## Supporting information

## Enhancing photovoltaic properties of low bandgap terpolymers based on benzodithiophene and phenanthrophenazine by introducing different second acceptor units

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## 1. Photovoltaic properties of terpolymer based PSCs at different conditions



Fig. S1a *J-V* curves of the PBDTT-PPzIID/PC<sub>71</sub>BM-based PSCs at different blend ratios (w/w) under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

Table S1a Photovoltaic properties of the PBDTT-PPzIID/PC\_{71}BM-based PSCs at

| D/A Ratio | $J_{\rm sc}$ / mA cm <sup>-2</sup> | $V_{\rm oc}/~{ m V}$ | FF/ % | PCE <sub>max</sub> /% |
|-----------|------------------------------------|----------------------|-------|-----------------------|
| 1/1       | 2.67                               | 0.76                 | 26.3  | 0.54                  |
| 1/2       | 4.05                               | 0.75                 | 39.4  | 1.19                  |
| 1/3       | 4.19                               | 0.76                 | 45.5  | 1.45                  |
| 1/4       | 3.91                               | 0.76                 | 43.9  | 1.31                  |

different blend ratios (w/w) under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.



**Fig. S1b** *J-V* curves of the PBDTT-PPzDPP/PC<sub>71</sub>BM-based PSCs at different blend ratios (*w/w*) under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

Table S1b Photovoltaic properties of the PBDTT-PPzDPP/PC71BM-based PSCs at

| D/A Ratio | $J_{\rm sc}$ / mA cm <sup>-2</sup> | $V_{\rm oc}/~{ m V}$ | FF/ % | PCE <sub>max</sub> /% |
|-----------|------------------------------------|----------------------|-------|-----------------------|
| 1/1       | 3.49                               | 0.69                 | 35.8  | 0.86                  |
| 1/2       | 4.34                               | 0.72                 | 48.7  | 1.51                  |
| 1/3       | 3.96                               | 0.69                 | 49.3  | 1.34                  |

different blend ratios (w/w) under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.



**Fig. S2a** *J-V* curves of the PBDTT-PPzIID/PC<sub>71</sub>BM-based PSCs at different DIO additive concentrations under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

**Table S2a** Photovoltaic properties of the PBDTT-PPzIID/PC<sub>71</sub>BM-based PSCs at different DIO additive concentrations under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

| DIO additive concentrations | $J_{\rm sc}/~{ m mA~cm^{-2}}$ | V <sub>oc</sub> / V | FF/ % | PCE <sub>max</sub> /% |
|-----------------------------|-------------------------------|---------------------|-------|-----------------------|
| 1%                          | 4.75                          | 0.76                | 51.1  | 1.85                  |
| 2%                          | 6.27                          | 0.76                | 52.2  | 2.49                  |
| 3%                          | 7.14                          | 0.76                | 48.9  | 2.66                  |



**Fig. S2b** *J-V* curves of the PBDTT-PPzDPP/PC<sub>71</sub>BM-based PSCs at different DIO additive concentrations under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

**Table S2b** Photovoltaic properties of the PBDTT-PPzDPP/PC<sub>71</sub>BM-based PSCs at different DIO additive concentrations under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

| DIO additive concentrations | $J_{\rm sc}/~{\rm mA~cm^{-2}}$ | $V_{ m oc}/~{ m V}$ | FF/ % | PCE <sub>max</sub> /% |
|-----------------------------|--------------------------------|---------------------|-------|-----------------------|
| 1%                          | 4.55                           | 0.70                | 51.1  | 1.76                  |
| 2%                          | 5.58                           | 0.70                | 59.4  | 2.32                  |
| 3%                          | 6.93                           | 0.70                | 58.7  | 2.85                  |



**Fig. S3a** *J-V* curves of the PBDTT-PPzIID/PC<sub>71</sub>BM-based PSCs at different spin-

coating rates under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

Table S3a Photovoltaic properties of the PBDTT-PPzIID/PC71BM-based PSCs at

| spin-coating<br>rates/ rpm | film<br>thickness/ nm | $J_{\rm sc}/~{ m mA~cm^{-2}}$ | $V_{\rm oc}/{ m V}$ | FF/ % | PCE <sub>max</sub> /% |
|----------------------------|-----------------------|-------------------------------|---------------------|-------|-----------------------|
| 1750                       | 103                   | 7.79                          | 0.75                | 51.8  | 3.01                  |
| 2000                       | 96                    | 7.55                          | 0.76                | 53.7  | 3.09                  |
| 2250                       | 90                    | 7.45                          | 0.76                | 55.0  | 3.12                  |
| 2500                       | 85                    | 7.41                          | 0.76                | 54.9  | 3.10                  |

different spin-coating rates under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.



**Fig. S3b** *J-V* curves of the PBDTT-PPzDPP/PC<sub>71</sub>BM-based PSCs at different spincoating rates under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

**Table S3b** Photovoltaic properties of the PBDTT-PPzDPP/PC<sub>71</sub>BM-based PSCs at

| spin-coating<br>rates/ rpm | film<br>thickness/ nm | $J_{\rm sc}/~{\rm mA~cm^{-2}}$ | $V_{ m oc}/~{ m V}$ | FF/ % | PCE <sub>max</sub> /% |
|----------------------------|-----------------------|--------------------------------|---------------------|-------|-----------------------|
| 1750                       | 107                   | 9.52                           | 0.69                | 58.5  | 3.82                  |
| 2000                       | 98                    | 9.67                           | 0.69                | 61.3  | 4.06                  |
| 2250                       | 93                    | 10.0                           | 0.69                | 60.9  | 4.18                  |
| 2500                       | 89                    | 9.64                           | 0.69                | 60.2  | 3.98                  |

different spin-coating rates under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.



**Fig. S4** *J-V* curves of the terpolymers/PC<sub>71</sub>BM-based PSCs at different CB/CHCl<sub>3</sub> ratios under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

Table S4 Photovoltaic properties of the terpolymers/PC<sub>71</sub>BM-based PSCs at different

| Terpolymers               | $J_{\rm sc}$ / mA cm <sup>-2</sup> | $V_{\rm oc}/~{ m V}$ | FF/ % | PCE <sub>max</sub> /% |
|---------------------------|------------------------------------|----------------------|-------|-----------------------|
| PBDTT-PPzIID <sup>a</sup> | 8.20                               | 0.73                 | 51.3  | 3.08                  |
| PBDTT-PPzIID <sup>b</sup> | 7.49                               | 0.73                 | 50.6  | 2.77                  |
| PBDTT-PPzDPP a            | 11.2                               | 0.67                 | 60.2  | 4.51                  |
| PBDTT-PPzDPP <sup>b</sup> | 8.77                               | 0.69                 | 62.6  | 3.79                  |

CB/CHCl<sub>3</sub> ratios under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

<sup>a</sup> CB/CHCl<sub>3</sub> ratio is 9/1; <sup>b</sup> CB/CHCl<sub>3</sub> ratio is 8/2.



**Fig. S5a** *J-V* curves of the PBDTT-PPzIID/PC<sub>71</sub>BM-based PSCs at different temperature under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

Table S5a Photovoltaic properties of the PBDTT-PPzIID/PC $_{71}$ BM-based PSCs at

| Temperature/ °C | $J_{\rm sc}$ / mA cm <sup>-2</sup> | $V_{\rm oc}/~{ m V}$ | FF/ % | PCE <sub>max</sub> /% |
|-----------------|------------------------------------|----------------------|-------|-----------------------|
| 80              | 8.43                               | 0.75                 | 51.5  | 3.24                  |
| 90              | 7.73                               | 0.76                 | 52.0  | 3.06                  |
| 100             | 5.30                               | 0.78                 | 53.3  | 2.19                  |

different temperature under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.



**Fig. S5b** *J-V* curves of the PBDTT-PPzDPP/PC<sub>71</sub>BM-based PSCs at different temperature under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

Table S5b Photovoltaic properties of the PBDTT-PPzDPP/PC71BM-based PSCs at

| Temperature/ °C | $J_{\rm sc}$ / mA cm <sup>-2</sup> | $V_{\rm oc}/~{ m V}$ | FF/ % | PCE <sub>max</sub> /% |
|-----------------|------------------------------------|----------------------|-------|-----------------------|
| 80              | 9.94                               | 0.69                 | 60.5  | 4.12                  |
| 90              | 8.49                               | 0.70                 | 60.6  | 3.61                  |
| 100             | 4.75                               | 0.72                 | 58.8  | 2.00                  |

different temperature under illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.