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Schiff base derivative doped chiral nematic liquid crystals with large wavelength shift driven by temperature and light

Lei Ren^a, Wanli He^{*a,b}, Meiju Wei^a, Shiguang Luo^a, Daipeng Yao^a, Zhou Yang^{*a,b},
Dong Wang^a, Hui Cao^a

a. Department of Materials Physics and Chemistry, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, P. R. China. E-mail: hewanli@mater.ustb.edu.cn.

b. Beijing Key Laboratory of Function Materials for Molecule & Structure Construction, School of Materials Science and Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Beijing 100083, P.R. China.

1. Experimental

2-hydroxy-4-(oct-3-yloxy)benzaldehyde (I) was synthesized through routine methods. of 2,4-dihydroxybenzaldehyde (1.0g, 7.2mol) and 2-ethylhexyl bromide (1.5g, 8.0mol) were placed in a 100 ml single-necked flask and dissolved in 250 ml of acetone, then K₂CO₃ (1.0g, 7.2mol) and an appropriate amount of KI were poured into the flask. The mixture was refluxed at 60°C for 30 hours, allowed to stand for a while, then filtered and washed with dichloromethane (10ml×3). The filtrate was dried to give yellow solid. The product was observed with TLC plate by using ethyl acetate: petroleum ether (1:1) solvent system, R_f=0.8. The product was extracted by column chromatography using ethyl acetate: petroleum ether (1:2) solvent system, and the solvent was evaporated to give yellow oil which was dried in vacuum oven, then obtained yellow liquid of 0.97 g, yield: 54%. FT-IR(KBr, cm⁻¹): 3260(-OH stretching), 2959, 2873(-CH₃ stretching), 2930, 2860(-CH₂- stretching), 2745(-CHO stretching), 1642, 1509, 1221, 1119, 1018, 803, 639. ¹H-NMR (400MHz, CDCl₃): 11.473(1H,s,OH), 9.701(1H,s,CHO), 7.40-7.42(1H,d,ArH), 6.52-6.54(1H,m,ArH), 6.41-6.43(1H,d,ArH), 8.04-8.10(2H,d,ArH), 3.88-3.91(2H,d,-CH₂-), 1.70-1.80(1H,m,-CH-), 1.20-1.55(8H,m,-CH₂-), 0.89-0.94(6H,m,-CH₃).

[1,1'-binaphthyl]-2,2'-diylbis(4-nitrobenzoate) (II) was synthesized through routine methods. 1,1'-bi-2-naphthol (1.0g, 3.5mol) and p-nitrobenzoic acid (1.3g, 7.7mol) were placed in a 100 ml single-necked flask and dissolved in 100 ml of dichloromethane. Then EDC (2.0g, 105mol) and an appropriate amount of DMAP were poured into the flask. The mixture was stirred at room temperature for 30 h, and the filtrate was spun dry. The crude product was extracted with dichloromethane and water, and the organic layer was dried to obtain pink sticky substance. The product was observed with TLC plate by using dichloromethane solvent system, R_f= 0.76, and the product was extracted by column chromatography using ethyl acetate: petroleum ether (1:2) solvent system. The solvent was dried to give yellow oil, which was dried in vacuum oven to give solid of 1.64 g, yield: 80%. FT-IR(KBr, cm⁻¹): 1741(C=O stretching), 1525, 1348(-NO₂ stretching), 1262(-C-O-C- stretching). ¹H-NMR(400MHz, CDCl₃): 7.34-7.48(4H,m,ArH), 7.48-7.60(4H,m,ArH), 7.66-7.74(4H,d,ArH), 7.92-7.98(2H,d,ArH), 8.00-8.04(2H,d,ArH), 8.045-8.10(2H,d,ArH).

[1,1'-binaphthyl]-2,2'-diylbis(4-aminobenzoate) (III) was synthesized through routine methods. [1,1'-binaphthyl]-2,2'-diylbis(4-nitrobenzoate)(1.0g, 1.7mol) was placed in a 250 ml single-necked flask and dissolved by using ethanol: water(4:1):1 solvent system, then reduced iron powder (0.5g, 8.6mol) and ammonium chloride (0.9g, 17.1mol) were poured into the flask. The mixture was refluxed at 90°C for 30 h, and allowed to stand for suction filtration. Light yellow solution was dried to give pale yellow solid. The product was observed with TLC plate by using dichloromethane solvent system, $R_f = 0.29$. And the product was extracted by using ethyl acetate: petroleum ether(1:2) solvent system. The solvent was spun dry to give yellow solid, which was dried in vacuum oven to give yellow solid, 0.58 g, yield: 65%. FT-IR(KBr, cm^{-1}): 3475, 3405(-NH₂ stretching), 1710(C=O stretching), 1619(-NH bending).¹H-NMR(400MHz, CDCl₃):7.94-8.00(2H,d,ArH),7.88-7.92(2H,d,ArH), 7.56-7.60(2H,d,ArH), 7.47-7.51(4H,d,ArH),7.41-7.45(2H,m,ArH), 7.36-7.40(2H,d,ArH), 7.30-7.40(2H,m,ArH), 6.42-6.47(4H,d,ArH),3.90-4.04(4H,m,-NH₂).

[1,1'-binaphthyl]-2,2'-diylbis(4-((4-(oct-3-yloxy)benzylidene)amino)benzoate) (NACN) was synthesized through routine methods. 2-hydroxy-4-(oct-3-yloxy)benzaldehyde (1.0g, 4.0mol) and [1,1'-binaphthyl]-2,2'-diylbis(4-aminobenzoate) (2.3g, 4.4mol) was placed in a 250 ml single-necked flask and dissolved in 50 ml of ethanol, and a few drops of acetic acid were added drop wise as catalyst. The mixture was stirred at room temperature for 24 hours, and the filtrate was dried to give yellow solid. The product was observed with TLC plate by using ethyl acetate: petroleum ether (1:3) solvent system, $R_f = 0.4$. The eluent was extracted by column chromatography by using ethyl acetate: petroleum ether(1:3) solvent system, and the solvent was evaporated to dryness to give yellow solid, which was crystallized from ethanol, and then recrystallized in ethanol, chilled overnight, filtered, and dried to give yellow solid of 0.84 g, yield: 22%. Optical rotations: $[\alpha]^{20}_D = -262.69^\circ$. MALDI-TOF,m/z: 990.0(989.22). FT-IR(KBr, cm^{-1}): 3060 (-OH), 2958, 2872(-CH₃ stretching),2926,2854(-CH₂- stretching),1731(C=O stretching),1627(C=N stretching),1589,1259 (-C-O-C- stretching), 1164, 1064, 801,692. ¹H-NMR(400MHz, CDCl₃): 13.35(1H,s,-OH),8.45-8.48(1H,s,ArH),7.99-8.05(1H,d,ArH),7.91-7.98(1H,d,ArH),7.65-7.72(2H,d,ArH),7.59-7.64(2H,d,ArH),7.46-7.52(1H,t,ArH),7.42-7.46(1H,d,ArH),7.35-7.40(1H,t,ArH),7.24-7.28(1H,d,ArH),7.08-7.13(2H,d,ArH),6.49-6.54(2H,d,ArH),3.85-3.95(2H,m,-CH₂-),1.73-1.83(1H,m,-CH-),1.40-1.56(4H,m,-CH₂-),1.25-1.40(4H,m,-CH₂-),0.90-1.00(6H,m,-CH₃).

2. Measurement

Fabrication of the LC Cell: To obtain homogeneous alignment, 2.0 wt% polyvinyl alcohol (PVA) in aqueous solution was coated onto the inner surfaces of the cell substrates by spin-casting. The deposited film was dried at 80.0°C for about 30.0 min and subsequently rubbed with textile cloth under the pressure of 2.0 g cm² along one direction. The samples were filled into the cell by capillary action in the temperature range of the CLC phase.

Characterization: The chemical structures of NACN were determined by NMR (Bruker AV 400) and FTIR (Nicolet-510P). The optical textures were observed by POM device (Olympus BX-51) equipped with hot stage calibrated to an accuracy of 0.1°C (Linkam LK-600PM). The phase-transition temperatures were investigated by differential scanning calorimetry (DSC) (Mettler DSC822e) at the heating rate of 10.0°C/min under dry nitrogen purge. The spectra of selective transmission were obtained with UV/VIS/NIR spectrophotometer (JASCO V-570) while the transmittance of the blank cell was normalized as 100.0%. The thermogravimetric analysis of NACN were investigated by (Thermogravimetric Analysis, TG) (TA naichi) at a heating rate of 10.0°C/min under a dry nitrogen purge. The specific optical rotations analysis of NACN were investigated by spectropolarimeter at room temperature.

3. Supplementary Results

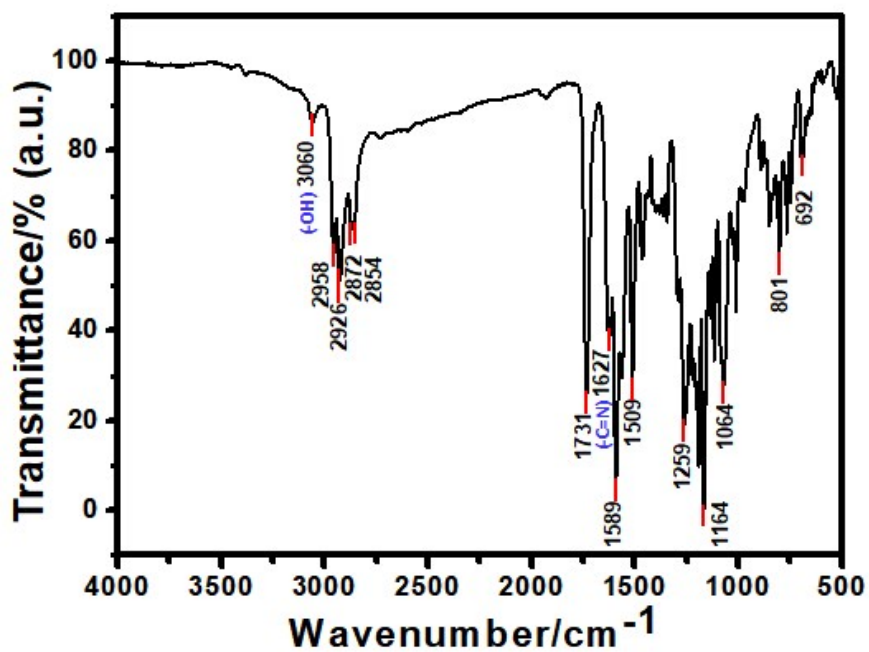


Figure S1. The FTIR spectra of NACN

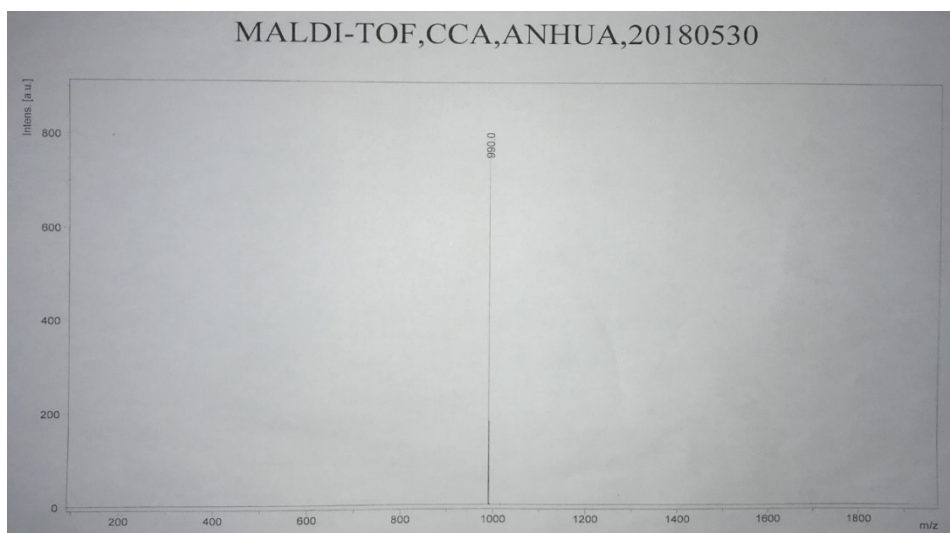


Figure S2. The Mass Spectrometry of NACN

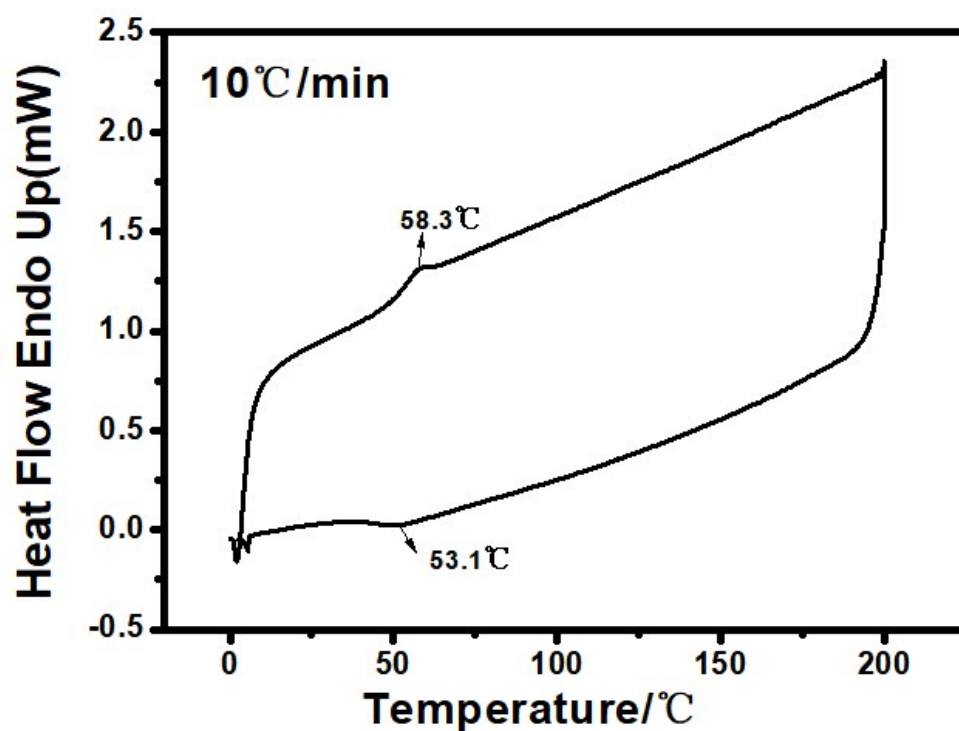
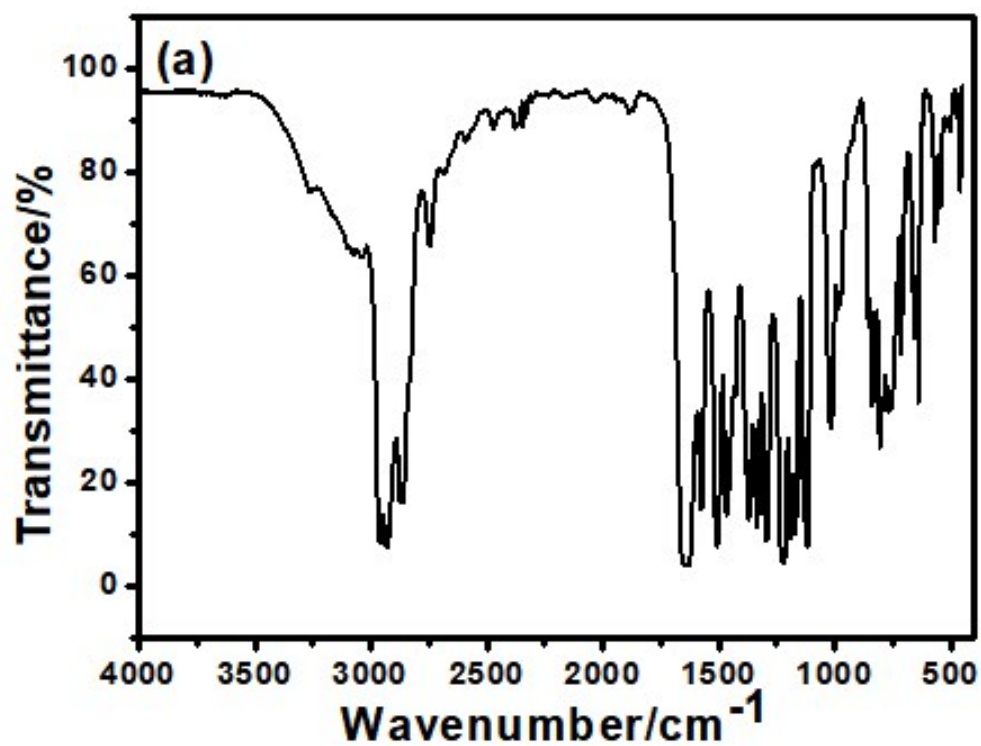


Figure S3. The temperatures and enthalpies of the transition of NACN with heating rate of 10.0°C/min under dry nitrogen purge



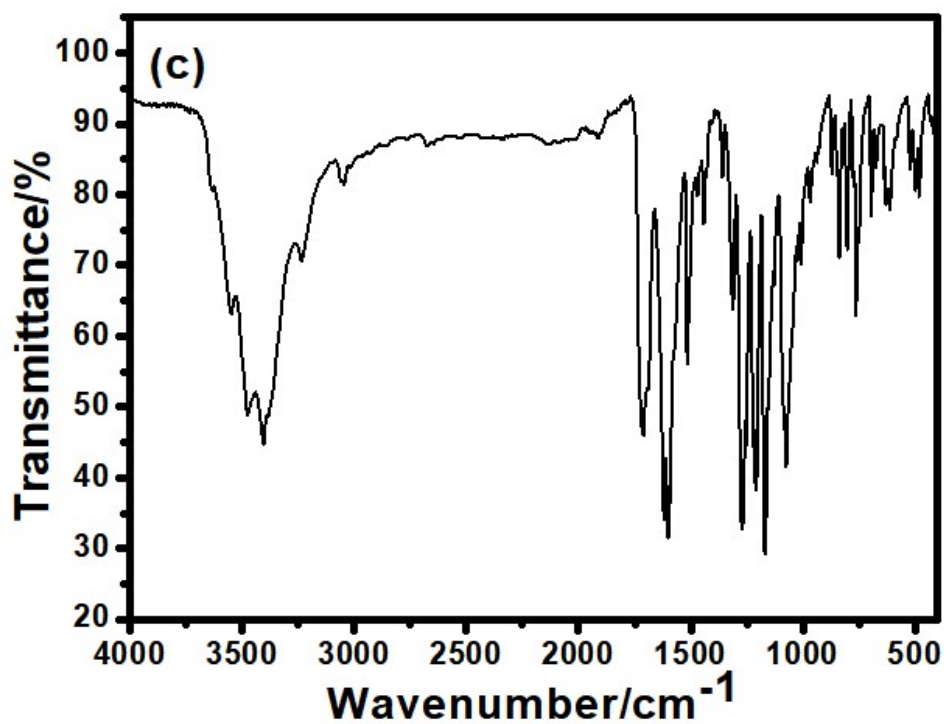
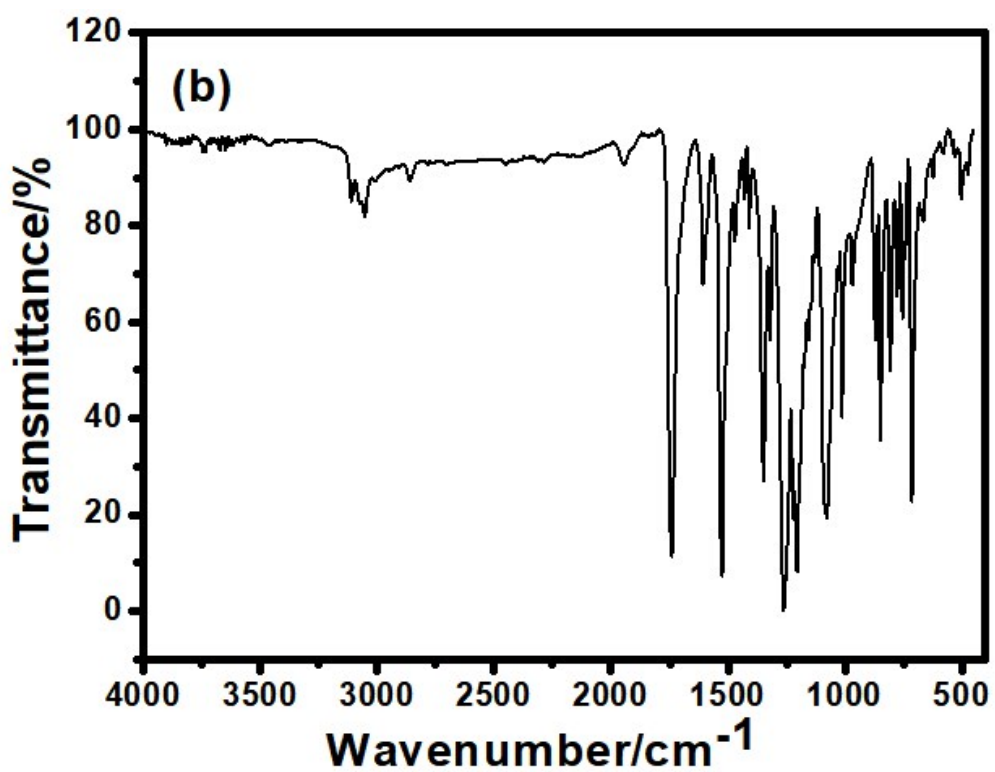
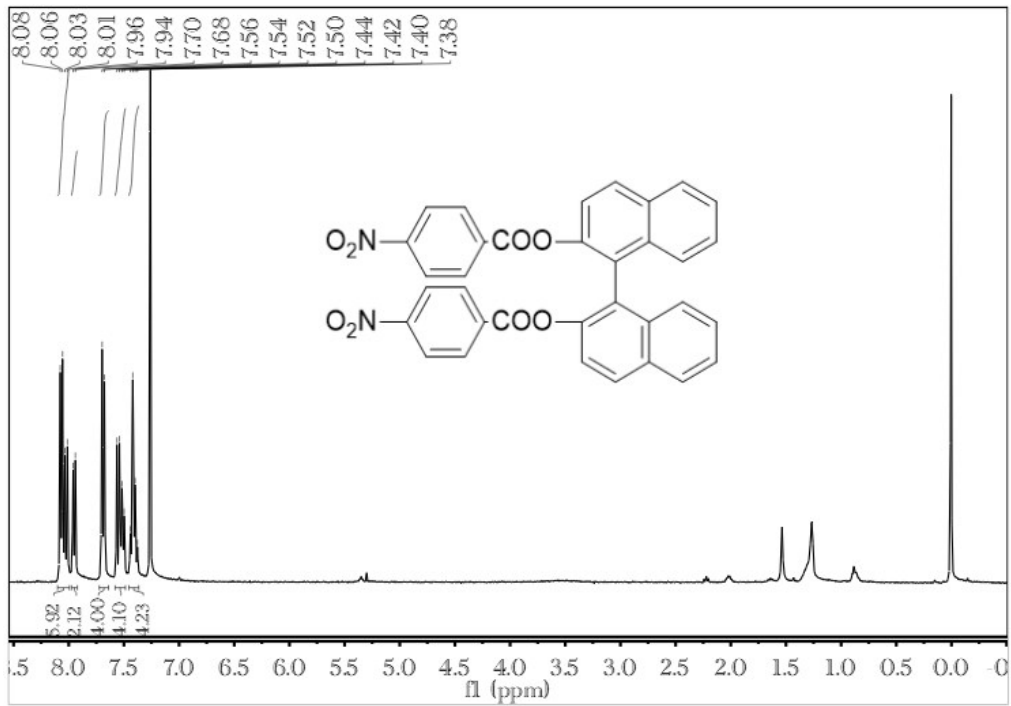
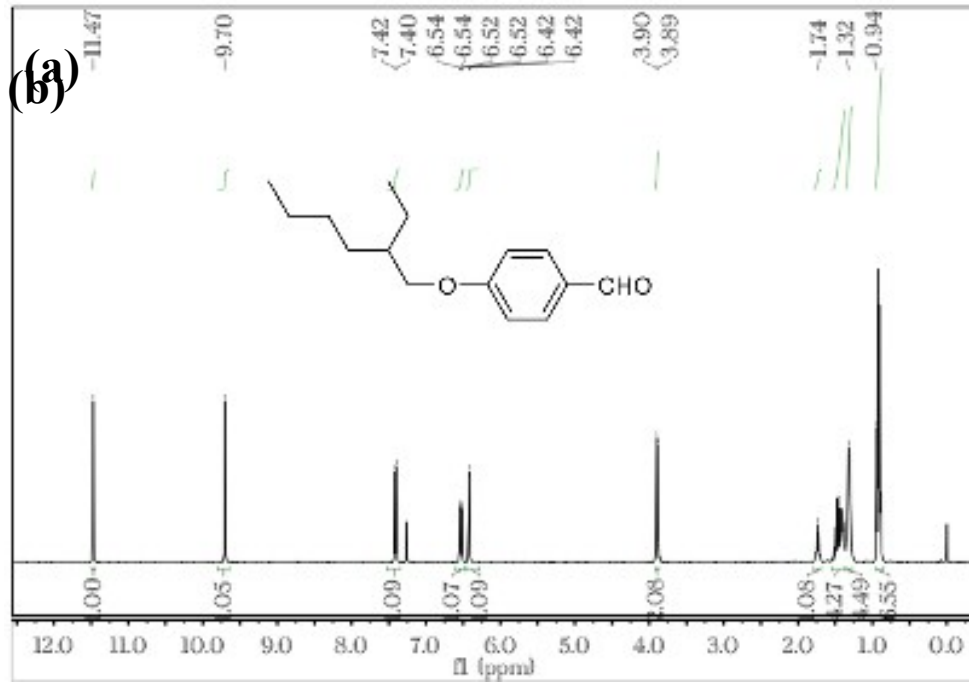


Figure S4.(a) The FTIR spectra of 2-hydroxy-4-(octan-3-yloxy)benzaldehyde; (b) The FTIR spectra of [1,1'-binaphthalene]-2,2'-diyl bis(4-nitrobenzoate); (c) The FTIR spectra of [1,1'-binaphthalene]-2,2'-diyl bis(4-aminobenzoate)



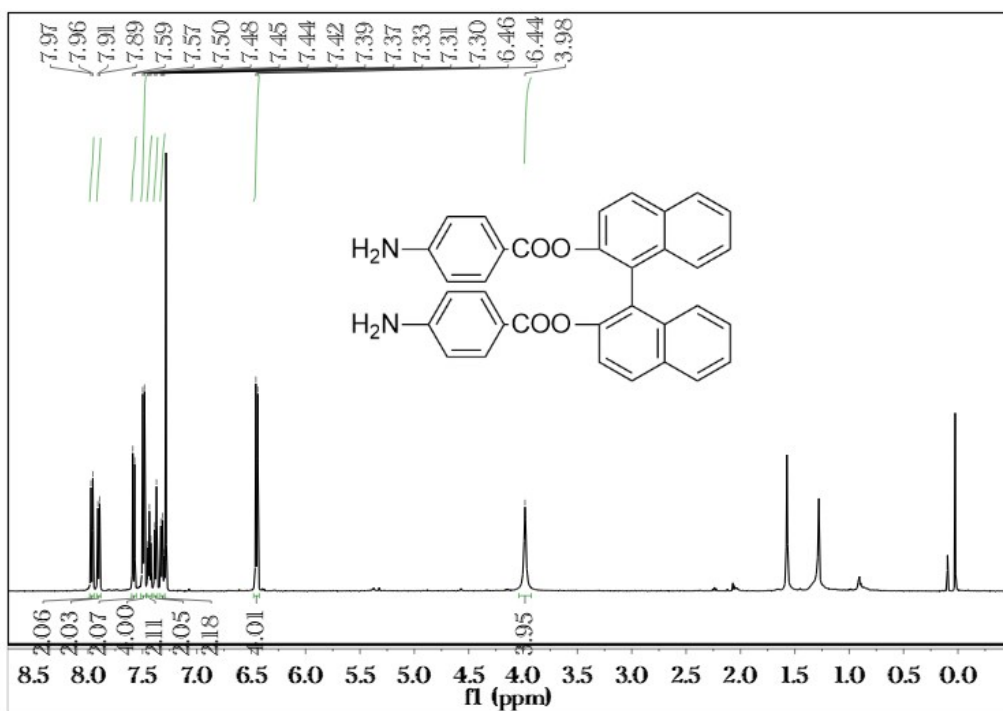


Figure S5. (a) The ^1H NMR of 2-hydroxy-4-(octan-3-yloxy)benzaldehyde; (b) The ^1H NMR of [1,1'-binaphthalene]-2,2'-diyl bis(4-nitrobenzoate); (c) The ^1H NMR of [1,1'-binaphthalene]-2,2'-diyl bis(4-aminobenzoate)

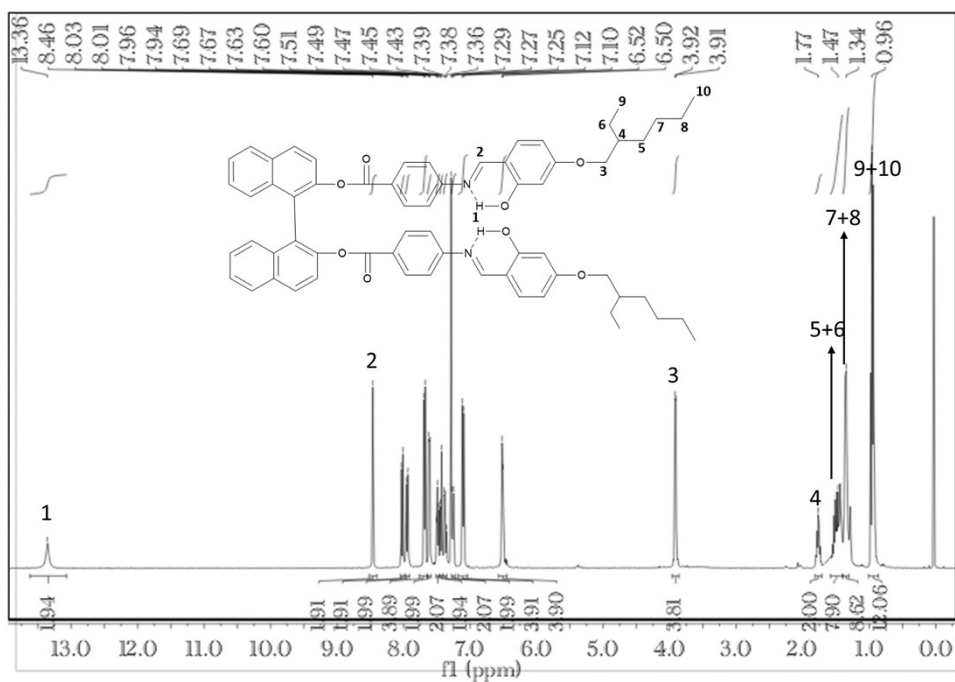


Figure S6. The ^1H -NMR of NACN

Rudolph Research Analytical

This sample was measured on an Autopol V, Serial #83050
Manufactured by Rudolph Research Analytical, Hackettstown, NJ, USA.

Measurement Date : Monday, 28-OCT-2019

Set Temperature : 20.0

Time Delay : Disabled

Delay between Measurement : Disabled

n	Average	Std.Dev.	% RSD	Maximum	Minimum		
3	-262.69	0.00	0.00	-262.69	-262.69		
S.No	Time	Result	Scale	OR °Arc	WLG.nm	Lg.mm	Temp.
1	16:22:44	-262.69	SR Plus	-0.352	589	100.00	20.0
2	16:22:52	-262.69	SR Plus	-0.352	589	100.00	20.0
3	16:22:59	-262.69	SR Plus	-0.352	589	100.00	20.0

Figure S7. The specific optical rotations of NACN at room temperature

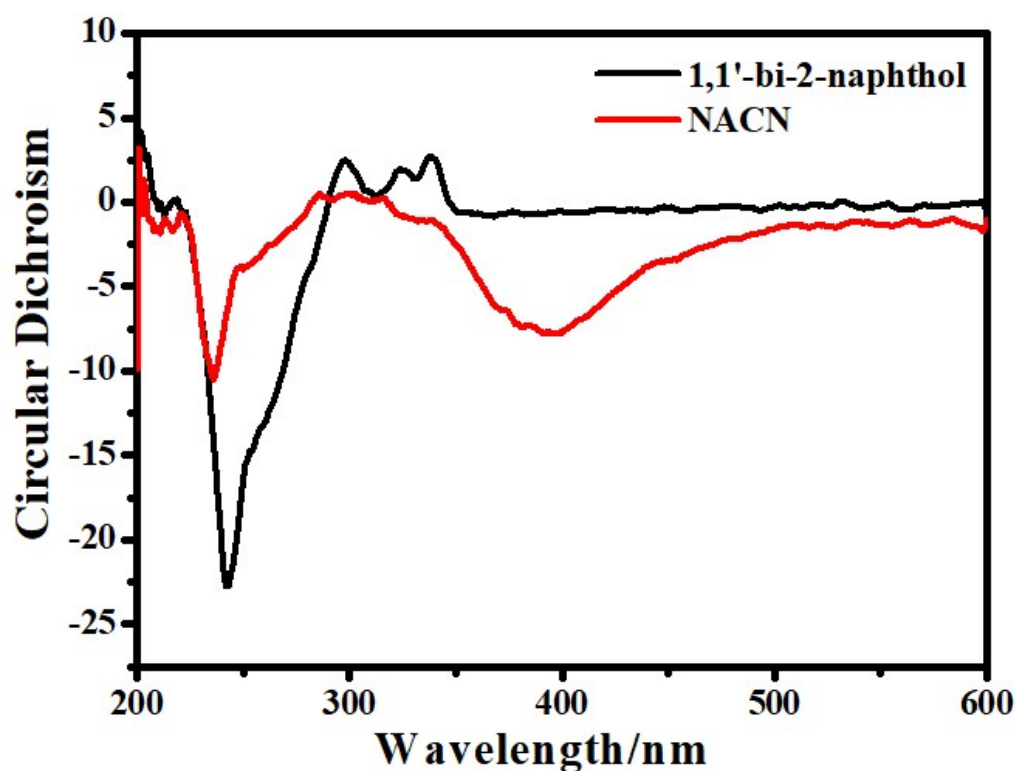


Figure S8. The circular dichroism of NACN and its raw material

The circular dichroism of NACN and its raw material 1,1'-bi-2-naphthol was consistent, as shown in figure S8. The CD spectra results indicated that the NACN and (S)-(s)-1,1'-bi-2-naphthol had the same helical senses of chirality.

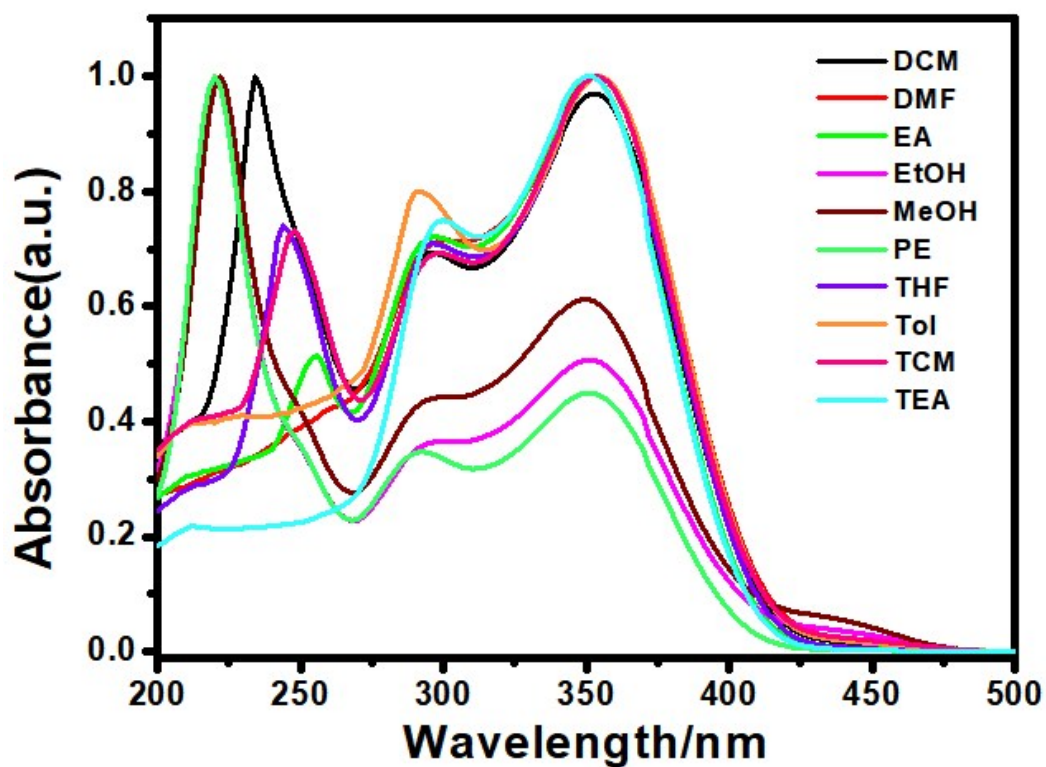


Figure S9. The UV absorption spectrum of NACN in different solvent

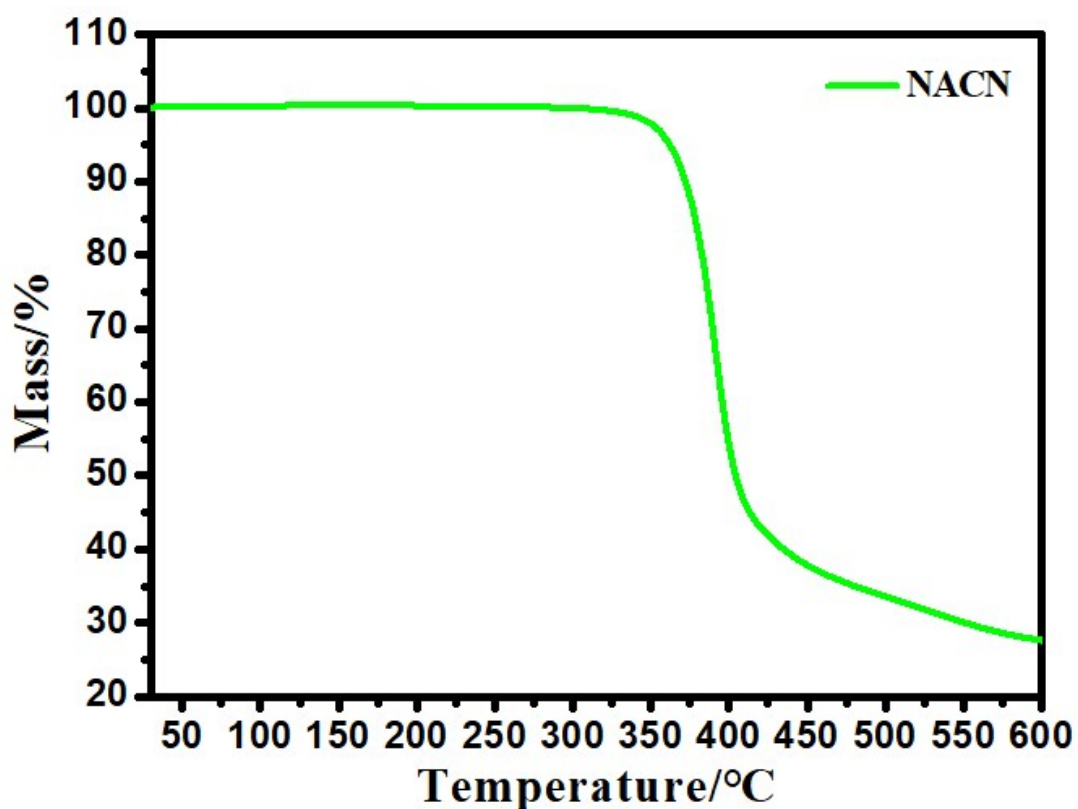
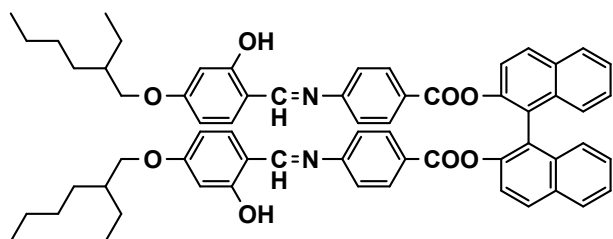


Figure S10. The thermogravimetric analysis of NACN

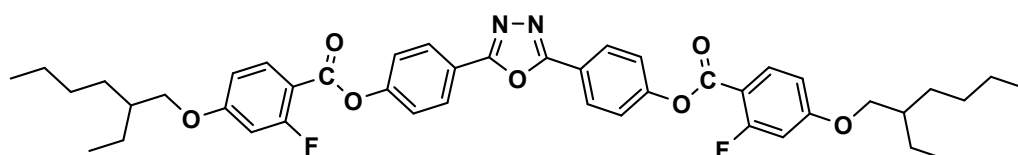
The mass of NACN hardly changed during heating within 320 °C, as shown in figure S10, which indicated that the NACN was stable during the heating process under 320 °C.

(a) N-LC: **SLC-7011** (YongSheng Hua qing Liquid Crystal Co., Ltd, $n_o=1.673$, $n_e=1.838$, $\Delta n=0.165$, TN-I = 68.0°C); **SLC1717** (Yong Sheng Hua qing Liquid Crystal Co., Ltd, $n_o=1.519$, $n_e=1.720$, $\Delta n = 0.201$, TN-I = 92.0°C); **BHR 32100** (Beijing BaYi Space LCD Technology Co., Ltd., $n_o=1.517$, $n_e=1.752$, $\Delta n = 0.235$, TN-I = 98.0°C); **BHR40120** (Beijing BaYi Space LCD Technology Co., Ltd., $n_o=1.505$, $n_e=1.750$, $\Delta n = 0.245$, TN-I = 135°C)

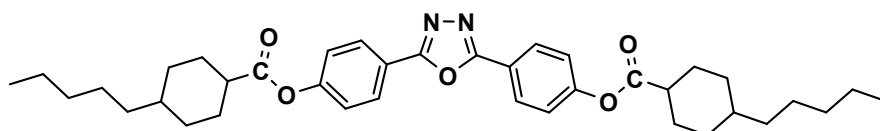
(b) Chiral dopant: **NACN** (left handed)



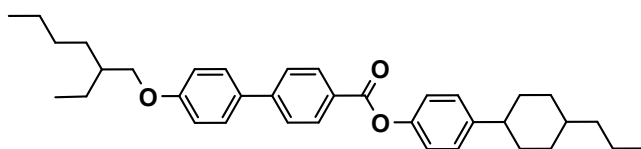
(c) Bend dopant: **C₆ZF-OXD-C₆ZF**



Bend dopant: **C₅C-OXD-C₅C**



(d) Other dopant: **C₆HPBC₃**



Other dopant: **C₆HPBC₅**

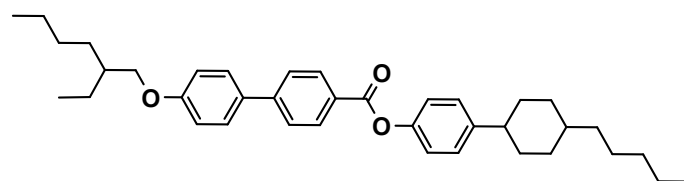
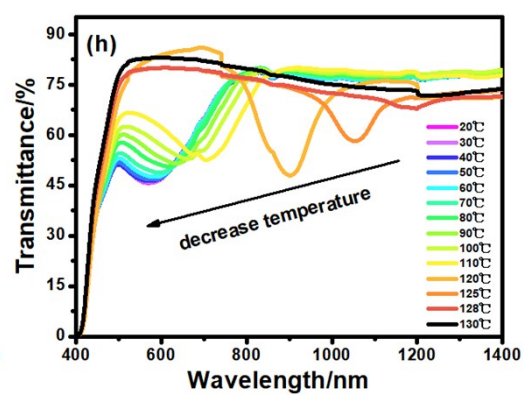
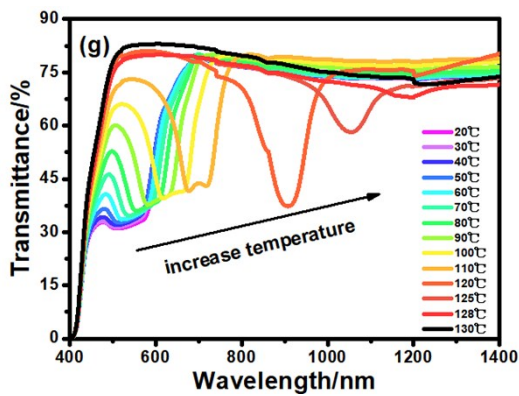
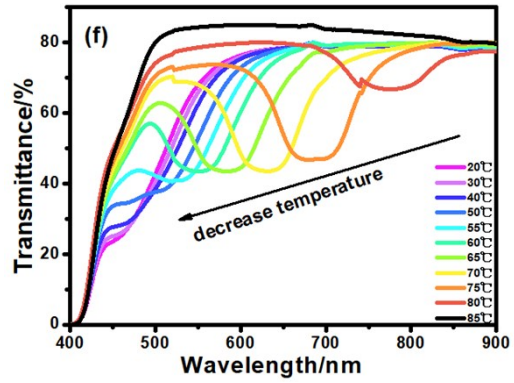
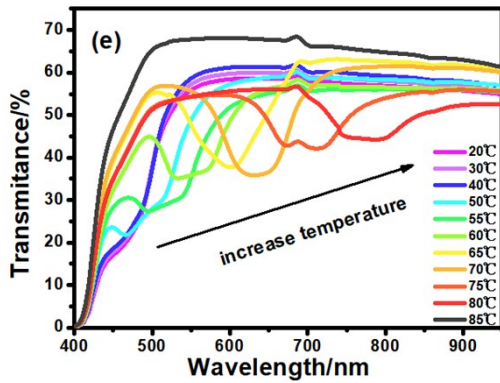
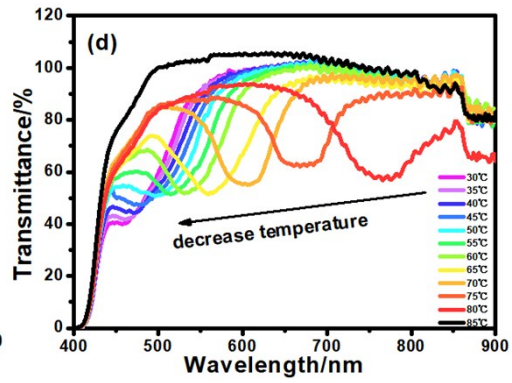
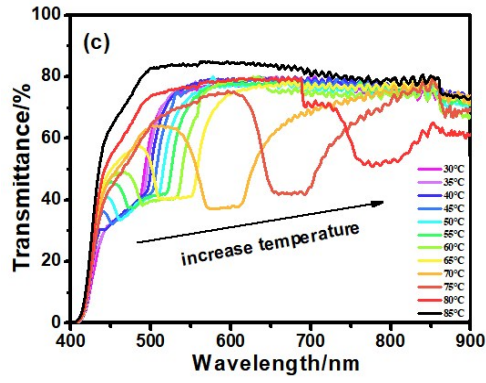
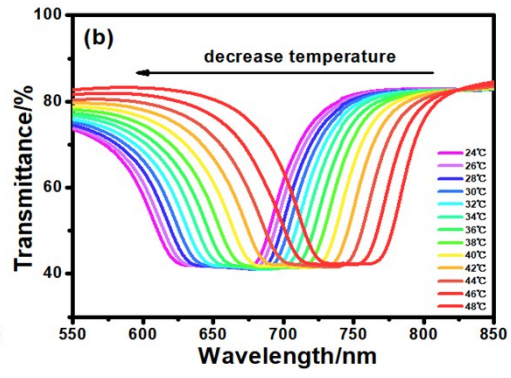
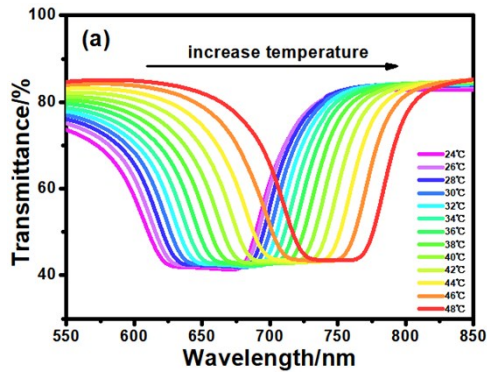


Figure S11. The materials used in this work



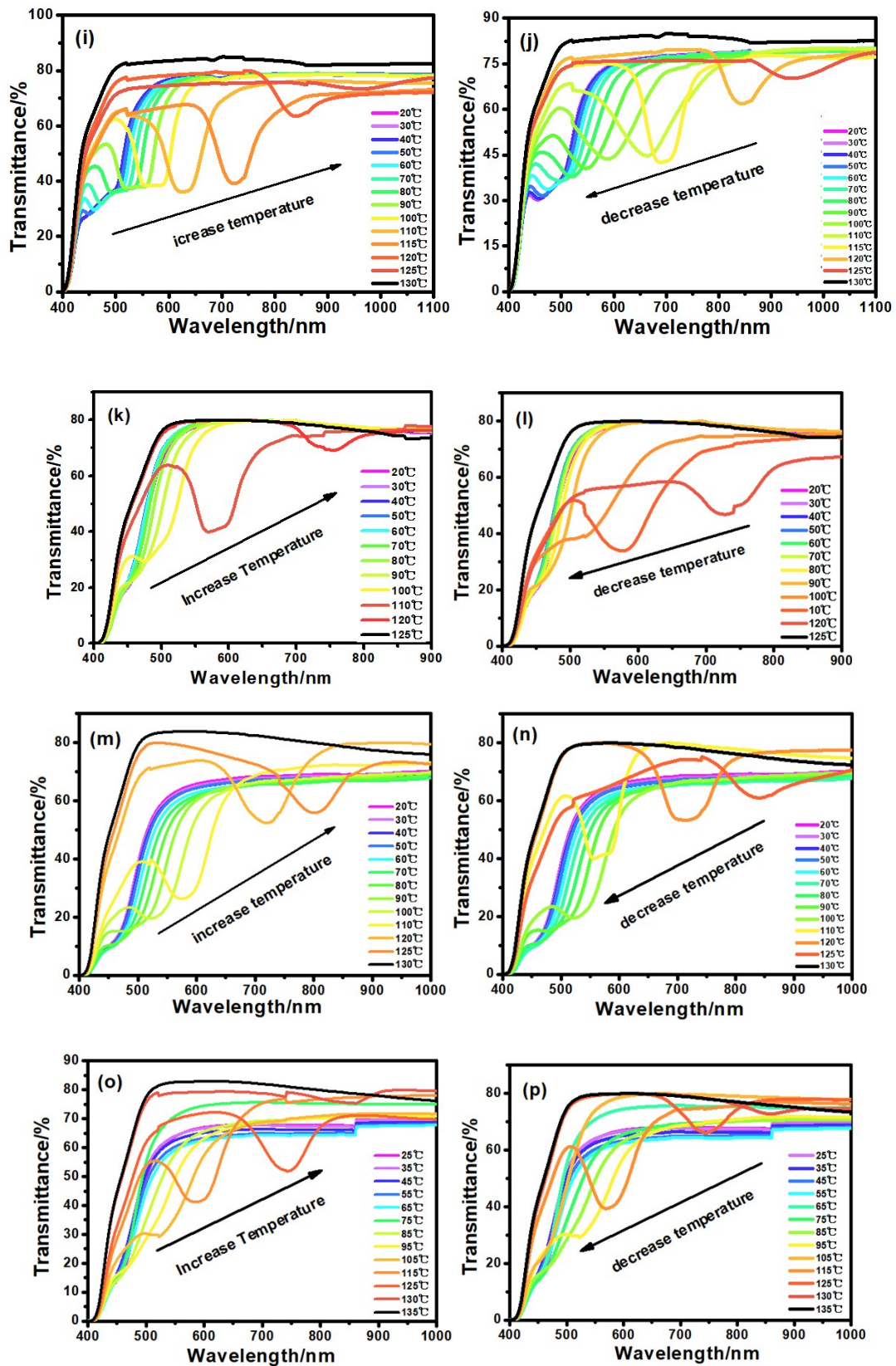


Figure S12. The elective reflection wavelength of samples with increasing temperature and decreasing temperature; (sample 1 (a, b), sample 2 (c, d), sample 3(e, f), sample 4(g, h), sample 5(i, j), sample 6(k, l), sample 7(m, n), sample 8 (o, p)

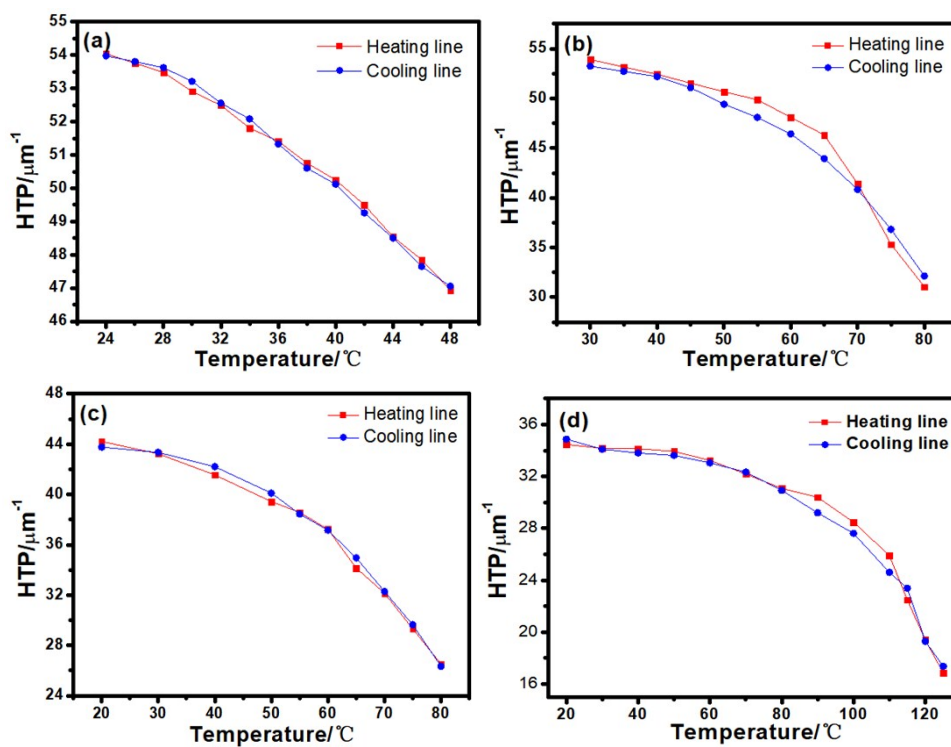


Figure S13. The calculated values of HTP for samples ((a)1, (b)2,(c)3, (d)4) during heating and cooling

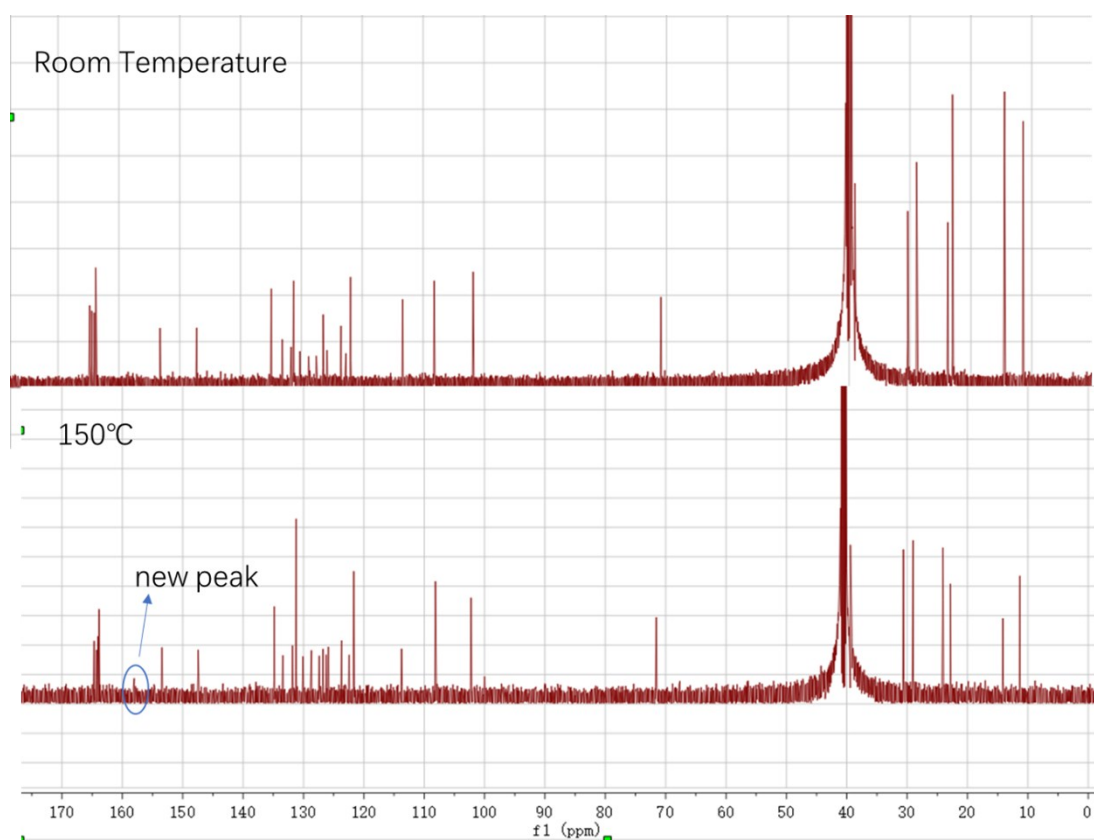


Figure S14. The ^{13}C -NMR of NACN at room temperature and at 150°C . A new weak peak at 158 ppm appeared after heating, which indicated a new keto structure was formed.

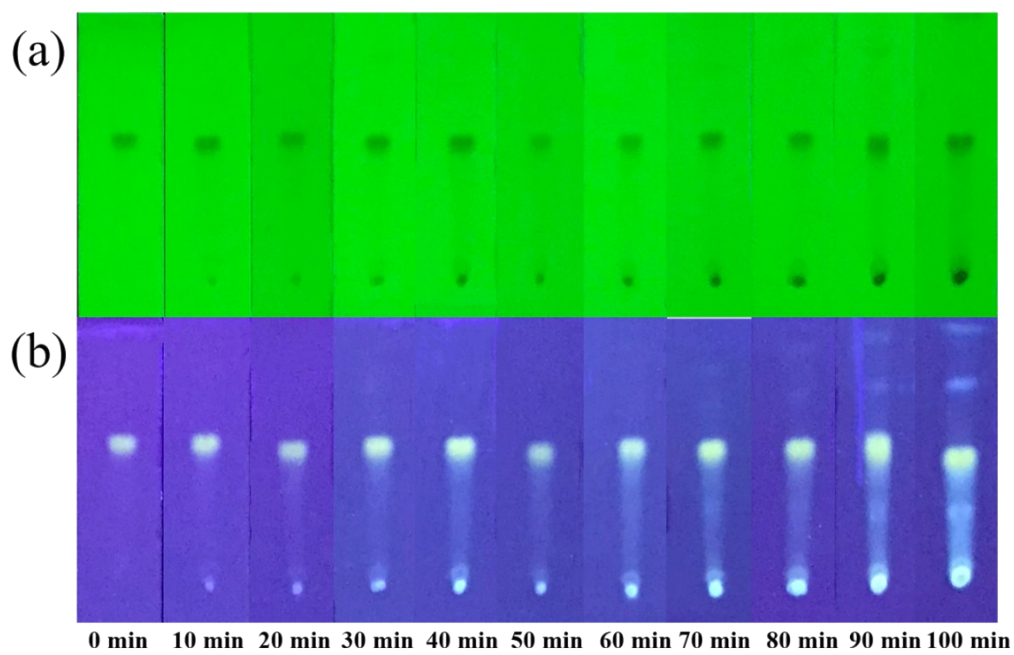


Figure S15. The photography of TLC points of the compound NACN in dichloromethane during UV irradiation (365nm, 10 mW/cm²) detected by UV Lamps (a)254-nm and (b)365-nm