

## Electronic Supplementary Information:

### Main-chain second-order nonlinear optical polyaryleneethynylenes containing isolation chromophore: enhanced nonlinear optical property, improved optical transparency and stability

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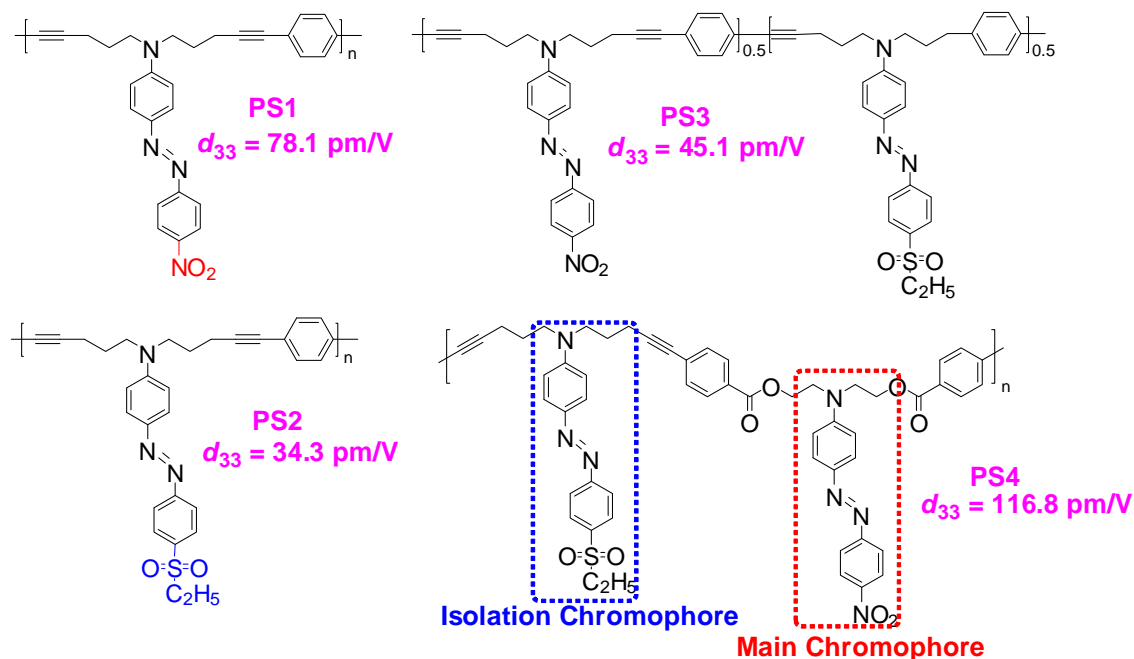


Chart S1. The structures and  $d_{33}$  values of NLO polymers PS1-PS4.

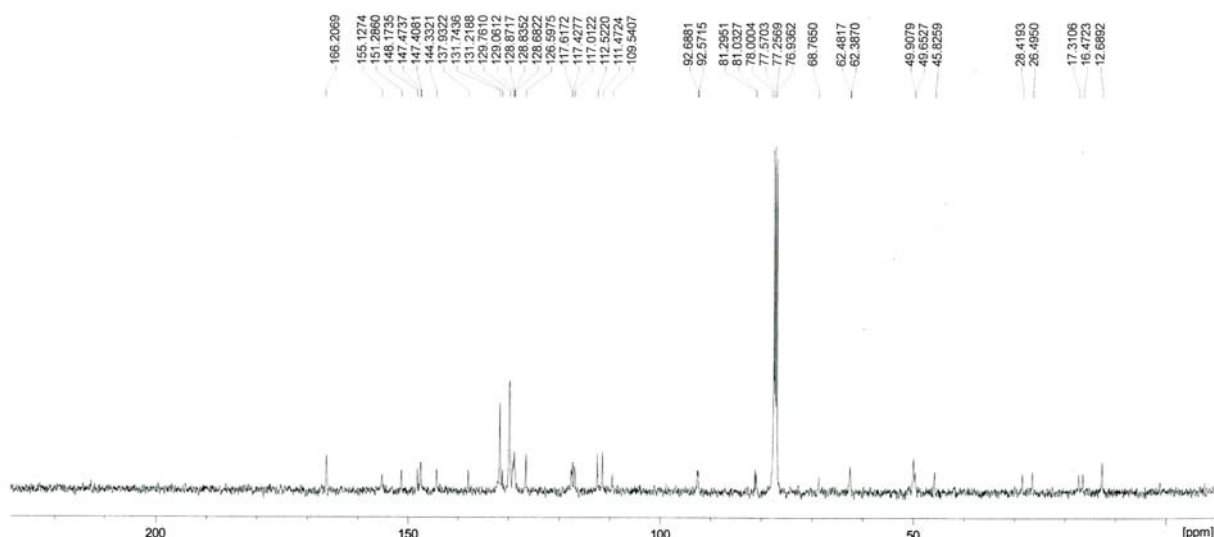


Fig. S1  $^{13}\text{C}$  NMR spectrum of polymer P1 in chloroform- $d$ .

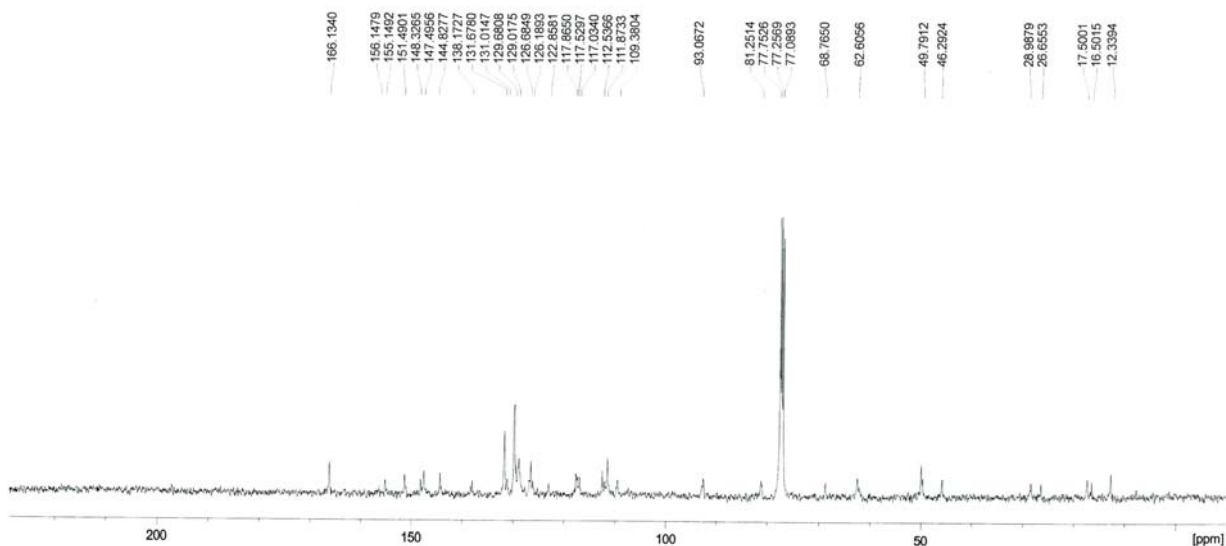


Fig. S2  $^{13}\text{C}$  NMR spectrum of polymer **P2** in chloroform-*d*.

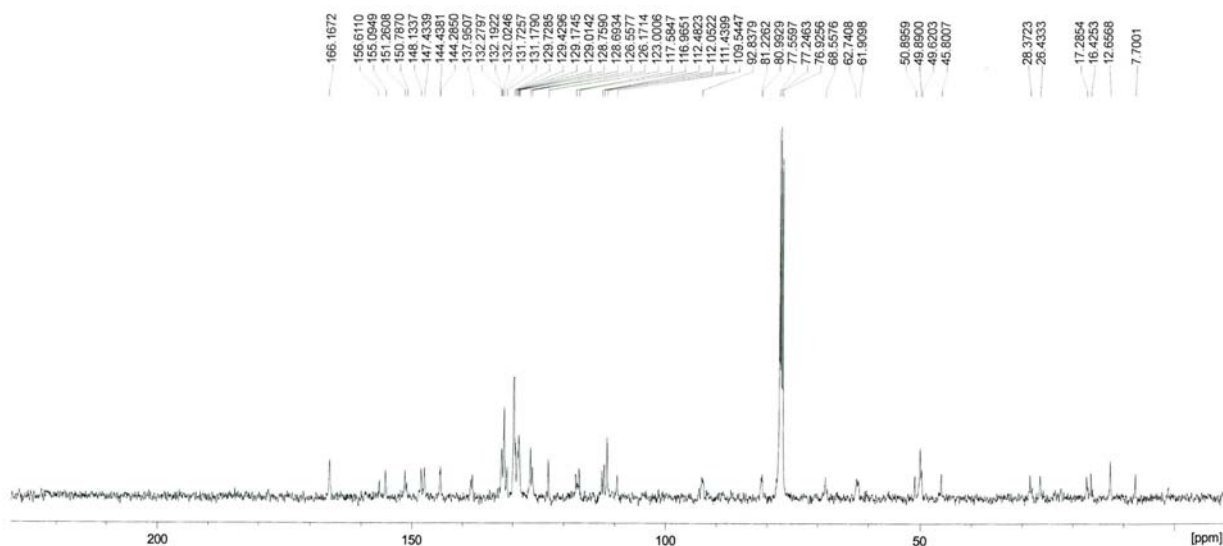


Fig. S3  $^{13}\text{C}$  NMR spectrum of polymer **P3** in chloroform-*d*.

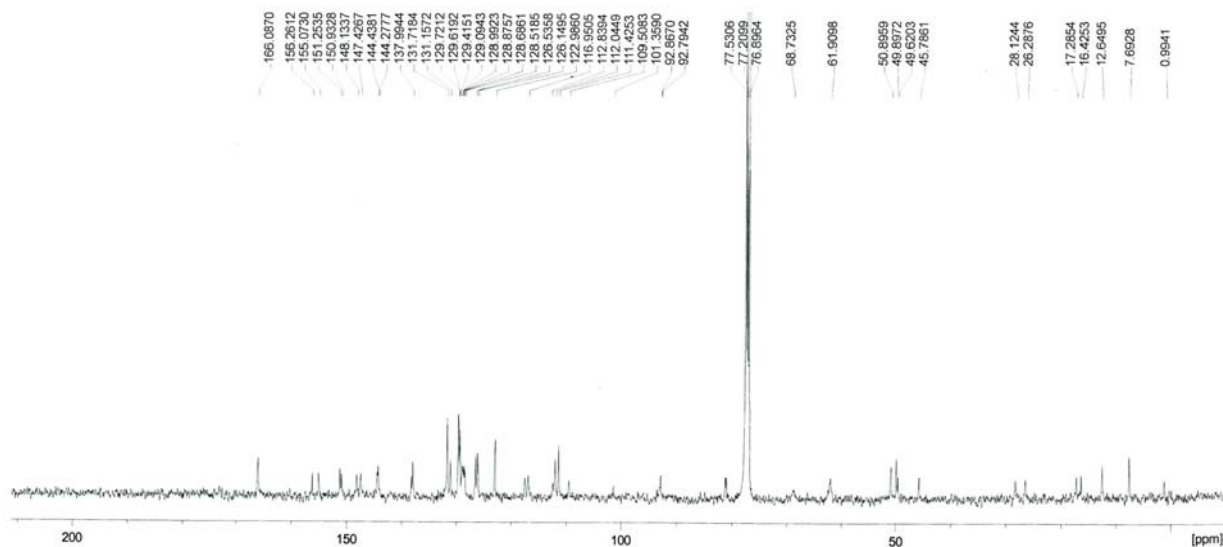


Fig. S4  $^{13}\text{C}$  NMR spectrum of polymer **P4** in chloroform-*d*.

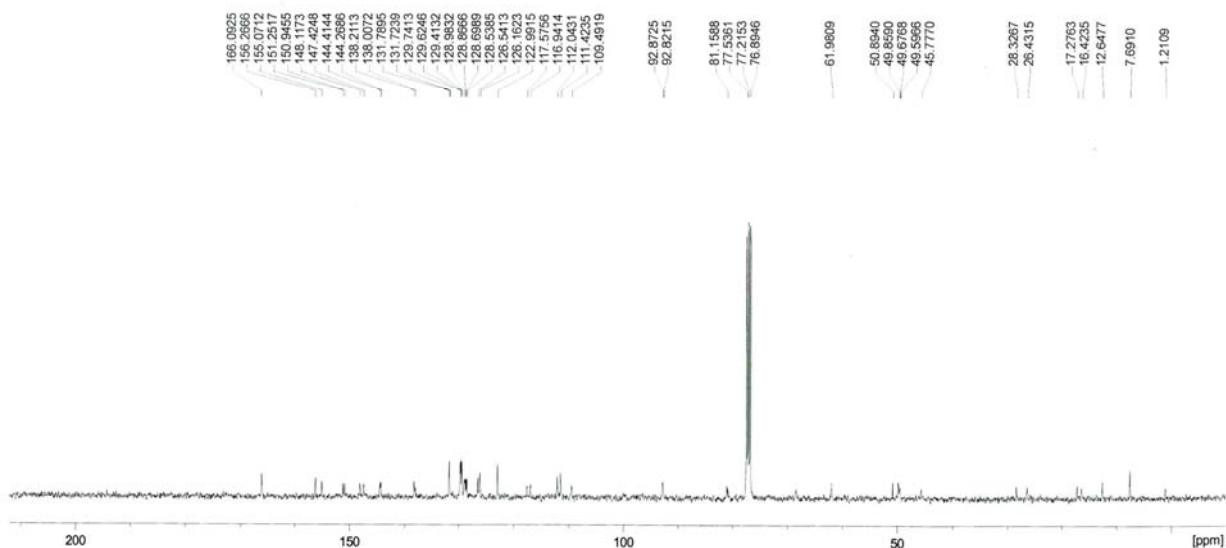


Fig. S5  $^{13}\text{C}$  NMR spectrum of polymer **P5** in chloroform-*d*.

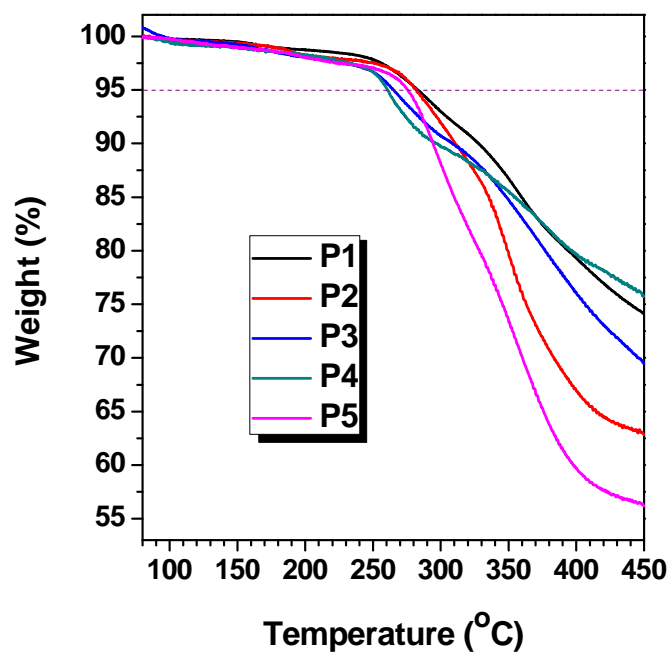


Fig. S6 TGA thermograms of polymers **P1-P5**, measured in nitrogen at a heating rate of 10 °C/min.

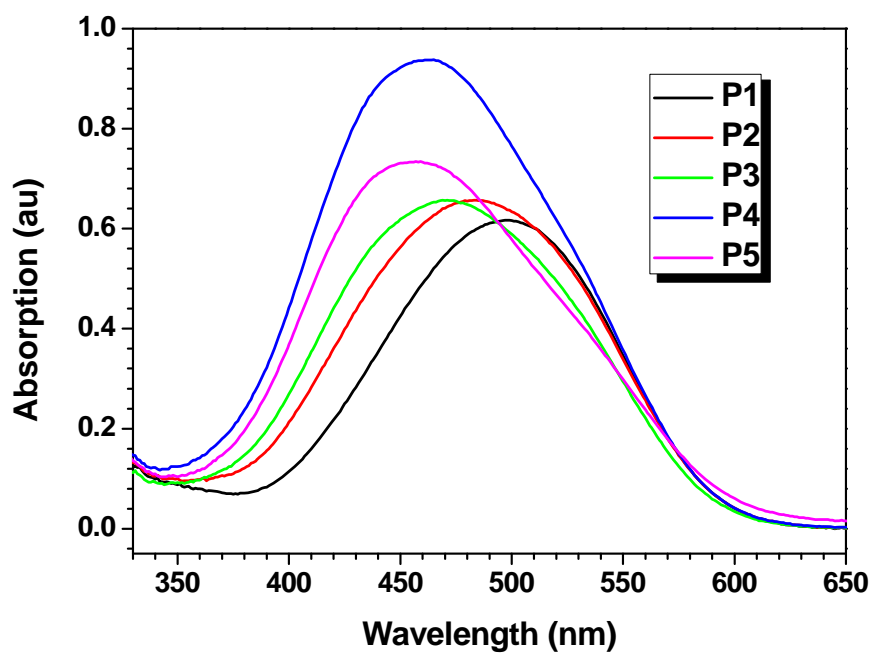


Fig. S7 UV-vis spectra of polymers **P1-P5** in THF (0.02 mg/mL).

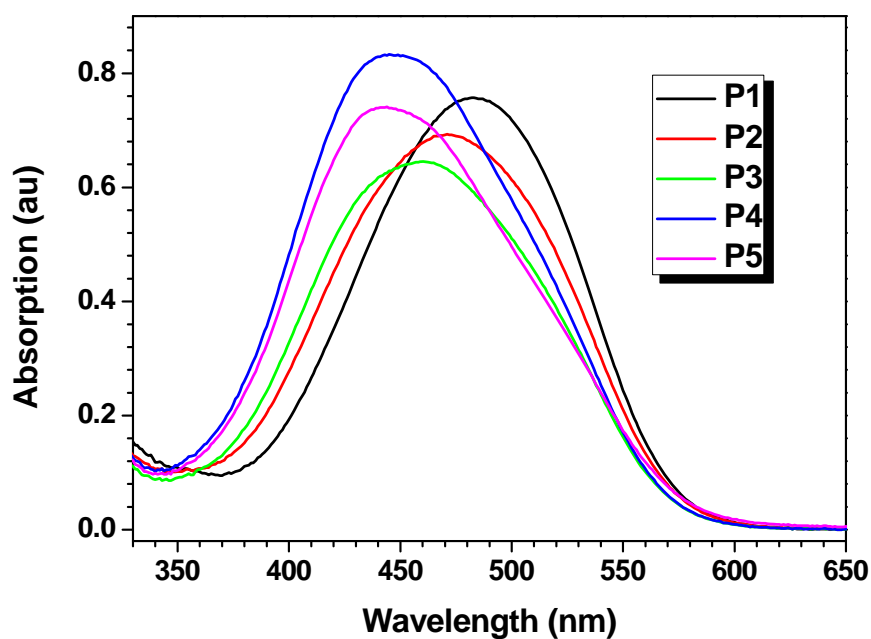


Fig. S8 UV-vis spectra of polymers **P1-P5** in 1,4-dioxane (0.02 mg/mL).

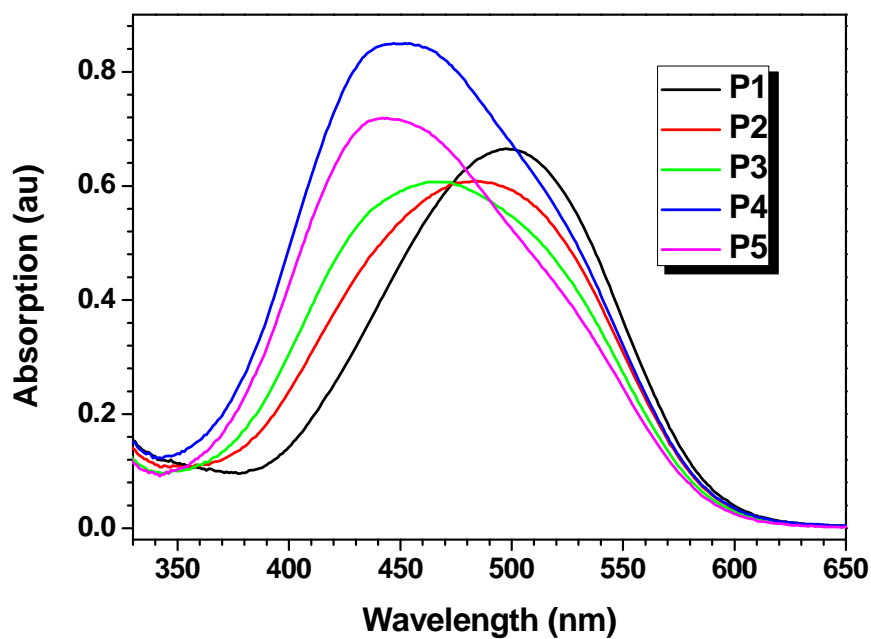


Fig. S9 UV-vis spectra of polymers **P1-P5** in dichloromethane (0.02 mg/mL).

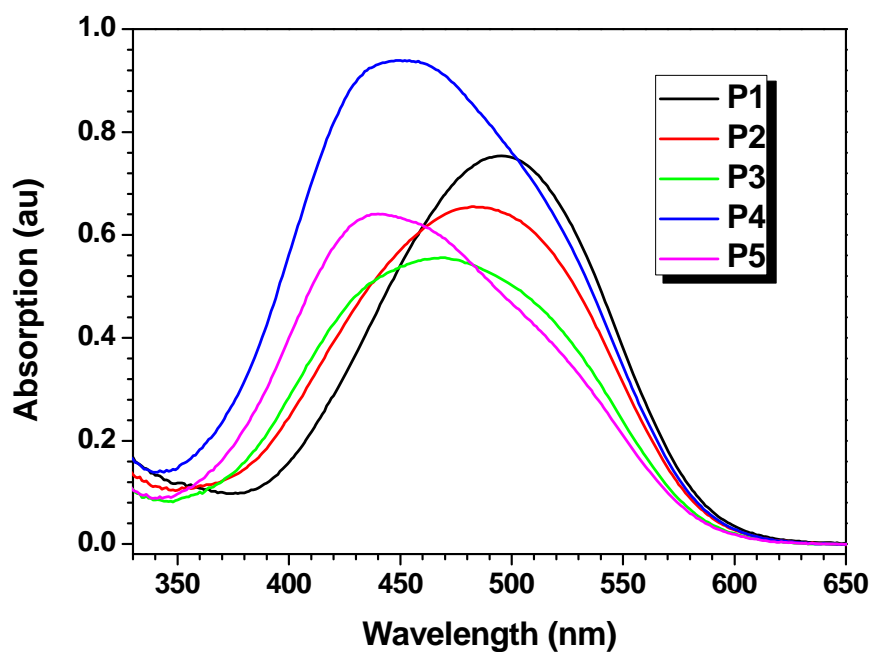


Fig. S10 UV-vis spectra of polymers **P1-P5** in chloroform (0.02 mg/mL).

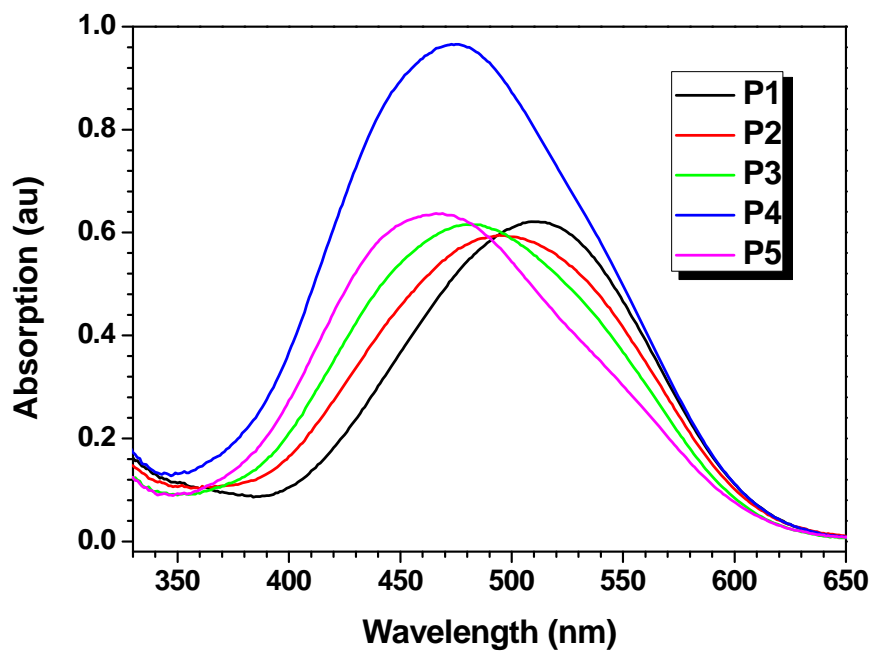


Fig. S11 UV-vis spectra of polymers **P1-P5** in DMSO (0.02 mg/mL).

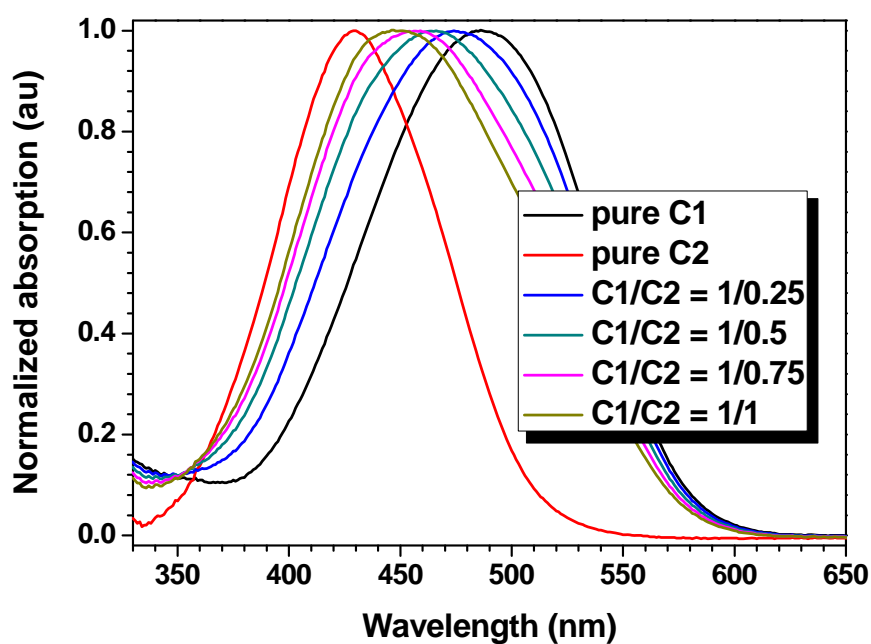


Fig. S12 Normalized UV-Vis spectra of THF solutions of chromophores **C1**, **C2** and their mixture with different ratio. (the concentration of **C1** was  $1 \times 10^{-5}$  mmol/mL).

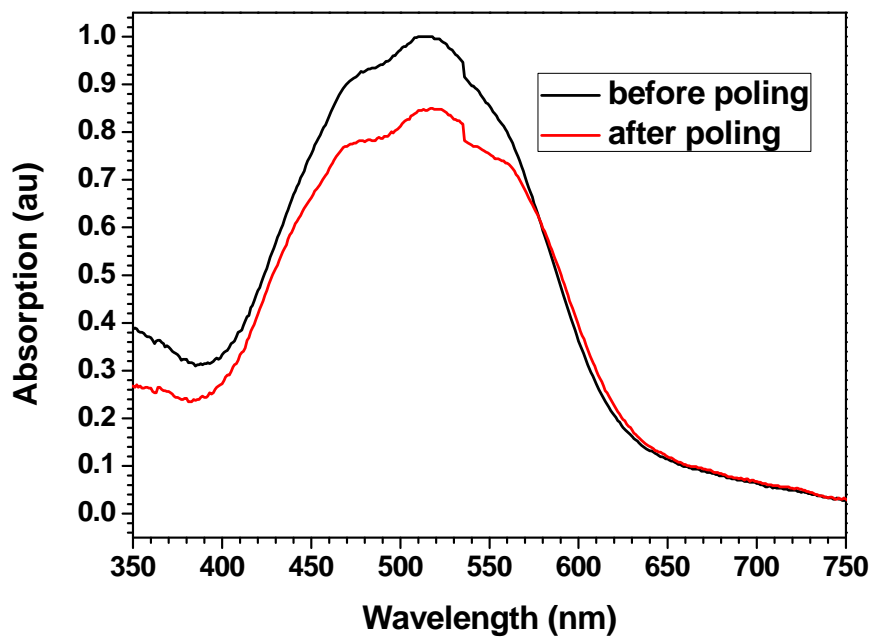


Fig. S13 Absorption spectra of the film of **P1** before and after poling.

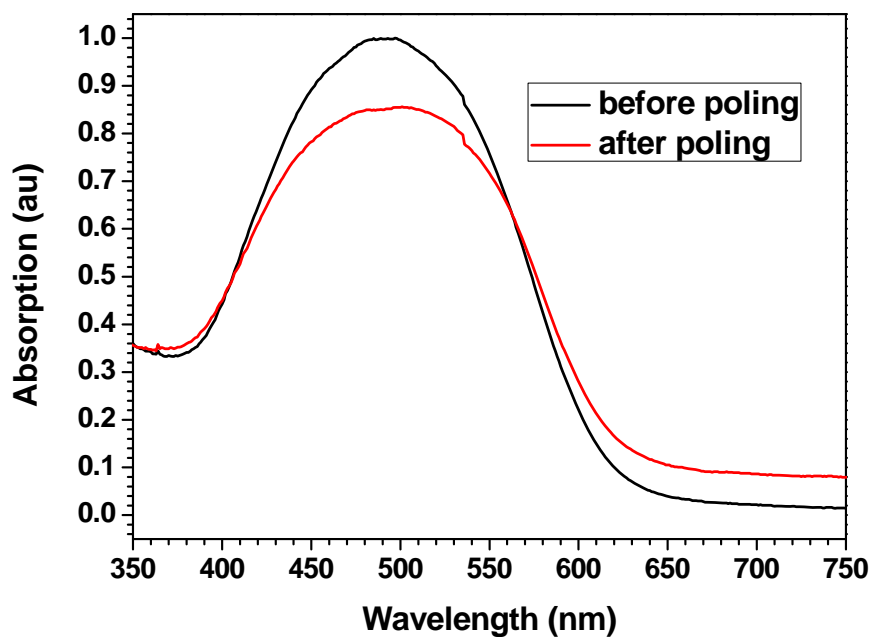


Fig. S14 Absorption spectra of the film of **P2** before and after poling.

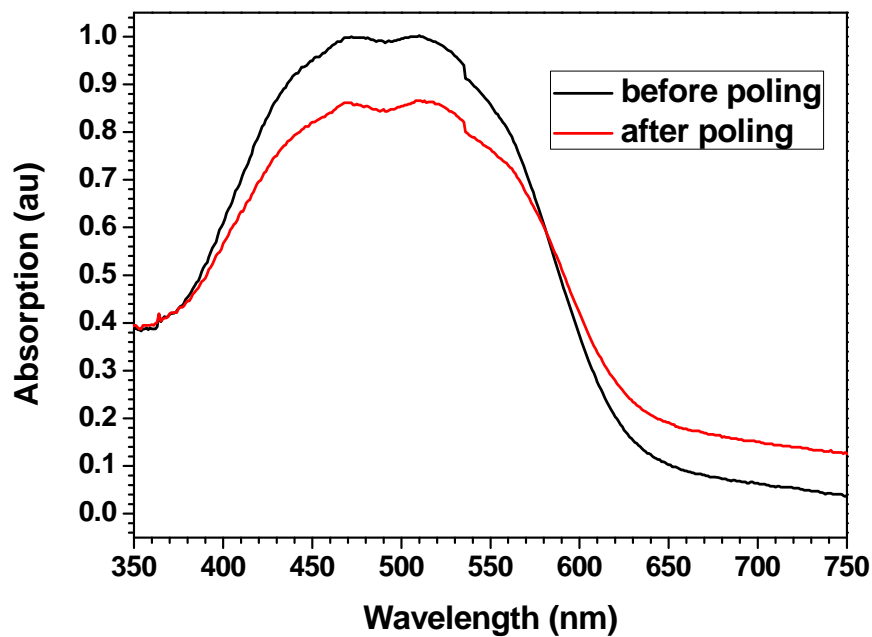


Fig. S15 Absorption spectra of the film of **P3** before and after poling.

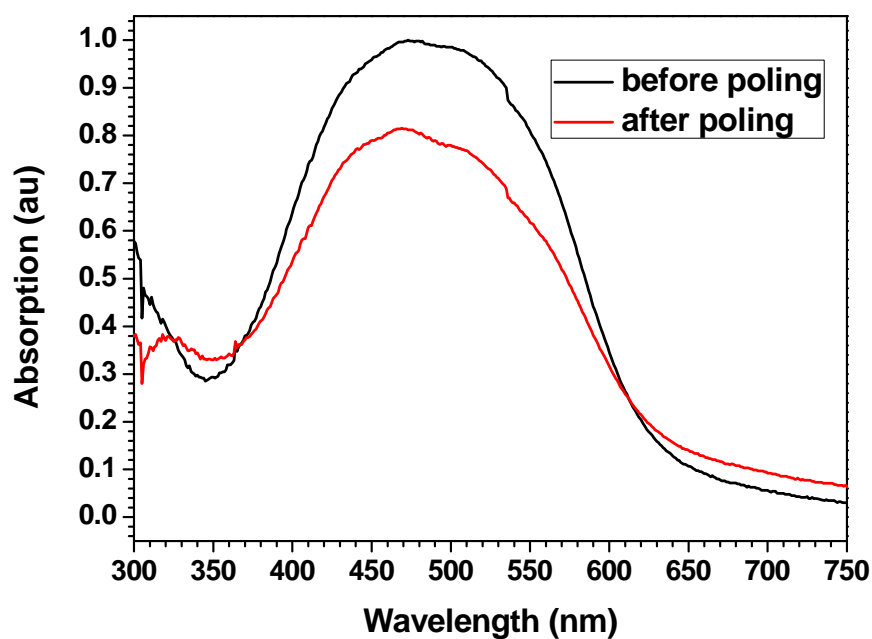


Fig. S16 Absorption spectra of the film of **P4** before and after poling.



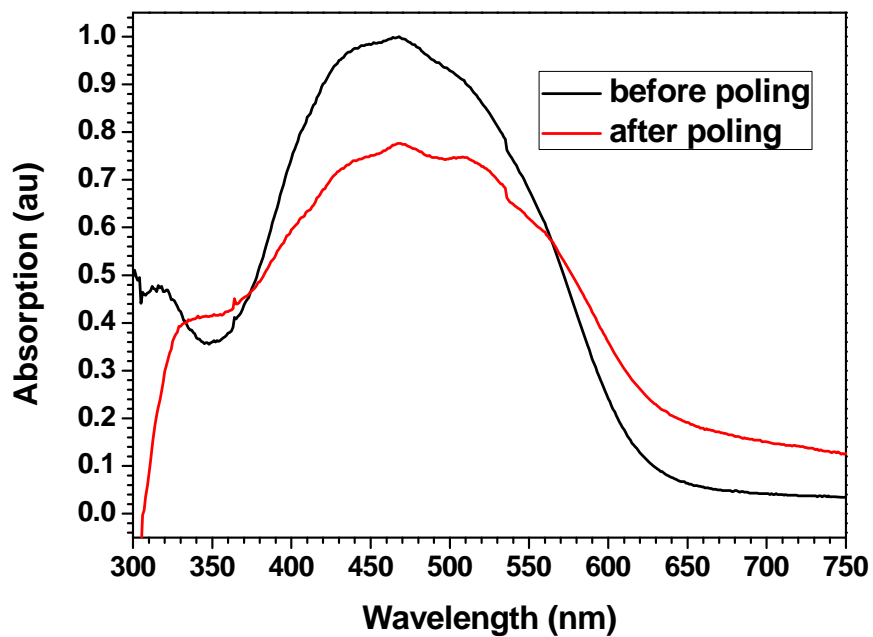


Fig. S17 Absorption spectra of the film of **P5** before and after poling.

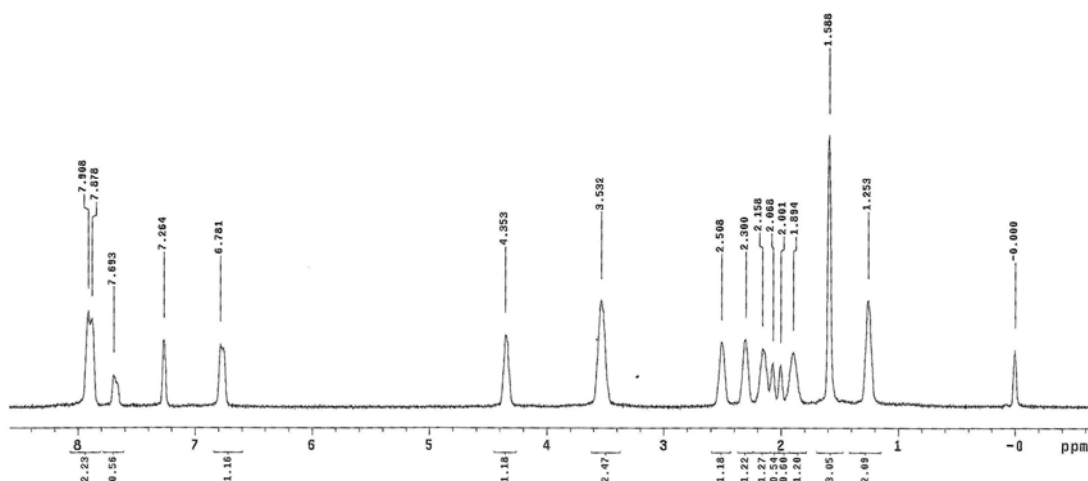
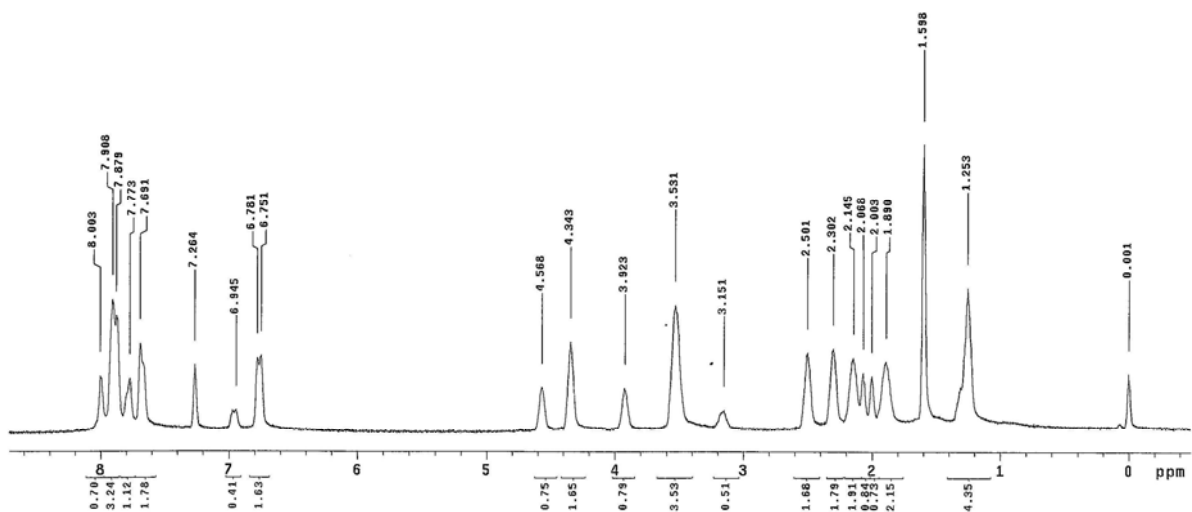
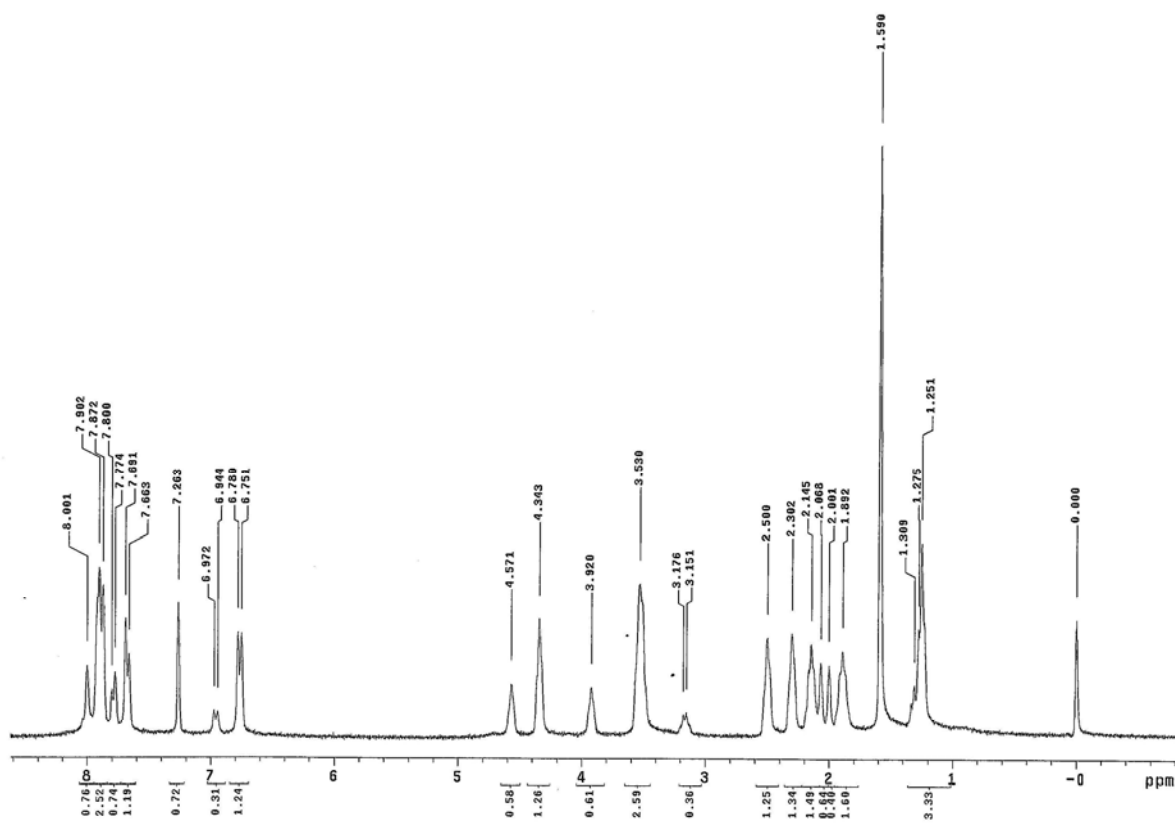


Fig. S18 <sup>1</sup>H NMR spectrum of **C2** and **C1** mixed with the ratio of 0:1 in chloroform-*d*.



**Fig. S19** <sup>1</sup>H NMR spectrum of C2 and C1 mixed with the ratio of 0.25:1 in chloroform-*d*.



**Fig. S20** <sup>1</sup>H NMR spectrum of C2 and C1 mixed with the ratio of 0.5:1 in chloroform-*d*.

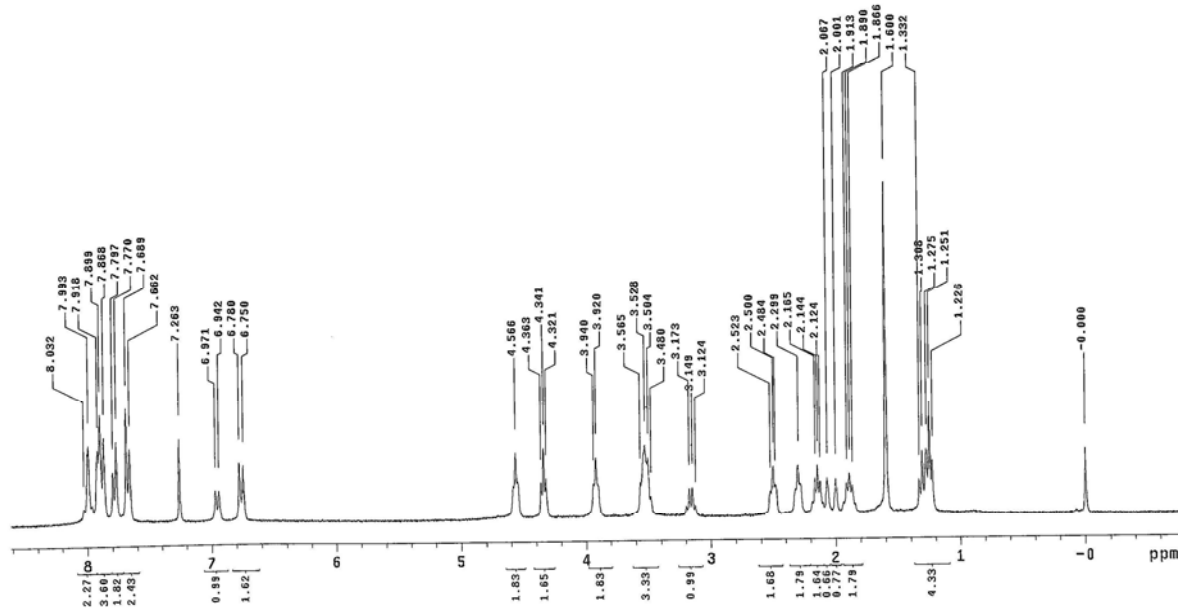


Fig. S21 <sup>1</sup>H NMR spectrum of C2 and C1 mixed with the ratio of 0.75:1 in chloroform-*d*.

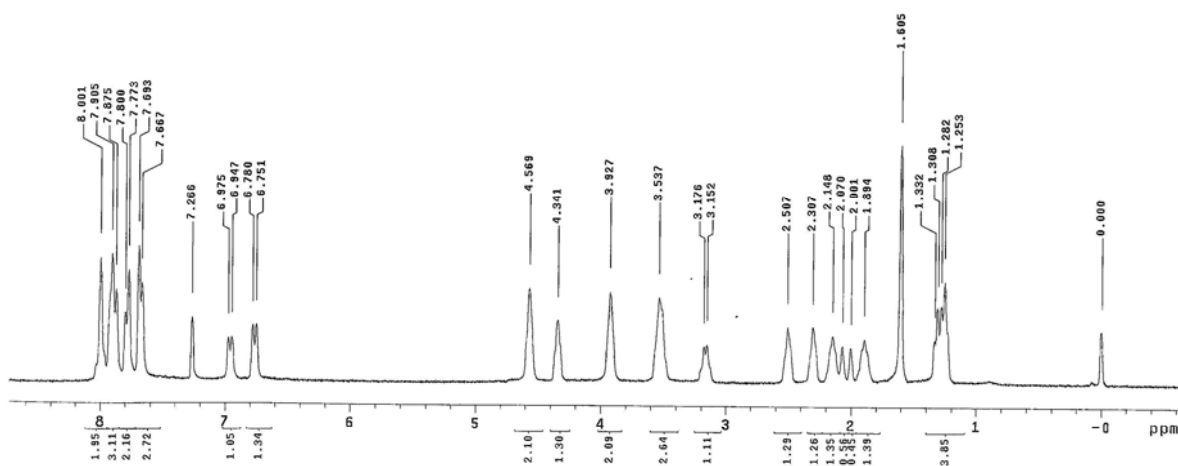


Fig. S22 <sup>1</sup>H NMR spectrum of C2 and C1 mixed with the ratio of 1:1 in chloroform-*d*.