

Electronic Supplementary Information for:

**Perylene and naphthalene diimide polymers for all-polymer solar cells:  
A comparative study of chemical copolymerization and physical blend**

Shuixing Dai,<sup>ab</sup> Pei Cheng,<sup>cd</sup> Yuze Lin,<sup>c</sup> Yifan Wang,<sup>cd</sup> Lanchao Ma,<sup>cd</sup> Qidan Ling, <sup>\*a</sup> and Xiaowei Zhan<sup>\*b</sup>

<sup>a</sup> Fujian Key Laboratory of Polymer Materials, College of Materials Science and Engineering, Fujian Normal University, Fuzhou 350007, China.

<sup>b</sup> Department of Materials Science and Engineering, College of Engineering, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Peking University, Beijing 100871, China.

E-mail: xwzhan@pku.edu.cn

<sup>c</sup> Beijing National Laboratory for Molecular Sciences and Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

<sup>d</sup> University of Chinese Academy of Sciences, Beijing 100049, China.

**Table S1** Photovoltaic performance of P3HT: PPDI100 blend with different weight ratio

D/A (w/w) <sup>a</sup>	<i>V</i> <sub>OC</sub> (V)	<i>J</i> <sub>SC</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%) <sup>b</sup>
3.5:1	0.618	2.81	62.8	1.09 (1.07)
3:1	0.621	3.40	65.4	1.38 (1.31)
2.5:1	0.611	2.99	61.3	1.12 (1.11)
1.5:1	0.606	1.90	60.8	0.70 (0.68)
1:1	0.620	0.78	55.5	0.27 (0.26)
1:1.5	0.592	0.18	33.9	0.04 (0.03)

<sup>a</sup>Annealing at 150 °C for 10 min in N<sub>2</sub> atmosphere. <sup>b</sup>Average PCE in brackets.

**Table S2** Photovoltaic performance of P3HT: PPDI75-*co*-NDI25 blend with different weight ratio

D/A (w/w) <sup>a</sup>	<i>V</i> <sub>OC</sub> (V)	<i>J</i> <sub>SC</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%) <sup>b</sup>
3:1	0.639	2.84	55.3	1.00 (0.95)
2.5:1	0.632	2.90	60.3	1.11 (1.05)
2:1	0.638	2.55	56.4	0.92 (0.87)
1:1	0.629	2.45	57.6	0.89 (0.84)
1:2	0.620	2.37	36.6	0.54 (0.52)

<sup>a</sup>Annealing at 150 °C for 10 min in N<sub>2</sub> atmosphere. <sup>b</sup>Average PCE in brackets.

**Table S3** Photovoltaic performance of P3HT: PPDI50-*co*-NDI50 blend with different weight ratio

D/A (w/w) <sup>a</sup>	<i>V</i> <sub>OC</sub> (V)	<i>J</i> <sub>SC</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%) <sup>b</sup>
3:1	0.649	3.22	61.3	1.28 (1.21)
2.5:1	0.652	3.29	61.4	1.32 (1.29)
2:1	0.650	2.35	55.3	0.84 (0.75)
1:1	0.610	1.59	56.1	0.54 (0.49)
1:2	0.595	1.04	58.7	0.36 (0.33)

<sup>a</sup>Annealing at 150 °C for 10 min in N<sub>2</sub> atmosphere. <sup>b</sup>Average PCE in brackets.

**Table S4** Photovoltaic performance of P3HT: PPDI25-*co*-NDI75 blend with different weight ratio

D/A (w/w) <sup>a</sup>	V <sub>OC</sub> (V)	J <sub>SC</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%) <sup>b</sup>
3.5:1	0.682	2.96	54.2	1.09 (1.07)
3:1	0.682	3.62	62.4	1.54 (1.45)
2.5:1	0.681	3.24	65.1	1.44 (1.36)
1.5:1	0.680	2.97	63.5	1.28 (1.22)
1:1	0.677	2.82	57.8	1.10 (1.04)
1:1.5	0.663	2.63	48.3	0.84 (0.77)

<sup>a</sup>Annealing at 150 °C for 10 min in N<sub>2</sub> atmosphere. <sup>b</sup>Average PCE in brackets.

**Table S5** Photovoltaic performance of P3HT: PNNDI100 blend with different weight ratio

D/A (w/w) <sup>a</sup>	V <sub>OC</sub> (V)	J <sub>SC</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%) <sup>b</sup>
2.5:1	0.707	2.18	51.6	0.80 (0.71)
2:1	0.706	2.87	55.3	1.12 (1.06)
1.5:1	0.716	1.95	59.7	0.84 (0.80)
1:1	0.720	1.00	40.6	0.29 (0.28)
1:1.5	0.678	0.69	34.5	0.16 (0.15)

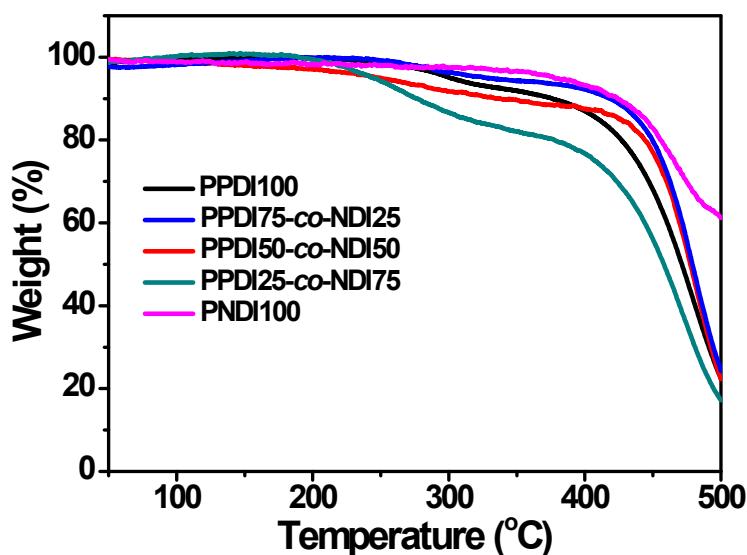
<sup>a</sup>Annealing at 150 °C for 10 min in N<sub>2</sub> atmosphere. <sup>b</sup>Average PCE in brackets.

**Table S6** Photovoltaic performance of P3HT: PPDI-*co*-NDI binary blend and P3HT: PPDI100: PNNDI100 ternary blend with different weight ratio

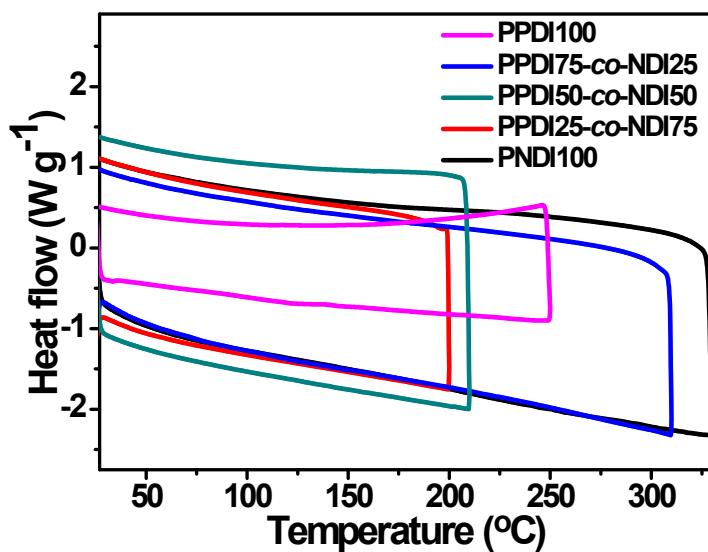
blend	D/A (w/w) <sup>a</sup>	V <sub>OC</sub> (V)	J <sub>SC</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%) <sup>b</sup>
P3HT: PPDI75- <i>co</i> -NDI25	2.5:1	0.632	2.90	60.3	1.11 (1.05)

P3HT: PPDI100: PNDI100	2.5:0.75:0.25	0.608	2.48	49.0	0.74 (0.72)
P3HT: PPDI50- <i>co</i> -NDI50	2.5:1	0.652	3.29	61.4	1.32 (1.29)
P3HT: PPDI100: PNDI100	2.5:0.5:0.5	0.632	2.25	55.4	0.79 (0.74)
P3HT: PPDI75- <i>co</i> -NDI25	3:1	0.682	3.62	62.4	1.54 (1.45)
P3HT: PPDI100: PNDI100	3:0.25:0.75	0.656	2.47	50.9	0.83 (0.80)

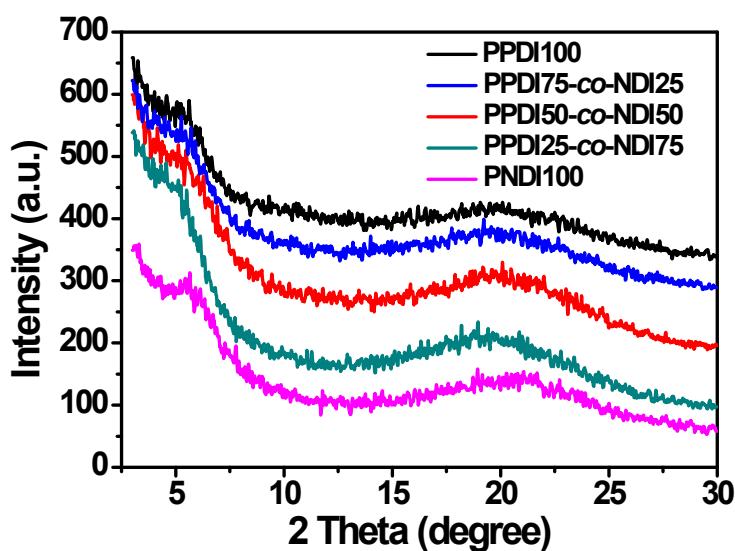
<sup>a</sup>Annealing at 150 °C for 10 min in N<sub>2</sub> atmosphere. <sup>b</sup>Average PCE in brackets.



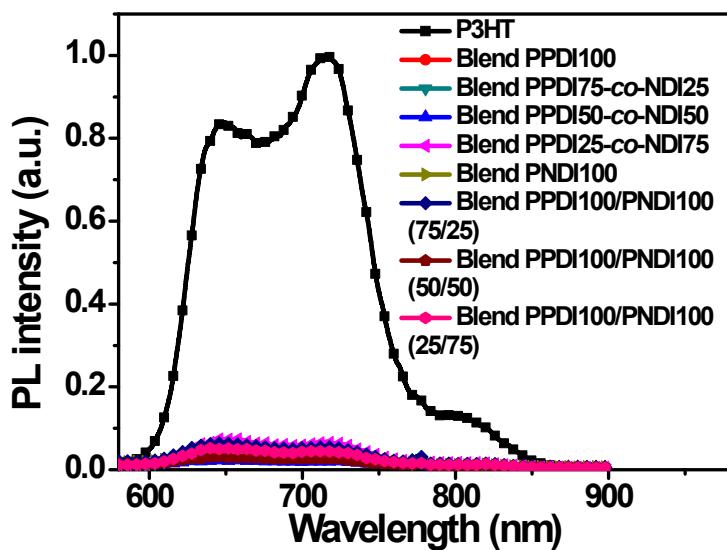
**Fig. S1** TGA curves of PPDI-*co*-NDI copolymers.



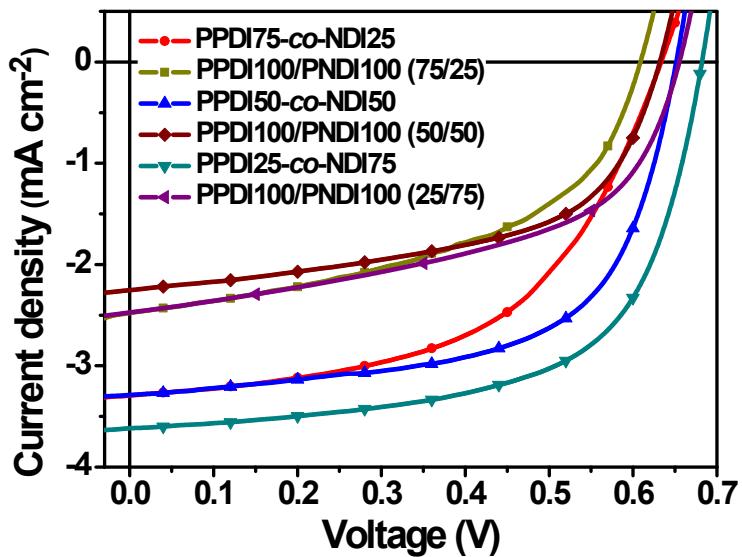
**Fig. S2** DSC curves of PPDI-*co*-NDI copolymers.



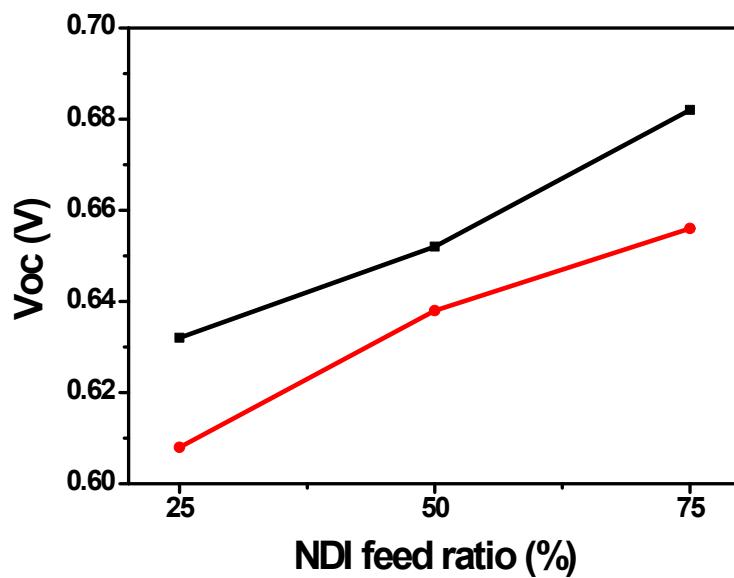
**Fig. S3** XRD patterns of films of PPDI-*co*-NDI copolymers.



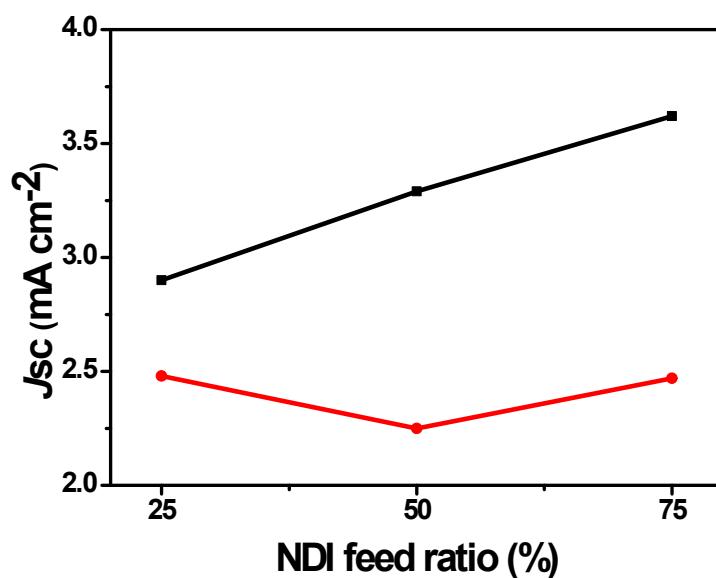
**Fig. S4** Photoluminescence spectra of P3HT neat film, P3HT: PPDI-*co*-NDI binary blended films and P3HT: PPDI100: PNDI100 ternary blended films (excitation at 520 nm).



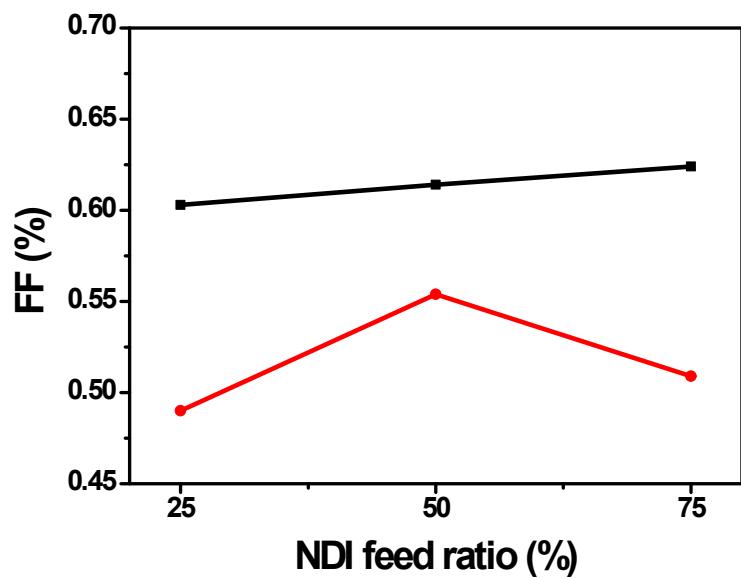
**Fig. S5**  $J$ - $V$  characteristics of device based on P3HT: PPDI-*co*-NDI binary blend and P3HT: PPDI100: PNDI100 ternary blend.



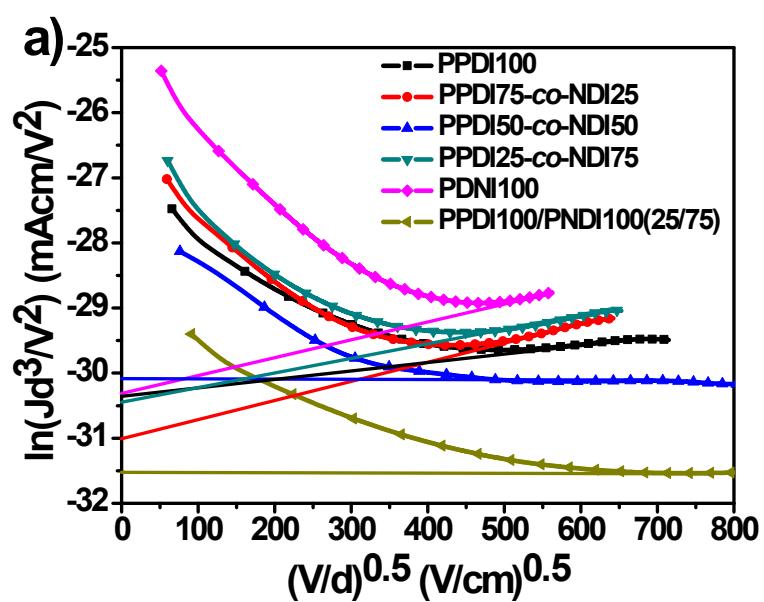
**Fig. S6**  $V_{OC}$  of P3HT: PPDI-*co*-NDI binary blend (black line) and P3HT: PPDI100: PNDI100 ternary blend (red line) vs. NDI feed ratio.

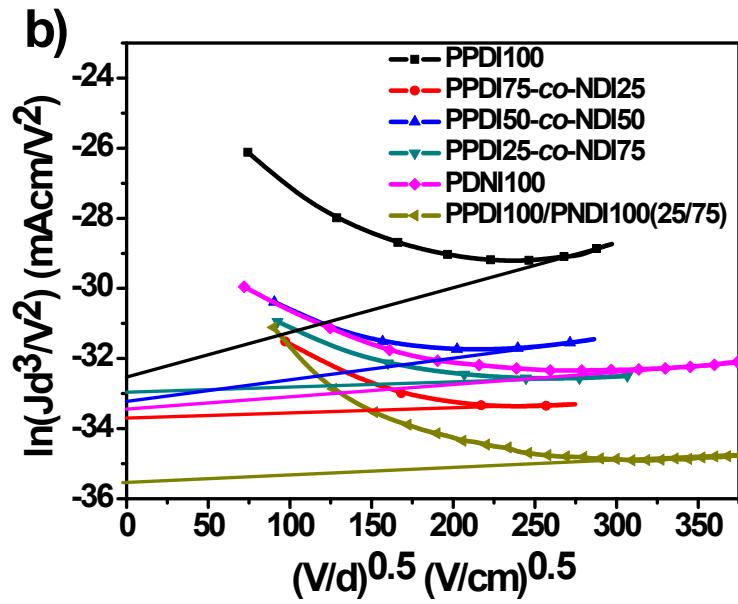


**Fig. S7**  $J_{SC}$  of P3HT: PPDI-*co*-NDI binary blend (black line) and P3HT: PPDI100: PNDI100 ternary blend (red line) vs. NDI feed ratio.

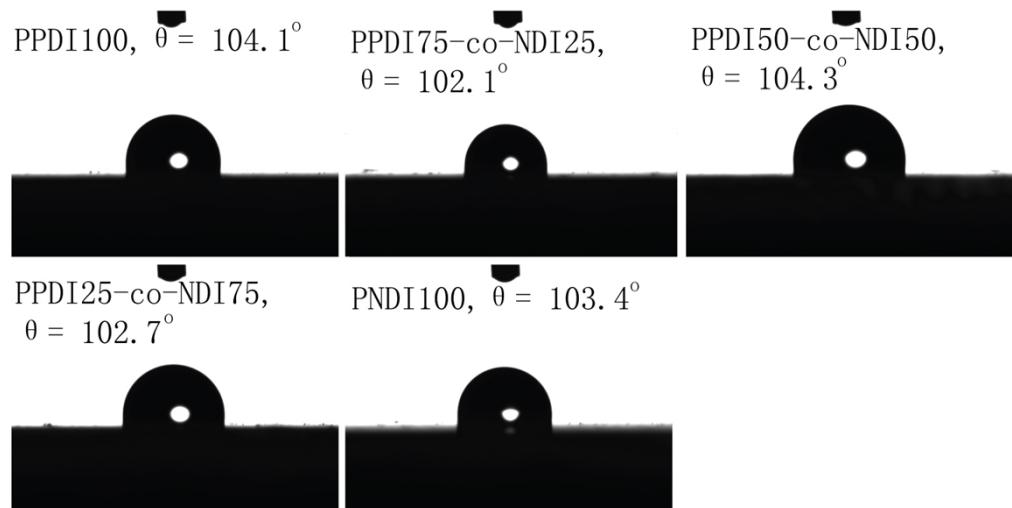


**Fig. S8** FF of P3HT: PPDI-*co*-NDI binary blend (black line) and P3HT: PPDI100: PNDI100 ternary blend (red line) vs. NDI feed ratio.





**Fig. S9** J-V characteristics measured under dark for (a) hole-only and (b) electron-only device based on P3HT: polymer acceptor blended film.



**Fig. S10** The contact angles ( $\theta$ ) of PPDI-*co*-NDI neat films spin-coated on a quartz substrate.