Electronic Supplementary Material (ESI) for Soft Matter.

# Supporting Information

for

# A homeotropic main-chain tolane-type liquid crystal elastomer film exhibiting high anisotropic thermal conductivity

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**General considerations.** 4-Iodophenol, 10-undecenol, 6-bromo-1-hexanol, triphenylphosphine (TPP), diisopropyl azodicarboxylate (DIAD), CuI, $PdCl_2(PPh_3)_2$, trimethylethynylsilane, dicyclohexylcarbodiimide (DCC), dimethylaminopyridine (DMAP), photoinitiator Lucirin 2,4,6-trimethylbenzoyldiphe-nylphosphine oxide (TPO), glyoxal bis(diallyl acetal) (GBDA) and pentaerythritol- tetrakis(3-mercaptopropionate) (PETMP) were purchased from Sigma-Aldrich. Dichloromethane and tetrahydrofuran were distilled from $CaH_2$ under nitrogen. Other chemical reagents were used without further purification. Anti-parallel surface-treated ITO-patterned 40 μm thick LC cells were received as gifts from Prof. Qing Li (Department of Electronic Engineering, Southeast University).

All NMR spectra were obtained using either a Bruker HW500 MHz spectrometer (AVANCE AV-500) or a Bruker HW300 MHz spectrometer (AVANCE AV-300) and recorded in $CDCl_3$ (internal reference 7.26 ppm). A high frequency linear amplifier (FLC ELECTRONICS AB model A800) was used to amplify the AC electric power produced by a Tektronix AFG2000-SC signal generator. The photopolymerization reactions were carried out under the irradiation of a UV lamp (20 $mW\cdot cm^{-2}$, $\lambda = 365$ nm; LP-40A, LUYOR Corporation). The thermal properties of the monomer and the xMELCP film were measured by using differential scanning calorimetry (DSC, TA Instruments Q10) under nitrogen purge at a heating rate of 10 °C /min. The liquid crystal textures of the monomer and the xMELCP film were examined using a polarizing optical microscope (Olympus BX53P) equipped with a Mettler PF82HT hot stage. The light transmittances of the LC samples were measured by using a photodetector (PD02, Instec Inc.).

X-ray scattering experiment was performed to ascertain the liquid crystal phase structure of the film and the monomer. The two dimensional X-ray scattering (2D-WAXS) experiments were performed using a Bruker D8Discover diffractometer with VANTEC 500 as a 2D detector. Corundum was used for calibration of the reflection peak positions. The diffraction patterns were recorded in the transmission mode at ambient temperature using uniaxially oriented film samples.

The thermal conductivity at room temperature was determined from the thermal diffusivity $\alpha$, density $\rho$ and specific heat $c$. The thermal conductivity $\lambda$ was calculated using the following Equation 1.[1]

$$\lambda = \alpha \times \rho \times c \,. \tag{1}$$

The thermal diffusivity ($\alpha$) of samples the films was measured by a method based on a Laser Flash Analysis (NETZSCH LFA LFA467 NanoFlash) at room temperature in a vacuum of 0.01 Pa.[2] In this method, the sample was prepared in a round shape with a 25.4 mm diameter as the sample holder was standard with fixed size and coated with a carbon layer on the entire surface by a carbon sprayer (KONTAKT CHEMIE) to enhance the thermal contact and to prevent direct transmission of the laser flash light through the specimen. Light pulse was used as a heating source to heat surface of sample firstly, and then infrared detector was used to measure the resulting temperature rise at four different positions. Ideally, light pulse width was close to infinitesimal, the thermal conduction process inside the sample was one-dimensional heat transfer from lower surface to upper surface, implying there was no lateral heat flux, no heat loss during the test process. The thermal diffusivity was determined by analyzing the temperature-versus-time curve based on the following Equation 2. [2]

$$\alpha = 0.1388 \times d^2 \times t_{1/2}^{-1}. \tag{2}$$

In Equation 2, $\alpha$ is the thermal diffusivity, $d$ is the thickness of the sample and $t_{1/2}$ is the half time of upper surface temperature rise to maximum after exposure to light pulses. Appropriate mathematical model was used to correct any deviation from ideal conditions during the actual measurement. Calculation Model "Cowan + Impulse Correction" and "In-plane + Impulse Correction" were used to modify thermal loss and calculate the thermal diffusivity in the normal direction and horizontal direction respectively.

The density ($\rho$) in Equation 2 is obtained according to Equation 3.

$$\rho = \frac{m}{V} \tag{3}$$

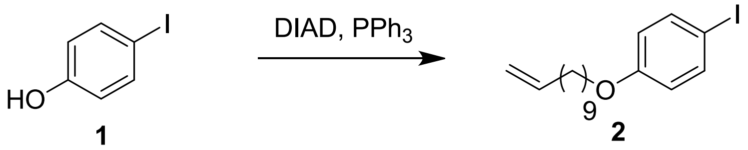
The mass ($m$) was available by weighing the sample using electronic precision balance. The volume ($V$) was determined by the superficial area and thickness of the sample. The thickness ($d$) was measured by a cardboard thickness detector working at specific contact area and pressure.

The specific heat capacity $c$ was measured by a differential scanning calorimeter (DSC, NETZSCH DSC 200 F3 Maia) at the heating rate of 10 $^{o}$C /min using sapphire method. Three tests including blank test, sapphire test, and sample test were carried out in turn. Firstly, the base curve of DSC was achieved by the blank test. The sapphire was selected as reference sample with known $c_{p_{standard}}$ = 0.78 J/g • K. Then the DSC curves, heat enthalpy change rate *dH/dt* as a function of time *t*, of the sample and sapphire were calibrated with the base curve. Comparing the DSC signal of sample with that of sapphire, $c_{p_{sample}}$ of the being tested sample could be calculated based on the following Equation 4:

$$\frac{DSC_{sample} - DSC_{blank}}{DSC_{standard} - DSC_{blank}} = \frac{c_{p_{sample}} \times m_{sample}}{c_{p_{standard}} \times m_{standard}} . \qquad (4)$$

$DSC_{sample}$, $DSC_{blank}$, $DSC_{standard}$ are the ordinate of the DSC curves corresponding to the sample, blank specimen, and standard specimen, respectively; $c_{p_{sample}}$ and $c_{p_{standard}}$ are the specific heat of the sample and standard specimen, respectively; $m_{sample}$ and $m_{standard}$ are the mass of the sample and sapphire, respectively.

## Synthesis of LC Monomer T6EE9.



**1-Iodo-4-(undec-10-en-1-yloxy)benzene (2).** The synthetic procedures is similar to that of the reference.[3] 4-Iodophenol (500 mg, 2.27 mmol) and triphenylphosphine ($PPh_3$, 710 mg, 2.71 mmol) were added to a reaction flask. 10-Undecenol (390 mg, 2.29 mmol) was added under $N_2$ and diluted with anhydrous THF (20 mL). DIAD (550 mg, 2.72 mmol) was added dropwise slowly into the reaction flask at 0 $^{o}$C. The reaction mixture was slowly warmed to room temperature and stirred at room temperature for 12 h. The resulting solution was concentrated and purified by flash chromatography (petroleum ether) to give the desired product **2** as a colorless oil (710 mg, Yield: 83 %). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 8.91 Hz, 2H), 6.67 (d, J = 8.88 Hz, 2H), 5.82 (m, 1H), 5.07 – 4.83 (m, 2H), 3.91 (t, J = 6.64 Hz, 2H), 2.04 (m, 2H), 1.84 – 1.68 (m, 2H), 1.48 – 1.26 (m, 12H).

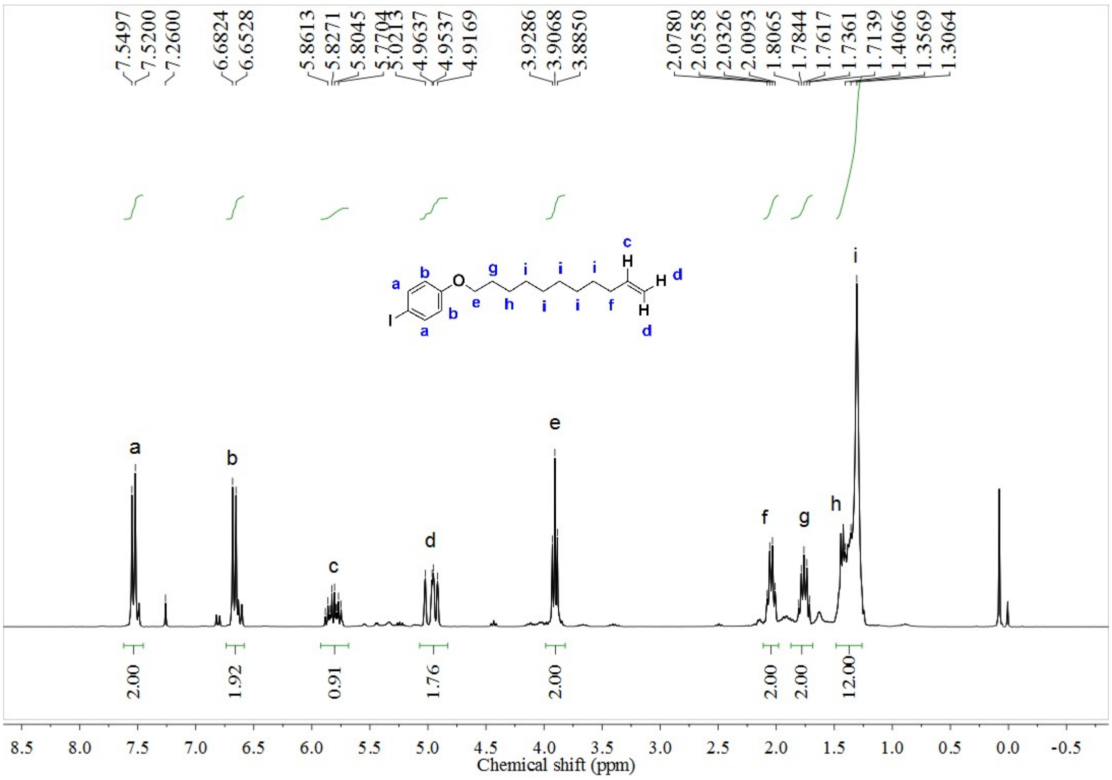
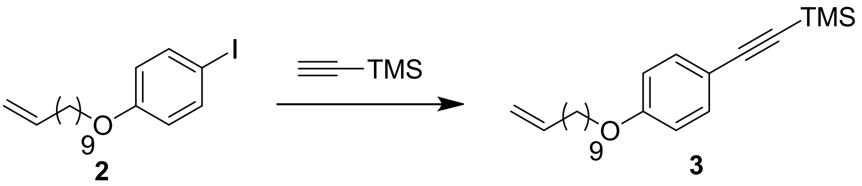


**Fig. S1** $^1$H NMR spectrum of compound **2**.



**Trimethyl((4-(undec-10-en-1-yloxy)phenyl)ethynyl)silane (3).** The synthetic procedures is similar to that of the references.[4-5] Compound **2** (650 mg, 1.75 mmol), CuI (50 mg, 0.26 mmol), $PdCl_2(PPh_3)_2$ (60 mg, 0.09 mmol) and triethylamine (0.73 mL, 5.25 mmol) were added into a reaction flask. Under an atmosphere of nitrogen, anhydrous THF and trimethylethynylsilane (190 mg, 1.90 mmol) were added. The reaction mixture was stirred at 40 °C overnight. The resulting solids were filtered off. The filtrate was concentrated and purified by flash chromatography (petroleum ether) to give the desired product **3** as a colorless oil (520 mg, Yield: 87 %). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, J = 8.76 Hz, 2H), 6.80 (d, J = 8.76 Hz, 2H), 5.82 (m, 1H), 4.97 (m, 2H), 3.94 (t, J = 6.56 Hz, 2H), 2.05 (q, J = 6.88 Hz, 2H), 1.84 – 1.70 (m, 2H), 1.31 (m, 12H), 0.24 (s, 9H) .

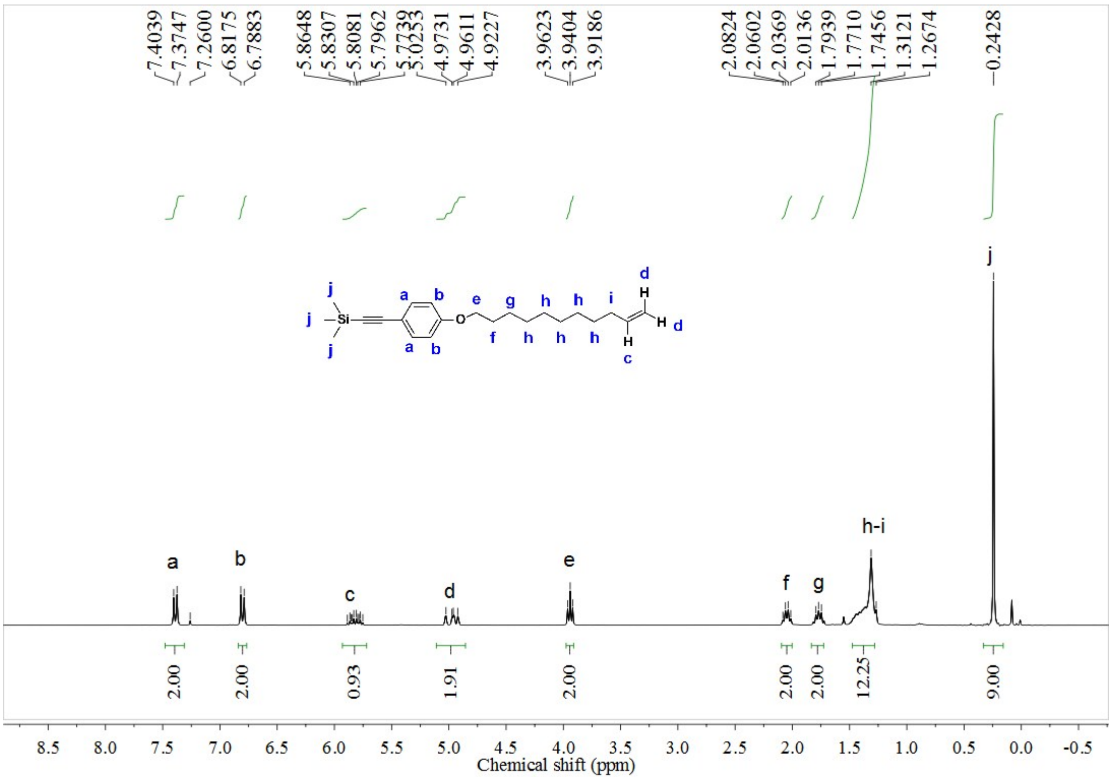
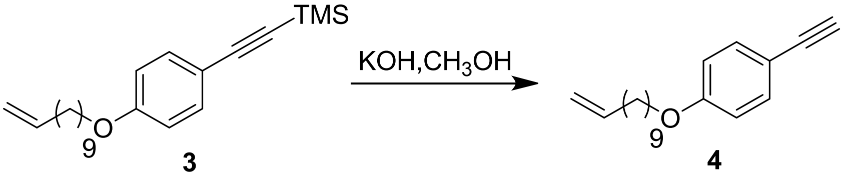


**Fig. S2** $^1$H NMR spectrum of compound **3**.



**1-Ethynyl-4-(undec-10-en-1-yloxy)benzene (4).** The synthetic procedures is similar to that of the reference.[6] In a reaction flask, compound **3** (400 mg, 1.15 mmol) was dissolved in a methanol solution, followed by the dropwise addition of an excess amount of aqueous KOH solution. The reaction mixture was stirred at room temperature for 2 h. Methanol was distilled off *via* rotovap. The resulting materials were diluted with a large amount of water and extracted with ethyl acetate. The organic layers were combined and dried over anhydrous sodium sulfate. The organic solution was concentrated to give the desired product **4** as a colorless oil (300 mg, Yield: 96 %). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.76 Hz, 2H), 6.83 (d, J = 8.76 Hz, 2H), 5.83 (m, 1H), 4.98 (m, 13.5 Hz, 2H), 3.95 (t, J = 6.54 Hz, 2H), 2.99 (s, 1H), 2.06 (q, J = 6.88 Hz, 2H), 1.85 – 1.72 (m, 2H), 1.38 (m, 12H).

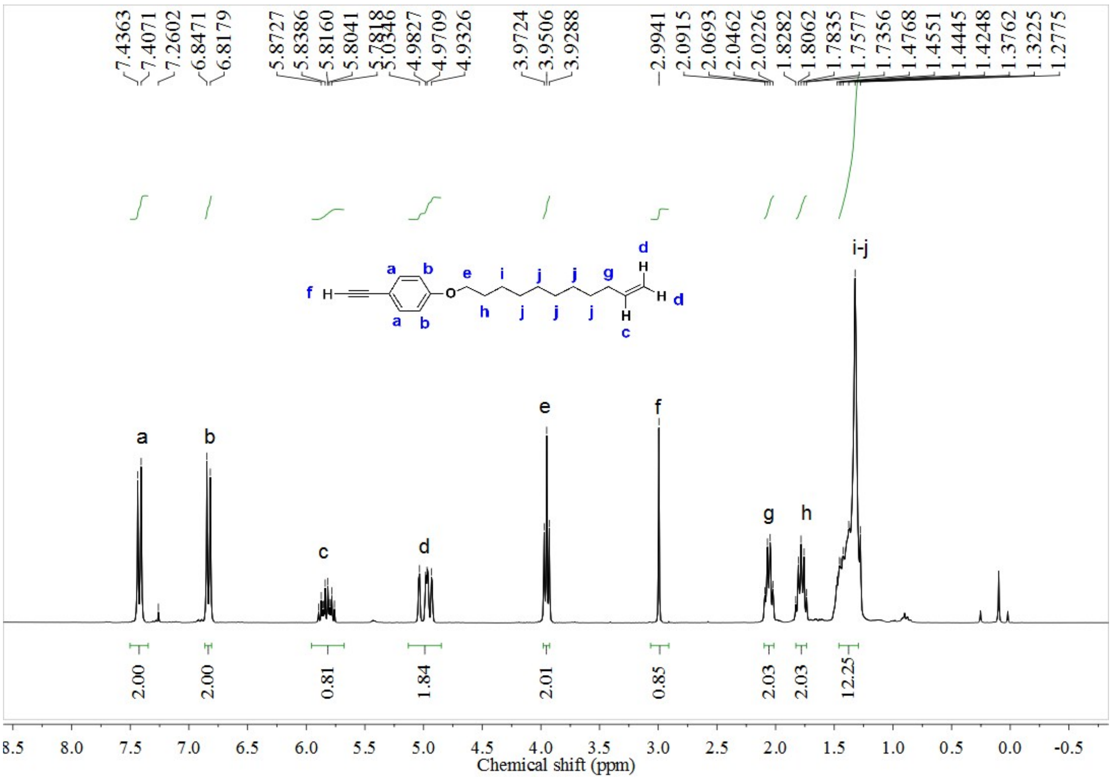
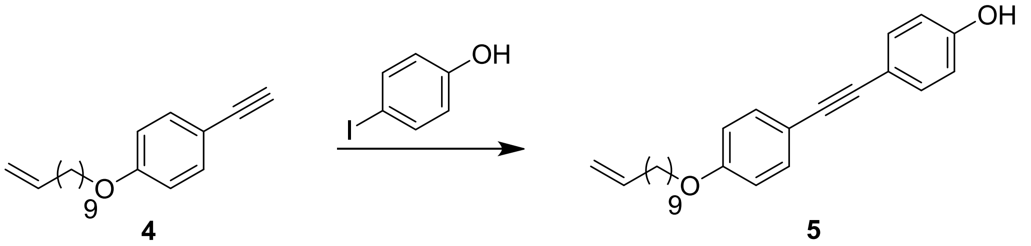


**Fig. S3** $^1$H NMR spectrum of compound **4**.



**4-((4-(Undec-10-en-1-yloxy)phenyl)ethynyl)phenol (5).** 4-Iodophenol (240 mg, 1.09 mmol), CuI (38 mg, 0.20 mmol), $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol) and triethylamine (0.42 mL, 3.00 mmol) were added into a reaction flask. Under an atmosphere of nitrogen, anhydrous THF and compound **4** (250 mg, 0.92 mmol) were added. The reaction mixture was stirred at 40 °C overnight. The resulting solids were filtered off. The filtrate was concentrated and purified by flash chromatography (petroleum ether : EtOAc, 20 : 1) to give the desired product **5** as a white solid (180 mg, Yield: 54 %). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 4H), 6.82 (m, 4H), 5.82 (m, 1H), 5.11 – 4.75 (m, 3H), 3.96 (t, J = 6.55 Hz, 2H), 2.05 (m, 2H), 1.86 – 1.71 (m, 2H), 1.49 – 1.28 (m, 12H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 159.03, 155.43, 139.20, 133.07, 132.84, 116.08, 115.46, 114.56, 114.11, 88.05, 87.71, 68.12, 33.78, 29.48, 29.39, 29.34, 29.20, 29.09, 28.92, 26.00.

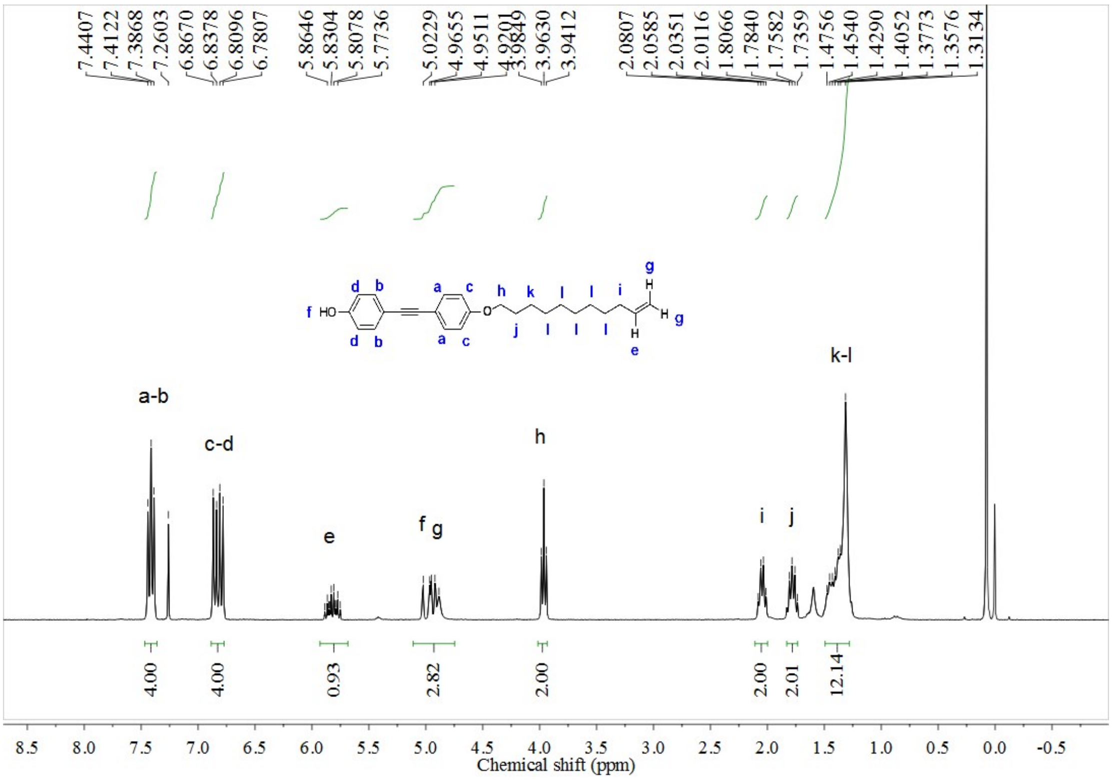


**Fig. S4** $^{1}$H NMR spectrum of compound **5**.

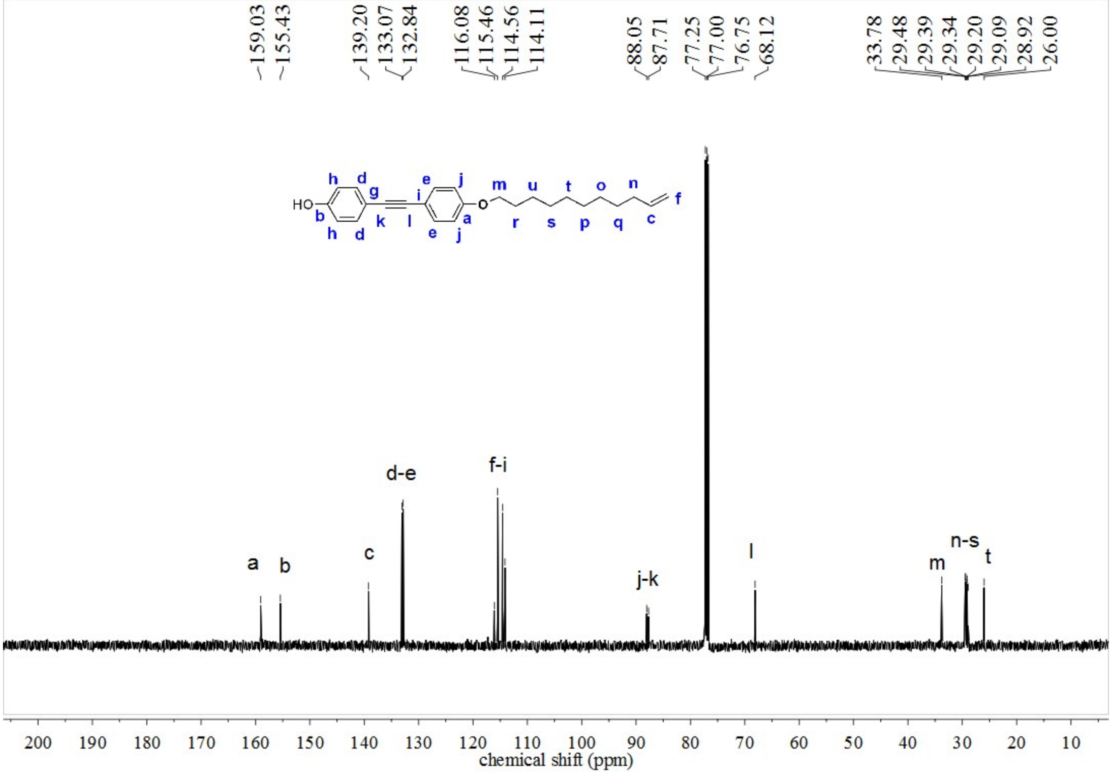
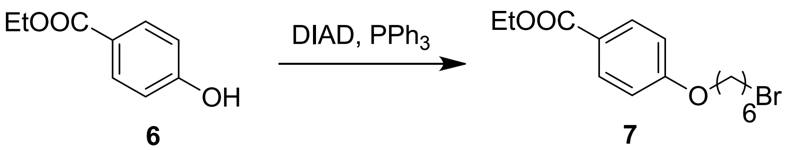


**Fig. S5** $^{13}$C NMR spectrum of compound **5**.



**6** **7**

**Ethyl 4-((6-bromohexyl)oxy)benzoate (7).** Compound **6** (500 mg, 3.01 mmol), and triphenylphosphine (1.26 g, 4.80 mmol) were dissolved in 20 mL dry THF. Under a nitrogen atmosphere, 6-bromo-1-hexanol (540 mg, 2.98 mmol), DIAD (970 mg, 4.80 mmol) were added into the above mixture at 0 °C. The reaction mixture was stirred at room temperature overnight and the solvent was removed *via* vacuum. The crude product was subsequently purified by flash column chromatography (petroleum ether : ethyl acetate, 20 : 1) to provide compound **7** as a white solid (790 mg, yield: 81%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 5.28 Hz, 2H), 6.88 (d, J = 5.28 Hz, 2H), 4.33 (q, J = 4.26 Hz, 2H), 3.99 (t, J = 3.84 Hz, 2H), 3.40 (t, J = 4.05 Hz, 2H), 1.91 – 1.84 (m, 2H), 1.82 – 1.77 (m, 2H), 1.52 – 1.46 (m, 4H), 1.36 (t, J = 4.28 Hz, 3H).

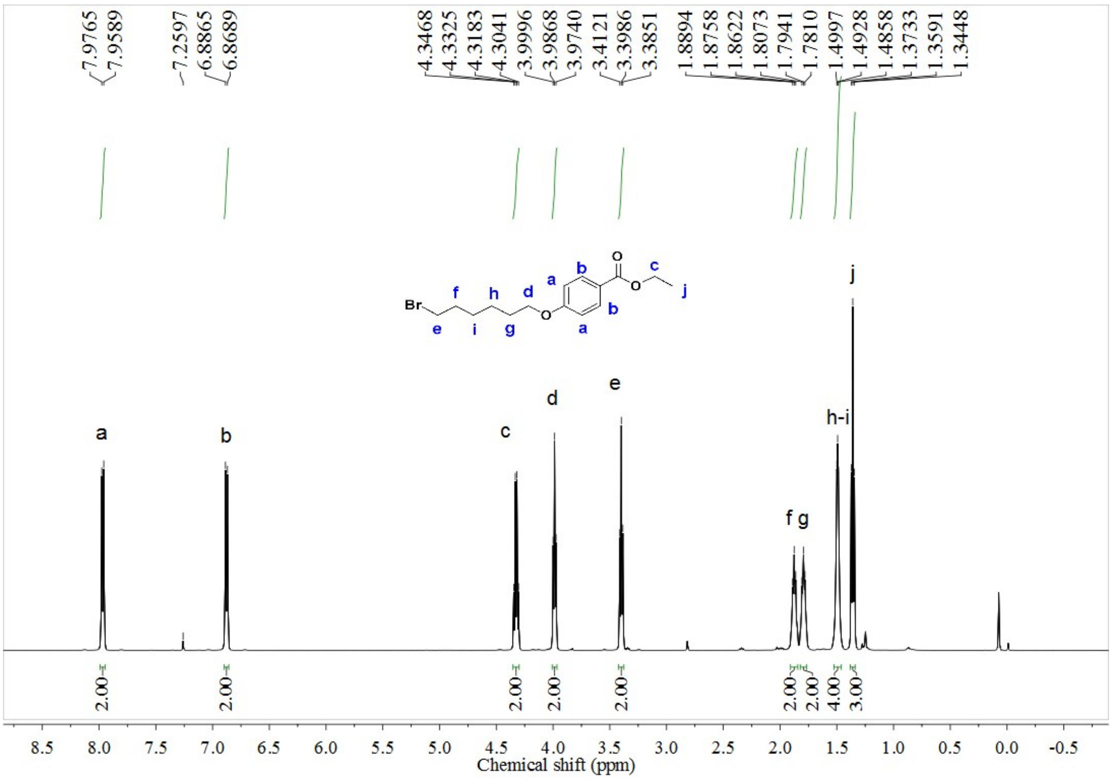
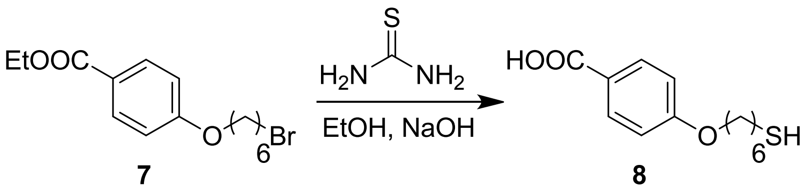


**Fig. S6** $^1$H NMR spectrum of compound **7**.



**4-((6-Mercaptohexyl)oxy)benzoic acid (8).**[7] Compound **7** (530 mg, 1.61 mmol), thiourea (190 mg, 2.50 mmol), ethanol (60 mL) were added into a 150 mL round-bottom flask under an atmosphere of nitrogen. The mixture was stirred at 88 ℃ for 20 h. After cooling to room temperature, the reaction mixture was diluted by sodium hydroxide solution (5 M, 1 mL) and the mixture was heated at reflux for 5 h at 85 °C. A hydrochloric acid solution (2.5 M) was slowly added into the above solution until the pH reached to 1.0. The solution was then diluted with 50 mL of distilled water and extracted with dichloromethane. The organic layer was concentrated and purified by flash chromatography (ethyl acetate) to give the desired product **8** as a white solid (330 mg, Yield: 81%). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.05 (d, J = 5.22 Hz, 2H), 6.93 (d, J = 5.22 Hz, 2H), 4.03 (t, J = 3.80 Hz, 2H), 2.55 (m, 2H), 1.82 (m, 2H), 1.66 (m, 2H), 1.49 (m, 4H), 1.34 (t, J = 4.64 Hz, 1H).

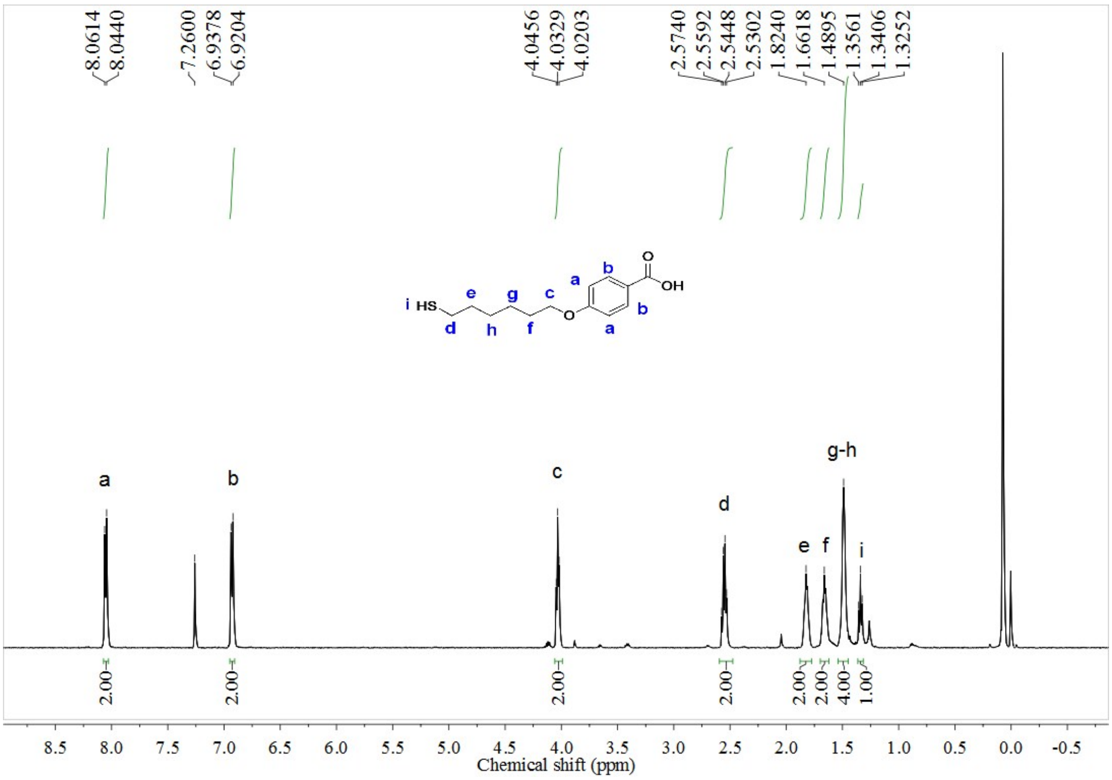
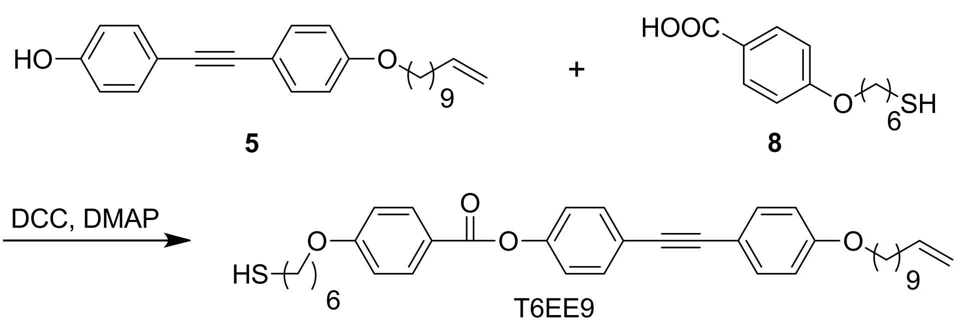


**Fig. S7** $^1$H NMR spectrum of compound **8**.



**4-((4-(Undec-10-en-1-yloxy)phenyl)ethynyl)phenyl4-((6-mercaptohexyl)oxy)benzoate (T6EE9).** Compound **5** (150 mg, 0.41 mmol), compound **8** (160 mg, 0.63 mmol), DMAP (27 mg, 0.22 mmol) and anhydrous dichloromethane were added into a 50 mL reaction flask. Under nitrogen atmosphere, DCC (130 g, 0.63 mmol) was added into the above flask at room temperature. The reaction mixture was stirred at room temperature for 12 h. After filtering off the solid, the resulting mixture was concentrated and purified by flash chromatography (petroleum ether : EtOAc, from 50 : 1 to 15 : 1) to give the desired monomer **T6EE9** (80 mg, yield: 33%) as a white solid. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J = 8.82 Hz, 2H), 7.55 (d, J = 8.61 Hz, 2H), 7.46 (d, J = 8.70 Hz, 2H), 7.19 (d, J = 8.58 Hz, 2H), 6.97 (d, J = 8.85 Hz, 2H), 6.87 (d, J = 8.76 Hz, 2H), 5.82 (m, 1H), 5.12 – 4.85 (m, 2H), 4.05 (t, J = 6.40 Hz, 2H), 3.97 (t, J = 6.54 Hz, 2H), 2.56 (m, 2H), 2.05 (m, 2H), 1.91 – 1.73 (m, 4H), 1.66 (m, 2H), 1.54 – 1.28 (m, 17H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 164.60, 163.54, 159.27, 150.66, 139.17, 133.00, 132.53, 132.29, 121.83, 121.45, 121.19, 115.02, 114.56, 114.32, 114.10, 89.51, 87.30, 68.12, 68.02, 33.82, 33.76, 29.47, 29.38, 29.33, 29.18, 29.08, 28.96, 28.91, 28.02, 25.98, 25.49, 24.48.

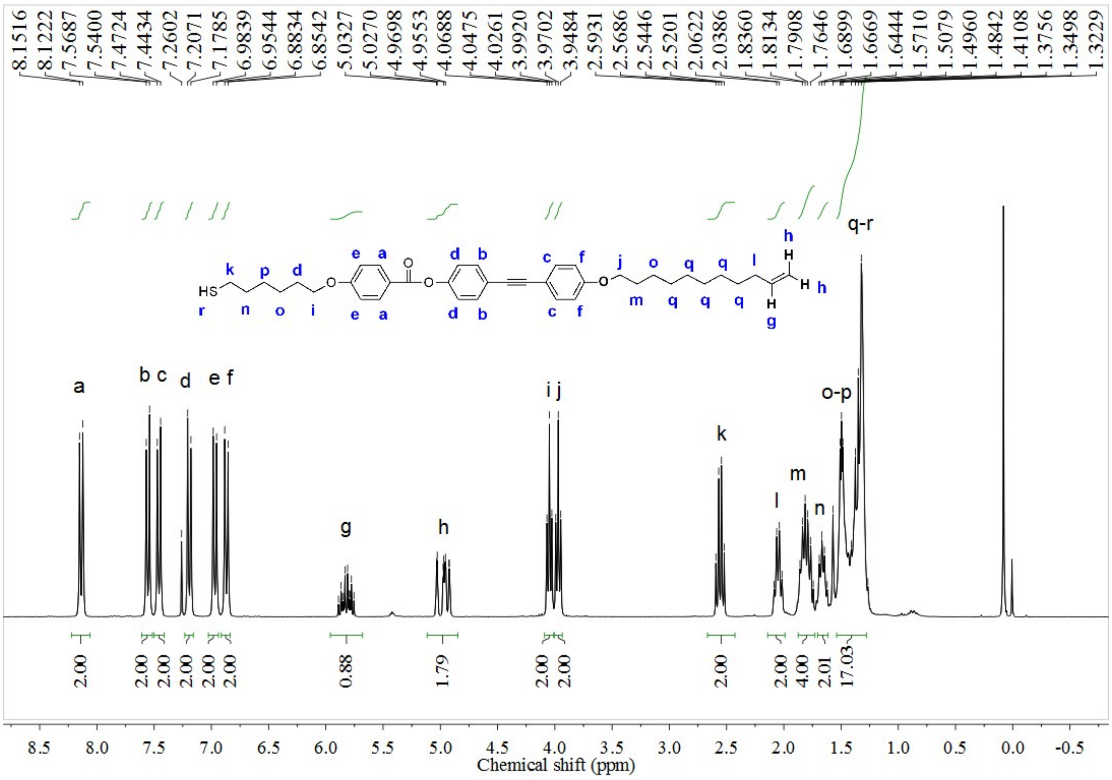


**Fig. S8** $^{1}$H NMR spectrum of **T6EE9**.

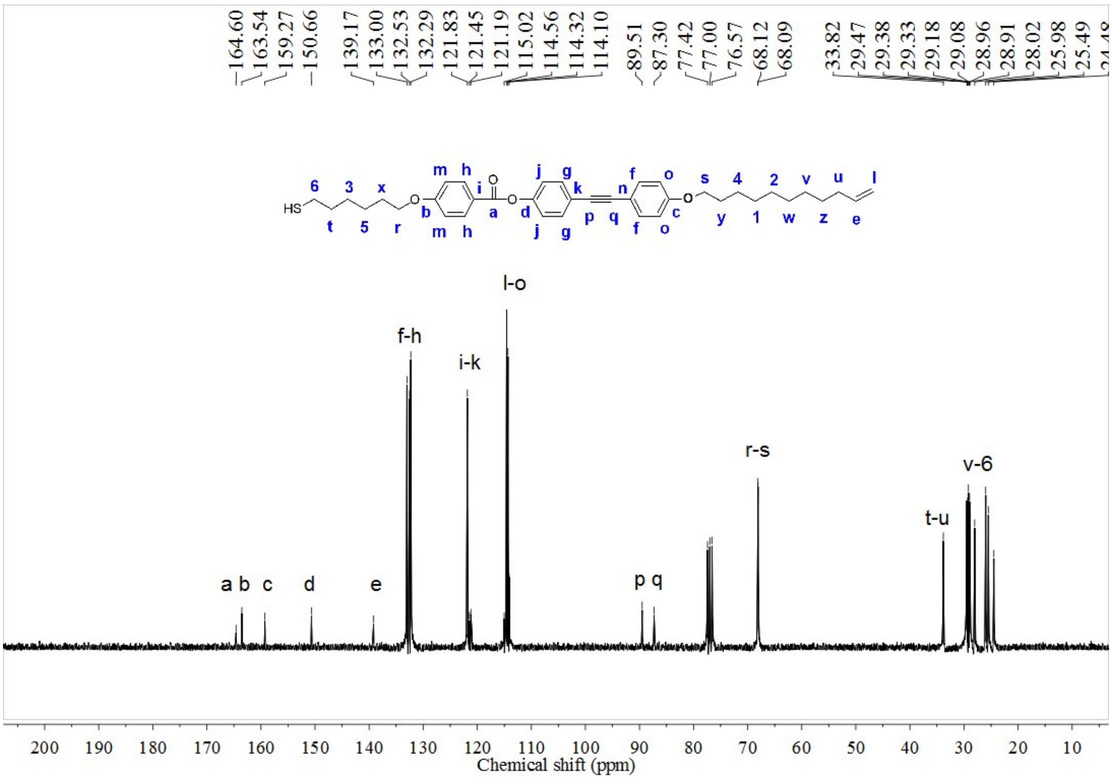


**Fig. S9** $^{13}$C NMR spectrum of **T6EE9**.

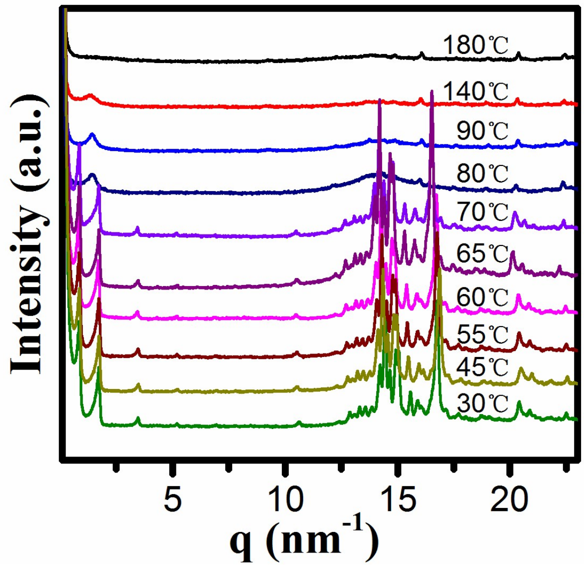


**Fig. S10** One-dimensional WAXS patterns of LC monomer **T6EE9**.

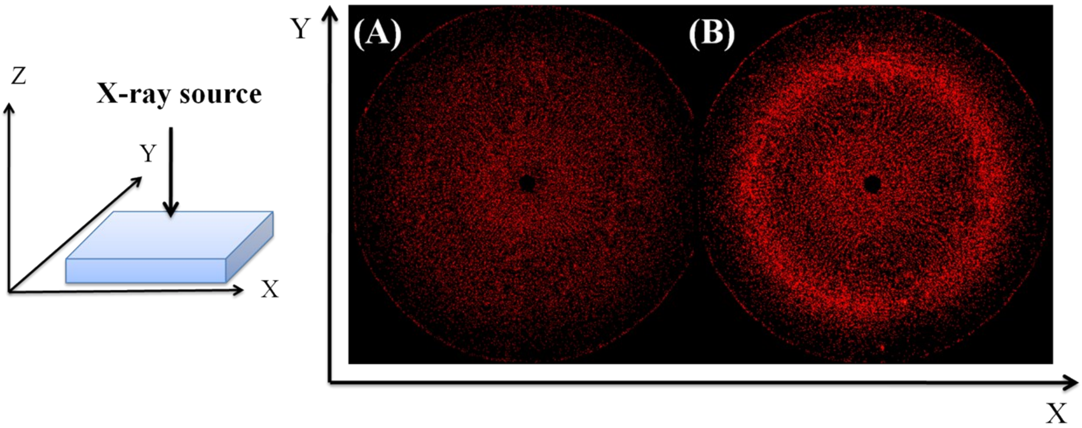


**Fig. S11** The ITO region (A) and the non-ITO region (B) of xMELCP films by the incident beam normal to the film plane, recorded at 25℃.

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## References:

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