

## Electronic Supplementary Information:

### Main chain dendronized hyperbranched polymers: Convenient synthesis and good second-order nonlinear optical performance

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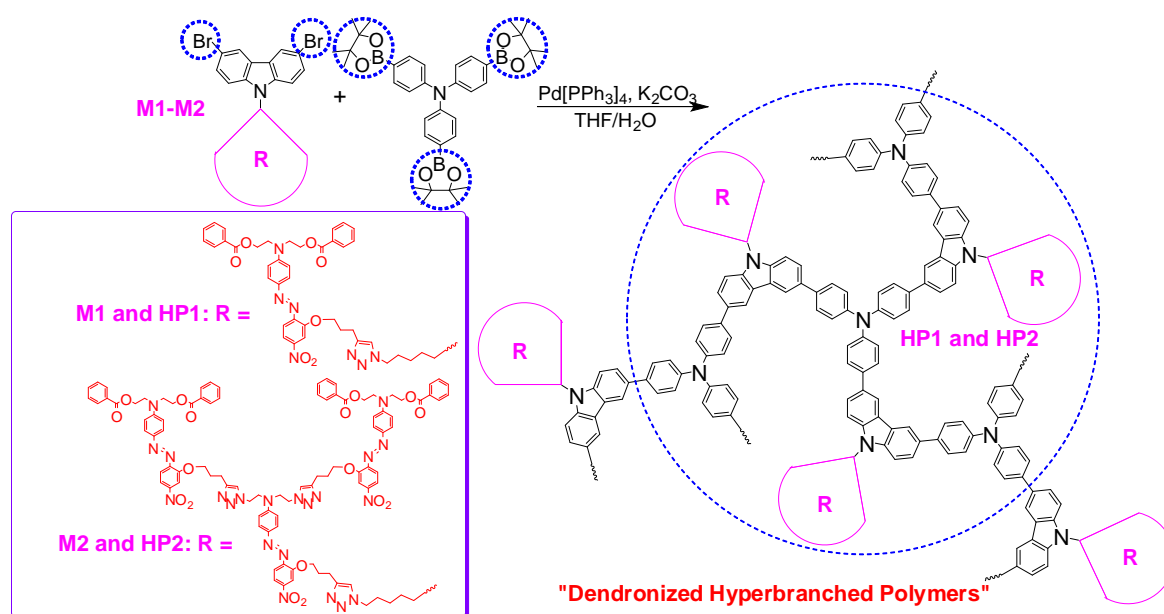
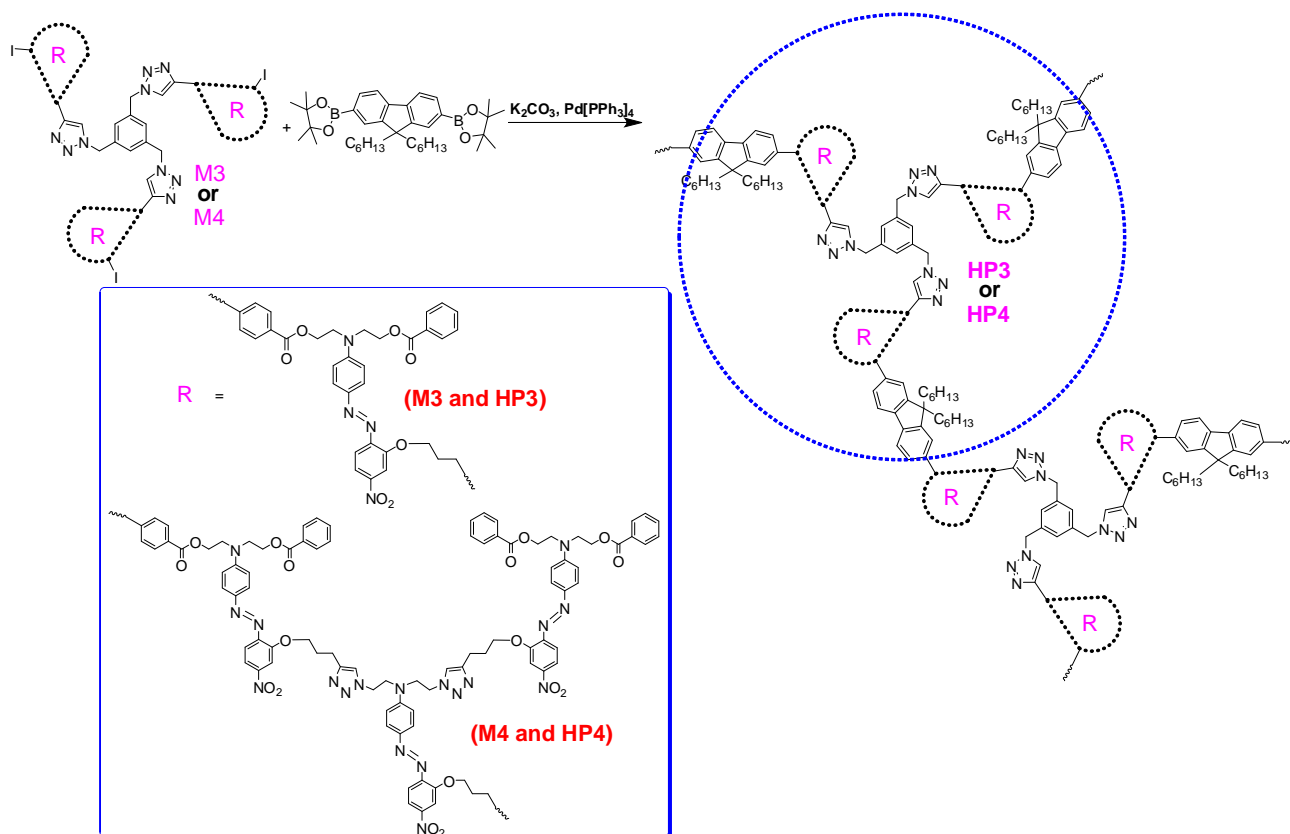
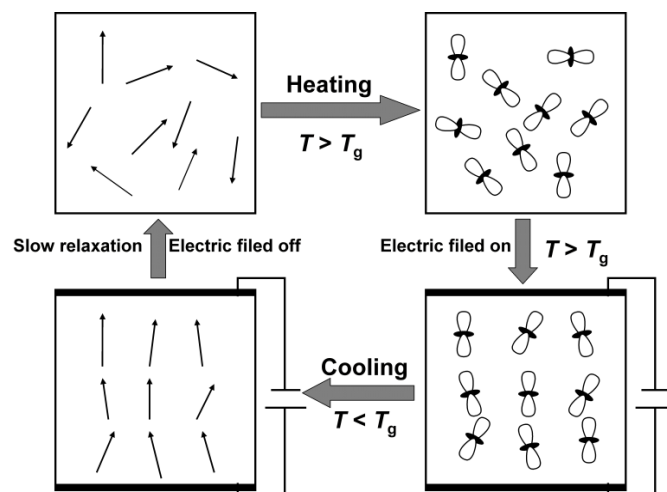


Chart S1. The structure of dendronized hyperbranched polymers **HP1** and **HP2**.



**Chart S2.** The structure of dendronized hyperbranched polymers **HP3** and **HP4**.



**Chart S3.** Graphical illustration of poling procedure for NLO polymers.

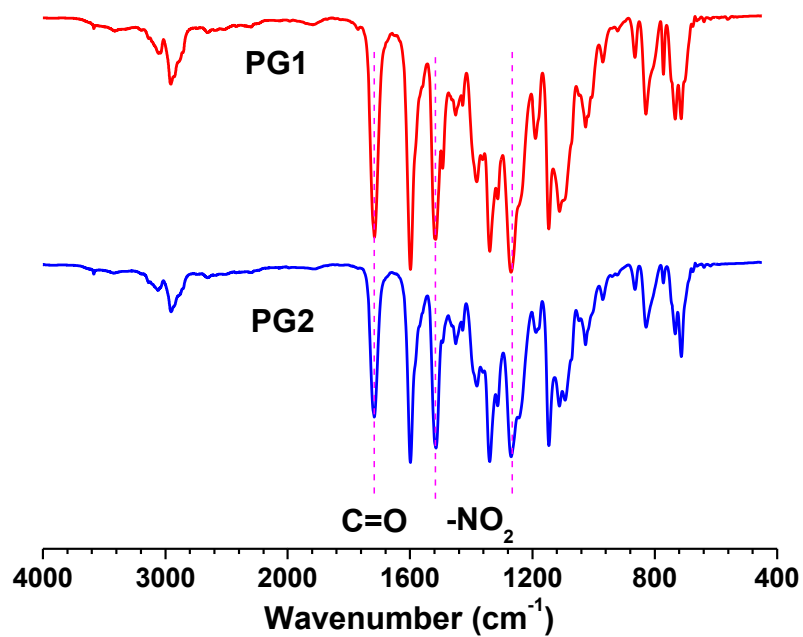


Fig. S1 The FT-IR spectra of main chain dendronized hyperbranched polymers PG1 and PG2.

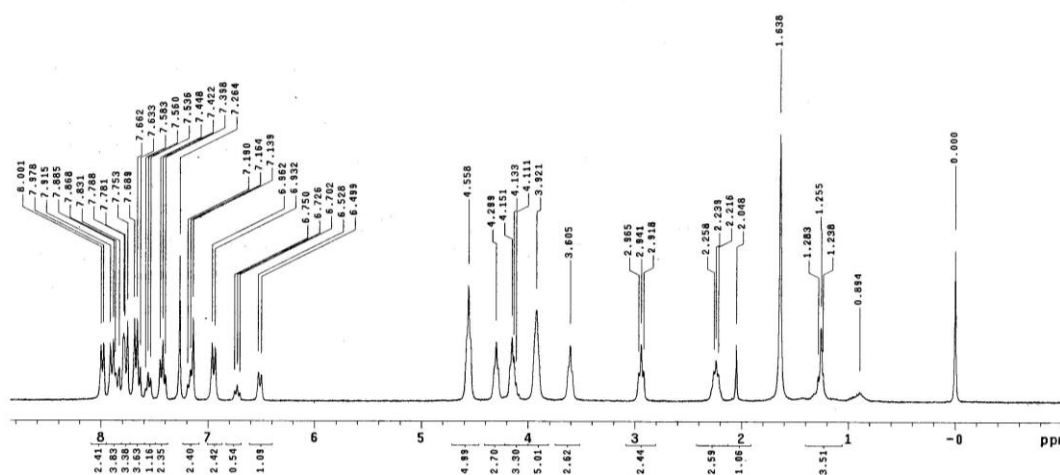


Fig. S2  $^1\text{H}$  NMR spectrum of MG1 in chloroform-*d*.

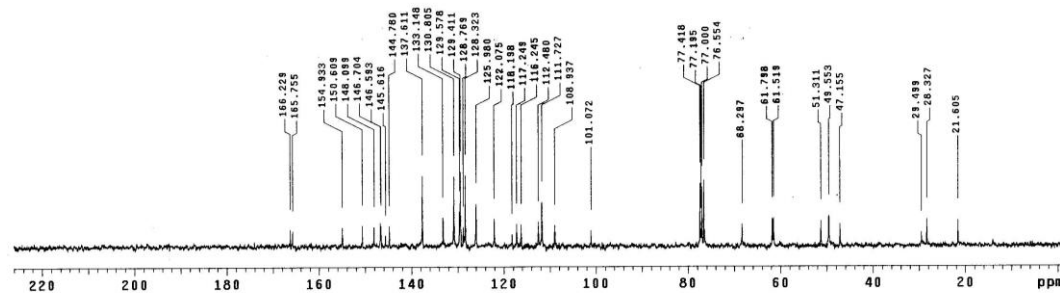


Fig. S3  $^{13}\text{C}$  NMR spectrum of MG1 in chloroform-*d*.

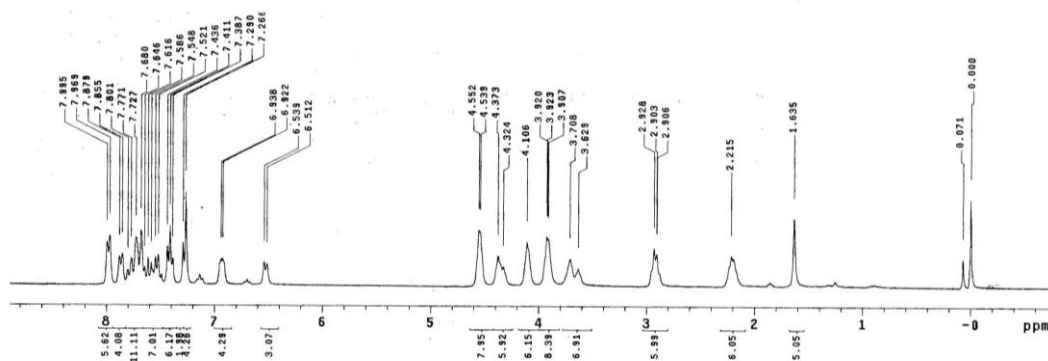


Fig. S4  $^1\text{H}$  NMR spectrum of MG2 in chloroform-*d*.

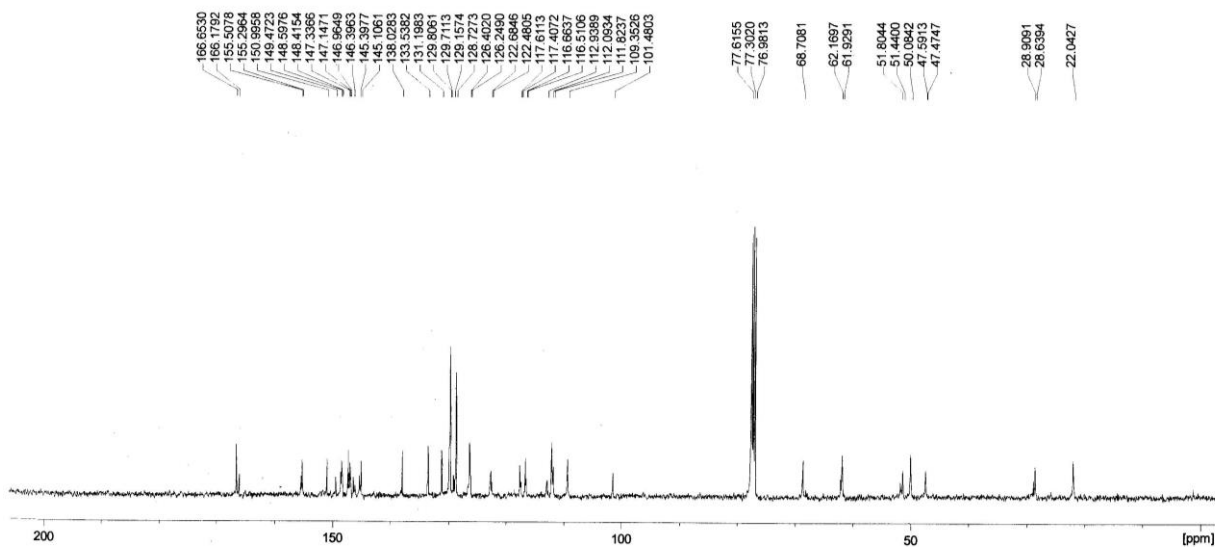


Fig. S5  $^{13}\text{C}$  NMR spectrum of MG2 in chloroform-*d*.

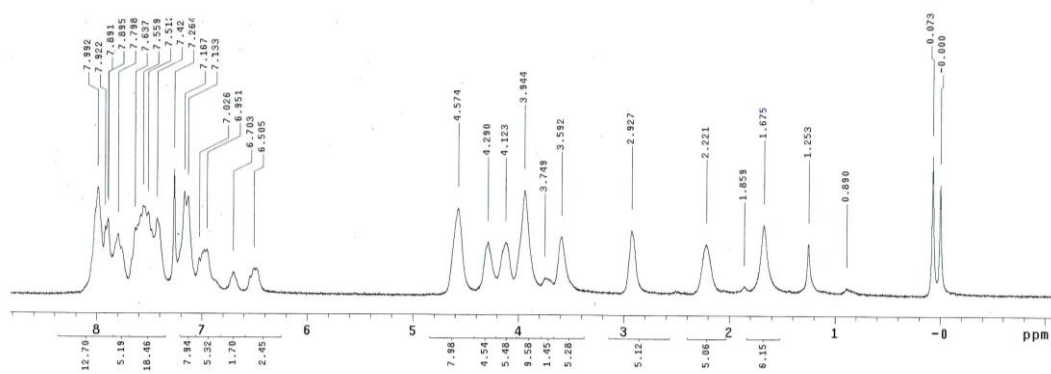


Fig. S6  $^1\text{H}$  NMR spectrum of PG1 in chloroform-*d*.

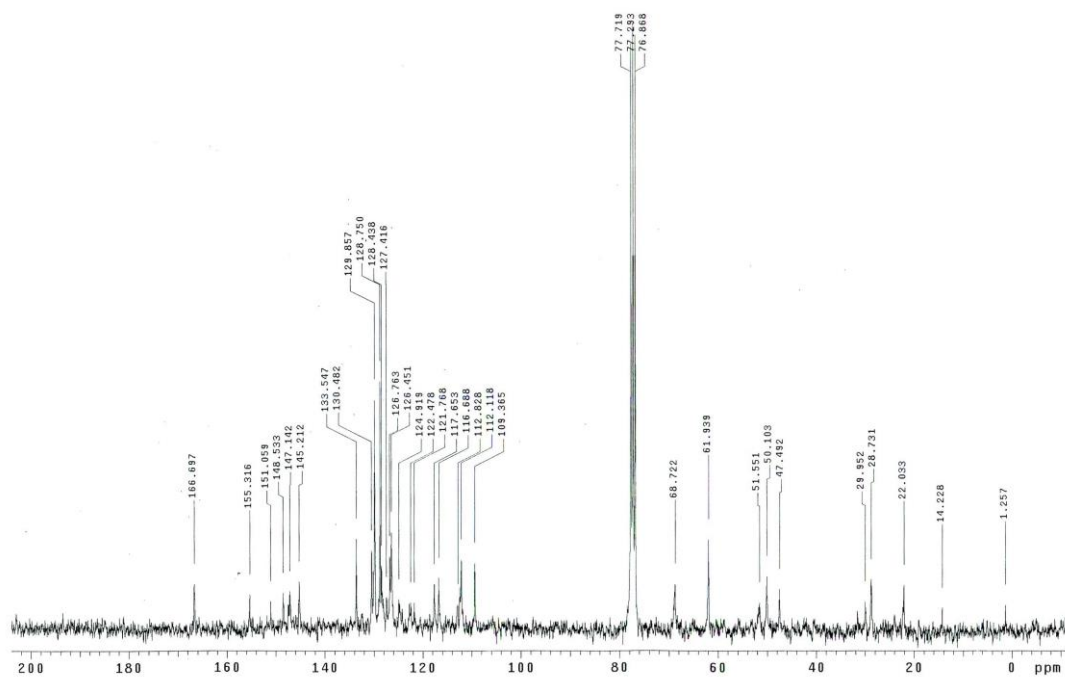


Fig. S7  $^{13}\text{C}$  NMR spectrum of PG1 in chloroform-*d*.

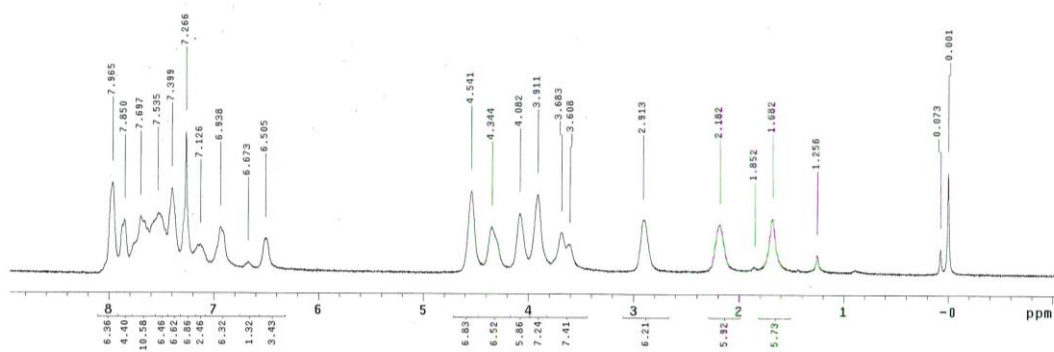
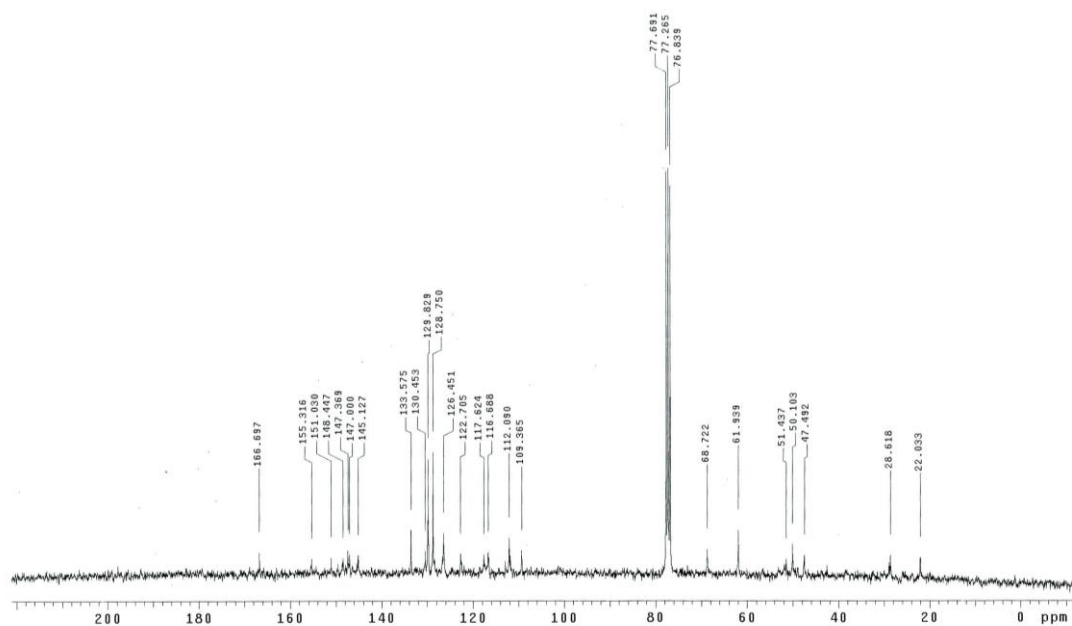
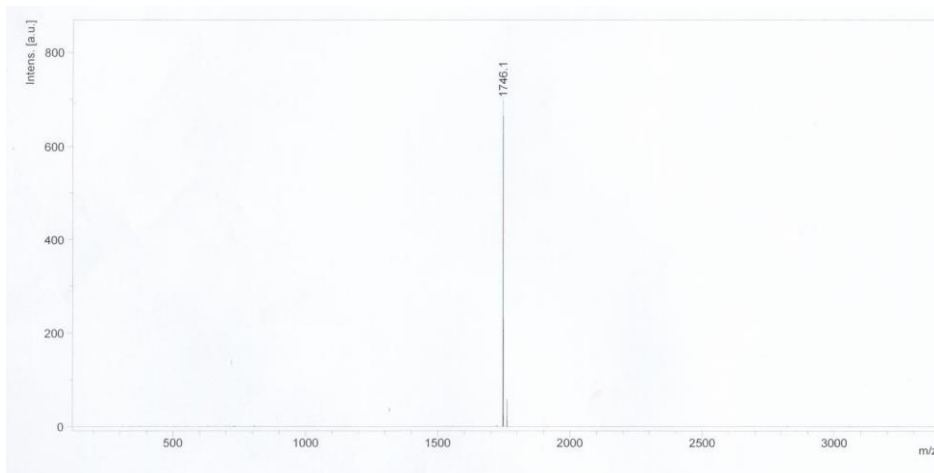


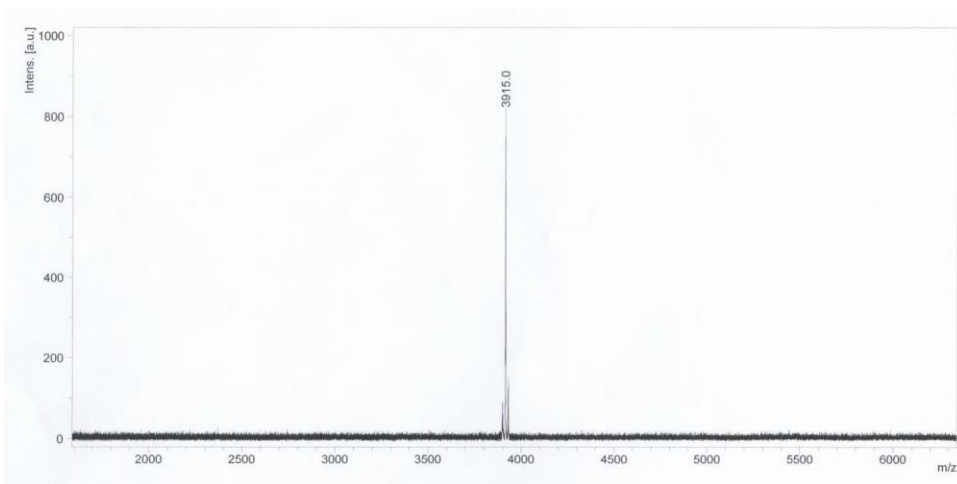
Fig. S8  $^1\text{H}$  NMR spectrum of PG2 in chloroform-*d*.



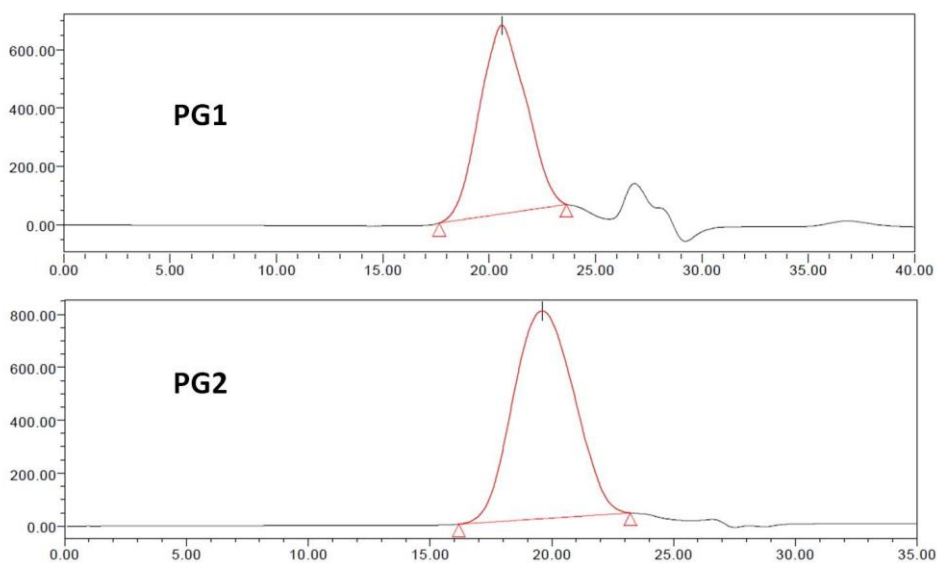
**Fig. S9**  $^{13}\text{C}$  NMR spectrum of **PG2** in chloroform-*d*.



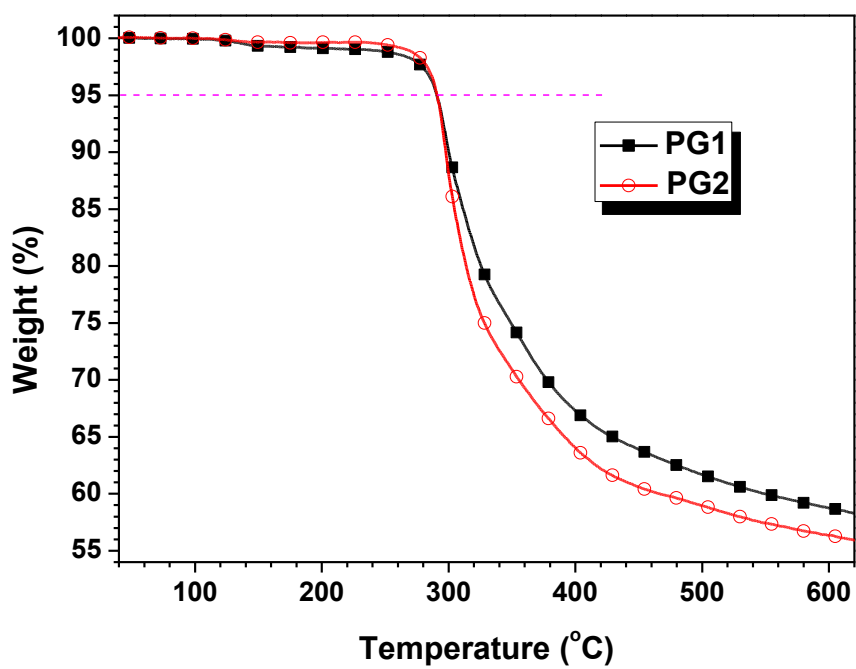
**Fig. S10** The MALDI-TOF mass spectrum of **MG1**.



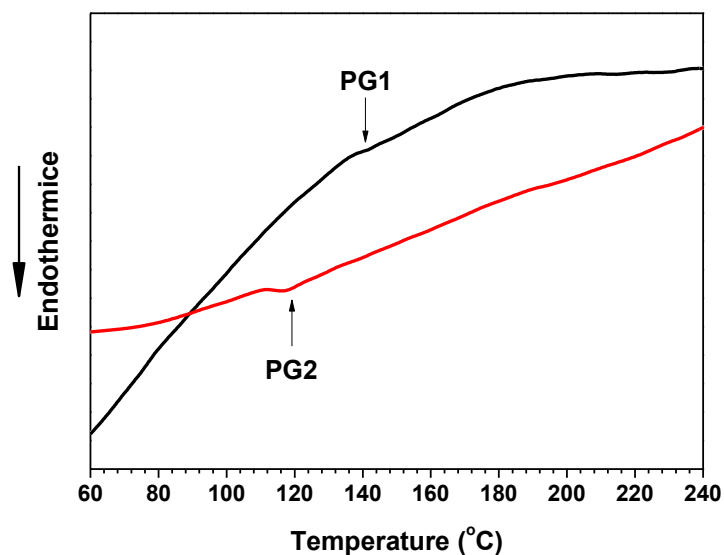
**Fig. S11** The MALDI-TOF mass spectrum of **MG2**.



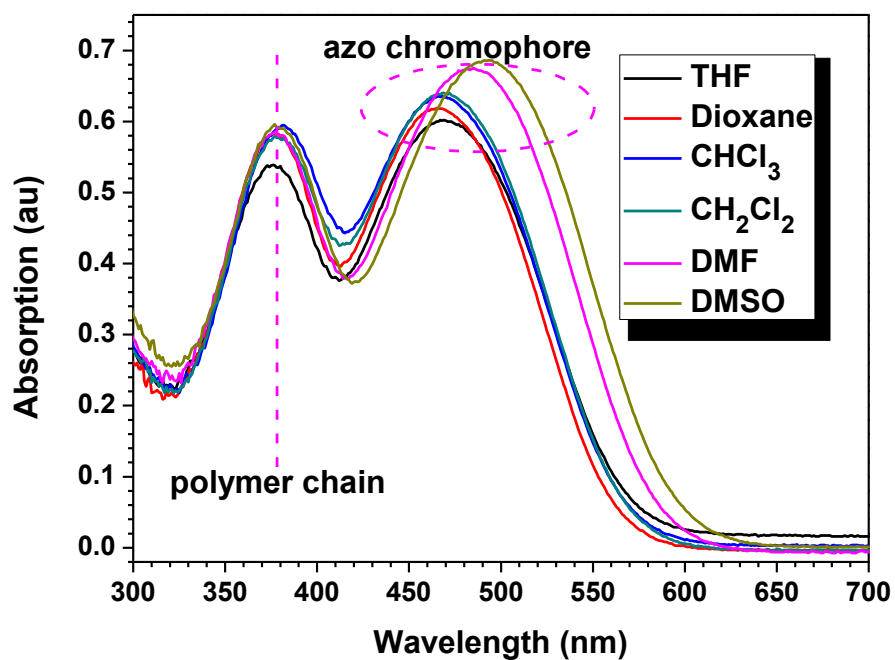
**Fig. S12** The GPC chromatograms of **PG1** and **PG2**.



**Fig. S13** TGA thermograms of main chain dendronized hyperbranched polymers **PG1** and **PG2**, measured in nitrogen at a heating rate of 10 °C/min.

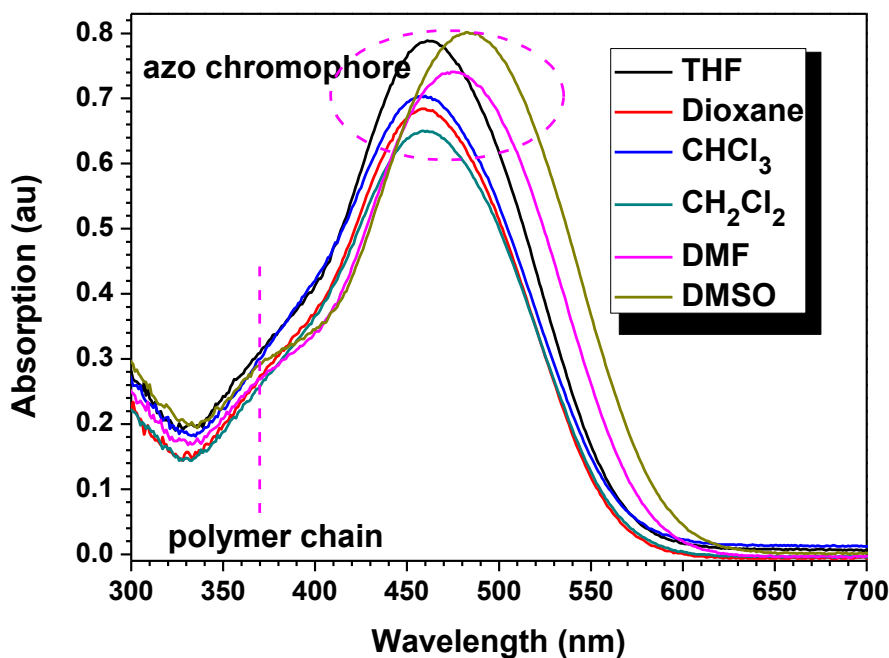


**Fig. S14** DSC thermograms of main chain dendronized hyperbranched polymers **PG1** and **PG2**, measured in nitrogen at a heating rate of 10 °C/min.



**Fig. S15** UV-Vis spectra of **PG1** in different solutions (0.02 mg/mL).





**Fig. S16** UV-Vis spectra of **PG2** in different solutions (0.02 mg/mL).

#### 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 ( $d_{33}$ ) 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 SHG intensities of the dendronized hyperbranched polymers and the quartz, as well as the film thickness of the tested thin films, we can calculate the  $d_{33}$  value of dendronized hyperbranched polymers easily.

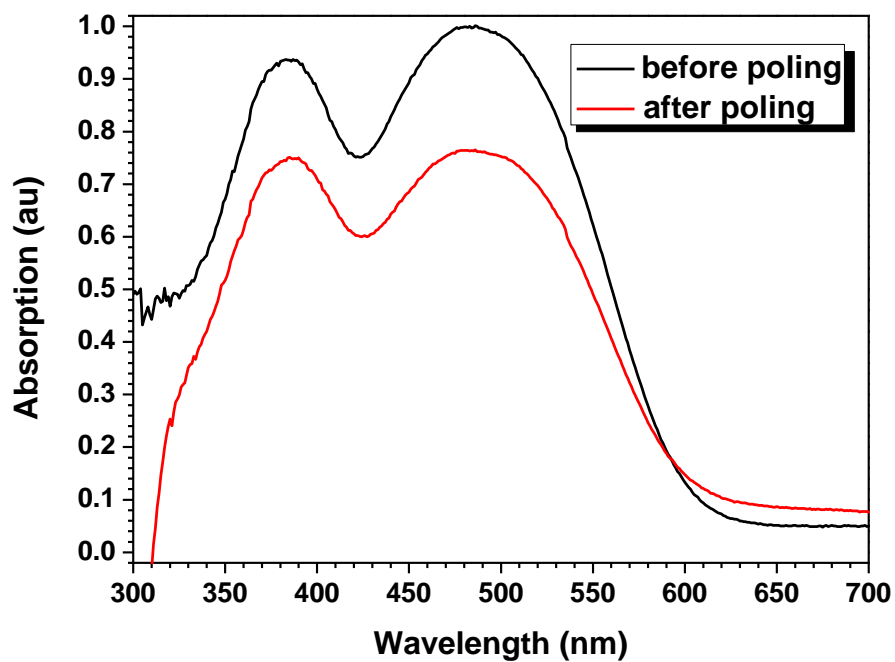


Fig. S17 Absorption spectra of the film of PG1 before and after poling.

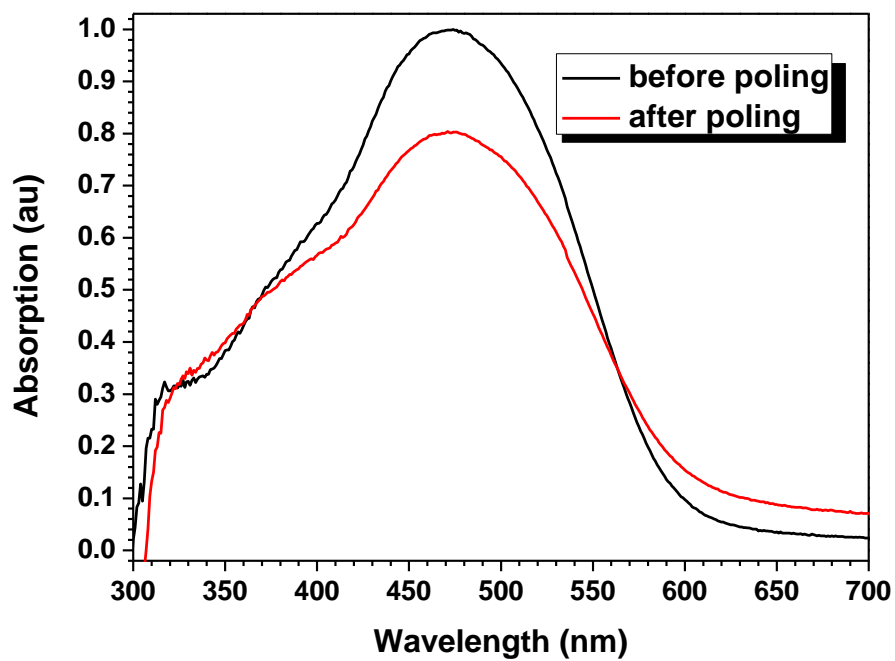


Fig. S18 Absorption spectra of the film of PG2 before and after poling.