

## Supporting Information

### **Syntheses and properties of low band gap polymers based on thienyl thienoindole as new electron rich unit for organic photovoltaics**

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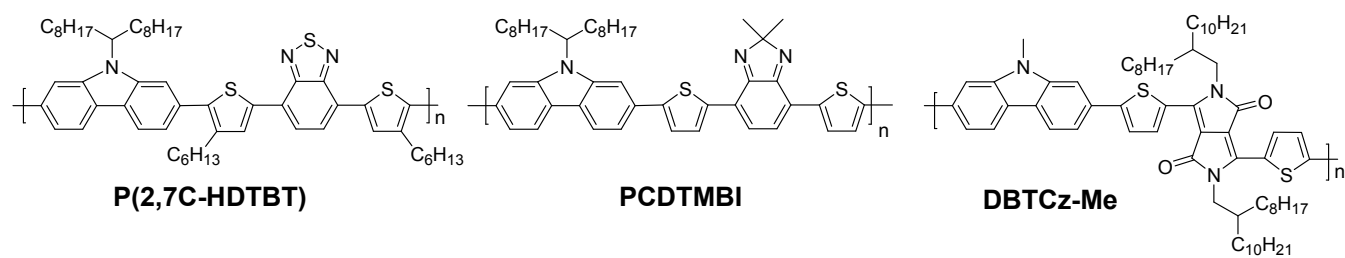
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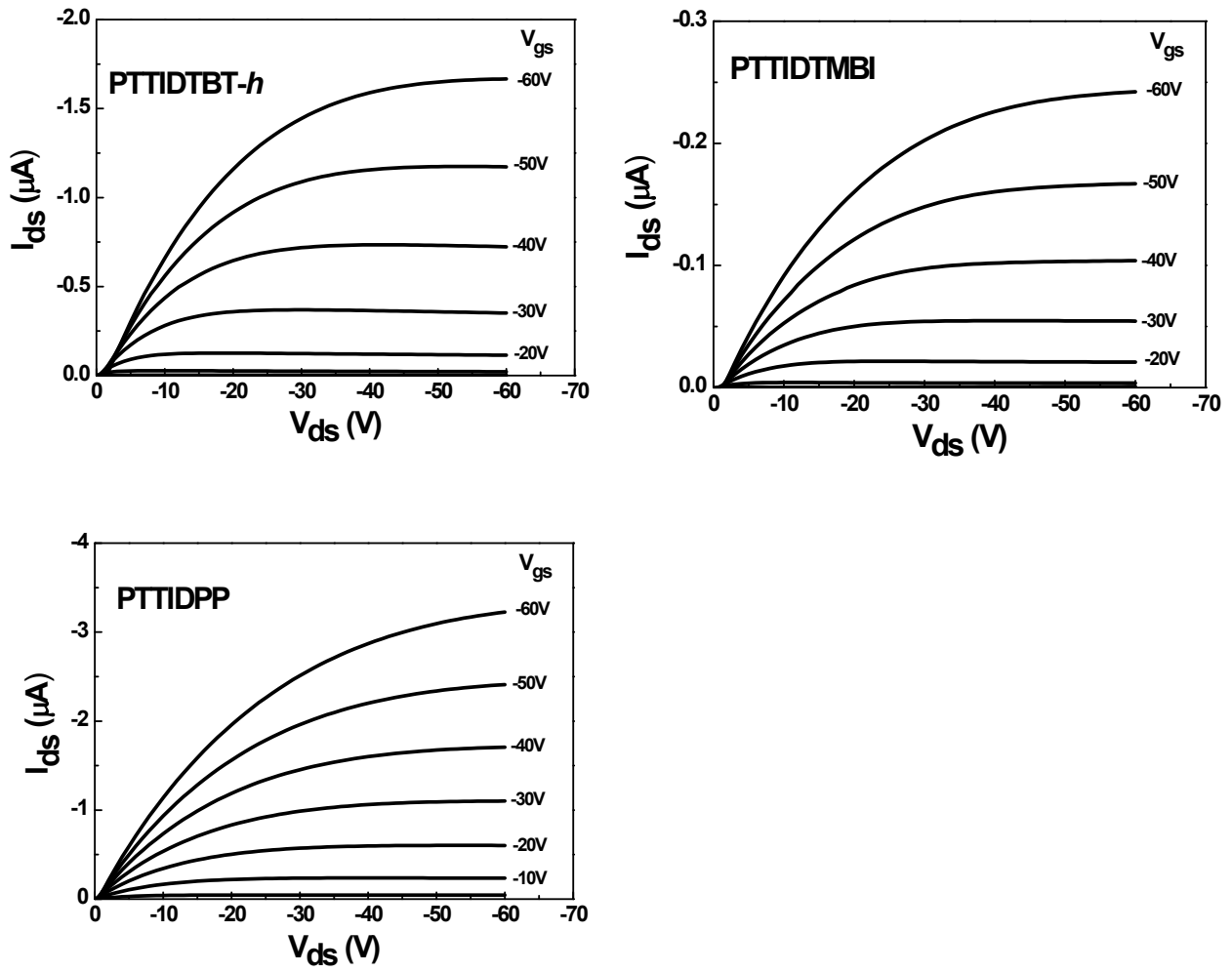
**Scheme S1.** Chemical structures of P(2,7C-HDTBT), PCDTMBI and DBTCz-Me.



**Table S1.** OFET device characteristics of polymers

| polymer            | Mobility<br>( $\text{cm}^2\text{s}^{-1}\text{V}^{-1}$ ) | $I_{\text{off}}$<br>(A) | $I_{\text{on}}$<br>(A) | $I_{\text{on}}/I_{\text{off}}$ | $V_{\text{T}}$<br>(V) |
|--------------------|---------------------------------------------------------|-------------------------|------------------------|--------------------------------|-----------------------|
| PTTIDTBT- <i>h</i> | $3.56 \times 10^{-3}$                                   | $3.35 \times 10^{-10}$  | $4.20 \times 10^{-6}$  | $1.25 \times 10^4$             | 7.98                  |
| PTTIDTMBI          | $3.30 \times 10^{-4}$                                   | $3.66 \times 10^{-10}$  | $4.09 \times 10^{-7}$  | $1.12 \times 10^3$             | -4.43                 |
| PTTIDPP            | $3.01 \times 10^{-3}$                                   | $3.42 \times 10^{-10}$  | $5.85 \times 10^{-6}$  | $1.71 \times 10^4$             | -2.36                 |

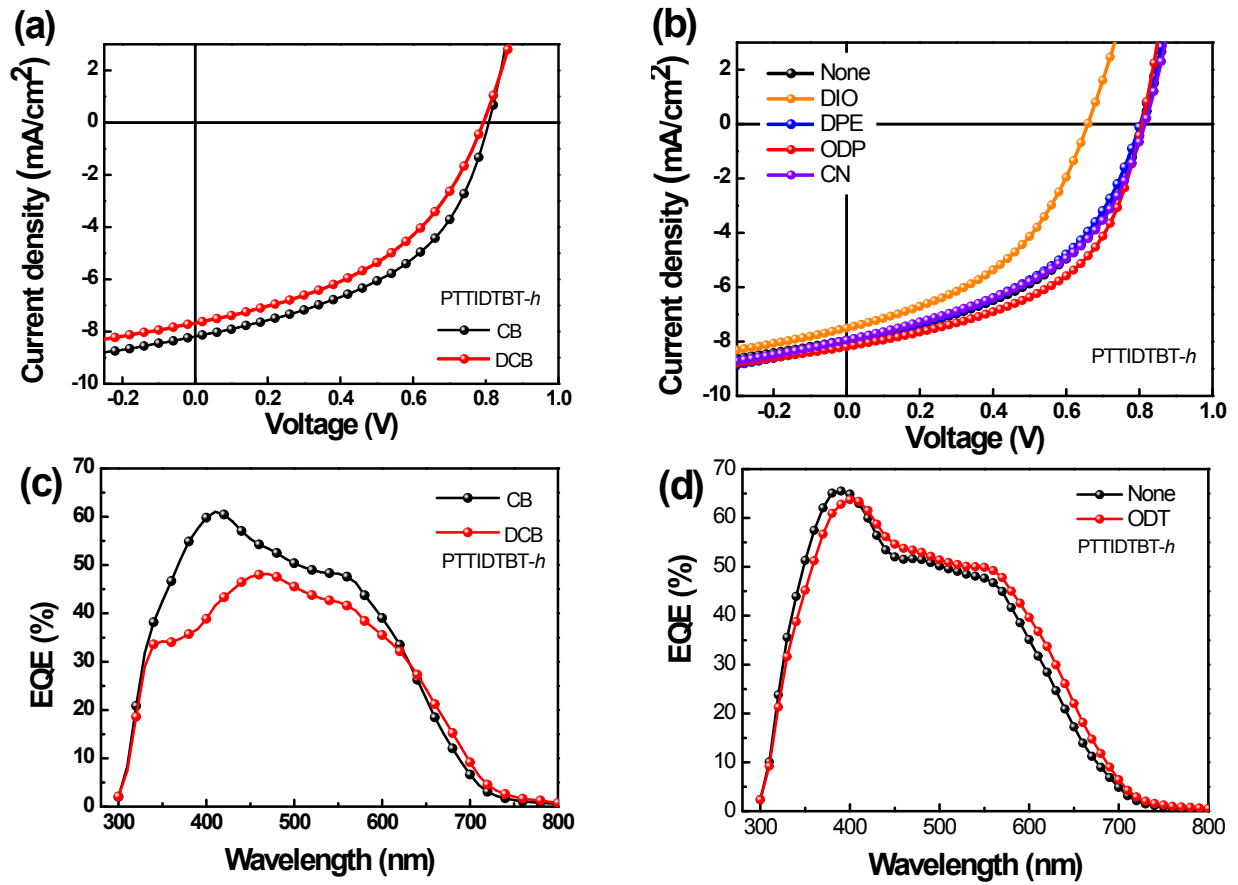
**Figure S1.** Output characteristics of polymers



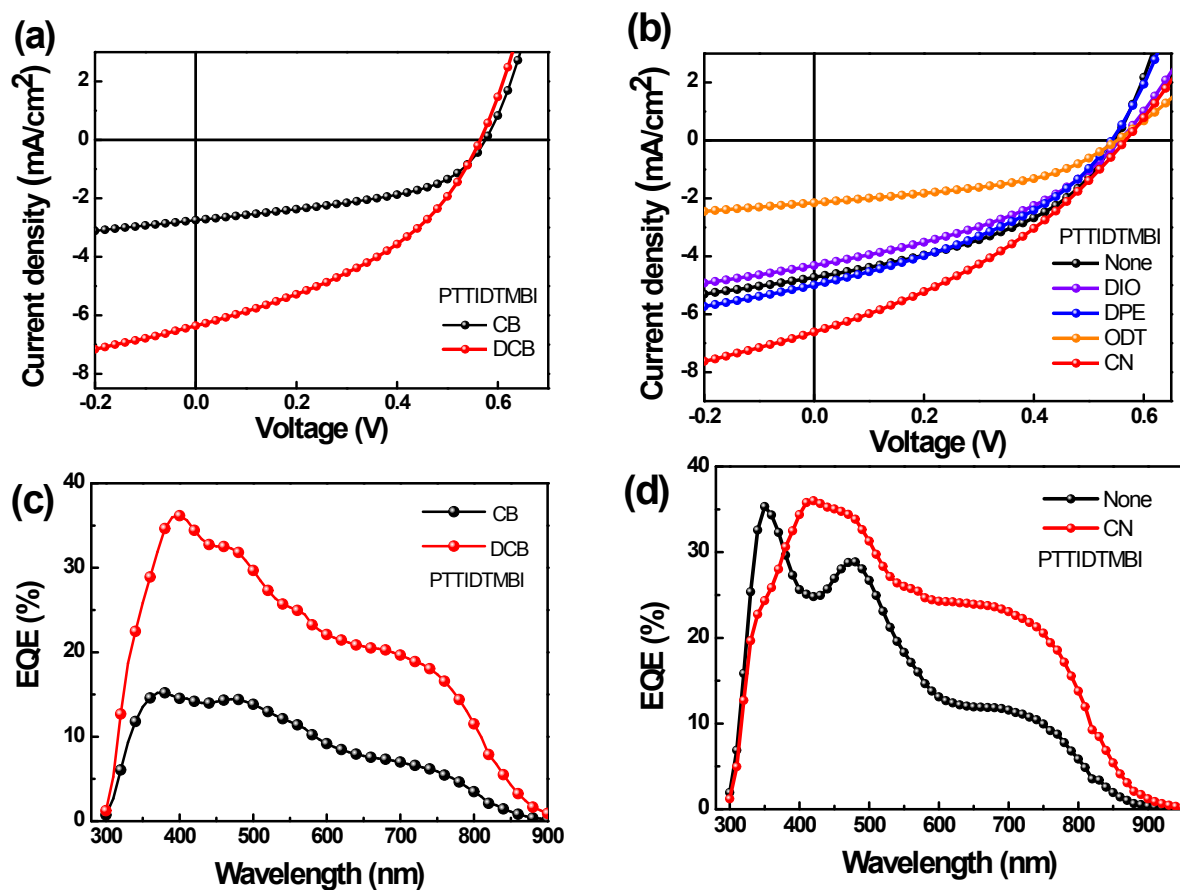
**Table S2.** Photovoltaic properties of the polymer solar cells

| polymer            | sol  | ratio | additive | thickness (nm) | thermal annealing (°C, min) | $J_{sc}$ (mA/cm <sup>2</sup> ) | $V_{oc}$ (V) | $FF$ | PCE (%) |
|--------------------|------|-------|----------|----------------|-----------------------------|--------------------------------|--------------|------|---------|
| PTTIDTBT- <i>h</i> | CB   | 1:1   | None     | 140            | None                        | 5.04                           | 0.71         | 0.35 | 1.26    |
|                    |      |       |          | 165            | None                        | 7.61                           | 0.74         | 0.39 | 2.20    |
|                    |      | 1:3   | None     | 165            | (80, 5)                     | 7.68                           | 0.77         | 0.41 | 2.42    |
|                    |      |       |          |                | None                        | 7.99                           | 0.79         | 0.43 | 2.67    |
|                    |      |       |          | 175            | (80, 5)                     | 7.72                           | 0.77         | 0.42 | 2.50    |
|                    |      |       |          |                | None                        | 8.19                           | 0.81         | 0.47 | 3.14    |
|                    | ODCB | 1:3   | None     | 185            | None                        | 7.96                           | 0.81         | 0.47 | 3.00    |
|                    |      |       | 2% DIO   | 130            | None                        | 7.50                           | 0.66         | 0.44 | 2.18    |
|                    |      |       | 2% DPE   | 150            | None                        | 8.05                           | 0.80         | 0.45 | 2.93    |
|                    |      |       | 2% ODT   | 130            | None                        | 8.19                           | 0.81         | 0.51 | 3.35    |
|                    |      |       | 2% CN    | 130            | None                        | 7.95                           | 0.82         | 0.46 | 2.98    |
|                    |      |       |          |                |                             |                                |              |      |         |
| PTTIDTMBI          | CB   | 1:1   | None     | 175            | None                        | 2.01                           | 0.58         | 0.46 | 0.53    |
|                    |      |       |          |                | (80, 5)                     | 2.01                           | 0.58         | 0.45 | 0.53    |
|                    |      | 1:3   |          | 165            | None                        | 2.75                           | 0.58         | 0.48 | 0.76    |
|                    |      |       |          |                | None                        | 2.10                           | 0.56         | 0.55 | 0.65    |
|                    | ODCB | 1:1   | None     | 160            | None                        | 6.36                           | 0.57         | 0.40 | 1.44    |
|                    |      | 1:3   | 2% DIO   | 165            | None                        | 4.31                           | 0.56         | 0.39 | 0.93    |
|                    |      |       | 2% DPE   | 120            | None                        | 4.99                           | 0.54         | 0.37 | 1.01    |
|                    |      |       | 2% ODT   | 120            | None                        | 2.15                           | 0.55         | 0.45 | 0.53    |
|                    |      |       | 2% CN    | 165            | None                        | 6.62                           | 0.57         | 0.35 | 1.30    |
|                    |      |       |          |                |                             |                                |              |      |         |
| PTTIDPP            | CB   | 1:1   | None     | 170            | None                        | 4.85                           | 0.49         | 0.42 | 1.00    |
|                    |      |       |          |                | None                        | 2.25                           | 0.43         | 0.47 | 0.46    |
|                    |      | 1:3   |          | 150            | (80, 5)                     | 2.26                           | 0.41         | 0.44 | 0.41    |
|                    |      |       |          |                | None                        | 2.75                           | 0.46         | 0.56 | 0.71    |
|                    | ODCB | 1:1   | None     | 180            | None                        | 6.01                           | 0.49         | 0.44 | 1.30    |
|                    |      |       | 2% DIO   | 155            | None                        | 6.38                           | 0.47         | 0.33 | 0.98    |
|                    |      |       | 2% DPE   | 155            | None                        | 7.08                           | 0.45         | 0.41 | 1.33    |

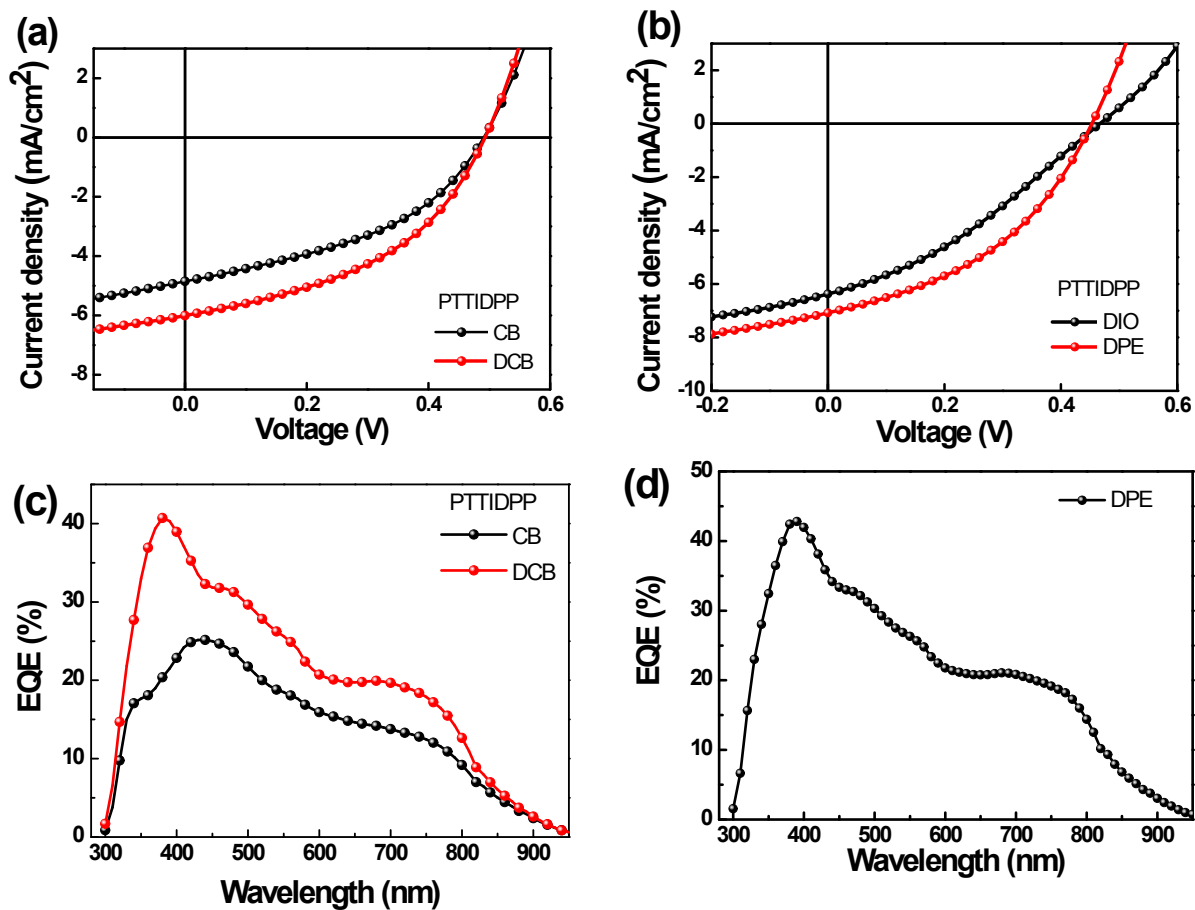
**Figure S2.** Current density-voltage characteristics of the (a) PTTIDTBT-*h*:PC<sub>71</sub>BM (1:3) blend under the illumination of AM 1.5G, 100 mW/cm<sup>2</sup>, (b) PTTIDTBT-*h*:PC<sub>71</sub>BM (1:3) processed with additives. EQE curves of the (c) PTTIDTBT-*h*:PC<sub>71</sub>BM (1:3), (d) PTTIDTBT-*h*:PC<sub>71</sub>BM (1:3) processed with DPE under the illumination of AM 1.5G, 100 mW/cm<sup>2</sup>



**Figure S3.** Current density-voltage characteristics of the (a) PTTIDTMBI:PC<sub>71</sub>BM (1:1) blend under the illumination of AM 1.5G, 100 mW/cm<sup>2</sup>, (b) PTTIDTMBI:PC<sub>71</sub>BM (1:1) processed with additives. EQE curves of the (c) PTTIDTMBI:PC<sub>71</sub>BM (1:1), (d) PTTIDTMBI:PC<sub>71</sub>BM (1:1) processed with CN under the illumination of AM 1.5G, 100 mW/cm<sup>2</sup>



**Figure S4.** Current density-voltage characteristics of the (a) PTTIDPP:PC<sub>71</sub>BM (1:1) blend under the illumination of AM 1.5G, 100 mW/cm<sup>2</sup>, (b) PTTIDPP:PC<sub>71</sub>BM (1:1) processed with additives. EQE curves of the (c) PTTIDPP:PC<sub>71</sub>BM (1:1), (d) PTTIDPP:PC<sub>71</sub>BM (1:1) processed with DPE under the illumination of AM 1.5G, 100 mW/cm<sup>2</sup>



**Figure S6.** The GIWAX data of polymers/PC<sub>71</sub>BM blend films. 2D patterns of polymers (a, c, e) and 1D patterns of out-of-plane direction (b, d, f).

