



Original article

Naphthylethyne based liquid crystals with high birefringence and characteristics of selective reflection



Yu-Zhen Zhao^a, Dong Wang^c, Ze-Min He^a, Gang Chen^b, Lan-Ying Zhang^b,
Hai-Quan Zhang^{a,*}, Huai Yang^{b,*}

^aState Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China

^bDepartment of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China

^cDepartment of Materials Physics and Chemistry, University of Science and Technology Beijing, Beijing 100083, China

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ABSTRACT

A series of high birefringence liquid crystalline molecules with cyano, isothiocyanato and trifluoromethyl terminal compounds based on naphthylethyne core were successfully synthesized and characterized. The molecular structures of the intermediates and resulting compounds were confirmed by Fourier transform infrared (FT-IR), nuclear magnetic resonance (NMR), mass spectrometry (MS), and elemental analysis (EA). Their thermal stability, transition temperatures, and phase sequences were investigated by simultaneous thermal analyzer polarized (STA), optical microscopy (POM) and differential scanning calorimetry (DSC). The birefringence was measured by using an Abbe refractometer. In addition, the selective reflection characteristics with naphthylethyne compounds were also studied.

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1. Introduction

Design and synthesis of novel liquid crystalline molecules are a focus of research in the field of liquid crystal displays (LCDs) [1–4]. Liquid crystals (LCs), which exhibit high values of birefringence (Δn), are potentially useful for incorporation into electro-optic devices, including various display configurations, such as super-twisted nematic liquid crystal displays (STN-LCDs), scattering-type polymer-dispersed liquid crystal displays (PDLCDs), reflective liquid crystal displays, and spatial light modulators [5–7]. With the rapid development of information technology, design and synthesis of highly birefringent liquid crystalline materials has become an important issue due to the fact that highly birefringent liquid crystals are urgently needed for fast third-order non-linear switching devices [8]. In addition, a number of new applications of highly birefringent liquid crystals have been reported, for example, in reflectors, polarizers, organic light-emitting diodes (OLEDs) and for improving viewing angles in compensation films [9–13].

In the past few years, many highly birefringent materials have been obtained by introducing highly polarizable end-groups and by increasing the molecular π -electron conjugation length [14–16]. Naphthylethyne skeletons with cyano or isothiocyanato terminating groups have also been reported as candidates for high birefringence LC compounds [17]. However, the optical properties of UV absorption and selective reflection have not yet been reported. In the present study, our objective has been to obtain a series of LC molecules with high Δn values based on naphthylethyne and the optical properties of UV absorption spectrum and selective reflection.

2. Experimental

The ¹H NMR and ¹³C NMR spectra were recorded on an AVANCZ 400 spectrometer at 298 K using CDCl₃ as a solvent and tetramethylsilane (TMS) as an internal standard. FT-IR spectra were recorded on a Perkin-Elmer spectrophotometer using a powdered sample on a KBr plate. UV–vis absorption spectra were recorded on a UV-3100 spectrophotometer. Polarizing optical micrographs (POM) were recorded on an Olympus BX51 equipped with a hot stage (LinkamLK-600PM). The Δn was evaluated according to the guest–host method [8] by using an Abbe

* Corresponding authors.

E-mail addresses: hqzhang@ysu.edu.cn (H.-Q. Zhang), yanghuai@pku.edu.cn (H. Yang).

refractometer (2WAJ), and differential scanning calorimetry (DSC) was recorded on a Perkin–Elmer Pyris 6.

Reagents were purchased from commercial sources (Aldrich) and used without further purification, apart from triethylamine (TEA) and tetrahydrofuran (THF), which were distilled under argon before use.

The synthetic routes of the target liquid crystal compounds are shown in Scheme 1.

2-Bromo-6-pentyloxy-naphthalene: 2-Bromopentane (4.5 g, 30 mmol) was added dropwise through a syringe to a suspension of 6-bromo-2-naphthol (3.3 g, 15 mmol) and K_2CO_3 (6.2 g, 45 mmol) in DMF (30 mL). The solution was stirred at 90 °C for 4 h. After the reaction completed, the solvent was removed by vacuum distillation. The crude product was purified by column chromatography (silica gel, hexane: CH_2Cl_2 = 4:1) to give the target product (3.94 g, 90%) as a white solid. 1H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.69 (d, 1H, J = 8.0 Hz), 7.54 (d, 1H, J = 8.0 Hz), 7.51 (d, 2H, J = 8.0 Hz), 7.18 (d, 1H, J = 8.0 Hz), 7.11 (s, 1H), 4.03 (t, 2H), 1.88 (m, 2H), 1.44 (m, 2H), 1.29 (m, 2H), 0.96 (t, 3H); FTIR (cm^{-1}): ν 3108, 2925, 2854, 1604, 1483, 1466, 1345, 1216, 1184, 997, 882, 803, 720; MALDI-TOF-MS (dithranol): m/z : calcd. for $C_{15}H_{17}BrO$: 292.03, found: 293.14 [MH] $^+$.

Trimethyl-(6-pentyloxynaphthalen-2-ylethynyl)-silane: 2-Bromo-6-pentyloxynaphthalene (2.92 g, 10 mmol) and TMSA (1.17 g, 12 mmol) were dissolved in 100 mL dry triethylamine (Et_3N); tetrahydrofuran (THF) (1:1), then, $Pd(PPh_3)_4$ (0.28 g, 0.24 mmol) and CuI (0.09 g, 0.48 mmol) were added. The reaction mixture was stirred at room temperature for 8 h under an Ar atmosphere. Upon completion, the solvent was removed in vacuo and the crude material purified by column chromatography on silica gel (hexane: CH_2Cl_2 = 2:1) to give the target compound (2.57 g, 83%) as a white solid. 1H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.72 (d, 1H, J = 8.0 Hz), 7.67 (d, 1H, J = 8.0 Hz), 7.53 (d, 2H, J = 8.0 Hz), 7.16 (d, 1H, J = 8.0 Hz), 7.10 (s, 1H), 4.04 (t, 2H), 1.88 (m, 2H), 1.44 (m, 2H), 1.28 (m, 2H), 0.96 (t, 3H), 0.08 (s, 9H); FTIR (cm^{-1}): ν 3109, 2924, 2853, 2185, 2174, 1604, 1483, 1466, 1345, 1212, 1184, 995, 882, 800, 724; MALDI-TOF-MS (dithranol): m/z : calcd. for $C_{20}H_{26}OSi$: 310.17, found: 310.47 [M].

2-Ethynyl-6-pentyloxynaphthalene: K_2CO_3 (2.76 g, 20 mmol) was added to a solution of trimethyl-(6-pentyloxynaphthalen-2-ylethynyl)-silane (2.17 g, 7 mmol) in 80 mL THF:MeOH (7:3). The reaction mixture was stirred at room temperature for 3 h. Upon completion, the mixture was filtered by suction filtration. The solvent was removed in vacuo and the crude product was purified by column chromatography (CH_2Cl_2 as the eluent) to give the target compound (1.51 g, 91%) as a white solid. 1H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.73 (d, 1H, J = 8.0 Hz), 7.68 (d, 1H, J = 8.0 Hz),

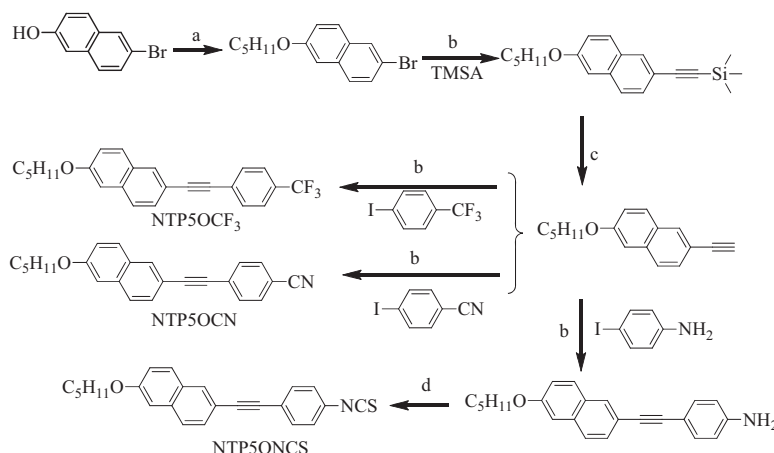
7.56 (d, 2H, J = 8.0 Hz), 7.17 (d, 1H, J = 8.0 Hz), 7.13 (s, 1H), 4.09 (t, 2H), 3.06 (s, 1H), 1.89 (m, 2H), 1.44 (m, 2H), 1.28 (m, 2H), 0.96 (t, 3H); FTIR (cm^{-1}): ν 3297, 3109, 2924, 2853, 2185, 2108, 2045, 1604, 1483, 1466, 1345, 1212, 1184, 995, 882, 800, 724; MALDI-TOF-MS (dithranol): m/z : calcd. for $C_{17}H_{18}O$: 238.13, found: 238.32 [M].

4-(6-Pentyloxynaphthalene-2-ylethynyl)-benzonitrile (NTP5OCN): The synthesis of NTP5OCN used the same method as described for the preparation of 1-bromo-6-pentyloxy-naphthalene and 4-iodo-benzonitrile. The product was a white solid, yield: 78%. 1H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.78 (d, 1H, J = 8.0 Hz), 7.70 (d, 1H, J = 8.0 Hz), 7.59 (d, 1H, J = 8.0 Hz), 7.56 (d, 2H, J = 8.0 Hz), 7.24 (d, 2H, J = 8.0 Hz), 7.21 (d, 1H, J = 8.0 Hz), 7.17 (s, 1H), 4.04 (t, 2H), 1.87 (m, 2H), 1.44 (m, 2H), 1.26 (m, 2H), 0.96 (t, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 134.7, 132.1, 132.0, 131.9, 129.4, 128.0, 128.5, 128.3, 127.0, 120.0, 118.6, 116.9, 111.2, 106.6, 94.7, 87.5, 68.2, 28.9, 28.3, 22.5, 14.1; FTIR (cm^{-1}): ν 3109, 2924, 2853, 2243, 2239, 2185, 2108, 2045, 1604, 1483, 1466, 1345, 1212, 1184, 995, 882, 800, 724. MALDI-TOF-MS (dithranol): m/z : calcd. for $C_{24}H_{21}NO$: 339.15, found: 339.42 [M].

4-(6-Pentyloxynaphthalene-2-ylethynyl)-trifluoromethyl-phenyl (NTP5OCF₃): The synthesis of NTP5OCF₃ used the same method as described for the preparation of A with a yield of 76% as a white solid. 1H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.73 (d, 1H, J = 8.0 Hz), 7.68 (d, 1H, J = 8.0 Hz), 7.62 (d, 1H, J = 8.0 Hz), 7.54 (d, 2H, J = 8.0 Hz), 7.21 (d, 2H, J = 8.0 Hz), 7.17 (d, 1H, J = 8.0 Hz), 7.13 (s, 1H), 4.09 (t, 2H), 1.89 (m, 2H), 1.44 (m, 2H), 1.28 (m, 2H), 0.96 (t, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 134.5, 131.8, 131.7, 129.9, 129.4, 128.8, 128.3, 127.4, 126.9, 125.3, 125.2 (q, J = 220 Hz), 119.9, 117.2, 106.6, 92.6, 87.6, 68.1, 28.9, 28.3, 22.5, 14.1; FTIR (cm^{-1}): ν 3109, 2924, 2853, 2185, 2108, 2045, 1604, 1483, 1466, 1345, 1212, 1184, 995, 882, 800, 724 cm^{-1} . MALDI-TOF-MS (dithranol): m/z : calcd. for $C_{24}H_{21}F_3O$: 382.15, found: 382.42 [M].

4-(6-Pentyloxynaphthalene-2-ylethynyl)-phenylamine: The synthesis used the same method as described for the preparation of A with a yield of (73%) as a yellow solid. 1H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.74 (d, 1H, J = 8.0 Hz), 7.69 (d, 1H, J = 8.0 Hz), 7.53 (d, 1H, J = 8.0 Hz), 7.31 (d, 2H, J = 8.0 Hz), 7.16 (d, 1H, J = 8.0 Hz), 7.10 (s, 1H), 6.58 (d, 2H, J = 8.0 Hz), 4.04 (t, 2H), 4.0 (s, 2H), 1.87 (m, 2H), 1.44 (m, 2H), 1.26 (m, 2H), 0.96 (t, 3H); FTIR (cm^{-1}): ν 3451, 3447, 3109, 2924, 2853, 2185, 2108, 2045, 1604, 1483, 1466, 1345, 1212, 1184, 995, 882, 800, 724. MALDI-TOF-MS (dithranol): m/z : calcd. for $C_{23}H_{23}NO$: 329.18, found: 329.43 [M].

2-(4-Isothiocyanto-phenylethynyl)-6-pentyloxy-naphthalene (NTP5ONCS): 4-(6-Pentyloxynaphthalene-2-ylethynyl)-phenylamine (1.27 g, 4 mmol) was dissolved in 30 mL $CHCl_3$, then $CaCO_3$ (0.8 g, 8 mmol) and $CSCl_2$ (0.68 g, 6 mmol) were added. The



Scheme 1. The synthesis routes and reagents: a, $C_5H_{11}Br$, K_2CO_3 , DMF; b, Et_3N , THF, $Pd(PPh_3)_4$, CuI; c, K_2CO_3 , MeOH; d, $CSCl_2$, $CaCO_3$.

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