

## Supporting Information

for

### A Calamitic Mesogenic Near-Infrared Absorbing Croconaine Dye/Liquid Crystalline Elastomer Composite

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### **General considerations:**

Croconic acid was purchased from Alfa Aesar Inc. 2,5-Dihydroxybenzoic acid, hexamethylene diacrylate and 2-thiophenethiol were purchased from TCI Inc. 4-Butyloxybenzoic acid, methyl isonipecotate, dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), 2,2-dimethoxy-2-phenylacetophenone (DMPA), 4-hydroxybutylacrylate, and n-decyl alcohol were purchased from Aladdin (Shanghai) Inc. Dichloromethane, toluene and DMF were distilled from CaH<sub>2</sub> under nitrogen. Other chemical reagents were used without purification. All non-aqueous reactions were conducted in oven-dried glasswares, under a dry nitrogen atmosphere. All flash chromatography were performed using Macherey-Nagel MN Kieselgel 60 (0.063-1.2 mm). Antiparallel liquid crystal cells (S100A220UG180) were purchased from Instec Inc.

All <sup>1</sup>H spectra and <sup>13</sup>C NMR 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<sub>3</sub> (internal reference 7.26 ppm). High-resolution mass spectra were obtained with Waters Micromass Q-TOF micro system mass spectrometer in positive ion mode. Differential scanning calorimetry (DSC) spectra were recorded on a TA Instruments Q100 instrument (New Castle, DE) under nitrogen purge at a heating rate of 10 °C/min. UV-vis spectra were obtained with a TU-1810 ultraviolet-visible spectrophotometer (UV/VIS spectrometer) (Beijing Purkinje General Corp., China).

A UV lamp (20 mW·cm<sup>-2</sup>, λ = 365 nm; LP-40A; LUYOR Corporation) was used to irradiate on the LC mixture samples to perform the photo-crosslinking reactions. Fluke Thermal Imager (FLK-TI95) was used to measure the instant temperature changes of the film surfaces. All NIR-responsive experiments were performed using a 808 nm semiconductor laser source (Output power: 8W, Center wavelength: 808 ± 3 nm, Nanjing Latron Laser Company, China).

The preparatios of these films were performed on a Mettler PF82HT hot stage. Polarized optical microscopy (POM) observations of the liquid crystalline textures of the films were performed on an Olympus BX53P microscope with a Mettler PF82HT

hot stage. The images were captured using a Microvision MV-DC200 digital camera with a Phenix Phmias2008 Cs Ver2.2 software. X-ray scattering experiments were performed with a high-flux small angle X-ray scattering instrument (SAXSess, Anton Paar) equipped with Kratky block-collimation system and a temperature control unit (Anton Paar TCS300). At each single steady temperature, both small angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) were simultaneously recorded on an imaging-plate (IP) which extended to high-angle range (the  $q$  range covered by the IP was from 0.06 to 29  $\text{nm}^{-1}$ ,  $q = 4\pi(\sin \theta)/\lambda$ , where the wavelength  $\lambda$  is 0.1542 nm of Cu  $K\alpha$  radiation and  $2\theta$  is the scattering angle) at 40 kV and 40 mA for 30 min.

#### **The preparation procedure of LCE/YHD796 composite film**

LC monomer **A444** (30.11 mg,  $4.76 \times 10^{-2}$  mmol), hexamethylene diacrylate (1.20 mg,  $5.29 \times 10^{-3}$  mmol), 2,2-dimethoxy-2-phenylacetophenone (0.34 mg,  $1.33 \times 10^{-3}$  mmol) and **YHD796** (0.42 mg,  $0.53 \times 10^{-3}$  mmol) were mixed and dissolved in  $\text{CH}_2\text{Cl}_2$  which was then evaporated to provide the LC mixture. The mixture was filled by capillarity into an antiparallel homogeneous-aligned LC cell with 20  $\mu\text{m}$  gap placed on a hot stage which set the temperature at 120  $^\circ\text{C}$ . The LC cell was slowly cooled down to 60  $^\circ\text{C}$  at a rate of -1.0  $^\circ\text{C}$  per minute and annealed at 60  $^\circ\text{C}$  for ca. 2 h to achieve a fine planar alignment. A subsequent UV irradiation was carried out under a stream of nitrogen gas (using a zip-lock bag). After UV irradiation (365 nm, 20  $\text{mW}\cdot\text{cm}^{-2}$ ) for 1.5 h, the LC cell was placed into a 40% hydrofluoric acid solution for 3 days to dissolve up the glass cell and give the desired LCE/**YHD796** composite as a free-standing film.

#### **The preparation procedure of pure LCE film**

LC monomer **A444** (29.63 mg,  $4.69 \times 10^{-2}$  mmol), hexamethylene diacrylate (1.17 mg,  $5.18 \times 10^{-3}$  mmol) and 2,2-dimethoxy-2-phenylacetophenone (0.33 mg,  $1.29 \times 10^{-3}$  mmol) were mixed and dissolved in  $\text{CH}_2\text{Cl}_2$  which was then evaporated to provide the LC mixture. The mixture was filled by capillarity into an antiparallel homogeneous-

aligned LC cell with 20  $\mu\text{m}$  gap placed on a hot stage which set the temperature at 120  $^{\circ}\text{C}$ . The LC cell was slowly cooled down to 60  $^{\circ}\text{C}$  at a rate of -1.0  $^{\circ}\text{C}$  per minute and annealed at 60  $^{\circ}\text{C}$  for ca. 2 h to achieve a fine planar alignment. A subsequent UV irradiation was carried out under a stream of nitrogen gas (using a zip-lock bag). After UV irradiation (365 nm, 20  $\text{mW}\cdot\text{cm}^{-2}$ ) for 0.5 h, the LC cell was placed into a 40% hydrofluoric acid solution for 3 days to dissolve up the glass cell and give the desired pure LCE as a free-standing film.

### **Synthesis of YHD1**

#### **1-Thiophen-2-yl-piperidine-4-carboxylic acid methyl ester (6)**

Methyl isonipecotate (2.79 g, 19.51 mmol), thiophene-2-thiol (1.62 g, 13.93 mmol) and 20 mL of toluene were added into a 50 mL three-neck round-bottom flask equipped with a magnetic stirrer, a nitrogen inlet tube and a water-cooled condenser. The resulting mixture was heated to reflux for 3 h. After cooling to room temperature, the mixture was transferred into a 100 mL round-bottom flask, and diluted with ethyl acetate. The solvents were concentrated by rotary evaporation to provide a crude light-yellow solid. The crude sample was purified by column chromatography (petroleum ether : ethyl acetate = 10/1) to give the desired product **6** (1.96 g, yield: 62.6 %) as a white solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.77 (m, 1H), 6.60 (m, 1H), 6.13 (d,  $J = 5$  Hz, 1H), 3.73 (s, 3H), 3.52 (m, 2H), 2.84 (m, 2H), 2.44 (m, 1H), 2.02 (m, 2H), 1.93 – 1.82 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 174.94, 159.37, 126.05, 112.42, 105.77, 51.63, 40.41, 25.73.

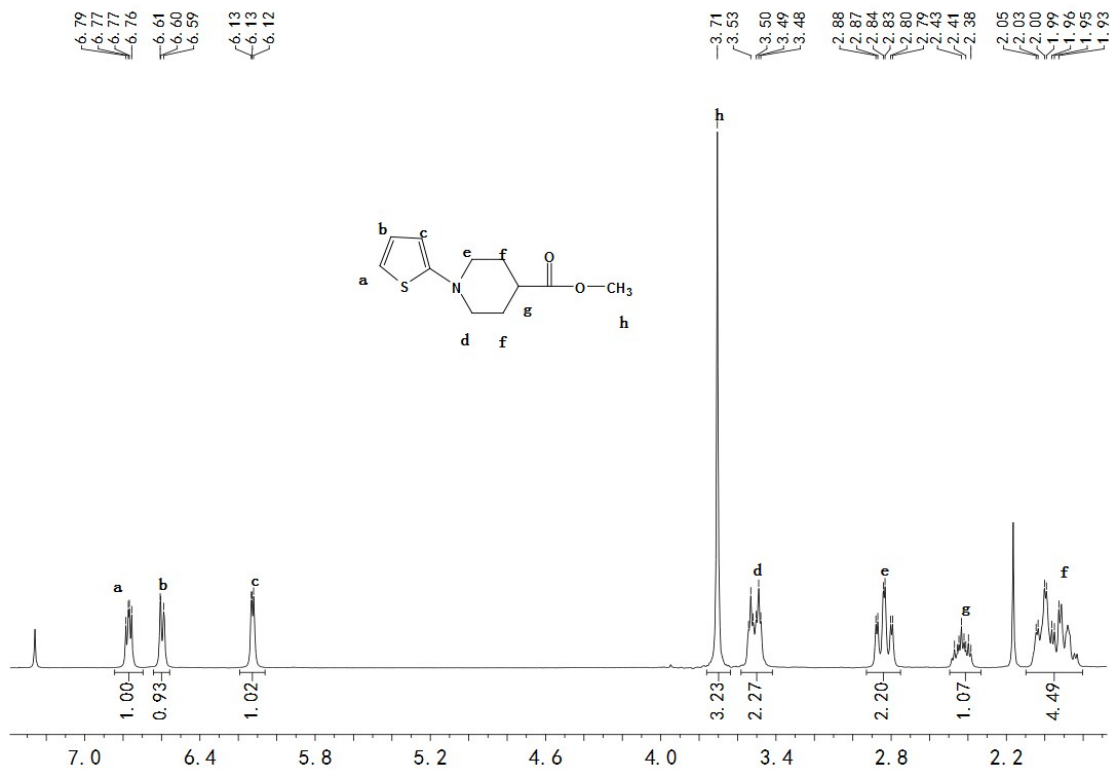


Figure S1. <sup>1</sup>H NMR spectrum of Compound 6.

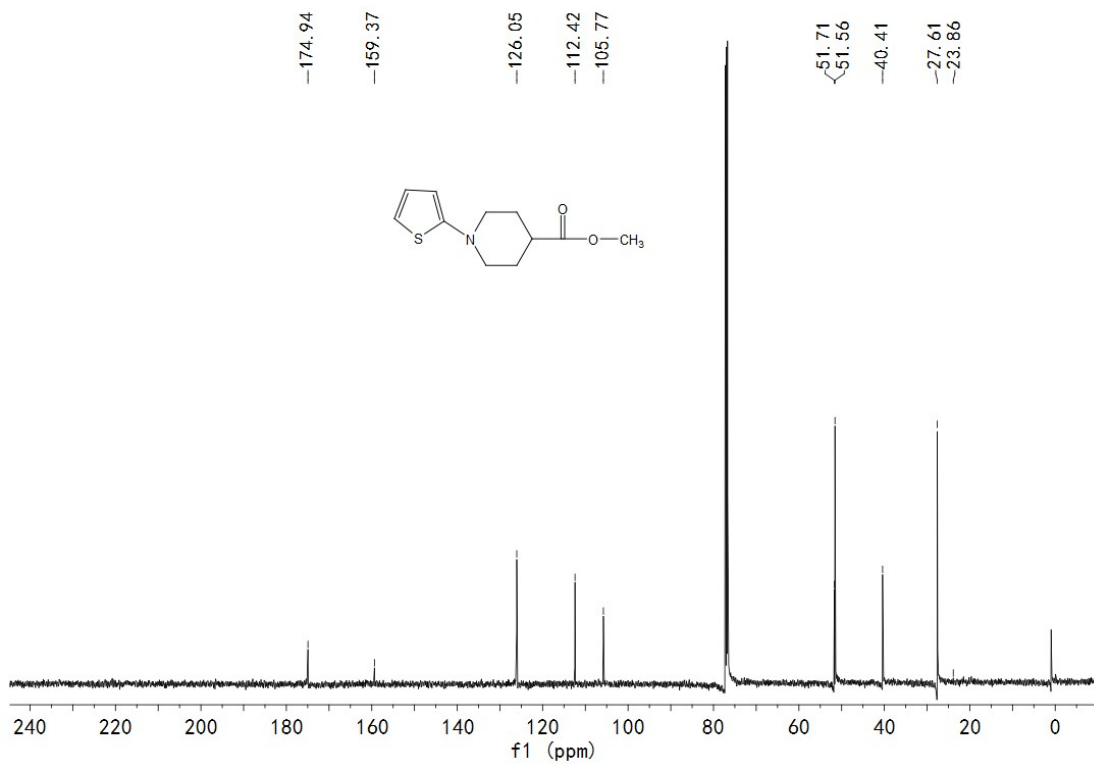


Figure S2. <sup>13</sup>C NMR spectrum of Compound 6.

### 2,5 -bis[(4-carboxylic-piperidylamino) thiophenyl]-croconium (2, YHD1).

Croconic acid **7** (0.14 g, 0.98 mmol) and compound **6** (0.45 g, 1.99 mmol) were added into a solution of 30 mL toluene/n-butanol (v/v, 1/1) under nitrogen atmosphere. The reaction mixture was heated to reflux for 1h. After cooled to room temperature, the precipitate was collected by filtration, washed with methanol and dried under vacuum to give the desired product **YHD1** (0.59 g, yield 55.3%) as a black solid. M.P. 236 – 237 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.65 (m, 2H), 6.54 (m, 2H), 3.92 (m, 4H), 3.71 (s, 6H), 3.43 (m, 4H), 2.67 (m, 2H), 2.09 (m, 4H), 1.92 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 173.60, 140.91, 124.15, 112.76, 52.05, 50.37, 39.53, 31.85, 29.62, 29.28, 27.84, 27.42.

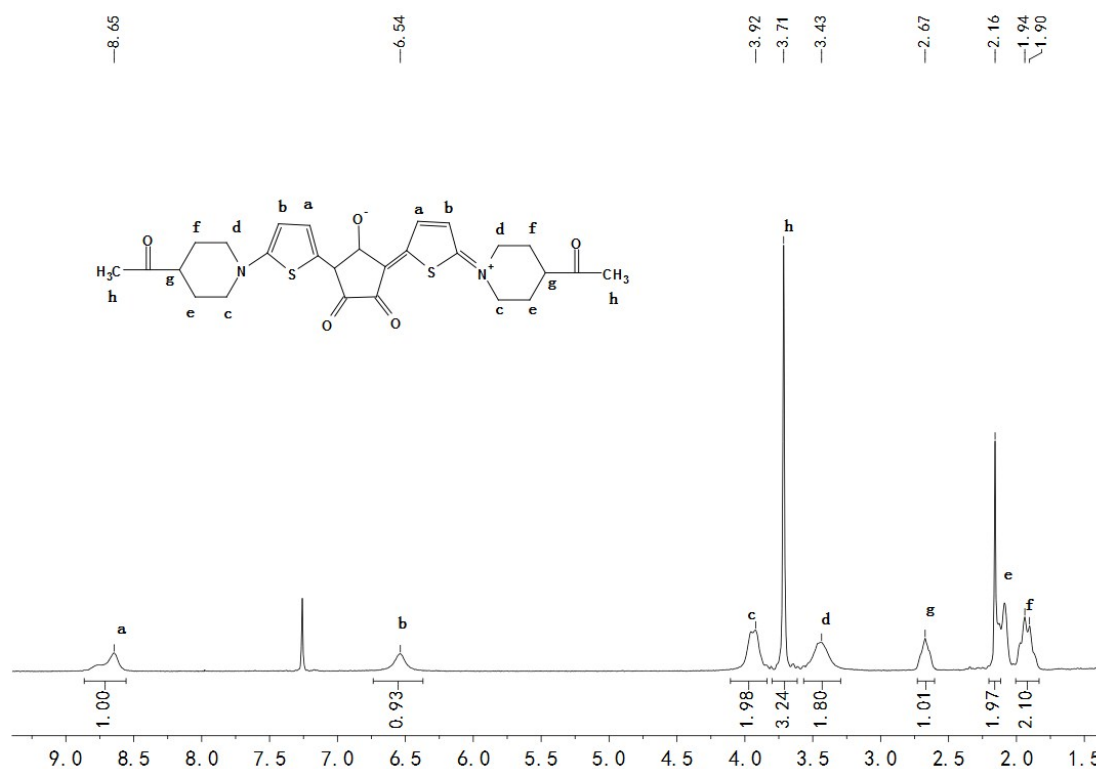
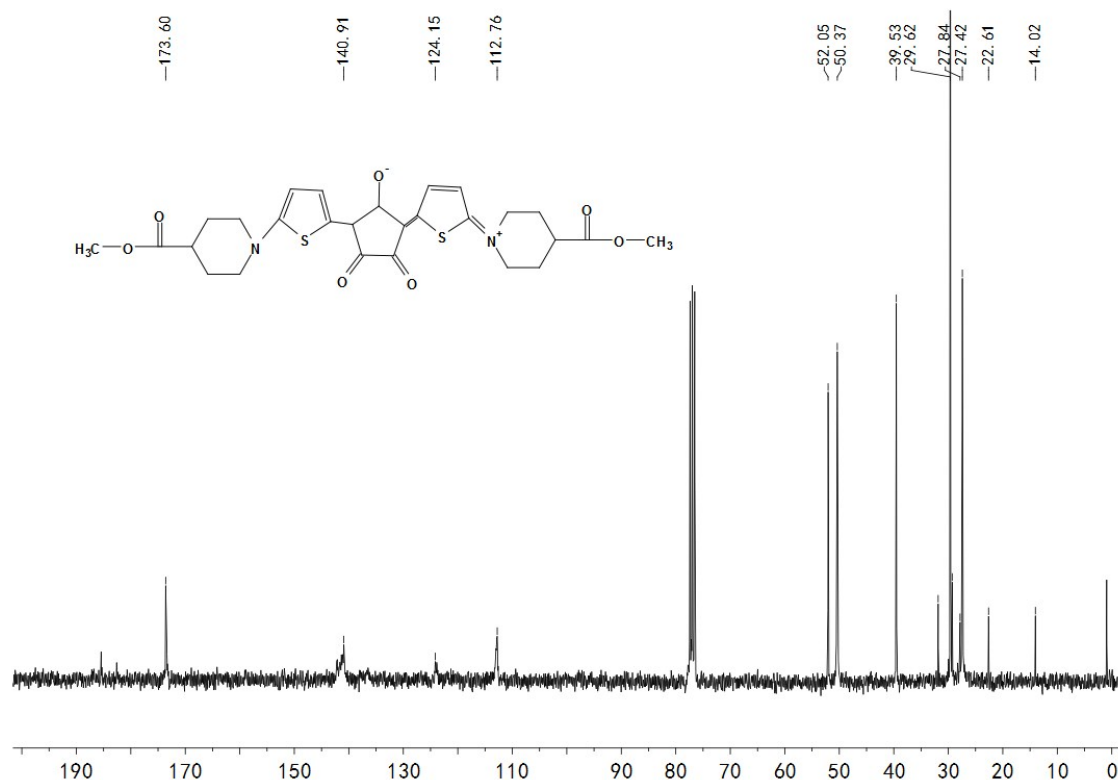


Figure S3. <sup>1</sup>H NMR spectrum of YHD1.

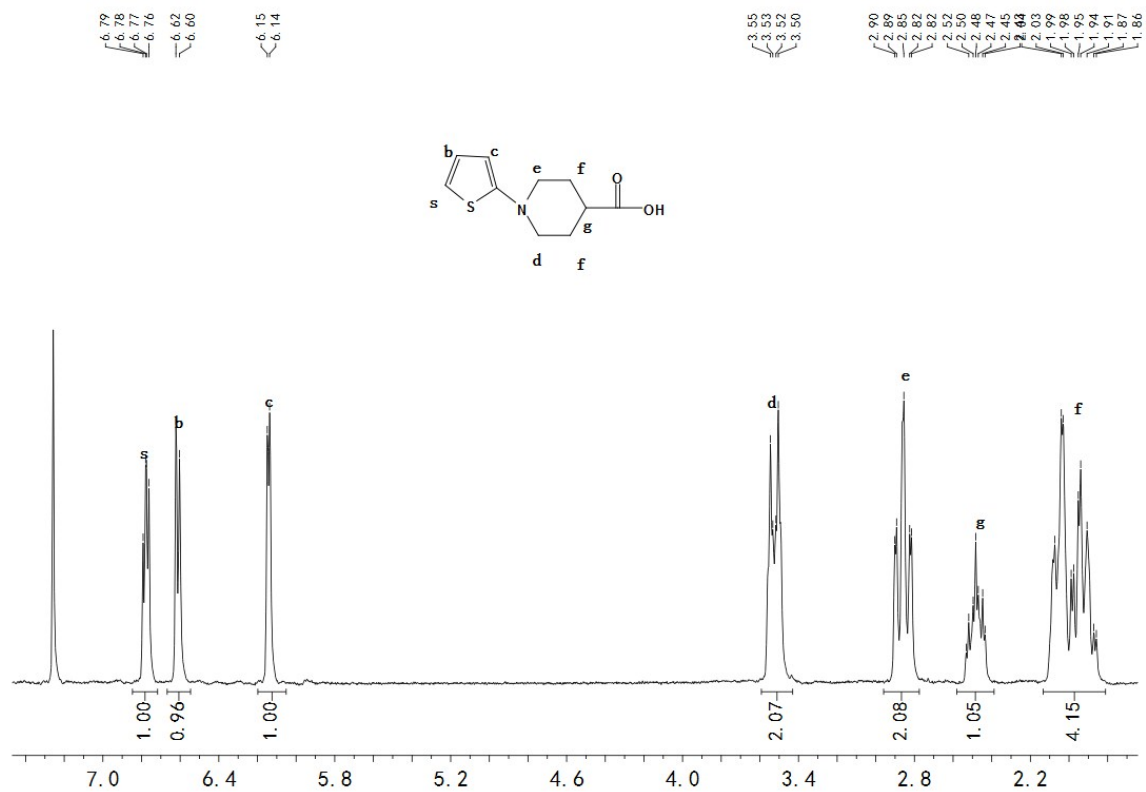


**Figure S4.**  $^{13}\text{C}$  NMR spectrum of **YHD1**.

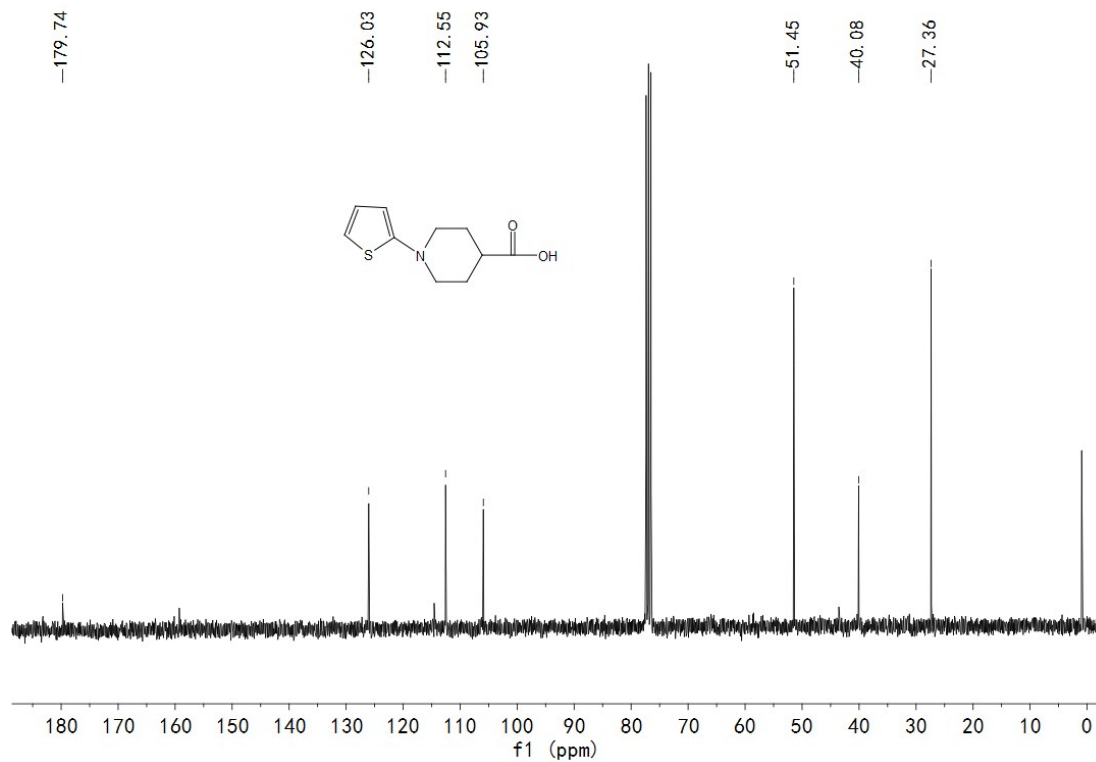
### **Synthesis of YHD796**

#### **1-Thiophen-2-yl-piperidine-4-carboxylic acid (**8**).**

Compound **6** (1.00 g 4.45 mmol) and 25 mL of 0.5 N sodium hydroxide solution were added into a 100 mL round-bottom flask. The reaction mixture was heated at reflux temperature for 3h. After cooled to room temperature, the mixture was acidified with 10 mL of aqueous acetic acid (conc. 10%). The precipitate product was collected by filtration and dried under vacuum, to give intermediate **8** as a white solid (0.76 g, yield 80.8%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.78 (dd,  $J = 6.0, 3.0$  Hz, 1H), 6.61 (d,  $J = 6.0$  Hz, 1H), 6.14 (d,  $J = 3.0$  Hz, 1H), 3.52 (m, 2H), 2.94 – 2.76 (m, 2H), 2.48 (m, 1H), 1.96 (m, 4H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 179.74, 160.59, 126.03, 112.55, 105.93, 51.45, 40.08, 27.36.



**Figure S5.** <sup>1</sup>H NMR spectrum of Compound 8.



**Figure S6.** <sup>13</sup>C NMR spectrum of Compound 8.



### 1-Thiophen-2-yl-piperidine-4-carboxylic acid decyl ester (9).

Compound **8** (0.76 g, 3.60 mmol), n-decyl alcohol (0.68 g, 4.34 mmol), DMAP (0.02 g, 0.18 mmol) and dry CH<sub>2</sub>Cl<sub>2</sub> (25 mL) were added into a 50 mL Schlenk-type flask. Under a nitrogen atmosphere, DCC (0.88 g, 4.27 mmol) was added into the above flask in one portion at 0 °C, the reaction solution was stirred at room temperature for 24 h. After filtering off the precipitate, the solute was concentrated by rotary evaporation and the crude oil was purified by column chromatography (petroleum ether : ethyl acetate = 15/1) to give the product **9** (0.70 g, yield 55.6%) as a colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 6.77 (dd, *J* = 6.0, 3.0 Hz, 1H), 6.60 (t, *J* = 6.0 Hz, 1H), 6.13 (m, 1H), 4.16 – 4.03 (t, *J* = 8.3 Hz, 2H), 3.51 (m, 2H), 2.84 (m, 2H), 2.42 (m, 1H), 2.07 – 1.87 (m, 4H), 1.40 – 1.22 (m, 16H), 0.89 (t, *J* = 6.6 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 174.51, 126.02, 112.31, 105.65, 64.64, 51.55, 40.57, 31.84, 29.60, 28.99, 28.60, 27.66, 25.88, 22.62, 14.04.

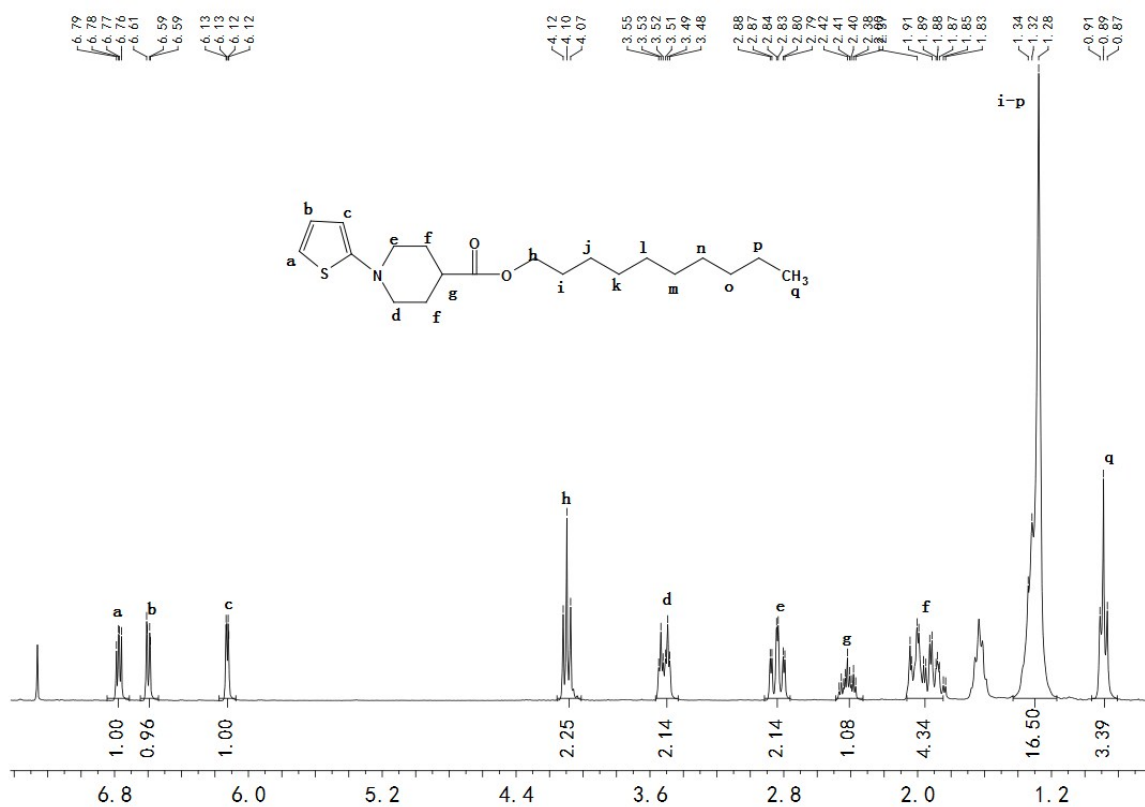
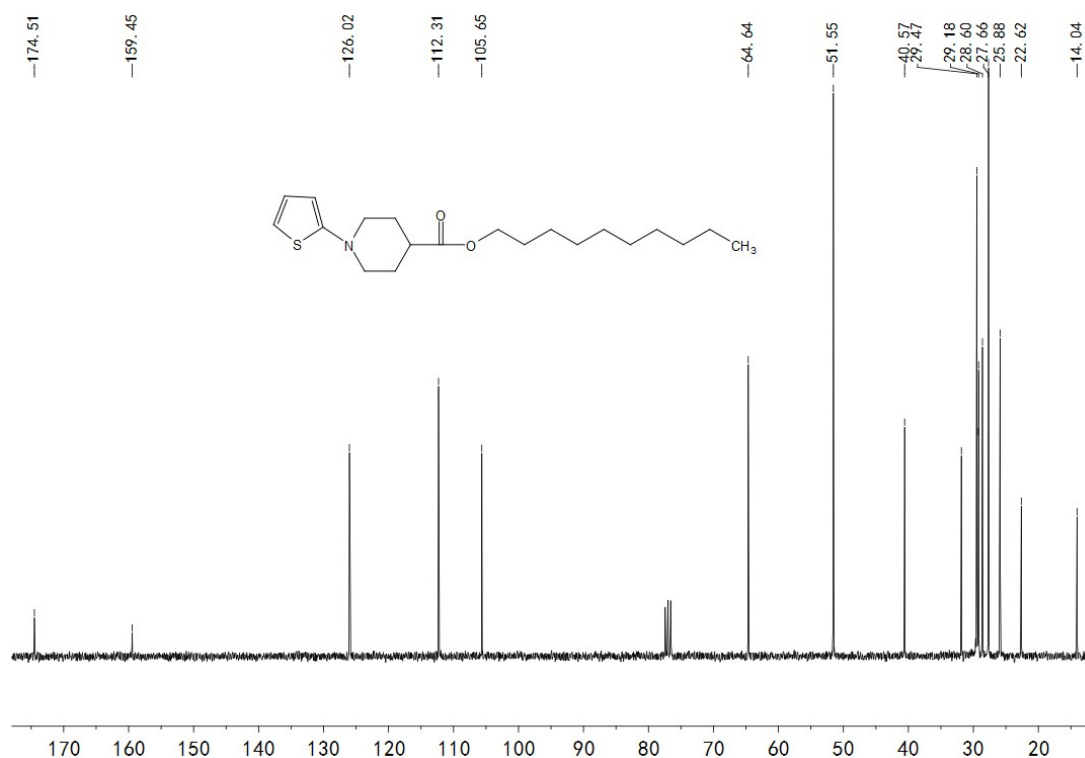


Figure S7. <sup>1</sup>H NMR spectrum of Compound **9**.



**Figure S8.**  $^{13}\text{C}$  NMR spectrum of Compound **9**.

**2,5-Bis[(decyl-4-carboxylate-piperidylamino) thiophenyl]-croconium (YHD796).**

Croconic acid **7** (0.14 g, 0.98 mmol) and compound **9** (0.69 g, 1.96 mmol) were added into a solution of 30 mL toluene/n-butanol (v/v, 1/1) under nitrogen atmosphere. The reaction mixture was heated to reflux for 1 h. After cooled to room temperature, the mixture was transferred into a 100 mL round-bottom flask and diluted with 15 mL dichloromethane. These solvents were concentrated by rotary evaporation and the resulting crude black solid was purified by column chromatography ( $\text{CH}_2\text{Cl}_2$  : methanol = 50/1) to give the desired product **YHD796** (0.64 g, yield 79.9%) as a black solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.67 (m, 2H), 6.50 (m, 2H), 4.08 (t,  $J$  = 8.3 Hz, 4H), 3.89 (m, 4H), 3.41 (m, 4H), 2.63 (m, 2H), 1.95 (m, 8H), 1.65 (m, 4H), 1.26 (m, 28H), 0.85 (t,  $J$  = 6.0 Hz, 6H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 173.21, 141.21, 124.29, 113.00, 65.15, 50.41, 39.71, 31.81, 30.64, 24.09, 22.59, 14.02. ESI-MS  $m/z$ : 831.6 [ $m+\text{Na}$ ] $^+$ , calculated for **YHD796**, 808.6.

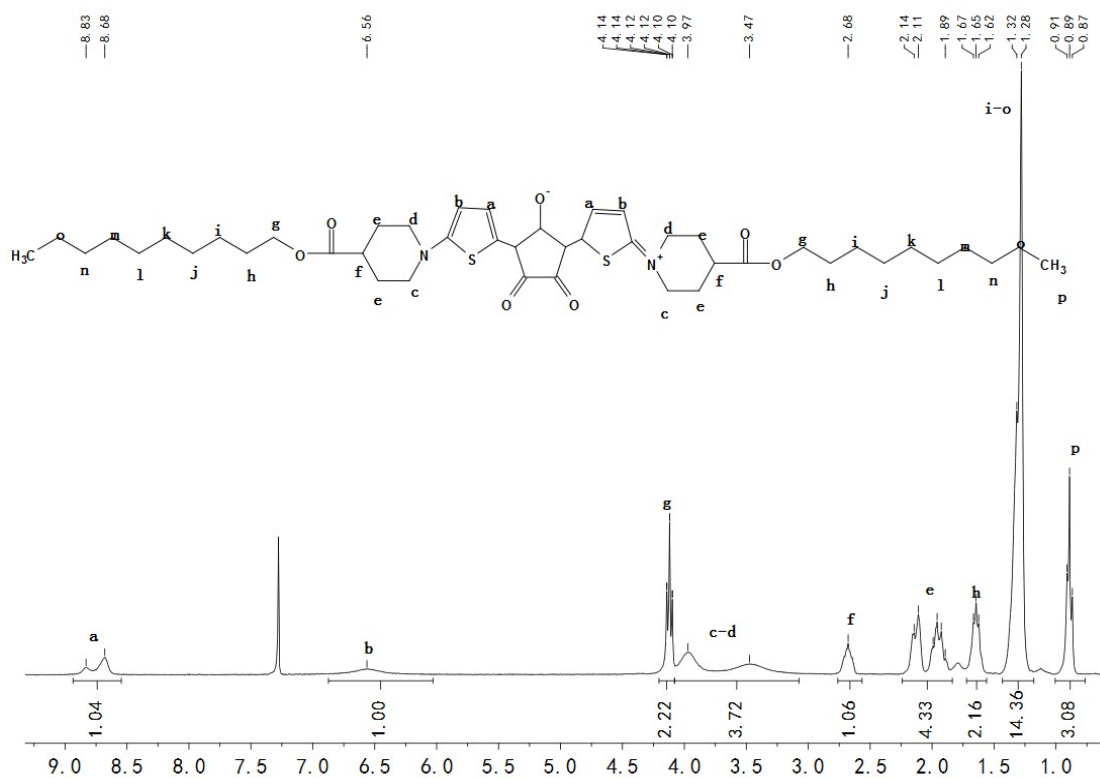


Figure S9. <sup>1</sup>H NMR spectrum of YHD796.

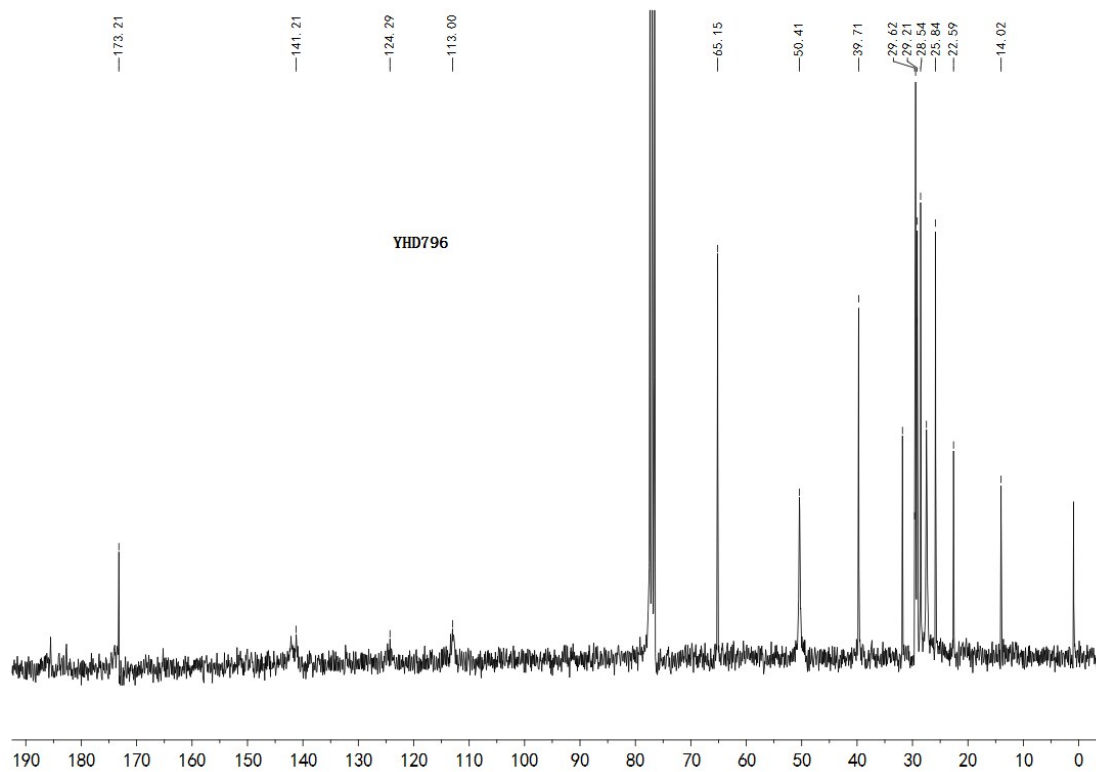
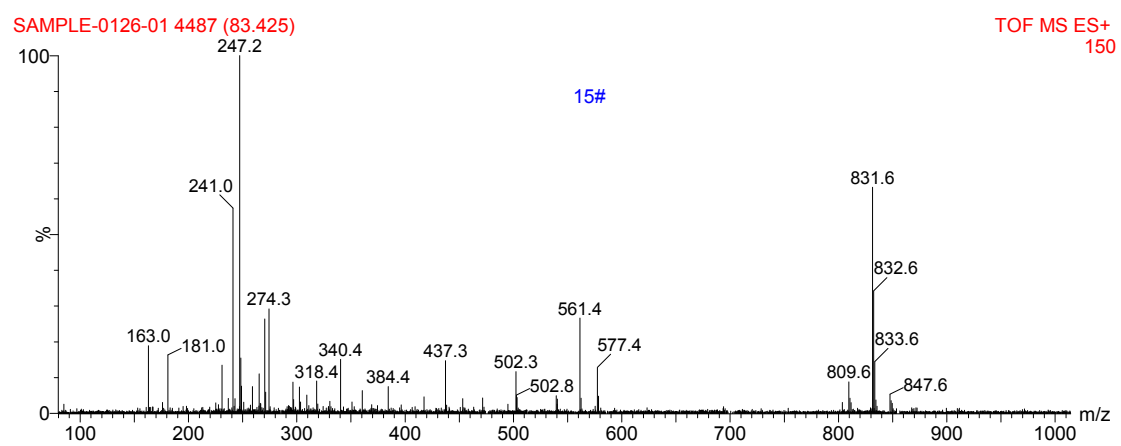


Figure S10. <sup>13</sup>C NMR spectrum of YHD796.



**Figure S11.** ESI-MS spectrum of YHD796.

### Synthesis of A444

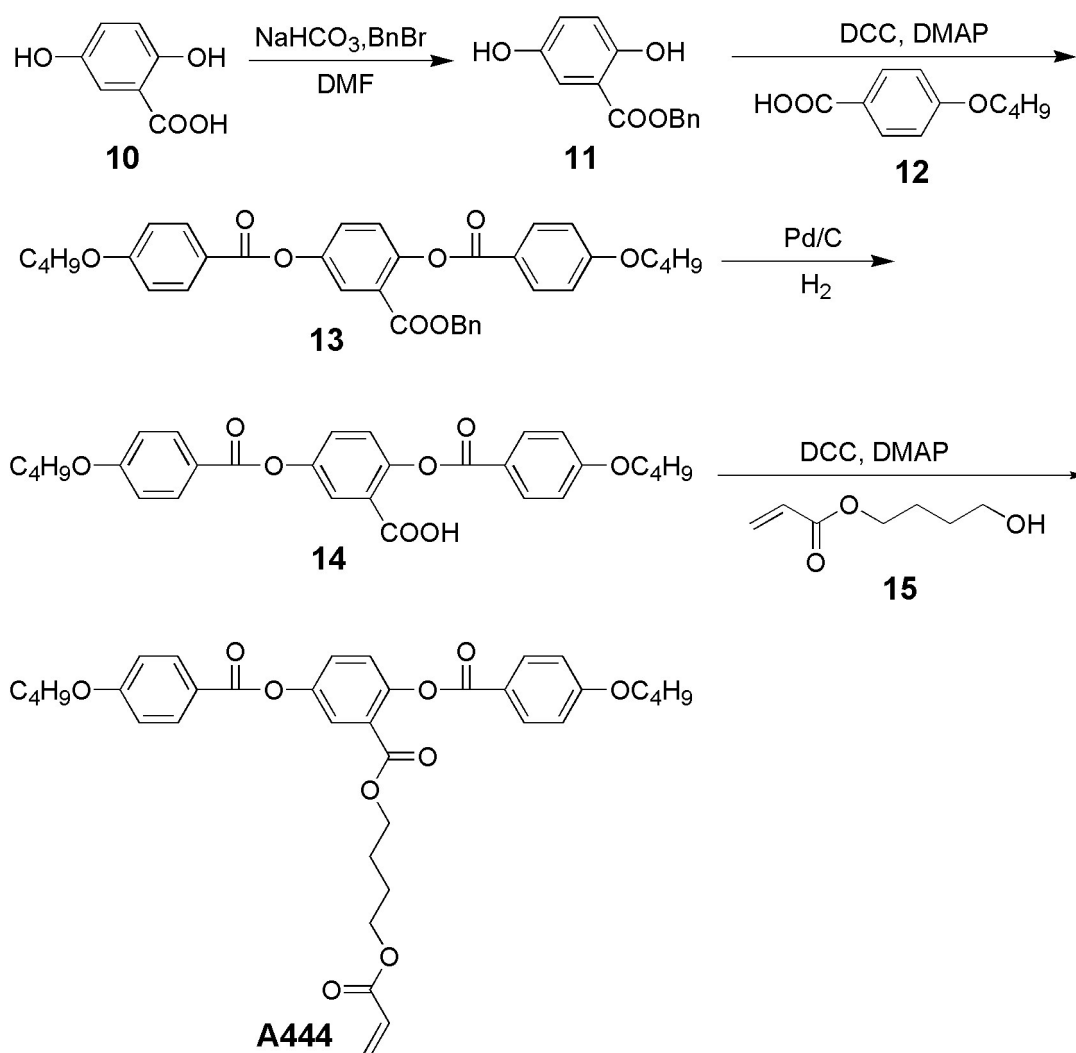


Figure S12. The synthetic route of A444.

### Benzyl 2,5-Dihydroxybenzoate (**11**).

2,5-Dihydroxybenzoic acid (6.16 g, 40.00 mmol) was dissolved in dry DMF (60 mL). NaHCO<sub>3</sub> (9.90 g, 117.86 mmol) was added and the reaction mixture was stirred at 70 °C for 1 h. Benzyl bromide (5.71 g, 31.33 mmol) were then added slowly and the mixture was stirred at 70 °C for additional 7 h. After cooling to room temperature, the reaction mixture was diluted with 150 mL water and extracted twice with 1:1 n-hexane/ethyl acetate (70 mL). The organic layer was washed twice with water, followed by drying over anhydrous magnesium sulfate. Then, the filtrate was concentrated under reduced pressure to give crude products. The final purification was carried out by column chromatography to give the product **11** (6.33 g, Yield: 64.8 %) as a white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.47 - 7.34 (m, 5H), 7.31 (d, *J* = 3.05 Hz, 1H), 7.04 - 6.81 (m, 2H), 5.36 (s, 2H), 4.52 (s, 2H).

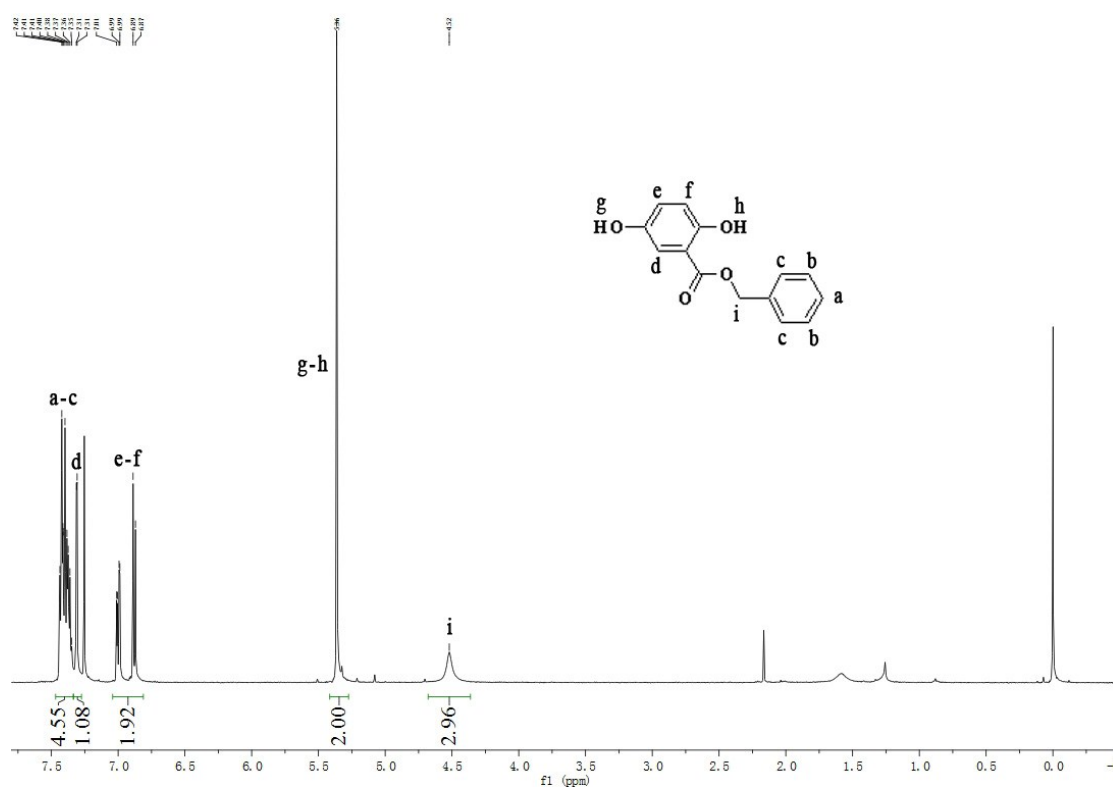


Figure S13. <sup>1</sup>H NMR spectrum of Compound **11**.

### Benzyl 2,5-Di(4'-butyloxybenzoyloxy)benzoate (**13**).

4-Butyloxybenzoic acid (**12**) (7.66 g, 39.52 mmol), compound **11** (4.38 g, 17.95 mmol), DMAP (0.58 g, 4.75 mmol) and dry CH<sub>2</sub>Cl<sub>2</sub> (70 mL) were added into a 250 mL round-bottom flask. Under a nitrogen atmosphere, DCC (8.1 g, 39.30 mmol) was added into the above flask in one portion at r.t. The reaction mixture was stirred at r.t. for 12 h. After filtering off the solids, the reaction solution was then concentrated by rotary evaporation and the resulting crude solid was recrystallized in methanol to give the desired product **13** (9.2 g, Yield: 85.9%) as a white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 8.25 - 8.01 (m, 4H), 7.9 (d, *J* = 2.85 Hz, 1H), 7.26 - 7.24 (m, 7H), 7.04 - 6.86 (m, 4H), 5.19 (s, 2H), 4.06 (t, *J* = 6.45 Hz, 4H), 1.8 (m, 4H), 1.5 (m, 4H), 1.0 (t, *J* = 7.25 Hz, 6H).

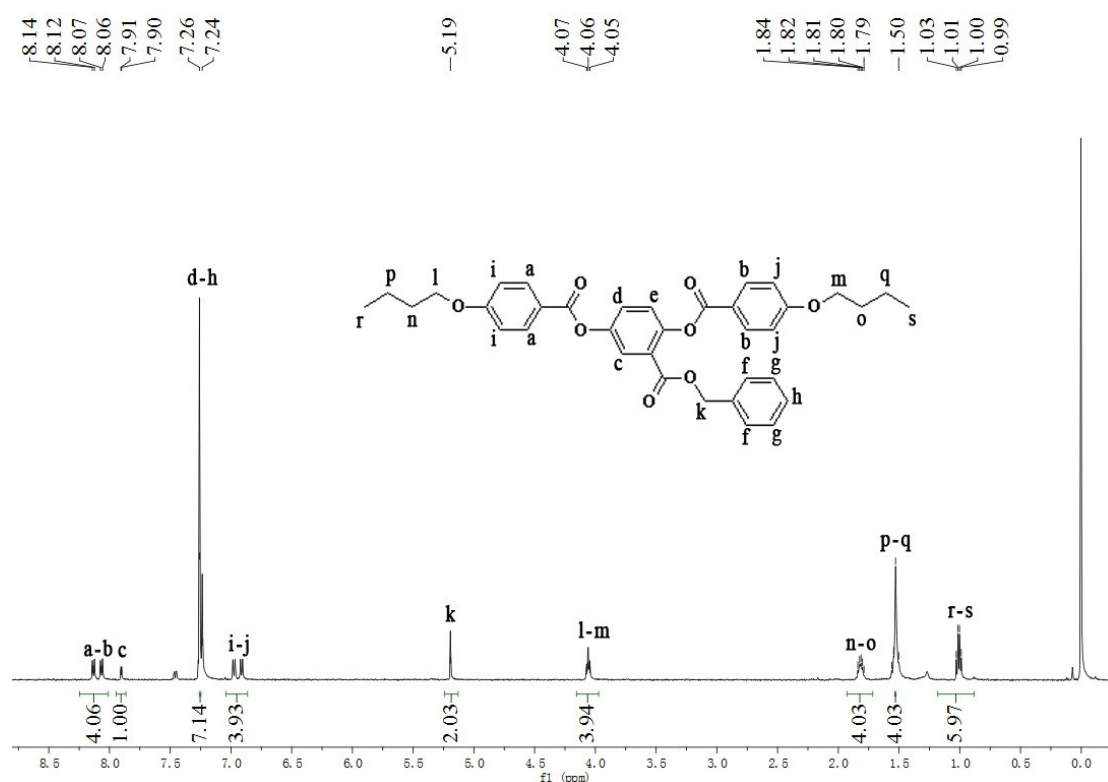


Figure S14. <sup>1</sup>H NMR spectrum of Compound **13**.





### 2,5-Di(4'-butyloxybenzoyloxy)benzoic Acid (**14**).

Hydrogen was allowed to bubble through a stirred suspension of 10 % Pd/C (1.51 g) in 100 mL of dichloromethane for 15 minutes. Benzyl ether **13** (6.22 g, 10.42 mmol) was added, and the reaction mixture was stirred at r.t. for 10 h. After filtering through a celite pad, the filtrate was concentrated, and the product **14** (4.81 g, 92.3 %) was further dried under vacuum.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.23-8.07 (m, 4H), 7.9 (d,  $J = 2.85$  Hz, 1H), 7.69-7.38 (dd,  $J = 8.7, 2.9$  Hz, 2H), 7.04 - 6.92 (m, 4H), 4.06 (t,  $J = 3.5$  Hz, 4H), 1.83 (m, 4H), 1.52 (m, 4H), 1.00 (m, 6H).

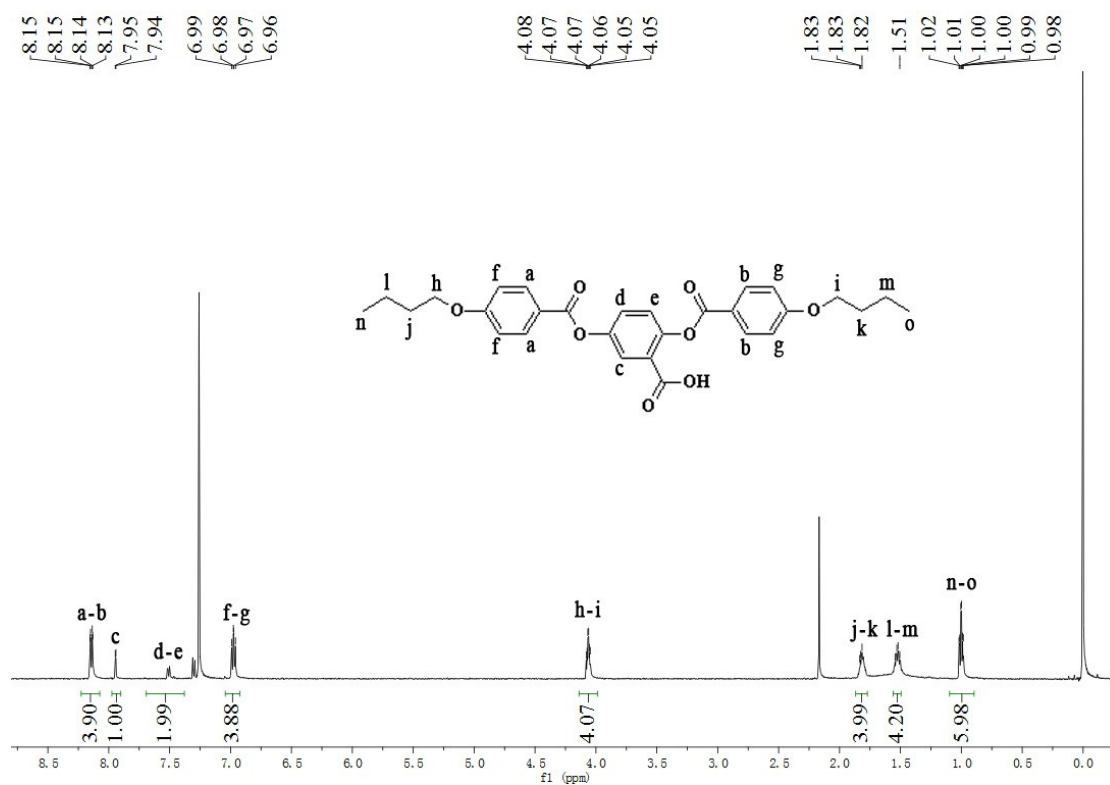


Figure S14.  $^1\text{H}$  NMR spectrum of Compound **14**.

### 2,5-Bis-(4-butoxy-benzoyloxy)-benzoic-4-hydroxybutyl acrylate ester (A444).

Compound **14** (1.29 g, 2.54 mmol), 4-hydroxybutyl acrylate (0.44 g, 3.05 mmol), DMAP (0.01 g, 0.13 mmol) and dry CH<sub>2</sub>Cl<sub>2</sub> (25 mL) were added into a 50 mL Schlenk-type flask. Under a nitrogen atmosphere, DCC (0.53 g, 2.54 mmol) was added into the above flask in one portion at 0 °C, the reaction mixture was stirred at room temperature for 24 h. After filtering off the solids, the solvents were concentrated by rotary evaporation and the crude solid was purified by column chromatography (petroleum ether : ethyl acetate = 15/1) to give the product **A444** (0.96 g, yield 60.2%) as a white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.15 (m, 4H), 7.89 (d, *J* = 2.7 Hz, 1H), 7.46 (t, *J* = 6.3 Hz, 1H), 7.32 – 7.24 (m, 1H), 6.98 (d, *J* = 6.5 Hz, 4H), 6.36 (d, *J* = 17.3 Hz, 1H), 6.08 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.79 (d, *J* = 10.4 Hz, 1H), 4.21 (t, *J* = 6.0 Hz, 2H), 4.05 (m, 6H), 1.91 – 1.74 (m, 4H), 1.71 – 1.49 (m, 8H), 1.00 (t, *J* = 7.4 Hz, 6H).

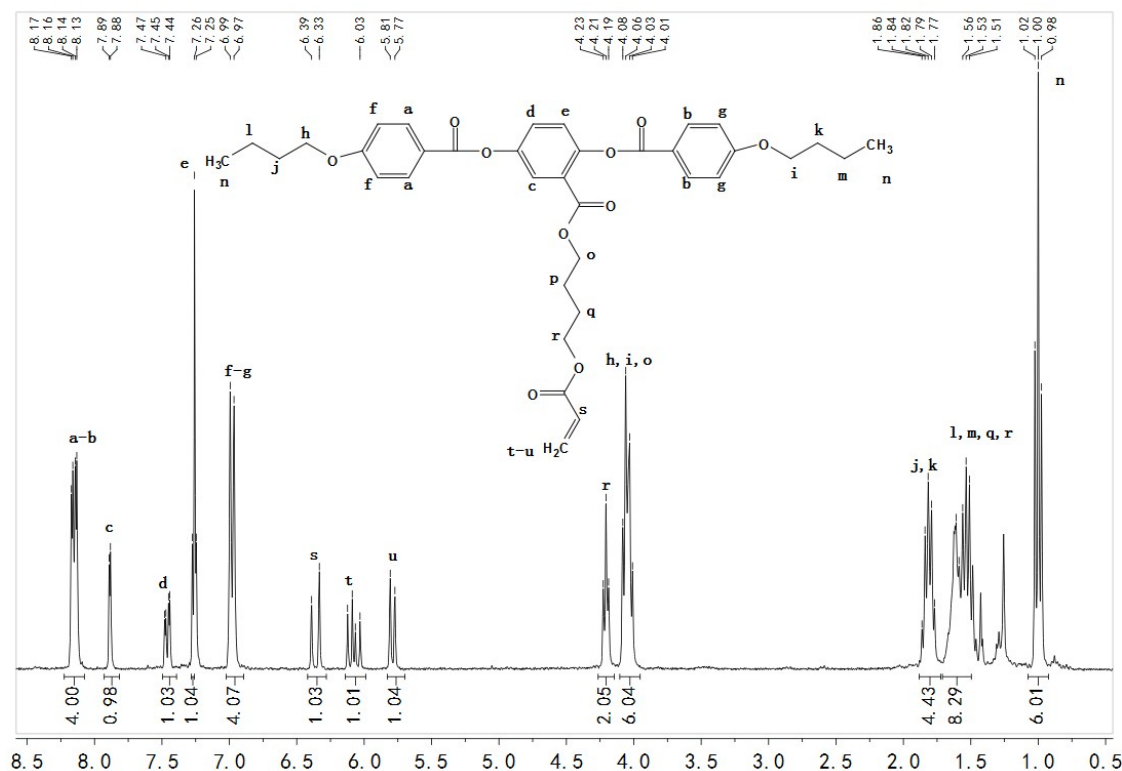
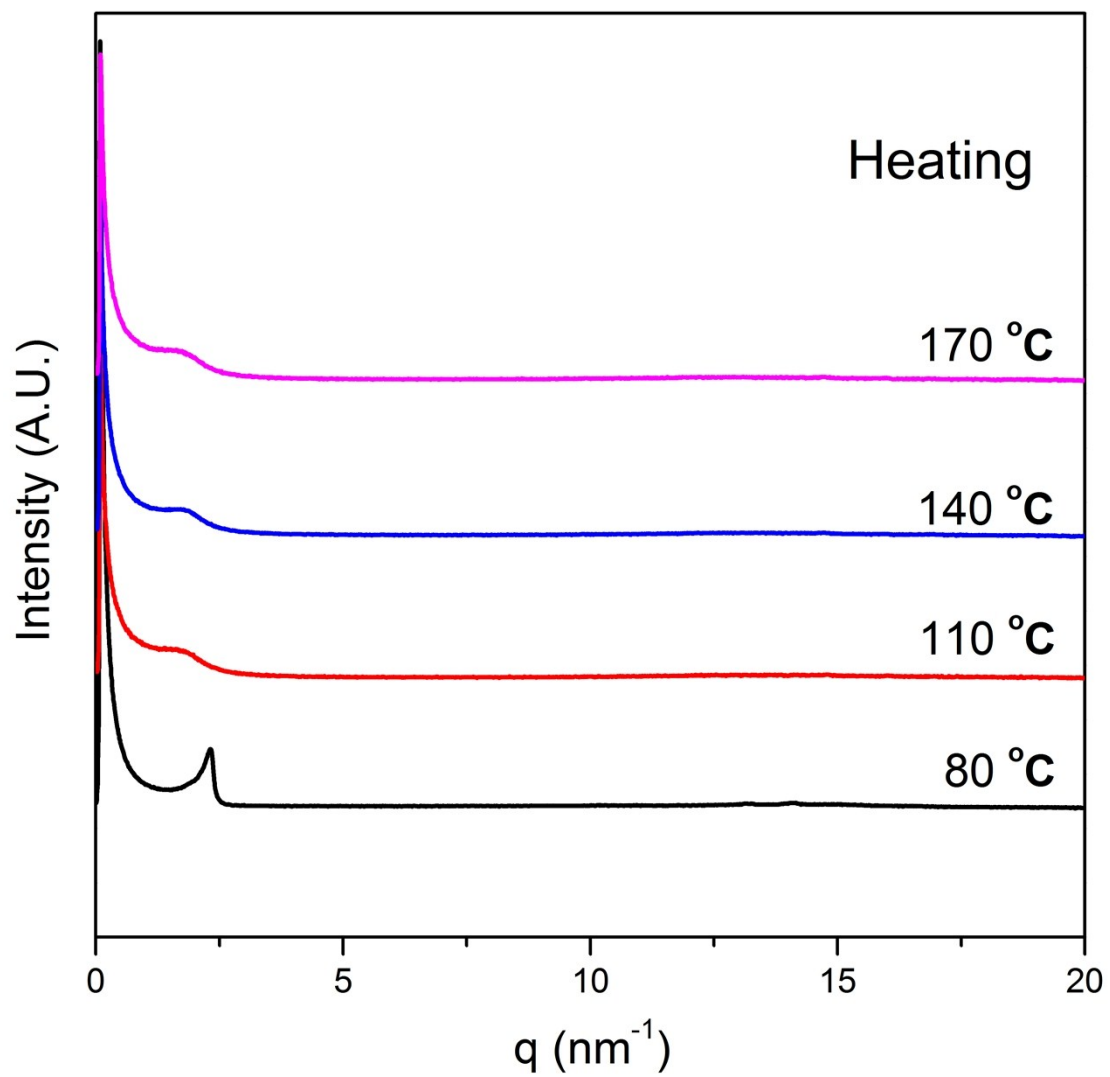
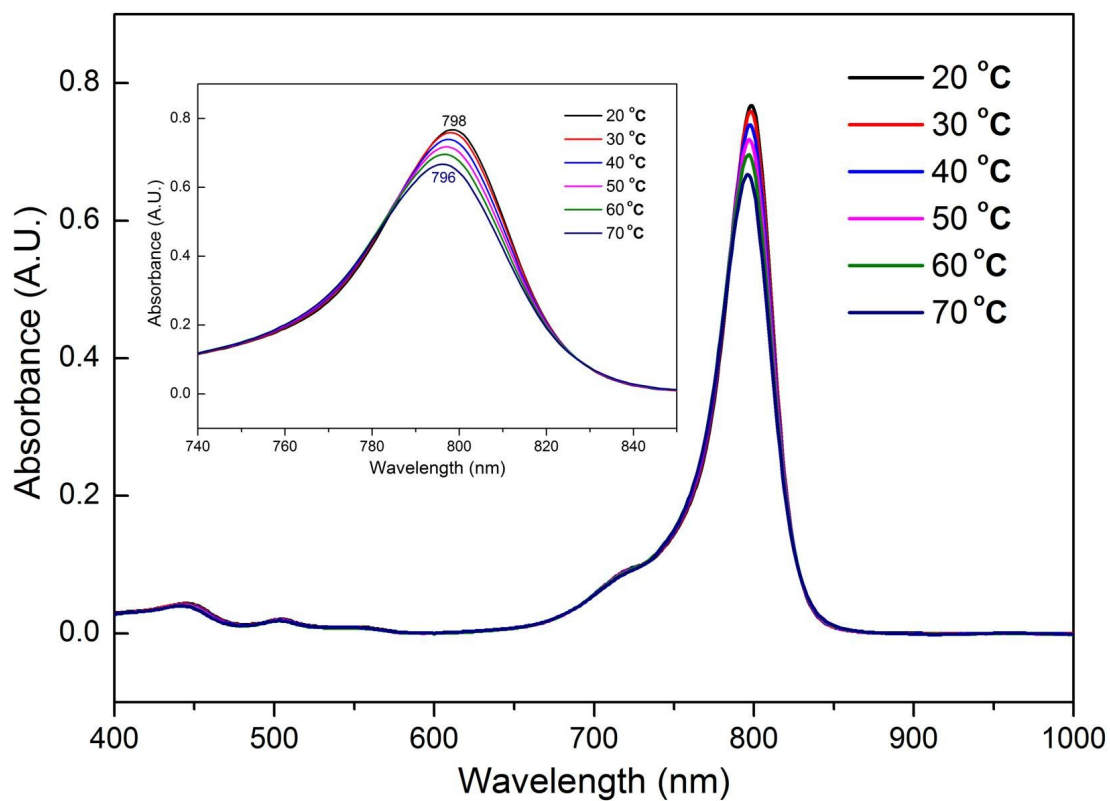


Figure S15. <sup>1</sup>H NMR spectrum of LC monomer **A444**.



**Figure S16.** One-dimensional WAXS patterns of YHD796 on heating.



**Figure S17.** UV-vis absorption spectra of **YHD796** (conc. =  $3.00 \times 10^{-3}$  mg/mL, dissolved in DMF) at varied temperatures.