

# Synthesis of Thiophene-Based Derivatives and the Effects of Their Molecular Structure on the Mesomorphic Behavior and Temperature Range of Liquid-Crystalline Blue Phases

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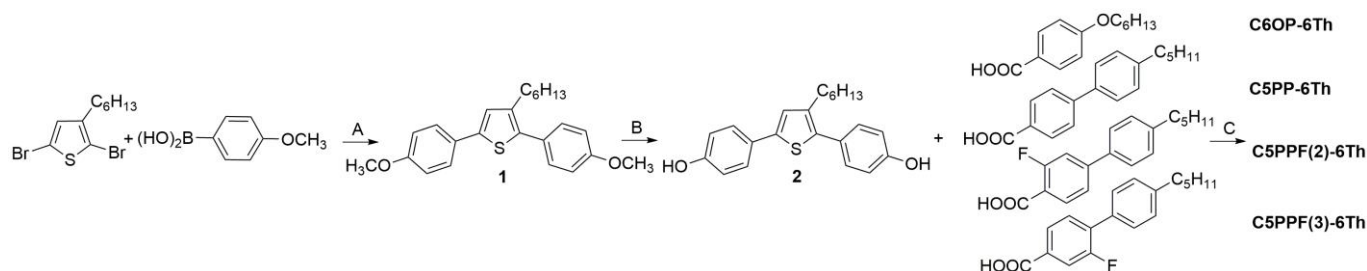
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# Supporting information

## 1. Materials Synthesis



**Scheme 1.** Synthetic route of the studied compounds. Reagents and conditions: (A) Pd(PPh<sub>3</sub>)<sub>4</sub>, aq. K<sub>2</sub>CO<sub>3</sub>, alcohol, toluene, 80 °C; (B) BBr<sub>3</sub>, RT; (C) DCC, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, RT.

### 1.1. 3-hexyl-2,5-bis(4-methoxyphenyl) thiophene (1)<sup>1</sup>

All chemicals and solvents were purchased from commercial supplies and used without further purification. A mixture of anhydrous potassium carbonate (41.4 g; 330 mmol), p-methoxyphenylboronic acid (16.7 g; 110 mmol), 3-hexyl-2,5-dibromothiophene (13.04 g; 40 mmol), cetyltrimethylammonium bromide (1.5 g; 5 mmol) were added into a three port round flask equipped with a stirrer and a thermometer. Add toluene (30 mL), ethanol (30 mL), and deionized water (30 mL) into the flask in turn. Then the mixture was mixed by ultrasonic vibration for 30 min under the protection of nitrogen. Put the flask in oil bath, vacuum the system, and add high purity nitrogen. Then palladium acetate (0.3 g; 0.12 mmol) acted as the catalyst was added into the flask. This mixture was heated to 80 °C and stirred for 12 h. The reactants then were poured into a 1000 mL beaker. The separating funnel was used to separate the liquid. Dichloromethane (200 mL) was used for multiple extraction, leaving the organic layer. Anhydrous magnesium sulfate (MgSO<sub>4</sub>) was added into the organic layer for drying. After filtration, the filtrate was evaporated and filtrated through silica using dichloromethane/mineral ether and recrystallization from ethanol yielded yellow powders of 3-hexyl-2,5-bis(4-methoxyphenyl) thiophene (6.8 g, 45%). FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2856, 2955 (-CH<sub>2</sub>-, -CH<sub>3</sub> stretching), 1606 (C=C shaking of benzene ring), 1505, 1289 (C-O stretching of ester bond), 1253, 1176 ( $\nu$ -O stretching), 1031, 828, 552, 509. <sup>1</sup>H NMR (400 MHz, DMSO,  $\delta$ ): 7.37-7.54 (m, 4H, ArH), 7.07 (s, 1H, ThH), 6.90-6.97 (m, 4H, ArH), 3.84-3.85 (t, 6H, Ar-O-CH<sub>3</sub>), 0.85-2.63 (m, 13H, Th-(CH<sub>2</sub>)<sub>5</sub>-CH<sub>3</sub>).

### 1.2. 3-hexyl-2,5-bis(4-hydroxyphenyl) thiophene (2)<sup>1</sup>

A 200 mL Schlenk flask was charged with 3-hexyl-2,5-bis(4-methoxyphenyl) thiophene (6.1 g, 0.016 mol) and dry dichloromethane (50 mL) under argon. In a separate flask, the boron tribromide (4.7 mL, 0.048 mol) was dissolved in dry dichloromethane (10 mL) and added to the reaction flask via a cannula at -78 °C. The yellow solution was allowed to warm up to room temperature and was stirred at room temperature for 24 h. After that, the deionized water (50 mL) was added dropwise into the flask at -78 °C, and the resulting mixture was stirred for 12 h at room temperature. After agitation, the reaction mixture was poured into 400 mL of deionized water and a blue colored precipitate was filtered off. The crude product was then recrystallized from acetidin for three times to yield 3-hexyl-2,5-bis(4-hydroxyphenyl) thiophene as pale blue solid powders (4.6 g, 82%). FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3316 (H-bonded OH), 2922, 2856, (-CH<sub>2</sub>-, -CH<sub>3</sub> stretching), 1609 (C=C shaking of benzene ring), 1504, 1214, 1175 ( $\nu$ -O stretching), 834, 826, 648, 538, 508. <sup>1</sup>H NMR (400 MHz, DMSO,  $\delta$ ): 7.37-7.54 (m, 4H, ArH), 7.07 (s, 1H, ThH), 6.90-6.97 (m, 4H, ArH), 5.35 (m, 2H, Ar-OH), 0.85-2.63 (m, 13H, Th-(CH<sub>2</sub>)<sub>5</sub>-CH<sub>3</sub>).

### 1.3. C6OP-6Th

*p*-hexoxybenzoic acid (2.22 g, 10 mmol), 3-hexyl-2,5-bis(4-hydroxyphenyl) thiophene (1.76 g, 5 mmol) and *N,N'*-dicyclohexylcarbodiimide (DCC) (3.1 g, 15 mmol) in dichloromethane (100 mL) with catalytic amount of 4-dimethylamino pyridine (DMAP) (0.18 g, 1.5 mmol) were stirred at room temperature for 24 h. *N,N'*-dicyclohexylurea formed was filtered off. The filtrate was washed with deionized water and dried over MgSO<sub>4</sub>. Solvent was removed under the reduced pressure and chromatographed over a column of silica gel using acetidin/ mineral ether as an eluent, and then recrystallized from ethanol yielded yellow colored powders (1.7 g, 45 %). FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2870-2936 (-CH<sub>2</sub>-, -CH<sub>3</sub> stretching), 1778, 1732 (C=O), 1683, 1606 (C=C shaking of benzene ring), 1579, 1511, 1468, 1429 (C-C shaking of benzene ring), 1391, 1257 (C-O stretching of ester bond), 1025, 995, 936, 846, 771, 647, 552. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.64-7.83 (s, 2H, ArH), 7.50-7.52 (m, 5H, ArH), 7.19-7.28 (m, 8H, ArH), 6.93-6.95 (m, 2H, ThH, ArH), 4.06-4.11 (s, 4H, Ar-CH<sub>2</sub>-), 2.72-2.75 (s, 2H, -CH<sub>2</sub>-), 0.87-1.97 (m, 33H, Ar-O-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub>, Th-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>4</sub>-CH<sub>3</sub>)

#### 1.4. C5PP-6Th

The procedure of compound C6OP-6Th was followed except using 4'-pentyl-[1,1'-biphenyl]-4-carboxylic acid. Yield: 40%. FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2921, 2856 (-CH<sub>2</sub>-, -CH<sub>3</sub> stretching), 1732 (C=O stretching of ester bond), 1605 (C=C shaking of benzene ring), 1499, 1464 (C-C shaking of benzene ring), 1399, 1268, 1203 (C-O stretching of ester bond), 1167, 1078, 1016, 877, 820, 763, 693. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.26-8.27 (s, 4H, ArH), 7.73-7.75 (s, 4H, ArH), 7.53-7.68 (m, 6H, ArH), 7.21-7.32 (m, 11H, ArH, ThH), 2.66-2.69 (s, 6H, Ar-CH<sub>2</sub>-), 0.87-1.55 (m, 29H, Ar-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub>, Th-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>4</sub>-CH<sub>3</sub>).

#### 1.5. C5PPF(2)-6Th

The procedure of compound C6OP-6Th was followed except using 3-fluoro-4'-pentyl-[1,1'-biphenyl]-4-carboxylic acid. Yield: 40%. FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2925, 2854 (-CH<sub>2</sub>-, -CH<sub>3</sub> stretching), 1732 (C=O stretching of ester bond), 1620 (C=C shaking of benzene ring), 1556, 1499 (C-C shaking of benzene ring), 1398, 1279, 1204 (C-O stretching of ester bond), 1166, 1056 (-F stretching), 874, 809, 766, 689. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.04-8.07 (s, 2H, ArH), 7.97-8.00 (s, 2H, ArH), 7.59-7.69 (m, 10H, ArH), 7.53-7.55 (m, 9H, ArH), 7.21-7.32 (s, 2H, ArH, ThH), 2.66-2.70 (s, 6H, Ar-CH<sub>2</sub>-), 0.87-1.69 (m, 29H, Ar-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub>, Th-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>4</sub>-CH<sub>3</sub>).

#### 1.6. C5PPF(3)-6Th

The procedure of compound C6OP-6Th was followed except using 2-fluoro-4'-pentyl-[1,1'-biphenyl]-4-carboxylic acid. Yield: 40%. FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2928, 2856 (-CH<sub>2</sub>-, -CH<sub>3</sub> stretching), 1734 (C=O stretching of ester bond), 1605 (C=C shaking of benzene ring), 1500, 1428 (C-C shaking of benzene ring), 1400, 1282, 1208 (C-O stretching of ester bond), 1167, 1076 (-F stretching), 1008, 927, 868, 755. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.26-8.27 (s, 4H, ArH), 7.73-7.75 (s, 4H, ArH), 7.53-7.68 (m, 8H, ArH), 7.21-7.32 (m, 9H, ArH, ThH), 2.66-2.70 (s, 6H, Ar-CH<sub>2</sub>-), 0.87-1.55 (m, 29H, Ar-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub>, Th-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>4</sub>-CH<sub>3</sub>).

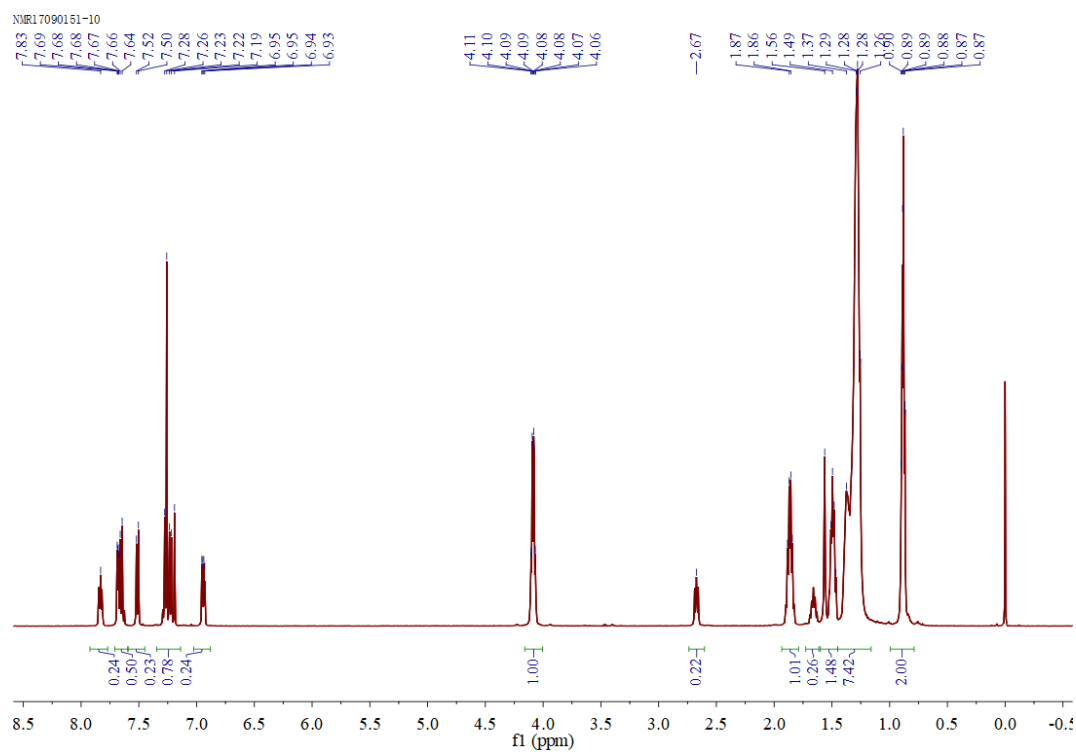


Figure S1. The  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) spectra of C6O-6Th.

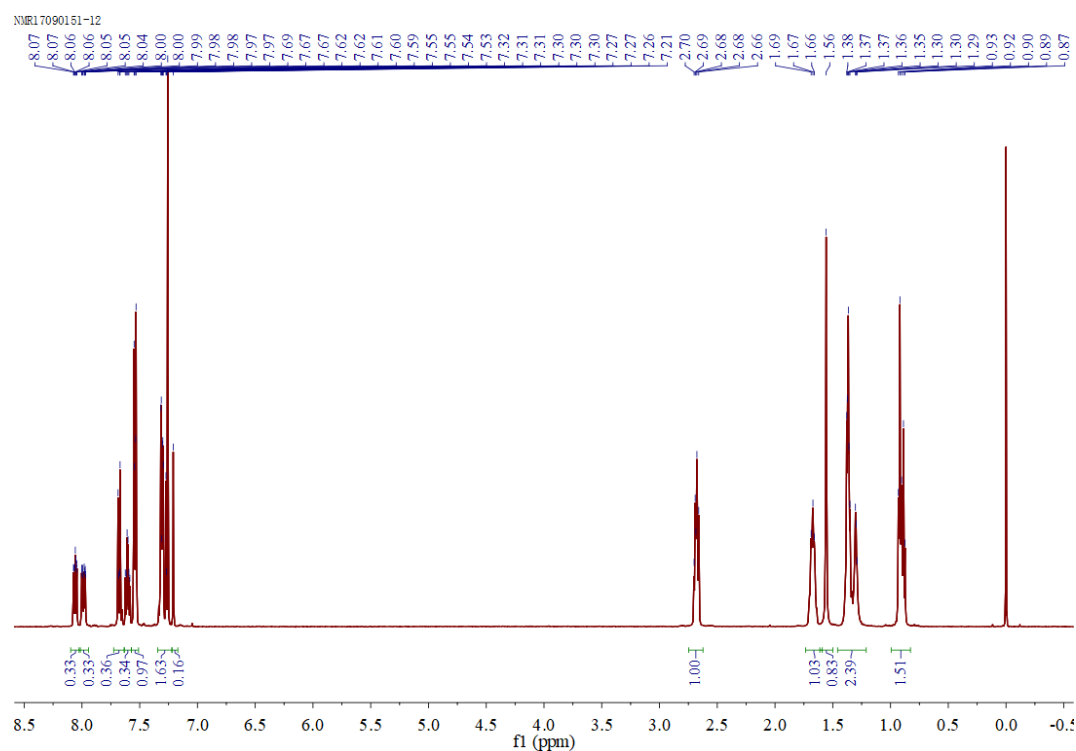
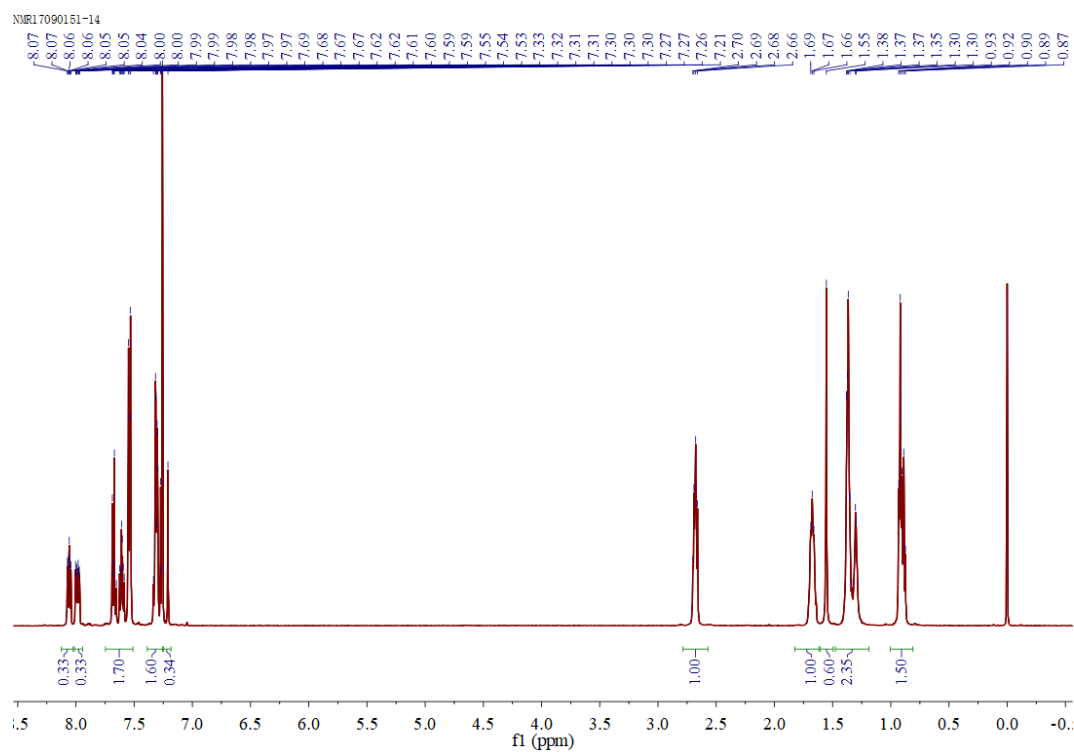
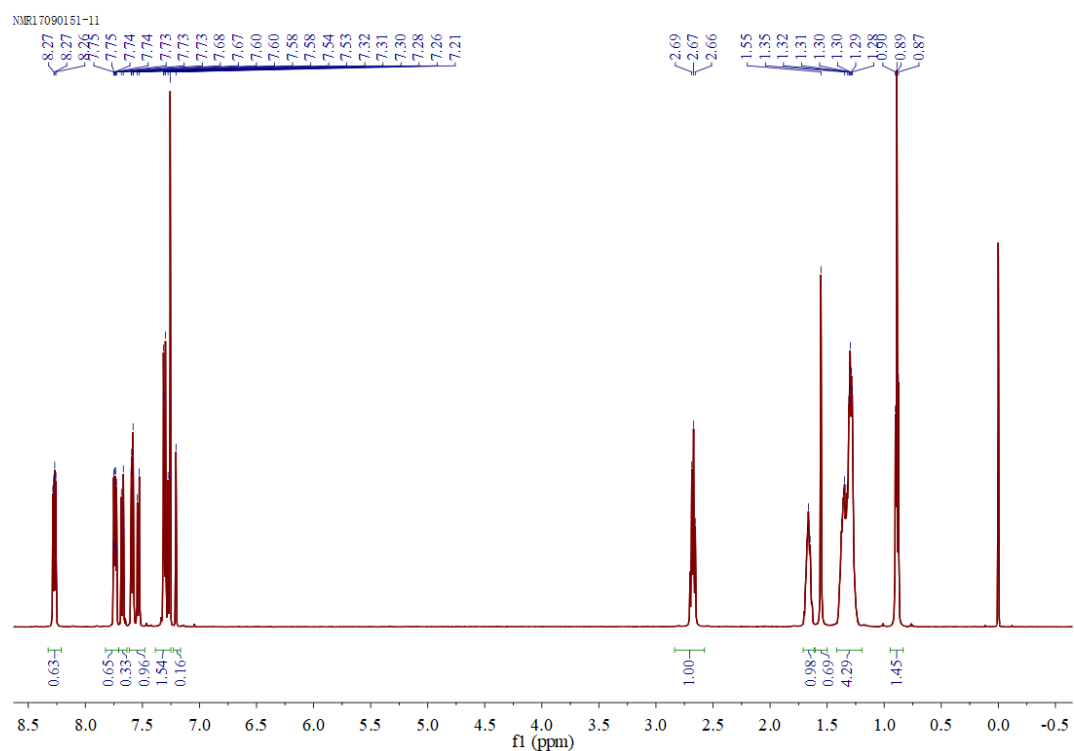


Figure S2. The  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) spectra of C5PP-6Th.



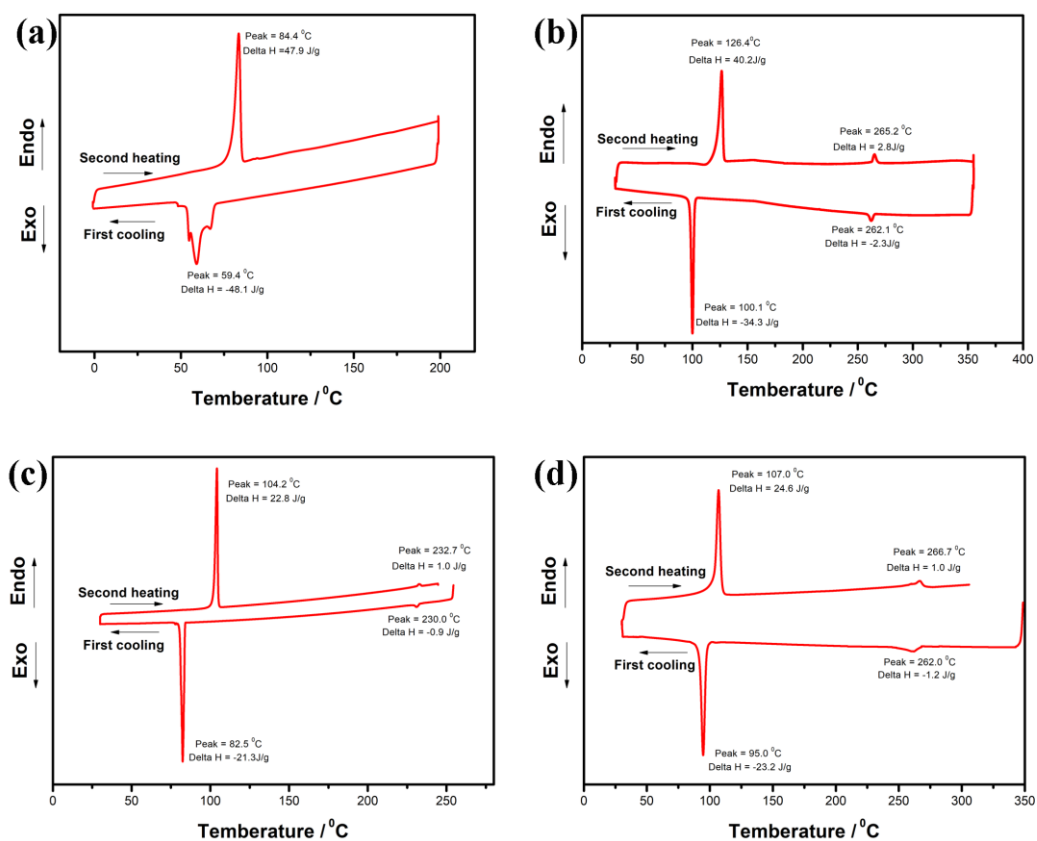
**Figure S3.** The  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) spectra of C5PPF(2)-6Th.



**Figure S4.** The  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) spectra of C5PPF(3)-6Th.

## 2. The DSC curves

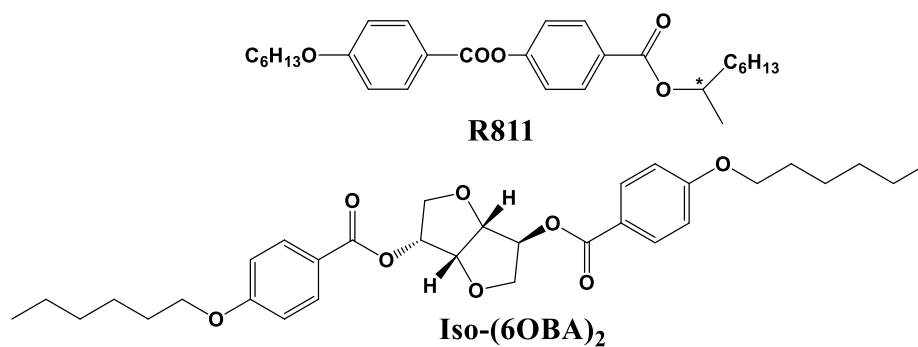
The temperatures and enthalpies of the transition investigated by DSC at a scanning rate of  $10.0\text{ }^\circ\text{C min}^{-1}$  under a dry nitrogen purge are shown in Figure S5.



**Figure S5.** The DSC thermograms of compound (a) C6OP-6Th, (b) C5PP-6Th, (c) C5PPF(2)-6Th and (d) C5PPF(3)-6Th with the heating as well as cooling scans at the rate of 10 °C min<sup>-1</sup>.

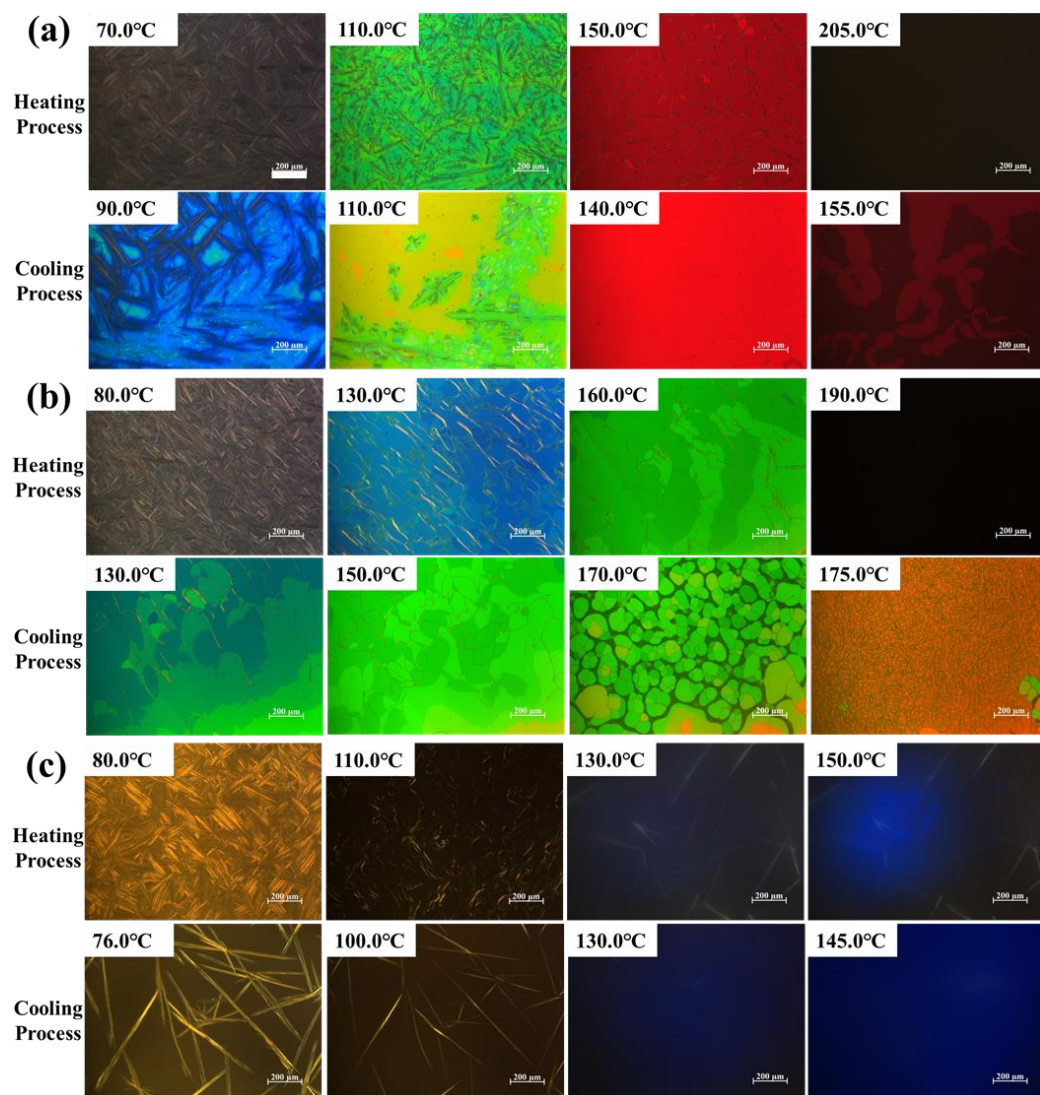
### 3. Chemical structure

The chemical structure of chiral dopant R811 and Iso-(6OBA)<sub>2</sub> are shown in Figure S6.

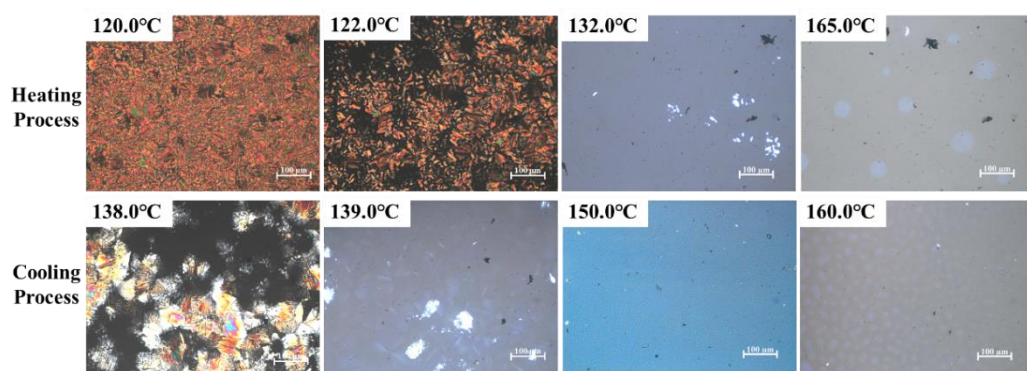


**Figure S6.** The chemical structure of chiral dopant R811 and Iso-(6OBA)<sub>2</sub>.

### 4. BP Behavior of C5PP-6Th doped with chiral compounds



**Figure S7.** Typical POM textures in LC cells with parallel treatment of A1, A2 and A4 for C5PP-6Th blended with different contents of chiral dopant R811. The scale bar is 200  $\mu\text{m}$ .



**Figure S8.** Typical POM textures in LC cells with no parallel treatment of A3. The scale bar is 100  $\mu\text{m}$ .

## Reference

1. Cheng, X.H., Dong, X., Zheng, T., Ye, H. and Wei, G.H. Synthesis and Mesomorphic Behavior of 3-Alkyl-2,5-bis[p-(hexa-2,4-dienyloxy)phenyl]-Thiophene Derivatives. *Chin. J. Chem.* **2008**, *26*, 146–149. <https://doi.org/10.1002/cjoc.200890010>.