Supporting Information

Synthesis and characterization of chiral smectic side-chain liquid crystalline elastomers containing nematic and chiral mesogens

Ying Jiang, Yuehua Cong and Baoyan Zhang

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

Contents

1. Synthesis and analytical data

In ^{1}H NMR spectra, **M_1**, **M_2** and **CL** exhibits chemical shift values around 1.0-2.7, 4.9-6.0 and 6.9-8.5 ppm corresponding to the featured protons of methylene protons, olefinic protons, and aromatic protons, respectively. The integration results confirmed the proton numbers of each observed range of shift values. From FT-IR spectra, due to **M_1**, **M_2** and **CL** all have several ester groups, the wavenumber shift of C=O stretching from 1710-1750 can be easily observed. The strong and multiple peaks nearby 2850-3000 and 3060 cm^{-1} for long chain alkyl and alkene are also very obvious in these three compounds. The distinguished stretching vibration peaks of the cyano group at 2230~2260 cm^{-1} is the unique evidence of the chemical structure of M_1.

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 ℃ 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 (23.5g, 68%); mp 87 ℃ (lit.[1, 2] 88-89 ℃).

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, detected the hydrolyzing degree by TLC, and ended reaction when no intermediate **1** observed. The resultant yellow slurry was poured into 500 mL deionized water, then freezed in 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. Then the crude product was recrystallized by 100 mL absolute ethanol to give a white powder solid (8.1g, 88.2%); mp 168 ℃. (lit. [1, 2] 163.7 ℃).

1.1.3 Synthesis of $\mathbf{M_1}$ 4'-((6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexanoyl)oxy)-[1,1'-biphenyl]-4-yl dodec-11-enoate

Intermediate **2** (2.9g, 9.36 mmol) was completely dissolved in 120 mL dichloromethane (DCM) by magnetic stirring, then N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI, 3.64g, 18.72 mmol) was added to form carboxylic acid activator. After triethylamine (TEA, 2.8g, 28 mmol) was dropped, a transparent solution was formed. 4-Dimethylaminopyridine (DMAP, 0.61g, 5 mmol) and 4'-hydroxy-[1,1'-biphenyl]-4-yl undec-10-enoate (2.64g, 7.5 mmol) were dissolved in 20 mL DCM, slowly added dropwise into the reactor. Kept the temperature below 10 ℃ and reacted overnight, then reacted at 40 ℃ (slightly reflux) for further 48 h. The resultant solution was washed by 250 mL 3M HCl solution, 250 mL saturated sodium bicarbonate solution, and 250 mL saturated sodium chloride solution in sequence, and then washed by 250 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 (9:1) mixture as the eluent. Recrystallization from ethanol gave the desired product. Yield: 43%. ^{1}H NMR (Bruker AV 600; Bruker, 600 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: δ = 7.70 – 6.98 (m, 16H, Ar-*H*), 5.83 (ddt, *J* = 16.9, 10.2, 6.7, 1H, CH_2 = C*H*-), 5.03 – 4.93 (m, 2H, CH_2 = CH-), 4.07 (t, *J* = 6.3, 2H, -OCH_2-), 2.66 – 1.30 (m, 24H, -(CH_2)$_8$- and -(CH_2)$_4$-); IR (KBr) ν_{max}/cm^{-1}: 3075(=CH), 2941–2845(–CH3, –CH2–), 2223(–CN), 1750-1730 (C=O), 1604, 1501 (Ar–), 1258-1074 (C-O); Elemental anal. calcd. for $C_{43}H_{47}NO_5$: C 78.51, H 7.20, N 2.13, O 12.16; Found: C 78.59, H 7.25, N 2.19, O 12.11.

1.2 Syntheses of $\mathbf{M_2}$

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 ℃.

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 **3** (16.32g, 60mmol), triphenylphosphine (21g, 80 mmol), and (*S*)-octan-2-ol (7.1g, 55 mmol) were dissolved in dry tetrahydrofuran (100 mL), and 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 all the triphenylphosphine transferred into triphenylphosphine oxide. Then washed by saturated sodium chloride (250 mL) and deionized water (250 mL) separately. The organic layer was dried by anhydrous magnesium sulfate for 5 minutes, filtered, and evaporated the dichloromethane. The obtained viscous solid product was mixed with petroleum ether (boiling range 60-90 ℃), 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. Crude product was purified by column chromatography [400 mesh silica gel; 5% v/v ethyl acetate in petroleum ether (boiling range 60-90 ℃)] 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 **4** (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 **4** was disappeared. The solvent was removed by evaporation. Put water (250 mL) into the residual viscous solid, then filtered and collected the filter cake, which was dried in vacuum oven (30 ℃), and a white solid was collected. The crude product was purified by recrystallization from the mixture of 20% v/v ethyl acetate in petroleum ether (boiling range 60-90 ℃), and a pure white crystal product was obtained. Yield 93%, mp 84-87 ℃, $[\alpha]_D^{RT}$ = -30.7 °(0.025 g ml^{-1}, CH_2Cl_2).

1.2.4 Synthesis of $\mathbf{M_2}$ (*R*)-4'-((octan-2-yloxy)carbonyl)-[1,1'-biphenyl]-4-yl (4'-(undec-10-enoyloxy)-[1,1'-biphenyl]-4-yl) adipate

To a solution of 6-oxo-6-((4'-(undec-10-enoyloxy)-[1,1'-biphenyl]-4-yl)oxy)hexanoic acid (3.33g, 6.93 mmol) in dichloromethane (100 mL) was added 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI, 2.8g, 14.4 mmol). Triethylamine (TEA, 1.82g, 18 mmol) was injected by a syringe. Under stirring for a while the solution become completely transparent. Intermediate **5** (2g, 6.13 mmol) and 4-dimethylaminopyridine (DMAP, 0.878g, 7.2mmol) were dissolved in dichloromethane (50 mL), and added dropwise into the reactor. The reaction continued for 48 hours. Washed the reaction solution by 1 M HCl (250 mL), saturated sodium bicarbonate (250 mL) and saturated sodium chloride (250 mL) separately, and subsequently washed by deionized water (250 mL) twice. Kept the organic layer and dried it 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 (100 mL) and passed through a short chromatography column [400 mesh silica gel; 10% v/v ethyl acetate in petroleum ether (boiling range 60-90 ℃)] to give a white solid product. Yield 48%. ^{1}H NMR (Bruker AV 600; Bruker, 600

MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: δ = 8.11 – 7.16 (m, 16H, Ar-*H*), 5.83 (ddt, *J* = 17.0, 10.2, 6.7, 1H, CH_2 = C*H*-), 5.19 (h, *J* = 6.0, 1H), 5.05 – 4.91 (m, 2H, CH_2 = CH-), 2.66 – 1.30 (m, 40H, -(CH_2)$_8$-, -(CH_2)$_4$-, -(CH_2)$_5$-, and -(CH_3)$_2$); IR (KBr) v_{max}/cm^{-1}: 3076(=CH), 2935–2840 (–CH_3, –CH_2–), 1750-1708 (C=O), 1606, 1494 (Ar–), 1468, 1384 (CH_3), 1251-1100 (C-O). Elemental anal. calcd. for C50H60O8: C 76.11, H 7.66, O 16.22; Found: C 76.31, H 7.59, O 16.11. $[\alpha]_D^{RT}$ = -20.2 °.

1.3 Syntheses 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 under 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 91.4%, mp 314 ℃. IR (KBr) v_{max}/cm^{-1}:3414(-OH), 1703 (C=O), 1603, 1510 (Ar–), 1587 (C=C), 1280-1080 (C-O).

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 ℃ for further 6 hours. The material was washed 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 ℃)] 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

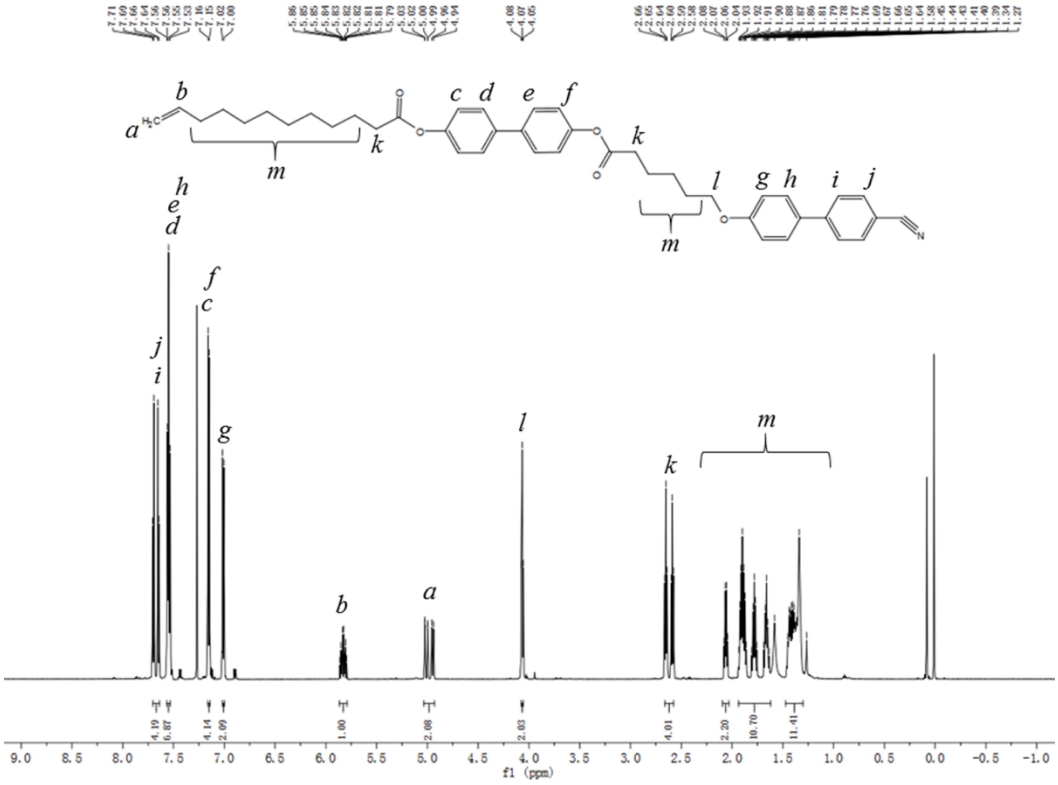

Fig. S1. ^{1}H NMR spectrum of M_1 (600MHz, $CDCl_3$)

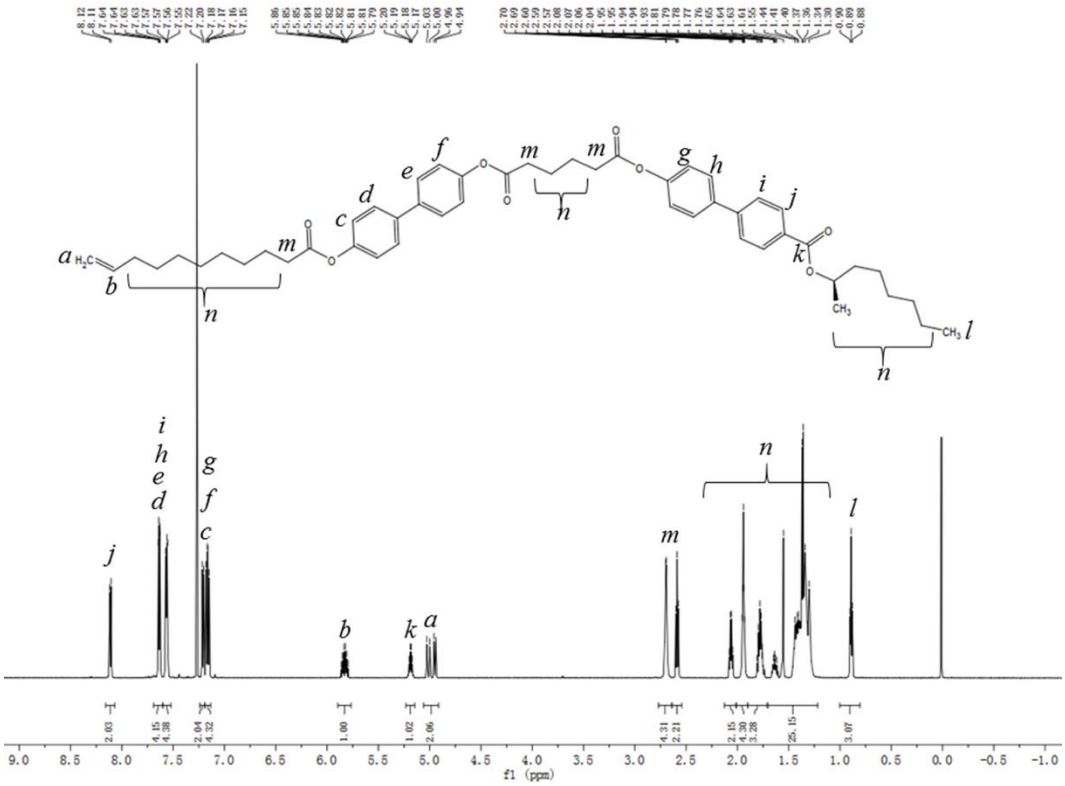

Fig. S2. ^{1}H NMR spectrum of M_2 (600MHz, $CDCl_3$)

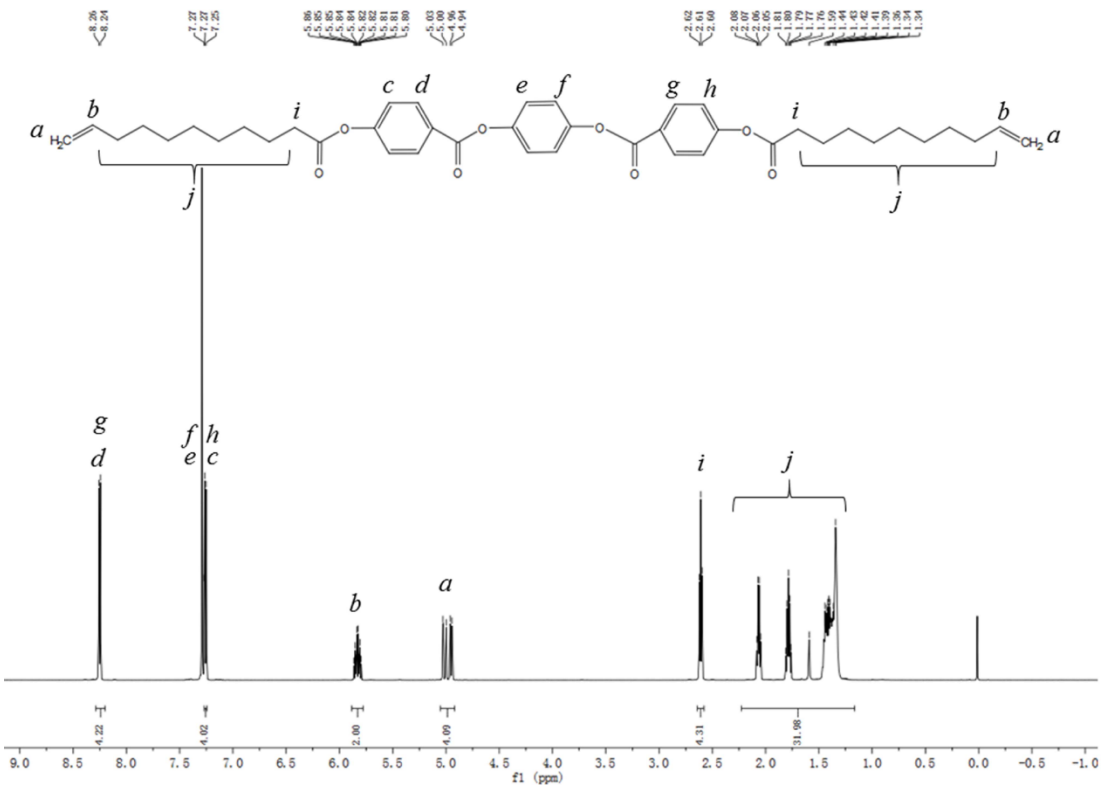

Fig. S3. ^{1}H NMR spectrum of CL (600MHz, $CDCl_3$)

3. FT-IR spectrograms

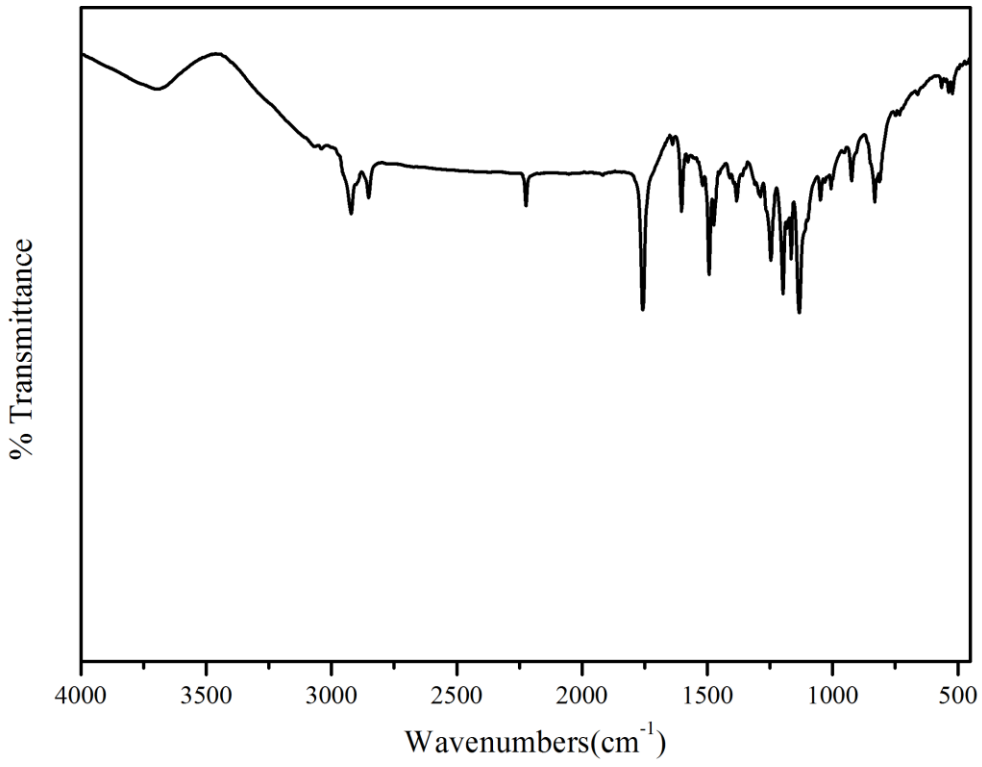

Fig. S4. FT-IR Spectrogram spectrum of M_1

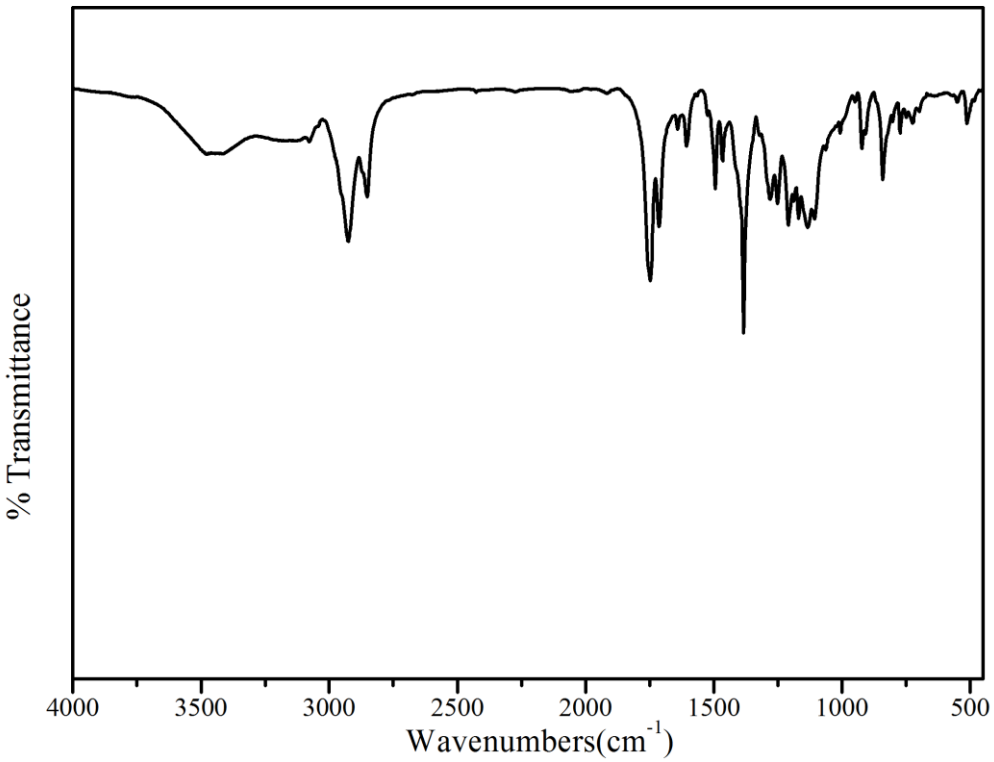

Fig. S5. FT-IR Spectrogram spectrum of M_2

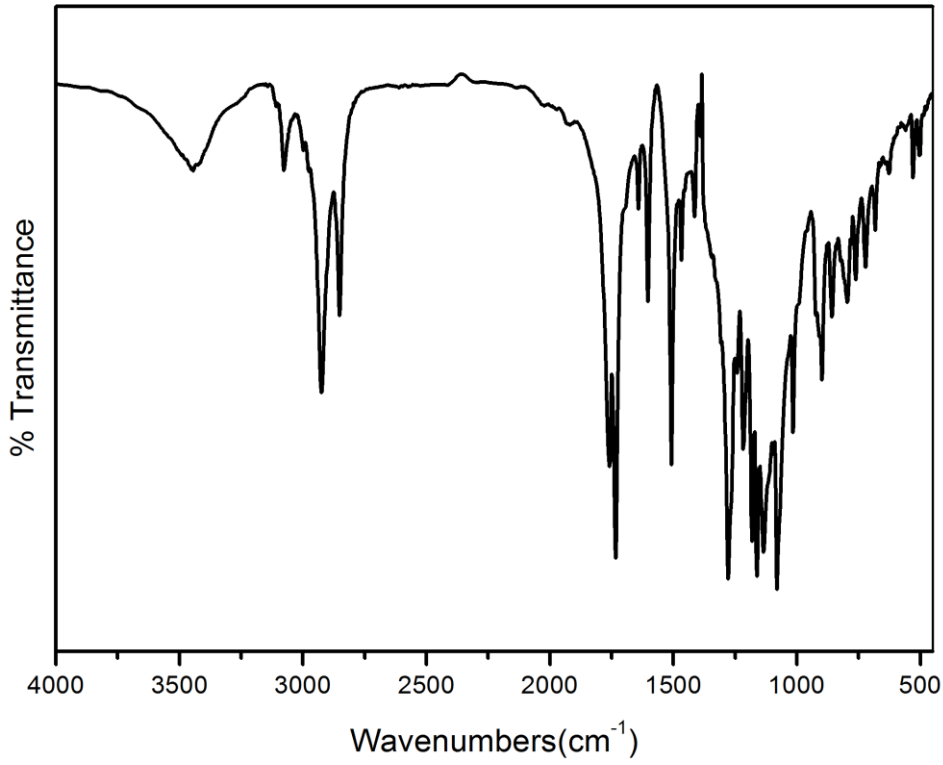

Fig. S6. FT-IR Spectrogram spectrum of CL

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