

Electronic supplementary information for

**Effects of Rigid Core and Flexible Tails on the Phase Behaviors of
Polynorbornene-Based Mesogen-Jacketed Liquid Crystalline Polymers**

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Synthesis of 2'-amino-(4',4''-bis(*p*-carboxylate)-terphenyl) (M-1)

2,5-Dibromoaniline (5.00 g, 19.9 mmol), 4-(methoxycarbonyl) phenylboronic (14.4 g, 80.0 mmol), and Pd(PPh₃)₄ (2.30 g, 1.99 mmol) were dissolved in the mixed solvent of 80 mL of H₂O and 40 mL of THF in a 250 mL round-bottomed flask. The mixture was refluxed under a nitrogen atmosphere at 80 °C for 24 h. After the mixture was cooled to ambient temperature, THF was removed by rotary evaporation, and the remaining mixture was extracted three times with 50 mL of CH₂Cl₂. The organic layers were combined and dried by MgSO₄. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (silica gel, CH₂Cl₂), resulting in 2.10 g of a light yellow solid. Yield: 29%. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 8.14 (d, 2H), 8.12 (d, 2H), 7.67 (d, 2H), 7.60 (d, 2H), 7.23 (d, 1H), 7.10 (dd, 1H), 7.03 (d, 1H), 7.10 (dd, 1H), 3.96 (s, 3H), 3.95 (s, 3H).

Synthesis of 2'-amino-(4',4''-bis(*p*-dicarboxylic acid)-terphenyl) (M-2)

M-1 (2.10 g, 5.80 mmol) and NaOH (11.6 g, 290 mmol) were dissolved in the mixed solvent of 50 mL of dioxane and 20 mL of H₂O, and the mixture was refluxed at 100 °C overnight. After the mixture was cooled to ambient temperature, the solvent was removed by rotary evaporation. The residue was dissolved in water. A dilute hydrochloric acid solution was added until the pH of the mixture was about 2, and a light yellow solid appeared. After filtration and drying under an infrared lamp, the product was obtained as a light yellow powder. Yield: 90%. ¹H NMR (400 MHz, DMSO, δ, ppm): 8.05 (m, 4H), 7.79 (d, 2H), 7.69 (d, 2H), 7.60 (d, 2H), 7.57 (s, 1H), 7.45 (d, 1H), 7.38 (d, 1H).

Synthesis of *N*-(4',4''-bis(*p*-carboxylphenyl)-terphenyl)-2'-*cis*-5-norbornene-*exo*-2,3-dicarboximide (NbTpA, M-3)

cis-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (0.800 g, 4.90 mmol) and glacial acetic acid (30.0 mL) were charged in a 100 mL round-bottomed flask. **M-2** (0.500 g, 1.50 mmol) was added to the reaction mixture at 120 °C in about 30 min. Then the reaction mixture was refluxed

for 12 h. After being cooled to ambient temperature, the mixture was poured into cold water (~150 mL) and vigorously stirred for 2 h. After filtration and drying under an infrared lamp, the product was obtained as a white powder. Yield: 80%. ¹H NMR (400 MHz, DMSO, δ , ppm): 13.00 (s, 2H), 8.06 (t, 2H), 7.96 (m, 4H), 7.86 (d, 2H), 7.70 (m, 2H), 7.55 (d, 2H), 7.34 (t, 2H), 2.94 (s, 2H), 2.74 (d, 2H), MS (HR-ESI): [M-H]⁻/z, Calcd 479.2; Found 478.2.

Synthesis of NbTpCn

NbTpC16. 1-Bromohexadecane (1.00 g, 3.30 mmol), NbTpA (0.200 g, 0.600 mmol), and KHCO₃ (0.300 g, 3.00 mmol) were dissolved in 50 mL of *N,N*-dimethylformamide (DMF), and the mixture was refluxed at 100 °C for 24 h. After being cooled to ambient temperature, the mixture was poured into cold water. Then the solution was extracted three times with 50 mL of dichloromethane (CH₂Cl₂). The organic layers were combined and dried by MgSO₄. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (silica gel, CH₂Cl₂), resulting in 0.200 g of a white powder. Yield: 61%. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.03–8.12 (m, 4H), 7.79–7.66 (m, 3H), 7.38–7.58 (m, 4H), 6.20–6.28 (d, 2H), 4.43 (m, 4H), 3.08–3.35 (d, 2H), 2.61–2.74 (d, 2H), 1.77 (m, 4H), 1.26–1.54 (m, 54H), 0.88 (t, 6H). MS (HR-ESI): [M + H]⁺/z, Calcd 815.5; Found 816.5. Anal. Calcd for C₆₁H₈₅NO₆: C, 78.92; H, 9.23; N, 1.51. Found: C, 78.81; H, 9.29; N, 1.58.

NbFpC8. NbTpC8 was a colorless liquid prepared from **M-3** and 1-bromooctane. Yield: 50%. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.04–8.12 (m, 4H), 7.67–7.77 (m, 3H), 7.36–7.4 (m, 4H), 6.21–6.27 (d, 2H), 4.32 (m, 4H), 3.08–3.35 (d, 2H), 2.61–2.75 (d, 2H), 1.77 (m, 4H), 1.29–1.79 (m, 22H), 0.89 (m, 6H). MS (HR-ESI): [M + H]⁺/z, Calcd 703.4; Found 704.4.

NbFpC12. NbTpC12 was a colorless liquid prepared from **M-3** and 1-bromododecane. Yield: 55%. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.03–8.11 (m, 4H), 7.69–7.75 (m, 3H), 7.36–7.57 (m, 4H), 6.20–6.28 (d, 2H), 4.32 (m, 4H), 3.08–3.35 (d, 2H), 2.61–2.74 (d, 2H), 1.77 (m, 4H), 1.27–1.62 (m, 38H), 0.88 (t, 6H). MS (HR-ESI): [M + H]⁺/z, Calcd 815.5; Found 816.5.

Synthesis of NbFpC16 and NbFpC10,6

NbFpC16. C16-OH (0.500 g, 1.500 mmol), NbTpA (0.200 g, 0.600 mmol), *N,N*-diisopropylcarbodiimide (DIC, 0.200 g, 1.50 mmol), and 4-(dimethylamino)pyridine (DMAP, 0.0200 g, 0.160 mmol) were dissolved in CH₂Cl₂ (50.0 mL) in a 100 mL round-bottomed flask and stirred at ambient temperature for 24 h. After the solvent was evaporated, the crude product was purified by silica gel column chromatography with CH₂Cl₂ and subsequent recrystallization from methanol. Yield: 60%. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 8.12–8.20 (m, 4H), 7.68–7.73 (m, 3H), 7.03–7.09 (m, 4H), 6.85–6.89 (m, 4H), 6.16–6.23 (d, 2H), 3.89 (m, 4H), 3.06–3.30 (d, 1H), 2.58–2.71 (d, 1H), 1.72 (m, 4H), 1.20–1.40 (m, 52H), 0.81 (t, 6H). MS (HR-ESI): [M + H]⁺/z, Calcd 1111.7; Found 1112.7. Anal. Calcd for C₇₉H₉₃NO₈: C, 78.81; H, 8.43; N, 1.26. Found: C, 78.81; H, 8.39; N, 1.32.

NbFpC10,6. NbFpC10,6 was prepared from NbTpA and C10,6-OH. Yield: 50%. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 8.19–8.29 (m, 4H), 7.75–7.81 (m, 3H), 7.43–7.62 (m, 4H), 7.13 (m, 4H), 6.96 (d, 4H), 6.23–6.29 (d, 2H), 3.84 (m, 4H), 3.13–3.37 (d, 1H), 2.65–2.78 (d, 1H), 1.29–1.78 (m, 50H), 0.89 (m, 6H). MS (HR-ESI): [M + H]⁺/z, Calcd 1111.7; Found 1112.7. Anal. Calcd for C₇₉H₉₃NO₈: C, 78.81; H, 8.43; N, 1.26. Found: C, 79.01; H, 8.49; N, 1.22.

Results

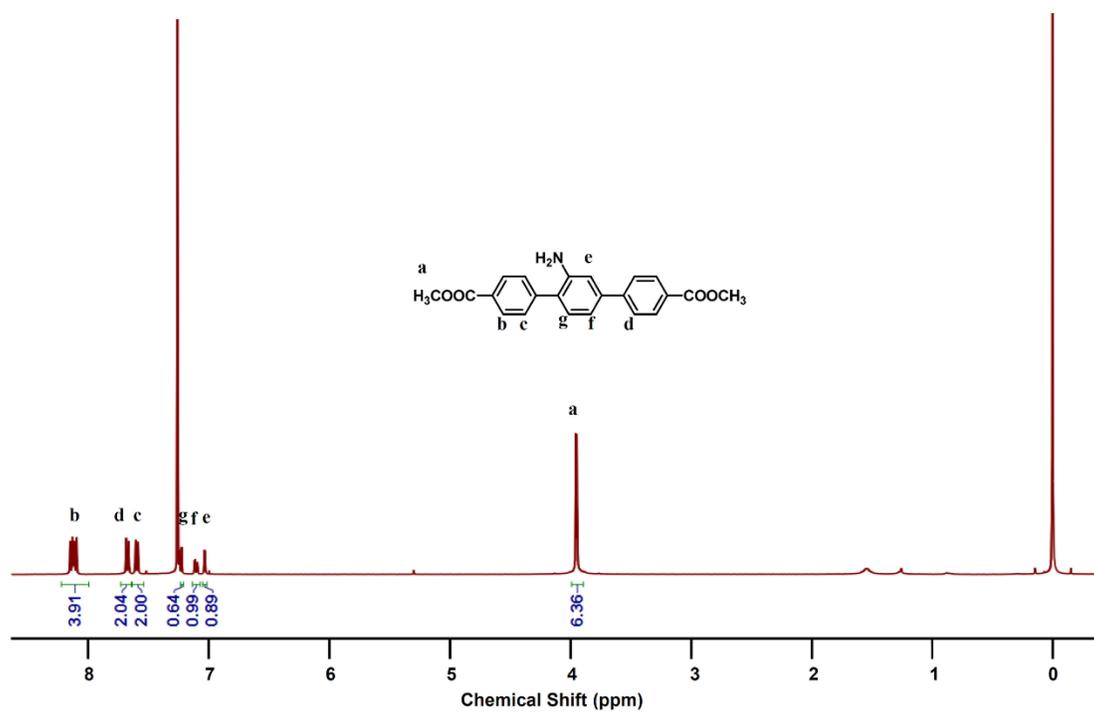


Fig. S1 ^1H NMR spectrum of **M-1** in CDCl_3 .

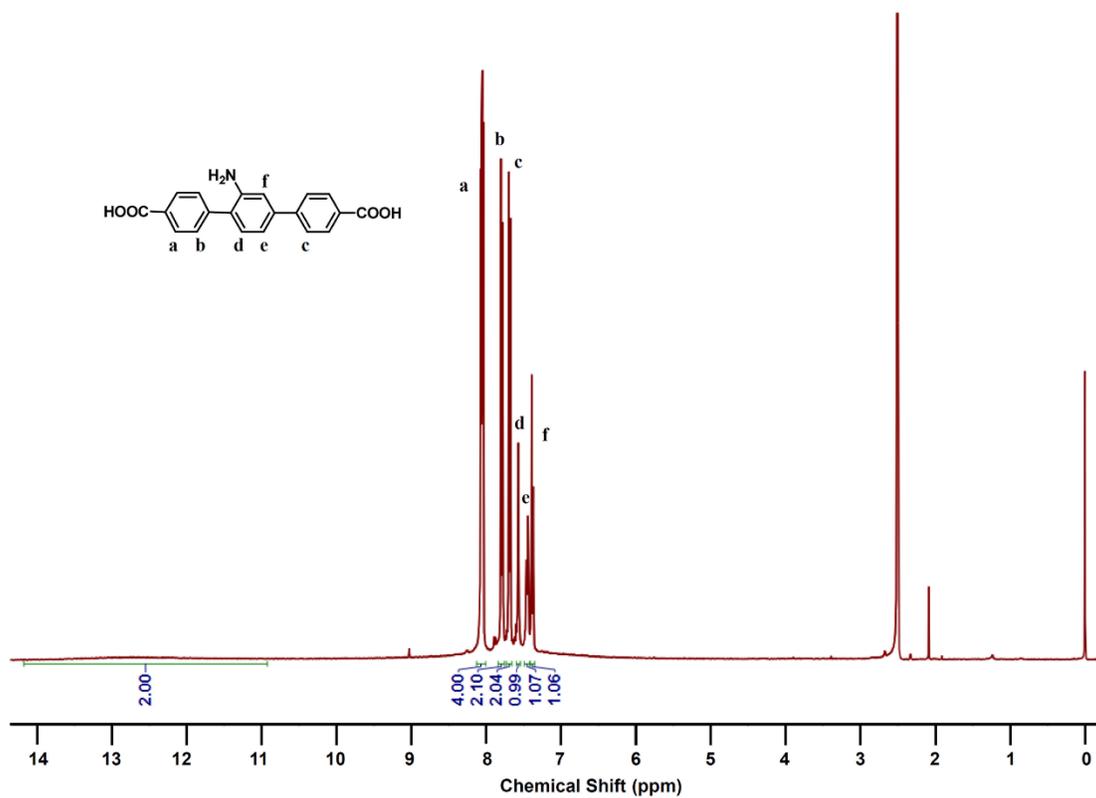


Fig. S2 ^1H NMR spectrum of **M-2** in CDCl_3 .

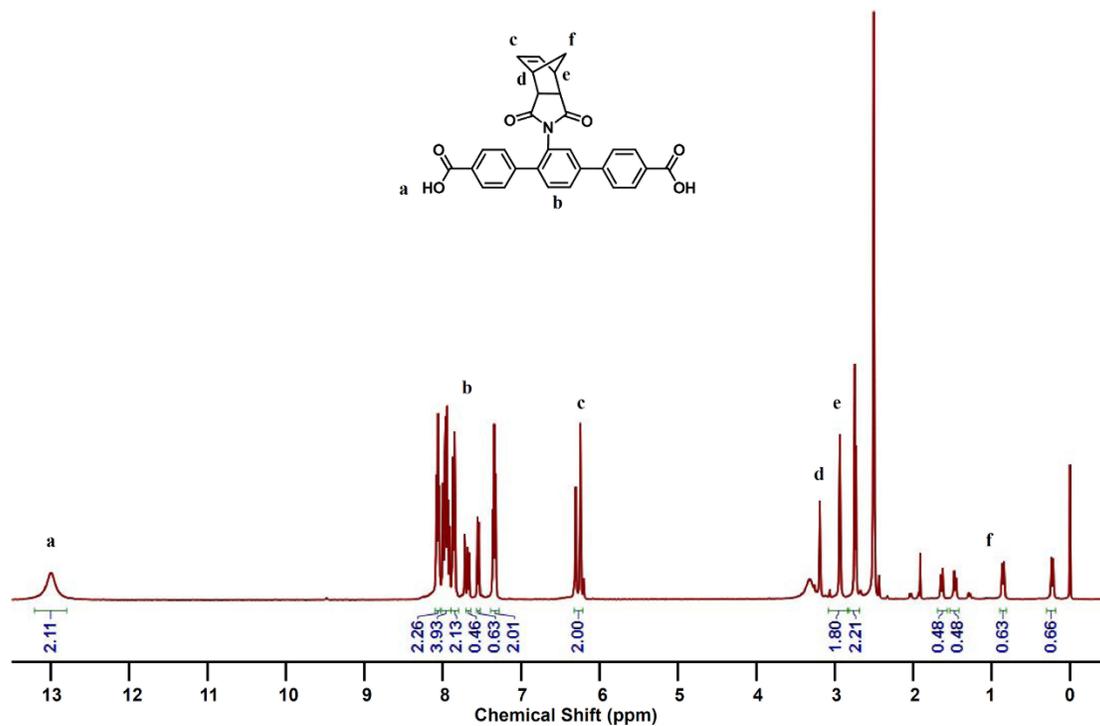


Fig. S3 ¹H NMR spectrum of **M-3** in CDCl₃.

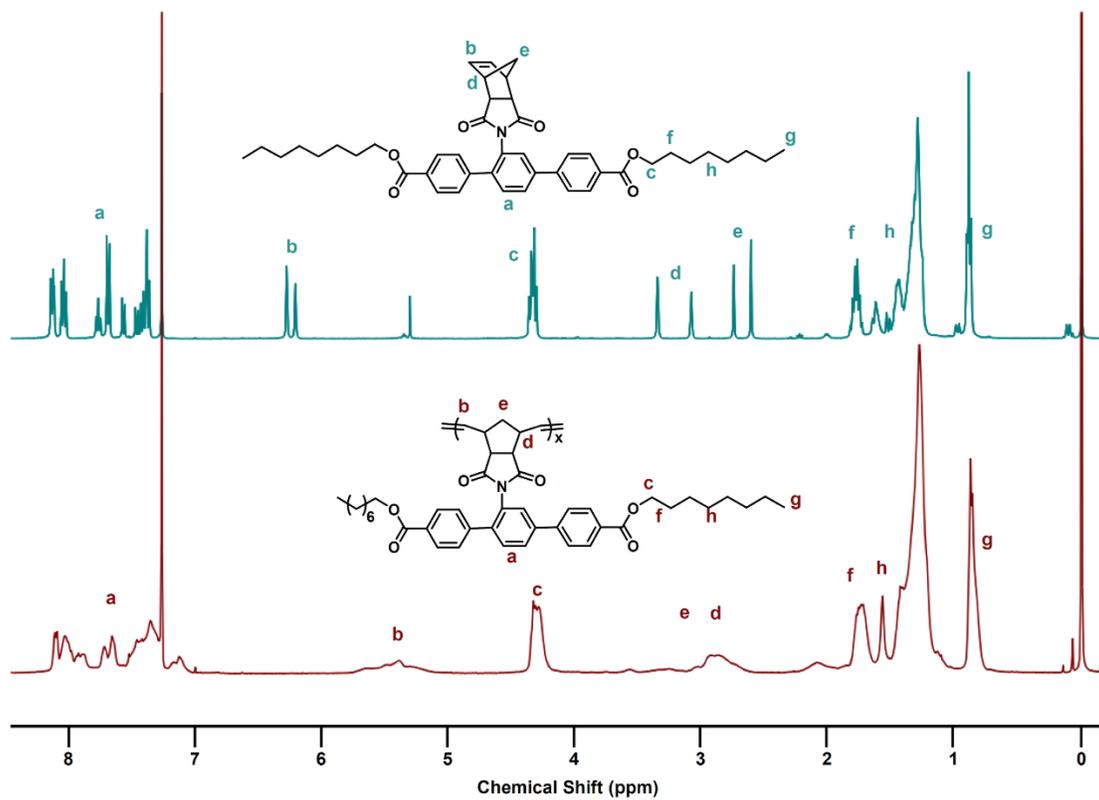


Fig. S4 ¹H NMR spectra of NbTpC8 (top) and PNbTpC8 (bottom) in CDCl₃.

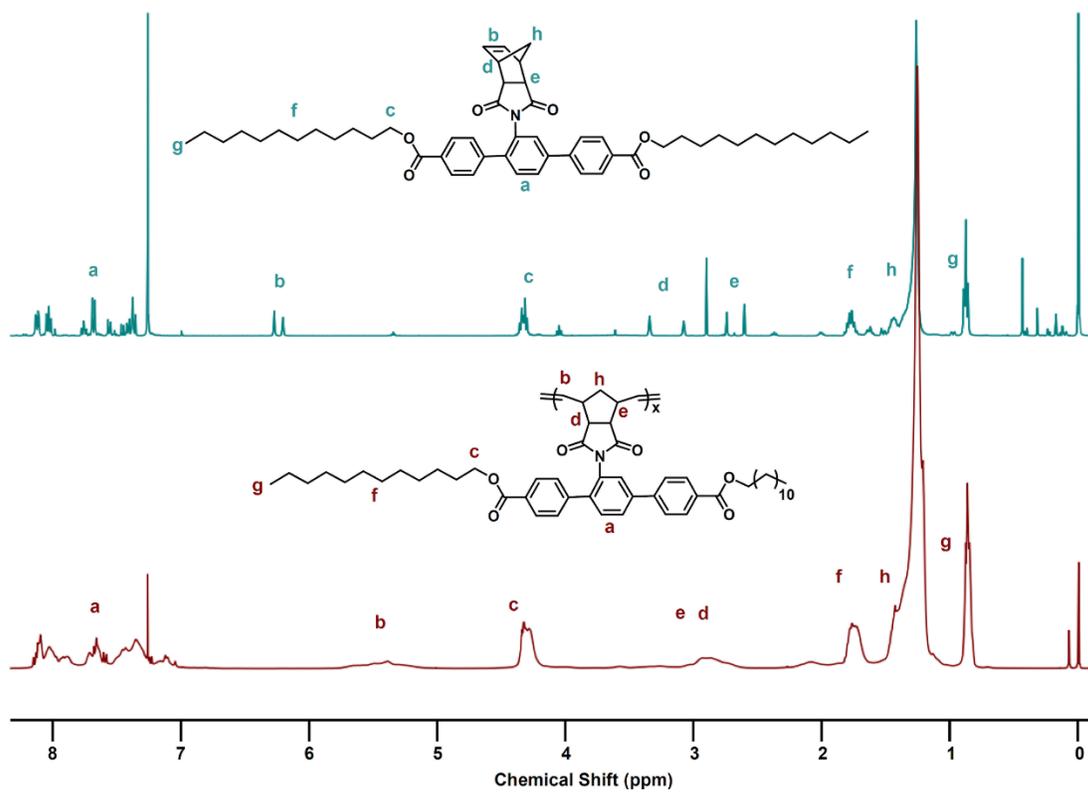


Fig. S5 ¹H NMR spectra of NbTpC12 (top) and PNbTpC12 (bottom) in CDCl₃.

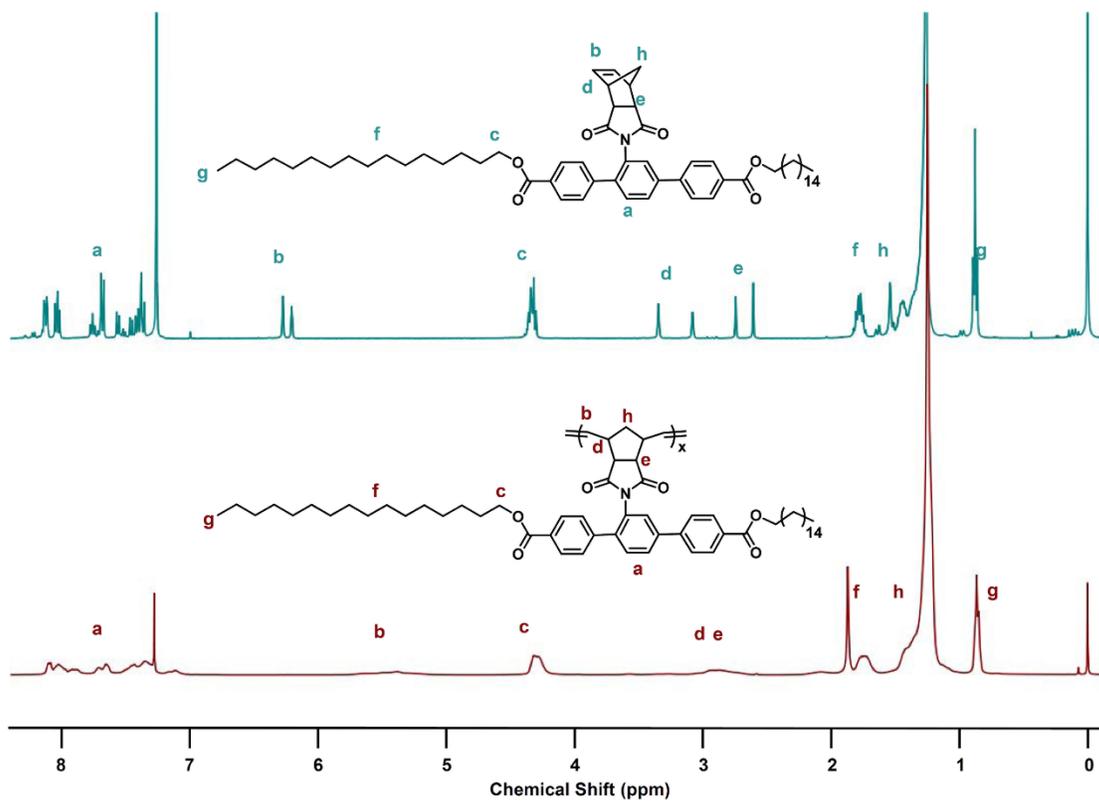


Fig. S6 ¹H NMR spectra of NbTpC16 (top) and PNbTpC16 (bottom) in CDCl₃.

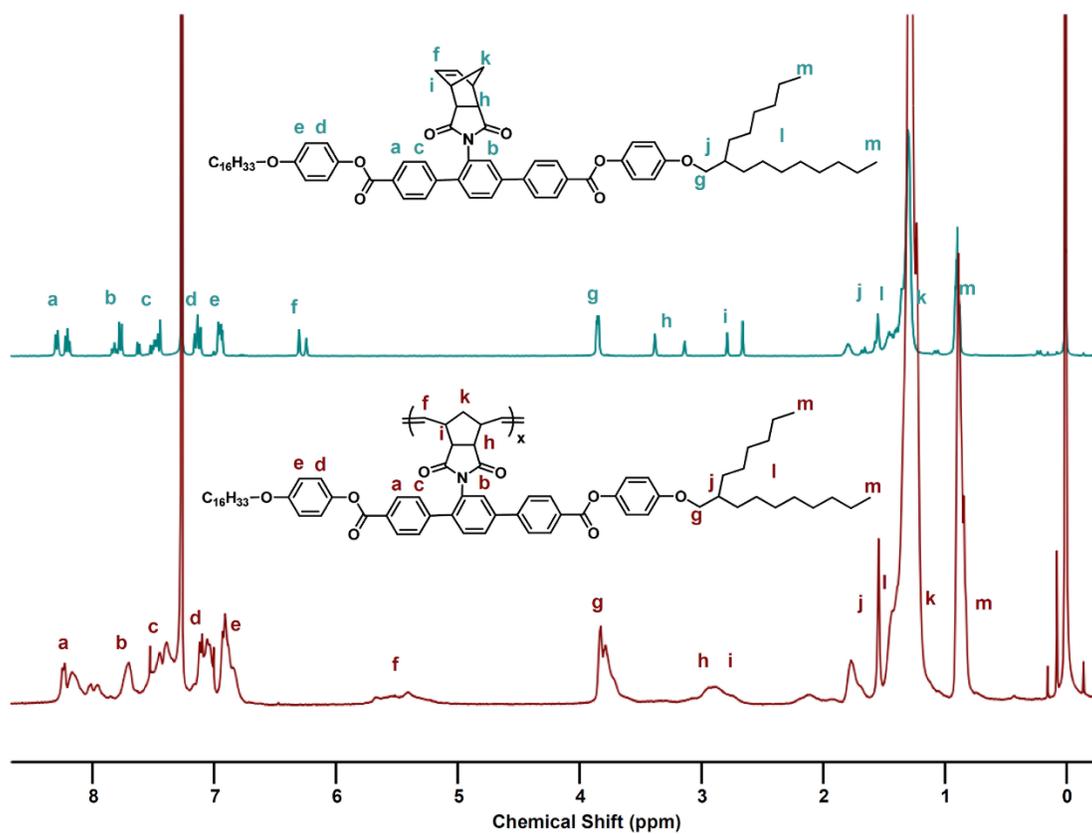


Fig. S7 ^1H NMR spectra of NbFpC10,6 (top) and PNbFpC10,6 (bottom) in CDCl_3 .

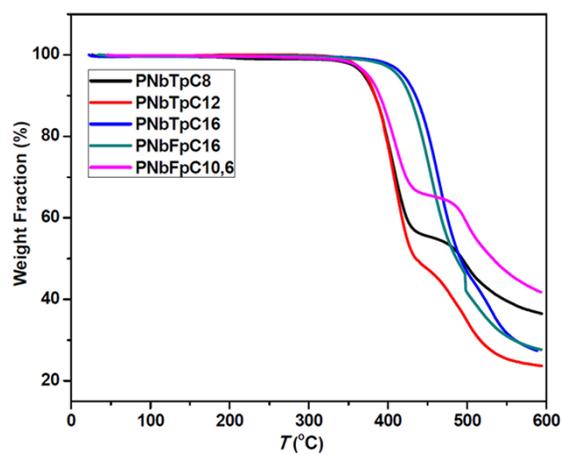


Fig. S8 TGA curves of all polymers at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere.

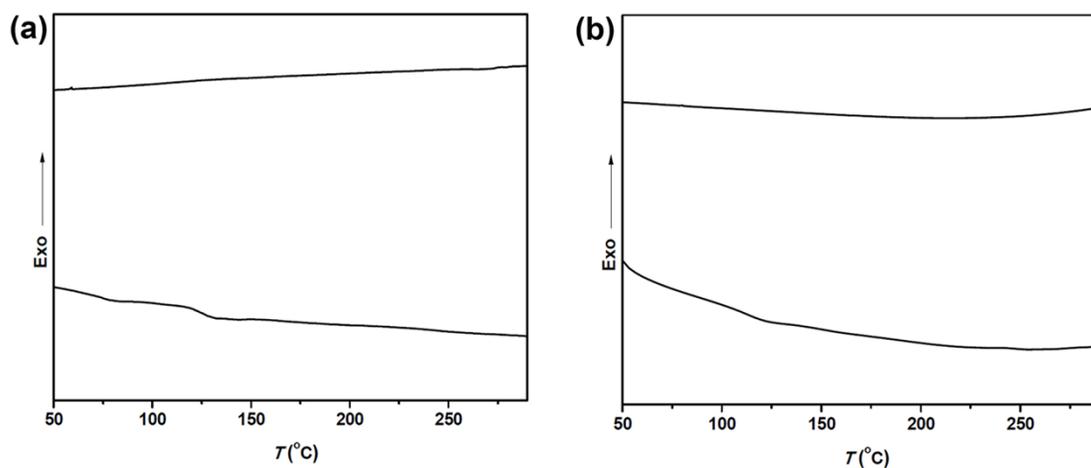


Fig. S9 DSC traces of PNBtpC8 (a) and PNBtpC16 (b) during the first cooling processes at a rate of $3\text{ }^{\circ}\text{C min}^{-1}$ and the second heating processes at a rate of $20\text{ }^{\circ}\text{C min}^{-1}$ under a nitrogen atmosphere.

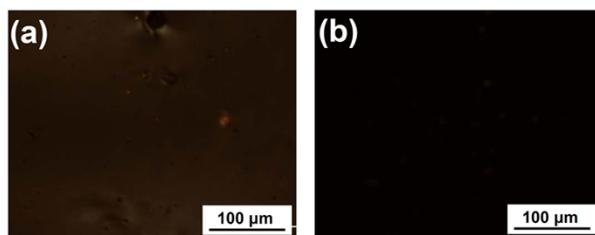


Fig. S10 PLM micrographs of PNBtpC12 (a) and PNBtpC16 (b) at $150\text{ }^{\circ}\text{C}$.

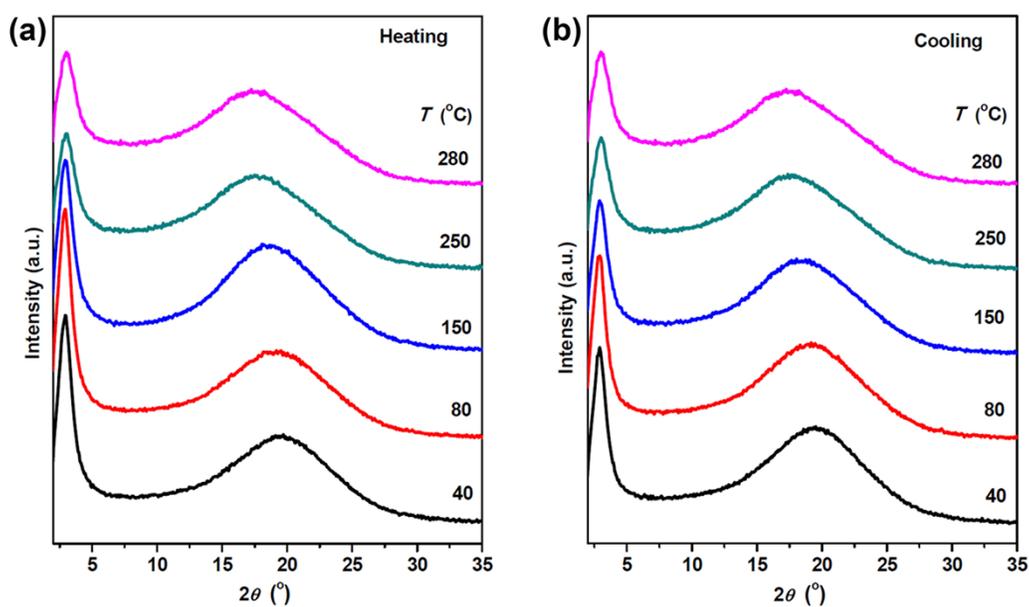


Fig. S11 1D WAXD profiles of PNBfPc12 during the first heating (a) and subsequent cooling (b) processes.

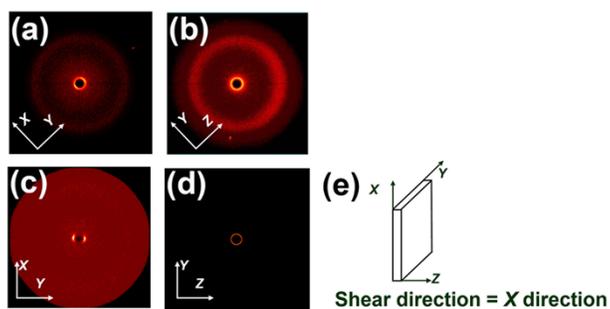


Fig. S12 2D WAXD patterns of PNBfTpC12 with the X-ray beam perpendicular (a) and parallel (b) to the shear direction, those of PNBfPc10,6 with the X-ray beam perpendicular (c) and parallel (d) to the shear direction, and the shear geometry (e).