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Supporting information

The synthesis and photovoltaic properties of A-D-A-type small molecules containing diketopyrrolopyrrole terminal units

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1. The UV-Vis absorption of compound A in chloroform.

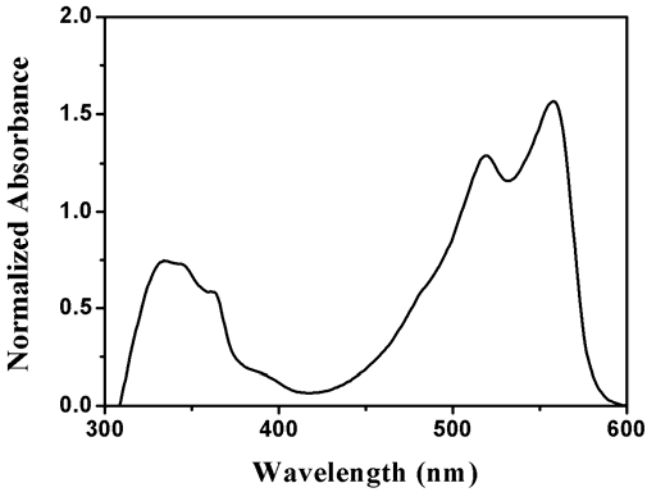


Fig.1 The UV-Vis absorption of compound A in chloroform.

2. I-V characteristic of the PV device with P3HT as donor.

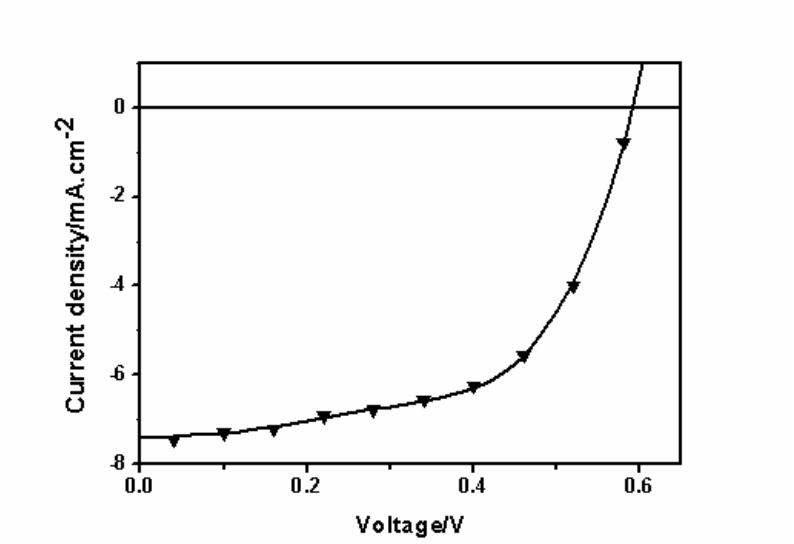
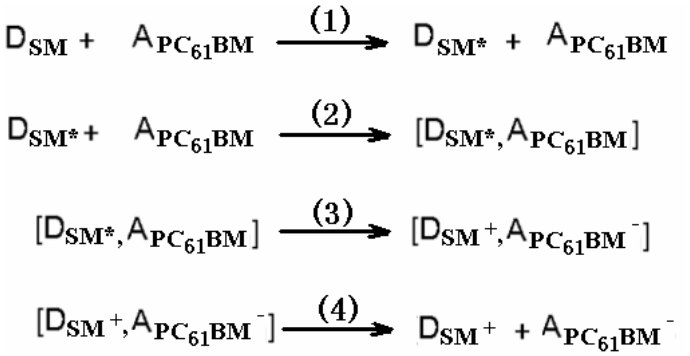


Fig.2 I-V characteristics of the PV device with the structure of ITO/PEDOT:PSS/P3HT:$PC_{61}BM$/LiF/Al under an illumination of AM 1.5 G (80 mW cm^{-2}).

3. Mechanism for photoinduced charge separation.



Scheme. 1 Mechanism for photoinduced charge separation of synthesized donor molecules (D_{SM}) and acceptor PCBM (A_{PCBM}): (1) photoexcitation of D_{SM}; (2) diffusion of the exciton and formation of an encounter pair; (3) electron transfer to form a geminate pair; (4) charge separation.

The elementary steps in the process of fluorescence quenching were described as following: (1) absorption of light and generation of excitons (D_{SM*}); (2) diffusion of the exciton and formation of an encounter pair ([D_{SM*},A_{PCBM}]); (3) electron transfer within the encounter pair to form a geminate pair ([D_{SM+},A_{PCBM}-]); (4) the geminate pair completely separated to cause the fluorescence quenching.

4. Synthetic procedures

3,6-dibromocarbazole [14a] A solution of carbazole (1.5 g, 9.0 mmol), dried silica gel (30 g), N-bromosuccinimide (NBS) (3.21 g, 18 mmol) in dichloroethane (220 mL) was stirred at room temperature under N_2 atmosphere in the dark for 18 h. After filtered, the filtrate was washed with brine (3×100 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The crude product was purified by recrystallization with ethanol to afford compound **1** as a light gray solid (2.27 g, 78%). M.p.: 204-208 °C.

3,6-dibromo-9-octylcarbazole (1) [14b] A solution of compound 1 (2.51 g, 7.7 mmol), $Bu_4N^+Br^-$ (0.10 g, 0.30 mmol), 1-bromooctane (2.4 g, 12.5 mmol), potassium hydroxide (0.82 g, 14.7 mmol) in acetone (25 mL) was refluxed for 6 h. After being cooled to room temperature, the mixture was filtered and the solvent was removed under reduced pressure. Then the crude product was purified by recrystallization with ethanol to afford compound **2** as a white solid (3.21 g, 95%). ^{1}H-NMR ($CDCl_3$, ppm, 400 MHz) δ = 8.13 (d, *J* = 2.0 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 2.0 Hz, 2H), 4.23 (t, *J* = 7.2 Hz, 2H), 1.85-1.78 (m, 2H), 1.25-1.22 (m, 10H), 0.86-0.82 (m, 3H). M.p.: 84-87 °C.

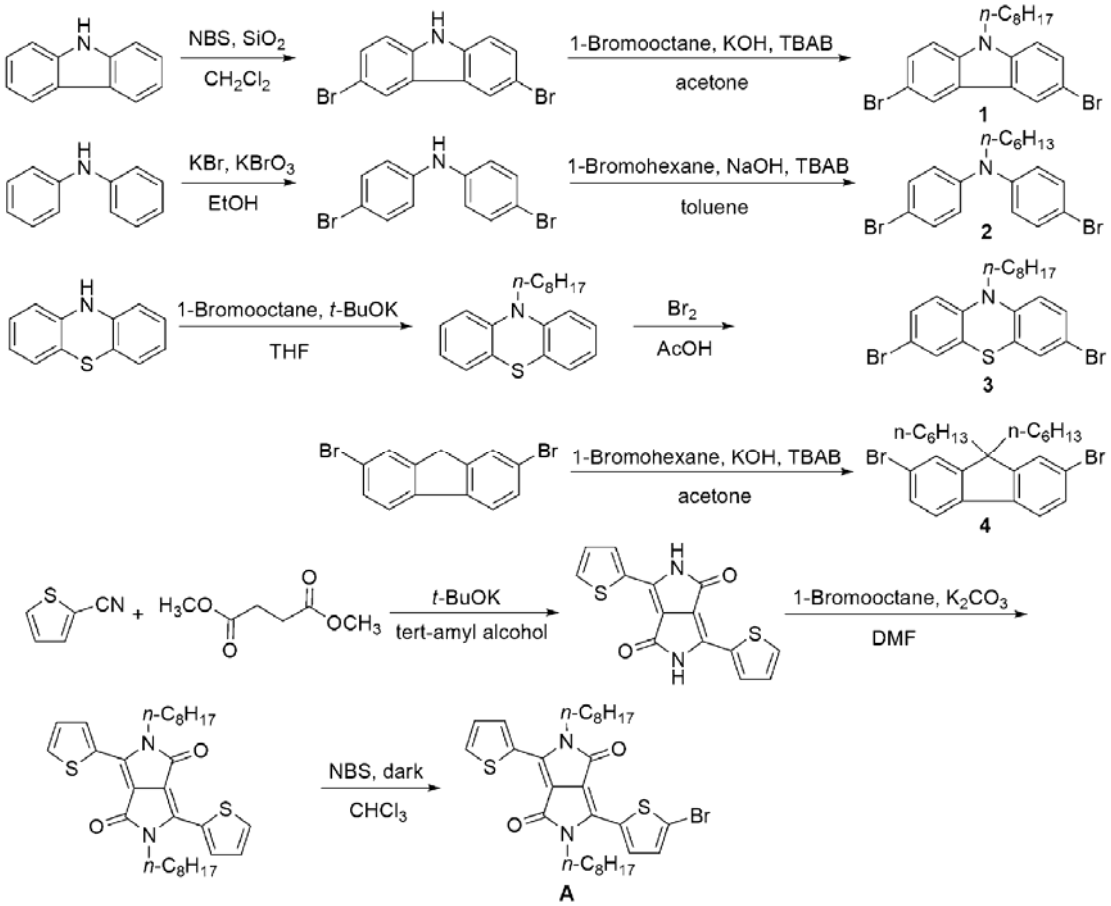


Fig 3. Synthetic routes of dibromo-donors and compound A

Bis(4-bromophenyl)amine [15] A solution of diphenylamine (0.51 g, 3.0 mmol), potassium bromide (0.52 g, 4.4 mmol), potassium bromate (0.37 g, 2.2 mmol) in acetic acid (30 mL) was heated at 100 °C for 24 h. After the mixture was cooled to room temperature, 10 mL of 0.2 M aqueous solution of sodium sulfite was added. The mixture was then extracted with chloroform three times (3×20 mL). The combined organic layer was washed by deionized water and dried with anhydrous Na_2SO_4. After solvent evaporation, the crude product was purified by silica gel chromatography using a mixture of hexane/dichloromethane (2:1 v/v) as eluent. The compound **3** was obtained as a light gray solid in 65% yield (0.64 g). M.p.: 106-109 °C.

Bis(4-bromophenyl)hexylamine (2)[15] To a solution of compound 5 (0.98 g, 3.0 mmol), $Bu_4N^+Br^-$(0.19 g, 0.60 mmol) in toluene (15 mL) and 50 wt% NaOH aqueous solution (15 mL), 1-bromohexane (0.59 g, 3.6 mmol) was added by a syringe. The mixture was then refluxed for 24 h under stirring. After this mixture was cooled to room temperature, the organic layer was separated and the water layer was extracted with dichloromethane three times. The combined organic layer was washed with $NaHCO_3$ and water and then dried over anhydrous Na_2SO_4. The crude product was purified by a silica gel chromatography using hexane/dichloromethane (8:1 v/v) as eluent. Compound **4** was obtained as a white solid in 65% yield (0.81 g). ^{1}H-NMR ($CDCl_3$, ppm, 400 MHz) δ = 7.34 (d, *J* = 9.2 Hz, 4H), 6.84 (d, *J* = 8.8 Hz, 4H), 3.60 (t, *J* = 7.6 Hz, 2H), 1.64-1.56 (m, 2H), 1.32-1.25 (m, 5H), 0.89-0.85 (m, 4H)

10-Octyl-phenothiazine [13b] To a solution of 10H-phenothiazine (0.99 g, 5.0 mmol) in dry THF (10 mL), potassium tert-butoxide (0.62 g, 5.53 mmol)was added. After stirred at room temperature for 2h, 1-bromooctane (1.93 g, 10 mmol) was added by syringe, then the mixture was stirred at 66 °C for 3 h. After cooling to room temperature, the crude product was filtrated through a short plug of silica gel, and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography using hexane as eluent to afford compound **5** as a yellow oil (0.68 g, 50%).

3,7-Dibromo-10-Octyl-phenothiazine (3)[13b] To a solution of compound 5 (3.1 g, 10 mmol) in acetic acid (3.8 mL), bromine (0.51 mL, 10 mmol) was added dropwise . After stirred for 1 h at room temperature, another portion of bromine (0.51 mL, 10 mmol) was added to the reaction mixture. The solution was stirred for 18 h at room temperature, and then saturated aqueous solution of sodium sulfite (2.7 mL) and diethyl ether (3.9 mL) were added to stir for another 2 h. Then the organic phase was separated, the water layer was extracted with diethyl ether and the combined organic layer was dried with anhydrous Na_2SO_4. After the solvents were removed under reduced pressure, the residue was purified by silica gel chromatography using hexane as eluent to afford compound **6** as a yellow oil (2.9 g, 61%). ^{1}H-NMR ($CDCl_3$, ppm, 400 MHz) δ = 7.23-7.20 (m, 4H), 6.67 (d, *J* = 8.8 Hz, 2H), 3.73 (t, *J* = 7.2 Hz, 2H), 1.74-1.69 (m, 2H), 1.36-1.24 (m, 10H), 0.88-0.83 (m, 3H).

2,7-dibromo-9,9-di-n-hexylfluorene (4)[13c] To a solution of 2, 7-dibromofluorene (0.65 g, 2.0 mmol), $Bu_4N^+Br^-$ (0.10 g, 0.30 mmol) in toluene (6 mL) and aqueous NaOH (50 wt%; 3 mL), 1-bromohexane (0.74 g, 4.5 mmol) was added by syringe, then the mixture was kept at 80°C for 48h. After cooled to room temperature, the organic layer was separated and the water layer was extracted with dichloromethane. The combined organic layer was washed with deionized water and then dried over anhydrous Na_2SO_4. Compound **7** as a colorless oil (0.72 g, 74%) was obtained after column chromatography using n-hexane as the eluent. ^{1}H-NMR ($CDCl_3$, ppm, 400 MHz) δ = 7.52 (d, *J* = 8.4 Hz, 2H), 7.45 (sd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 4H), 1.93-1.89 (m, 4H), 1.15-1.03 (m, 12H), 0.80-0.73 (m, 6H), 0.60-0.0.54 (m, 4H)

3, 6-dithien-2-yl-2, 5-dihydropyrrolo[3, 4-c]pyrrole-1, 4-dione [16] To a solution of potassium tert-butoxide (4.0 g, 35.7 mmol) in t-amyl alcohol (25 mL), 2-thiophenecarbonitrile (3.3 g, 30 mmol) was added by a syringe under nitrogen. The mixture was warmed up to 100-110°C, and a solution of dimethyl succinate (1.5 g, 10 mmol) in t-amyl alcohol (8 mL) was dropped slowly over 1 h. then the reaction was kept at the same temperature for about 1 h, and the byproduct of methanol was distilled off for about 2 h. After being cooled to 65°C, the mixture was diluted with methanol (50 mL) and neutralized with acetic acid. Then the suspension was filtered, the purple filter cake was washed by hot methanol and water and dried in vacuum. The crude product could be used directly without further purification (2.42g, 76%).

3,6-dithien-2-yl-2,5-di-n-octyl-pyrrolo[3, 4-c]pyrrole-1, 4-dione [16] A solution of compound 8 (0.30 g, 1.0 mmol) and anhydrous K_2CO_3 (0.41 g, 3.0 mmol) in 10 ml anhydrous *N*,*N*-dimethylformamide (DMF) was heated to 60 °C and stirred for 1 h under nitrogen. Then *n*-octyllbromide (0.58 g, 3.0 mmol) was added dropwise, the

mixture was stired at 80 °C for another 20 h. When cooled to room temperature, 40 mL of distilled water was poured into the system, the resulting suspension was stirred at room temperature for 1 h. The solid was collected by vacuum filtration, washed with distilled water and methanol several times, the crude product was purified by silica gel chromatography using CH_2Cl_2 as eluent to get compound **9** as a purple solid (0.26 g, 49%). M.p.: 139-143 °C.

3-(5-Bromo-thiophen-2-yl)-2,5-di-n-octyl-6-(thiophen-2-yl)-pyrrolo[3,4-c]pyrrole-1,4-dione (A)[12] To a solution of compound 9 (0.53 g, 1.0 mmol) in $CHCl_3$ (35 mL), NBS (0.18 g, 1.0 mmol) in $CHCl_3$ (17 mL) was dropwised at 0 °C over 5 h without light. Then the mixture was stirred at room temperature overnight. After that, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography using a mixture of hexane/dichloromethane (1:9 v/v) as eluent to obtain compound **A** as purple solid in 61% yield (0.42 g). ^{1}H- NMR ($CDCl_3$, ppm, 400 MHz) δ = 8.94 (d, *J* = 4.0 Hz, 1H), 8.67 (d, *J* = 4.4 Hz, 1H), 7.65 (d, *J* = 4.8 Hz, 1H), 7.28 (t, *J* = 4.4 Hz, 1H), 7.23 (d, *J* = 4.4 Hz, 1H), 4.08–3.97 (m, 4H), 1.77–1.70 (m, 4H), 1.45–1.27 (m, 19H), 0.89–0.86 (m, 7H). M.p.: 152-154 °C.

5. ^{1}H-NMR and ^{13}C-NMR spectra of the molecules

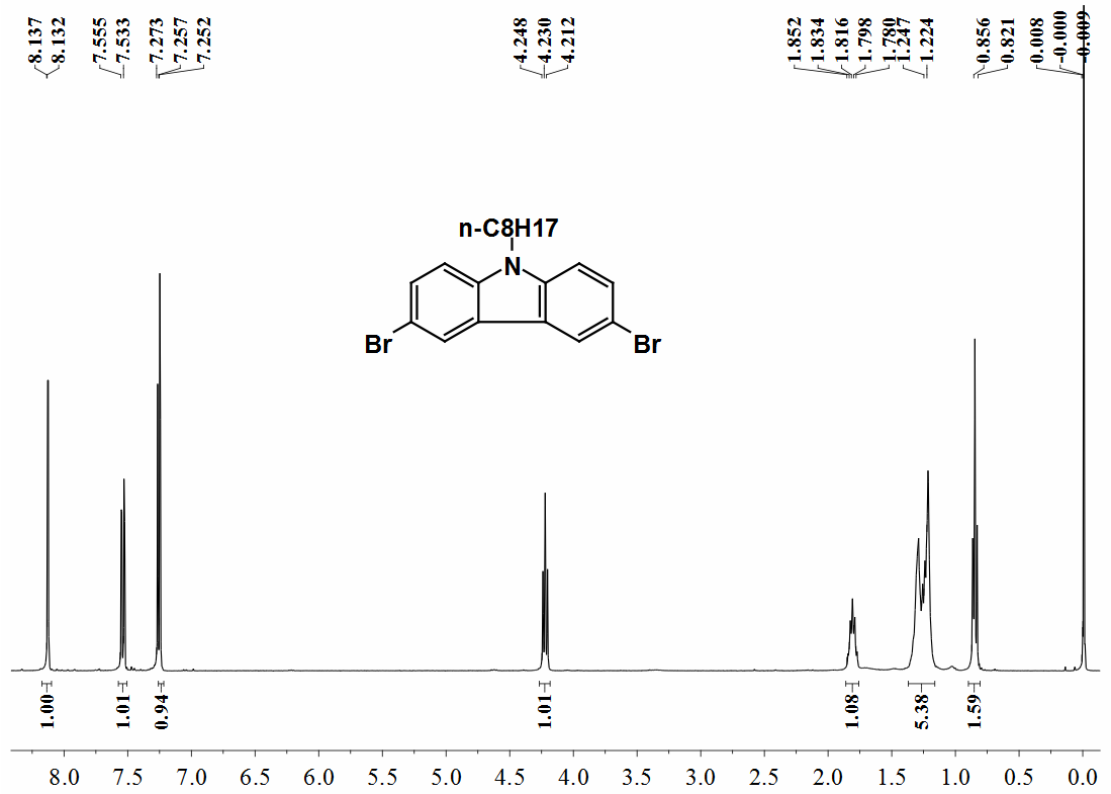


Fig. 4 ^{1}H-NMR spectrum of compound **1**

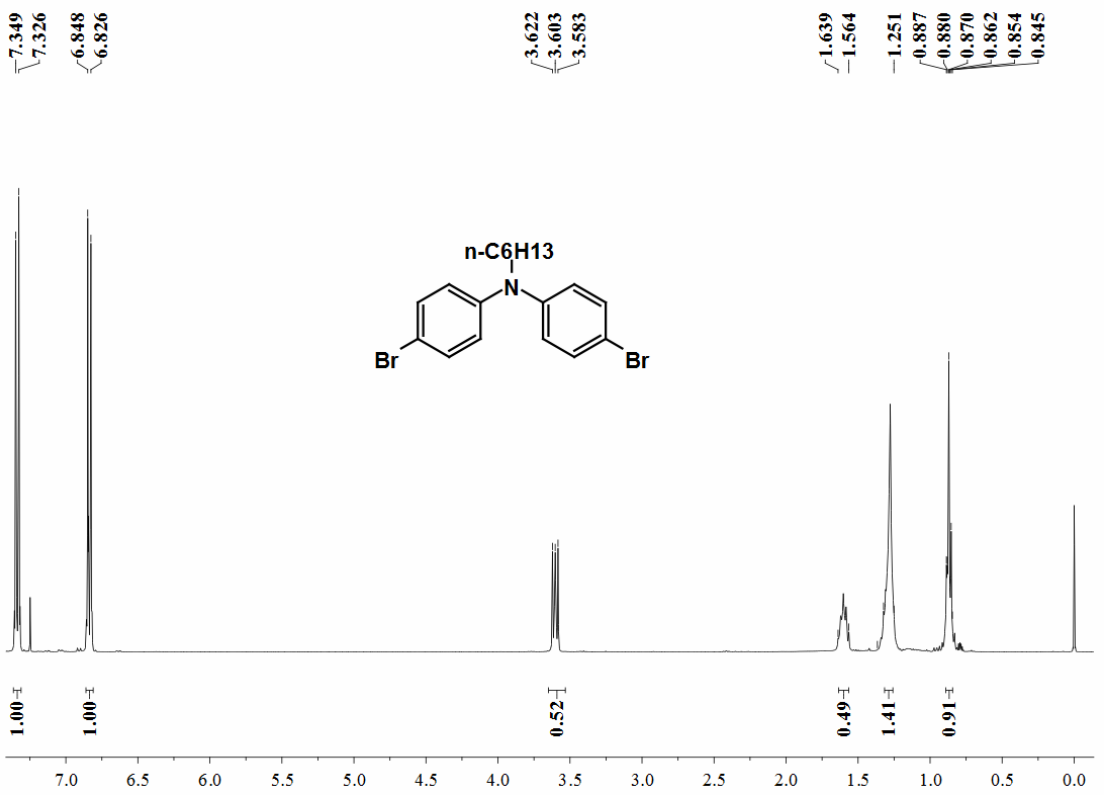


Fig. 5 ^{1}H-NMR spectrum of compound **2**

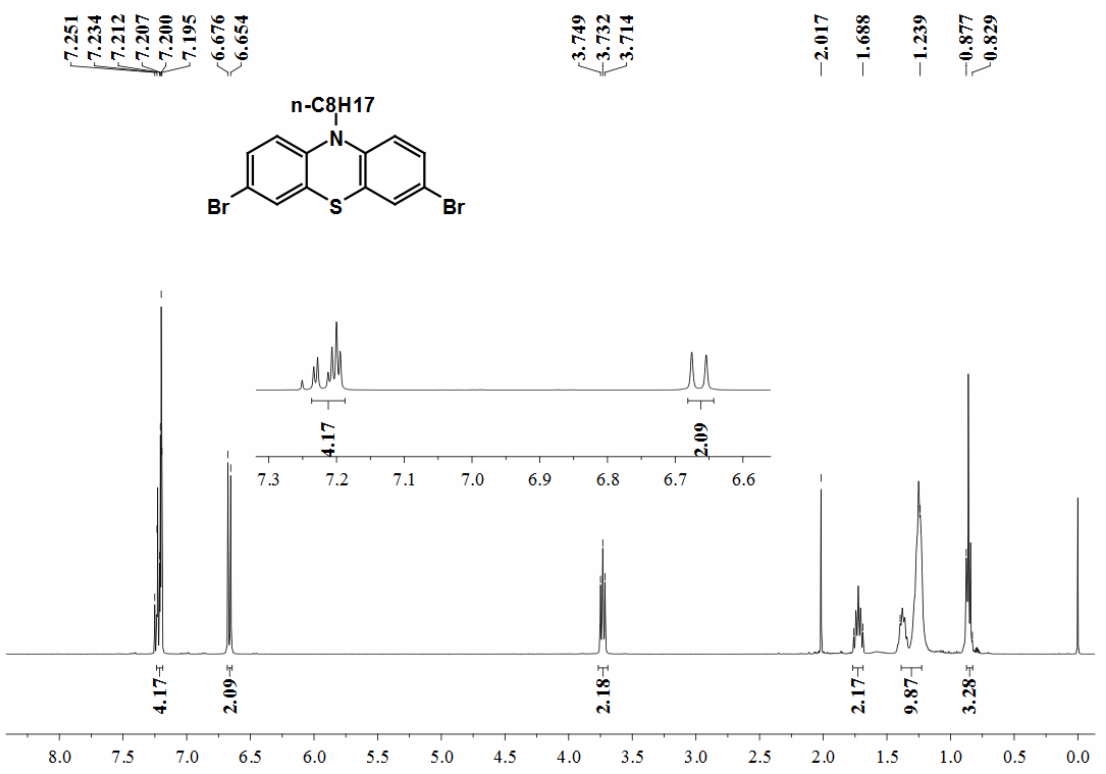


Fig. 6 ^{1}H-NMR spectrum of compound **3**

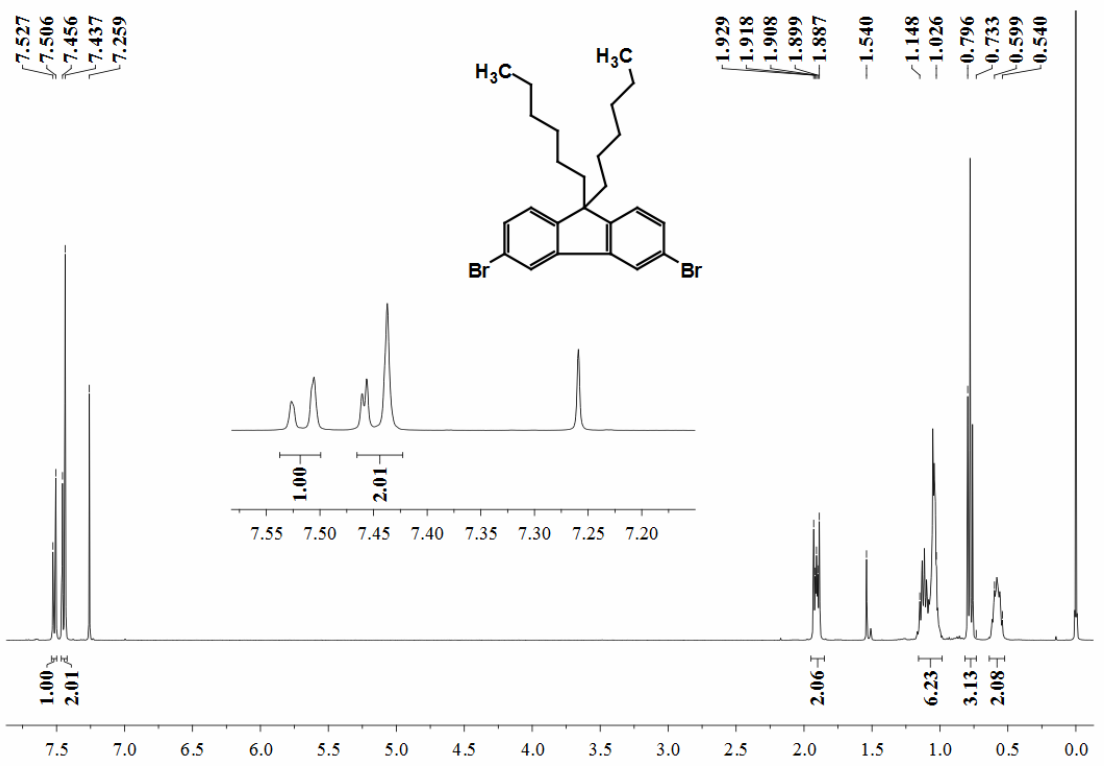


Fig. 7 ^{1}H-NMR spectrum of compound **4**

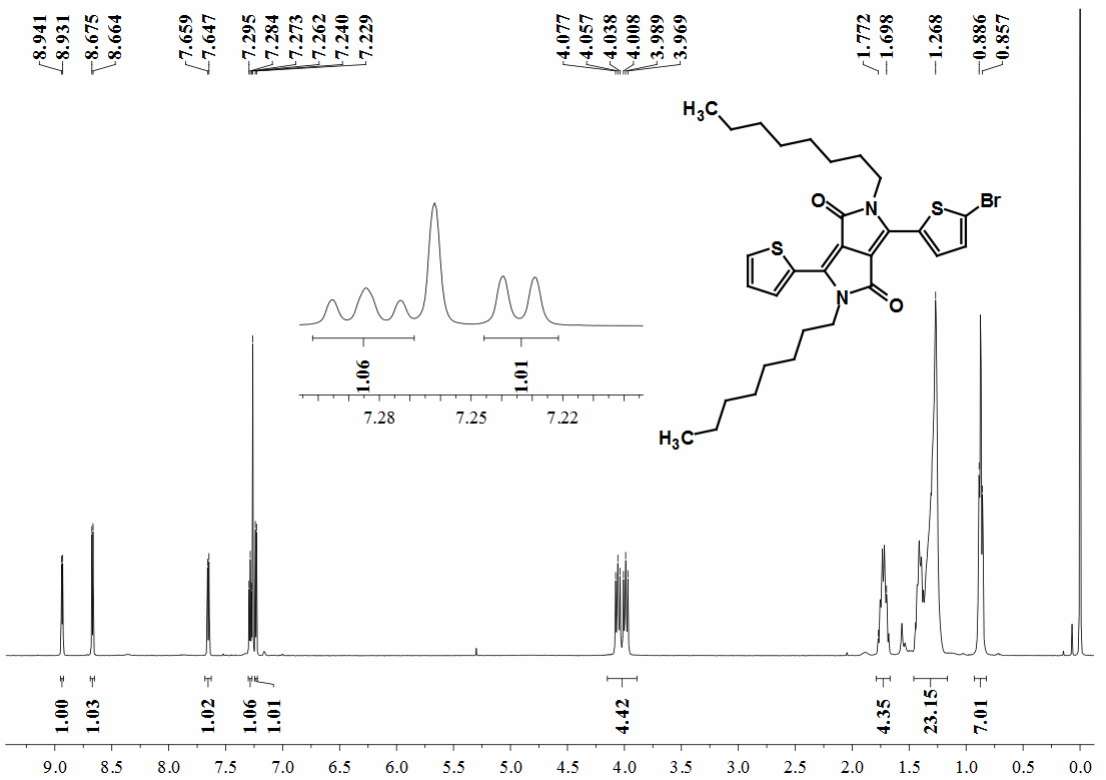


Fig. 8 ^{1}H-NMR spectrum of compound **A**

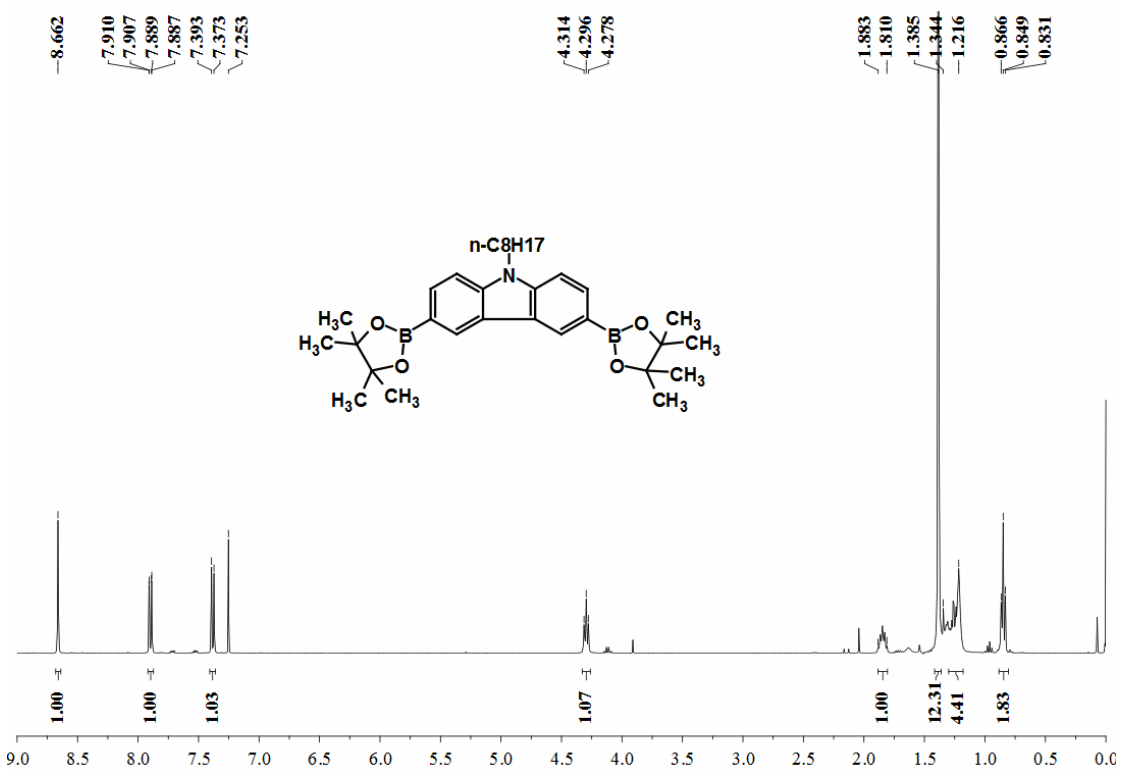


Fig. 9 [1]H-NMR spectrum of compound **D1**

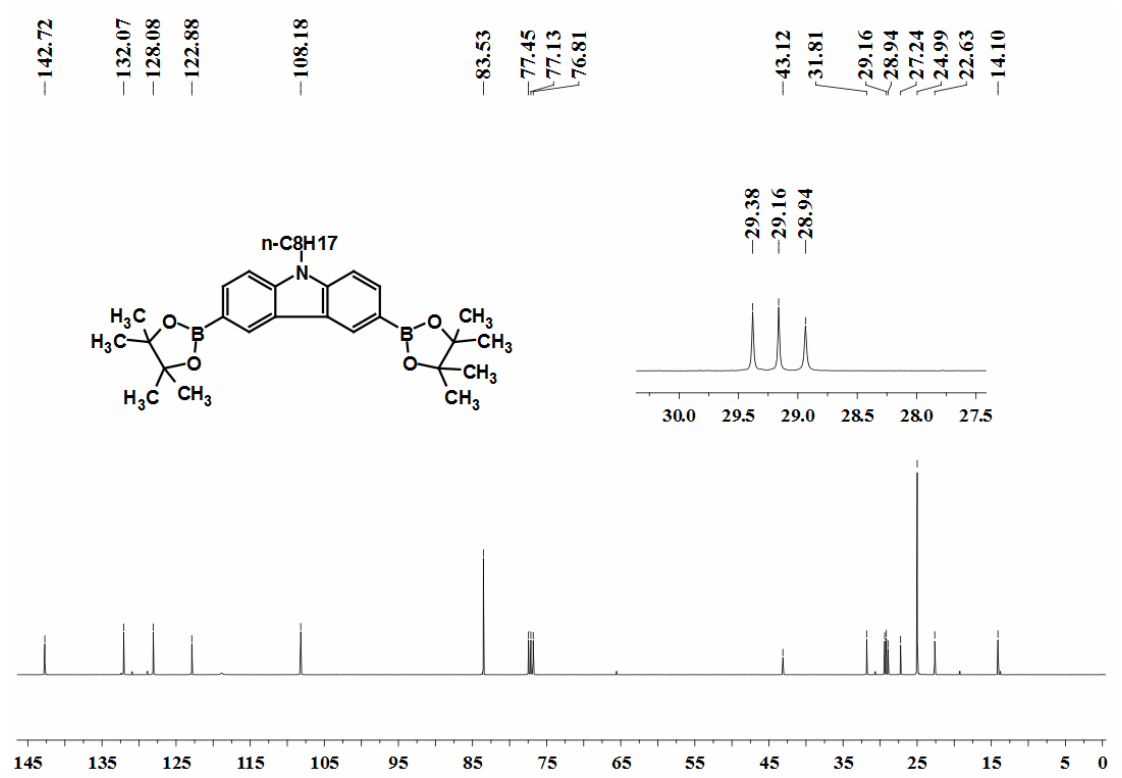


Fig. 10 [13]C-NMR spectrum of compound **D1**

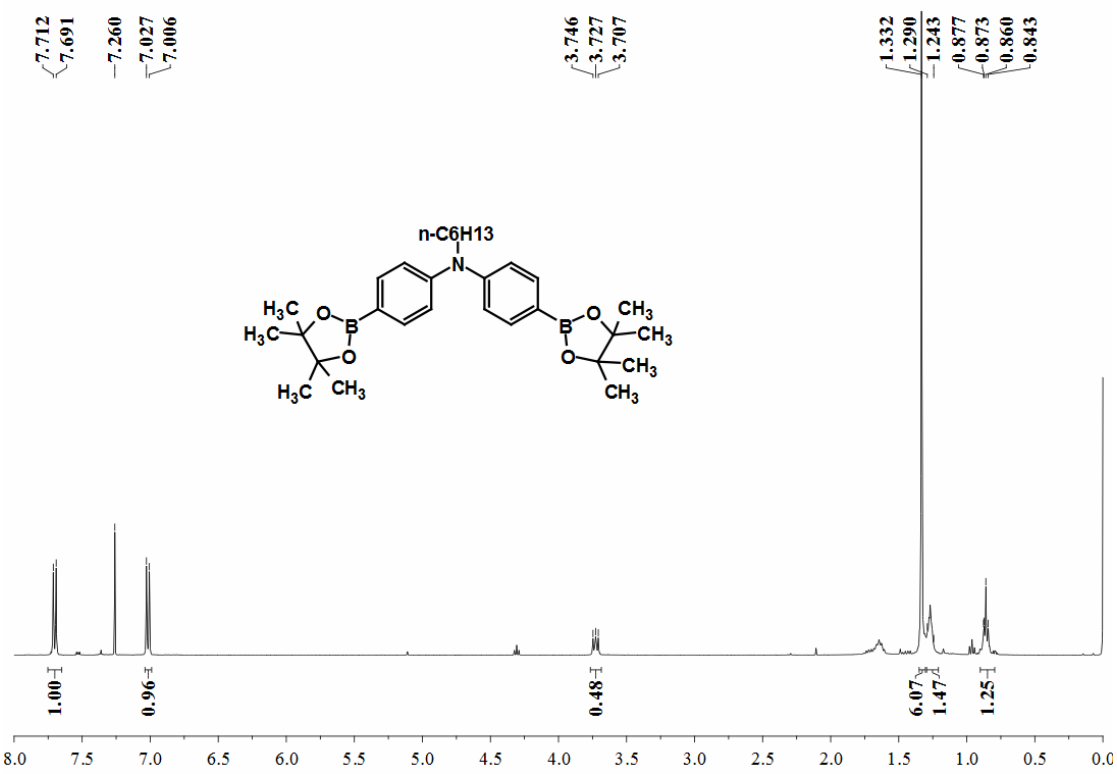


Fig. 11 ^{1}H-NMR spectrum of compound **D2**

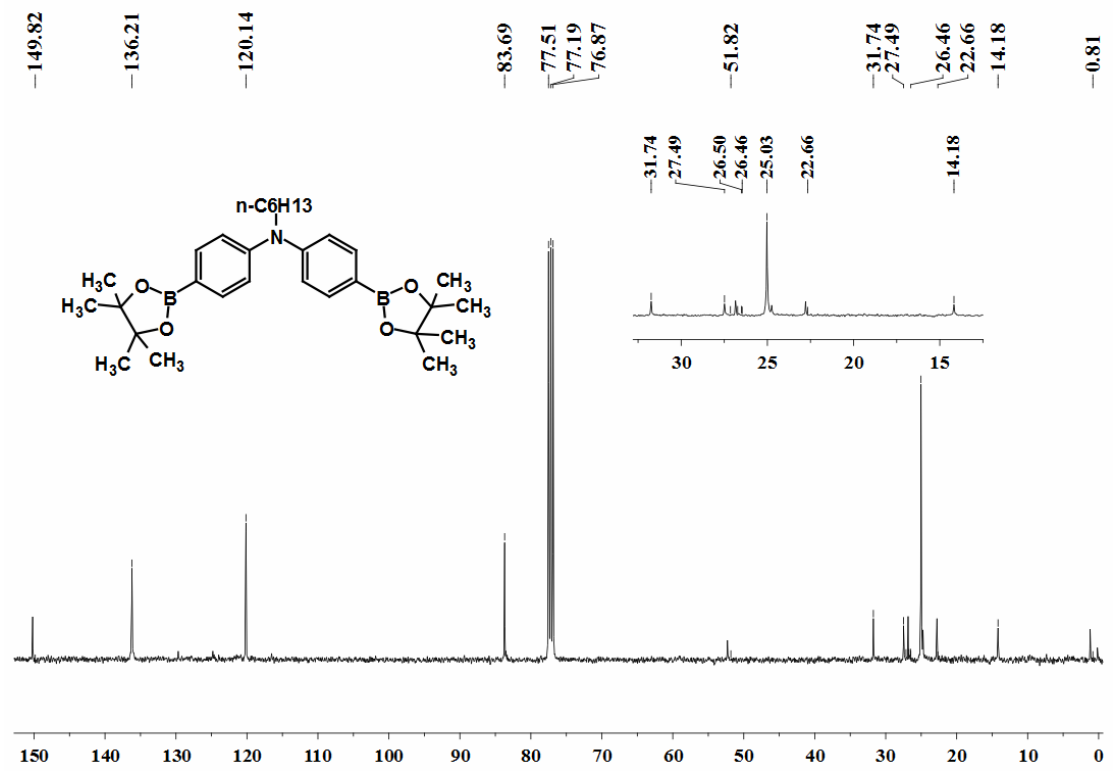


Fig. 12 ^{13}C-NMR spectrum of compound **D2**

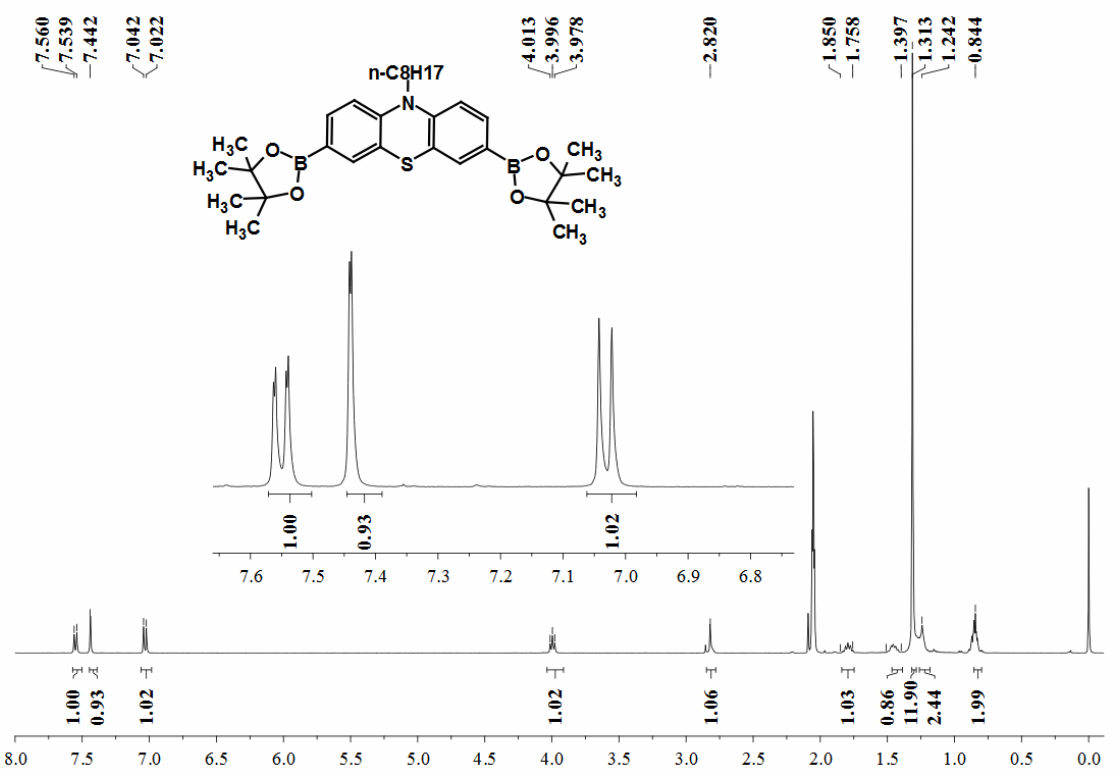


Fig. 13 ^{1}H-NMR spectrum of compound **D3**

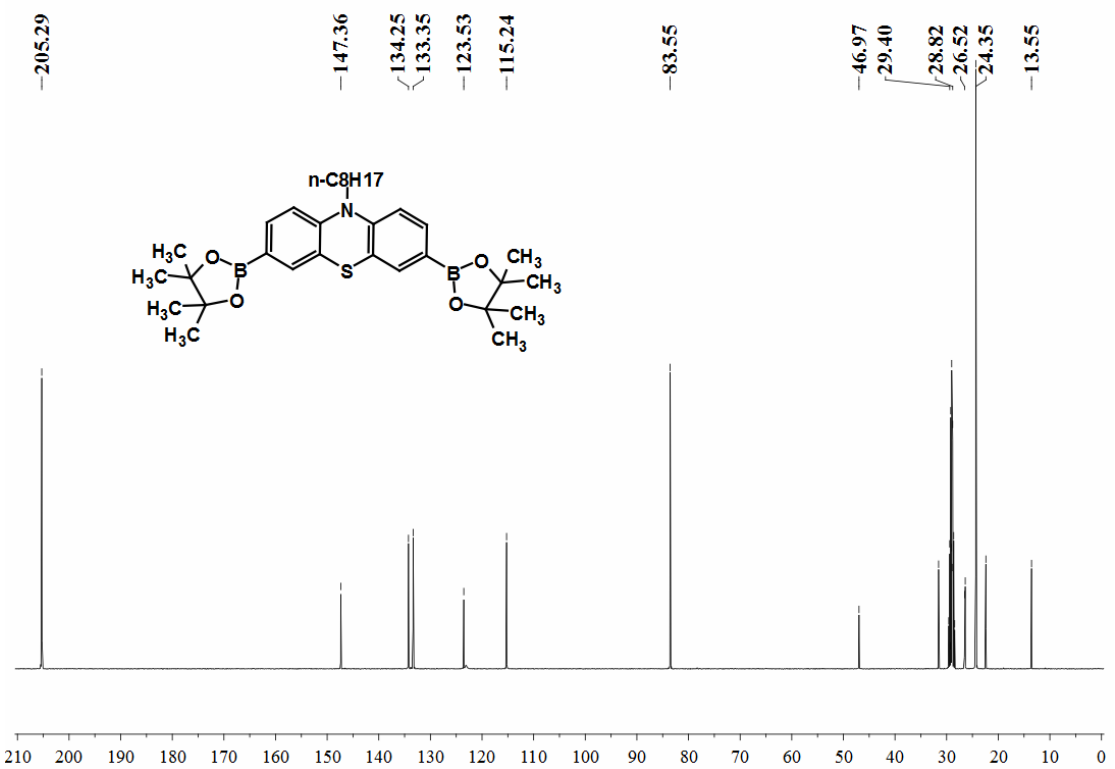


Fig. 14 ^{13}C-NMR spectrum of compound **D3**

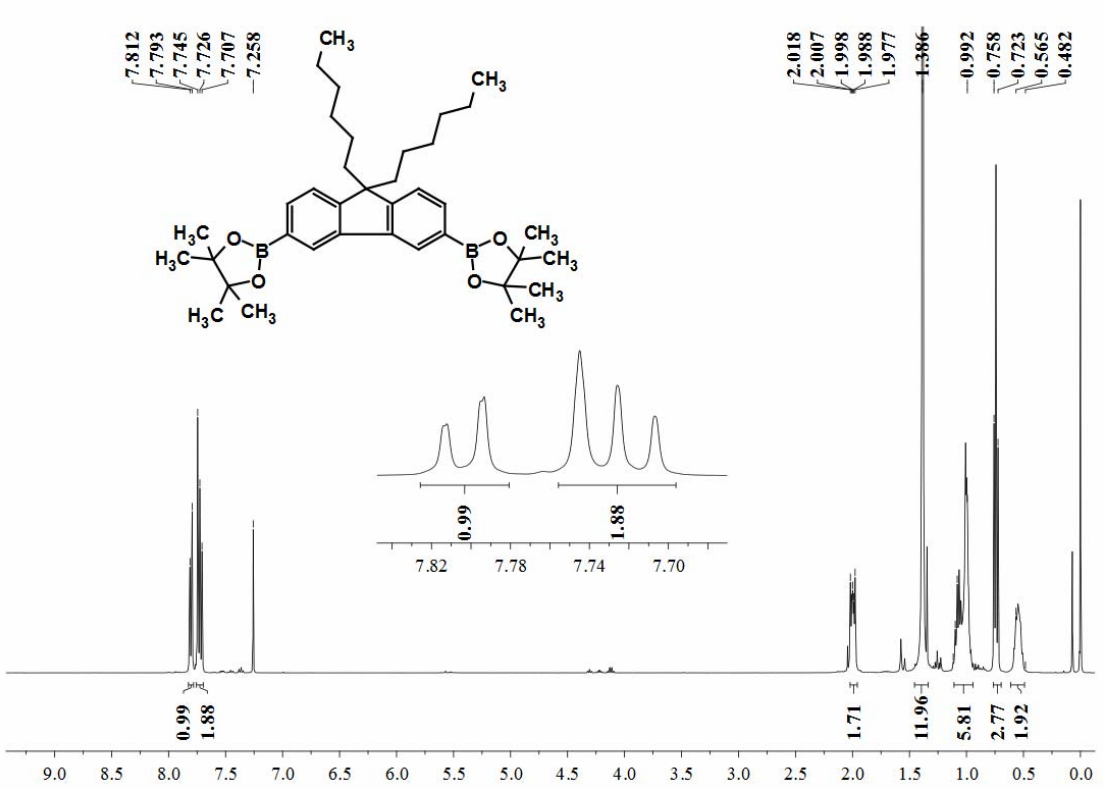


Fig. 15 ^{1}H-NMR spectrum of compound **D4**

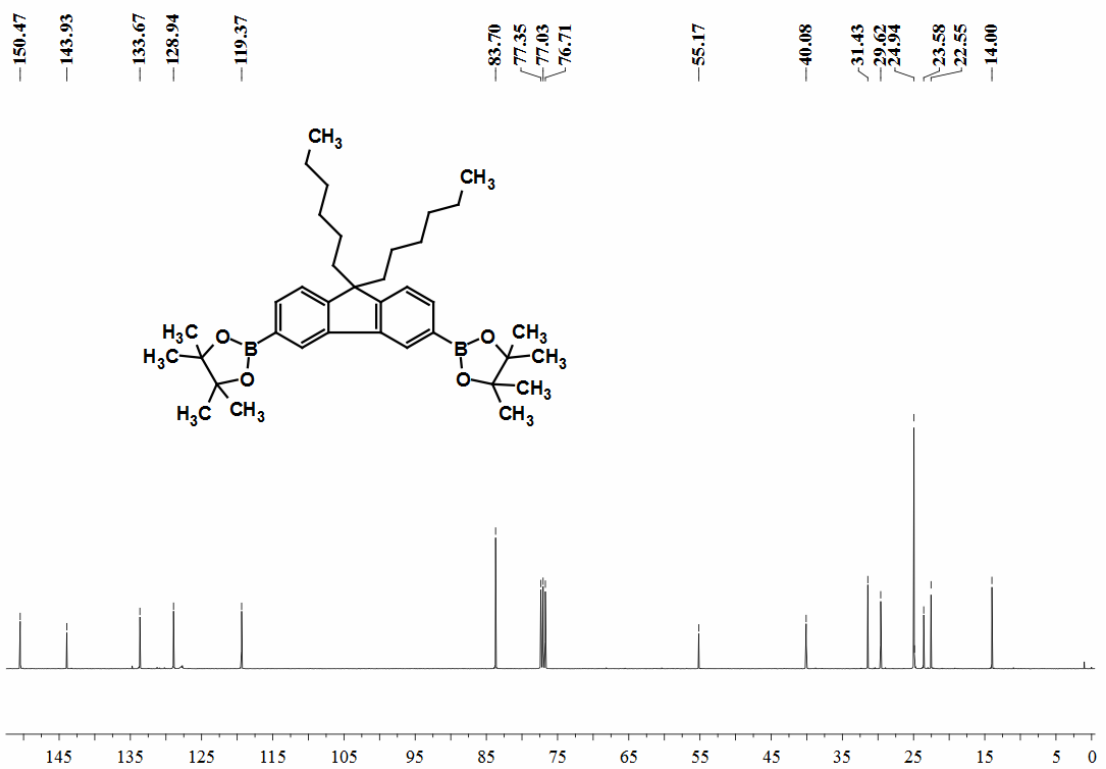


Fig. 16 ^{13}C-NMR spectrum of compound **D4**

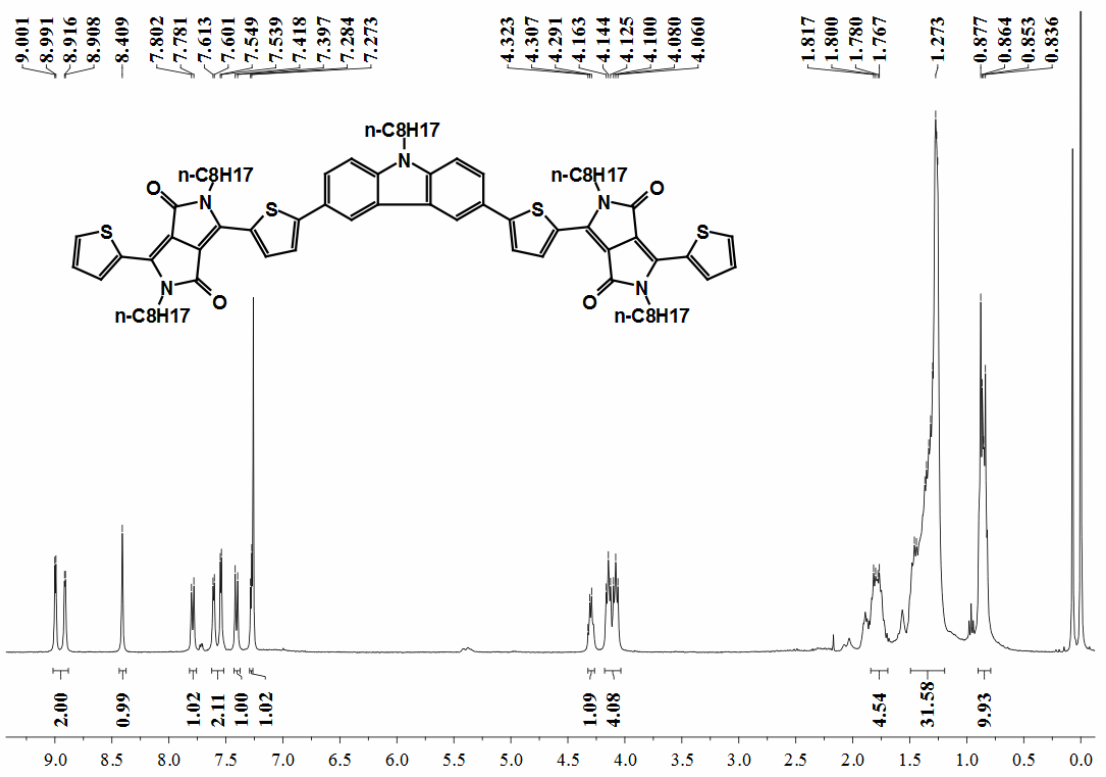


Fig. 17 ^{1}H-NMR spectrum of **Cz(TDPP)$_2$**

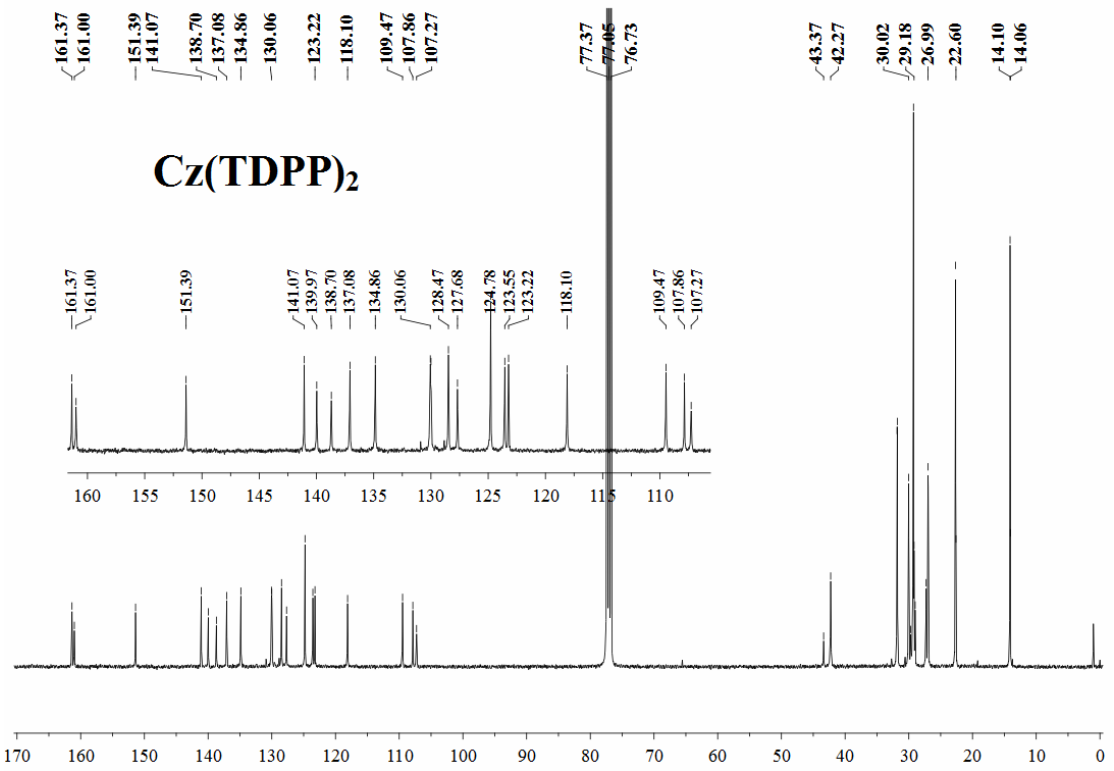


Fig. 18 ^{13}C-NMR spectrum of **Cz(TDPP)$_2$**

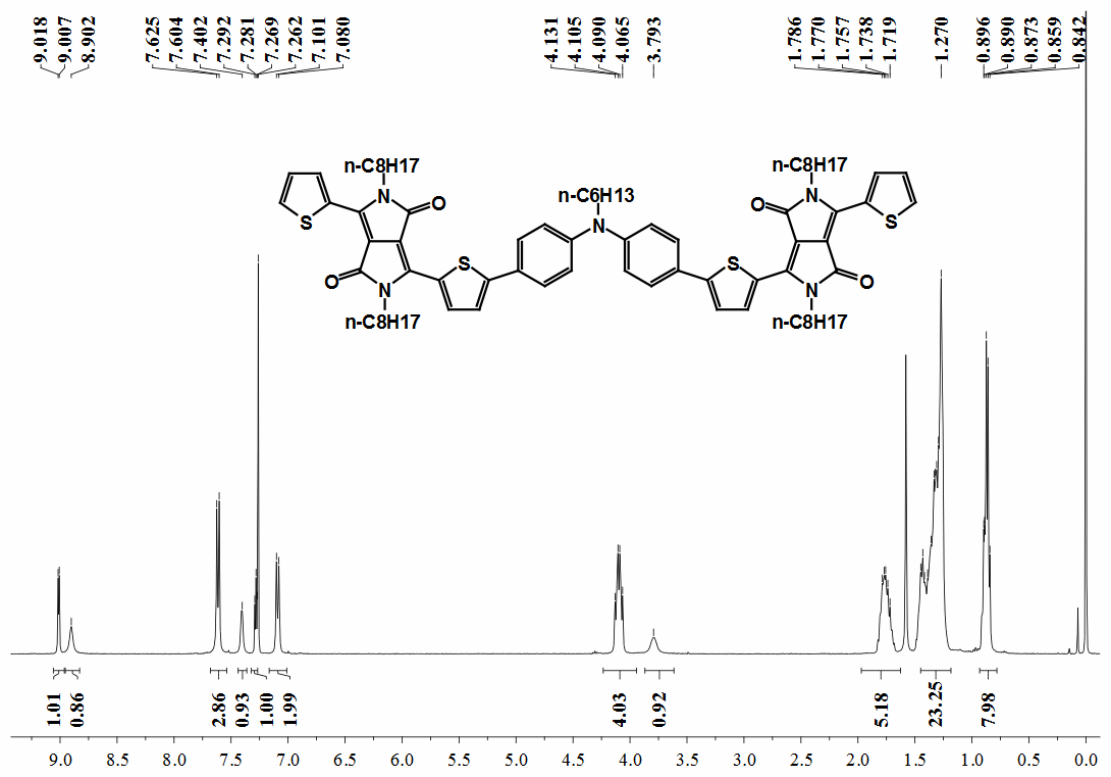


Fig. 19 ^{1}H-NMR spectrum of **DPA(TDPP)$_2$**

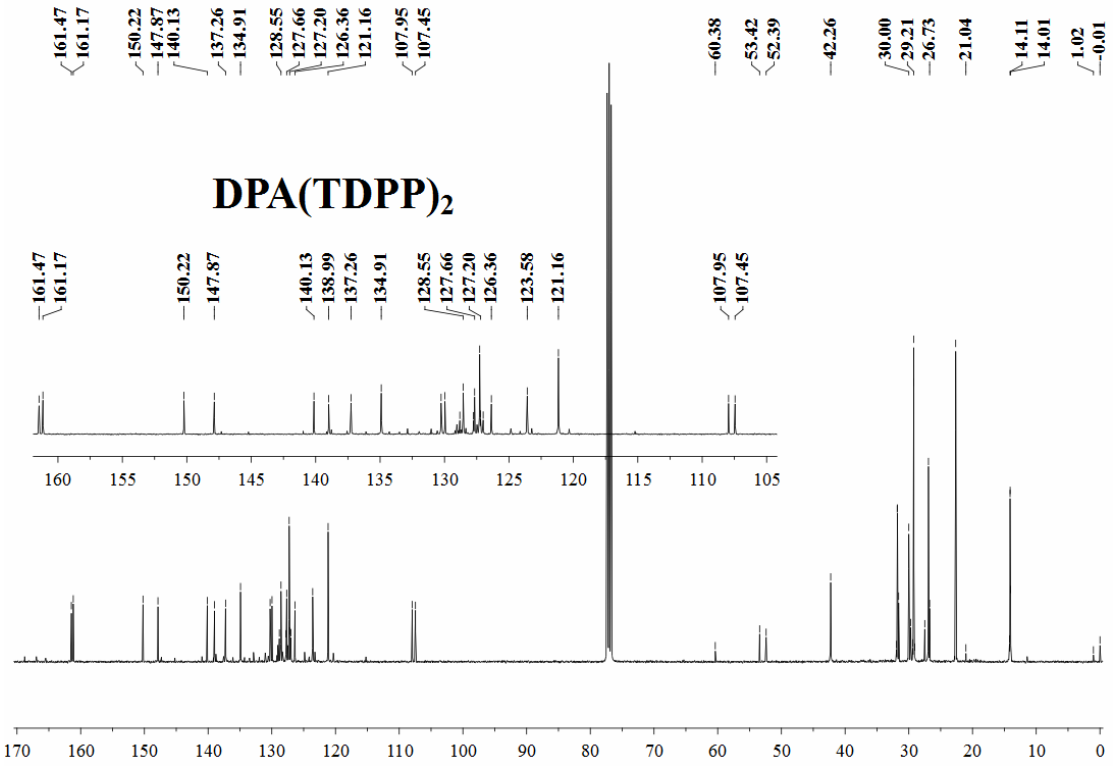


Fig. 20 ^{13}C-NMR spectrum of **DPA(TDPP)$_2$**

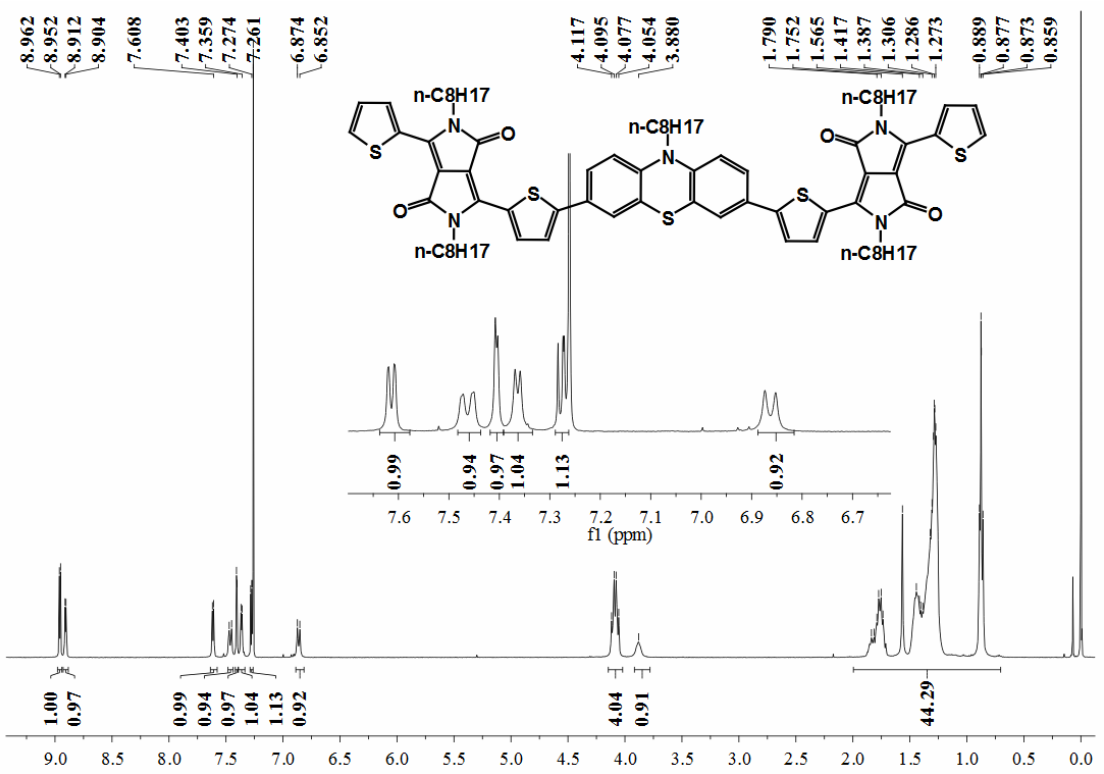


Fig. 21 ^{1}H-NMR spectrum of **PTZ(TDPP)$_2$**

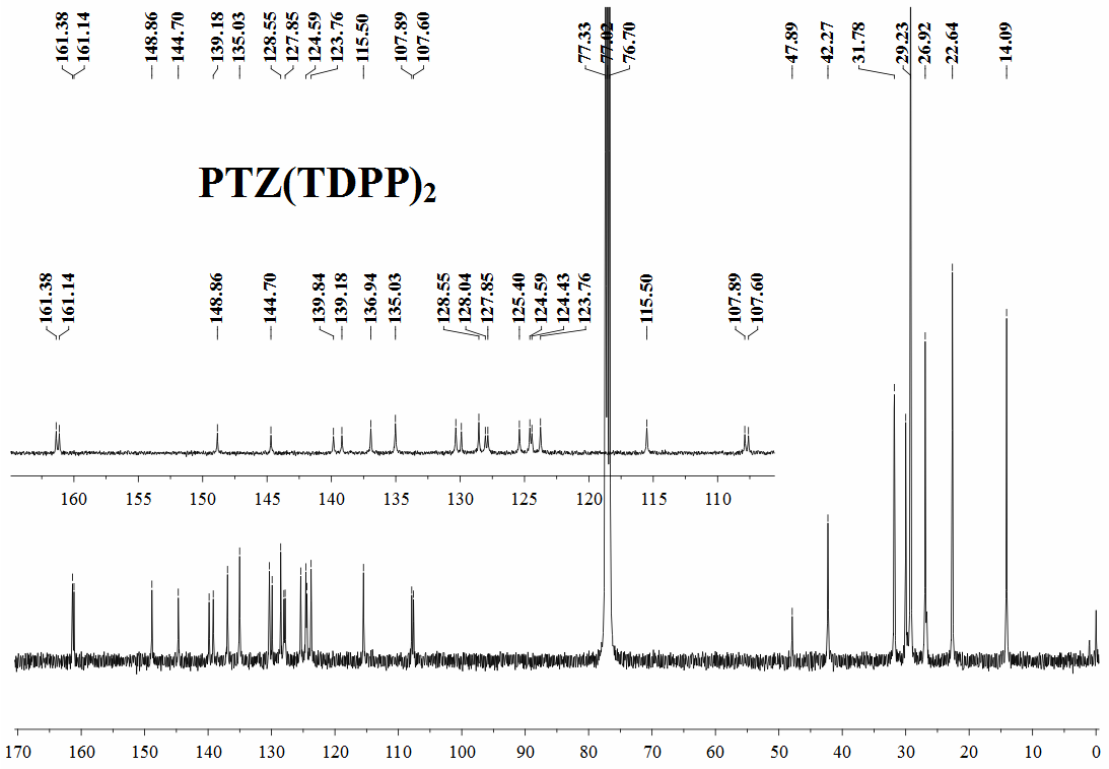


Fig. 22 ^{13}C-NMR spectrum of **PTZ(TDPP)$_2$**

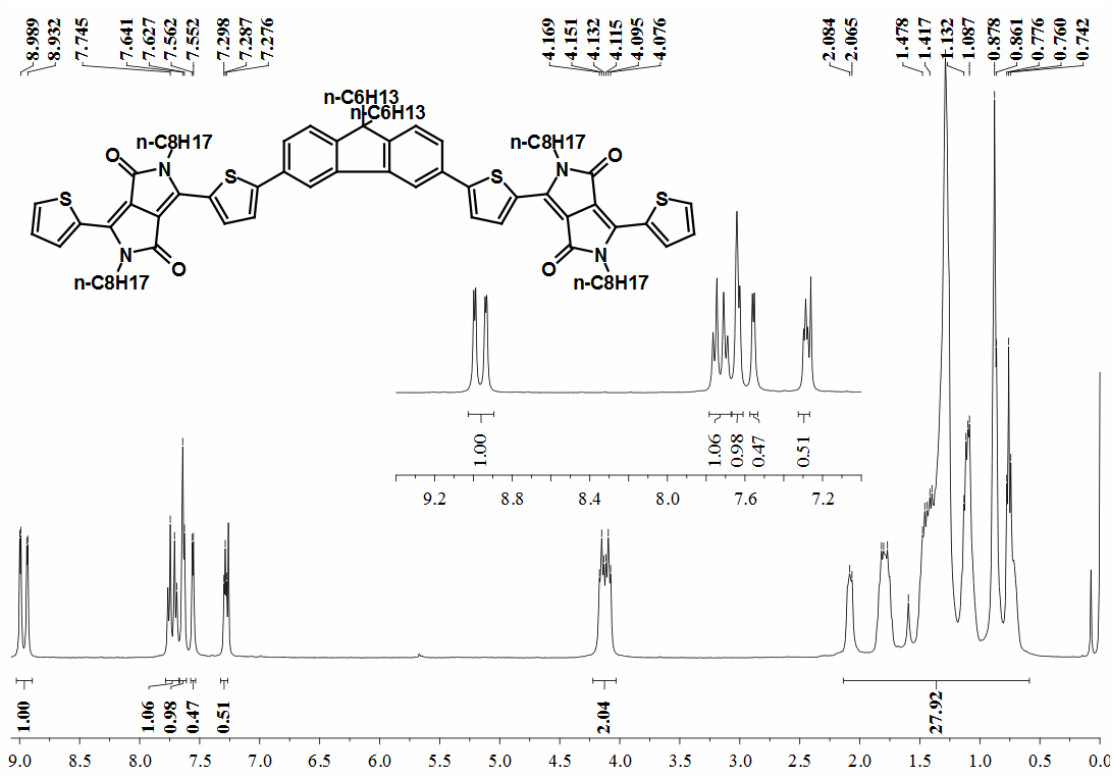


Fig. 23 ^{1}H-NMR spectrum of **FL(TDPP)$_2$**

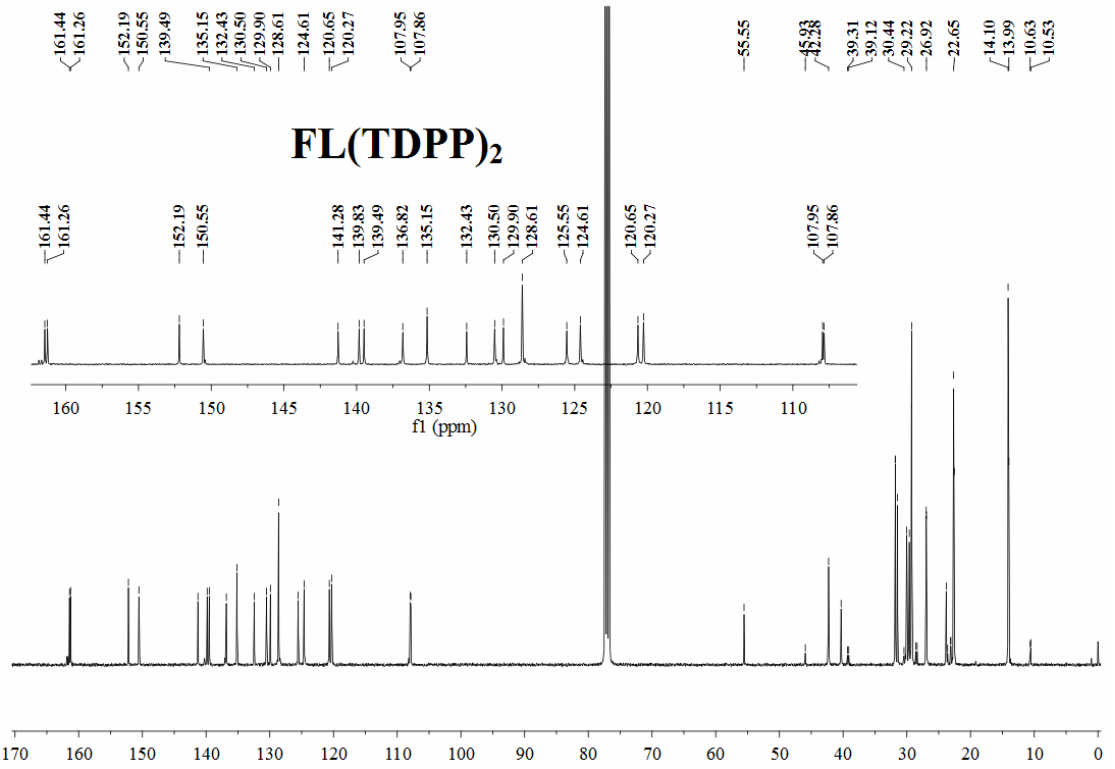


Fig. 24 ^{13}C-NMR spectrum of **FL(TDPP)$_2$**