Electronic Supplementary Information for:

The integration of“X” type dendron into polymers to further improve the comprehensive NLO performance

Runli Tang,[a,d] Hong Chen,[a,d] Shengmin Zhou,[a] Binwen Liu,[b] Dong Gao,[c] Huiyi Zeng,[b] and Zhen Li*[a]

[a] Department of Chemistry, Hubei Key Lab on Organic and Polymeric Opto-Electronic Materials, Wuhan University, Wuhan, 430072, China.

E-mail: lizhen@whu.edu.cn or lichemlab@163.com; Fax: +86-27-68756757; Tel: +86-27-68755363

[b] Fujian Institute of Research on the Structure of Matter, the Chinese Academy of Sciences, Fuzhou 350002, China.

[c] Institute of Chemistry, The Chinese Academy of Sciences, Beijing10080, China.

[d] The authors contributed equally to this paper.

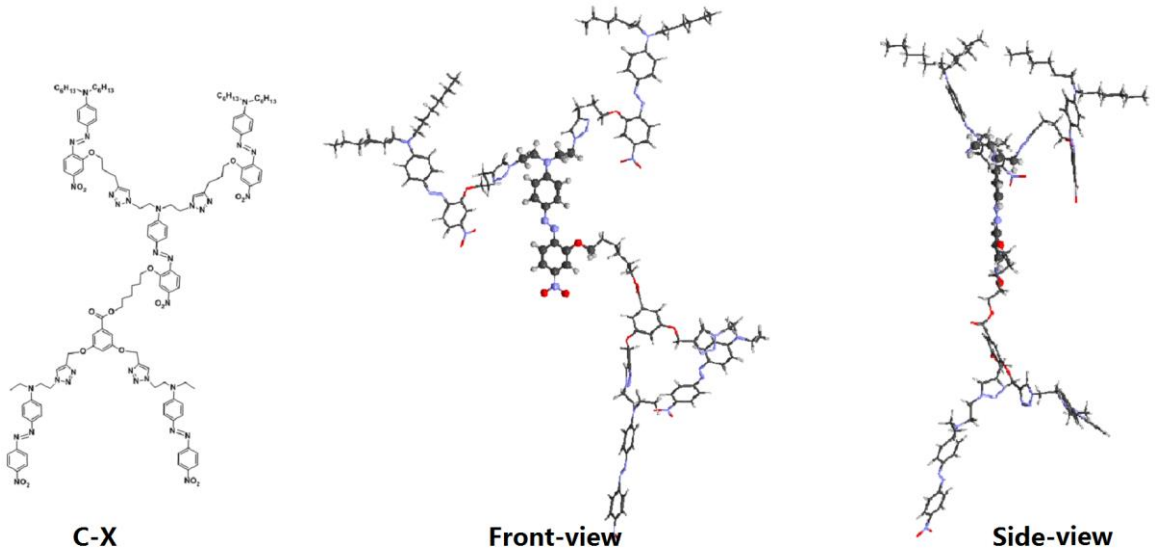


Figure S1. "X" type dendrimer **C-X** and its calculated conformation.

Experimental Section

Materials

Tetrahydrofuran (THF) was dried over Na-K alloy and distilled under an atmosphere of dry nitrogen. *N*, *N*-Dimethylformamide (DMF) was dried over CaH_2 and distilled under an atmosphere of dry nitrogen. Compounds R1-R3 were synthesized according to our previous work.[1]

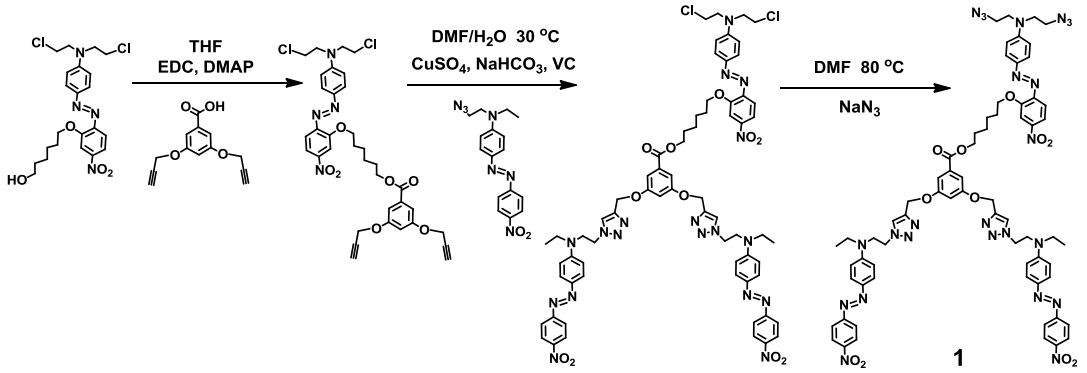
Instrumentation

^1H and ^{13}C NMR spectra were measured on a Varian Mercury300, or Bruker ARX400 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. UV-visible spectra were obtained using a Shimadzu UV-2550 spectrometer. HR-MS was measured by high resolution fourier

transform ion cyclotron resonance mass spectrometer (FT-ICR-MS), APEX II (Bruker). MALDI-TOF was measured by Voyager-DE-STR MALDI-TOF mass spectrometer (ABI, American). Thermal analysis was performed on METTLER TOLEDO ATAR^{e} TGA/DSC 1 thermal analyzer at a heating rate of 10 ^{o}C/min in nitrogen at a flow rate of 50 cm^{3}/min for thermogravimetric analysis (TGA).

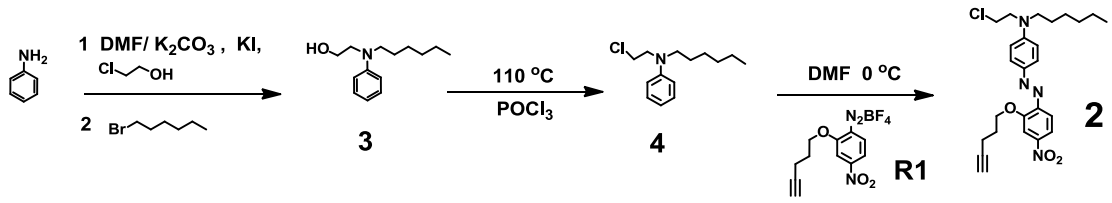
Synthesis

As shown in Scheme S1, compound **1** was synthesized according to our previous work,[2] further characterized. MALDI-TOF MS: m/z calcd for $C_{67}H_{70}N_{24}O_{11}$: 1409.6 $[M+Na]^{+}$; found: 1409.7.



Scheme S1 The synthetic route to compound **1**.

As shown in Scheme S2, compound **2** was synthesized:



Scheme S2. The synthetic route to compound **2**.

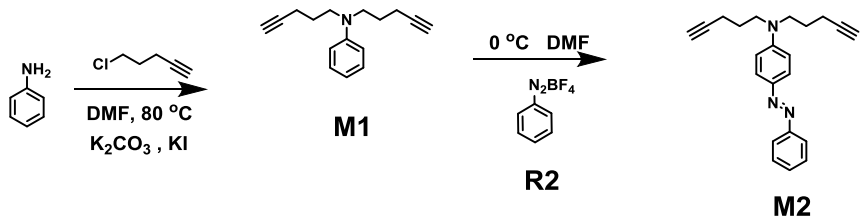
Compound **3**: Aniline (9.30 g, 0.1 mol) was dissolved in DMF, then 2-chloroethanol (8.05 g, 0.1 mol), K_2CO_3 (27.63 g, 0.2 mol) and KI (3.32 g, 0.02 mol) were added. After the reaction mixture was stirred for 24 h at 80 ^{o}C, another batch of 1-bromohexanel (16.50 g, 0.1 mol), K_2CO_3 (13.82 g, 0.1 mol) and KI (16.60 g, 0.01 mol) was added. The resultant mixture was stirred for another 24 h at 80 ^{o}C, cooled to room temperature, then filtered to remove the solid. The filtrate was poured into a lot of water, extracted with chloroform, and washed with water for several times. The organic layer was dried over magnesium sulfate. The resultant crude product was purified by column chromatography on silica gel using chloroform/petroleum ether (2/1) as eluent to afford colorless oil. (14.26 g, 64.8 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 0.89 (t, J=6.3, 3H, -CH3),

1.30 (dd, 6H, -CH2-), 1.58 (dd, 2H, -CH2-), 1.72 (t, J=6.0 Hz, 1H, -OH), 3.33-3.28 (dd, 2H, -CH2-), 3.49-3.45 (dd, 2H, -CH2-), 3.81-3.75 (dd, 2H, -CH2-), 6.76-6.68 (dd, 3H, ArH), 7.25-7.19 (dd, 2H, Ar2). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ (ppm): 14.20, 22.83, 26.92, 31.84, 52.00, 53.31, 60.13, 112.97, 116.70, 129.42, 148.54.

Compound **4**: compound **3** (4.00 g, 18.1 mmol) was dissolved in $POCl_3$ (2.78 g, 18.1 mmol) in an ice bath, then the resultant mixture was stirred for 2 h at 100 ^{o}C, cooled to room temperature. Ice water was added into the mixture in an ice bath, some sodium carbonate solution was added to adjust the pH value to 7.0. The mixture was extracted by chloroform, and the organic layer was combined and dried over magnesium sulfate. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent, to afford a colorless oil (3.93 g, 91.4 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.25 (t, J=5.1 Hz, 3H, -CH3), 1.61-1.49 (dd, 2H, -CH2-), 1.89-1.93 (dd, 2H, -CH2), 3.73-3.65 (dd, 4H, -CH2-), 3.87-3.73 (dd, 2H, -CH2-), 3.89-3.85 (dd, 2H, -CH2-), 4.24 (t, J=6.9 2H, -CH2-), 6.80 (dd, 2H, ArH), 7.69 (d, J=9.0 Hz, 1H, ArH), 7.94-7.87 (dd, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ (ppm): 14.24, 22.86, 26.92, 27.52, 31.87, 40.41, 51.62, 53.05, 111.88, 116.56, 129.64, 147.26.

Compound **2**: compound **4** (479.5 mg, 2.0 mmol) and **R1** (638.0 mg, 2.0 mmol) were dissolved in DMF, stirred for 24 h at 0 ^{o}C. Then the mixture was poured into a lot of ice water, and some sodium bicarbonate was added to adjust the pH value to 7.0. The resultant deep red precipitate was filtered, washed with water, and further purified by column chromatography on silica gel using chloroform/petroleum ether (3/1) as eluent, to afford a red powder (725.0 mg, 77.0 %). HR-MS: m/z calcd for $C_{25}H_{31}Cl_1N_4O_3$: 470.2585 $[M]^+$; found: 470.2086. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 0.91 (t, 3H, -CH3), 1.35 (dd, 6H, -CH2-), 1.66 (dd, 2H, -CH2), 2.00 (s, 1H, -CCH), 2.19-2.13 (dd, 2H, -CH2-), 2.51 (t, J=7.2, 2H, -CH2-), 3.45 (t, J=7.5, 2H, -CH2-), 3.68-3.66 (dd, 2H, -CH2-), 3.76-3.74 (dd, 2H, -CH2-), 4.35 (t, J=6.3, 2H, -CH2), 6.76 (d, 2H, ArH), 7.69 (d, J=8.4, 1H, ArH), 7.92-7.88 (dd, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ (ppm): 14.20, 15.34, 22.82, 26.84, 27.57, 28.22, 31.79, 40.11, 51.99, 52.92, 68.29, 69.40, 83.40, 109.41, 111.55, 116.81, 117.59, 126.44, 144.78, 147.21, 148.43, 150.70, 155.26.

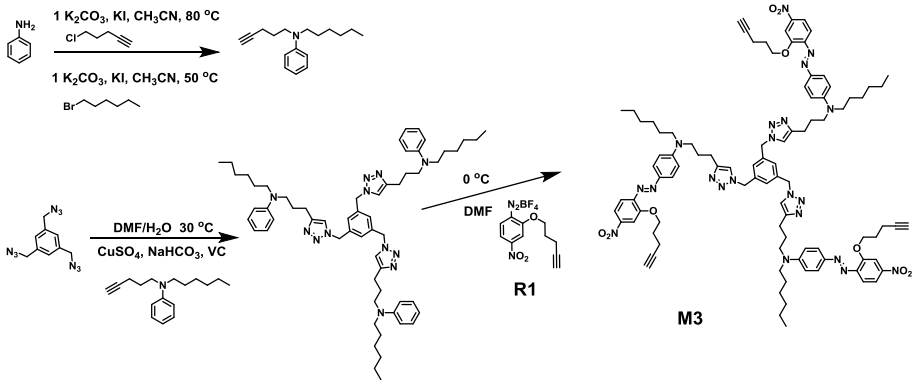
As shown in Scheme S3, compound **M1** was synthesized according to our previous work,[2d, 3] and **M2** was synthesized as following:



Scheme S3. The synthetic route to **M1** and **M2**

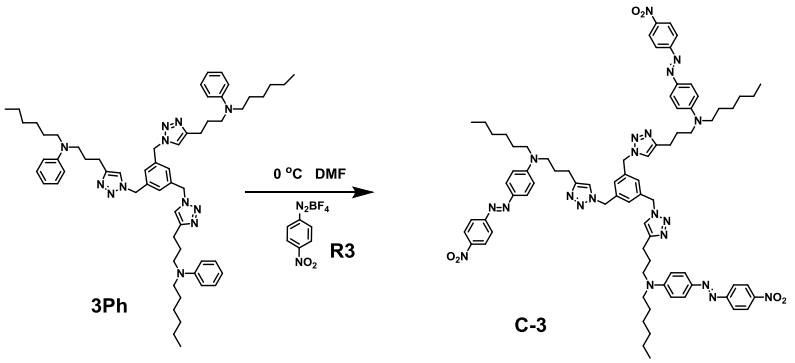
M2: **Mon1** (225.3 mg, 1.0 mmol), and **R2** (191.9 mg, 1.0 mmol) were dissolved in DMF (5 mL), the resultant mixture was allowed to stir at 0 ℃ overnight, and then poured into a lot of water. The precipitate was collected and washed several times with water, and purified by column chromatography using ethyl acetate/petroleum ether (1/8) as eluent to yield an orange oil (295.0 mg, 89.6 %). HR-MS: m/z calcd for $C_{22}H_{23}N_3$: 329.1892 $[M]^+$; found: 329.1887. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 1.87 (t, *J*=6.9 Hz, 4H, -CH_2-), 2.28 (br, 4H, -CH_2-), 2.05 (s, 2H, -C≡CH), 2.28 (br, 4H, -CH_2-), 3.55 (t, *J*=6.9 Hz, 4H, -CH_2-), 6.80 (d, *J*=9.0 Hz, 2H, -ArH), 7.37 (m, 1H, -ArH), 7.47 (t, *J*=7.2 Hz, 4H, -ArH), 7.87-7.81 (m, 4H, -ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ (ppm): 153.41, 150.29, 143.74, 129.57, 129.13, 125.38, 122.38, 111.60, 83.50, 69.54, 50.12, 26.01, 16.16.

As shown in Scheme S4, compound **M3** was synthesized according to our previous work.[4]



Scheme S4. The synthetic route to **M3**

As shown in Scheme S5, compound **C-3** was synthesized:



Scheme S5. The synthetic route to **C-3**

Compound **C-3**: Compound **3Ph** (66.0 mg, 0.06 mmol), and **R3** (53.1 mg, 0.22 mmol) were dissolved in DMF (6 mL), the resultant mixture was allowed to stir at 0 ℃ overnight, and then poured into a lot of water. The precipitate was collected, washed several times with water, and purified by column chromatography using dichloromethane/ethyl acetate (1/2) as eluent to yield a red solid (78.3 mg, 82.3 %). MALDI-TOF MS: m/z calcd for $C_{78}H_{93}N_{21}O_6$: 1420.7 $[M]^+$; found: 1420.9. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 0.89 (br, 9H, -CH_2-), 1.32 (m, 18H, -CH_2-), 2.00 (m, 6H, -CH_2-), 2.73 (t, *J*=7.5 Hz, 6H, -CH_2-), 3.37 (t, *J*=6.9 Hz, 6H, -CH_2-), 3.46 (t, *J*=6.9 Hz, 6H, -CH_2-), 5.43 (s, 6H, -CH_2-), 6.65 (m, *J*=8.7 Hz, 6H, -ArH), 7.12 (s, 3H, -ArH), 7.22 (s, 3H, -ArH), 7.89-7.80 (m, 12H, -ArH), 8.32 (d, *J*=9.0 Hz, 6H, -ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ (ppm): 156.7, 151.4, 147.6, 147.1, 143.2, 136.9, 127.2, 126.2, 124.6, 122.4, 120.9, 111.2, 53.3, 51.1, 50.6, 31.5, 27.1, 26.7, 26.5, 22.9, 22.5, 13.9.

References

1 (a) Z. Li, W. Wu, P. Hu, X. Wu, G. Yu, Y. Liu, C. Ye, Z. Li, J. Qin, *Dyes and Pigments* 2009, **81**, 264; (b) Z. a. Li, G. Yu, W. Wu, Y. Liu, C. Ye, J. Qin, Z. Li, *Macromolecules* 2009, **42**, 3864; (c) W. Wu, C. Li, G. Yu, Y. Liu, C. Ye, J. Qin, Z. Li, Chemistry 2012, 18, 11019; (d) Z. Li, A. Qin, J. W. Y. Lam, Y. Dong, Y. Dong, C. Ye, I. D. Williams, B. Z. Tang, Macromolecules 2006, 39, 1436.

2 R. Tang, S. Zhou, W. Xiang, Y. Xie, H. Chen, Q. Peng, G.Yu, B. Liu, H. Zeng, Q. Li and Z. Li, *J. Mater. Chem. C*, 2015, **3**, 4545.

3 Z. a. Li, W. Wu, C. Ye, J. Qin, Z. Li, *Polymer* 2012, **53**, 153.

4 R. Tang, H. Chen, S. Zhou, W. Xiang, X. Tang, B. Liu, Y. Dong, H. Zeng and Z. Li, *Polym. Chem*., 2015, DOI: 10.1039/C5PY00155B.

The ^{1}H NMR and ^{13}C NMR spectra of related compounds:

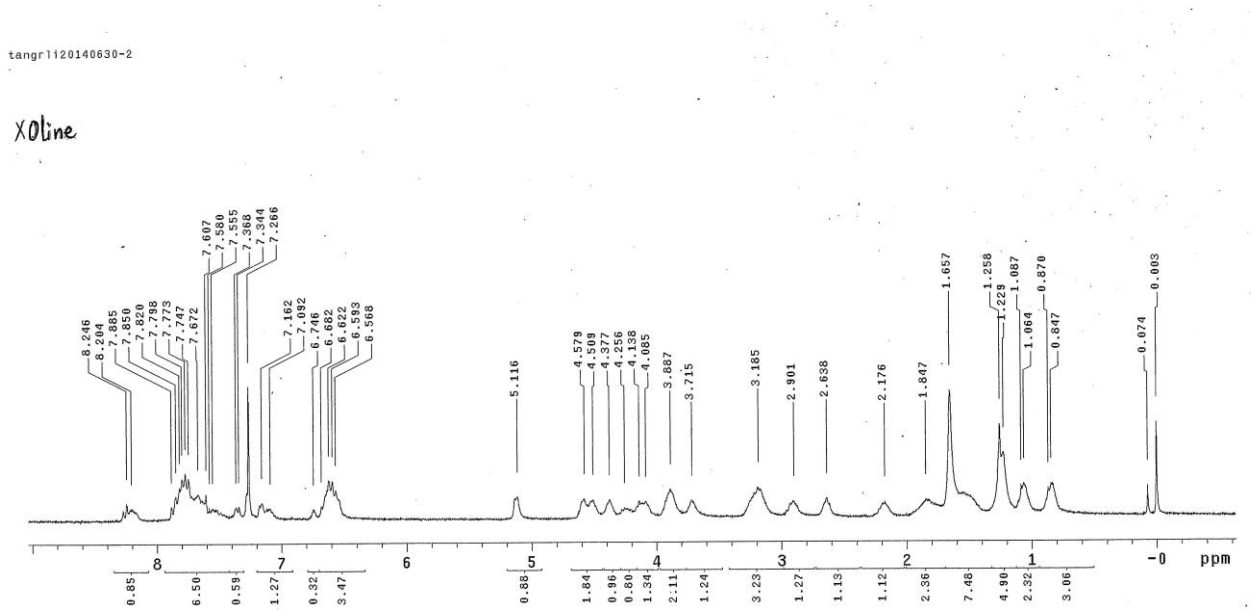


Fig.S2. The ^{1}H NMR spectrum of polymer **P1** in chloroform-*d*.

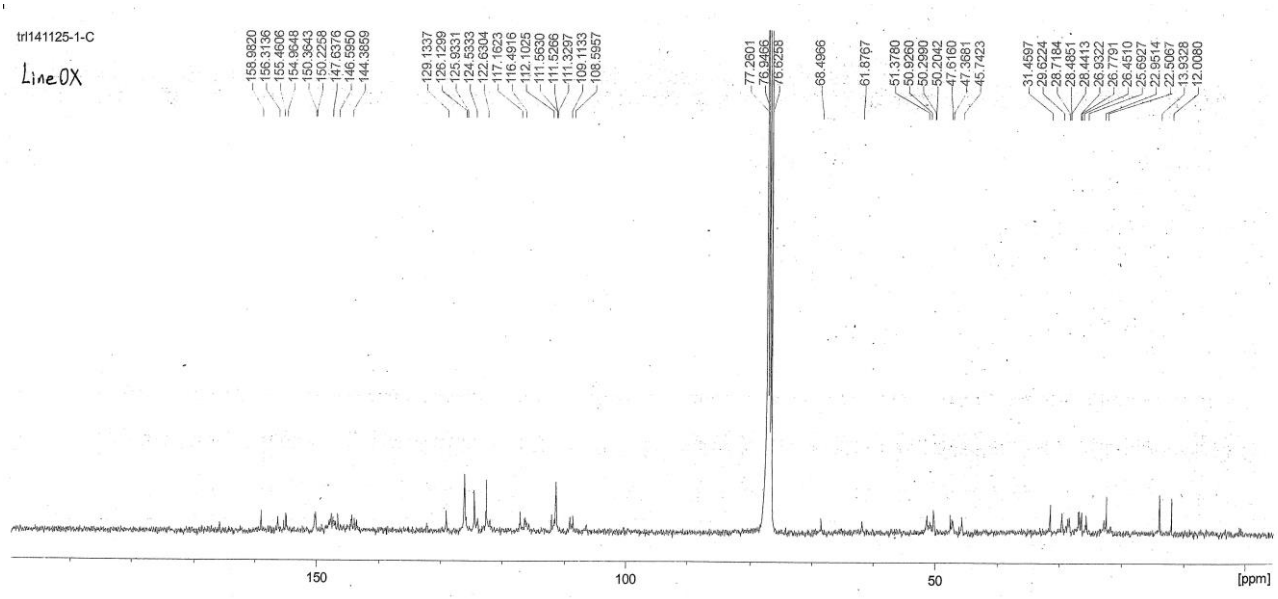


Fig.S3. The ^{13}C NMR spectrum of polymer **P1** in chloroform-*d*.

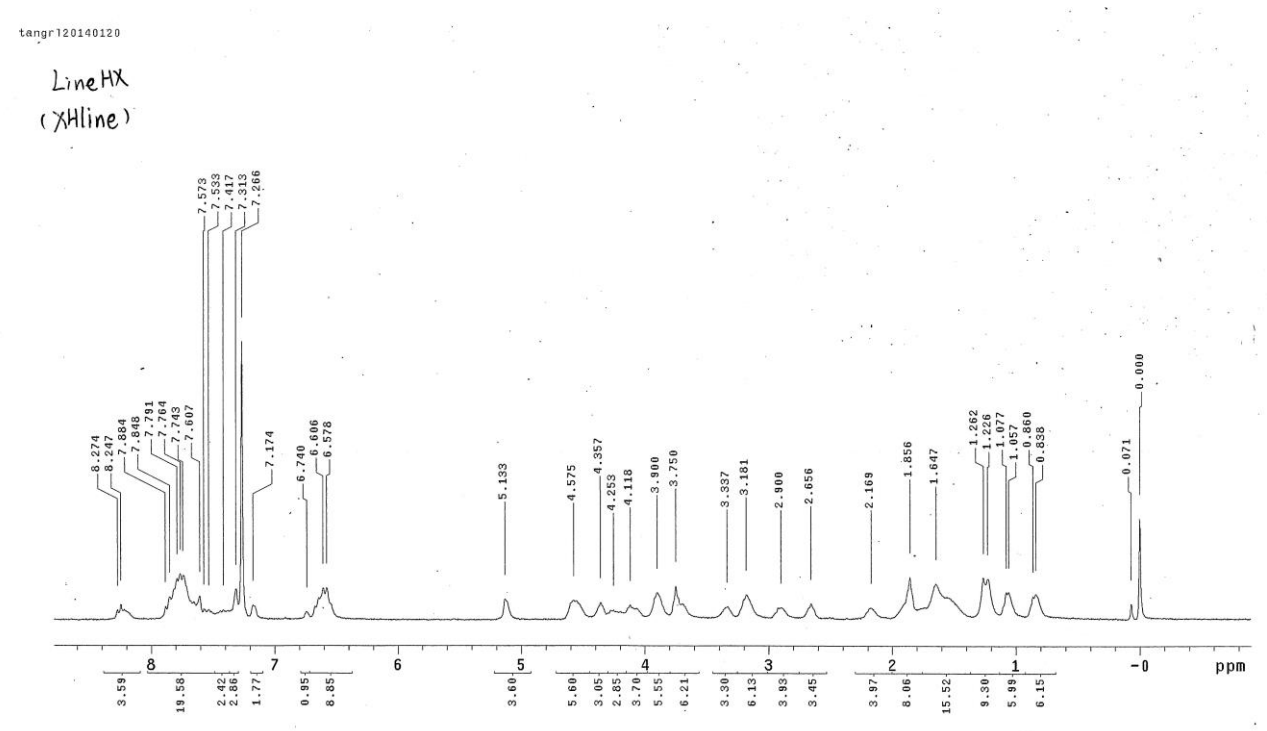


Fig.S4. The ^{1}H NMR spectrum of polymer **P2** in chloroform-*d*.

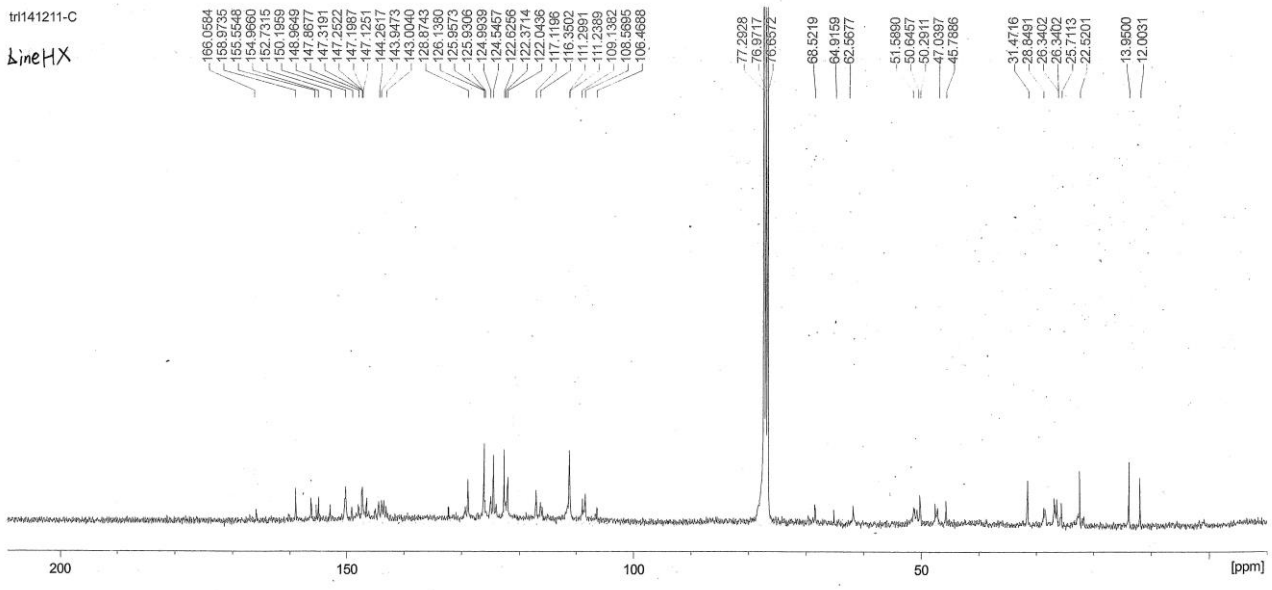


Fig.S5. The ^{13}C NMR spectrum of polymer **P2** in chloroform-*d*.

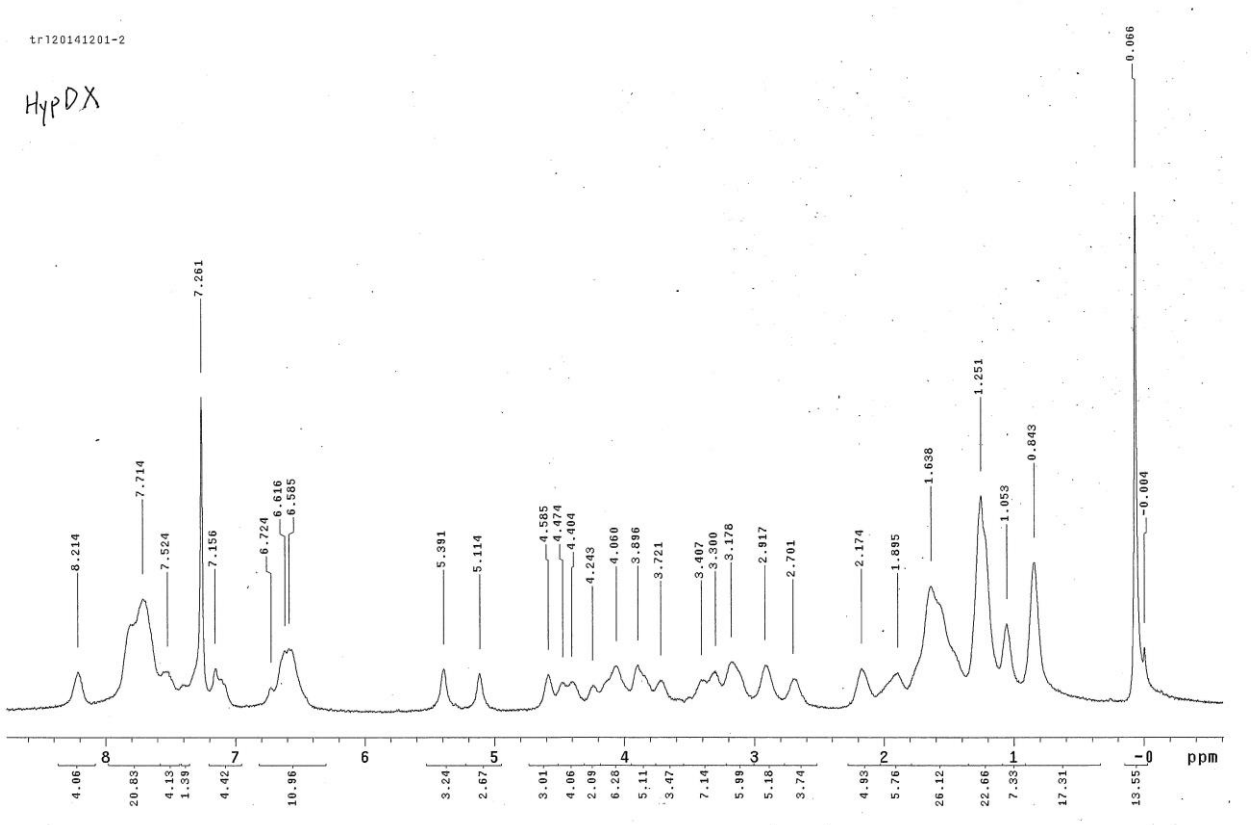


Fig.S6. The ^{1}H NMR spectrum of polymer **P3** in chloroform-*d*.

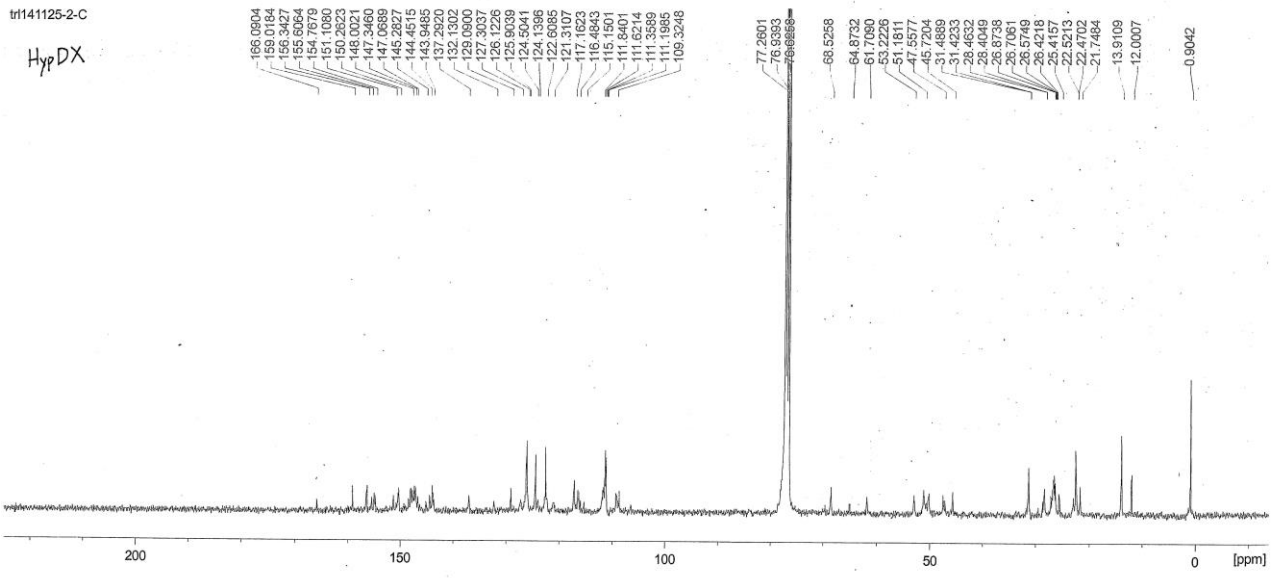


Fig.S7. The ^{13}C NMR spectrum of polymer **P3** in chloroform-*d*.

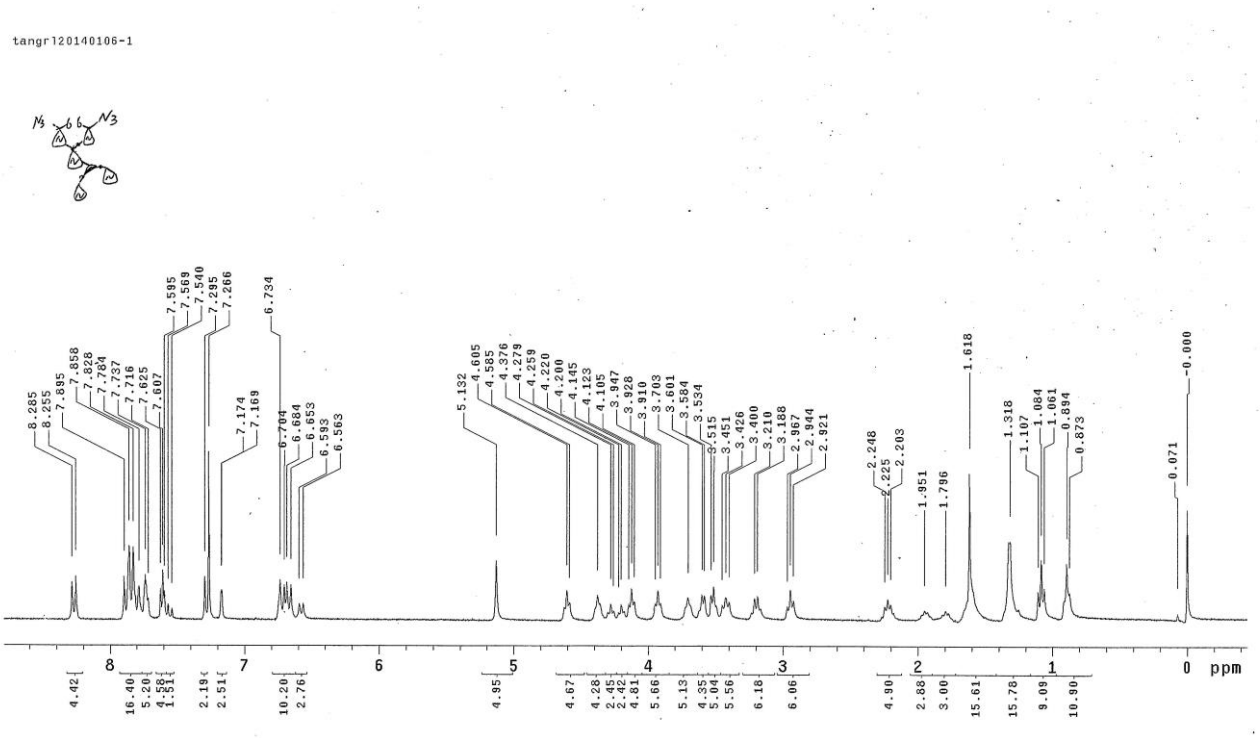


Fig.S8. The ^{1}H NMR spectrum of **MX** in chloroform-*d*.

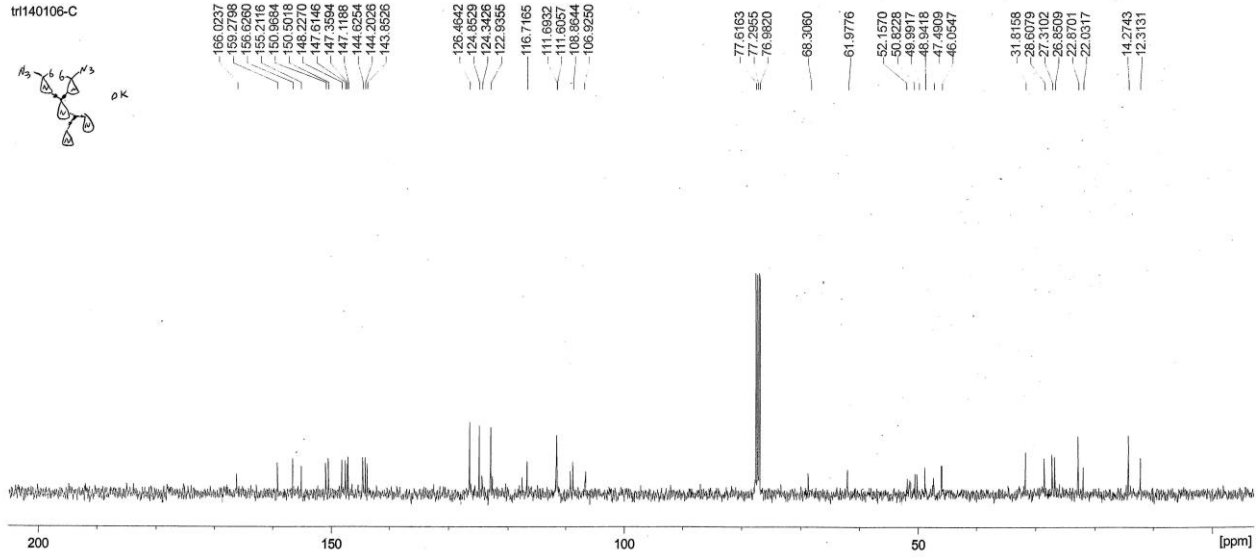


Fig.S9. The ^{13}C NMR spectrum of **MX** in chloroform-*d*.

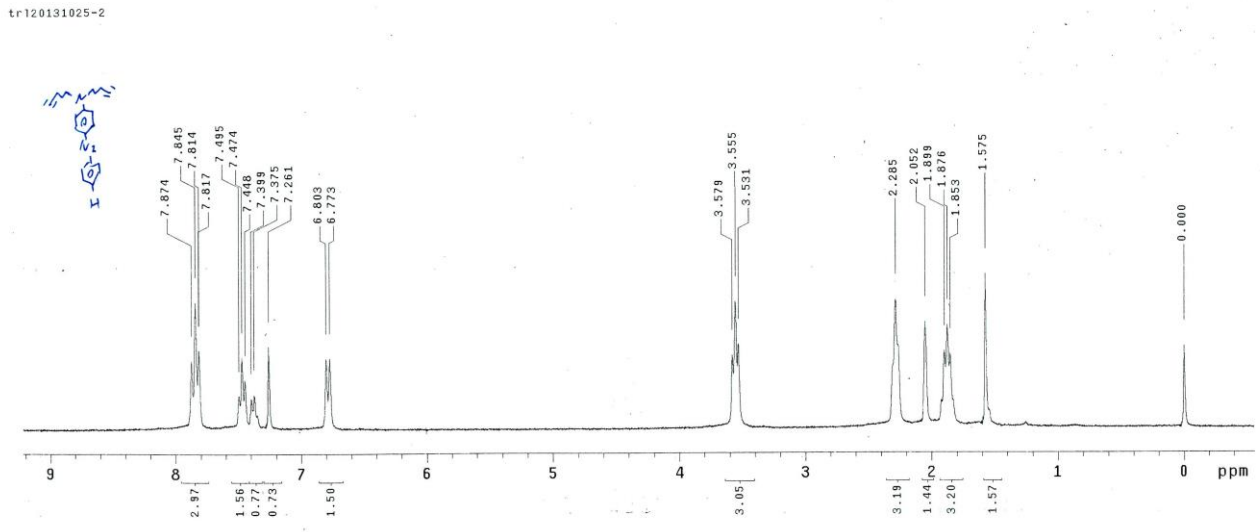


Fig.S10. The ^{1}H NMR spectrum of **M2** in chloroform-*d*.

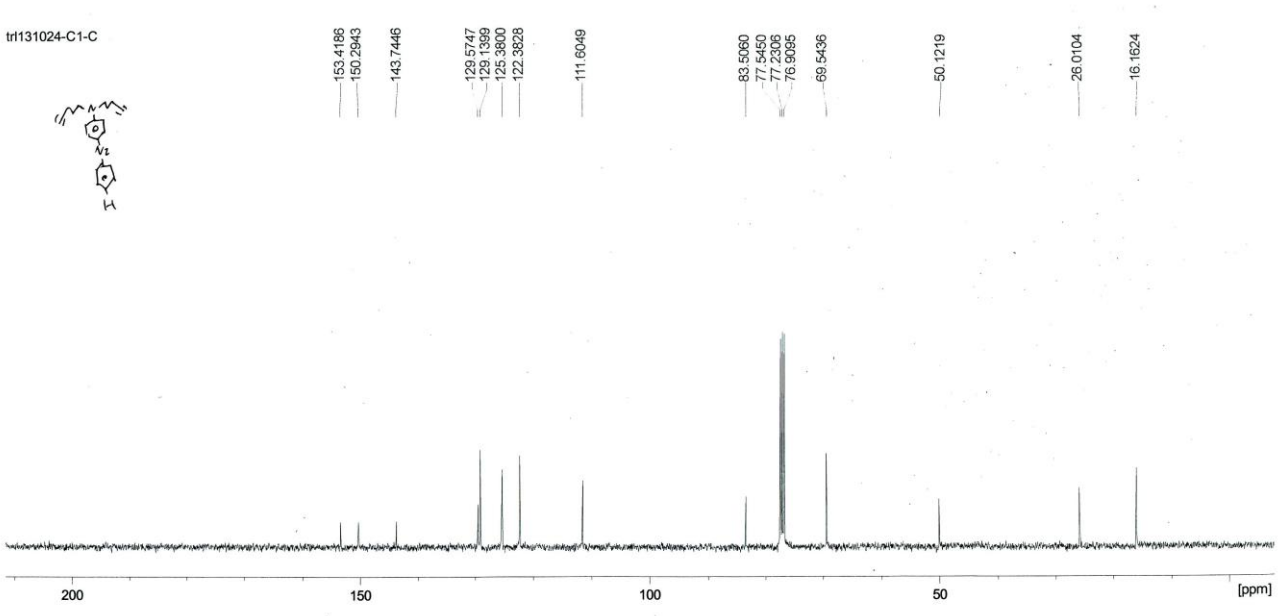


Fig.S11. The ^{13}C NMR spectrum of **M2** in chloroform-*d*.

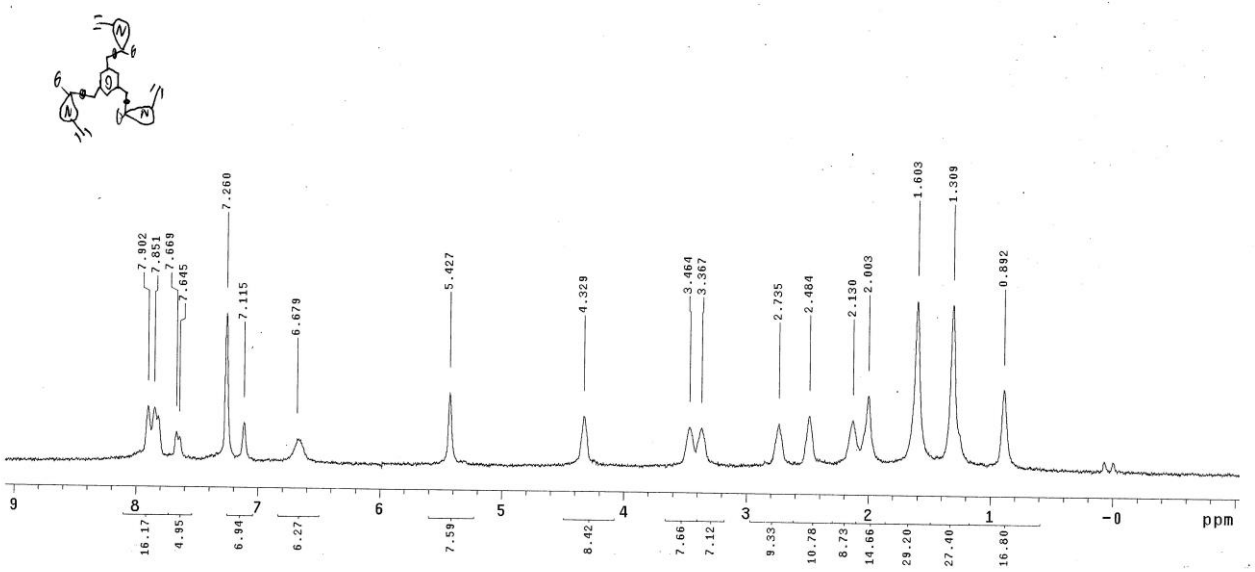


Fig.S12. The ^{1}H NMR spectrum of **M3** in chloroform-*d*.

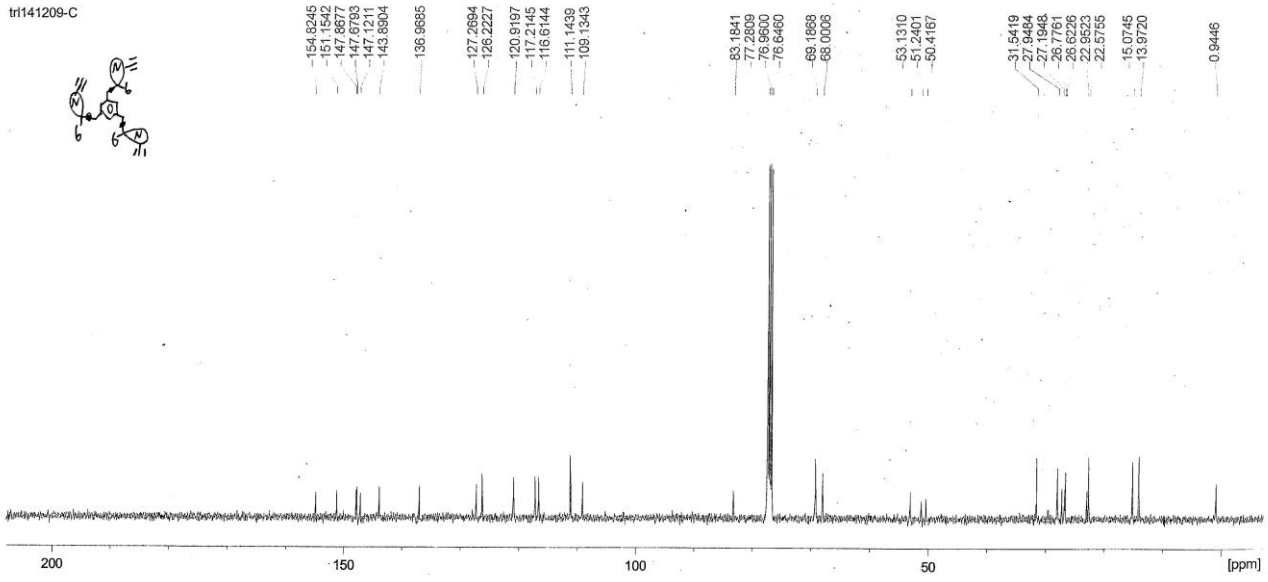


Fig.S13. The ^{13}C NMR spectrum of **M3** in chloroform-*d*.

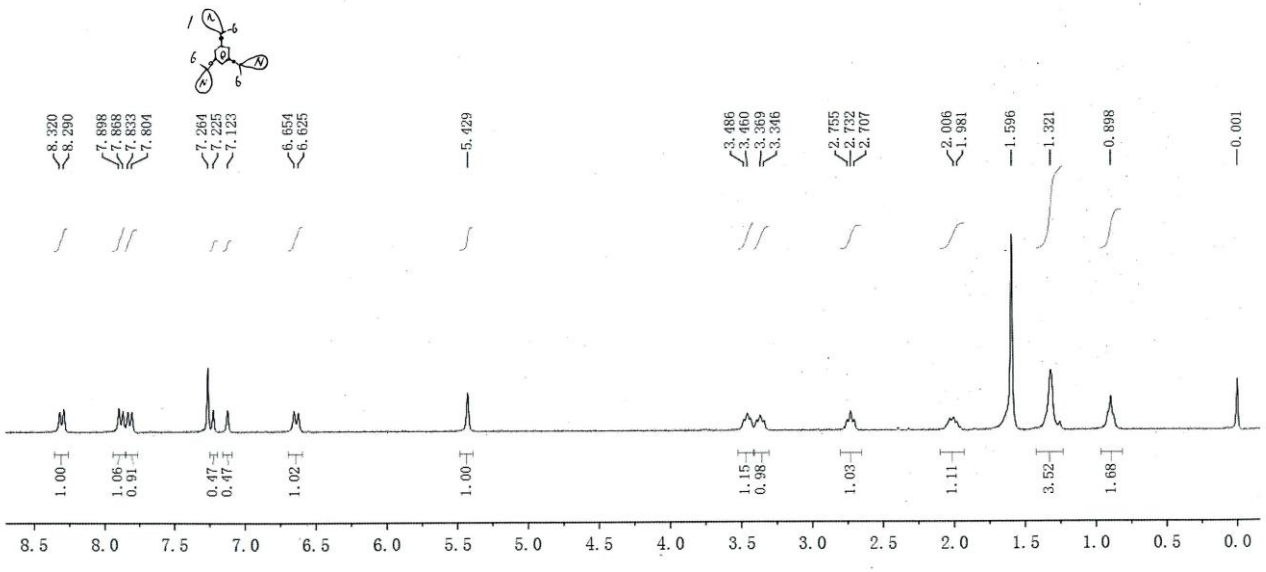


Fig.S14. The ^{1}H NMR spectrum of **C-3** in chloroform-*d*.

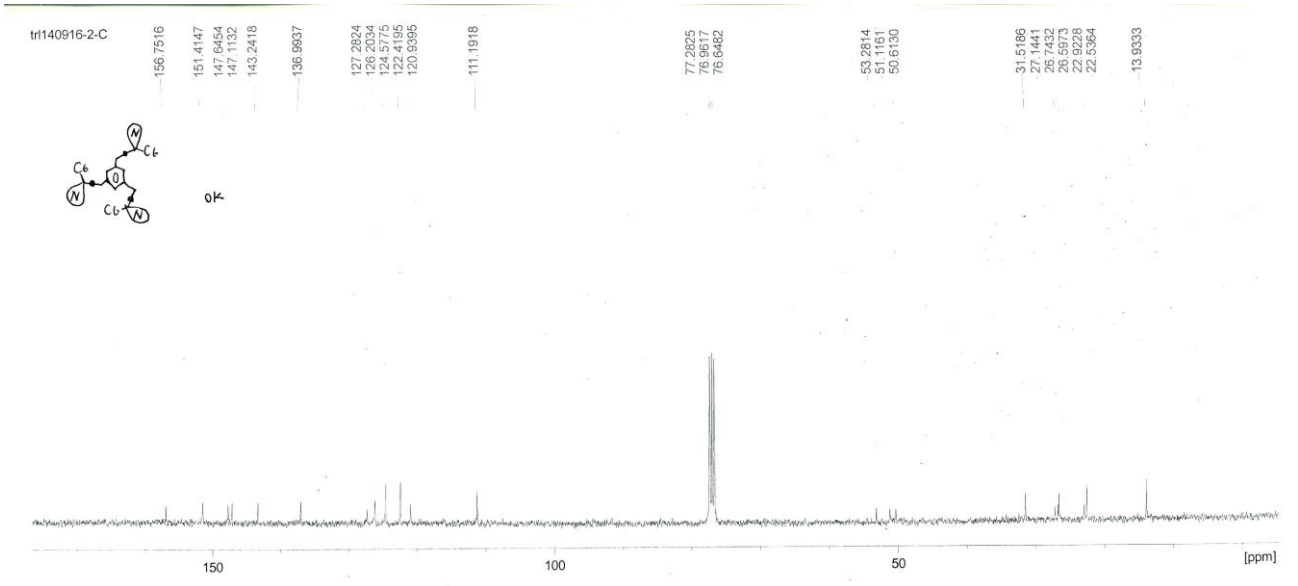


Fig.S15. The ^{13}C NMR spectrum of **C-3** in chloroform-*d*.

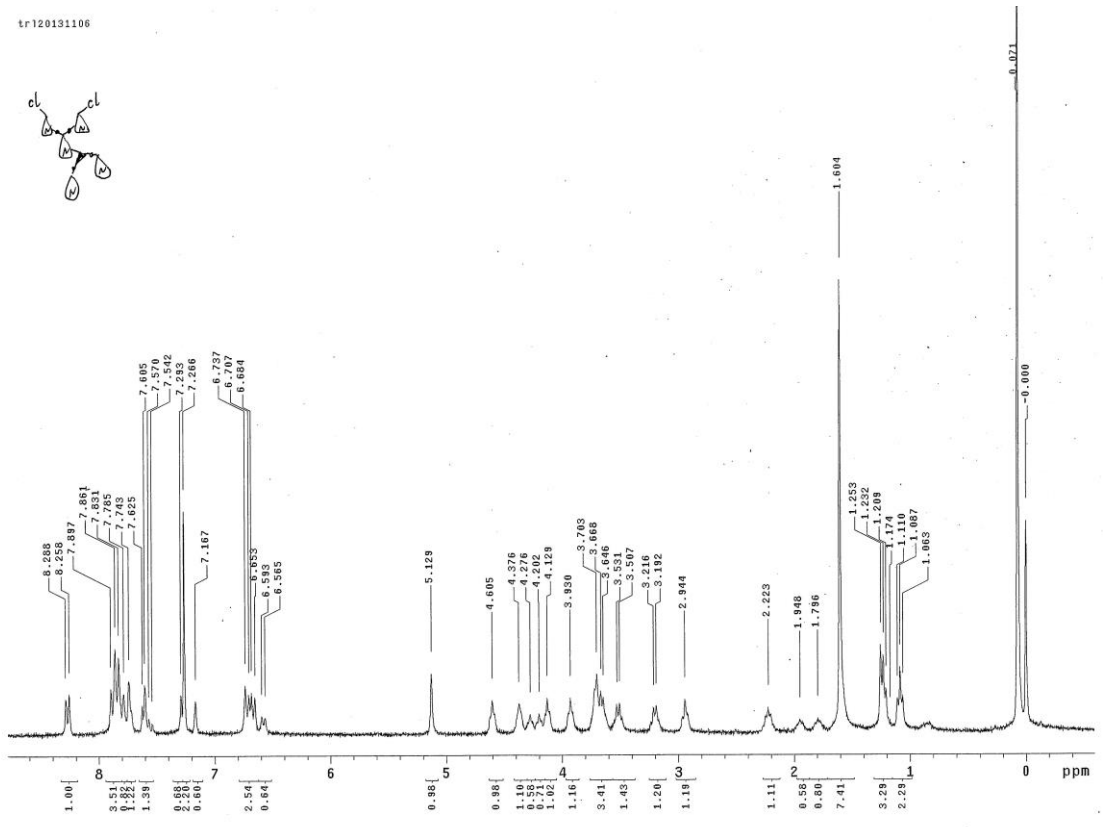


Fig.S16. The ^{1}H NMR spectrum of **X-2Cl** in chloroform-*d*.

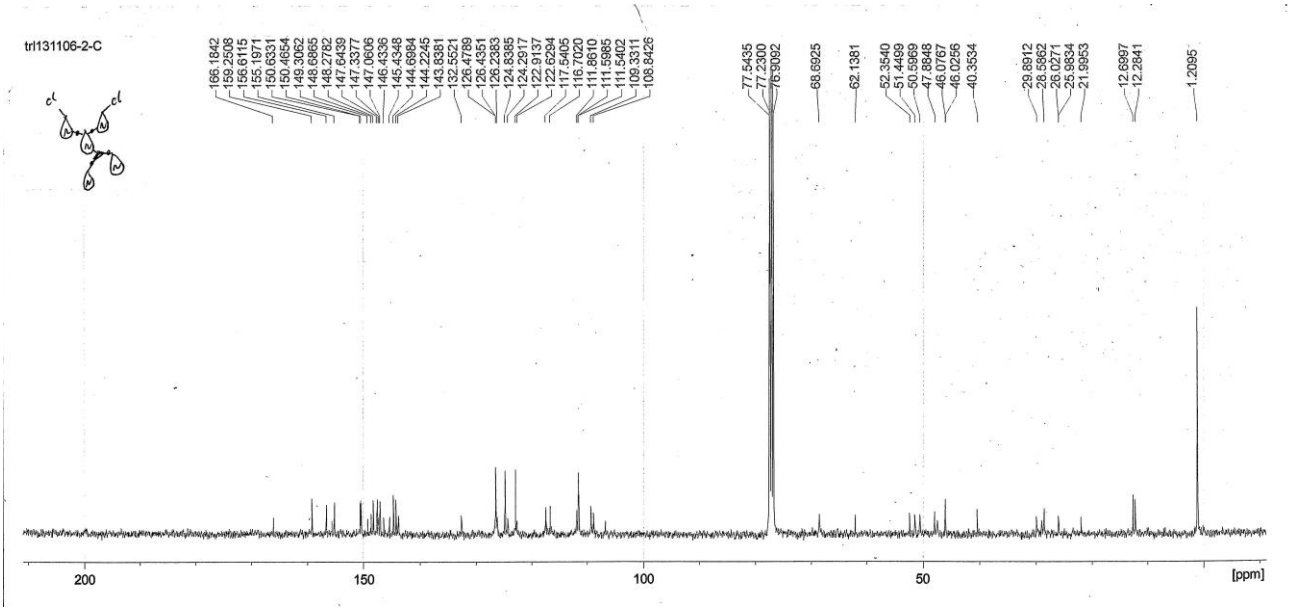


Fig.S17. The ^{13}C NMR spectrum of **X-2Cl** in chloroform-*d*.

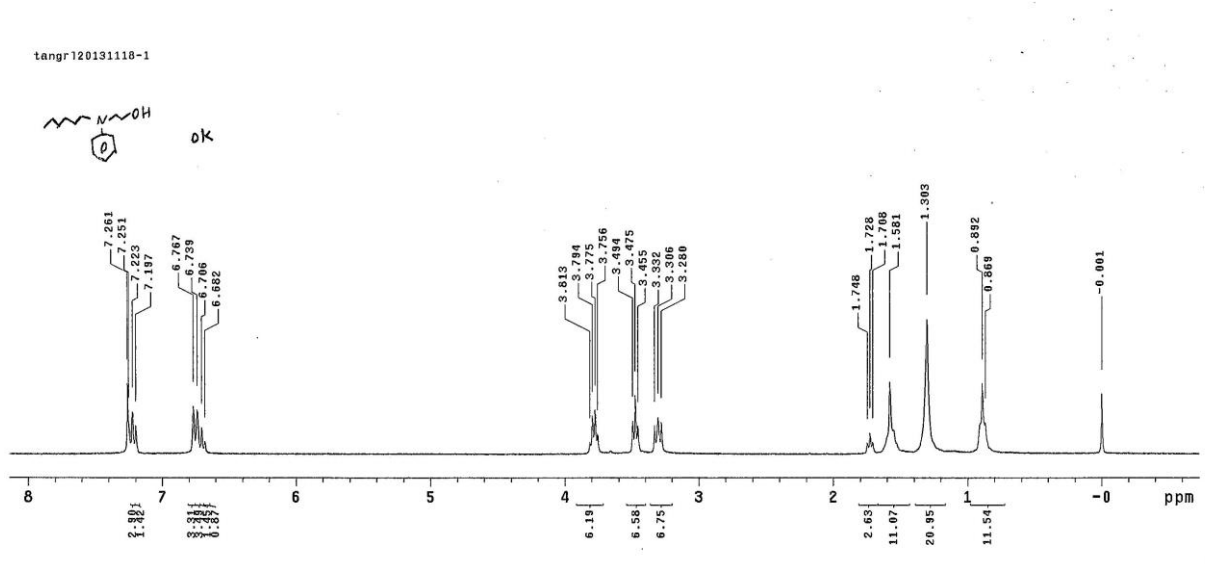


Fig.S18. The ^{1}H NMR spectrum of **3** in chloroform-*d*.

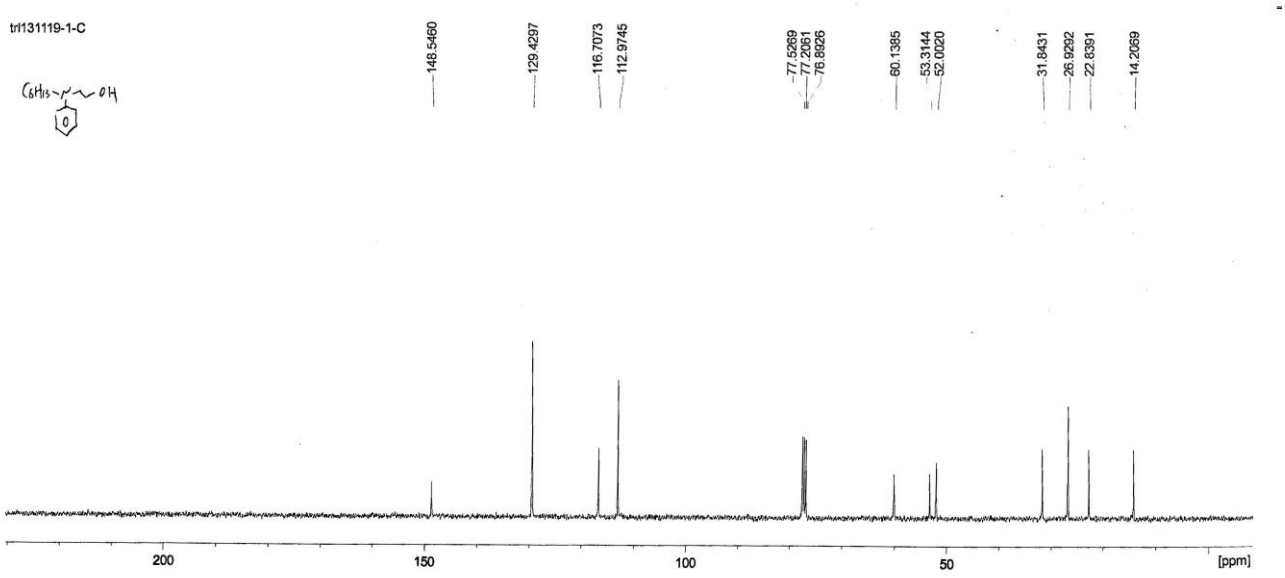


Fig.S19. The ^{13}C NMR spectrum of **3** in chloroform-*d*.

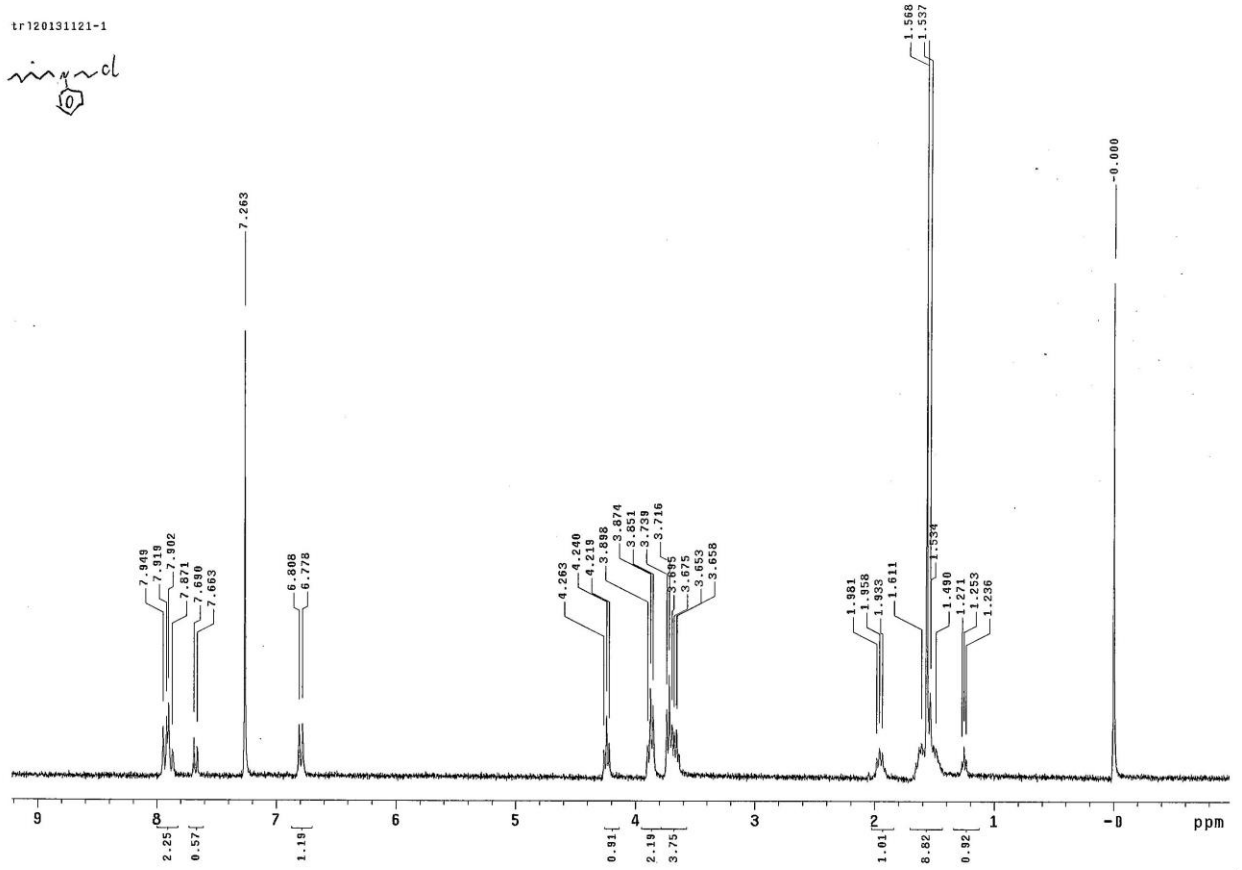


Fig.S20. The ^{1}H NMR spectrum of **4** in chloroform-*d*.

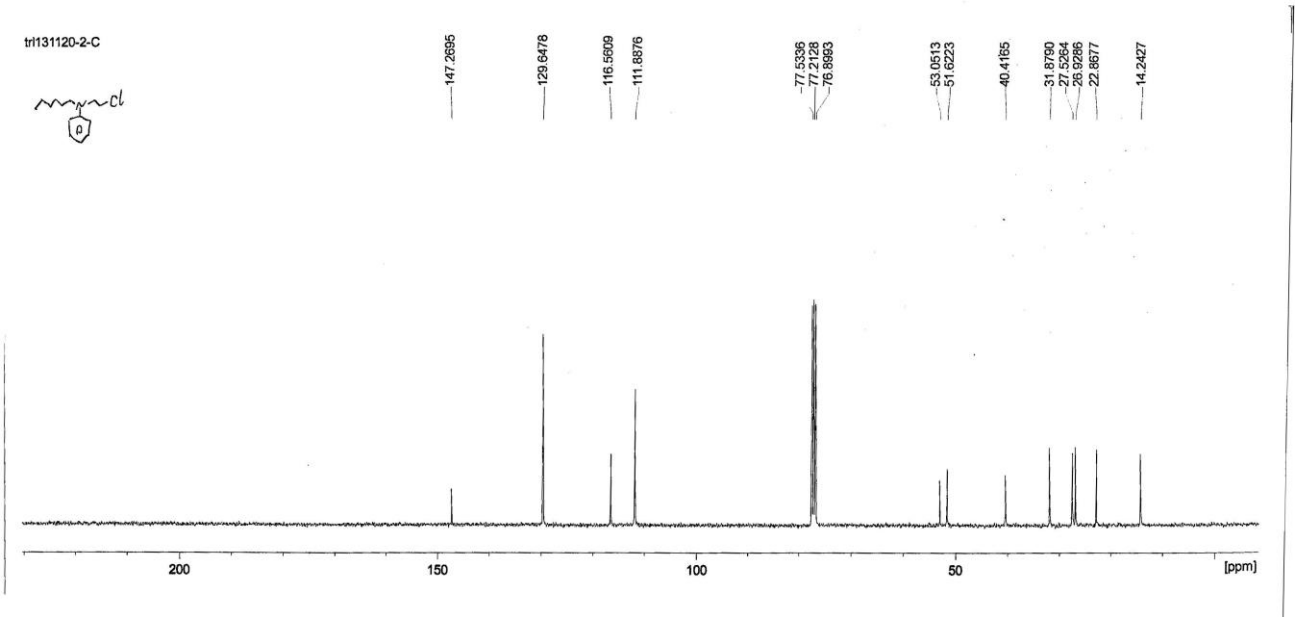


Fig.S21. The ^{13}C NMR spectrum of **4** in chloroform-*d*.

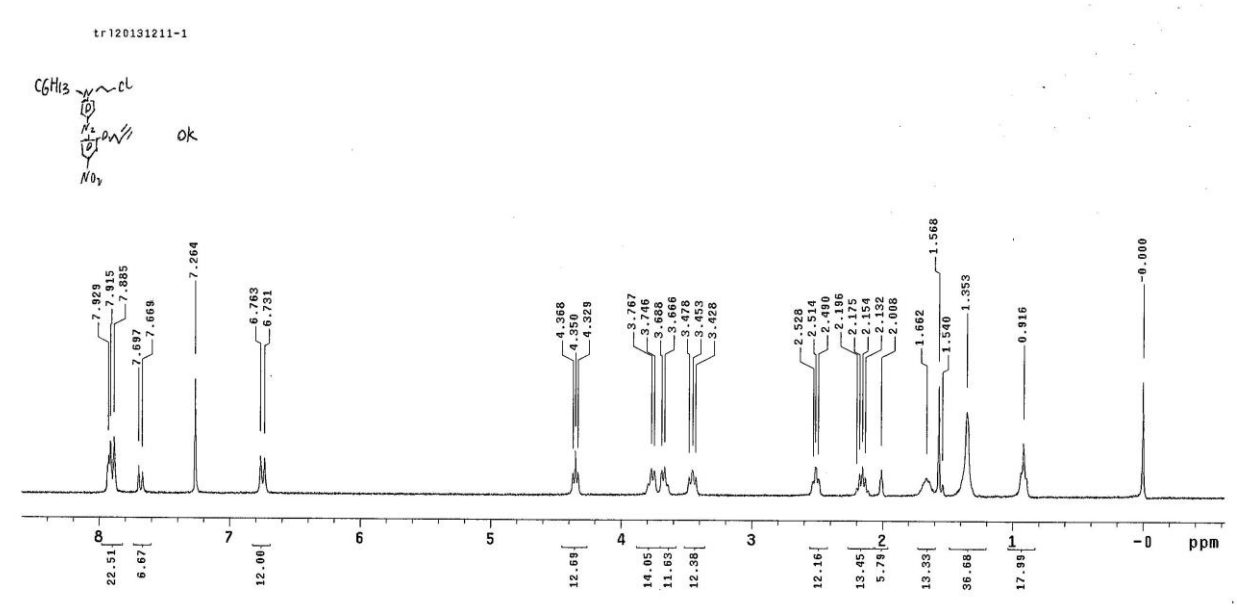


Fig.S22. The ^{1}H NMR spectrum of **2** in chloroform-*d*.

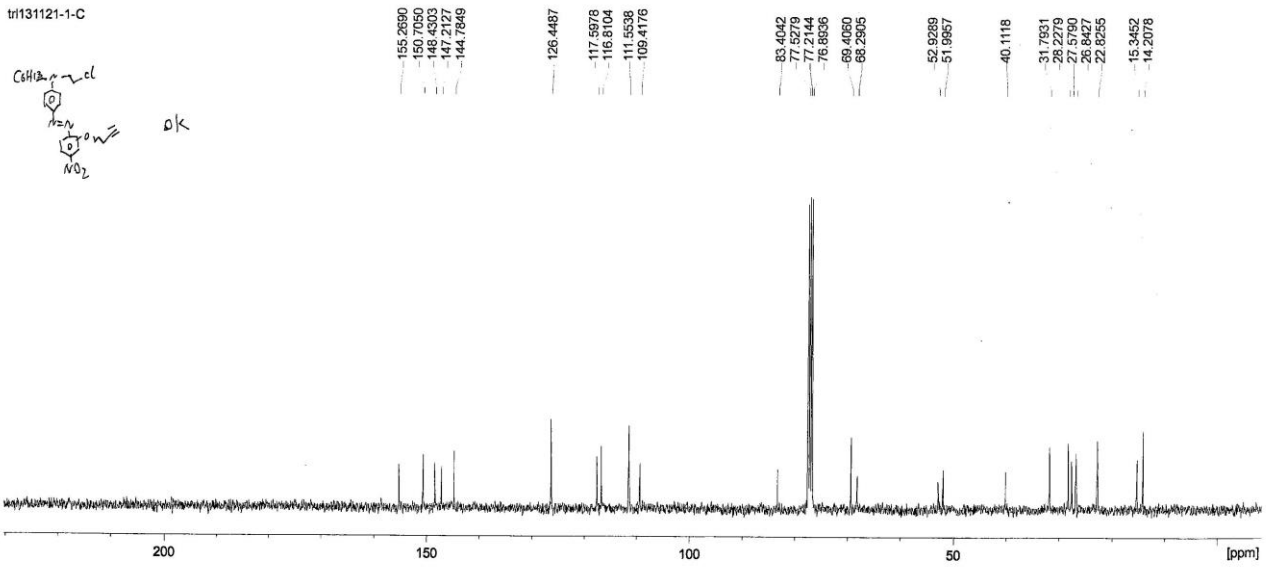


Fig.S23. The ^{13}C NMR spectrum of **2** in chloroform-*d*.

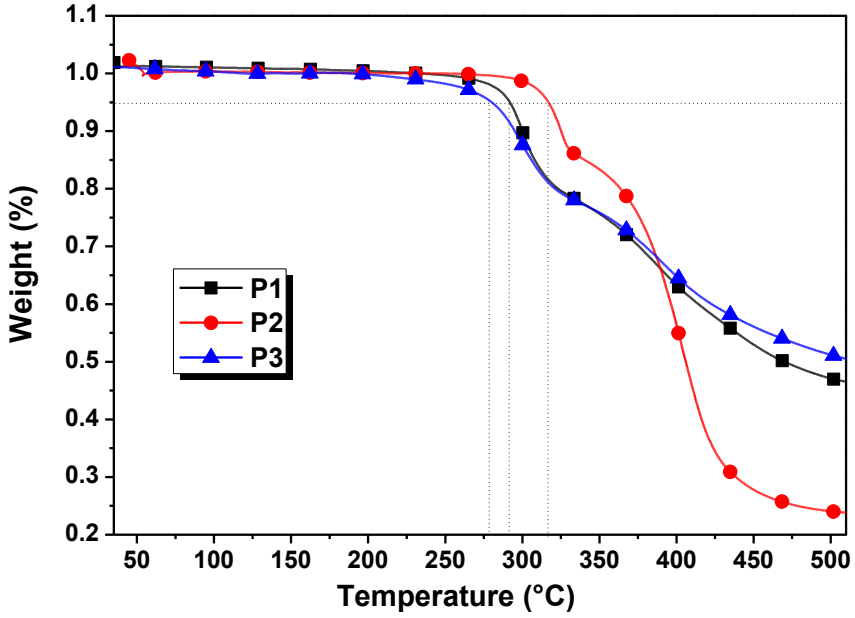


Fig. S24. TGA thermograms of polymers measured in nitrogen at a heating rate of 10 ℃/min.

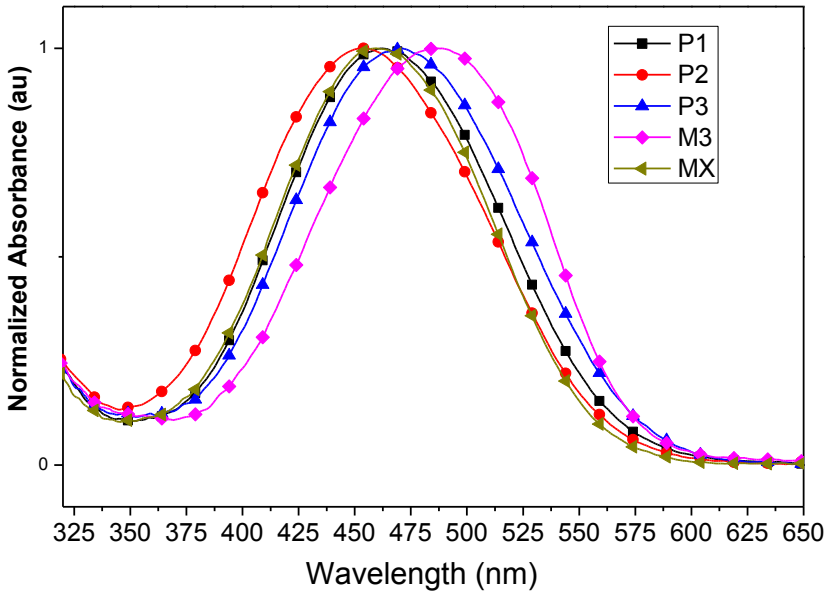


Fig. S25. UV-vis absorption spectra of monomers and polymers in 1,4-dioxane.

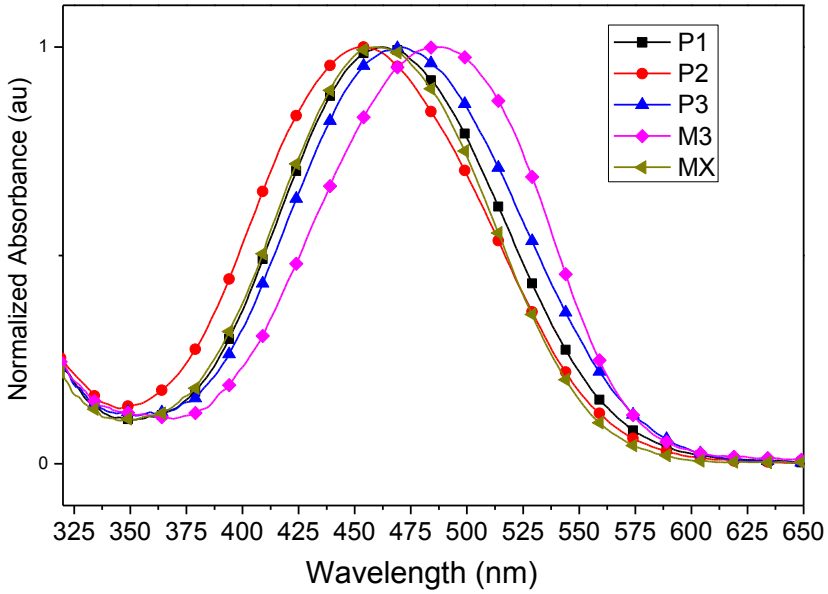


Fig. S26. UV-vis absorption spectra of monomers and polymers in CH_2Cl_2.

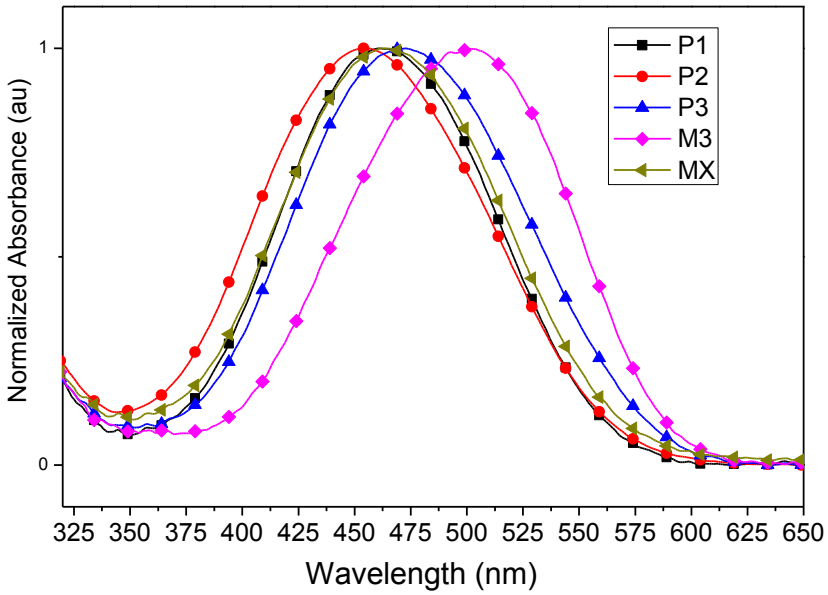


Fig. S27. UV-vis absorption spectra of monomers and polymers in $CHCl_3$.

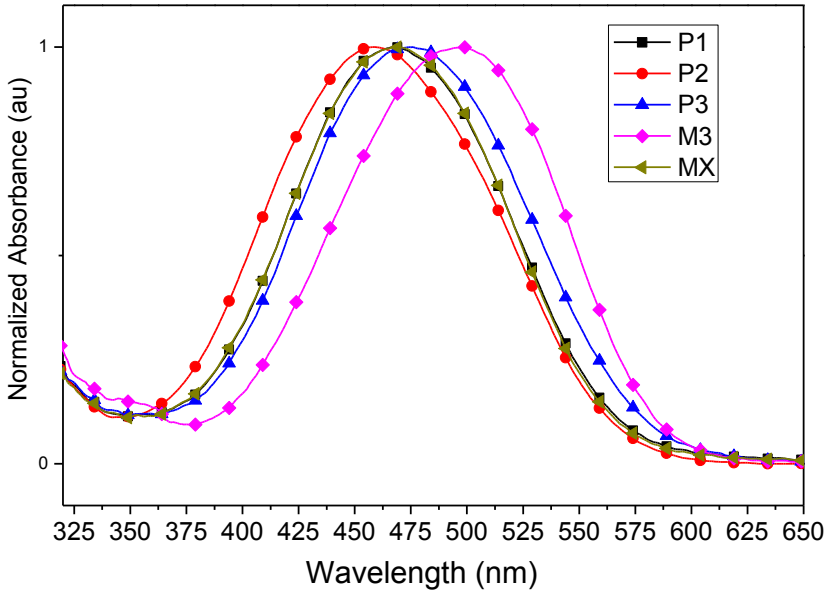


Fig. S28. UV-vis absorption spectra of monomers and polymers in THF.

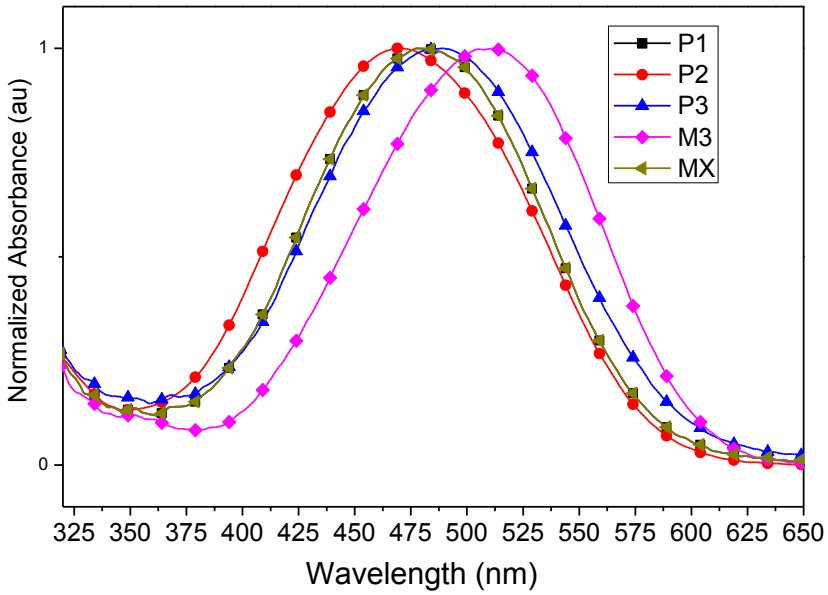


Fig. S29. UV-vis absorption spectra of monomers and polymers in DMF.

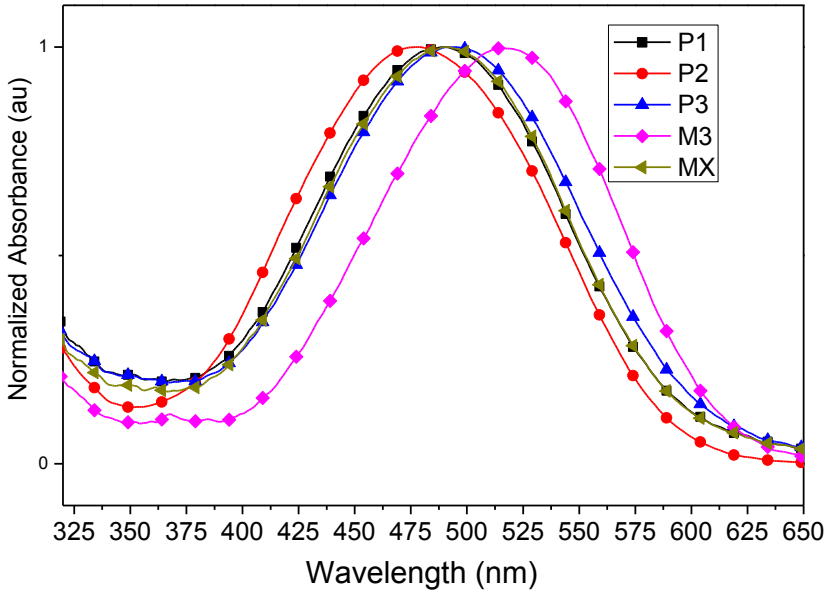


Fig. S30. UV-vis absorption spectra of monomers and polymers in DMSO.

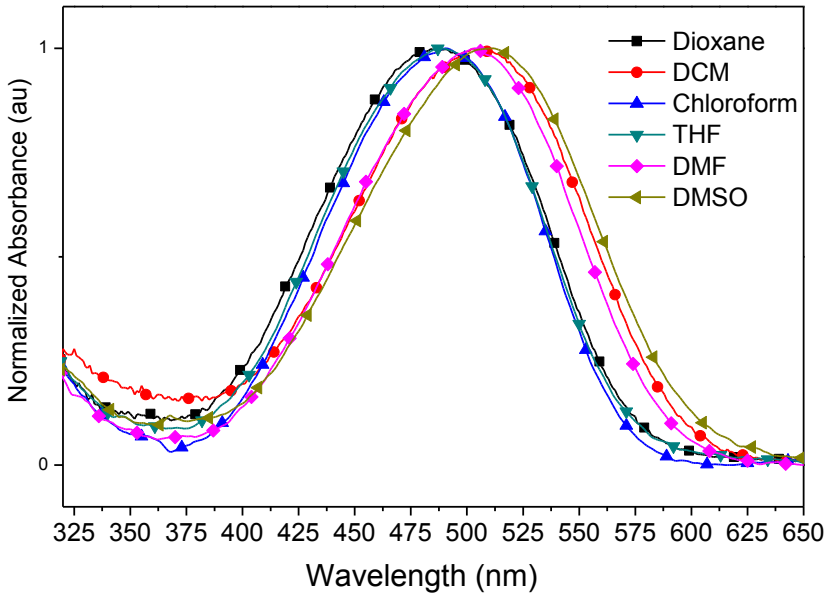
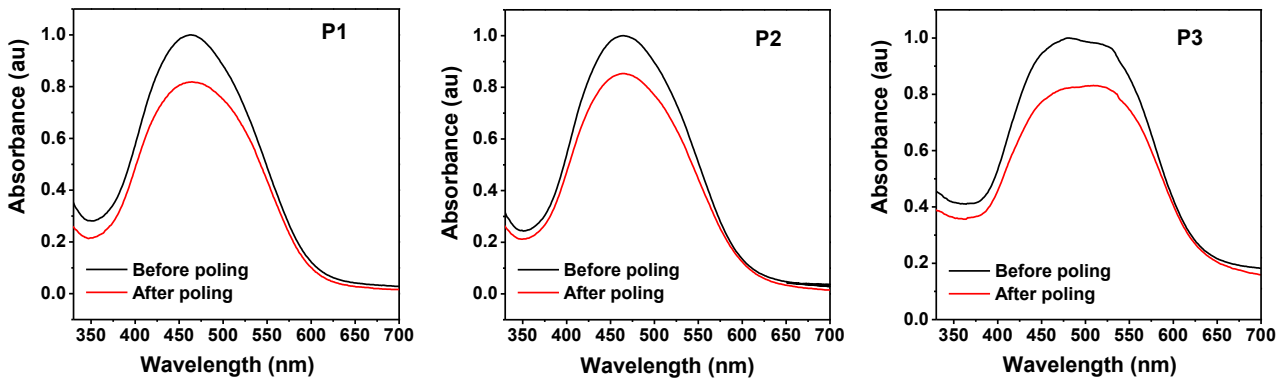


Fig. S31. UV-vis absorption spectra of **C-3** in different solvents.



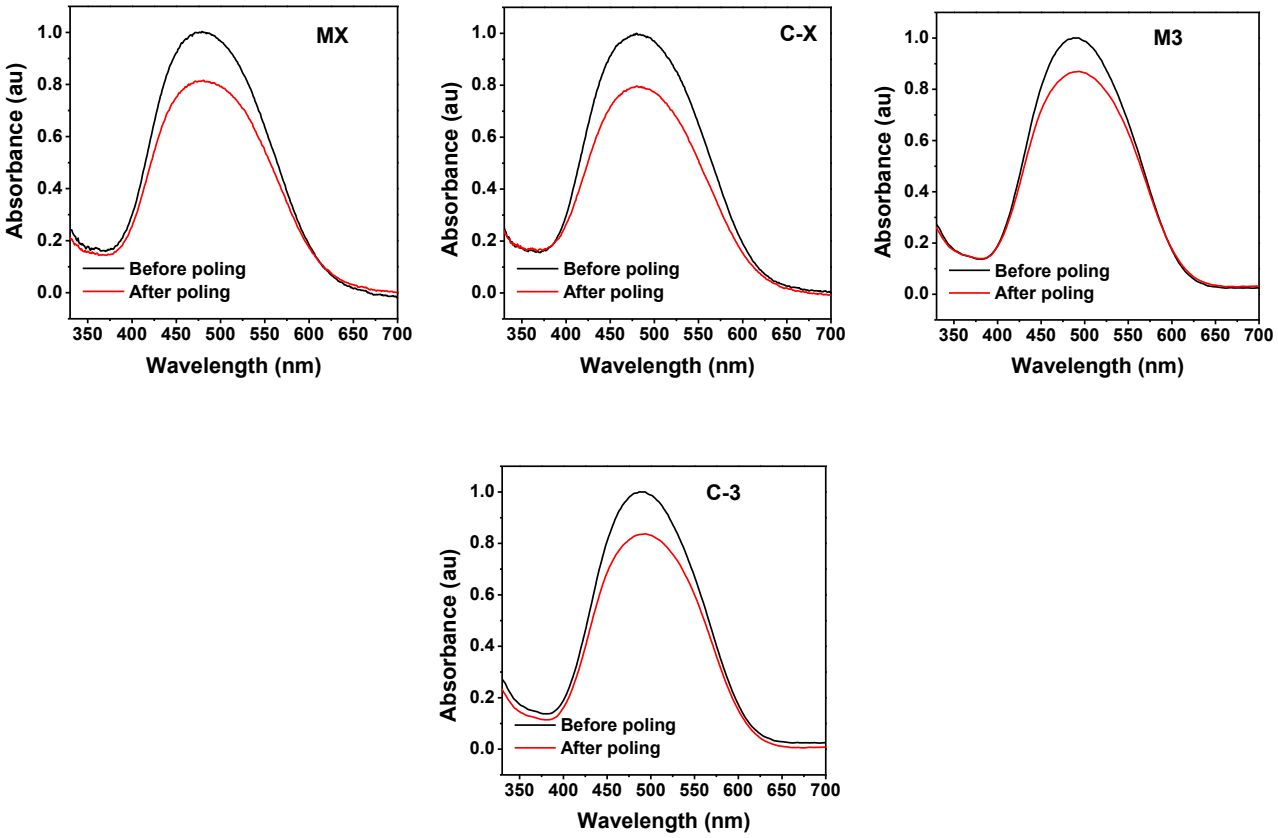


Fig. S32. UV-vis absorption spectra of each film before and after poling (poled for 30 min at voltage of 7.0 kV).

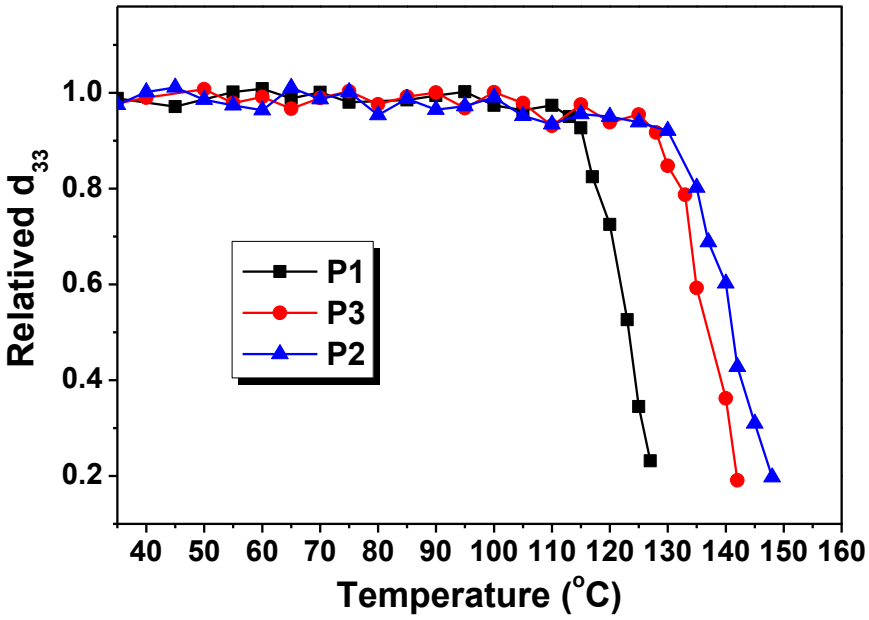


Fig. S33. Decay curves of the SHG coefficients of thin films (poled under 8.0 KV voltage) as a function of temperature.

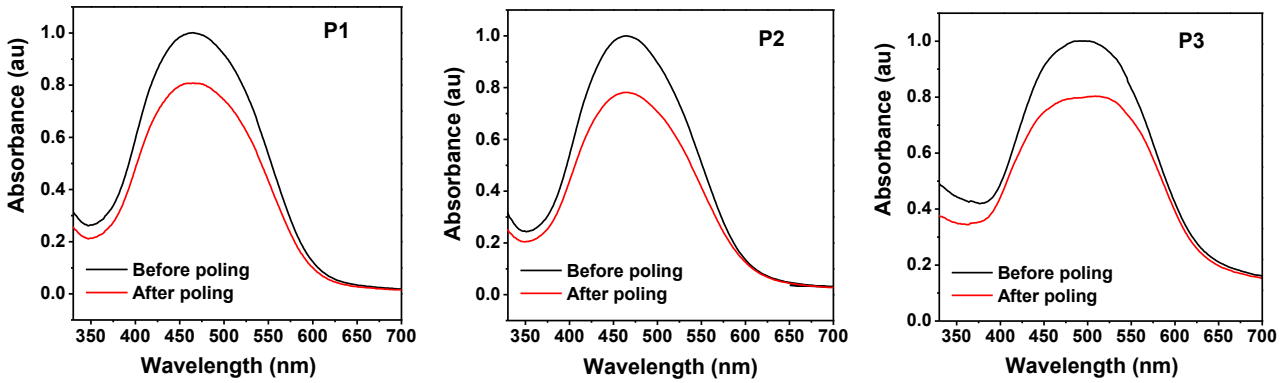


Fig. S34. UV-vis absorption spectra of each film before and after poling ((poled for 30 min at voltage of 8.0 kV).