

## Electronic Supplementary Information:

### The self-assembly effect in NLO polymers containing isolation chromophores: enhanced NLO coefficient and stability

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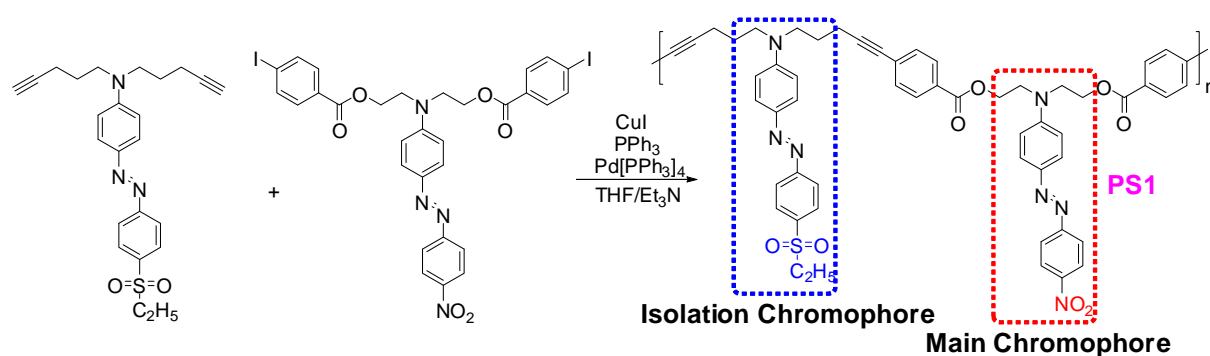


Chart S1 The structure of NLO polymer PS1 containing isolation chromophore.

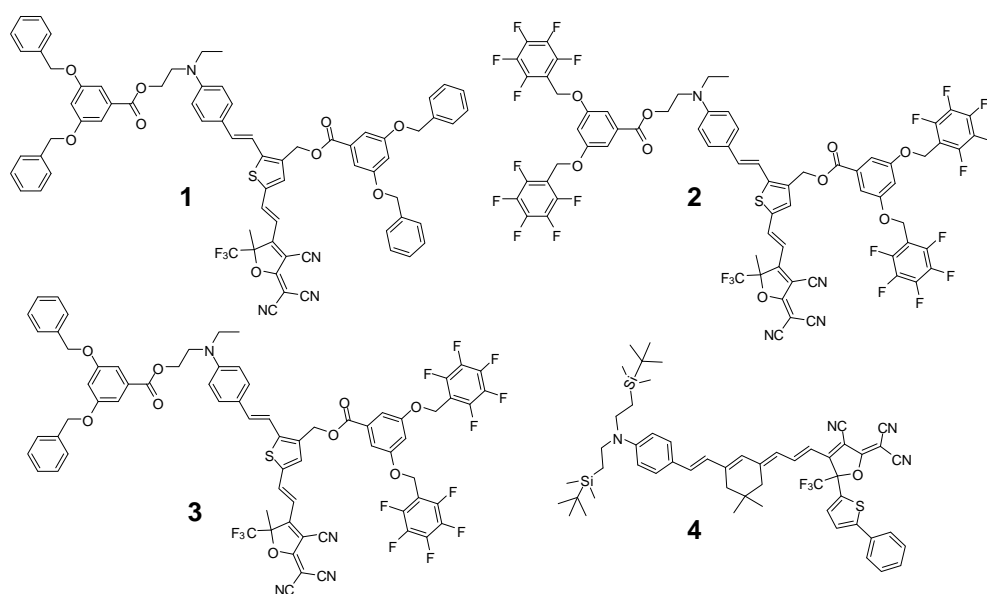
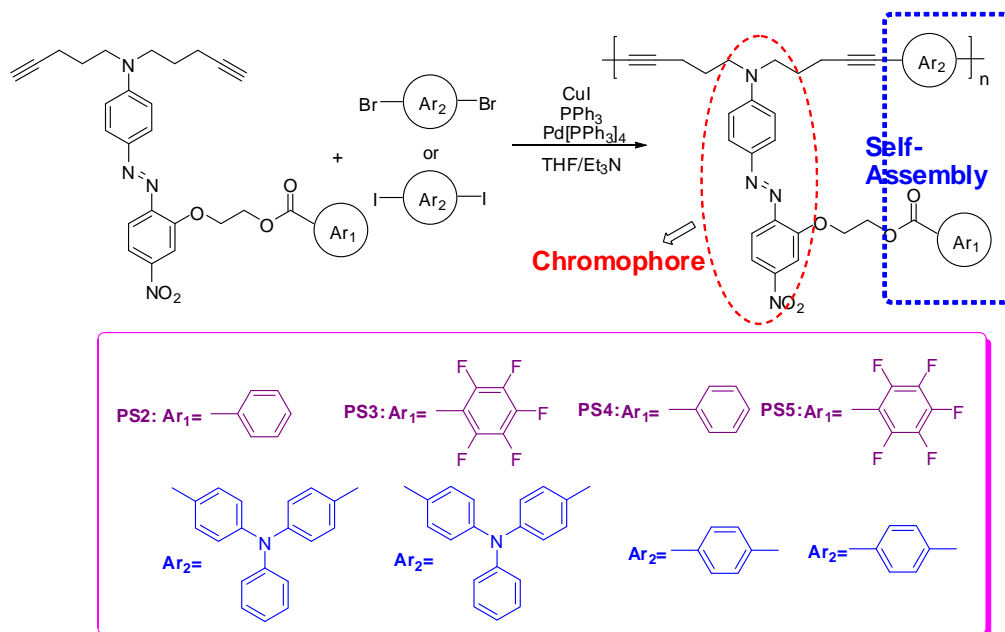
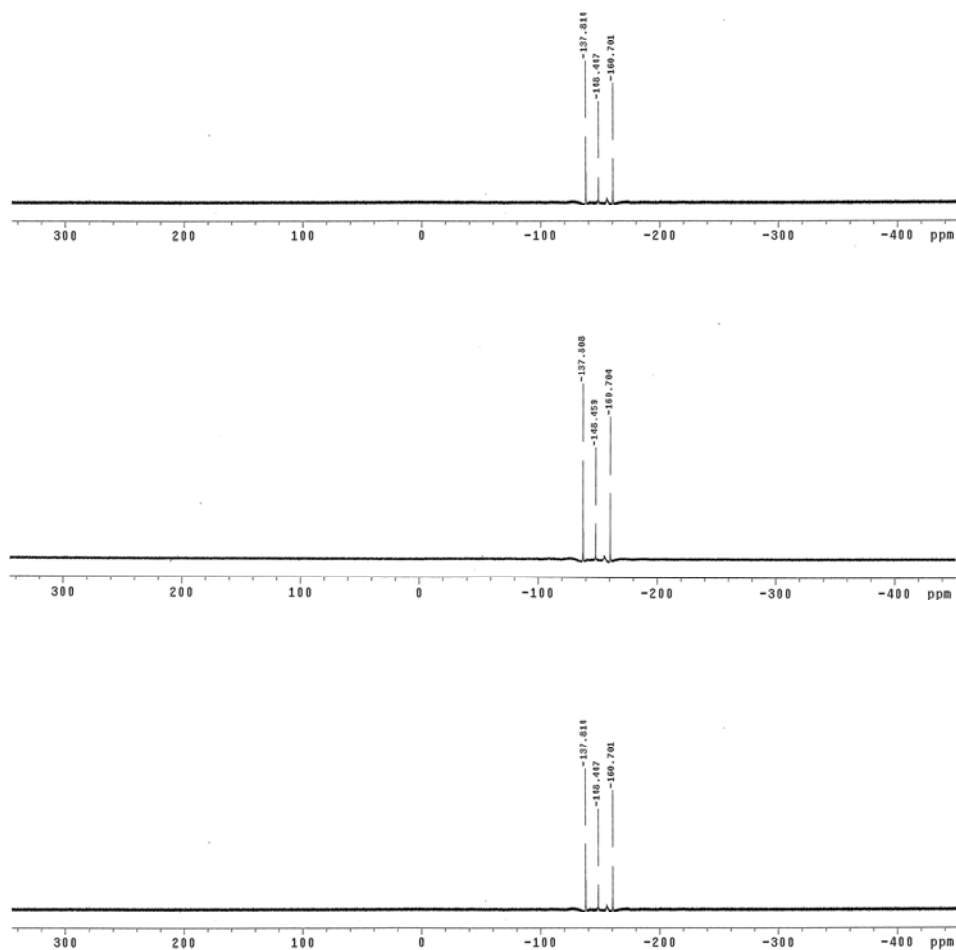


Chart S2 The structure of dendron-substituted NLO chromophores containing perfluoroaromatic rings.



**Chart S3** The structures of NLO polymers **PS2-PS5** with different types of isolation groups.



**Fig. S1** The <sup>19</sup>F NMR spectra of **P2** (up), **P3** (middle) and **P4** (down).

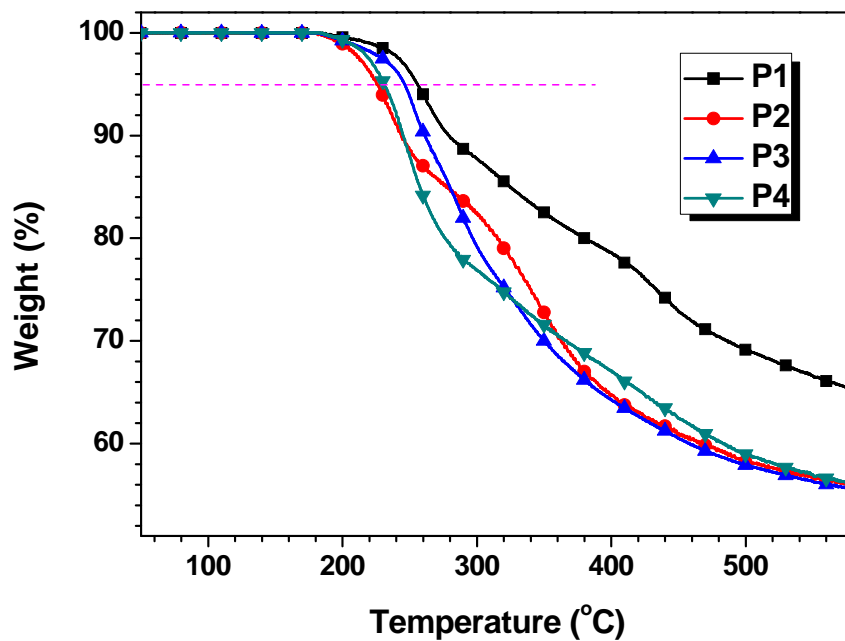


Fig. S2 TGA thermograms of **P1-P4**, measured in nitrogen at a heating rate of 10 °C/min.

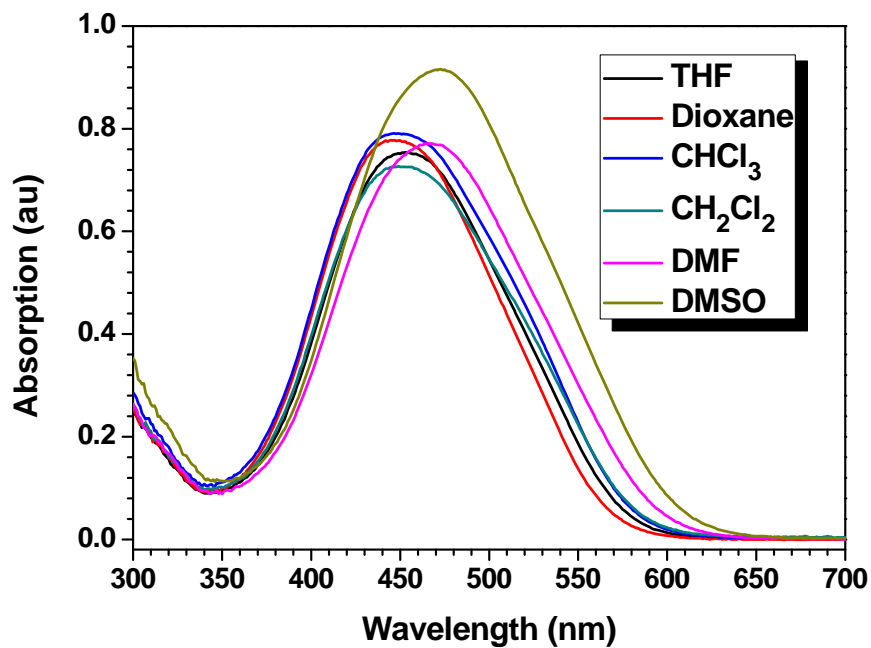


Fig. S3 UV-vis spectra of polymer **P1** in different solvents (0.02 mg/mL).

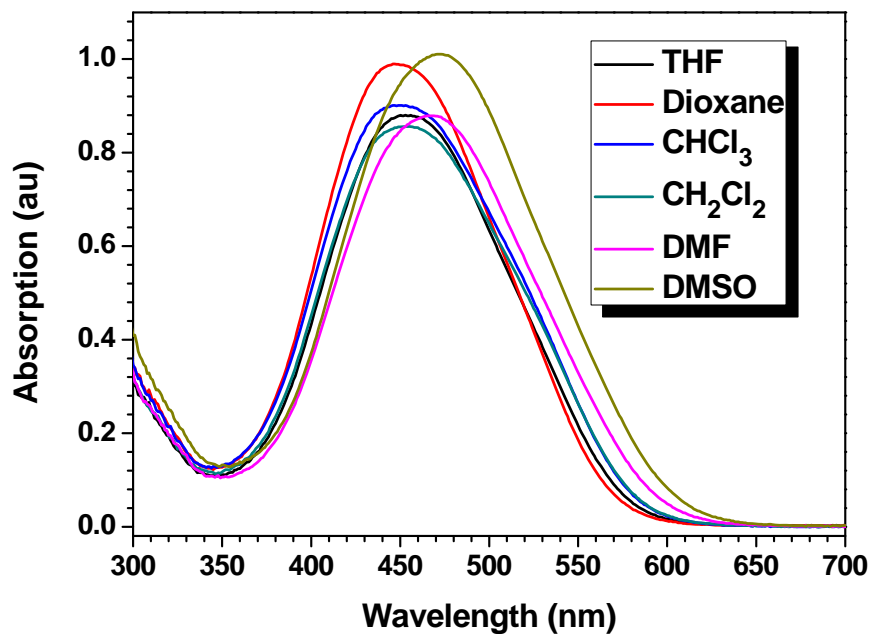


Fig. S4 UV-vis spectra of polymer **P2** in different solvents (0.02 mg/mL).

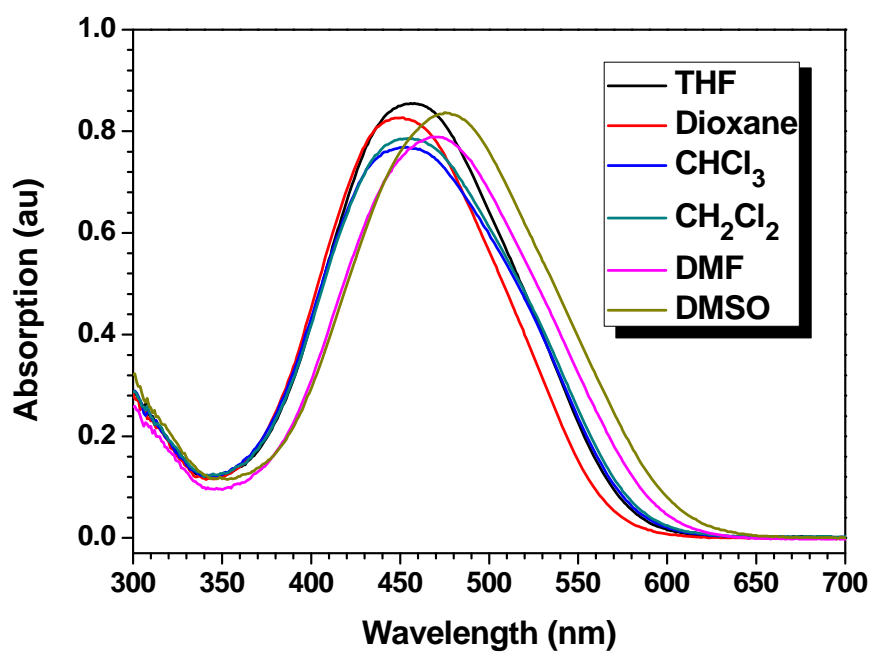


Fig. S5 UV-vis spectra of polymer **P3** in different solvents (0.02 mg/mL).

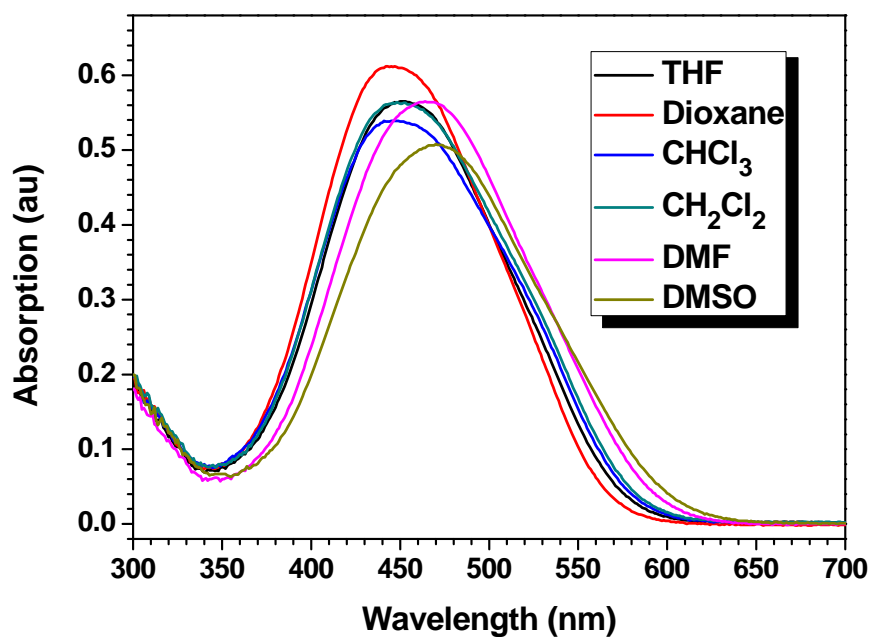


Fig. S6 UV-vis spectra of polymer **P4** in different solvents (0.02 mg/mL).

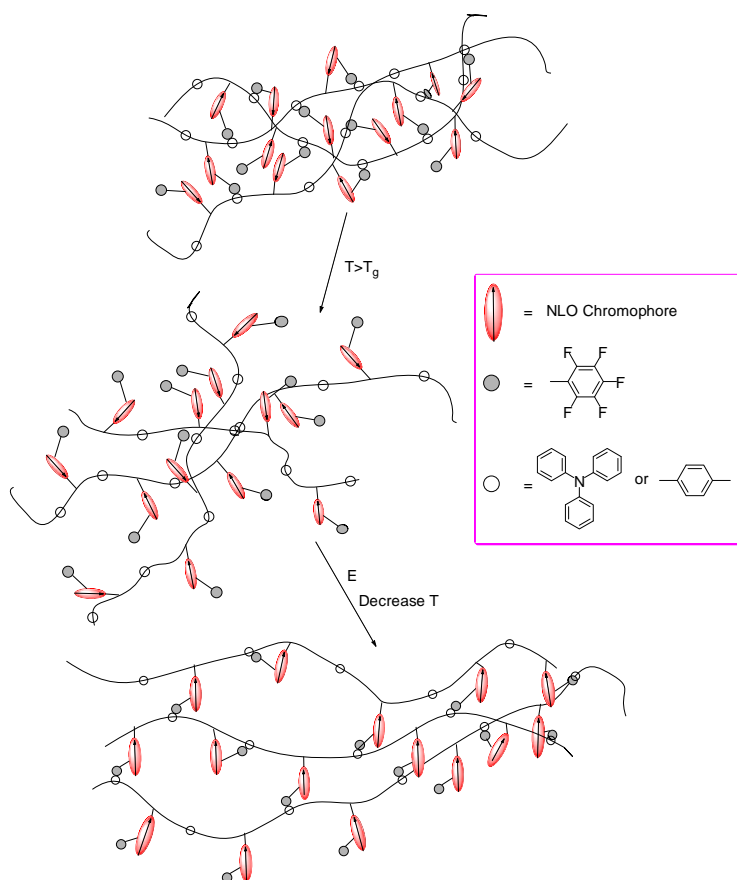
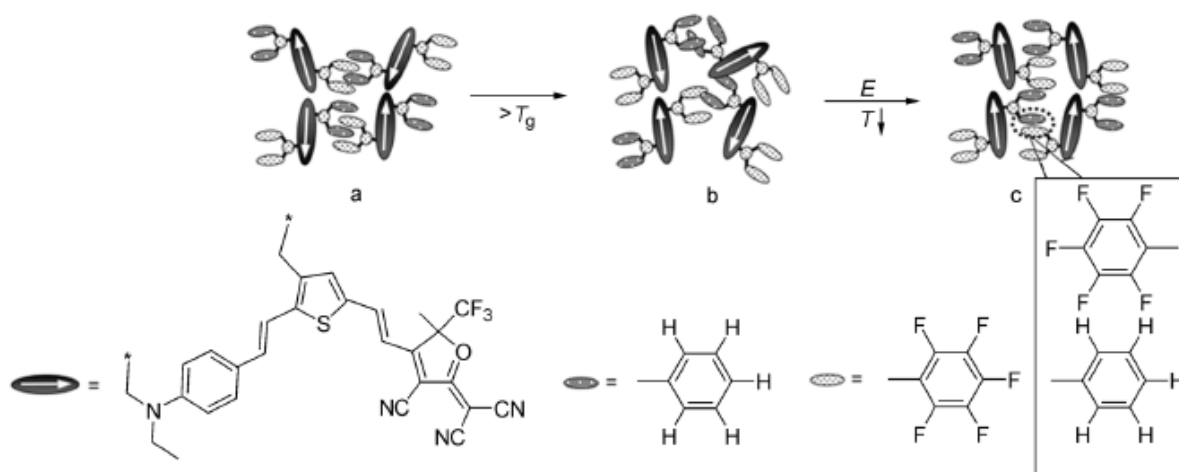


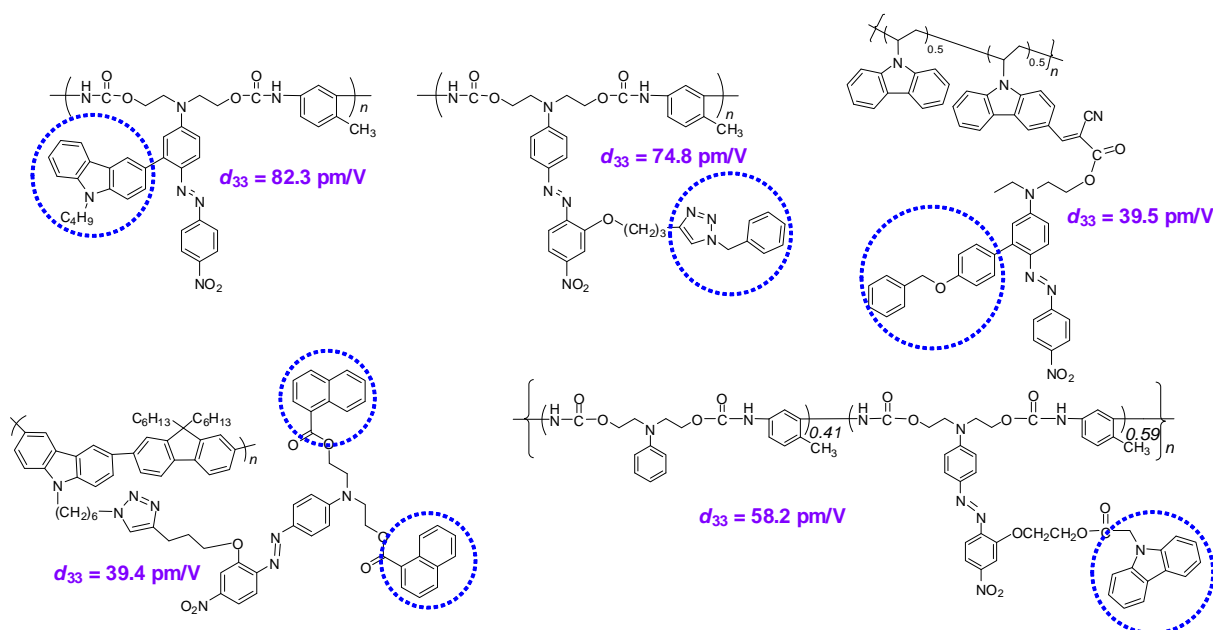
Fig. S7 Graphical illustration of the alignment formation of self-assembled polymers.



**Fig. S8** Graphical illustration of the alignment formation of self-assembled chromophore **3** by Ar-ArF interactions: (a) locked random dipoles (shown as arrows) before poling; (b) unlocked random dipoles before poling; (c) locked acentric dipoles after poling followed by cooling.

**Table S1.** The maximum absorption of hyperbranched polymers ( $\lambda_{\max}$ , nm).

	THF	1,4-dioxane	chloroform	dichloromethane	DMF	DMSO
<b>P1</b>	454	447	447	449	465	473
<b>P2</b>	456	446	447	455	468	473
<b>P3</b>	456	452	454	454	470	475
<b>P4</b>	453	443	447	448	464	470



**Chart S4** Some NLO polymers and their  $d_{33}$  values.

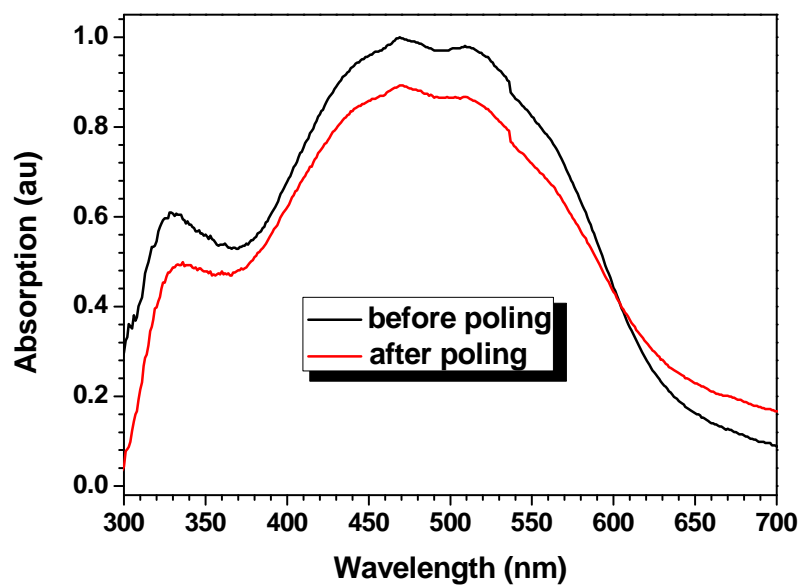


Fig. S9 Absorption spectra of the film of **P3** before and after poling.

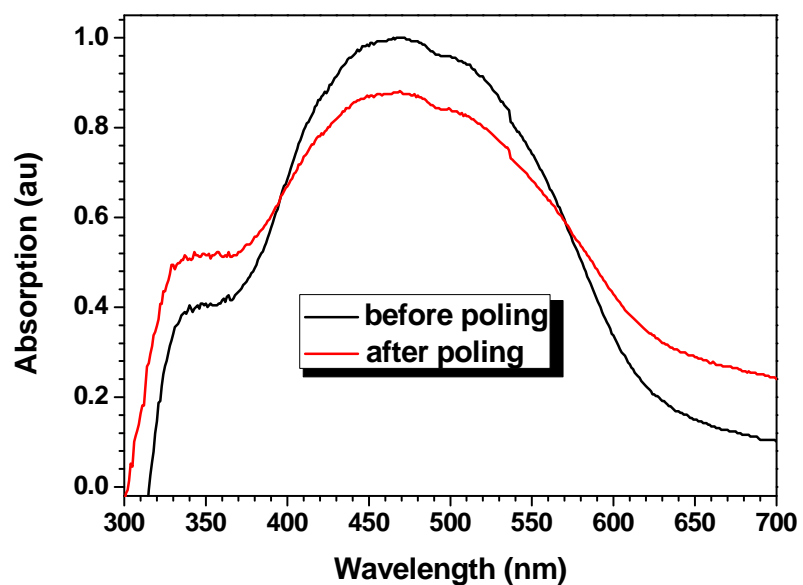


Fig. S10 Absorption spectra of the film of **P4** before and after poling.