

# Supplementary Material

## **Perovskite Solar Cells Based on Hole Transporting Conjugated Polymers by Direct Arylation Polycondensation**

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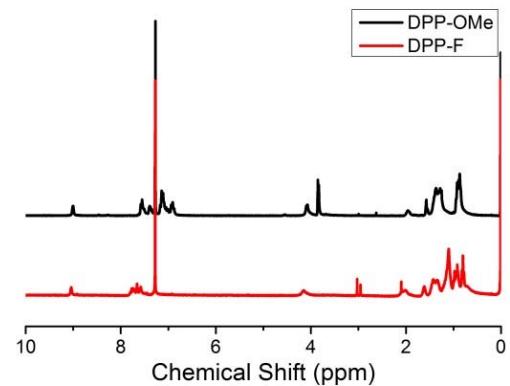
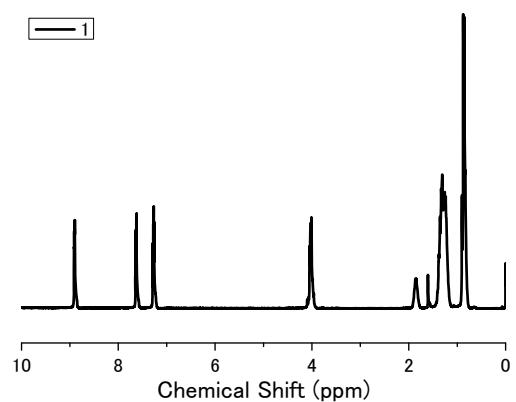
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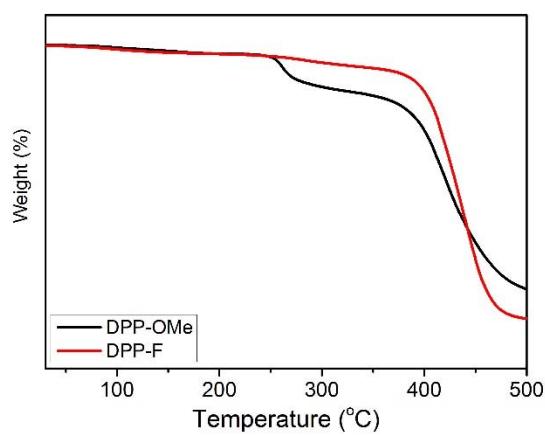
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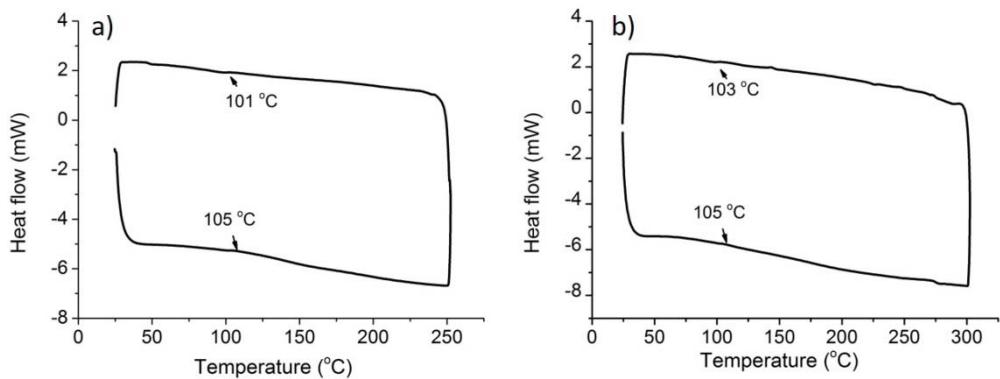
Phone: +81-3-5734-3774, Fax: +81-3-5734-3774.



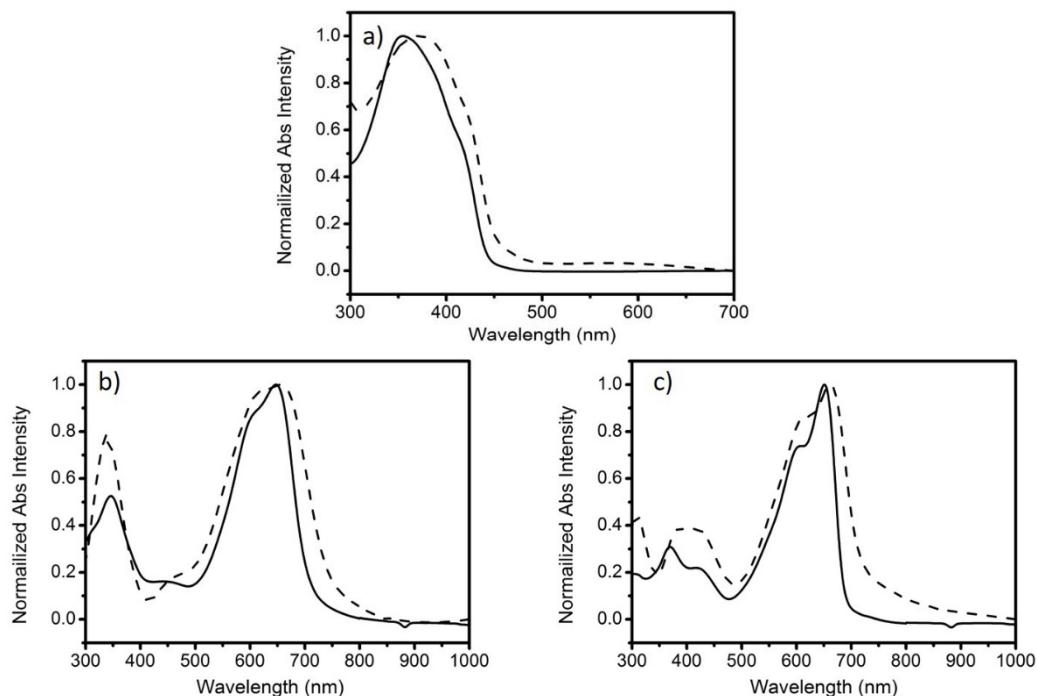
**Fig. S1**  $^1\text{H}$ -NMR spectra of **1**, **DPP-OMe**, and **DPP-F** in  $\text{CDCl}_3$ .



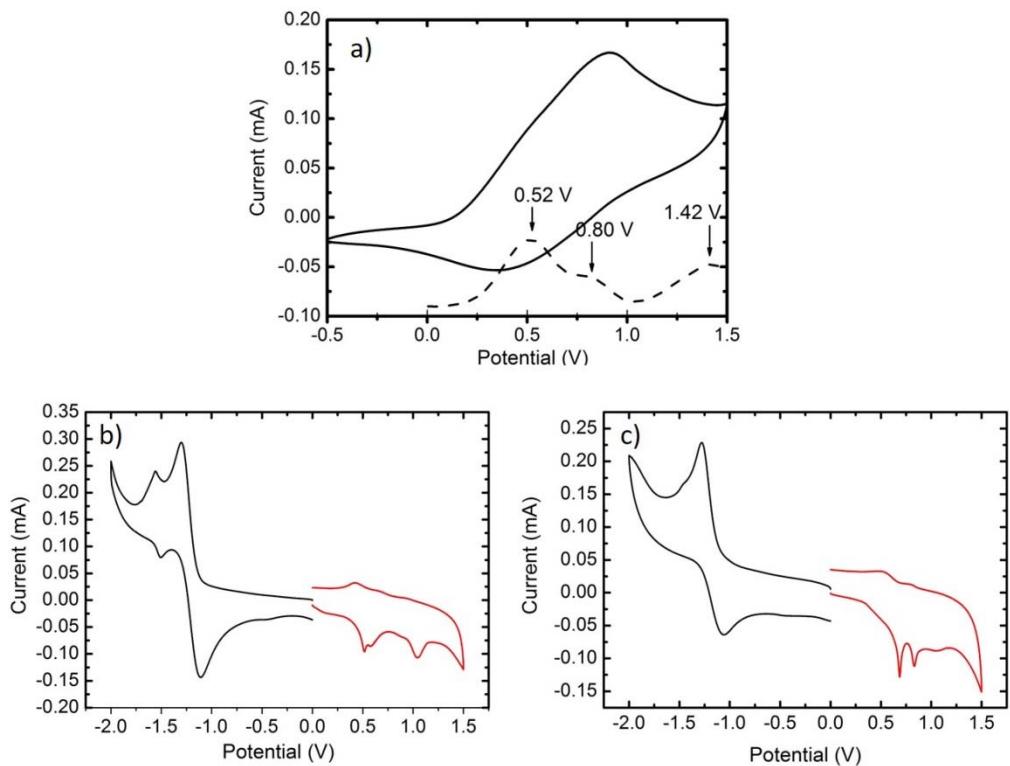
**Fig. S2** Thermogravimetric analysis (TGA) curves of **DPP-OMe** and **DPP-F** under nitrogen flow ( $50 \text{ mL min}^{-1}$ ) at the heating rate of  $10^\circ\text{C min}^{-1}$ .



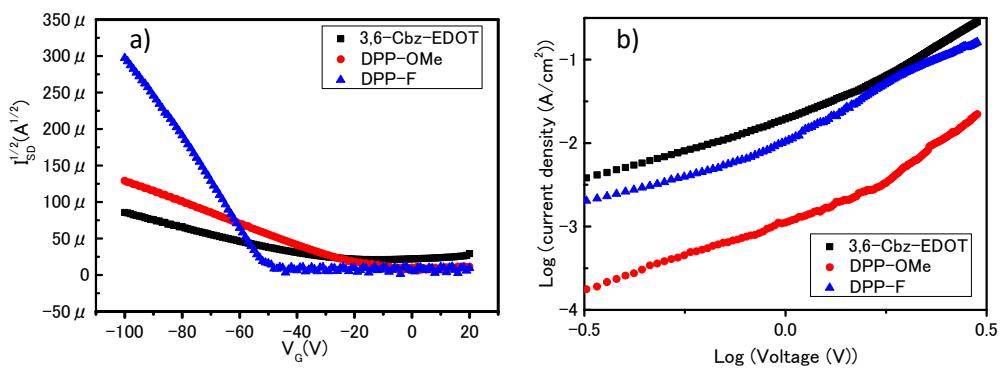
**Fig. S3** Differential scanning calorimetry (DSC) curves of (a) **DPP-OMe** and (b) **DPP-F** under nitrogen flow ( $50 \text{ mL min}^{-1}$ ) at the scanning rate of  $10 \text{ }^{\circ}\text{C min}^{-1}$  (second heating and cooling processes).



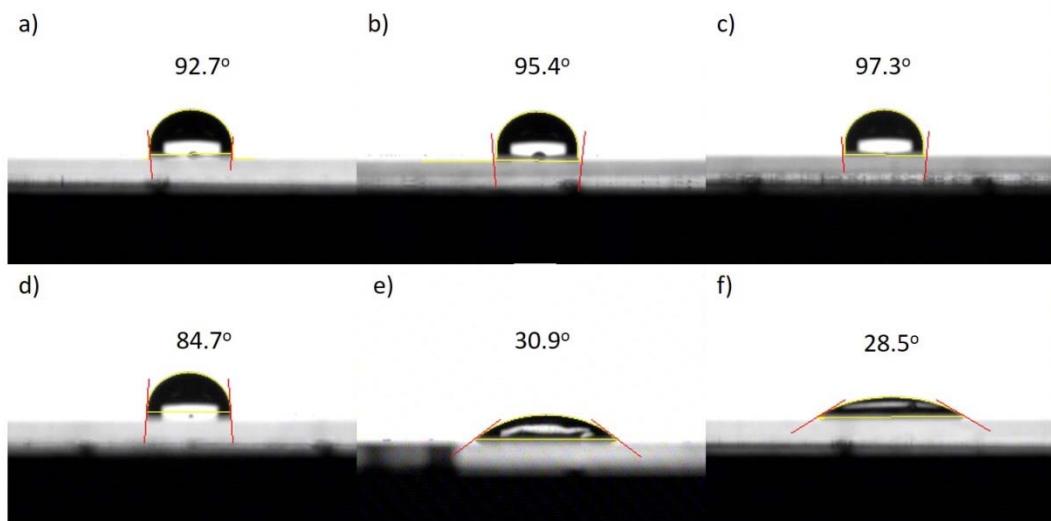
**Fig. S4** Normalized UV-vis absorption of (a) **3,6-Cbz-EDOT**, (b) **DPP-OMe** and (c) **DPP-F** in  $\text{CH}_2\text{Cl}_2$  measured at  $10^{-5} \text{ M}$  repeat unit $^{-1}$  (solid line) and film states (dash line).



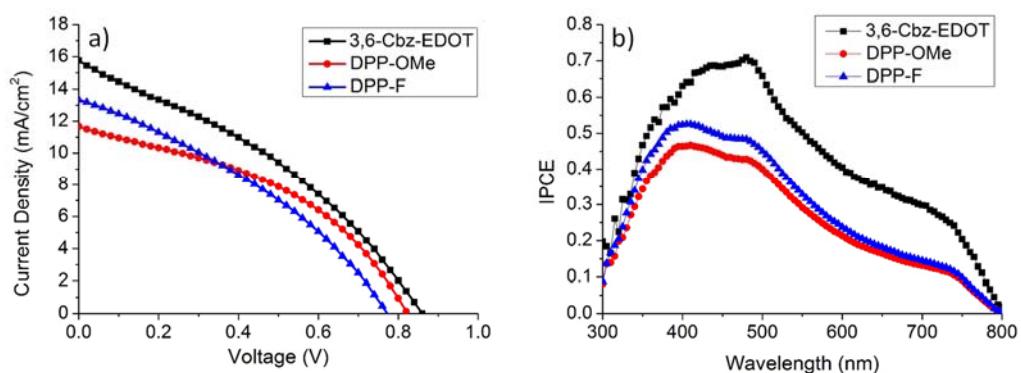
**Fig. S5** Cyclic voltammetry of films of (a) 3,6-Cbz-EDOT, (b) DPP-OMe and (c) DPP-F on a glassy carbon electrode, measured in CH<sub>3</sub>CN with 0.1 M (nC<sub>4</sub>H<sub>9</sub>N)<sub>4</sub>PF<sub>6</sub> at the scanning rate of 0.1 V s<sup>-1</sup> under flowing nitrogen. Potentials vs. Ag/Ag<sup>+</sup>.



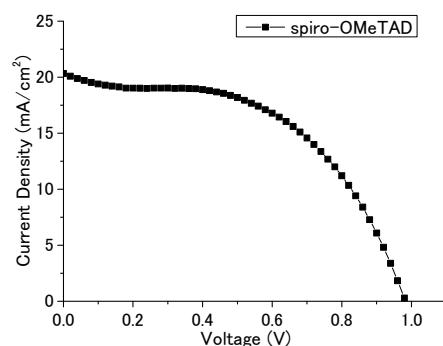
**Fig. S6** (a) Transfer characteristics of the thin film transistors and (b) log-log plots of the SCLC measurements of the as-cast HTM films.



**Fig. S7** Contact angles of water on the films of (a) 3,6-Cbz-EDOT, (b) DPP-OMe, (c) DPP-F, (d) TBP doped 3,6-Cbz-EDOT, (e) Li-TFSi doped 3,6-Cbz-EDOT and (f) both TBP and Li-TFSi doped 3,6-Cbz-EDOT.



**Fig. S8** (a) Current–voltage (J-V) curves and (b) IPCE spectra of the PSCs based on the polymeric HTMs without dopants.



**Fig. S9** Current–voltage (J-V) curve of the PSC based on spiro-OMeTAD with TBP and Li-TFSi.

## Solar cell parameters

### Undoped 3,6-Cbz-EDOT

No	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
<b>1 average</b>	<b>15.76</b>	<b>0.86</b>	<b>0.35</b>	<b>4.70</b>
forward	16.31	0.86	0.34	4.77
backward	15.21	0.86	0.36	4.67
<b>2 average</b>	<b>15.35</b>	<b>0.83</b>	<b>0.30</b>	<b>3.83</b>
forward	15.21	0.83	0.30	3.82
backward	15.49	0.83	0.30	3.84
<b>3 average</b>	<b>15.10</b>	<b>0.78</b>	<b>0.37</b>	<b>4.39</b>
forward	14.83	0.73	0.39	4.31
backward	15.35	0.83	0.35	4.47
<b>Average</b>	<b>15.40</b>	<b>0.82</b>	<b>0.34</b>	<b>4.30</b>

### Doped 3,6-Cbz-EDOT (Li-TFSi only)

No	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
<b>1 average</b>	<b>17.46</b>	<b>0.95</b>	<b>0.40</b>	<b>6.65</b>
forward	17.42	0.95	0.37	6.12
backward	17.49	0.95	0.43	7.21
<b>2 average</b>	<b>17.50</b>	<b>0.94</b>	<b>0.38</b>	<b>6.37</b>
forward	17.99	0.94	0.35	5.97
backward	17.01	0.95	0.42	6.81
<b>3 average</b>	<b>17.45</b>	<b>0.94</b>	<b>0.37</b>	<b>6.14</b>
forward	17.66	0.94	0.36	6.05
backward	17.24	0.95	0.38	6.24
<b>Average</b>	<b>17.47</b>	<b>0.94</b>	<b>0.38</b>	<b>6.39</b>

### Doped 3,6-Cbz-EDOT (TBP only)

No	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
<b>1 average</b>	<b>15.64</b>	<b>0.93</b>	<b>0.46</b>	<b>6.76</b>
forward	15.92	0.93	0.44	6.42
backward	15.36	0.94	0.49	7.10
<b>2 average</b>	<b>15.55</b>	<b>0.94</b>	<b>0.47</b>	<b>6.88</b>
forward	15.57	0.93	0.44	6.37
backward	15.52	0.94	0.51	7.42
<b>3 average</b>	<b>15.76</b>	<b>0.93</b>	<b>0.47</b>	<b>6.92</b>
forward	15.98	0.93	0.44	6.53
backward	15.54	0.93	0.51	7.33
<b>Average</b>	<b>15.65</b>	<b>0.93</b>	<b>0.47</b>	<b>6.85</b>

**Doped 3,6-Cbz-EDOT (both Li-TFSi and TBP)**

No	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	FF	PCE (%)
<b>1 average</b>	<b>18.36</b>	<b>0.91</b>	<b>0.48</b>	<b>8.17</b>
forward	18.08	0.89	0.47	7.63
backward	18.64	0.93	0.50	8.72
<b>2 average</b>	<b>17.68</b>	<b>0.92</b>	<b>0.50</b>	<b>8.12</b>
forward	18.01	0.90	0.46	7.39
backward	17.35	0.94	0.55	8.89
<b>3 average</b>	<b>17.40</b>	<b>0.92</b>	<b>0.51</b>	<b>8.11</b>
forward	17.85	0.90	0.46	7.42
backward	16.95	0.94	0.56	8.86
<b>Average</b>	<b>17.81</b>	<b>0.92</b>	<b>0.50</b>	<b>8.13</b>

**Undoped DPP-OMe**

No	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	FF	PCE (%)
<b>1 average</b>	<b>11.37</b>	<b>0.83</b>	<b>0.39</b>	<b>3.70</b>
forward	10.91	0.74	0.31	2.48
backward	11.84	0.90	0.50	5.30
<b>2 average</b>	<b>11.67</b>	<b>0.82</b>	<b>0.41</b>	<b>3.97</b>
forward	11.30	0.82	0.40	3.74
backward	12.04	0.83	0.42	4.19
<b>3 average</b>	<b>12.02</b>	<b>0.83</b>	<b>0.43</b>	<b>4.32</b>
forward	11.79	0.83	0.43	4.19
backward	12.26	0.84	0.44	4.47
<b>Average</b>	<b>11.69</b>	<b>0.83</b>	<b>0.41</b>	<b>4.00</b>

**Doped DPP-OMe (both Li-TFSi and TBP)**

No	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	FF	PCE (%)
<b>1 average</b>	<b>11.12</b>	<b>0.82</b>	<b>0.49</b>	<b>4.47</b>
forward	11.08	0.82	0.47	4.29
backward	11.15	0.82	0.51	4.67
<b>2 average</b>	<b>11.07</b>	<b>0.77</b>	<b>0.46</b>	<b>3.97</b>
forward	11.07	0.76	0.44	3.73
backward	11.08	0.78	0.49	4.24
<b>3 average</b>	<b>11.03</b>	<b>0.76</b>	<b>0.45</b>	<b>3.75</b>
forward	10.80	0.73	0.44	3.48
backward	11.26	0.78	0.46	4.03
<b>Average</b>	<b>11.07</b>	<b>0.78</b>	<b>0.47</b>	<b>4.06</b>

**Undoped DPP-F**

No	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	FF	PCE (%)
<b>1 average</b>	<b>12.78</b>	<b>0.77</b>	<b>0.35</b>	<b>3.48</b>
forward	12.26	0.78	0.37	3.58
backward	13.30	0.76	0.33	3.38
<b>2 average</b>	<b>13.33</b>	<b>0.77</b>	<b>0.34</b>	<b>3.54</b>
forward	13.41	0.78	0.36	3.75
backward	13.26	0.77	0.33	3.43
<b>3 average</b>	<b>13.78</b>	<b>0.78</b>	<b>0.30</b>	<b>3.25</b>
forward	14.36	0.79	0.33	3.77
backward	13.19	0.77	0.27	2.76
<b>Average</b>	<b>13.30</b>	<b>0.77</b>	<b>0.33</b>	<b>3.42</b>

**Doped DPP-F (both Li-TFSi and TBP)**

No	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	FF	PCE (%)
<b>1 average</b>	<b>12.54</b>	<b>0.80</b>	<b>0.39</b>	<b>3.88</b>
forward	11.71	0.80	0.45	4.27
backward	13.37	0.79	0.34	3.59
<b>2 average</b>	<b>13.66</b>	<b>0.78</b>	<b>0.38</b>	<b>4.08</b>
forward	13.14	0.79	0.43	4.42
backward	14.18	0.77	0.35	3.83
<b>3 average</b>	<b>13.67</b>	<b>0.73</b>	<b>0.40</b>	<b>3.94</b>
forward	13.14	0.73	0.43	4.14
backward	14.18	0.72	0.37	3.80
<b>Average</b>	<b>13.29</b>	<b>0.77</b>	<b>0.39</b>	<b>3.97</b>