

Supporting information

Synthesis and investigation of novel cinnamic-acid-derived hydrogen-bonded mesogens with wide blue phase

Wanli He, Zhou Yang, Hui Cao, Guojie Wang, Huai Yang*

*Department of Materials Physics and Chemistry, School of Materials Science and Engineering, University of Science and Technology Beijing, 100083, P. R. China

1. Synthesis of the hydrogen-bonded (H-bonded) liquid crystal (LC) complexes

All the starting materials were commercially available from Beijing Chemical Product Factory (BJCPF) and used without further purification. The target compounds were prepared by routine methods as shown in Figure S1 and characterized by fourier transform infrared spectroscopy (FT-IR) using a Nicolet 510P FTIR spectrometer, nuclear magnetic resonance (^1H NMR) using Bruker AV400 instrument in CDCl_3 , Elemental analysis using a Carlo Erba 1106 model elemental analyzer. The purities were analyzed by high performance Liquid chromatography (HPLC) with UV detection at 254 nm.

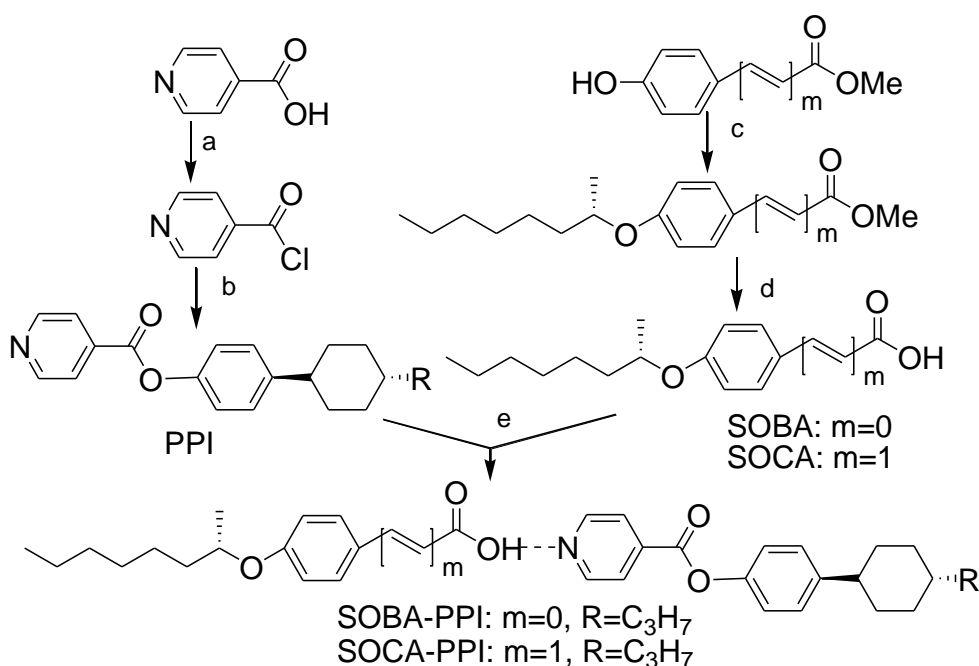


Figure S1. (A) Synthetic routes of the H-bonded LC complexes: a) SOCl_2 ; b) alkyl-trans-cyclohexyl phenol, NET_3 , THF; c): K_2CO_3 , (R)-octan-2-yl 4-methylbenzenesulfonate, butan-2-one; d) NaOH , H_2O ; HCl ; e) THF

Synthesis of 4-(4-trans-propylcyclohexyl) phenol isonicotinate

4-(4-trans-propylcyclohexyl) phenol isonicotinate (PPI) was synthesized by two steps starting with isonicotinic acid as shown in Figure S1. Thionylchloride (60.0 mL) was added slowly to a stirred mixture of isonicotinic acid (24.6 g, 0.2mol) and DMF (1.0 mL) at room temperature. The acid begins to dissolve into solution with lively releasing gas which should be conducted into NaOH solution for absorption.

After stirred for another 12.0 hours, excess thionyl chloride was removed in vacuum when the temperature had risen to about 40.0 °C, and cold petroleum ether (200.0 mL) was stirred into the residue. The crude product was filtered, washed with petroleum ether and dried in vacuo at room temperature. Yield: 35.0 g (95.0%) of white crystals sufficiently pure for the preparation of the activated esters. To a stirred suspension of last isonicotinoylchloride hydrochloride (8.9 g, 50.0 mmol) and 4-(4-trans-propylcyclohexyl) phenol (10.9 g, 50.0 mmol, purity > 99.0%) in THF (200.0 mL) was added triethylamine (20.0 mL, 0.14 mol) over 30.0 minutes. The suspension was stirred at room temperature for 12.0 hours, filtered and concentrated in vacuum. The residue was dissolved in hexane (300.0 mL), treated with activated carbon and recrystallized from hexane as a white needle solid.

Yield: 79.5%. Purity: 99.0% by HPLC. FT-IR (KBr, cm^{-1}): 2918, 2848 ($-\text{CH}_2-$, $-\text{CH}_3$ stretching), 1739 ($\text{C}=\text{O}$ stretching), 1564, 1508, 1446 (aromatic $\text{C}=\text{C}$), 1409, 1277, 1203, 1087, 967, 874, 822, 758, 701, 548. ^1H NMR (400 MHz, CDCl_3 , δ): 0.90-0.94 (t, 3H, $-(\text{CH}_2)_2\text{CH}_3$), 1.06-1.94 (m, 4H, methylene; 9H, cyclohexane), 2.49-2.52 (t, 1H, cyclohexane), 7.13-7.30 (dd, 4H, $-\text{O}-\text{ArH}-$), 8.02-8.03 (d, 2H, pyridine Hs), 8.86-8.90 (d, 2H, pyridine Hs). Elemental analysis: Calc'd for $\text{C}_{21}\text{H}_{25}\text{NO}_2$: C 77.98%, H 7.79%, N 4.33%; found C 77.95%, H 7.70%, N 4.35%.

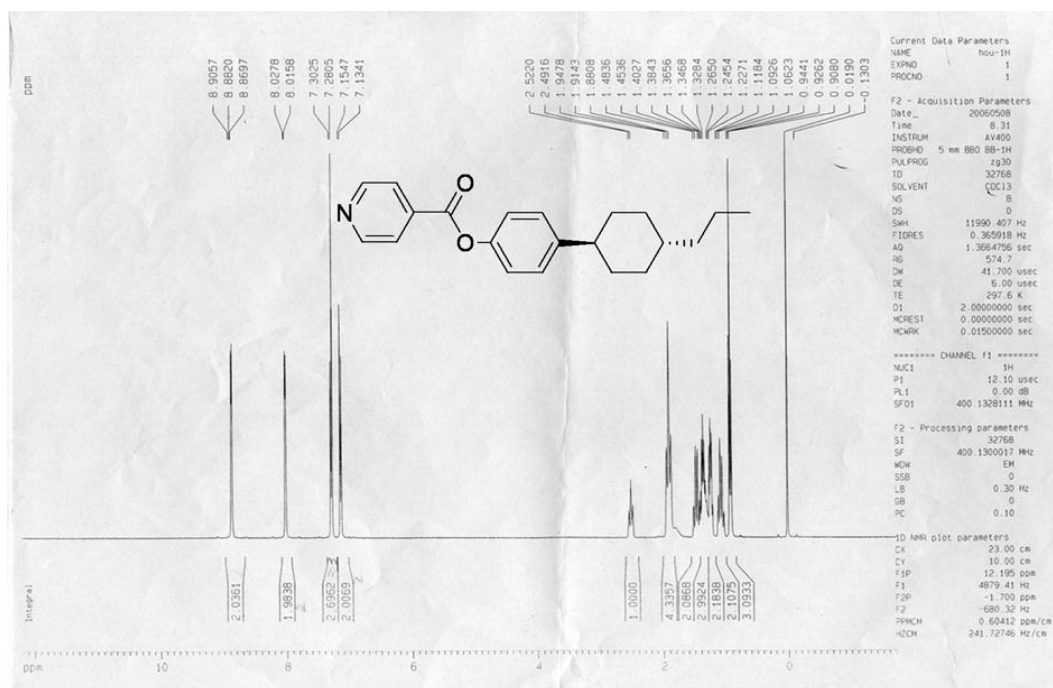


Figure S2. The spectrum of ^1H NMR of PPI

Synthesis of (S)-4-(2-octanyloxy) cinnamic acid

(S)-4-(2-octanyloxy) cinnamic acid (SOCA) was prepared as Figure S1 shown, the process was described in full as following. TsCl (1.5 mmol) in solvent (1.0 ml) was added to a stirred solution of an R-2-octanol (1.0 mmol), Et₃N 2 mmol) and Me₃N.HCl (0.1 mmol) in acetonitrile (1.0 mL) at 0-5 °C,

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and the mixture was stirred for 1 h. To decompose an excess TsCl, N,N-dimethylethylenediamine (ca. 130 mg) was added to the mixture, which was stirred for 10 min. Water was added to the mixture, which was extracted with EtOAc. The organic phase was washed with water and brine, dried (Na₂SO₄) and concentrated. The obtained crude product was purified by silica-gel column chromatography (CH₂Cl₂) to give the desired (R)-octan-2-yl 4-methylbenzenesulfonate.

To a solution of methyl 4-hydroxycinnamate (6.4 g, 36.0 mmol), K₂CO₃ (10 g, 72.4 mmol) and (R)-octan-2-yl 4-methylbenzenesulfonate (10.0g, 36.0mmol) in dry butan-2-one (90.0 mL) was stirred at reflux temperature for about 10h under a nitrogen atmosphere. TLC analysis indicated completion of the reaction. The solution was washed by 4.0 wt% NaOH and water, dried over anhydrous MgSO₄ and finally evaporated to remove the solvent. The resulting residue was purified via column chromatography (silica gel, petroleum ether/ethyl acetate) as colorless oil. The intermediate was hydrolyzed by potassium hydroxide (2.8 g, 40.0 mmol) in 100.0 mL of water and refluxed for 5.0 hours under a nitrogen atmosphere. Then the solvent was poured into cold water and acidified to pH=1 by hydrochloric acid solution. The resulting precipitate was extracted with ether, thoroughly washed with water, and dried over anhydrous MgSO₄. The ether was removed to give the crude SOCA, which crystallized to give a white needle solid.

Yield: 79.5%. Purity: 98.6% by HPLC. FT-IR (KBr cm⁻¹): 3250-2632 (acidic -OH stretching), 2915, 2849 (-CH₂-, -CH₃ stretching), 1718 (C=O stretching), 1631, 1571, 1447(aromatic C=C), 1398, 1334, 1312, 1249(C-O-Ar stretching), 1155, 1048, 839, 769, 677, 622, 579, 526. ¹H NMR (400 MHz, CDCl₃): 0.89-0.92(t, 3H, -(CH₂)₅CH₃), 1.31-1.40 (m, 11H, -OCH(CH₃)CH₂(CH₂)₄CH₃), 1.57-1.77 (m, 2H, Ar-OCH(CH₃)CH₂-), 4.41-4.45 (m, 1H, Ar-OCH(CH₃)CH₂-), 6.31-6.35 (d, 1H, ethylene), 6.90-6.92 (d, 2H, ArH), 7.50-7.52 (d, 2H, ArH), 7.75-7.79 (d, 1H, ethylene). Elemental analysis: Calc'd for C₁₇H₂₄O₃: C 73.88%, H 8.75%; found C 73.70%, H 8.70%.

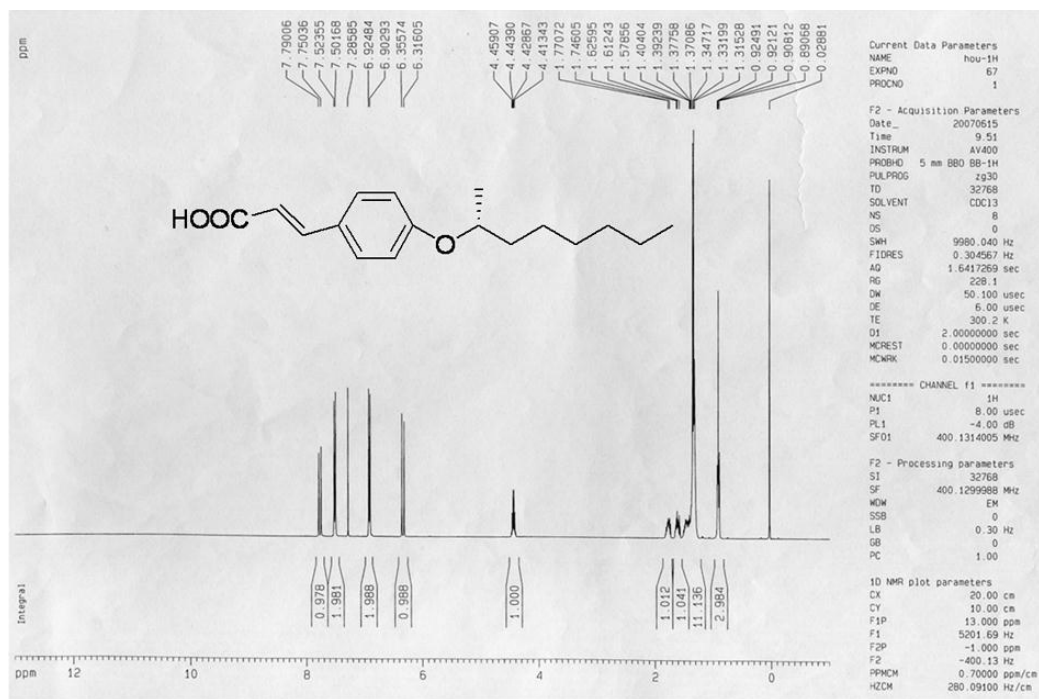


Figure S3. The spectrum of ¹H NMR of SOCA

Synthesis of (S)-4-(2-octanyloxy) benzoic acid

(S)-4-(2-octanyloxy)benzoic acid (SOBA) was synthesized by the same procedure used for SOCA. Yield: 85.5%. Purity: 98.0% by HPLC. FT-IR (KBr, cm⁻¹): 3100-2666 (acidic -OH stretching), 2930, 2856 (-CH₂-, -CH₃ stretching), 2666, 2544, 1677 (C=O stretching), 1606, 1513 (aromatic C=C), 1426, 1257 (C-O-Ar stretching), 1173, 1120, 1031, 936, 848, 777, 697, 643, 551. ¹H NMR (400 MHz, CDCl₃, δ): 0.89-0.92 (t, 3H, -(CH₂)₅CH₃), 1.29-1.44 (m, 11H, -OCH(CH₃)CH₂(CH₂)₄CH₃), 1.59-1.61 (m, H, Ar-OCH(CH₃)CH₂-), 1.73-1.77 (m, H, Ar-OCH(CH₃)CH₂-), 4.44-4.48 (m, 1H, Ar-OCH(CH₃)CH₂-), 6.89-6.92 (d, 2H, ArH), 8.03-8.05 (d, 2H, ArH). Elemental analysis: Calc'd for C₁₅H₂₂O₃: C 71.97%, H 8.86%; found C 71.91%, H 8.90%.

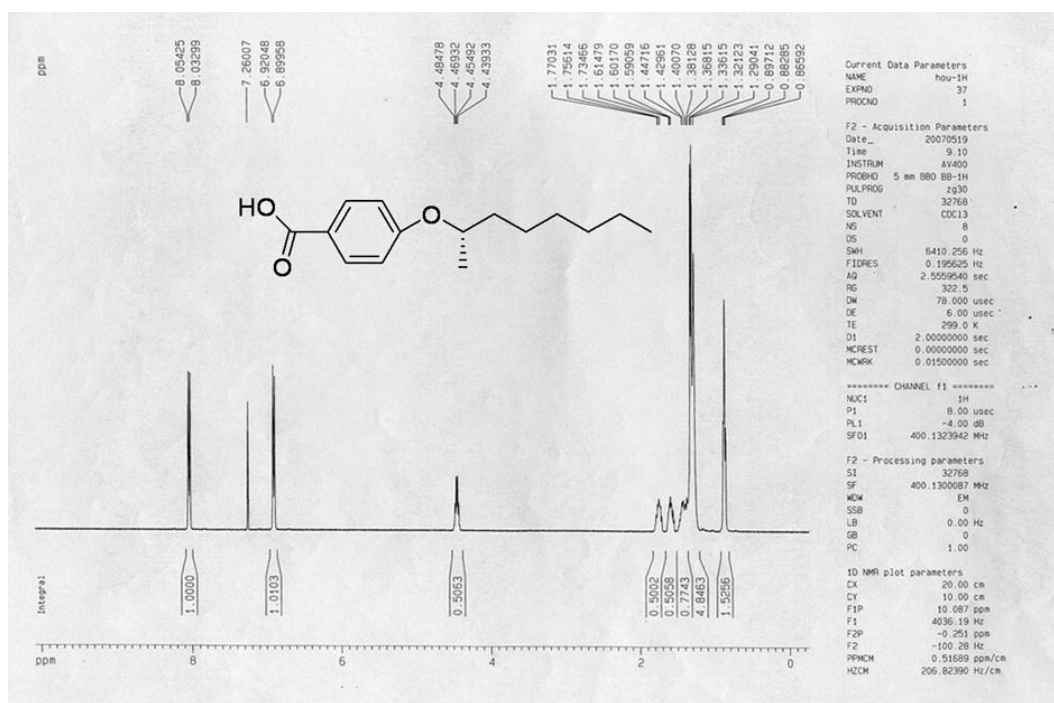


Figure S4. The spectrum of ¹H NMR of SOBA

Synthesis of H-bonded LC complexes

The requisite amounts of chiral alkoxy benzoic acids and achiral acceptor were dissolved in 1.0 mL of THF and followed by slowly removing the solvent under reduced pressure. The resulting solid was dried in vacuum for about 24.0 hours.

2. The FTIR spectroscopy of the hydrogen-bonded complexes

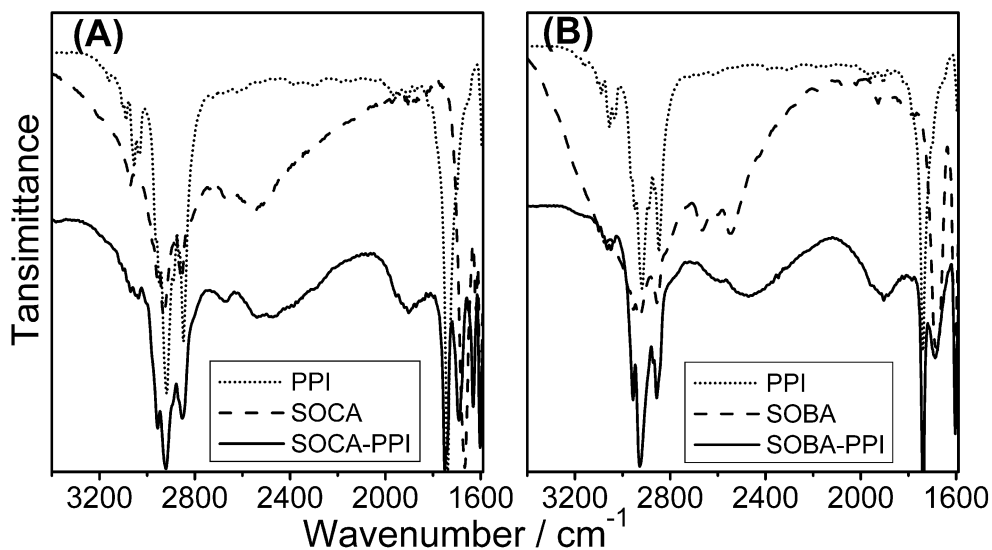


Figure S5. The plots of FT-IR spectra for the precursors and the 1:1 H-bonded complexes: a) the cinnamic-acid-derived system; b) the benzoic-acid-derived system.

The formation of the H-bond in the complexes could be directly confirmed by IR spectra. The Figure S5 show the H-bond precursors and the H-bonded mesogens in the benzoic-acid-derived system and cinnamic-acid-derived system, respectively. The two H-bonded characteristic peaks centered at about 2500 cm^{-1} and 1900 cm^{-1} in the H-bonded complexes were absence in the precursors of SOBA, SOCA and PPI, which indicates existence of a stably strong hydrogen bond in complexes.

3. The thermal behavior of the H-bonded complexes

The thermal behavior of the H-bonded complexes were studied with a Perkin-Elmer DSC 6 instrument, as Figure S6 shown, and observed by using an Olympus BX-51 polarizing optical microscope (POM) equipped with a Linkam Scientific LTS 350 heating/ freezing stage at a heating rate of $0.5\text{ }^{\circ}\text{C}/\text{min}$, respectively, as Figure S7 shown. The phase transition temperatures were obtained by DSC measurement except those of SmA-TGBA*, TGBA*-N* and N*-BP* phase transitions which could be only observed with POM since these transitions are second order or very weak first order transitions and difficult to be measured with DSC.

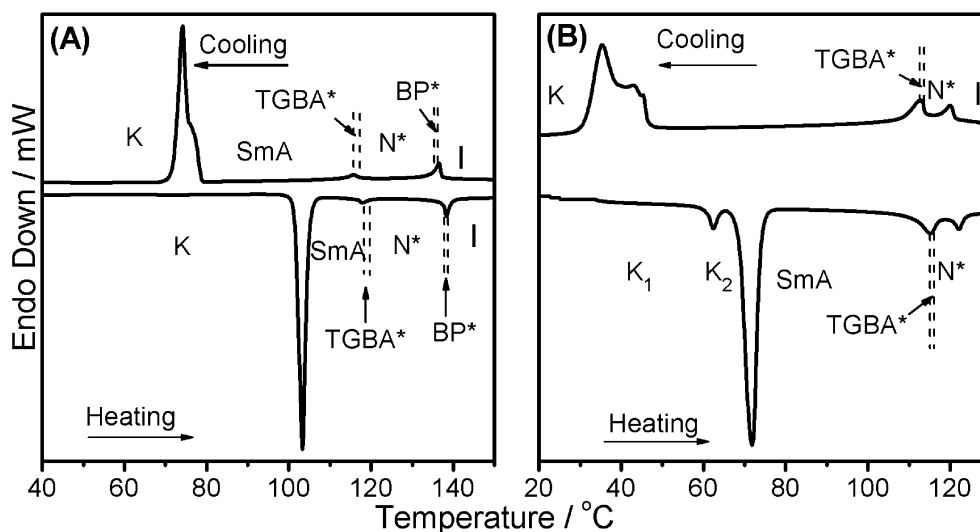


Figure S6. The plots of DSC curves for the 1:1 H-bonded complexes: a) SOCA-PPI; b) SOBA-PPI. K: crystalline phase; SmA: smetic A phase; TGBA*: twist-grain-boundary A phase; N*: chiral nematic phase; BP*: blue phase; I: isotropic phase. Unfortunately, the weak phase transitions of SmA-TGBA*, TGBA*-N* and N*-BP* were not appeared in the DSC cures but obviously observed by POM.

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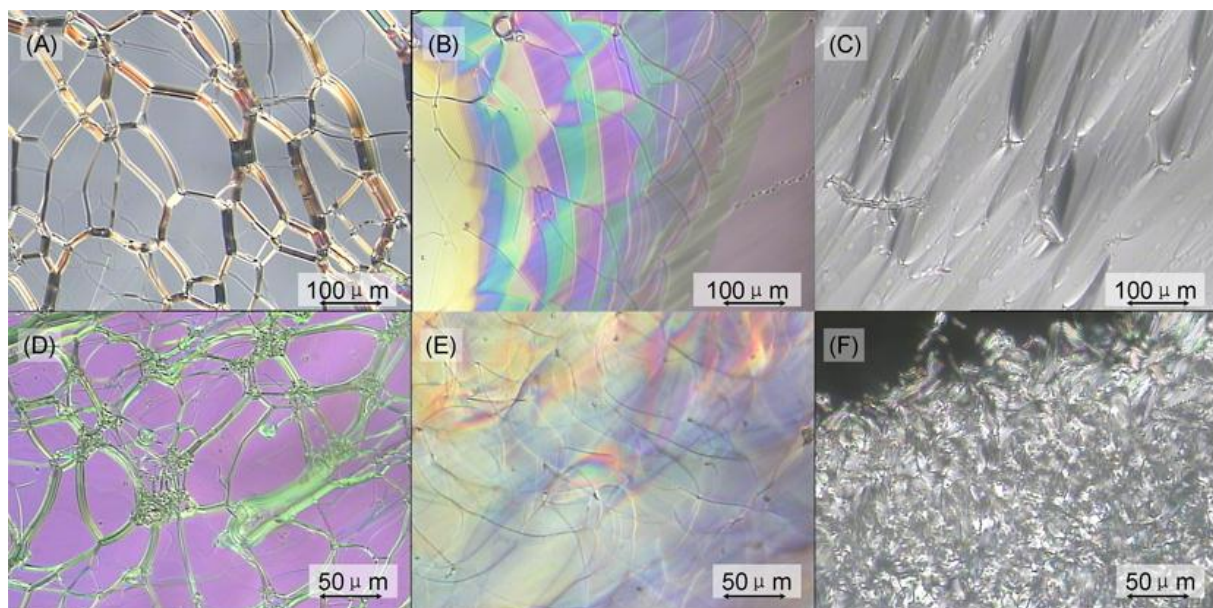


Figure S7. The optical textures of the mesophases in the H-bonded complexes: (A) The oily streaks texture of N* for SOBA-PPI at 120.5 °C; (B) The grandjean texture of TGBA* phase for SOBA-PPI mediating the N* (left part) and SmA* (right area) at 116.6 °C under a planarly oriented condition; (C) The fan-shaped texture of SmA* for SOBA-PPI at 110.0 °C. (D) The grandjean texture of N* for SOCA-PPI at 125.5 °C; (E) The grandjean texture of TGBA* for SOCA-PPI at 118.5 °C; (F) Coexisting of the fingerprint texture of TGBA* phase and the pseudo-isotropic texture (left top part) for SOCA-PPI at 118.0 °C under a homeotropically oriented condition;