

*Electronic Supplementary Information (ESI)*

**Di(naphthalen-2-yl)-1,2-diphenylethene-based polymers: aggregation-enhanced emission and explosive detection**

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**General**

THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. Chemicals and reagents were purchased from Aldrich and J&K Scientific Ltd., and used as received without further purification. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker AV 500 spectrometer in deuterated chloroform using tetramethylsilane (TMS;  $\delta = 0$ ) as internal reference. UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer. Photoluminescence was recorded on a Perkin-Elmer LS 55 spectrofluorometer. Fluorescent lifetime was determined using a Hamamatsu time-resolved spectrometer C11367-11 QuantaTaurus-Tau. Mass spectra were recorded on an Agilent 1290 Infinity LC/6530 Q-TOF MS. Thermogravimetric analysis was carried on a TA TGA Q5000 under dry nitrogen at a heating rate of 10 °C min<sup>-1</sup>. The number ( $M_n$ ) and weight average ( $M_w$ ) molecular weights and polydispersity indices (PDI or  $M_w/M_n$ ) of the polymers were estimated by a Waters Associates gel permeation chromatography (GPC 2414) system equipped with RI and UV detectors. The ground-state geometries were optimized using the density function theory (DFT) method with B3LYP hybrid functional at the basis set level of 6-31G(d). All the calculations were performed using Gaussian 09 package.

### ***Explosive detection***

A solution of picric acid (PA) in THF with a concentration of  $2 \text{ mg mL}^{-1}$  was prepared by dissolving an appropriate amount of PA in THF. Photoluminescence titration was carried out by adding aliquots of PA solution into solutions of P1–P3 in THF/water mixtures with a water fraction of 90 vol%.

### ***Synthesis***

**(4-Bromophenyl)(naphthalen-2-yl)methanone (3)<sup>1</sup>:** A solution of *n*-BuLi (5 mL, 12.08 mmol) in *n*-hexane was added dropwise to a solution of 2-bromonaphthalene (2.5 g, 12.08 mmol) in dry THF (50 mL) under N<sub>2</sub> at  $-40^\circ\text{C}$ . After stirring for 1 h, the solution was transferred to excess 4-bromobenzoyl chloride (2.8 g, 12.76 mmol) in dry THF (30 mL). The resulting mixture was kept at  $-40^\circ\text{C}$  for 30 min. The mixture was then warmed to room temperature, and K<sub>2</sub>CO<sub>3</sub> solution (1 M, 5 mL) was added to the mixture. The mixture was extracted with ethyl acetate by three times. The combined organic layers were washed with water, and dried over anhydrous MgSO<sub>4</sub>. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. White solid of **3** was obtained in 75% yield. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$ (TMS, ppm): 8.22 (s, 1H), 7.97–7.88 (m, 4H), 7.73–7.71 (m, 2H), 7.68–7.65 (m, 2H), 7.64–7.61 (m, 1H), 7.58–7.55 (m, 1H). <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$ (TMS, ppm): 195.2, 136.8, 135.3, 134.5, 132.2, 131.7, 131.6, 131.5, 129.4, 128.5, 128.4, 127.8, 127.2, 127.0, 125.4.

**1,2-Bis(4-bromophenyl)-1,2-di(naphthalen-2-yl)ethene (4):** To a mixture of (4-bromophenyl)(naphthalen-2-yl)methanone (1.56 g, 5 mmol), zinc dust (0.78 g, 12 mmol) in 80 mL dry THF was added dropwise titanium (IV) chloride (1.15 g, 6 mmol) under N<sub>2</sub> at  $-78^\circ\text{C}$ . After stirring for 20 min, the reaction mixture was warmed to room temperature and then heated to reflux for 12 h. The mixture was cooled to room temperature and poured into water, and extracted with dichloromethane by three times. The combined organic layers were washed with saturated brine solution and water, and dried over anhydrous MgSO<sub>4</sub>. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. White solid of **4** was obtained in 52% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$ (TMS, ppm): 7.79 (d, 1H, *J* = 7.5 Hz), 7.71 (d, 1H, *J* = 7.5 Hz),

7.66–7.64 (m, 2H), 7.58 (d, 1H,  $J = 7.5$  Hz), 7.54–7.52 (m, 3H), 7.48–7.37 (m, 4H), 7.32 (d, 2H,  $J = 8.0$  Hz), 7.23–7.16 (m, 4H), 7.00–6.97 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 142.6, 142.4, 140.7, 140.6, 140.52, 140.48, 133.2, 133.1, 132.32, 132.28, 131.2, 131.1, 130.61, 130.56, 129.2, 128.0, 127.6, 127.51, 127.49, 127.3, 126.2, 126.1, 125.9, 121.0, 120.9. MS (APCI):  $m/z$  589.0185 ( $\text{M}^+$ ,  $\text{C}_{34}\text{H}_{22}\text{Br}_2$ , calcd 588.0088).

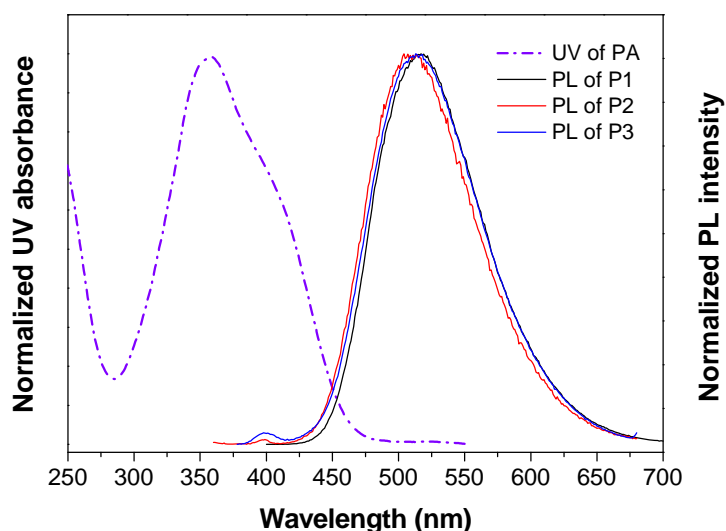
**P1:** 1,5-Cyclooctadiene (cod, 0.08 mL, 0.712 mmol, dried over  $\text{CaH}_2$ ) was added to a solution of bis(1,5-cyclooctadiene)nickel(0) ( $[\text{Ni}(\text{COD})_2]$ , 196 mg, 0.712 mmol) and 2,2'-bipyridyl (96 mg, 0.712 mmol) in dehydrated DMF (10 mL), and the mixture was heated at 80 °C for 1 h. To the resulting purple solution was added **4** (120 mg, 0.2 mmol) at 80 °C, and the mixture was stirred at that temperature for 72 h to afford a deep purple suspension. After cooling to room temperature, HCl (1 M, 4 mL) was added to the mixture. After filtration, the residue was washed with  $\text{H}_2\text{O}$  by three times. The residue was dissolved in THF and added into 300 mL of methanol to obtain P1 as a yellow solid in 76% yield.  $M_w = 6300$ ;  $M_w/M_n = 2.5$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.74–7.14 (ArH).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 143.0, 142.9, 142.8, 141.5, 141.4, 141.3, 140.9, 138.3, 133.3, 132.1, 130.7, 130.6, 129.7, 128.0, 127.5, 127.1, 126.1, 125.8.

**P2:** To a mixture of **4** (148.4 mg, 0.25 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-*n*-octylfluorene (160.6 mg, 0.25 mmol) and  $\text{K}_2\text{CO}_3$  (345.0 mg, 2.5 mmol) in THF/ $\text{H}_2\text{O}$  (8.75 mL, v/v = 6:1). After degassed and purged with  $\text{N}_2$ ,  $\text{Pd}(\text{PPh}_3)_4$  (12 mg, 0.01 mmol) was added. The mixture was refluxed for 28 h and then extracted with dichloromethane and washed with 100 mL brine three times. The organic layers were combined and dried with anhydrous  $\text{MgSO}_4$ . After solvent evaporation, the residue was dissolved in THF and added into 300 mL of methanol to obtain P2 as a yellow solid in 78% yield.  $M_w = 20600$ ;  $M_w/M_n = 2.9$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.81–7.24 (ArH), 2.03 (– $\text{CCH}_2$ –), 1.18–1.06 (– $\text{CH}_2$ –), 0.81 – 0.80 (– $\text{CH}_2$ –), 0.71 (– $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 151.7, 142.8, 141.6, 141.0, 140.1, 139.4, 133.2, 132.1, 130.6, 129.8, 128.8, 128.1, 127.6, 127.2, 126.4, 125.8, 121.0, 119.9, 55.3, 40.4, 31.7, 30.0, 29.2, 23.8, 22.6, 14.0.

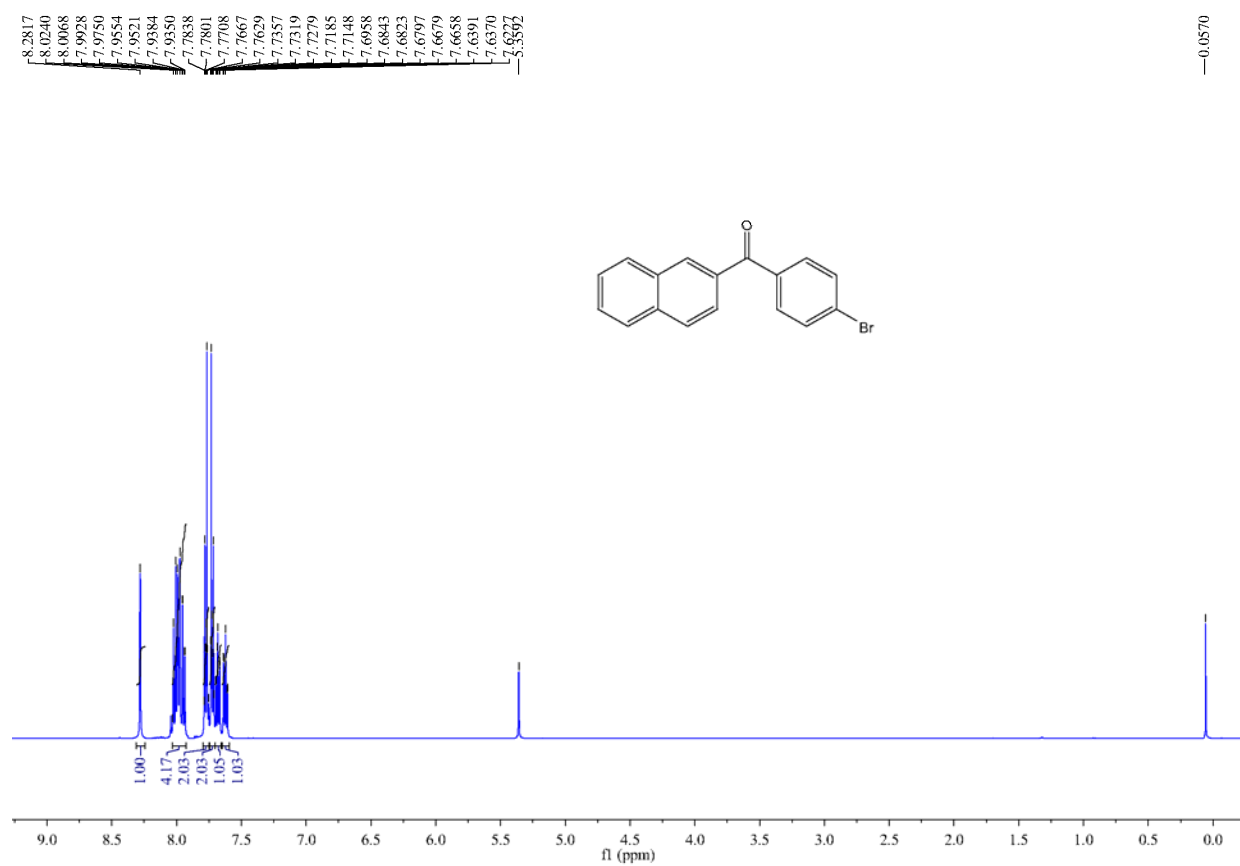
**P3:** The procedure was analogous to that described for P2. A yellow solid of P3 was obtained in 68% yield.  $M_w = 16000$ ;  $M_w/M_n = 2.9$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 8.16–8.08 (ArH), 7.81–7.26 (ArH), 4.33 (–NCH<sub>2</sub>–), 1.91–1.88 (–CH<sub>2</sub>–), 1.41–1.25 (–CH<sub>2</sub>–), 0.86–0.84 (–CH<sub>3</sub>).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 142.9, 142.7, 141.7, 141.6, 141.5, 141.1, 140.1, 138.4, 133.3, 132.2, 130.7, 129.8, 128.8, 128.1, 127.6, 127.2, 126.8, 125.8, 121.9, 126.6, 118.5, 106.8, 43.0, 31.8, 30.4, 29.7, 29.4, 29.2, 29.0, 27.3, 22.6, 14.1.

## References

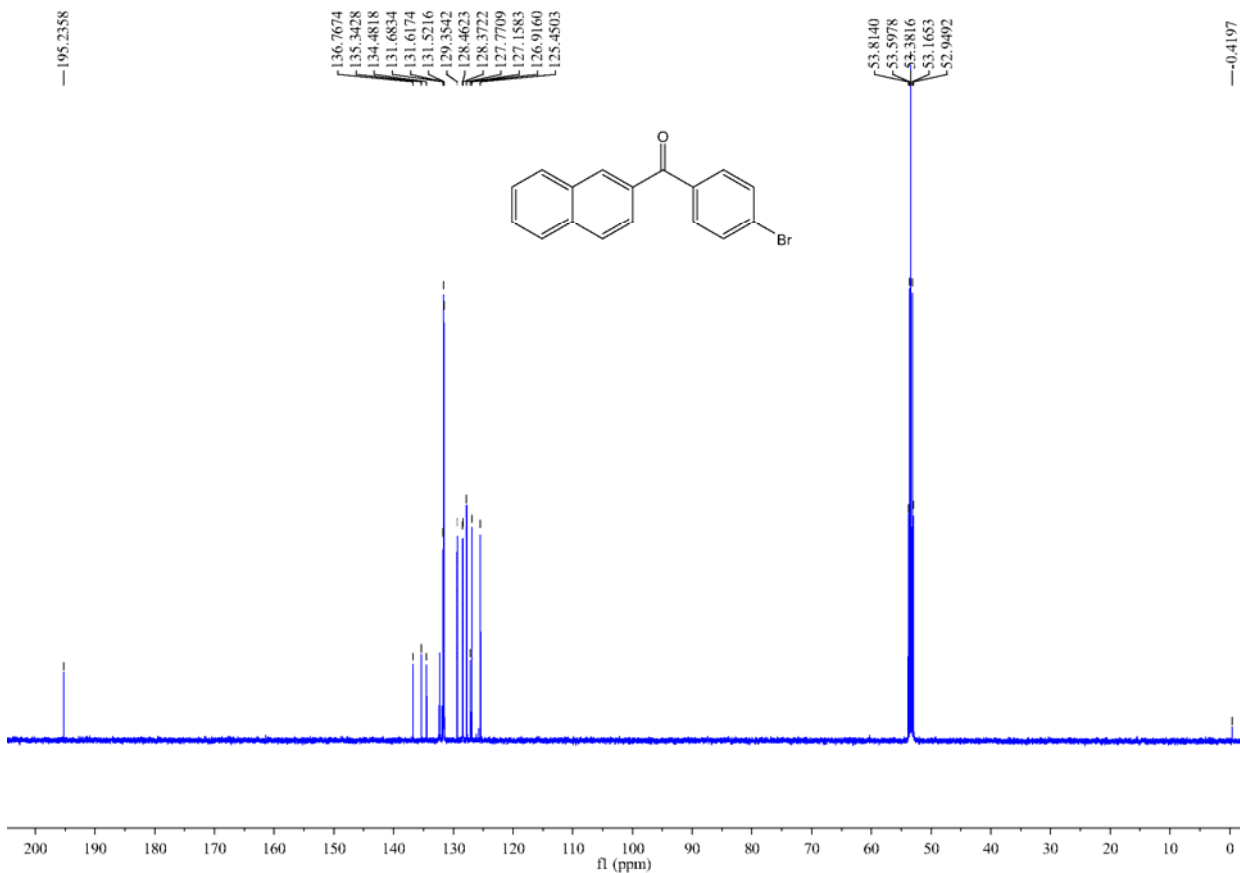
(1) A. T. Biju and F. Glorius, *Angew. Chem. Int. Ed.*, 2010, **49**, 9761.



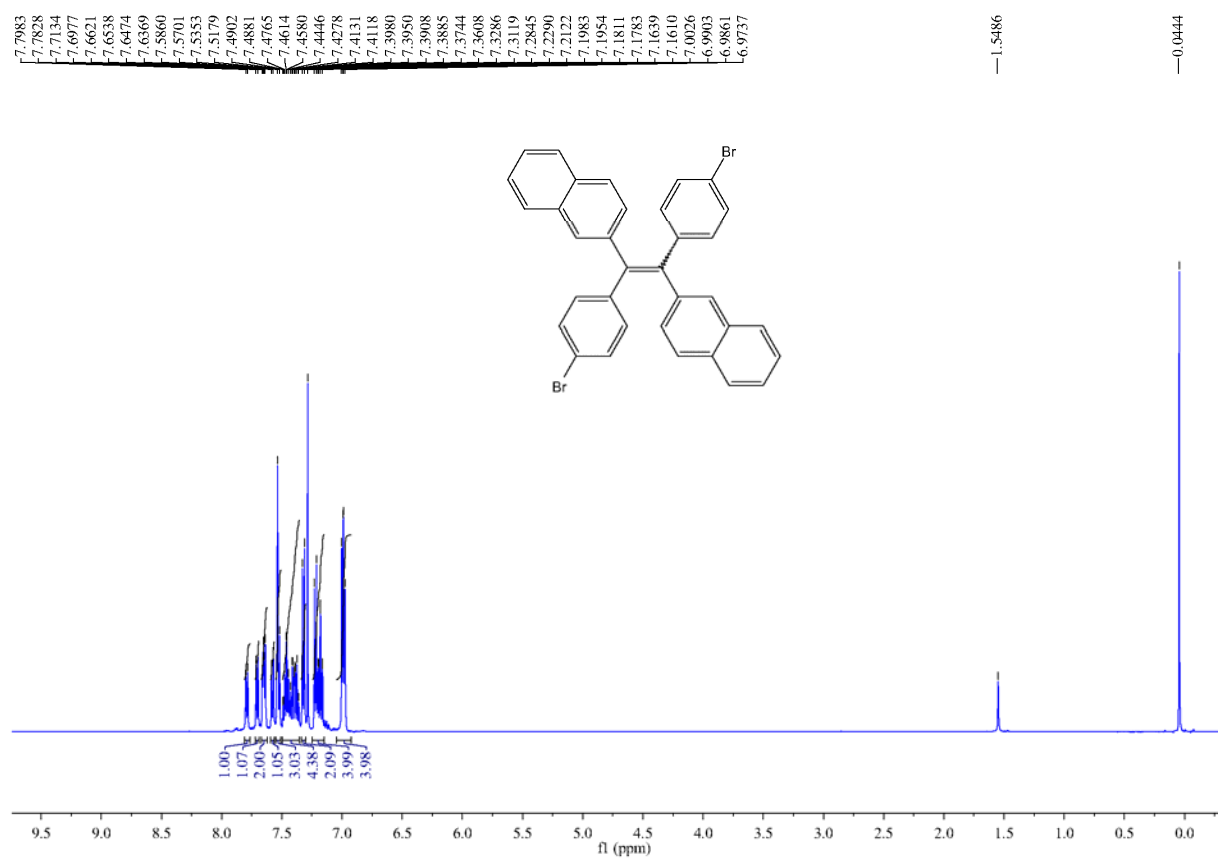
**Fig. S1** Absorption spectrum of PA and PL spectra of P1–P3 in THF/water mixtures ( $f_w = 90$  vol%).



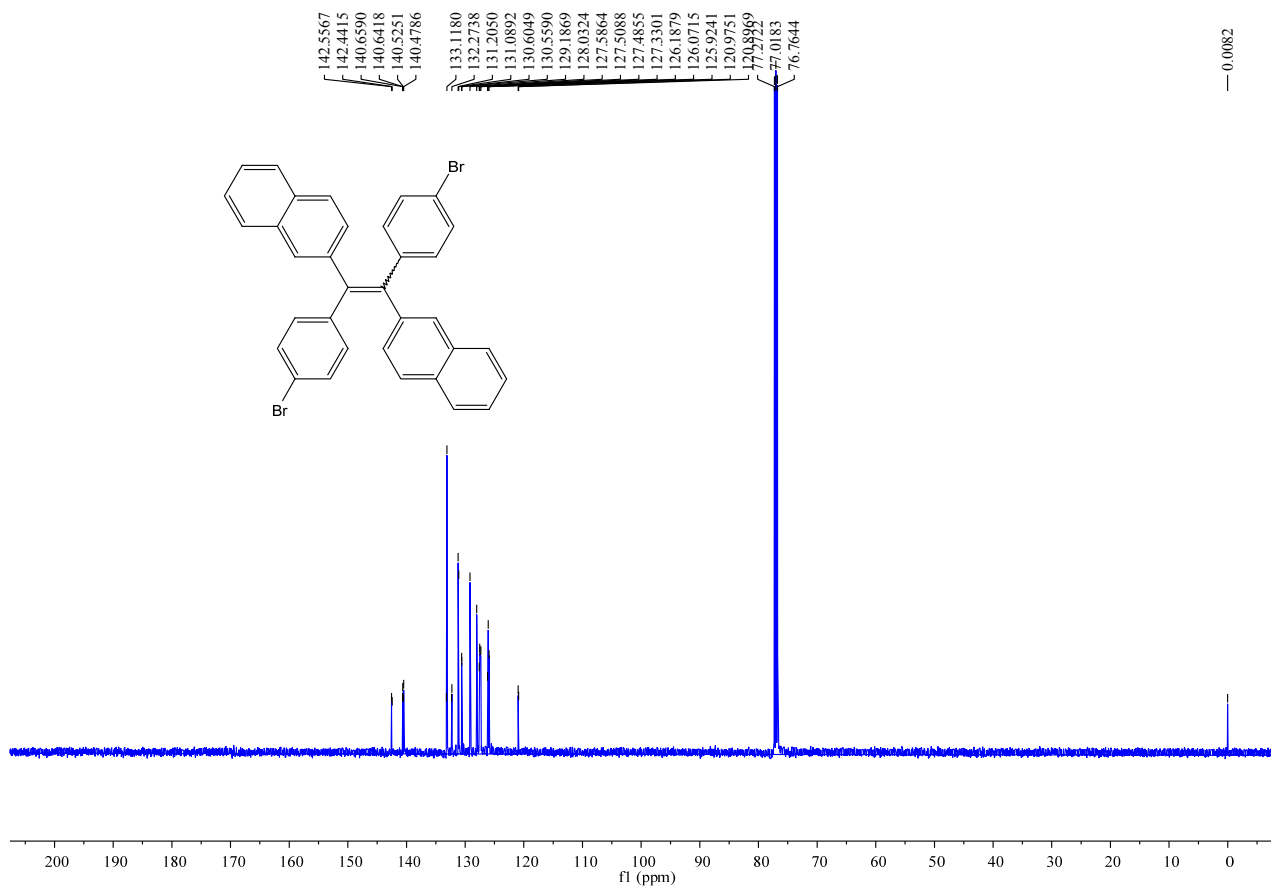
**Fig. S2** <sup>1</sup>H NMR spectrum of compound **3**.



**Fig. S3** <sup>13</sup>C NMR spectrum of compound **3**.



**Fig. S4** <sup>1</sup>H NMR spectrum of compound 4.



**Fig. S5** <sup>13</sup>C NMR spectrum of compound 4.

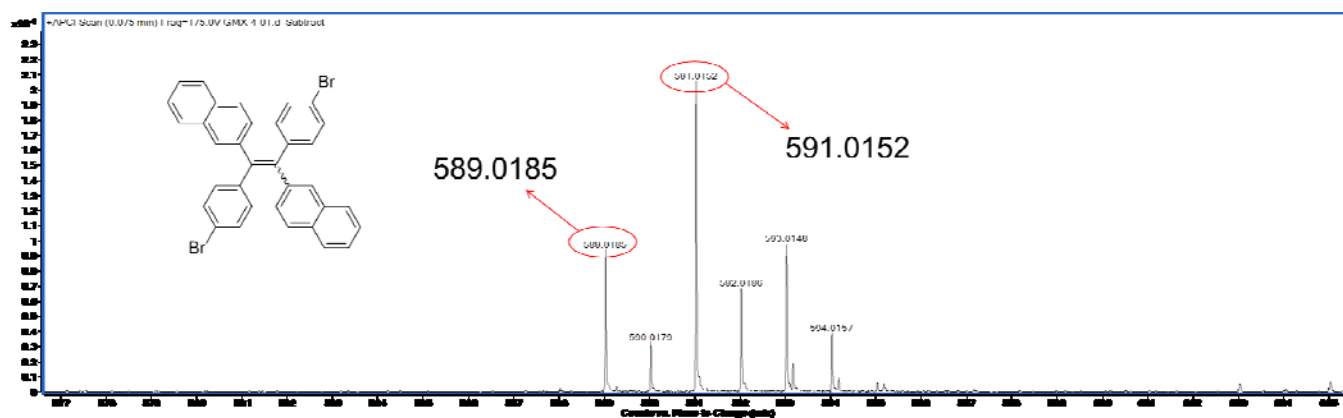


Fig. S5 HRMS spectrum of compound 4.

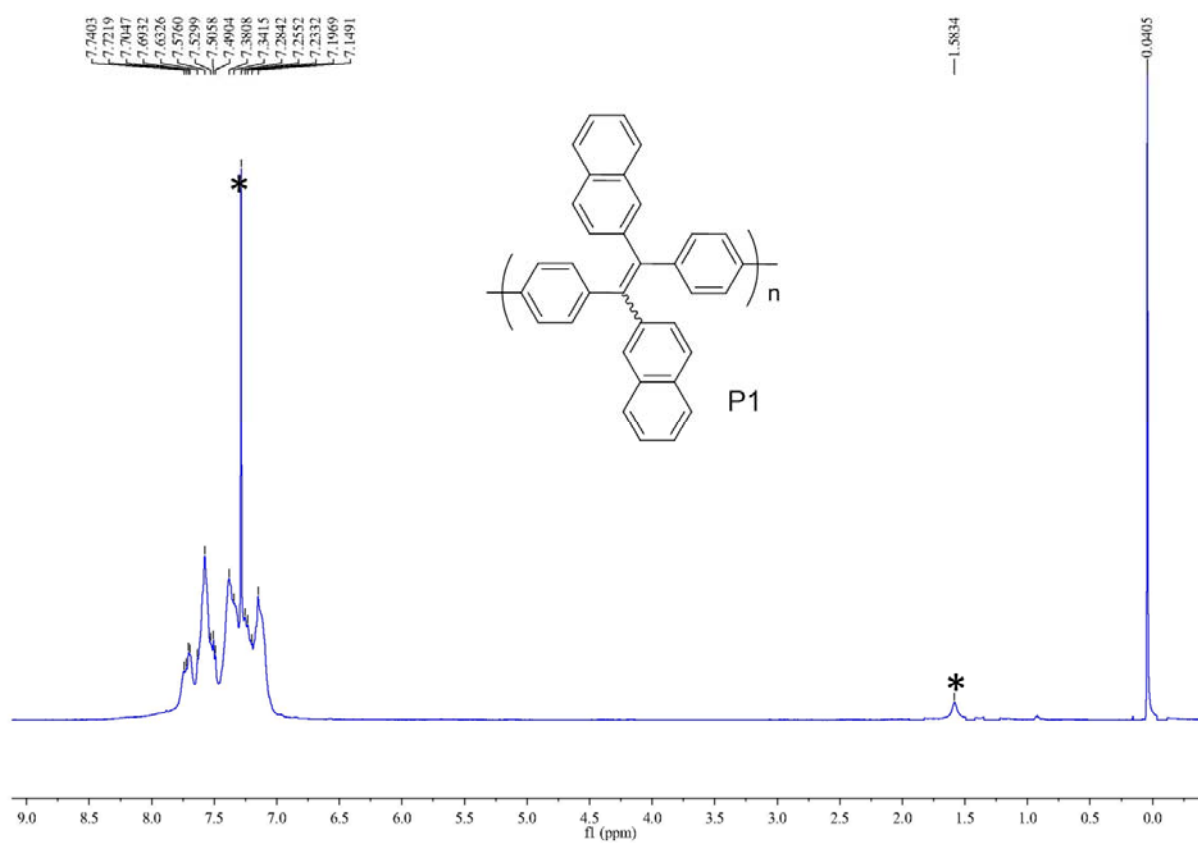


Fig. S7  $^1\text{H}$  NMR spectrum of P1.

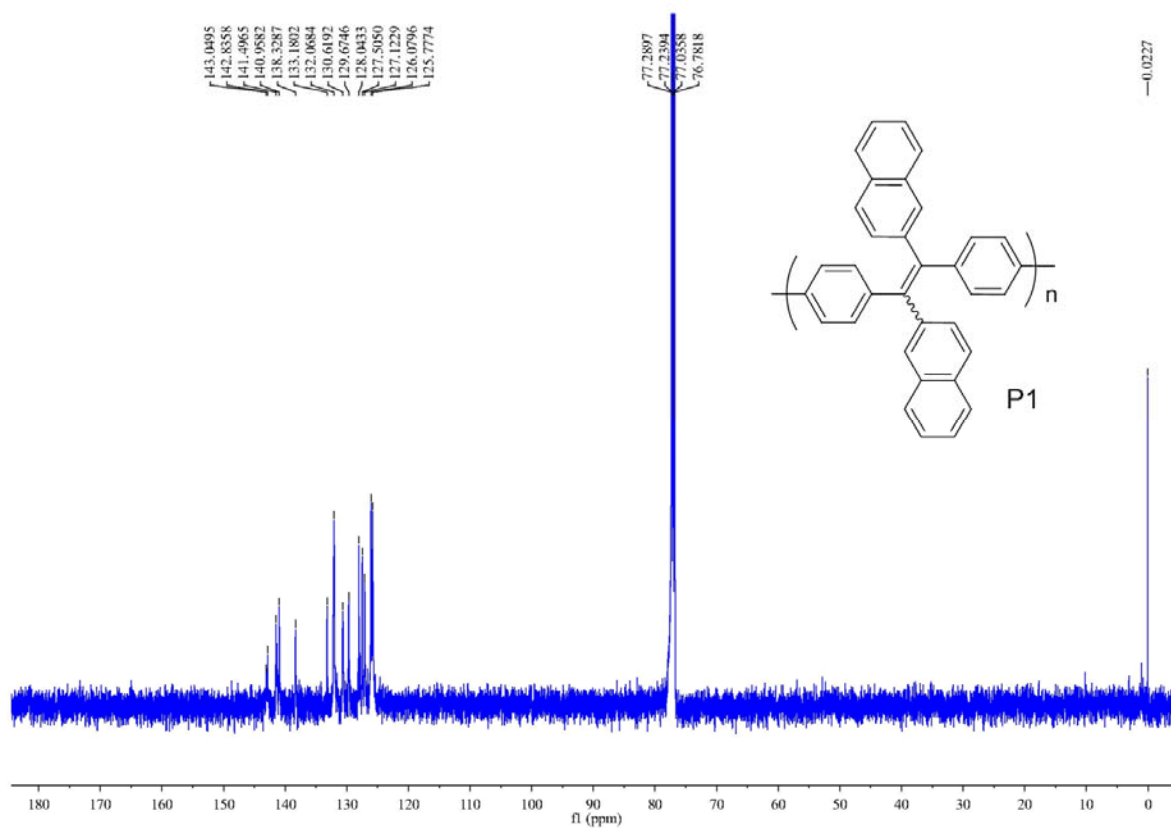


Fig. S8 <sup>13</sup>C NMR spectrum of compound P1.

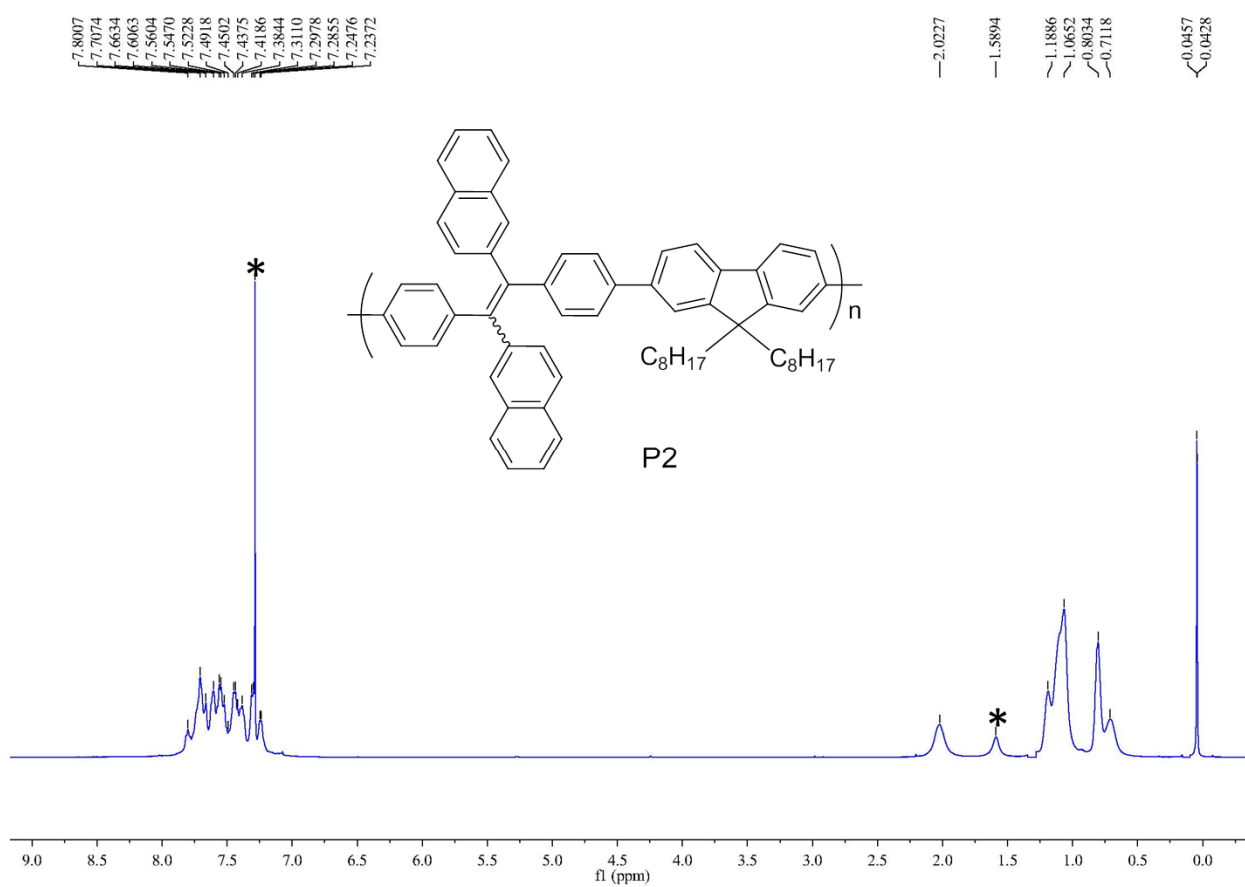


Fig. S9 <sup>1</sup>H NMR spectrum of P2.



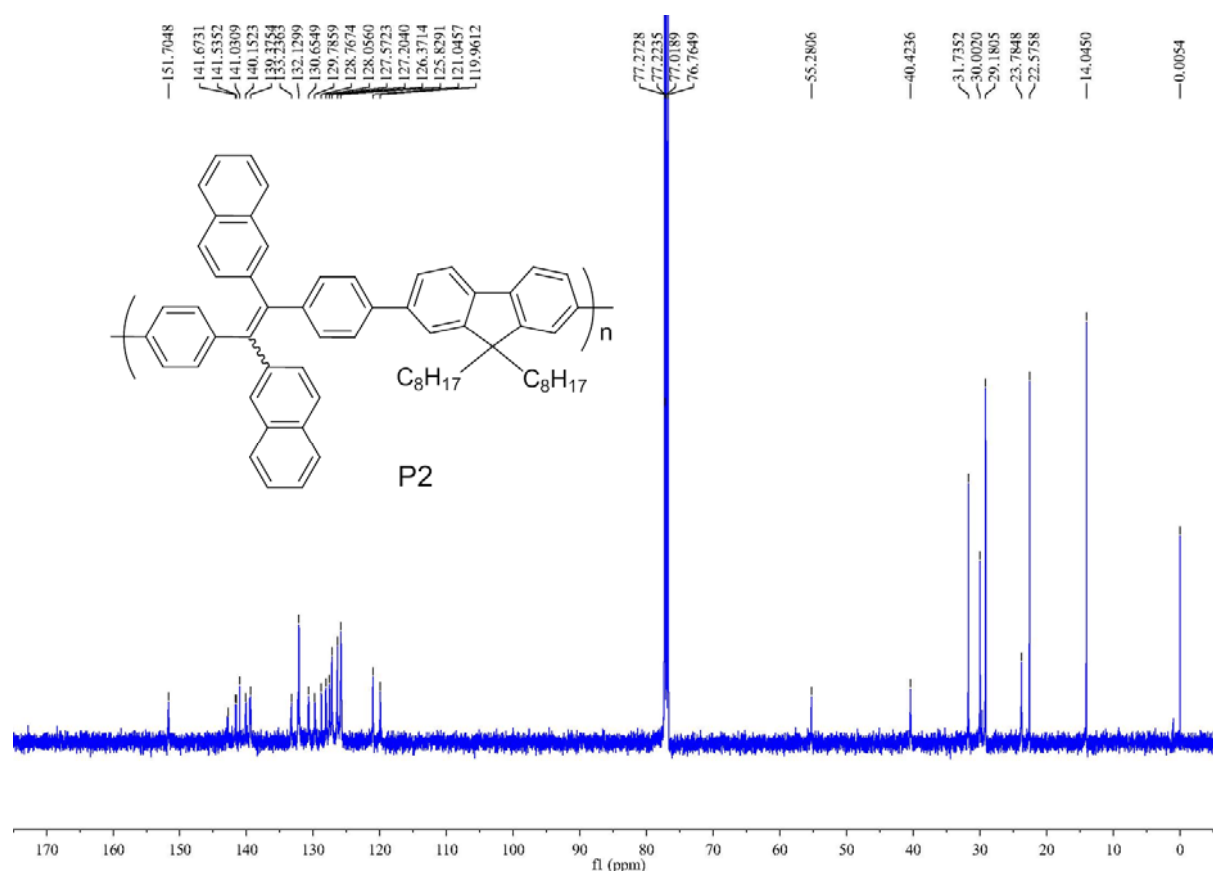


Fig. S10 <sup>13</sup>C 3NMR spectrum of P2.

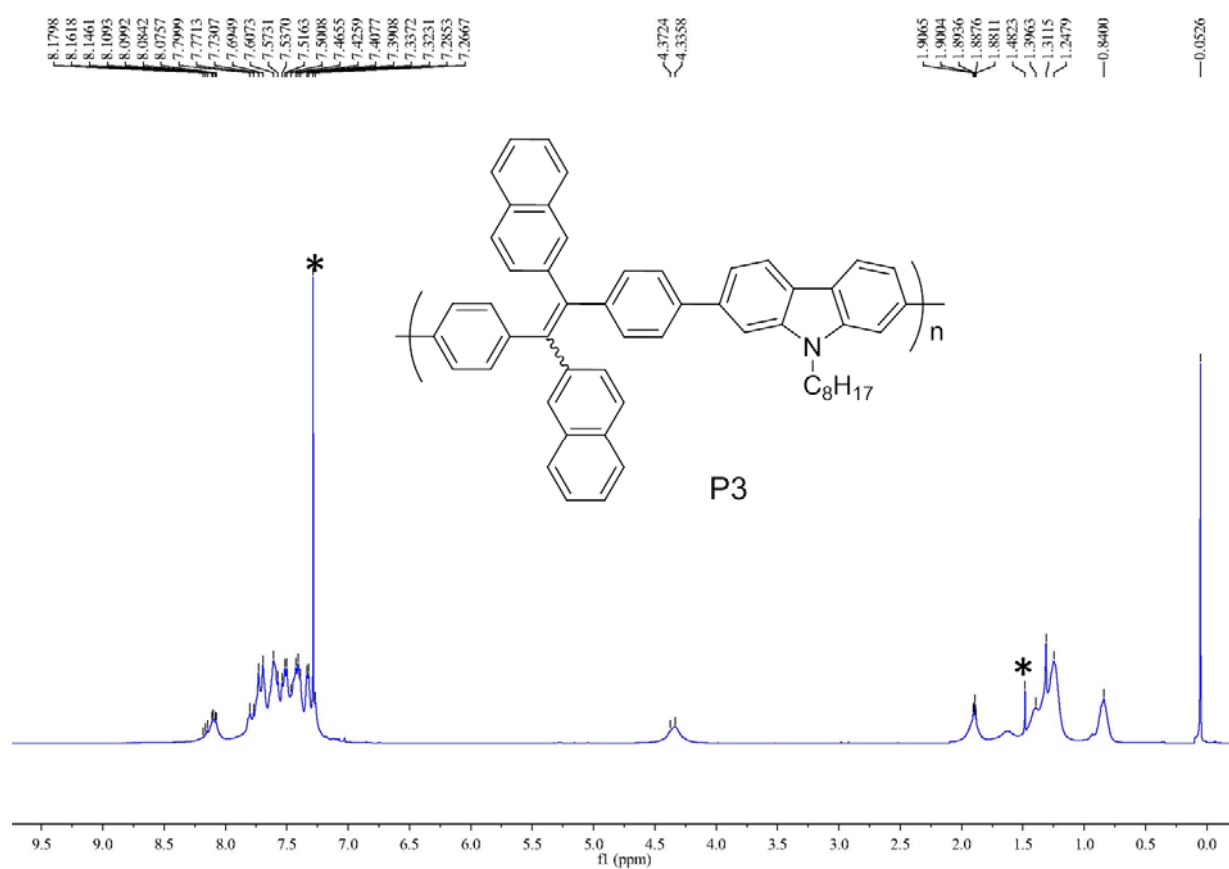
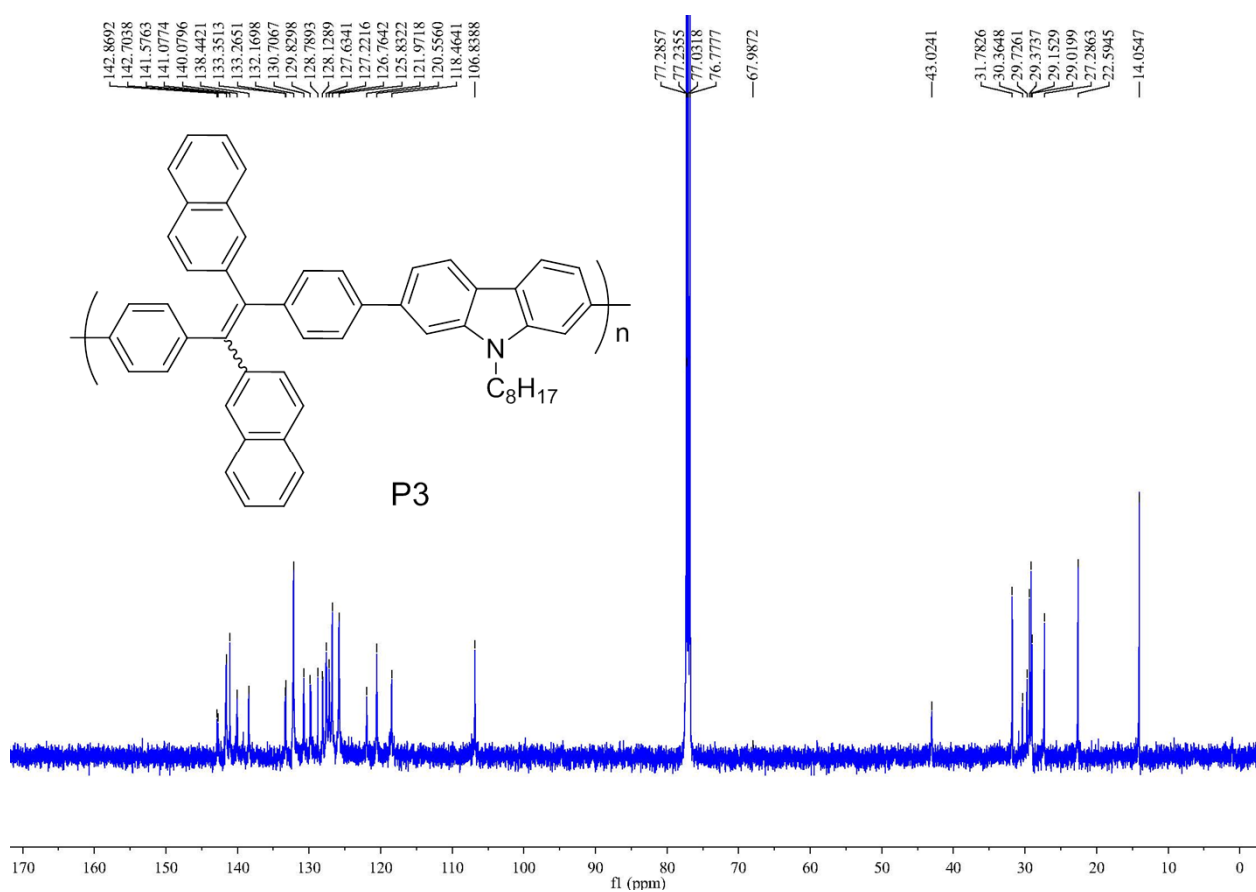


Fig. S11 <sup>1</sup>H NMR spectrum of P3.



**Fig. S12**  $^{13}\text{C}$  NMR spectrum of P3.