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# Structure-properties relationship in diketopyrrolopyrrole based small molecules using functional terminal side chains via direct arylation: a joint experimental and theoretical study

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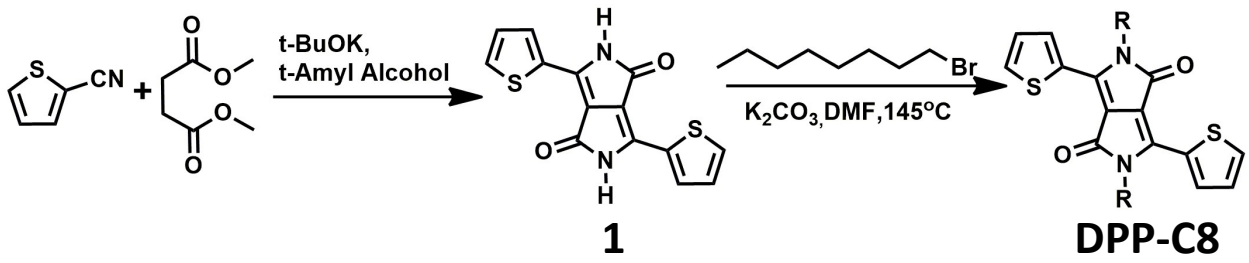
**1. Synthetic procedure**




**Synthesis of 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1)**

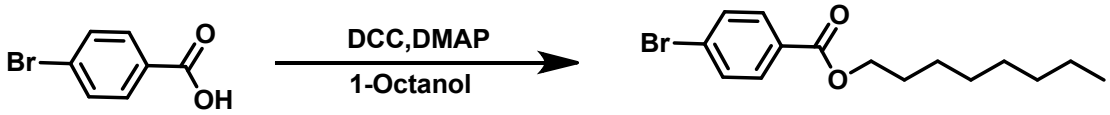
In an two neck 250 mL round bottom flask t-BuOK (6.0 g, 53.55 mmol) was taken under nitrogen atmosphere. To this t-amylalcohol (40 mL) and 2-thiophene carbonitrile (4.9 g, 45 mmol) was added and it was heated to 110 °C. Then a solution of dimethylsuccinate (2.2 g, 15 mmol) in t-amyl alcohol (15 mL) was slowly added drop by drop for one hour. Then it was continued for additional two hours at 110 °C. Then the reaction mixture was cooled to 65 °C and diluted with 75 mL of methanol. Then it was neutralized with acetic acid and reflux for 10 minutes. Then it was cooled, filtered washed with hot methanol and water gives a dark purple solid and it was used directly for next step without additional purification. (6.2g, 46% yield)

**Synthesis of 2,5-dioctyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP-C8)**

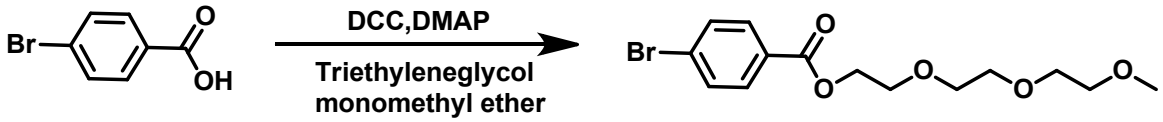
In an two neck 250 mL round bottom flask Compound 1 (5.0 g, 16.64mmol) and anhydrous potassium carbonate (9.2g, 66.58mmol) were dissolved in N,N-dimethylformamide (100 mL) was taken under nitrogen atmosphere and it was heated to 145 °C for one hour. 1-bromooctane (12.8g, 66.58mmol) was added to the reaction mixture by syringe. The reaction was continued for 24 h at 145 °C. Then it was cooled to room temperature, poured in ice cold water and filtered. The filtered crude product was purified by column chromatograpy using hexane – chloroform (1:1) as an eluent gave a dark puple solid.(3.8g, 43.67% yield) $^1$H NMR (400 MHz, *CDCl3*) δ 8.89 (dd, 2H) 7.62 (dd, 2H), 7.27 (dd, 2H), 4.03 (m, 4H), 1.86 (m, 2H), 1.38 – 1.25 (m, 16H), 0.85 (m, 12H); 13C NMR (100 MHz, *CDCl3*) δ 161.75, 140.42,135.25, 130.49, 129.83, 128.41, 107.94, 45.86, 39.08, 30.23, 28.36, 23.55, 23.05, 14.01, 10.48.

**Synthesis of 1-bromo-4-(octyloxy)benzene (M1)**


**Synthesis of octyl 4-bromobenzoate (M2)**




**2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-bromobenzoate (M3)**




**Synthesis of 1-bromo-4-(octyloxy)benzene (M1)**

In an two neck 250 ml round bottom flask 4-Bromophenol (5.0g, 29.06 mmol) and anhydrous potassium carbonate (4.82g, 34.88mmol) were dissolved in N,N-dimethylformamide (50 mL).To this 1-Bromooctane (6.73g, 34.88mmol) was added to the reaction mixture by syringe. The reaction was continued for 24 h at 80 °C. Then it was cooled to room temperature, washed with water and extracted in ethylacetate, dried in anhydrous sodium sulphate and purified by column chromatograpy using hexane gave a clear yellow viscous liquid.(6.91g, 83.43% yield) $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.51 – 7.31 (m, 2H), 6.79-6.71 (m, 2H), 3.91 (t, *J*=6.6, 2H), 1.83 – 1.69 (m, 2H), 1.51-1.23 (m, 10H), 1.05 – 0.78 (m, 3H).$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 158.31, 132.19, 116.32, 112.58, 68.28, 31.86, 29.39, 29.34, 29.25, 26.06, 22.70, 14.13.

**Synthesis of octyl 4-bromobenzoate (M2)**

In an two neck 250 ml round bottom flask 4-Brombenzoic acid (5.0g, 24.87 mmol), N,N'-Dicyclohexylcarbodiimide (5.64g, 27.30mmol)and 4-Dimethylaminopyridine (0.303g, 2.48mmol) were dissolved in dichloromethane (100 mL).To this 1-Octanol (3.56g, 27.30mmol) was added to the reaction mixture by syringe. The reaction was stirred for 24 h at room temperature. Then it was filtered off, washed with water, dried in anhydrous sodium sulphate and purified by column

chromatograpy using hexane – ethylacetate (95:5) gave a yellow viscous liquid. (5.39g, 69.58mmol) 1H NMR (400 MHz, CDCl3) δ = 8.01 – 7.76 (m, 2H), 7.66 – 7.44 (m, 2H), 4.28 (t, J=6.7, 2H), 1.85 – 1.64 (m, 2H), 1.50 – 1.19 (m, 10H), 0.91 – 0.79 (m, 3H). 13C NMR (101 MHz, CDCl3) δ = 165.88, 131.64, 131.07, 129.44, 127.88, 65.40, 31.79, 29.25, 29.20, 28.68, 26.03, 22.65, 14.08.

**Synthesis of octyl 4-bromobenzoate (M3)**

In an two neck 250 ml round bottom flask 4-Brombenzoic acid (5.0g, 24.87 mmol), N,N'-Dicyclohexylcarbodiimide (5.64g, 27.30mmol)and 4-Dimethylaminopyridine (0.303g, 2.48mmol) were dissolved in dichloromethane (100 mL).To this 1-Octanol (.56g, 27.30mmol) was added to the reaction mixture by syringe. The reaction was stirred for 24 h at room temperature. Then it was filtered off, washed with water, dried in anhydrous sodium sulphate and purified by column chromatograpy using hexane – ethylacetate (80:20) gave a yellow viscous liquid. (4.11g, 47.67mmol) 1H NMR (400 MHz, CDCl3) δ = 8.03 – 7.76 (m, 2H), 7.63 – 7.36 (m, 2H), 4.43-4.39 (m, 2H), 3.79-3.75 (m, 2H), 3.69 – 3.55 (m, 6H), 3.50 – 3.43 (m, 2H), 3.34 – 3.27 (m, 3H). 13C NMR (101 MHz, CDCl3) δ = 165.67, 131.61, 131.19, 129.00, 128.00, 71.86, 70.64, 70.57, 70.53, 69.07, 64.30, 58.96.

**Synthetic procedure for PDPP-OC8**

In an two neck round bottom flask 2,5-dioctyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.350g, 0.66mmol), 1-bromo-4-(octyloxy)benzene (0.570g, 2.01mmol), $K_2CO_3$ (276mg, 2.00mmol), pivalic acid (0.022g, 0.22mmol) and $Pd(OAc)_2$ (7.5mg, 0.003mmol) was taken and it was dissolved in N,N'-dimethylacetamide (3ml) and it was stirred at 110°C for 16h under nitrogen atmosphere. Then it was cooled to room temperature and precipitated in 100ml of methanol. The crude product was purified by column chromatography using $CH_2Cl_2$ and petroleum ether (2:1, v/v) as eluent followed by thrice recrystallisation with ethyl acetate gave brownish red solid. Yield (357mg, 58%). $^1$H NMR (400 MHz, CDCl3) δ = 8.95 (d, J=4.1, 2H), 7.59 (d, J=8.7, 4H), 7.34 (d, J=4.1, 2H), 6.92 (d, J=8.7, 4H), 4.10 (t, J=6.5, 4H), 3.98 (t, J=6.5, 4H),1.82 -1.76 (m, 8H), 1.51 – 1.23 (m, 40H), 0.9-0.852 (m, 12H). $^{13}$C NMR (101 MHz, CDCl3) δ = 161.30, 159.88, 149.99, 139.25, 136.80, 127.79, 127.45, 125.72, 123.47, 115.05, 107.61, 68.22, 42.28, 31.83, 30.95, 30.02, 29.38, 29.25, 26.95, 26.04, 22.68, 22.65, 14.13. Elemental Analysis,

Calculated (%): C, 74.63; H, 8.64; N, 3.00; S, 6.87; Found: C, 74.01; H, 8.69; N, 3.07; S, 6.97. MS (MALDI) m/z:Calculated for $C_{58}H_{80}N_2O_4S_2$, 933.396, found: 932.621

**Synthetic procedure for PDPP-EC8**

In an two neck round bottom flask 2,5-dioctyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.30g, 0.57mmol), octyl 4-bromobenzoate (0.537g, 1.71mmol), $K_2CO_3$ (0.237g, 1.71mmol), pivalic acid (0.019g, 0.18mmol) and $Pd(OAc)_2$ (0.006g, 0.0286mmol) was taken and it was dissolved in N,N'-dimethylacetamide (3ml) and it was stirred at 110°C for 16h under nitrogen atmosphere. Then it was cooled to room temperature and precipitated in 100ml of methanol. The crude product was purified by column chromatography using f $CH_2Cl_2$ and petroleum ether (1:1, v/v) as eluent followed by thrice recrystallisation with ethyl acetate gave dark blue solid. Yield (0.322mg, 57%). $^1$H NMR (400 MHz, CDCl3) δ = 8.97 (d, J=3.7, 2H), 8.06 (d, J=7.9, 4H), 7.71 (d, J=7.9, 4H), 7.54 (d, J=3.8, 2H), 4.31 (t, J=6.5, 4H), 4.11 (t, J=6.5, 4H), 1.85 – 1.73 (m, 8H), 1.47-1.26 (m, 40H), 0.98 – 0.82 (m, 12H). $^{13}$C NMR (101 MHz, CDCl3) δ = 165.99, 161.19, 148.17, 139.32, 137.02, 136.70, 130.38, 129.94, 125.75, 108.44, 65.38, 42.34, 31.81, 30.03, 29.27, 29.22, 28.72, 26.93, 26.05, 22.66, 22.64, 14.10. Elemental Analysis, Calculated (%): C, 72.84; H, 8.15; N, 2.83; S, 6.48; Found: C, 72.71; H, 8.26; N, 2.99; S, 6.79. MS (MALDI) m/z: Calculated for $C_{60}H_{80}N_2O_6S_2$, 989.417, found: 988.845

**Synthetic procedure for PDPP-EG**

In an two neck round bottom flask 2,5-dioctyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.3g, 0.57mmol), 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-bromobenzoate (0.595g, 1.71mmol), K2CO3 (0.237g, 1.71mmol), pivalic acid (0.19 mg, 0.19mmol) and $Pd(OAc)_2$ (0.006g, 0.028mmol) was taken and it was dissolved in N,N'-dimethylacetamide (2ml) and it was stirred at 110°C for 16h under nitrogen atmosphere. Then it was cooled to room temperature and precipitated in 100ml of methanol. The crude product was purified by column chromatography using f $CH_2Cl_2$ and petroleum ether (9:1, v/v) as eluent followed by thrice recrystallisation with ethyl acetate gave dark blue solid. Yield (367mg, 61%). $^1$H NMR (400 MHz, CDCl3) δ = 8.96 (d, J=4.1, 2H), 8.08 (d, J=8.4, 4H), 7.71 (d, J=8.4, 4H), 7.54 (d, J=4.2, 2H), 4.50 – 4.47 (m, 4H), 4.14 – 4.09 (m, 4H), 3.87 – 3.83 (m, 4H), 3.76 – 3.64 (m, 12H), 3.55 (dd, J=5.6, 3.6, 4H), 3.38 (s, 6H), 1.78 (d, J=5.4, 4H), 1.53 – 1.22 (m, 20H), 0.87 (t, J=6.7, 6H). 13C NMR

(101 MHz, CDCl3) δ = 165.89, 161.19, 148.10, 139.33, 137.19, 136.70, 130.56, 129.99, 129.93, 125.88, 125.76, 108.46, 71.94, 70.72, 70.66, 70.61, 69.22, 64.33, 59.06, 42.34, 31.81, 30.03, 29.22, 26.93, 22.64, 14.12. Elemental Analysis, Calculated (%): C, 65.88; H, 7.24; N, 2.65; S, 6.07; Found: C, 65.73; H, 7.26; N, 2.77; S, 6.19. MS (MALDI) m/z: Calculated for $C_{58}H_{76}N_2O_{12}S_2$, 1057.360, found: 1057.566

**Synthetic procedure for PDPP-CHO**

In an two neck round bottom flask 2,5-dioctyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.5g, 0.95mmol), 4-bromobenzaldehyde (53g, 2.85mmol), $K_2CO_3$ (0.39g, 2.85mmol), pivalic acid (0.032g, 0.31mmol) and $Pd(OAc)_2$ (0.011g, 0.047mmol) was taken and it was dissolved in N,N'-dimethylacetamide (3ml) and it was stirred at 110°C for 16h under nitrogen atmosphere. Then it was cooled to room temperature and precipitated in 100ml of methanol. The crude product was purified by column chromatography using $CH_2Cl_2$ and petroleum ether (4:1, v/v) as eluent followed by thrice recrystallisation with ethyl acetate gave dark blue solid. Yield (0.327mg, 47%). $^1$H NMR (400 MHz, CDCl3) δ = 10.03 (2 H, s), 8.98 (2 H, s), 7.89 (6 H, d, *J* 36.6), 7.61 (4 H, s), 4.12 (4 H, s), 1.37 (24 H, d, *J* 72.5), 0.86 (6 H, s).

**Synthetic procedure for PDPP-CNEC8**

In an two neck round bottom flask PDPP-CHO (0.25g, 0.34mmol) was taken and it was dissolved in chloroform (15ml) and it was stirred for 30 minutes under nitrogen atmosphere. To that octylcyanoacetate (0.673g, 3.41mmol) and triethylamine (0.1g, 1.71mmol) was added. The reaction was continued with stirring for 48 hours at room temperature. Then it was washed with water, dried in anhydrous sodium sulphate and purified by column chromatograpy using hexane – chloroform (60:40) as eluent followed by thrice recrystallisation with ethyl acetate gave dark blue solid. Yield (0.26g, 70%). 1H NMR (400 MHz, CDCl3) δ = 8.99 (d, J=4.0, 2H), 8.15 (s, 2H), 8.00 (d, J=8.1, 4H), 7.73 (d, J=8.1, 4H), 7.55 (d, J=4.1, 2H), 4.29 (t, J=6.7, 4H), 4.11 – 4.06 (m, 4H), 1.81 – 1.73 (m, 8H), 1.49 – 1.26 (m, 40H), 0.88 (t, J=6.6, 12H). 13C NMR (101 MHz, CDCl3) δ = 162.47, 161.00, 153.24, 147.50, 139.10, 137.25, 136.99, 131.90, 131.43, 130.46, 126.26, 115.53, 108.71, 102.81, 66.94, 42.40, 31.82, 31.78, 30.08, 29.70, 29.25, 29.23, 29.19, 29.17, 28.50, 26.96, 25.80, 22.65, 14.12, 14.10. Elemental Analysis, Calculated (%): C, 72.62; H, 7.57; N, 5.13; S,

5.88; Found: C, 72.49; H, 7.76; N, 5.31; S, 6.01. MS (MALDI) m/z: Calculated for $C_{66}H_{82}N_4O_6S_2$, 1091.510, found: 1091.638

**2. $^1$H-NMR and $^{13}$C-NMR spectra**

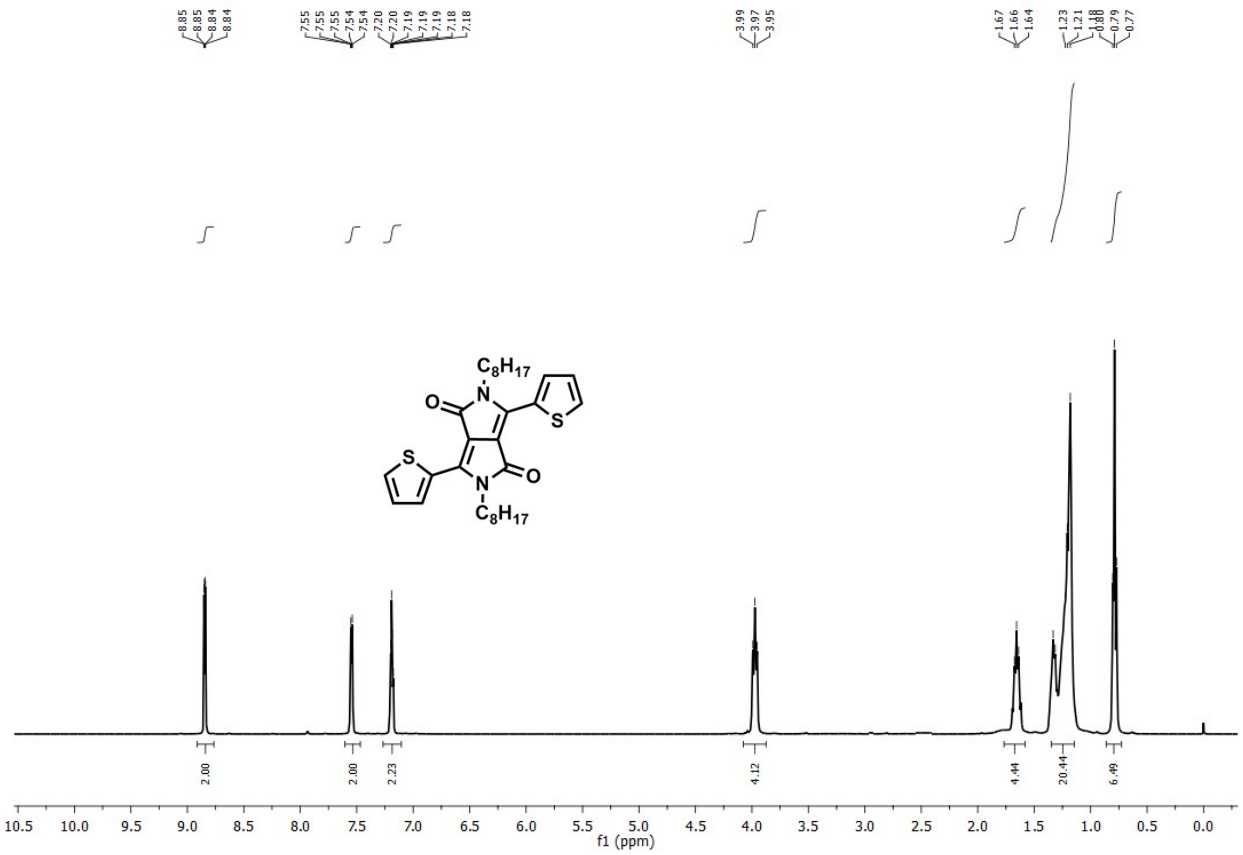



**Fig. S1 $^1$ H-NMR of compound DPP-C8 in $CDCl_3$.**

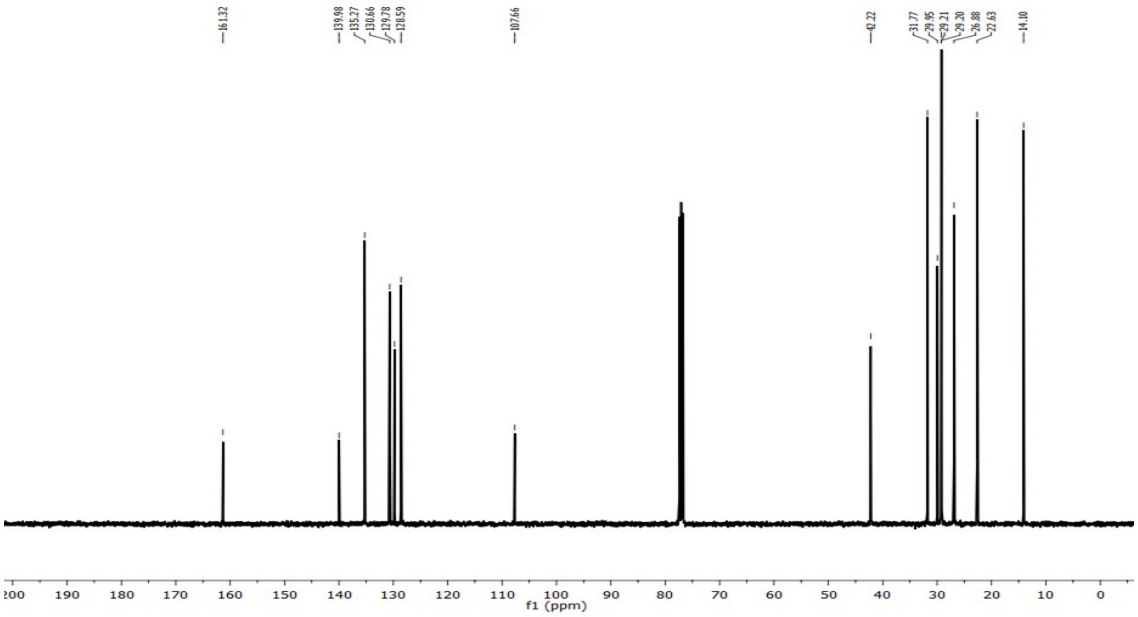



**Fig. S2 [13] C-NMR of compound DPP-C8 in CDCl3.**

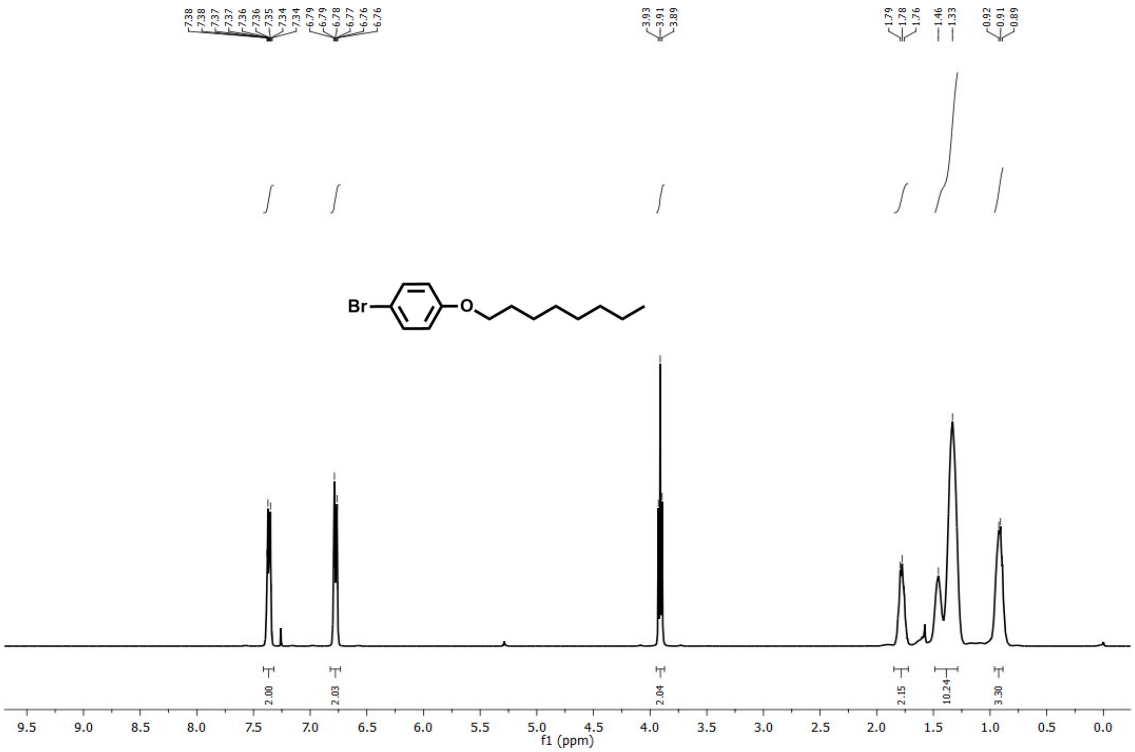



**Fig. S3 [1] H-NMR of compound M1 in $CDCl_3$.**

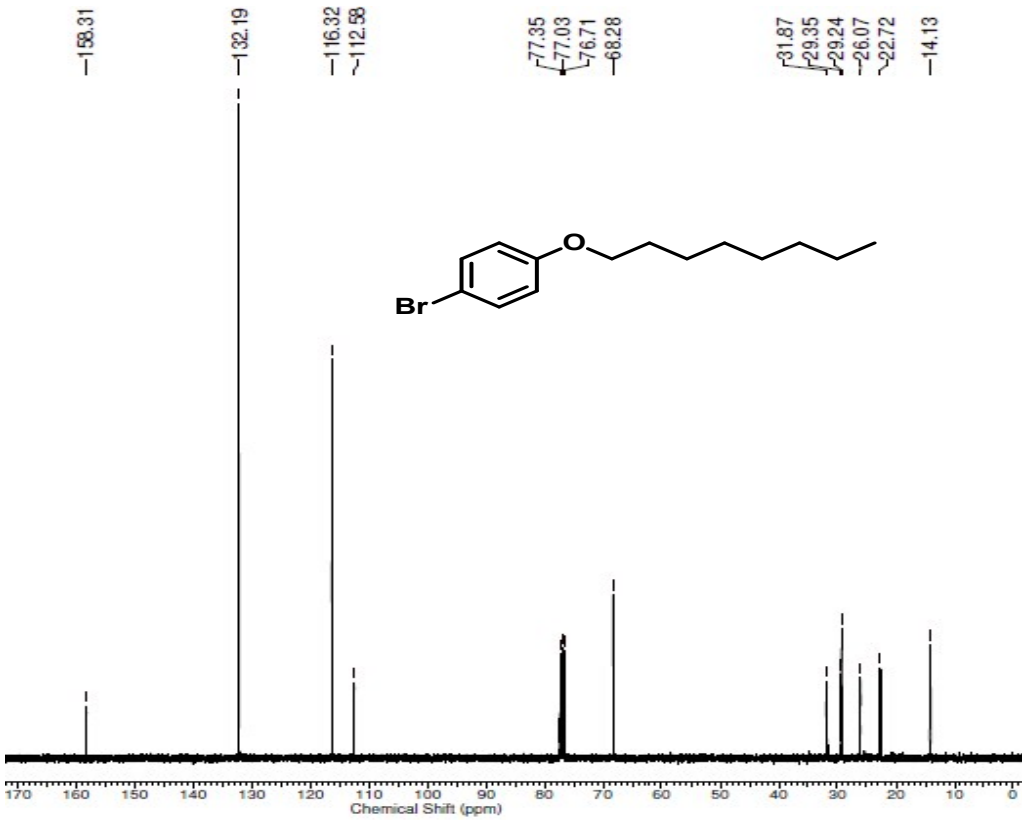
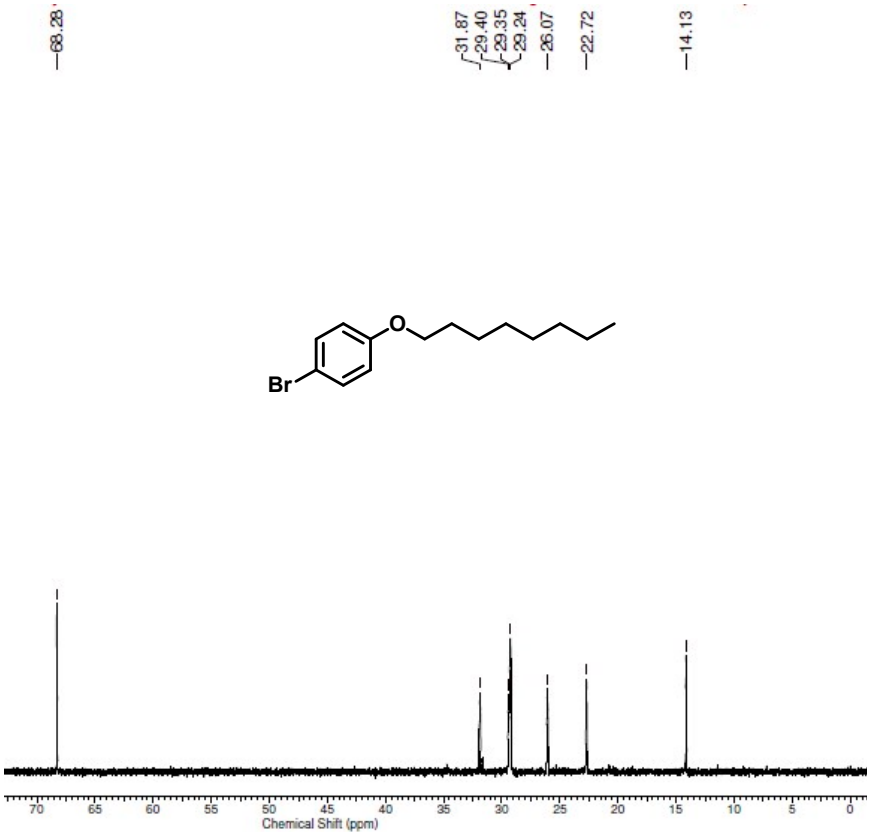



**Fig. S4 $^{13}$C-NMR of compound M1 in $CDCl_3$.**



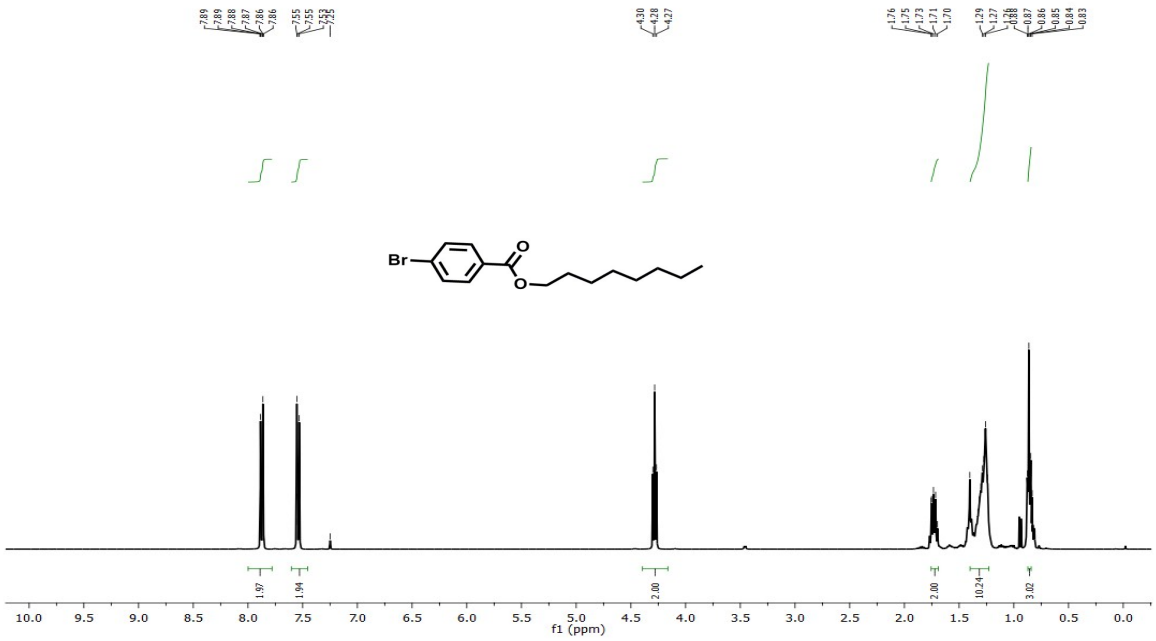



**Fig. S5 [1] H-NMR of compound M2 in $CDCl_3$.**

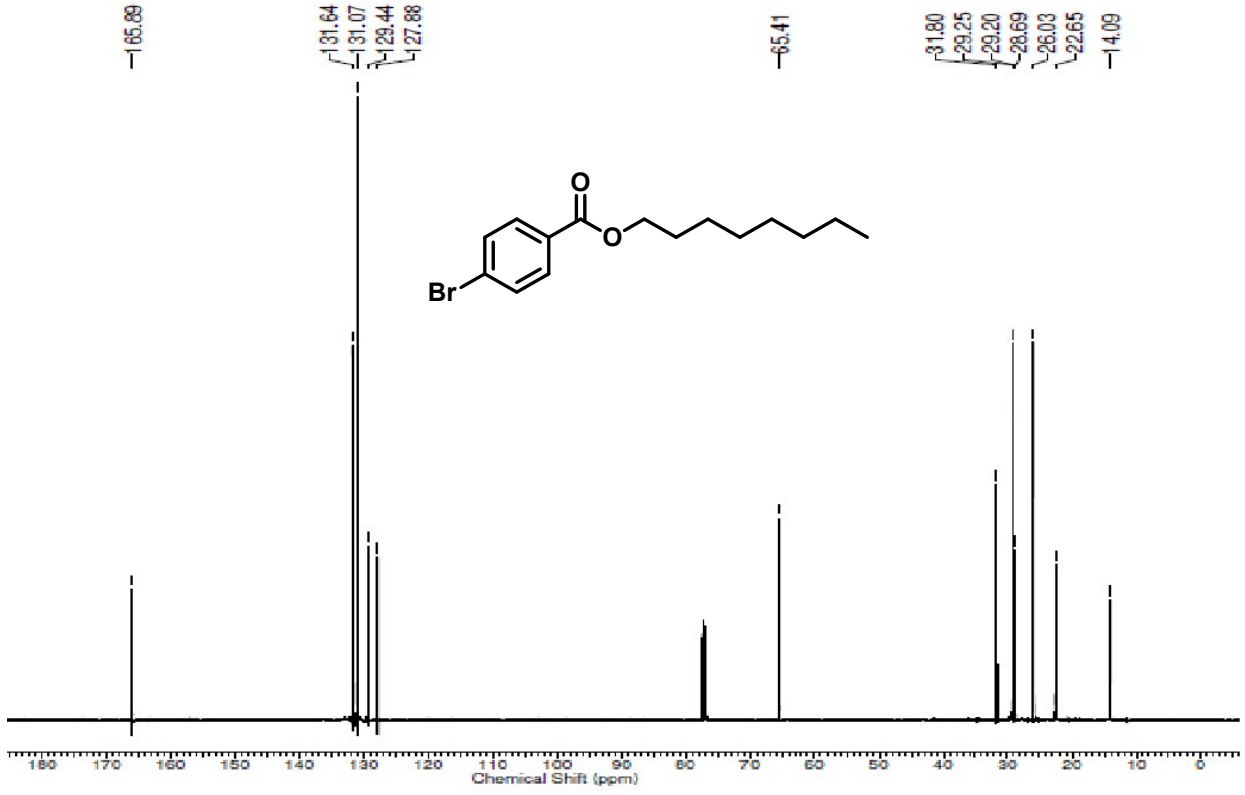



**Fig. S6 [13] C-NMR of compound M2 in $CDCl_3$.**

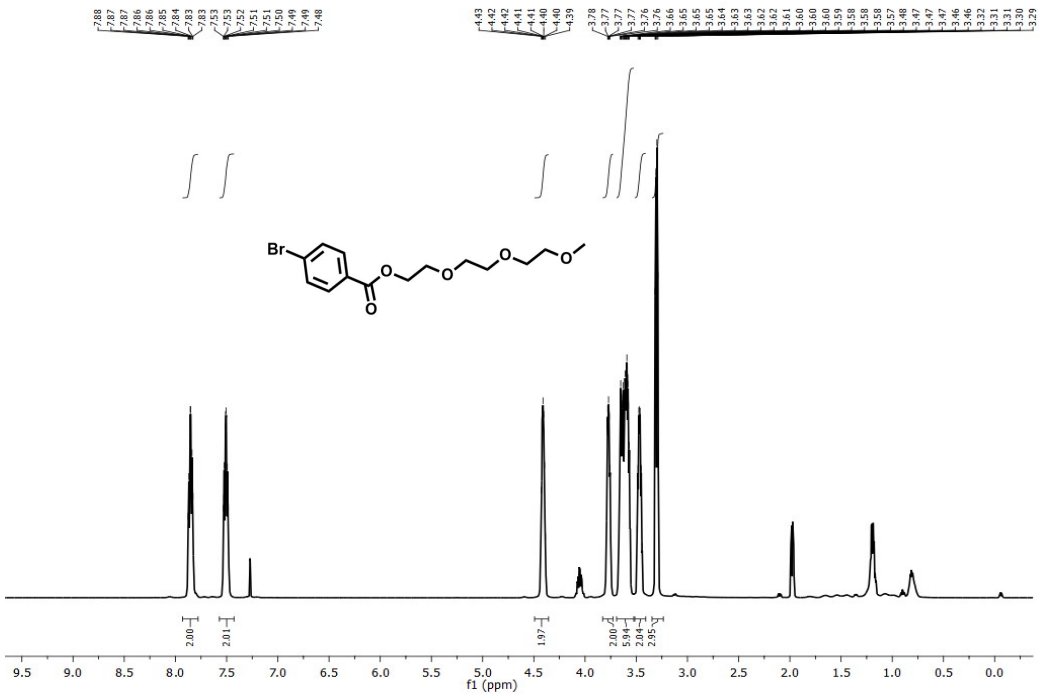



**Fig. S7 [1] H-NMR of compound M3 in CDCl3.**

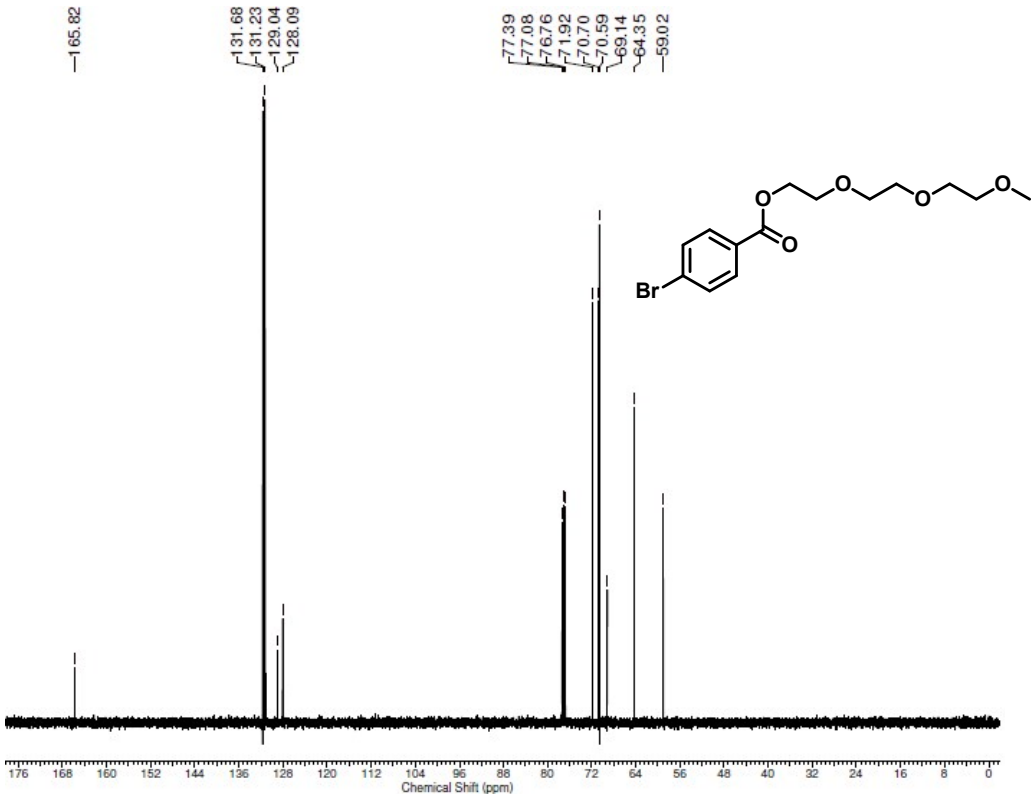



**Fig. S8 [13] C-NMR of compound 3 in $CDCl_3$.**

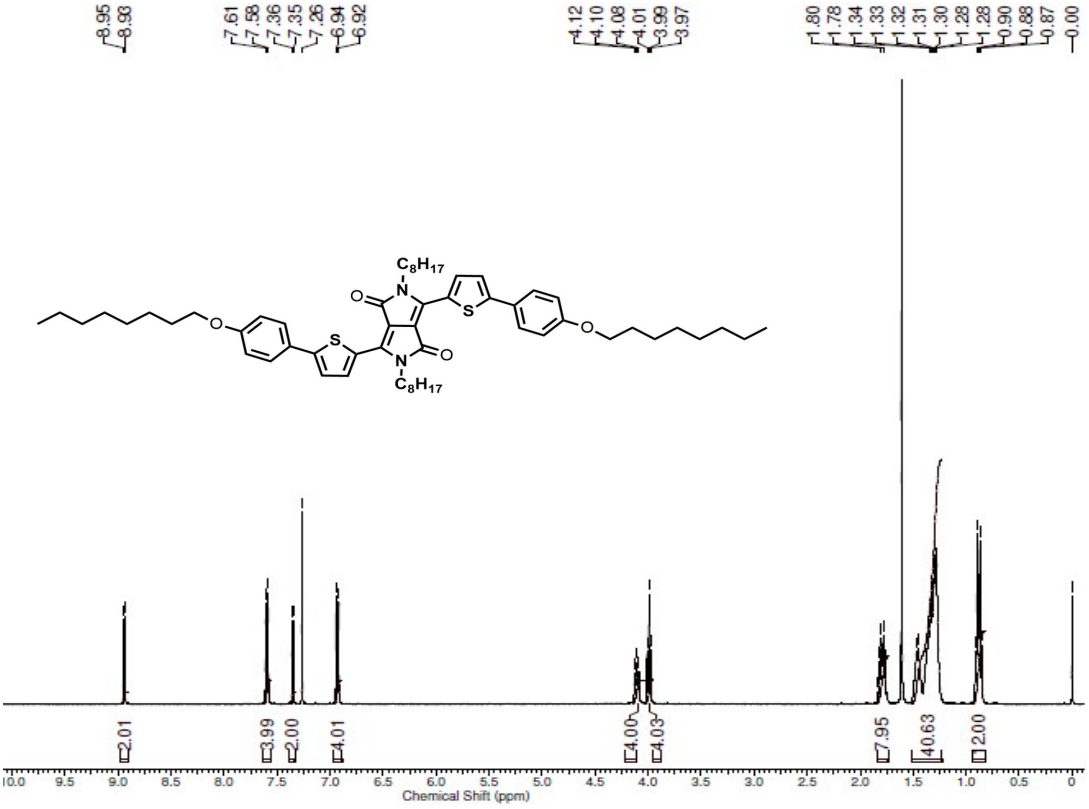



**Fig. S9 [1] H-NMR of compound PDPP-OC8 in $CDCl_3$.**

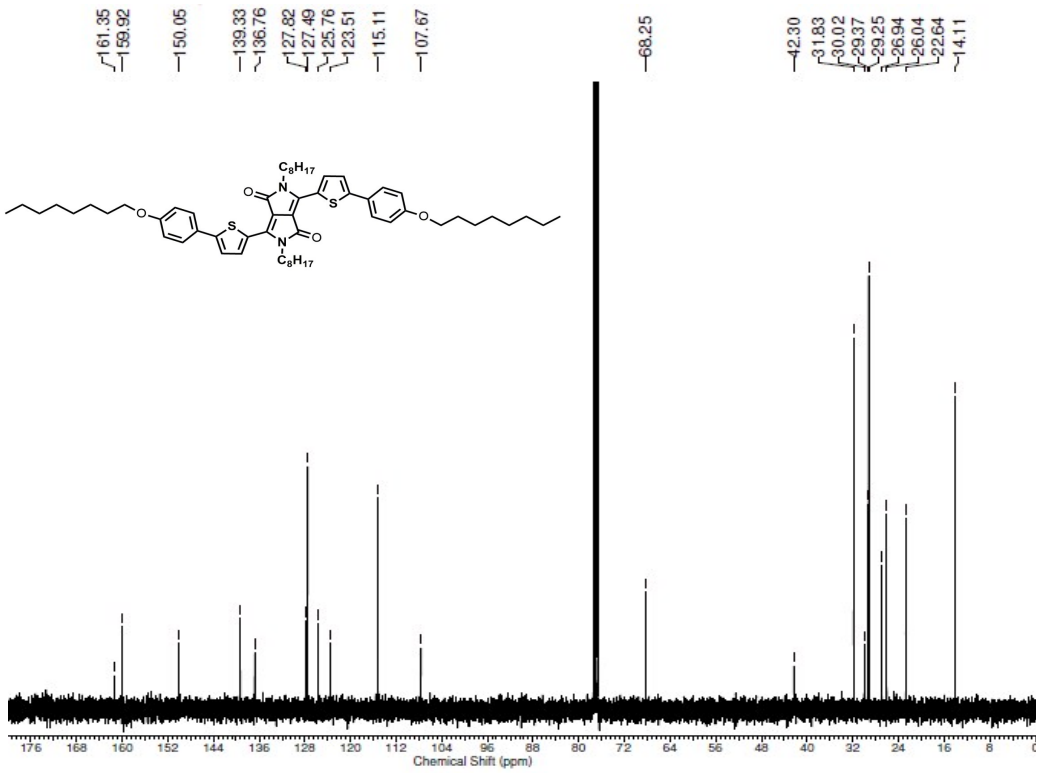
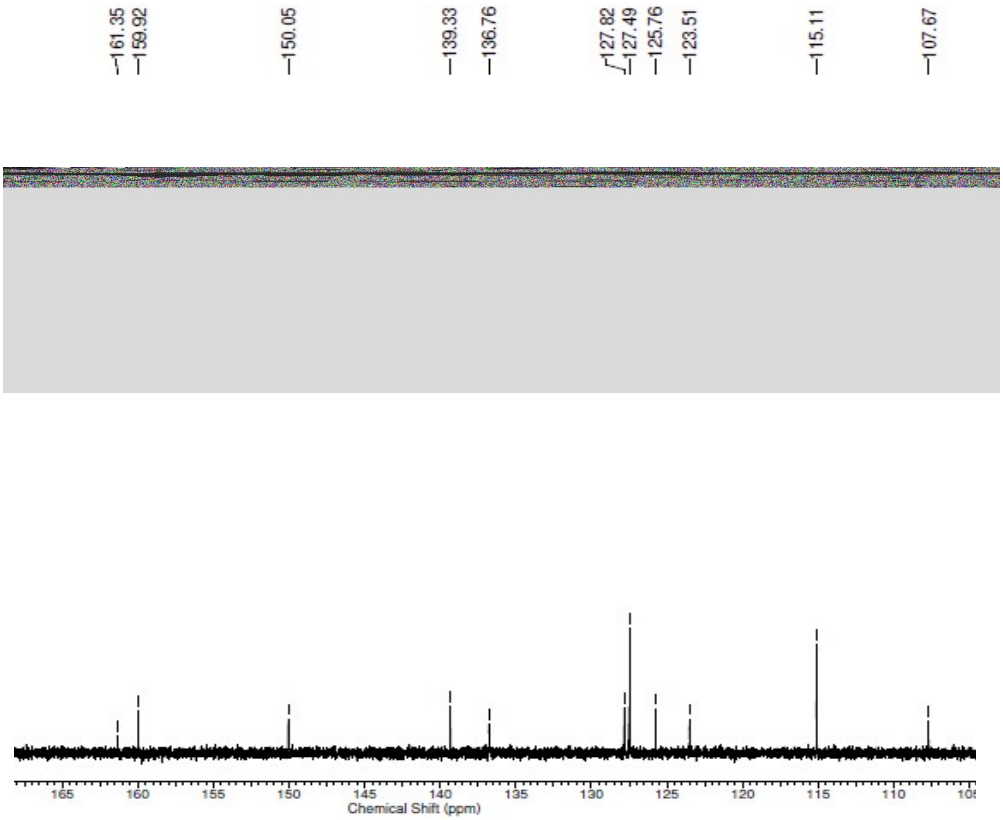


**Fig. S10 [13] C-NMR of compound PDPP-OC8 in $CDCl_3$**



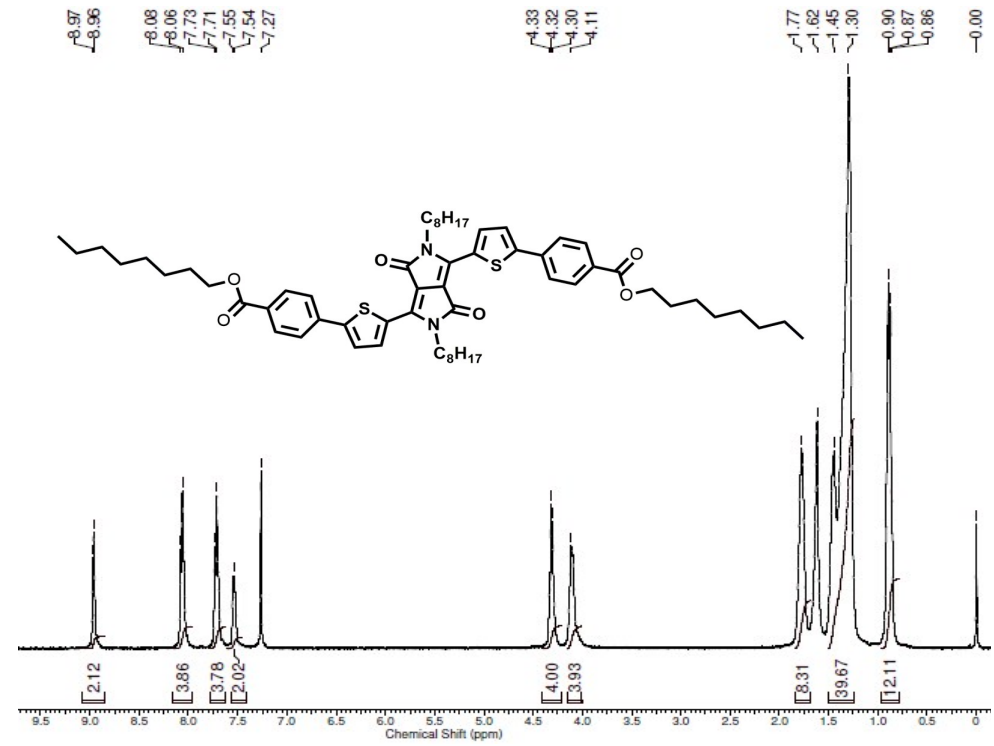




**Fig. S11 [1] H-NMR of compound PDPP-EC8 in $CDCl_3$.**

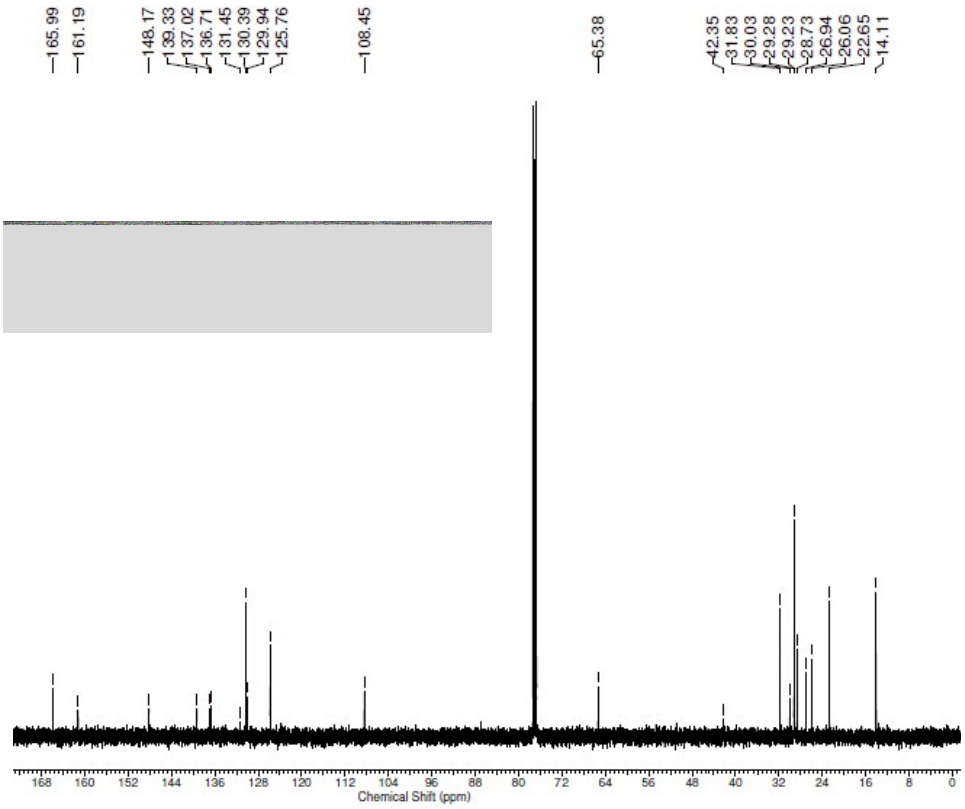
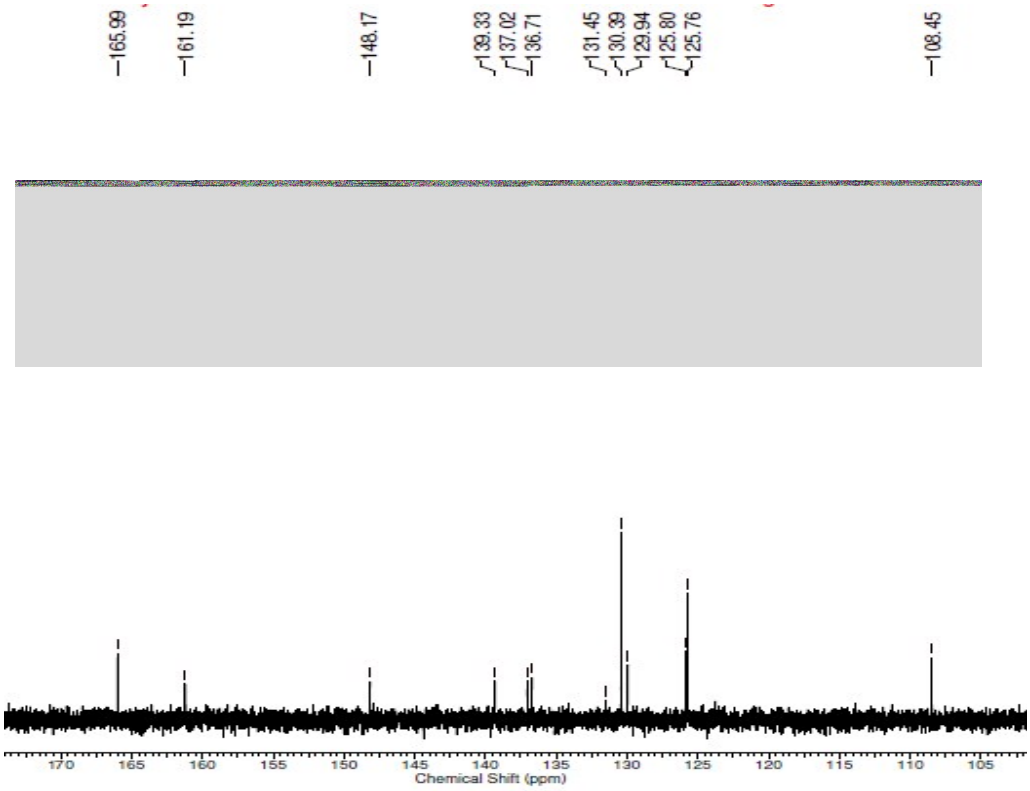



**Fig. S12 [13] C-NMR of compound PDPP-EC8 in $CDCl_3$.**



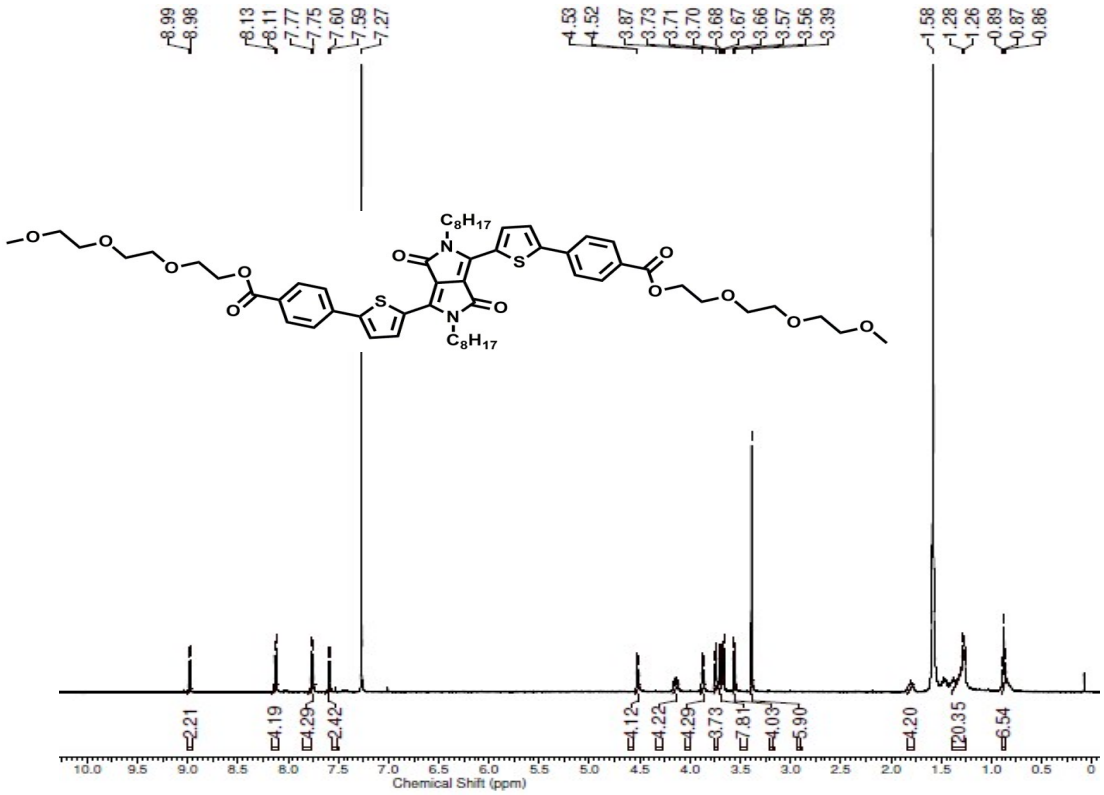
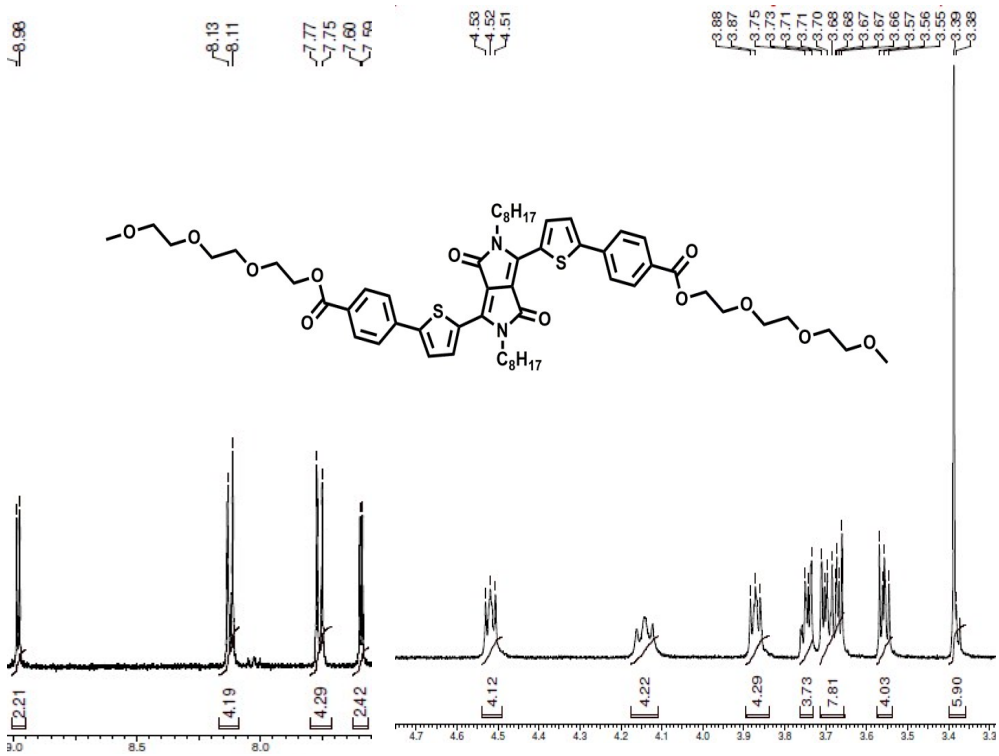



**Fig. S13 [1] H-NMR of compound PDPP-EG in $CDCl_3$.**



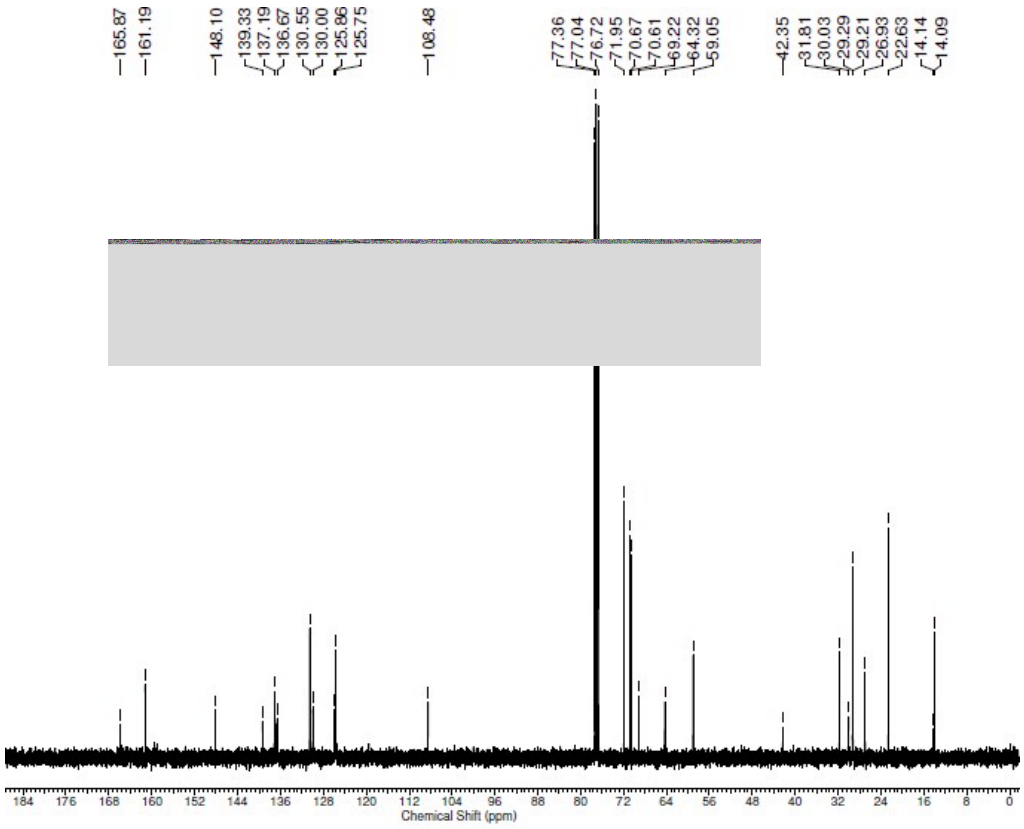
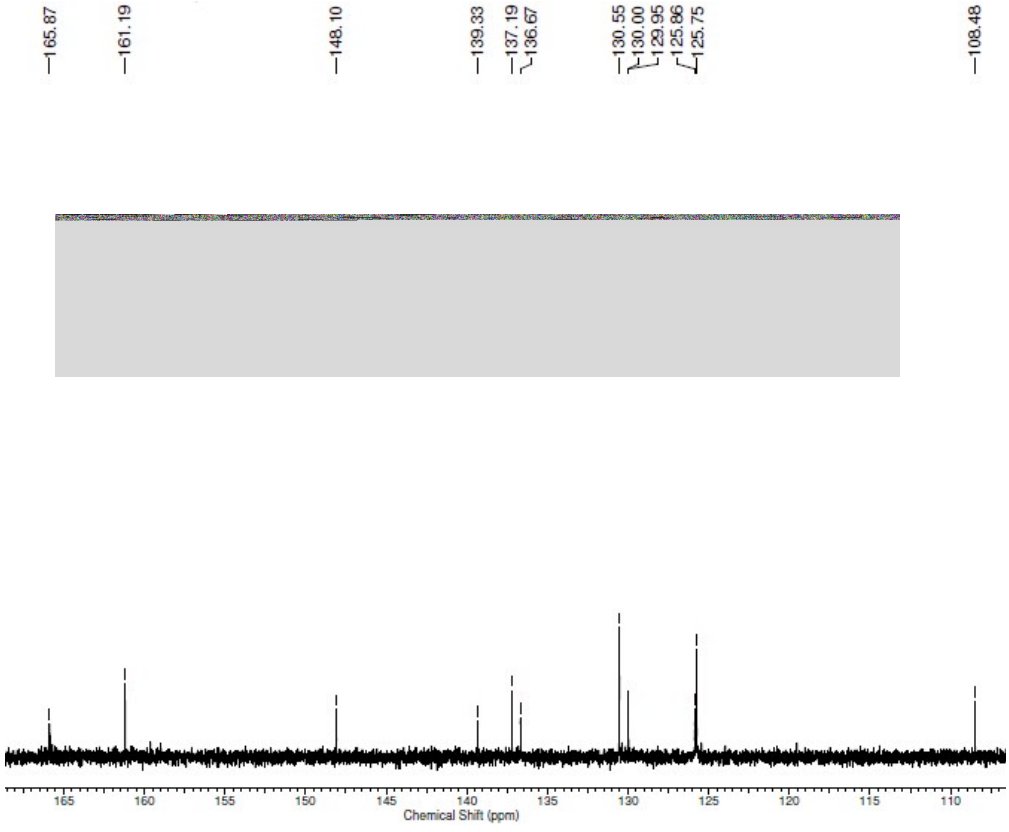



**Fig. S14 $^{13}$C-NMR of compound PDPP-EG in $CDCl_3$.**



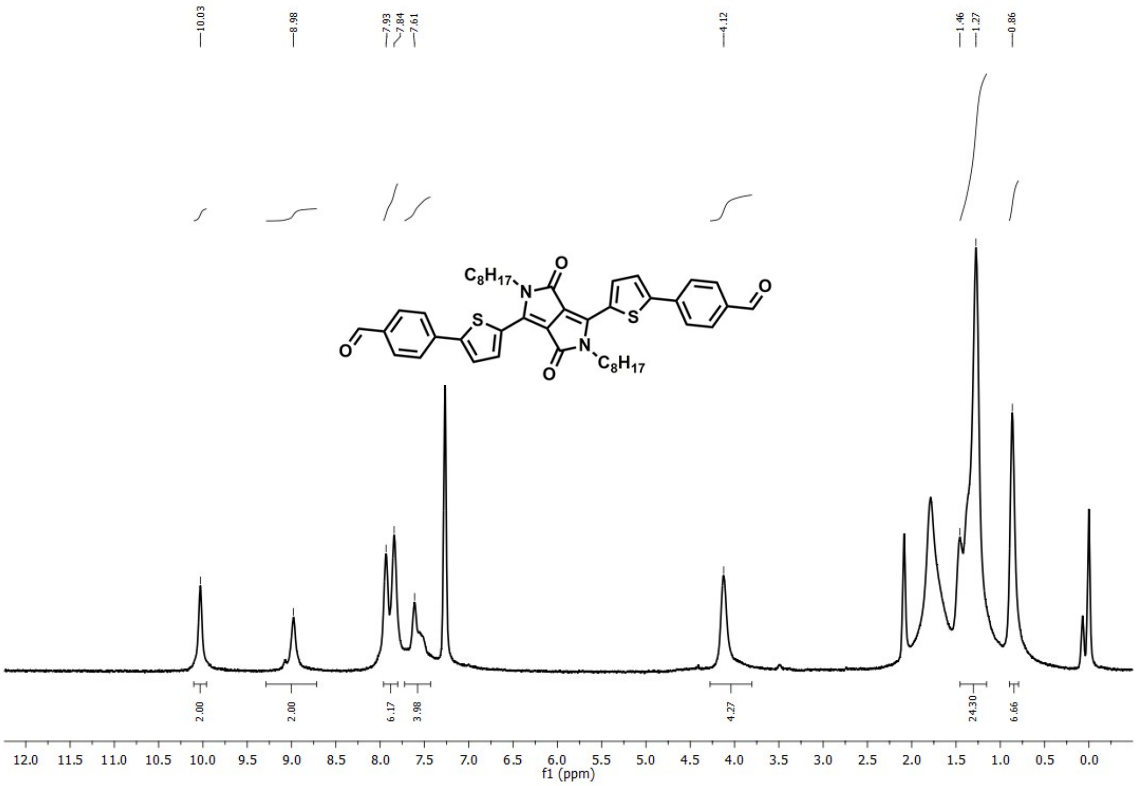



**Fig. S15 [1] H-NMR of compound PDPP-CHO in CDCl3**

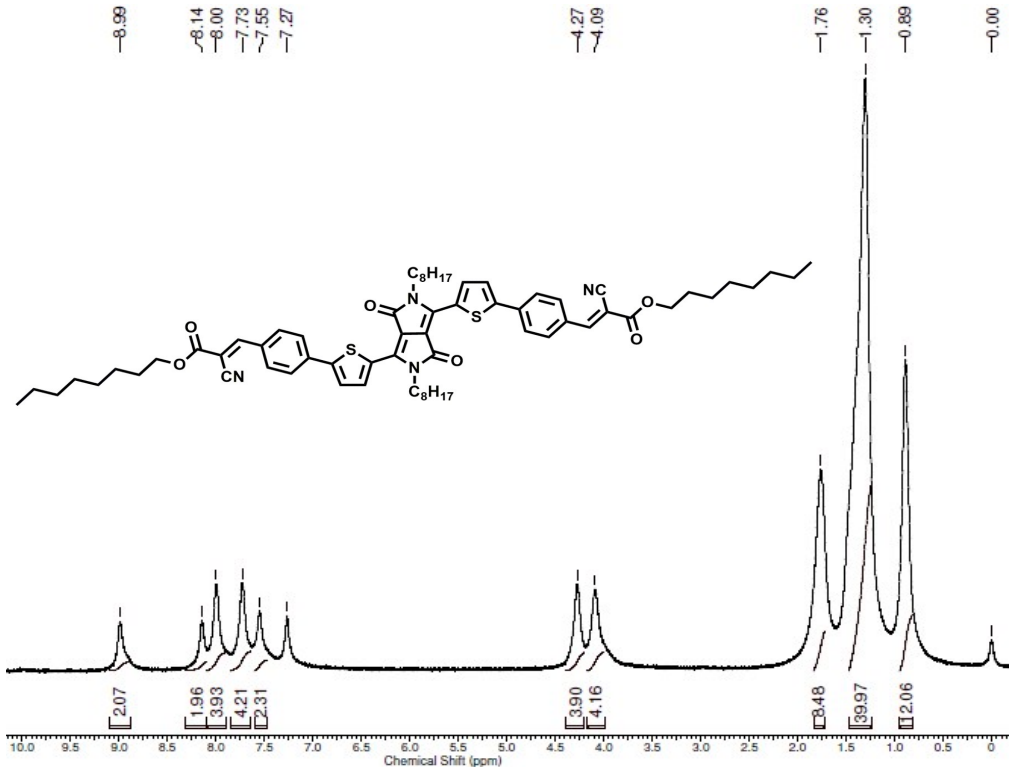



**Fig. S16 [1] H-NMR of compound PDPP-CNEC8 in $CDCl_3$.**

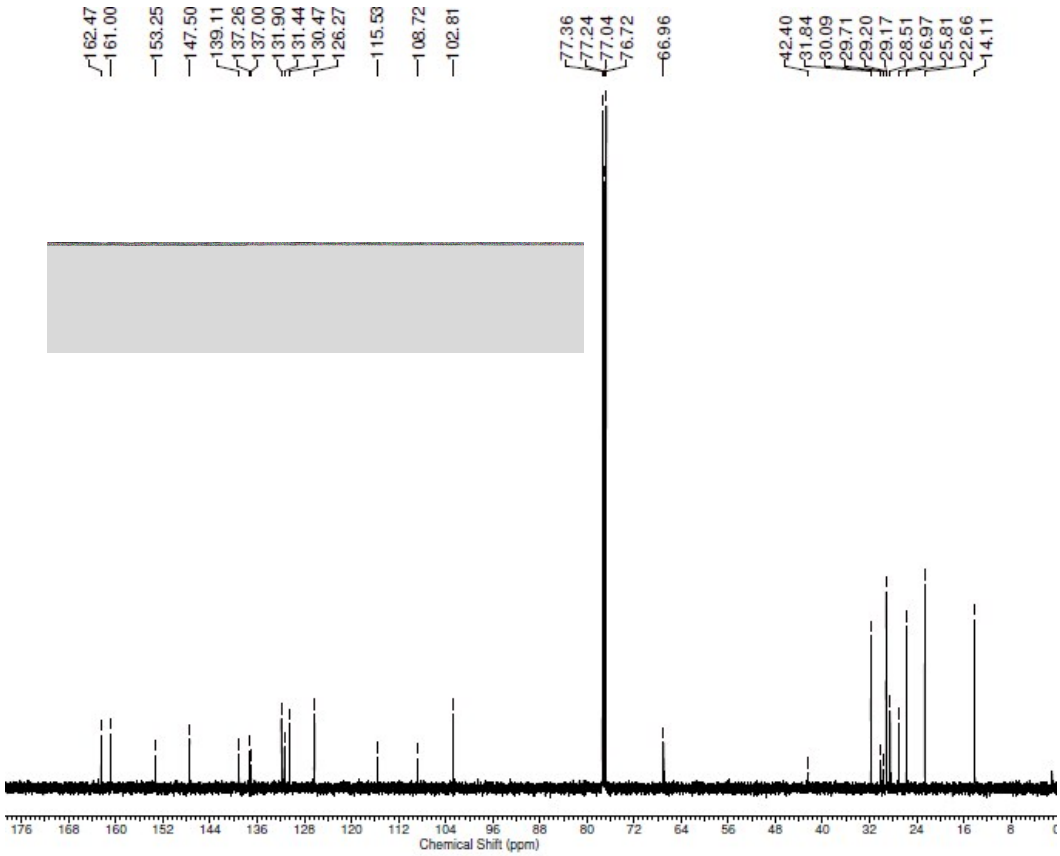
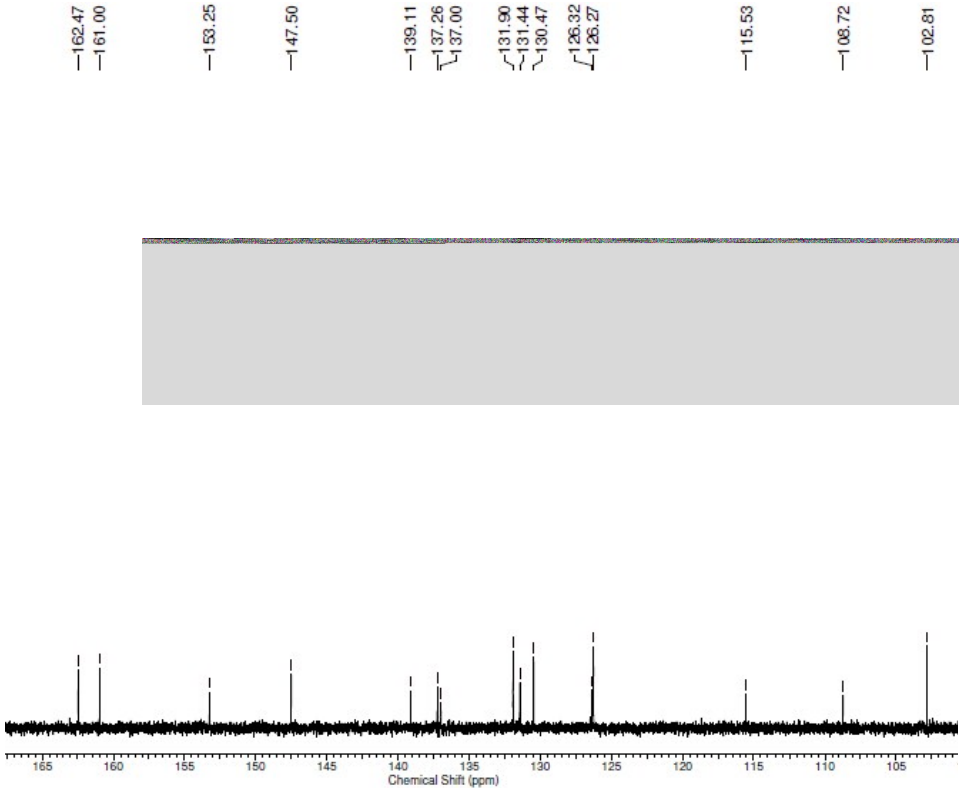



**Fig. S17 [13] C-NMR of compound PDPP-CNEC8 in CDCl3**



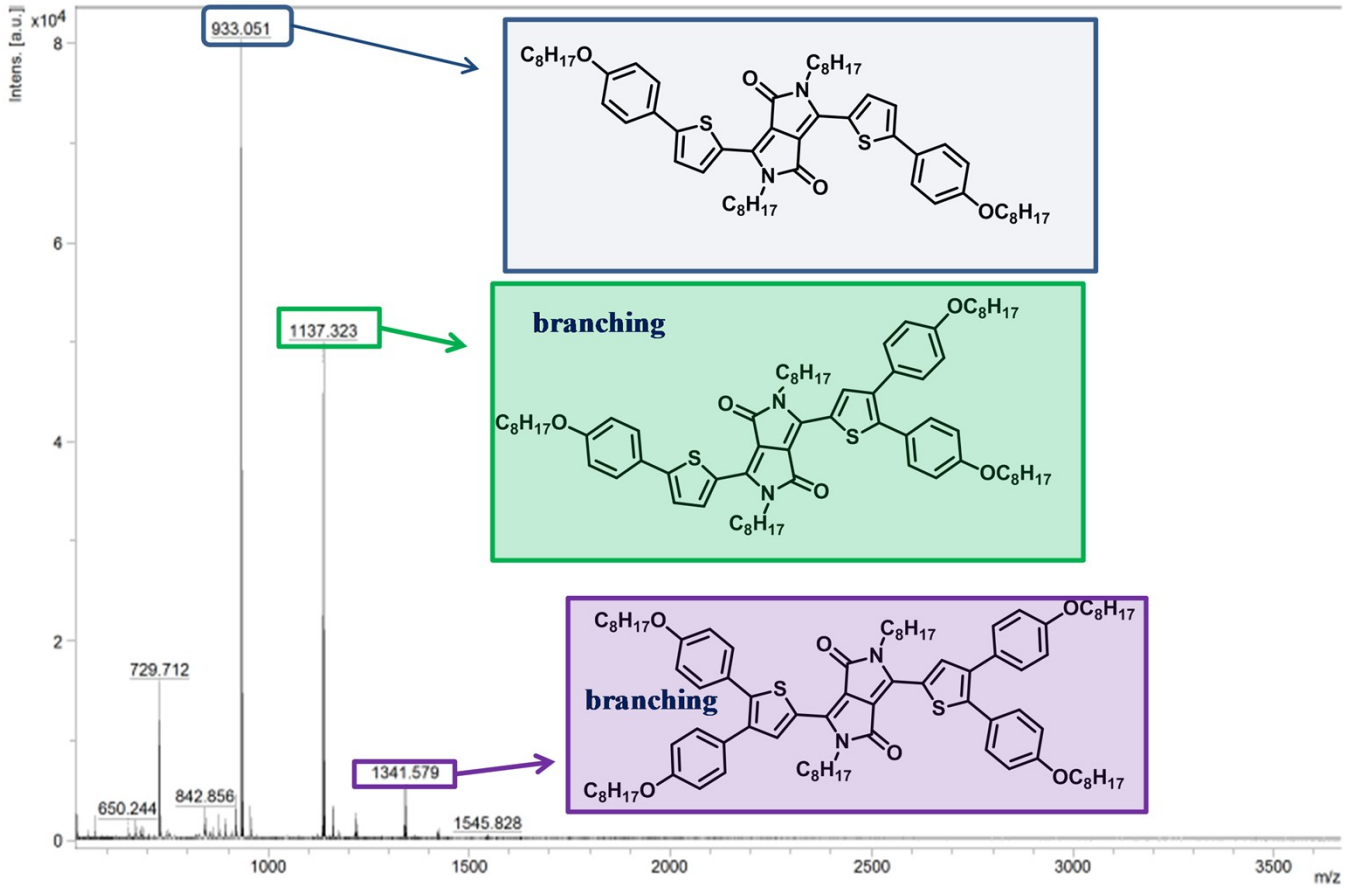



**Fig. S18. MALDI mass spectrum of compound PDPP-OC8 after column chromatograpy, showing some side products formed during direct arylation (the exact position of branching point and regioselectivity on dpp are unknown) .**

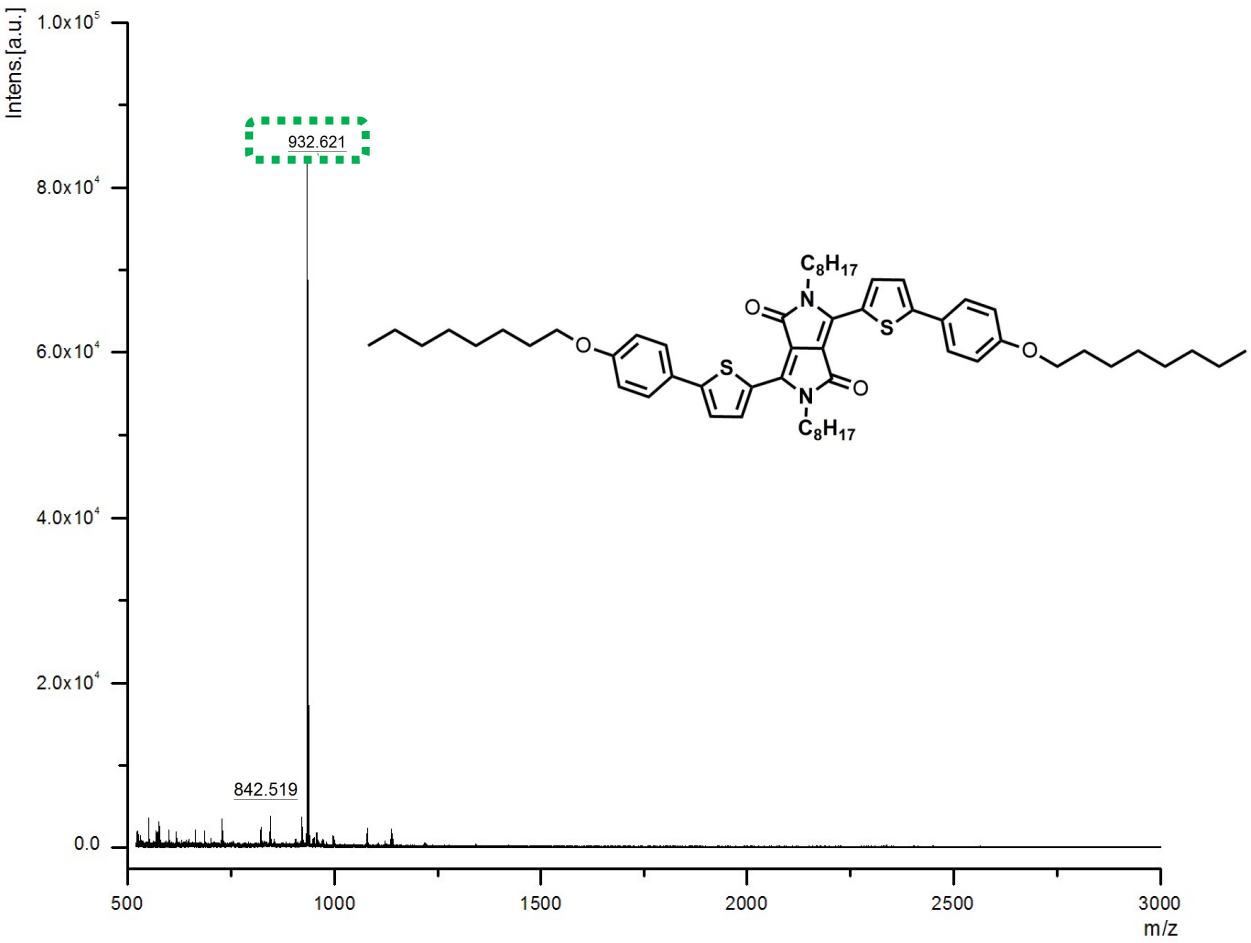



**Fig. S19. MALDI mass spectrum of compound PDPP-OC8 after column chromatograpy followed by recrystallisation thrice with ethyl acetate.**

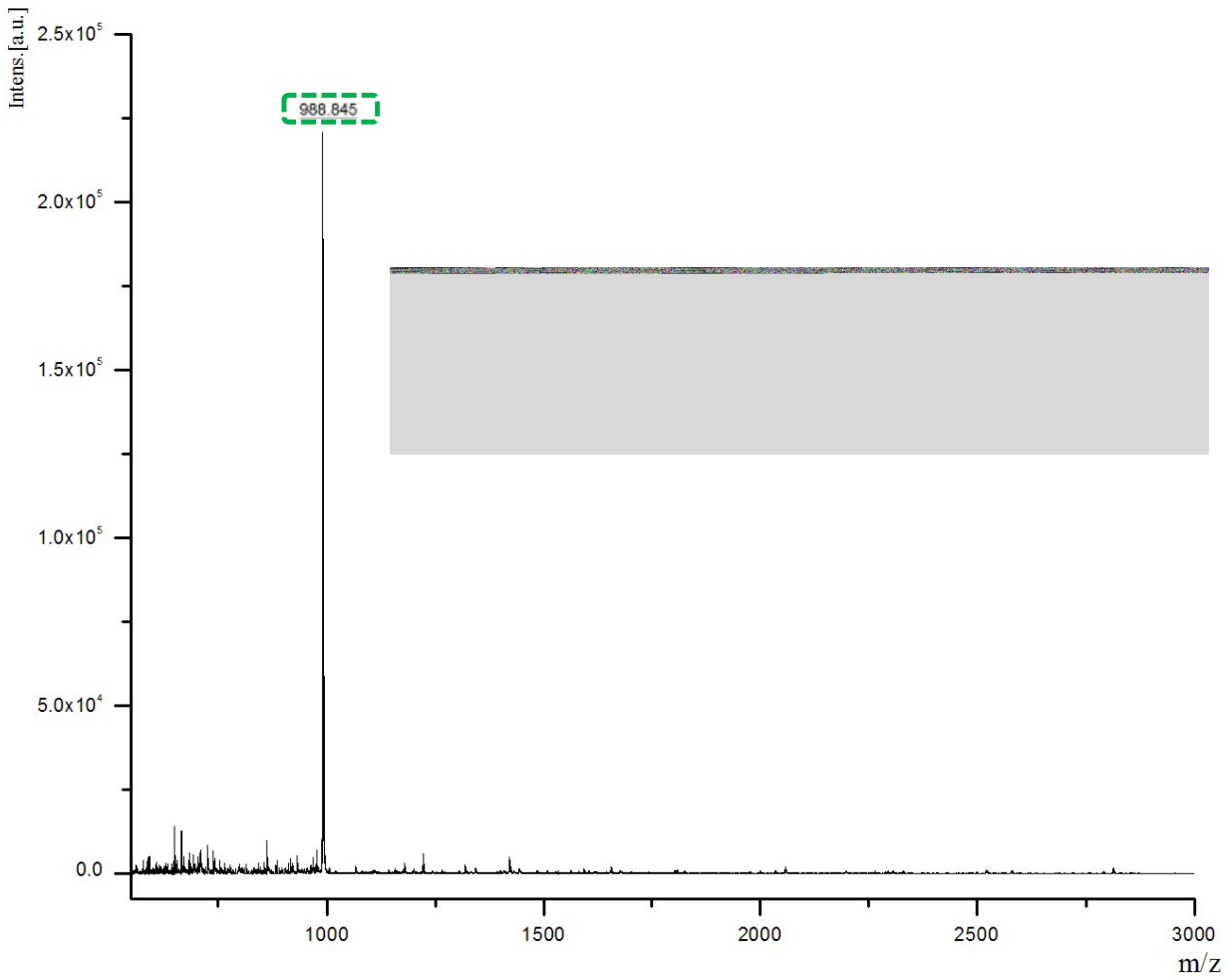



**Fig. S20. MALDI mass spectrum of compound PDPP-EC8 after column chromatograpy followed by recrystallisation thrice with ethyl acetate.**

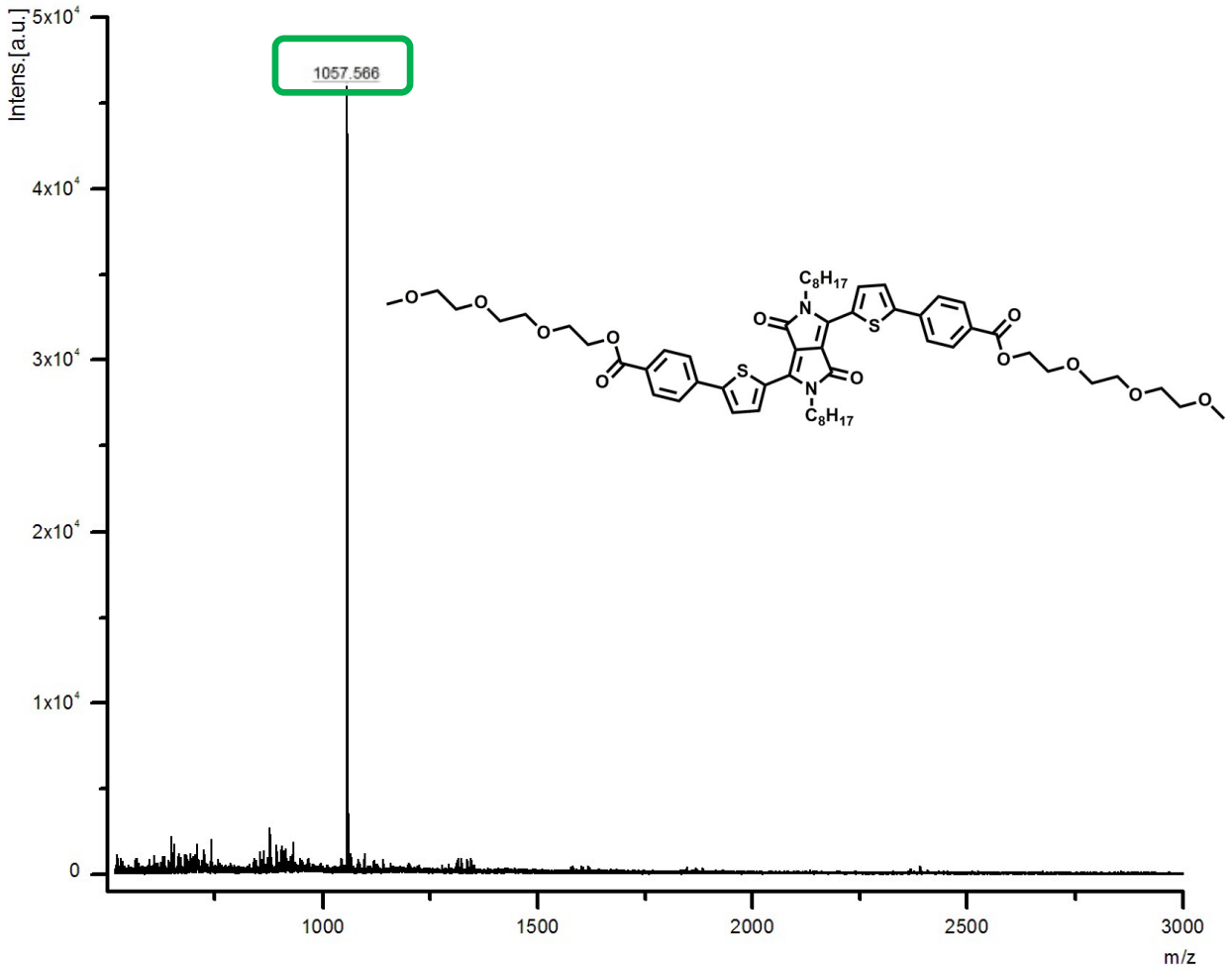



**Fig. S21. MALDI mass spectrum of compound PDPP-EG after column chromatograpy followed by recrystallisation thrice with ethyl acetate.**

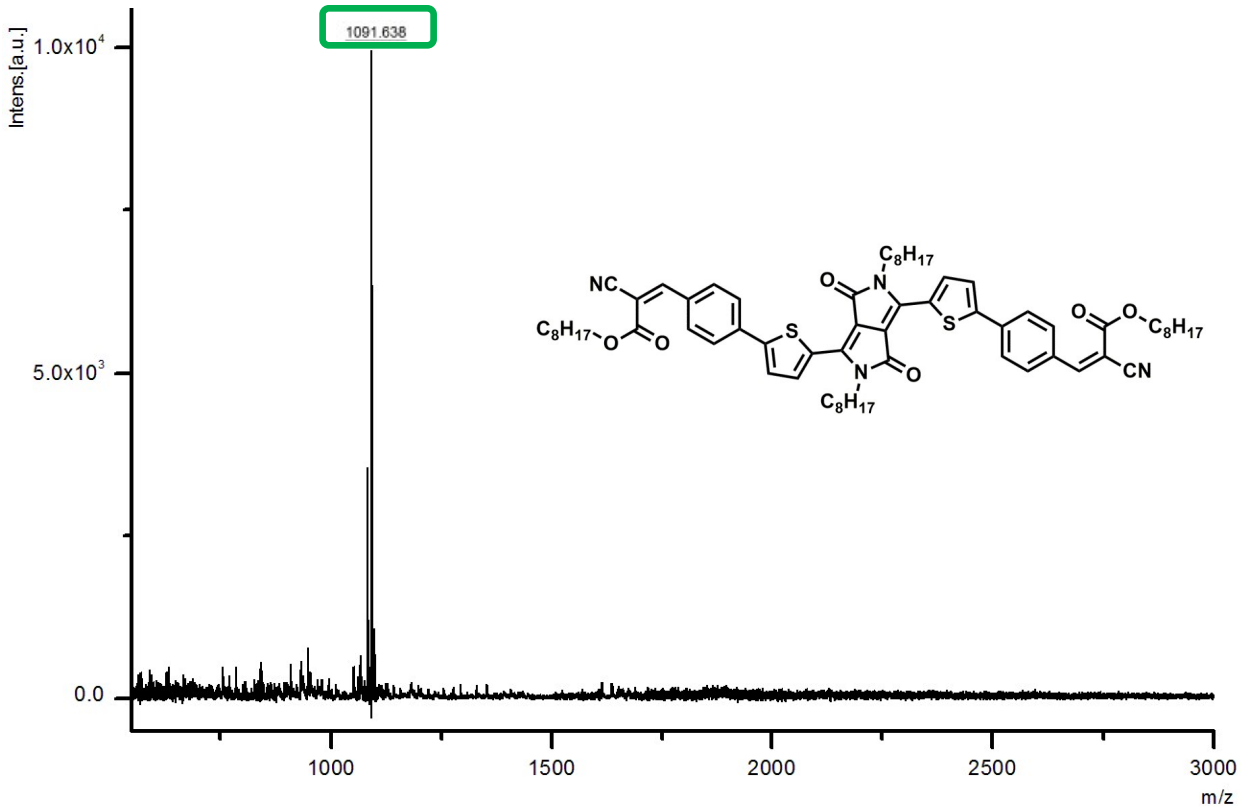



**Fig. S22. MALDI mass spectrum of compound PDPP-CNEC8 after column chromatograpy followed by recrystallisation thrice with ethyl acetate**