Electronic Supplementary Information

A detailed study on the thermal, photo-physical, electrochemical properties and OFET applications of D-π-A-π-D structured unsymmetrical diketopyrrolopyrrole materials

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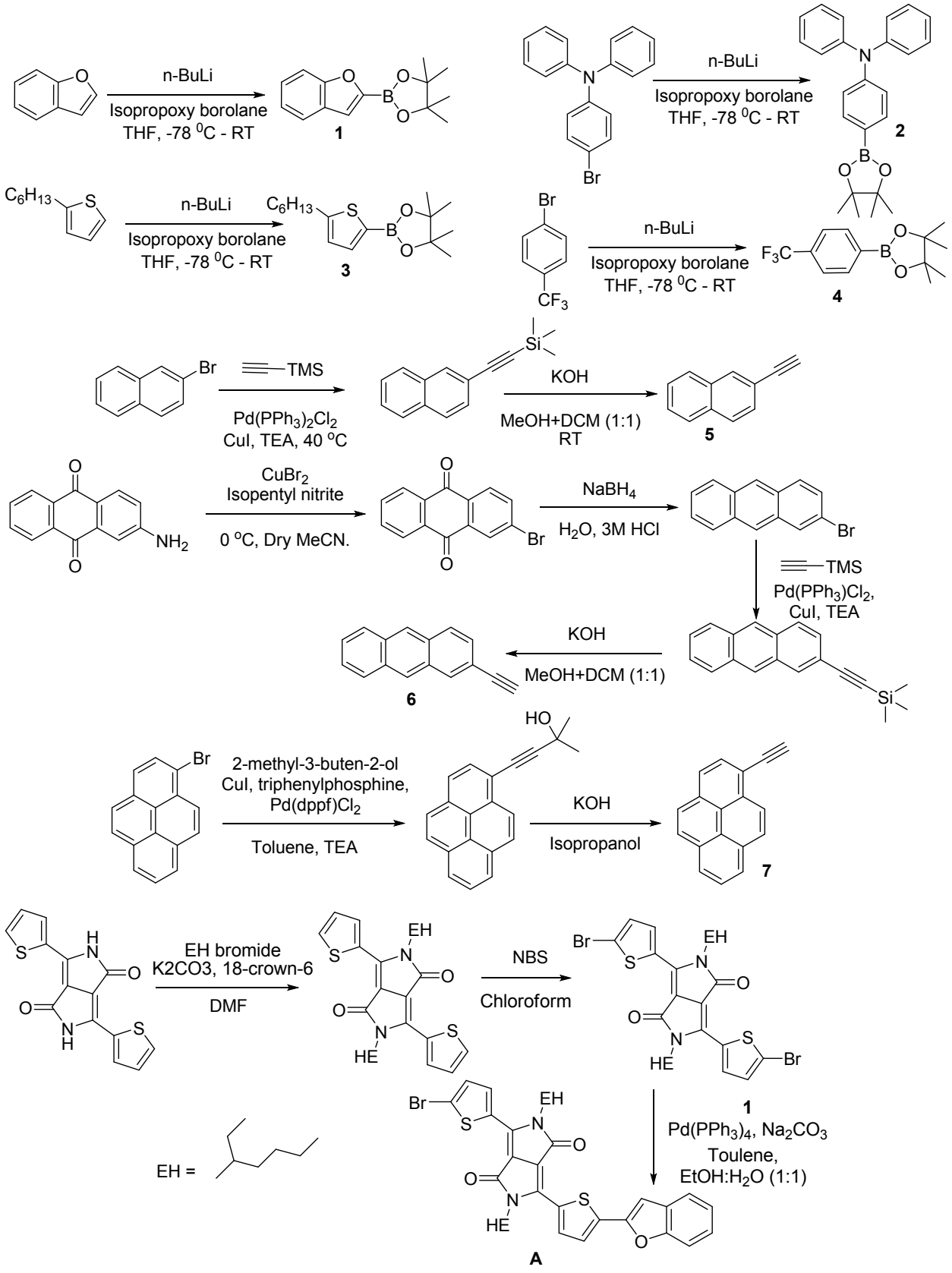
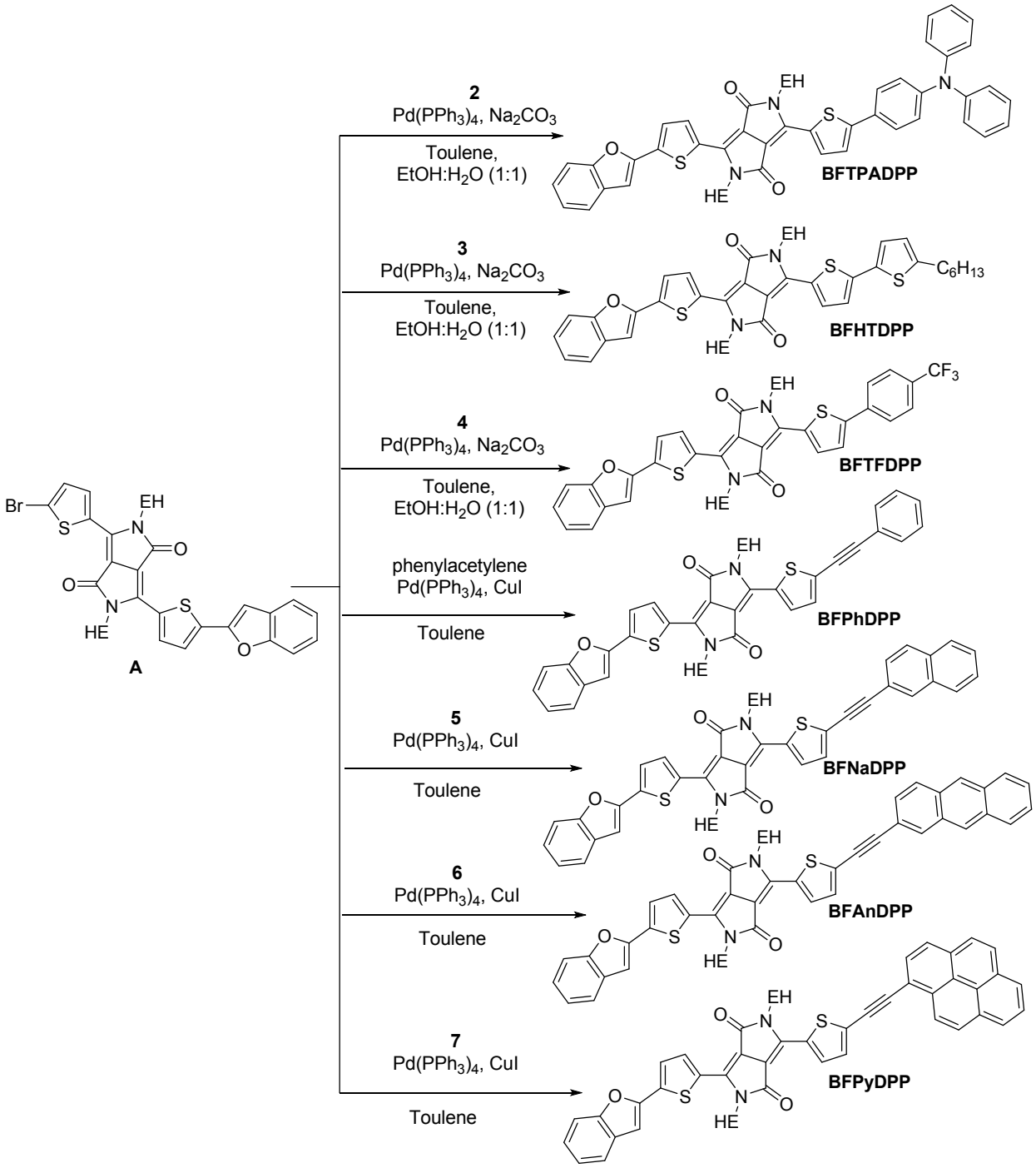


Scheme 1. Scheme for the synthesis of precursors of target DPP-derivatives



Scheme 2. Scheme for the synthesis of the target DPP-derivatives

Experimental Section:

Materials and instruments

All the materials for synthesis were purchased from commercial suppliers and used without further purifcation. Dry DMF (dried over molecular sieves), dry toluene (dried on sodium wire) and freshly distilled THF (distilled over sodium/benzophenone) were used in all experiments. NMR spectra were recorded using Bruker Avance (300 MHz) or Varian Inova (500 MHz) spectrometers. HRMS spectra were obtained on a Thermofinngan mass spectrometer. Absorption spectra were recorded on a Cary 5000 UV-VIS-NIR spectrophotometer. Fluorescence measurements were performed on a Cary Eclipse fluorescence spectrophotometer. Cyclic voltammetric measurements were performed on a PC-controlled CHI 62C electrochemical analyzer in dichloromethane (CH_2Cl_2) at a scan rate of 100 mV s^{-1}. Tetrabutylammonium perchlorate (0.1 M) was used as supporting electrolyte. The glassy carbon, standard calomel electrode (SCE) and platinum wire were used as working, reference and counter electrodes, respectively. The potential of reference electrode was calibrated using ferrocene internal standard. All the potentials were reported against SCE. All measurements were carried out at room temperature. TGA and DSC experiments were conducted on Exstar TG/TGA 7200 and Exstar DSC 7020 instruments, respectively with 10 °C/min heating and cooling rate. Fluorescence lifetimes were measured using a Fluorog-3 time correlated single photon counting (TCSPC) instrument using NanoLed laser at 610 nm for excitation.

DFT calculations:

Density Functional Theory (DFT) calculations were performed using Gaussian 09 ab initio quantum chemical software package.[1] DFT was used for obtaining the ground-state properties, and time-dependent DFT (TDDFT) was used for the estimation of ground to excited-state transitions. The geometries were optimized until the maximum internal forces acting on all the atoms and the stress were less than 4.5×10 eV/Å and 1.01×10^{-3} kbar respectively. The minima were further confirmed by vibrational analysis with zero negative frequencies. No symmetry constraints were applied during the geometry optimization. The gas phase relaxations of atomic positions of all the seven derivatives was carried out by employing the hybrid Becke, three-parameter,[2,3] Lee-Yang-Parr[2-4] exchange-correlation functional (B3LYP) and a 6-31G (d,p)

basis.[5-7] These relaxed geometries were used as inputs for further calculations. To perform the calculations without compromising the results, long alkyl chains were replaced with methyl groups. The geometries were then used to obtain the frontier molecular orbitals (FMOs), vertical and adiabatic ionization potential, vertical and adiabatic electron affinities and also subjected to the single-point TDDFT studies (first 20 vertical singlet–singlet transitions) to obtain the UV-Vis spectra of the derivatives. The integral equation formalism polarizable continuum model (PCM)[8, 9] within the self-consistent reaction field (SCRF) theory has been used for TDDFT calculations to describe the solvation of the derivatives in chloroform solvent. The TDDFT calculations were performed with various functionals like B3LYP, cam-B3LYP[9] and M06-2X.[10] The software GaussSum 3.0[11] was employed to simulate the absorption spectrum and to interpret the nature of transitions. The percentage contributions of individual units present in the dyes to the respective molecular orbitals were calculated.

OFET fabrication

Bottom-contact/bottom-gate OFET devices were fabricated using n-doped-Si/SiO_2 substrates where Si and SiO_2 were used as the gate electrode and gate dielectric, respectively. The substrates were cleaned using ultrasonication in acetone, and in iso-propanol. The cleaned substrates were dried under oven at 100 °C for 20 minutes. The substrates were modified with OTS to form a SAM monolayer and transferred into a glove box. Thin films of the small molecules were deposited on the treated substrates by spin coating the small molecule solution (8 mg/mL) in chloroform, optionally followed by thermal annealing at 100 °C, under Argon. The OFET devices had a channel length (L) varied from 2.5 to 20 μm and a channel width (W) of 10 mm. The measurements of the OFETs were carried out in Argon filled glove box using a Agilent 4156 semiconductor parameter analyzer on a probe stage. The carrier mobility, μ, was calculated from the data in the linear and saturated regime according to the equation $I_{SD} = (W/L)C_i\mu(V_G - V_T)V_D$ for linear and $I_{SD} = (W/2L)C_i\mu(V_G - V_T)^2$ for saturation, where I_{SD} is the drain current, W and L are channel width and length, respectively. C_i (C_i = 14.9 nF) is the capacitance per unit area of the gate dielectric layer and V_G and V_T are the gate voltage and threshold voltage, respectively. V_G-V_T of the device was determined from the relationship between the square root of I_{SD} at the saturated regime.

Synthesis of boronic ester intermediates

2-(benzofuran-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1**):

To a 50 mL two-neck round-bottom flask containing benzofuran (2.00 g, 17 mmol), dry THF (20 mL) was added and the resulting solution was cooled to -78 °C (dry ice/acetone). To this solution, n-BuLi (2.0 M, 6.8 mL, 17 mmol) was added drop wise. After stirring for 30 minutes at -78 °C, the temperature of the reaction mixture was allowed to reach RT and stirred at RT for 1 h followed by cooling down to -78 °C. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4 mL, 23 mmol) was added drop wise to the reaction mixture at -78 °C and the resulting solution was warmed to RT and stirred at RT overnight. After completion of the reaction monitored using TLC, the reaction was quenched at -78 °C by adding saturated NH_4Cl solution and extracted three times with ethyl acetate (3x50 mL). The combined ethyl acetate extract was dried over anhydrous Na_2SO_4 and the solution was filtered and concentrated under reduced pressure. The residue obtained was purified using column chromatography to yield the title compound as yellow solid (Yield: 96%, 4.00 g).

^{1}H NMR (500 MHz, δ ppm): 7.63 (d, J = 7.78 Hz, 1H), 7.57 (d, J = 8.39 Hz, 1H), 7.40 (s, 1H), 7.36-7.32 (m, 1H), 7.23 (t, J = 7.17 Hz, 1H), 1.39 (s, 12H).

Similar procedure was adopted to synthesize 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Yellow liquid, Yield: 68%) and 4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (Off-white solid, Yield: 83%).

2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**): ^{1}H NMR (500 MHz, δ ppm): 7.49-7.44 (m, 1H), 7.47 (d, J = 3.02 Hz, 1H), 6.86 (d, J = 3.02 Hz, 1H), 2.88-2.81(m, 2H), 1.73-1.64 (m, 2H), 1.41-1.25 (m, 18H), 0.91-0.85 (m, 3H).

4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (**4**): ^{1}H NMR (500 MHz, δ ppm): 7.91 (d, J = 8.80 Hz, 2H), 7.61 (d, J = 8.24 Hz, 2H), 1.35 (s, 12H).

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylamine (**2**):

In a 50 mL two-neck round-bottom flask, 4-bromo-N,N-diphenylaniline (2.00 g, 6.1 mmol) was dissolved in dry THF (20 mL) and the mixture was cooled down to -78 °C (dry ice/acetone). To

this mixture, n-BuLi (2.0 M, 3.7 mL, 7.4 mmol) was added under N_2 atmosphere and stirred for 1 h at -78 °C followed by the drop wise addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.40 g, 7.4 mmol). The reaction mixture was allowed to reach RT and stirred at RT overnight. After the disappearance of the starting materials in TLC, reaction was quenched by adding water (20 mL) and thus obtained aqueous solution was extracted with chloroform (3x50 mL). The combined chloroform extract was dried over anhydrous Na_2SO_4 and the solution was filtered and concentrated under reduced pressure. The residue obtained was purified using column chromatography to get the title compound as white solid (Yield: 61%, 1.40 g).

^{1}H NMR (500 MHz, δ ppm): 7.68-7.65 (m, 2H), 7.27-7.22 (m, 4H), 7.12-7.08 (m, 4H), 7.06-7.01 (m, 4H), 1.33 (s, 12H)

Synthesis of ethynyl intermediates

The synthetic precursors, 2-ethynylnaphthalene (**5**), 2-ethynylanthracene (**6**) and 1-ethynylpyrene (**7**) were synthesized from their corresponding bromo derivatives. The corresponding bromo derivatives were first reacted with acetylene reagents followed by the de-protection yielded the required ethynyl precursors. Ethynyltrimethylsilane and 2-methyl-3-buten-2-ol were used as acetylene reagents for 2-bromonaphthalene, 2-bromoanthracene and 1-bromopyrene, respectively. General synthetic procedure for the ethynylation and de-protection are given below.

2-bromoanthracene:

2-bromoanthracene was prepared in a two step procedure using 2-aminoanthraquinone as synthetic precursor.

To a 500 mL two-neck round-bottom flask containing copper (II) bromide (20.00 g, 89.5 mmol) dissolved in dry acetonitrile (100 mL), isopentyl nitrite (12.00 mL, 89.5 mmol) was added at 0 °C and the mixture was stirred for 30 minutes at 0 °C. The temperature of the reaction mixture was allowed to reach RT, stirred at RT for 30 minutes followed by cooling down to 0 °C. To the resultant solution, 2-Aminoanthraquinone (10.00 g, 44.7 mmol) dissolved in THF (150 mL) was quickly added and the solution was stirred for 2 h at 0 °C. After completion of reaction, organic solvents were removed by rotary evaporation to give a dark brown solid. To the above solid, water (200 mL) was added and the resulting slurry was vacuum filtered. The residue obtained

was thoroughly washed with water and dissolved in dichloromethane. The insoluble materials were filtered and the dichloromethane layer was dried over anhydrous Na_2SO_4. The dichloromethane solution was filtered and concentrated under reduced pressure. The residue obtained was purified using column chromatography to give 2-bromoanthraquinone as a yellow solid (Yield: 31%, 4.00 g).

To a solution of 2-Bromoanthraquinone (8.50 g, 29.6 mmol) in isopropyl alcohol and THF mixture (1:1, 200 mL) at 0 °C, $NaBH_4$ (6.70 g, 177 mmol) was added and the reaction mixture was stirred at 0 °C for 3 h. The solution was then warmed to RT and additional $NaBH_4$ (3.35 g, 89 mmol) was added. The resulting solution was stirred at RT for 12 h followed by the addition of water (10 mL). The resultant mixture was stirred at RT for an additional 12 h. After the completion of the reaction, solvent was removed by rotary evaporation. To the residue obtained, HCl (3M) was slowly added until the bubbling was ceased followed by the addition of additional 3M HCl (30 mL). The resulting solution was stirred under reflux conditions for 6 h and cooled down to RT and concentrated under reduced pressure. The resultant suspension was filtered and the obtained residue was dissolved in dichloromethane. The dichloromethane solution was dried over anhydrous Na_2SO_4 and filtered. The solution obtained was concentrated under reduced pressure and the residue was purified using column chromatography to give the title compound (Yield: 22%, 2.20 g).

Ethynylation of 2-bromonaphthalene and 2-bromoanthracene

To a two-neck 50 mL round-bottom flask, corresponding bromo derivative (10 mmol), bis(triphenylphosphine)palladium(II) dichloride (10 mol%) and CuI (10 mol%) were added and fitted to a reflux condenser. The reaction vessel was evacuated and filled with N_2 gas. Freshly distilled triethylamine (5 mL) was added to the reaction vessel and the resultant solution was purged with N_2 gas for 15 minutes. Ethynyltrimethylsilane (15 mmol) was added drop wise to the reaction mixture and the resultant mixture was heated to 40 °C and stirred at this temperature overnight. After completion of the reaction monitored using TLC, insoluble materials were removed by filtration through celite and the filtrate was concentrated and partitioned between water and ethyl acetate. The ethyl acetate layer collected and the aqueous layer was washed with ethyl acetate (3x20 mL). The combined ethyl acetate extract was dried over anhydrous Na_2SO_4

and filtered. The solution obtained was concentrated and the residue was purified using column chromatography to obtain the title compound.

Trimethyl(naphthalen-2-ylethynyl)silane (Yield: 80%, 1.5 g). (anthracen-2-ylethynyl)trimethyl silane (Yield: 80%, 2.1 g).

Silyl de-protection of trimethyl(naphthalen-2-ylethynyl)silane and (anthracen-2-ylethynyl)trimethylsilane:

To the solution of corresponding ethynyltrimethylsilane (6.5 mmol) in dichloromethane and methanol mixture (1:1, 40 mL), potassium hydroxide (13 mmol) was added and the resultant solution was stirred for 3 h at RT. After the complete disappearance of starting materials monitored using TLC, the reaction mixture was poured into water and extracted with ethyl acetate (3x20 mL). The combined organic extract was dried over anhydrous Na_2SO_4 and filtered. The solution obtained was concentrated and the residue was purified using column chromatography to give the desired compound over 90% yield.

2-ethynylnaphthalene (**5**): ^{1}H NMR (500 MHz, δ ppm): 8.02 (s, 1H), 7.82-7.76 (m, 3H), 7.52-7.47 (m, 3H), 3.14 (s, 1H).

2-ethynylanthracene (**6**): ^{1}H NMR (500 MHz, δ ppm): 8.39 (d, J = 3.5 Hz, 2H), 8.22 (s, 1H), 8.02-7.98 (m, 2H), 7.96-7.93.(m, 1H), 7.50-7.45 (m, 3H), 3.20 (s, 1H).

2-methyl-4-(pyren-1-yl)but-3-yn-2-ol:

To a two-neck 100 mL round-bottom flask, 1-bromopyrene (2.00 g, 7.1 mmol), 2-methyl-3-buten-2-ol (4.78 g, 56.9 mmol), triphenylphosphine (0.75 g, 9.8 mmol), CuI (0.40 g, 2.13 mmol) and dichloro[1,1′-bis(diphenylphosphino)ferrocene] palladium (II) dichloromethane complex (1:1) (116 mg, 20 mol%) were added and fitted to a reflux condenser. The reaction vessel was evacuated and filled with N_2 gas. Dry toluene (8 mL) and freshly distilled triethylamine (30 mL) were added to the reaction vessel and the resultant solution was purged with N_2 gas for 15 minutes. The resultant mixture was heated to 80 °C and stirred at this temperature overnight. After completion of the reaction, reaction mixture was cooled to RT and partitioned between water and ethyl acetate. Ethyl acetate layer was collected and the aqueous layer was washed with ethyl acetate (3x20 mL). The combined ethyl acetate extract was dried over anhydrous Na_2SO_4

and filtered. The solution obtained was concentrated and the residue was purified using column chromatography to obtain the desired compound (Yield: 84%, 1.7 g).

^{1}H NMR (500 MHz, δ ppm): 8.51-8.48 (m, 1H), 8.22-8.13 (m, 3H), 8.09-8.06 (m, 3H), 8.03-7.99 (m, 2H), 2.30-2.27 (m, 1H), 1.80 (s, 6H).

1-ethynylpyrene (**7**):

2-methyl-4-(pyren-1-yl)but-3-yn-2-ol (1.50 g, 5.27 mmol) and KOH (0.65 g, 11 mmol) were dissolved in isopropanol (30 mL) in a 50 mL two-neck round-bottom flask and the mixture was heated to 80 °C and stirred at this temperature for 3 h. After the disappearance of the starting materials monitored using TLC, the reaction mixture was cooled RT and poured into water. The aqueous solution was extracted three times with ethyl acetate (3x50 mL). The combined organic extract was dried over anhydrous Na_2SO_4 and filtered. The solution obtained was concentrated and the residue was purified using column chromatography to yield the title compound (Yield: 93%, 1.1 g).

^{1}H NMR (500 MHz, δ ppm): 8.60-8.57 (m, 1H) 8.24-8.15 (m, 4H), 8.11-8.08 (m, 2H), 8.05-8.01 (m, 2H), 3.62 (s, 1H).

Synthesis of diketopyrrolopyrrole (DPP) intermediates

2,5-Bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4c]pyrrole-1,4(2H,5H)-dione[12]:

In a two-neck round-bottom flask, 3,6-dithiophen-2-yl-2,5-dihydro- pyrrolo[3,4-c]pyrrole-1,4-dione (20.00 g, 66.66 mmol) and anhydrous K_2CO_3 (29.85 g, 216 mmol) were dissolved in dry DMF (400 mL) and this solution was purged with N_2 gas for 30 minutes. The resultant solution was stirred under heating at 120 °C for 1 h followed by the drop wise addition of 2-Ethylhexyl bromide (38.62 g, 200 mmol) and catalytic amount of 18-crown-6. The temperature of the reaction mixture was raised to 150 °C and stirred overnight at 150 °C. After the completion of the reaction, the reaction mixture was cooled to RT and partitioned between chloroform and water. The chloroform layer was collected and the aqueous layer was washed with $CHCl_3$ (3x50 mL). The combined organic extract was dried over anhydrous Na_2SO_4 and filtered. The solution obtained was concentrated and the residue was purified using column chromatography to yield the desired compound as a dark red solid (Yield: 22%, 8.0 g).

3,6-bis(5-bromothien-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dion[12]:

In a 250 mL two-neck round-bottom flask, 2,5-Bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4c]pyrrole-1,4(2H,5H)-dione (4.00 g, 7.62 mmol) was dissolved in chloroform (80 mL) and this solution was cooled to 0 °C. After stirring at 0 °C for 20 minutes, NBS (2.88 g, 16.7 mmol) was added portion wise over 30 minutes and the resultant mixture was stirred for another 30 minutes to complete the reaction. After the completion of reaction, solvent was removed under reduced pressure and the resulting solid was purified using column chromatography to yield the target compound (Yield: 78%, 4.1 g).

3-(5-(benzofuran-2-yl)thiophen-2-yl)-6-(5-bromothiophen-2-yl)-2,5-bis(2 ethylhexyl)pyrrolo [3,4-c] pyrrole-1,4(2H,5H)-dione (**A**):

To a 250 mL two-neck round-bottom flask, 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl) pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (2.00 g, 2.93 mmol), 2-(benzofuran-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.71g, 2.93 mmol), $Pd(PPh_3)_4$ (67 mg, 5 mol%) and Na_2CO_3 (4.95 g, 460 mmol) were added and fitted to reflux condenser. The reaction vessel was evacuated and filled with N_2 gas. Dry toluene (70 mL) was added to the flask and the mixture was purged with N_2 gas for 30 minutes. A solution of H_2O and EtOH mixture (2:1, 44.5 mL) was added to the reaction mixture and the mixture was heated to 90 °C and stirred at this temperature overnight. After completion of the reaction, reaction mixture was cooled to RT and diluted with ethyl acetate and water. The organic layer was collected and the aqueous layer was extracted with ethyl acetate (3x50 mL). The combined ethyl acetate extract was dried over anhydrous Na_2SO_4 and filtered. The solution obtained was concentrated and the residue was purified using column chromatography to obtain the desired compound (Yield: 28%, 0.6 g).

^{1}H NMR (500 MHz, δ ppm): 8.98 (d, J = 4.15 Hz, 1H), 8.65 (d, J = 4.15 Hz, 1H), 7.60-7.56 (m, 2H), 7.51 (d, J = 8.06 Hz, 1H), 7.36-7.30 (m, 1H), 7.26 (m, 1H), 7.22 (d, J = 4.15 Hz, 1H), 7.05 (s, 1H), 4.08-3.93 (m, 2H), 1.96-1.82 (m, 2H), 1.41-1.27 (m, 16H), 0.91-0.86 (m, 12H). ^{13}C NMR (125 MHz, δ ppm): 161.6, 161.3, 154.9, 149.9, 140.1, 138.8, 138.1, 136.7, 135.2, 135.1, 131.4, 129.4, 128.8, 128.5, 125.4, 125.4, 123.5, 121.2, 118.7, 111.2, 108.3, 103.7, 46.0, 39.2, 39.1, 30.3, 30.2, 29.7, 28.5, 28.3, 23.6, 23.6, 23.1, 23.0, 14.1, 14.0, 10.5.

Synthesis of target DPP-derivatives

3-(5-(benzofuran-2-yl)thiophen-2-yl)-6-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**BFTPADPP**):

To a 50 mL two-neck round-bottom flask, **1** (0.20 g, 0.277 mmol), N,N-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (0.20 g, 0.55 mmol), $Pd(PPh_3)_4$ (6 mg, 5 mol%) and Na_2CO_3 (0.47 g, 4.4 mmol) were added and fitted to a reflux condenser. The reaction vessel was evacuated and filled with N_2 gas. Freshly degassed toluene (20 mL) was added to the reaction vessel followed by the addition of H_2O and EtOH mixture (2:1, 10.5 mL). The resulting solution was purged with N_2 gas for 30 minutes and heated to 90 °C and stirred at this temperature overnight. Reaction progress was monitored using TLC. After completion of the reaction, reaction mixture was cooled to RT and partitioned between with chloroform and water. The choloform layer was collected and the aqueous layer was extracted with chloroform (3x10 mL). The combined chloroform extract was dried over anhydrous Na_2SO_4 and filtered. The solution obtained was concentrated. The residue obtained was washed several times with pure methanol and re-crystallized in toluene to yield the title compound (Yield: 89%, 0.22 g).

^{1}H NMR (500 MHz, δ ppm): 9.05 (d, J = 4.27 Hz, 1H), 8.95 (d, J = 4.12 Hz, 1H), 7.60-7.56 (m, 2H), 7.54-7.51 (m, 3H), 7.38 (d, J = 4.27 Hz, 1H), 7.35-7.27 (m, 6H), 7.16-7.13 (m, 4H), 7.11-7.04 (m, 5H), 4.13-4.04 (m, 4H), 1.99-1.91 (m, 2H), 1.43-1.26 (m, 16H), 0.94-0.84 (m, 12H); ^{13}C NMR (125 MHz, δ ppm): 161.8, 161.5, 154.9, 150.3, 150.1, 148.6, 147.0, 140.5, 138.6, 137.6, 137.4, 136.0, 129.7, 129.4, 128.9, 127.6, 126.9, 126.4, 125.4, 125.2, 125.0, 123.7, 123.5, 122.7, 121.1, 111.2, 108.8, 107.8, 103.4, 46.0, 39.2, 39.1, 30.3, 29.7, 28.5, 23.6, 23.1, 14.0, 10.6, 10.5.

ESI-HRMS (Positive mode, m/z): 884.38991 ($M+H^+$), Calc. for C_{56} H_{58} O_3 N_3 S_2 is 884.39141.

Similar procedure was adopted to synthesize 3-(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(5-(4 (trifluoromethyl)phenyl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H) dione (**BFTFDPP**) (Yield: 80%, 0.17 g) and 3-(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(5'-hexyl-2,2'-bithiophen-5-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**BFHTDPP**) (Yield: 84%, 0.20 g)

BFTFDPP: ^{1}H NMR (500 MHz, δ ppm): 9.01 (d, J = 4.12 Hz, 1H), 8.94 (d, J = 4.12 Hz, 1H), 7.79-7.79 (m, 2H), 7.77-7.66 (m, 2H), 7.61-7.58 (m, 2H), 7.55-7.51 (m, 2H), 7.39-7.32 (m, 1H),

7.26 (s, 1H), 7.07 (s, 1H), 4.14-4.04 (m, 4H), 1.98-1.90 (m, 2H), 1.46-1.26 (m, 16H), 0.95-0.86 (m, 12H); ^{13}C NMR (125 MHz, δ ppm): 161.7, 161.5, 154.9, 149.9, 147.2, 140.0, 138.1, 136.7, 136.5, 136.4, 130.1, 130.0, 129.4, 128.8, 126.2, 125.7, 125.4, 125.34, 123.5, 121.2, 111.2, 108.8, 108.6, 103.7, 46.0, 39.3, 30.3, 28.6, 28.5, 23.7, 23.1, 14.1, 10.6, 10.5.
ESI-HRMS (Positive mode, m/z): 785.30386 ($M+H^+$), Calc. for C_{45} H_{48} O_3 N_2 F_3 S_2 is 785.30530.

BFHTDPP: ^{1}H NMR (500 MHz, δ ppm): 8.97 (dd, J = 10.99 Hz, 2H), 7.60-7.57 (m, 2H), 7.5-7.50 (m, 1H), 7.35-7.31 (m, 1H), 7.26 (m, 1H), 7.24 (d, J = 4.12 Hz, 1H), 7.15 (d, J = 3.66 Hz, 1H), 7.05 (s, 1H), 6.76-6.74 (m, 1H), 4.14-4.00 (m, 4H), 2.85-2.80 (m, 2H), 1.97-1.90 (m, 2H), 1.73-1.67 (m, 2H), 1.43-1.26 (m, 22H), 0.94-0.86 (m, 15H); ^{13}C NMR (125 MHz, δ ppm): 161.7, 161.5, 154.9, 150.1, 147.9, 143.8, 140.2, 138.8, 137.4, 137.2, 136.0, 133.5, 129.7, 128.9, 127.3, 125.4, 125.2, 125.1, 124.0, 123.5, 121.1, 111.2, 108.1, 103.5, 46.0, 39.2, 31.5, 30.3, 28.7, 28.5, 23.7, 23.1, 22.5, 14.1, 10.6.
ESI-HRMS (Positive mode, m/z): 807.36672 ($M+H^+$), Calc. for C_{48} H_{59} O_3 N_2 S_3 is 807.36823.

The target DPP derivatives **BFPhDPP**. **BFNaDPP**. **BFAnDPP** and **BFPyDPP** were synthesized from **1** and the corresponding ethynyl precursors by adopting Sonogashira coupling reaction protocol. General procedure for their synthesis is given below.

To a 100 mL two-neck round-bottom flask, **1** (1 mmol), CuI (7 mol%), $Pd(PPh_3)_4$ (2 mol%) and the corresponding acetylene compound were added and fitted to a reflux condenser. The reaction vessel was evacuated and filled with N_2 gas. Dry toluene (30 mL) to and dry diethylamine (2 mL) were added to the reaction vessel and the resulting solution was purged with N_2 gas for 20 minutes. The reaction mixture was heated to reflux temperature and stirred at this temperature overnight. After completion of reaction monitored using TLC, water (50 mL) was added to the reaction mixture and the resulting solution was extracted with chloroform (3x50 mL). The combined organic extract was subjected to serial washings with water followed by brine solution. Thus obtained chloroform solution was dried over anhydrous Na_2SO_4 and filtered. The solution obtained was concentrated and the residue was purified using column chromatography.

3-(5-(benzofuran-2-yl)thiophen-2-yl)-2.5-bis(2-ethylhexyl)-6-(5-(phenylethynyl)thiophen-2-yl)pyrrolo[3.4-c]pyrrole-1.4(2H.5H)-dione (**BFPhDPP**) (Yield: 85%, 0.17 g)

BFPhDPP: ^{1}H NMR (500 MHz, δ ppm): 9.02 (d, J = 4.12 Hz, 1H), 8.91(d, J = 4.12 Hz, 1H), 7.62-7.51 (m, 5H), 7.41-7.37 (m, 4H), 7.34 (t, J = 8.0 Hz, 1H), 7.28 (s, 1H), 7.07 (s, 1H), 4.14-4.00 (m, 4H), 1.98-1.89 (m, 2H), 1.45-1.25 (m, 16H), 0.95-0.86 (m, 12H); ^{13}C NMR (125 MHz, δ ppm): 161.6, 161.6, 161.5, 140.6, 139.3, 135.5, 135.3, 132.9, 132.8, 131.5, 130.8, 130.5, 129.8, 129.0, 128.6, 128.5, 128.3, 122.3, 108.7, 108.0, 97.7, 97.5, 82.3, 46.0, 45.9, 39.1, 39.1, 30.1, 30.1, 28.3, 23.5, 23.0, 14.0, 10.5.
ESI-HRMS (Positive mode, m/z): 741.31702 ($M+H^+$), Calc. for C_{46} H_{49} O_3 N_2 S_2 is 741.31791.

3-(5-(benzofuran-2-yl)thiophen-2-yl)-2.5-bis(2-ethylhexyl)-6-(5-(naphthalen-2-ylethynyl)thiophen-2-yl)pyrrolo[3.4-c]pyrrole-1.4(2H.5H)-dione (**BFNaDPP**) (Yield: 86%, 0.19 g).

BFNaDPP: ^{1}H NMR (500 MHz, δ ppm): 9.02 (d, J = 4.12 Hz, 1H), 8.94 (d, J = 4.12 Hz, 1H), 8.09 (s, 1H), 7.86-7.83 (m, 3H), 7.61-7.57 (m, 3H), 7.54-7.51 (m, 3H), 7.44-7.42 (m, 1H), 7.36-7.32 (m, 1H), 7.28 (s, 1H), 7.07 (s, 1H), 4.13-4.02 (m, 4H), 1.98-1.91 (m, 2H), 1.44-1.27 (m, 16H), 0.95-0.88 (m, 12H); ^{13}C NMR (125 MHz, δ ppm): 161.6, 161.5, 154.9, 149.9, 139.9, 139.1, 138.1, 136.7, 135.5, 133.1, 133.0, 132.9, 131.7, 130.6, 129.4, 128.8, 128.4, 128.2, 127.9, 127.9, 127.8, 127.8, 127.1, 126.8, 125.4, 125.4, 123.5, 121.1, 119.5, 111.2, 108.9, 108.6, 103.7, 98.2, 82.7, 46.1, 46.0, 39.2, 39.1, 30.3, 30.1, 29.7, 29.6, 28.5, 28.3, 23.6, 23.5, 23.1, 14.1, 10.5.
ESI-HRMS (Positive mode, m/z): 791.33216 ($M+H^+$), Calc. for C_{50} H_{51} O_3 N_2 S_2 is 791.33356.

3-(5-(anthracen-2-ylethynyl)thiophen-2-yl)-6-(5-(benzofuran-2-yl)thiophen-2-yl)-2.5-bis(2-ethylhexyl)pyrrolo[3.4-c]pyrrole-1.4(2H.5H)-dione (**BFAnDPP**) (Yield: 87%, 0.20 g).

BFAnDPP: ^{1}H NMR (500 MHz, δ ppm): 9.04-9.02 (m, 1H), 8.96-8.94 (m, 1H), 8.43-8.39 (m, 2H), 8.27-8.24 (m,1H), 8.04-7.97 (m, 3H), 7.61-7.58 (m, 2H), 7.54-7.48 (m, 4H), 7.46-7.44 (m, 1H), 7.36-7.32 (m, 1H), 7.29-7.27 (m, 1H), 7.08-7.05 (m, 1H), 4.13-4.03 (m 4H), 1.99-1.91 (m, 2H), 1.45-1.28 (m, 16H), 0.96-0.88 (m, 12H); ^{13}C NMR (125 MHz, δ ppm): 161.6, 161.5, 155.0, 154.8, 149.9, 136.7, 135.5, 133.0, 132.4, 132.1, 130.7, 130.7, 128.8, 128.5, 128.3, 128.2, 126.8, 126.6, 126.3, 125.9, 125.4, 125.3, 123.5, 121.2, 119.0, 111.2, 108.7, 103.7, 98.6, 98.0, 92.5, 83.3, 46.1, 46.1, 39.2, 39.1, 30.3, 30.1, 28.5, 28.3, 23.6, 23.1, 14.1, 10.5.
ESI-HRMS (Positive mode, m/z): 841.34820 ($M+H^+$), Calc. for C_{54} H_{53} O_3 N_2 S_2 is 841.34921.

3-(5-(benzofuran-2-yl)thiophen-2-yl)-2.5-bis(2-ethylhexyl)-6-(5-(pyren-1 ylethynyl)thiophen-2-yl)pyrrolo[3.4-c]pyrrole-1.4(2H.5H)-dione (**BFPyDPP**) (Yield: 91%, 0.22 g).

BFPyDPP: ^{1}H NMR (500 MHz, δ ppm): 9.01 (dd, J = 18.76 Hz, 2H), 8.58 (d, J = 9.00 Hz, 1H), 8.27-8.19 (m, 4H), 8.16-8.10 (m, 2H), 8.07-8.03 (m, 2H), 7.60-7.57 (m, 2H), 7.55-7.50 (m, 2H), 7.36-7.31 (m, 1H), 7.26 (m, 1H), 7.05 (s, 1H), 4.15-4.03 (m, 4H), 2.01-1.92 (m, 2H), 1.48-1.28 (m, 16H), 0.98-0.88 (m, 12H); ^{13}C NMR (125 MHz, δ ppm): 161.5, 161.4, 154.9, 149.9, 139.7, 139.0, 138.0, 136.7, 135.6, 132.9, 131.8, 131.7, 131.1, 130.9, 130.7, 129.4, 128.8, 128.6, 128.5, 127.1, 126.3, 125.9, 125.8, 125.6, 125.4, 125.3, 125.1, 124.5, 124.3, 124.1, 123.5, 121.1, 116.5, 111.2, 108.8, 108.6, 103.6, 97.4, 88.0, 46.1, 46.0, 39.2, 39.2, 30.3, 30.2, 28.5, 28.4, 23.6, 23.1, 14.1, 10.5.

ESI-HRMS (Positive mode, m/z): 865.34798 ($M+H^{+}$), Calc. for $C_{56}H_{53}O_3N_2S_2$ is 865.34921.

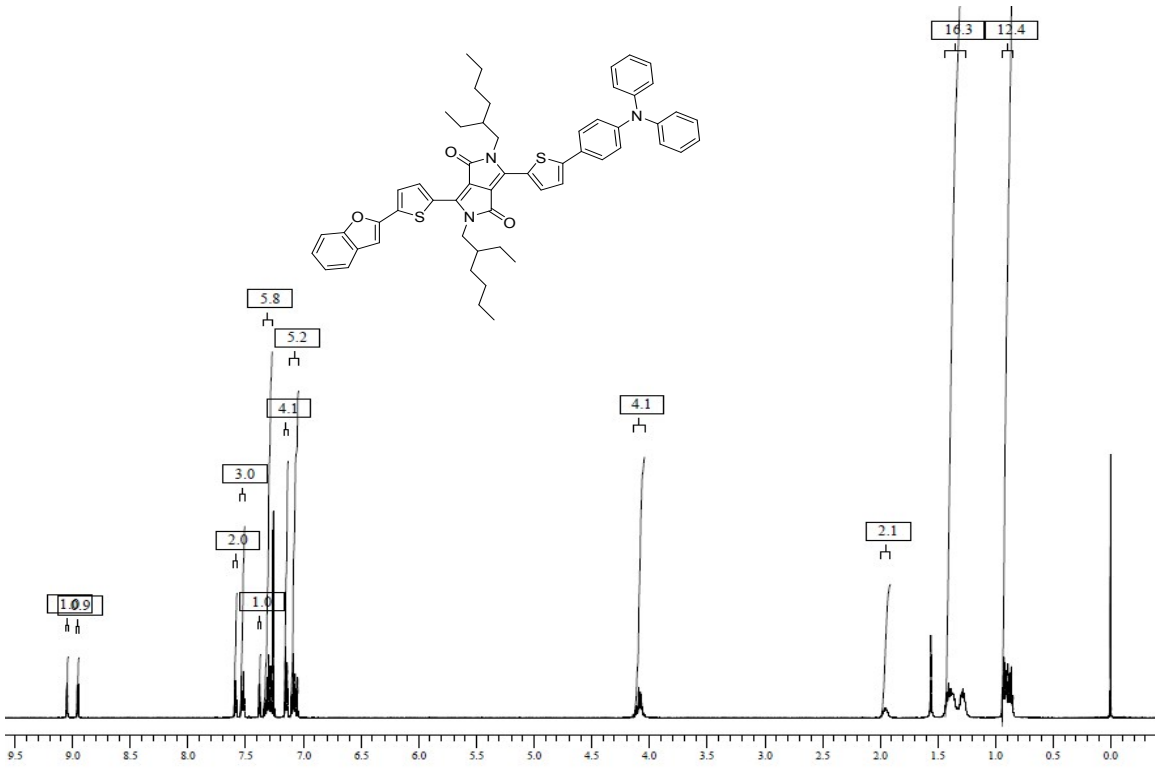


Fig. S1. [1]H NMR spectrum of **BFTPADPP**

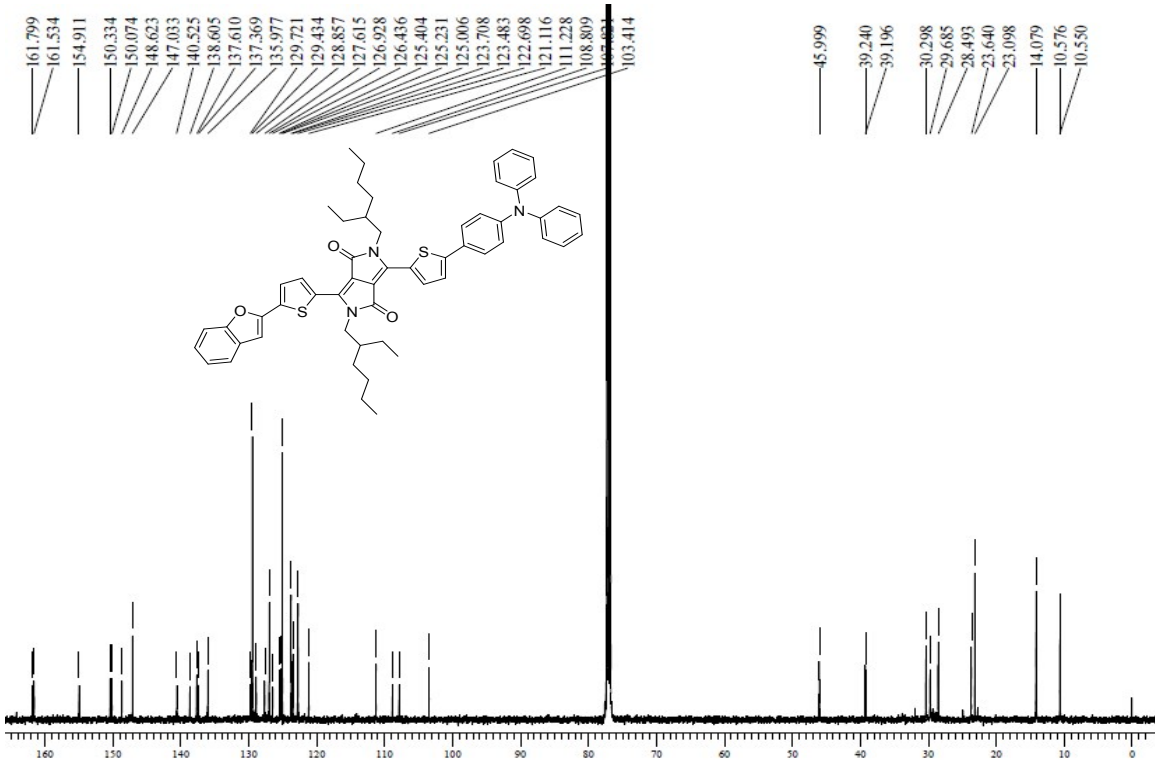


Fig. S2. [13]C NMR spectrum of **BFTPADPP**

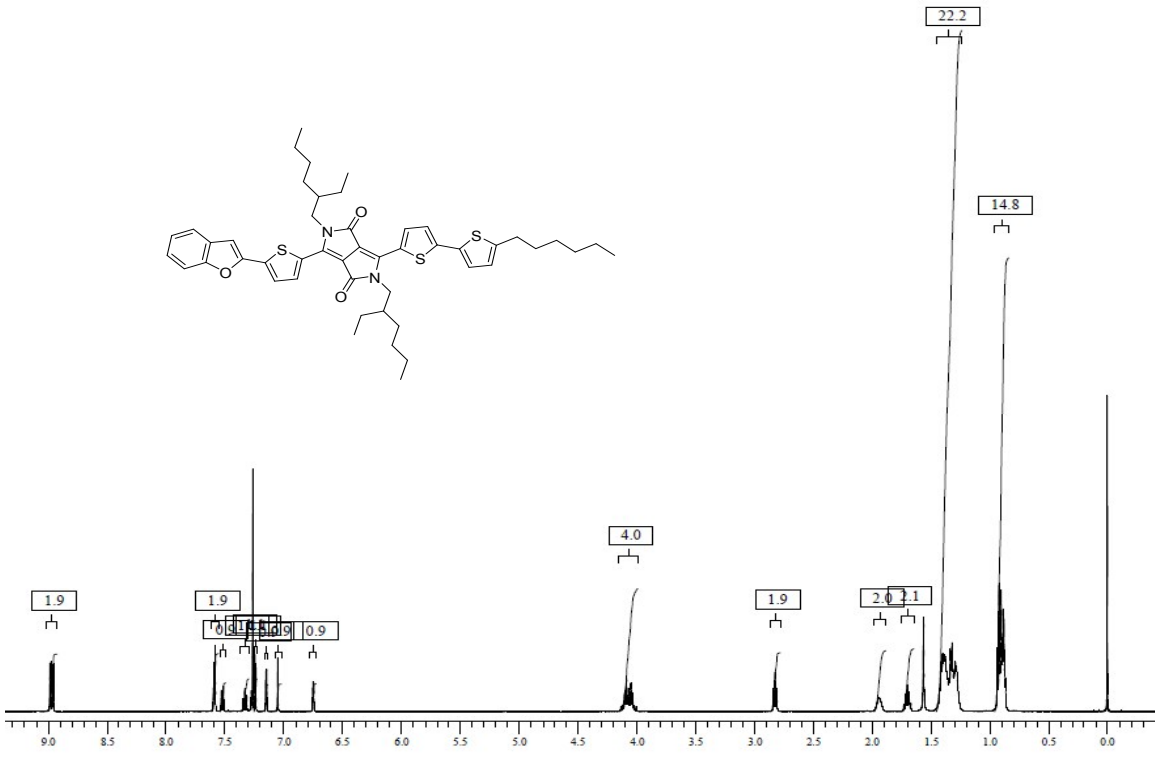


Fig. S3. ^{1}H NMR spectrum of **BFHTDPP**

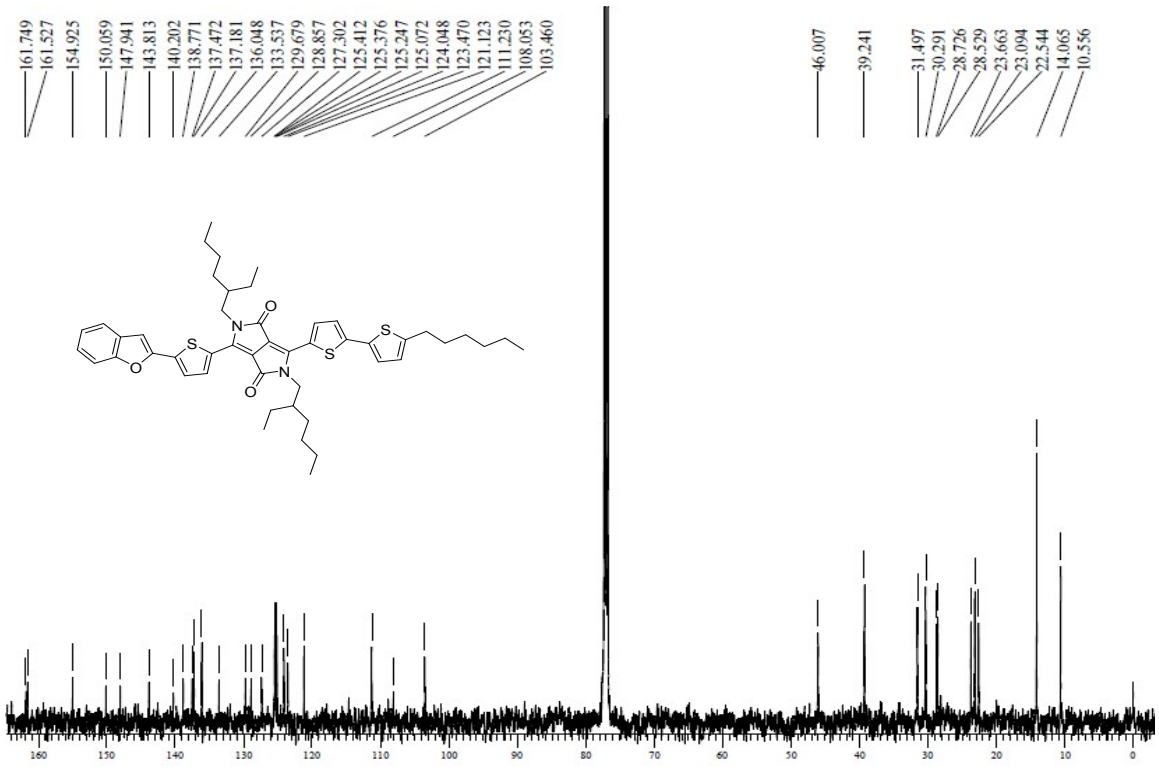


Fig. S4. ^{13}C NMR spectrum of **BFHTDPP**

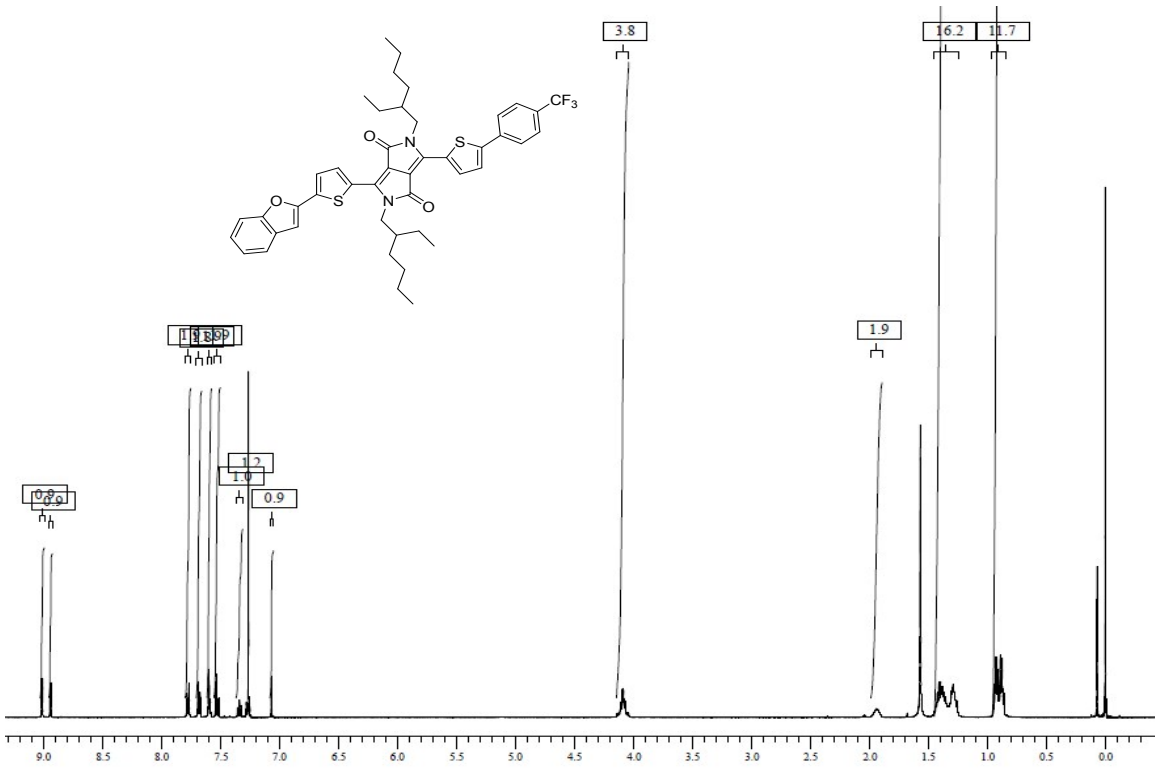


Fig. S5. ^{1}H NMR spectrum of **BFTFDPP**

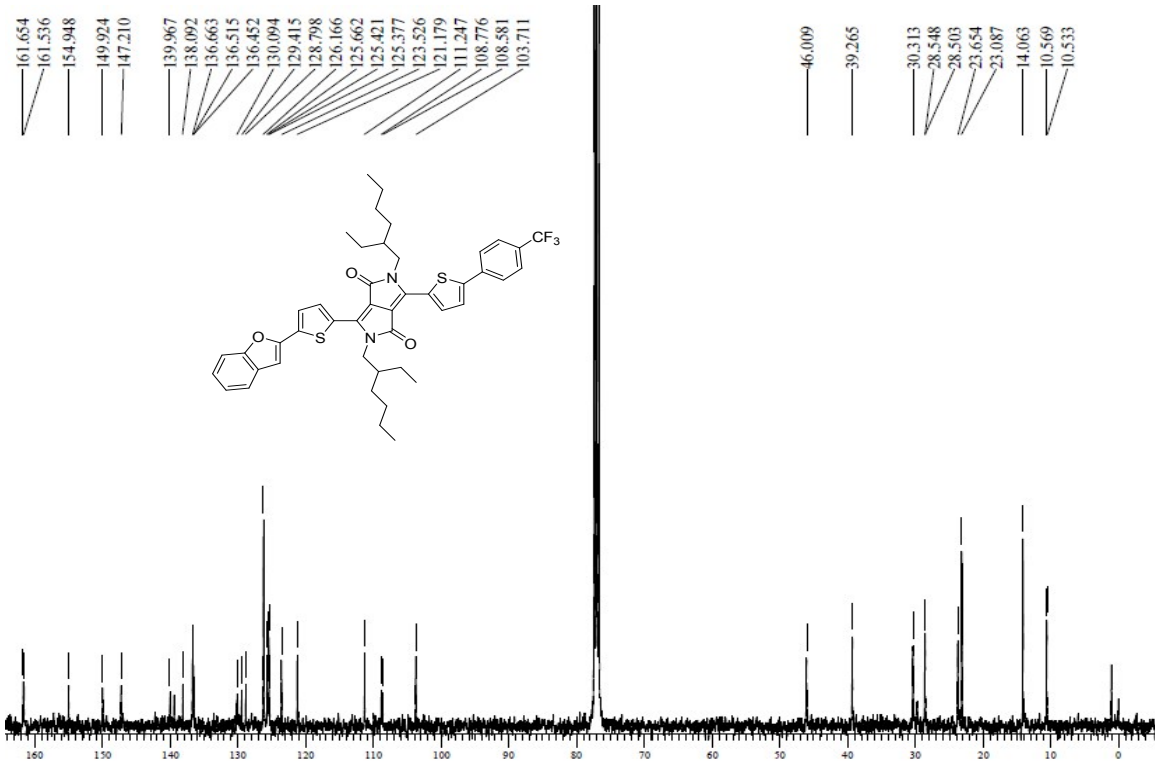


Fig. S6. ^{13}C NMR spectrum of **BFTFDPP**

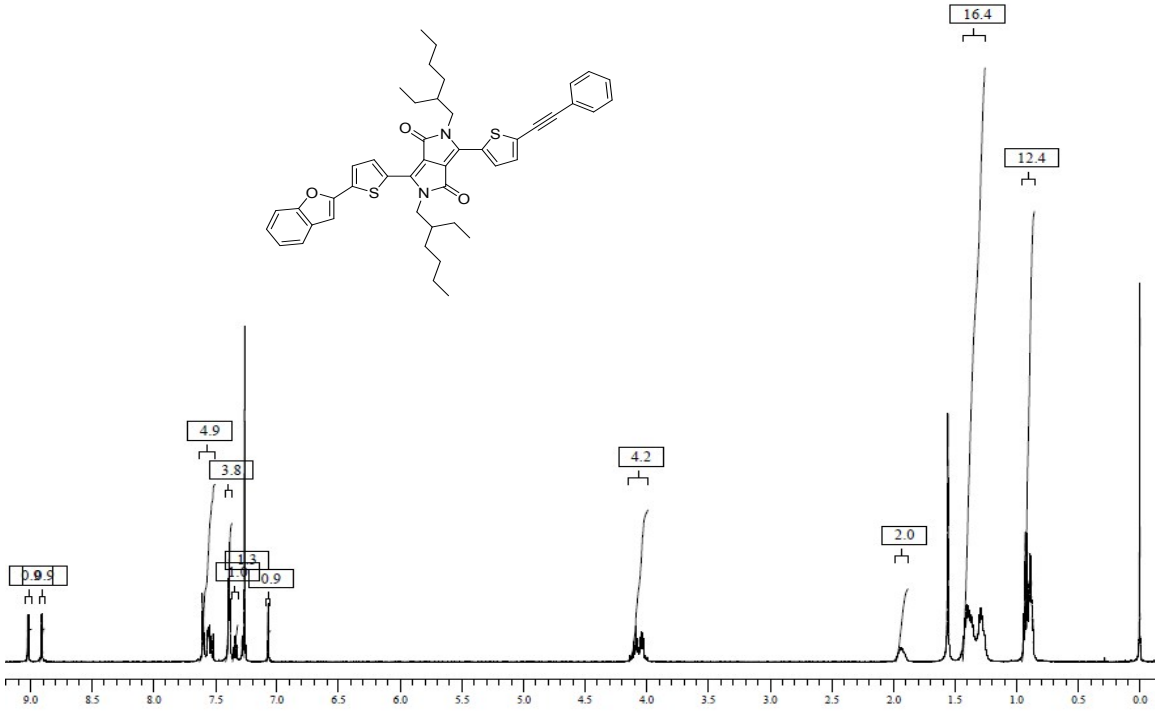


Fig. S7. ^{1}H NMR spectrum of **BFPhDPP**

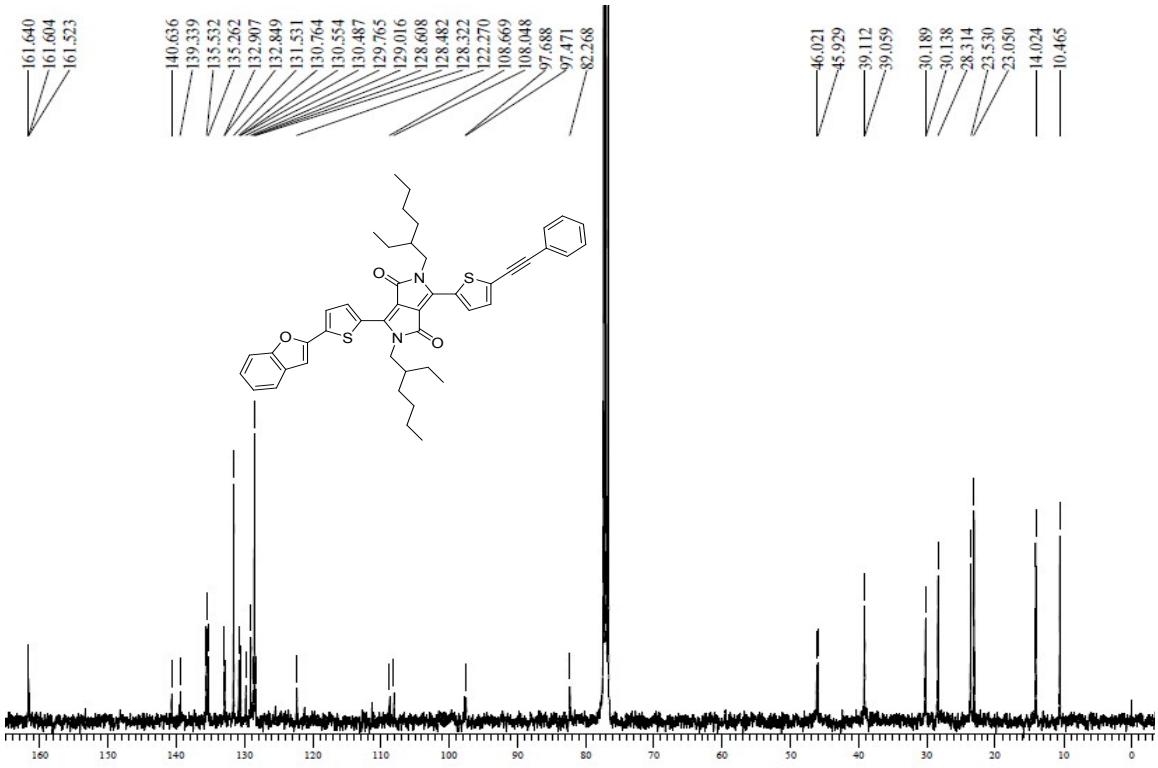


Fig. S8. ^{13}C NMR spectrum of **BFPhDPP**

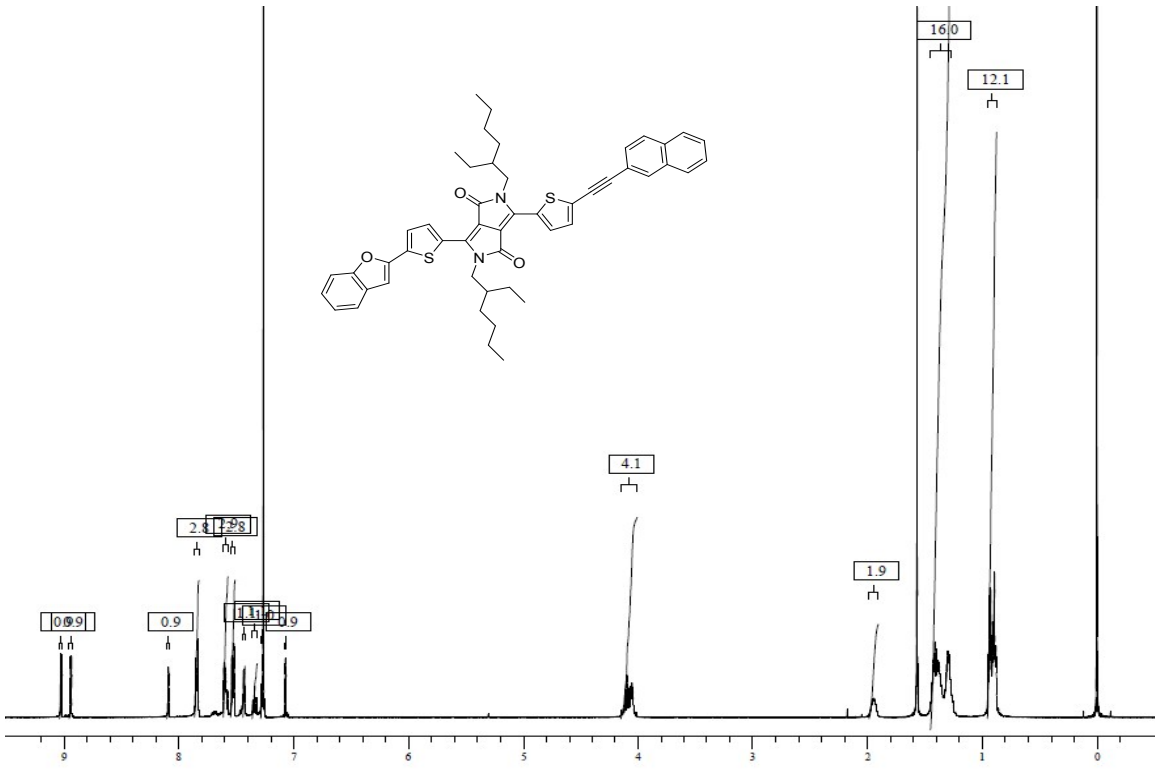


Fig. S9. [1]H NMR spectrum of **BFNaDPP**

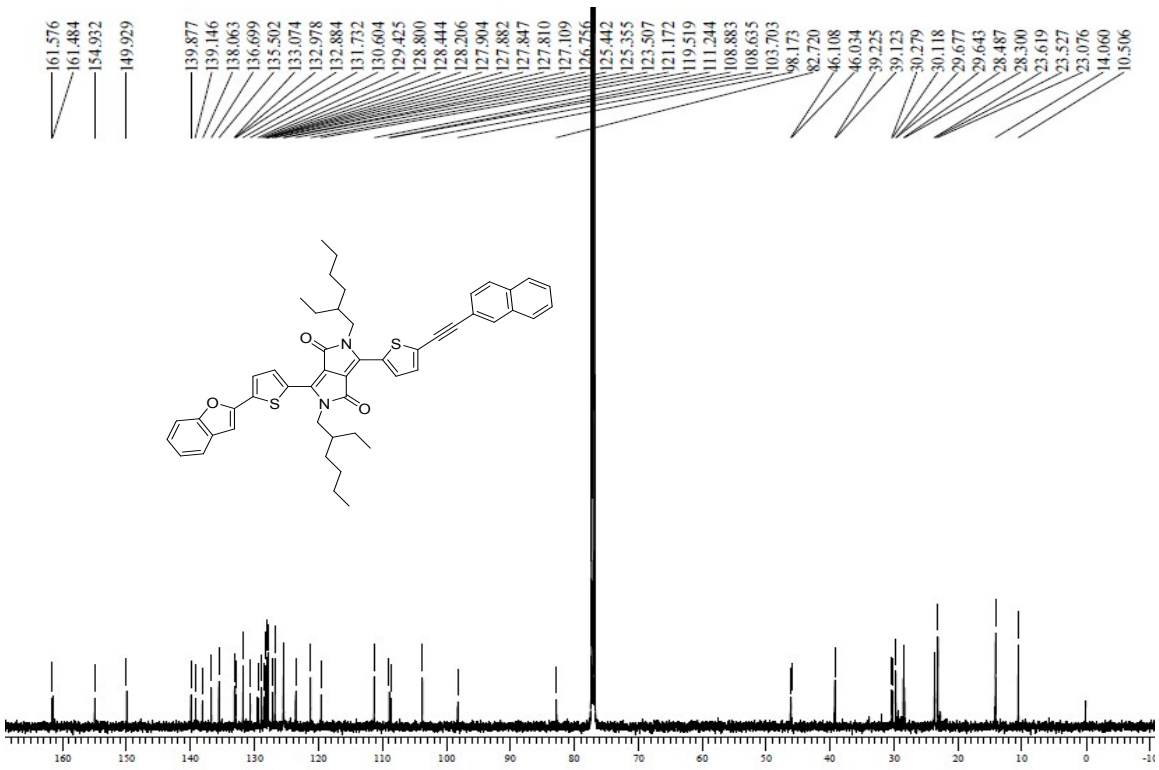


Fig. S10. [13]C NMR spectrum of **BFNaDPP**

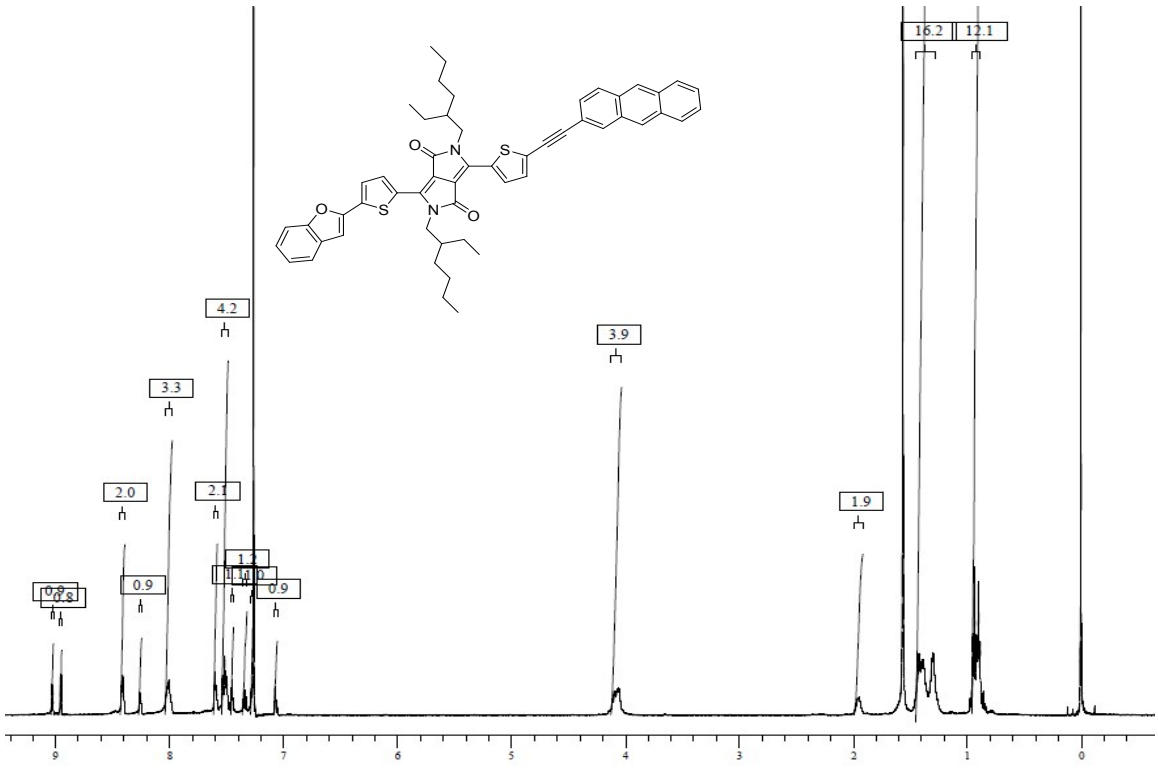


Fig. S11. [1]H NMR spectrum of **BFAnDPP**

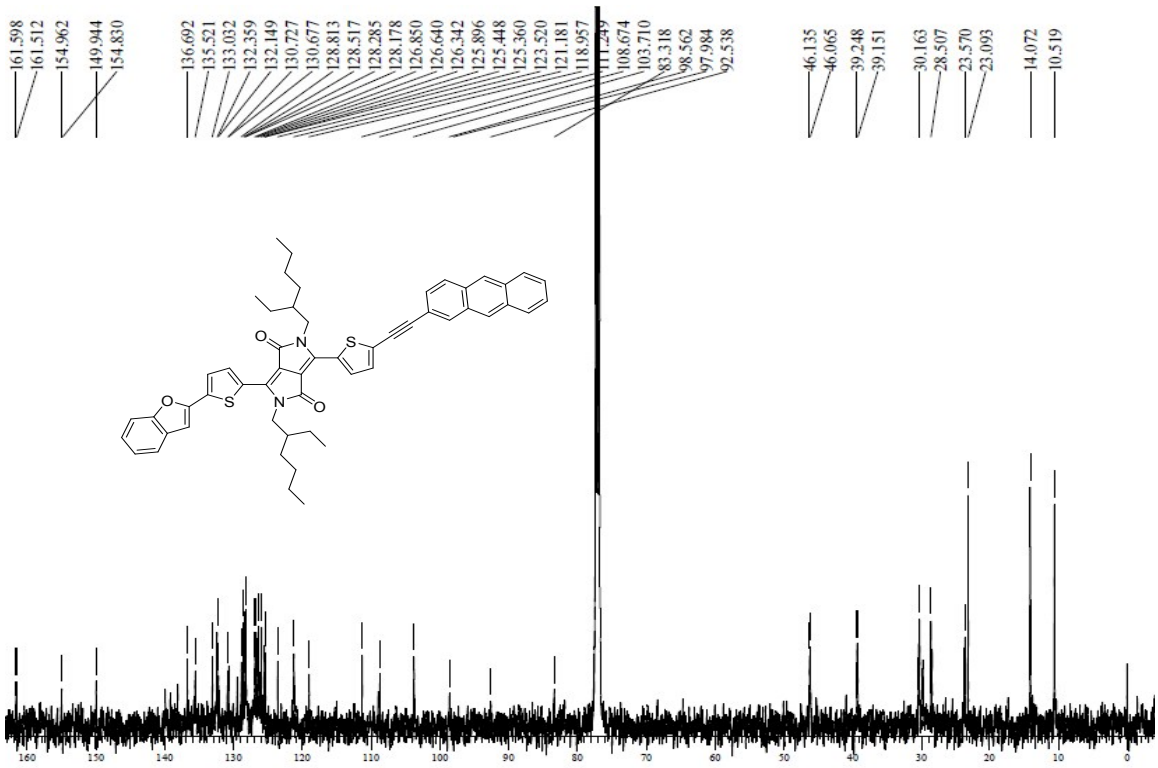


Fig. S12. [13]C NMR spectrum of **BFAnDPP**

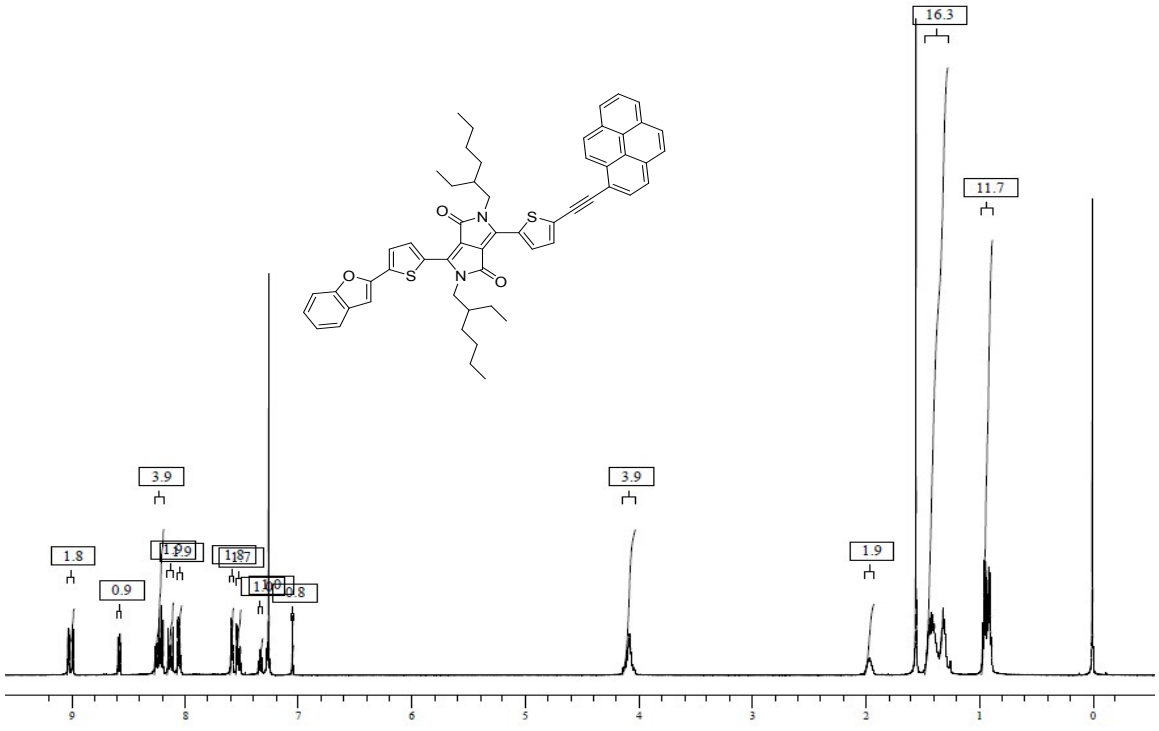


Fig. S13. [1]H NMR spectrum of **BFPyDPP**

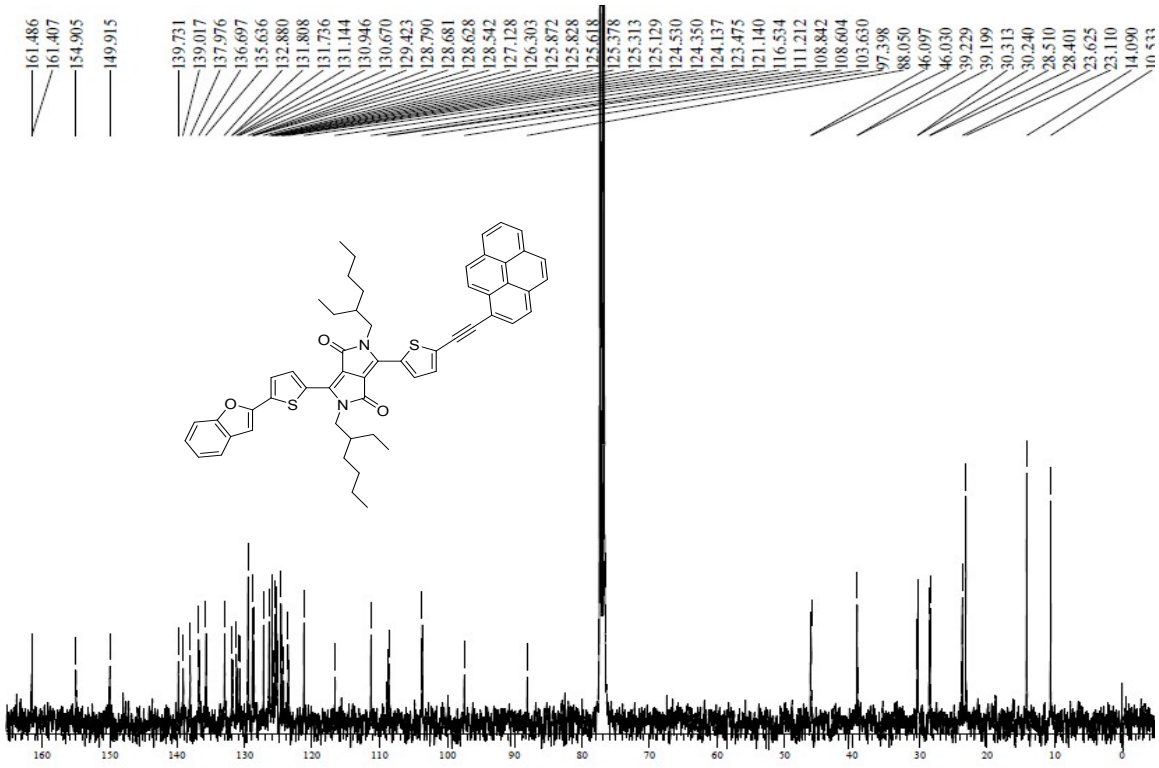


Fig. S14. [13]C NMR spectrum of **BFPyDPP**

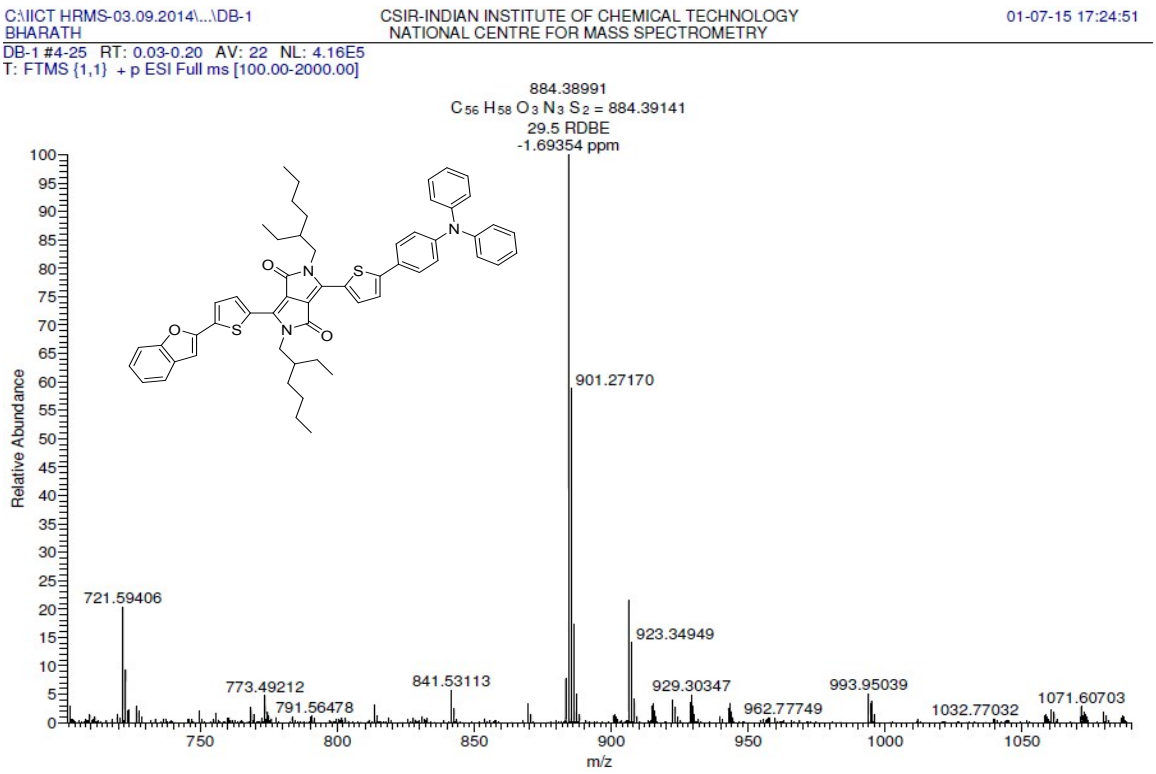


Fig. S15. ESI-HRMS spectrum of **BFTPADPP**

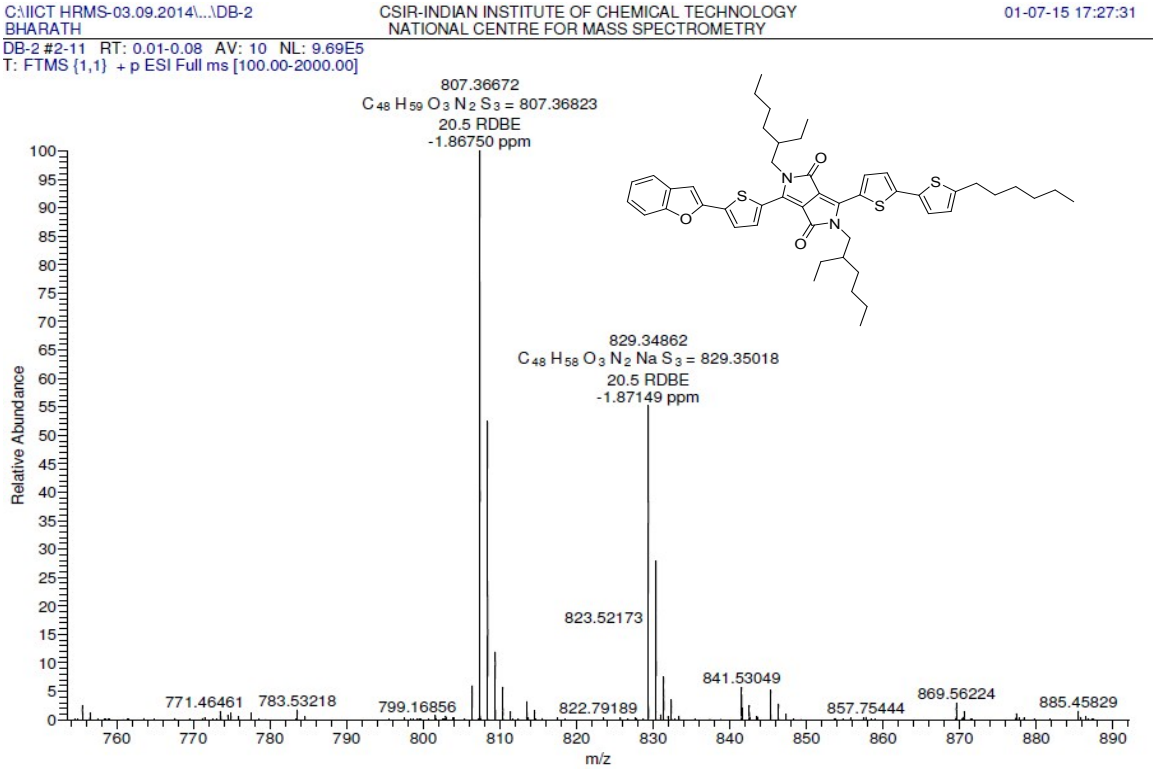


Fig. S16. ESI-HRMS spectrum of **BFHTDPP**

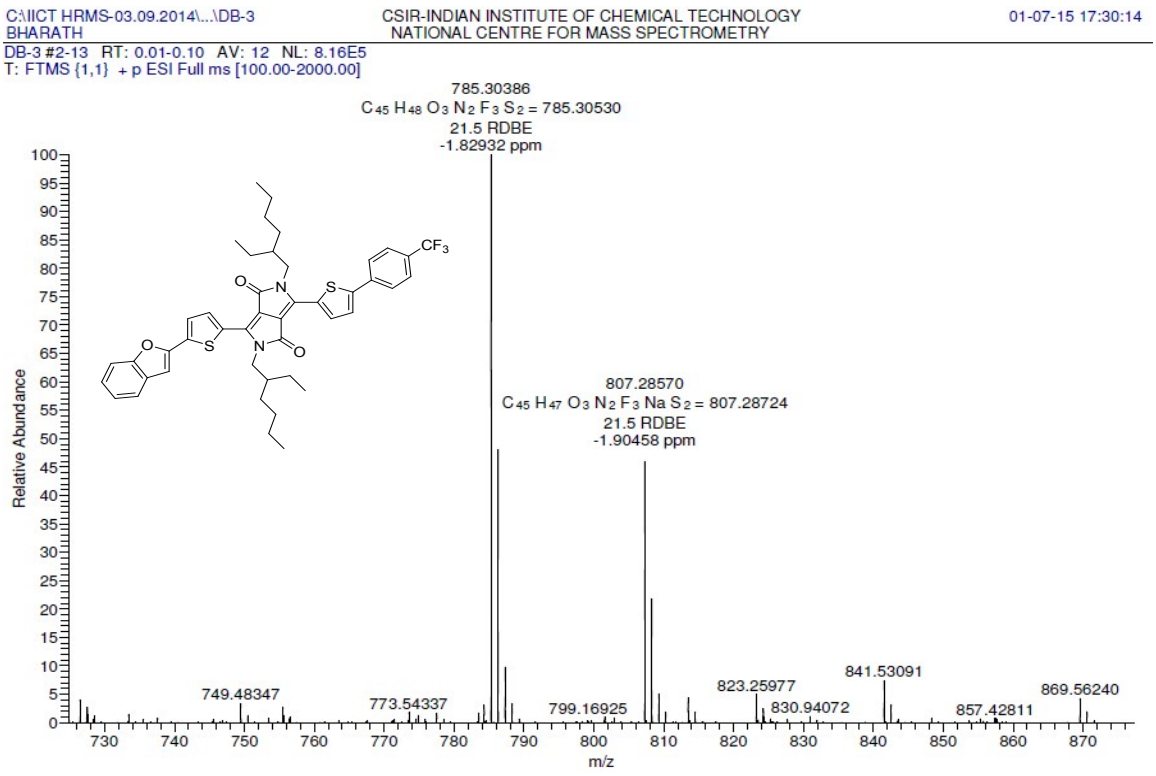


Fig. S17. ESI-HRMS spectrum of **BFTFDPP**

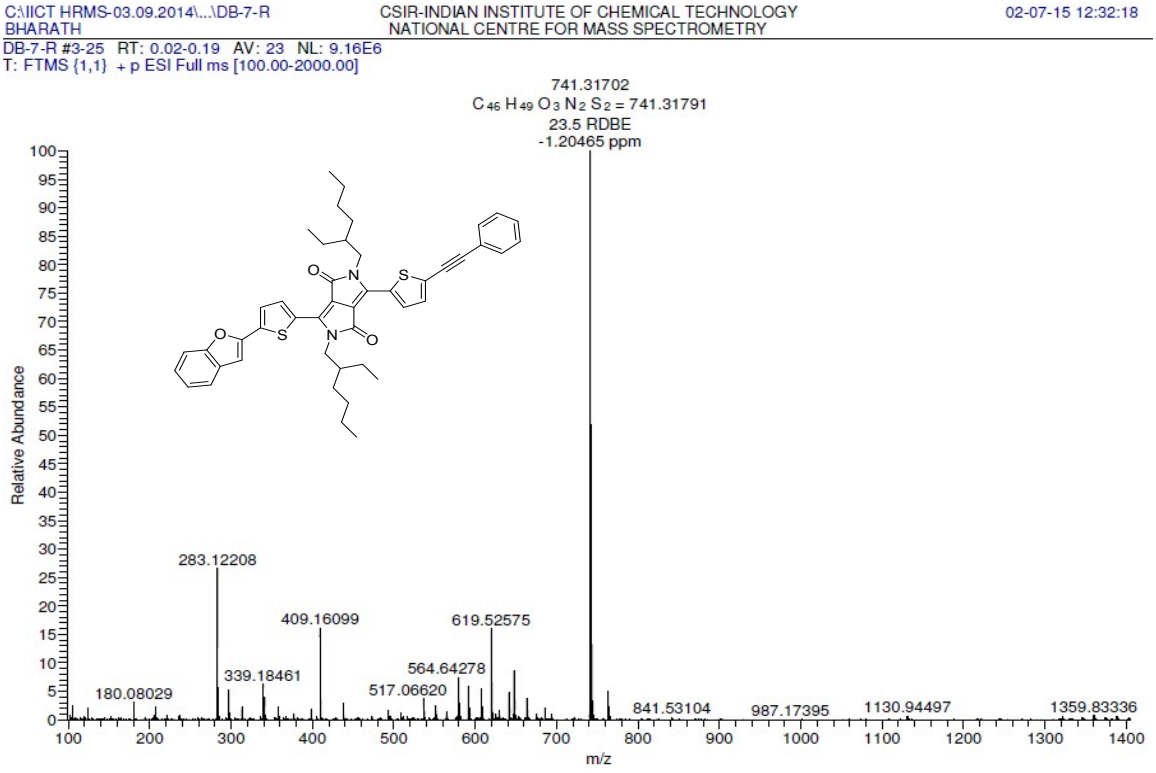


Fig. S18. ESI-HRMS spectrum of **BFPhDPP**

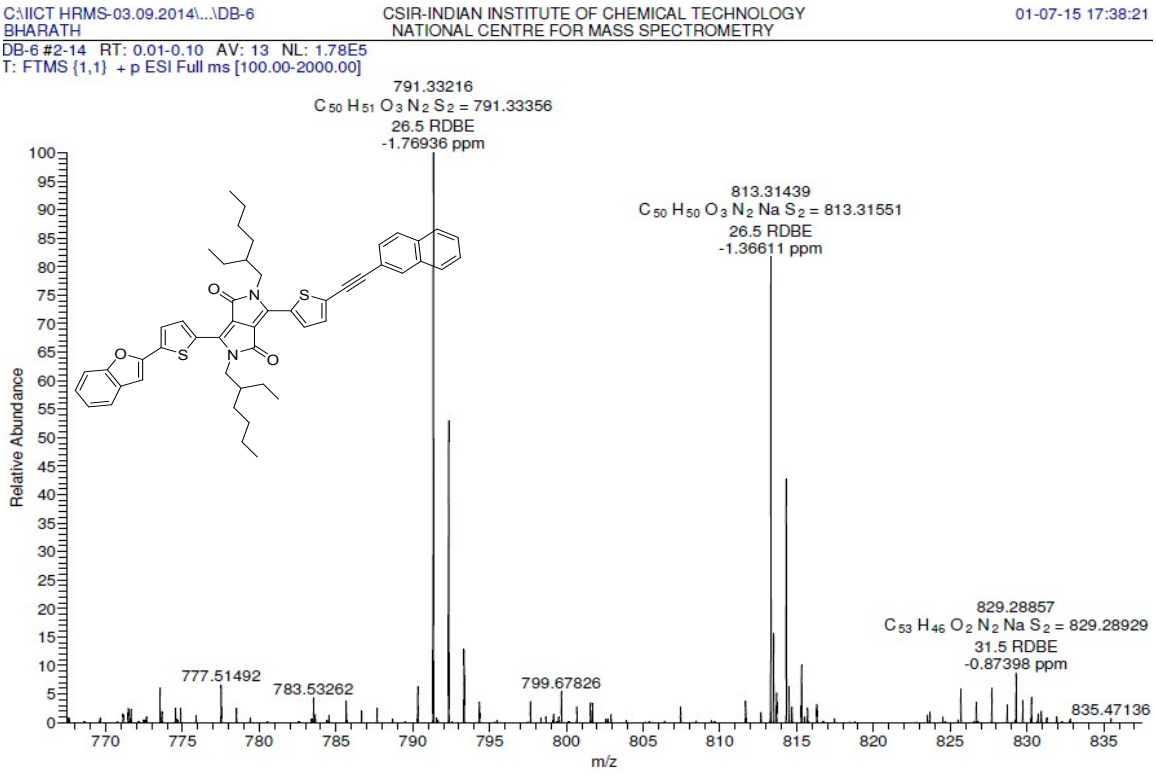


Fig. S19. ESI-HRMS spectrum of **BFNaDPP**

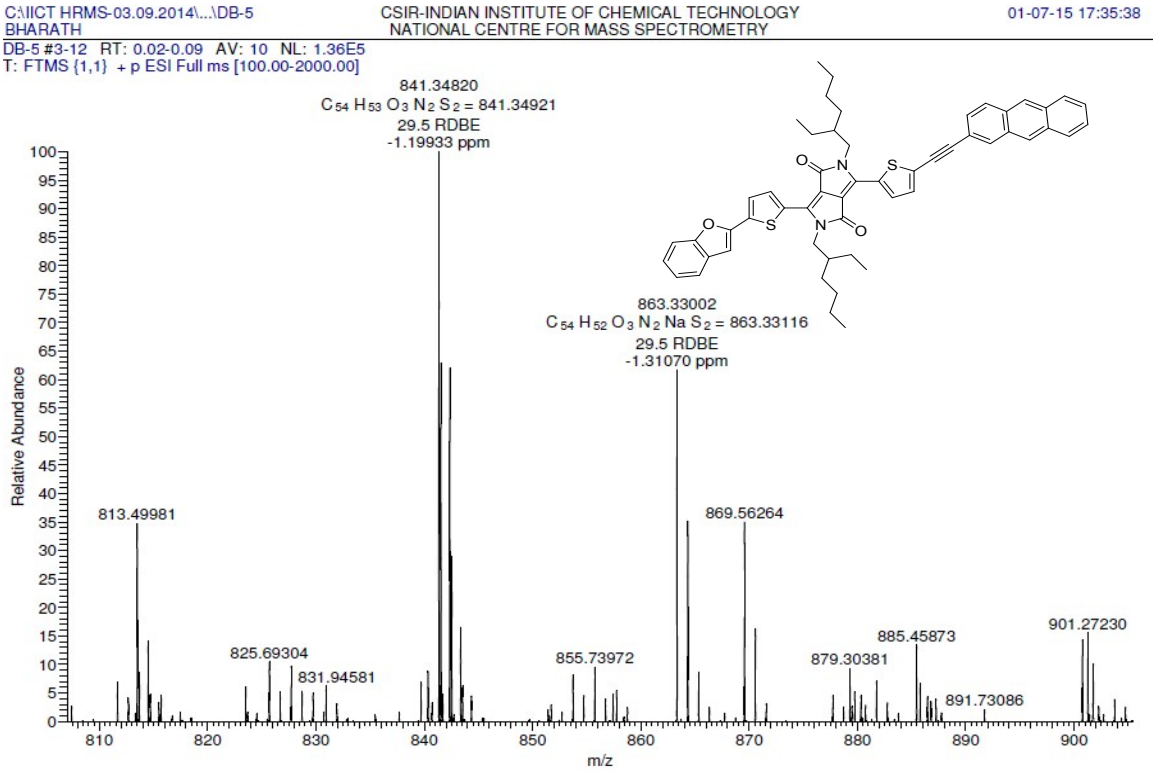


Fig. S20. ESI-HRMS spectrum of **BFAnDPP**

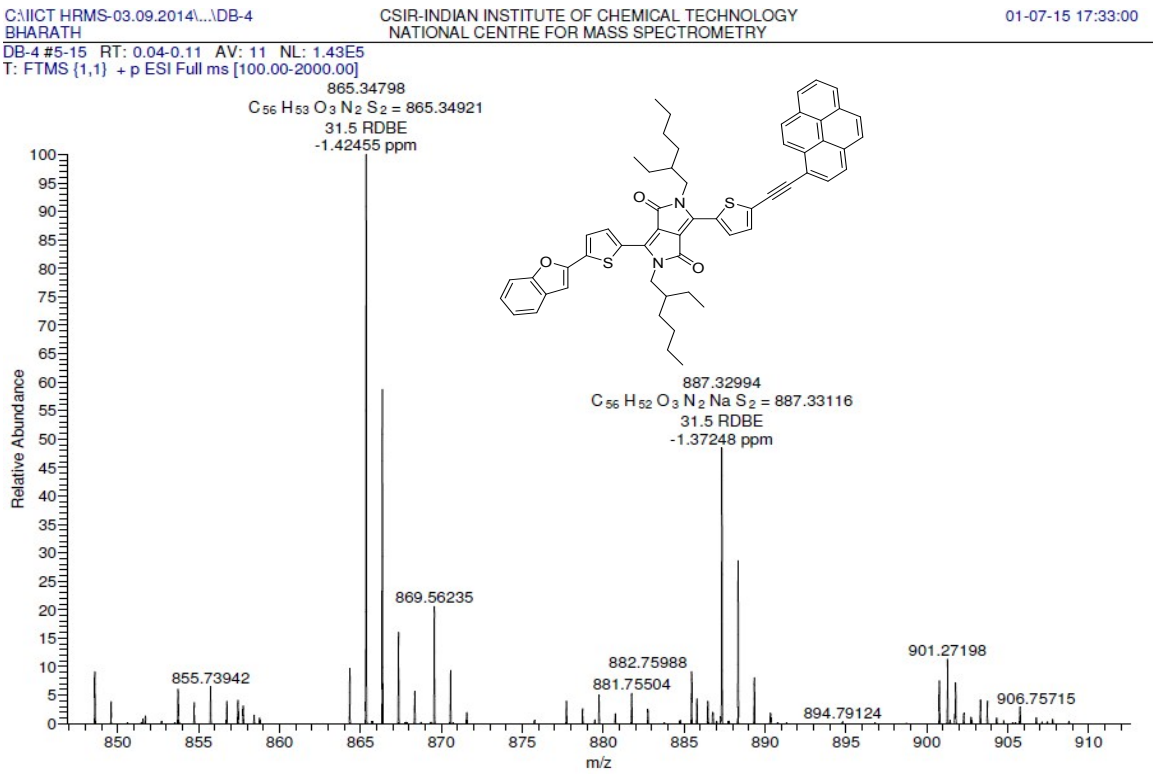


Fig. S21. ESI-HRMS spectrum of **BFPyDPP**

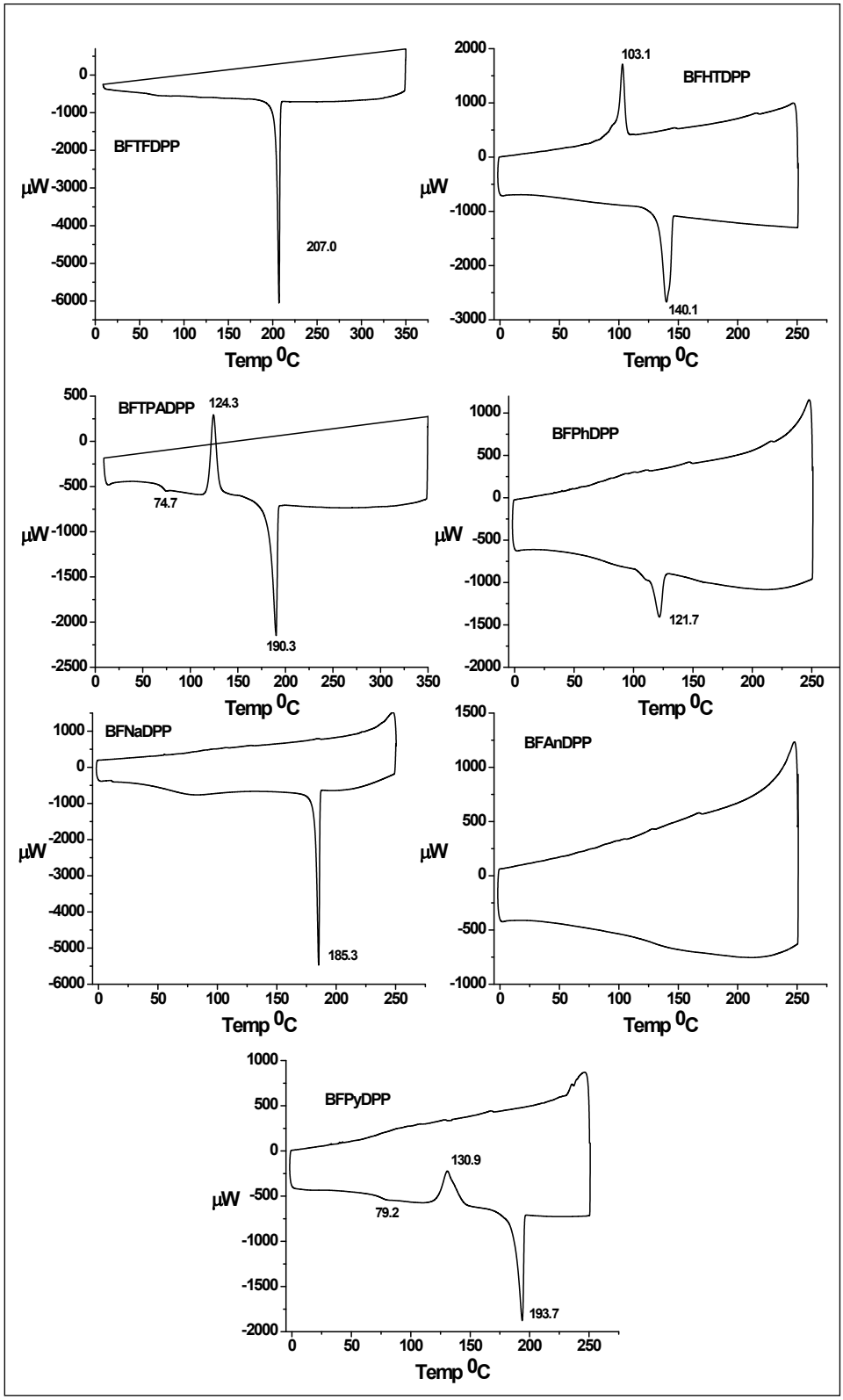


Fig. S22. DSC thermograms of the synthesized DPP-derivatives

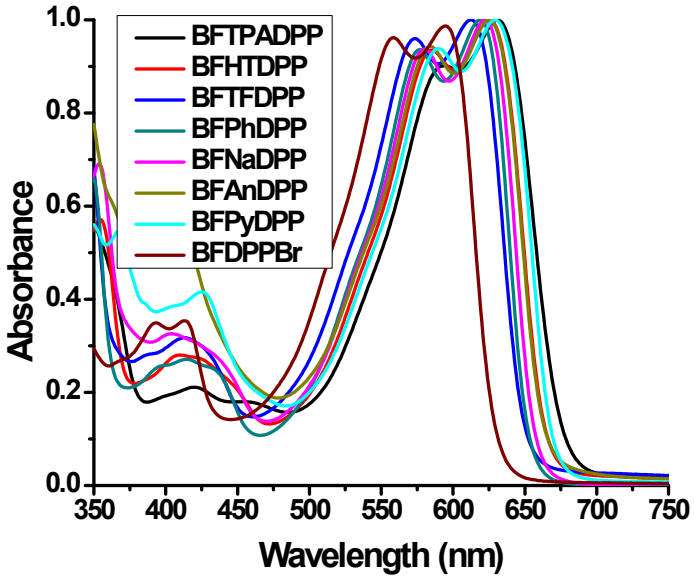


Fig. S23. Normalized UV-Visible absorption spectra of the synthesized DPP-derivatives and their synthetic precursor **BFDPPBr**.

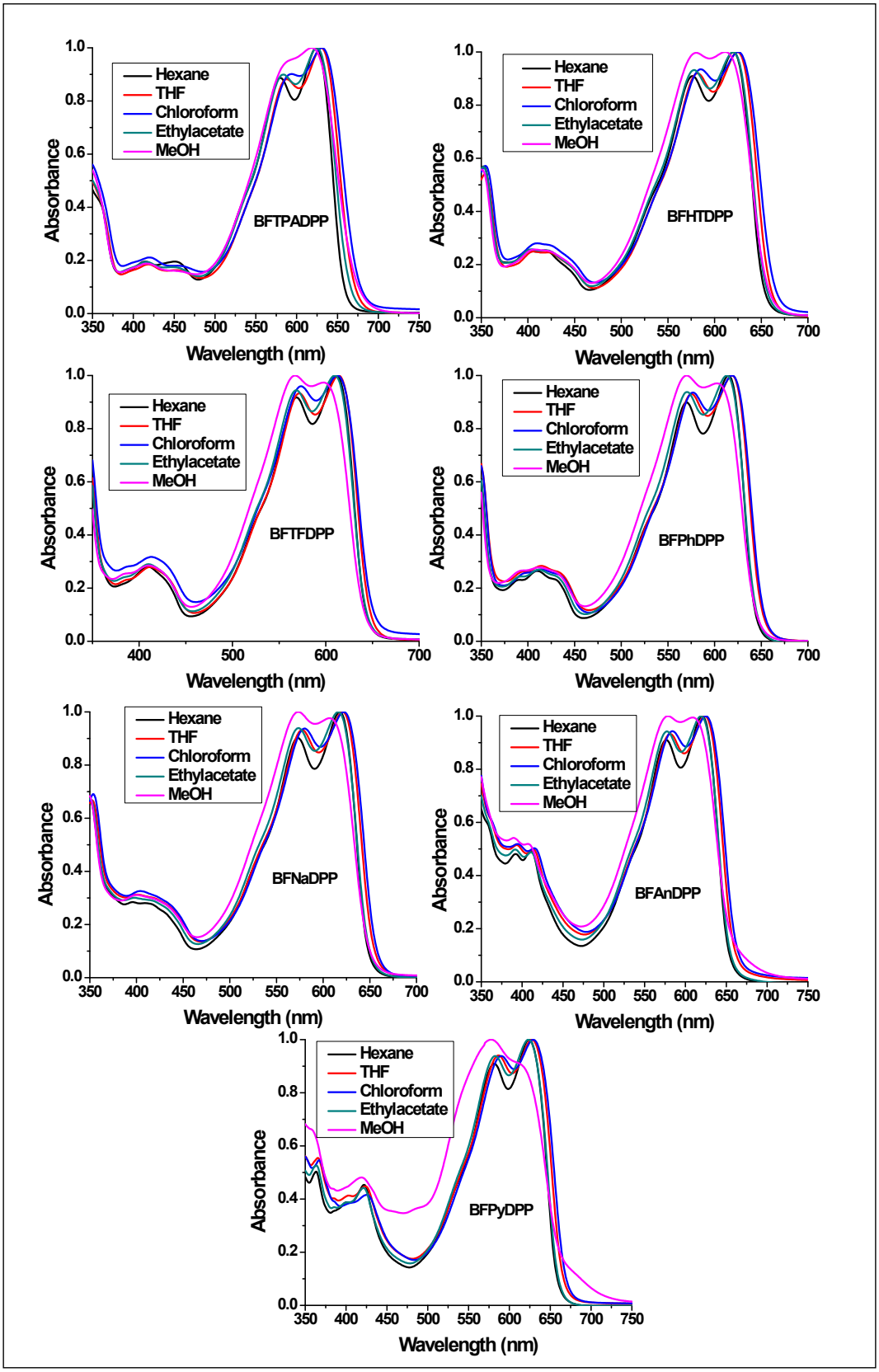


Fig. S24. Normalized absorption spectra of the synthesized DPP-derivatives in various solvents

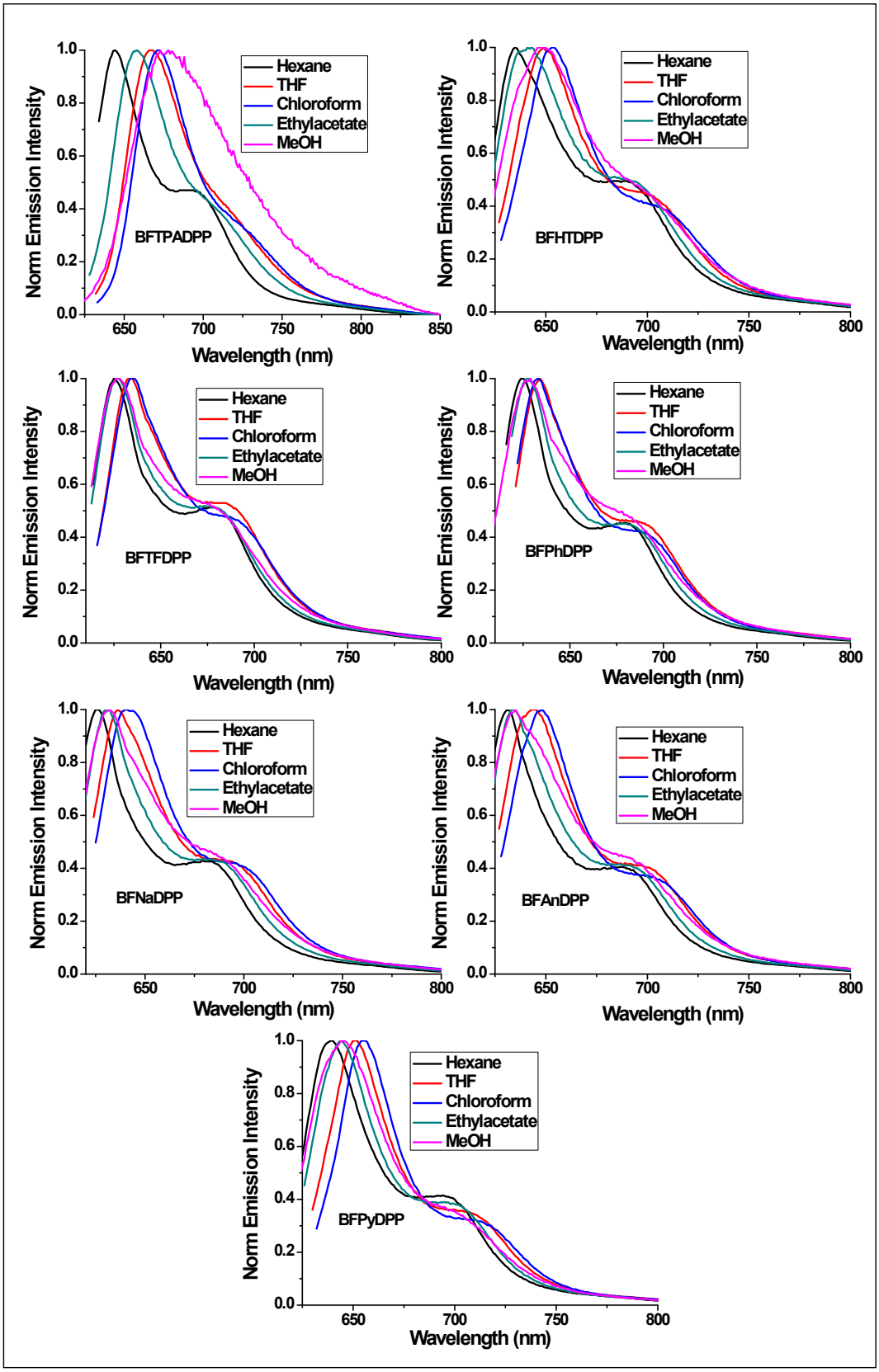


Fig. S25. Normalized emission spectra of the synthesized DPP-derivatives in various solvents

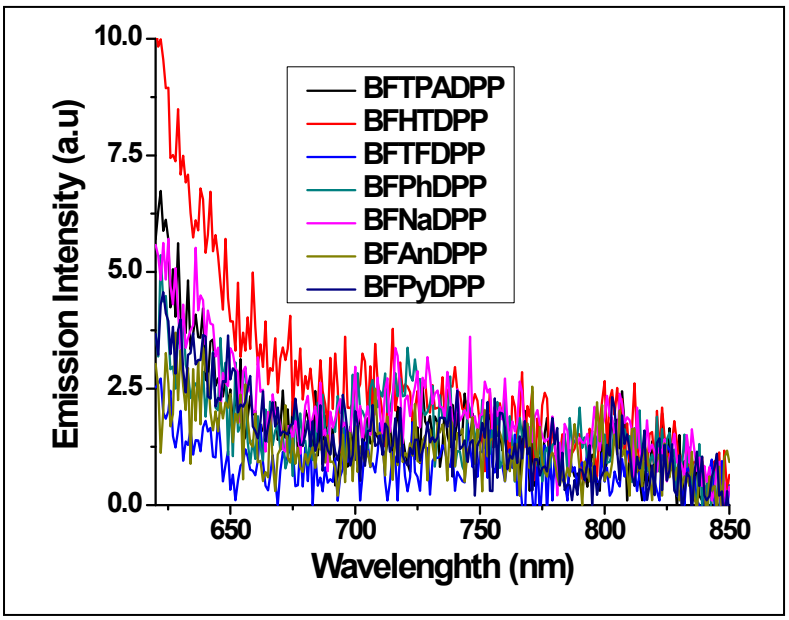


Fig. S26. Emission spectra of the synthesized DPP-derivatives in their thin film state

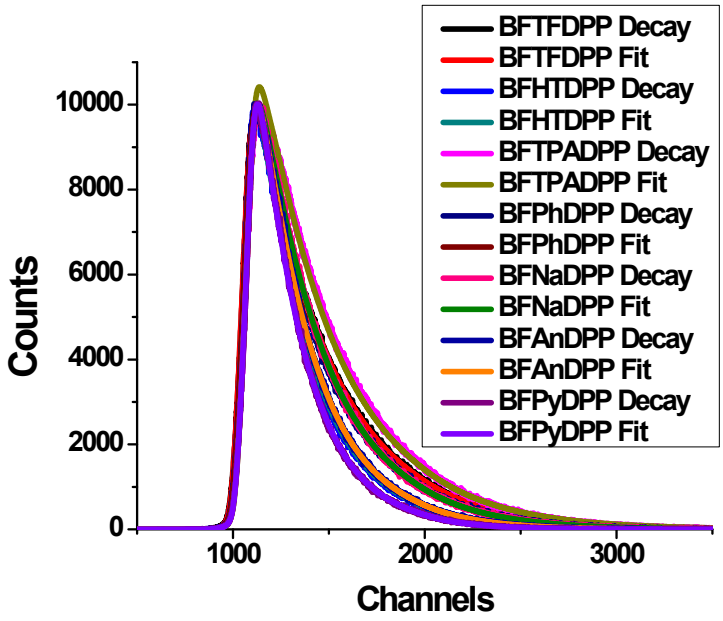


Fig. S27. TCSPC data and their corresponding fit curves of the synthesized DPP-derivatives

Table S1: HOMO (**H**) energy, LUMO (**L**) energy and HOMO-LUMO gap ($\mathbf{E_{H-L}}$), ground state dipole moment (μ_{gs}), transition dipole moments (μ_{ge}), adiabatic electron affinity ($\mathbf{EA_a}$) and adiabatic ionization potential ($\mathbf{IP_a}$) of the DPP-derivatives calculated at B3LYP/6-31G (d,p) level.

Material code	H (eV)	L (eV)	E_{H-L} (eV)	μ_{gs}	μ_{ge}	IP_a (eV)	EA_a (eV)
BFTPADPP	-4.68	-2.61	2.07	3.25	5.99	5.48	-1.71
BFHTDPP	-4.76	-2.70	2.06	2.02	5.46	5.70	-1.72
BFTFDPP	-4.97	-2.86	2.11	3.43	5.21	5.94	-1.91
BFPhDPP	-4.85	-2.79	2.06	0.74	5.71	5.79	-1.83
BFNaDPP	-4.84	-2.79	-2.05	1.08	6.08	5.74	-1.88
BFAnDPP	-4.83	-2.81	2.02	1.34	6.46	5.68	-1.93
BFPyDPP	-4.80	-2.81	1.99	1.54	6.66	5.63	-1.95

Table S2. Absorption maxima (λ_{max}), oscillator strength (f), main orbital transitions and coefficients of wave functions (**CI)** of the DPP-derivatives calculated at B3LYP/6-31G (d,p) in chloroform solvent phase.

Material code	λmax(nm)	f	CI
BFTPADPP	678	1.858	HOMO→LUMO (0.7054)
BFHTDPP	657	1.674	HOMO→LUMO (0.7103)
BFTFDPP	638	1.549	HOMO→LUMO (0.7102)
BFPhDPP	658	1.798	HOMO→LUMO (0.7099)
BFNaDPP	666	1.973	HOMO→LUMO (0.7090)
BFAnDPP	680	2.152	HOMO→LUMO (0.7081)
BFPyDPP	697	2.2427	HOMO→LUMO (0.7067)

Table S3: Absorption maxima (λ_{max}), oscillator strength (f), main orbital transitions, coefficients of wave functions (**CI)** of the DPP-derivatives calculated at M062X/6-31G (d,p) level in chloroform solvent phase

Material code	λmax(nm)	f	CI
BFTPADPP	579	1.6013	HOMO->LUMO (97%)
BFHTDPP	577	1.801	HOMO->LUMO (93%)
BFTFDPP	564	1.4845	HOMO->LUMO (98%)
BFPhDPP	577	1.692	HOMO->LUMO (97%)
BFNaDPP	580	1.827	HOMO→LUMO (0.6955)
BFAnDPP	585	1.971	HOMO→LUMO (0.6885)
BFPyDPP	594	2.0779	HOMO->LUMO (94%)

Table S4: Absorption maxima (λ_{max}), oscillator strength (f), main orbital transitions, coefficients of wave functions (**CI)** calculated at cam-B3LYP/6-31G (d,p) level in chloroform solvent phase.

Material code	λmax(nm)	f	CI
BFTPADPP	575	1.6181	HOMO->LUMO (96%)
BFHTDPP	572	1.7997	HOMO->LUMO (90%)
BFTFDPP	560	1.5029	HOMO->LUMO (96%)
BFPhDPP	574	1.7151	HOMO->LUMO (96%)
BFNaDPP	577	1.850	HOMO→LUMO (0.6898)
BFAnDPP	581	1.989	HOMO→LUMO (0.6811)
BFPyDPP	590	2.1023	HOMO->LUMO (91%)

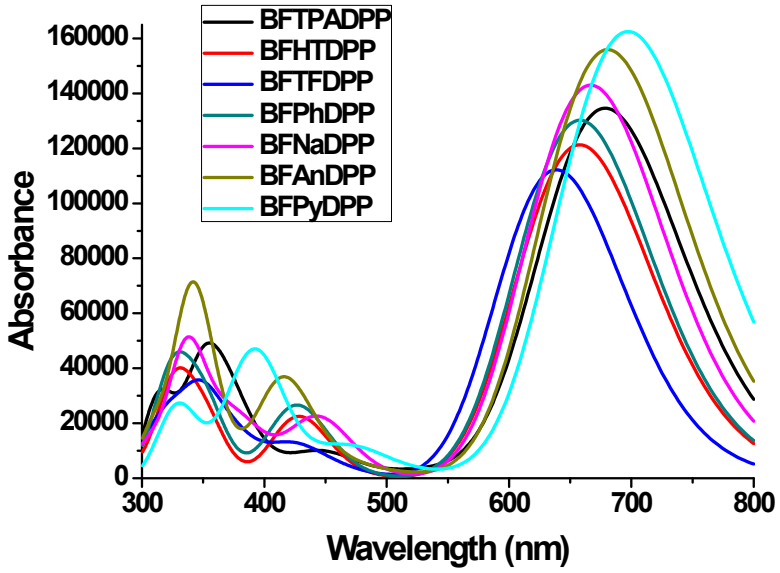


Fig. S28. Theoretically generated UV-visbile absorption spectra of synthesized DPP-derivatives

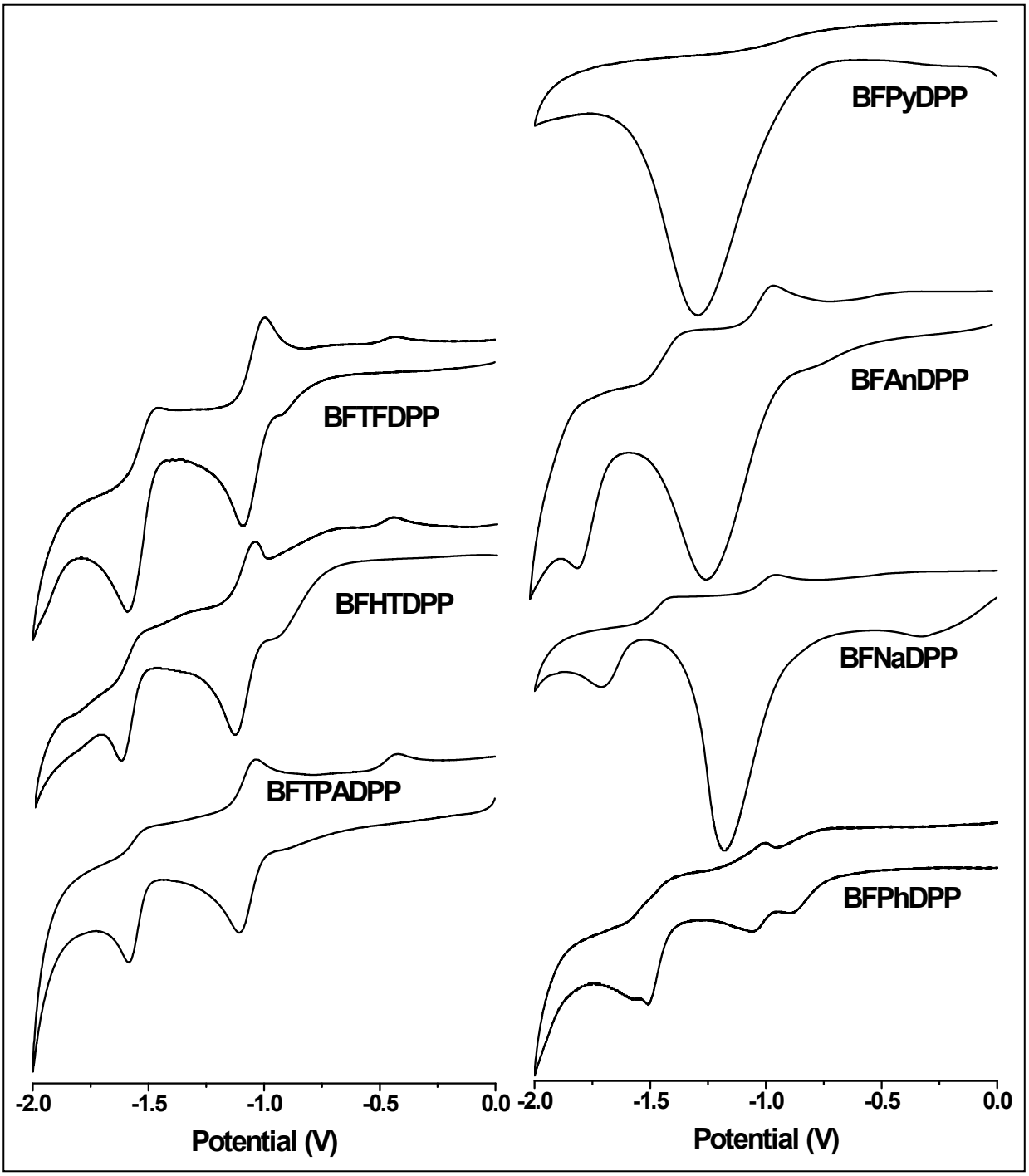


Fig. S29. Cylcic voltagramms represent the reversible reduction behaviour of the synthesized DPP-derivatives

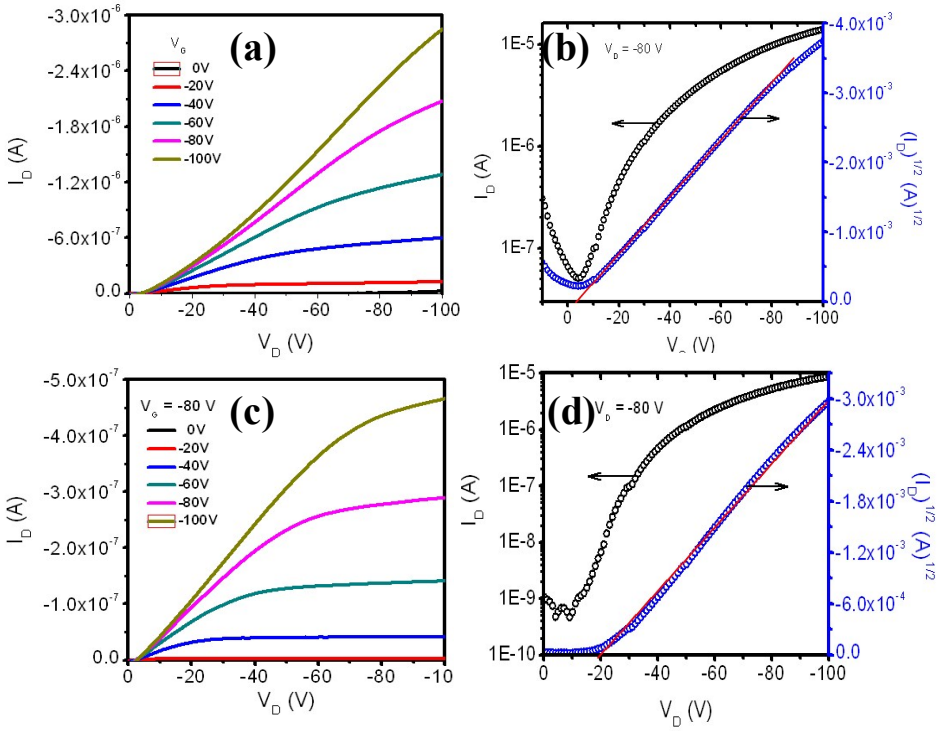


Fig. S30. Output (**a**) and transfer (**b**) characteristics of **BFTPADPP** and Output (**c**) and transfer (**d**) characteristics for compound **BFHTDPP** after annealed at 100° C

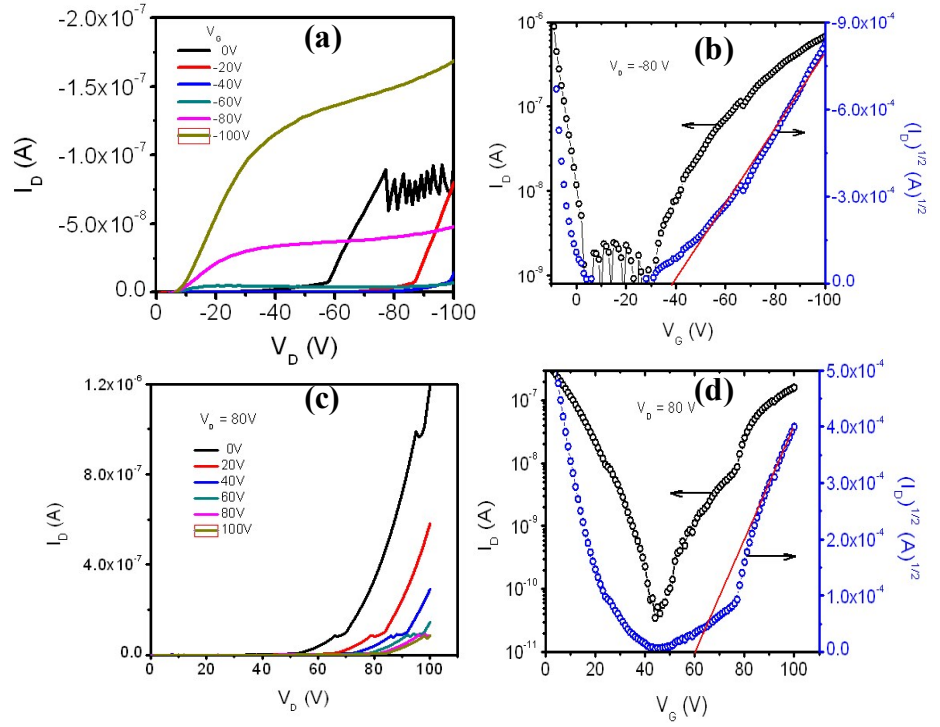


Fig. S31. Output (**a**) and transfer (**b**) characteristics for hole and Output (**c**) and transfer (**d**) characteristics for electron in **BFTFDPP** after annealed at 100° C

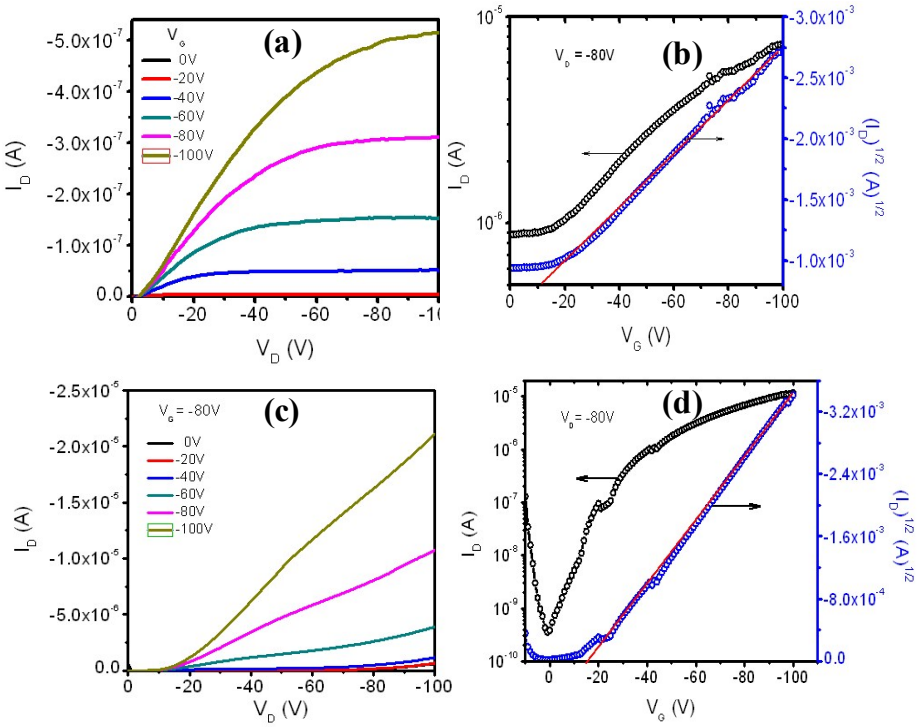


Fig. S32. Output (**a**) and transfer (**b**) characteristics of **BFPhDPP** and Output (**c**) and transfer (**d**) characteristics of **BFNaDPP** after annealed at 100° C

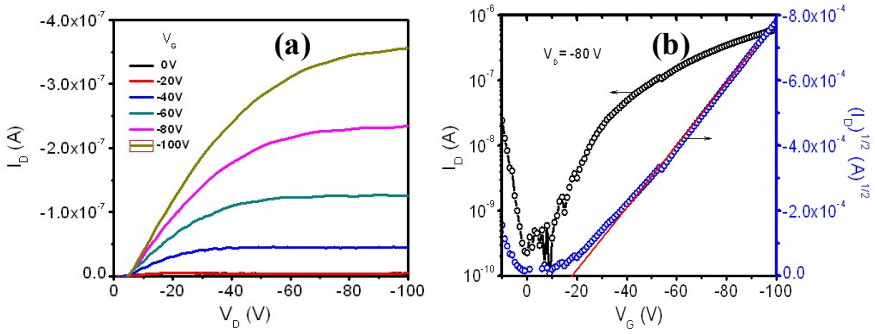


Fig. S33. Output (**a**) and transfer (**b**) characteristics of **BFAnDPP**

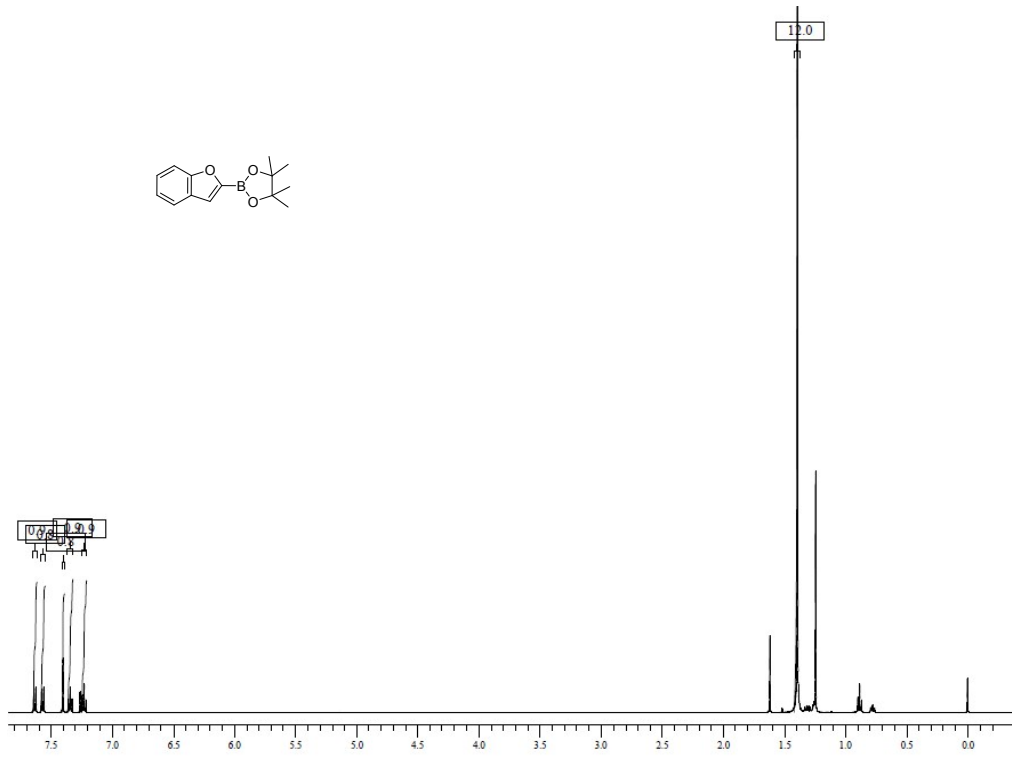


Fig. S34. [1]H NMR spectrum of **1**

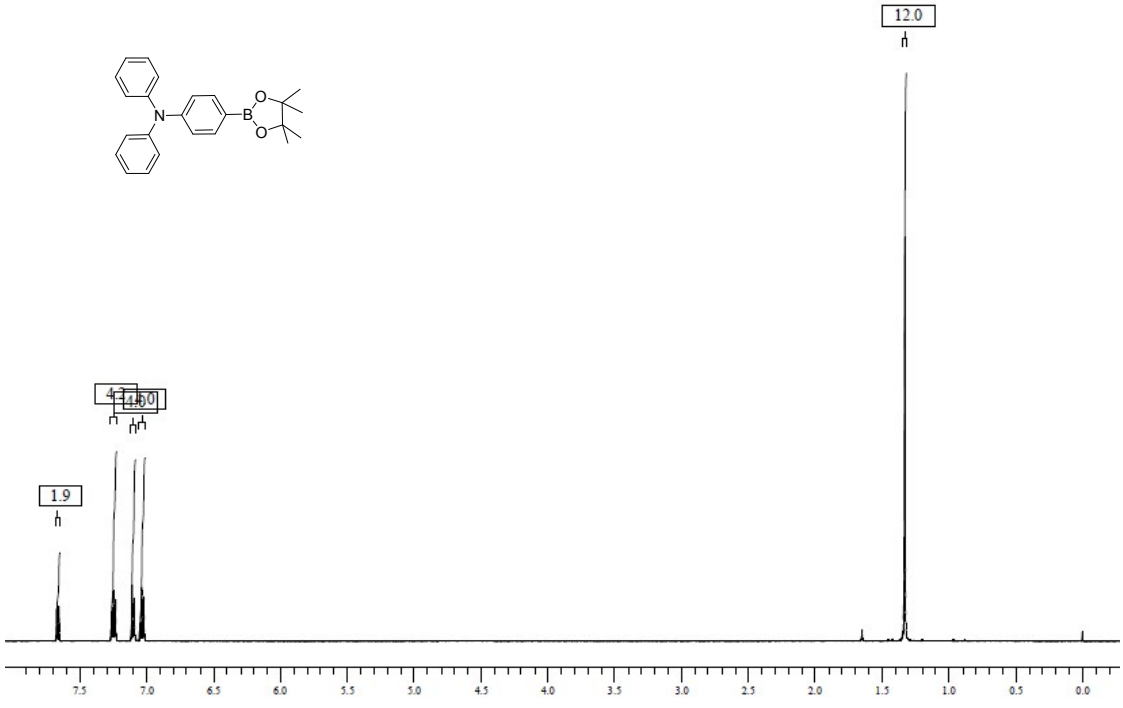


Fig. S35. [1]H NMR spectrum of **2**

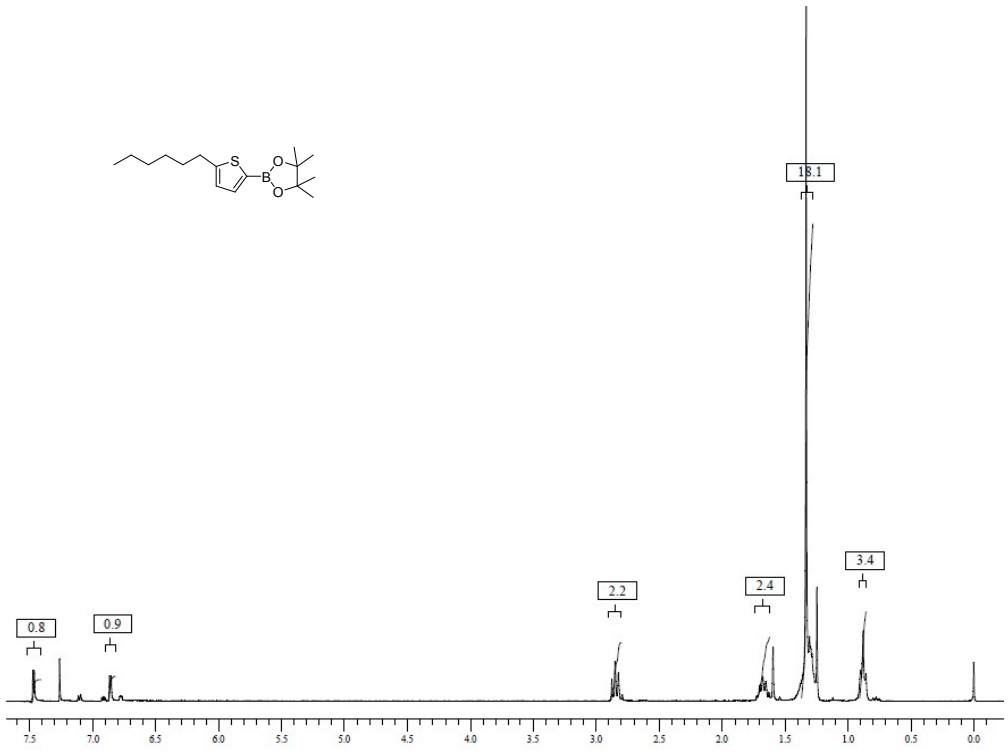


Fig. S36. ^{1}H NMR spectrum of **3**

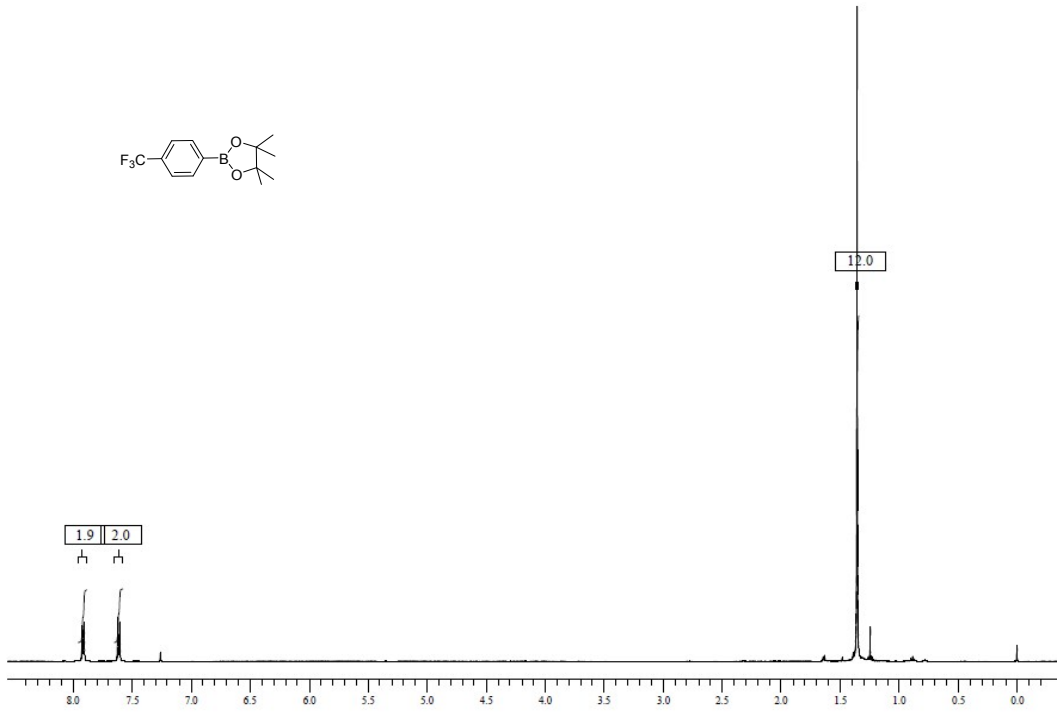


Fig. S37. ^{1}H NMR spectrum of **4**

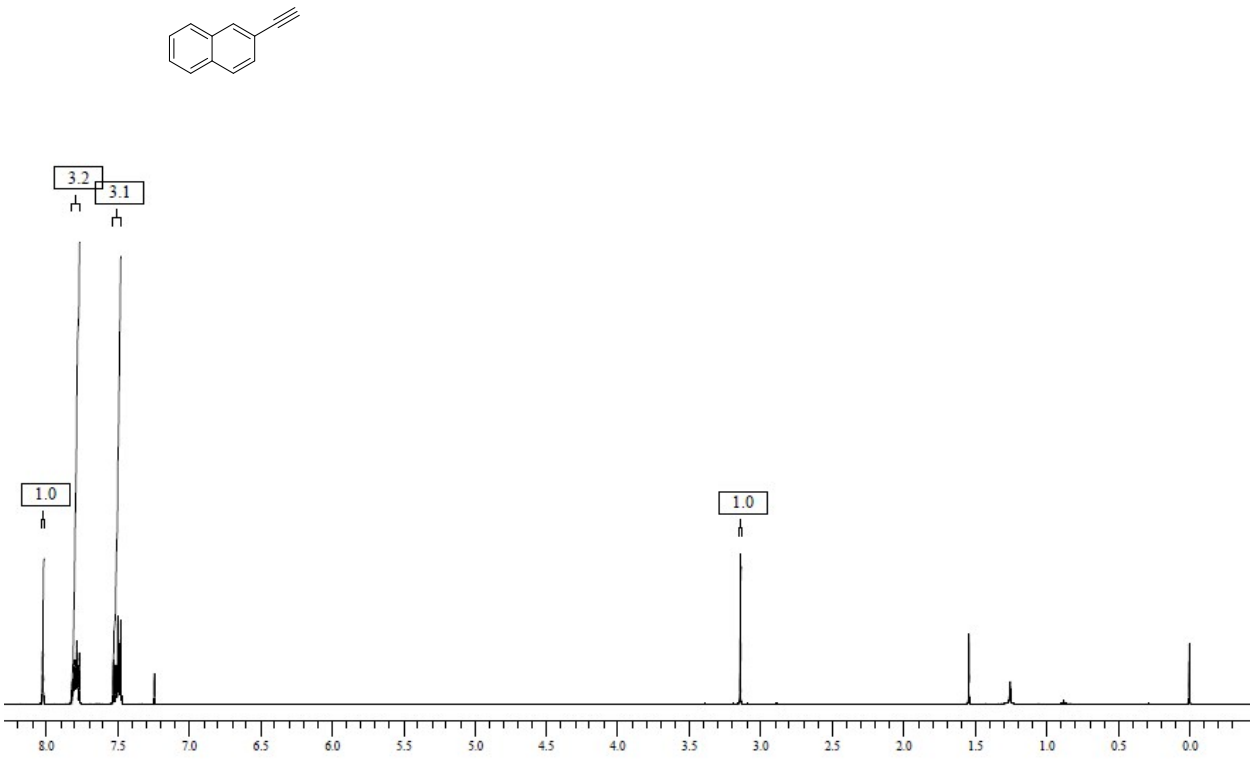


Fig. S38. [1]H NMR spectrum of **5**

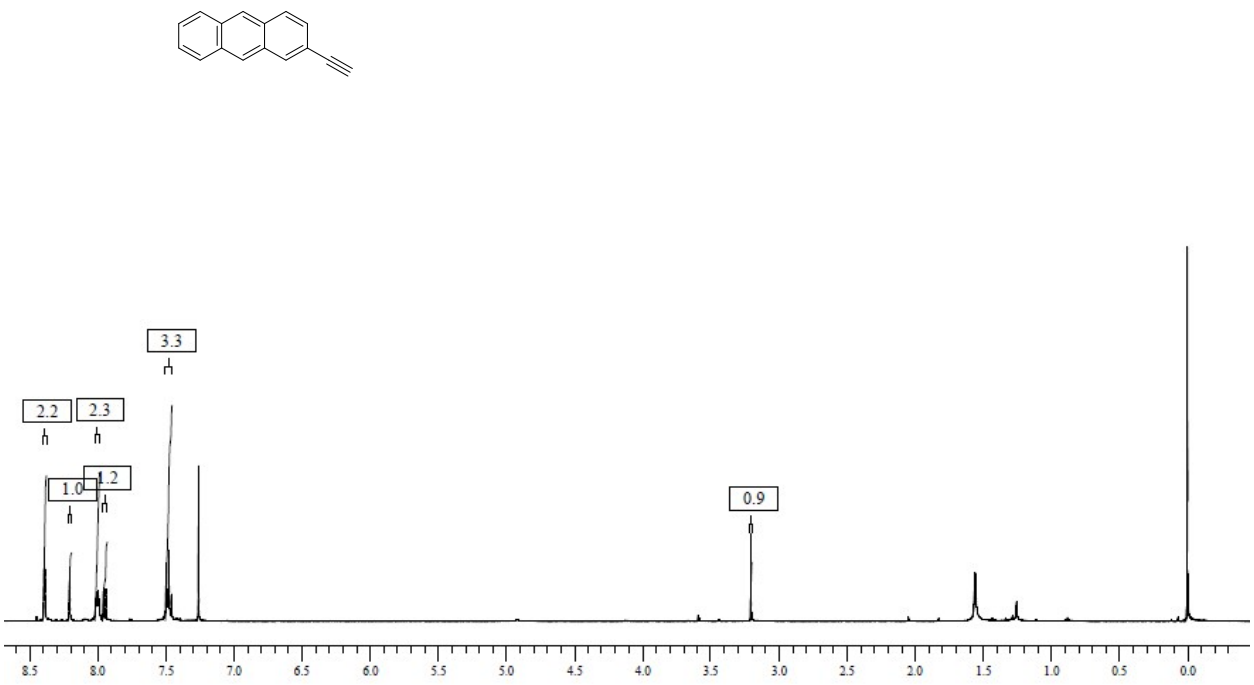


Fig. S39. [1]H NMR spectrum of **6**

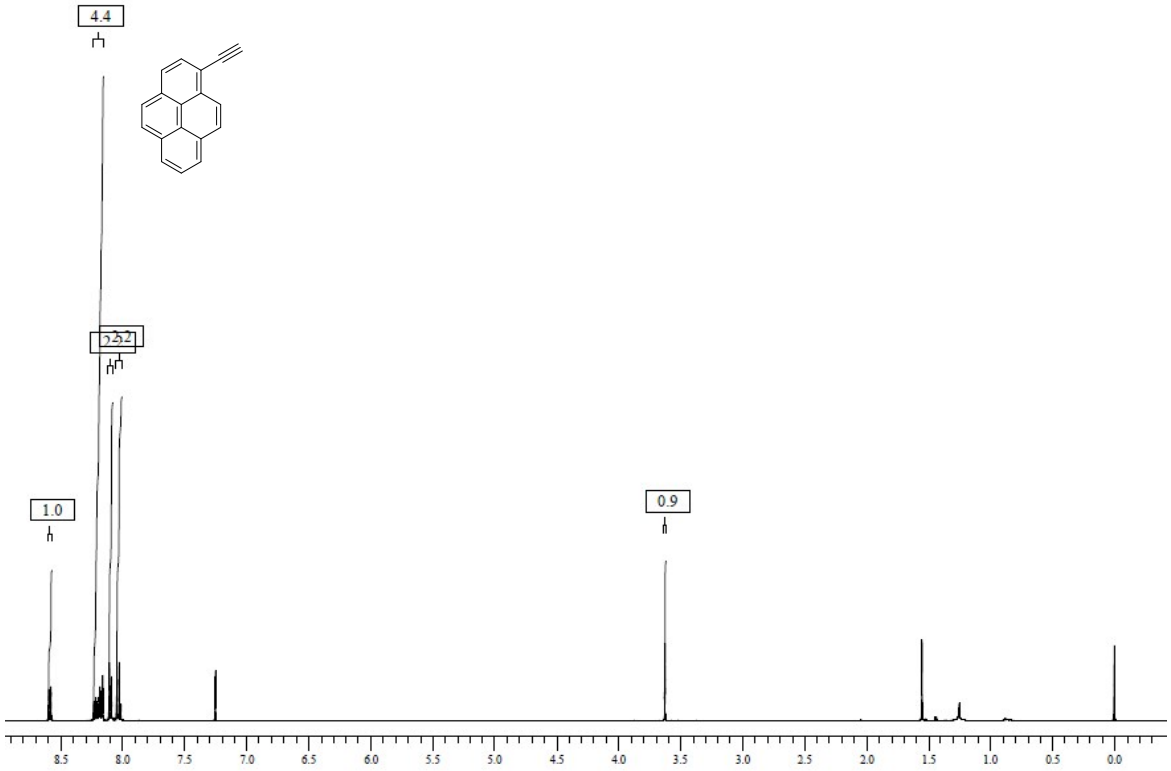


Fig. S40. [1]H NMR spectrum of **7**

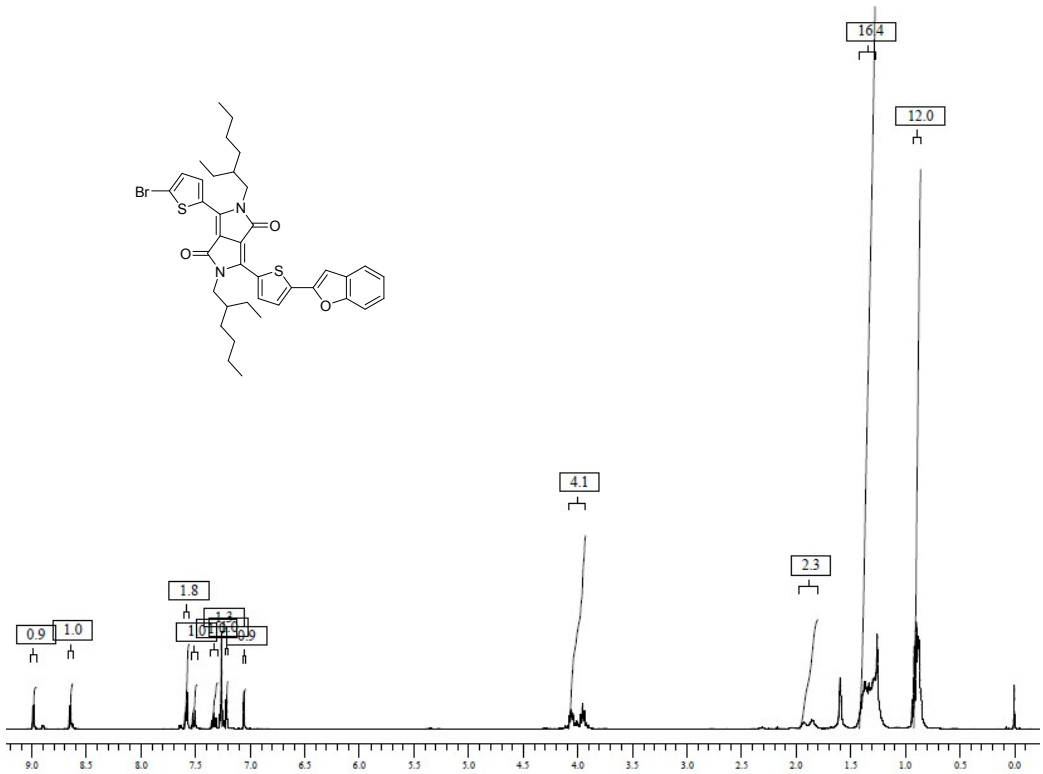


Fig. S41. [1]H NMR spectrum of **A**

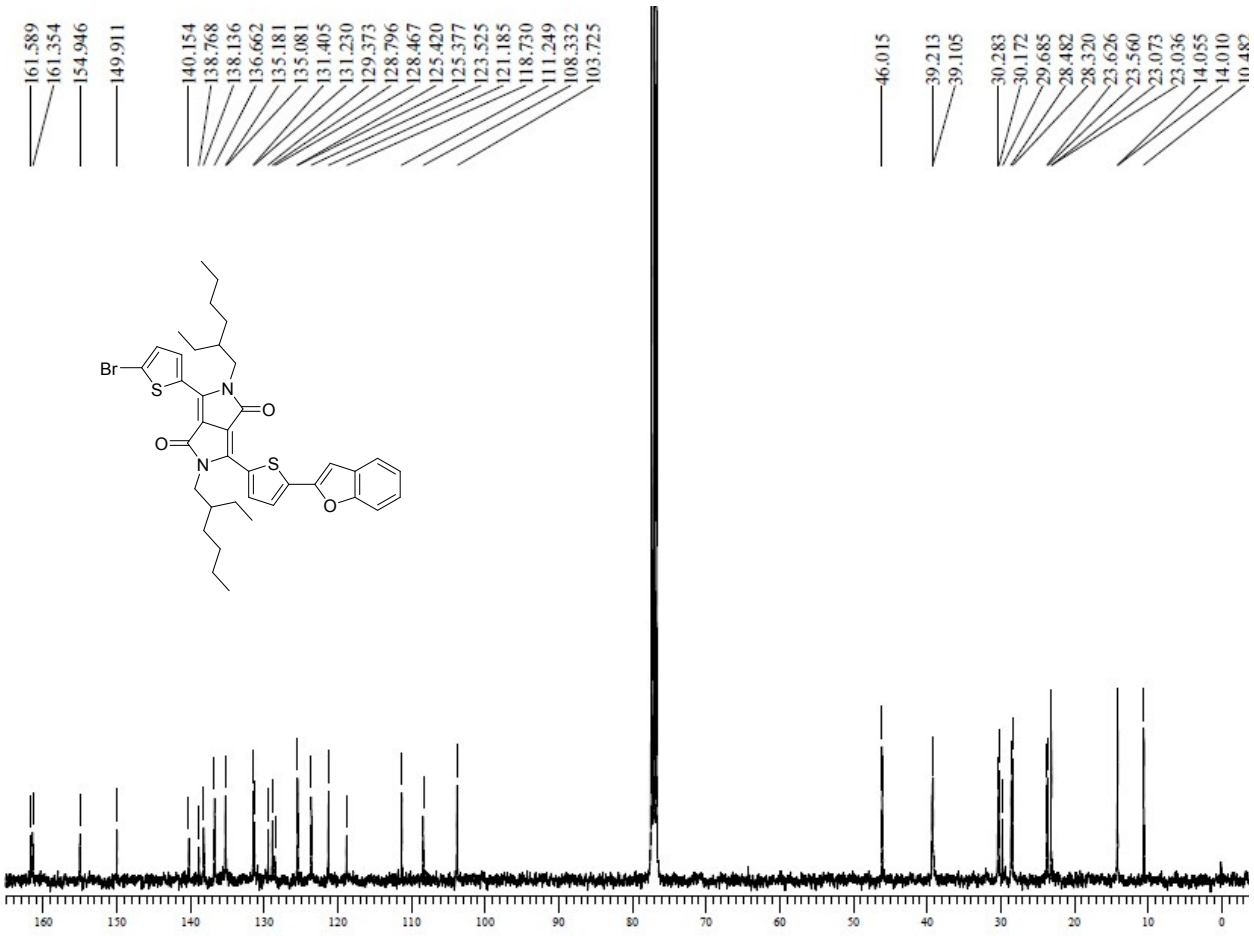


Fig. S42. ^{13}C NMR spectrum of **A**

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