

## Three-dimensional molecular donors combined with polymeric acceptors for high performance fullerene-free organic photovoltaics

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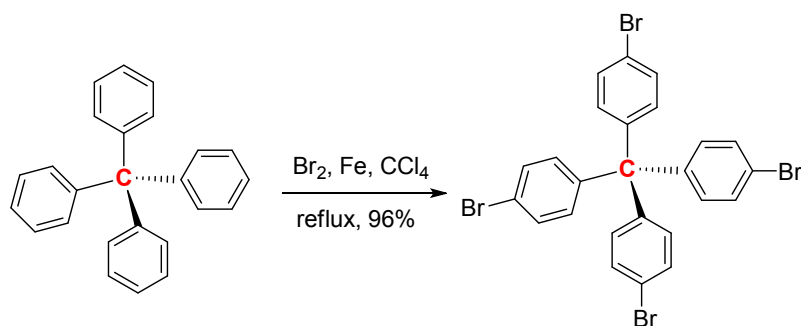
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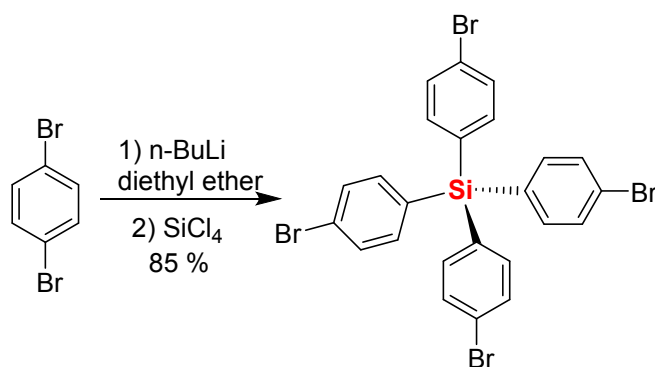
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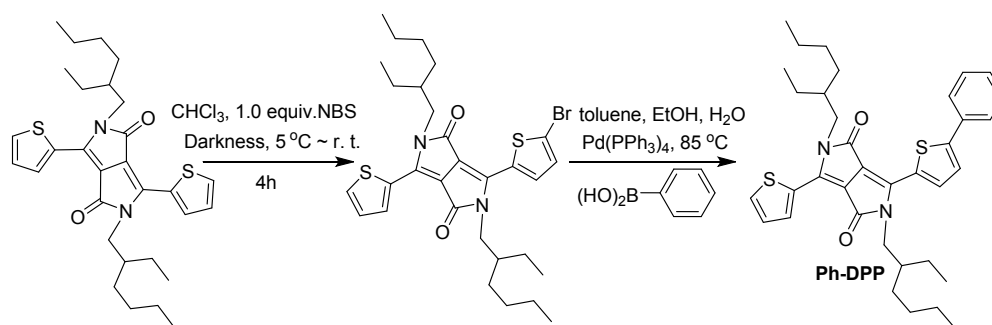
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**Synthesis of Intermediates TBPM, TBPS and Ph-DPP****Scheme S1**

Scheme S1 shows the synthetic route of intermediate compound **TBPM**, according to the reported procedure.<sup>[S1]</sup> Tetraphenylmethane (1.6 g, 5 mmol) was warmed with stirring to 30-35 °C in 25 mL CCl<sub>4</sub> containing 0.05 g iron filings. Bromine (4 g, 25 mmol) was added cautiously and slowly, maintaining the temperature. A solution of aqueous alkali (KOH) was used in a bubbler trap attached to the end of a condenser to avoid HBr fumes. After several hours at 30-35 °C the solution was refluxed for 1 day at which time the dark-brown solution had become paler and all the initially insoluble tetraphenylmethane had dissolved. The solution was then cooled to room temperature and red-brown crystals were collected. After crystallization from a chloroform-methanol mixture, pale, off-white crystals were obtained. Yield, 3.2 g (96%); **TBPM**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.55 –7.53 (d, *J* = 8.4, 8H), 7.35 –7.32 (d, *J* = 8.4, 8H).

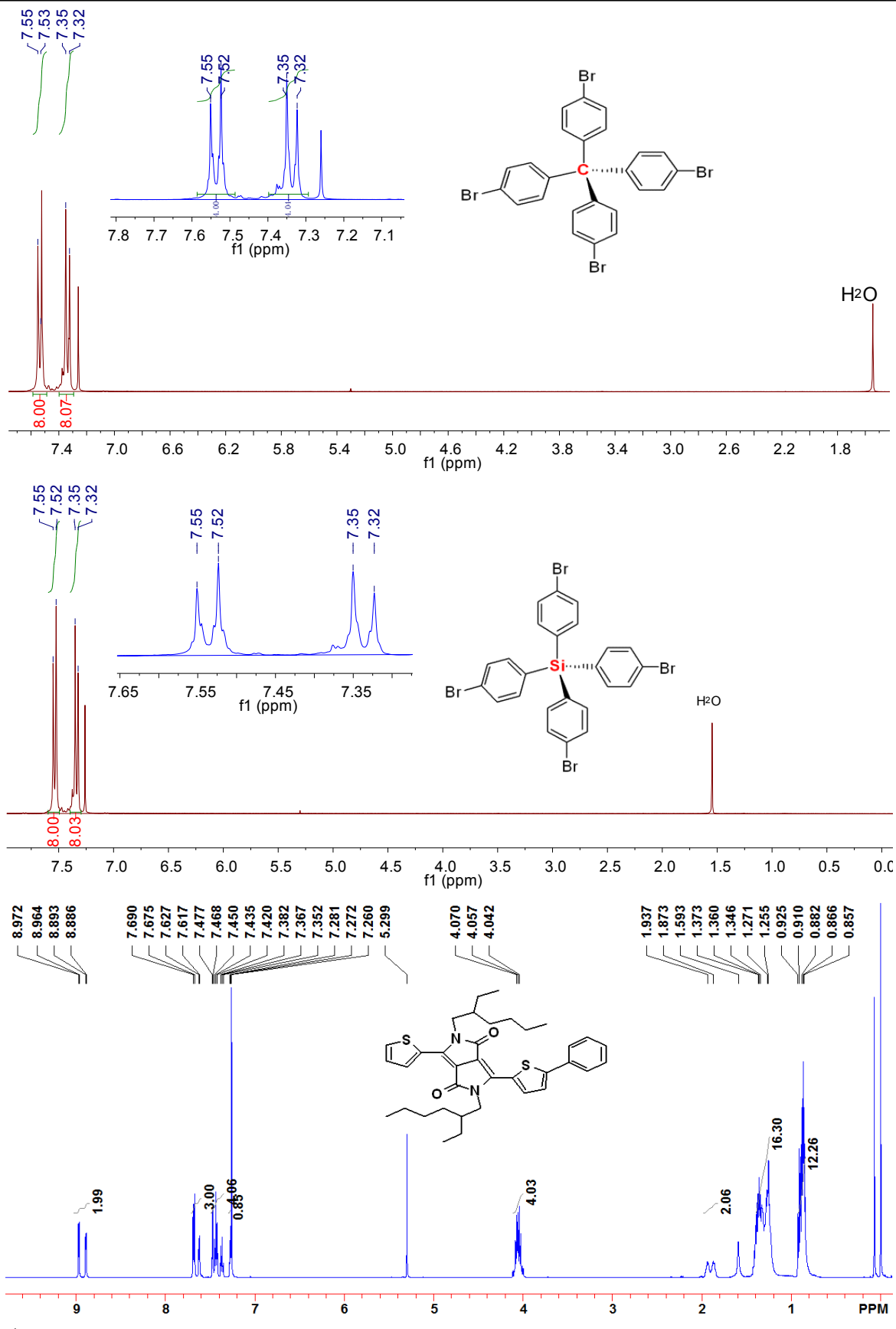
**Scheme S2**

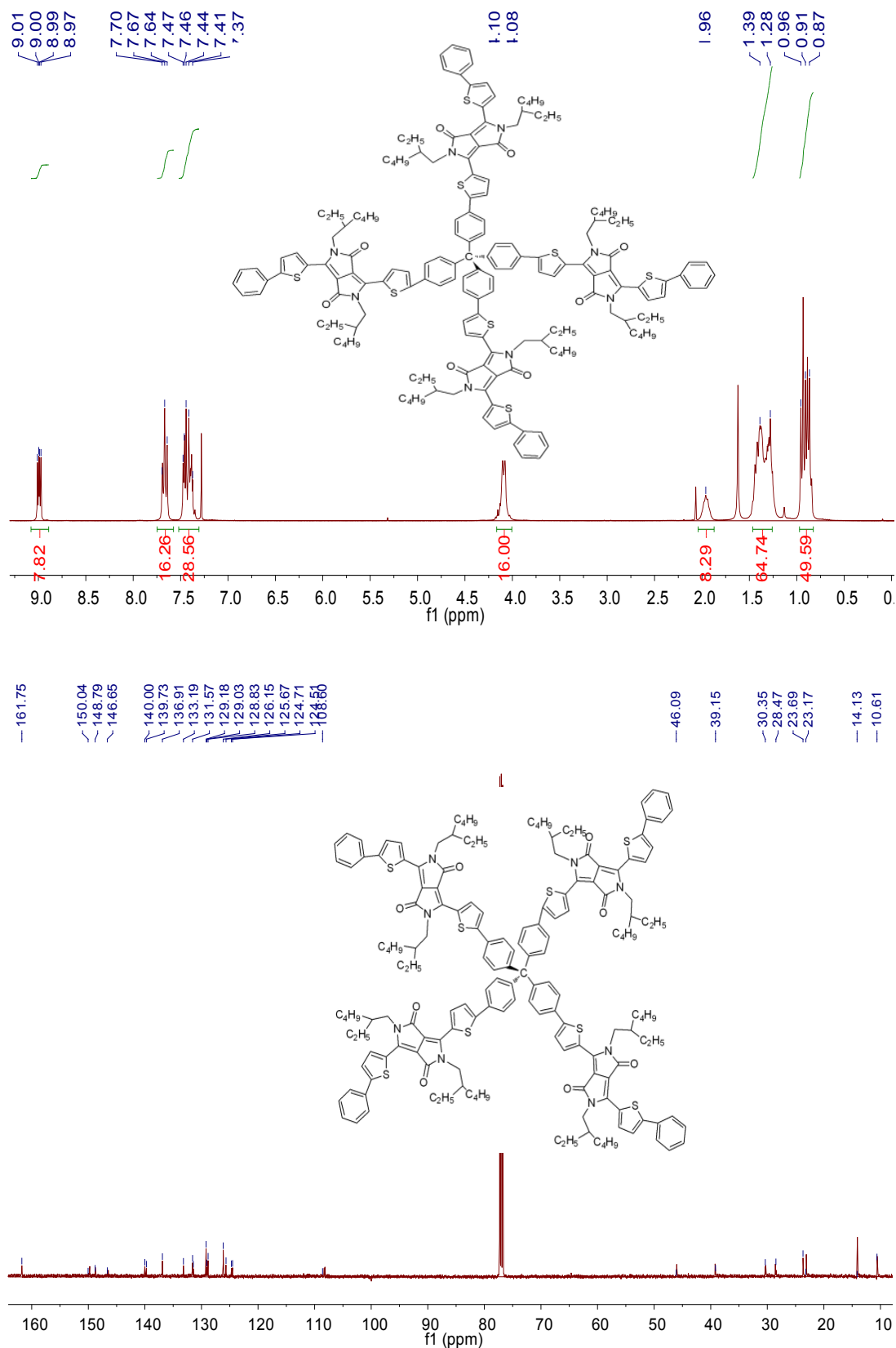
Scheme S2 shows the synthetic route of intermediate compound **TMPS**. Based on the reported procedure with slight modifications,<sup>[S2]</sup> detailed procedures are as follows. A solution of 1,4-dibromobenzene (11.8 g, 50 mmol) in anhydrous ether (125 mL) was stirred at  $-10^{\circ}\text{C}$  under argon and treated dropwise with a solution of butyllithium (20 mL, 2.5 M in hexane, 50 mmol). The resulting mixture was kept at  $-10^{\circ}\text{C}$  for 15 min, and then  $\text{SiCl}_4$  (1.43 mL, 12.5 mmol) was added dropwise. The mixture was stirred at  $-10^{\circ}\text{C}$  for 30 min and at  $25^{\circ}\text{C}$  for 12 h. Then 1 M aqueous HCl was added, and the resulting mixture was extracted with ether. The combined extracts were washed with  $\text{H}_2\text{O}$  and brine, dried over  $\text{MgSO}_4$ , and filtered. Volatiles were removed by evaporation under reduced pressure, and the residue was recrystallized twice from ethanol to afford colorless crystal of tetrakis(4-bromophenyl)silane. **TMPS**:  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 –7.51 (d,  $J = 8.4$ , 8H), 7.42 –7.32 (d,  $J = 8.4$ , 8H).

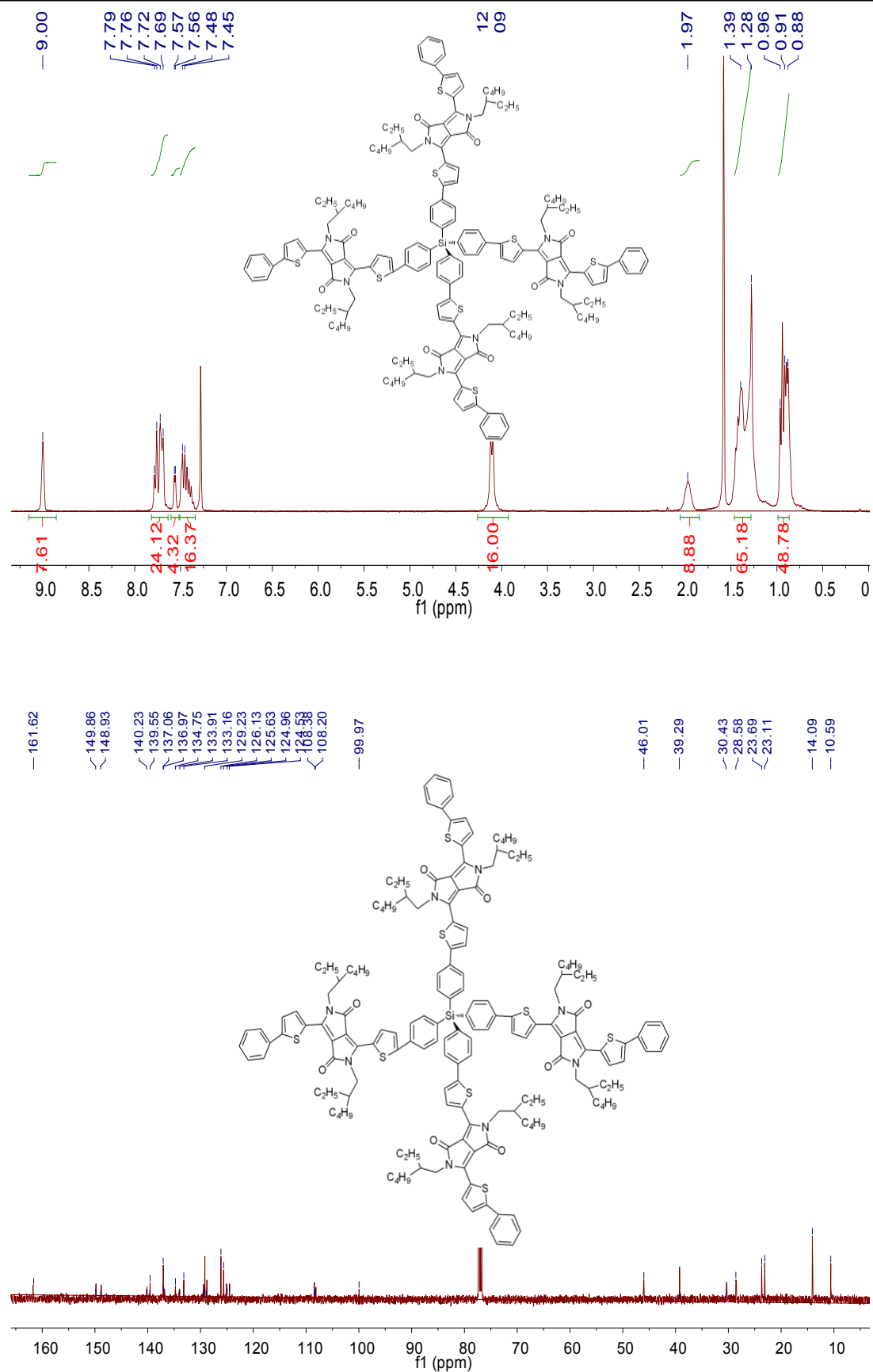


**Scheme S3**

Scheme S3 shows the synthetic route of intermediate compound **Ph-DPP**, according to our previously reported procedure.<sup>[S3]</sup> **Ph-DPP**:  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.90 (d,  $J = 3.9$  Hz, 1H), 8.64 (d,  $J = 4.2$  Hz, 1H), 7.65 (d,  $J = 5.1$  Hz, 1H), 7.29 – 7.18 (m, 2H), 4.03–3.92 (m, 4H), 1.84(m, 2H), 1.38–1.23 (m, 16H), 0.91–0.83 (m, 12H).

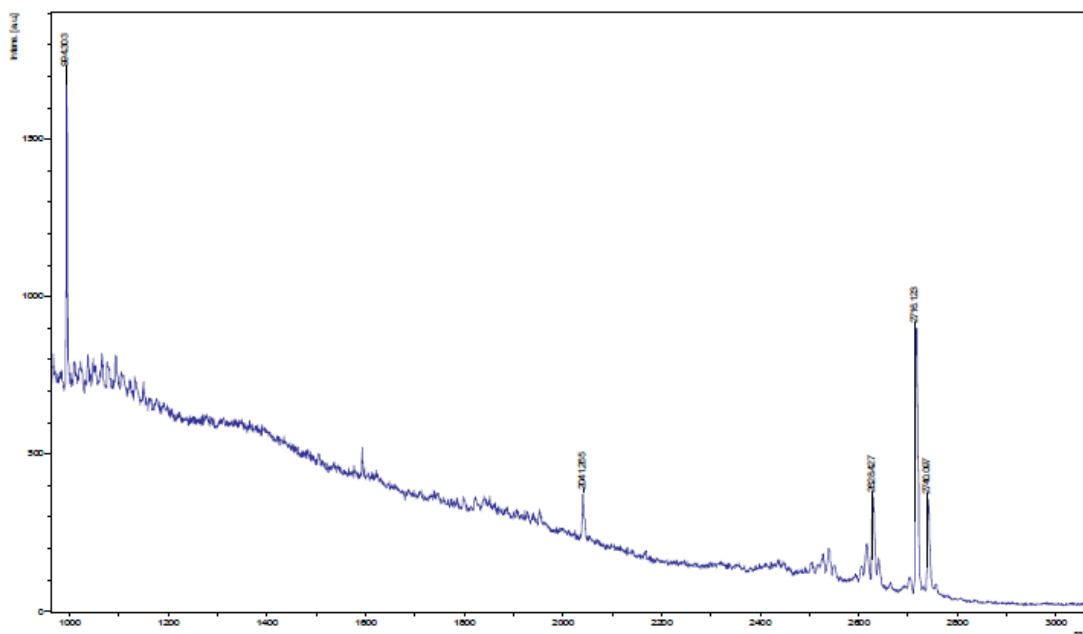
**Fig. S1** <sup>1</sup>H NMR spectra of TBPM, TBPS and Ph-DPP

**Fig. S2** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of C-DPP.

**Fig. S3**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of Si-DPP.

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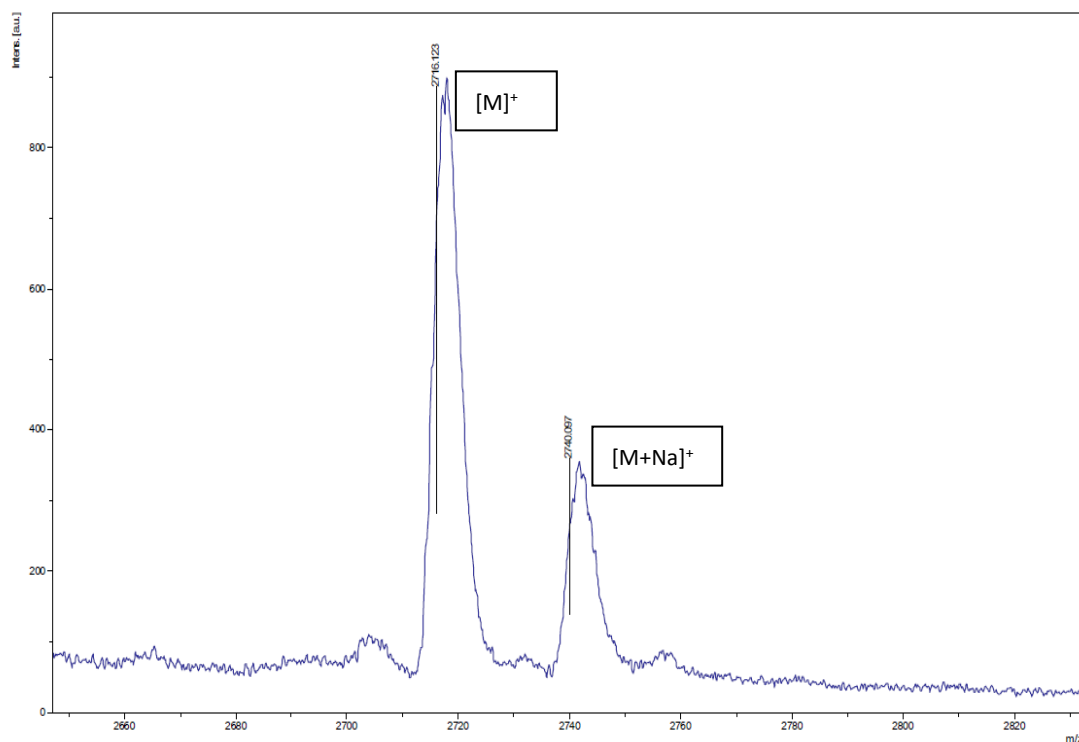
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MALDI SPECTRUM

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**Fig. S4** MALDI-TOF MS spectrum of **C-DPP**, calcd: 2715.89; found: 2716.12.

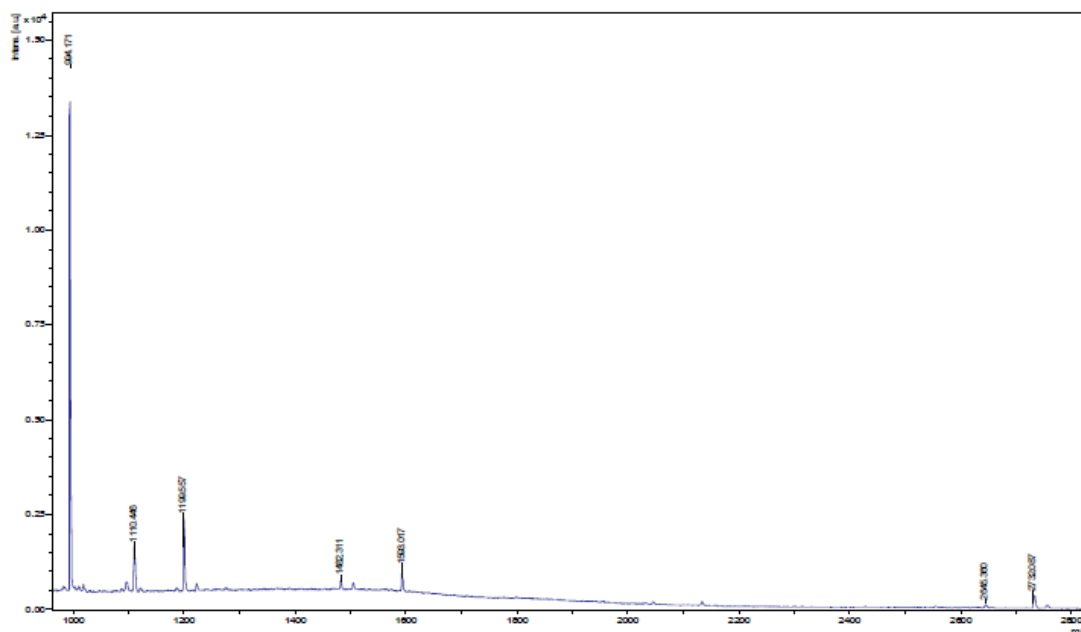
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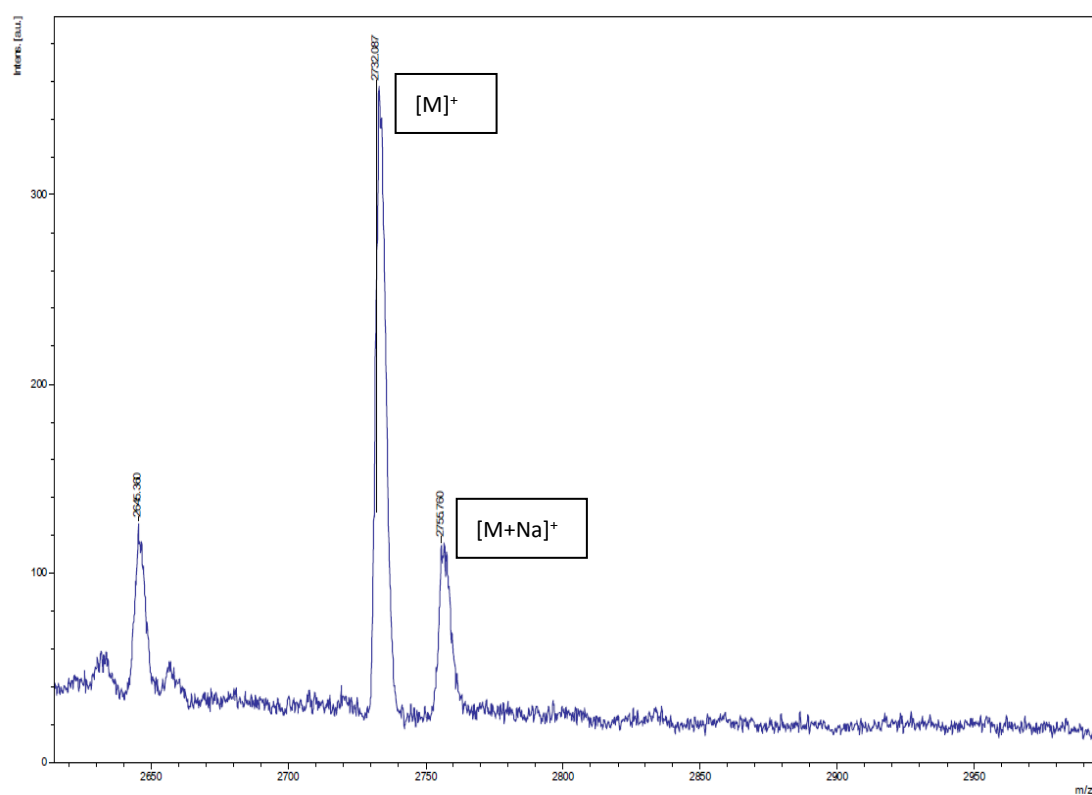
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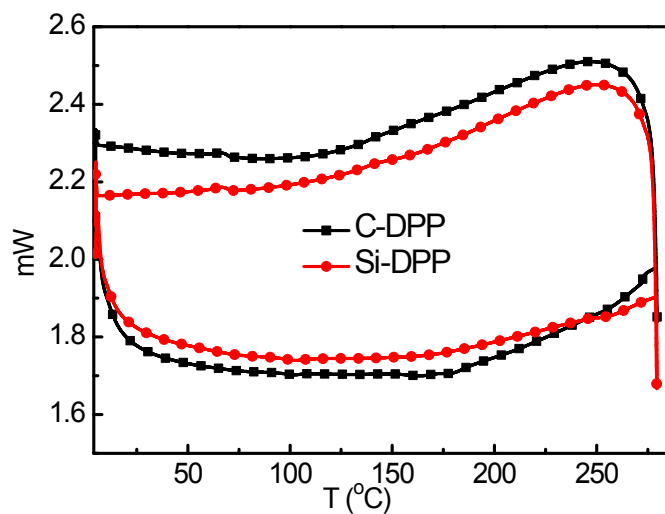
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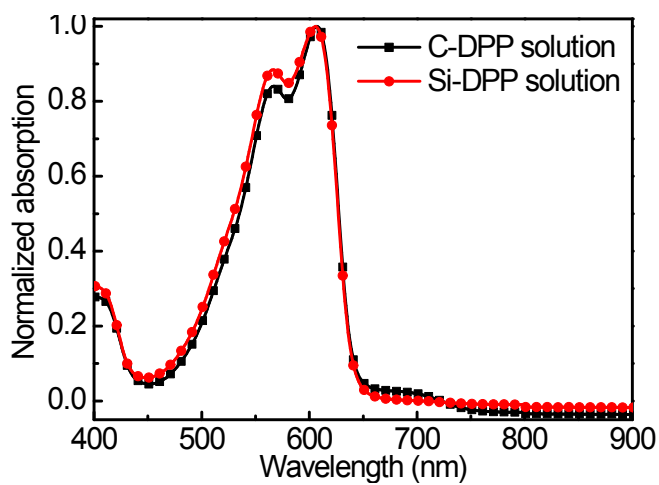
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**Fig. S5** MALDI-TOF MS spectrum of **Si-DPP**, calcd: 2731.97; found: 2732.09.

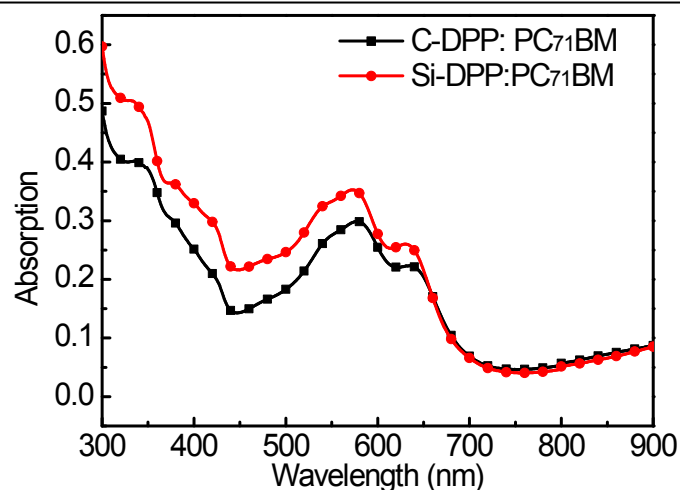




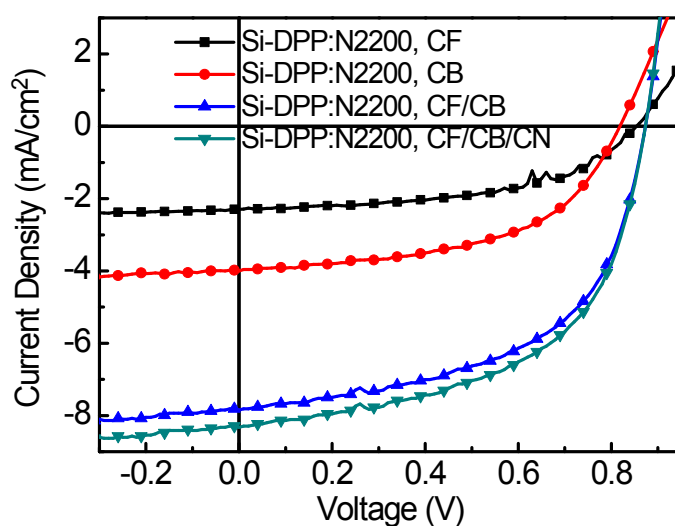
**Fig. S6** DSC curves of **C-DPP** and **Si-DPP** (neither melting nor re-crystallization was detected).



**Fig. S7** UV-vis absorption spectra of **C-DPP** and **Si-DPP** solutions in  $\text{CHCl}_3$ .



**Fig. S8** UV-vis absorption spectra of BHJs of C-DPP:PC<sub>71</sub>BM and Si-DPP: PC<sub>71</sub>BM. (They show mainly the features of 3D-DPPs absorption, along with the absorption less than 350 nm arising from PC<sub>71</sub>BM.)

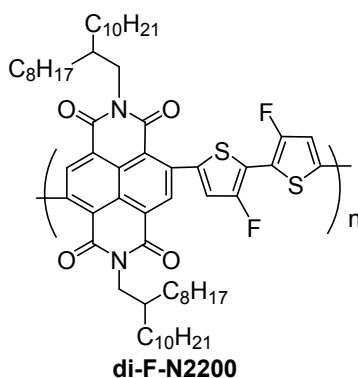


**Fig. S9** J-V curves of Si-DPP:N2200 processed by various solvents.

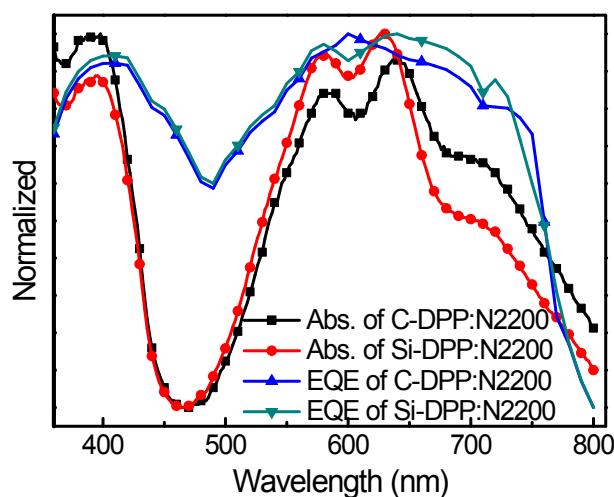
**Table S1** Effects of processing solvents on the OPV performance of Si-DPP:N2200.

Solvents	V <sub>oc</sub> [V]	J <sub>sc</sub> [mA cm <sup>-2</sup> ]	FF	PCE [%]
CF	0.85	2.29	0.52	1.03
CB	0.82	4.00	0.53	1.73
CF/CB <sup>a)</sup>	0.87	7.85	0.55	3.76
CF/CB/CN <sup>b)</sup>	<b>0.87</b>	<b>8.32</b>	<b>0.56</b>	<b>4.02</b>

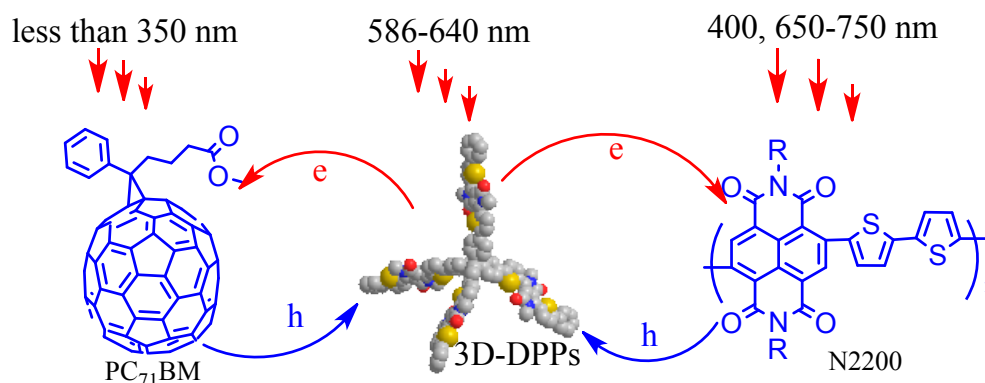
<sup>a)</sup> CF/CB (1:1, v/v); <sup>b)</sup> CF/CB/CN (1:1:0.03, v/v)



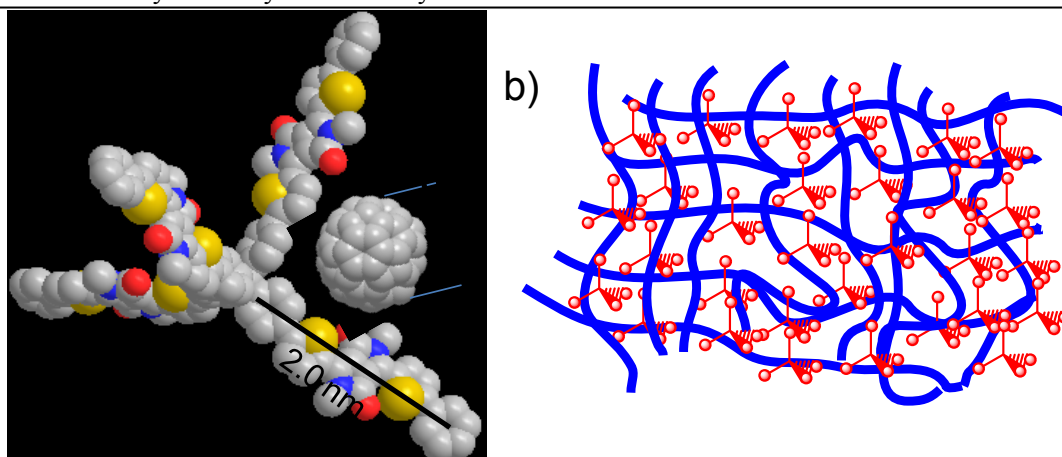
**Fig. S10** The structure of di-F-N2200.



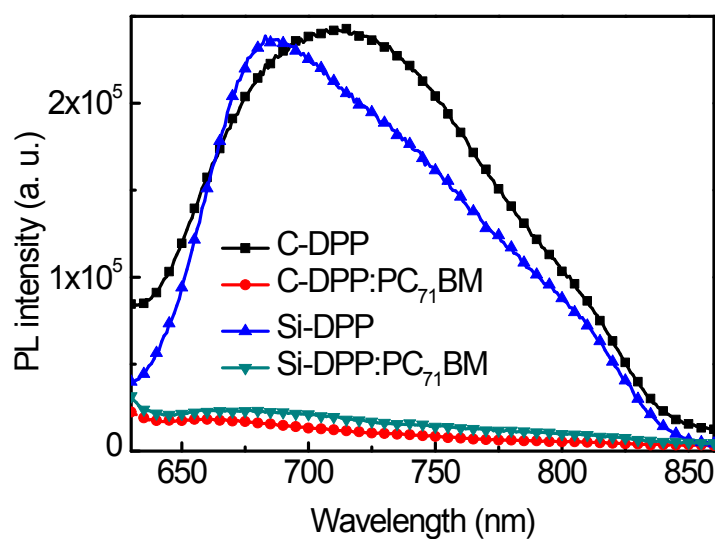
**Fig. S11** Normalized UV-vis absorption and IPCE spectra of 3D-DPP:N2200 BHJs.  
(The trends of UV-vis and EQE spectra of 3D-DPP:N2200 BHJs correlate well with each other).



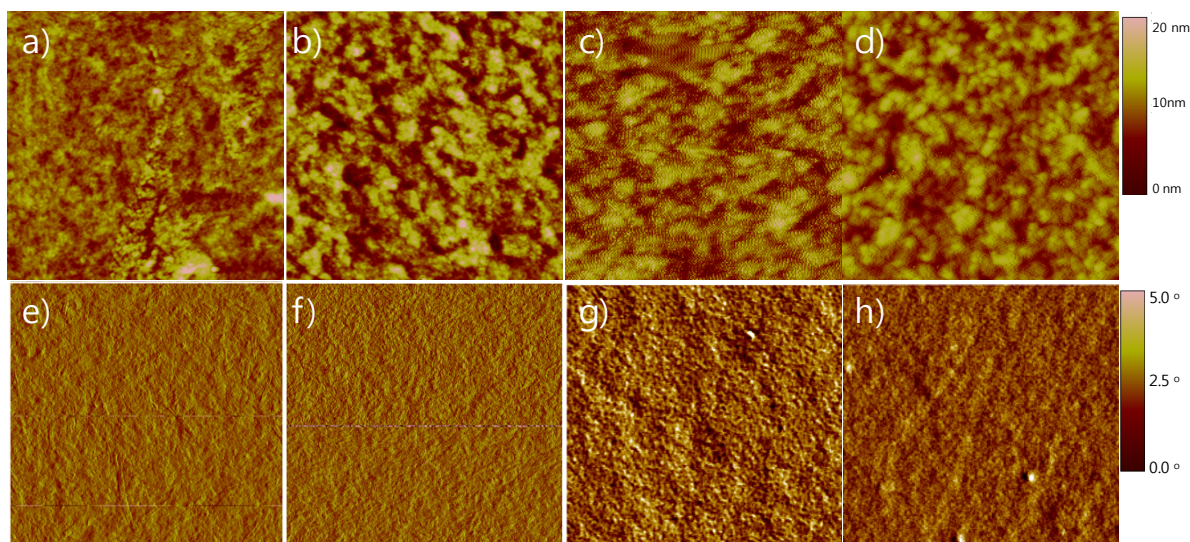
**Fig. S12** Photo-absorption and photo-generated charge transfer between 3D-DPP donors with N2200 and PC<sub>71</sub>BM acceptors (As compared with 3D-DPPs:PC<sub>71</sub>BM, both the photon-generated electron on donors (3D-DPPs) transferring to acceptor (N2200) and the photon-generated hole on acceptor transferring to donors contributes to the enhanced  $J_{SCS}$ ).



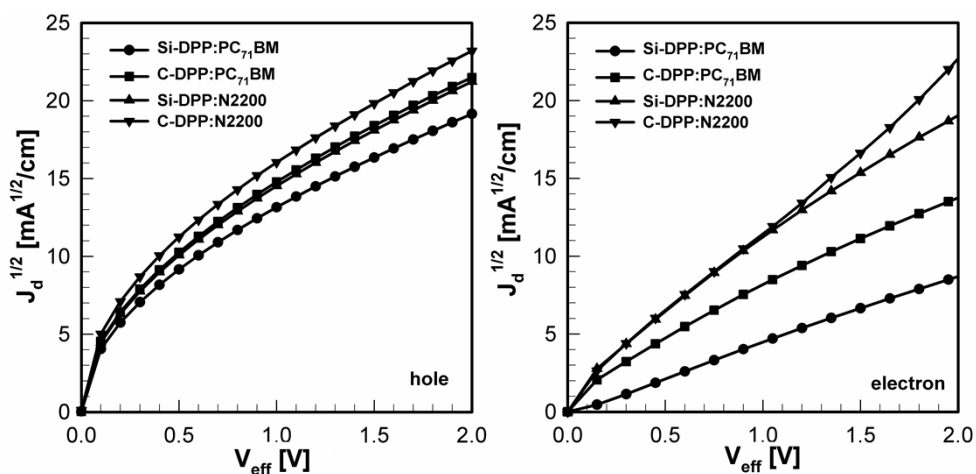
**Fig. S13** Proposed models for the D-A distributions in the BHJs of 3D-DPP:PC<sub>71</sub>BM and 3D-DPP:N2200. (a) The intimate D-A mixing between 3D-DPPs and PCBM will enhance the quenching of PL emission, however, but it will prevent the formation of suitable phase separation and adversely affect charge separation; b) The blend of crystalline N2200 and amorphous 3D-DPPs allows easier nanoscale phase separation, facilitating better charge separation and transport.)



**Fig. S14** Steady PL spectra of **C-DPP** and **Si-DPP** films, and **C-DPP:PC<sub>71</sub>BM** and **Si-DPP:PC<sub>71</sub>BM** BHJs (excited at 600 nm).



**Fig. S15** AFM height images (a, b, c, d) and corresponding phase images (e, f, g, h) of BHJs C-DPP:N2200, Si-DPP:N2200, C-DPP:PC<sub>71</sub>BM, and Si-DPP:PC<sub>71</sub>BM. Scale: 2  $\mu\text{m}$   $\times$  2  $\mu\text{m}$ .



**Fig. S16** J-V curves for a) hole-only and b) electron-only devices.

## References

- [S1] L. M. Wilson, A. C. Griffin, *J. Mater. Chem.*, 1993, **3**, 991.
- [S2] J.-H. Fournier, X. Wang, J. D. Wuest, *Can. J. Chem.*, 2003, **81**, 376.
- [S3] S. Liu, M. Shi, J. Huang, Z. Jin, X. Hu, J. Pan, H. Li, A. K.-Y. Jen, H.-Z. Chen, *J. Mater. Chem. A*, 2013, **1**, 2795.