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** $^1$H NMR spectrum of MG1 in chloroform-$d$.

**Fig. S3** $^{13}$C NMR spectrum of MG1 in chloroform-$d$. 
Fig. S4 $^1$H NMR spectrum of MG2 in chloroform-$d$.

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

Fig. S6 $^1$H NMR spectrum of PG1 in chloroform-$d$. 
Fig. S7 $^{13}$C NMR spectrum of PG1 in chloroform-$d$.

Fig. S8 $^1$H NMR spectrum of PG2 in chloroform-$d$. 
**Fig. S9** $^{13}$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).
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:

$$\frac{d_{33,x}}{d_{11,q}} = \frac{\chi_x^{(2)}}{\chi_q^{(2)}} = \frac{I_x I_{c,q}}{I_q I_s} F$$

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, $I_{c,q}$ 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.