Supporting Information

Wide band gap diketopyrrolopyrrole-based conjugated polymers incorporating biphenyl units applied in polymer solar cells

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The supporting information contains the experimental part, synthesis route for monomers and polymers (Scheme S1), absorption spectra of the polymers in chloroform solution (Fig. S1), electrochemical properties and LUMO offset (Fig. S2 and Table S1), X-ray diffraction patterns of the thin films of DPP polymers (Fig. S3), ambipolar transfer characteristics for FETs for the DPP polymers (Fig. S4), the influence of solvent additive on device performance (Table S2), the AFM height and phase images of the optimized DPP-polymers:[70]PCBM blend films (Fig. S5), and ^{1}H and ^{13}C-NMR of the monomers and polymers (Fig. S6-S16).

Materials and Measurement. All synthetic procedures were performed under argon atmosphere. Commercial chemicals were used as received. Dry solvents were distilled over 4 Å molecular sieves. [70]PCBM (purity ~95%) was purchased from Solenne BV. 3,6-Bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-di(2'-octyldodecyl)-pyrrolo[3,4c]pyrrolo-1,4-dione (**5**) was synthesized according to literature procedures.[1] 4,4'-Biphenyldiboronic acid bis(pinacol)ester (**6**) was purchased from Aldrich Chemical Co. and recrystallized from isopropanol before use in polymerization reactions.

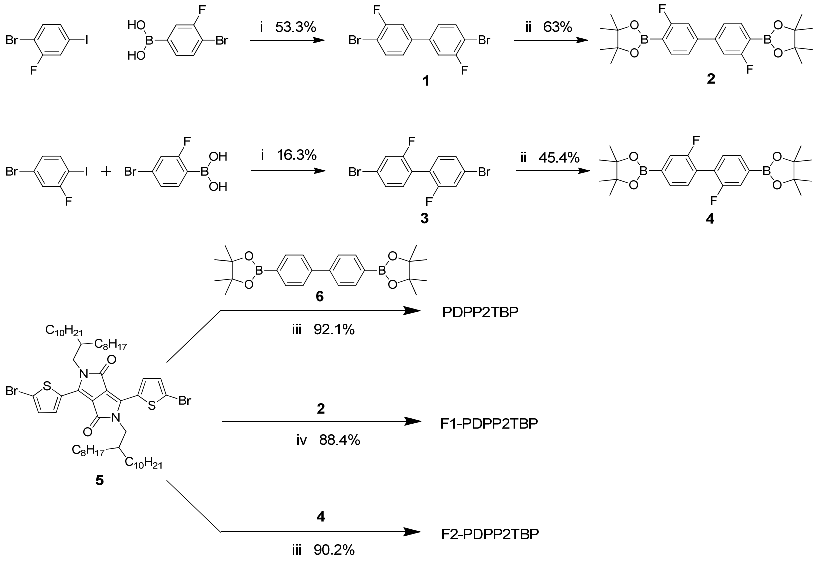
^{1}H-NMR and ^{13}C-NMR spectra were recorded at 400 MHz and 100 MHz on a VARIAN mercury spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Molecular weights were determined with GPC at 140 °C with $CHCl_3$ as the eluent for PDPP2TBP or 80 °C with *o*-DCB as the eluent for F1 and F2-PDPP2TBP on a PL-GPC 120 system using a PL-GEL 5u MIXED-C column and against polystyrene standards. Electronic spectra were recorded on a Perkin Elmer Lambda 900 UV/vis/nearIR spectrophotometer. AFM images were taken on a Veeco MultiMode AFM connected to a Nanoscope III controller operating in tapping mode using PPP-NCH-50 probes (Nanosensors). TEM was performed on a Tecnai G^2 Sphera TEM (FEI) operated at 200 kV.

Cyclic voltammetry was conducted with a scan rate of 0.1 V s^{-1} under an inert atmosphere with 1 M tetrabutylammonium hexafluorophosphate in *o*-DCB as the electrolyte. The working electrode was a platinum disk, the counter electrode was a silver electrode and an Ag/AgCl quasi-reference electrode was used. The concentration of the sample in the electrolyte was approximately 1 mM, based on monomers. Fc/Fc^+ was used as an internal standard. The polymers solution in *o*-DCB (1 mg/ml) were heated to 140 °C to solublize the polymers.

XRD was measured on a Bruker D4 Endeavor diffractometer using Cu Kα radiation with a wavelength of 0.15406 nm. Scans were done from 2 – 35 degrees (2θ) with scan speed of 0.2 seconds/step and increments of 0.01 degree/step. Samples for XRD were prepared by drop casting 300 μL of a 7 mg/ml polymer solution in chloroform on to a (911) surface of a silicon wafer.

Field-effect transistors were fabricated using heavily doped silicon wafers as the common gate electrode with a 200 nm thermally oxidized SiO_2 layer as the gate dielectric. Using conventional photolithography, gold source and drain electrodes were defined in a bottom contact device configuration with a channel width and length of 2500 μm and 10 μm, respectively. A 10 nm layer of titanium was used, acting as an adhesion layer for the gold on SiO_2. The SiO_2 layer was exposed to the vapor of the primer hexamethyldisilazane for 60 min. prior to semiconductor deposition in order to passivate the surface of the dielectric. Polymer films were spun from a chloroform solution (4 mg/ml) at 1500 rpm for 30 s. Freshly prepared devices were annealed in a dynamic vacuum of 10^{-5} mbar at 150 °C for 3 h to remove traces of the solvent. All electrical measurements were performed in vacuum using an HP 4155C semiconductor parameter analyzer.

Photovoltaic devices were made by spin coating poly(ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP AI 4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). The photoactive layer were deposited by spin coating a chloroform solution containing the polymers and [70]PCBM with 1:2 (w/w) ratio and the appropriate amount of *o*-DCB or 1-chloronaphthalene (1-CN). LiF (1 nm) and Al (100 nm) were deposited by vacuum evaporation at ~2 × 10^{-7} mbar as the back electrode. The active area of the cells was 0.09 or 0.16 cm^2 and no size dependence was found between these two dimensions. *J*–*V* characteristics were measured under ~100 mW cm^{-2} white light from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB 120 daylight filter, using a Keithley 2400 source meter. Short circuit currents under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The spectral response was measured under simulated 1 sun operation conditions using bias light from a 532 nm solid state laser (Edmund Optics). Light from a 50 W tungsten halogen lamp (Osram64610) was used as probe light and modulated with a mechanical chopper before passing the monochromator (Oriel, Cornerstone 130) to select the wavelength. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Stanford Research Systems SR 830). A calibrated Si cell was used as reference. The device was kept behind a quartz window in a nitrogen filled container. The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak 150 profilometer.



Scheme S1 Synthesis route of DPP based monomers and polymerization for these polymers. (i) $Pd(PPh_3)_4/K_2CO_3$ (aq)/Aliquat 336 in toluene/THF(4:1, v/v) at 80 °C. (ii) (i) $Pd(dppf)Cl_2{\cdot}CH_2Cl_2/KOAc$ in 1,4-dioxane (10 mL) at 80 °C. (iii) Suzuki polymerization to PDPP2TBP and F2-PDPP2TBP using $Pd_2(dba)_3/PPh_3/K_3PO_4$ (aq)/Aliquat 336 in toluene at 115 °C. (iv) Suzuki polymerization to F1-PDPP2TBP using $Pd(PPh_3)_4/K_2CO_3$ (aq)/Aliquat 336 in toluene at 80 °C.

4,4'-dibromo-3,3'-difluoro-1,1'-biphenyl (1). To a degassed mixture of 1-bromo-2-fluoro-4-iodobenzene (0.73 g, 2.4 mmol), 4-bromo-3-fluorobenzeneboronic acid (0.525 g, 2.4 mmol), 2 M K_2CO_3 in H_2O (1.5 mL), toluene (16 mL), THF (4 mL), and Aliquat 336 (0.5 mL), was added tetrakis(triphenylphosphine)palladium(0) (138 mg, 0.12 mmol). The mixture was stirred at 50 °C for 24 h and then up to 80 °C for another 24 h. The resulting mixture was cooled to room temperature after which it was poured out in chloroform, washed by water and brine, and dried by evaporation. The resulting solid was subjected to column chromatography (silica, eluent heptane) and then crystallized from heptane at −20 °C to afford **1** (0.45 g, 53.3%). ^{1}H NMR δ (ppm): 7.61 (m, 2H), 7.30 (m, 2H), 7.21 (m, 2H). ^{13}C NMR δ (ppm): 160.63, 158.16, 140.27, 134.05, 123.55, 114.80, 109.40.

2,2'-(3,3'-difluoro-[1,1'-biphenyl]-4,4'-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2). To a degassed mixture of **1** (200 mg, 0.57 mmol), bis(pinacolato)diboron (364.9 mg, 1.44 mmol), potassium acetate (169 mg, 1.72 mmol in 1,4-dioxane (10 mL)), was added [1,1'-bis(diphenylphosphino)ferrocene]dichloro-palladium (II) (1:1) (46.5 mg, 0.057 mmol). The mixture was stirred at 80 °C for 18 h. The resulting mixture was cooled to room temperature after which it was poured out in chloroform, washed by water and brine, and dried by evaporation. The crude product was purified by crystallization from isopropanol (10 mL) to yield 160 mg (63%) of white crystals. ^{1}H NMR δ (ppm): 7.80 (m, 2H), 7.37 (m, 2H), 7.28 (d, 2H), 1.37 (s, 24H). ^{13}C NMR δ (ppm): 168.80, 166.29, 144.71, 137.35, 122.17, 113.70, 83.98, 24.81.

4,4'-dibromo-2,2'-difluoro-1,1'-biphenyl (3). Same procedure as for **1** was used, but now 4-bromo-2-fluoro-1-iodobenzene (0.69 g, 2.3 mmol) and 4-bromo-2-fluorobenzeneboronic acid (0.5 g, 2.3 mmol) were used as the monomers. Yield: 0.13 g (16.3%). ^{1}H NMR δ (ppm): 7.37 (m, 4H), 7.23 (m, 2H). ^{13}C NMR δ (ppm): 160.69, 160.68, 158.15, 158.13, 132.29, 132.26, 132.23, 127.63, 127.61, 12.59, 122.74, 122.70, 122.65, 121.68, 121.64, 121.58, 121.54, 119.86, 119.76, 119.69, 119.59, 119.51, 119.41.

2,2'-(2,2'-difluoro-[1,1'-biphenyl]-4,4'-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4). The same procedure as for **2** was used, but now **3** (130 mg, 0.37 mmol), bis(pinacolato)diboron (237 mg, 0.93 mmol), potassium acetate (110 mg, 1.12 mmol) and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (II) (1:1) (30.5 mg, 0.037 mmol) were added. Yield: 75 mg (45.4%). ^{1}H NMR δ (ppm): 7.65 (m, 2H), 7.58 (m, 2H), 7.40 (m, 2H), 1.36 (s, 24H). ^{13}C NMR δ (ppm): 160.70, 158.20, 130.98, 130.17, 126.20, 121.50, 84.14, 24.84.

PDPP2TBP. To a degassed solution of monomer **5** (79.97 mg, 0.078 mmol), **6** (31.87 mg, 0.078 mmol) in H_2O (0.5 mL) and toluene (3 mL) containing 2 M K_3PO_4, tris(dibenzylideneacetone)dipalladium(0) (2.16 mg, 2.4 μmol) and triphenylphosphine (2.52 mg, 9.6 μmol) were added. The mixture was stirred at 115 °C for 24 h, after which it was precipitated in methanol. The solids were filtered off, redissolved in 1,1,2,2-tetrachloroethane (TCE) (80 mL) at 140 °C and treated with 28% NH_3 solution in water (50 mL) at 80 °C for 1 h. The layers were separated and the organic layer was stirred with EDTA (100 mg) for 2 h, after which water (100 mL) was added and the liquids were stirred for 1 h. The layers were separated and the organic layer was reduced in volume by evaporating most of the TCE. The polymer was precipitated in acetone and filter through a Soxhlet thimble. The polymer was extracted with acetone, hexane and dichloromethane. The resulting solid was soluble in TCE at 140 °C and precipitated in acetone. The polymer was collected by filtering over a 0.45 μm PTFE membrane filter and dried in a vacuum oven to yield **PDPP2TBP** (73 mg, 92.1%) as a dark powder. GPC ($CHCl_3$, 140 °C): $M_n = 49.0$ kg mol^{-1}, PDI = 3.61.

F1-PDPP2TBP. To a degassed solution of monomer **5** (70.31 mg, 0.069 mmol), **2** (30.5 mg, 0.069 mmol) in H_2O (0.5 mL) and toluene (3 mL) containing 2 M K_2CO_3, tetrakis(triphenylphosphine)palladium(0) (3.99 mg, 3.5 μmol) was added. The mixture was stirred at 80 °C for 24 h, after which it was precipitated in methanol. Same purification procedure as for PDPP2TBP was used. Yield: 64 mg (88.4%). GPC (*o*-DCB, 80 °C): $M_n = 67.6$ kg mol^{-1}, PDI = 4.11.

F2-PDPP2TBP. Same procedure as for **PDPP2TBP** was used, but now **5** (67.86 mg, 0.067 mmol) and **4** (29.44 mg, 0.067 mmol) was used as the monomers. Yield: 63 mg (90.2%). GPC (*o*-DCB, 80 °C): $M_n = 72.0$ kg mol^{-1}, PDI = 1.98.

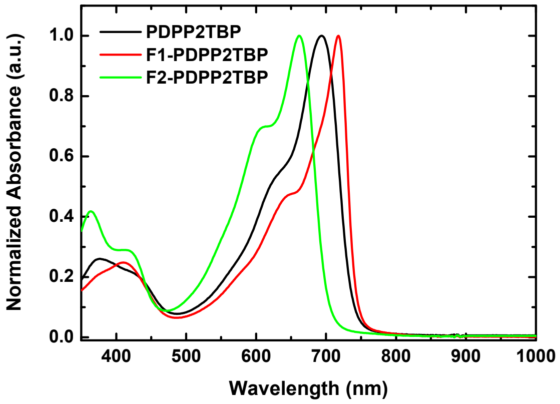


Fig. S1 Electronic absorption spectra of the DPP polymers in $CHCl_3$ solution.

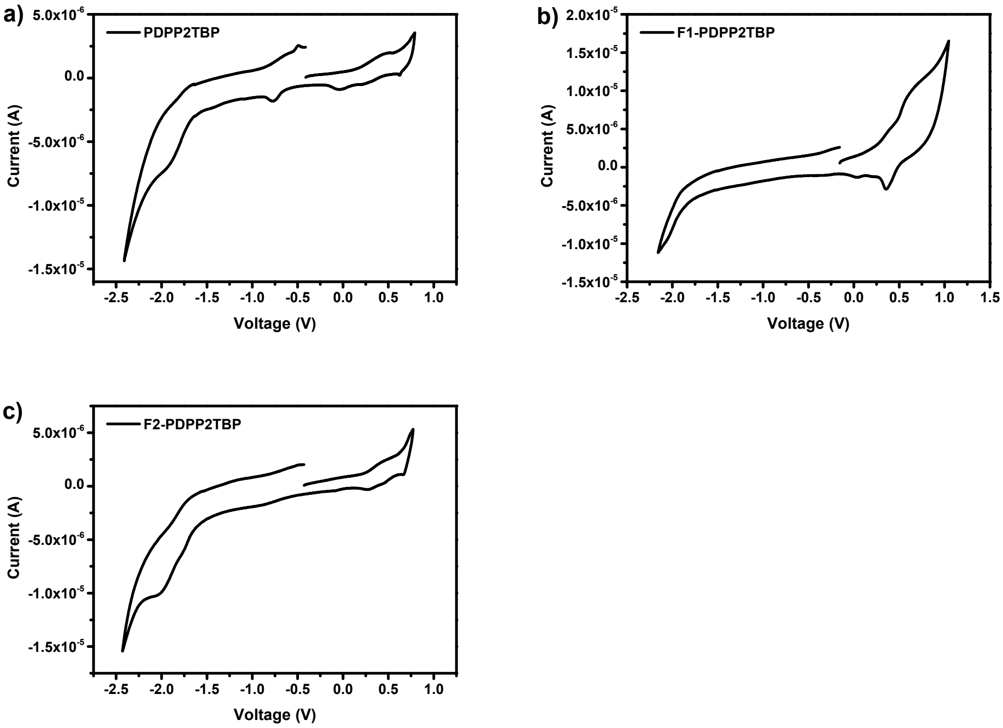


Fig. S2 Cyclic voltammograms of the DPP polymers in *o*-DCB. Potential vs. Fc/Fc$^+$.

Table S1 Electrochemical properties, energy level and LUMO offset of the DPP polymers related to [70]PCBM.

Polymer	E_{red}[a] (V)	E_{ox}[a] (V)	E_g^{cv} (eV)	E_{HOMO}[b] (eV)	E_{LUMO}[c] (eV)	α[d] (eV)
PDPP2TBP	-1.64	0.16	1.8	-5.39	-3.59	0.57
F1-PDPP2TBP	-1.60	0.21	1.81	-5.44	-3.63	0.53
F2-PDPP2TBP	-1.60	0.25	1.85	-5.48	-3.63	0.53
[70]PCBM	-1.07[e]	-	-	-	-4.16	-

[a] Versus Fc/Fc$^+$. [b] E_{HOMO} = -5.23 eV- eE_{ox}. [c] E_{LUMO} = -5.23 eV- eE_{red}. [d] $\alpha = e(E_{LUMO}$([70]PCBM – E_{LUMO} (polymer)). [e] Ref 2.

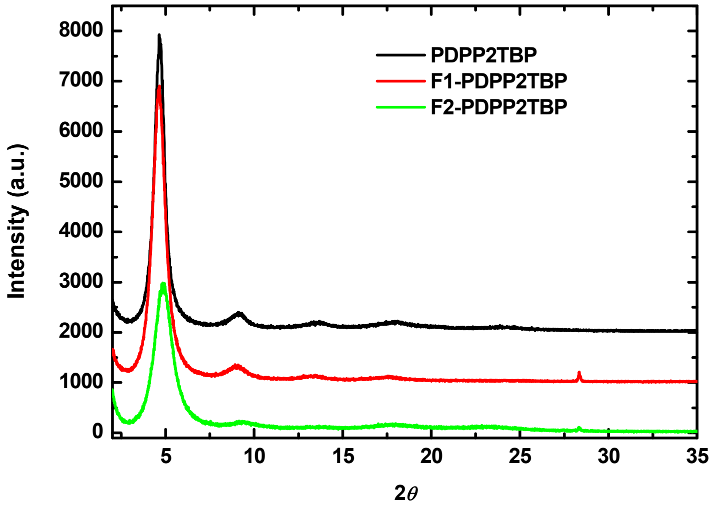


Fig. S3 X-ray diffraction patterns of thin films of the DPP polymers (vertically offset for clarity). *d*-Spacings for PDPP2TBP, F1-PDPP2TBP and F2-PDPP2TBP are 1.89 nm, 1.90 nm and 1.80 nm.

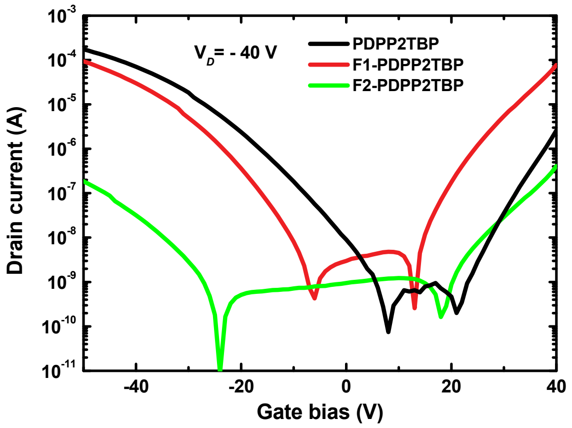


Fig. S4 Ambipolar transfer characteristics for FETs for the DPP polymers recorded at a drain bias of V_D = -40 V. The length and width of the transistor are 40 μm and 10 mm, respectively.

Table S2 Optimized solar cells of the PDPP2TBP polymers with [70]PCBM cast from chloroform with co-solvent (*o*-DCB or 1-CN).

Polymer	Co-solvent	Thickness (nm)	J_{sc} [a] (mA cm^{-2})	V_{oc} (V)	FF	PCE [a] (%)
PDPP2TBP	*o*-DCB 5%	90	11.4	0.79	0.62	5.6
PDPP2TBP	1-CN 3%	90	11.5	0.80	0.63	5.7
F1-PDPP2TBP	*o*-DCB 10%	105	6.7	0.89	0.62	3.7
F1-PDPP2TBP	1-CN 3%	105	7.0	0.87	0.48	2.9
F2-PDPP2TBP	*o*-DCB 10%	100	7.1	0.94	0.55	3.7
F2-PDPP2TBP	1-CN 3%	100	7.7	0.93	0.56	4.1

[a] J_{sc} and PCE were calculated by integrating the EQE spectrum with the AM1.5G spectrum.

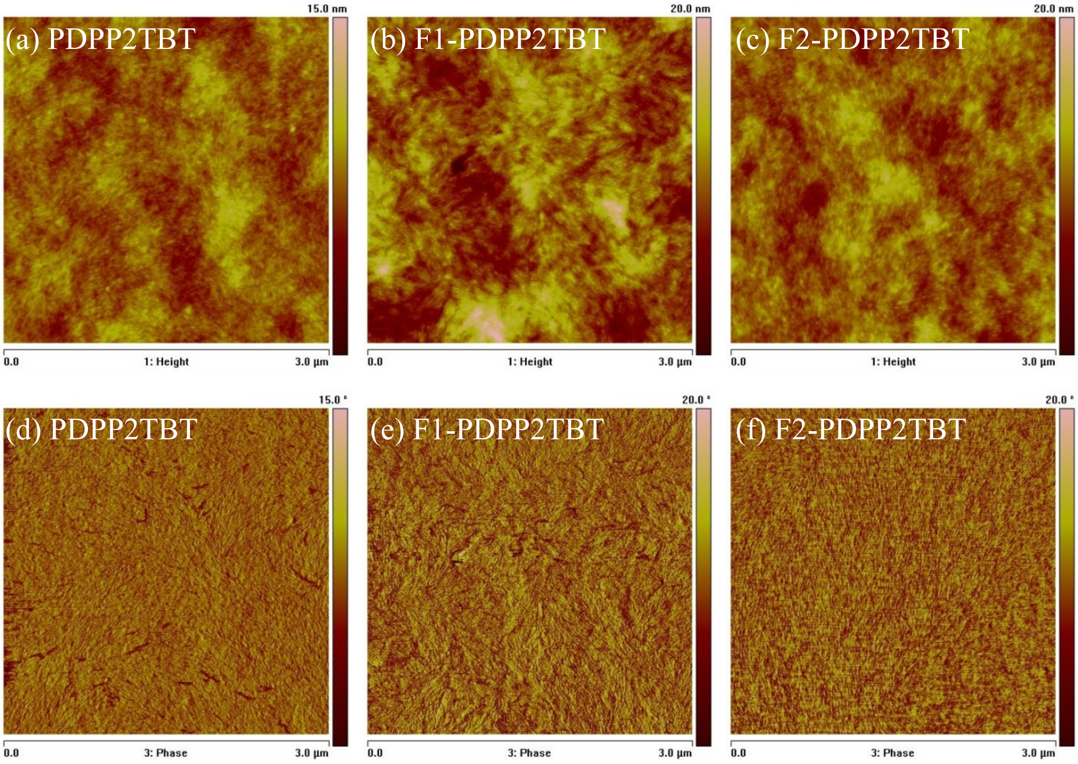


Fig. S5 AFM height and phase images of the optimized DPP polymer:[70]PCBM blend films. (a-c) height images and (d-f) phase images. The root mean square (RMS) roughness for these layers is 1.11 nm, 1.78 nm and 1.58 nm for PDPP2TBP, F1-PDPP2TBP and F2-PDPP2TBP.

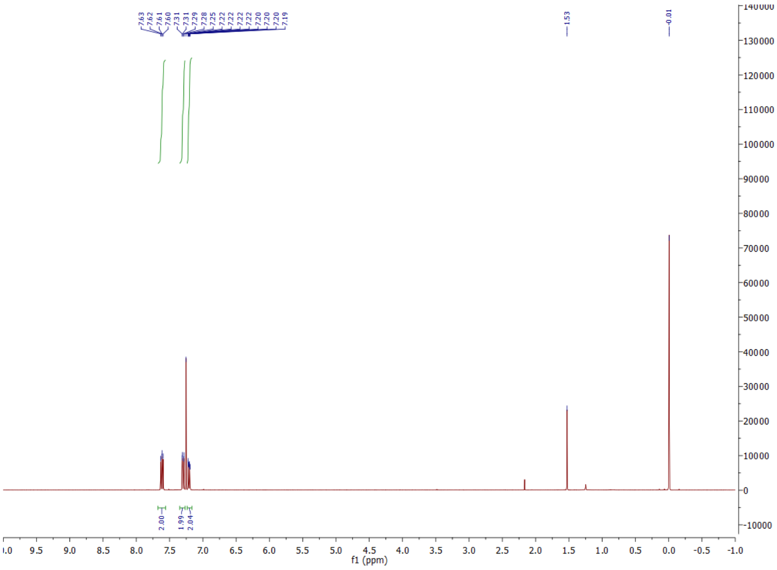


Fig. S6 ^{1}H-NMR of compound **1**.

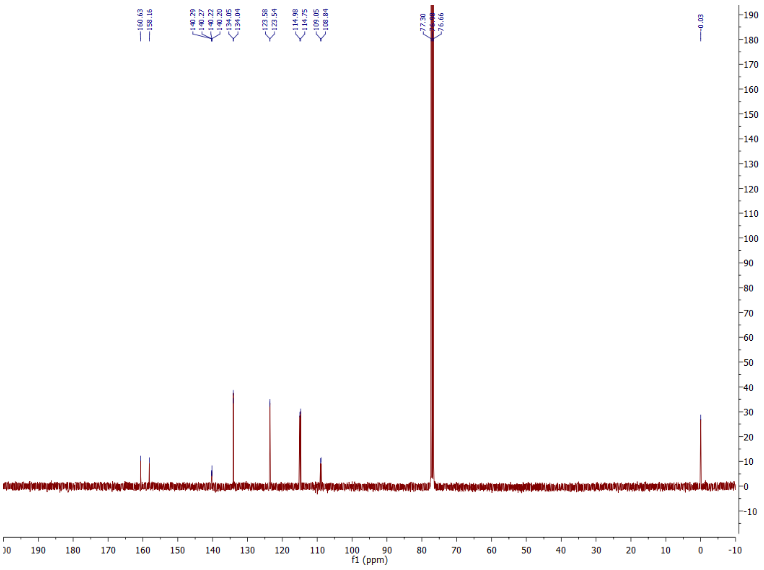


Fig. S7 ^{13}C-NMR of compound **1**.

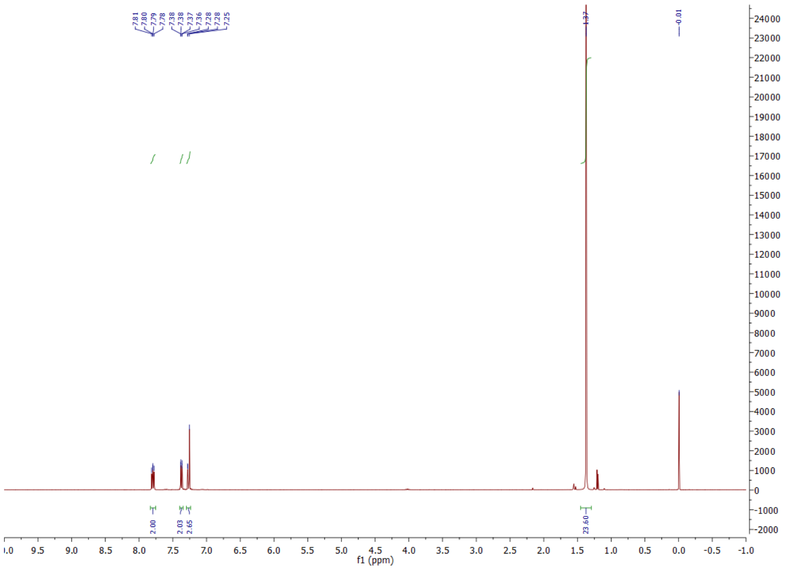


Fig. S8 ^{1}H-NMR of compound **2**.

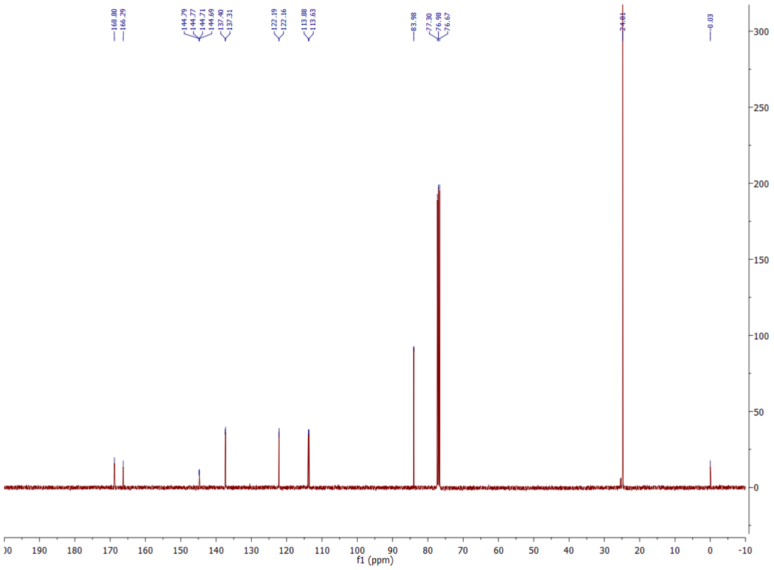


Fig. S9 ^{13}C-NMR of compound **2**.

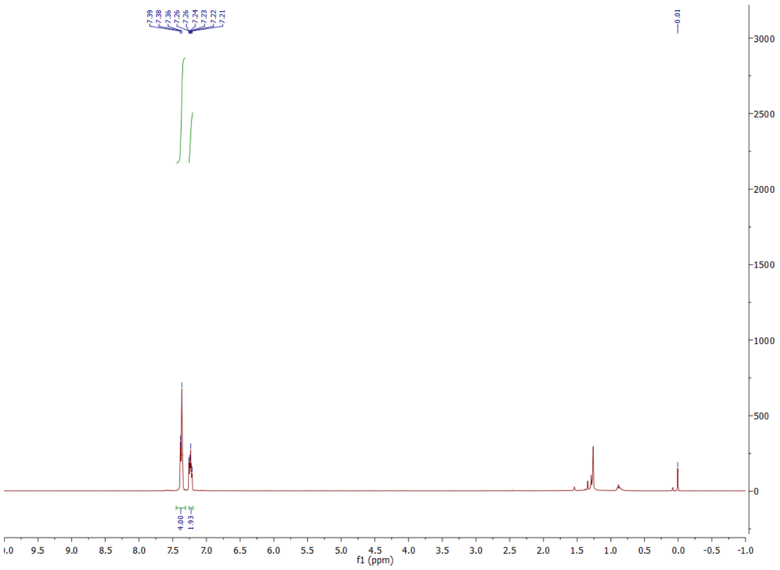


Fig. S10 ^{1}H-NMR of compound **3**.

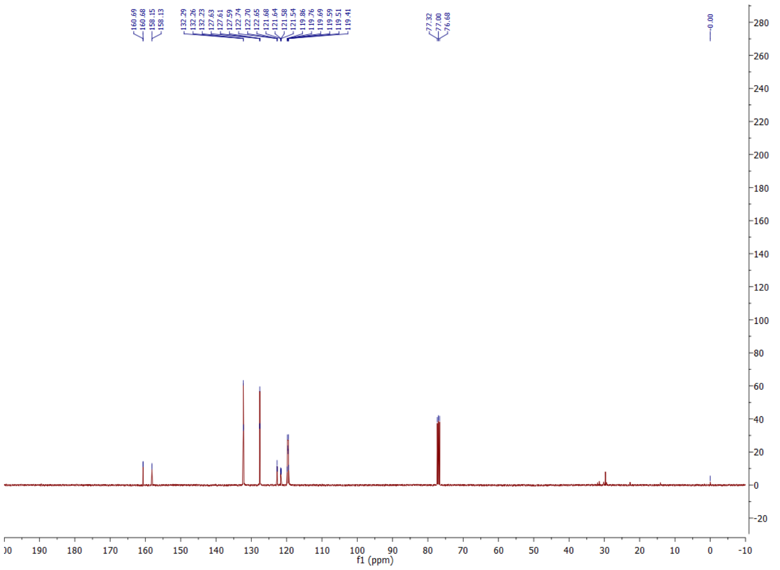


Fig. S11 ^{13}C-NMR of compound **3**.

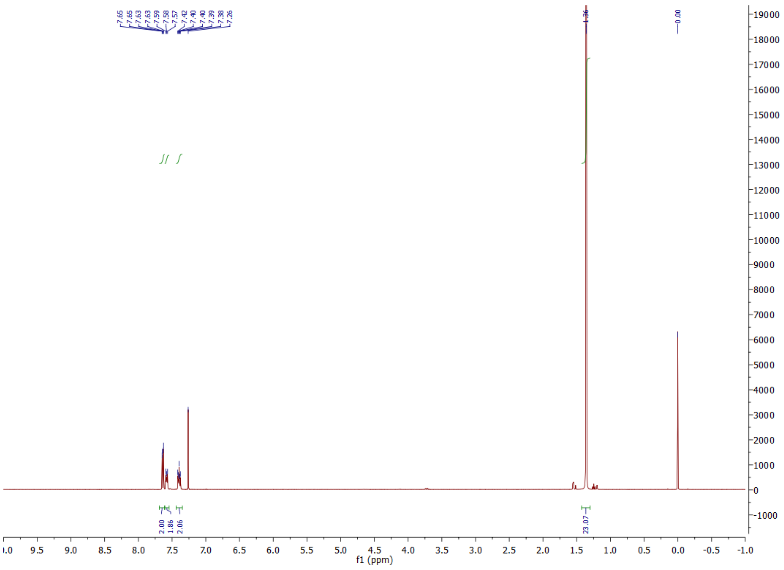


Fig. S12 ^{1}H-NMR of compound **4**.

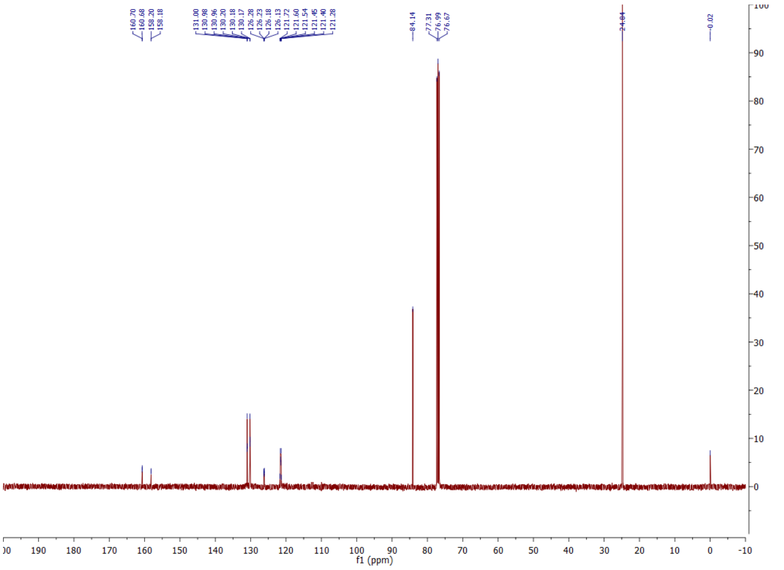


Fig. S13 ^{13}C-NMR of compound **4**.

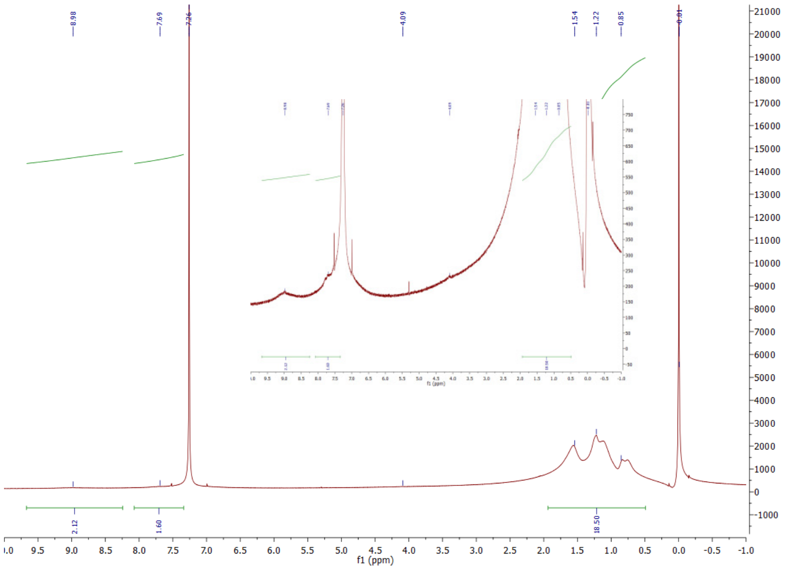


Fig. S14 ^{1}H-NMR of PDPP2TBP. The inset shows the spectrum at increased vertical scale.

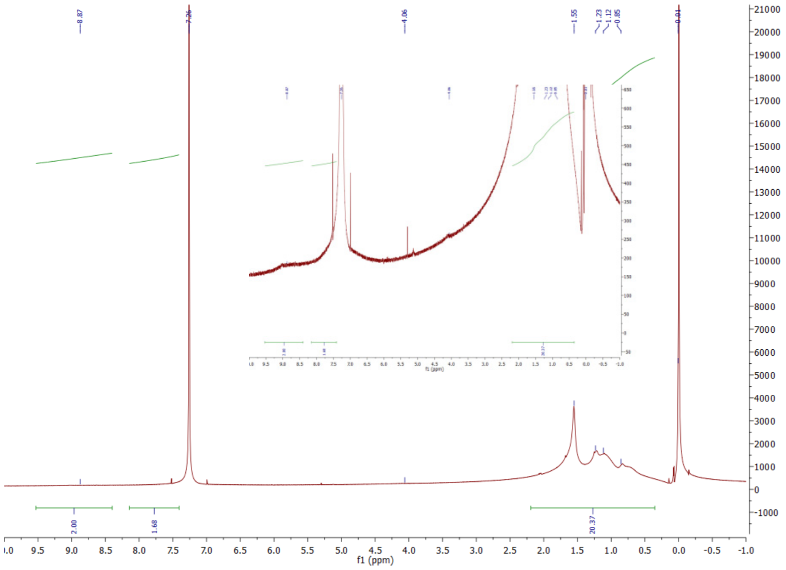


Fig. S15 ^{1}H-NMR of F1-PDPP2TBP. The inset shows the spectrum at increased vertical scale.

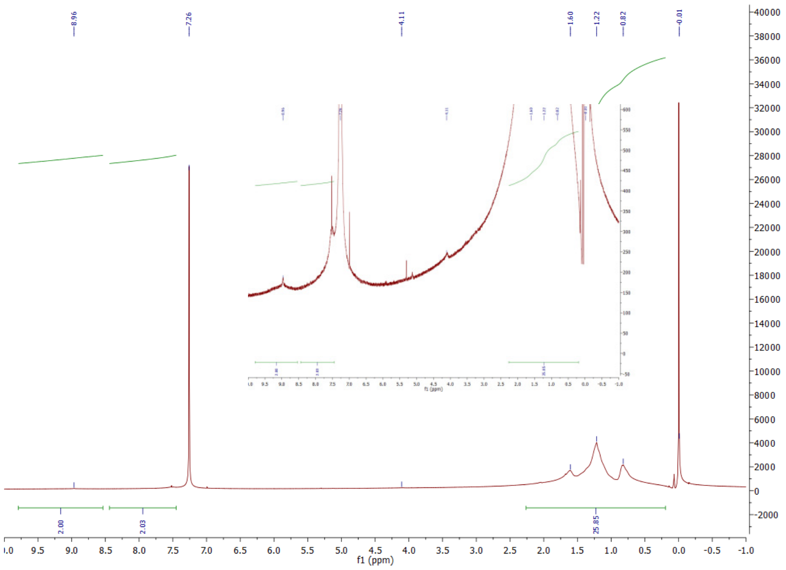


Fig. S16 ^{1}H-NMR of F2-PDPP2TBP. The inset shows the spectrum at increased vertical scale.

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[1] G. B. Zhang, Y. Y. Fu, Z. Y. Xie and Q. Zhang, *Sol. Energy Mater. Sol. Cells*, 2011, **95**, 1168-1173.

[2] M. M. Wienk, J. M. Kroon, W. J. H. Verhees, J. Knol, J. C. Hummelen, P. A. van Hal and R. A. J. Janssen, *Angew. Chem., Int. Ed.*, 2003, **42**, 3371.