Electronic Supplementary Information:

Main-chain second-order nonlinear optical polyaryleneethynlenes containing isolation chromophore: enhanced nonlinear optical property, improved optical transparency and stability

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Chart S1. The structures and $d_{33}$ values of NLO polymers PS1-PS4.

Fig. S1 $^{13}$C NMR spectrum of polymer P1 in chloroform-$.d$. 
Fig. S2 ¹³C NMR spectrum of polymer P2 in chloroform-\textit{d}.

Fig. S3 ¹³C NMR spectrum of polymer P3 in chloroform-\textit{d}.

Fig. S4 ¹³C NMR spectrum of polymer P4 in chloroform-\textit{d}. 
**Fig. S5** $^{13}$C NMR spectrum of polymer P5 in chloroform-$d$.

**Fig. S6** TGA thermograms of polymers P1-P5, measured in nitrogen at a heating rate of 10 °C/min.
**Fig. S7** UV-vis spectra of polymers P1-P5 in THF (0.02 mg/mL).

**Fig. S8** UV-vis spectra of polymers P1-P5 in 1,4-dioxane (0.02 mg/mL).
Fig. S9 UV-vis spectra of polymers P1-P5 in dichloromethane (0.02 mg/mL).

Fig. S10 UV-vis spectra of polymers P1-P5 in chloroform (0.02 mg/mL).
**Fig. S11** UV-vis spectra of polymers P1-P5 in DMSO (0.02 mg/mL).

**Fig. S12** Normalized UV-Vis spectra of THF solutions of chromophores C1, C2 and their mixture with different ratio. (the concentration of C1 was $1 \times 10^{-5}$ mmol/mL).
Fig. S13 Absorption spectra of the film of P1 before and after poling.

Fig. S14 Absorption spectra of the film of P2 before and after poling.
Fig. S15 Absorption spectra of the film of P3 before and after poling.

Fig. S16 Absorption spectra of the film of P4 before and after poling.
Fig. S17 Absorption spectra of the film of P5 before and after poling.

Fig. S18 $^1$H NMR spectrum of C2 and C1 mixed with the ratio of 0:1 in chloroform-$d$. 
**Fig. S19** $^1$H NMR spectrum of C2 and C1 mixed with the ratio of 0.25:1 in chloroform-$d$.

**Fig. S20** $^1$H NMR spectrum of C2 and C1 mixed with the ratio of 0.5:1 in chloroform-$d$. 
Fig. S21 $^1$H NMR spectrum of C2 and C1 mixed with the ratio of 0.75:1 in chloroform-$d$.

Fig. S22 $^1$H NMR spectrum of C2 and C1 mixed with the ratio of 1:1 in chloroform-$d$. 