Supporting Information

Amorphous ternary charge cascade molecules for bulk heterojunction photovoltaics.

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Characterization of neat SF-(PDI)$_4$ and SF-(DPP)$_4$.

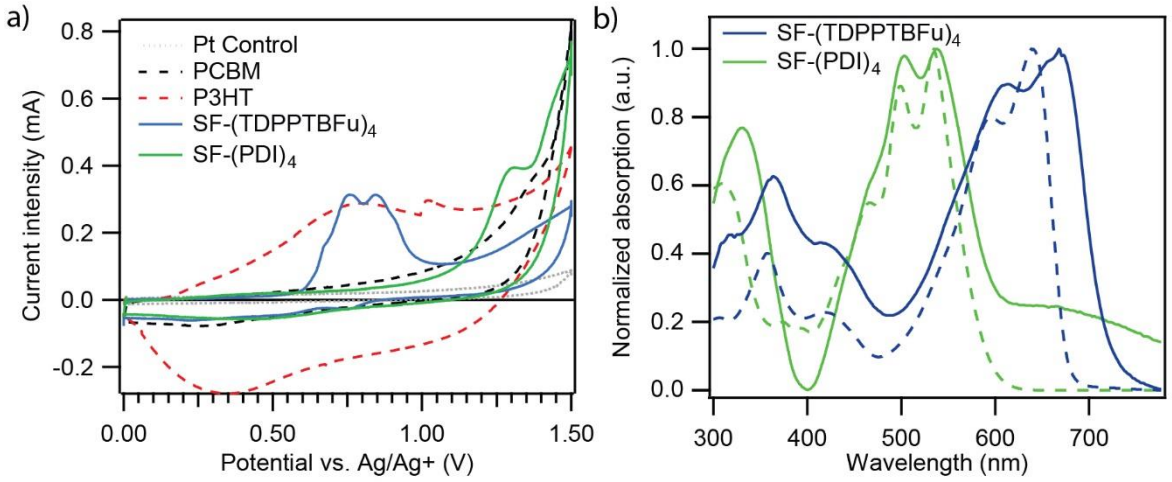

Figure S1. a) cyclic voltammetry of drop casted films over a platinum working electrode within a 0.5 M tetrabutylammonium hexafluorophosphate solution in acetonitrile at a sweeping rate of 50 mV s-1 vs. and Ag/Ag+ reference electrode. Two irreversible oxidation waves at -5.4 eV and -6.0 eV vs vacuum were found for SF-(DPP)$_4$ and SF-(PDI)$_4$ respectively, which we attributed to the highest occupied molecular orbital (HOMO) of the molecules. b) ultra-violet and visible absorption spectra of SF-(DPP)$_4$ and SF-(PDI)$_4$ in CHCl3 (dashed lines) and in solid state thin films (solid lines). The bandgap for SF-(DPP)$_4$ and SF-(PDI)$_4$, estimated from onset absorption, are found to be 1.7 eV and 2.05 eV respectively. The lowest unoccupied molecular orbital (LUMO) energy was inferred from the HOMO and the bandgap.

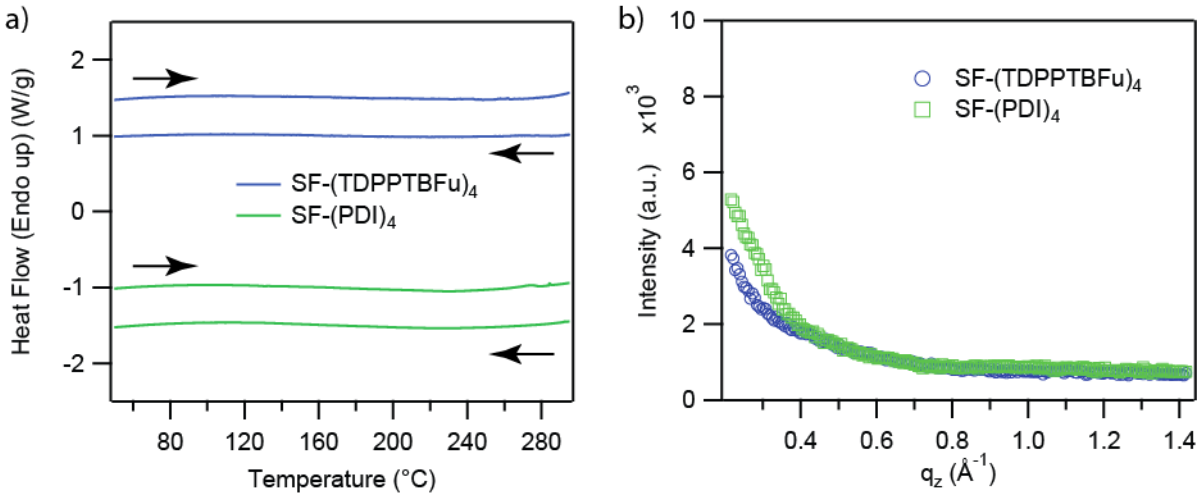

Figure S2. *(a) Differential scanning calorimetry second heating and cooling curves of drop casted SF-(DPP)$_4$ and SF-(PDI)$_4$ from dichlorobenzene at 80 °C with a scan rate of 10 °C/min. Black arrows indicate scan direction. (b) Out of plane grazing incident wide angle X-ray diffraction of neat SF-(DPP)$_4$ and SF-(PDI)$_4$ thin films.*

Crystallinity data of P3HT and PCBM blended with SF-(PDI)$_4$.

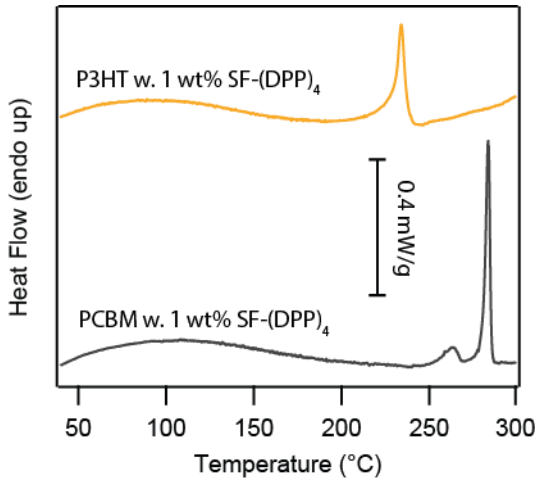

Figure S3. *differential scanning calorimetry second heating curves of P3HT and PCBM containing 1 wt% SF-(DPP)$_4$*

Crystal correlation length calculation from diffraction pattern.

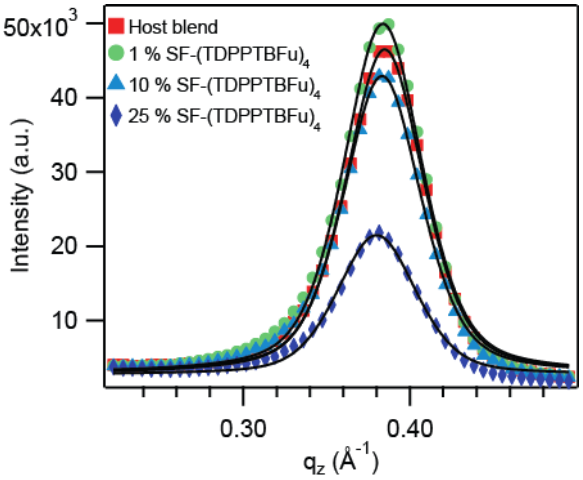

Figure S4. *Out of plane grazing incident wide angle X-ray diffraction of thin films with varying amount of ternary additive. Solid black lines are the respective Pseudo-Voigt fit.*

Crystal correlation length was obtained according to Scherrer's equation:

$$CCL = \frac{2\pi}{FWHM}$$

where FWMH is the full width at half maximum obtained by fitting the diffracted peak with a Pseudo-Voigt equation.

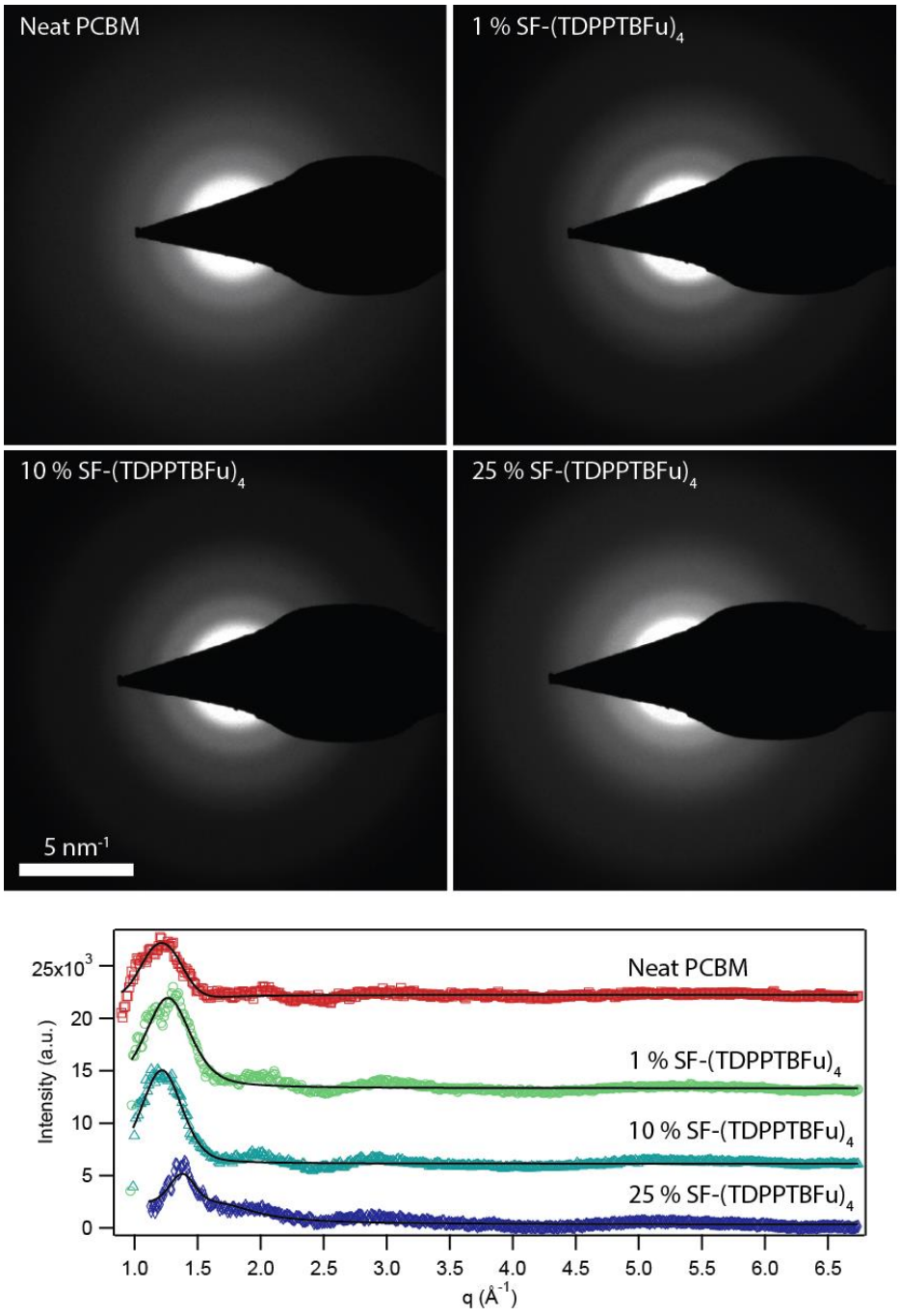

Figure S5. *Electron diffraction pattern of films with varying amount of ternary additive. Bottom graph shows cross sections of the diffraction intensity vs. q-vector. Solid black lines are the respective Pseudo-Voigt fit.*

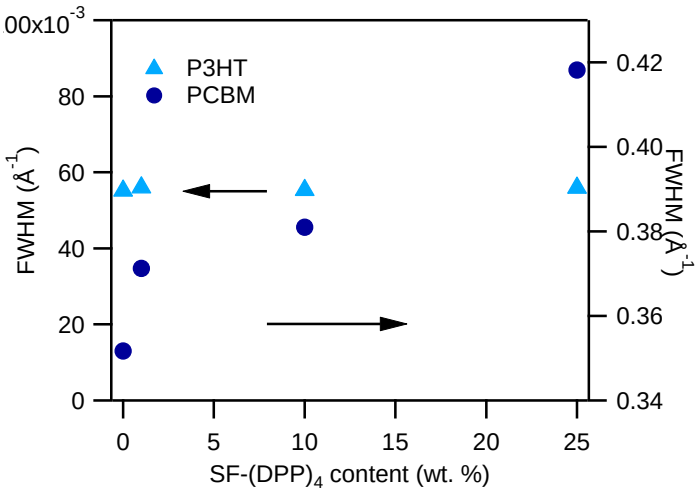

Figure S6. *Crystal correlation length of PCBM and P3HT as a function of* SF-(DPP)$_4$ *content.*

OPV device optimization.

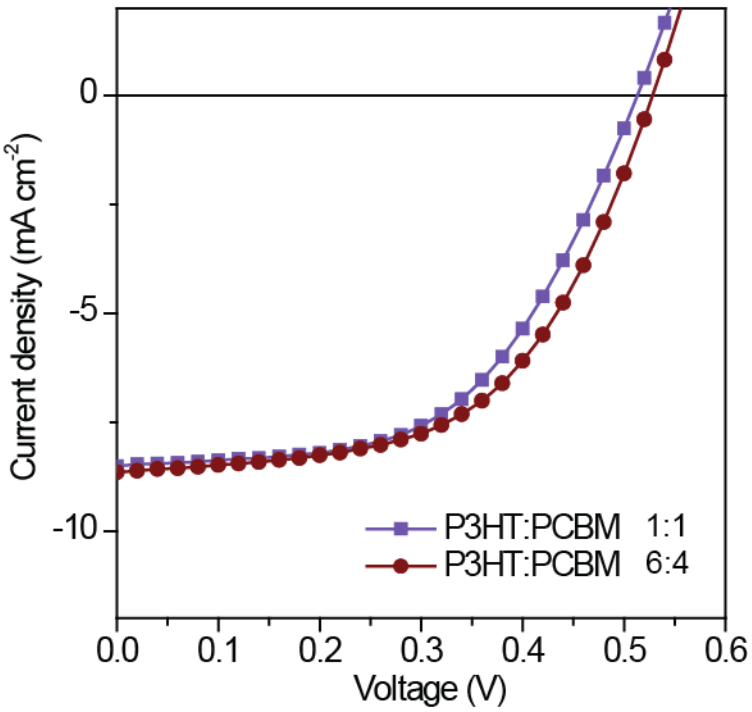

Figure S7. *Typical JV curves for P3HT:PCBM blends at 1:1 and 6:4 ratios.*

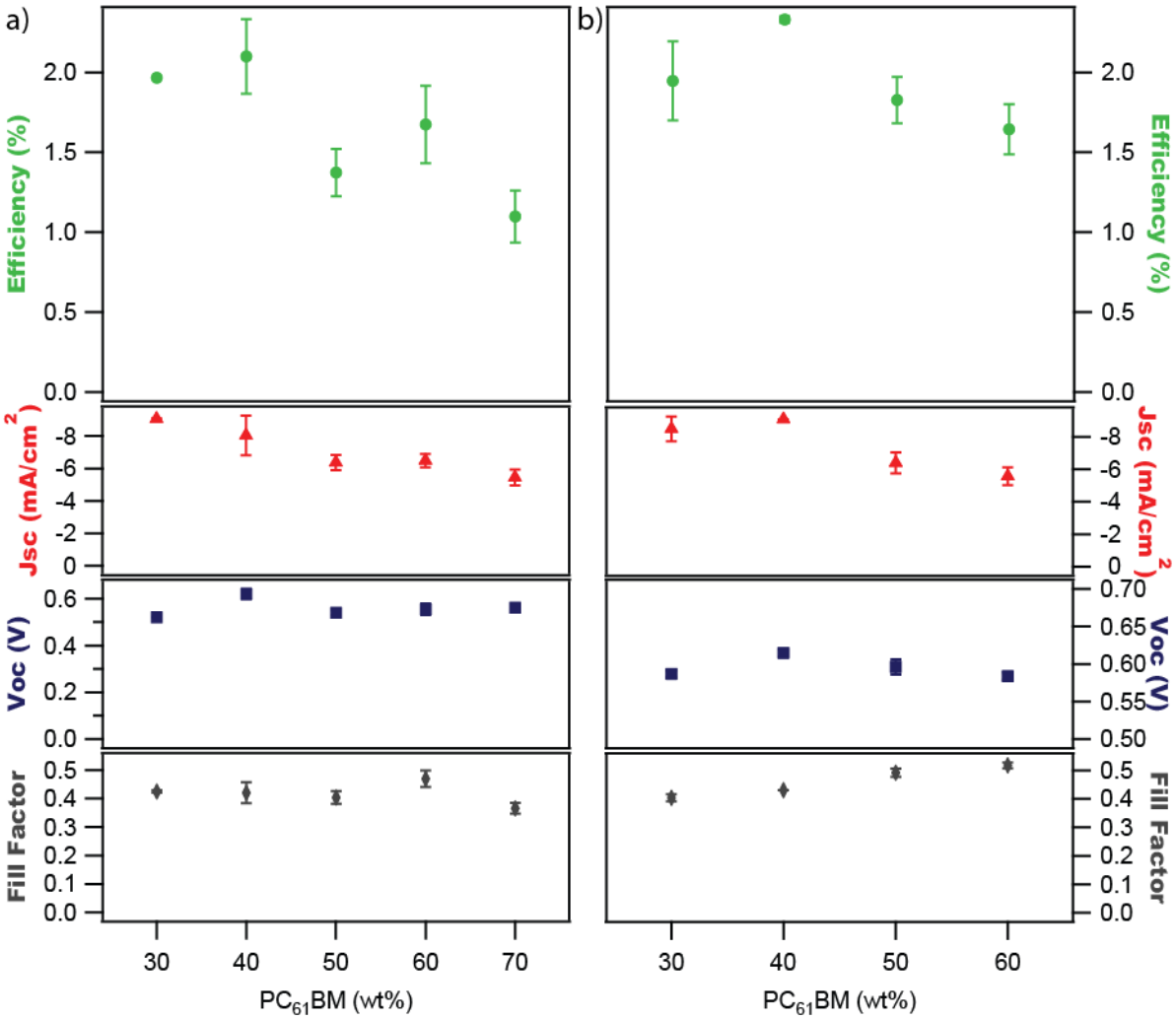

Figure S8. *Average figures of merit of devices containing 5 wt% (a) SF-(DPP)$_4$ and (b) SF-(PDI)$_4$ in function of PCBM content. Optimum efficiency is found at 6:4 P3HT:PCBM ratio, which is identical to the host blend optimum.*

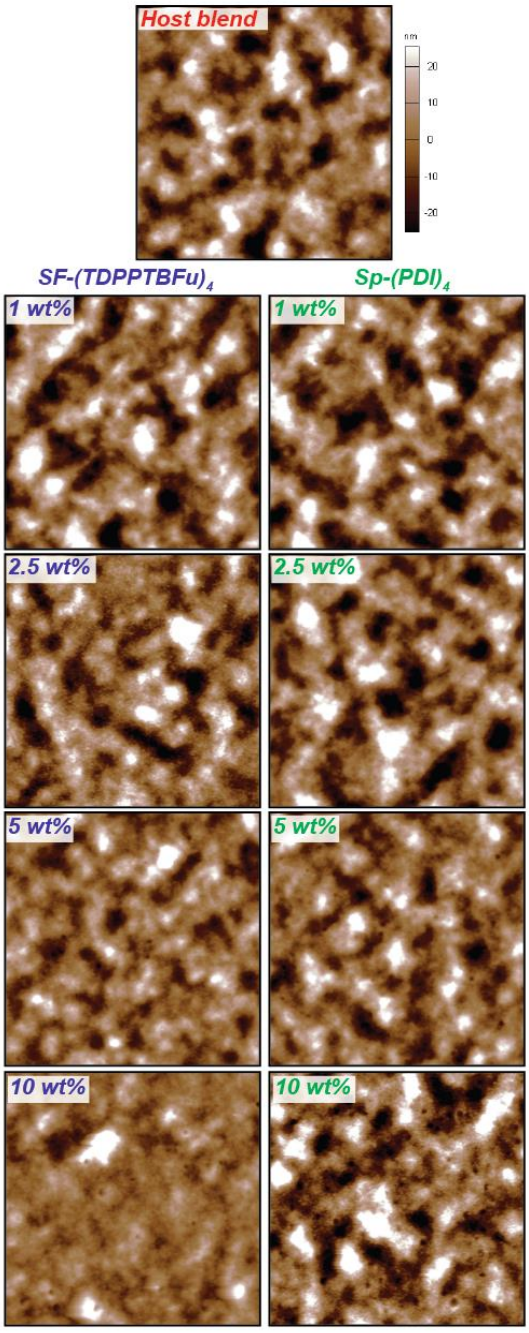

Figure S9. *Atomic force microscopy height images (5 um x 5 um) of host blend and with additive. The slightly smoother surface at 10 wt% SF-(DPP)$_4$ might arise from the capping layer formation on the surface.*

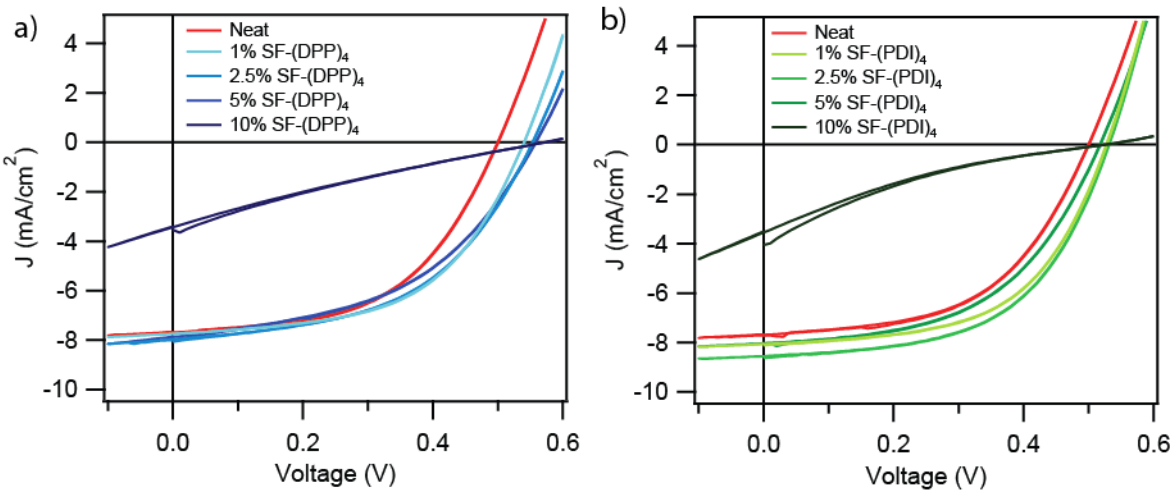

Figure S10. *Typical JV curves for P3HT:PCBM blends containing varying amount of (a) SF-(DPP)$_4$ and (b) SF-(PDI)$_4$.*

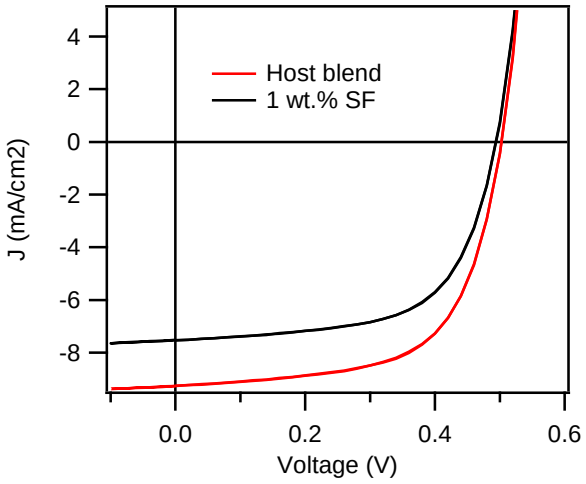

Figure S11. *JV curve of P3HT:PCBM host blend and containing 1 wt.% SF molecule (9,9'-spirobifluorene). Performances are decreased as expected from the large bandgap of the spirocore acting as an insulator inside the blend.*

OPV device characterization.

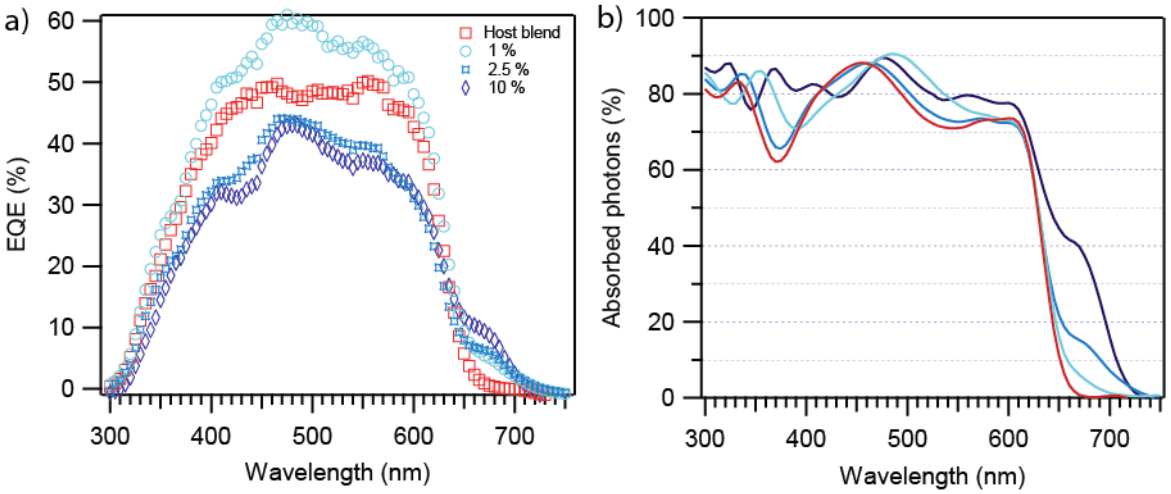

Figure S12. *(a) External quantum efficiency and (b) ratio of absorbed photons for host blend film and blended with 1, 2.5 and 10 wt% SF-(DPP)$_4$.*

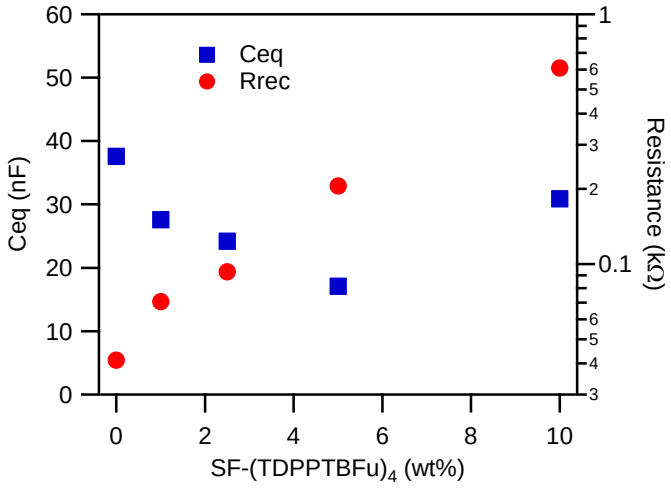

Figure S13. *Equivalent capacitance of the constant phase element (blue squares) and resistance (red dots) in function of SF-(DPP)$_4$ content.*

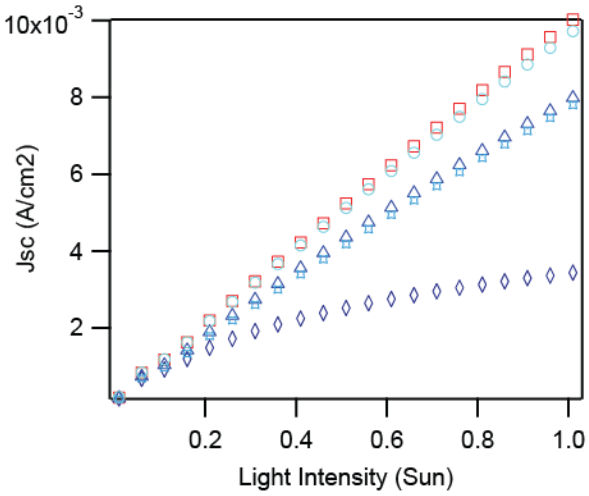

Figure S14. *Light intensity dependence of Jsc for neat P3HT:PCBM devices and blended with 1, 2.5, 5 and 10 wt% SF-(DPP)$_4$*

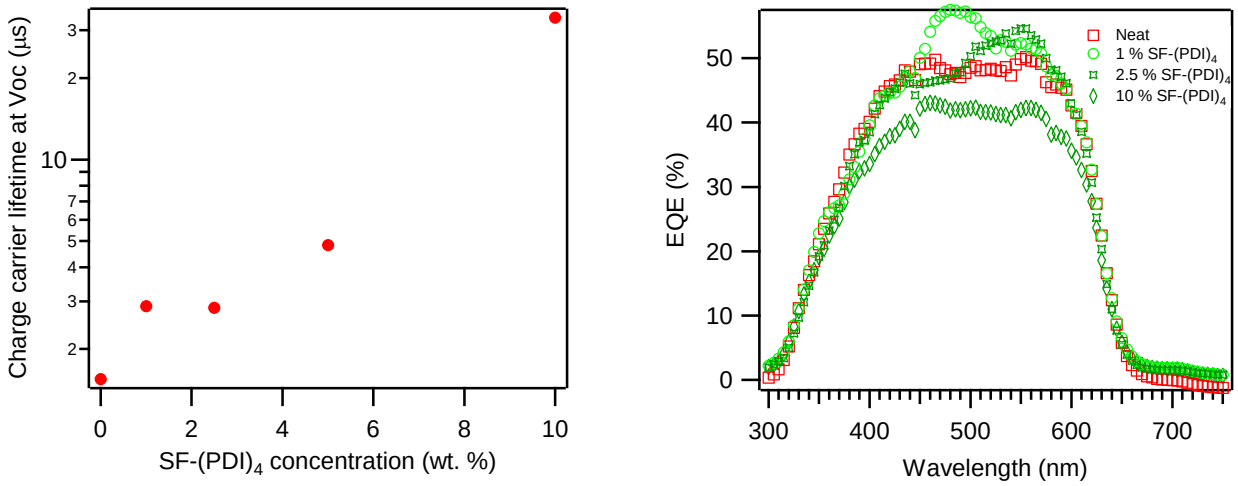

Figure S15: *(left) lifetimes extracted out of impedence spectrscopy under 1 Sun at OC for as function of SF-(PDI)4 content. (right) external quantum efficiency for P3HT.PCBM host blend and containing varying amount of SF-(PDI)$_4$.*

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Synthesis Experimental Procedures

General

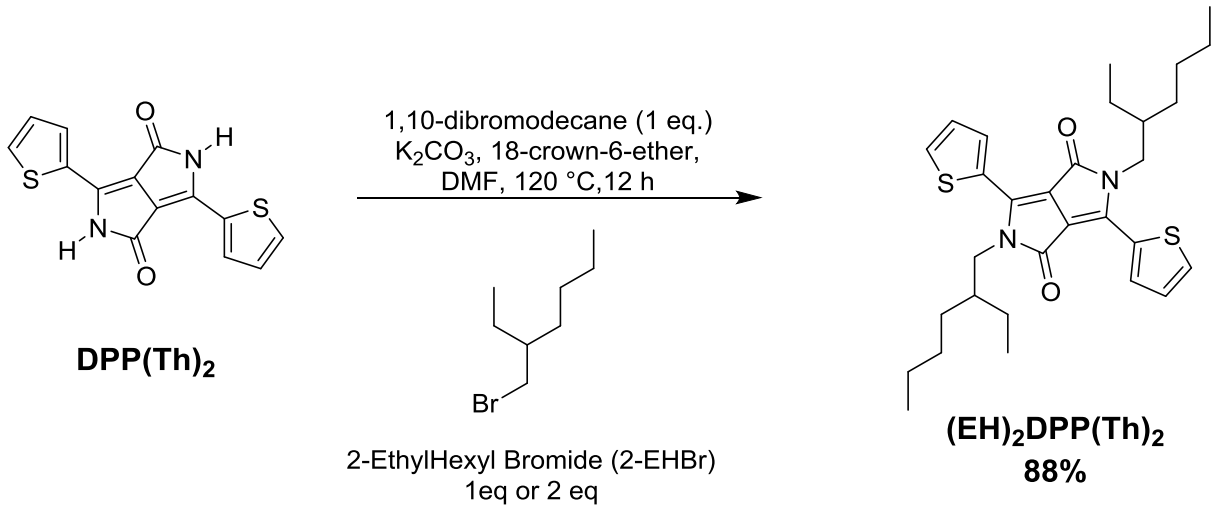
All reagents were of commercial reagent grade (Sigma-Aldrich, Acros and Fluorochem) and were used without further purification. Toluene, Chloroform, Tetrahydrofuran (Fisher Chemical, HPLC grade) and chlorobenzene (Alfa Aesar, HPLC grade) were purified and dried on a Pure Solv-MD Solvent Purification 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 grades). The (1H) and (13C) NMR spectra were recorded at room temperature 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 1H or 13C signals in $CDCl_2$ (1H: 7.26, 13C: 77.16) and dichloromethane-d_2 (2H: 5.32, 13C:53.84). EI-MS spectrum was recorded on an EI/CI-1200L GC-MS (Varian) instrument. Atomatic-Pressure-Photoinonization-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, 2,5-Dihydroxybenzoic acid as matrix. Both materials 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 monomeric units of the SF Cascade molecules

Synthesis of the spiro-core (SF-$Bpin_4$) was performed following the literature procedures by Wu, Schumm *et. al*. *J. Org. Chem*, **1996**, 61 ,20, 6906-6921, and the synthesis of 2,5-Dihydro-3,6-di-2-thienyl-pyrrolo[3,4-*c*]pyrrole-1,4-dione ($DPP(Th)_2$ based on *J. Polym. Sci. A Polym. Chem.* **2010**, 48, 1669-1675.

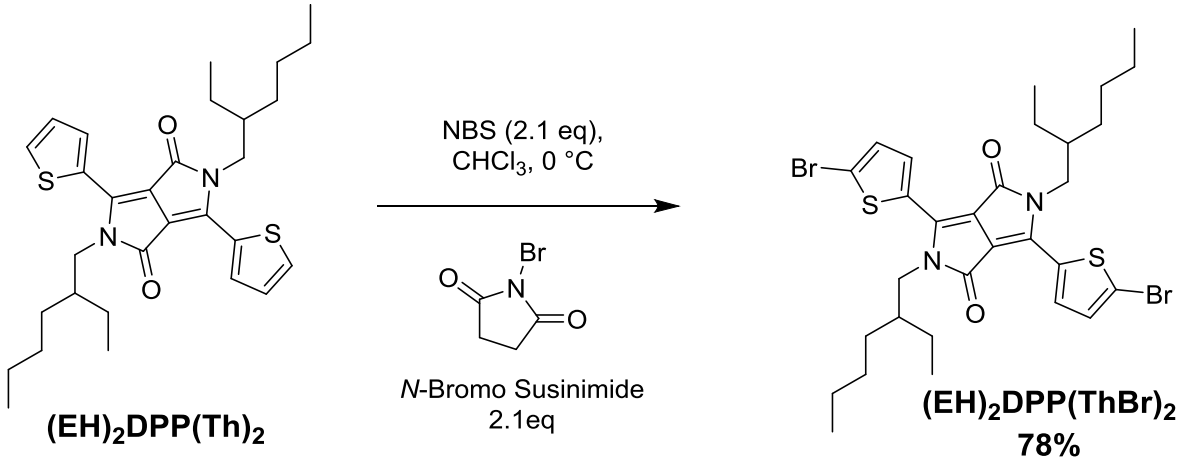
Procedure for Monomeric units of SF-(DPP)$_4$

Alkylation of DPP(Th)$_2$ with 2-ethylhexylbromide



DPP(Th)$_2$(1eq) and anhydrous K2CO3 were stirred in anhydrous (DMF) under Argon at 130 °C for 1 h. 2-EthylhexylBromide (2.5eq) was then added drop wise and the reaction mixture was stirred at 130 °C for a further 20 h for a symmetric alkylation of the DPP(Th)$_2$ core. 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 to obtain the **EH$_2$DPP(Th)$_2$** as red crystals after recrystallization with Ethanol with a yield of 88%; 1H 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.[C30H40N2O2S2]: 524.78.

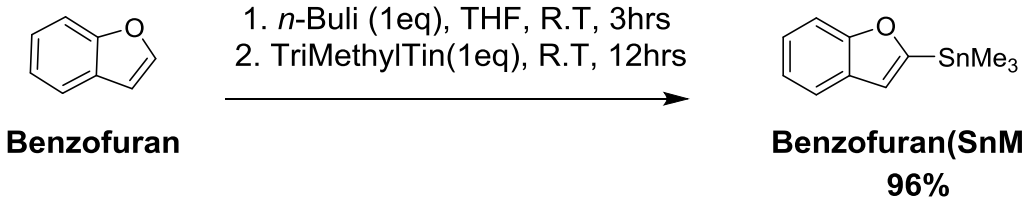
Bromination of EH$_2$DPP(Th)$_2$



To a solution of **EH$_2$DPP(Th)$_2$** in an Argon filled chloroform flask, wrapped in aluminium foil to exclude light at 0°C, N-bromosuccinimide(2.1eq) and left o stir overnight. After completed the

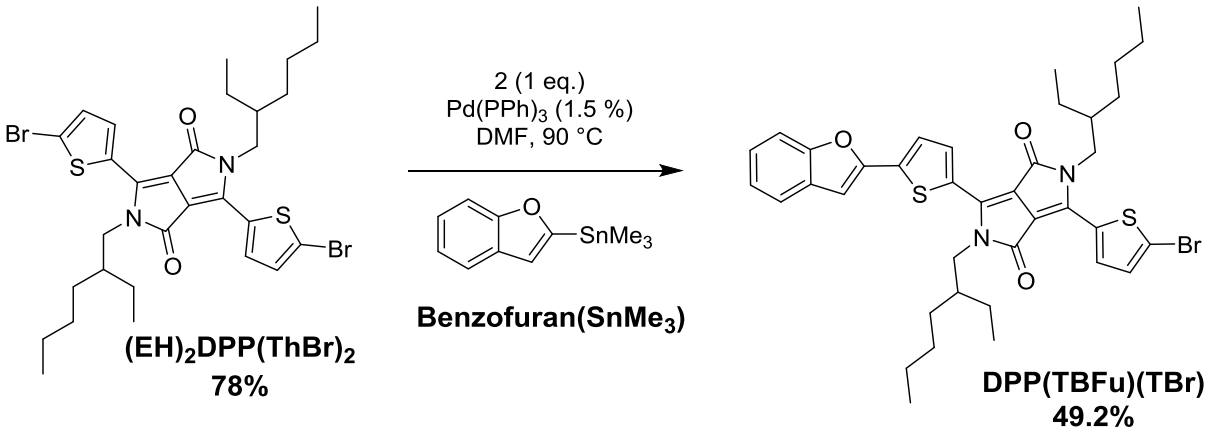
crude was poured into cold methanol, and left to stir for 1h. The precipitate was filtered and the solid was washed with methanol (2 × 200 mL) then dried under vacuum. The crude product was recrystallized from Hexane/chloroform to give the product as a dark purple solid of **$(EH)_2DPP(ThBr)_2$** (Yield =78%);1H 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. [C22H22Br2N2O2S2]: 570.36.

Stannylation of Benzofuran



Benzofuran(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_2O (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 MgSO4, followed by solvent removal under vacuum to afford a yellow-oil of **4a** at a yield of 96%**;** ^{1}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_C (300MHz, $CDCl_3$) 193.83, 155.18, 127.76, 127.14, 124.09, 123.39, 116.76, 112.55, -9.55.

General Procedure for Stille Coupling reaction of $(EH)_2DPP(ThBr)_2$



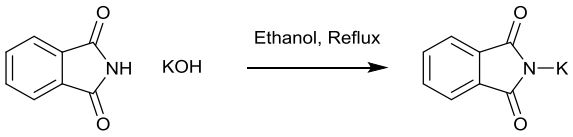
In a 100 mL oven-dried Schlenk flask, $EHDPP(TBr)_2$ (2.89 g, 4.24 mmol), $BFSnMe_3$ **2** (1.19 g, 4.24 mmol) and tetrakistriphenylphosphine palladium(0) (0.489 g, 0.423mmol) were placed. The

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 $CHCl_3$ until the washings were colourless. The organic extract was then dried with $MgSO_4$, 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%). ^{1}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* $[M]^+$= 721.1962

<u>Procedure for Monomeric units of SF-(PDI)$_4$</u>

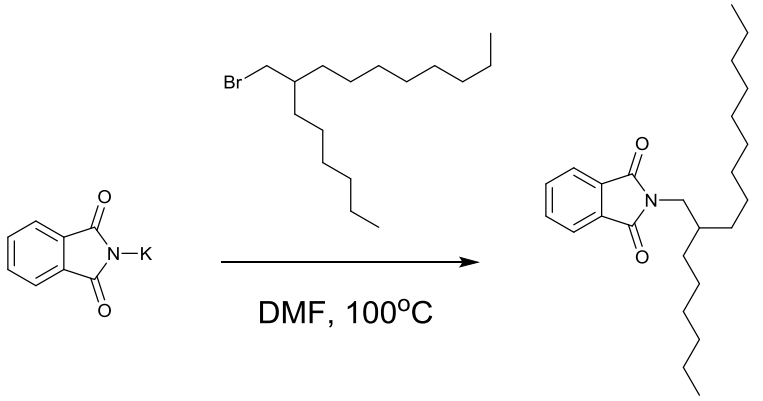
Synthetic steps of 2-hexyldecan-1-amine (HDNH$_2$)

Potassium 1,3-dioxoisoindolin-2-ide



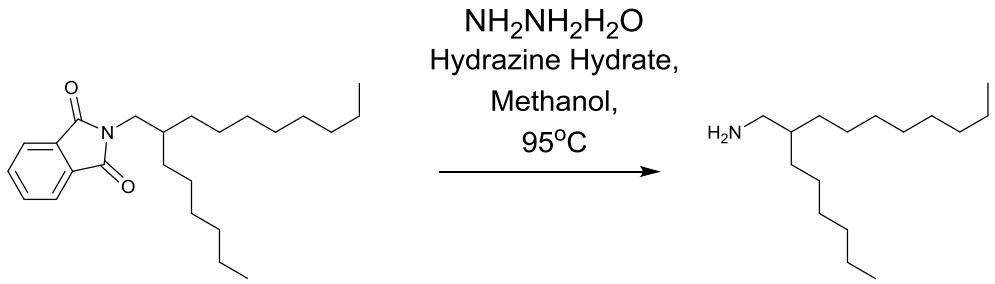
Phthalimide (4) (20 g, 0.136 mol) was added to 400ml absolute ethanol. The mixture was gently heated under reflux and then the hot solution was decanted into a solution of potassium hydroxide (7.6 g, 0.136 mole) in water (7.5 ml) and ethanol (23 ml). The mixture was stirred and cooled quickly to room temperature, and the precipitate was filtered with suction. The crystals obtained were washed with 12ml of acetone twice to remove any unchanged phthalimide. The yield of air-dried potassium phthalimide is 18.6 g. (82%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.88 (dt, *J* = 7.6, 3.7 Hz, 2H), 7.84 – 7.75 (dd, *J* = 5.5, 3.1 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.36 , 123.65; MS: 184.99 (APPI).

Synthesis of 2-(3-hexylundecyl)isoindoline-1,3-dione



Potassium phthalimide (7.5 g, 0.0404 mol) was added to a solution of 2-decyl-1-tetradecylbromide (15.7 g, 0.0376 mol) in 45 ml dry DMF. The reaction was stirred for 16 hours at 90C. After cooling to room temperature, the reaction mixture was poured into 150 ml water and extracted with dichloromethane (3 x 100 ml). The combined organic layers were washed with 200 ml 0.2 N KOH, water, saturated ammonium chloride, dried over anhydrous MgSO4, and concentrated under reduced pressure. The resulting crude yellow oil was purified via column chromatography (silica gel: dichloromethane) giving 5 as a pale yellow oil (17.83 g, 98 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.66 (dd, *J* = 5.6, 3.0 Hz, 2H), 3.53 (d, *J* = 7.2 Hz, 2H), 1.85 (h, *J* = 6.3 Hz, 1H), 1.41 – 1.16 (m, 26H), 0.88 – 0.77 (m, 6H); MS:2371.28MS: 371.28 (APPI): Calcd. [C24H37NO2]: 371.28.

Synthesis of 2-hexyldecan-1-amine ($HDNH_2$)

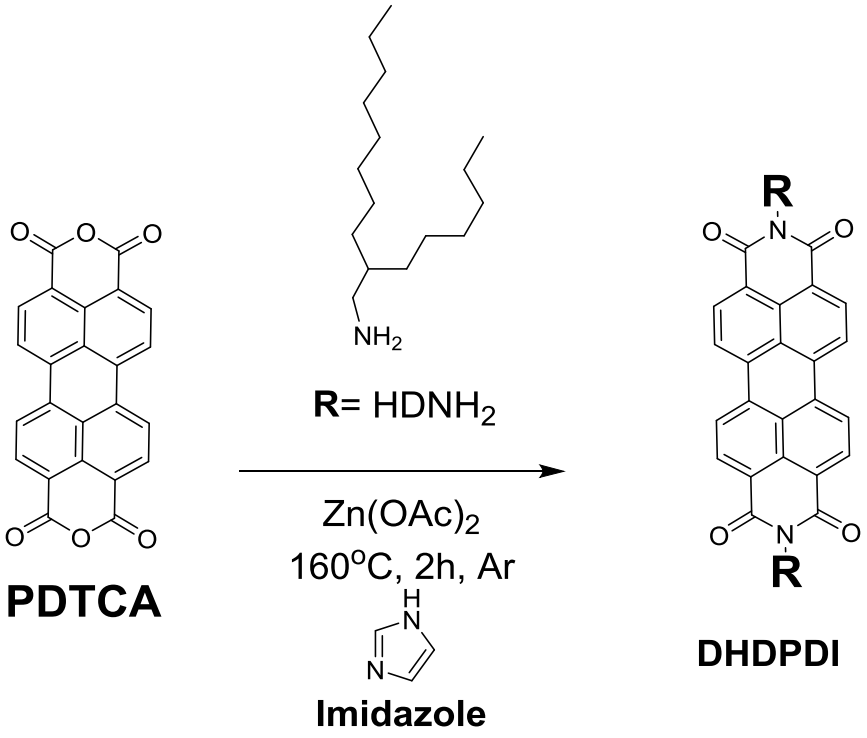


The alkyl Phthalimide (1eq) adn Hydrazine hydrate (3eq) was dissolved in methanol (10g per 100mL), and left to stir at 95°C. The reaction was monitored by TLC until all the starting imide has disappeared and the reaction was stopped. Reaction mixture was then transferred to an RBF, and methanol was evaporated. DCM (100mL) was the added into the crude, and was then washed with 10% KOH. Phase separation of the organic layer was done with DCM and the crude was dried and solvent evaporated to afford a yellow oil of the alkyl amine. ^{1}H NMR (400 MHz, Chloroform-

d) δ 3.38 (s, 1H), 2.57 (d, *J* = 4.2 Hz, 2H), 1.97 (s, 1H), 1.24 (s, 26H), 0.86 (t, *J* = 6.5 Hz, 6H). MS: 241.28 (APPI): Calcd. [C16H35N]: 241.28

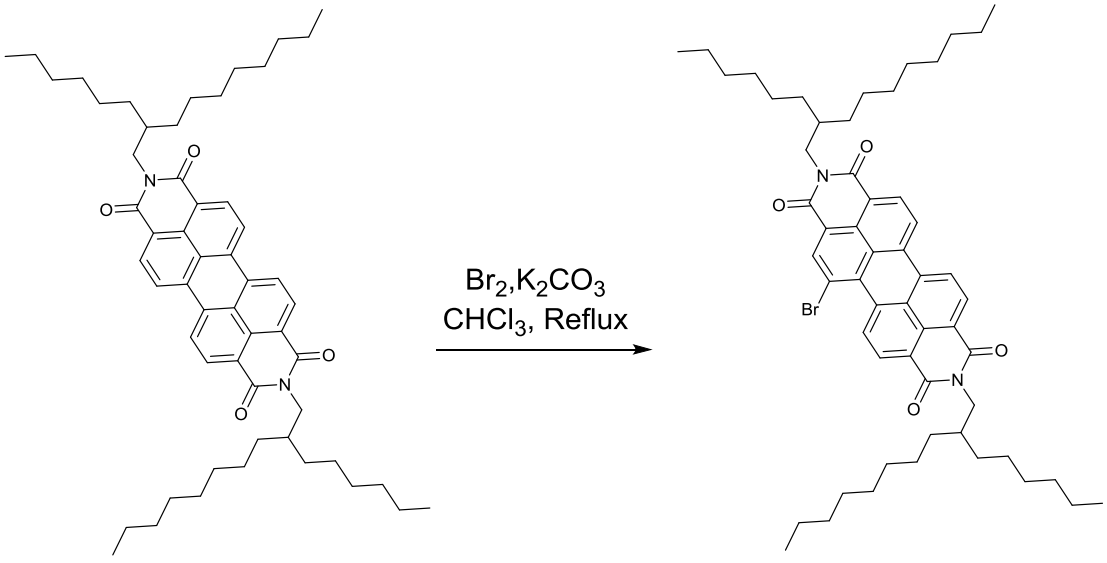
Synthetic steps of HD-PDIMBr

Alkylation of PDTCA with $HDNH_2$



A mixture of perylene-3,4,9,10-tetracarboxylicdianhydride PTCDA (1.0 mmol), Zn(OAc)2 (0.75 mmol),imidazole (4.0 g) and the respective alkyl amine (3.0mmol) was vigorously stirred at 160 °C for 2 h. After cooling to r.t., the mixture was dissolved in minimum amount of THF and precipitated in 300 mL 2N HCl/MeOH 2:1 V/V. The precipitate was collected by filtration, washed with H2O followed by MeOH and dried at 80 °C in vacuum. The crude product was further purified by column chromatography using Chloroform as eluent. **DHDPDI** was obtained as a bright red powder at an average Yield 68%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 7.8 Hz, 4H), 8.13 (d, *J* = 8.1 Hz, 4H), 4.08 (d, *J* = 7.3 Hz, 4H), 1.98 (p, *J* = 6.4, 6.0 Hz, 2H), 1.47 – 1.37 (m, 2H), 1.35 (s, 4H), 0.86 (q, *J* = 6.5 Hz, 24H); MS: 838.56 (APPI): Calcd. [C56H74N2O4]: 839.22.

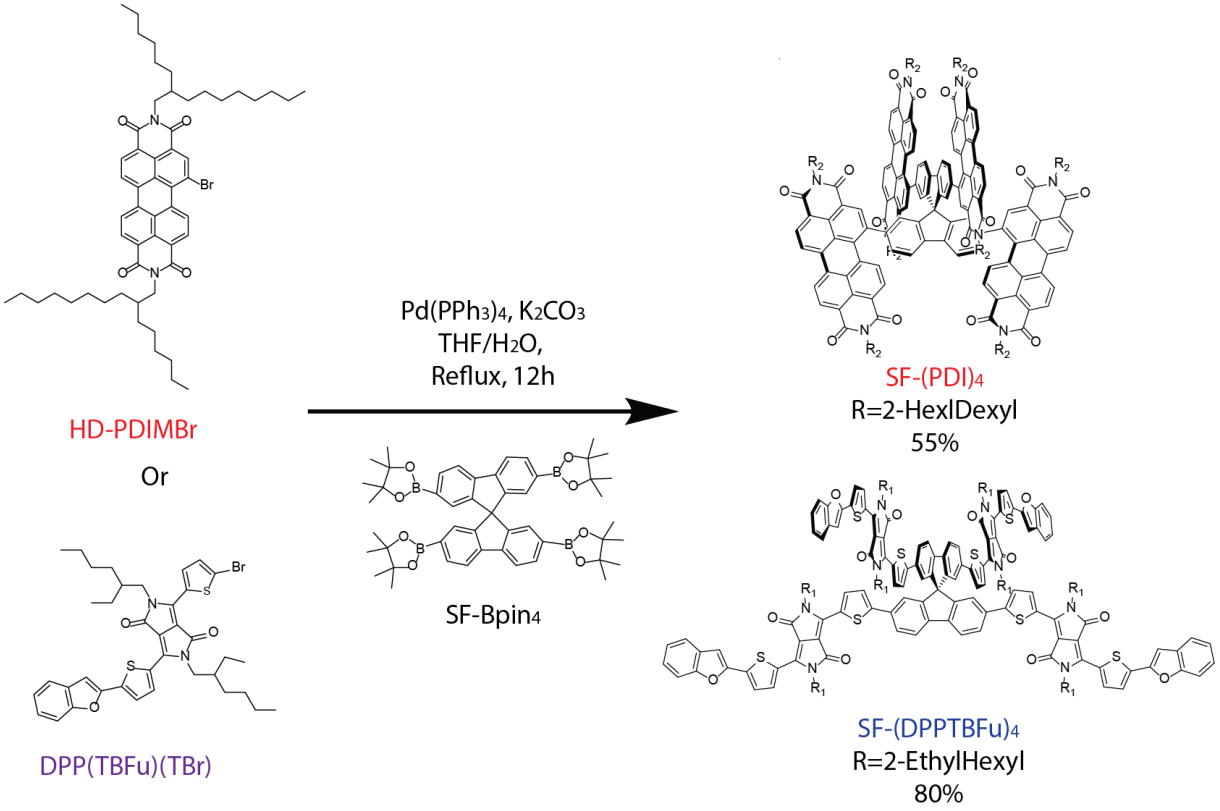
Mono Bromination of DHDPDI



DHDPDI **DHDPDIMBr**

A mixture of DHDPDI (3.5 g, 6.6 mmol), K2CO3 (3.5g, 25.4 mmol), 70mL CHCl3 and 17mL Br2 was stirred at reflux for 4h. The excess bromine was removed by adding aqueous Na2SO3. Then, the crude product was purified by silica gel column chromatography with dichloromethane as eluent. DHDPDIMBr (1.9 g, 42%) were obtained as red solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.54 (d, *J* = 8.3 Hz, 1H), 8.62 (s, 1H), 8.49 – 8.39 (m, 3H), 8.25 (dd, *J* = 8.2, 4.8 Hz, 2H), 4.08 (dd, *J* = 17.3, 7.3 Hz, 4H), 1.99 (dq, *J* = 17.8, 6.0 Hz, 2H), 1.53 – 1.18 (m, 48H), 0.87 (q, *J* = 6.8, 6.3 Hz, 12H); MS: 916.48 (APPI): Calcd. [C56H73BrN2O4]: 918.11

General Synthetic Procedure for Suzuki Coupling reaction of the DPP(TBFu)(TBr) and HE-PDIMbr with SF-Bpin$_4$



Scheme S1. Final Suzuki Coupling reaction of the respective DPP(TBFu)(Tbr) and HD-PDIMBr chromophoric unit with the central spiro core SF-Bpin$_4$

A mixture of SF-Bpin$_4$ (1eq), DPP(TBFu)(Tbr) or HD-PDIMBr (4.5eq), Pd(PPh$_3$)$_4$ (10%), Potassium Carbonate (1M), was added into a solution of THF/H_2O (Volume Ratio-10:3), and was degassed using a vacuum/argon flushing cycle three times before refluxing at 66°C for 24h under Argon atmosphere. After 24h, the reaction mixture was then cooled to r.t. and precipitated in excess methanol which was filtered with celite, and extracted extracted with $CHCl_3$. The crude solution was then washed with brine dried over $MgSO_4$, and organic extract was concentrated in vacuum. The residue was then purified by flash column chromatography (eluent: dichloromethane:*n*-hexane = 1:1) to get the product as SF-(PDI)$_4$ as a red solid with a yield of 55%, while a dark green solid was obtained for SF-(DPPTBFu)$_4$ with a yield of 80%.

^{1}H and ^{13}C NMR and Mass Characterization

SF-(PDI)$_4$: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (s, 4H), 8.71 (d, *J* = 8.0 Hz, 4H), 8.47 (d, *J* = 8.1 Hz, 4H), 8.24 (s, 8H), 8.06 (d, *J* = 7.8 Hz, 4H), 7.35 (d, *J* = 9.4 Hz, 8H), 7.25 (d, *J* = 8.6 Hz, 4H), 6.95 (d, *J* = 8.2 Hz, 4H), 4.25 (d, *J* = 7.4 Hz, 16H), 3.68 (b, 8H), 3.37 (t, *J* = 10.5 Hz, 8H), 2.14 (b, 8H), 1.68 – 0.96 (m, 192H), 0.85 (dt, *J* = 18.8, 5.5 Hz, 48H); ^{13}C NMR (101MHz,

Chloroform-*d*) 163.69, 163.56, 162.95, 162.56, 161.75, 151.65, 143.40, 141.66, 141.04, 135.10, 134.11, 133.98, 133.76, 131.91, 130.66, 128.95, 128.80, 128.47, 128.36, 128.09, 127.40, 126.53, 124.72, 123.57, 123.24, 123.16, 122.82, 122.36, 122.01, 121.40, 44.94, 44.09, 36.77, 36.50, 36.35, 31.96, 31.93, 31.86, 31.80, 31.70, 31.46, 30.20, 30.17, 30.02, 29.96, 29.87, 29.82, 29.70, 29.65, 29.60, 29.53, 29.37, 29.34, 29.30. (MALDI-TOF): *m/z* $[M]^+$= 3665.21

SF-$(DPPTBFu)_4$: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.97 (d, *J* = 4.0 Hz, 4H), 8.85 (d, *J* = 3.9 Hz, 4H), 8.02 (d, *J* = 8.0 Hz, 4H), 7.83 (d, *J* = 8.0 Hz, 4H), 7.60 (d, *J* = 7.5 Hz, 8H), 7.53 (d, *J* = 8.2 Hz, 4H), 7.41 – 7.31 (m, 8H), 7.28 (b, 4H), 7.13 (s, 4H), 7.06 (s, 4H), 4.03 (dp, *J* = 14.8, 7.4, 6.3 Hz, 16H), 1.89 (dq, *J* = 25.4, 6.7 Hz, 8H), 1.48 – 1.05 (m, 64H), 0.88 (tt, *J* = 16.4, 7.3 Hz, 48H); ^{13}C NMR (101 MHz, $CDCl_3$) 161.72, 161.58, 154.97, 150.03, 149.34, 139.80, 139.35, 137.77, 136.68, 136.32, 133.58, 129.58, 128.94, 128.86, 125.45, 125.34, 124.89, 123.53, 121.46, 121.34, 121.18, 53.44, 45.93, 39.23, 31.61, 30.32, 29.72, 28.47, 28.40, 23.75, 23.65, 23.08, 23.03, 22.67, 14.14, 14.06, 10.63, 10.56. (MALDI-TOF): *m/z* $[M]^+$= 2872.117

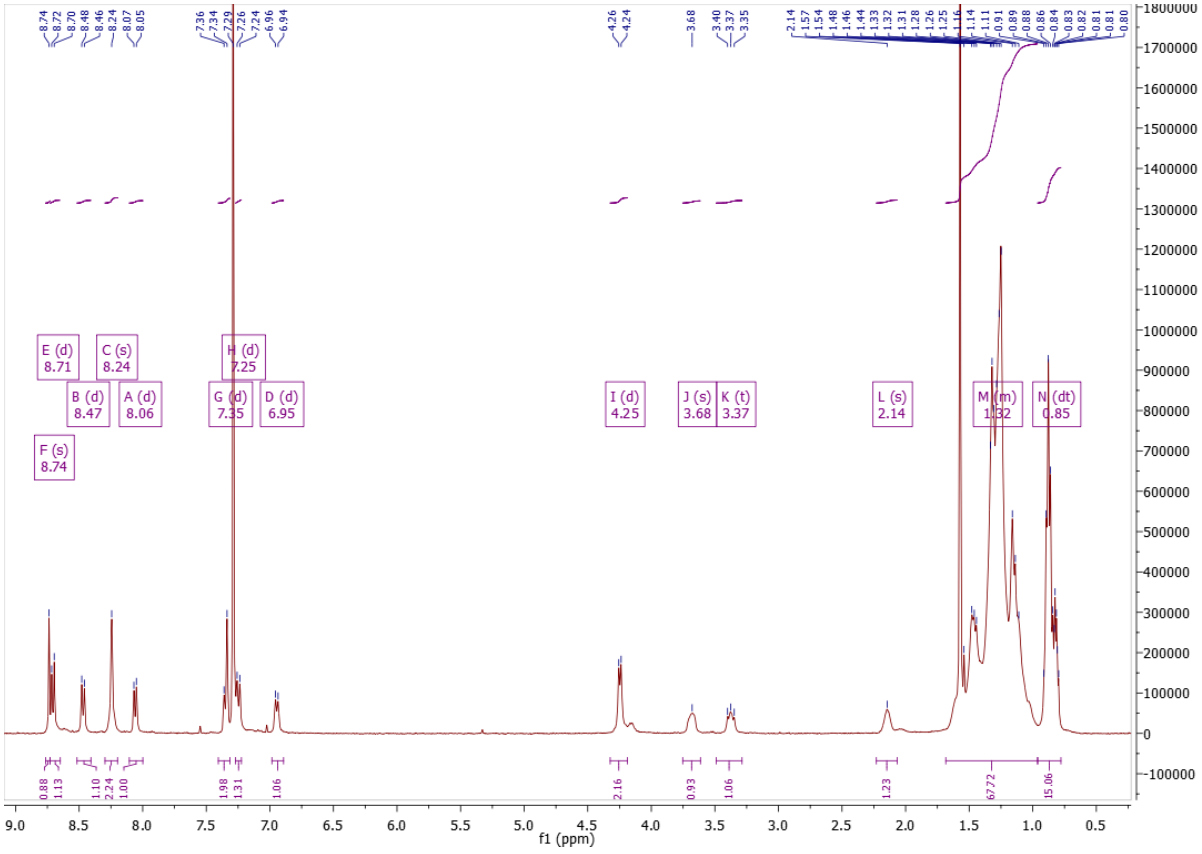


Figure S16. ***^{1}H NMR of*** *SF-$(PDI)_4$*

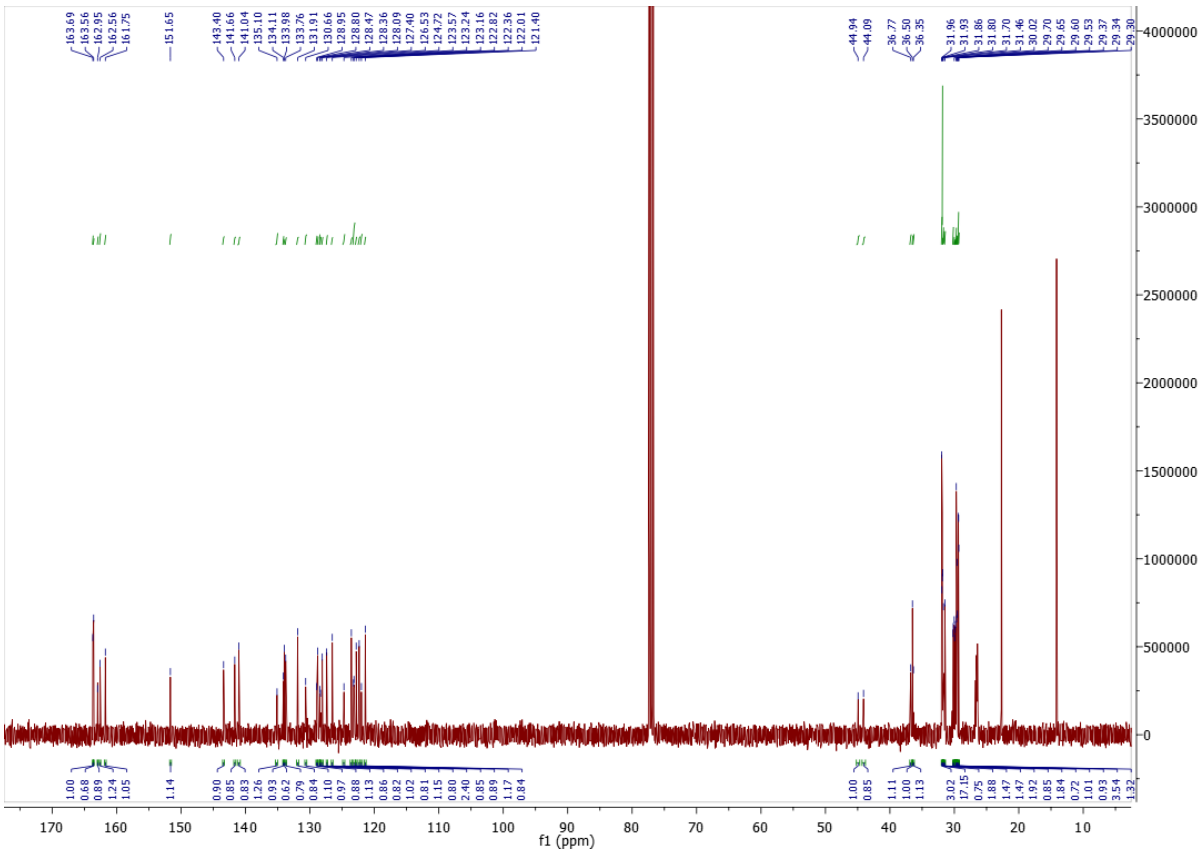


Figure S17. ***^{13}C NMR of*** *SF-(PDI)$_4$*

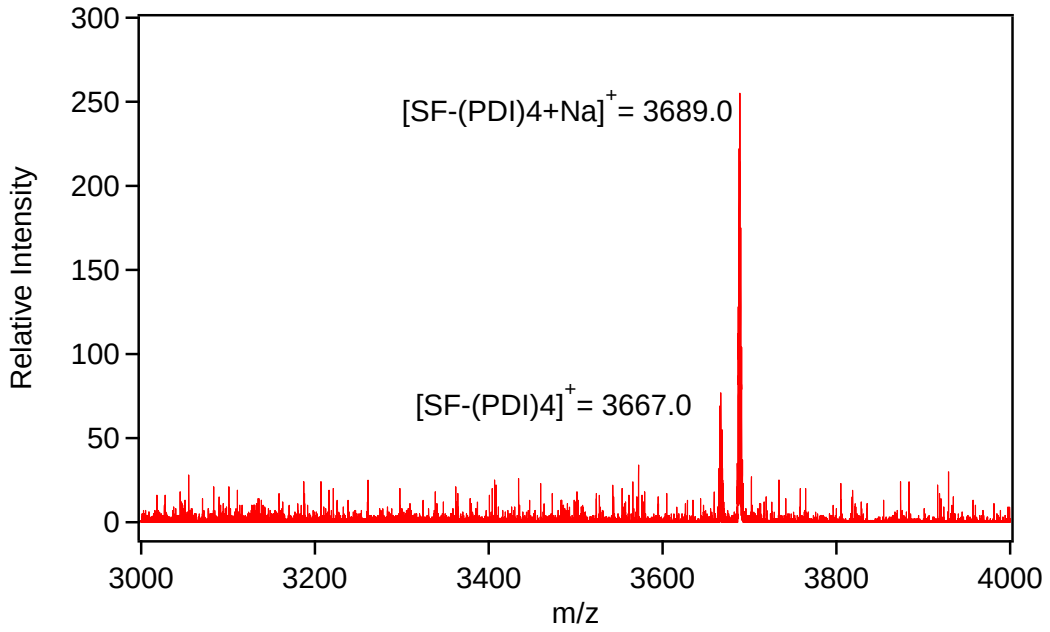


Figure S18. MALDI-TOF Analysis of SF-(PDI)$_4$ using 2,5-Dihydroxybenzoic acid matrix

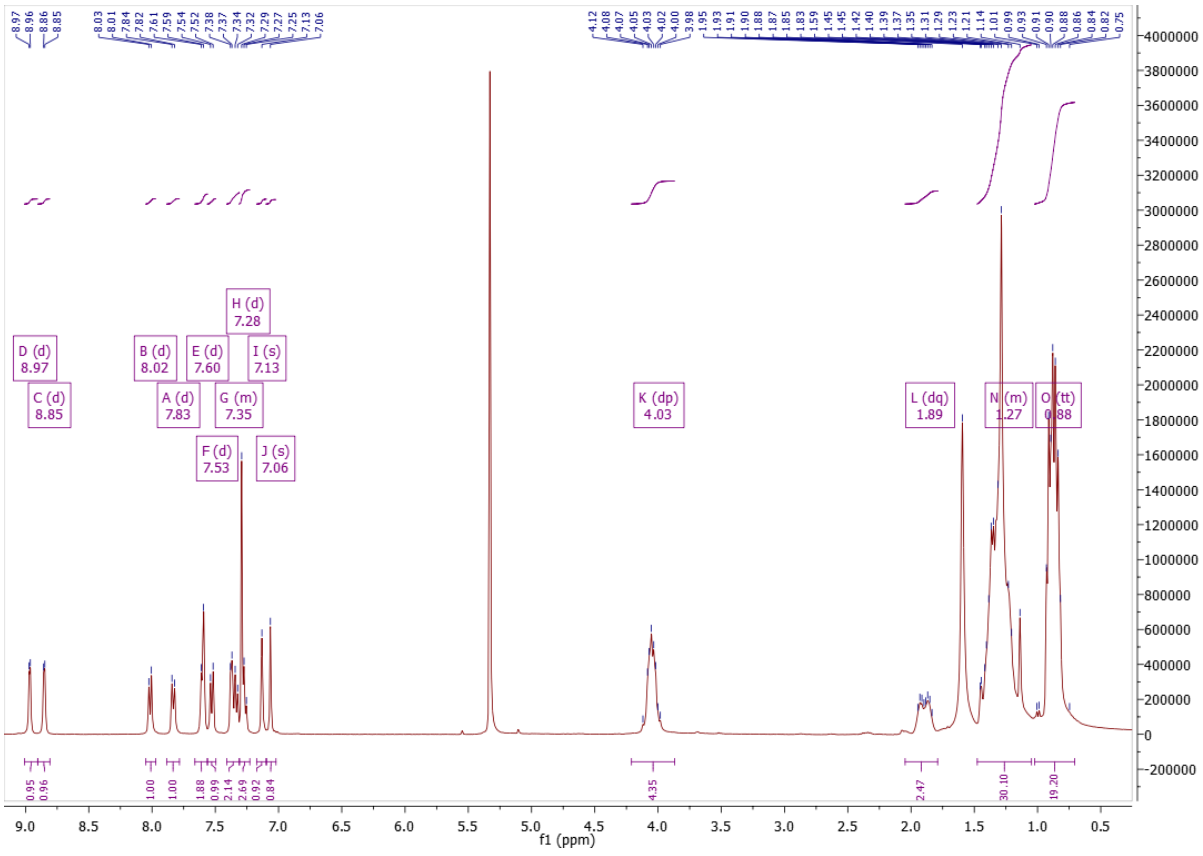


Figure S19. ***^{1}H NMR of*** *SF-(DPPTBFu)$_4$*

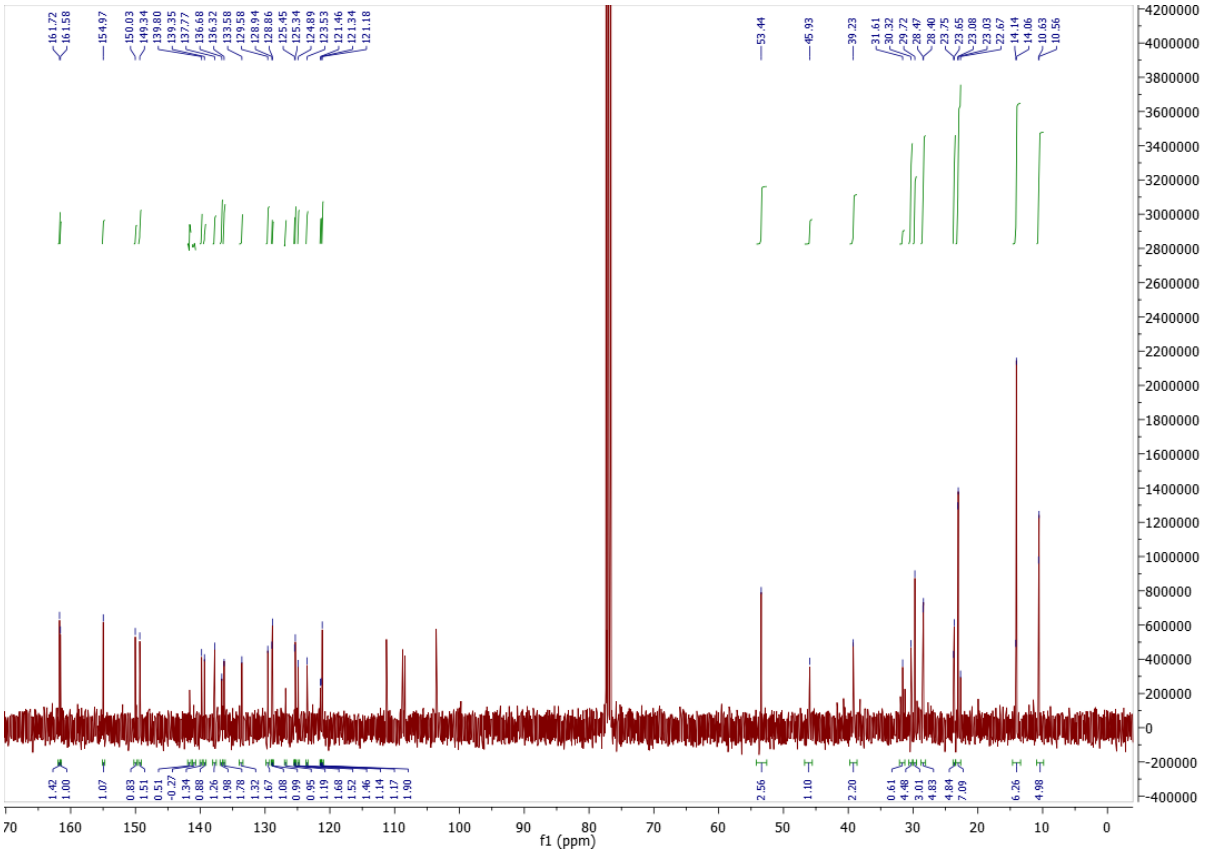


Figure S20. ***^{13}C NMR of*** *SF-(DPPTBFu)$_4$*

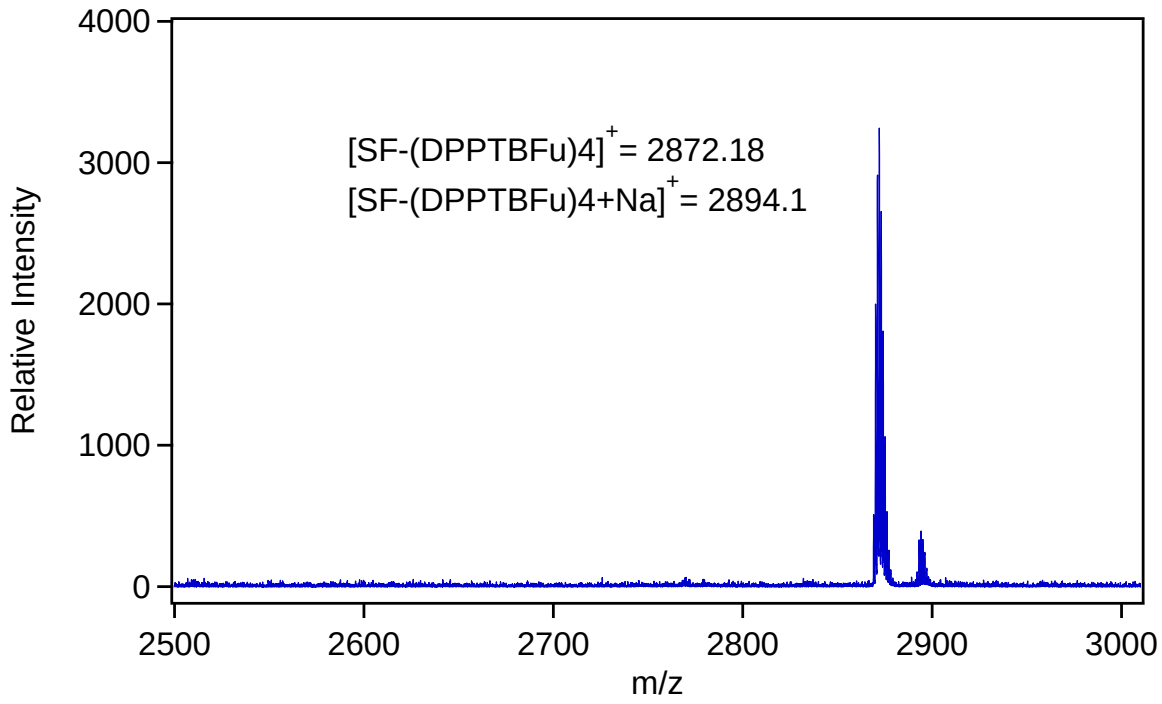


Figure S21. MALDI-TOF Analysis of SF-(DPPTBFu)$_4$ using 2,5-Dihydroxybenzoic acid matrix