

Electronic Supplementary Information for:

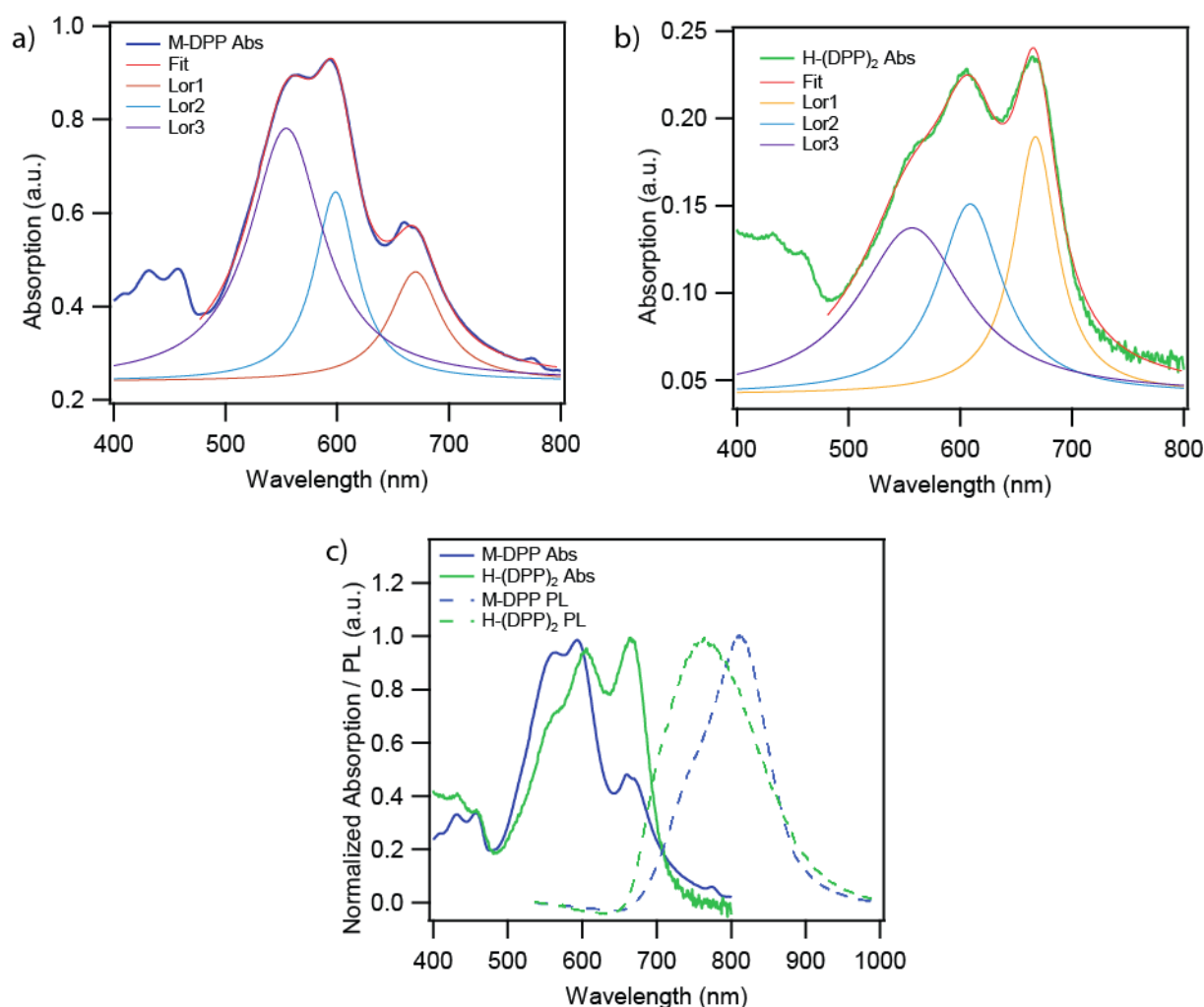
**Engineering the self-assembly of diketopyrrolopyrrole-based molecular semiconductors via an aliphatic linker strategy**

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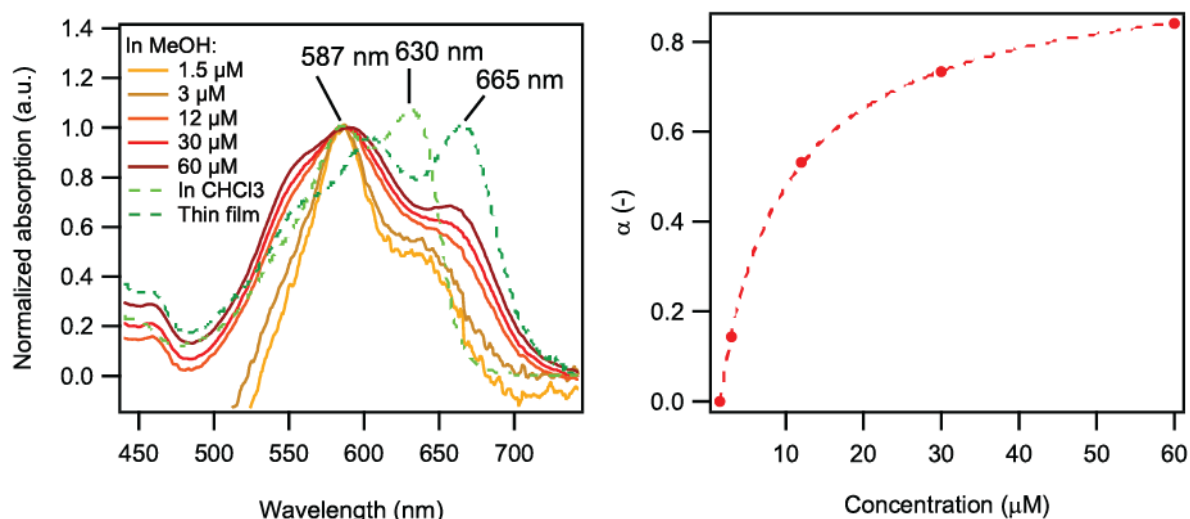
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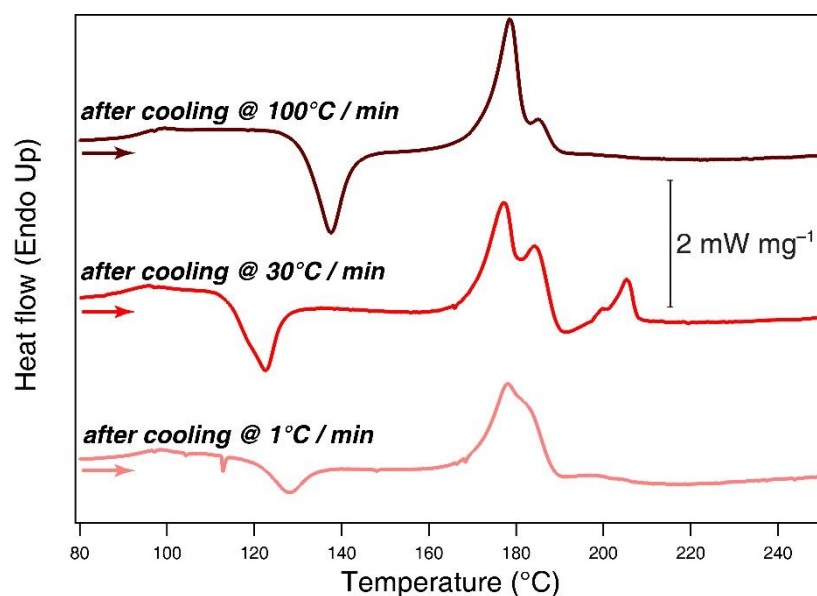
**Additional Figures:**



**Figure S1.** Deconvoluted absorption spectrum of a) M-DPP and b) H-(DPP)<sub>2</sub> using a sum of 3 Lorentzian functions for the fitting. c) Absorption spectrum (solid) and emission spectrum (dashed) of H-(DPP)<sub>2</sub> (green) and M-DPP (blue) in solid state.



**Figure S2.** (a) Absorption spectrum of H-(DPP)<sub>2</sub> in methanol at different concentration. Light green dashed line shows absorption spectrum of H-(DPP)<sub>2</sub> dissolved in CHCl<sub>3</sub> while dark green dashed line shows solid state absorption. (b) Aggregated fraction obtained from the absorption at 700 nm in function of concentration in MeOH. Fitting for cooperative self-assembly is shown in dashed line.



**Figure S3.** Differential scanning calorimetry heating curves of H-(DPP)<sub>2</sub> drop-casted sample at 10°C/min after cooling from the melt at different speed as indicated.

**Table S1.** Average hole mobility ( $\mu_h$ ) extracted from saturated and linear regime, on/off ratio and threshold voltage of the different OFET devices presented in this study in annealed conditions. Parameters for as cast devices are given in parenthesis.

| Active layer                        | Content (wt. %) | $\mu_{Sat}$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) | $\mu_{Lin}$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) <sup>1</sup> | On/off ratio                               | $V_T$ (V)    |
|-------------------------------------|-----------------|-----------------------------------------------------------|------------------------------------------------------------------------|--------------------------------------------|--------------|
| Neat M-DPP                          | -               | $6.5 \times 10^{-4}$<br>( $3.0 \times 10^{-5}$ )          | $2.2 \times 10^{-4}$                                                   | $7.0 \times 10^2$<br>(85.2)                | -10<br>(-11) |
| Neat H-(DPP) <sub>2</sub>           | -               | $2.4 \times 10^{-5}$<br>( $1.1 \times 10^{-5}$ )          | $9.7 \times 10^{-6}$                                                   | $1.0 \times 10^2$<br>(38)                  | -5<br>(-10)  |
| Neat V-(DPP) <sub>2</sub>           | -               | $< 1 \times 10^{-6}$                                      | $< 1 \times 10^{-6}$                                                   | $< 10$                                     | -10          |
| Blend<br>M-DPP:H-(DPP) <sub>2</sub> | 1               | $7.9 \times 10^{-4}$<br>( $1.7 \times 10^{-5}$ )          | $4.1 \times 10^{-4}$                                                   | $1.7 \times 10^3$<br>(85.5)                | -11<br>(-15) |
|                                     | 5               | $8.3 \times 10^{-4}$<br>( $1.7 \times 10^{-5}$ )          | $3.9 \times 10^{-4}$                                                   | $3.0 \times 10^3$<br>( $5.1 \times 10^2$ ) | -6<br>(-11)  |
|                                     | 10              | $1.1 \times 10^{-3}$<br>( $1.7 \times 10^{-5}$ )          | $4.8 \times 10^{-4}$                                                   | $3.4 \times 10^3$<br>( $1.2 \times 10^2$ ) | -5<br>(-10)  |
|                                     | 25              | $7.9 \times 10^{-5}$<br>( $1.3 \times 10^{-5}$ )          | -                                                                      | $3.9 \times 10^2$<br>(76)                  | -20<br>(-30) |
| Blend<br>M-DPP:V-(DPP) <sub>2</sub> | 1               | $1.6 \times 10^{-3}$<br>( $1.5 \times 10^{-5}$ )          | $6.4 \times 10^{-4}$                                                   | $4.7 \times 10^3$<br>(61)                  | -6<br>(-25)  |
|                                     | 5               | $2.0 \times 10^{-3}$<br>( $3.0 \times 10^{-5}$ )          | $7.7 \times 10^{-4}$                                                   | $2.6 \times 10^3$<br>(45)                  | -7<br>(-17)  |
|                                     | 10              | $3.0 \times 10^{-3}$<br>( $1.7 \times 10^{-4}$ )          | $9.2 \times 10^{-4}$                                                   | $6.4 \times 10^3$<br>( $4.7 \times 10^2$ ) | -9<br>(-13)  |
|                                     | 25              | $1.6 \times 10^{-4}$<br>( $2.4 \times 10^{-5}$ )          | -                                                                      | $1.1 \times 10^3$<br>( $1.3 \times 10^2$ ) | -8<br>(-12)  |

<sup>1</sup>Measured on more than 6 months old devices.

Charge carrier mobility in the saturated regime (when  $V_D > (V_G - V_T)$ ) was extracted using the following expression for the saturated current:

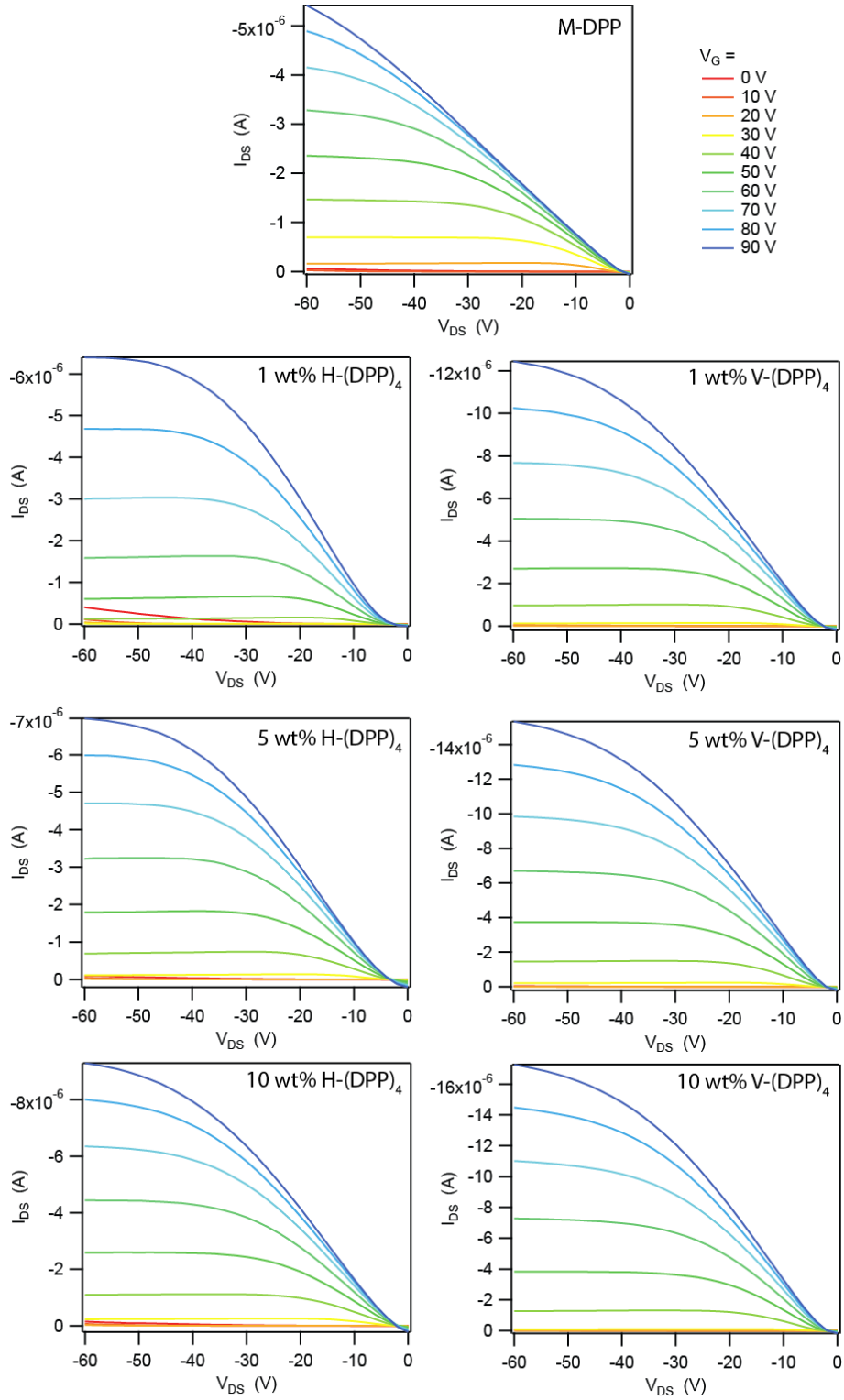
$$I_{DS} = \mu_{sat} C_i \frac{W}{2L} (V_G - V_T)^2$$

Where,  $C_i$  is the gate dielectric capacitance,  $W$  the channel width,  $L$  the channel length,  $V_T$  the threshold voltage and  $V_G$  the gate voltage.  $V_D > (V_G - V_T)$ .

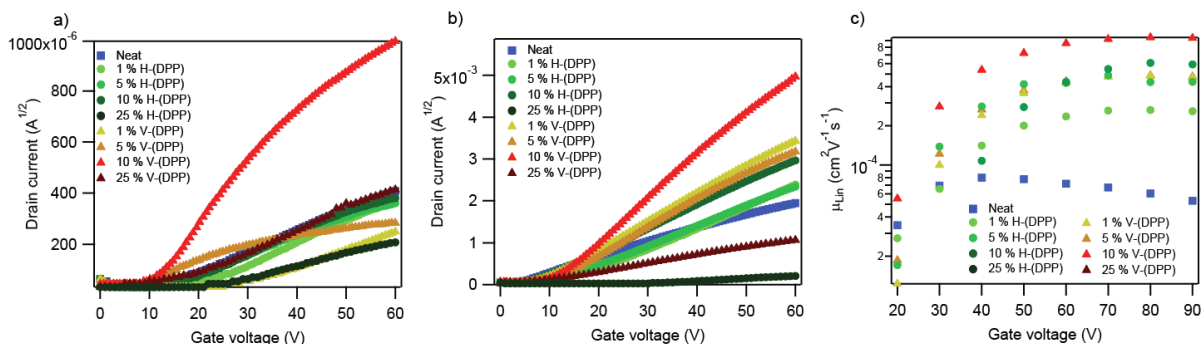
While in linear regime (when  $V_D << (V_G - V_T)$ ), the drain current can be expressed as:

$$I_{DS} = \mu_{lin} C_i \frac{W}{L} (V_G - V_T) V_D$$

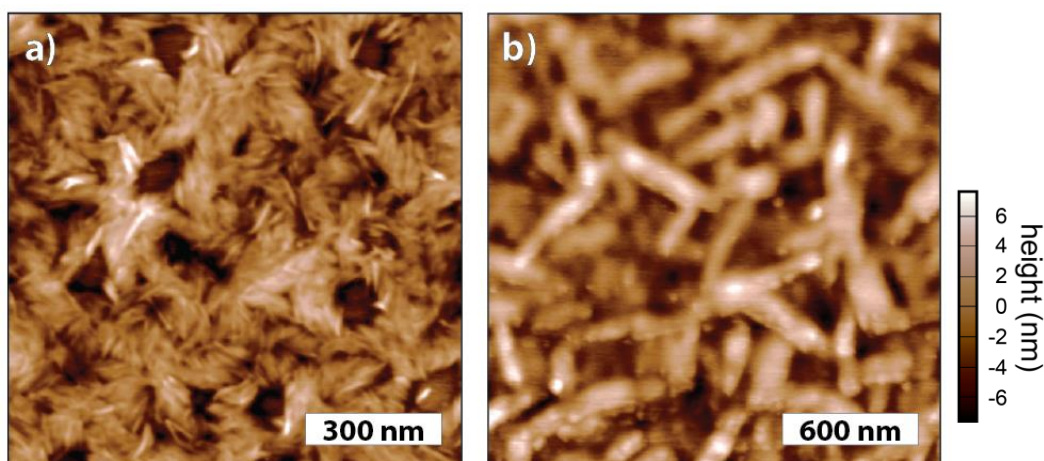
With  $V_D$  is the drain voltage.



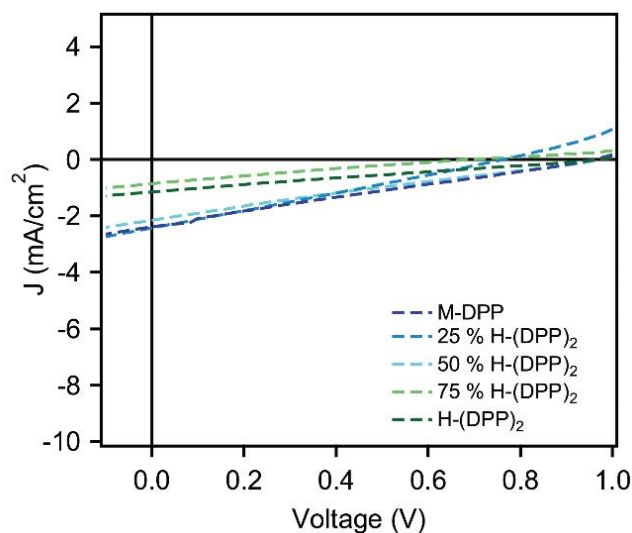
**Figure S4.** Output curves for transistors (channel length 20  $\mu\text{m}$ , channel width of 1 cm) prepared with neat M-DPP, 1, 5, 10 wt% H-(DPP)<sub>2</sub> and 1, 5, 10 wt% V-(DPP)<sub>2</sub> and annealed at 110  $^{\circ}\text{C}$  for 10 min. Measured on more than 6 months old devices.



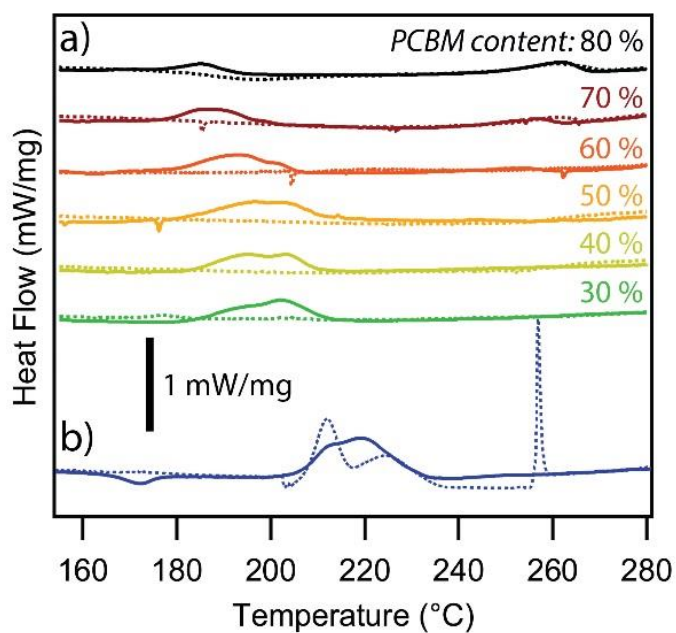
**Figure S5.** OFET device characteristics. (a) – (c) Show the output curves for transistors (channel length 20  $\mu\text{m}$ , channel width of 1 cm) prepared with neat M-DPP, 10 wt% H-(DPP)<sub>2</sub>, 10 wt% V-(DPP)<sub>2</sub>, respectively, and annealed at 110  $^{\circ}\text{C}$  for 10 min. d) and e) show the transfer curves for the Neat M-DPP and blend transistors as cast (b) and after annealing (c) at 110 $^{\circ}\text{C}$  for 10 min. (g) shows the extracted linear mobility as a function of gate voltage.



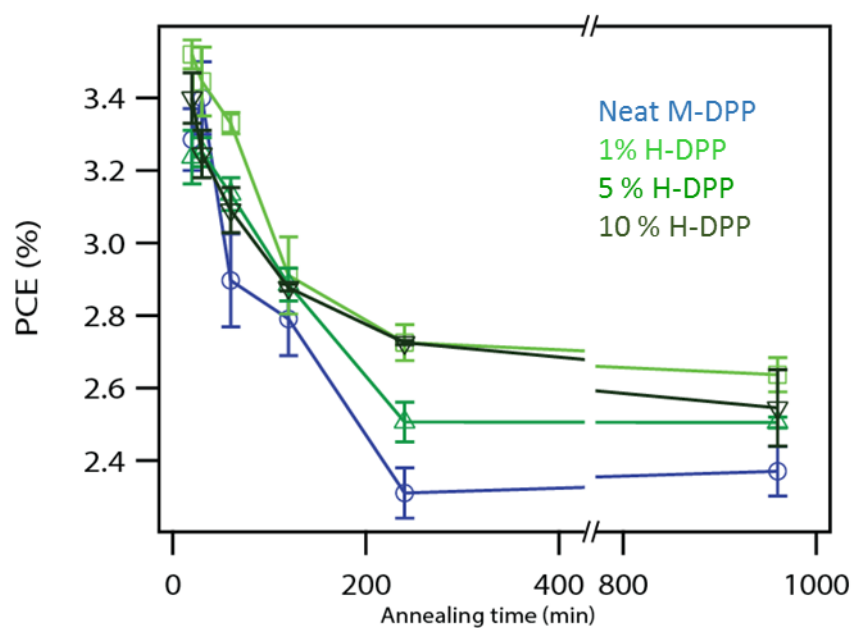
**Figure S6.** AFM height images of neat H-(DPP)<sub>2</sub> (a) and M-DPP (b).



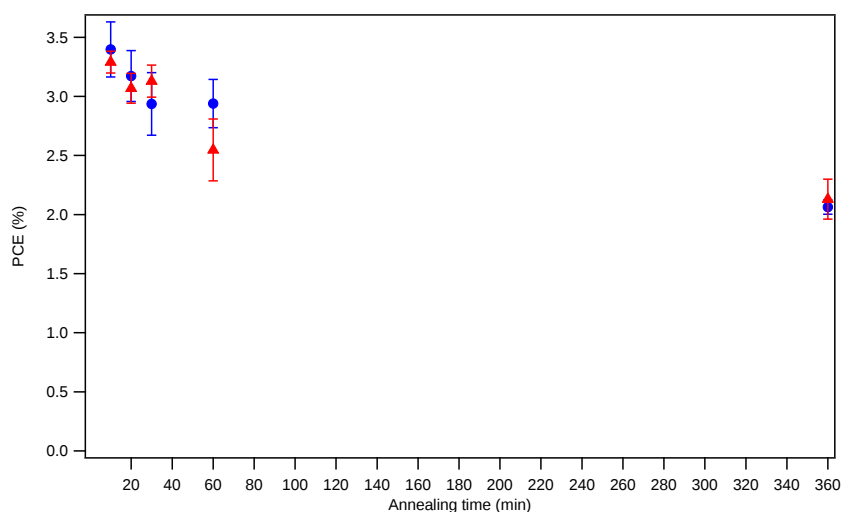
**Figure S7.** J-V curves of (as-cast, unannealed) photovoltaic devices based on bulk heterojunction Donor:PC<sub>61</sub>BM at a weight ratio of 6:4. The donor component consists of M-DPP with added dimer as indicated.



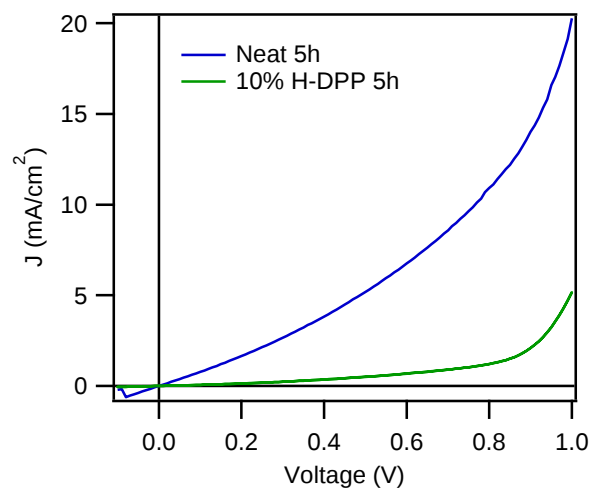
**Figure S8.** Heating curves measured by differential scanning calorimetry for a) different ratios of H-(DPP)<sub>2</sub>:PCBM blends and b) M-DPP:PCBM (6:4) on first heating (solid line) and second heating (dashed line). (exothermic down)



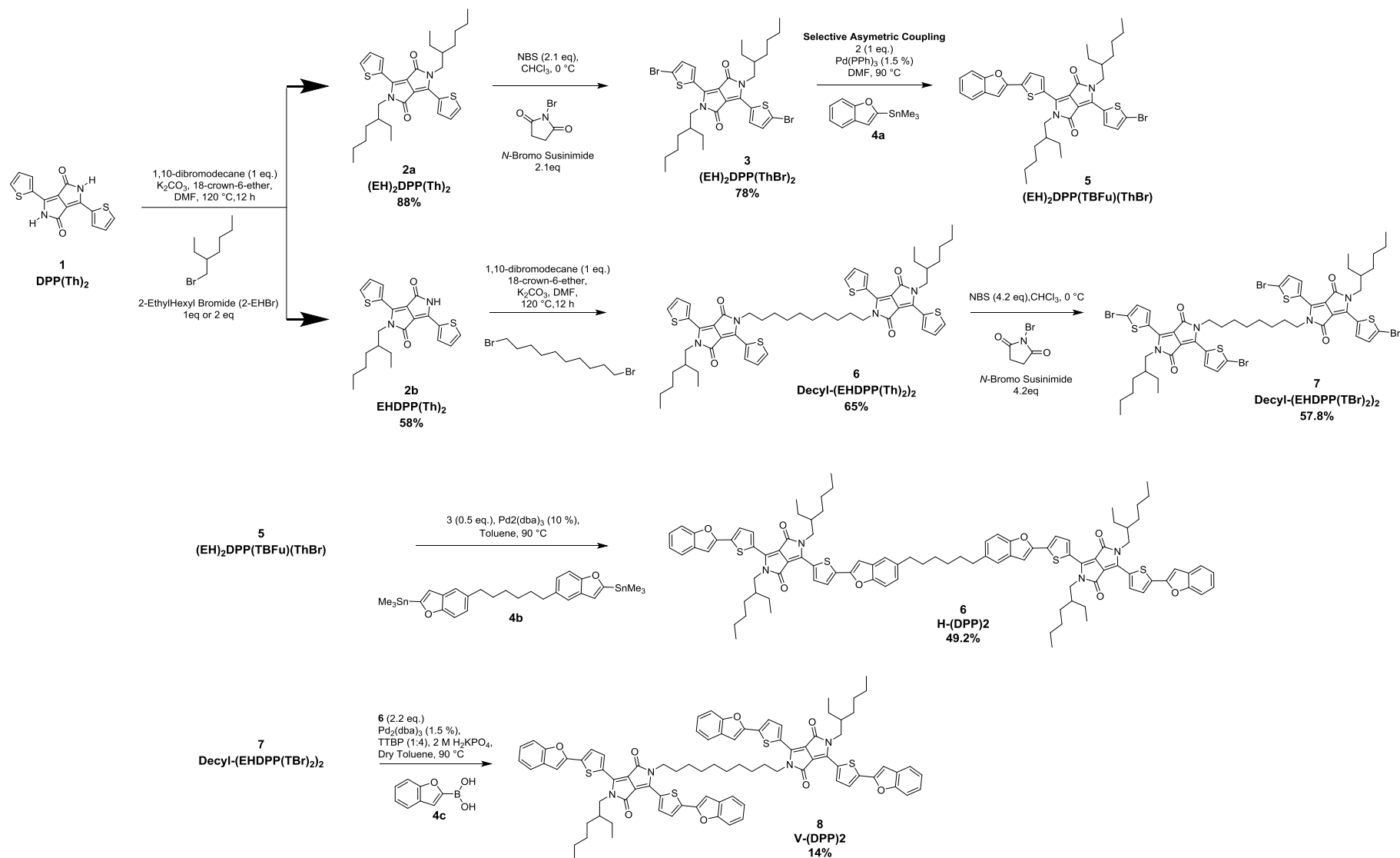
**Figure S9.** PCE stability during annealing at 100°C with and without H-(DPP)<sub>2</sub> in the wt% indicated.



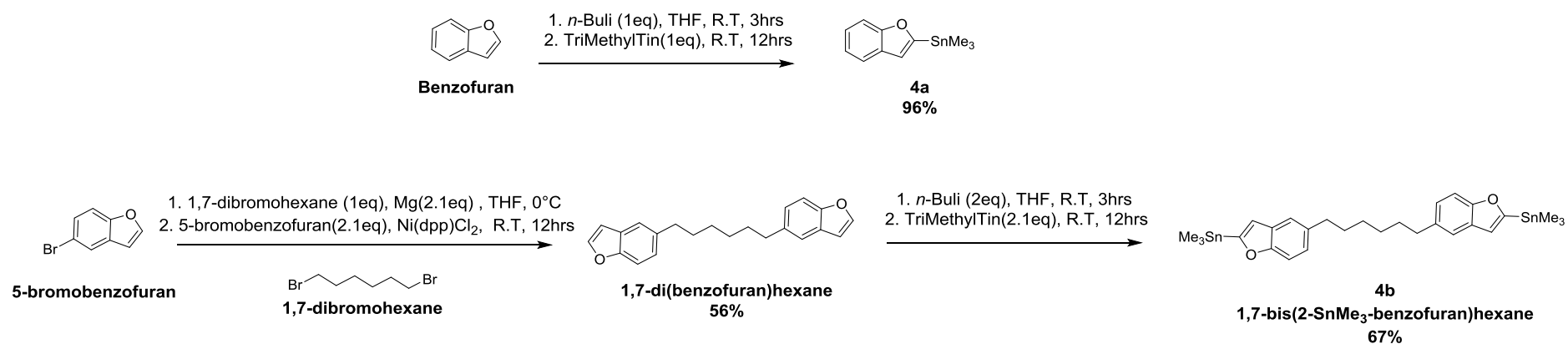
**Figure S10.** PCE stability during annealing at 100°C with (red triangles) and without (blue circles) 10 wt% V-(DPP)<sub>2</sub>.



**Figure S11.** JV curves in dark conditions of M-DPP:PCBM neat and with 10 wt% H-(DPP)<sub>2</sub> after 5h annealing prior to aluminium deposition.



**Scheme S1. Full Synthetic Route of H-(DPP)<sub>2</sub> and V-(DPP)<sub>2</sub>**



**Scheme S2. Stannylation of Benzofuran moieties**

## Synthetic Procedures

All reagents were of commercial reagent grade (Sigma-Aldrich, Acros and Fluorochem) and were used without further purification. Toluene, Chloroform, Tetrahydrofuran (Fisher Chemical, HPLC grade) and chlorobenzene (Alfa Aesar, HPLC grade) were purified and dried on a Pure Solv-MD Solvent Purification System (Innovative Technology, Amesbury, United States) apparatus. Normal phase silica gel chromatography was performed with an Acros Organic silicon dioxide (pore size 60 Å, 40–50 µm technical grade). The (<sup>1</sup>H) and (<sup>13</sup>C) NMR spectra were recorded at room temperature unless otherwise stated using per-deuterated solvents as internal standards on a NMR Bruker Advance III-400 spectrometer (Bruker, Rheinstetten, Germany). Chemical shifts are given in parts per million (ppm) referenced to residual <sup>1</sup>H or <sup>13</sup>C signals in CDCl<sub>3</sub> (<sup>1</sup>H: 7.26, <sup>13</sup>C: 77.16) and dichloromethane-*d*<sub>2</sub> (2H: 5.32, <sup>13</sup>C:53.84). EI-MS spectrum was recorded on an EI/CI-1200L GC-MS (Varian) instrument. Atomic-Pressure-Photoionization-Source(APPI) MS spectrum was recorded on an ESI/APCI LC-MS Autopurification System with a ZQ Mass detector (Waters, Milford, United States) instrument using a positive mode. Matrix-Assisted-Laser-Desorption/Ionization Time of Flight (MALDI-TOF) MS spectrum was recorded on a Bruker MALDI-TOF AutoFlex speed instrument using alpha-cyano-4-hydroxycinnamic acid, and 2,5-Dihydroxybenzoic acid as matrix. DPP(TBFu)<sub>2</sub> was synthesized according to literature procedure (*Adv. Funct. Mater.* **2009**, *19*, 3063-3069). Both H-(DPP)<sub>2</sub> and V-(DPP)<sub>2</sub> were purified using a Biotage Isolera™ Spektra Accelerated Chromatographic Isolation System™ with a Biotage ZIP® Sphere cartridges (60µm spherical silica) before device fabrication. Synthesis of 2,5-Dihydro-3,6-di-2-thienyl-pyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP(Th)<sub>2</sub> - **1**) (see *J. Polym. Sci. A Polym. Chem.* **2010**, *48*, 1669-1675)

### Preparation of stannylated Benzofuran moieties (Scheme S2)

**1,6-di(benzofuran)hexane** was synthesized based on our previously published procedure (*Chem. Sci.* 2014, *5*, 4922-4927): To a solution of 1,6-dibromohexane (2.0g, 8.2mmol) in dried tetrahydrofuran (80 mL), magnesium turnings (418.4mg, 17.2mmol) was added dropwise at 0°C over an 1hrs under argon. This was then allowed to warm up to room temperature and left to stir for 4h. 5-bromobenzofuran (3.39g, 17.2mmol) and dichloro[1,3-bis(diphenylphosphino)propane]nickel (5%eq, 0.41mmol) were added quickly at –30°C and was then left to stir at room temperature for 12hrs. Saturated ammonium chloride was added to quench the reaction (approximately 30-40mL). Diethyl ether was then used to extract the organic phase from the crude mixture, subsequently washed with brine and dried over magnesium sulfate, filtered and concentrated under vacuum. This was then subjected to silica gel chromatography using hexane as an elution solvent to obtain a white solid after precipitation in methanol affording the product (2.1g, 80.5%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.63 (s, 2H), 7.45 (d, *J* = 11.0 Hz, 4H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.75 (s, 2H), 2.74 (t, *J* = 7.8 Hz, 2H), 1.70 (p, *J* = 7.2 Hz, 2H), 1.35 (dd, *J* = 20.6, 6.6 Hz, 8H). δ<sub>c</sub> ( 400MHz CDCl<sub>3</sub>) 145.01, 137.43, 124.99, 120.39, 110.93, 106.42, 35.92, 32.19, 29.76, 29.74, 29.63, 29.58, 29.34.

### General procedure for the stannylation of Benzofuran and 1,6-di(benzofuran)hexane to produce 4a and 4b

1-Benzofuran or 1,6-di(benzofuran)hexane (1eq) was placed in an oven-dried 100 mL Schlenk flask and degassed by three vacuum/nitrogen cycles. Anhydrous THF (20 mL) was injected and the solution was cooled to -78 °C for 15mins after which, *N*-butyllithium (2.5M in hexanes, at 1.1 and 2.1 eq respectively) was added slowly, and the reaction was left stirring for 1-2hrs. Tributyltin chloride (1.1 and 2.1 eq

respectively) was added slowly, the reaction was allowed to heat up to room temperature over 12 hours. H<sub>2</sub>O (5-20 mL) was then added to quench the reaction, after which the crude was then concentrated under vacuum, diluted with water (200 mL), 1 M NaOH (50 mL) and extracted with hexanes. The organic phase was collected, dried under MgSO<sub>4</sub>, followed by solvent removal under vacuum to afford a yellow-oil of **4a** at a yield of 96% and a white solid of **4b** at a yield of 67%.

**4a:** <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 16.3, 7.6 Hz, 2H), 7.33 (dt, *J* = 16.5, 7.6 Hz, 2H), 7.05 (d, *J* = 2.2 Hz, 1H), 0.54 (d, *J* = 2.1 Hz, 9H); δ<sub>c</sub> (300MHz, CDCl<sub>3</sub>) 193.83, 155.18, 127.76, 127.14, 124.09, 123.39, 116.76, 112.55, -9.55.

**4b:** <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.3 Hz, 3H), 7.37 (s, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.90 (s, 2H), 2.71 (t, *J* = 7.6 Hz, 5H), 1.77 – 1.57 (m, 6H), 1.43 – 1.16 (m, 24H), 0.44 (s, 18H); δ<sub>c</sub> (300MHz, CDCl<sub>3</sub>) 136.86, 127.98, 124.42, 119.60, 117.40, 110.45, 35.89, 32.24, 29.74, 29.72, 29.63, 29.57, 29.29, -9.19. δ<sub>c</sub> (101 MHz, CDCl<sub>3</sub>) 136.86, 127.98, 124.42, 119.60, 117.40, 110.45, 35.89, 32.24, 29.74, 29.72, 29.63, 29.57, 29.29.

### Preparation of diketopyrrolopyrrole(DPP) derivatives (Scheme S1)

#### General Procedure for the symmetric and asymmetric alkylation of DPP(Th)<sub>2</sub> (**1**), EHDPP(Th)<sub>2</sub> (**2b**), and Decyl-(EHDPP(Th)<sub>2</sub>)<sub>2</sub> (**6**)

**DPP(Th)<sub>2</sub> (1)** or **EHDPP(Th)<sub>2</sub> (2b)** and anhydrous K<sub>2</sub>CO<sub>3</sub> were stirred in anhydrous (DMF) under Argon at 130 °C for 1 h. 2-EthylhexylBromide or 1,10-dibromodecane was then added drop wise and the reaction mixture was stirred at 130 °C for a further 20 h for an asymmetric or symmetric alkylation respectively. The reaction mixture was allowed to cool to room temperature then it was poured into ice water (1 L) and the resulting suspension was stirred for 1 h. After the solid was dried under vacuum to give the crude product, and separated via silica gel column chromatography using Hexane: Chloroform as eluent.

For **(EH)<sub>2</sub>DPP(Th)<sub>2</sub> (2a)**, 1eq of **DPP(Th)<sub>2</sub> (1)** and 2.5eq of 2-EthylhexylBromide was used to obtain the final product as red crystals after recrystallization with Ethanol (Average Yield 88%); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.92 (d, *J* = 3.9 Hz, 2H), 7.65 (d, *J* = 5.0 Hz, 2H), 7.30 (d, *J* = 4.3 Hz, 2H), 4.13 – 3.98 (m, 4H), 1.89 (p, *J* = 6.3 Hz, 2H), 1.33 (dd, *J* = 37.4, 16.5, 9.2, 5.0 Hz, 8H), 0.89 (dt, *J* = 9.1, 7.1 Hz, 6H). MS: 524.25 (APPI): Calcd.[C<sub>30</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>]: 524.78.

For **EHDPP(Th)<sub>2</sub> (2b)**, 1eq of **DPP(Th)<sub>2</sub> (1)** and 2-EthylhexylBromide was used to obtain the product as a red powder after precipitation with Hexane:Chloroform at average Yield 58%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.86 (d, *J* = 3.7 Hz, 1H), 8.49 (s, 1H), 8.40 (d, *J* = 3.7 Hz, 1H), 7.69 (d, *J* = 5.1 Hz, 1H), 7.63 (d, *J* = 5.0 Hz, 1H), 7.37 – 7.23 (m, 5H), 4.06 (q, *J* = 7.1 Hz, 2H), 1.89 (q, *J* = 6.7 Hz, 1H), 1.48 – 1.18 (m, 8H), 0.98 – 0.82 (m, 7H). δ<sub>c</sub> (101 MHz, CDCl<sub>3</sub>) 135.46, 132.18, 130.89, 130.61, 129.23, 128.49, 45.91, 39.11, 30.22, 28.35, 23.54, 23.07. MS: 412.13 (APPI): Calcd. [C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>]: 412.57.

For **Decyl-(EHDPP(Th)<sub>2</sub>)<sub>2</sub> (6)**, 2eq of **EHDPP(Th)<sub>2</sub> (2b)** and 1.0eq of 1,10-dibromodecane was used to obtain the product as a dark red solid with an average yield of 65% after separation via chromatography using CHCl<sub>3</sub> as eluent, and precipitation in CH<sub>2</sub>Cl<sub>2</sub>:Methanol; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.00 – 8.77 (dd, *J* = 26.7, 3.9 Hz, 4H), 7.70 – 7.56 (d, *J* = 5.1 Hz, 4H), 7.36 – 7.18 (m, 4H), 4.18 – 3.92 (dh, *J* = 14.8, 7.4, 6.6 Hz, 8H), 2.08 – 1.63 (m, 12H), 1.49 – 1.11 (m, 12H), 0.96 – 0.74 (q, *J* = 7.2 Hz, 12H); δ<sub>c</sub> (101 MHz, CDCl<sub>3</sub>) 161.76, 161.36, 140.38, 140.06, 135.38, 135.17, 130.69, 130.64, 130.59, 130.57, 129.84, 129.73, 128.65,

28.40, 108.05, 107.57, 63.03, 45.86, 42.18, 39.09, 32.74, 30.22, 29.91, 29.25, 29.16, 29.09, 29.05, 28.35, 26.79, 26.76, 25.64, 23.52, 23.08, 14.05, 10.50.

#### General Procedure for the bromination of DPP(Th)<sub>2</sub> (**1**) and Decyl-(EHDPP(Th)<sub>2</sub>)<sub>2</sub> (**6**)

To a solution of **1** or **6** in an Argon filled chloroform flask, wrapped in aluminium foil to exclude light at 0°C, N-bromosuccinimide at 2.1eq and 4.2eq respectively. After the reaction was completed as indicated from TLC, the mixture was poured into cold methanol, and left to stir for 1h. The precipitate was filtered and the solid was washed with methanol (2 × 200 mL) then dried under vacuum. The crude product was recrystallized from Hexane/chloroform to give the product as a dark purple solid of (EH)<sub>2</sub>DPP(ThBr)<sub>2</sub> (**3**) and Decyl-(EHDPP(TBr)<sub>2</sub>)<sub>2</sub> (**7**).

**(3)** (Yield =78%); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.67 (d, *J* = 4.2 Hz, 4H), 7.25 (d, *J* = 4.2 Hz, 4H), 3.97 (h, *J* = 7.8 Hz, 4H), 1.86 (q, *J* = 6.5 Hz, 2H), 1.45 – 1.21 (m, 16H), 0.91 (q, *J* = 7.4 Hz, 12H); MS: 567.95 (APPI): Calcd. [C<sub>22</sub>H<sub>22</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>]: 570.36.

**(7)** (Yield=57.8%); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.68 (dd, *J* = 23.8, 4.1 Hz, 4H), 7.29 (s, 5H), 6.97 (d, *J* = 3.7 Hz, 1H), 3.97 (tq, *J* = 14.9, 7.3 Hz, 2H), 3.58 – 3.36 (m, 1H), 1.85 (q, *J* = 6.5 Hz, 1H), 1.72 (p, *J* = 8.3, 7.6 Hz, 1H), 1.49 – 1.08 (m, 22H), 1.00 – 0.75 (m, 7H). MS (APPI): *m/z* [M]<sup>+</sup> = 1273.10

#### General Procedure for Stille Coupling the optimization of (EH)<sub>2</sub>DPP(TBFu)(ThBr) (**5**)

In a 100 mL oven-dried Schlenk flask, EHDPP(TBr)<sub>2</sub> (2.89 g, 4.24 mmol), B<sub>2</sub>SnMe<sub>3</sub> **2** (1.19 g, 4.24 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.489 g, 0.423mmol) were placed. The flask was then degassed by three vacuum/nitrogen cycles. Anhydrous DMF or toluene (15 mL) was then injected into the flask and the solution mixture was stirred for 12h at 100 °C under Argon. After cooling to room temperature, the reaction mixture was poured into water (300 mL) with brine (30 mL). The precipitate was filtered over Celite, washed with water and methanol, and then washed with CHCl<sub>3</sub> until the washings were colourless. The organic extract was then dried with MgSO<sub>4</sub>, and the solvent was removed under vacuum and the product was purified by column chromatography (hexane/DCM) to afford EHDPP(TBFu)(ThBr) as a dark blue solid (1.50g, 49.2%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.03 – 8.95 (d, *J* = 4.2 Hz, 1H), 8.68 – 8.61 (d, *J* = 4.2 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.56 – 7.48 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.30 (td, *J* = 8.2, 7.8, 1.4 Hz, 1H), 7.30 – 7.20 (s, 9H), 7.09 – 7.04 (s, 1H), 4.14 – 4.03 (m, 2H), 4.03 – 3.91 (m, 2H), 2.01 – 1.77 (m, 1H), 1.48 – 1.16 (m, 12H), 1.01 – 0.78 (m, 14H). MS (ESI): *m/z* [M]<sup>+</sup> = 721.1962

#### Hexyl-(EHDPP(TBFu)<sub>2</sub>)<sub>2</sub> (**6**) H-(DPP)<sub>2</sub>

In a 50 ml oven-dried Schlenk flask 144 mg of 1,6-bis(2-(trimethylstannyl)benzofuran-5-yl)hexane (144mg, 0.22mmol) and EHDPP(TBFu)(ThBr) (353mg, 0.49mmol) were added in 10 ml of anhydrous chlorobenzene under an Argon atmosphere using 2 mol% of tris(dibenzylideneacetone)dipalladium and tri(o-tolyl)-phosphine as a catalyst. After, 24hours the reaction was left to cool down, and the crude was allowed to precipitate in methanol, and collected via filtration with several hexane and methanol washings. The crude was then filtered over Celite, washed with water and methanol, and then washed with CHCl<sub>3</sub> until the washings were colourless. The organic extract was then dried with MgSO<sub>4</sub>, and the solvent was removed under vacuum and the product was purified by column chromatography (hexane/DCM) to afford H-DPP as a dark blue solid (1.50g, 49.2%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.99 (t, *J* = 3.0 Hz, 4H), 7.55 (q, *J* = 5.2, 4.1 Hz, 6H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 6.9 Hz, 2H), 7.23 (s, 4H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.01 (s, 2H), 6.94 (s, 2H), 4.17 – 3.97 (m, 5H), 2.68 (t, *J* = 7.6 Hz, 2H), 1.93 (q, *J* = 6.5 Hz, 3H), 1.67 (t, *J* = 7.3 Hz, 3H), 1.35 (dq, *J* = 45.5, 12.4, 10.0 Hz, 24H), 0.91 (dt, *J* = 13.5, 7.0 Hz, 15H); δ<sub>c</sub> (400 MHz,

CD<sub>2</sub>Cl<sub>2</sub>) 125.40, 125.37, 123.55, 121.25, 111.15, 103.72, 103.59, 53.96, 53.89, 53.69, 53.62, 53.42, 53.35, 53.15, 52.88, 29.96, 28.51, 28.12, 26.37, 23.10; MS (MALDI-TOF):  $m/z$  [M]<sup>+</sup> = 1596.19

See Figures S12-S14 for the <sup>1</sup>H NMR, <sup>13</sup>C NMR, and MALDI-TOF MS results.

#### **N-EthylHexy-N-Decyl-Bis-EHDPP(TBFu)<sub>2</sub> (7) V-(DPP)<sub>2</sub>**

In a 50mL Schleck flask, Decyl-(EHDPP(TBr)<sub>2</sub>)<sub>2</sub> (0.128mg, 0.11mmol) Benzofuran-2-boronic acid (73mg, 0.45mmol), tris(dibenzylideneacetone)dipalladium(0) (2.8 mg, mmol), and tri-tert-butylphosphonium tetrafluoroborate (3.6mg, mmol) was mixed with 15mL of anhydrous toluene and 2mL of 2.0 M potassium phosphate and the resulting mixture was degassed for 10 min. The reaction mixture was stirred and heated to 90°C under argon overnight. After which the reaction mixture was allowed to cool down to room temperature, and poured into 300mL of methanol and then stirred for 1h. The precipitated solid was then collected by vacuum filtration and washed with several portions of distilled water, methanol, isopropanol, and petroleum ether. The solid was then washed with hot methanol, and precipitated several times in methanol/Hexane/CH<sub>2</sub>Cl<sub>2</sub>. The crude product was purified by flash chromatography using chloroform as eluent, and the solvent was removed in vacuum to obtain a pure product of V-DPP(0.020mg, 14%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.08 – 8.92 (d, *J* = 4.3 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.60 – 7.53 (d, *J* = 8.6 Hz, 1H), 7.41 – 7.33 (t, *J* = 7.7 Hz, 1H), 7.33 – 7.25 (d, *J* = 1.3 Hz, 25H), 7.16 – 7.10 (s, 1H), 4.73 – 4.56 (t, *J* = 11.4 Hz, 1H), 4.23 – 4.07 (d, *J* = 15.3 Hz, 1H), 3.58 – 3.46 (d, *J* = 5.3 Hz, 2H), 3.25 – 3.19 (s, 0H), 1.99 – 1.84 (s, 1H), 1.83 – 1.67 (s, 1H), 1.69 – 1.48 (d, *J* = 1.4 Hz, 32H), 1.42 – 1.24 (d, *J* = 32.4 Hz, 3H), 1.24 – 1.12 (s, 1H), 1.12 – 0.97 (m, 1H), 0.97 – 0.82 (dt, *J* = 14.6, 6.7 Hz, 6H); δ<sub>c</sub> (600 MHz, CDCl<sub>3</sub>) 161.69, 154.92, 149.98, 139.64, 138.03, 136.78, 136.47, 129.46, 128.85, 125.55, 125.45, 123.61, 121.29, 111.35, 108.67, 103.77, 77.37, 77.16, 77.11, 76.86, 46.00, 42.89, 42.73, 39.22, 38.07, 29.83, 28.48, 23.53, 23.23, 14.29, 10.57; MS (MALDI-TOF):  $m/z$  [M+Na]<sup>+</sup> = 1450.9.

See Figures S15-S17 for the <sup>1</sup>H NMR, <sup>13</sup>C NMR, and MALDI-TOF MS results.

$^1\text{H}$  and  $^{13}\text{C}$  Nuclear Magnetic Resonance (NMR) and Mass spectra of  $H\text{-(DPP)}_2$  and  $V\text{-(DPP)}_2$

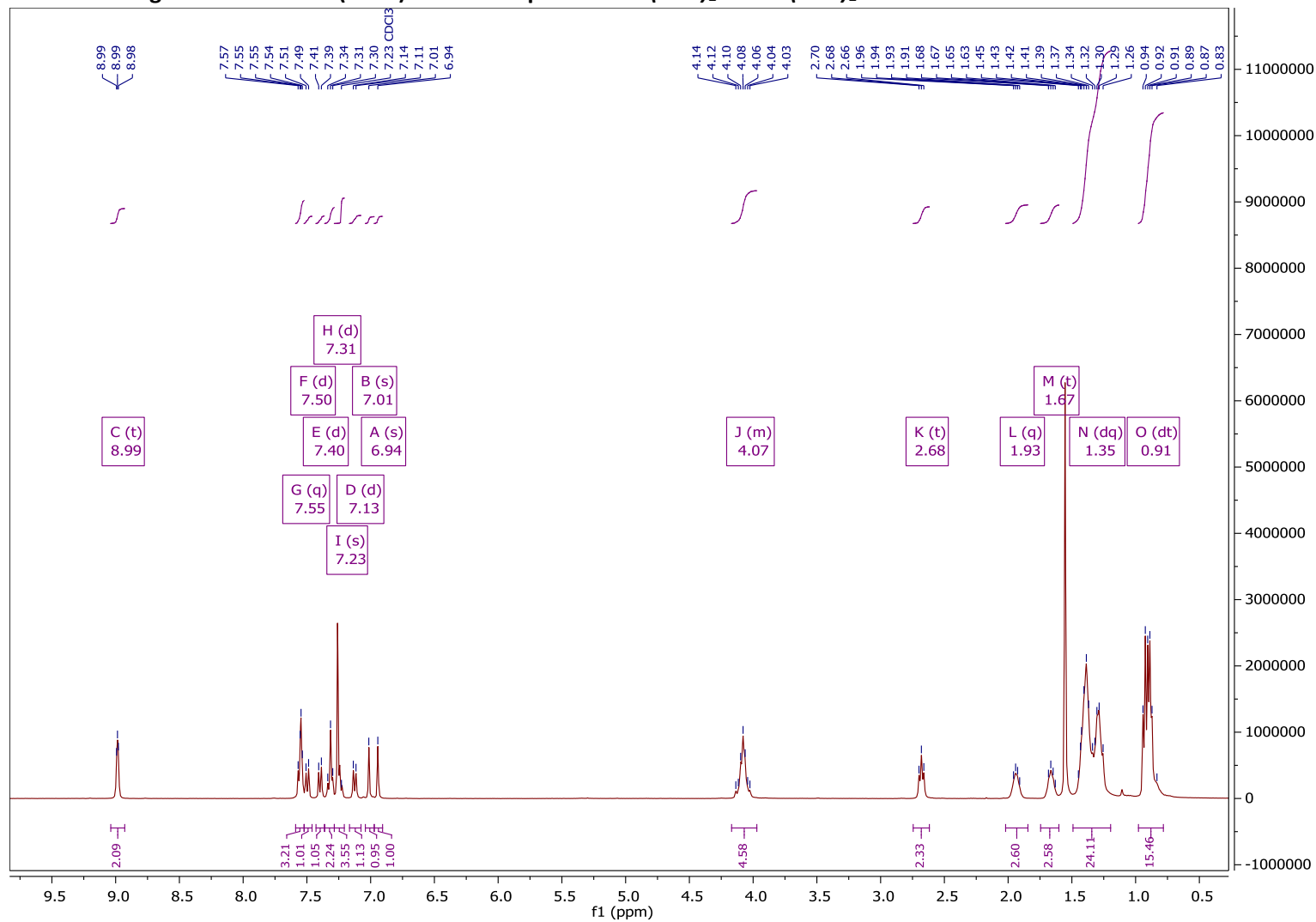
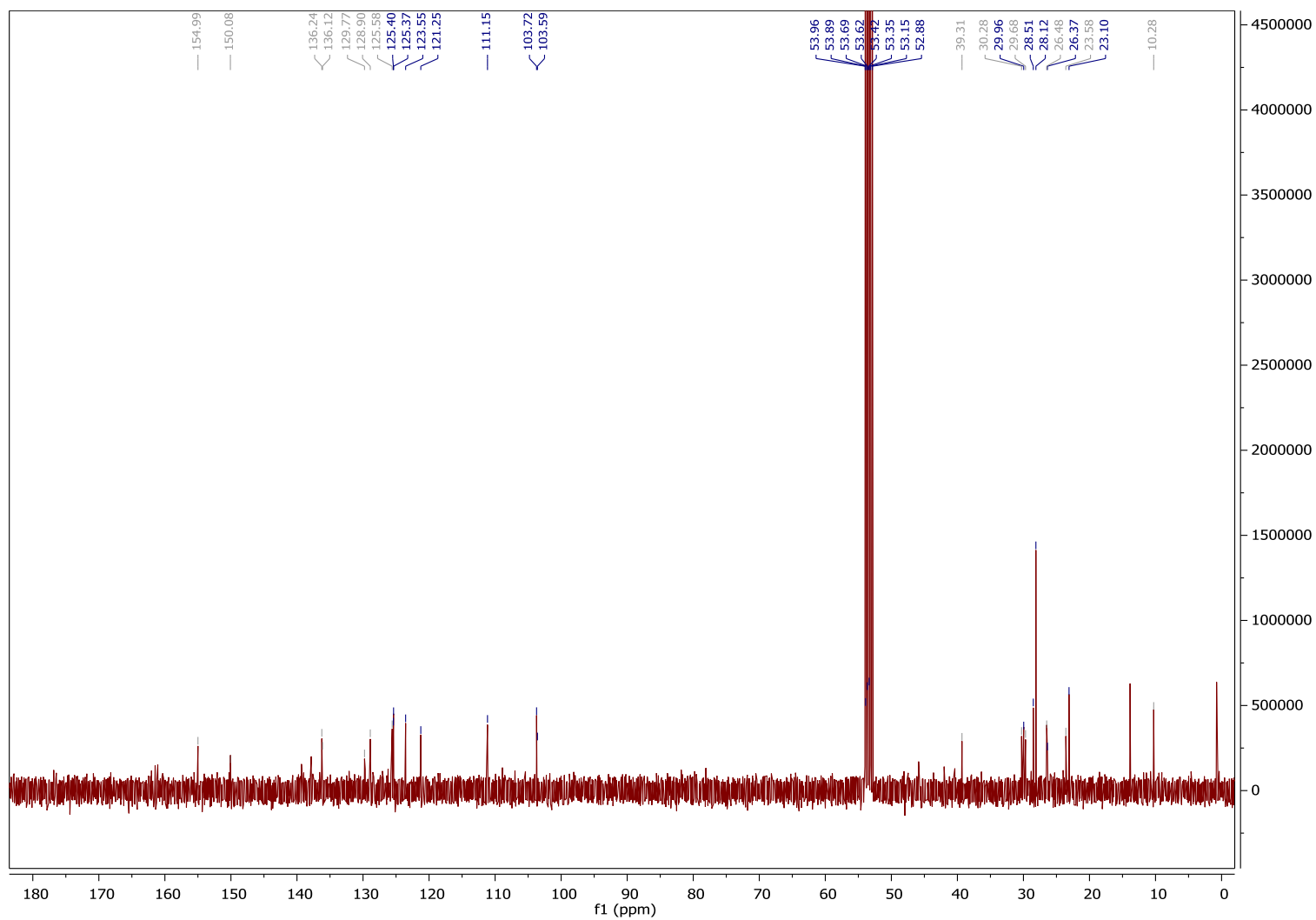


Figure S12.  $^1\text{H}$  NMR of  $H\text{-(DPP)}_2$



**Figure S13.**  $^{13}\text{C}$  NMR of  $\text{H}-(\text{DPP})_2$

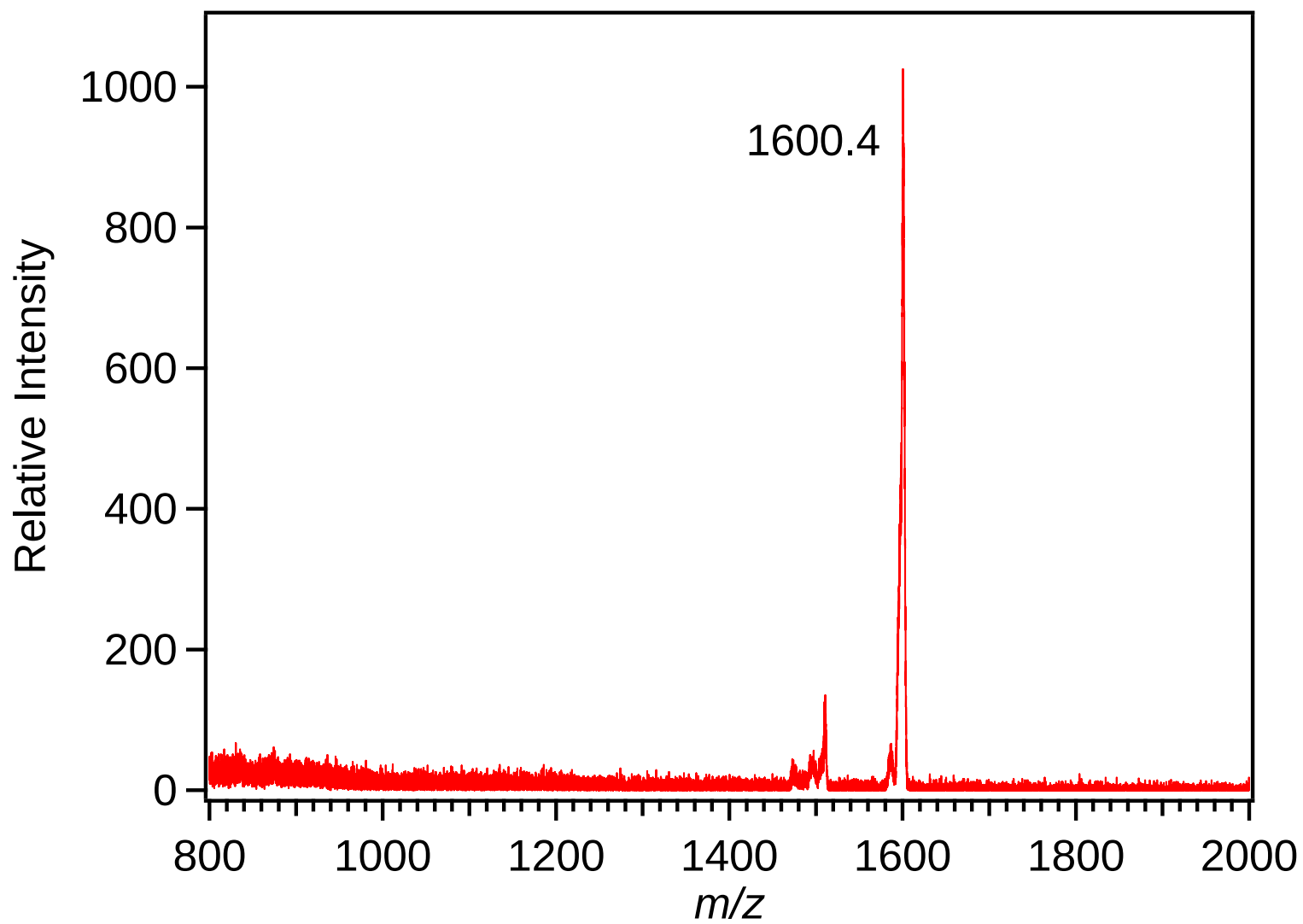


Figure S14. MALDI-TOF Mass Spectra of  $H-(DPP)_2$

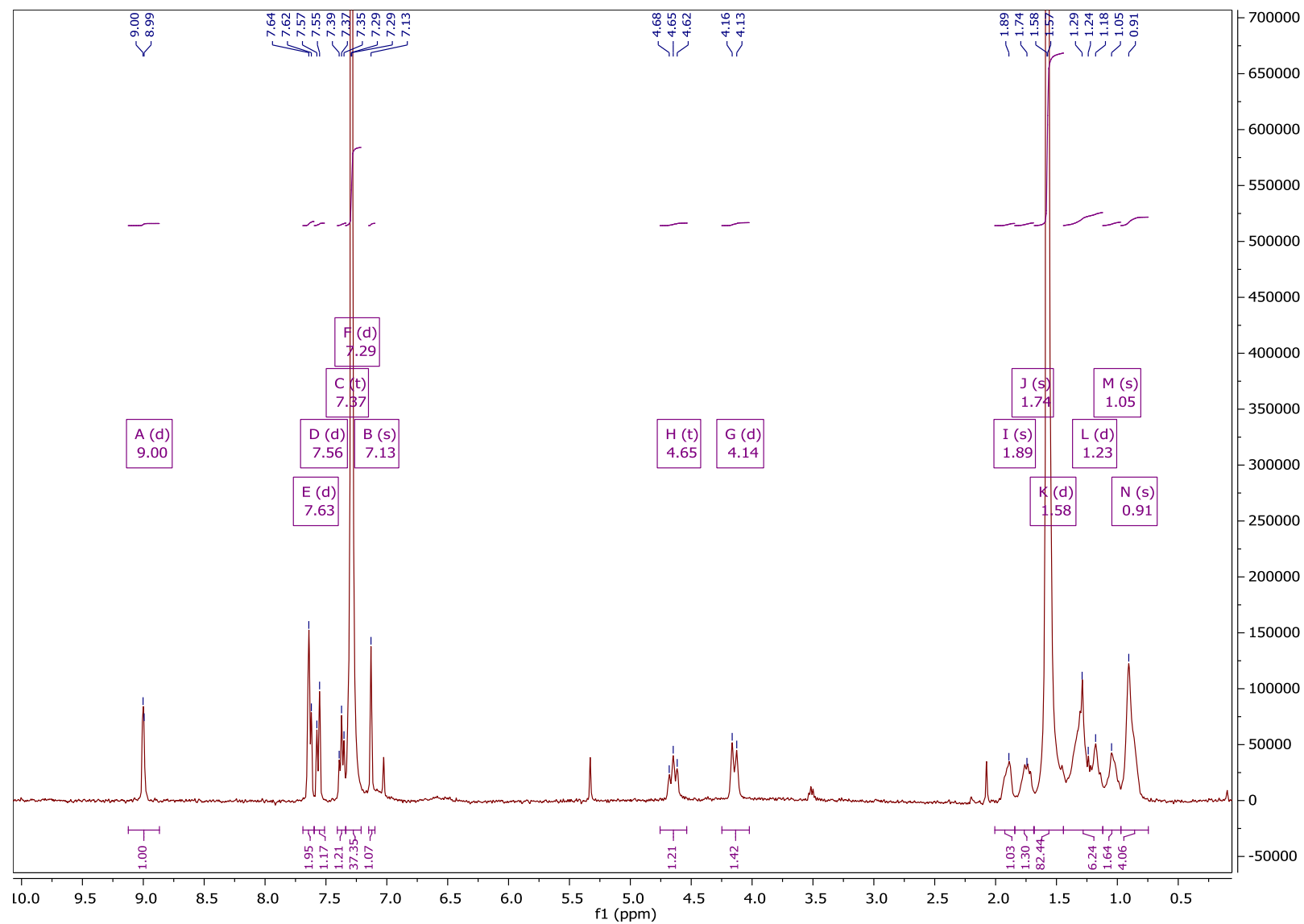
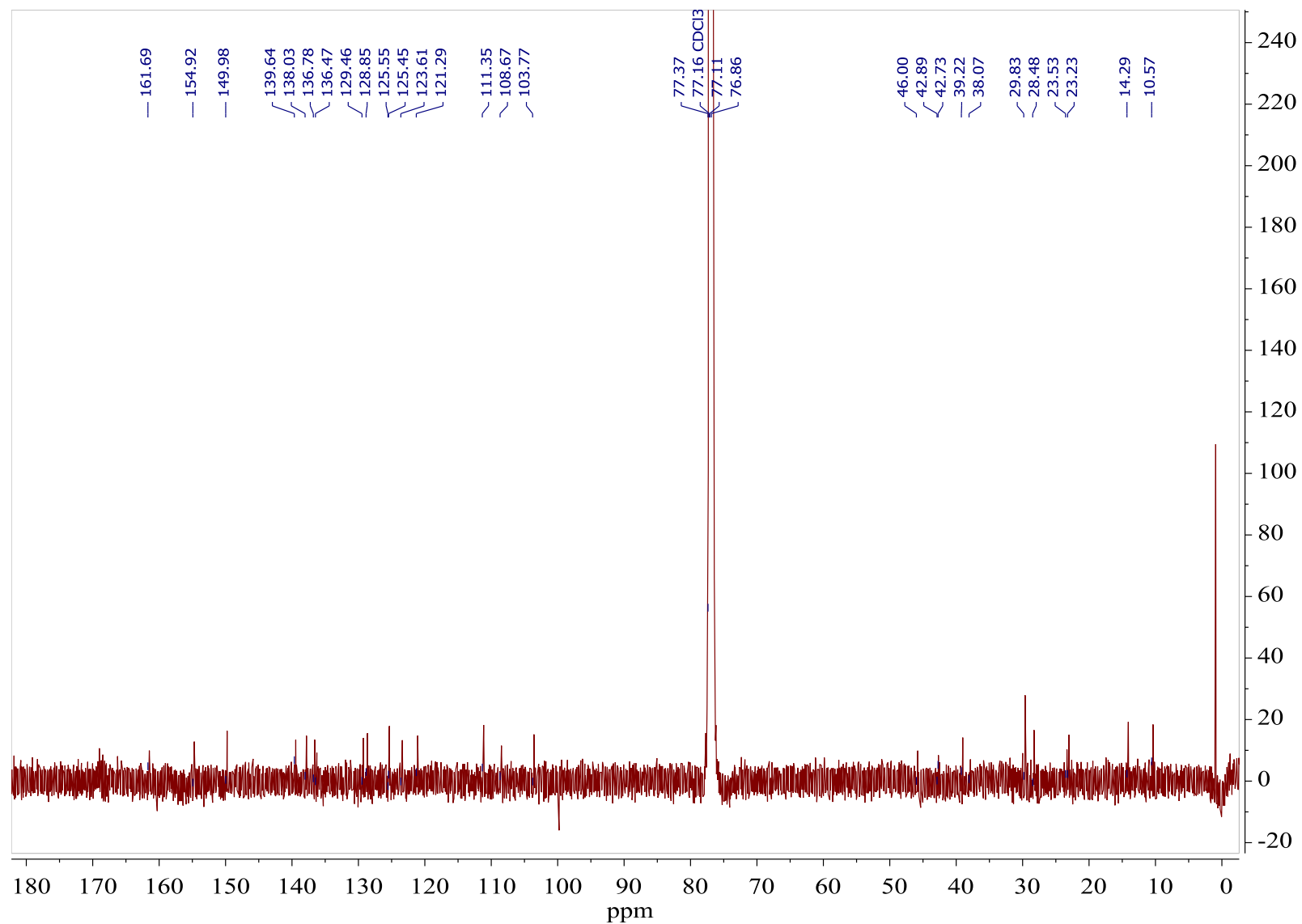


Figure S15.  $^1\text{H}$  NMR of  $\text{V}-(\text{DPP})_2$



**Figure S16**  $^{13}\text{C}$  NMR of  $\text{V}-(\text{DPP})_2$  ( $^{13}\text{C}$  NMR spectra was only obtained at  $0^\circ\text{C}$  using a AVANCE III HD 600 MHz High at 20000 Scans using  $\text{CDCl}_3$  as solvent at a concentration of  $0.5\text{mg/mL}$ . The low resolution is probably due to the low concentration used during the experiment, which was required due to the low solubility of  $\text{V}-(\text{DPP})_2$  as discussed in the main text.

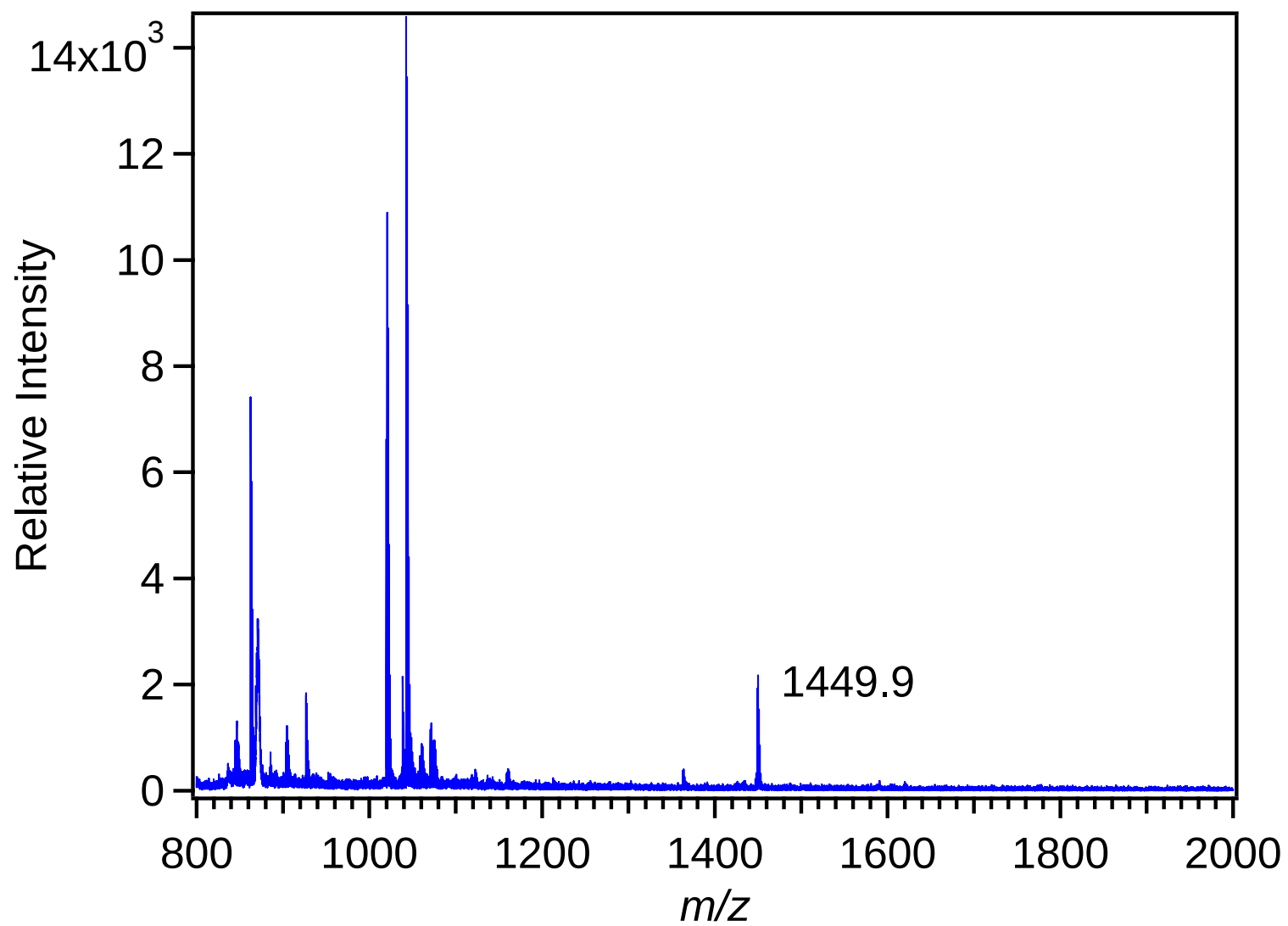


Figure S17. MALDI-TOF Mass Spectra of V-(DPP)<sub>2</sub>