

## Supporting Information

### Excimer Emission Induced Intra-system Self-absorption Enhancement - A Novel Strategy to Realize High Efficiency and Excellent Stability Ternary Organic Solar Cells Processed in Green Solvent

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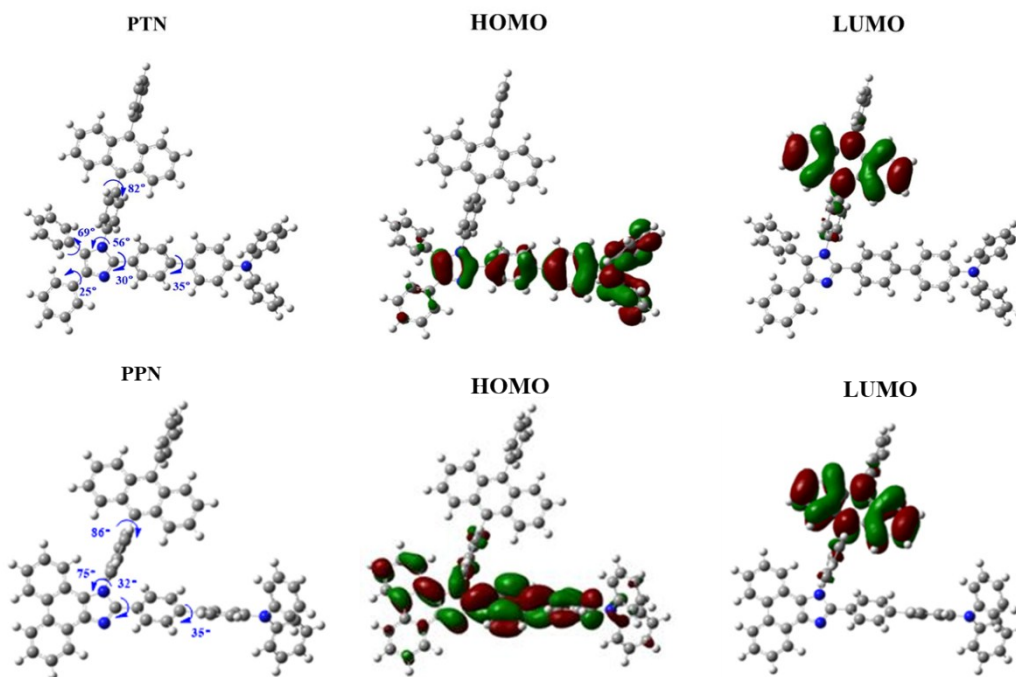
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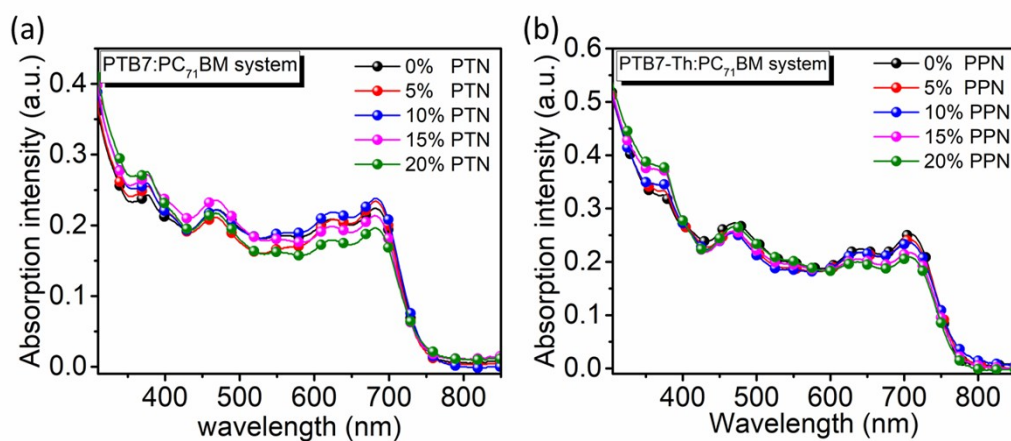
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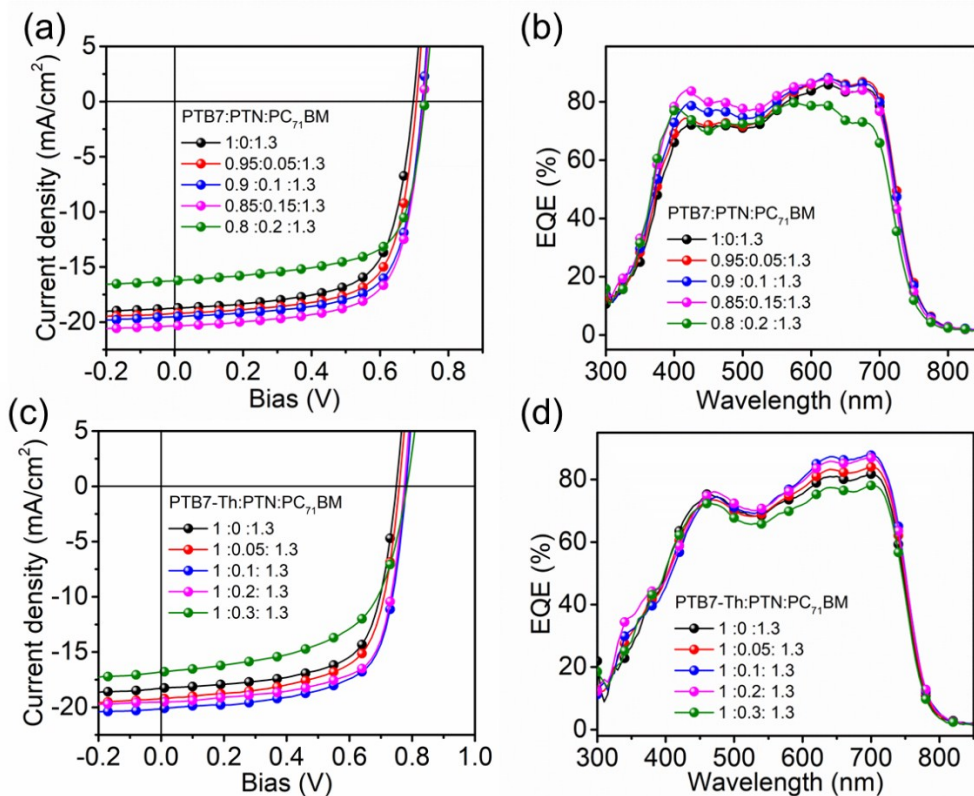
<sup>‡</sup> Xiaoyang Du and Bin Liu contributed equally to this work.



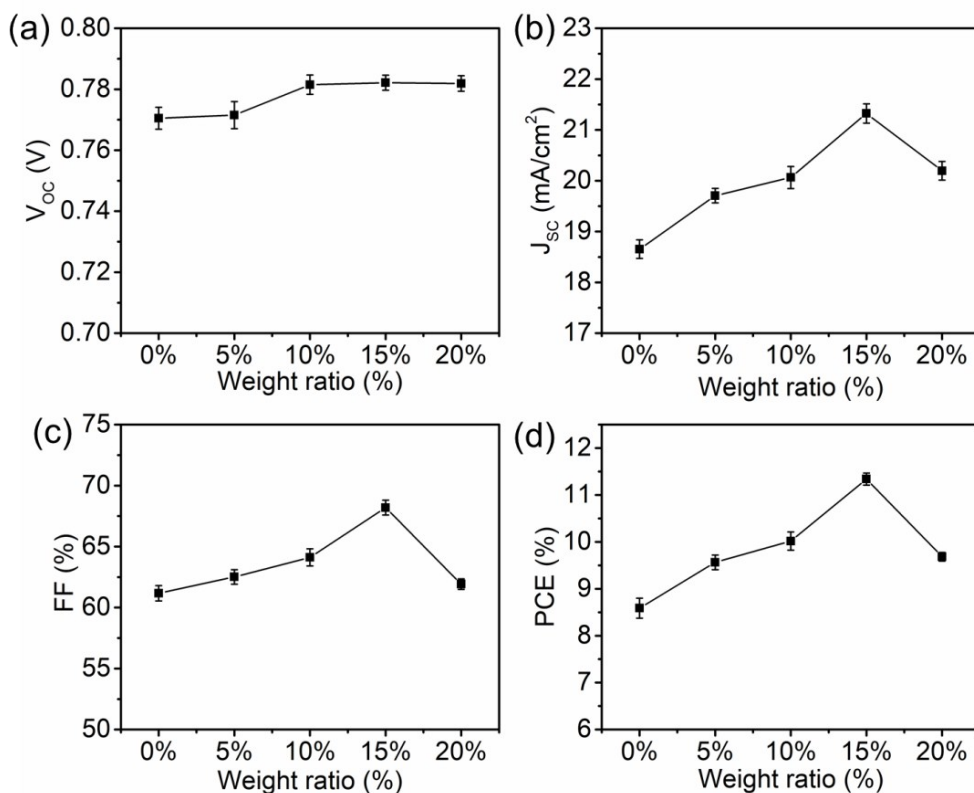
**Figure S1.** Calculated HOMO and LUMO distributions of PTN and PPN.



**Figure S2.** (a) absorption spectra of PTB7: PTN: PC<sub>71</sub>BM based ternary films; (b) absorption spectra of PTB7-Th: PPN: PC<sub>71</sub>BM based ternary films.



**Figure S3.** J-V (a) and EQE (b) curves for PTB7:PTN:PC<sub>71</sub>BM based OSCs; J-V characteristics (c) and EQEs (d) of PTB7-Th:PTN:PC<sub>71</sub>BM based OSCs with consistent PTB7-Th.



**Figure S4.** (a)-(d) V<sub>OC</sub>, J<sub>SC</sub>, FF, and PCE values of PTB7-Th:PTN:PC<sub>71</sub>BM contained device with different PTN contents. These data were collected from 20 samples.

**Table S1.** Performance summaries of PTB7: PTN: PC<sub>71</sub>BM based OSCs

<b>PTB7:PTN:PC<sub>71</sub>BM</b>	<b>V<sub>oc</sub> (V)</b>	<b>J<sub>sc</sub> (mA/cm<sup>2</sup>)</b>	<b>J<sub>calc</sub><sup>a</sup> (mA/cm<sup>2</sup>)</b>	<b>FF (%)</b>	<b>PCE(average)<sup>b</sup> (%)</b>
<b>100:0:130</b>	<b>0.71</b>	<b>18.22</b>	<b>18.03</b>	<b>63.02</b>	<b>8.16 (7.99)</b>
<b>95:5:130</b>	<b>0.72</b>	<b>19.61</b>	<b>18.96</b>	<b>68.99</b>	<b>9.77 (9.36)</b>
<b>90:10:130</b>	<b>0.72</b>	<b>19.98</b>	<b>19.40</b>	<b>69.60</b>	<b>10.10 (9.82)</b>
<b>85:15:130</b>	<b>0.72</b>	<b>20.65</b>	<b>19.88</b>	<b>70.14</b>	<b>10.43 (10.21)</b>
<b>80:20:130</b>	<b>0.72</b>	<b>16.98</b>	<b>16.45</b>	<b>67.71</b>	<b>8.28 (8.03)</b>
<b>85:15:130<sup>c</sup></b>	<b>0.73</b>	<b>19.82</b>	<b>19.47</b>	<b>71.30</b>	<b>10.32 (9.89)</b>

<sup>a</sup> J<sub>calc</sub> means the calculated from EQE spectra; <sup>b</sup> Statistical data obtained from 20 devices; <sup>c</sup> devices performed with CB solvent