Electronic supplementary information (ESI)

## Benzothiadiazole-benzodithiophene-based random copolymers for efficient thick-film polymer solar cells via solvent vapor annealing approach

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**Fig. S1** J-V curves of solar cells based on **P2FBT-75**:PC<sub>71</sub>BM system with different D/A ratios.

 Table S1
 The photovoltaic parameters with different D/A ratios based on P2FBT 

 75:PC<sub>71</sub>BM system

| P2FBT-                                |           |                 | _              |      |                        |
|---------------------------------------|-----------|-----------------|----------------|------|------------------------|
| <b>75</b> :PC <sub>71</sub> BM Weight | Thickness | V <sub>oc</sub> | $J_{ m sc}$    | FF   | $PCE_{max}(PCE_{ave})$ |
| Ratio                                 | (nm)      | (V)             | $(mA cm^{-2})$ |      | (%)                    |
| 1:1                                   | 150       | 0.92            | 4.42           | 0.45 | 1.88 (1.84)            |
| 1:1.5                                 | 130       | 0.91            | 5.12           | 0.51 | 2.36 (2.33)            |
| 1:2                                   | 130       | 0.91            | 4.98           | 0.52 | 2.36 (2.31)            |
| 1:2.5                                 | 140       | 0.91            | 4.11           | 0.55 | 2.03 (1.96)            |



**Fig. S2** J-V curves of solar cells based on **P2FBT-50**:PC<sub>71</sub>BM system with different D/A ratios.

Table S2 The photovoltaic parameters with different D/A ratios based on P2FBT-50:PC<sub>71</sub>BM system

| <b>P2FBT-50</b> :PC <sub>71</sub> BM | Thickness | $V_{\rm oc}$ | $J_{ m sc}$    | FF   | PCE <sub>max</sub> (PCE <sub>ave</sub> ) |
|--------------------------------------|-----------|--------------|----------------|------|--|
| Weight Ratio                         | (nm)      | (V)          | $(mA cm^{-2})$ |      | (%)                                      |
| 1:1                                  | 130       | 0.90         | 4.42           | 0.42 | 1.76 (1.57)                              |
| 1:1.5                                | 140       | 0.88         | 5.54           | 0.45 | 2.23 (2.20)                              |
| 1:2                                  | 140       | 0.89         | 4.50           | 0.47 | 1.91 (1.85)                              |
| 1:2.5                                | 130       | 0.87         | 4.03           | 0.52 | 1.82 (1.80)                              |



**Fig. S3** J-V curves of solar cells based on **P2FBT-25**:PC<sub>71</sub>BM system with different D/A ratios.

**Table S3** The photovoltaic parameters with different D/A ratios based on P2FBT-25:PC71BM system

| <b>P2FBT-25</b> :PC <sub>71</sub> BM | Thickness | $V_{\rm oc}$ | $J_{ m sc}$    | FF   | PCE <sub>max</sub> (PCE <sub>ave</sub> ) |
|--------------------------------------|-----------|--------------|----------------|------|--|
| Weight Ratio                         | (nm)      | (V)          | $(mA cm^{-2})$ |      | (%)                                      |
| 1:1                                  | 140       | 0.93         | 5.27           | 0.48 | 2.39 (2.12)                              |
| 1:1.5                                | 150       | 0.91         | 6.03           | 0.48 | 2.67 (2.64)                              |
| 1:2                                  | 150       | 0.91         | 5.09           | 0.52 | 2.41 (2.39)                              |
| 1:2.5                                | 150       | 0.91         | 3.92           | 0.49 | 1.76 (1.70)                              |



**Fig. S4** J-V curves of solar cells based on **P2FBT-75**:PC<sub>71</sub>BM (1:1.5) system with different spin speed (r/s).

**Table S4** The photovoltaic parameters based on **P2FBT-75**:PC71BM (1:1.5) systemwith different spin speed (r/s)

| <b>P2FBT-75</b> :PC <sub>71</sub> BM | Thickness | $V_{\rm oc}$ | $J_{ m sc}$    | FF   | PCE <sub>max</sub> (PCE <sub>ave</sub> ) |
|--------------------------------------|-----------|--------------|----------------|------|--|
| Spin Speed (r/s)                     | (nm)      | (V)          | $(mA cm^{-2})$ |      | (%)                                      |
| 800                                  | 130       | 0.91         | 5.12           | 0.51 | 2.36 (2.33)                              |
| 1000                                 | 100       | 0.92         | 5.92           | 0.58 | 3.16 (3.13)                              |



**Fig. S5** J-V curves of solar cells based on **P2FBT-50**:PC<sub>71</sub>BM (1:1.5) system with different spin speed (r/s).

**Table S5** The photovoltaic parameters based on **P2FBT-50**:PC<sub>71</sub>BM (1:1.5) system with different spin speed (r/s)

| <b>P2FBT-50</b> :PC <sub>71</sub> BM | Thickness | $V_{\rm oc}$ | $J_{ m sc}$    | FF   | $PCE_{max}(PCE_{ave})$ |
|--------------------------------------|-----------|--------------|----------------|------|------------------------|
| Spin Speed (r/s)                     | (nm)      | (V)          | $(mA cm^{-2})$ |      | (%)                    |
| 800                                  | 140       | 0.88         | 5.54           | 0.45 | 2.23 (2.20)            |
| 1000                                 | 100       | 0.90         | 5.02           | 0.57 | 2.59 (2.51)            |



**Fig. S6** J-V curves of solar cells based on **P2FBT-25**:PC<sub>71</sub>BM (1:1.5) system with different spin speed (r/s).

**Table S6** The photovoltaic parameters based on **P2FBT-25**:PC71BM (1:1.5) systemwith different spin speed (r/s)

| <b>P2FBT-25</b> :PC <sub>71</sub> BM | Thickness | $V_{\rm oc}$ | $J_{ m sc}$    | FF   | PCE <sub>max</sub> (PCE <sub>ave</sub> ) |
|--------------------------------------|-----------|--------------|----------------|------|--|
| Spin Speed (r/s)                     | (nm)      | (V)          | $(mA cm^{-2})$ |      | (%)                                      |
| 800                                  | 150       | 0.91         | 6.03           | 0.48 | 2.67 (2.64)                              |
| 1000                                 | 100       | 0.93         | 5.80           | 0.55 | 2.98 (2.91)                              |

**75**:PC<sub>71</sub>BM system  $J_{\rm sc}$  (mA cm<sup>-2</sup>) Active layer (1:1.5) DIO  $V_{\rm oc}$  (V) FF PCE (%)<sup>*a*</sup> **P2FBT-75**: PC<sub>71</sub>BM 0.5% 0.88 7.05 0.45 2.83 (2.81) **P2FBT-75**: PC<sub>71</sub>BM 1% 0.91 8.99 0.57 4.71 (4.64) **P2FBT-75**: PC<sub>71</sub>BM 2% 0.88 7.36 0.46 3.02 (2.95) **P2FBT-75**: PC<sub>71</sub>BM 3% 0.88 7.23 0.42 2.71 (2.70) **P2FBT-75**: PC<sub>71</sub>BM 5% 0.90 7.72 0.43 3.04 (3.00)

 Table S7
 Photovoltaic parameters with different contents of DIO based on P2FBT

<sup>*a*</sup> The values in parentheses stand for the average PCEs from over 10 devices.



**Fig. S7** PCE versus difference solvent vapor annealing time (s) of the optimal PSC devices based on **P2FBT-75**:PC<sub>71</sub>BM system.

**Table S8** The optimal photovoltaic parameters with  $CH_2Cl_2$  and THF vapor annealingwith 30 s of optimal PSC devices

| Active layer (1:1.5)                  | SVA                             | $V_{\rm oc}\left({ m V} ight)$ | $J_{\rm sc}$ (mA cm <sup>-2</sup> ) | FF   | PCE (%) <sup>a</sup> |
|---------------------------------------|---------------------------------|--------------------------------|-------------------------------------|------|----------------------|
| <b>P2FBT-2</b> 5: PC <sub>71</sub> BM | CH <sub>2</sub> Cl <sub>2</sub> | 0.87                           | 8.31                                | 0.51 | 3.71 (3.66)          |
| <b>P2FBT-50</b> : PC <sub>71</sub> BM | $CH_2Cl_2$                      | 0.86                           | 8.48                                | 0.43 | 3.17 (2.92)          |
| <b>P2FBT-75</b> : PC <sub>71</sub> BM | $CH_2Cl_2$                      | 0.89                           | 10.15                               | 0.53 | 4.81 (4.69)          |
| <b>P2FBT-75</b> : PC <sub>71</sub> BM | THF                             | 0.90                           | 6.91                                | 0.43 | 2.74 (2.49)          |

<sup>*a*</sup> The values in parentheses stand for the average PCEs from over 10 devices.