

Electronic Supplementary Information for:

A series of dendronized hyperbranched polymers with dendritic chromophore moieties in the periphery: convenient synthesis and large nonlinear optical effects

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Table of Contents

1. Graphical illustration of poling procedure for NLO polymers.	Chart S1	2
2. The structure of the dendrimers and similar hyperbranched polymer in previous work	Chart S2	2
3. The structure of the dendronized hyperbranched polymers in previous work.	Chart S3	3
4. The structure of the similar dendrimers in previous work.	Chart S4	3
5. The maximum absorption wavelengths of the DHPs.	Table S1	4
6. The synthesis of sulfonyl-based azo chromophore S2 .	Scheme S1	4-5
7. The synthesis of model molecule S5	Scheme S2	4-6
8. The ¹ H NMR and ¹³ C NMR spectra of related compounds.	Fig. S1-S16	7-14
9. The MALDI-TOF mass of S3 , Initiator and S5 .	Fig. S17-19	15-16
10. FT-IR spectra of Initiator , P1 , P2 and P3 .	Fig. S20	16
11. The GPC chromatograms of P1 , P2 and P3 .	Fig. S21	17
12. The TGA thermograms of PMMA and S5	Fig. S22	17
13. The UV-vis spectra of DHPs in solutions.	Fig. S23-28	18-20
14. The UV-vis spectra of DHPs in films.	Fig. S29-31	21-22
15. Calculation of the NLO coefficients.		22-23

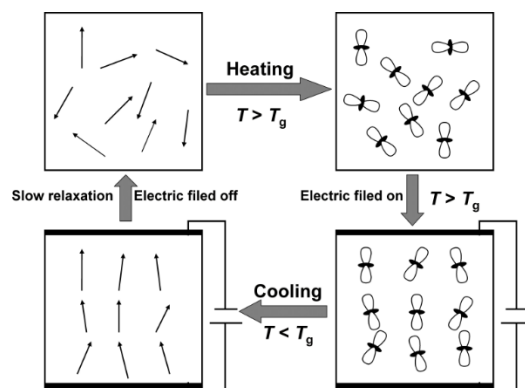


Chart S1. Graphical illustration of poling procedure for NLO polymers.

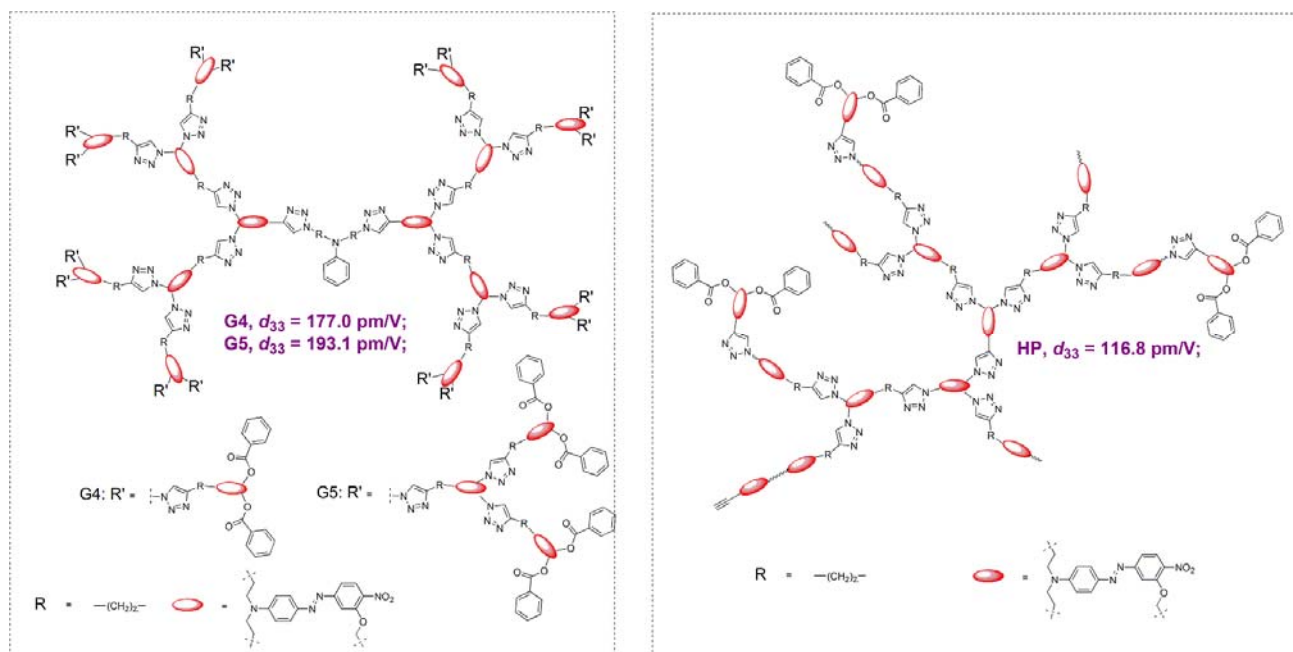


Chart S2. The structure of the dendrimers and similar hyperbranched polymer in previous work.

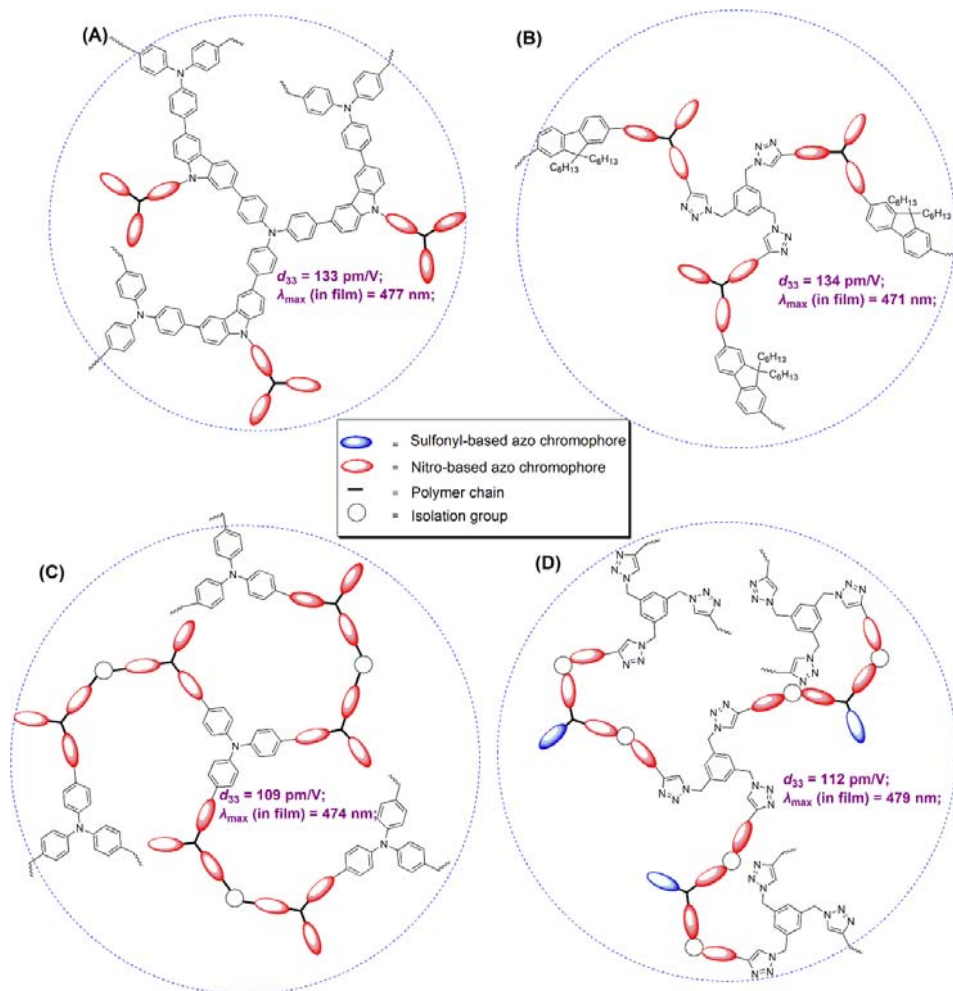


Chart S3. The structure of the dendronized hyperbranched polymers in previous work.

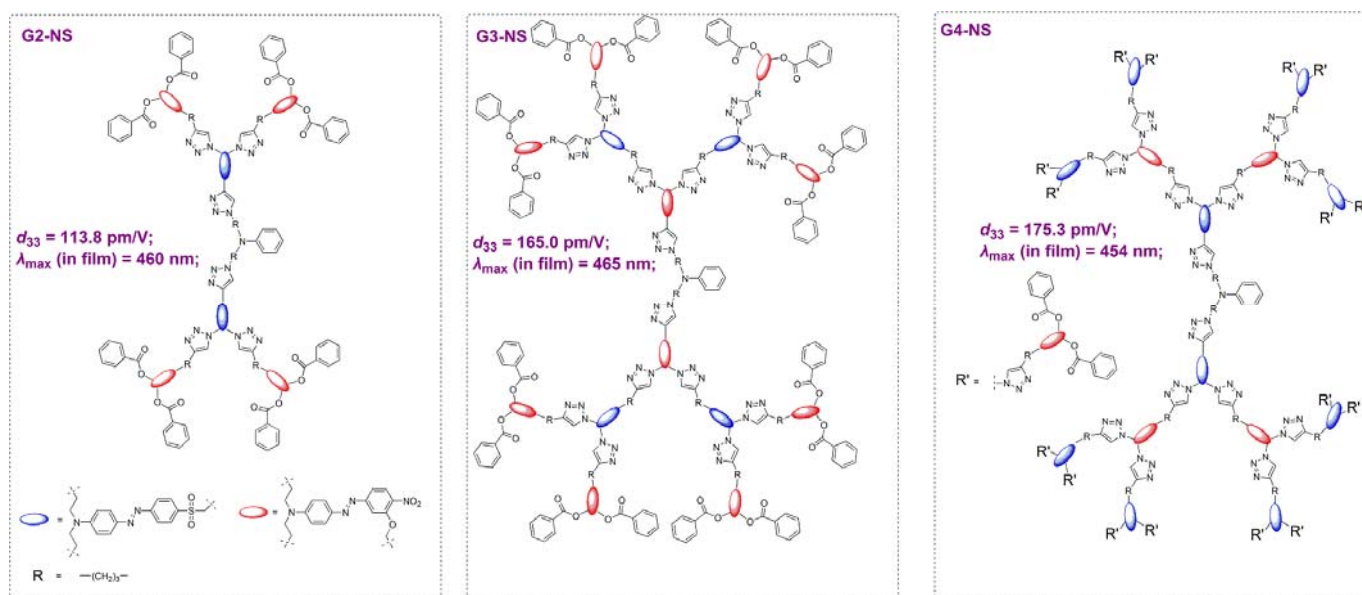
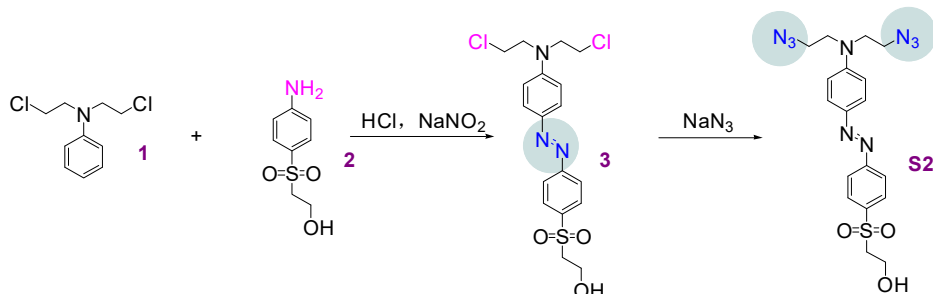
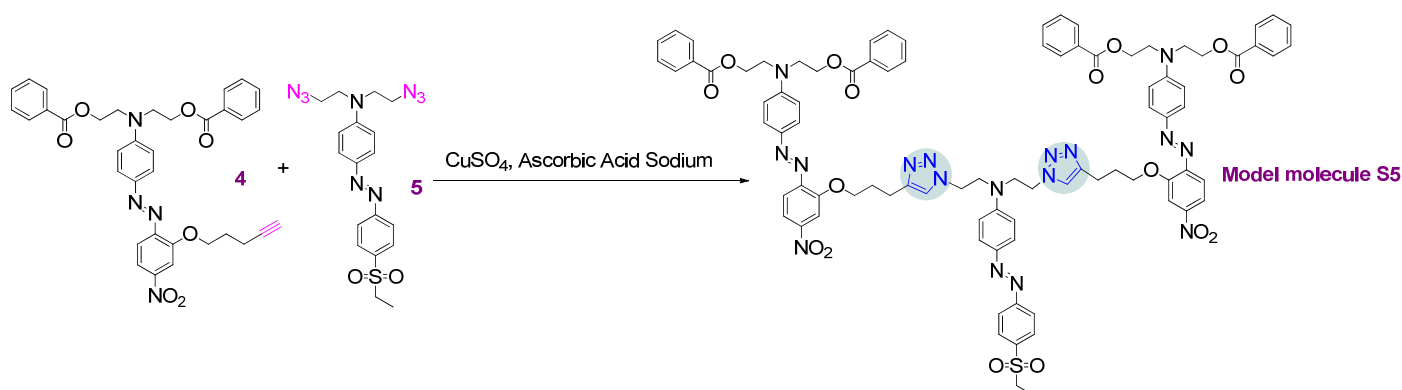


Chart S4. The structure of the similar dendrimers in previous work.

Table S1. The maximum absorption wavelengths of the DHPs. (λ_{\max} , nm, 0.02 mg/mL).

	THF	1,4-dioxane	chloroform	dichloromethane	DMF	DMSO	film ^a
P1	445	439	441	441	460	467	452
P2	445	439	436	440	462	467	450
P3	446	439	438	442	462	468	449

^a In the preparation of polymer thin films, the DHPs were dissolved in THF (concentration ~ 4 wt%), and the residual solvent was removed by heating the films in a vacuum before the NLO measurement.

**Scheme S1.** The synthesis of sulfonyl-based azo chromophore **S2**.**Scheme S2.** The synthesis of model molecule **S5**.

Materials

Compounds **1**¹, **2**², **4**³ and **5**⁴ were prepared according to the literature and our previous work, respectively. All other reagents were used as received.

Synthesis of compound **3**

Compound **2** (1.51 g, 7.5 mmol) was added to hydrochloric acid solution (about 18 wt%), and aqueous solution of NaNO₂ (621.0 mg, 9 mmol) was added slowly and stirred at 0 °C for 30 min. Then,

compound **1** (1.64 g, 7.5 mmol) was dissolved in DMF (12 mL) and dropped to the mixture and stirred for 10 h, then poured in to a lot of water and extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography using dichloromethane/ethyl acetate (5/1, v/v) as elute to afford red solid (1.63 g, 50.4%). ¹H NMR (400 MHz, CDCl₃, 298K), δ (TMS, ppm): 2.61 (s, 1H, -OH), 3.31-3.45 (m, 2H, -SO₂CH₂-), 3.71 (t, *J* = 6.9 Hz, 4H, -CH₂Cl), 3.87 (t, *J* = 6.9 Hz, 4H, -NCH₂-), 3.94-4.10 (m, 2H, -OCH₂-), 6.79 (d, *J* = 9.2 Hz, 2H, ArH), 7.86-8.11 (m, 6H, ArH). ¹³C NMR (100 MHz, CDCl₃), δ (TMS, ppm): 40.3, 53.5, 56.5, 58.5, 111.8, 123.2, 126.3, 129.2, 138.8, 144.6, 149.8, 156.3.

Synthesis of compound S2

Compound **3** (1.08 g, 2.5 mmol), NaN₃ (1.46 g, 22.5 mmol) and DMF were added into a flask, the resultant mixture was allowed to stir at 80 °C overnight, and then poured into a lot of water and extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography using petroleum ether/ethyl acetate (1/1, v/v) as elute to afford red solid (893.6 mg, 80.6%). ¹H NMR (400 MHz, CDCl₃, 298K), δ (TMS, ppm): 2.77 (s, 1H, -OH), 3.34-3.48 (m, 2H, -SO₂CH₂-), 3.61 (t, *J* = 6.0 Hz, 4H, -CH₂N₃), 3.74 (t, *J* = 6.0 Hz, 4H, -NCH₂-), 4.09 (d, *J* = 32.0 Hz, 2H, -OCH₂-), 6.84 (d, *J* = 9.2 Hz, 2H, ArH), 7.87-8.17 (m, 6H, ArH). ¹³C NMR (100 MHz, CDCl₃), δ (TMS, ppm): 48.9, 50.9, 56.5, 58.5, 112.0, 123.2, 126.2, 129.2, 138.7, 144.6, 150.0, 156.4.

Synthesis of compound S5

Chromophore **4** (136.5 mg, 0.22 mmol), **5** (42.6 mg, 0.10 mmol), CuSO₄•5H₂O (10 mol%), NaHCO₃ (20 mol%), and ascorbic acid (20 mol%) were dissolved in THF (2.5 mL)/H₂O (0.5 mL) under nitrogen in a Schlenk flask. After the mixture was stirred at room temperature for 3 h, the reaction was stopped by the

addition of water. It was then extracted with chloroform, and washed with brine. The organic layer was dried over anhydrous magnesium sulfate and purified by column chromatography using THF/chloroform (1/2, v/v) as the eluent to afford red solid **S5** (130.0 mg, 77.9%). ¹H NMR (400 MHz, CDCl₃, 298K), δ (TMS, ppm): 1.43 (s, 3H, -CH₃), 2.13-2.16 (m, 4H, -CH₂-), 2.95 (s, 4H, -CH₂C-), 3.13 (q, J = 7.4 Hz, 1H, -SCH₂-), 3.72 (s, 4H, -NCH₂-), 3.93 (t, J = 5.9 Hz, 8H, -NCH₂-), 4.14 (s, 4H, -NCH₂-), 4.37 (s, 4H, -OCH₂-), 4.56 (t, J = 6.0 Hz, 8H, -COOCH₂-), 6.56 (d, J = 9.0 Hz, 2H, ArH), 6.92-7.01 (m, 4H, ArH), 7.24 (s, 2H, C=CH), 7.42 (t, J = 7.7 Hz, 8H, ArH), 7.55 (t, J = 7.4 Hz, 4H, ArH), 7.63 (d, J = 8.8, 1.0 Hz, 2H, ArH), 7.80 (dd, J = 19.7, 8.1 Hz, 6H, ArH), 7.87-7.93 (m, 6H, ArH), 7.98 ((t, J = 10.1 Hz, 10H, ArH). ¹³C NMR (100 MHz, CDCl₃), δ (TMS, ppm): 21.9, 28.5, 30.4, 47.4, 50.0, 51.3, 56.5, 58.5, 61.8, 68.7, 76.8, 77.2, 77.5, 109.4, 112.0, 116.7, 122.5, 123.2, 125.6, 126.3, 128.6, 129.2, 129.7, 133.5, 145.1, 147.0, 147.3, 148.4, 149.5, 150.9, 155.2, 156.1, 166.6. MALTDI-TOF MS: calcd for (C₈₈H₈₅N₁₇O₁₆S): *m/z* [M+Na]⁺: 1691.8; found: *m/z* 1691.8.

References

1. X. Shen, H. Liu, Y. Li, and S. Liu, *Macromolecules*, 2008, **41**, 2421-2425.
2. Z. Li, S. Dong, G. Yu, Z. Li, Y. Liu, C. Ye, J. Qin, *Polymer*, 2007, **48**, 5520-5529.
3. Z. Li, Q. Zeng, G. Yu, Z. Li, C. Ye, Y. Liu and J. Qin, *Macromol. Rapid Commun.*, 2008, **29**, 136-141.
4. R. Tang, H. Chen, S. Zhou, W. Xiang, X. Tang, B. Liu, Y. Dong, H. Zeng, Z. Li, *Polym. Chem.*, 2015, **6**, 5580-5589.

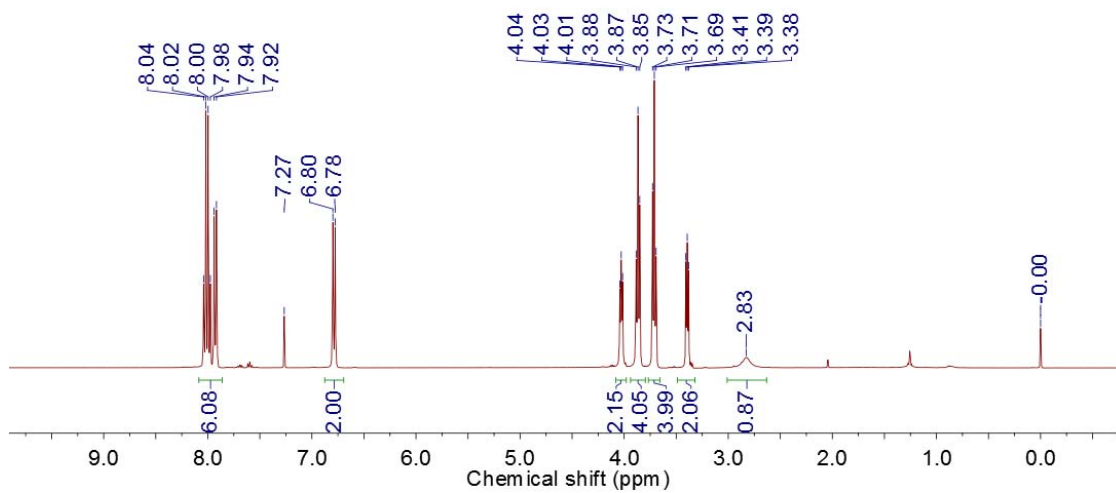


Fig. S1. ^1H NMR spectrum of compound **3** (CHCl_3 -*d*).

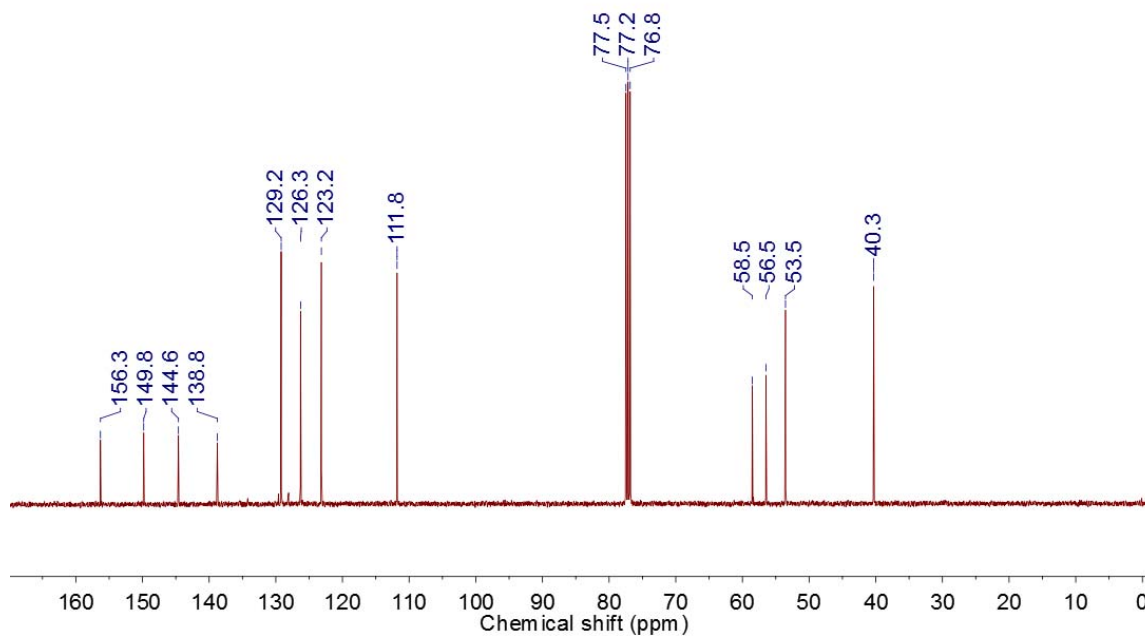


Fig. S2. ^{13}C NMR spectrum of compound **3** (CHCl_3 -*d*).

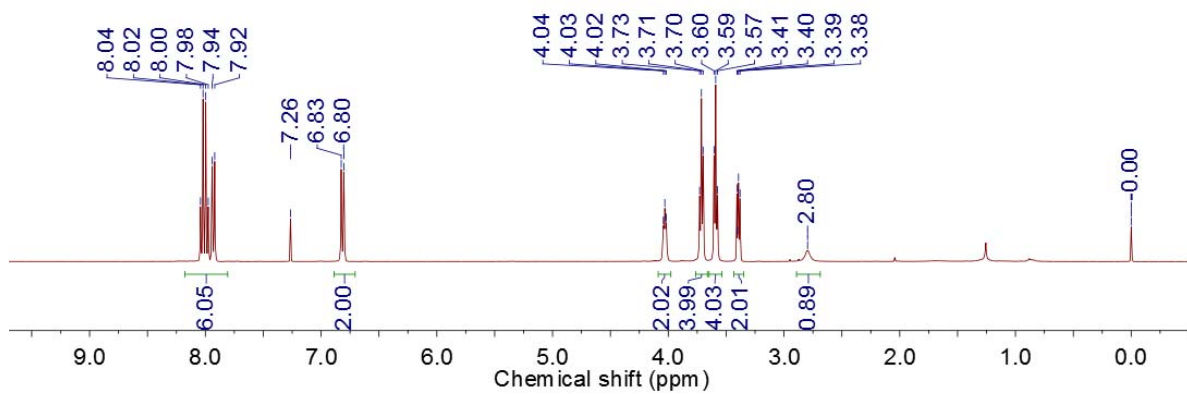


Fig. S3. ^1H NMR spectrum of compound S2 (CHCl_3-d).

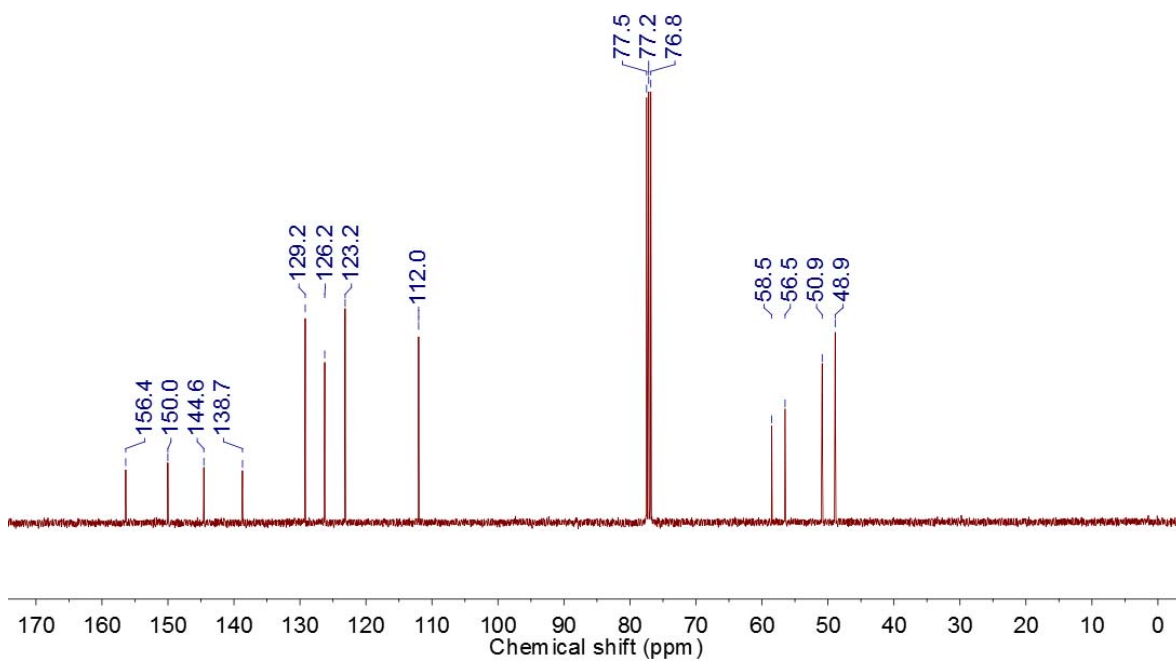


Fig. S4. ^{13}C NMR spectrum of S2 (CHCl_3-d).

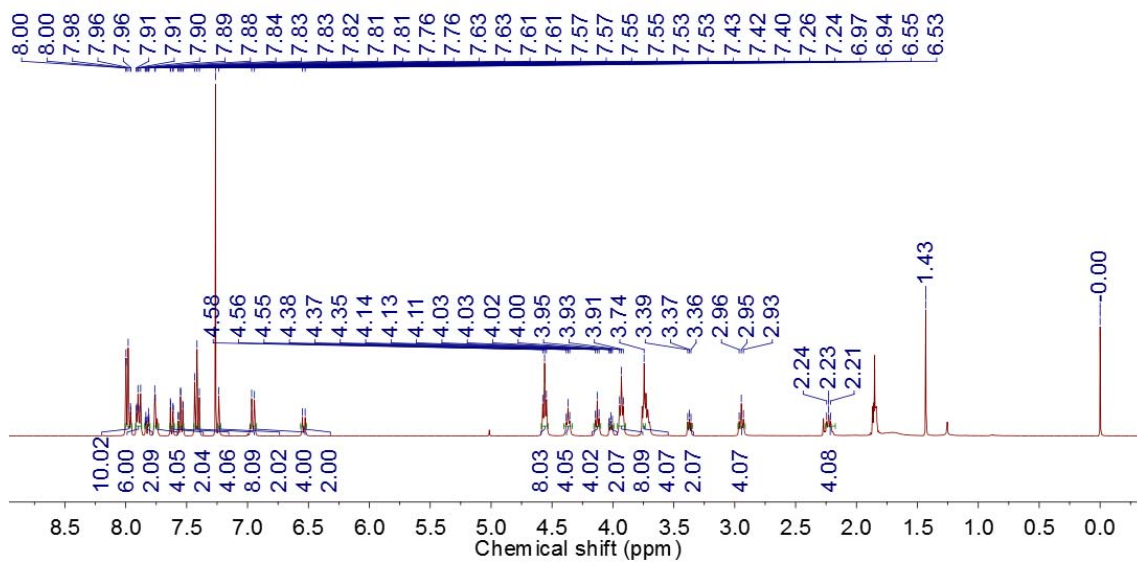


Fig. S5. ^1H NMR spectrum of S3 (CHCl_3-d).

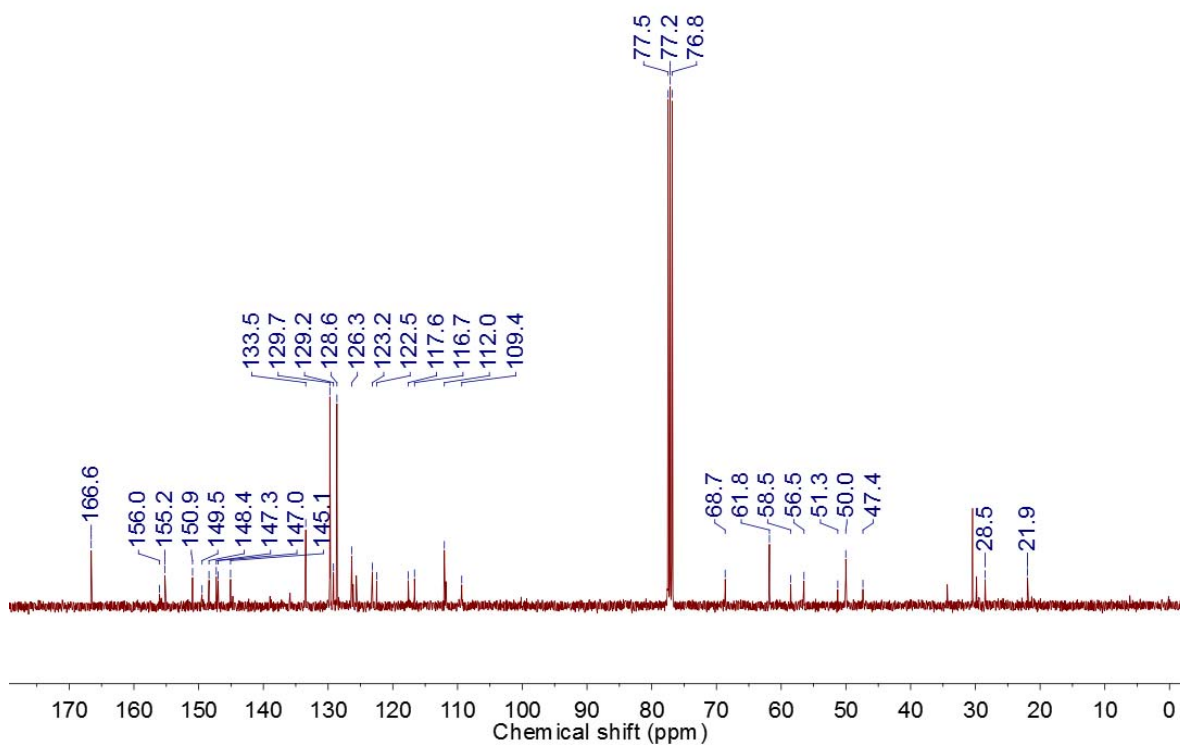


Fig. S6. ^{13}C NMR spectrum of S3 (CHCl_3-d).

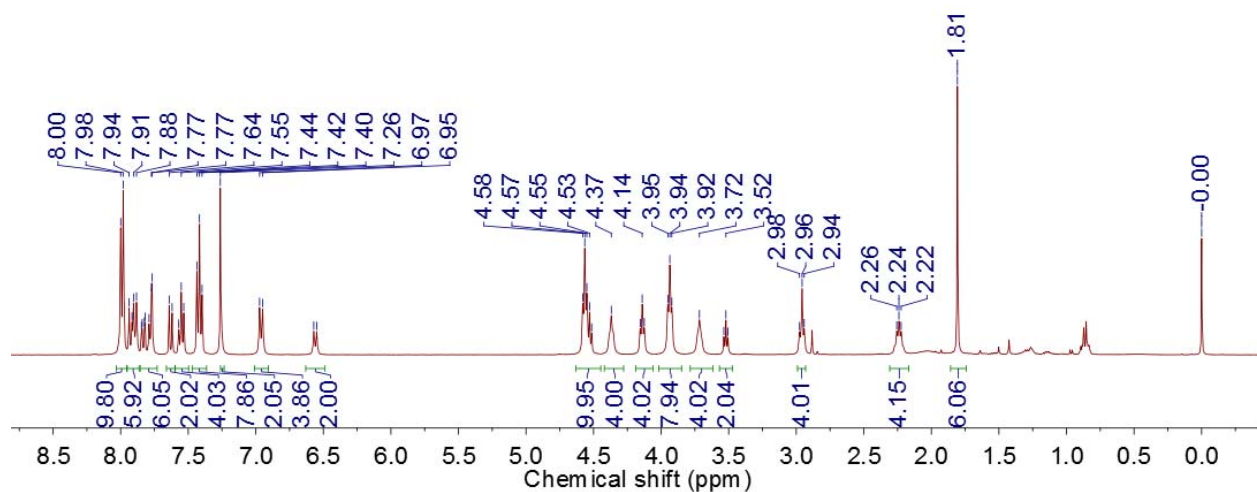


Fig. S7. ^1H NMR spectrum of **Initiator** ($\text{CHCl}_3\text{-}d$).

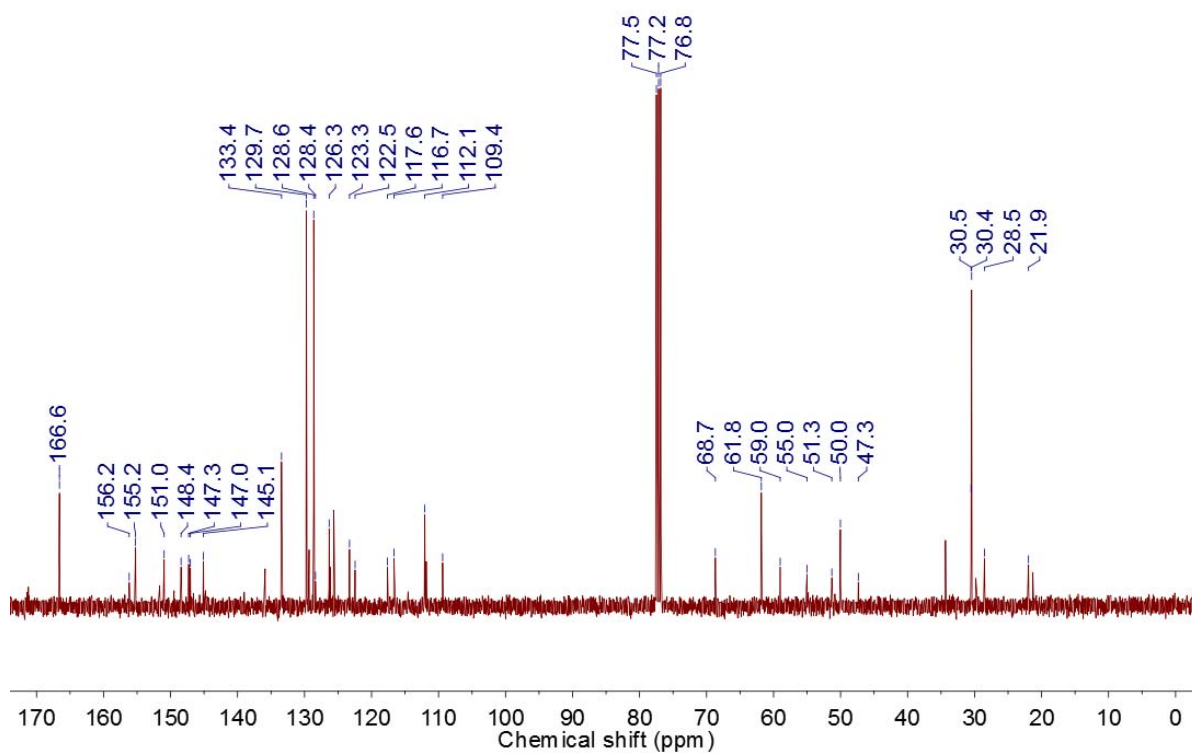


Fig. S8. ^{13}C NMR spectrum of **Initiator** ($\text{CHCl}_3\text{-}d$).

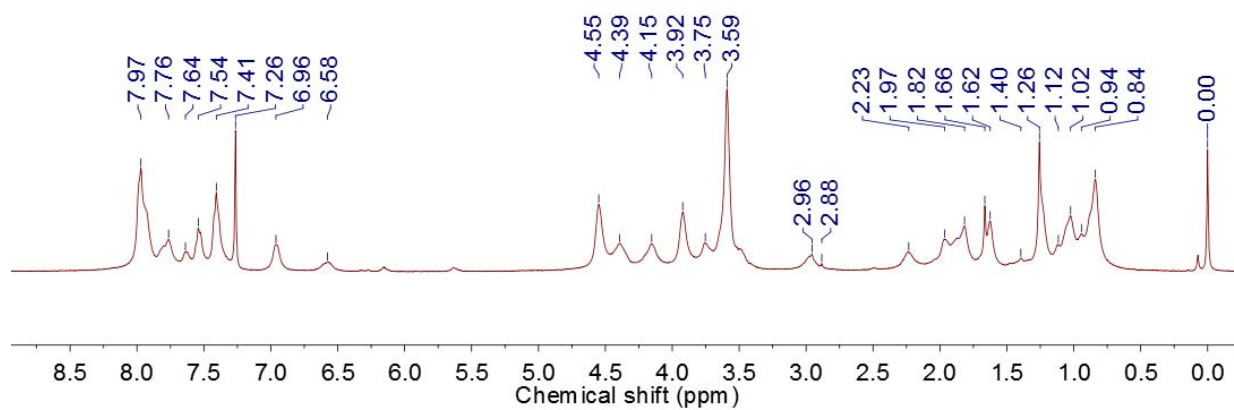


Fig. S9. ^1H NMR spectrum of P1 ($\text{CHCl}_3\text{-}d$).

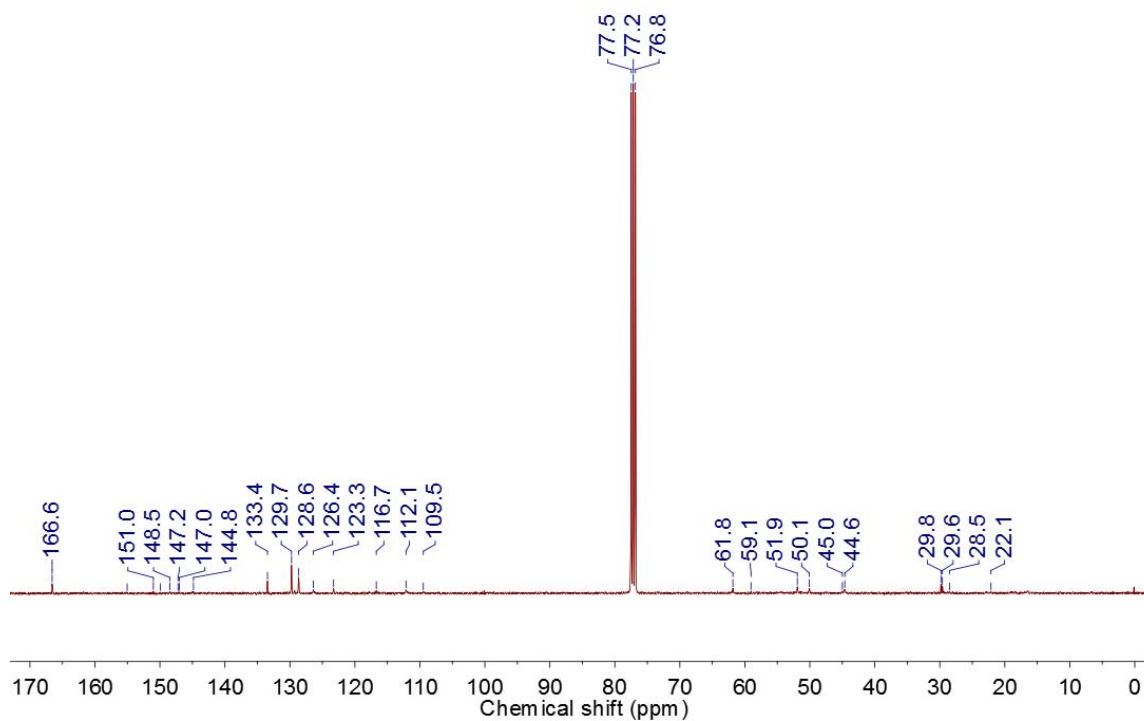


Fig. S10. ^{13}C NMR spectrum of P1 ($\text{CHCl}_3\text{-}d$).

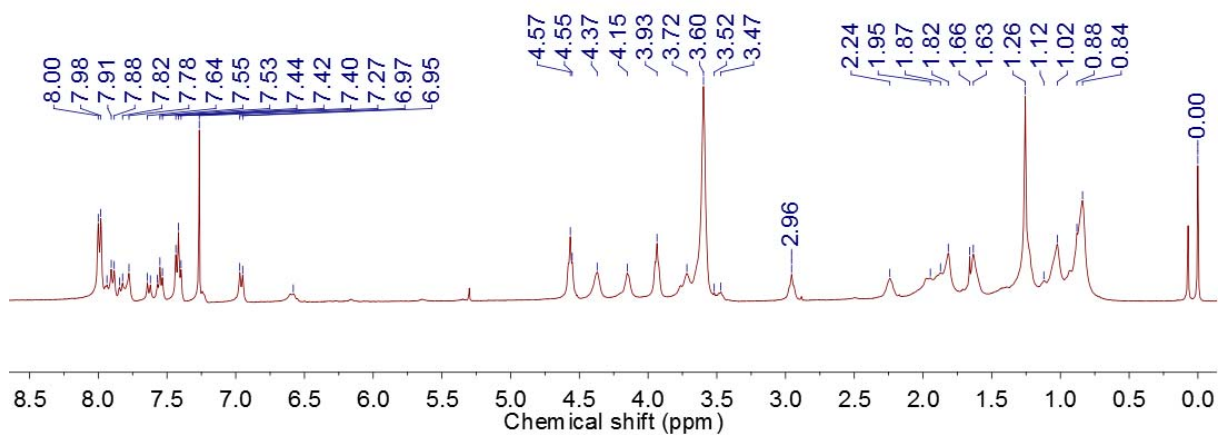


Fig. S11. ^1H NMR spectrum of P2 (CHCl_3-d).

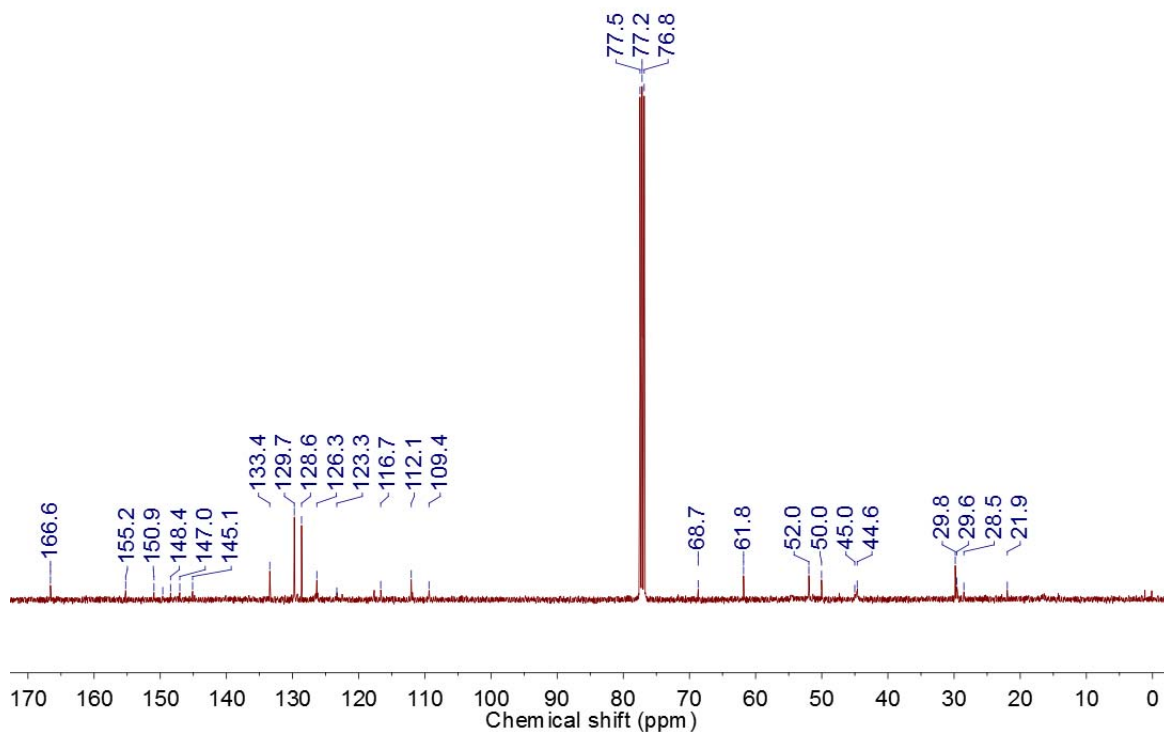


Fig. S12. ^{13}C NMR spectrum of P2 (CHCl_3-d).

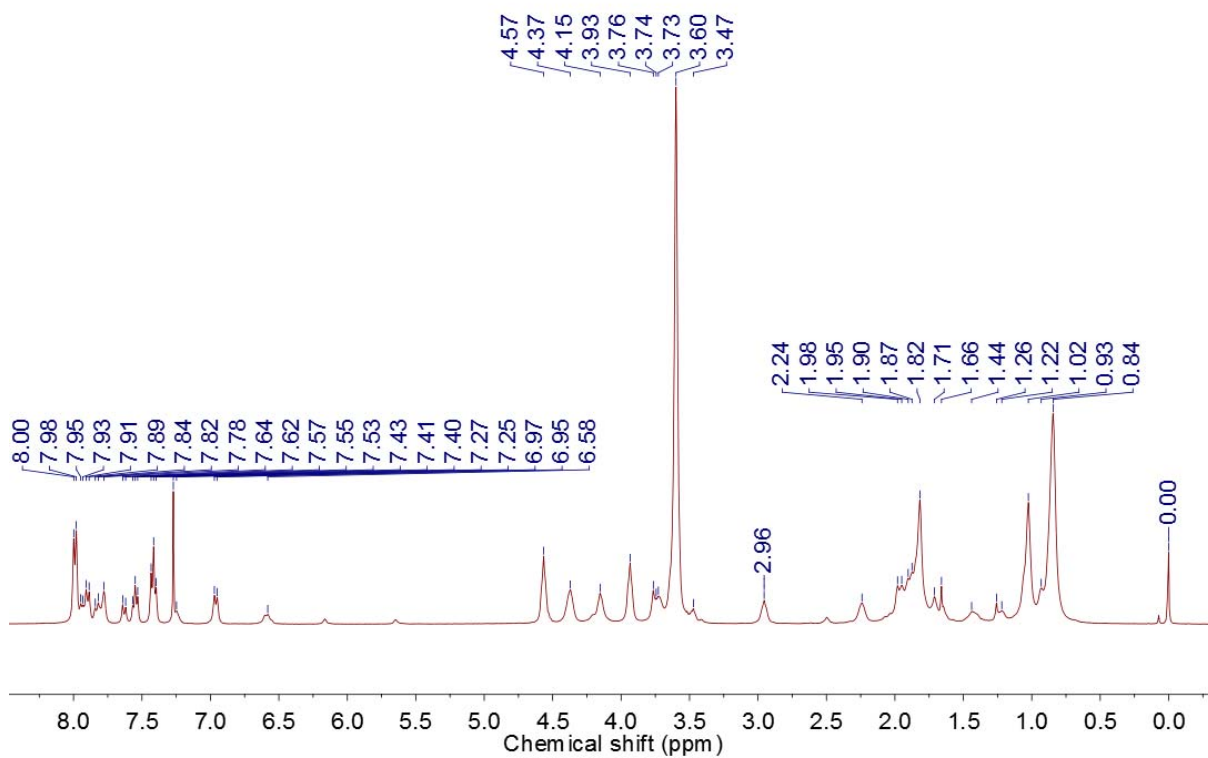


Fig. S13. ^1H NMR spectrum of P3 (CHCl_3-d).

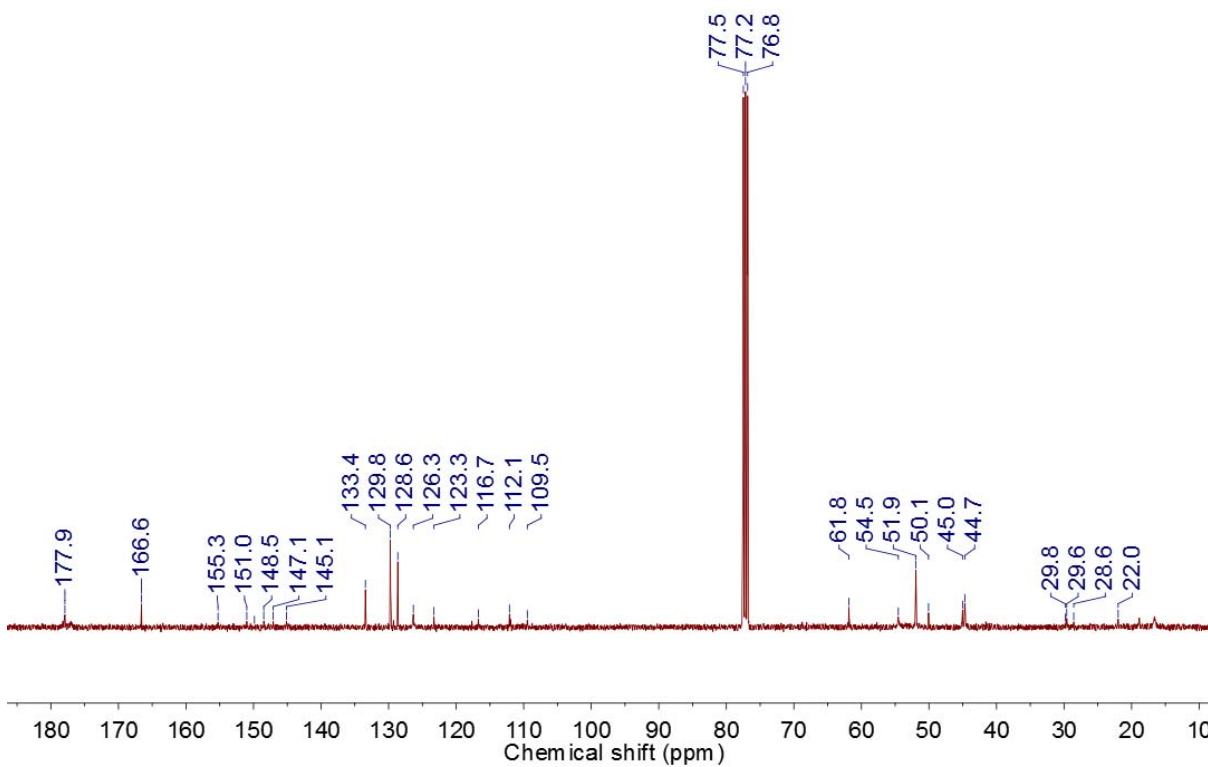


Fig. S14. ^{13}C NMR spectrum of P3 (CHCl_3-d).

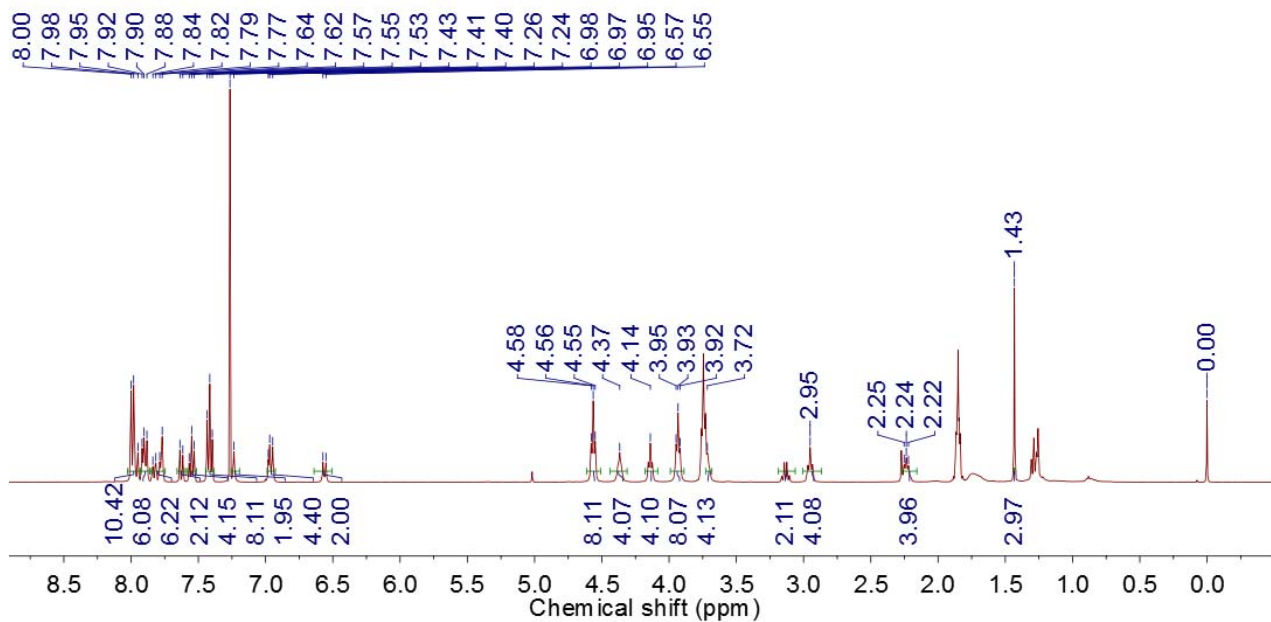


Fig. S15. ^1H NMR spectrum of S5 (CHCl_3 -*d*).

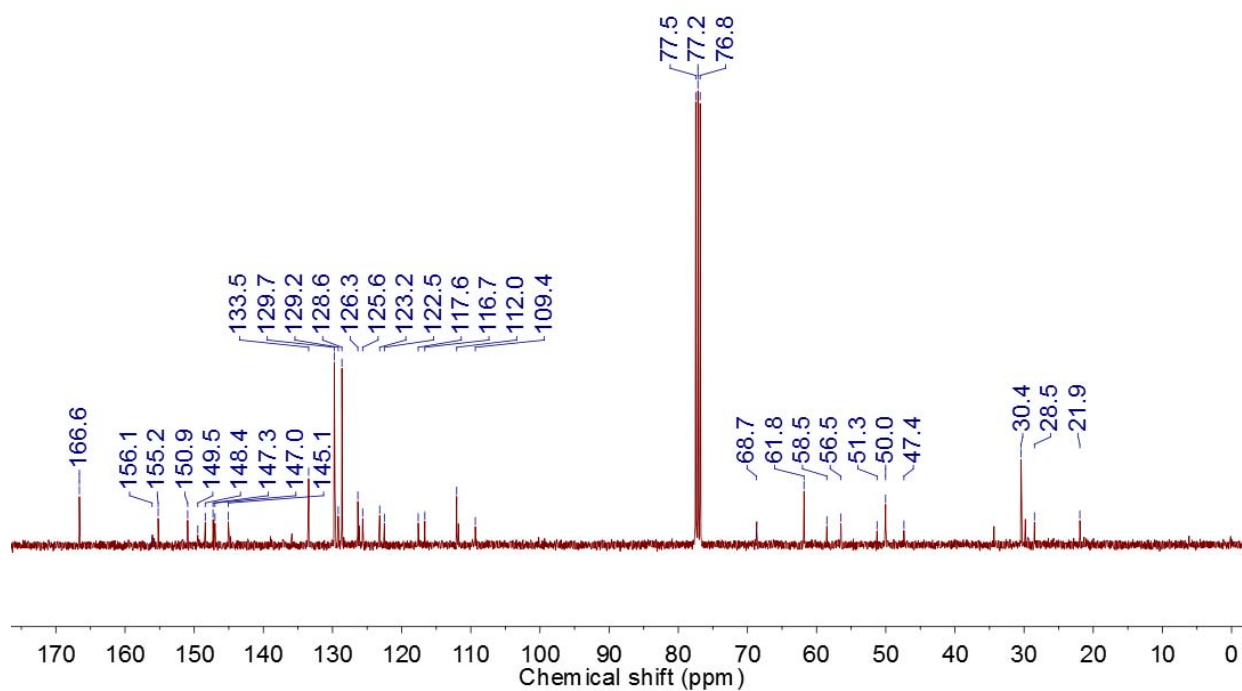


Fig. S16. ^{13}C NMR spectrum of S5 (CHCl_3 -*d*).

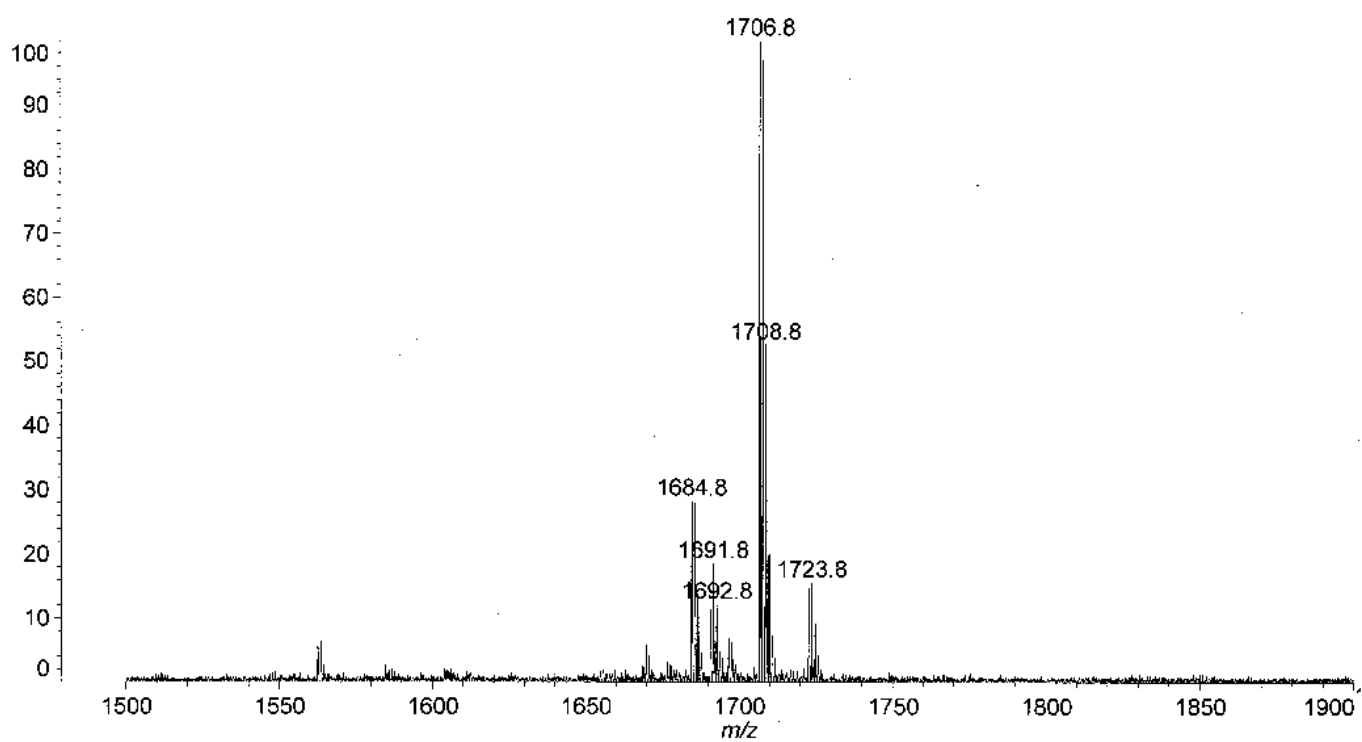


Fig. S17. The MALDI-TOF mass spectrum of S3.

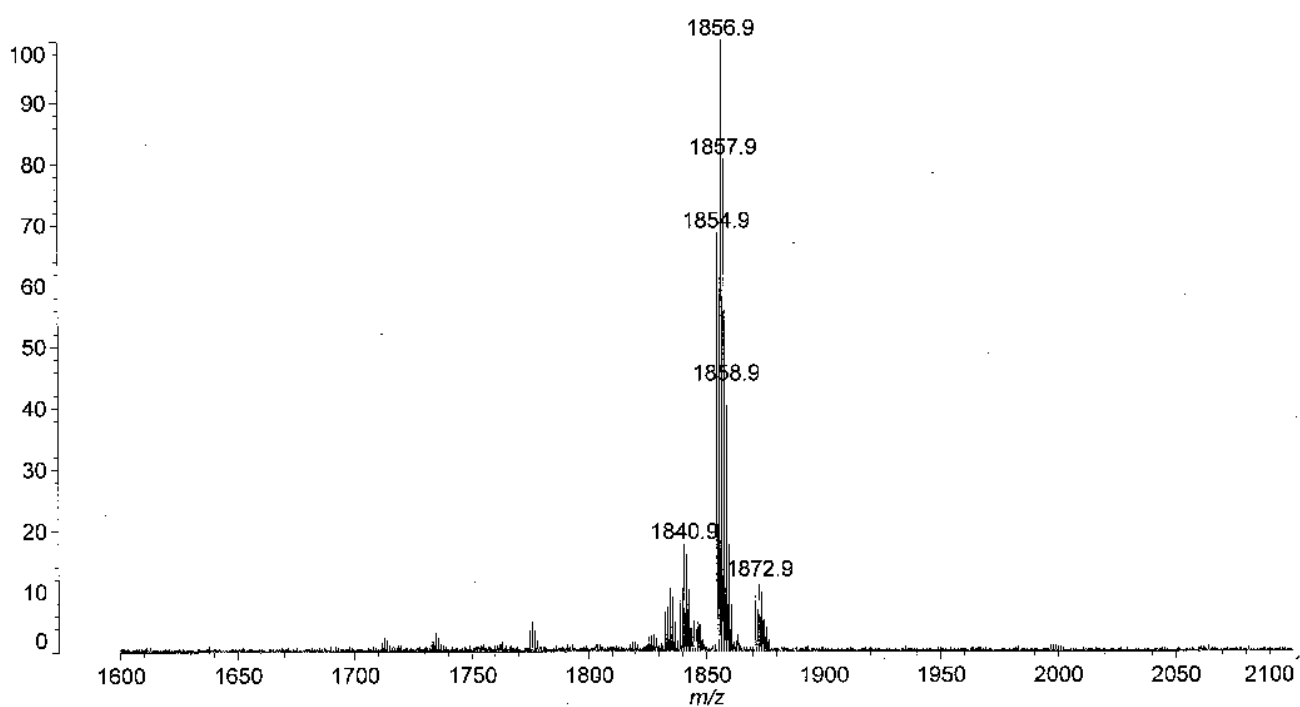


Fig. S18. The MALDI-TOF mass spectrum of Initiator.

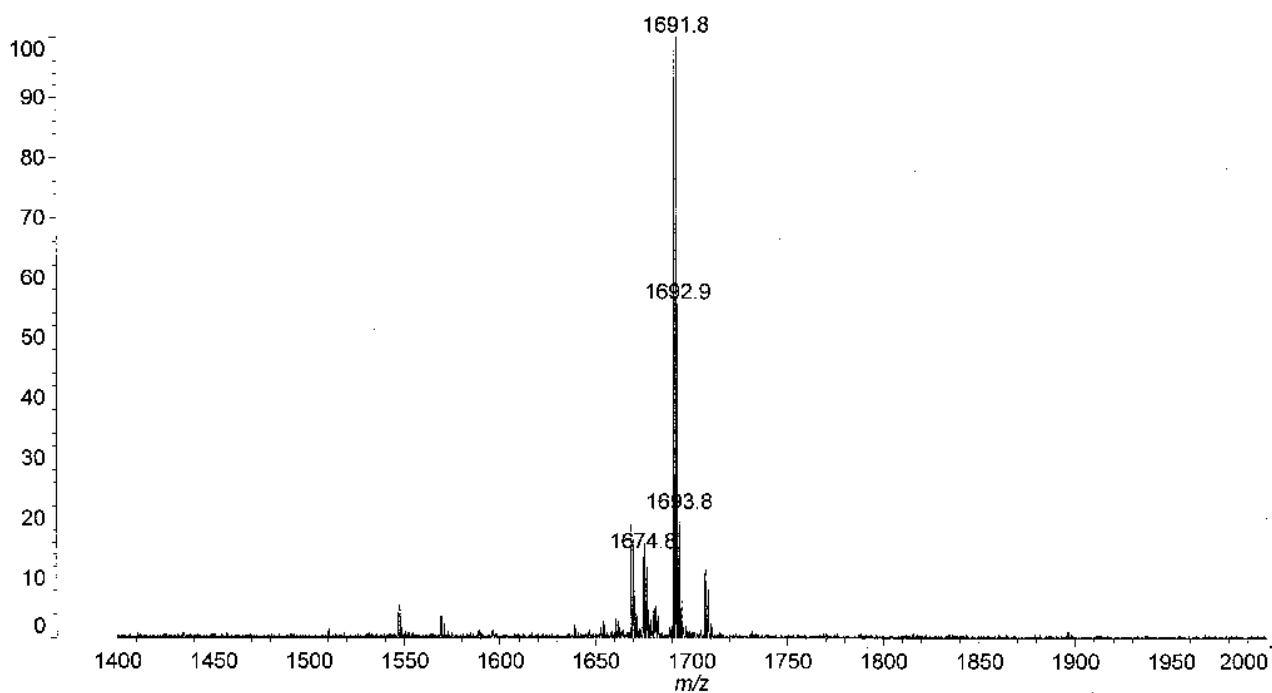


Fig. S19. The MALDI-TOF mass spectrum of S5.

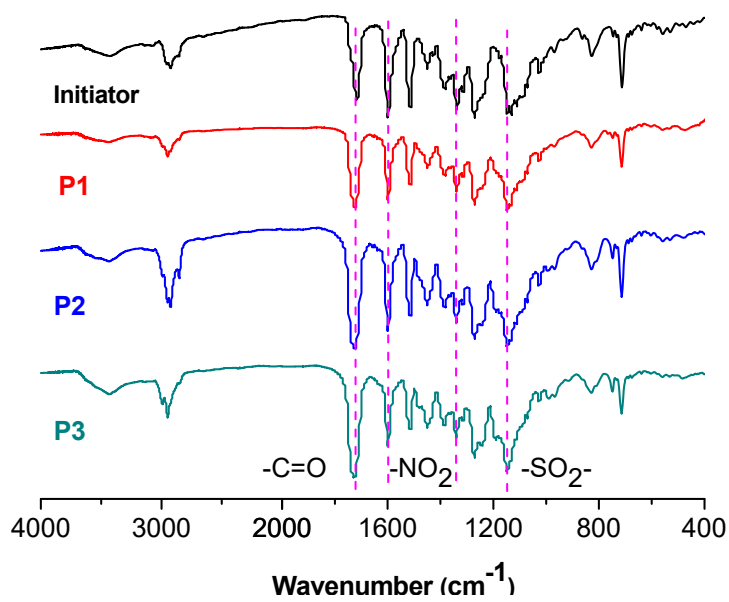


Fig. S20. FT-IR spectra of Initiator, P1, P2 and P3.

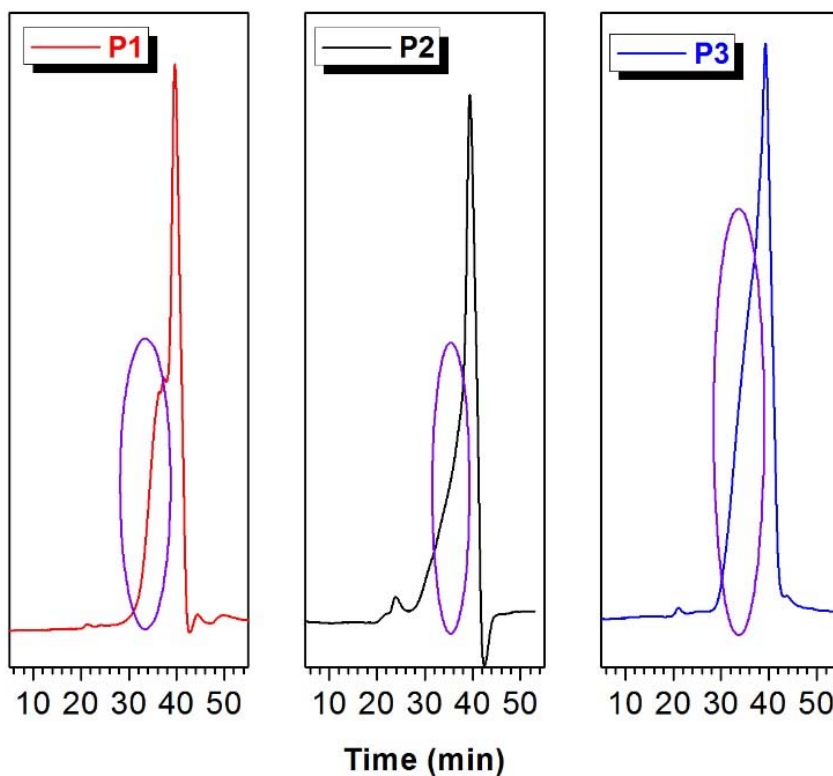


Fig. S21. The GPC chromatograms of P1, P2 and P3.

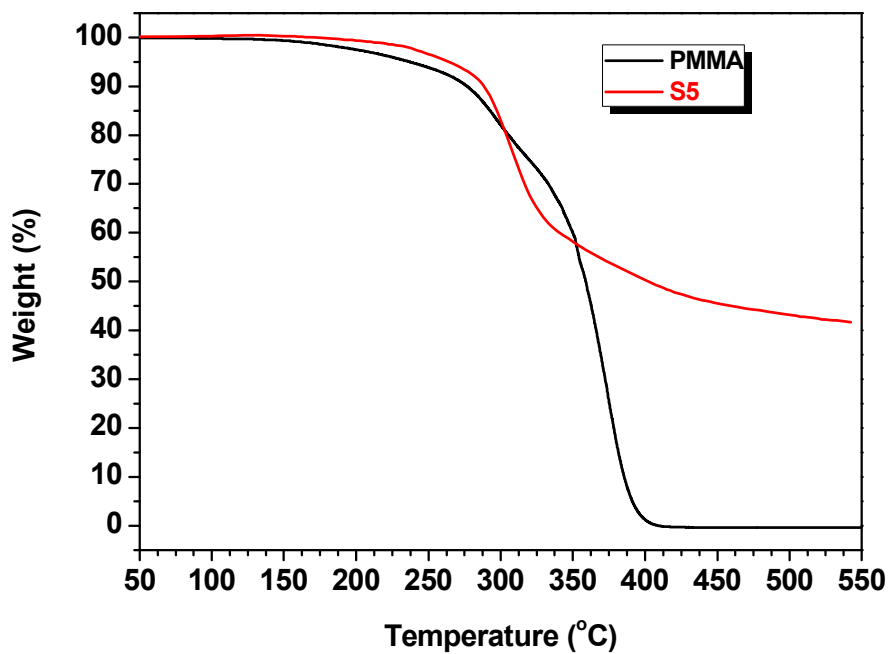


Fig. S22. The TGA thermograms of PMMA and S5, measured in nitrogen at a heating rate of 10 °C/min.

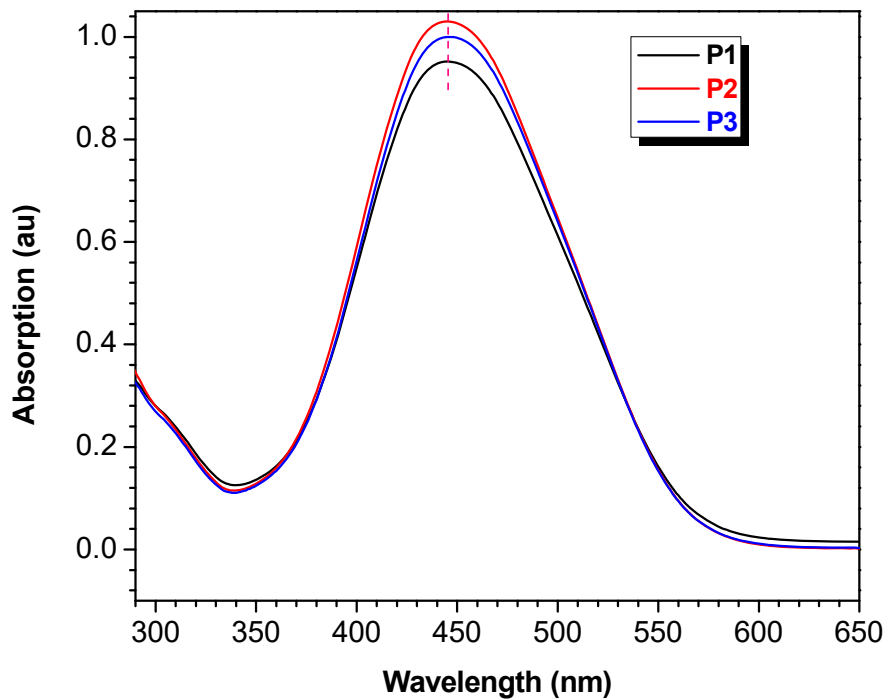


Fig. S23. UV-vis spectra of THF solutions of DHPs (0.02 mg/mL).

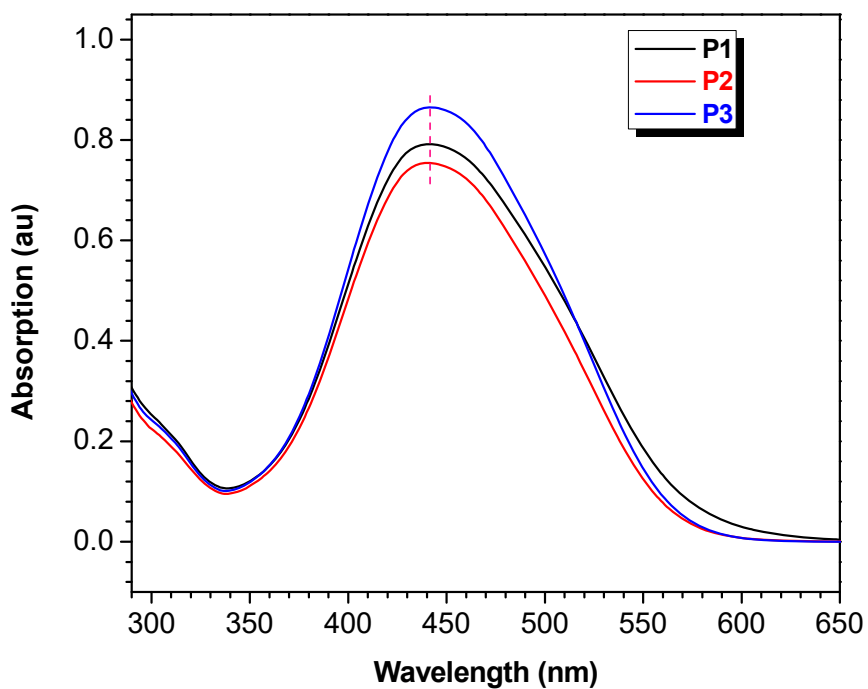


Fig. S24. UV-vis spectra of CH₂Cl₂ solutions of DHPs (0.02 mg/mL).

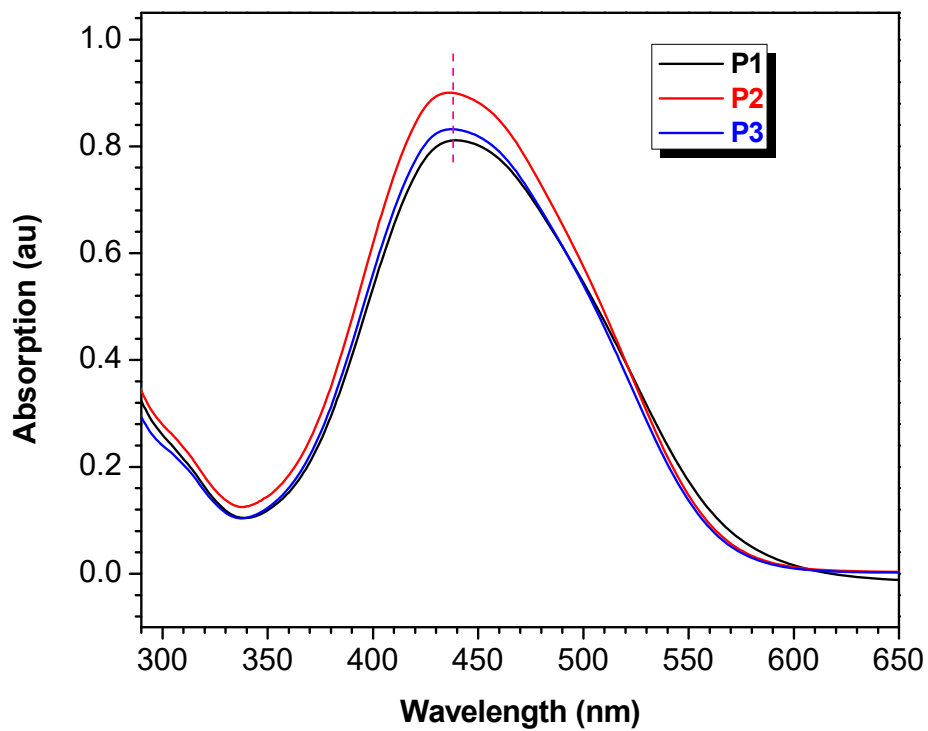


Fig. S25. UV-vis spectra of CHCl₃ solutions of DHPs (0.02 mg/mL).

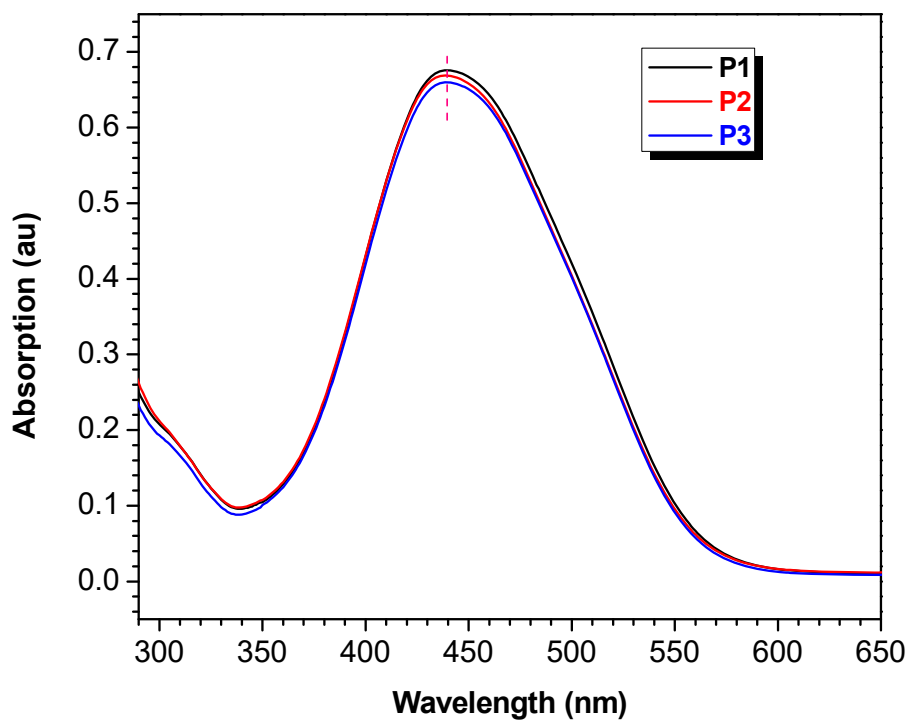


Fig. S26. UV-vis spectra of dioxane solutions of DHPs (0.02 mg/mL).

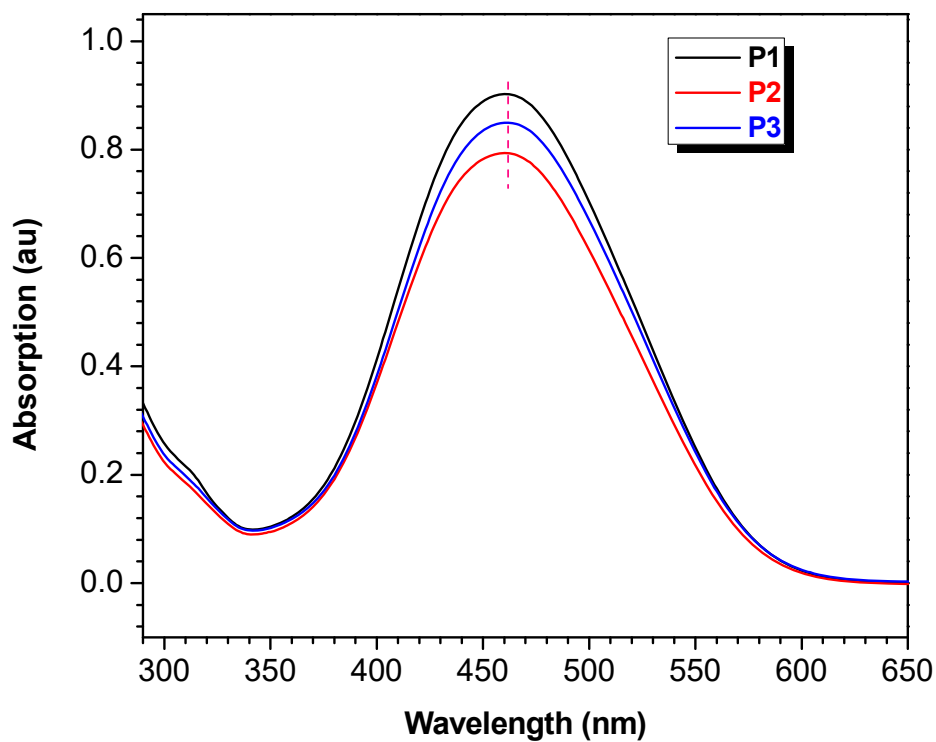


Fig. S27. UV-vis spectra of DMF solutions of DHPs (0.02 mg/mL).

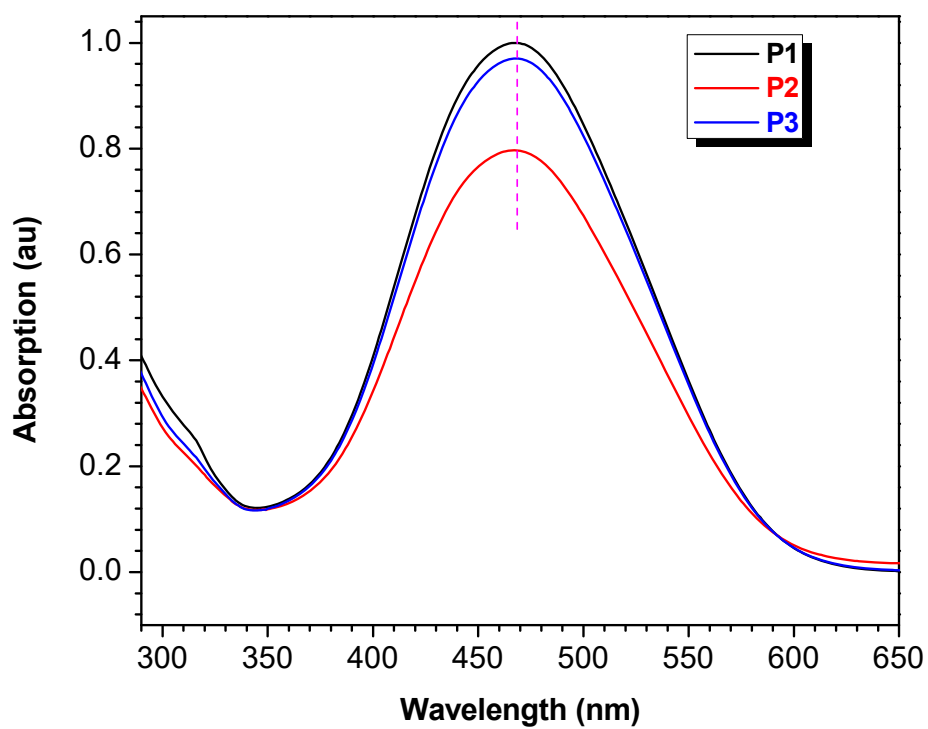


Fig. S28. UV-vis spectra of DMSO solutions of DHPs (0.02 mg/mL).

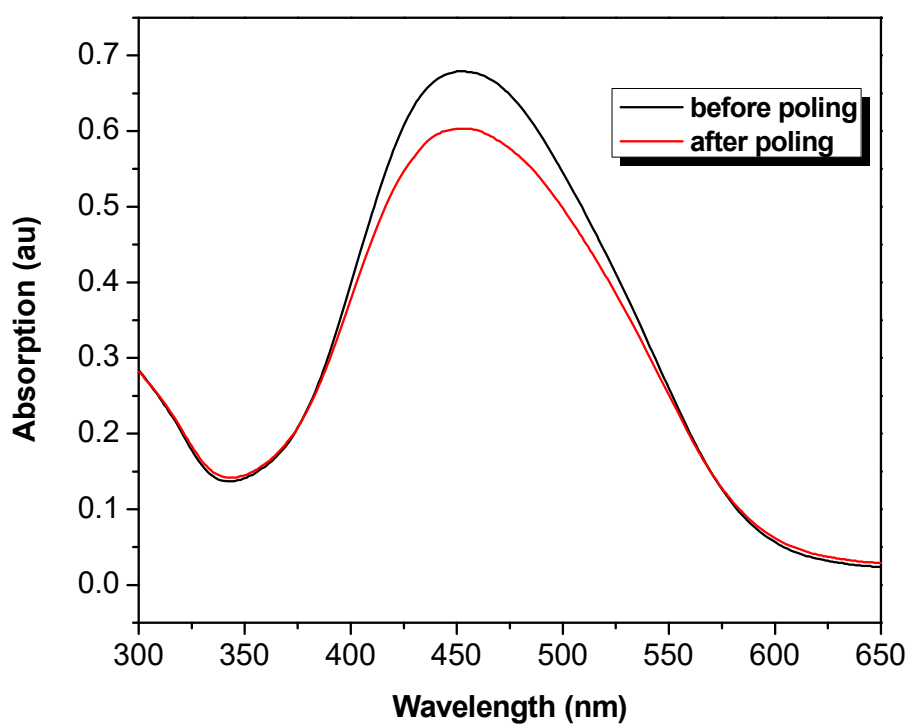


Fig. S29. UV-vis absorption spectra of the film of P1 before and after poling.

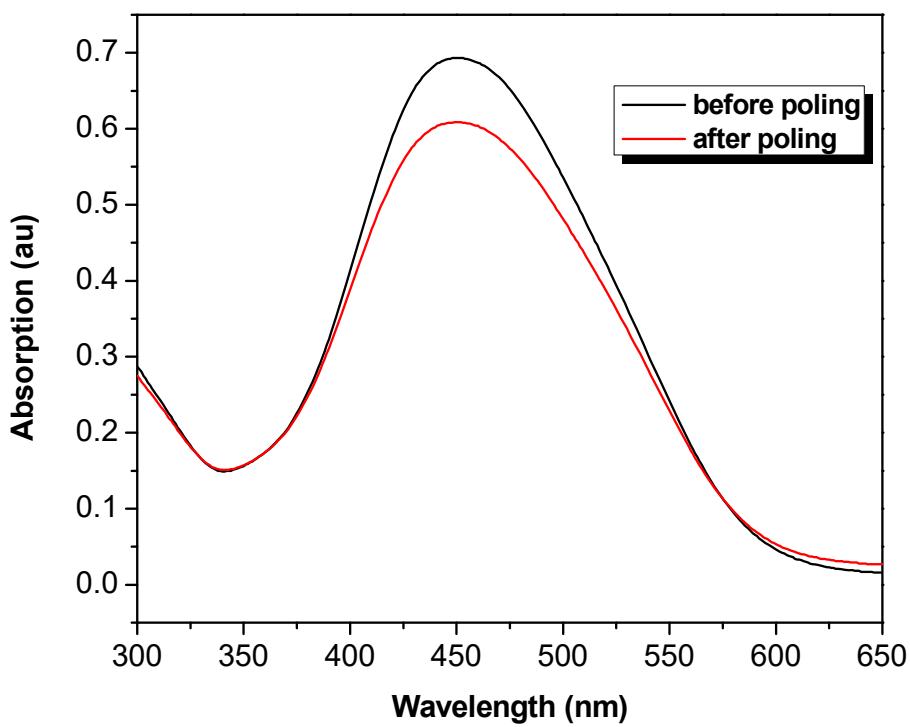


Fig. S30. UV-vis absorption spectra of the film of P2 before and after poling.

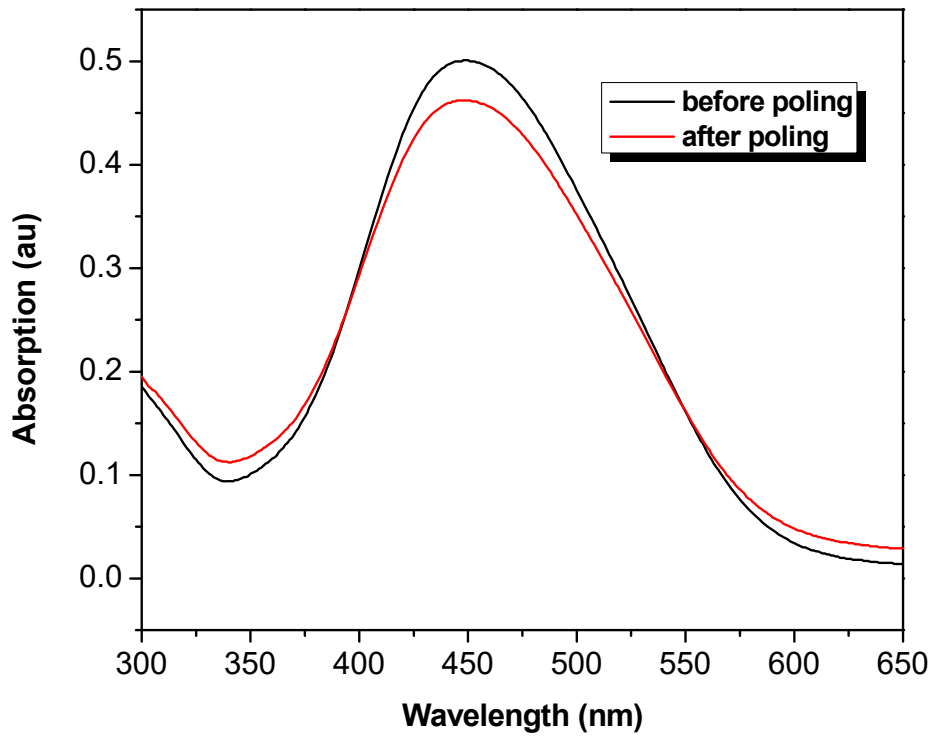


Fig. S31. UV-vis absorption spectra of the film of **P3** before and after poling.

Calculation of the NLO coefficients:

In this paper, we used second harmonic generation (SHG) processes, a typical second-order NLO effect, to express the NLO coefficients of the dendronized hyperbranched polymers. Calculation of the SHG coefficients for the poled films is based on the following equation:

$$\frac{d_{33,s}}{d_{11,q}} = \frac{\chi_s^{(2)}}{\chi_q^{(2)}} = \sqrt{\frac{I_s}{I_q}} \frac{l_{c,q}}{l_s} F$$

Where $d_{11,q}$ is d_{11} of the quartz crystals, which is equal to 0.45 pm/V. I_s and I_q are the SHG intensities of the sample and the quartz, respectively, $l_{c,q}$ is the coherent length of the quartz, l_s is the thickness of the polymer film, and F is the correction factor of the apparatus and is equal to 1.2 when l_c is much greater than l_s . Thus, from the experimental data, the d_{33} values of the **DHPs** were calculated at a fundamental wavelength of 1064 nm. To avoid the phenomenon that the d_{33} value of the same NLO polymer could be

different when measured by different methods or different testing system at different time, we tested all the samples at the same time.

we also calculated their nonresonant d_{33} values ($d_{33(\infty)}$), according to the following equation:

$$\frac{d_{33}}{d_{\infty}} = \omega_0^4 / [(\omega_0^2 - \omega^2)(\omega_0^2 - 4\omega^2)]$$

Where ω_0 was the frequency of the λ_{\max} of **DHPs** in film; ω was the frequency of the laser.