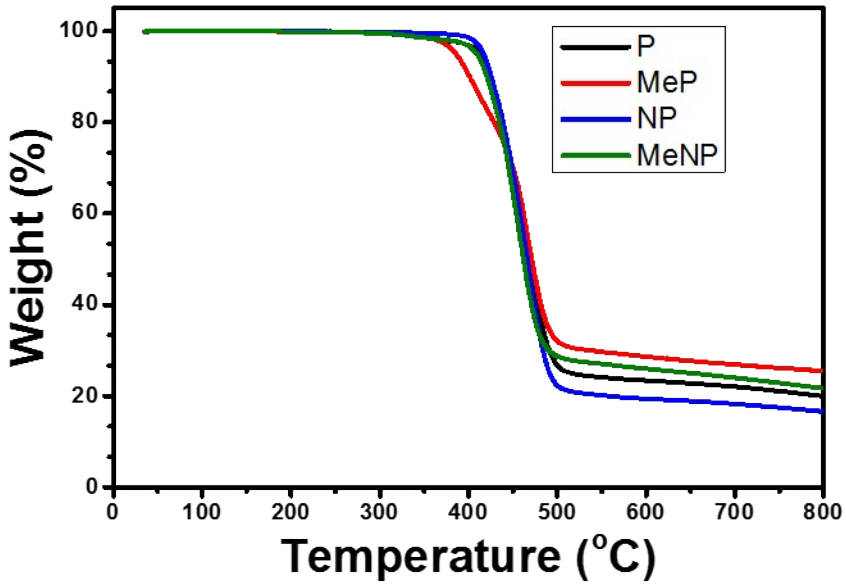

Figure S3. DSC trace of (a) **PA1**, (b) **PA2**, (c) **PA3**, and (d) **PA4** in the temperature range from 45 °C to 295 °C (b).

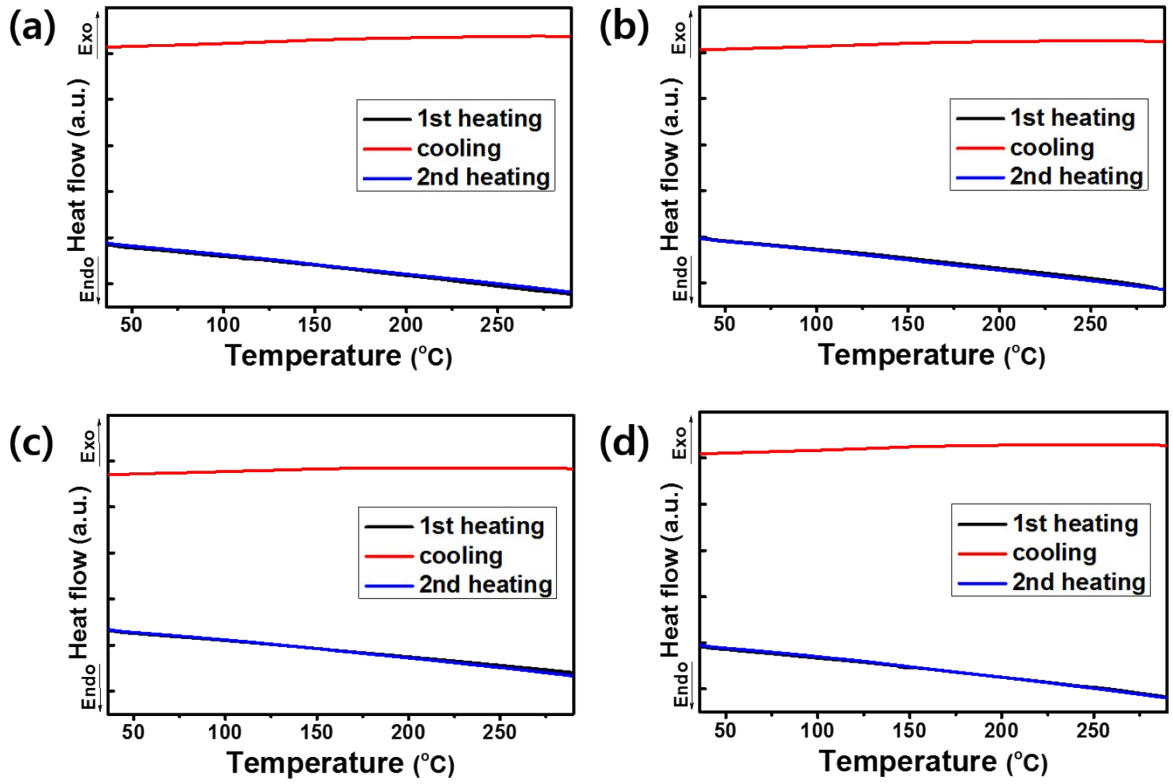

Figure S4. Top views (left) and side views (right) of the optimized structure of the polymer repeating units of (a) **PA1**, (b) **PA2**, (c) **PA3**, and (d) **PA4** calculated by using the density functional theory (DFT) at the B3LYP/6-311G(d,p) level.

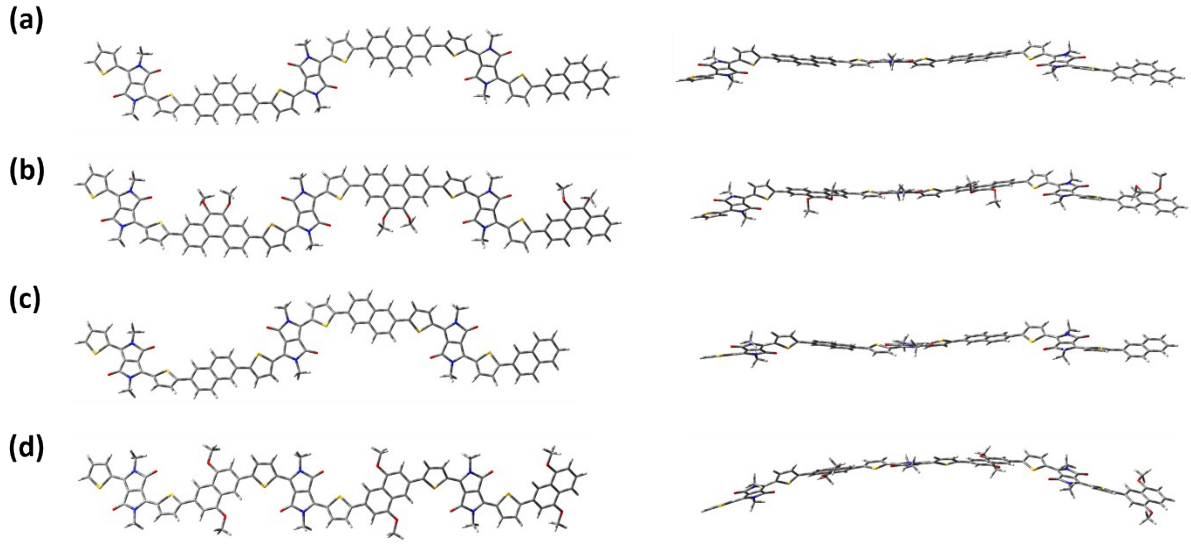

Figure S5. HOMO (bottom) and LUMO (top) surface contour plots of (a) **PA1**, (b) **PA2**, (c) **PA3**, and (d) **PA4**

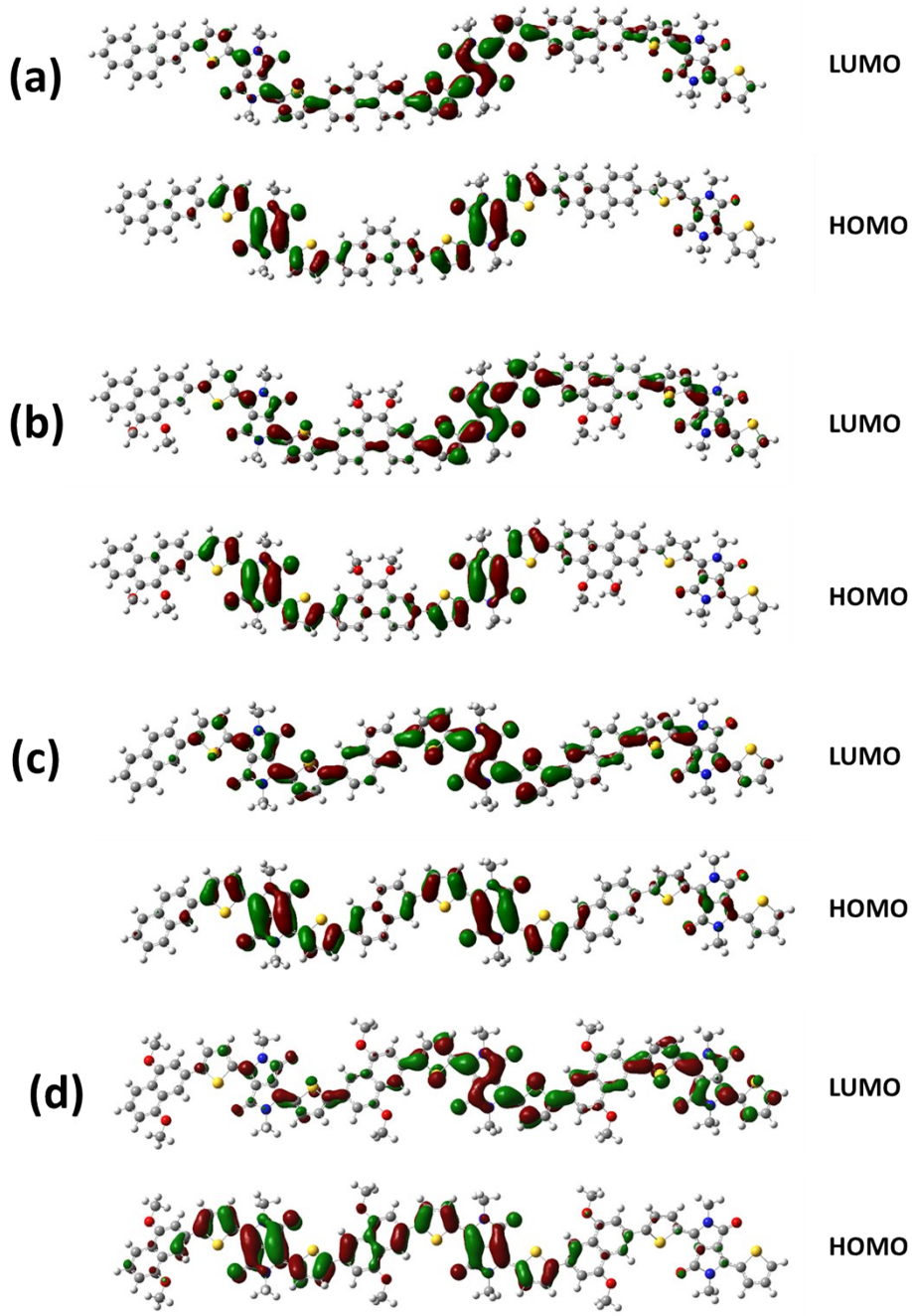

Figure S6. Calculated UV-Vis absorption spectra using TD-DFT with a CAM-B3LYP functional and basis set of 6-311g(d,p).

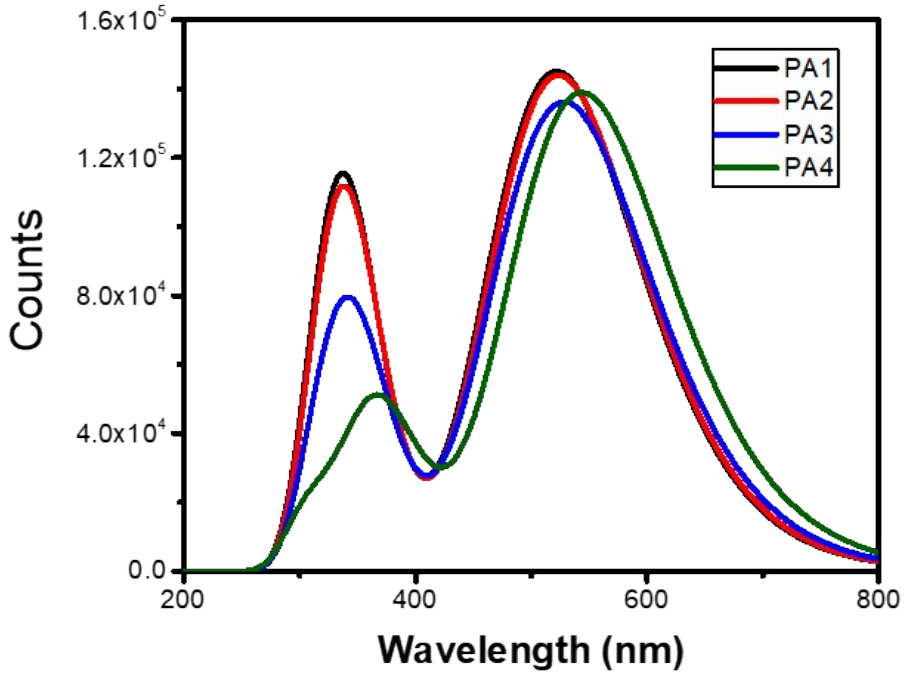

Figure S7. Temperature dependent absorption spectra of (a) **PA1**, (b) **PA2**, (c) **PA3**, and (d) **PA4** in *o*-DCB with increasing the temperature from 40 to 110 °C.

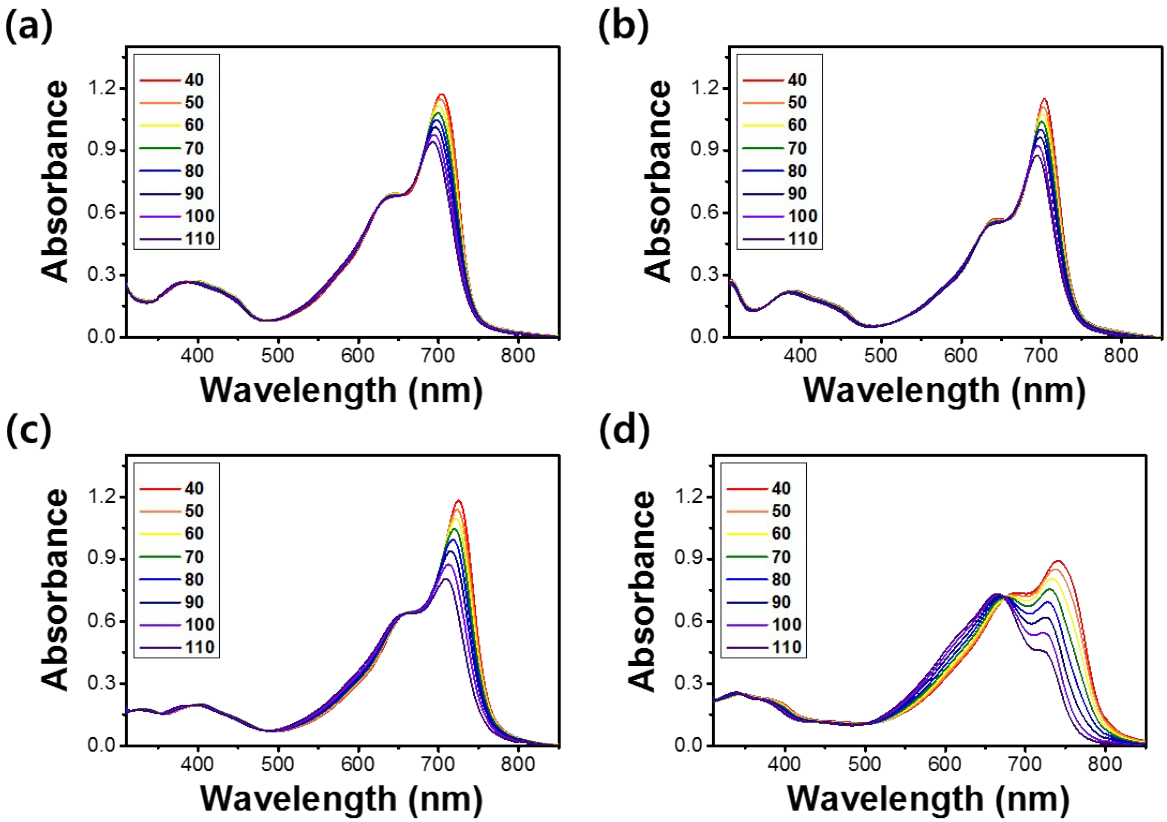

Figure S8. Cyclic voltammograms of polymer thin films

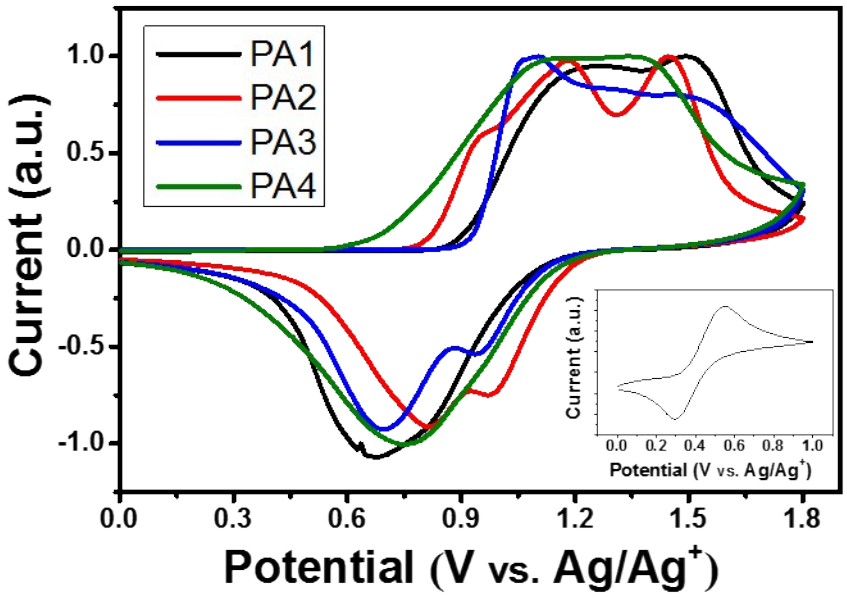

Figure S9. Tapping-mode AFM height images (1μm x 1μm) of pristine (left) and thermally-treated films of (a) **PA1**, (b) **PA2**, (c) **PA3**, and (d) **PA4.**

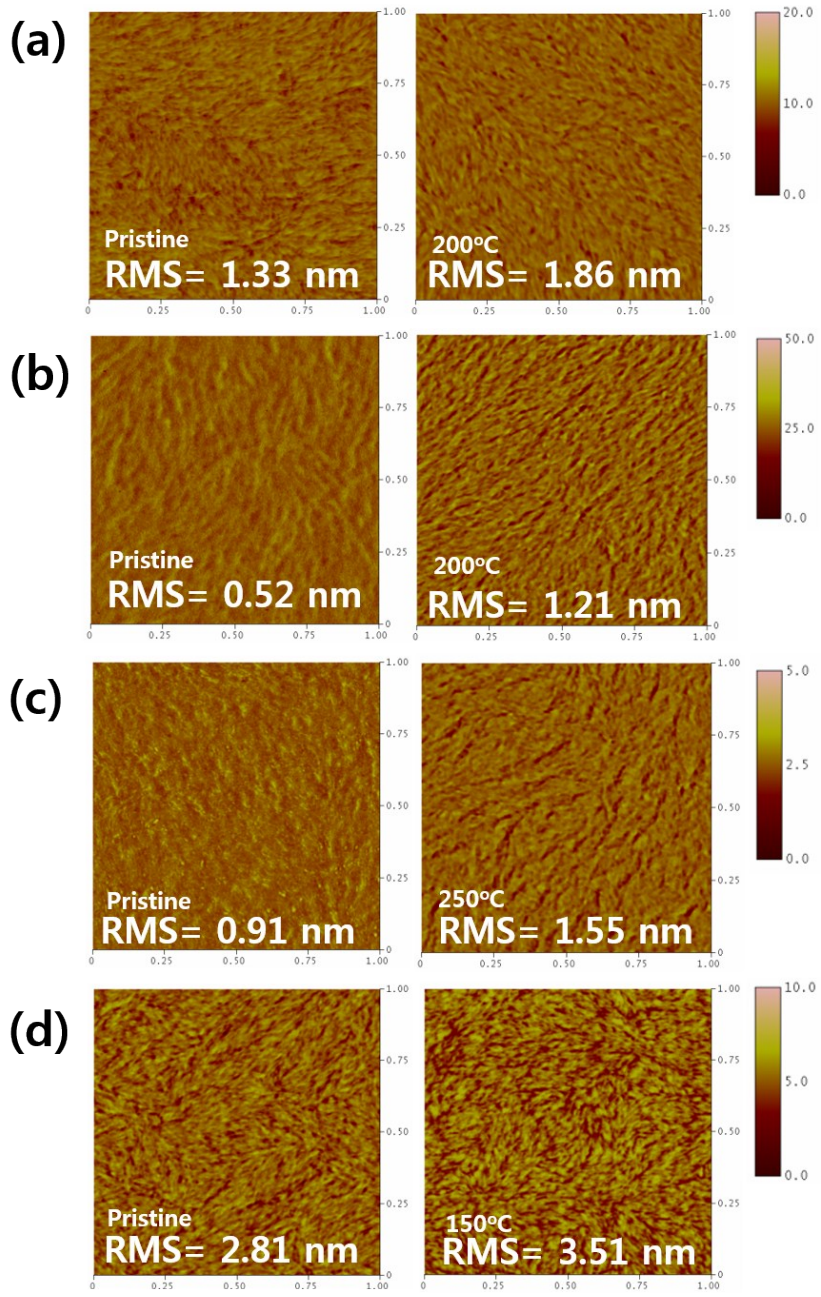

Figure S10. GIWAXD 2D patterns of (a) **PA1**, (b) **PA2**, (c) **PA3**, and (d) **PA4** thin films on Si/SiO_2 substrates

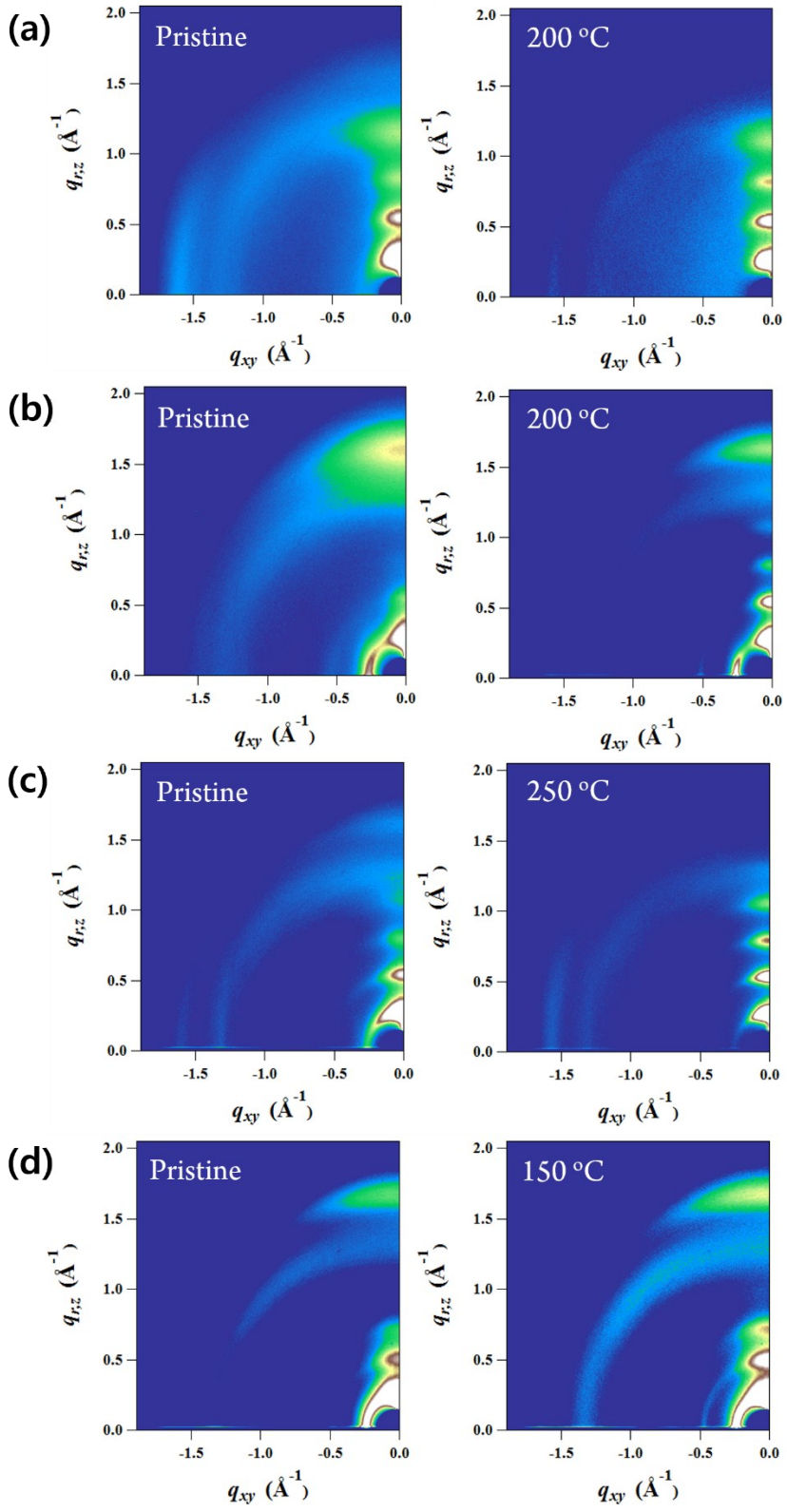

Figure S11. Output characteristics of OFET devices of (MeO)PA-based polymer films after annealing: (a) **PA1** at at 200 °C, (b) **PA2** at at 200 °C, (c) **PA3** at at 250 °C, and (d) **PA4** at at 150 °C.

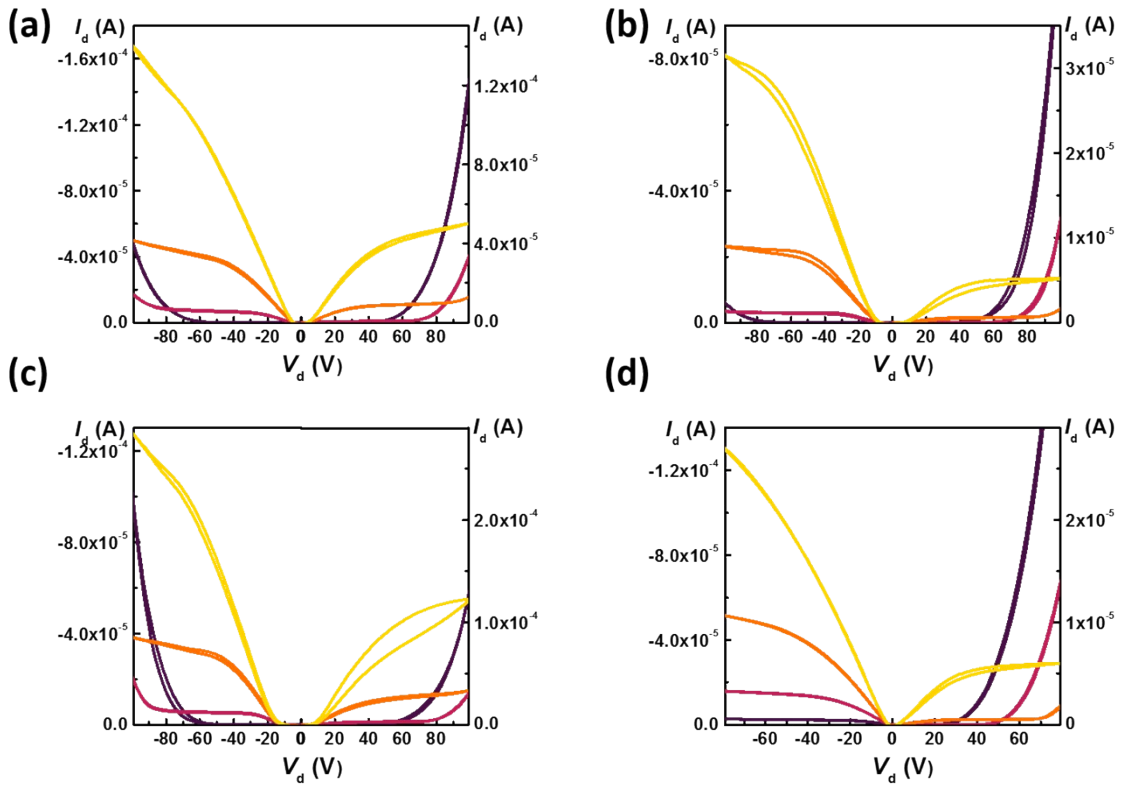

Figure S12. (a) transfer and (b) output characteristics of PA1-based OFET casted using trichloroethylene solution after annealing at 200 °C.

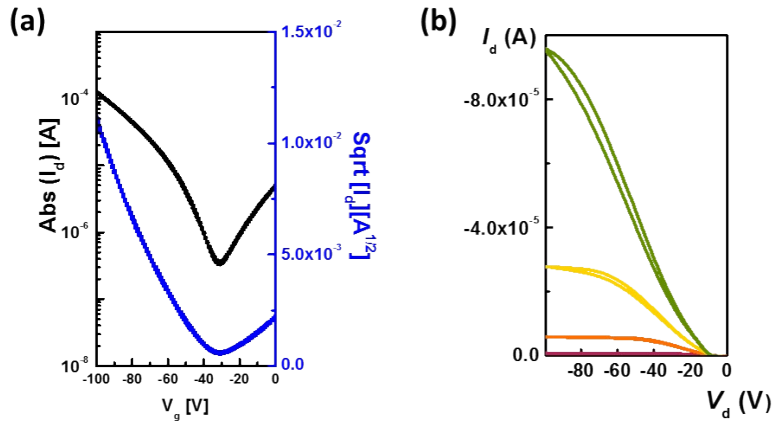

Figure S13. (a) Measured J_{sc} of (MeO)PA copolymers:$PC_{71}BM$ solar cells plotted against light intensity on a logarithmic scale. (b) V_{oc} of (MeO)PA copolymers:PC71BM solar cells

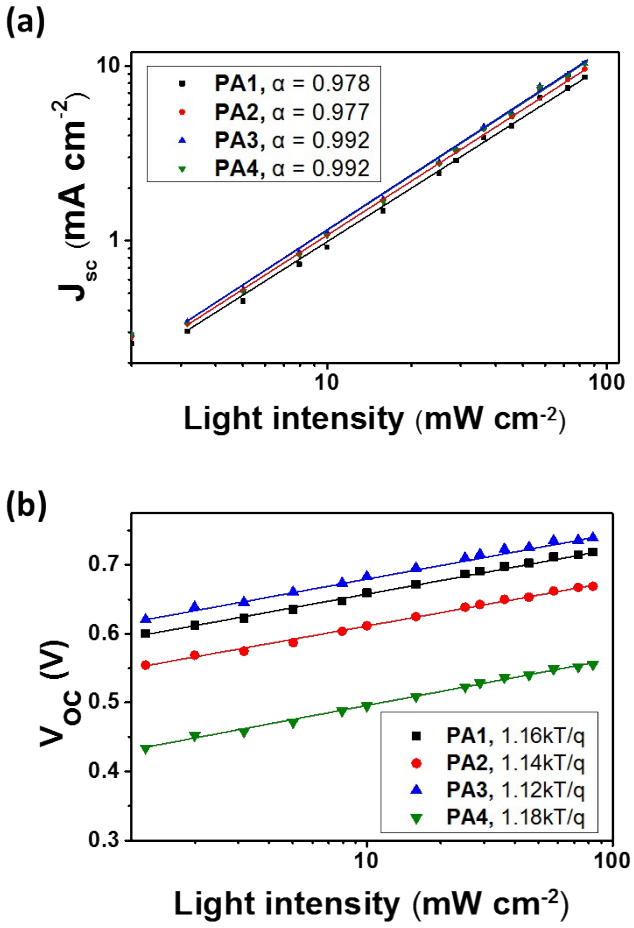

Table S1. Photovoltaic characterisics of the devices based on PA1:PCBM.

PCBM	Solvent condition	Device structure	Weight ratio (w/w)	V_{oc} (V)	J_{sc}(mA/cm^2)	FF (%)	PCE (%)
$PC_{61}BM$	Chloroform:DCB =4:1	Normal	1:1	0.76	7.0	49	2.6
			1:2	0.75	7.6	62	3.5
			1:3	0.76	6.8	70	3.6
			1:4	0.74	5.7	73	3.1
$PC_{71}BM$	Chloroform:DCB =4:1	Normal	1:1	0.76	7.7	54	3.2
			1:2	0.75	8.6	71	4.6
			1:3	0.74	10.2	67	5.0
			1:4	0.72	9.0	71	4.6
$PC_{71}BM$	Chloroform with 3v/v% DPE	Normal	1:1	0.72	8.5	48	2.9
			1:2	0.72	11.2	51	4.1
			1:3	0.73	11.3	53	4.4
			1:4	0.73	11.2	58	4.8
$PC_{71}BM$	Chloroform with 3v/v% DPE	Invert	1:1	0.72	8.5	48	2.9
			1:2	0.70	11.0	64	4.9
			1:3	0.72	11.5	63	5.3
			1:4	0.71	10.6	66	5.0

Figure S14. Characteristic J−V curves of BHJ solar cells fabricated from (a) PA1:$PC_{61}BM$ (cast from chloroform:*o*-dichlorobenzene=4:1 (v/v) cosolvent) with normal structure, (b) PA1:$PC_{71}BM$ (cast from chloroform:*o*-dichlorobenzene=4:1 (v/v) cosolvent) with normal structure, (c) PA1:$PC_{71}BM$ (cast from chloroform containing 3% diphenylether) with normal structure, and (d) PA1:$PC_{71}BM$ (cast from chloroform containing 3% diphenylether) with inverted structure.

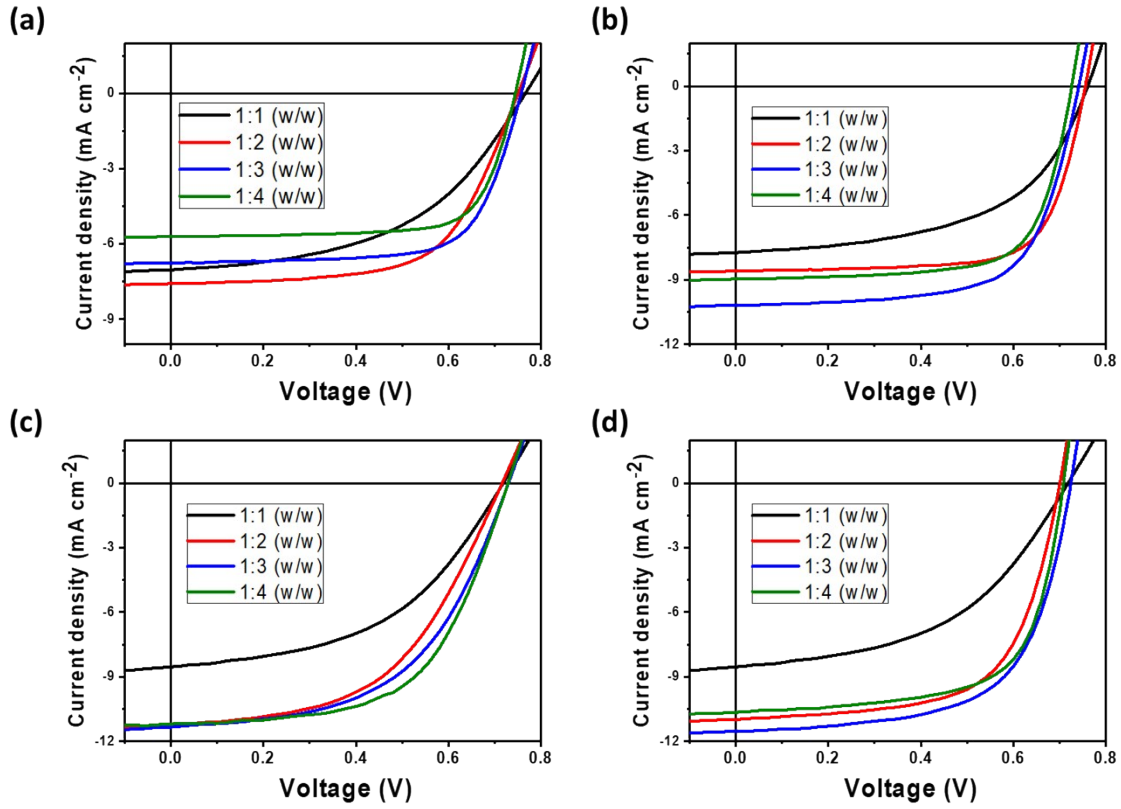

Table S2. Photovoltaic characterisics of the devices based on PA2:PCBM.

PCBM	Solvent condition	Device structure	Weight ratio (w/w)	V_{oc} (V)	J_{sc}(mA/cm^2)	FF (%)	PCE (%)
$PC_{61}BM$	CB	Normal	1:1	0.73	2.4	51	0.9
			1:2	0.72	7.0	58	2.9
			1:3	0.72	5.9	63	2.7
			1:4	0.72	5.2	66	2.5
$PC_{61}BM$	CB with 4% CN	Normal	1:1	0.73	5.6	52	2.1
			1:2	0.71	8.2	54	3.1
			1:3	0.71	5.8	63	2.6
			1:4	0.71	5.4	64	2.5
$PC_{61}BM$	CB	Normal	1:1	0.73	5.6	52	2.1
			1:2	0.71	8.2	54	3.1
			1:3	0.71	5.8	63	2.6
			1:4	0.71	5.4	64	2.5
$PC_{71}BM$	CB with 4% CN	Normal	1:1	0.73	7.7	47	2.6
			1:2	0.73	9.1	46	3.0
			1:3	0.74	7.8	57	3.3
			1:4	0.74	6.0	65	2.9
$PC_{71}BM$	CF	Normal	1:3	0.66	0.5	62	0.2
	CF with 4% CN			0.75	7.9	54	3.2
	CF:DCB=4:1			0.73	9.2	62	4.1
	DCB			0.71	9.6	46	3.1
	DCB with 4% CN			0.72	9.4	55	3.7
$PC_{71}BM$	Chloroform with 3v/v% DPE	Normal	1:1	0.68	9.3	47	3.0
			1:2	0.67	11.2	40	3.0
			1:3	0.68	12.3	57	4.8
			1:4	0.66	11.8	59	4.6
$PC_{71}BM$	Chloroform with 3v/v% DPE	Invert	1:1	0.69	9.7	40	2.7
			1:2	0.68	11.8	39	3.1
			1:3	0.68	12.1	53	4.4
			1:4	0.69	11.4	54	4.3

Figure S15. Characteristic J−V curves of BHJ solar cells fabricated from (a) PA2:$PC_{61}BM$ (cast from chlorobenzene and chlorobenzene with 4% chloronaphthalene) with normal structure, (b) PA2:$PC_{71}BM$ (cast from chlorobenzene and chlorobenzene with 4% chloronaphthalene) with normal structure, (c) PA2:$PC_{71}BM$ (cast from various solvent condition) with normal structure, (d) PA2:$PC_{71}BM$ (cast from chloroform containing 3% diphenylether) with normal structure, and (e) PA2:$PC_{71}BM$ (cast from chloroform containing 3% diphenylether) with inverted structure.

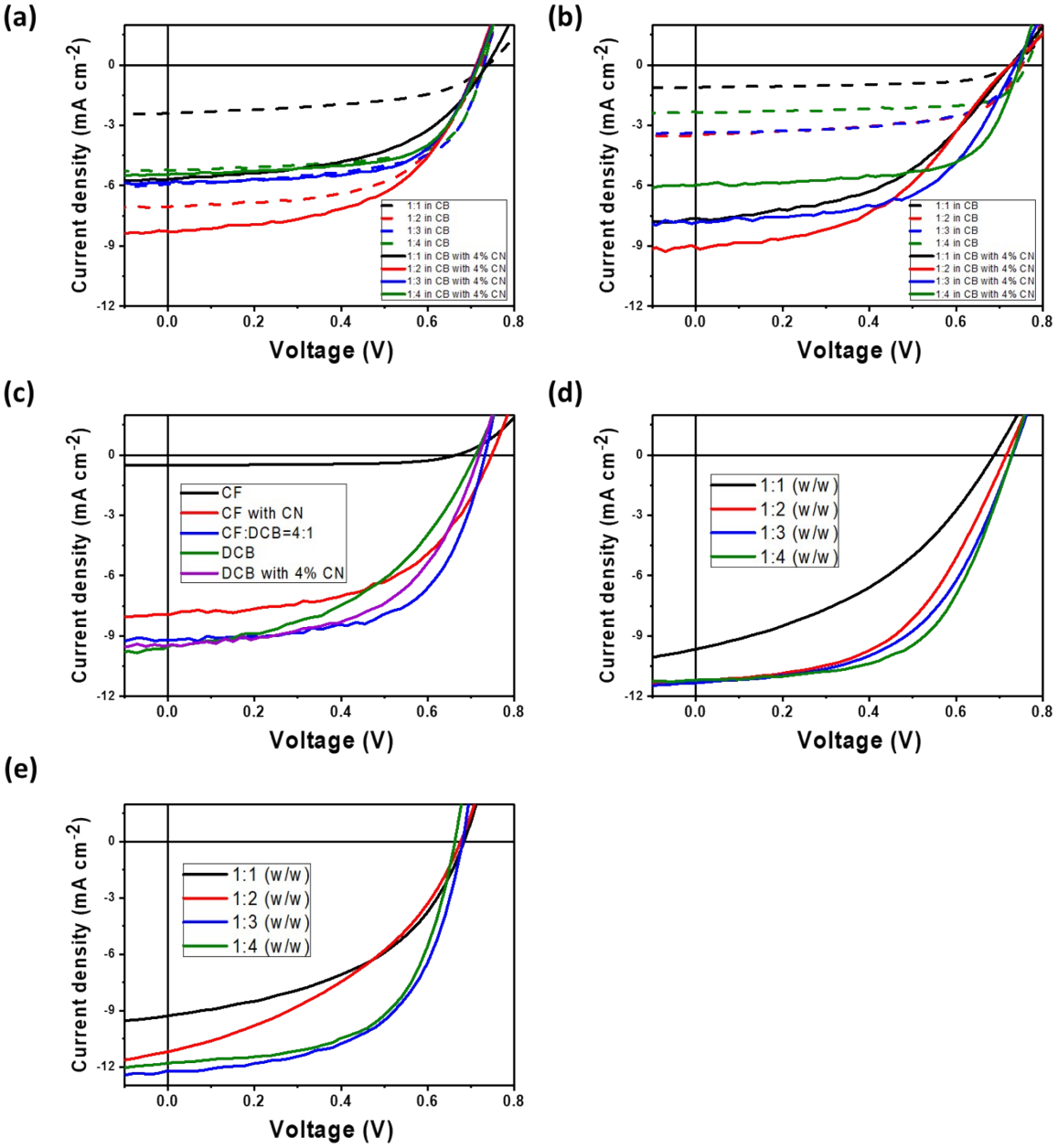

Table S3. Photovoltaic characterisics of the devices based on PA3:PCBM.

PCBM	Solvent condition	Device structure	Weight ratio (w/w)	V_{oc} (V)	J_{sc}(mA/cm^2)	FF (%)	PCE (%)
$PC_{61}BM$	Chloroform:DCB =4:1	Normal	1:1	0.78	4.7	60	2.2
			1:2	0.76	7.8	67	3.9
			1:3	0.76	8.0	66	4.1
			1:4	0.75	7.2	70	3.8
$PC_{71}BM$	Chloroform:DCB =4:1	Normal	1:1	0.77	6.4	63	3.0
			1:2	0.76	7.8	66	3.9
			1:3	0.74	8.0	58	3.4
			1:4	0.77	5.6	70	3.0
$PC_{71}BM$	Chloroform with 3v/v% DPE	Normal	1:1	0.76	10.7	50	4.1
			1:2	0.76	11.7	55	4.9
			1:3	0.76	10.9	61	5.1
			1:4	0.74	10.1	62	4.6
$PC_{71}BM$	Chloroform with 3v/v% DPE	Invert	1:1	0.76	10.6	56	4.5
			1:2	0.75	12.6	57	5.4
			1:3	0.75	12.6	61	5.8
			1:4	0.75	11.7	56	4.9

Figure S16. Characteristic J−V curves of BHJ solar cells fabricated from (a) PA3:$PC_{61}BM$ (cast from chloroform:*o*-dichlorobenzene=4:1 (v/v) cosolvent) with normal structure, (b) PA3:$PC_{71}BM$ (cast from chloroform:*o*-dichlorobenzene=4:1 (v/v) cosolvent) with normal structure, (c) PA3:$PC_{71}BM$ (cast from chloroform containing 3% diphenylether) with normal structure, and (d) PA3:$PC_{71}BM$ (cast from chloroform containing 3% diphenylether) with inverted structure.

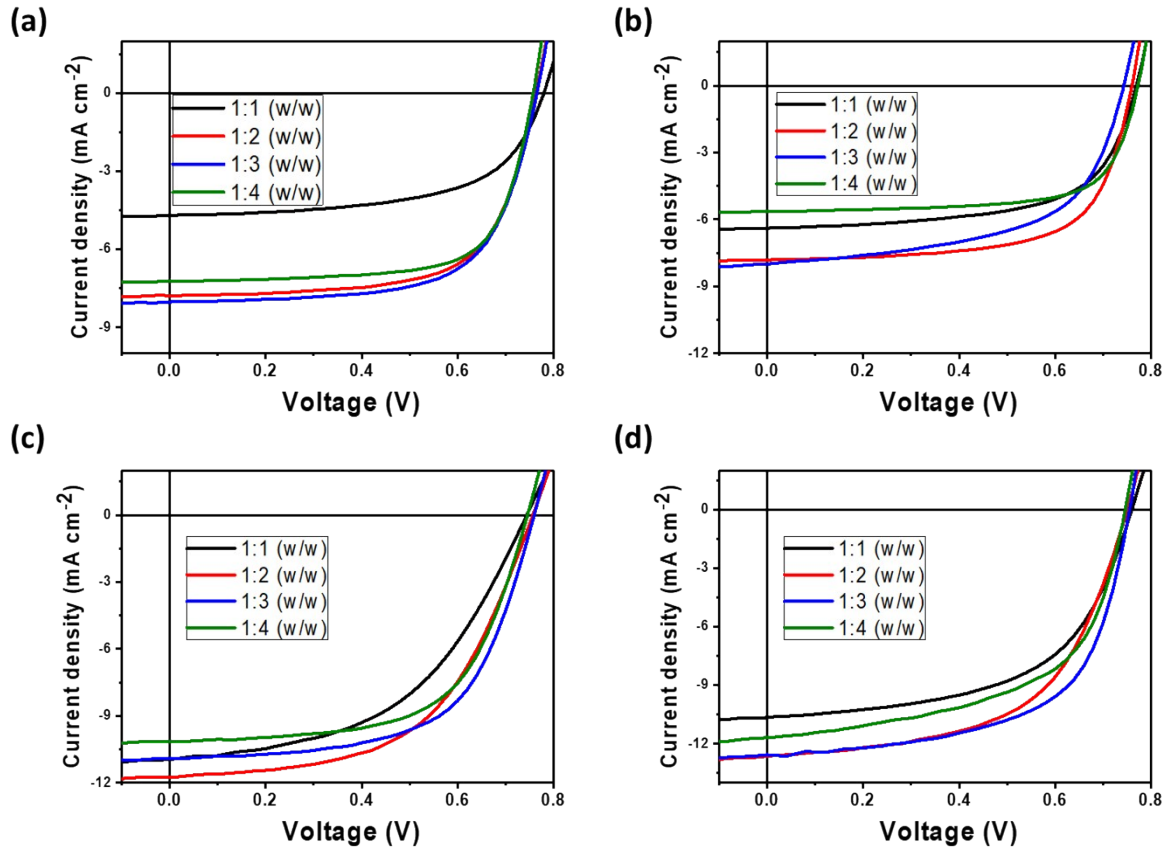

Table S4. Photovoltaic characterisics of the devices based on PA4:PCBM.

PCBM	Solvent condition	Device structure	Weight ratio (w/w)	V_{oc} (V)	J_{sc}(mA/cm^2)	FF (%)	PCE (%)
$PC_{61}BM$	Chloroform:DCB =4:1	Normal	1:1	0.57	5.9	49	1.7
			1:2	0.58	6.8	51	2.0
			1:3	0.60	6.8	69	2.8
			1:4	0.59	8.1	70	3.3
$PC_{71}BM$	Chloroform:DCB =4:1	Normal	1:1	0.57	7.4	55	2.3
			1:2	0.59	9.9	65	3.8
			1:3	0.58	11.3	64	4.2
			1:4	0.55	11.6	57	3.6
$PC_{71}BM$	Chloroform with 3v/v% DPE	Normal	1:1	0.56	10.2	54	3.1
			1:2	0.57	11.7	54	3.6
			1:3	0.57	10.2	53	3.1
			1:4	0.57	10.1	53	3.1
$PC_{71}BM$	Chloroform with 3v/v% DPE	Invert	1:1	0.56	11.7	57	3.7
			1:2	0.56	13.7	52	4.0
			1:3	0.57	12.5	58	4.1
			1:4	0.56	13.8	45	3.5

Figure S17. Characteristic J−V curves of BHJ solar cells fabricated from (a) PA4:$PC_{61}BM$ (cast from chloroform:*o*-dichlorobenzene=4:1 (v/v) cosolvent) with normal structure, (b) PA4:$PC_{71}BM$ (cast from chloroform:*o*-dichlorobenzene=4:1 (v/v) cosolvent) with normal structure, (c) PA4:$PC_{71}BM$ (cast from chloroform containing 3% diphenylether) with normal structure, and (d) PA4:$PC_{71}BM$ (cast from chloroform containing 3% diphenylether) with inverted structure.