

**Two Donor - One Acceptor (2D/1A) Random Terpolymer Comprising of
Diketopyrrolopyrrole Quaterthiophene with Various Donor π -Linkers for Organic
Photovoltaic Application**

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Synthesis

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

In a two-necked round-bottom flask, 11.2 g (100 mmol) *t*-BuOK was taken. To this 6.54 g (60 mmol) 2-thiophene carbonitrile in 50 mL *t*-amyl alcohol was added. The reaction mixture was heated to 110 °C. 2.92 g (20 mmol) dimethyl succinate in 16 ml *t*-amyl alcohol was added dropwise over a period of two hours at 110 °C. Then it was continued for another 2 hours at 110 °C. Then it was cooled to 65 °C and diluted with 100 mL of methanol. The reaction mixture was neutralized with glacial acetic acid, filtered and washed with methanol and warm water. A dark purple solid was obtained with 52% yield and it was used directly for next step without further purification.

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

2.0 g (6.65 mmol) of 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione and 3.65 g (26.63 mmol) of potassium carbonate were dissolved in 50 mL of DMF. The reaction mixture was heated to 110 °C. To this 8.1 g (26.63 mmol) of 2-hexyl-1-bromodecane was added drop by drop. Then the reaction mixture was continued for 24 hours at 110 °C. Then it was cooled poured into 200 ml of water and extracted with chloroform. The organic layer was dried with MgSO₄, filtered and concentrated. Then it was purified by column chromatography using hexane/chloroform (7:3) gave a purple solid with yield (36%). δ_{H} (400 MHz, CDCl₃) 8.87 (2 H, d, *J* 3.7), 7.62 (2 H, d, *J* 4.8), 7.26 (2 H, t, *J* 4.2), 4.01 (4 H, d, *J* 7.6), 1.90 (2 H, s), 1.43 – 1.09 (48 H, m), 0.85 (12 H, dd, *J* 13.9, 6.8). δ_{C} (101 MHz, CDCl₃) 161.76, 140.44, 135.21, 130.46,

129.85, 128.38, 107.95, 46.21, 37.73, 31.88, 31.76, 31.19, 30.00, 29.67, 29.49, 29.29, 26.20, 26.17, 22.66, 22.63, 14.11, 14.08..

Synthesis of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (M1).

In a single neck 100 ml round-bottom flask 1.0 g (1.10 mmol) of **2** was taken and it was dissolved in 50 mL of CHCl₃. To this 432 mg (2.5 mmol) was added in one portion. The reaction mixture was stirred in dark for 48 hours. Then it was poured in water and extracted in chloroform. The crude product was purified by column chromatography using hexane/chloroform (3:7) as an eluent give purple product with 60% yield. δ H (400 MHz, CDCl₃) 8.62 (2 H, d, J 4.1), 7.22 (2 H, d, J 4.1), 3.92 (4 H, d, J 7.6), 1.88 (2 H, s), 1.44 – 1.07 (48 H, m), 0.86 (12 H, d, J 6.3)^b. δ C (101 MHz, CDCl₃) 161.39, 139.41, 135.31, 131.42, 131.17, 118.97, 108.02, 46.33, 37.75, 31.88, 31.76, 31.17, 29.98, 29.65, 29.50, 29.29, 26.17, 26.14, 22.68, 22.63, 14.12, 14.08. MS (MALDI) : Calculated for C₄₆H₇₀Br₂N₂O₂S₂, 906.998, found: 907.087.

Synthesis of 3,3'''-dihexyl-2,2':5',2'':5'',2'''-quaterthiophene (3).

To a two-necked round-bottom flask 2.0 g (6.2 mmol) of 5,5'-dibromo-2,2'-bithiophene and 3.8 g (13 mmol) was taken and it was dissolved in 50 mL of THF. To this 2 M aqueous K₂CO₃ (10 mL) and tetrakis(triphenylphosphine)palladium(0) 358mg (0.31 mmol) was added and it was purged with N₂ thoroughly. Then it was allowed to stirred overnight at 70°C. After that the reaction mixture was poured in water and extracted in DCM. The organic layer was dried with MgSO₄, filtered and concentrated. Then it was purified by column chromatography using hexane/chloroform (9:1) gave a yellow viscous liquid with yield of 80%. δ H (400 MHz, CDCl₃)

7.20 (2 H, d, *J* 5.2), 7.15 (2 H, d, *J* 3.7), 7.05 (2 H, d, *J* 3.8), 6.97 (2 H, d, *J* 5.2), 2.95 – 2.66 (4 H, m), 1.77 – 1.62 (4 H, m), 1.49 – 1.19 (12 H, m), 0.92 (6 H, t, *J* 6.8); δ C (101 MHz, CDCl₃) 139.90, 136.83, 135.37, 130.36, 130.10, 126.55, 123.87, 123.84, 31.70, 30.67, 29.32, 29.24, 22.65, 14.11.

Synthesis of **5**, 5'''-dibromo-3,3'''-dihexyl-2,2':5',2'':5'',2'''-quaterthiophene (**M2**).

In a single neck 100 ml round-bottom flask 1.0 g (2 mmol) of **3** was taken and it was dissolved in a 1:1 mixture of 50 mL of CHCl₃/acetic acid. At ice cold condition 747 mg (4.2 mmol) of NBS was added in portion wise over the Course of 15 minutes. Then it was stirred at room temp for 18 hours. Then it was poured in water and extracted in chloroform. The crude product was purified by column chromatography using hexane/chloroform (9:1) as an eluent gives a yellow powder as product with 60% yield. δ H (400 MHz, CDCl₃) 7.11 (2 H, d, *J* 3.8), 6.97 (2 H, d, *J* 3.8), 6.91 (2 H, s), 2.89 – 2.54 (4 H, m), 1.61 (4 H, dd, *J* 14.7, 7.1), 1.46 – 1.24 (12 H, m), 0.90 (6 H, t, *J* 6.8). δ C (101 MHz, CDCl₃) 140.54, 137.05, 134.09, 132.73, 131.73, 126.97, 124.01, 110.68, 31.62, 30.51, 29.24, 29.12, 22.60, 14.11. MS (MALDI) :Calculated for C₂₈H₃₂Br₂S₄, 656.621, found: 656.983

Synthesis of Polymers

Synthesis of P4TFDPP

A mixture of **M1** 180 mg (0.2 mmol), **M2** 131 mg (0.2 mmol) and 9, 9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester 200 mg (0.4 mmol) was taken and it was dissolved in 10 mL of toluene. To this 2M aqueous potassium carbonate (2 mL), Aliquat (1 drop) and tetrakis(triphenylphosphine)palladium 36 mg (32 μ mol) was added and purged with N₂

thoroughly. The solution was stirred and refluxed for 24 hours. Then it was cooled to room temperature and precipitated in methanol. The crude polymer was purified using Soxhlet extraction by methanol, acetone and chloroform. The chloroform fraction was concentrated and dried in vacuum to recover the target polymer as a shiny green solid (yield 61%). δ_{H} (400 MHz, CDCl_3) 8.99 (2 H, br), 7.89 – 7.39 (14 H, br), 7.15 (4 H, br), 4.13 (4 H, br), 2.84 (4 H, br), 2.05 (2 H, br), 1.90 (8 H, br), 1.57 – 0.96 (102 H, br), 0.95 – 0.56 (30 H, br). Elemental Analysis, calculated (%) C, 77.93; H, 8.86; N, 1.47; S, 10.07; Found: C, 76.96; H, 8.81; N, 1.29; S, 10.28

Synthesis of P5TDPP

A mixture of **M1** 221 mg (0.24 mmol), **M2** 160 mg (0.24 mmol) and 2,5-Bis(trimethylstannyl)thiophene 200 mg (0.48 mmol) was taken and it was dissolved in 10 mL of toluene. To this tetrakis (triphenylphosphine) palladium 28 mg (24 μmol) was added and purged with N_2 thoroughly. The solution was stirred and refluxed for 24 hours. Then it was cooled to room temperature and precipitated in methanol. The crude polymer was purified using Soxhlet extraction by methanol, acetone and chloroform. The chloroform fraction was concentrated and dried in vacuum to recover the target polymer as a dark brown solid (yield 58%). δ_{H} (400 MHz, CDCl_3) 8.91 (2 H, br), 7.53 (2 H, br), 7.35 (2 H, br), 7.20 – 6.89 (8 H, br), 4.06 (4 H, br), 2.77 (4 H, br), 2.34 (2 H, br), 2.10 – 1.98 (4 H, br), 1.25 (60 H, br), 0.97 – 0.76 (18 H, br). Elemental Analysis, calculated (%) C, 69.84; H, 7.72; N, 1.99; S, 18.19; Found: C, 70.21; H, 7.81; N, 2.09; S, 19.08

Synthesis of P4TVDPP

A mixture of **M1** 149 mg (0.165 mmol), **M2** 108 mg (0.165 mmol) and trans-1,2-Bis(tributylstannyl)ethane 200 mg (0.33 mmol) was taken and it was dissolved in 10 mL of

toluene. To this tetrakis (triphenylphosphine) palladium 30 mg (26 μ mol) was added and purged with N₂ thoroughly. The solution was stirred and refluxed for 24 hours. Then it was cooled to room temperature and precipitated in methanol. The crude polymer was purified using Soxhlet extraction by methanol, acetone and chloroform. The chloroform fraction was concentrated and dried in vacuum to recover the target polymer as a dark brown solid (yield 53%). δ_H (400 MHz, CDCl₃) 8.91 (2 H, br), 7.95 – 7.31 (2 H, br), 7.20 – 6.66 (10 H, br), 4.03 (4 H, br), 2.75 (4 H, br), 1.25 (84 H, br). Elemental Analysis, calculated (%) C, 72.17; H, 8.39; N, 2.16; S, 14.82; Found: C, 72.61; H, 8.81; N, 2.29; S, 14.28

Synthesis of P4TPDPP

A mixture of **M1** 206 mg (0.22 mmol), **M2** 131 mg (0.225 mmol) and 1,4-Benzenediboronic acid bis(pinacol) ester 150 mg (0.45 mmol) was taken and it was dissolved in 10 mL of toluene. To this 2M aqueous potassium carbonate (2 mL), Aliquat (1 drop) and tetrakis(triphenylphosphine)palladium 36 mg (32 μ mol) was added and purged with N₂ thoroughly. The solution was stirred and refluxed for 24 hours. Then it was cooled to room temperature and precipitated in methanol. The crude polymer was purified using Soxhlet extraction by methanol, acetone and chloroform. The chloroform fraction was concentrated and dried in vacuum to recover the target polymer as a dark brown solid (yield 48%). δ_H (400 MHz, CDCl₃) 8.93 (2 H, br), 7.54 – 7.36 (6 H, br), 7.14 – 6.98 (10 H, br), 4.00 (4 H, br), 2.77 (4 H, br), 2.37-2.33 (2 H, br), 2.05 – 2.03 (4 H, br), 1.25 (60 H, br), 0.90 – 0.86 (20 H, br). Elemental Analysis, calculated (%) C, 73.87; H, 8.07; N, 2.00; S, 13.76; Found: C, 72.97; H, 6.81; N, 2.39; S, 13.28

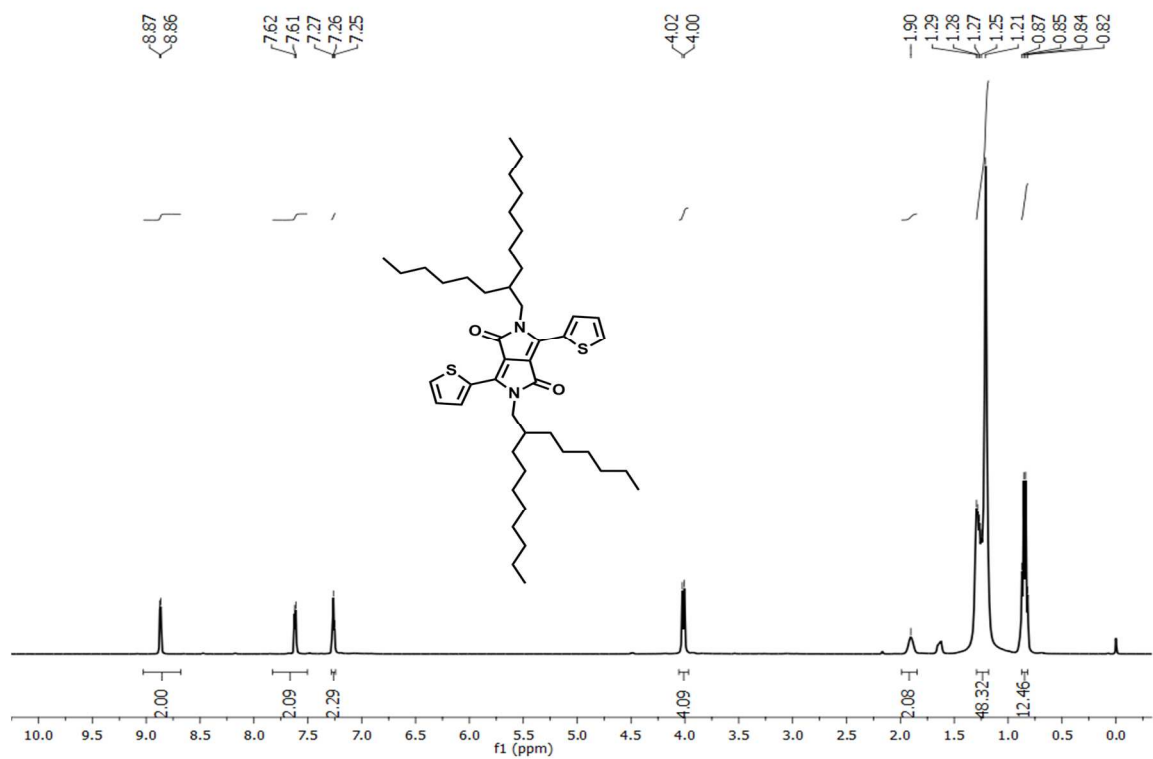


Fig. S1 ¹H-NMR of compound 2 in CDCl₃.

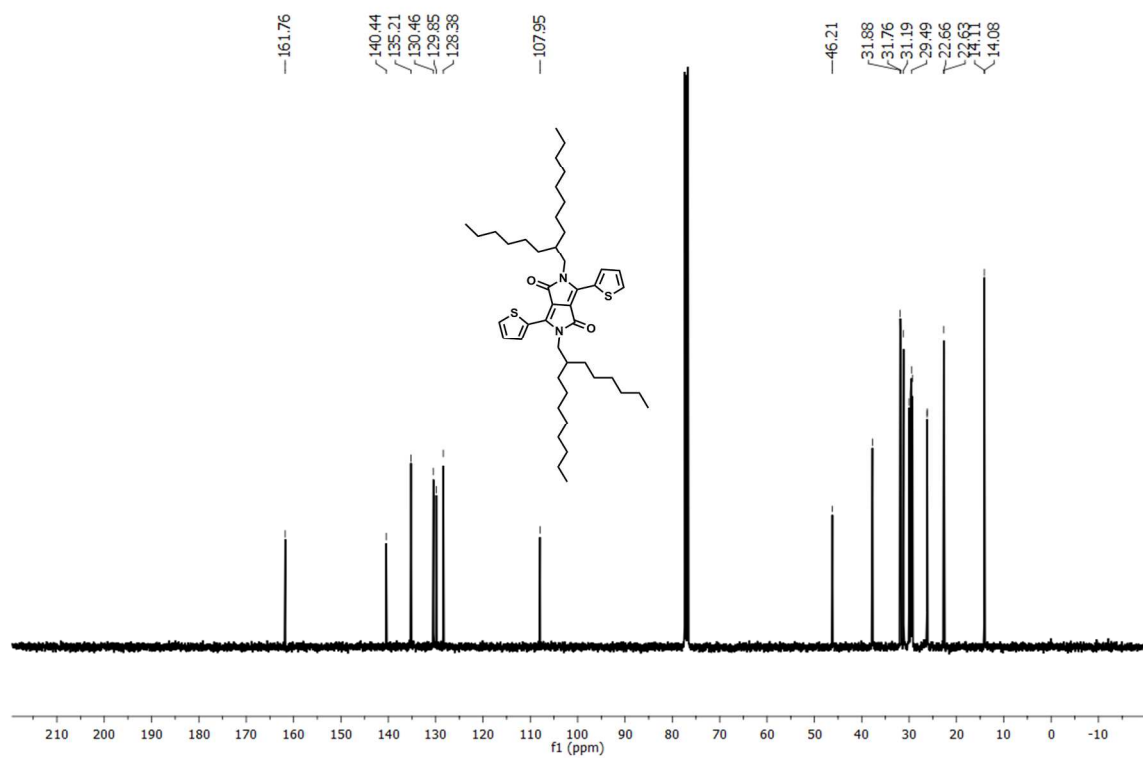


Fig. S2 ¹³C-NMR of compound 2 in CDCl₃.

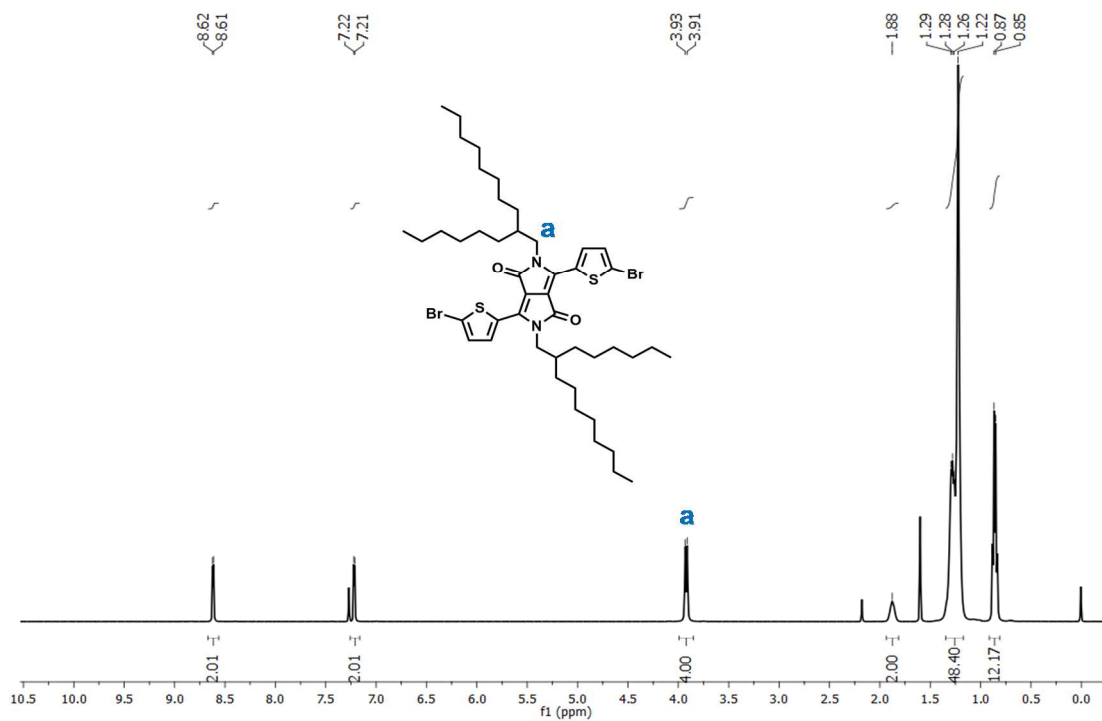


Fig. S3 ¹H-NMR of monomer M1 in CDCl₃.

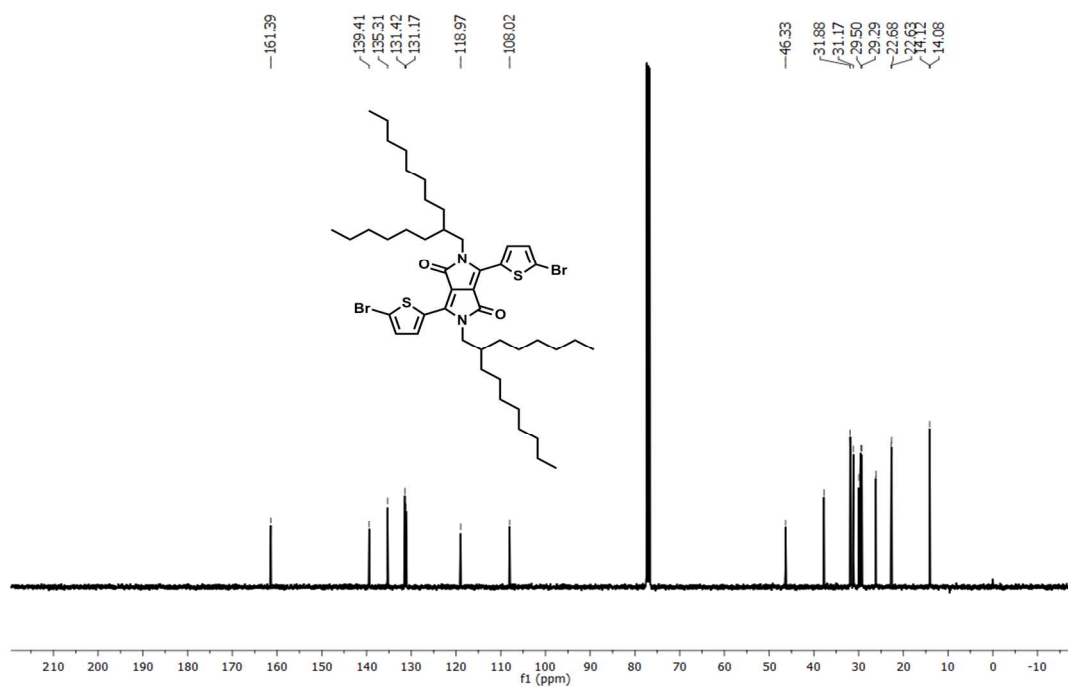


Fig. S4 ¹³C-NMR of monomer M1 in CDCl₃.

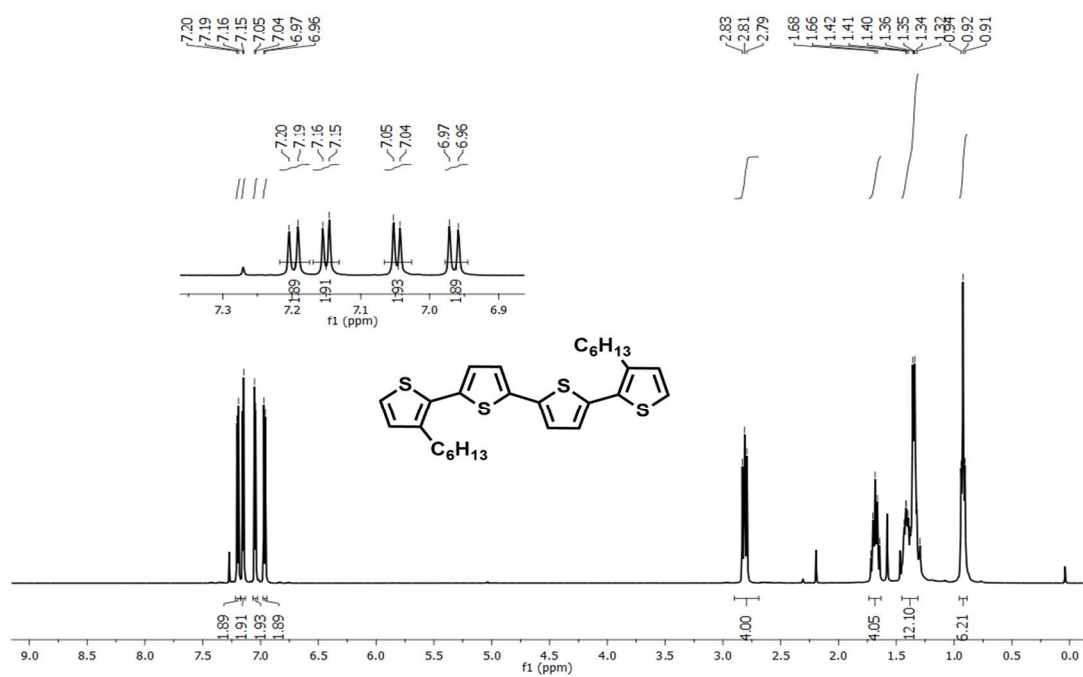


Fig. S5 ¹H-NMR of compound 3 in CDCl₃.

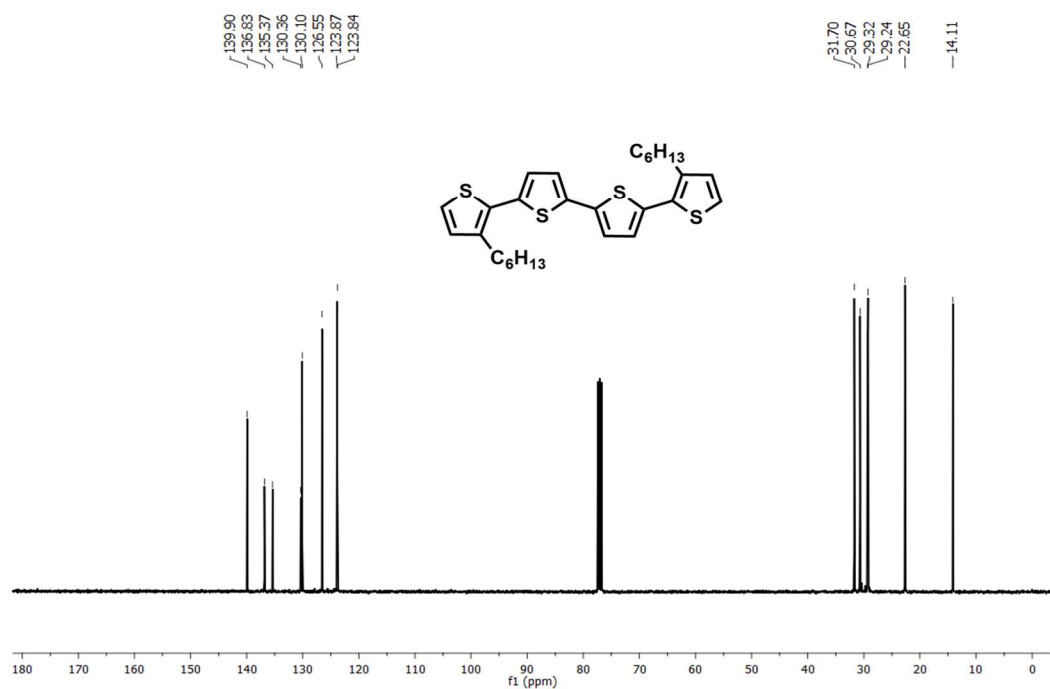


Fig. S6 ¹³C-NMR of compound 3 in CDCl₃.

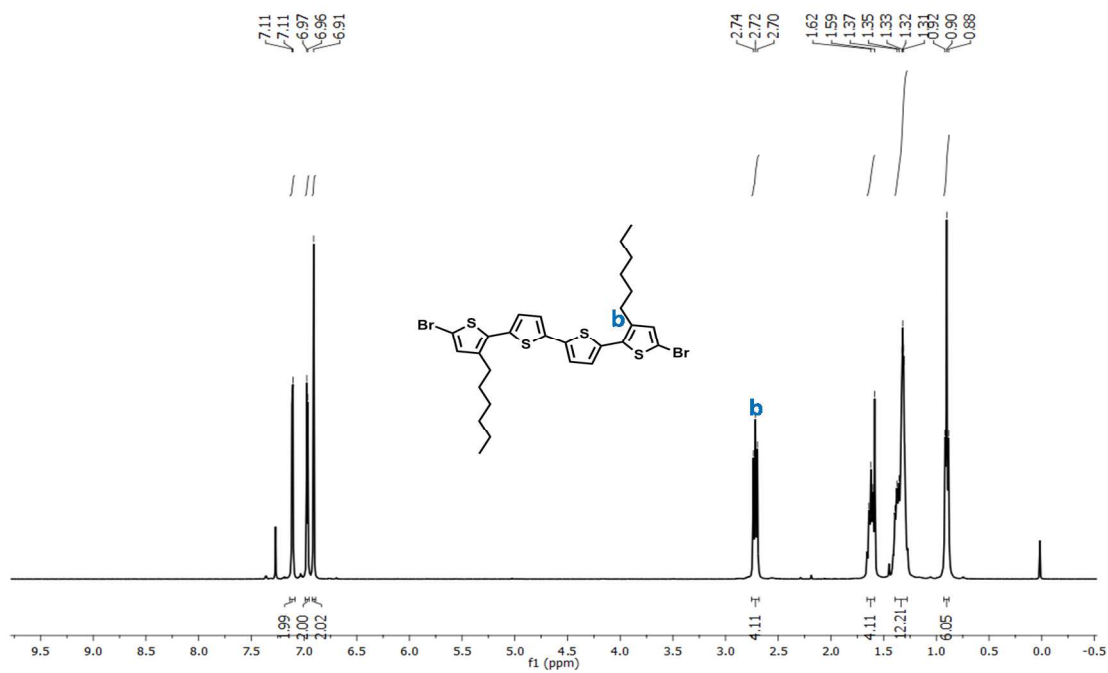


Fig. S7 ¹H-NMR of monomer M2 in CDCl₃.

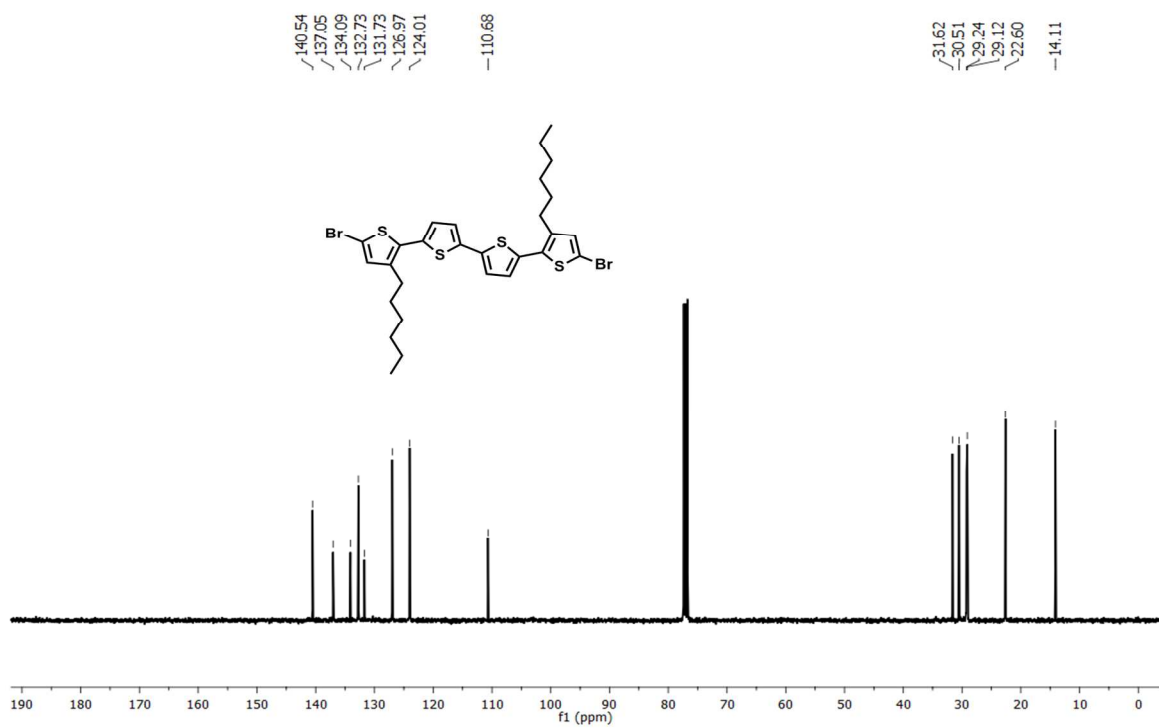


Fig. S8 ¹³C-NMR of monomer M2 in CDCl₃.

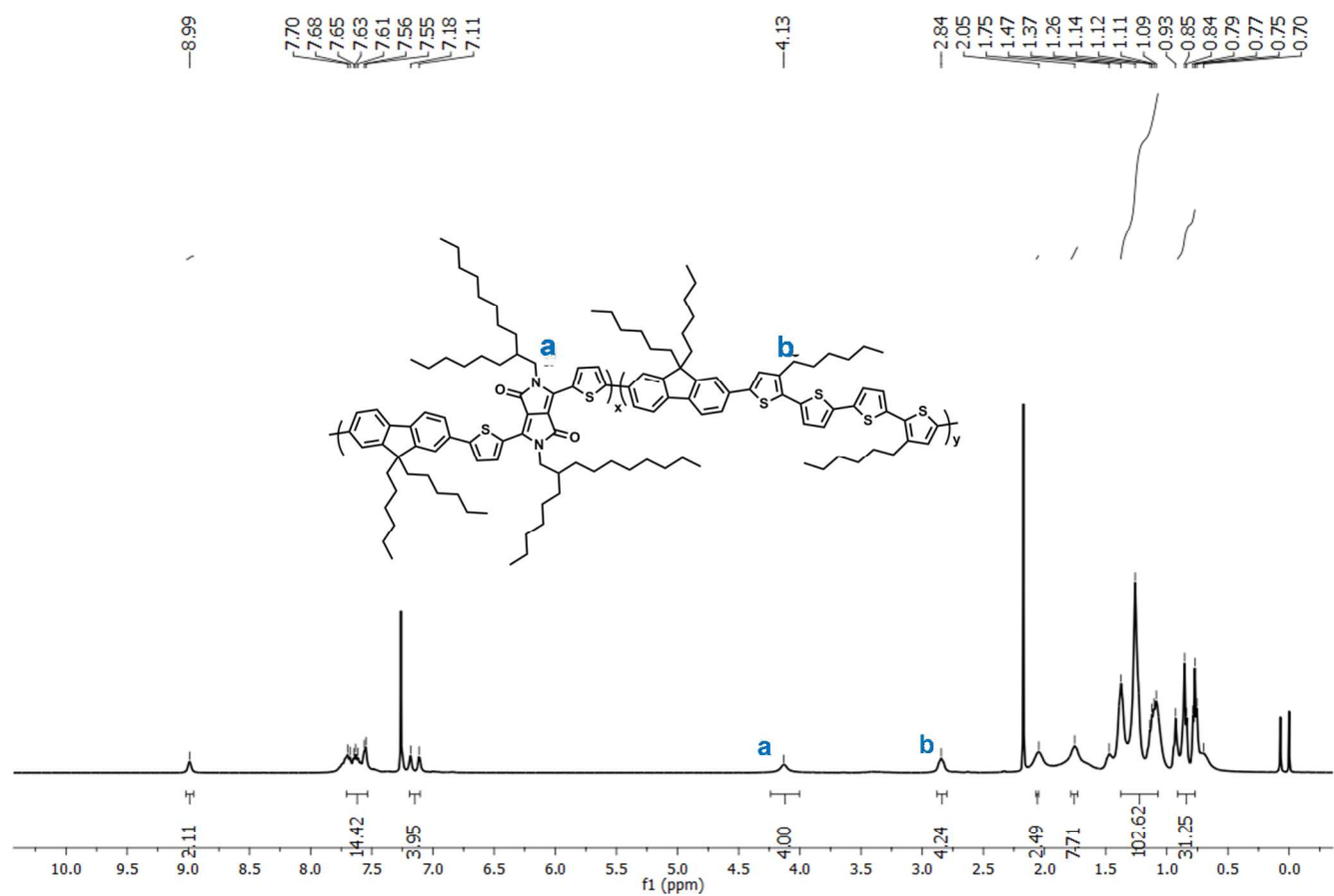


Fig. S9 ^1H -NMR of polymer P4TFDPP in CDCl_3 .

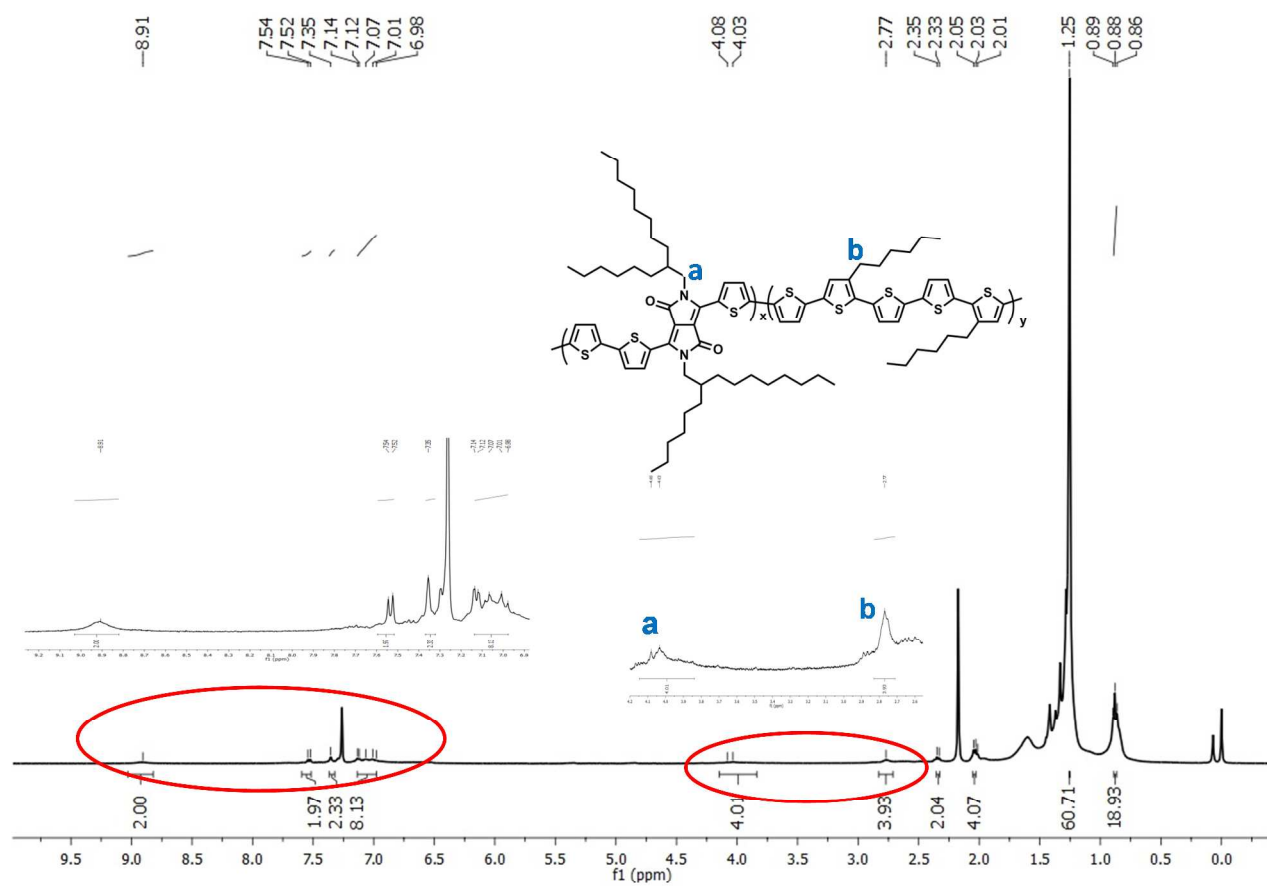


Fig. S10 ^1H -NMR of polymer P5TDPP in CDCl_3 .

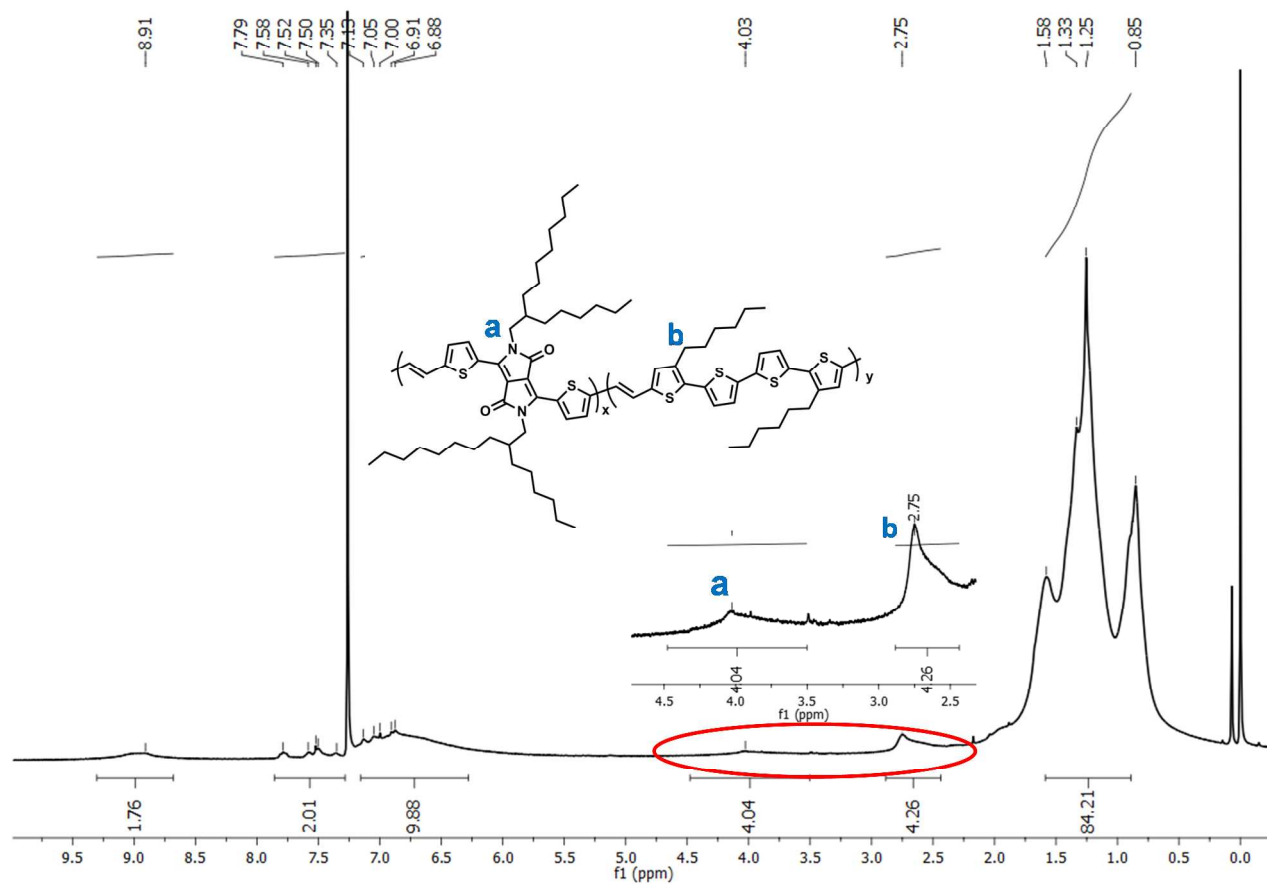


Fig. S11 ^1H -NMR of polymer P4TVDPP in CDCl_3 .

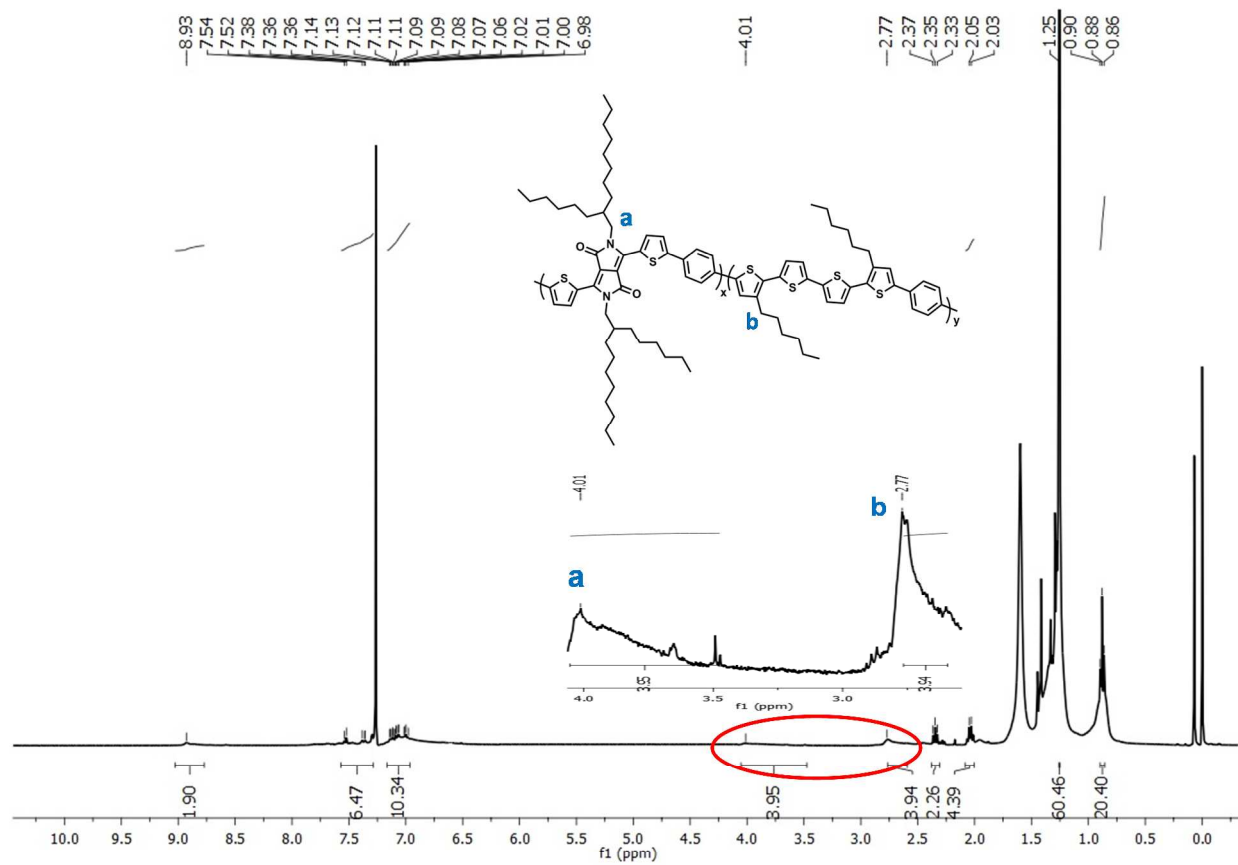


Fig. S12 ^1H -NMR of compound P4TPDPP in CDCl_3 .

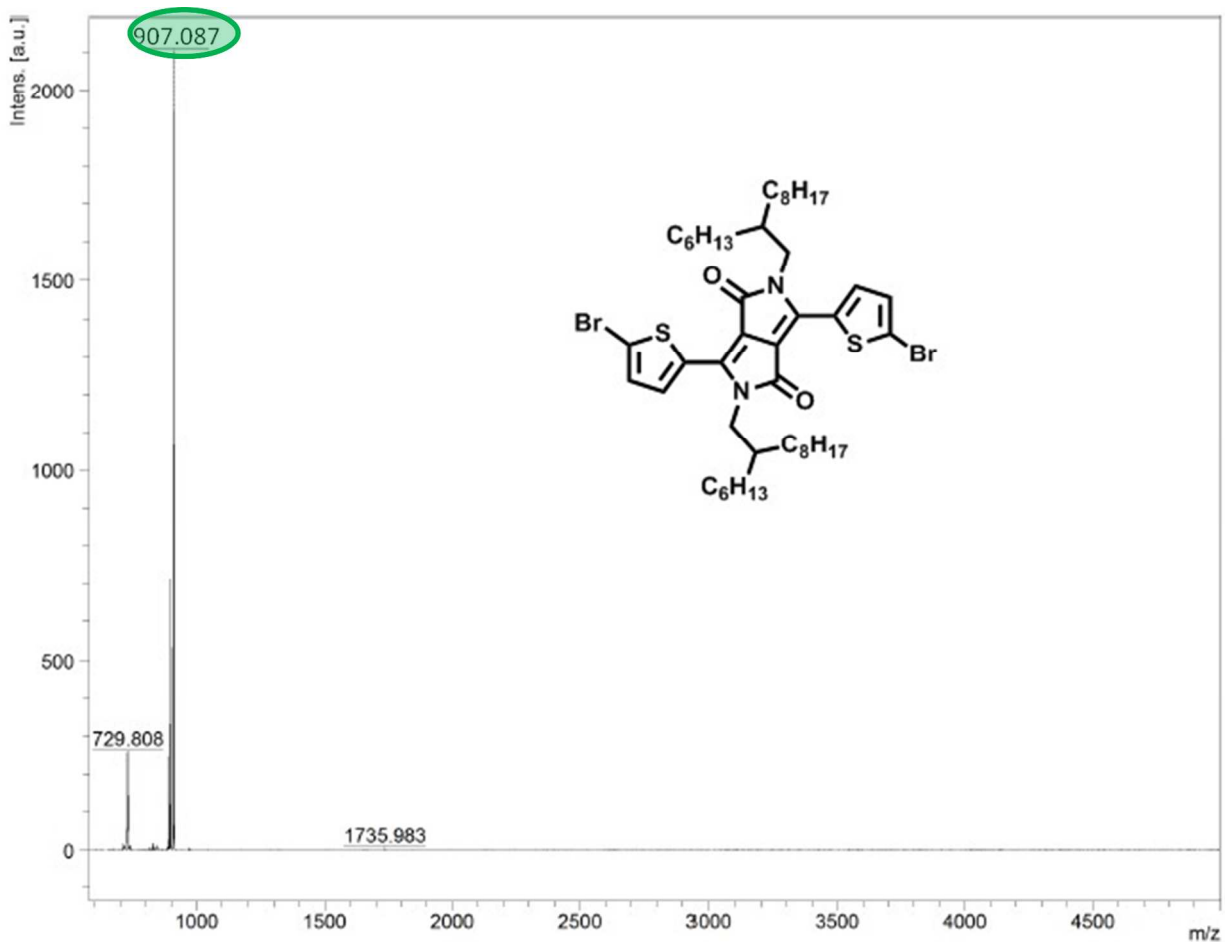


Fig. S13 MALDI mass spectrum of monomer M1.

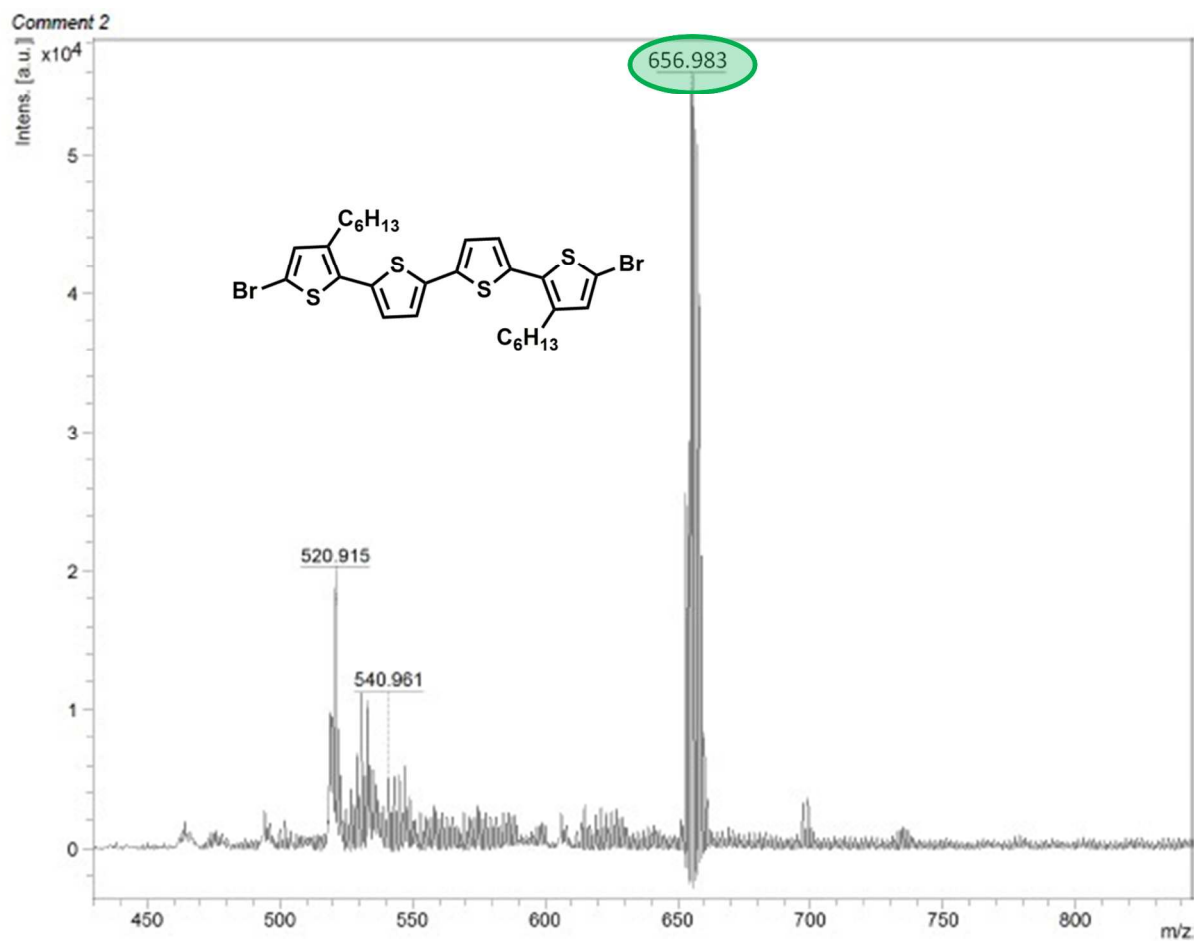


Fig. S14 · MALDI mass spectrum of monomer M2.