

## Electronic Supplementary Information:

### Aromatic/Perfluoroaromatic Self-Assembly Effect: an Effective Strategy to Improve NLO Effect

Wenbo Wu,<sup>a</sup> Qi Huang,<sup>a</sup> Cheng Ye,<sup>b</sup> Jingui Qin,<sup>a</sup> and Zhen Li\*<sup>a</sup>

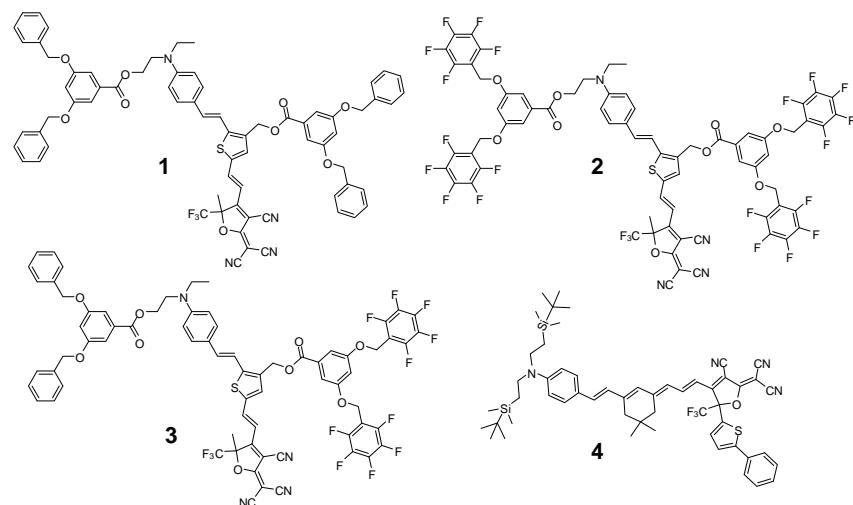


Chart S1.

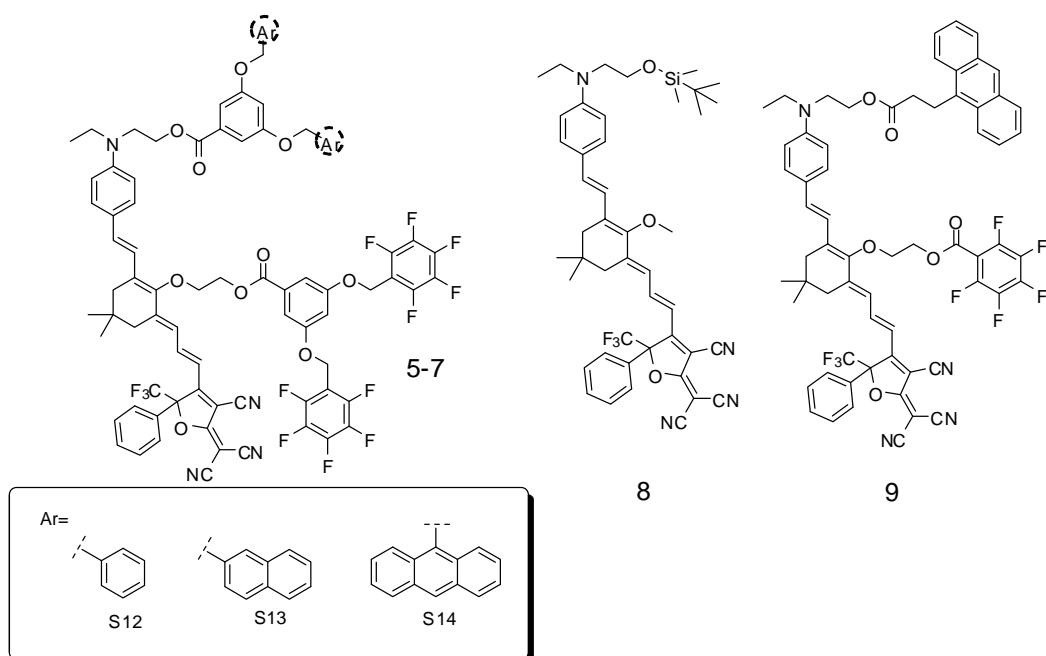


Chart S2.

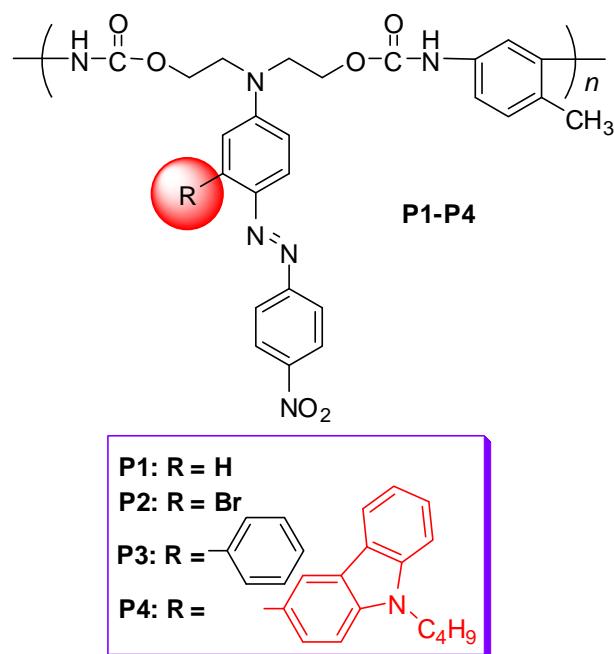


Chart S3.

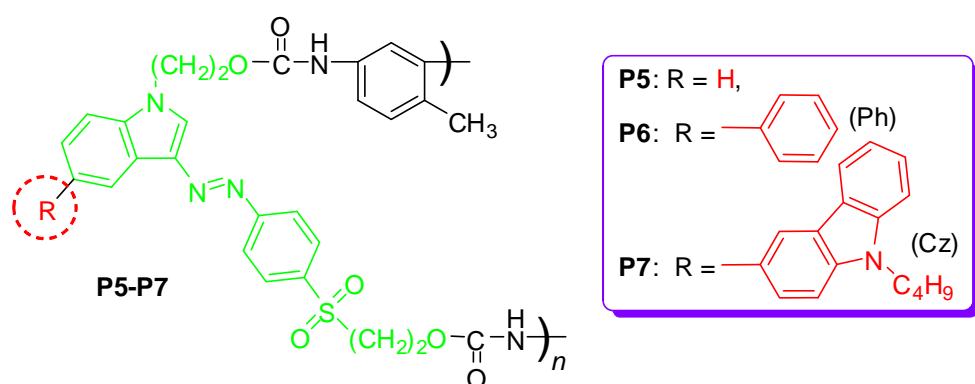


Chart S4.

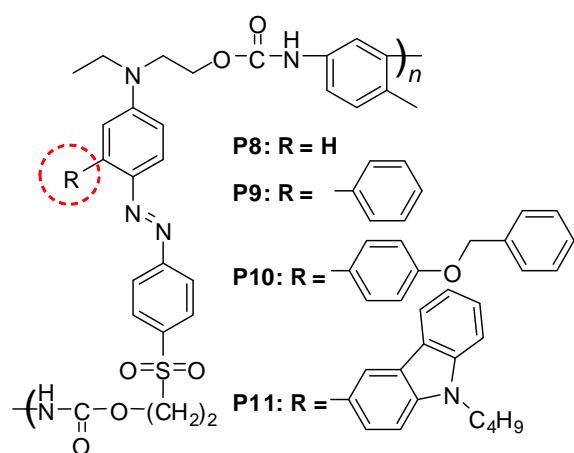


Chart S5.

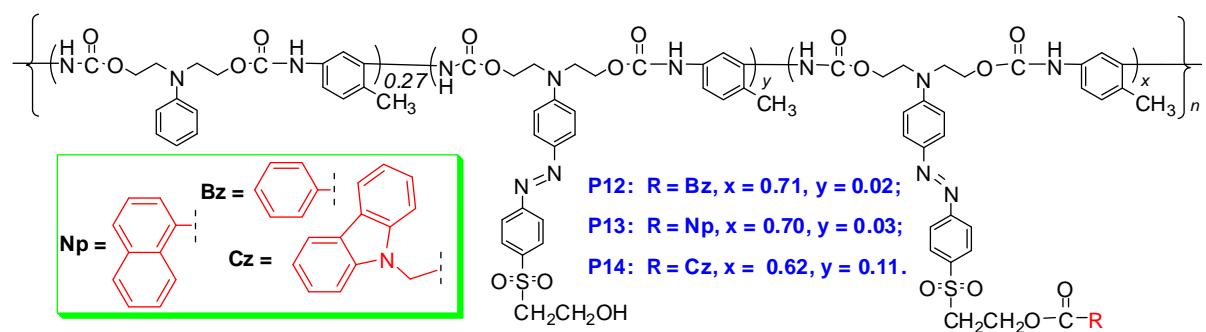


Chart S6.

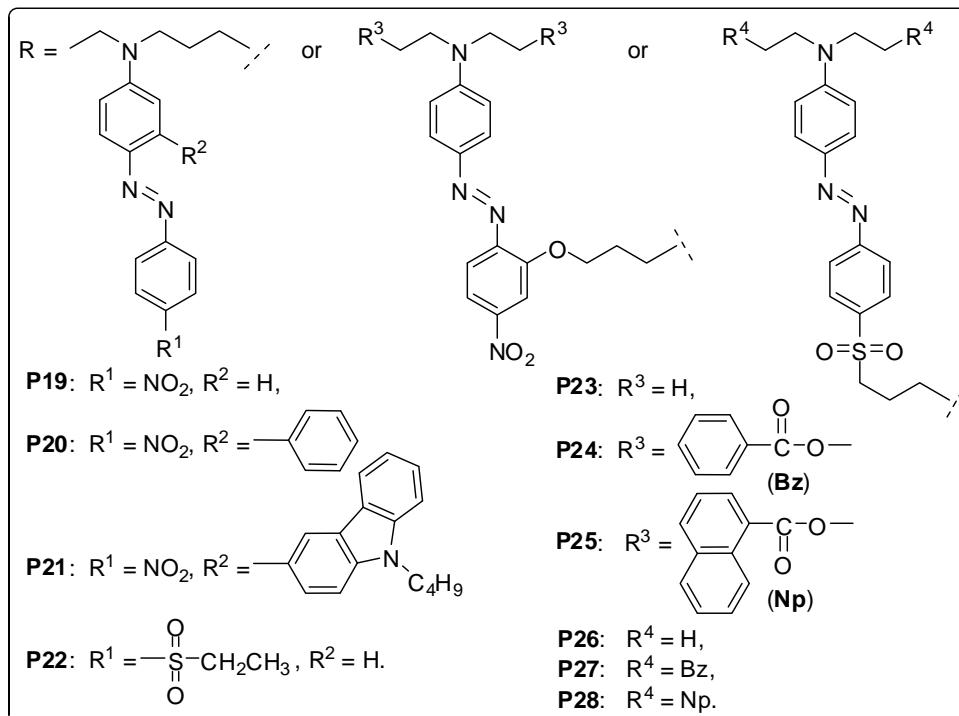
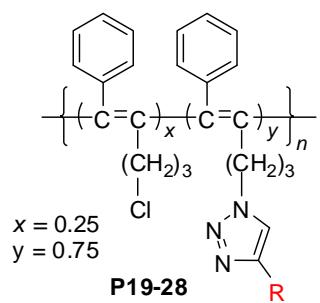


Chart S7.

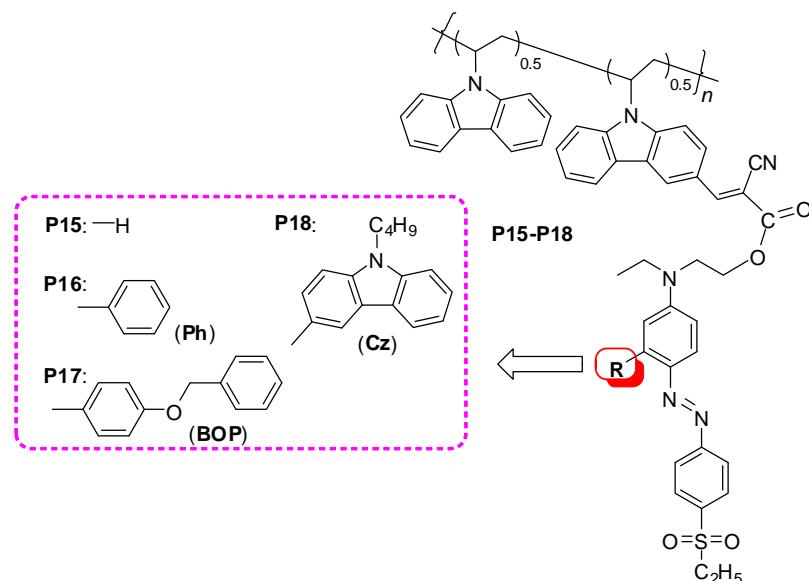


Chart S8.

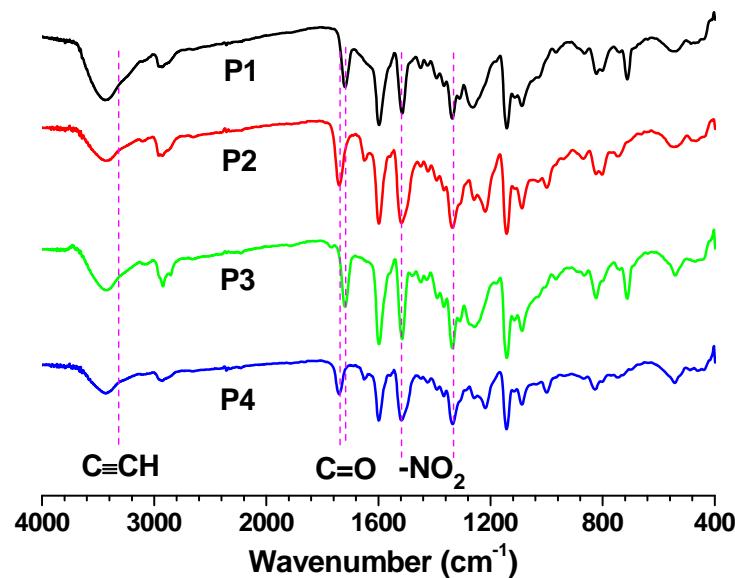
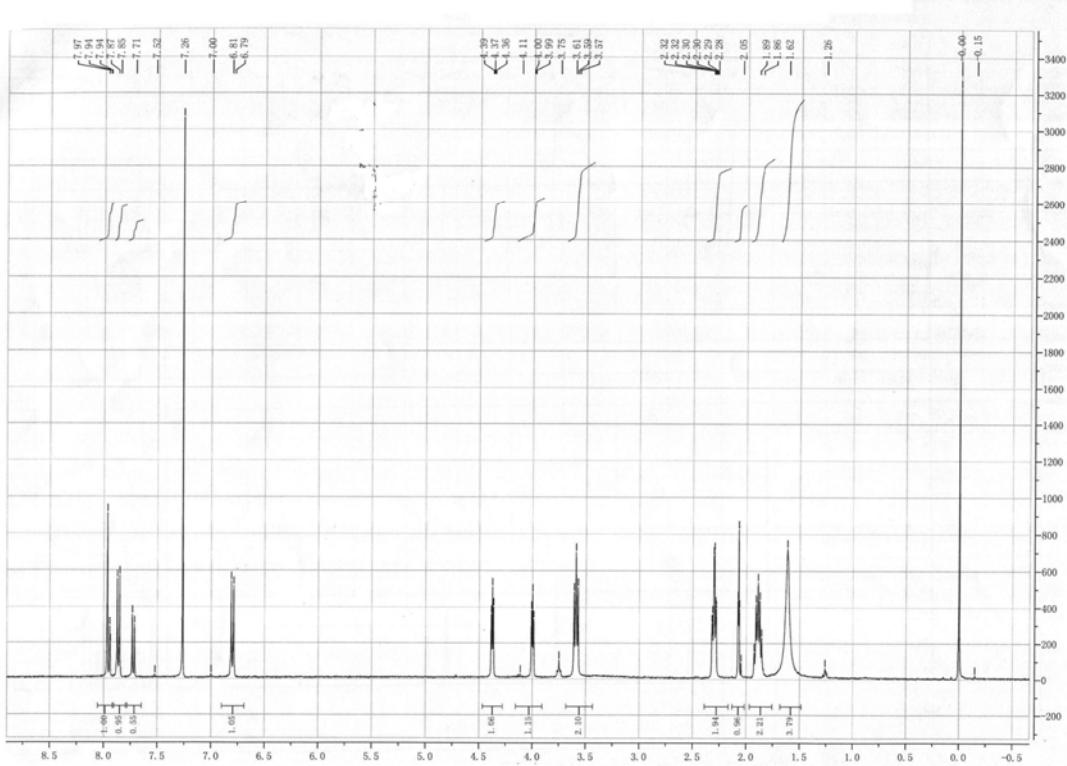
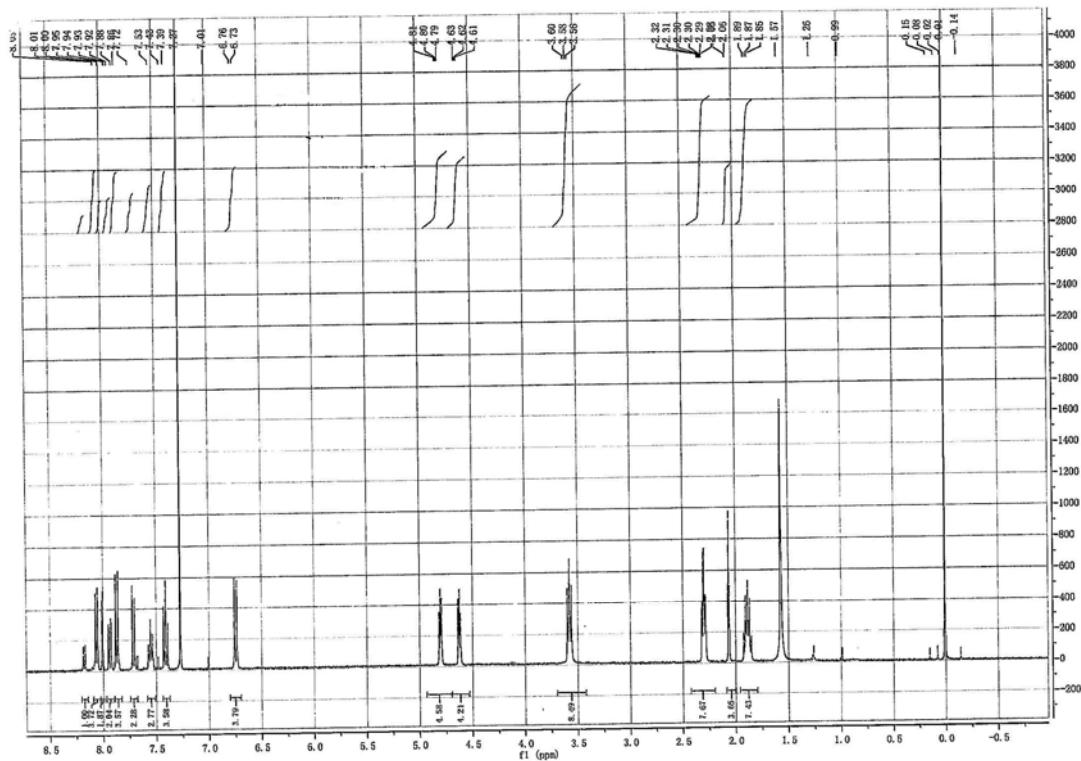


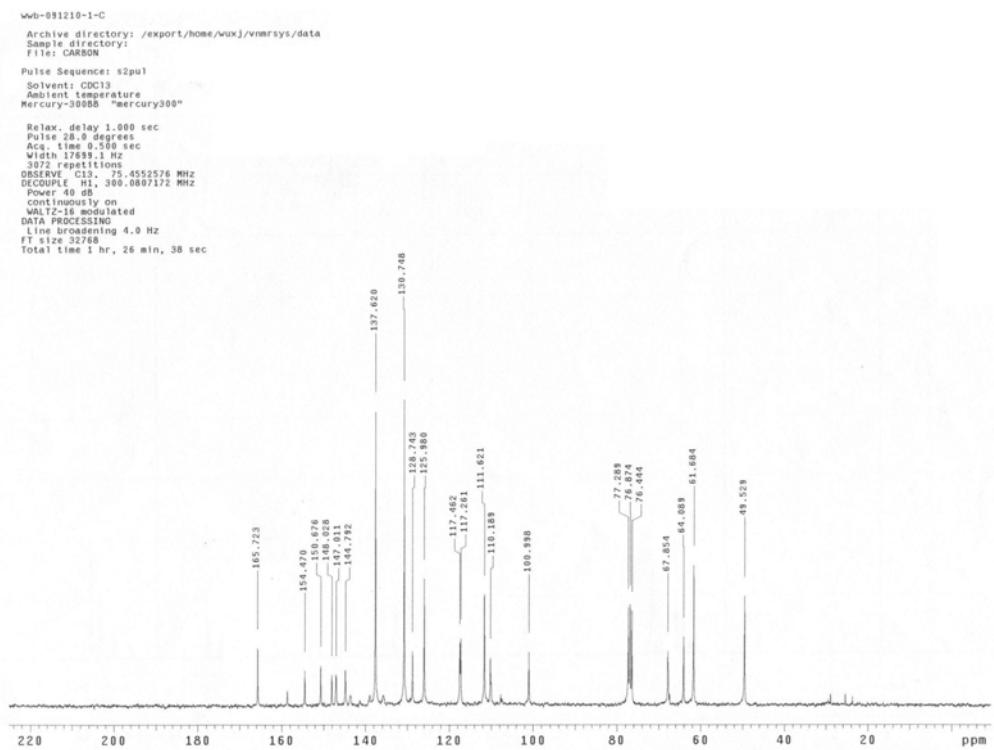
Fig. S1. The FT-IR spectra of polymers P1-P4.



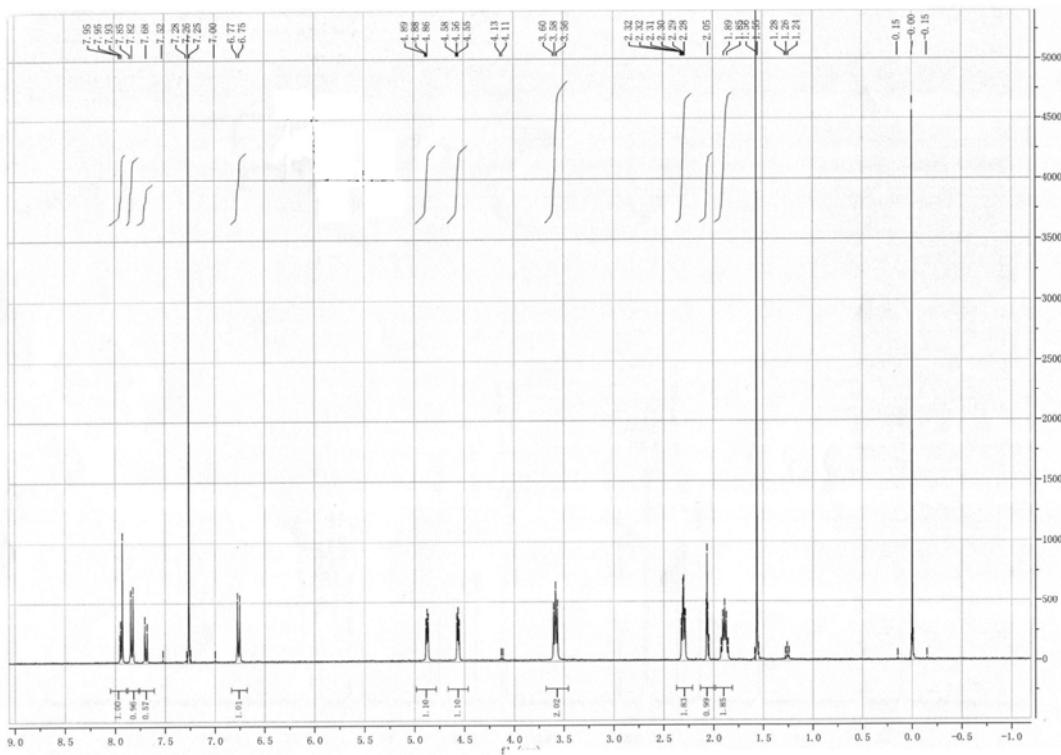
**Fig. S2.**  $^1\text{H}$  NMR spectrum of compound **S3** in chloroform-*d*.



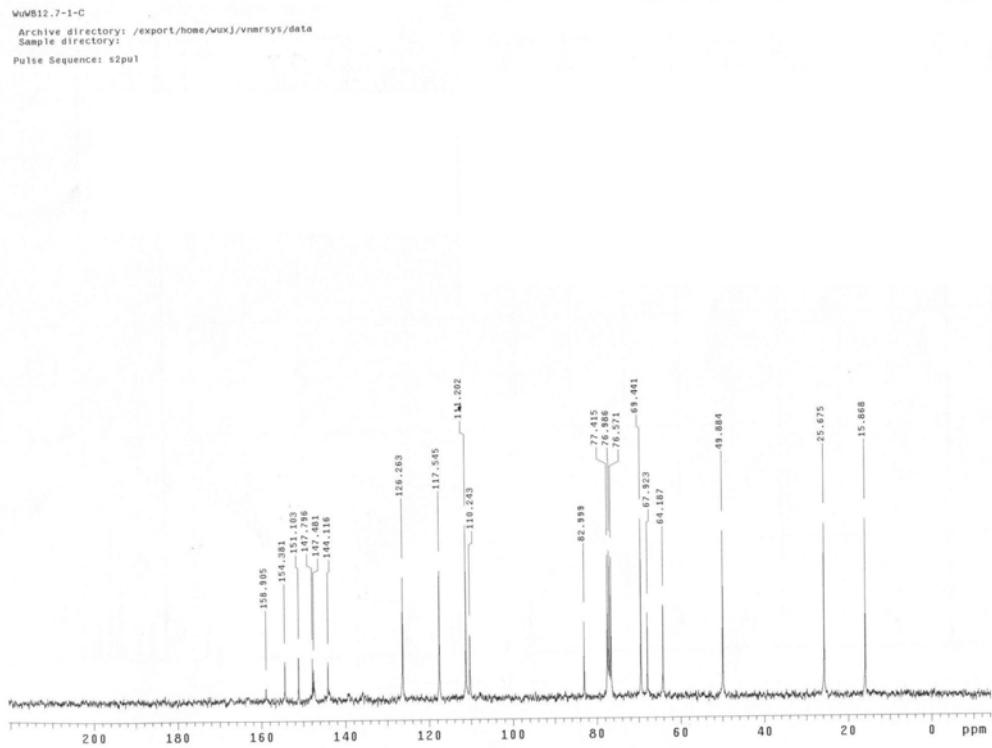
**Fig. S3.**  $^1\text{H}$  NMR spectrum of chromophore **C1** in chloroform-*d*.



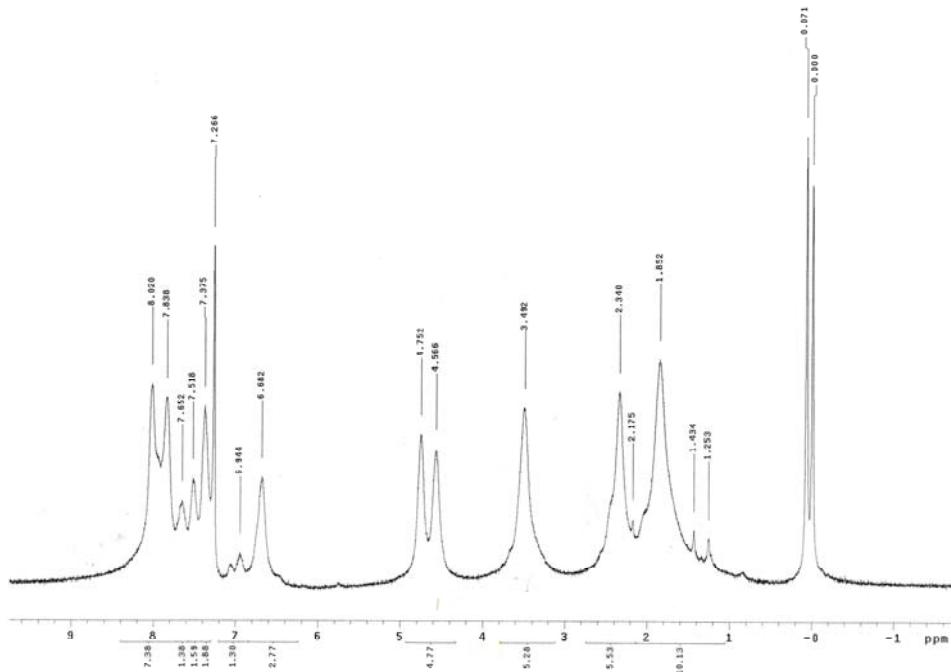
**Fig. S4.**  $^{13}\text{C}$  NMR spectrum of chromophore **C1** in chloroform-*d*.



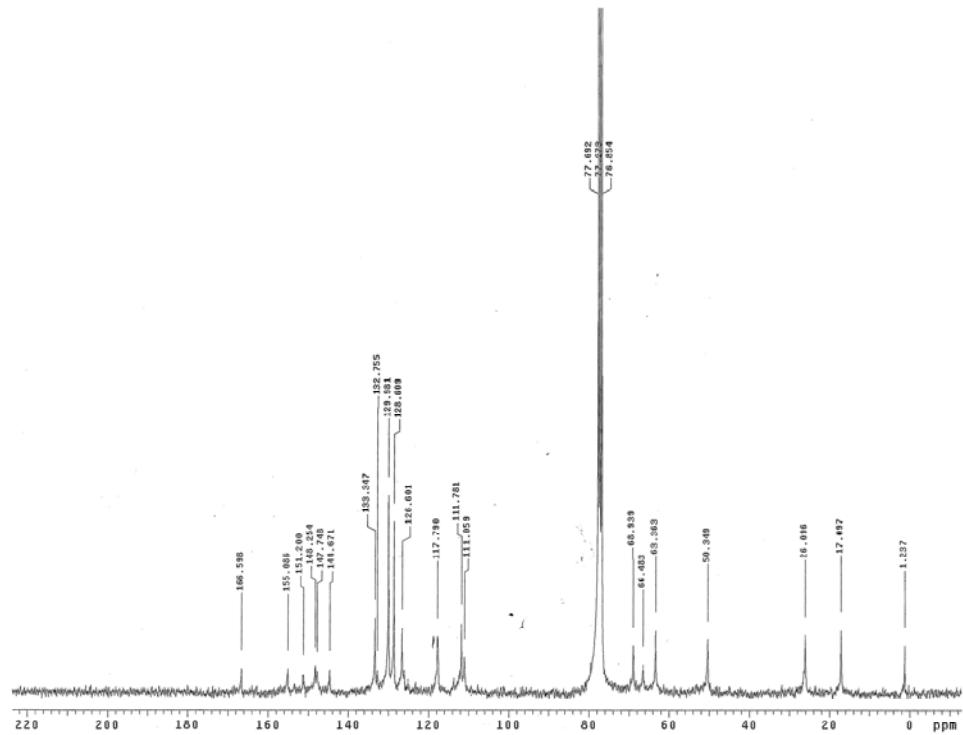
**Fig. S5.**  $^1\text{H}$  NMR spectrum of chromophore **C2** in chloroform-*d*.



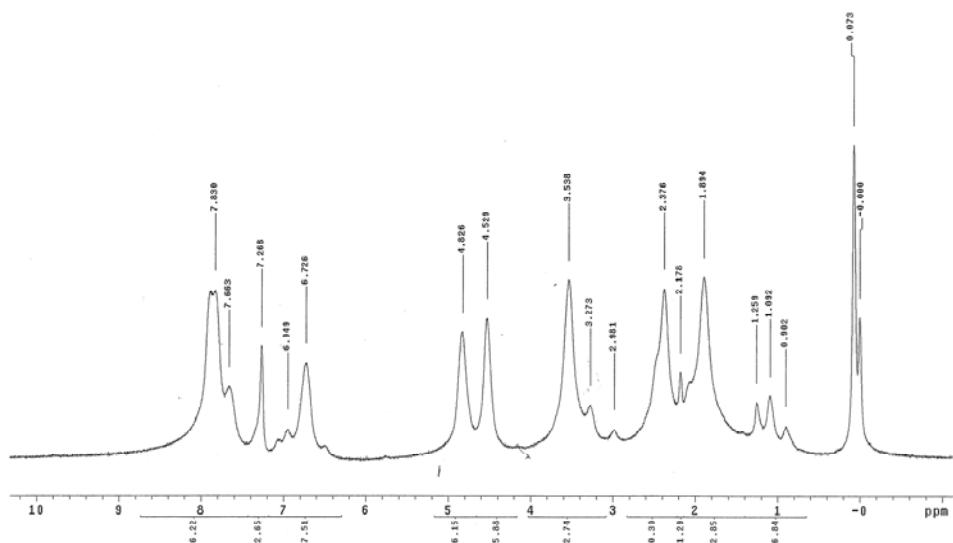
**Fig. S6.**  $^{13}\text{C}$  NMR spectrum of chromophore **C2** in chloroform-*d*.



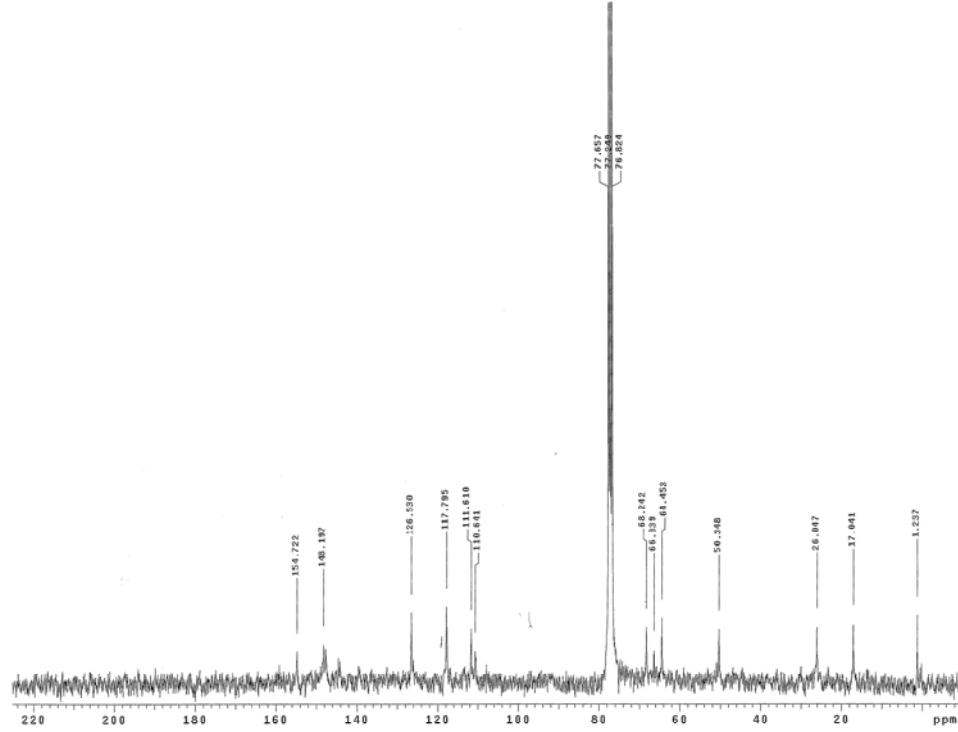
**Fig. S7.**  $^1\text{H}$  NMR spectrum of **P1** in chloroform-*d*.



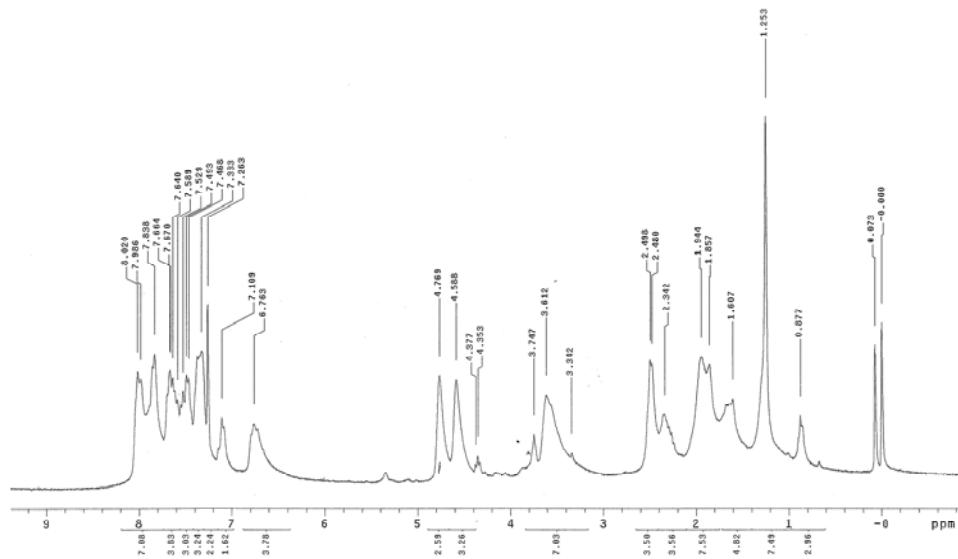
**Fig. S8.** <sup>13</sup>C NMR spectrum of **P1** in chloroform-*d*.



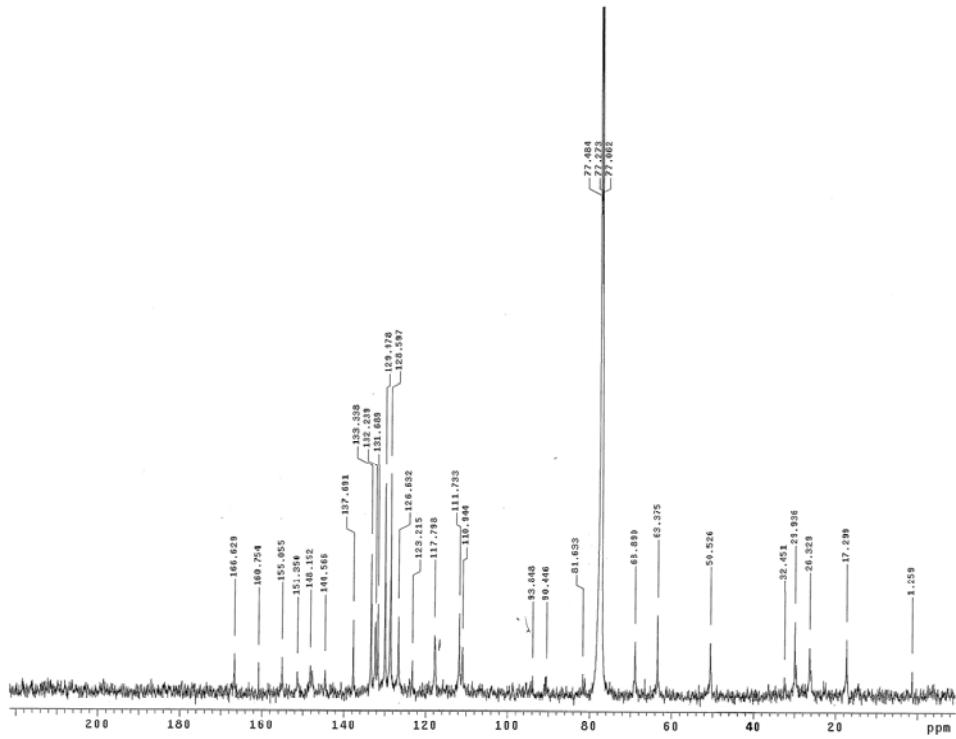
**Fig. S9.** <sup>1</sup>H NMR spectrum of **P2** in chloroform-*d*.



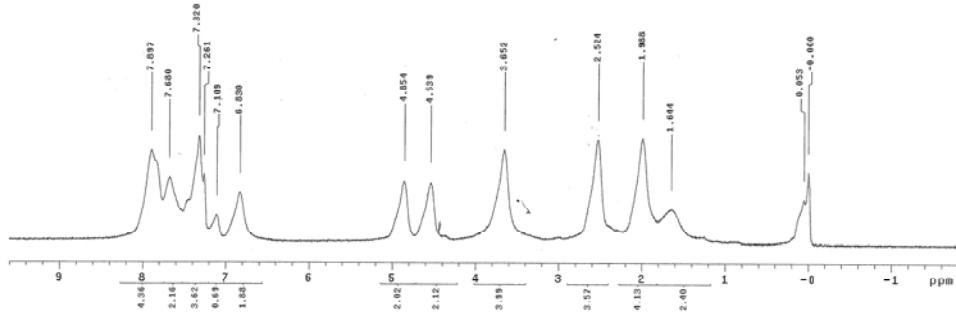
**Fig. S10.** <sup>13</sup>C NMR spectrum of **P2** in chloroform-*d*.



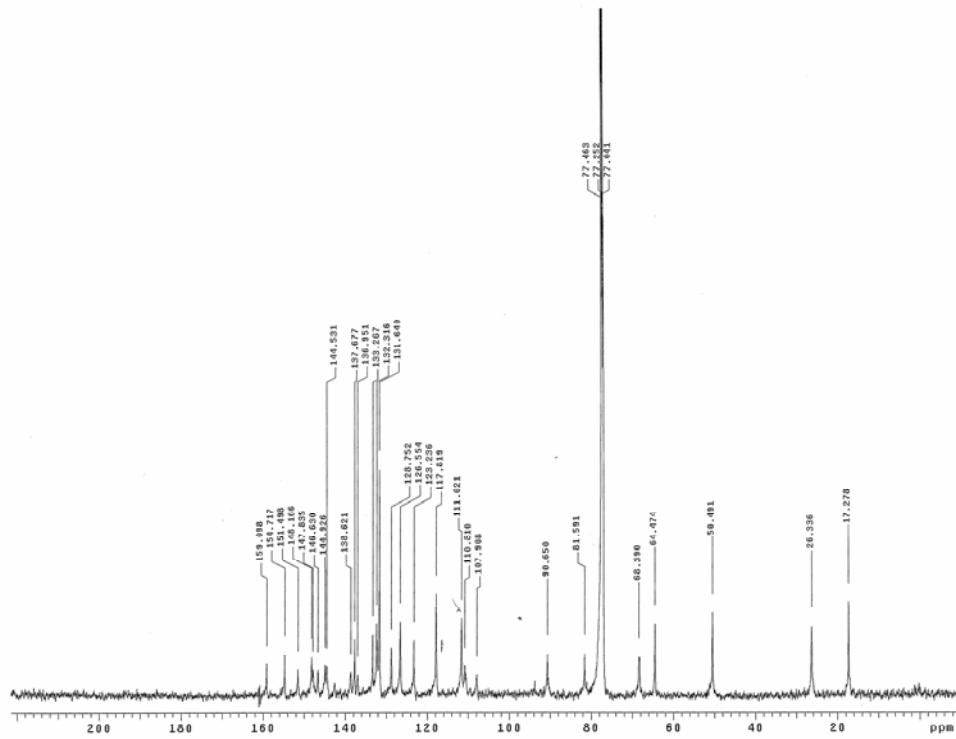
**Fig. S11.** <sup>1</sup>H NMR spectrum of **P3** in chloroform-*d*.



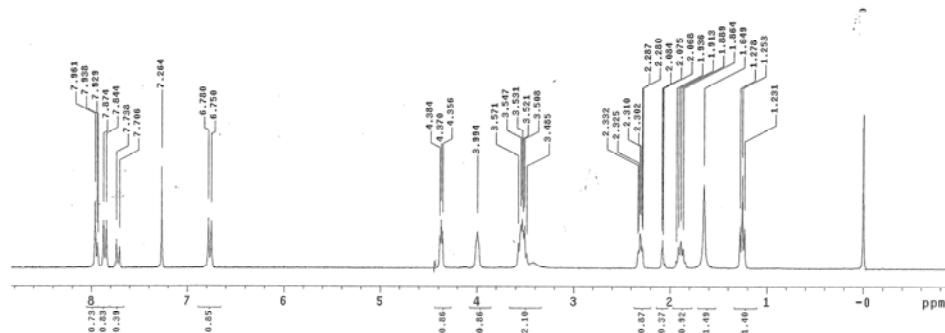
**Fig. S12.**  $^{13}\text{C}$  NMR spectrum of **P3** in chloroform-*d*.



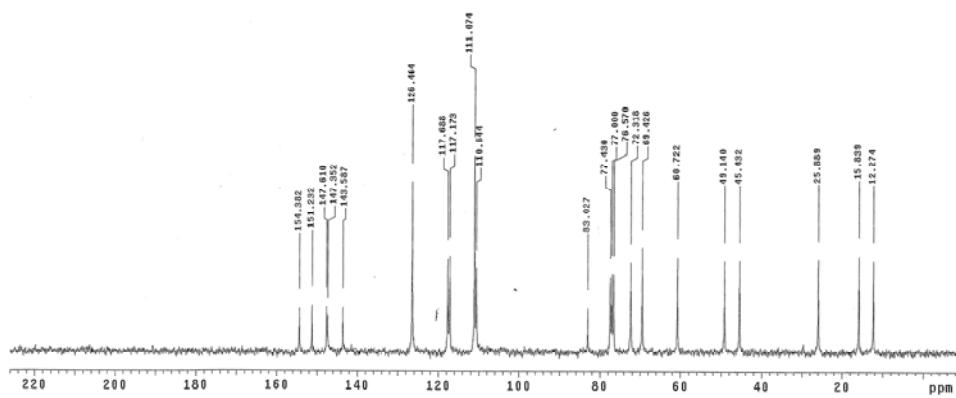
**Fig. S13.**  $^1\text{H}$  NMR spectrum of **P4** in chloroform-*d*.



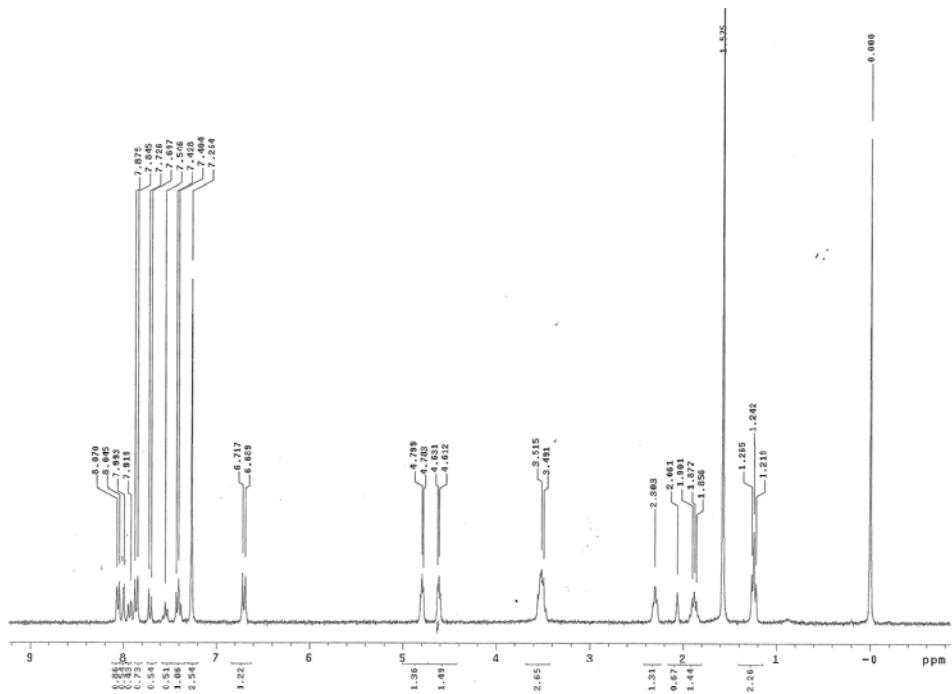
**Fig. S14.**  $^{13}\text{C}$  NMR spectrum of **P4** in chloroform-*d*.



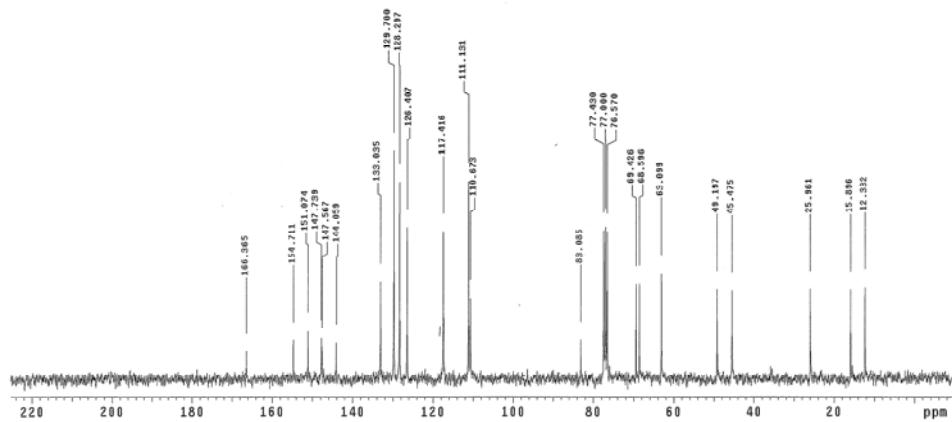
**Fig. S15.**  $^1\text{H}$  NMR spectrum of **S5** in chloroform-*d*.



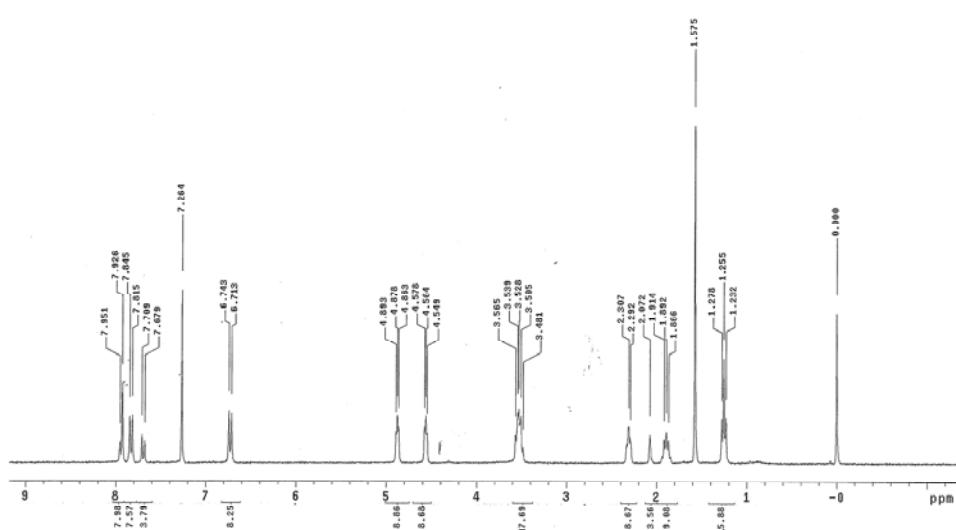
**Fig. S16.**  $^{13}\text{C}$  NMR spectrum of **S5** in chloroform-*d*.



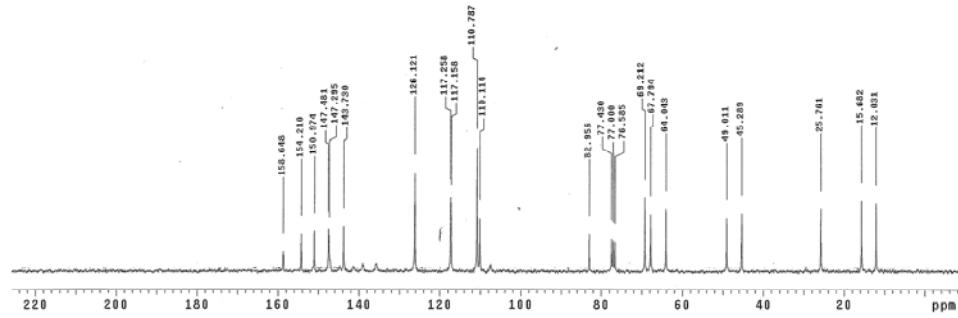
**Fig. S17.** <sup>1</sup>H NMR spectrum of M1 in chloroform-d.



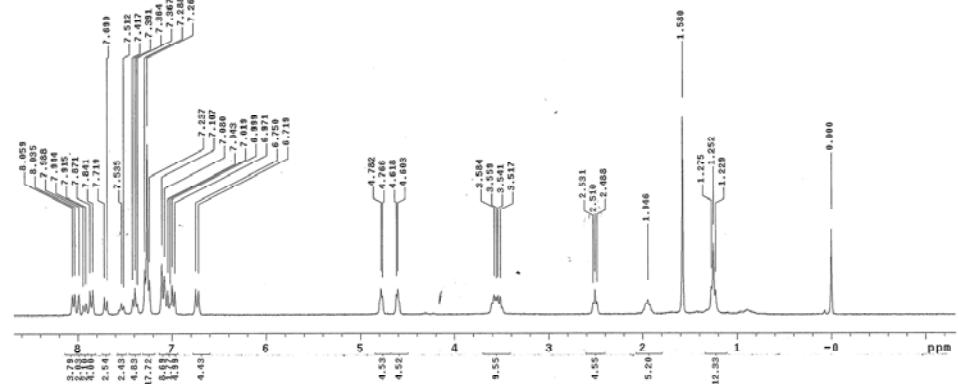
**Fig. S18.** <sup>13</sup>C NMR spectrum of M1 in chloroform-d.



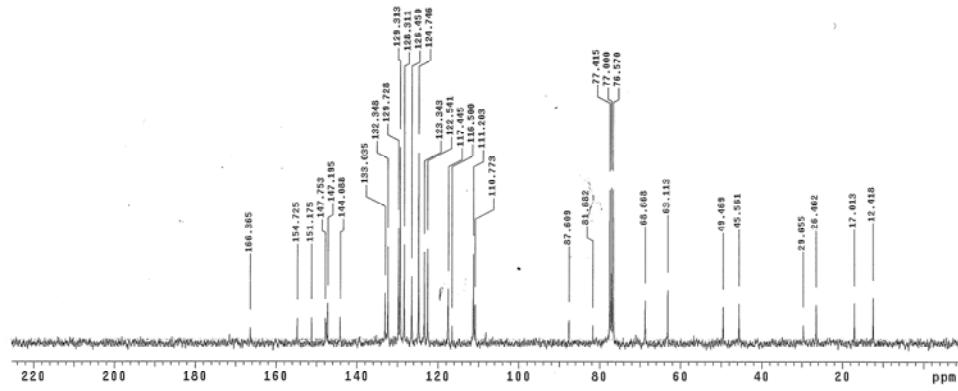
**Fig. S19.** <sup>1</sup>H NMR spectrum of M2 in chloroform-d.



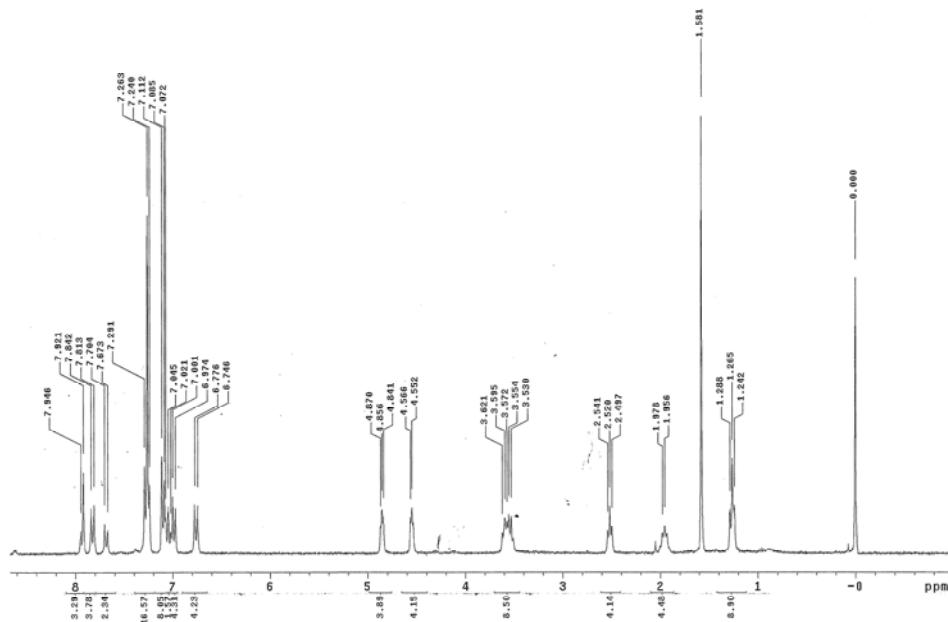
**Fig. S20.**  $^{13}\text{C}$  NMR spectrum of **M2** in chloroform-*d*.



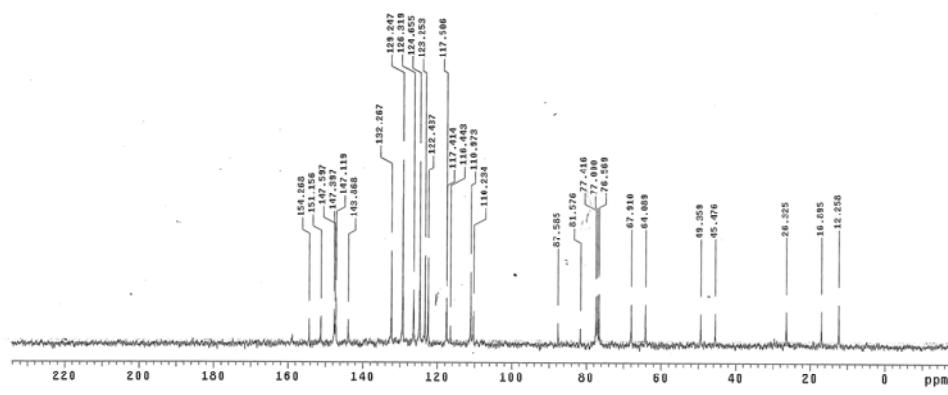
**Fig. S21.**  $^1\text{H}$  NMR spectrum of **M3** in chloroform-*d*.



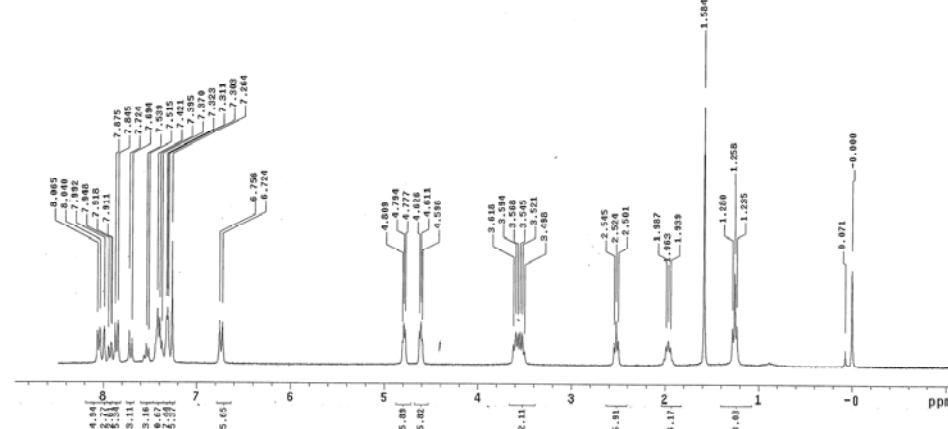
**Fig. S22.**  $^{13}\text{C}$  NMR spectrum of **M3** in chloroform-*d*.



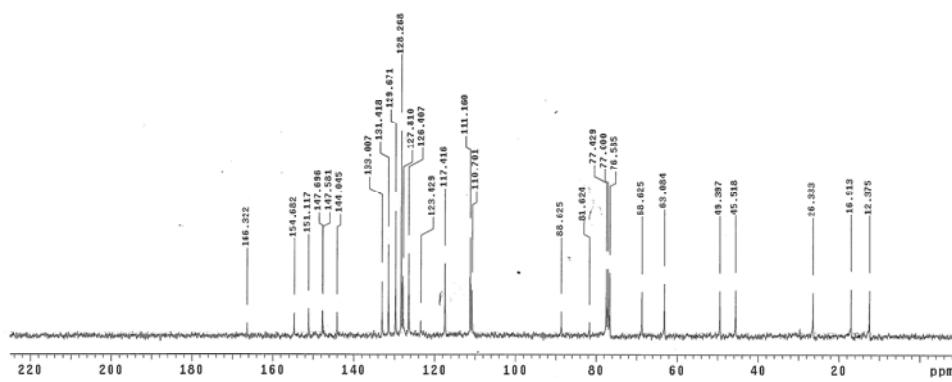
**Fig. S23.**  $^1\text{H}$  NMR spectrum of **M4** in chloroform-*d*.



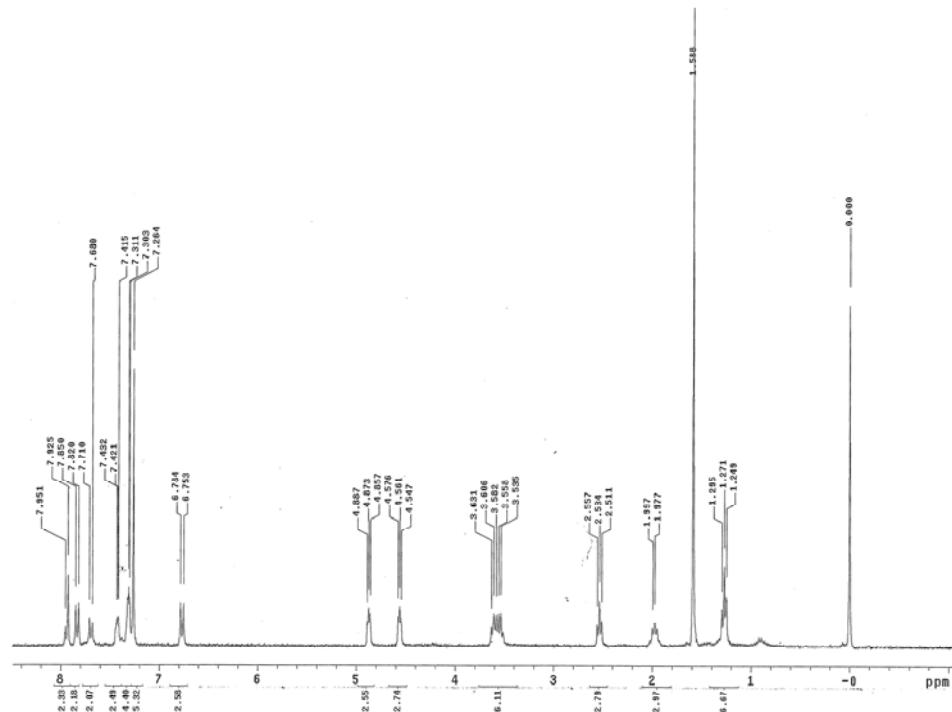
**Fig. S24.**  $^{13}\text{C}$  NMR spectrum of **M4** in chloroform-*d*.



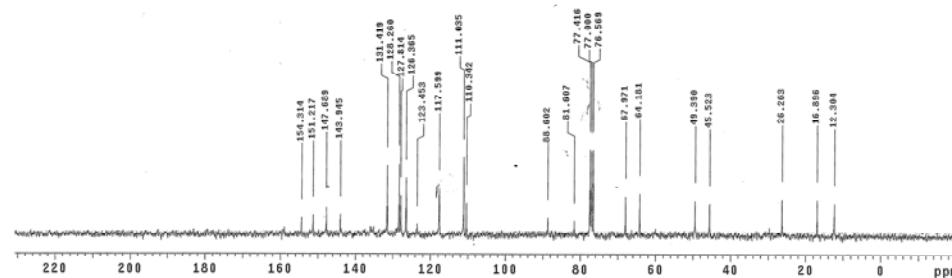
**Fig. S25.**  $^1\text{H}$  NMR spectrum of **M5** in chloroform-*d*.



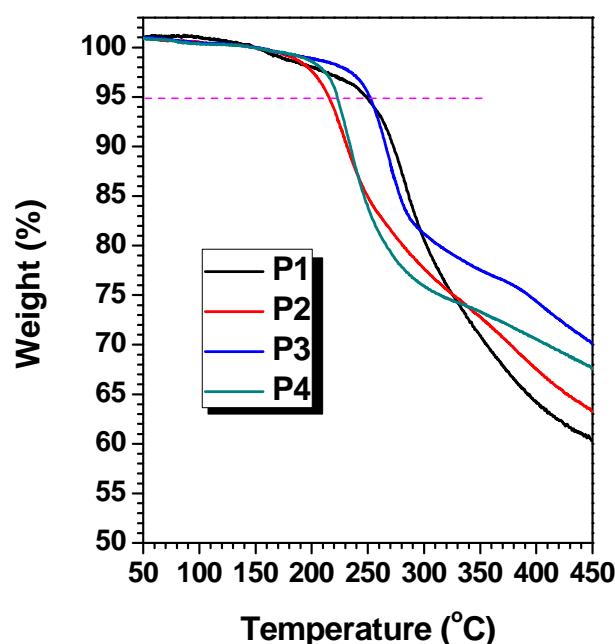
**Fig. S26.** <sup>13</sup>C NMR spectrum of M5 in chloroform-d.



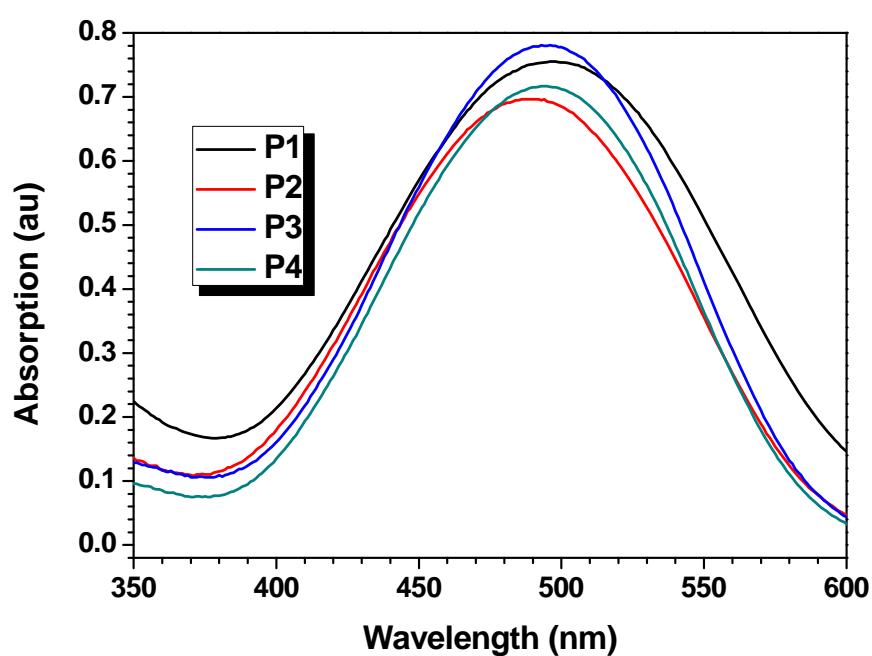
**Fig. S27.** <sup>1</sup>H NMR spectrum of M6 in chloroform-d.



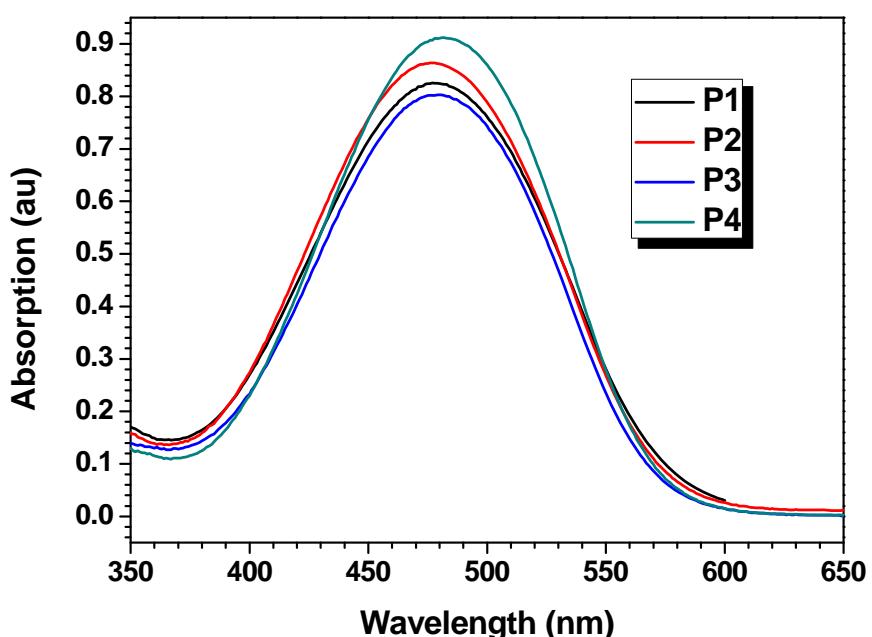
**Fig. S28.** <sup>13</sup>C NMR spectrum of M6 in chloroform-d.



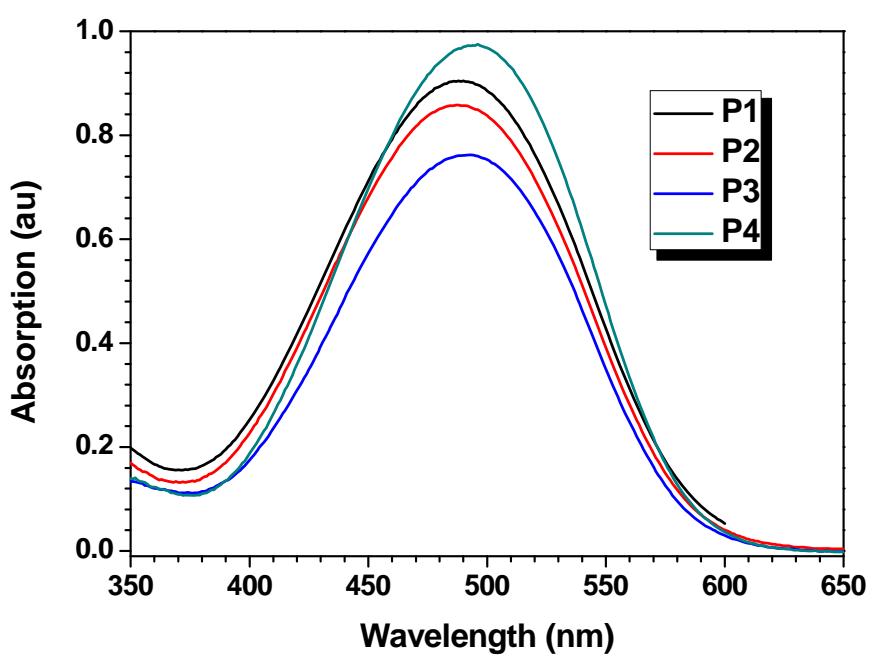
**Fig. S29.** TGA thermograms of polymers **P1-P4**, measured in nitrogen at a heating rate of 10 °C/min



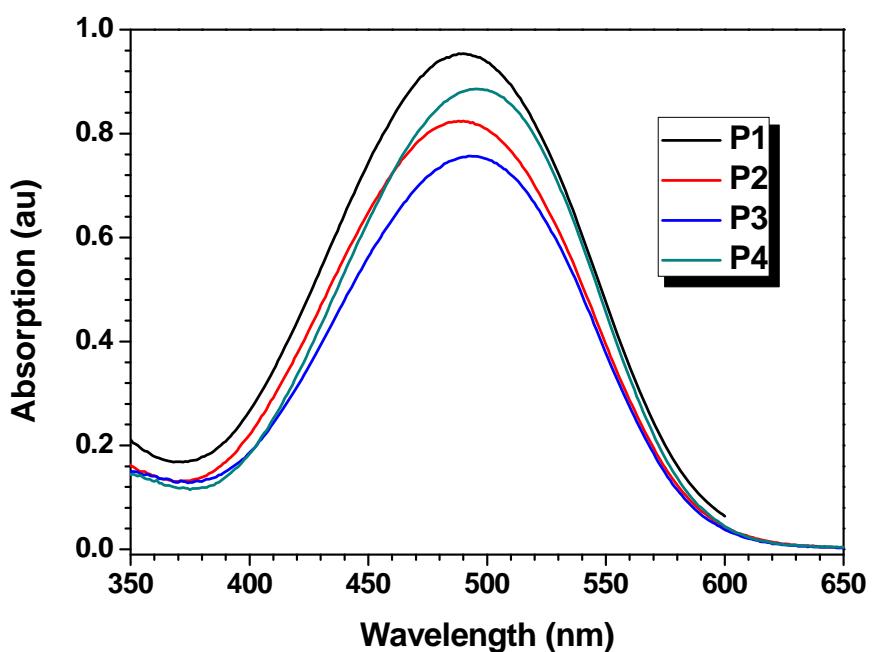
**Fig. S30.** UV-Vis spectra of polymers **P1-P4** in THF (0.02 mg/mL).



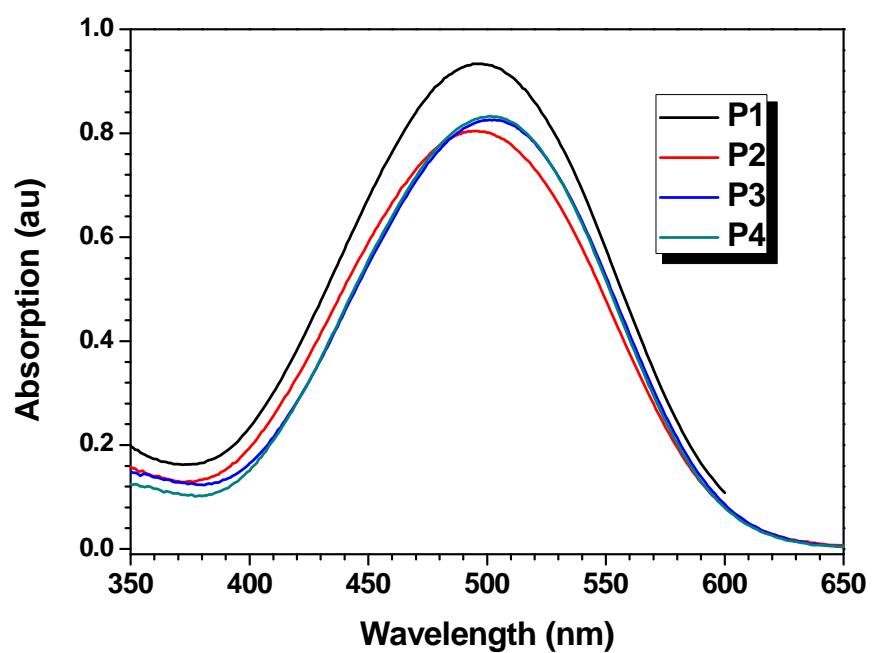
**Fig. S31.** UV-Vis spectra of polymers **P1-P4** in 1,4-dioxane (0.02 mg/mL).



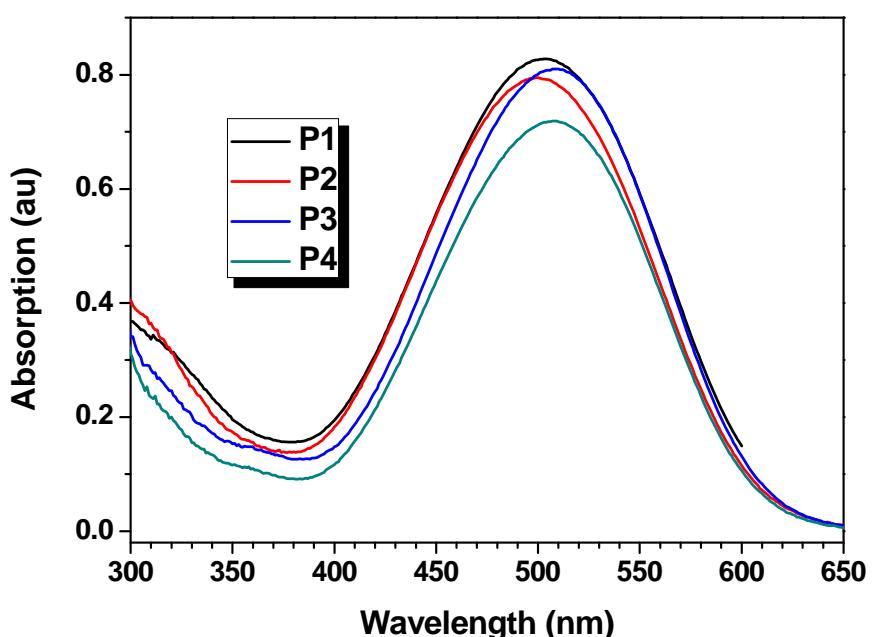
**Fig. S32.** UV-Vis spectra of polymers **P1-P4** in chloroform (0.02 mg/mL).



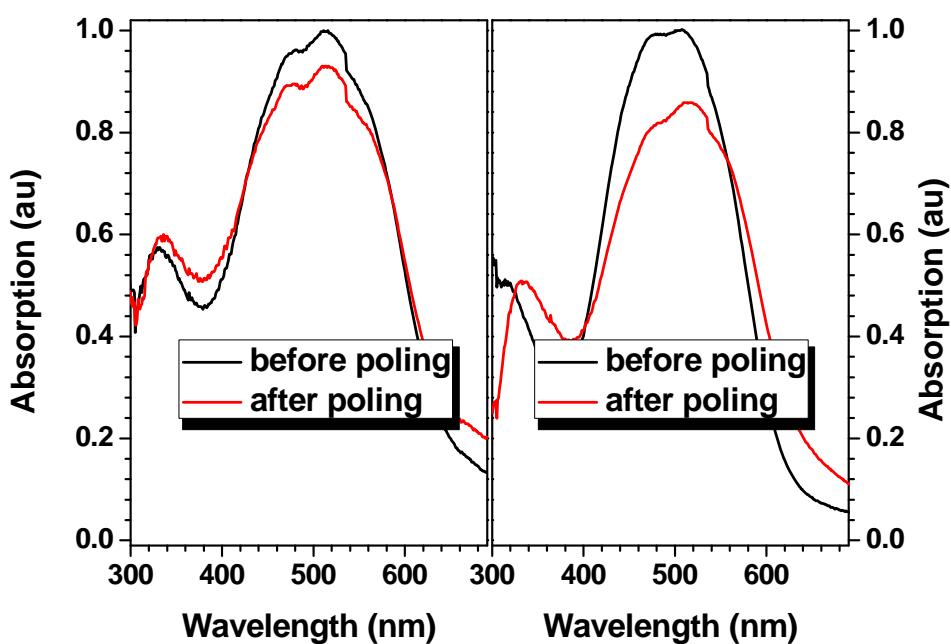
**Fig. S33.** UV-Vis spectra of polymers **P1-P4** in dichloromethane (0.02 mg/mL).



**Fig. S34.** UV-Vis spectra of polymers **P1-P4** in DMF (0.02 mg/mL).



**Fig. S35.** UV-Vis spectra of polymers **P1-P4** in DMSO (0.02 mg/mL).



**Fig. S36.** Absorption spectra of the film of **P1** (left) and **P2** (right) before and after poling.