

Electronic Supplementary Information

Photovoltaic poly (rod-coil) polymers based on benzodithiophene-centred A-D-A type conjugated segments and dicarboxylate-linked alkyl non-conjugated segments

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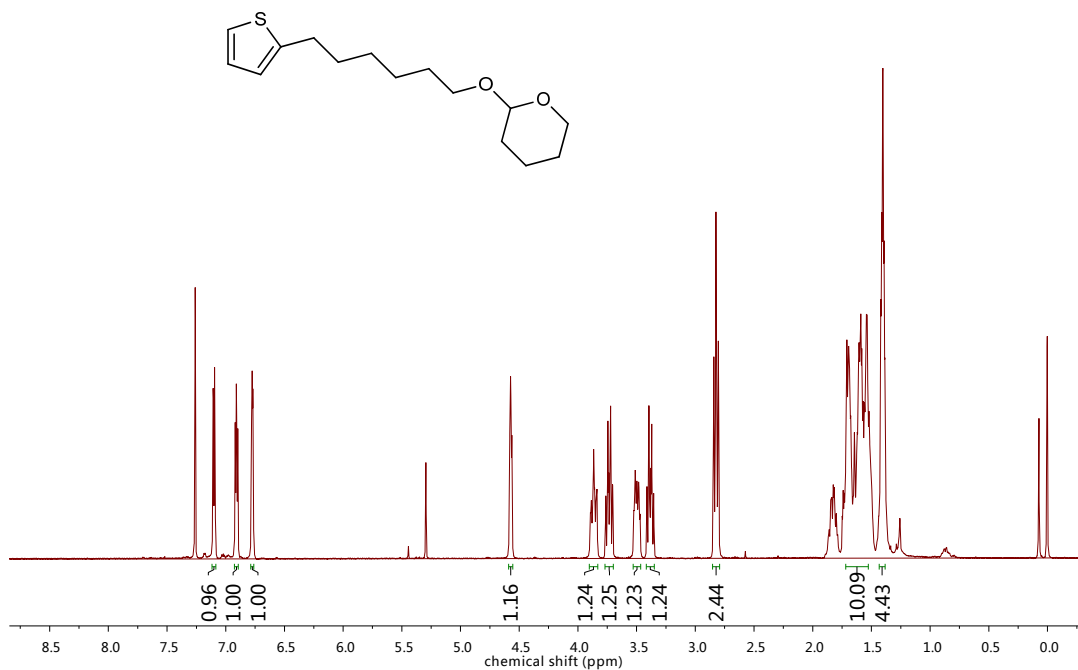


Fig. S1 ^1H NMR spectrum of compound 1 (CDCl_3).

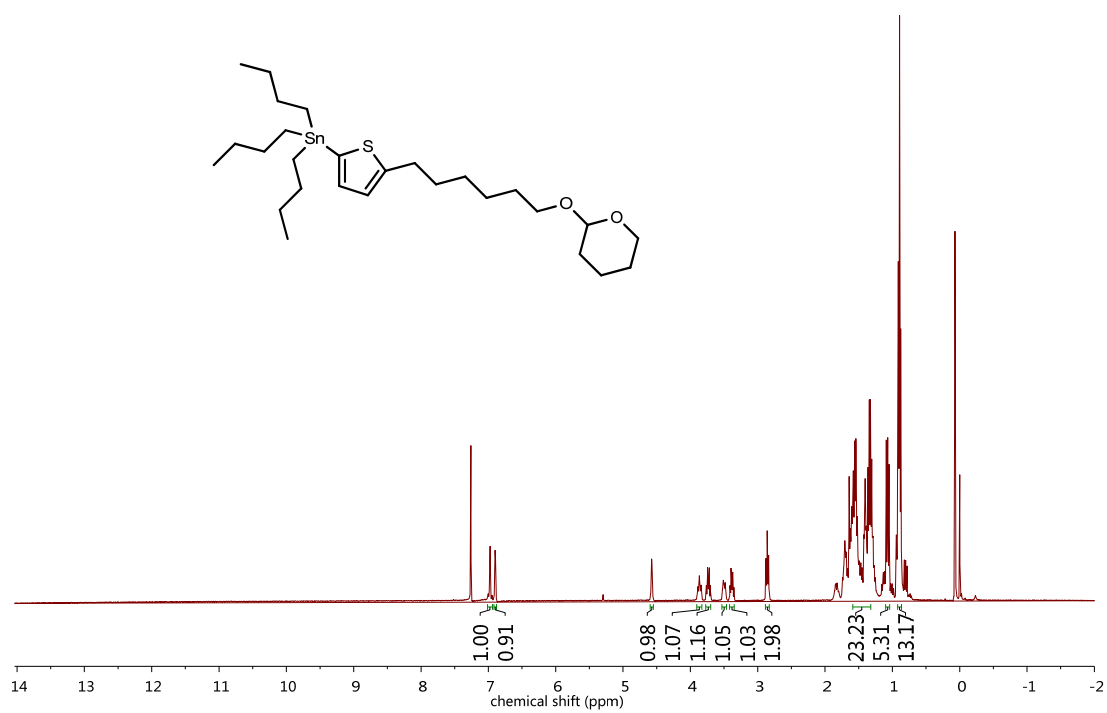


Fig. S2 ^1H NMR spectrum of compound 2 (CDCl_3).

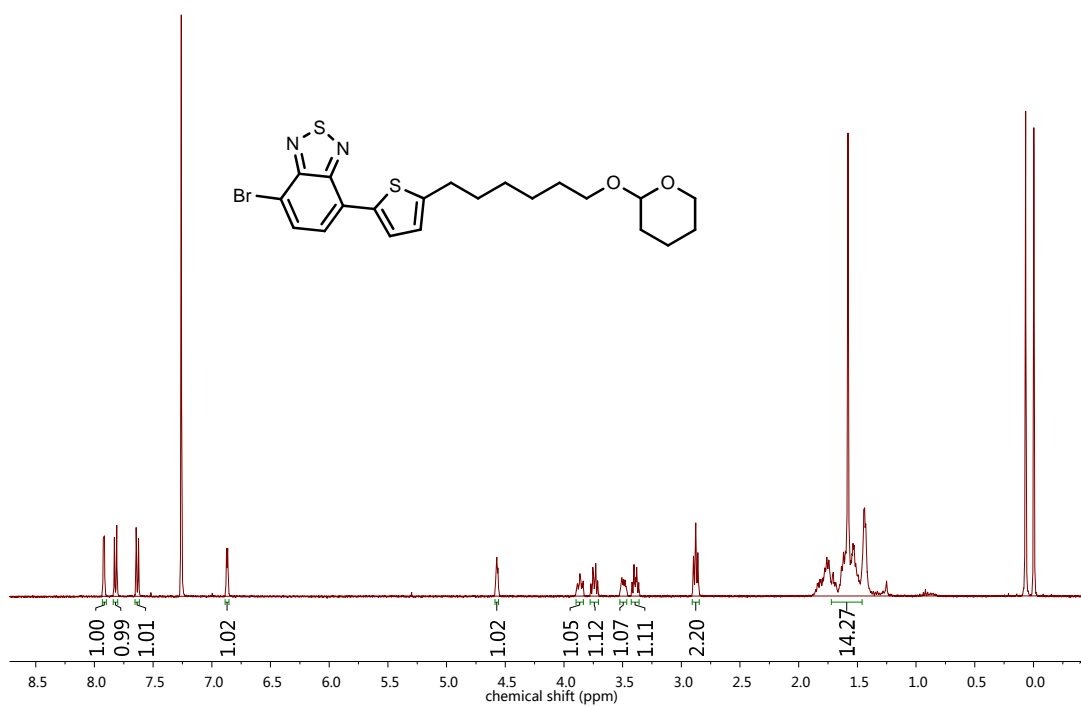


Fig. S3 ^1H NMR spectrum of compound 3 (CDCl_3).

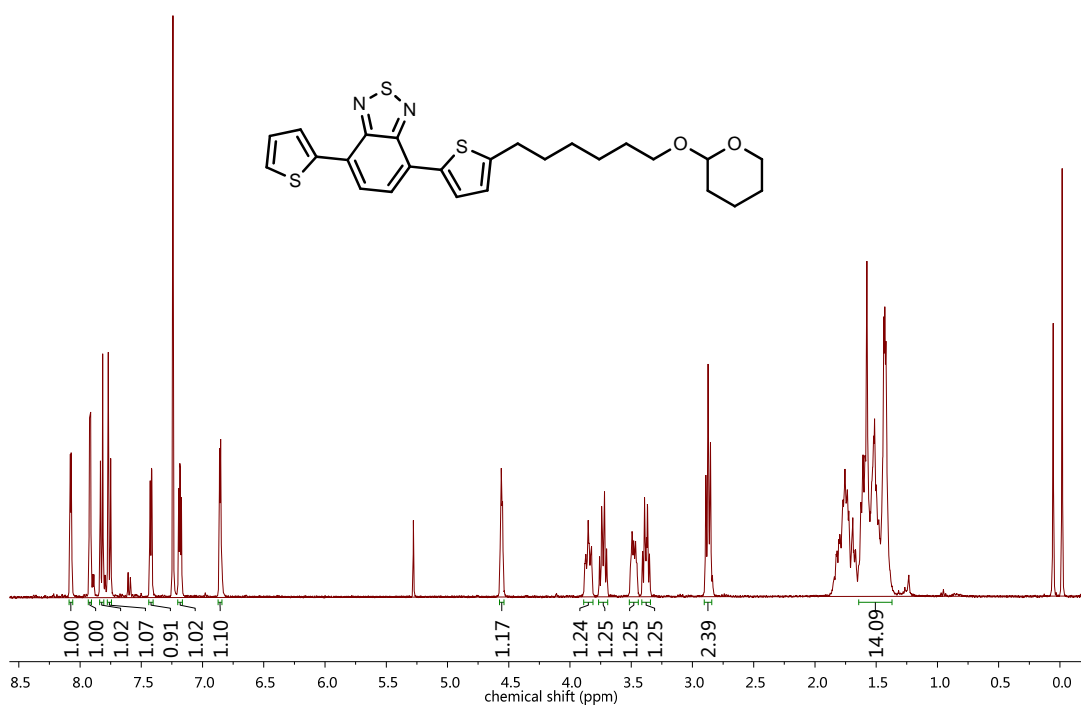


Fig. S4 ^1H NMR spectrum of compound 4 (CDCl_3).

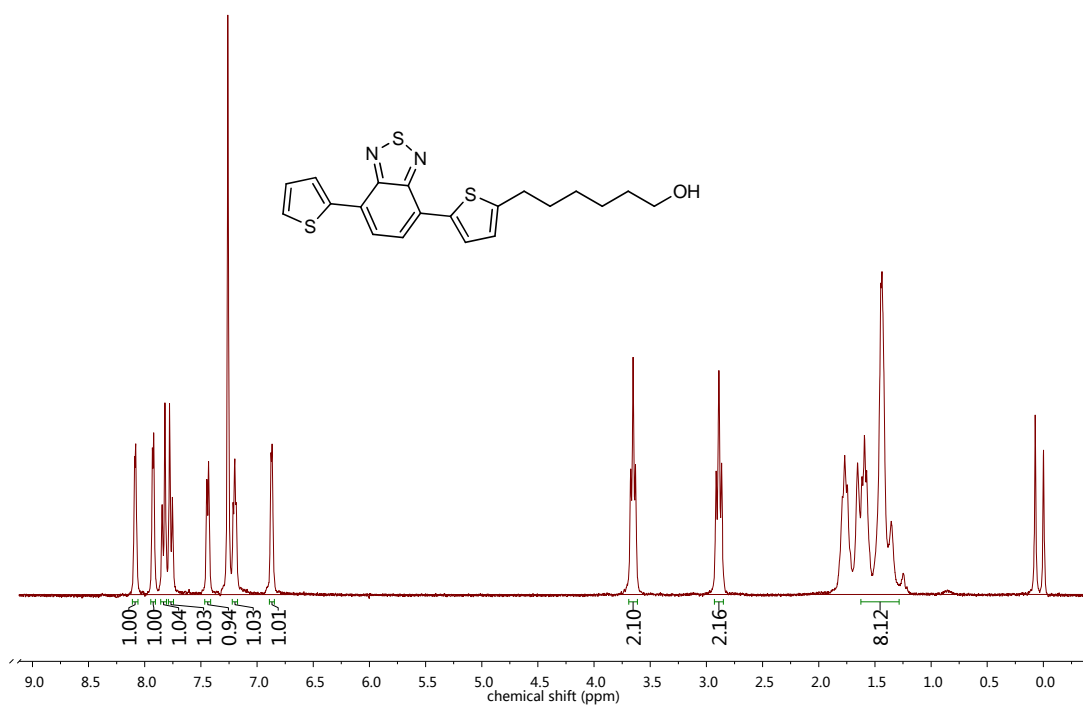


Fig. S5 ^1H NMR spectrum of compound 5 (CDCl_3).

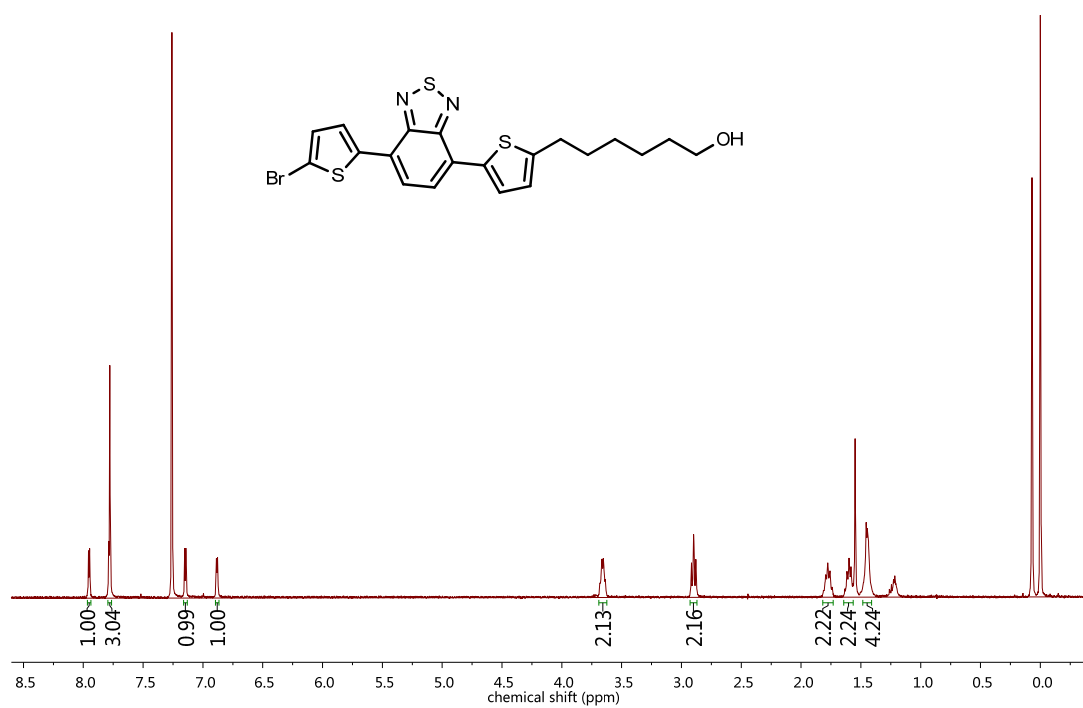


Fig. S6 ^1H NMR spectrum of compound 6 (CDCl_3).

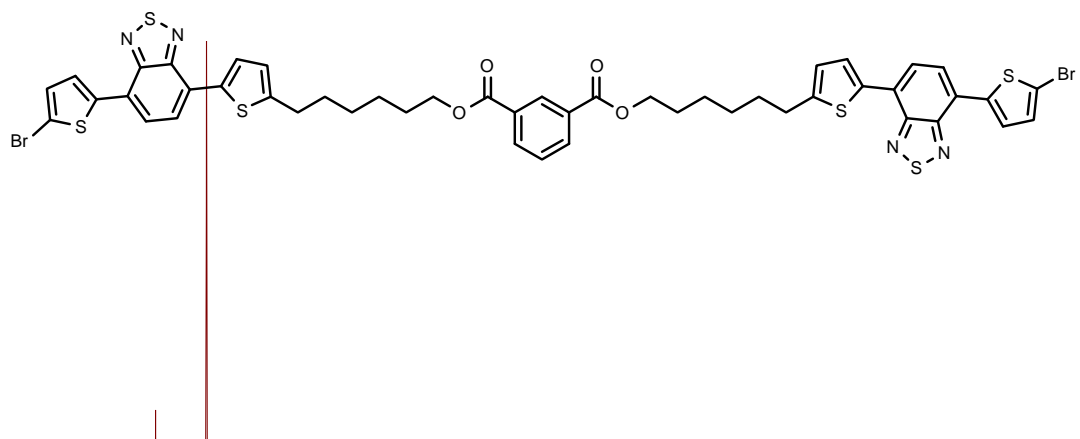


Fig. S7 ^1H NMR spectrum of compound 7 (CDCl_3).

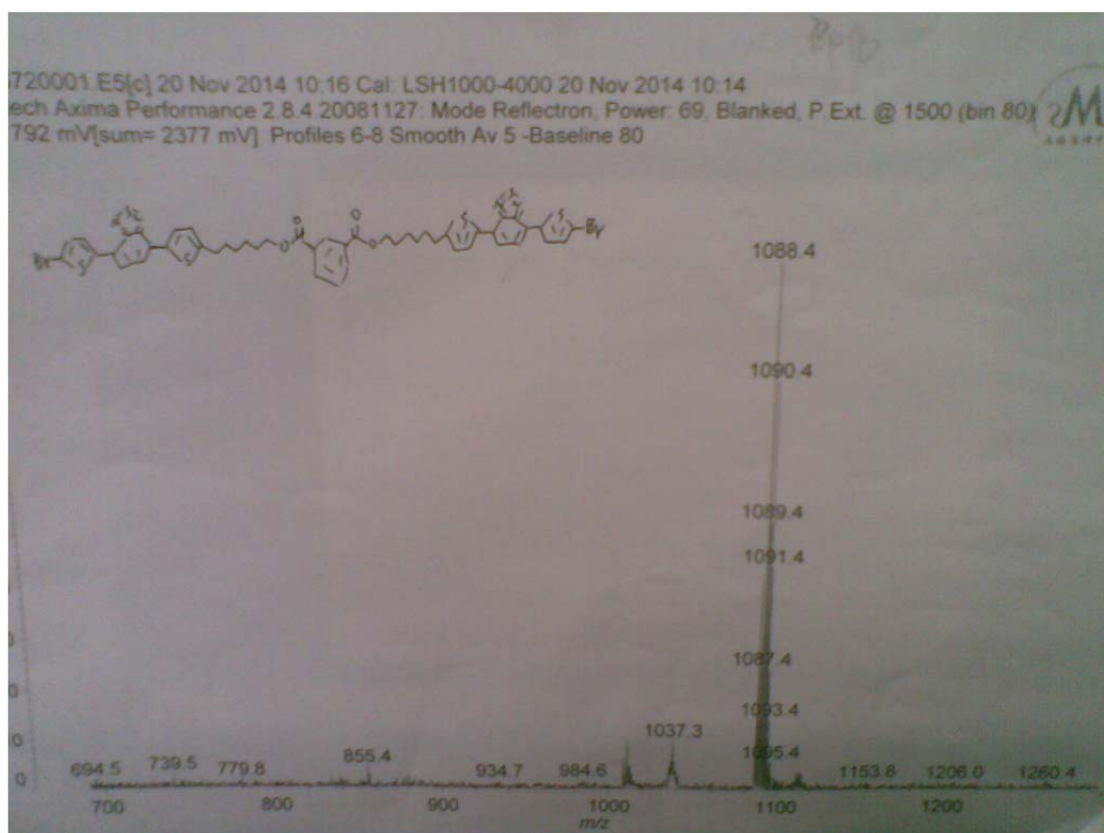


Fig. S8 MALDI-TOF MS of compound 7.

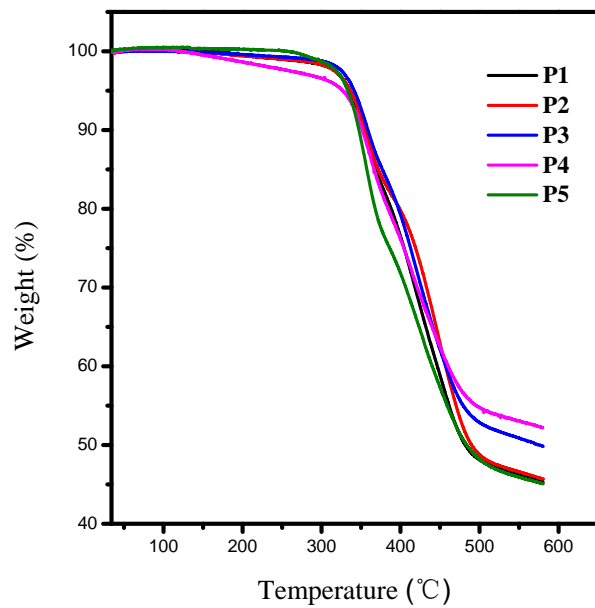


Fig. S9 TGA curves of P1, P2, P3, P4 and P5.

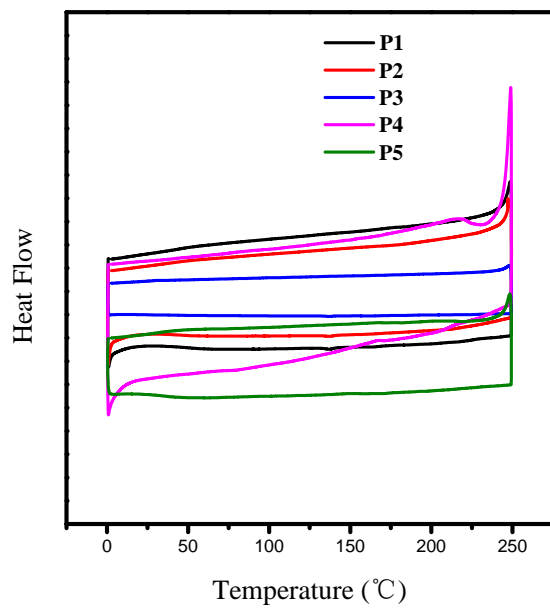


Fig. S10 DSC curves of P1, P2, P3, P4 and P5.

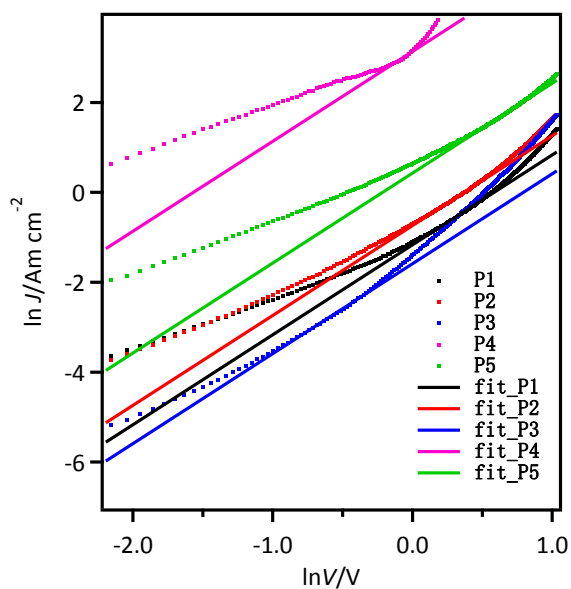


Fig. S11 $\ln J$ - $\ln V$ data in dark of hole-only devices based on **P1**, **P2**, **P3**, **P4** and **P5** in blending with PC_{61}BM and their SCLC fitting curves.

Table S1 Device parameters of **P1**/ PC_{61}BM -based solar cells under different conditions.

Solvent	P1 / PC_{61}BM	Spin-coating speed (rpm)	Annealing ($^{\circ}\text{C}$)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE ^a (%)	
CB	1/1	1000	100	0.61	1.82	26.9	0.30 (0.30)	
		700		0.62	1.67	26.6	0.28 (0.26)	
	1/1.5	1000		0.64	2.33	28.1	0.42 (0.41)	
		1500		0.72	2.21	29.1	0.46 (0.43)	
		2000		0.66	1.87	27.4	0.34 (0.32)	
	1/2	1000		0.72	1.59	28.3	0.33 (0.31)	
o-DCB	1/1.5	1500	60	0.59	2.02	28.6	0.34 (0.33)	
			80	0.65	2.03	28.2	0.37 (0.36)	
			100	0.73	2.19	29.8	0.47 (0.44)	
			120	0.65	2.25	28.5	0.42 (0.41)	
CF	1/1.5	1000	100	0.69	1.92	28.7	0.38 (0.37)	
				1000	0.70	1.41	26.5	0.26 (0.25)
				1500	0.70	2.02	29.9	0.42 (0.40)
		2500		0.68	2.04	26.9	0.37 (0.35)	

^a average value of PCE in the parenthesis.

Table S2 Device parameters of **P2/PC₆₁BM**-based solar cells under different conditions.

Solvent	P2/PC ₆₁ BM	Spin-coating speed (rpm)	Annealing (°C)	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE ^a (%)
o-DCB	1/1	1000	100	0.68	1.43	26.5	0.26 (0.25)
	1/1.5	700		0.72	1.68	27.2	0.33 (0.32)
		1000		0.75	2.04	27.3	0.42 (0.36)
		1500	60	0.66	1.69	28.3	0.32 (0.31)
			80	0.72	1.80	28.5	0.37 (0.35)
			100	0.76	1.99	33.8	0.51 (0.50)
			120	0.55	1.62	28.8	0.26 (0.25)
		140	0.43	1.81	27.0	0.21 (0.18)	
	2000	100	0.70	1.26	32.8	0.29 (0.27)	
	2500		0.58	0.95	33.5	0.18 (0.16)	
	1000		0.69	1.92	28.7	0.38 (0.37)	
	1/2		0.66	2.05	28.0	0.38 (0.36)	
	1/2.5		0.66	1.93	27.7	0.36 (0.33)	
	CB	1/2	1000	0.59	1.77	27.7	0.29 (0.26)
	Toluene			0.72	1.55	29.1	0.32 (0.30)
CF	1/1.5	0.77		1.30	27.7	0.30 (0.28)	
		0.72		2.05	28.7	0.42 (0.41)	
		0.73		2.12	28.2	0.44 (0.41)	
		2500	0.66	1.92	28.1	0.36 (0.33)	

^a average value of PCE in the parenthesis.

Table S3 Device parameters of **P3/PC₆₁BM**-based solar cells under different conditions.

Solvent	P3/PC₆₁BM	Spin-coating speed (rpm)	Annealing (°C)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE ^a (%)
CF	1/1.5	1000	100	0.76	1.54	28.9	0.34 (0.33)
		1500		0.74	1.49	30.8	0.34 (0.28)
		2500		0.76	1.61	27.4	0.33 (0.30)
CB		1000		0.71	1.32	30.4	0.28 (0.26)
		1500		0.73	1.66	30.0	0.36 (0.30)
		2500		0.70	1.49	28.3	0.30 (0.27)
<i>o</i> -DCB		1500	RT	0.58	1.38	26.8	0.21 (0.21)
			100	0.74	2.15	28.8	0.46 (0.42)
			120	0.62	1.26	27.6	0.22 (0.20)

^a average value of PCE in the parenthesis.**Table S4** Device parameters of **P4/PC₆₁BM**-based solar cells under different conditions.

Solvent	P4/PC₆₁BM	Spin-coating speed (rpm)	Annealing (°C)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE ^a (%)
<i>o</i> -DCB	1/1.5	500	RT	0.67	2.22	29.5	0.44 (0.40)
		1500		0.67	2.23	33.6	0.51 (0.43)
		2500		0.79	2.77	31.6	0.69 (0.64)

^a average value of PCE in the parenthesis.

Table S5 Device parameters of P5/PC₆₁BM-based solar cells under different conditions.

Solvent	P5/PC ₆₁ BM	Spin-coating speed (rpm)	Annealing (°C)	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE ^a (%)		
CF	3/1	1500	RT	0.91	1.65	27.4	0.41 (0.38)		
	2/1			0.84	2.56	31.4	0.68 (0.52)		
	1/1			0.84	2.40	35.7	0.72 (0.60)		
			100	0.87	2.32	33.5	0.68 (0.66)		
			120	0.87	1.88	32.0	0.53 (0.51)		
	1/1.5		1500	RT	0.85	2.87	34.2	0.84 (0.80)	
		1000			0.85	2.64	46.5	1.05 (0.93)	
		2000			0.83	2.67	49.4	1.09 (1.00)	
		2500			0.88	2.53	41.3	0.92 (0.76)	
		1/2			1500	0.87	2.12	44.2	0.82 (0.72)
					2500	0.87	2.15	50.7	0.99 (0.89)
	4000		0.84		2.18	52.3	0.96 (0.72)		
CB	1/1.5	1000	0.82		2.84	43.4	1.01 (0.99)		
		1500	0.82		2.85	41.8	0.98 (0.92)		
		2500	0.67		2.60	45.1	0.79 (0.70)		
o-DCB	1/1.5	1000	0.80		2.35	38.5	0.72 (0.52)		
		1500	0.83		2.32	45.8	0.88 (0.82)		
		2500	0.87	1.74	33.8	0.51 (0.49)			

^a average value of PCE in the parenthesis.