

## Supporting Information

### Near-infrared absorbing pyrrolopyrrole aza-BODIPY-based donor-acceptor polymers with reasonable photoresponse

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- i. <sup>1</sup>H NMR and absorption spectra of **P1**, **P2** and **P3**
- ii. Photovoltaic parameters for OPV device based on **P1–P3**:PC<sub>71</sub>BM

i.  $^1\text{H}$  NMR and absorption spectra of P1, P2 and P3

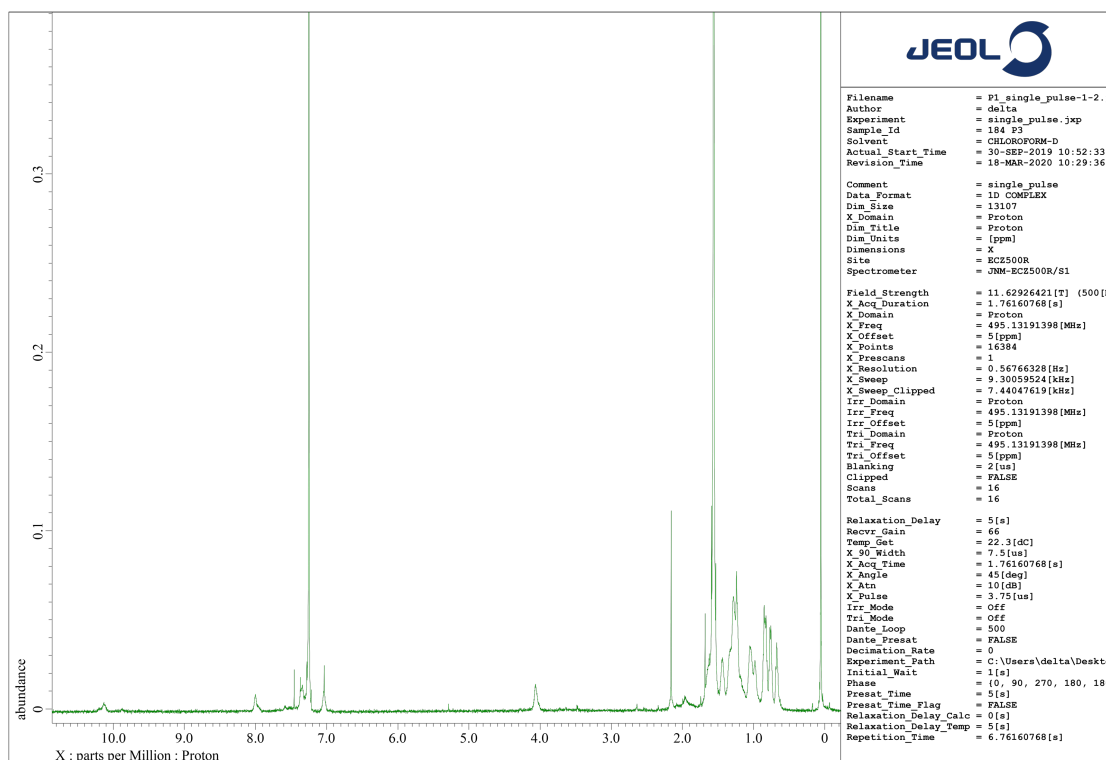


Fig. S1  $^1\text{H}$  NMR spectrum of P1 in  $\text{CDCl}_3$ .

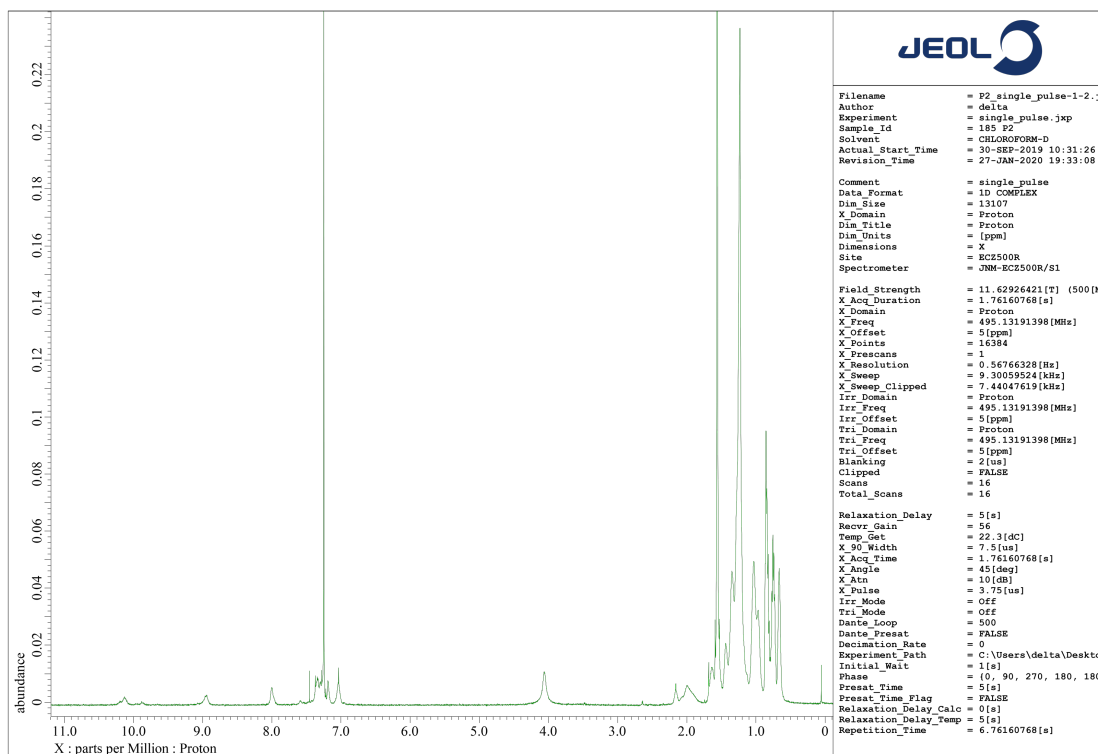


Fig. S2  $^1\text{H}$  NMR spectrum of P2 in  $\text{CDCl}_3$ .

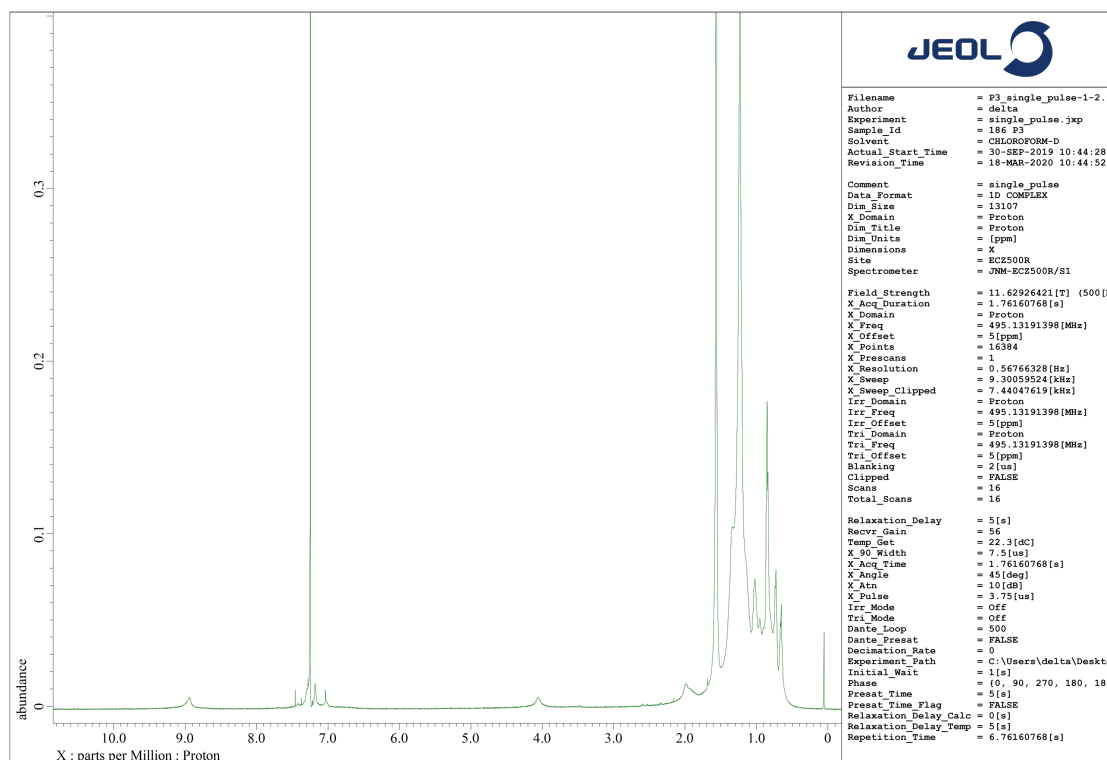


Fig. S3  $^1\text{H}$  NMR spectrum of **P3** in  $\text{CDCl}_3$ .

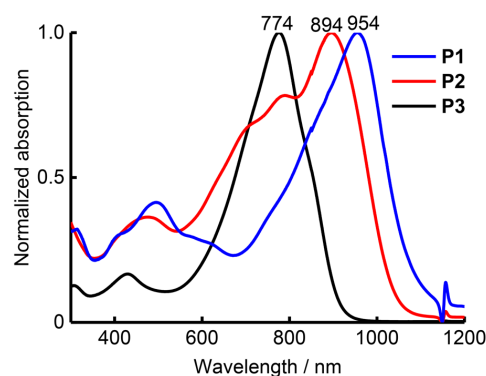


Fig. S4 UV/vis/NIR absorption spectra of **P1–P3** in  $\text{CHCl}_3$ .

## ii. Photovoltaic parameters for OPV device based on **P1–P3:PC<sub>71</sub>BM**

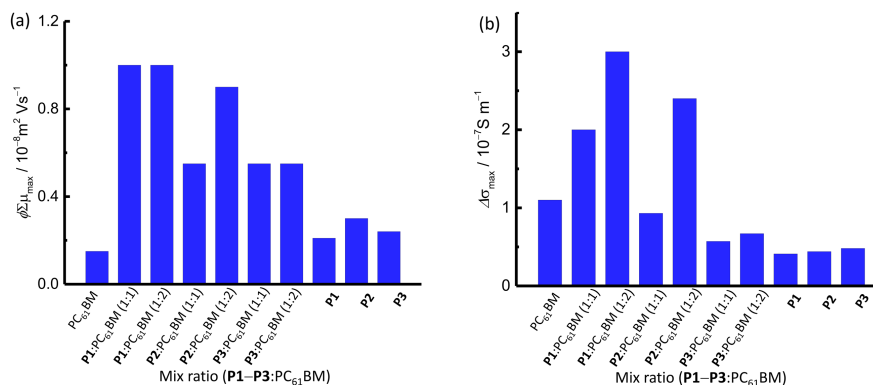
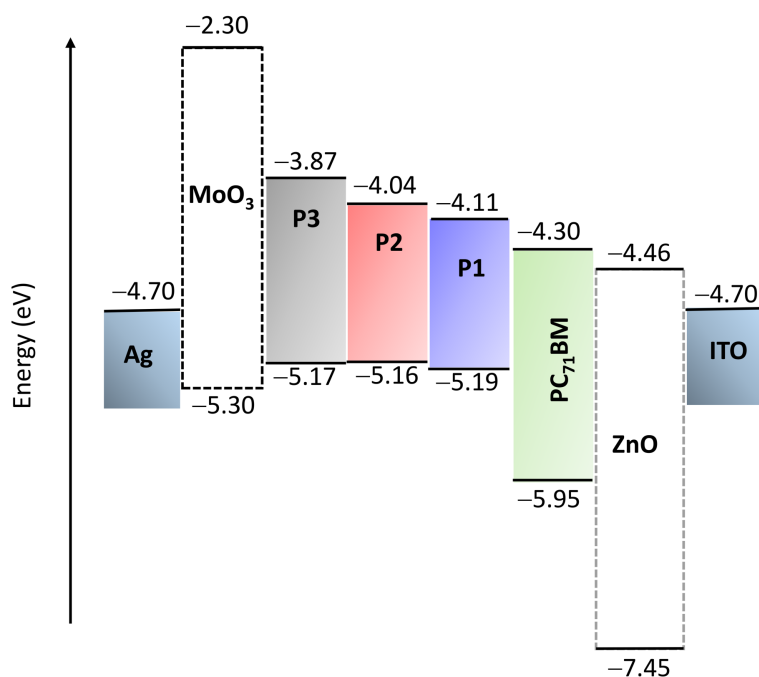


Fig. S5 (a) Maximum TRMC signals ( $\phi\Sigma\mu_{\text{max}}$ ) and (b) photoconductivity maxima ( $\Delta\sigma_{\text{max}}$ ) of drop-cast films of pristine **P1–P3** and PC<sub>61</sub>BM and a mixture of **P1–P3** and PC<sub>61</sub>BM at the ratio of 1:1 and 1:2 (w/w).

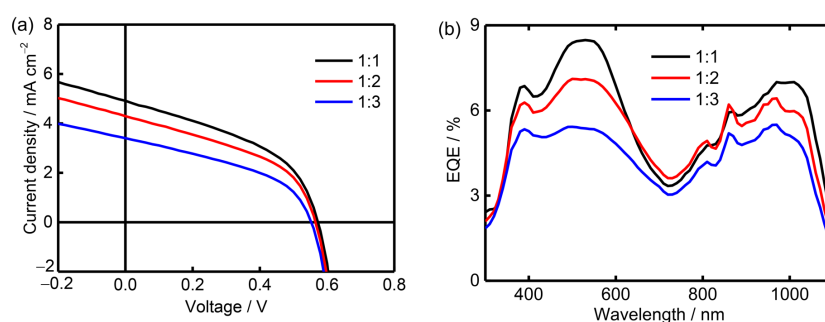


**Fig. S6** Inverted device structure of BHJ-OPVs based on **P1–P3**:PC<sub>71</sub>BM and the corresponding energy levels.

**Table S1** Device characteristics of **P1**:PC<sub>71</sub>BM BHJ-OPVs with various D/A blend ratios. Device conditions with the best PCE in the table are highlighted with a light blue background.

| Blend ratio                       | Solvent <sup>a</sup> | Thickness (nm) | $J_{sc}$ (mA cm <sup>-2</sup> ) | $V_{oc}$ (V) | FF   | PCE (%) |
|-----------------------------------|----------------------|----------------|---------------------------------|--------------|------|---------|
| <b>P1:PC<sub>71</sub>BM (1:1)</b> | CB                   | 66             | 4.92                            | 0.57         | 0.44 | 1.23    |
| P1:PC <sub>71</sub> BM (1:2)      | CB                   | 62             | 4.29                            | 0.57         | 0.44 | 1.07    |
| P1:PC <sub>71</sub> BM (1:3)      | CB                   | 76             | 3.40                            | 0.55         | 0.42 | 0.80    |

<sup>a</sup> CB: chlorobenzene.

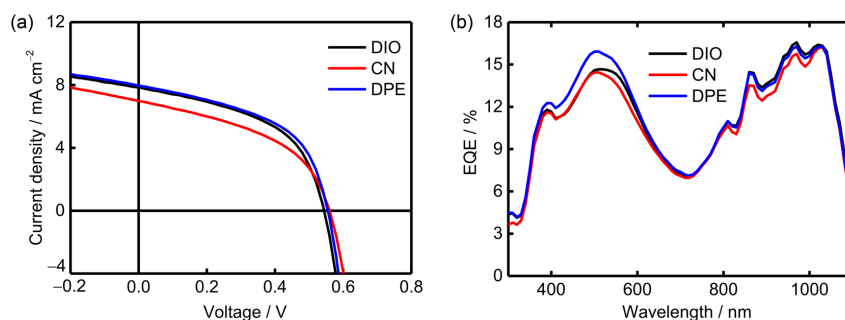


**Fig. S7** (a)  $J$ - $V$  curves and (b) EQE spectra of **P1**:PC<sub>71</sub>BM BHJ-OPVs with various D/A blend ratios corresponding to **Table S1**.

**Table S2** Device characteristics of **P1:PC<sub>71</sub>BM** BHJ-OPVs with different additives. Device conditions with the best PCE in the table are highlighted with a light blue background.

| Blend ratio                          | Solvent and additives <sup>a</sup> | Thickness (nm) | $J_{sc}$ (mA cm <sup>-2</sup> ) | $V_{oc}$ (V) | FF   | PCE (%) |
|--------------------------------------|------------------------------------|----------------|---------------------------------|--------------|------|---------|
| <b>P1:PC<sub>71</sub>BM</b><br>(1:1) | CB:DIO<br>(99.5:0.5 vol%)          | 65             | 7.82                            | 0.54         | 0.48 | 2.13    |
|                                      | CB:CN<br>(99.5:0.5 vol%)           | 70             | 6.98                            | 0.56         | 0.46 | 1.78    |
|                                      | CB:DPE<br>(99.5:0.5 vol%)          | 61             | 8.52                            | 0.55         | 0.48 | 2.27    |

<sup>a</sup> CB: chlorobenzene, DIO: 1,8-diiodooctane, CN: 1-chloronaphthalene, DPE: diphenyl ether.

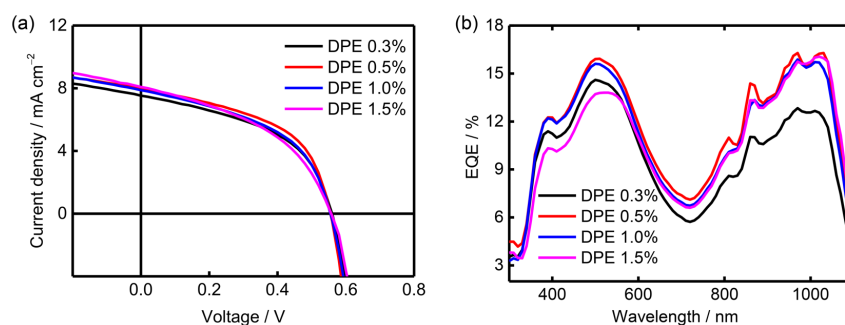


**Fig. S8** (a) *J*-*V* curves and (b) EQE spectra of **P1:PC<sub>71</sub>BM** BHJ-OPVs with different additives corresponding to **Table S2**.

**Table S3** Device characteristics of **P1:PC<sub>71</sub>BM** BHJ-OPVs with various DPE ratios. Device conditions with the best PCE in the table are highlighted with a light blue background.

| Blend ratio                          | Solvent and additives <sup>a</sup> | Thickness (nm) | $J_{sc}$ (mA cm <sup>-2</sup> ) | $V_{oc}$ (V) | FF   | PCE (%) |
|--------------------------------------|------------------------------------|----------------|---------------------------------|--------------|------|---------|
| <b>P1:PC<sub>71</sub>BM</b><br>(1:1) | CB:DPE<br>(99.7:0.3 vol%)          | 58             | 7.52                            | 0.56         | 0.48 | 2.01    |
|                                      | CB:DPE<br>(99.5:0.5 vol%)          | 61             | 8.52                            | 0.55         | 0.48 | 2.27    |
|                                      | CB:DPE<br>(99:1 vol%)              | 58             | 7.88                            | 0.55         | 0.48 | 2.08    |
|                                      | CB:DPE<br>(98.5:1.5 vol%)          | 78             | 8.06                            | 0.56         | 0.44 | 1.99    |

<sup>a</sup> CB: chlorobenzene, DPE: diphenyl ether

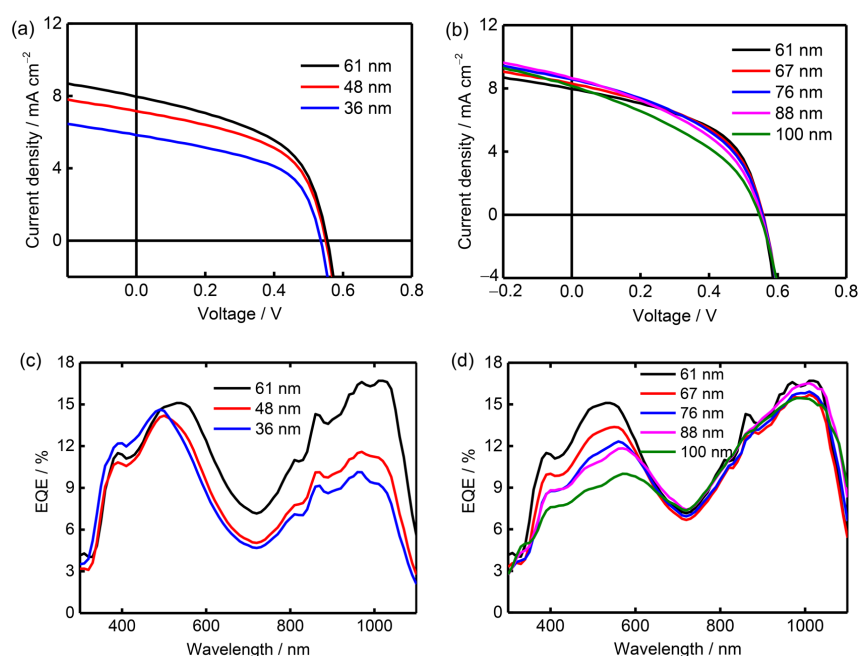


**Fig. S9** (a) *J*-*V* curves and (b) EQE spectra of **P1:PC<sub>71</sub>BM** BHJ-OPVs with various DPE ratios corresponding to **Table S3**.

**Table S4** Device characteristics of **P1:PC<sub>71</sub>BM** BHJ-OPVs with various thicknesses. Device conditions with the best PCE in the table are highlighted with a light blue background.

| Blend ratio                          | Solvent and additive <sup>a</sup> | Thickness (nm) | $J_{sc}$ (mA cm <sup>-2</sup> ) | $V_{oc}$ (V) | FF   | PCE (%) |
|--------------------------------------|-----------------------------------|----------------|---------------------------------|--------------|------|---------|
| <b>P1:PC<sub>71</sub>BM</b><br>(1:1) | <b>CB:DPE</b><br>(99.5:0.5 vol%)  | 36             | 5.83                            | 0.54         | 0.53 | 1.65    |
|                                      |                                   | 48             | 7.16                            | 0.55         | 0.52 | 2.06    |
|                                      |                                   | 61             | 8.52                            | 0.55         | 0.48 | 2.27    |
|                                      |                                   | 67             | 8.30                            | 0.56         | 0.47 | 2.18    |
|                                      |                                   | 76             | 8.58                            | 0.56         | 0.45 | 2.12    |
|                                      |                                   | 88             | 8.64                            | 0.55         | 0.42 | 2.00    |
|                                      |                                   | 100            | 8.15                            | 0.55         | 0.39 | 1.71    |

<sup>a</sup> CB: chlorobenzene, DPE: diphenyl ether.

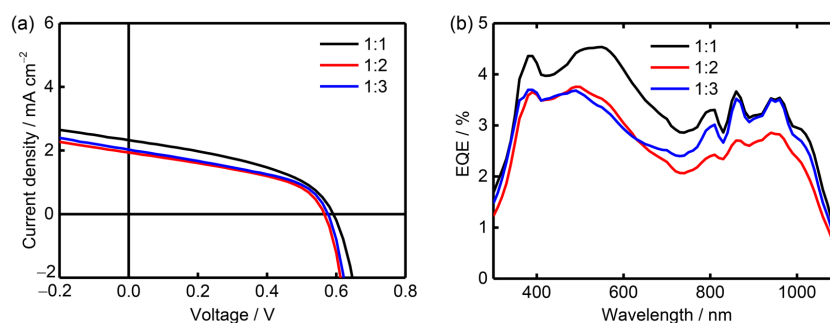


**Fig. S10** (a,b)  $J$ - $V$  curves and (c,d) EQE spectra of **P1:PC<sub>71</sub>BM** BHJ-OPVs with various thicknesses corresponding to **Table S4**.

**Table S5** Device characteristics of **P2:PC<sub>71</sub>BM** BHJ-OPVs with various D/A blend ratios. Device conditions with the best PCE in the table are highlighted with a light blue background.

| Blend ratio                       | Solvent <sup>a</sup> | Thickness (nm) | $J_{sc}$ (mA cm <sup>-2</sup> ) | $V_{oc}$ (V) | FF   | PCE (%) |
|-----------------------------------|----------------------|----------------|---------------------------------|--------------|------|---------|
| <b>P2:PC<sub>71</sub>BM (1:1)</b> | CB                   | 87             | 2.32                            | 0.59         | 0.43 | 0.59    |
| <b>P2:PC<sub>71</sub>BM (1:2)</b> | CB                   | 89             | 1.94                            | 0.57         | 0.44 | 0.48    |
| <b>P2:PC<sub>71</sub>BM (1:3)</b> | CB                   | 82             | 2.03                            | 0.58         | 0.43 | 0.51    |

<sup>a</sup> CB: chlorobenzene

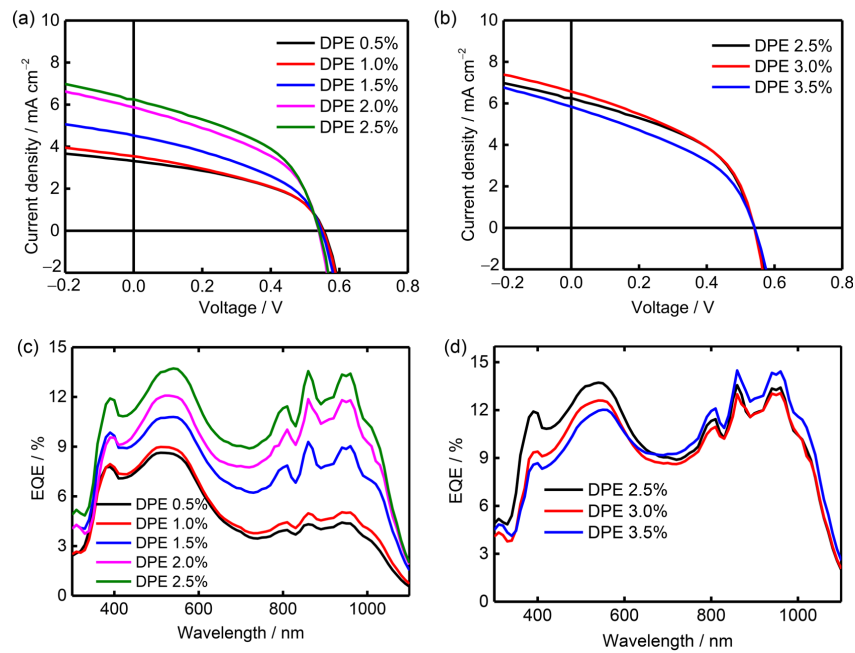


**Fig. S11** (a) *J*-*V* curves and (b) EQE spectra of **P2:PC<sub>71</sub>BM** BHJ-OPVs with various D/A blend ratios corresponding to **Table S5**.

**Table S6** Device characteristics of **P2:PC<sub>71</sub>BM** BHJ-OPVs with various DPE ratios. Device conditions with the best PCE in the table are highlighted with a light blue background.

| Blend ratio                       | Solvent and additive <sup>a</sup> | Thickness (nm) | $J_{sc}$ (mA cm <sup>-2</sup> ) | $V_{oc}$ (V) | FF   | PCE (%) |
|-----------------------------------|-----------------------------------|----------------|---------------------------------|--------------|------|---------|
| <b>P2:PC<sub>71</sub>BM (1:1)</b> | CB:DPE (99.5:0.5 vol%)            | 64             | 3.32                            | 0.55         | 0.45 | 0.83    |
|                                   | CB:DPE (99:1 vol%)                | 63             | 3.55                            | 0.55         | 0.43 | 0.84    |
|                                   | CB:DPE (98.5:1.5 vol%)            | 70             | 4.53                            | 0.55         | 0.42 | 1.04    |
|                                   | CB:DPE (98:2 vol%)                | 68             | 5.87                            | 0.54         | 0.45 | 1.42    |
|                                   | CB:DPE (97.5:2.5 vol%)            | 69             | 6.25                            | 0.54         | 0.46 | 1.56    |
|                                   | CB:DPE (97:3 vol%)                | 63             | 6.57                            | 0.54         | 0.44 | 1.56    |
|                                   | CB:DPE (96.5:3.5 vol%)            | 70             | 5.84                            | 0.54         | 0.41 | 1.30    |

<sup>a</sup> CB: chlorobenzene, DPE: diphenyl ether.

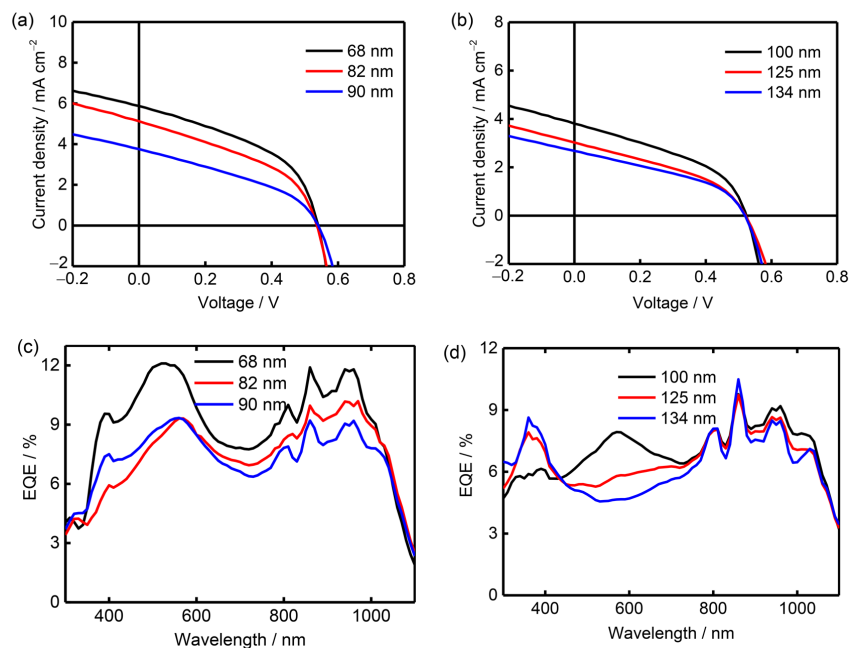


**Fig. S12** (a,b) *J*-*V* curves and (c,d) EQE spectra of **P2**:PC<sub>71</sub>BM BHJ-OPVs with various DPE ratios corresponding to **Table S6**.

**Table S7** Device characteristics of **P2**:PC<sub>71</sub>BM BHJ-OPVs with various thicknesses. Device conditions with the best PCE in the table are highlighted with a light blue background.

| Blend ratio                          | Solvent and additive <sup>a</sup> | Thickness (nm) | $J_{sc}$ (mA cm <sup>-2</sup> ) | $V_{oc}$ (V) | FF   | PCE (%) |
|--------------------------------------|-----------------------------------|----------------|---------------------------------|--------------|------|---------|
| <b>P2</b> :PC <sub>71</sub> BM (1:1) | CB:DPE (98:2 vol%)                | 68             | 5.87                            | 0.54         | 0.45 | 1.42    |
|                                      |                                   | 82             | 5.13                            | 0.54         | 0.42 | 1.15    |
|                                      |                                   | 90             | 3.75                            | 0.54         | 0.37 | 0.76    |
|                                      |                                   | 100            | 3.80                            | 0.52         | 0.41 | 0.82    |
|                                      |                                   | 125            | 3.02                            | 0.52         | 0.39 | 0.61    |
|                                      |                                   | 134            | 2.68                            | 0.52         | 0.40 | 0.55    |

<sup>a</sup> CB: chlorobenzene, DPE: diphenyl ether

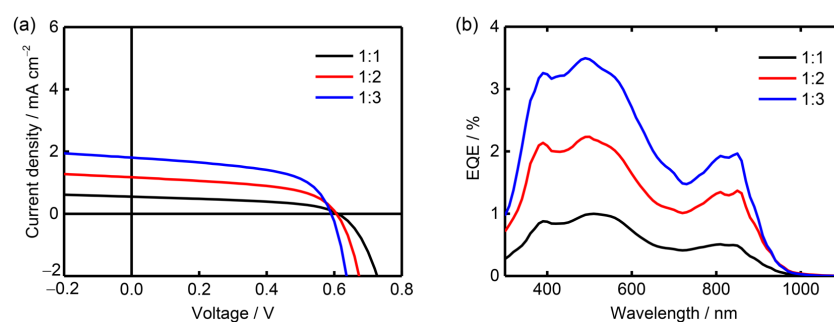


**Fig. S13** (a,b) *J*-*V* curves and (c,d) EQE spectra of **P2**:PC<sub>71</sub>BM BHJ-OPVs with various thicknesses corresponding to **Table S7**.

**Table S8** Device characteristics of **P3**:PC<sub>71</sub>BM BHJ-OPVs with various D/A blend ratios. Device conditions with the best PCE in the table are highlighted with a light blue background.

| Blend ratio                          | Solvent <sup>a</sup> | Thickness (nm) | $J_{sc}$ (mA cm <sup>-2</sup> ) | $V_{oc}$ (V) | FF   | PCE (%) |
|--------------------------------------|----------------------|----------------|---------------------------------|--------------|------|---------|
| <b>P3</b> :PC <sub>71</sub> BM (1:1) | CB                   | 132            | 0.55                            | 0.61         | 0.48 | 0.16    |
| <b>P3</b> :PC <sub>71</sub> BM (1:2) | CB                   | 113            | 1.18                            | 0.61         | 0.52 | 0.37    |
| <b>P3</b> :PC <sub>71</sub> BM (1:3) | CB                   | 88             | 1.81                            | 0.59         | 0.55 | 0.59    |

<sup>a</sup> CB: chlorobenzene.

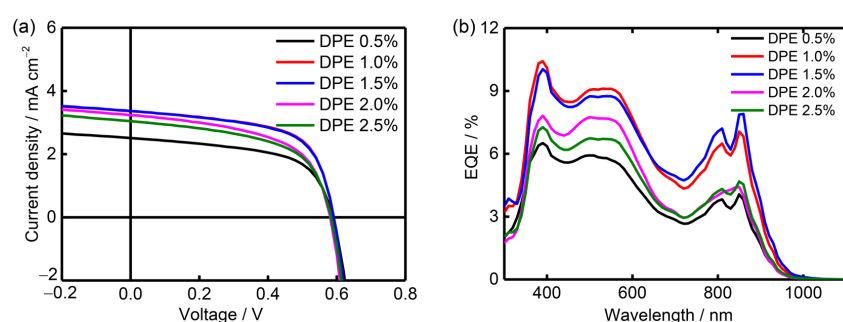


**Fig. S14** (a) *J*-*V* curves and (b) EQE spectra of **P3**:PC<sub>71</sub>BM BHJ-OPVs with various D/A blend ratios corresponding to **Table S8**.

**Table S9** Device characteristics of **P3:PC<sub>71</sub>BM** BHJ-OPVs with various DPE ratios. Device conditions with the best PCE in the table are highlighted with a light blue background.

| Blend ratio                          | Solvent and additive <sup>a</sup> | Thickness (nm) | $J_{sc}$ (mA cm <sup>-2</sup> ) | $V_{oc}$ (V) | FF   | PCE (%) |
|--------------------------------------|-----------------------------------|----------------|---------------------------------|--------------|------|---------|
| <b>P3:PC<sub>71</sub>BM</b><br>(1:3) | CB:DPE<br>(99.5:0.5 vol%)         | 66             | 2.51                            | 0.59         | 0.59 | 0.87    |
|                                      | CB:DPE<br>(99:1 vol%)             | 69             | 3.36                            | 0.59         | 0.62 | 1.23    |
|                                      | CB:DPE<br>(98.5:1.5 vol%)         | 70             | 3.37                            | 0.59         | 0.61 | 1.22    |
|                                      | CB:DPE<br>(98:2 vol%)             | 66             | 3.23                            | 0.58         | 0.56 | 1.05    |
|                                      | CB:DPE<br>(97.5:2.5 vol%)         | 70             | 3.04                            | 0.58         | 0.56 | 1.00    |

<sup>a</sup> CB: chlorobenzene, DPE: diphenyl ether.

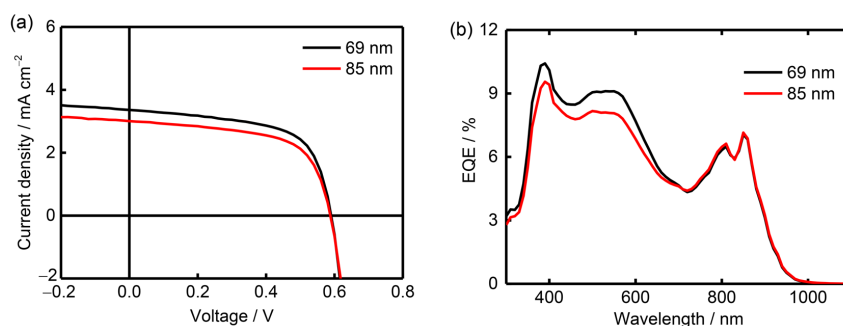


**Fig. S15** (a) *J*-*V* curves and (b) EQE spectra of **P3:PC<sub>71</sub>BM** BHJ-OPVs with various DPE ratios corresponding to **Table S9**.

**Table S10** Device characteristics of **P3:PC<sub>71</sub>BM** BHJ-OPVs with various thicknesses. Device conditions with the best PCE in the table are highlighted with a light blue background.

| Blend ratio                          | Solvent and additive <sup>a</sup> | Thickness (nm) | $J_{sc}$ (mA cm <sup>-2</sup> ) | $V_{oc}$ (V) | FF   | PCE (%) |
|--------------------------------------|-----------------------------------|----------------|---------------------------------|--------------|------|---------|
| <b>P3:PC<sub>71</sub>BM</b><br>(1:3) | CB:DPE<br>(99:1 vol%)             | 69             | 3.36                            | 0.59         | 0.62 | 1.23    |
|                                      |                                   | 85             | 3.00                            | 0.59         | 0.62 | 1.09    |

<sup>a</sup> CB: chlorobenzene, DPE: diphenyl ether



**Fig. S16** (a) *J*-*V* curves and (b) EQE spectra of **P3:PC<sub>71</sub>BM** BHJ-OPVs with various thicknesses corresponding to **Table S10**.