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

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1. Experimental

2-hydroxy-4-(oct-3-yloxy)benzaldehyde (I) was synthesized through routine methods. of 2,4-dihydroxybenzaldehyde (1.0 g, 7.2 mol) and 2-ethylhexyl bromide (1.5 g, 8.0 mol) were placed in a 100 ml single-necked flask and dissolved in 250 ml of acetone, then K\(_2\)CO\(_3\) (1.0 g, 7.2 mol) 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 (10 ml × 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(–CH\(_3\) stretching), 2930, 2860(–CH\(_2\)- stretching), 2745(–CHO stretching), 1642, 1509, 1221, 1119, 1018, 803, 639.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)):

- 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, –CH\(_2\)-), 1.70-1.80(1H, m, –CH-), 1.20-1.55(8H, m, –CH\(_2\)-), 0.89-0.94(6H, m, –CH\(_3\)).

[1,1'-binaphthyl]-2,2'-diylbis(4-nitrobenzoate) (II) was synthesized through routine methods. 1,1'-bi-2-naphthol (1.0 g, 3.5 mol) and p-nitrobenzoic acid (1.3 g, 7.7 mol) were placed in a 100 ml single-necked flask and dissolved in 100 ml of dichloromethane. Then EDC (2.0 g, 105 mol) 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: 54%. FT-IR(KBr, cm\(^{-1}\)):

- 1741(C=O stretching), 1525, 1348(-NO\(_2\) stretching), 1262(-C-O-C- stretching). \(^1\)H-NMR(400 MHz, CDCl\(_3\)):

- 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) 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 (-NH$_2$ stretching), 1710 (C=O stretching), 1619 (-NH bending).

$^1$H-NMR (400MHz, CDCl$_3$): 7.94-8.00 (2H, d, ArH), 7.88-7.92 (2H, d, ArH), 7.65-7.69 (2H, d, ArH), 7.47-7.51 (4H, d, ArH), 7.41-7.45 (2H, m, ArH), 7.36-7.40 (2H, m, ArH), 6.42-6.47 (4H, d, ArH), 3.90-4.04 (4H, m, -NH$_2$).

[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, 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 (-CH$_3$ stretching), 2926, 2854 (-CH$_2$ stretching), 1731 (C=O stretching), 1599, 1259 (-C-O-C- stretching), 1164, 1064, 801, 692. $^1$H-NMR (400MHz, CDCl$_3$): 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, -CH$_2$), 1.73-1.83 (1H, m, -CH$_2$), 1.40-1.56 (4H, m, -CH$_2$), 1.25-1.40 (4H, m, -CH$_2$), 0.90-1.00 (6H, m, -CH$_3$).

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 cm$^{-2}$ 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 $^1$H NMR of 2-hydroxy-4-(octan-3-yloxy)benzaldehyde; (b) The $^1$H NMR of [1,1'-binaphthalene]-2,2'-diyl bis(4-nitrobenzoate); (c) The $^1$H NMR of [1,1'-binaphthalene]-2,2'-diyl bis(4-aminobenzoate)

Figure S6. The $^1$H-NMR of NACN
Figure S7. The specific optical rotations of NACN at room temperature

Figure S8. 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, \( n_o = 1.673, \ n_e = 1.838, \ \Delta n = 0.165 \), \( TN-I = 68.0^\circ C \)); **SLC1717** (Yong Sheng Hua Qing Liquid Crystal Co., Ltd, \( n_o = 1.519, \ n_e = 1.720, \ \Delta n = 0.201 \), \( TN-I = 92.0^\circ C \)); **BHR 32100** (Beijing BaYi Space LCD Technology Co., Ltd., \( n_o = 1.517, \ n_e = 1.752, \ \Delta n = 0.235, \ TN-I = 98.0^\circ C \)); **BHR40120** (Beijing BaYi Space LCD Technology Co., Ltd., \( n_o = 1.505, \ n_e = 1.750, \ \Delta n = 0.245, \ TN-I = 135^\circ C \))

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

(c) Bend dopant: **C_6ZF-OXD-C_6ZF**

(d) Other dopant: **C_6HPBC_3**

Other dopant: **C_6HPBC_5**

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 150ºC
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