Supporting Information

Novel cholesteric liquid crystalline elastomers containing dimer type nematic and chiral liquid crystalline side-chains

Ying Jiang, Yuehua Cong and Baoyan Zhang

Center for Molecular Science and Engineering, Northeastern University, Shenyang 110004, PR, China

Contents

1. Synthesis and analytical data

1.1 Synthesis of M_1

1.1.1 Synthesis of intermediate **1** Ethyl 6-(4-cyanobiphenyl-4'-yloxy)hexanoate

Ethyl 6-bromohexanonate (33g, 149mmol), 4'-Hydroxy-4-biphenylcarbonitrile (20g, 103mmol), anhydrous potassium carbonate (20g, 145mmol) and potassium iodide (0.5g, 3mmol) were stirred in DMF (50 mL) for 48 hours at 50 °C under a nitrogen atmosphere. Evaporated most DMF and put remaining yellow solid into water (500 mL), added 3M HCl solution gradually to adjust the pH value to 5. The resultant white precipitate was filtered off and washed with abundant water. After drying, the crude product was then crystallized with absolute ethanol (100 mL), giving a white crystal powder. Yield: 68%. mp 87 °C (lit.[1, 2] 88-89 °C).

1.1.2 Synthesis of intermediate **2** 6-(4'-cyanobiphenyl-4'-yloxy)hexanoic acid

Intermediate **1** (10g, 29.7mmol) was mixed with 100 mL absolute ethanol at room temperature, then added lithium hydroxide (1.57g, 37.4mmol) and 20 mL deionized water, raised the temperature to flux. Detecting the hydrolyzing degree by TLC, and ended reaction when no ester **1** could be

observed. The resultant yellow slurry was poured into 500 mL deionized water, then frozen in the refrigerator for 30 min. Slowly adjusted the pH value to 2 by 3M HCl solution, a lot of white solid was precipitated. After filtration, the white precipitate was washed by deionized water several times and dried in oven. The crude product was recrystallized by 100 mL absolute ethanol to give a white powder solid. Yield: 88%. mp 168 °C (lit. [1, 2] 163.7 °C). ^{1}H NMR (Bruker AV 600; Bruker, 600 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.74-7.61 (m, 4H, Ar-*H*), 7.55-7.53 (d, 2H, Ar-*H*, *J* = 8.70 Hz), 7.01-6.98 (d, 2H, Ar-*H*, *J* = 8.61 Hz), 4.04-4.02 (t, 2H, -OCH_2-, *J* = 6.32 Hz), 2.44-2.41 (t, 2H, -CH_2-, *J* = 7.41 Hz), 1.93-1.46 (m, 12H, -(CH_2)$_2$-); IR (KBr) ν_{max}/cm^{-1}: 3500-3350(-OH), 2940–2850(–CH3, –CH2–), 2225(–CN), 1720-1690 (C=O), 1693, 1493 (Ar–), 1255-1150 (C-O). Elemental anal. calcd. for $C_{19}H_{19}NO_3$: C 73.77, H 6.19, N 4.53, O 15.52; Found: C 73.69, H 6.17, N 4.50, O 15.57.

1.1.3 Synthesis of **M$_1$** 4-((6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexanoyl)oxy) phenyl 4-(allyloxy) benzoate

Intermediate **2** (7.58g, 24 mmol) was completely dissolved in 200 mL dichloromethane (DCM) by magnetic stirring, then N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI, 10g, 52.2 mmol) was added to form the carboxylic acid activator. After triethylamine (TEA, 7.92g, 78.3 mmol) was dropped, a transparent solution was formed. 4-Dimethylaminopyridine (DMAP, 3.2g, 26.1 mmol) and 4-hydroxyphenyl 4-(allyloxy)benzoate (6g, 21.76 mmol) were dissolved in 40 mL DCM, slowly added into the reactor, kept the temperature below 10°C and reacted overnight. The reaction continued at 40°C for 48 h. The resultant solution was washed by 500 mL 3M HCl solution, 500 mL saturated sodium bicarbonate solution, and 500 mL saturated sodium chloride solution in sequence, and then washed by 500 mL deionized water twice. The organic layer was dried by anhydrous magnesium sulphate, after evaporation the white solid crude product was obtained, which was further purified by column chromatography on silica gel with a petroleum ether and ethyl acetate (8:1) mixture as the eluent. Recrystallization from ethanol gave the desired product. Yield: 38%. ^{1}H NMR (Bruker AV 600; Bruker, 600 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.16-8.13 (d, 2H, Ar-*H*, *J* = 8.84 Hz), 7.71-7.64 (q, 4H, Ar-*H*), 7.55-7.53 (d, 2H, Ar-*H*, *J* = 8.60 Hz), 7.23-7.12 (q, 4H, Ar-*H*), 7.03-6.99 (d, 4H, Ar-*H*, *J* = 8.78 Hz), 6.11-6.04 (m, 1H, CH_2 = C*H*-), 5.47-5.34 (dd, 2H, CH_2 = CH-, *J* = 18.46 Hz, 11.31 Hz), 4.66-4.63 (d, 2H, -OCH_2-, *J* = 5.29 Hz), 4.08-4.04 (t, 2H, -OCH_2-, *J* = 12.62 Hz), 2.66-2.61 (t, 2H, -CH_2-, *J* = 14.97 Hz), 1.93-1.84 (m, 4H, -(CH_2)$_2$-), 1.68-1.62 (q, 2H, -CH_2-); IR (KBr) ν_{max}/cm^{-1}: 3075(=CH), 2941–2850(–CH3, –CH2–), 2231(–CN), 1751-1720 (C=O), 1606, 1510 (Ar–), 1258-1074 (C-O). Elemental anal. calcd. for $C_{35}H_{31}NO_6$: C 74.85, H 5.66, N 2.49, O 17.09; Found: C 74.79, H 5.54, N 2.52, O 17.11.

1.2 Synthesis of M_2

1.2.1 Synthesis of intermediate **3** 4'-(methoxycarbonyloxy)biphenyl-4-carboxylic acid
Intermediate **3** was prepared according to the procedure of reported [3, 4]. Yield: 74.1%. mp 273 °C.

1.2.2 Synthesis of intermediate **4** (*R*)-octan-2-yl 4'-((methoxycarbonyl)oxy)-[1,1'-biphenyl]-4-carboxylate

Intermediate 4 (*R*)-octan-2-yl 4'-((methoxycarbonyl)oxy)-[1,1'-biphenyl]-4-carboxylate was prepared by a revised mitsunobu reaction. Intermediate 4 (16.32g, 60mmol), triphenylphosphine (21g, 80 mmol), and (*R*)-octan-2-ol (7.1g, 55 mmol) were dissolved in dry tetrahydrofuran (100 mL); then diisopropyl azodicarboxylate (14.14g, 70 mmol) was added dropwise under nitrogen atmosphere. The reaction was stirred for a further 24 h at room temperature and was monitored by TLC until fully completed. 10 mL water was dropped to make triphenylphosphine transferred into triphenylphosphine oxide. Then evaporated tetrahydrofuran and added DCM (250 mL) into the flask, washed by hydrogen peroxide (15%, 250 mL) several times until all the triphenylphosphine had been transferred into triphenylphosphine oxide. Then washed by saturated sodium (250 mL) and deionized water (250 mL) separately. The organic layer was dried by anhydrous magnesium sulfate for 5 minutes, filtered, and evaporated the DCM. The obtained viscous solid product was mixed with petroleum ether (boiling range 60-90 °C), stirred and heated up to small reflux for 5 minutes and then cooled down to room temperature. Filtered all the insoluble solid (mostly are the undesirable triphenylphosphine oxide and reduction product of diisopropyl azodicarboxylate), and evaporated the collected filtrate, a viscous transparent liquid was obtained. Further purified by column chromatography [400 mesh silica gel; 5% v/v ethyl acetate in petroleum ether (boiling range 60-90 °C)] to give a colorless oil. Yield: 76%.

1.2.3 Synthesis of intermediate 5 (*R*)-octan-2-yl 4'-hydroxy-[1,1'-biphenyl]-4-carboxylate

Intermediate 5 (*R*)-octan-2-yl 4'-hydroxy-[1,1'-biphenyl]-4-carboxylate was prepared by a revised procedure of reference [3, 4]. To a solution of Intermediate 5 (15g, 40 mmol) in absolute ethyl alcohol (130 mL) was added an aqueous ammonia solution (25%, 100 mL). The reaction mixture was stirred at room temperature for a while until the mixture turned into transparent liquid. Monitored the reaction by TLC until the spot of intermediate 5 was disappeared. The solvent was removed by evaporation. Put water (250 mL) into the residual viscous solid, then filtered and collected solid, which was dried in vacuum oven (30 °C), a white solid was collected. The crude product was purified by recrystallization of the mixture of 20% v/v ethyl acetate in petroleum ether (boiling range 60-90 °C), the pure white crystal product was obtained. Yield: 93%. mp 84-87 °C. ^{1}H NMR (Bruker AV 600; Bruker, 600 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.11-8.07 (d, 2H, Ar-*H*, *J* = 8.43 Hz), 7.62-7.52 (dd, 4H, Ar-*H*, *J* = 50.11 Hz, 8.52 Hz), 6.97-6.95 (d, 2H, Ar-*H*, *J* = 8.64 Hz), 5.30-5.28 (d, 1H, C*H*$_2$ = CH-, *J* = 4.45 Hz), 5.22-5.16 (h, 1H, C*H*$_2$ = CH-, *J* = 6.18 Hz), 1.86-1.20 (m, 14H, aliphatic *H*), 0.88-0.90 (t, 3H, -C*H*$_3$, *J* = 6.88 Hz). IR (KBr) v_{max}/cm^{-1}: 3450-3200 (-OH), 2980–2820(–CH3, –CH2–), 1710-1680 (C=O), 1575-1570, 1499 (Ar–), 1300-1185 (C-O). Elemental anal. calcd. for $C_{21}H_{26}O_3$: C 77.27, H 8.03, O 14.70; Found: C 77.33, H 8.11, O 14.68. $[\alpha]_D^{RT}$ = -30.7° (0.025 g ml^{-1}, CH_2Cl_2).

1.2.4 Synthesis of M_2 (*R*)-4-((4-(allyloxy)benzoyl)oxy)phenyl (4'-((octan-2-yloxy)carbonyl)-[1,1'-biphenyl]-4-yl) adipate

To a solution of 6-(4-((4-(allyloxy)benzoyl)oxy)phenoxy)-6-oxohexanoic acid (4g, 9.84 mmol) in dichloromethane (193 mL) was added 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI, 4.17g, 21.45 mmol). Triethylamine (TEA, 2.71g, 26.81 mmol) was then

injected by a syringe. Under stirring for a while the solution become completely transparent. Intermediate 5 (2.98g, 8.94 mmol) and 4-dimethylaminopyridine (DMAP, 1.31g, 10.73mmol) were dissolved in dichloromethane (129 mL), then added dropwise into the reactor. The reaction continued for 48 hours. Washed the reaction solution by 1 M HCl (500 mL), saturated sodium bicarbonate (500 mL) and saturated sodium chloride (500 mL) separately, and finally washed by deionized water (500 mL) twice. Kept the organic layer and dried by magnesium sulfate for 30 minutes. Collected the filtrate and evaporated the solvent, the crude product in white solid form was obtained. Recrystallized by absolute ethyl alcohol (500 mL) and passed through a short chromatography column [400 mesh silica gel; 20% v/v ethyl acetate in petroleum ether (boiling range 60-90 °C)] to give a white solid product. Yield: 45%. ^{1}H NMR (Bruker AV 600; Bruker, 600 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.16-8.15 (d, 2H, Ar-*H*, *J* = 8.79 Hz), 8.12-8.10 (d, 2H, Ar-*H*, *J* = 8.25 Hz), 7.66-7.62 (dd, 4H, Ar-*H*, *J* = 2.68 Hz, 2.92 Hz), 7.24-7.19 (q, 4H, Ar-*H*), 7.18-7.14 (d, 2H, Ar-*H*, *J* = 8.91 Hz), 7.03-6.99 (d, 2H, Ar-*H*, *J* = 9.04 Hz), 6.12-6.04 (m, 1H, CH_2 = C*H*-), 5.48-5.43 (dd, 1H, CH_2 = CH-, *J* = 1.48 Hz, 1.78 Hz), 5.37-5.33 (dd, 1H, CH_2 = CH-, *J* = 1.30 Hz, 1.31 Hz), 5.22-5.15 (sext, 1H, -C*H*-), 4.67-4.63 (d, 2H, -CH_2-, *J* = 5.42 Hz), 2.72-2.64 (q, 4H, -(CH_2)$_2$-), 1.96-0.87 (m, 20H, aliphatic *H*). IR (KBr) ν_{max}/cm^{-1}: 3079(=CH), 2930–2849(–CH_3, –CH_2–), 1748-1710 (C=O), 1606, 1503 (Ar–), 1255-1070 (C-O). Elemental anal. calcd. for C43H46O9: C 73.07, H 6.56, O 20.37; Found: C 73.19, H 6.38, O 20.31. $[\alpha]_D^{RT}$ = -24.9° (0.025 g ml^{-1}, CH_2Cl_2).

1.3 Synthesis of Crosslinking agent CL

1.3.1 Synthesis of intermediate 6 1,4-phenylene bis(4-hydroxybenzoate)

4-hydroxybenzoic acid (60.015g, 500 mmol) and hydroquinone (27.51g, 250 mmol) in *para*-xylene (600 mL) was added *p*-toluenesulfonic acid (3g, 17.5 mmol), an oil/water separator was amounted onto the flask and reacted in reflux for 48 hours, removed the generated water during the reaction. Filtered the material and collected the greyish filter cake. Washed by ethyl alcohol (100 mL) four times until the product turned into white solid. Yield: 91%. mp 314 °C. ^{1}H NMR (Bruker AV 600; Bruker, 600 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 10.54 (s, 2H, -O*H*), 8.02-8.00 (d, 4H, Ar-*H*, *J* = 8.33 Hz), 7.33 (s, 4H, Ar-*H*), 6.96-6.94 (d, 4H, Ar-*H*, *J* = 8.80 Hz). IR (KBr) ν_{max}/cm^{-1}:3414(-OH), 1703 (C=O), 1603, 1510 (Ar–), 1587 (C=C), 1280-1080 (C-O). Elemental anal. calcd. for C20H14O6: C 68.57, H 4.03, O 27.4; Found: C 68.11, H 4.16, O 27.39.

1.3.2 Synthesis of Crosslinking agent CL 1,4-phenylene bis(4-(undec-10-enoyloxy)benzoate)

Put Intermediate 6 (7g, 20 mmol) and triethylamine (8g, 80 mmol) into 1,4-dioxane (150 mL) stirring for 1 hour at room temperature. Added the mixture of 10-undecylenoyl chloride (16.55g, 80 mmol) in 1,4-dioxane (20 mL) dropwise and reacted at room temperature for 24 hours, then reacted at 60 °C for further 6 hours. The material was wash by massive deionic water several times, then washed by hot ethyl alcohol (300 mL) three times. The obtained crude product was passed through a short chromatography column [400 mesh silica gel; 20% v/v ethyl acetate in petroleum ether (boiling range 60-90 °C)] to give a white solid product. Yield: 58%. ^{1}H NMR (Bruker AV 600;

Bruker, 600 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.27-8.23 (d, 4H, Ar-*H*, *J* = 8.43 Hz), 7.27-7.24 (d, 4H, Ar-*H*, *J* = 8.67 Hz), 5.87-5.79 (m, 2H, CH_2 = C*H*-), 5.04-4.99 (dd, 2H, CH_2 = CH-, *J* = 1.39 Hz, 1.76 Hz), 4.97-4.93 (d, 2H, CH_2 = CH-, *J* = 9.72 Hz), 2.64-2.58 (t, 4H, -CH_2-), 2.10-1.29 (m, 32H, aliphatic *H*). IR (KBr) v_{max}/cm^{-1}: 3078(=CH), 2929–2845(–CH3, –CH2–), 1758-1715 (C=O), 1602, 1508 (Ar–), 1280-1070 (C-O). Elemental anal. calcd. for C42H50O8: C 73.88, H 7.38, O 18.74; Found: C 73.76, H 7.37, O 18.68. $[\alpha]_D^{RT}$ = -2.5° (0.025 g ml^{-1}, CH_2Cl_2).

2. ^{1}H NMR spectra

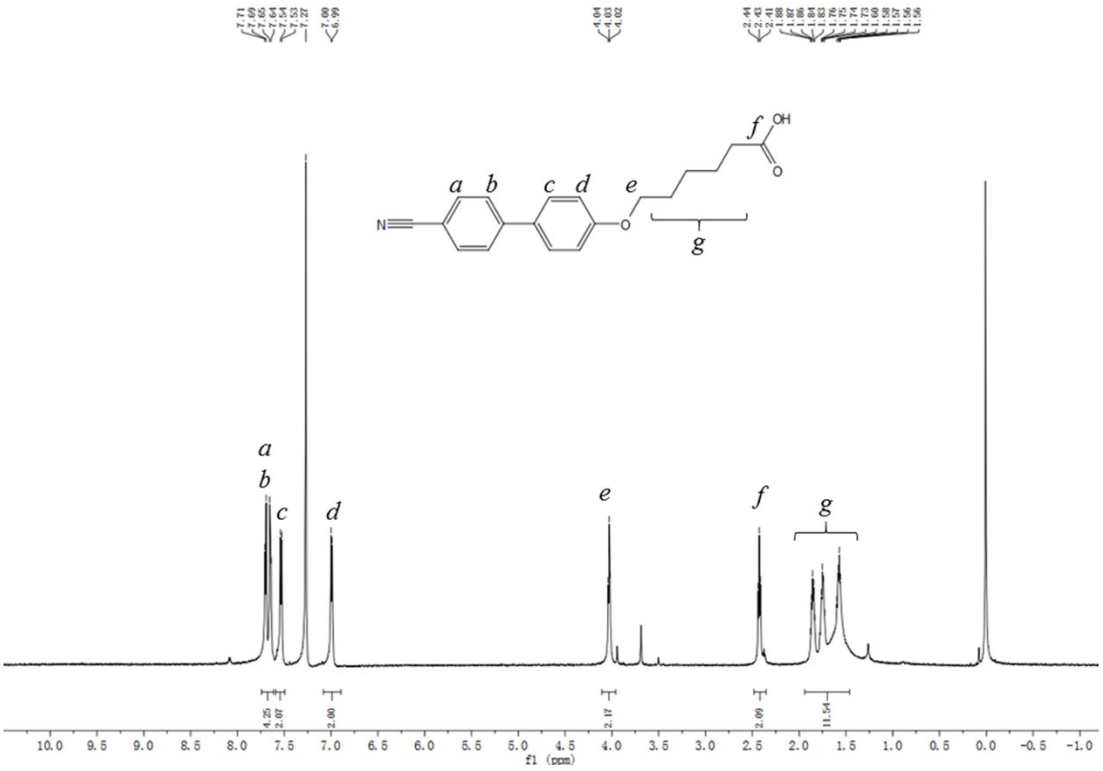

Fig. S1. ^{1}H NMR spectrum of Intermediate 2 (600MHz, $CDCl_3$)

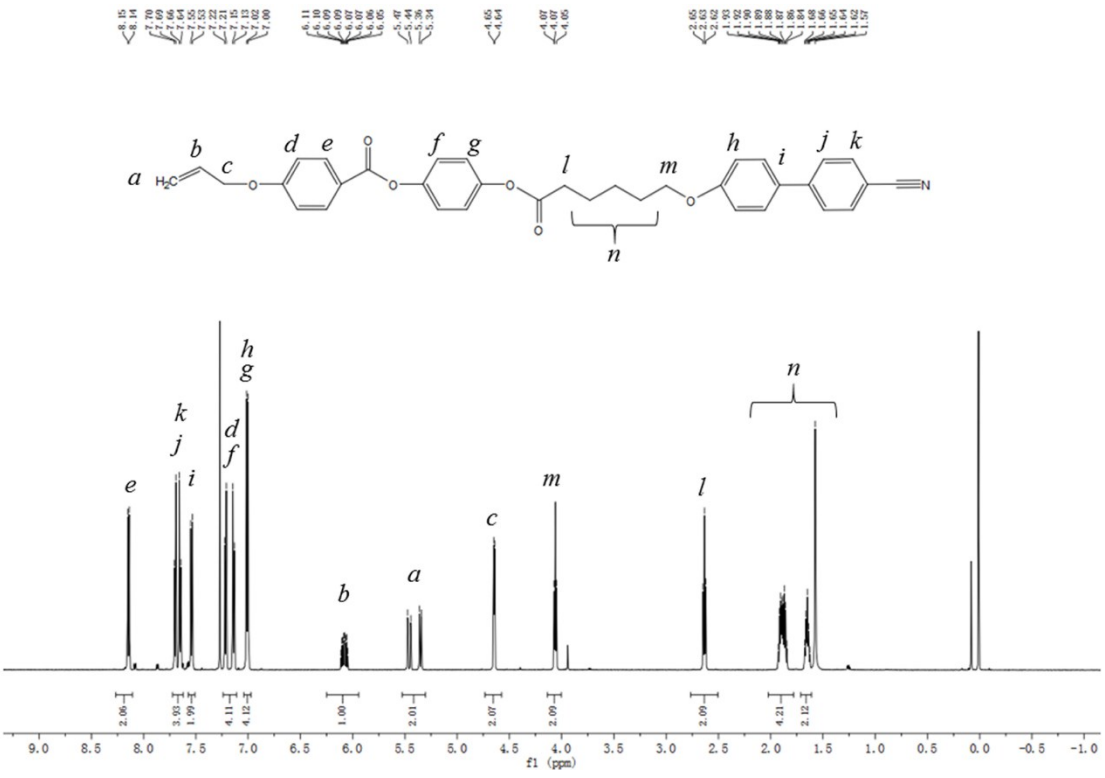

Fig. S2. ^{1}H NMR spectrum of M_1 (600MHz, $CDCl_3$)

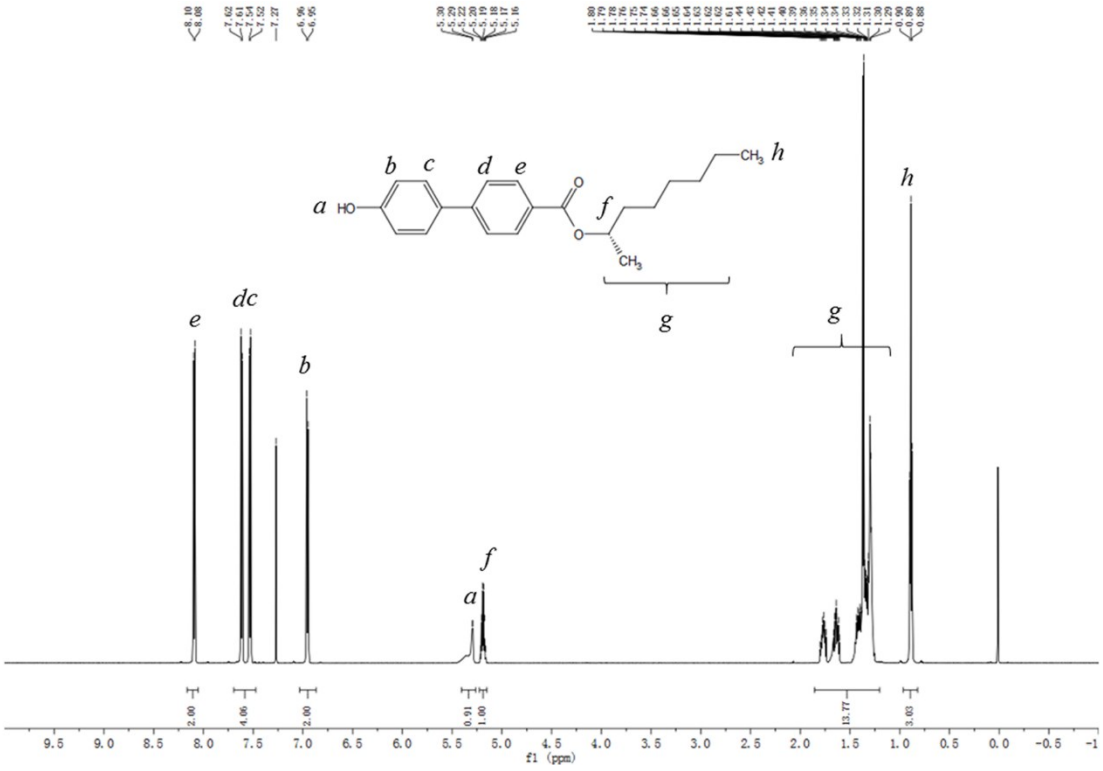

Fig. S3. ^{1}H NMR spectrum of Intermediate 5 (600MHz, $CDCl_3$)

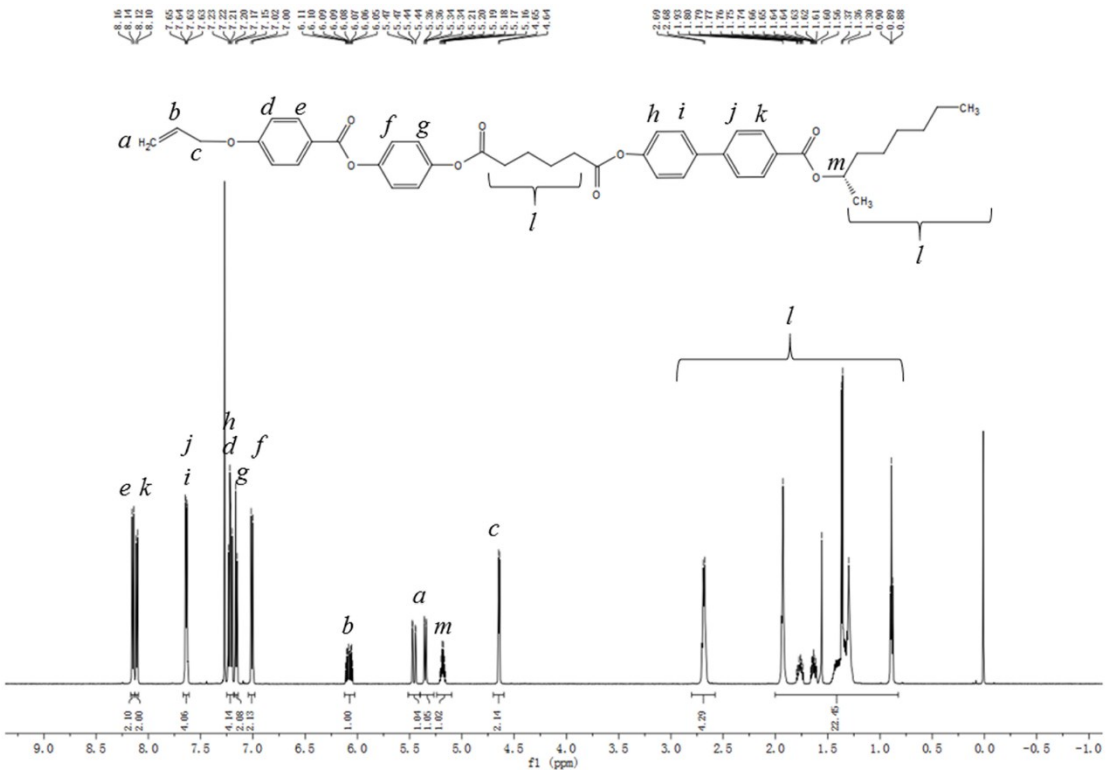

Fig. S4. ^{1}H NMR spectrum of M_2 (600MHz, $CDCl_3$)

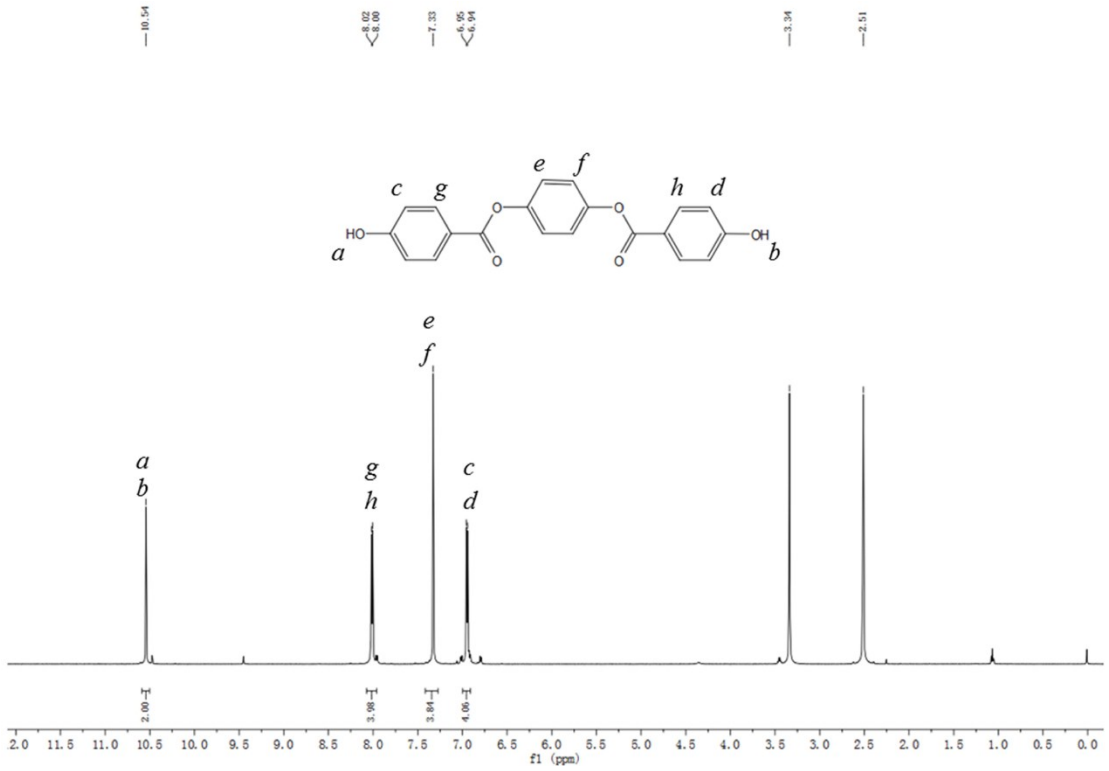

Fig. S5. ^{1}H NMR spectrum of Intermediate 6 (600MHz, DMSO-d_6)

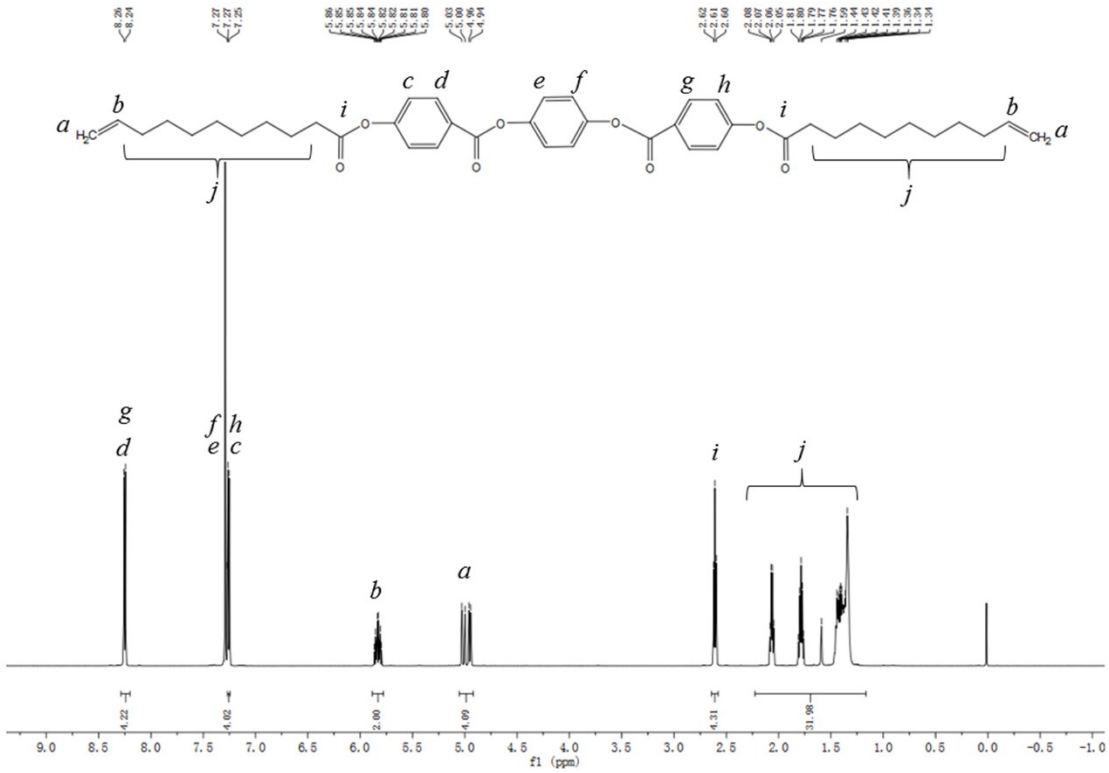

Fig. S6. ^{1}H NMR spectrum of CL (600MHz, $CDCl_3$)

3. FT-IR spectrograms

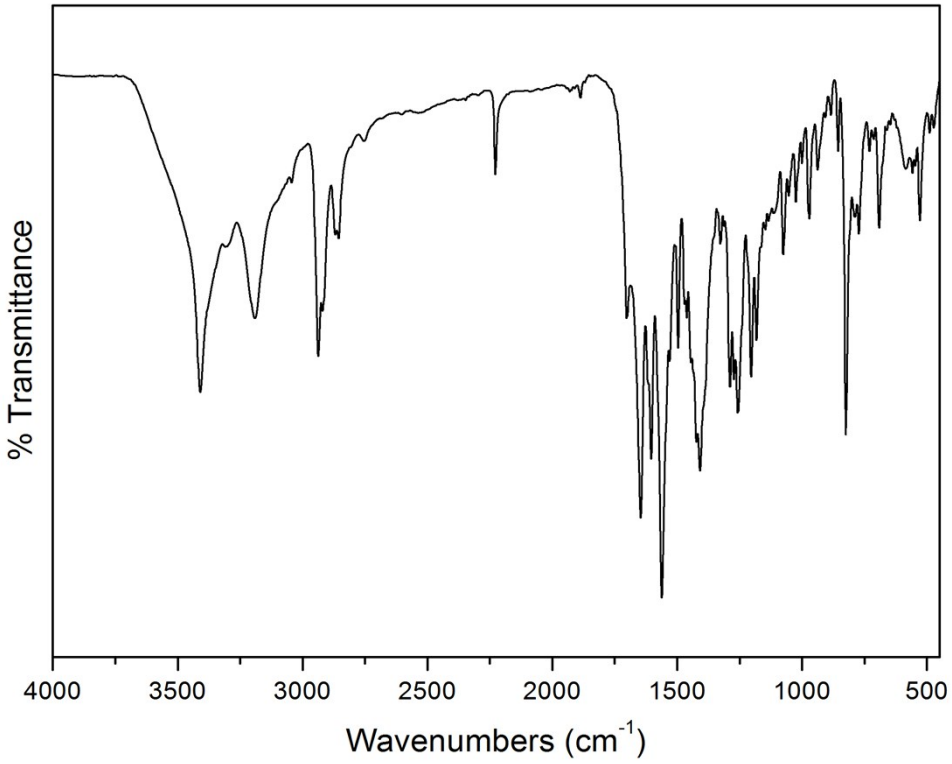

Fig. S7. FT-IR Spectrogram spectrum of Intermediate 2

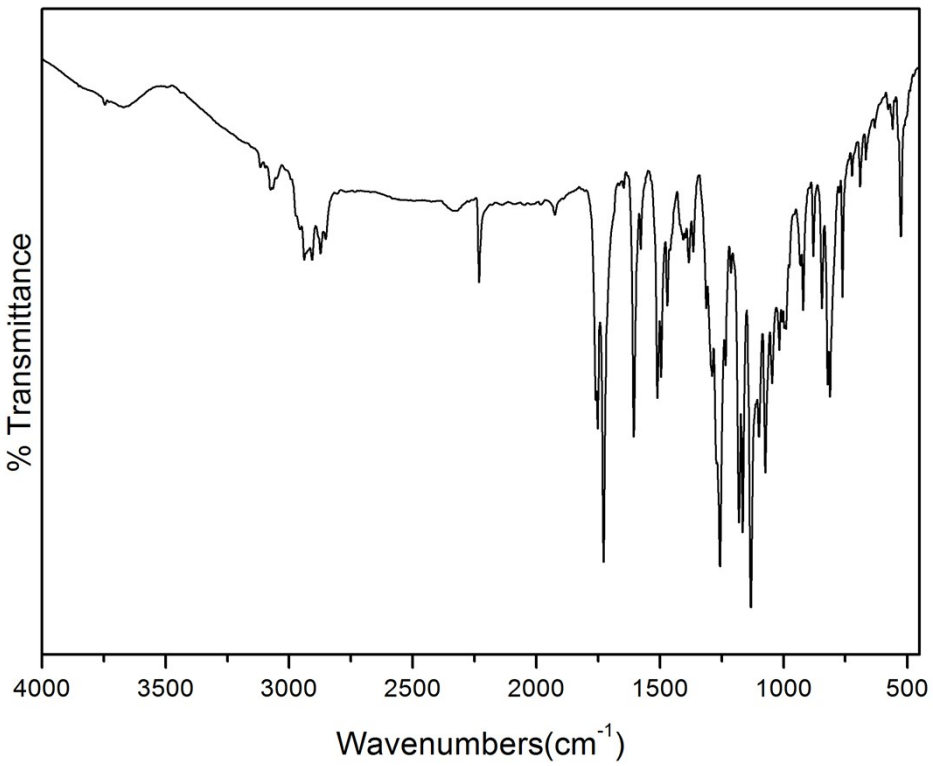

Fig. S8. FT-IR Spectrogram spectrum of M_1

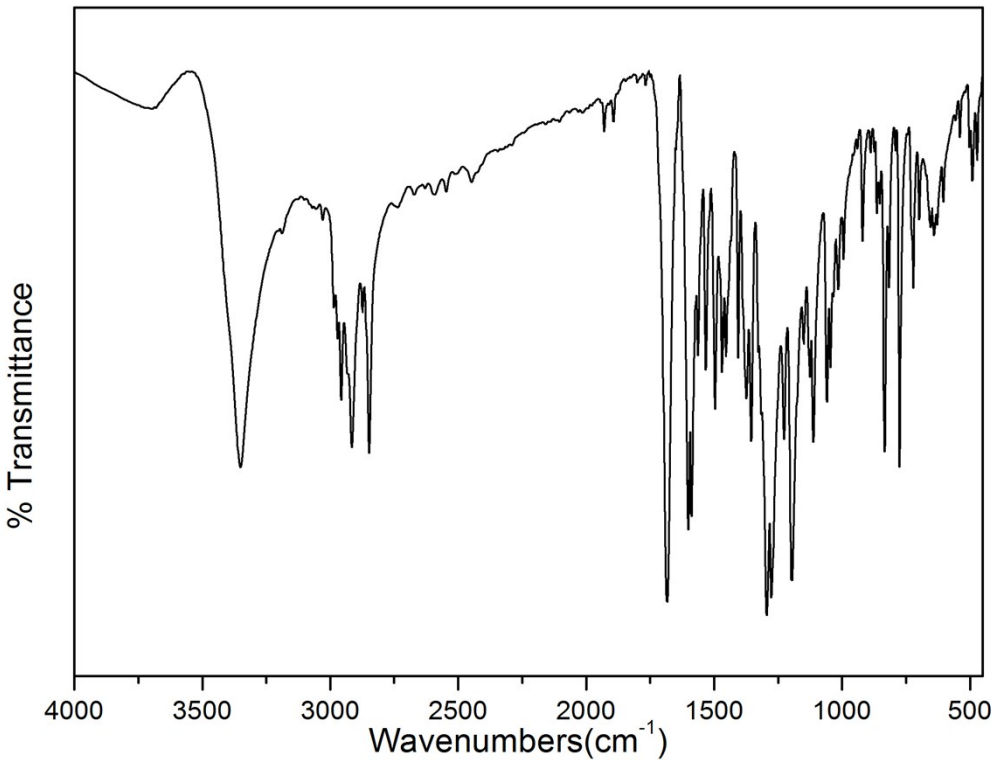

Fig. S9. FT-IR Spectrogram spectrum of Intermediate 5

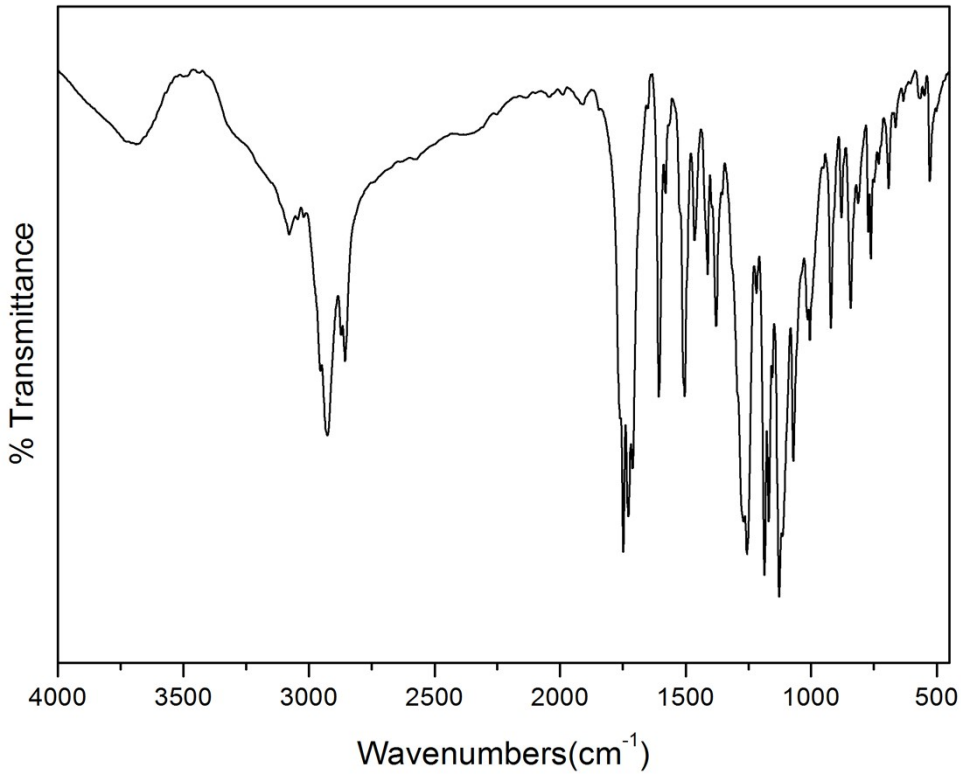

Fig. S10. FT-IR Spectrogram spectrum of M_2

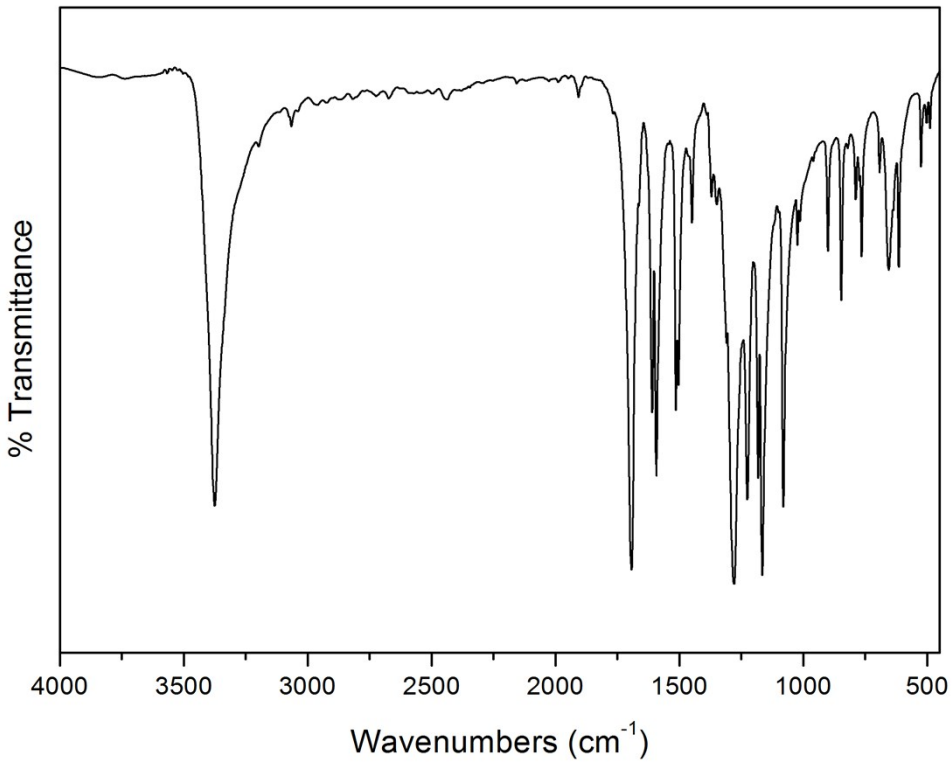

Fig. S11. FT-IR Spectrogram spectrum of Intermediate 6

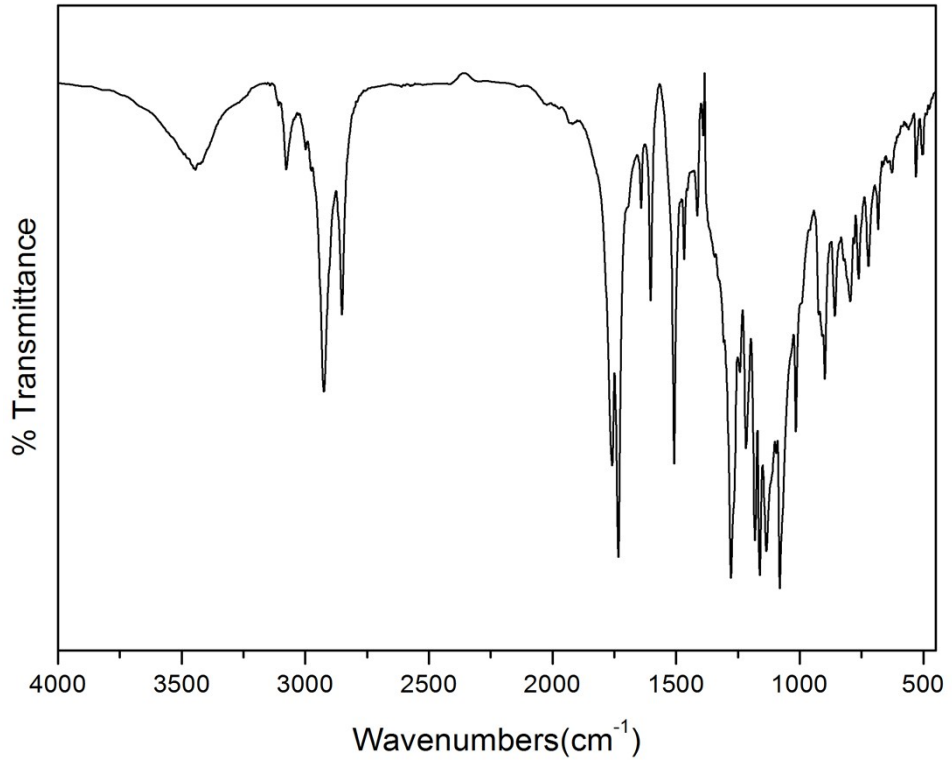

Fig. S12. FT-IR Spectrogram spectrum of CL

4. Additional textures

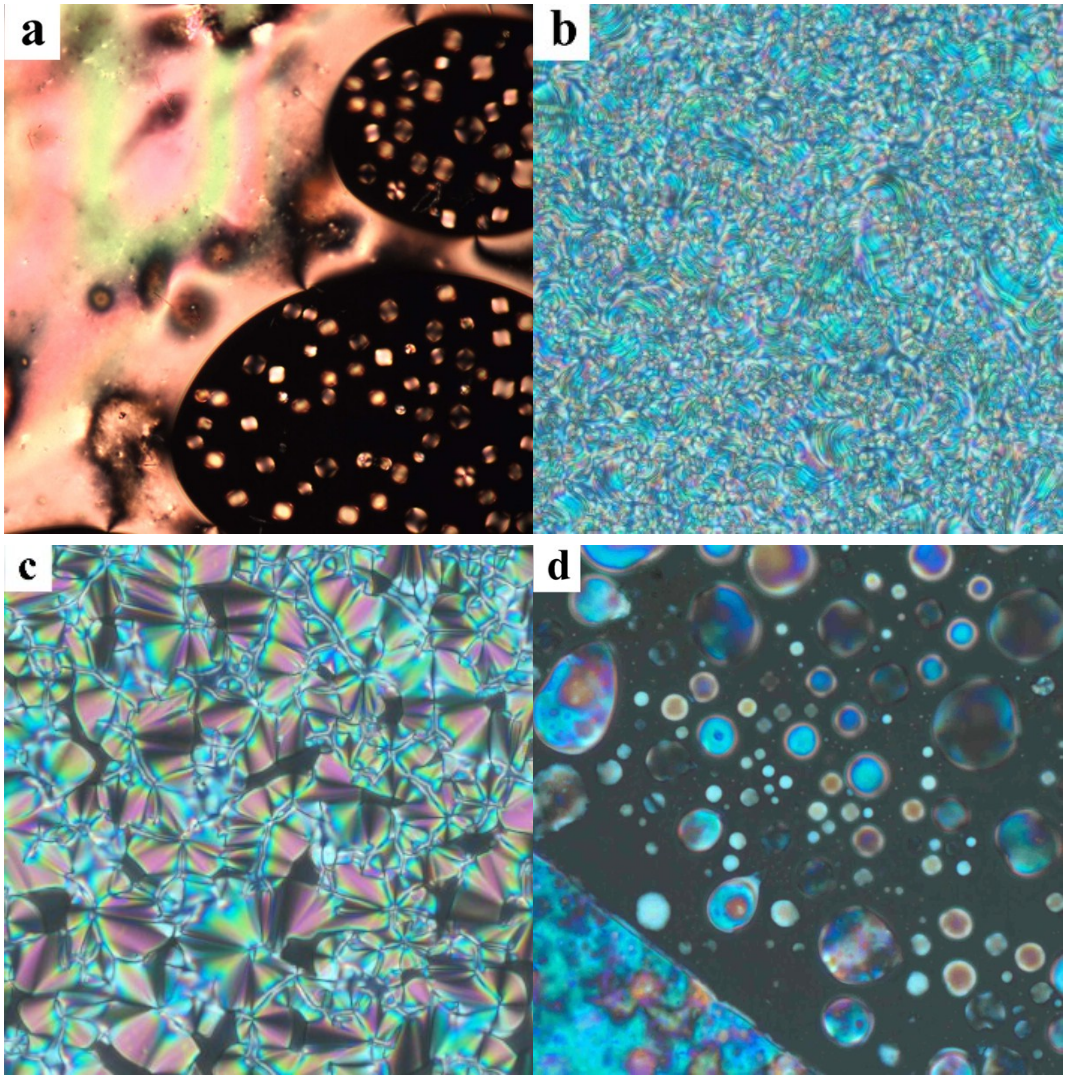

Fig. S13 Additional optical textures of M_1, M_2 and CL: (a) Coexistence of planar thread-like texture (on the left) with droplet texture (on the right) of nametic phase on heating to 222°C for M_1 (500×); (b) Crystallized lined texture of S_C* phase on cooling to 70 °C for M_2 (200×); (c) Fan-shaped focal conic texture of N^* phase on heating to 161 °C for M_2 (200×); (d) Coexistence of Planar thread-like texture (on the left) and droplet texture (on the right) of N phase on heating to 180°C for CL (500×).

5. heoretical molecule length of M_1, M_2 and CL

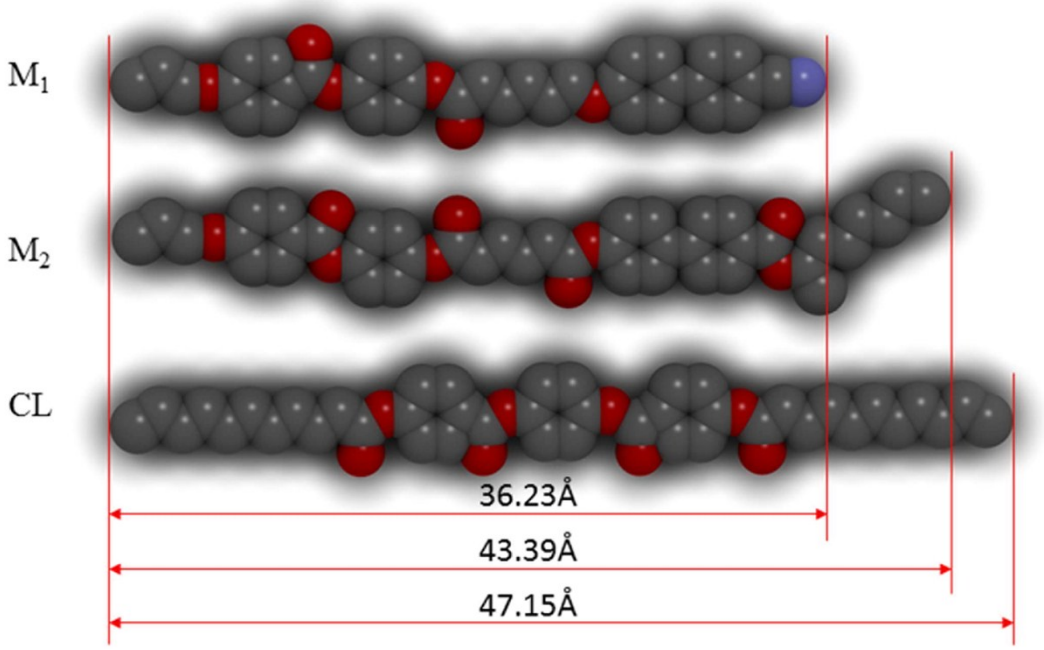

Fig. S14. Theoretical molecule length of M_1, M_2 and CL (with fully stretched mesomorphic units) calculated by using molecular modelling software Material Studios 6.0 from the calotte models (CPK, space-filling).

1. M. Sato and A. Yoshizawa, *Advanced Materials*, 2007, **19**, 4145-4148.
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