Liquid Crystals

ISSN: 0267-8292 (Print) 1366-5855 (Online) Journal homepage: http://www.tandfonline.com/loi/tlct20

Acetylene-containing highly birefringent rod-type reactive liquid crystals based on 2-methylhydroquinone

Hyein Jung, Ji Ho Yun, Inhye Jeon, Jinsoo Kim, Yun Ho Kim, Mi Hye Yi, Jinhan Cho, Eunkyoung Kim & Jae-Won Ka

To cite this article: Hyein Jung, Ji Ho Yun, Inhye Jeon, Jinsoo Kim, Yun Ho Kim, Mi Hye Yi, Jinhan Cho, Eunkyoung Kim & Jae-Won Ka (2018) Acetylene-containing highly birefringent rod-type reactive liquid crystals based on 2-methylhydroquinone, Liquid Crystals, 45:2, 279-291, DOI: 10.1080/02678292.2017.1323127

To link to this article: https://doi.org/10.1080/02678292.2017.1323127

LIQUID CRYSTALS, 2018
VOL. 45, NO. 2, 279–291
https://doi.org/10.1080/02678292.2017.1323127

Taylor & Francis
Taylor & Francis Group

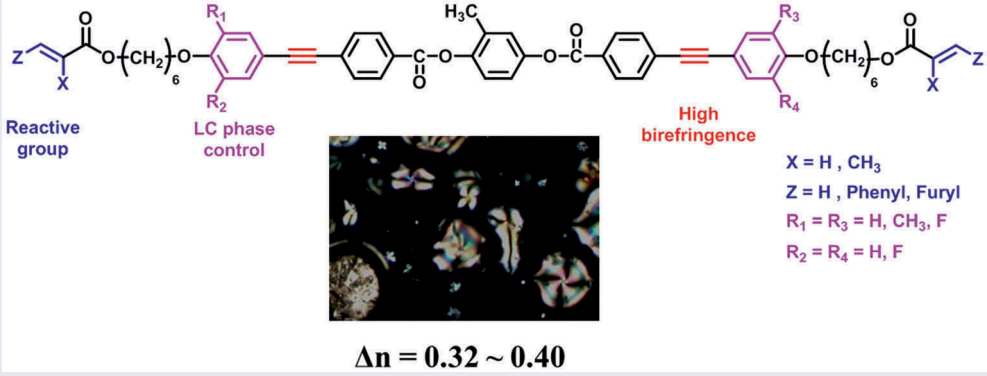
Acetylene-containing highly birefringent rod-type reactive liquid crystals based on 2-methylhydroquinone

Hyein Jung[a,c], Ji Ho Yun[a], Inhye Jeon[a,b], Jinsoo Kim[a], Yun Ho Kim[a], Mi Hye Yi[a], Jinhan Cho[b], Eunkyoung Kim[c] and Jae-Won Ka[a]

[a]Center for Advanced Functional Polymers, Korea Research Institute of Chemical Technology, Daejeon, Korea; [b]Departmehnt of Chemical and Biological Engineering, Korea University, Seoul, Korea; [c]Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul, Korea

ABSTRACT

New highly birefringent reactive liquid crystal materials based on the 2-methylhydroquinone core were designed and synthesised. Rod-type liquid crystal compounds bearing photo-crosslinkable reactive group of acryloyl, methacryloyl, cinnamoyl, furylacryloyl group were synthesised by introducing acetylene groups via Sonogashira coupling to obtain high birefringence, and lateral groups such as fluoro and methyl to adjust the temperature of the liquid crystal phase. The synthesised compounds were characterised using nuclear magnetic resonance spectroscopy, mass spectrometry and elemental analysis. In addition, their thermal behaviour was investigated using differential scanning calorimetry and polarised optical microscopy. After aligning the synthesised compounds, liquid crystal films were prepared by photo-irradiation. Photo-elastic modulator results showed that the obtained liquid crystal films had high birefringence (Δn) values of 0.32–0.40.



ARTICLE HISTORY
Received 8 November 2016
Accepted 20 April 2017

KEYWORDS
Liquid crystal; high birefringence; reactive LC; methylhydroquinone

1. Introduction

A reactive liquid crystal is a liquid crystal compound having a reactive end group, which can undergo crosslinking reactions when subjected to heat or light [1]. Photo-reactive liquid crystal compounds that are capable of cross-linking in the presence of light generally include cinnamoyl, methacrylate or acrylate groups [2–4]. Many studies have been actively conducted to control the optical and electrical properties of liquid crystals by aligning and fixing them using various methods. One of the key applications of reactive liquid crystal is in optical films [5], which can be widely used in both display and non-display applications, owing to the optical anisotropy of the liquid crystals.

An important factor for obtaining high-performance optical films using reactive liquid crystals is the birefringence of the liquid crystal film. A high-birefringence liquid crystal film can achieve performance similar to existing optical films by reducing its thickness [6]. Moreover, such a film can be utilised in new application fields, such as THz applications for telecommunication [7], tunable-focus lens [8] and holographic devices [9].

Many studies have been conducted to improve the birefringence of liquid crystal compounds and controlling various liquid crystal phase behaviours in accordance with π–electron conjugation, functional groups and compound structures [10,11]. Many high-

CONTACT Jae-Won Ka jwka@krict.re.kr
Supplemental data for this article can be accessed here.

birefringence liquid crystal compounds feature triple bonds or benzene rings with long π–π conjugation in the molecule, or highly polarisable functional groups such as NO_2, isothiocyanate (NCS) and cyano (CN) [12–15]. However, such structural motifs cause problems during film formation since they have decreased solubility in typical coating solvents used when designing molecules [16], as they contain polar groups or introduce long π–electron conjugation necessary to improve birefringence of the overall liquid crystal [17].

Studies on film alignment, film processing and evaluation of film properties have also been conducted. The LC 242 compound (containing a hydroquinone core, Figure 1) has been widely studied as a reactive liquid crystal compound [18–20]. An LC 242 film was formed through a photo-crosslinking reaction using UV irradiation, and its birefringence value was 0.14 ~ 0.18.

In this study, rod-type liquid crystal compounds featuring photo-crosslinkable acryloyl, methacryloyl, cinnamoyl and furylacryloyl groups were synthesised by introducing acetylene groups into the hydroquinone-focused liquid crystal compound to obtain high birefringence [21], and by introducing side groups (such as fluoro and methyl groups) [22] to control the temperature of the liquid crystal phase formation as shown in Figure 2. The correlations between molecular structure, liquid crystallinity, filming characteristics and birefringence were investigated.

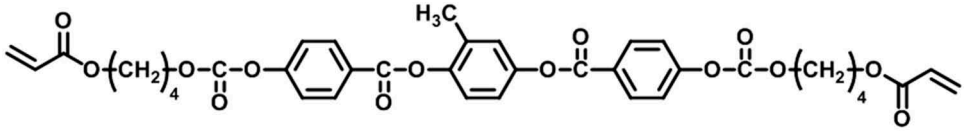
2. Experimental

2.1. Materials and measurements

Reagents and solvents were purchased from Aldrich, TCI and Duksan Chemical. Reaction products were purified using silica gel column chromatography (230–400 mesh, Merck). Proton nuclear magnetic resonance (NMR) spectra were recorded on Bruker 300–500 MHz instruments in DMSO-d_6 and $CDCl_3$ solvents with tetramethylsilane (TMS) as internal standard. Differential scanning calorimetry (DSC) measurements were conducted at heating and cooling rates of 10°C/min using a Perkin Elmer Diamond DSC. Polarised optical microscopy (POM) was performed using a Nikon Eclipse and INSTEC instrument at heating and cooling rates of 10°C/min. The alignment layer was rubbed using a rubbing machine (NMAIL instruments, RMS-50-D). The film thickness was measured using KLA-tencor instruments, Alpha-Step IQ Surface Profiler. Retardation measurements for birefringence were performed using a digital oscilloscope (Tektronix, TDS 2022B) in a He–Ne laser system.

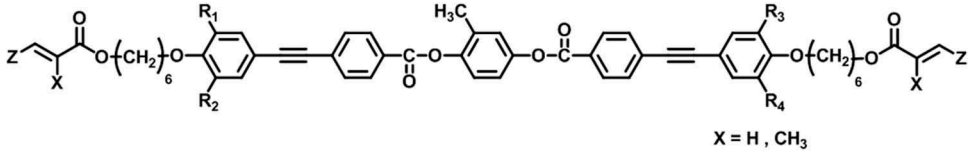
2.2 Preparation of LC film

Optical anisotropic films of compounds **9–12, 23–24** and the control LC 242 were produced as follows. Compounds **9, 10, 23** and **24** and a photo-initiator (6 wt% of LC) of 2,2-dimethoxy-2-phenylacetophenone /benzophenone in a 1:1 ratio were dissolved in 1,1,2,2-tetrachloroethane at 5 wt%. Compounds **11** and **12**, which do not require an initiator, were dissolved in 1,1,2,2,-tetrachloroethane at the same 5 wt% concentration. Subsequently, both solutions were spin-coated over rubbed alignment layers. After spin-coating, compounds **9–12** and **23** were baked at 220°C for 5 min, compound **24** at 250°C for 1 min and LC 242 at 120°C for 5 min. The baking temperatures used were based on the temperature needed to achieve proper alignment.



LC 242

Figure 1. The molecular structure of LC 242.



X = H , CH_3
Z = H , Phenyl, Furyl
$R_1 = R_3$ = H, CH_3, F
$R_2 = R_4$ = H, F

Figure 2. The molecular structure of the 2-methylhydroquinone core highly birefringent reactive liquid crystals.

After baking, the compounds were analysed by POM, followed by crystallisation. Compounds **9**–**12** films were cured with UV irradiation (365 nm, 0.4 J/cm^2) at 220°C, as were **23** (1 J/cm^2 at 180°C), **24** (1 J/cm^2 at 25°C) and LC 242 (0.8 J/cm^2 at 25°C). The thicknesses of the produced liquid crystal films were 0.20–0.23 µm.

2.3 Synthesis

2.3.1 2-Methyl-1,4-phenylene bis(4-iodobenzoate) (1)

A solution of 2-methylhydroquinone (2.1 g, 17 mmol), 4-iodobenzoyl chloride (10 g, 36 mmol) and pyridine (2.7 mL, 34 mmol) in tetrahydrofuran (200 mL) was stirred at 55°C for 12 h. After that, the reaction mixture was cooled to room temperature and the product was precipitated by adding water. A white powder was obtained by filtration and drying under vacuum (8.9 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.90 (4H, d, *J* = 2.2 Hz), 7.89 (4H, d, *J* = 2.2 Hz), 7.13 (3H, m), 2.24 (3H, s); ^{13}C NMR (300 MHz, $CDCl_3$) δ = 164.70, 164.32, 148.27, 146.93, 138.06, 137.99, 131.80, 131.71, 131.52, 128.87, 128.67, 124.07, 122.85, 120.00, 101.78, 101.72, 16.42; MS (EI) m/z: calcd for $C_{21}H_{14}I_2O_4$ 584.15, found: 584.6 $[M]^+$.

2.3.2 6-(4-Iodophenoxy)-1-hexanol (2)

4-Iodophenol (10 g, 45 mmol) and potassium carbonate (9.4 g, 68 mmol) were suspended in acetone (500 mL) for 30 min. 6-Bromohexan-1-ol (7.7 mL, 54 mmol) was then added dropwise and the solution was refluxed at 60°C for 12 h. After removing the solvent, water was added and the mixture was extracted with dichloromethane (3 × 150 mL). The organic phase was dried with anhydrous magnesium sulphate and evaporated. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (10:1) as an eluent to yield a colourless powder (15 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.53 (2H, d, *J* = 8.8 Hz), 6.66 (2H, d, *J* = 8.8 Hz), 3.90 (2H, t, *J* = 6.4 Hz), 3.64 (2H, t, *J* = 6.4 Hz), 1.86 (2H, m), 1.78 (2H, quint, *J* = 6.5 Hz), 1.61 (2H, m), 1.46 (2H, m) (OH, missing); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.90, 138.12, 116.88, 82.45, 67.91, 62.81, 32.61, 29.08, 25.81, 25.49.

2.3.3 6-[(4-Timethylsilylethynyl)phenoxy]-1-hexanol (3)

Compound **2** (10 g, 31 mmol), copper(I) iodide (0.59 g, 3.1 mmol), triphenylphosphine (0.82 g, 3.1 mmol) and bis (triphenylphosphine)palladium(II) dichloride (1.1 g, 1.5 mmol) were dissolved in tetrahydrofuran (100 mL) and triethylamine (100 mL) at room temperature under nitrogen. A solution of ethynyltrimethylsilane (9.5 mL, 62 mmol) in tetrahydrofurane (10 mL) and triethylamine (10 mL) was added using a syringe at 80°C. After 12 h, the cooled reaction mixture was poured into water and extracted using dichloromethane (3 × 150 mL). The organic phase was dried with anhydrous magnesium sulphate and evaporated. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (2:1) an eluent to yield a white solid (7.7 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.40 (2H, d, *J* = 8.8 Hz), 6.82 (2H, d, *J* = 8.8 Hz), 4.18 (2H, t, *J* = 6.4 Hz), 3.95 (2H, t, *J* = 6.4 Hz), 1.84 (2H, m), 1.73 (2H, m), 1.40 (4H, m), 0.28 (9H, s) (OH, missing); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.18, 133.35, 114.93, 114.22, 105.22, 92.22, 67.76, 62.66, 32.54, 29.05, 25.76, 25.45, 0.00.

2.3.4 6-(4-Ethynylphenoxy)-1-hexanol (4)

A reaction mixture of compound **3** (10 g, 34 mmol) and potassium carbonate (9.5 g, 68 mmol) in methanol (200 mL) was stirred at room temperature for 1 h. After removing the solvent, water was added and the mixture was extracted with dichloromethane (3 × 150 mL). The organic phase was dried with anhydrous magnesium sulphate and evaporated. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (5:1) an eluent to yield a light brown solid (5.3 g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.40 (2H, d, *J* = 8.8 Hz), 6.82 (2H, d, *J* = 8.8 Hz), 3.94 (2H, t, *J* = 6.4 Hz), 3.66 (2H, t, *J* = 6.4 Hz), 2.98 (1H, s), 1.80 (2H, quint, *J* = 6.7 Hz), 1.63 (2H, quint, *J* = 6.9 Hz), 1.22 (4H, m) (OH, missing); ^{13}C NMR (75MHz, $CDCl_3$) δ = 159.45, 133.55, 114.42, 113.90, 83.73, 75.70, 67.87, 62.84, 32.63, 29.11, 25.84, 25.51.

2.3.5 6-(4-Ethynylphenoxy)hexyl acrylate (5)

Compound **4** (10 g, 46 mmol) was suspended in pyridine (7.4 mL, 92 mmol) and dichloromethane (200 mL). Then, acryloyl chloride (4.6 mL, 55 mmol) was added dropwise and the solution was stirred at 40°C for 2 h. The reaction mixture was cooled to room temperature, water was added and the solution was extracted with dichloromethane (3 × 100 mL). The organic phase was dried with anhydrous magnesium sulphate and then evaporated. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (10:1) to give a white solid (10 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.41 (2H, d, *J* = 8.8 Hz), 6.82 (2H, d, *J* = 8.8 Hz), 6.40 (1H, dd, *J* = 17.3, 1.5 Hz), 6.12 (1H, dd, *J* = 17.3, 10.3 Hz), 5.82 (1H, dd, *J* = 10.3, 1.5 Hz), 4.16 (2H, t, *J* = 6.4 Hz), 3.95 (2H, t, *J* = 6.4 Hz), 2.99 (1H, s), 1.78 (2H, quint, *J* = 6.8 Hz), 1.69 (2H, quint, *J* = 6.9 Hz), 1.47 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.32, 159.40, 133.55, 130.59, 128.53, 114.38, 113.89, 83.70, 75.70, 67.77, 64.48, 29.02, 28.52, 25.70(two carbon); MS (EI) m/z: calcd for $C_{17}H_{20}O_3$ 272.34, found: 272.1 $[M]^+$.

2.3.6 6-(4-Ethynylphenoxy)hexyl methacrylate (6)

Compound **4** (10 g, 46 mmol) was suspended in pyridine (7.4 mL, 92 mmol) and tetrahydrofuran (200 mL). Then, methacryloyl chloride (5.4 mL, 55 mmol) was added dropwise and the solution was stirred at 60°C for 24h. The reaction mixture was cooled to room temperature, water was added and the solution was extracted with dichloromethane (3 × 100 mL). The organic phase was dried with anhydrous magnesium sulphate and then evaporated. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (20:1) to give a white solid (5.3 g, 40%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42 (2H, d, *J* = 8.8 Hz), 6.83 (2H, d, *J* = 8.8 Hz), 6.09 (1H, br), 5.54 (1H, br), 4.15 (2H, t, *J* = 6.6 Hz), 3.95 (2H, t, *J* = 6.4 Hz), 2.99 (1H, s), 1.94 (3H, s), 1.82 (2H, m), 1.73 (2H, m), 1.47 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.46, 159.40, 136.44, 133.53, 125.25, 114.38, 113.91, 83.69, 75.75, 67.76, 64.59, 29.02, 28.52, 25.76, 25.69, 18.33; MS (EI) m/z: calcd for $C_{18}H_{22}O_3$ 286.37, found: 286.8 $[M]^+$.

2.3.7 6-(4-Ethynylphenoxy)hexyl cinnamate (7)

Compound **4** (10 g, 46 mmol) was suspended in pyridine (7.4 mL, 92 mmol) and dichloromethane (200 mL). Then, cinnamoyl chloride (7.6 g, 46 mmol) was added dropwise and the solution was stirred at 40°C for 24 h. The reaction mixture was cooled to room temperature, water was added and the solution was extracted with dichloromethane (3 × 100 mL). The organic phase was dried with anhydrous magnesium sulphate and then evaporated. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (5:1) to give a white solid (12 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.67 (1H, d, *J* = 16.0 Hz) 7.52 (2H, m), 7.42 (2H, d, *J* = 2.6 Hz), 7.38 (3H, m), 6.84 (2H, d, *J* = 8.9 Hz), 6.43 (1H, d, *J* = 15.6 Hz), 4.22 (2H, t, *J* = 6.6 Hz), 3.96 (2H, t, *J* = 6.4 Hz), 2.98 (1H, s), 1.81 (2H, quint, *J* = 6.8 Hz), 1.74 (2H, quint, *J* = 6.9 Hz), 1.49 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.08, 159.40, 144.66, 134.36, 133.55, 130.25, 128.87, 128.04, 118.12, 114.38, 113.87, 83.70, 75.70, 67.77, 64.49, 29.02, 28.62, 25.75, 25.72; MS (EI) m/z: calcd for $C_{23}H_{24}O_3$ 348.44, found: 348.1 $[M]^+$.

2.3.8 6-(4-Ethynylphenoxy)hexyl (E)-3-(furan-2-yl) acrylate (8)

Compound **4** (10 g, 46 mmol) was suspended in pyridine (7.4 mL, 92 mmol) and dichloromethane (200 mL). Then, (*E*)-3-(furan-2-yl)acryloyl chloride (7.2 g, 46 mmol) was added dropwise and the solution was stirred for 24h at 60°C. The reaction mixture was cooled to room temperature, water was added and the solution was extracted with dichloromethane (3 × 100 mL). The organic phase was dried with anhydrous magnesium sulphate and then evaporated. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (5:1) to give a white solid (7.6 g, 50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.47 (1H, m), 7.43 (2H, d, *J* = 8.8 Hz), 7.39 (1H, s), 6.82 (2H, d, *J* = 8.8 Hz), 6.59 (1H, d, *J* = 3.4 Hz), 6.46 (1H, m), 6.31 (1H, d, *J* = 15.7 Hz), 4.20 (2H, t, *J* = 6.6 Hz), 3.99 (2H, t, *J* = 6.5 Hz), 2.99 (1H, s), 1.82 (2H, m), 1.73 (2H, m), 1.47 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.92, 159.44, 150.42, 139.31, 133.58, 129.89, 116.53, 116.17, 114.41, 113.91, 109.14, 83.74, 75.70, 67.81, 64.55, 29.05, 28.62, 25.76, 25.74; MS (EI) m/z: calcd for $C_{21}H_{22}O_4$ 338.40, found: 337.1 $[M]^+$.

2.3.9 2-Methyl-1,4-phenylene bis{4-[4-(6-acryloyloxyhexyloxy)phenyl]ethynyl}benzoate (9)

Compound **1** (10 g, 17 mmol), bis(triphenylphosphine) palladium(II) dichloride (2.0 g, 2.8 mmol), copper(I) iodide (0.80 g, 4.2 mmol) and triphenylphosphine (1.0 g, 3.8 mmol) were suspended in tetrahydrofuran (100 mL) and triethylamine (100 mL) under nitrogen. A solution of compound **5** (11 g, 41 mmol) in tetrahydrofuran (20 mL) was added using a syringe at 80°C. After 24 h, the cooled reaction mixture was poured into water and extracted using dichloromethane (3 × 150 mL). The organic phase was dried with anhydrous magnesium sulphate and evaporated. The residue was purified by silica gel column chromatography using a mixture of toluene/ethyl acetate (50:1) as an eluent to yield a beige solid (7.5 g, 50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.17 (4H, m), 7.63 (4H, m), 7.55 (4H, d, *J* = 8.8 Hz), 7.22 (3H, m), 6.89 (4H, d, *J* = 8.8 Hz), 6.43 (2H, dd, *J* = 17.3, 1.5 Hz), 6.13 (2H, dd, *J* = 17.3, 10.3 Hz), 5.82 (2H, dd, *J* = 10.3, 1.5 Hz), 4.18 (4H, t, *J* = 6.4 Hz), 3.99 (4H, t, *J* = 6.4 Hz), 2.27 (3H, s), 1.81 (4H, m), 1.70 (4H, m), 1.50 (4H, m), 1.44 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.31, 164.66, 164.29, 159.62, 148.37, 147.02, 133.30, 131.81, 131.48, 131.44, 130.54, 130.08, 129.30, 129.22, 128.56, 128.30, 124.09, 122.87, 120.01, 114.62, 114.45, 93.30, 87.41, 67.87, 64.47, 29.05, 28.54, 25.72 (two carbon), 16.46; MS (FAB) m/z: calcd for $C_{55}H_{52}O_{10}$ 872.3, found: 873 $[M + H]^+$.

2.3.10 2-Methyl-1,4-phenylene bis{4-[4-(6-methacryloyloxyhexyloxy)phenyl]ethynyl}benzoate (10)

Compound **1** (10 g, 17 mmol), bis(triphenylphosphine) palladium(II) dichloride (2.0 g, 2.8 mmol), copper(I) iodide (0.80 g, 4.2 mmol) and triphenylphosphine (1.0 g, 3.8 mmol) were suspended in tetrahydrofuran (100 mL) and triethylamine (100 mL) under nitrogen. A solution of compound **6** (12 g, 41 mmol) in tetrahydrofuran (20 mL) was added using a syringe at 80°C. After 24 h, the cooled reaction mixture was poured into water

and extracted using dichloromethane (3 × 150 mL). The organic phase was dried with anhydrous magnesium sulphate and evaporated. The residue was purified by silica gel column chromatography using a mixture of toluene/ethyl acetate (50:1) as an eluent to yield a beige solid (6.2 g, 40%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.17 (4H, m), 7.62 (4H, m), 7.49 (4H, d, *J* = 8.7 Hz), 7.20 (3H, m), 6.88 (4H, d, *J* = 8.7 Hz), 6.10 (2H, br), 5.54 (2H, br), 4.16 (4H, t, *J* = 6.6 Hz), 3.99 (4H, t, *J* = 6.4 Hz), 2.27 (3H, s), 1.94 (2H, m), 1.78 (4H, m), 1.72 (4H, m), 1.48 (8H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.48, 164.62, 164.25, 159.61, 148.35, 147.00, 136.47, 133.63, 133.50, 133.28, 132.10, 132.02, 131.78, 131.46, 131.42, 130.06, 129.28, 129.20, 128.28, 128.08, 125.20, 124.06, 122.85, 119.99, 114.60, 114.43, 93.29, 87.41, 67.85, 64.57, 29.03, 28.52, 25.76, 25.7, 18.30, 16.43; MS (FAB) m/z: calcd for $C_{57}H_{56}O_{10}$ 900.3, found: 902 $[M + H]^+$.

2.3.11 2-Methyl-1,4-phenylene bis{4-[4-(6-((2E)-3-phenylacryloyloxy)hexanoxy)phenyl]ethynyl} benzoate (11)

Compound **1** (10 g, 17 mmol), bis(triphenylphosphine) palladium(II) dichloride (2.0 g, 2.8 mmol), copper(I) iodide (0.80 g, 4.2 mmol) and triphenylphosphine (1.0 g, 3.8 mmol) were suspended in tetrahydrofuran (100 mL) and triethylamine (100 mL) under nitrogen. A solution of compound **7** (14 g, 41 mmol) in tetrahydrofuran (20 mL) was added using a syringe at 80°C. After 24 h, the cooled reaction mixture was poured into water and extracted using dichloromethane (3 × 150 mL). The organic phase was dried with anhydrous magnesium sulphate and evaporated. The residue was purified by silica gel column chromatography using a mixture of toluene/ethyl acetate (50:1) as an eluent to yield a beige solid (11 g, 63%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.18 (4H, m), 7.67 (2H, m), 7.62 (4H, m), 7.61 (4H, m), 7.39 (6H, m), 7.20 (3H, m), 6.88 (4H, d, *J* = 8.9 Hz), 6.45 (2H, d, *J* = 16.0 Hz), 4.23 (4H, t, *J* = 6.6 Hz), 4.00 (4H, t, *J* = 6.4 Hz), 2.27 (3H, s), 1.81 (4H, m), 1.76 (4H, m), 1.53 (8H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.05, 164.65, 164.28, 159.64, 148.38, 147.02, 144.66, 134.43, 133.30, 131.80, 131.48, 131.44, 130.24, 130.07, 129.31, 129.23, 128.87, 128.30, 128.10, 128.04, 124.08, 122.86, 120.01, 118.19, 114.63, 114.44, 93.32, 93.28, 87.42, 87.40, 67.88, 64.48, 29.05, 28.65, 25.76, 25.74, 16.45; MS (HRMS) m/z: calcd for $C_{67}H_{60}O_{10}$ 1024.4186, found: 1047.3567 $[M+Na]^+$.

2.3.12 2-Methyl-1,4-phenylene bis{4-[4-(6-((2E)-3-(2-furyl)acryloyloxy)hexanoxy)phenyl]ethynyl} benzoate (12)

Compound **1** (10 g, 17 mmol), bis(triphenylphosphine) palladium(II) dichloride (2.0 g, 2.8 mmol), copper(I) iodide (0.80 g, 4.2 mmol) and triphenylphosphine (1.0 g, 3.8 mmol) were suspended in tetrahydrofuran (100 mL) and triethylamine (100 mL) under nitrogen. A solution of compound **12** (14 g, 41 mmol) in tetrahydrofuran (20 mL) was added using a syringe at 80°C. After 24 h, the cooled reaction mixture was poured into water and extracted using dichloromethane (3 × 150 mL). The organic phase was dried with anhydrous magnesium sulphate and evaporated. The residue was purified by silica gel column chromatography using a mixture of toluene/ethyl acetate (50:1) as an eluent to yield a beige solid (6.9 g, 40%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.18 (4H, m) 7.62 (4H, m), 7.47 (4H, m), 7.42 (2H, m), 7.17 (3H, m), 6.88 (4H, d), 6.60 (2H, d, *J* = 3.4 Hz), 6.47 (2H, m), 6.31 (2H, d, *J* = 15.6 Hz), 4.20 (4H, t, *J* = 6.5 Hz), 4.00 (4H, t, *J* = 6.5 Hz), 2.27 (3H, s), 1.83 (4H, m), 1.74 (4H, m), 1.53 (8H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.08, 164.63, 164.26, 159.62, 150.91, 148.36, 147.00, 144.66, 133.28, 131.78, 131.46, 131.42, 130.99, 130.06, 129.30, 129.21, 128.28, 128.08, 124.06, 122.85, 119.99, 115.85, 114.63, 114.61, 114.41, 112.23, 93.32, 93.27, 87.38, 67.87, 64.39, 29.03, 28.63, 25.74, 25.71, 16.43; MS (FAB) m/z: calcd for $C_{63}H_{56}O_{12}$ 1004.3, found: 1005 $[M + H]^+$.

2.3.13 2,6-Difluoro-4-iodophenol (13)

2,6-Difluorophenol (10 g, 76 mmol) and *p*-toluenesulfonic acid (15 g, 76 mmol) were suspended in acetonitrile (500 mL) for 5 min. To the resulting solution was added *N*-iodosuccinimide (18 g, 76 mmol) carefully. After 24 h, the solution was poured over water and extracted with diethylether (1 × 100 mL). The organic phase was dried with anhydrous magnesium sulphate and evaporated. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (20:1) as an eluent (14 g, 70%). ^{1}H NMR (300 MHz, DMSO-d_6) δ = 10.49 (1H, S), 7.45 (2H, d, *J* = 9.1 Hz); MS (EI) m/z: calcd for $C_6H_3F_2IO$ 255.99, found: 255.9 $[M]^+$.

2.3.14 2-Methyl-4-iodophenol (14)

2-Methylphenol (10 g, 92 mmol) and *p*-toluenesulfonic acid (18 g, 92 mmol) were suspended in acetonitrile (500 mL) for 5 min. To the resulting solution was added *N*-iodosuccinimide (21 g, 92 mmol) carefully. After 24 h, the solution was poured over water and extracted with dichloromethane (3 × 100 mL). The organic phase was dried with anhydrous magnesium sulphate and evaporated. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (20:1) as an eluent (18 g, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42 (1H, m), 7.36 (1H, m), 6.55 (1H, d, *J* = 8.34 Hz), 4.67 (1H, s), 2.20 (3H, s).

2.3.15 6-(2,6-Difluoro-4-iodophenoxy)-1-hexanol (15)

Compound **13** (10 g, 39 mmol) and potassium carbonate (11 g, 78 mmol) were suspended in acetone (200 mL) for 30 min. 6-Bromo-hexan-1-ol (6.1 mL, 43 mmol) was then added dropwise and the solution was refluxed at 60°C for 24 h. After removing the solvent, water was added and the mixture was extracted with dichloromethane (3 × 150 mL). The organic phase was dried with anhydrous magnesium sulphate and evaporated. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (3:1) as an eluent (11 g, 81%). ^{1}H NMR (300 MHz, DMSO-d_6) δ = 7.56 (2H, d, *J* = 7.8 Hz), 4.36 (2H, t, *J* = 6.4 Hz), 4.08 (2H, t, *J* = 6.4 Hz) 1.67 (2H, m), 1.43 (6H, m) (OH, missing); MS (EI) m/z: calcd for $C_{12}H_{15}F_2IO_2$ 356.15, found: 355.9 $[M]^+$.

2.3.16 6-(2-Methyl-4-iodophenoxy)-1-hexanol (16)

Compound **14** (10 g, 43 mmol) and potassium carbonate (12 g, 85 mmol) were suspended in acetone (200 mL) for 30 min. 6-Bromohexan-1-ol (6.4 mL, 47 mmol) was then added dropwise and the solution was refluxed at 60°C for 24 h. After removing the solvent, water was added and the mixture was extracted with dichloromethane (3 × 150 mL). The organic phase was dried with anhydrous magnesium sulphate and evaporated. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (3:1) as an eluent (13 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.41 (2H, m), 6.56 (1H, d, *J* = 9.1 Hz), 3.93 (2H, t, *J* = 6.3 Hz), 3.66 (2H, t, *J* = 6.3 Hz), 2.16 (3H, s), 1.81 (2H, m), 1.55 (6H, m) (OH, missing).

2.3.17 6-[(4-Trimethylsilylethynyl-2,6-difluoro) phenoxy]-1-hexanol (17)

Compound **15** (10 g, 28 mmol), copper(I) iodide (2.4 g, 8.4 mmol), triphenylphosphine (1.5 g, 5.6 mmol) and bis(triphenylphosphine)palladium(II) dichloride (1.9 g, 5.6 mmol) were suspended in triethylamine (25 mL) under nitrogen. Then, a solution of ethynyltrimethylsilane (5.9 mL, 42 mmol) in tetrahydrofuran (10 mL) was added dropwise at 80°C over a span of 3 h. The resulting solution was concentrated by rotary evaporation. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (5:1) as an eluent to yield a yellow crystalline solid (8.2 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.05 (2H, d, *J* = 9 Hz), 4.18 (2H, t, *J* = 6.5 Hz), 3.68 (2H, t, *J* = 6.4 Hz), 1.67 (2H, m), 1.52 (6H, m), 0.28 (9H, s) (OH, missing); MS (EI) m/z: calcd for $C_{17}H_{24}F_2O_2Si$ 326.15, found: 326.0 $[M]^+$.

2.3.18 6-[(4-Trimethylsilylethynyl-2-methyl) phenoxy]-1-hexanol (18)

Compound **16** (10 g, 30 mmol), copper(I) iodide (1.7 g, 9.0 mmol), triphenylphosphine (1.6 g, 6.0 mmol) and bis(triphenylphosphine)palladium(II) dichloride (4.2 g, 6.0 mmol) were suspended in triethylamine (10 mL) under nitrogen. Then, a solution of ethynyltrimethylsilane (6.2 mL, 45 mmol) in tetrahydrofurane (10 mL) was added dropwise at 80°C. After 3 h, the resulting solution was concentrated by rotary evaporation. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (2:1) as an eluent to yield a brown crystalline solid (9.0 g, 99%). ^{1}H NMR (300 MHz, Acetone-d_6) δ = 7.28 (2H, m), 6.71 (1H, d, *J* = 8.1 Hz), 3.97 (2H, t, *J* = 6.4 Hz), 3.68 (2H, t, *J* = 6.4 Hz), 2.17 (3H, s), 1.78 (2H, m), 1.64 (6H, m), 0.24 (9H, s) (OH, missing).

2.3.19 6-[(4-Ethynyl-2,6-difluoro)phenoxy]-1-hexanol (19)

A reaction mixture of compound **17** (10 g, 31mmol) and potassium carbonate (4.2 g, 31 mmol) in methanol (200 mL) was stirred at room temperature for 1 h. After the reaction mixture concentrated by evaporation, the remaining residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (3:1) as an eluent (5.5 g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.03 (2H, d, *J* = 8.8 Hz), 4.17 (2H, t, *J* = 6.5 Hz), 3.69 (2H, t, *J* = 6.3 Hz), 3.06 (1H, s), 1.62 (2H, m), 1.49 (6H, m) (OH, missing); MS (EI) m/z: calcd for $C_{14}H_{16}F_2O_2$ 254.28, found: 254.1 $[M]^+$.

2.3.20 6-[(4-Ethynyl-2-methyl)phenoxy]-1-hexanol (20)

A reaction mixture of compound **18** (10 g, 33 mmol) and potassium carbonate (4.5 g, 33 mmol) in methanol (200 mL) was stirred at room temperature for 1 h. After the reaction mixture was concentrated by rotary evaporation. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl acetate (1:1) as an eluent to yield a yellow oil (5.0 g, 66%). ^{1}H NMR (300 MHz, Acetone-d_6) δ = 7.30 (2H, m), 6.74 (1H, d, *J* = 8.1 Hz), 3.98 (2H, t, *J* = 6.4 Hz), 3.67 (2H, t, *J* = 6.4 Hz), 2.96 (1H, s), 2.18 (3H, s), 1.83 (2H, quint, *J* = 6.5 Hz), 1.64 (2H, m), 1.49 (4H, m) (OH, missing).

2.3.21 6-[(4-Ethynyl-2,6-difluoro)phenoxy]hexyl acrylate (21)

Compound **19** (10 g, 39 mmol) was dissolved in triethylamine (5.6 mL, 78 mmol) and dichloromethane (200 mL). Then, acryloyl chloride (7.5 mL, 59 mmol) was added dropwise and the solution was stirred at 60° C for 2 h. The reaction mixture was cooled to room

temperature, water was added and the solution was extracted with dichloromethane (3 × 100 mL). The organic phase was dried with anhydrous magnesium sulphate and then evaporated. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl (20:1) as an eluent (9.7 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.03 (2H, d, *J* = 8.8 Hz), 6.43 (1H, dd, *J* = 17.3, 1.5 Hz), 6.16 (1H, dd, *J* = 17.3, 10.3 Hz), 5.84 (1H, dd, *J* = 10.3, 1.5 Hz), 4.18 (4H, m), 3.06 (1H, s), 1.87 (4H, m), 1.51 (4H, m); MS (EI) m/z: calcd for $C_{17}H_{18}F_2O_3$ 308.32, found: 308.1 $[M]^+$.

2.3.22 6-[(4-Ethynyl-2-methyl)phenoxy]hexyl acrylate (22)

Compound **20** (10 g, 43 mmol) was dissolved in triethylamine (6.2 mL, 86 mmol) and dichloromethane (200 mL).Then, acryloyl chloride (5.2 mL, 65 mmol) was added dropwise and the solution was stirred at 60° C for 2 h. The reaction mixture was cooled to room temperature, water was added and the solution was extracted with dichloromethane (3 × 100 mL). The organic phase was dried with anhydrous magnesium sulphate and then evaporated. The residue was purified by silica gel column chromatography using a mixture of hexane/ethyl (20:1) as an eluent (9.5 g, 77%).^{1}H NMR (300 MHz, Acetone-d_6) δ = 7.30 (2H, m), 6.73 (1H, d, *J* = 8.1 Hz), 6.42 (1H, dd, *J* = 17.3, 1.5 Hz), 6.16 (1H, dd, *J* = 17.3, 10.3 Hz), 5.83 (1H, dd, *J* = 10.3, 1.5 Hz), 4.19 (2H, m), 3.98 (2H, t, *J* = 6.3 Hz), 2.96 (1H, s), 2.17 (3H, s), 1.83 (4H, m), 1.52 (4H, m).

2.3.23 2-Methyl-1,4-phenylene bis{4-[4-(6-acryloyloxyhexyloxy)-2,6-difluorophenyl]ethynyl}-benzoate (23)

Compound **1** (10 g, 17 mmol), bis(triphenylphosphine) palladium(II) dichloride (2.0 g, 2.8 mmol), copper(I) iodide (1.4 g, 7.5 mmol) and triphenylphosphine (1.0 g, 3.8 mmol) were suspended in tetrahydrofurane (100 mL) and triethylamine (100 mL). A solution of compound **21** (12 g, 38 mmol) in tetrahydrofurane (20 mL) was added using a syringe at 90°C. After 24 h, the reaction mixture was poured into water and extracted using dichloromethane (3 × 150 mL). The organic phase was dried with magnesium sulphate and evaporated. The residue was purified by silica gel column chromatography using a mixture of toluene/ethyl acetate (100:1) as an eluent to yield a pale yellow solid (8.7 g, 54%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.22 (4H, m), 7.66 (4H, m), 7.23 (3H, m), 7.14 (4H, m), 6.44 (2H, dd, *J* = 17.3, 1.5 Hz), 6.17 (2H, dd, *J* = 17.3, 10.3 Hz), 5.84 (2H, dd, *J* = 10.3, 1.5 Hz), 4.21 (8H, m), 2.17 (3H, s), 1.82 (8H, m), 1.54 (8H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.32, 164.48, 164.12, 156.55, 156.49, 154.57, 154.51, 148.35, 147.01, 136.95, 131.82, 131.76, 131.71, 130.50, 130.16, 128.58, 128.09, 128.01, 124.09, 122.87, 120.02, 116.87, 115.89, 115.84, 115.75, 115.69, 89.19, 89.16, 75.94, 75.81, 74.66, 64.49, 29.81, 28.53, 25.64, 25.32, 16.46; MS (FAB) m/z: calcd for $C_{55}H_{48}F_4O_{10}$ 944.3, found: 945 $[M + H]^+$.

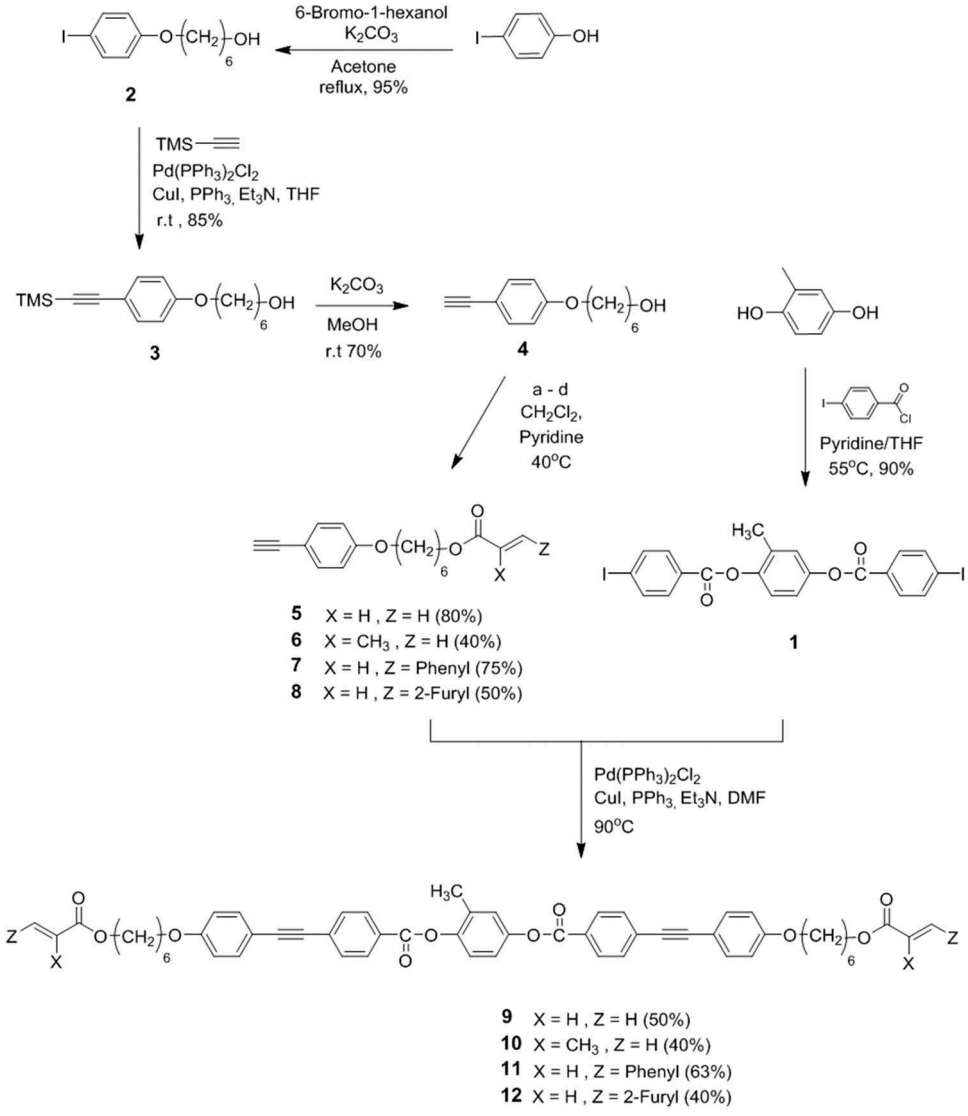
2.3.24 2-Methyl-1,4-phenylenebis{4-[4-(6-acryloyloxyhexyloxy)-2-methylphenyl]ethynyl}-benzoate (24)

Compound **1** (10 g, 17 mmol), bis(triphenylphosphine) palladium(II) dichloride (2.0 g, 2.8 mmol), copper(I) iodide (1.4 g, 7.5 mmol) and triphenylphosphine (1.0 g, 3.8 mmol) were suspended in tetrahydrofurane (100 mL) and triethylamine (100 mL). A solution of compound **22** (11 g, 38 mmol) in tetrahydrofurane (10 mL) was added using a syringe at 90°C. After 24 h, the reaction mixture was poured into water and extracted using dichloromethane (3 × 150 mL). The organic phase was dried with magnesium sulphate and evaporated. The residue was purified by silica gel column chromatography using a mixture of toluene/ethyl acetate (80:1) as an eluent to yield a brown solid (4.6 g, 30%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.19 (4H, m), 7.64 (4H, m), 7.38 (4H, m), 7.22 (3H, m), 6.80 (2H, m), 6.43 (2H, dd, *J* = 17.3, 1.5 Hz), 6.17 (2H, dd, *J* = 17.3, 10.3 Hz), 5.83 (2H, dd, *J* = 10.3, 1.5 Hz), 4.20 (4H, t, *J* = 6.6 Hz), 4.02 (4H, t, *J* = 6.3 Hz), 2.27 (3H, s), 2.22 (6H, s), 1.86 (4H, quint, *J* = 6.5 Hz), 1.75 (4H, quint, *J* = 6.8 Hz), 1.54 (8H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.31, 164.67, 164.31, 156.91, 148.44, 147.13, 135.19, 132.33, 131.56, 131.38, 130.54, 130.07, 129.45, 129.19, 128.56, 128.18, 127.53, 124.08, 122.86, 120.01 117.55, 117.38, 93.18, 87.66, 72.21, 64.51, 30.25, 28.58, 25.89, 25.80, 16.45, 16.18; MS (FAB) m/z: calcd for $C_{57}H_{56}O_{10}$ 900.3, found: 902 $[M + H]^+$.

3 Results and discussion

3.1 Synthesis of materials

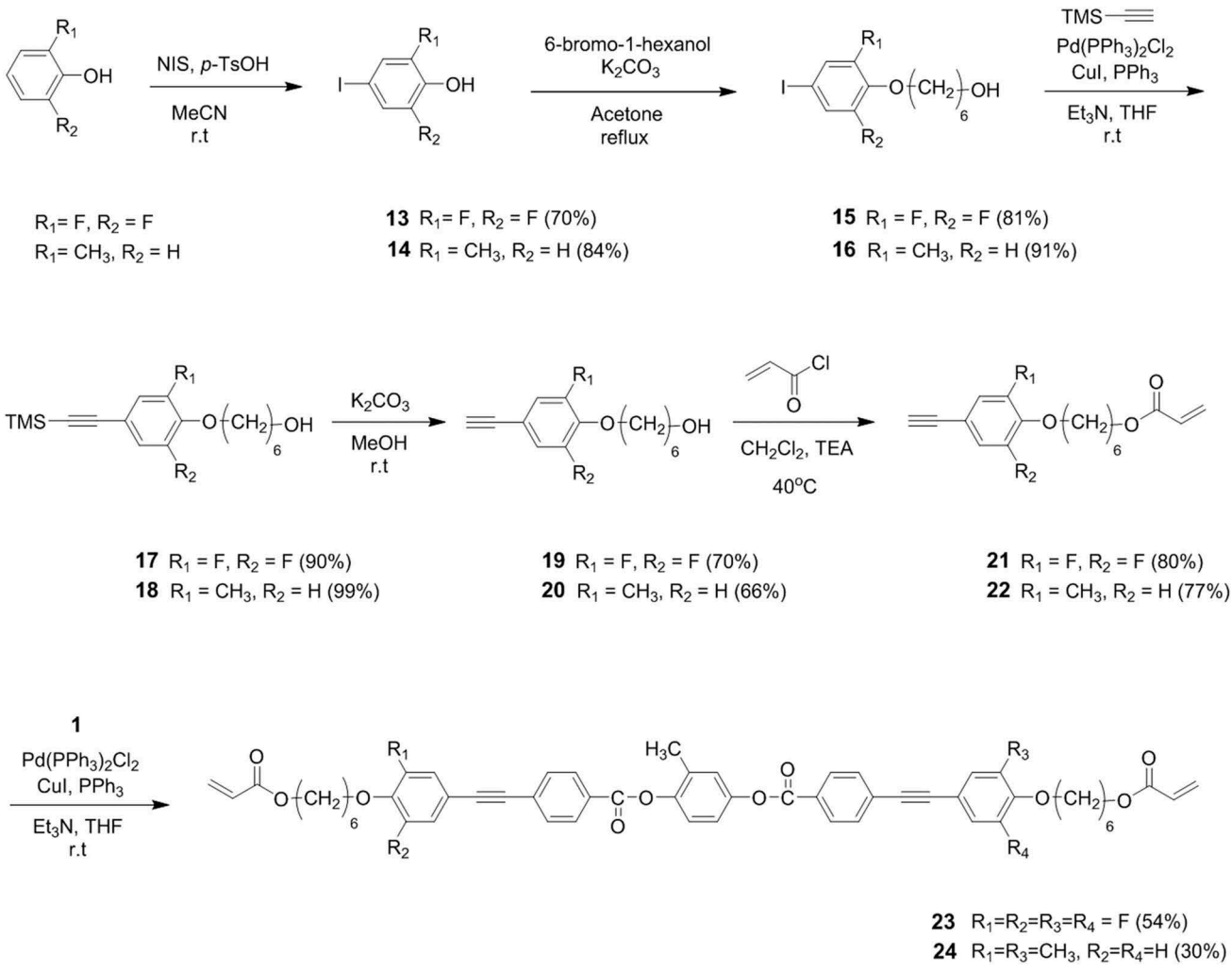
As shown in Scheme 1, compounds **9**–**12** were synthesised as high-birefringence reactive liquid crystal compounds based on a 2-methylhydroquinone core. Acryloyl, methacryloyl, cinnamoyloyl and furylacryloyl groups were introduced as reactive functional groups. The main intermediate compound, 2-methyl-1,4-phenylene bis(4-iodobenzoate) **1**, was obtained in 90% yield from esterification reaction of 2-methylhydroquinone and 4-iodobenzoyl chloride in the presence of pyridine at 55°C. Rod-shape liquid crystal compounds with high birefringence were obtained from acetylene-bearing compounds **5**–**8** via Sonogashira coupling



Scheme 1. Synthesis of high-birefringence rod-like molecules based on 2-methylhydroquinone. (a: acryloyl chloride, b: methacryloyl chloride, c: cinnamoyl chloride, d: furylacryloyl chloride).

reactions with the synthesised intermediate **1** [23,24]. Compounds **5–8** were synthesised using 4-iodophenol as a starting material. A substitution reaction with 6-bromo-1-hexanol was carried out in the presence of potassium carbonate (95%), followed by Sonogashira coupling with ethynyltrimethylsilane (85%) using bis (triphenylphosphine)palladium(II) dichloride as a catalyst and TMS elimination reaction using potassium carbonate (70%). Compounds **5–8** were formed using four different reactive functional groups through esterification using acryloyl chloride, methacryloyl chloride, cinnamoyl chloride and furylacryloyl chloride (40–80%). The highly birefringent reactive liquid crystals, acryloyl compound **9** (50%), methacryloyl compound **10** (40%), cinnamoyl compound **11** (60%) and furylacryloyl compound **12** (40%) were synthesised via Sonogashira coupling of the resultant triple bonds with the cores using a bis(triphenylphosphine)palladium(II) catalyst.

Different phenyl group substituents of the rod-shaped liquid crystal from a common 2-methylhydroquinone base were synthesised for controlling liquid crystal phase behaviour, such as compounds **23–24** in Scheme 2. First, phenolic compounds substituted with fluorine or methyl groups were iodinated using *N*-iodosuccinimde, resulting in 4-iodo-2-methylphenol (70%) and 2,6-difluoro-4-iodophenol (84%) [25]. These compounds were used as the starting materials to synthesise compounds **21** (80%) and **22** (77%) through the same method described for **5–8**. Compounds **23** (54%) and **24** (30%) were obtained from the synthesised compounds **1, 21** and **22** via Sonogashira coupling reaction using bis(triphenylphosphine)palladium (II) as a catalyst.



Scheme 2. Synthesis of high-birefringence rod-like molecules based on 2-methylhydroquinone with lateral substituents.

3.2 Thermal properties

The thermal behaviour of the synthesised compounds was investigated using DSC and POM. The synthesised compounds were examined between 180°C and room temperature, with temperature changes at a rate of 10° C/min [26]. From the DSC results in Figure 3, $T_{Cr\text{-}N}$ of compounds **9**–**12** and **23**–**24** indicate crystal (Cr) to mesophase transitions during second heating, while $T_{N\text{-}Cr}$ in Figure 4 indicates transitions from the nematic (N) phase to the crystal phase during second cooling [12]. A broad exothermic peak was present near 250°C during third heating in DSC for these compounds, confirming the presence of thermal polymerisation.

In the case of compound **9**, a narrow endothermic peak was present at 111°C, indicating a Cr to N transition, while the exothermic peak at 79°C indicated a N to Cr transition. In accordance with reactive group types, $T_{Cr\text{-}N}$ values were 105°C for methacryloyl compound **10**, 147°C for cinnamoyl compound **11** and 104° C for furylacryloyl compound **12**, confirming that the nematic phase in all compounds was maintained until a certain heat curing temperature.

The phase transition temperature of compound **23**, which features a difluoro substituent to adjust the temperature of the liquid crystal phase, was 83°C, a lower value than compound **9** (without substituent). In the case of compound **24** (dimethyl substituent), this temperature was 103°C. The $T_{N\text{-}Cr}$ values of compounds **10**–**12** were 76°C, 89°C and 67°C respectively. The phase transition of compound **23** was observed at 60°C, while the dimethyl-substituted compound maintained a nematic phase even during cooling. Thus, a wide range of processing temperatures is available during film forming process by UV irradiation after LC alignment.

The liquid crystal phase behaviour of the synthesised reactive liquid crystal compounds could also be determined using POM. Figure 5 shows nematic phase images during second heating or cooling of the synthetic compounds placed between orthogonal polarisation plates. After the Cr to N transition, the nematic

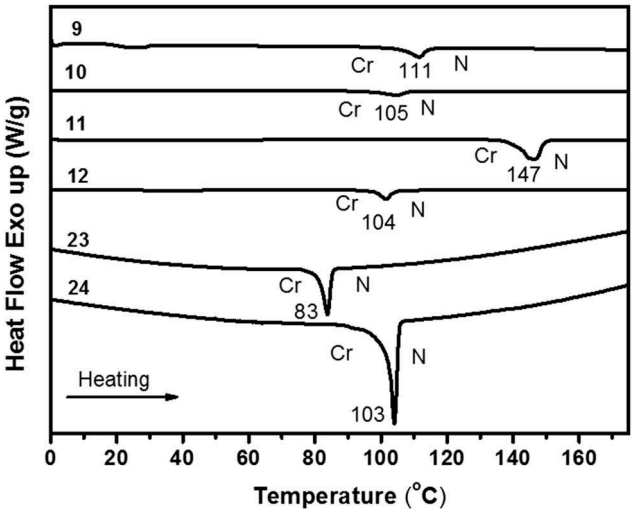


Figure 3. DSC results of compounds **9–12** and **23–24** from 2nd heating and cooling with rate 10°C/min (N_D: discotic nematic, I: isotropic).

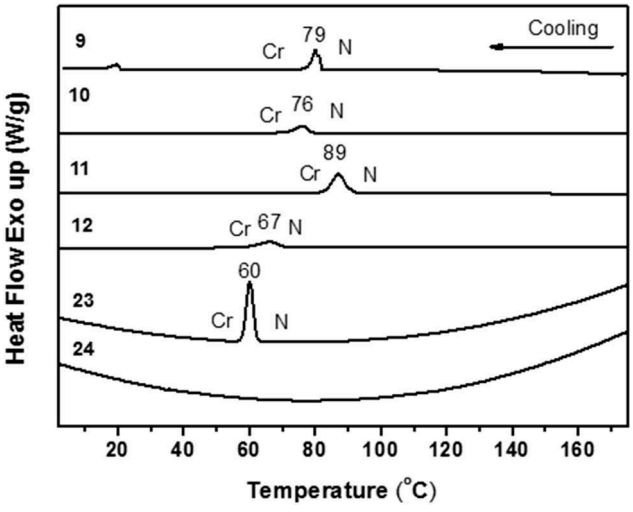


Figure 4. DSC results of compounds **9–12** and **23–24** from 2nd heating and cooling with rate 10°C/min (N_D: discotic nematic, I: isotropic).

phase was maintained until a certain heat curing temperature, consistent with the DSC results.

3.3 Optical properties

The alignment of the liquid crystal layers is shown in Figure 6. Here, black corresponds to a polariser angle of 0° and white at 45° based on the crossed polariser. Birefringence values of the LC films as shown in Figure 7 were analysed using photo-elastic modulators [27]. The intensity of light was determined by positioning the aligned liquid crystal films at 45° between the polariser and analyser along the polarising axis and by rotating the films with a constant angle. In Figure 7,

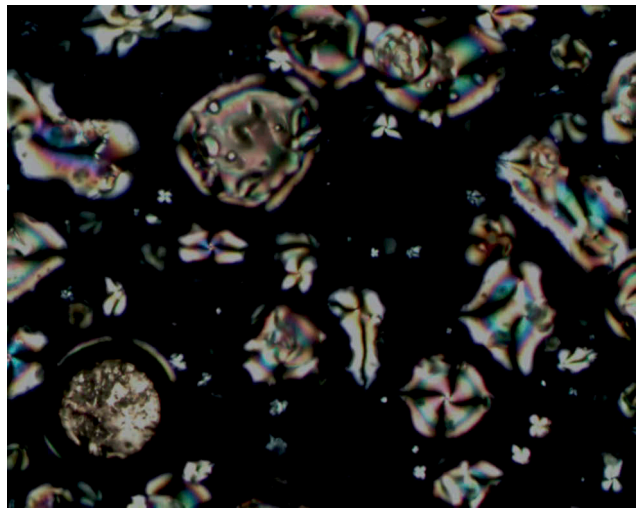


Figure 5. Nematic phase POM images of **24** at 110°C on 2nd heating (10°C/min, ×200 magnification).

retardation of the LC films was measured three times. Since the three retardation values showed similar patterns, birefringence could be calculated with minimal error. Birefringence (Δn) is normally calculated using the optical retardation of a known material (R_{standard}) and a sample (R_{sample}), their voltages (V_{standard} and V_{sample}, respectively) and film thickness (d) [28–30].

$$R_{\text{sample}} = R_{\text{standard}} \times \left(\frac{V_{\text{sample}}}{V_{\text{standard}}}\right) \quad (1)$$

$$R_{\text{standard}} = \frac{\lambda}{4}(\lambda = \text{laser wavelength}, 633\text{nm}) \quad (2)$$

$$R_{\text{sample}} = \Delta n \times d \quad (3)$$

Table 1 shows Δn values based on the optical contrasts (R_{sample}) of compounds **9–12** and **23–24**. The control LC 242 exhibited a Δn value of 0.24. It showed slightly high birefringence value than previous literatures (0.14–0.18) [31]. When measuring films under similar conditions and with the same thickness as the LC 242, the acetylene-containing compounds had enhanced Δn values of 0.32–0.40.

4. Conclusions

Novel rod-shape liquid crystals were synthesised by modifying 2-methylhydroquinone with cross-linkable functional groups and substituents to obtain high birefringence films. Sonogashira coupling was employed to introduce acetylene, and six compounds with modified end-functional groups, acryloyl compound **9**, methacryloyl compound **10**, cinnamoyl compound **11**, furylacryloyl compound **12**, difluoro-substituted compound **23** and methyl-substituted compound **24**, were synthesised. These new

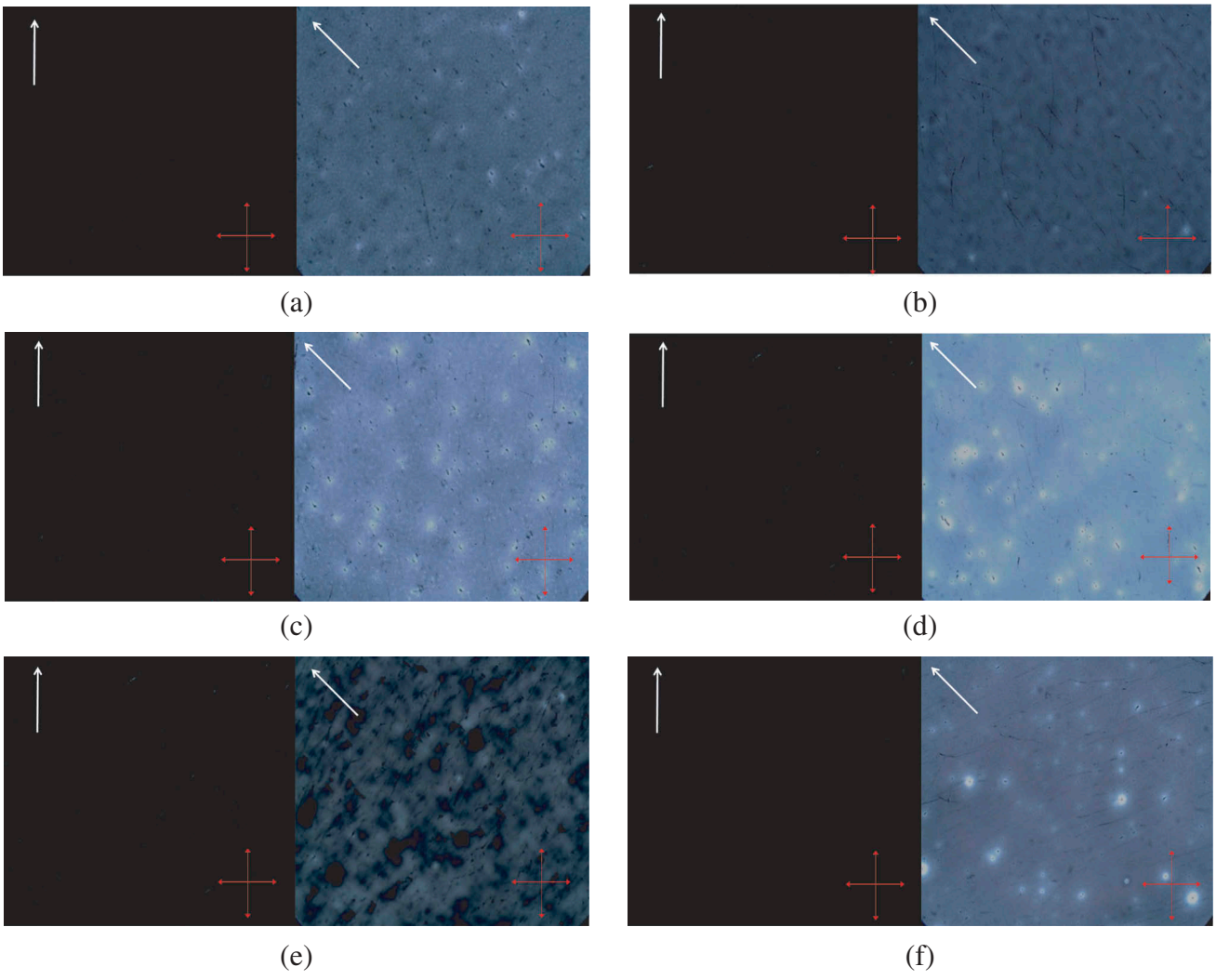


Figure 6. POM images of compounds **5–8, 23–24 (**5 wt.% in 1,1,2,2-tetrachloroethane) film on rubbed alignment layer after being cured under UV irradiation (365 nm, 10 mJ/cm^2) (×100 magnification, ↑: rubbing direction, +: crossed polarizer). (a) Compound **9** (0.21 µm thickness). (b) Compound **10** (0.20 µm thickness). (c) Compound **11** (0.21 µm thickness). (d) Compound **12** (0.22 µm thickness). (e) Compound **23** (0.20 µm thickness). (f) Compound **24** (0.25 µm thickness).

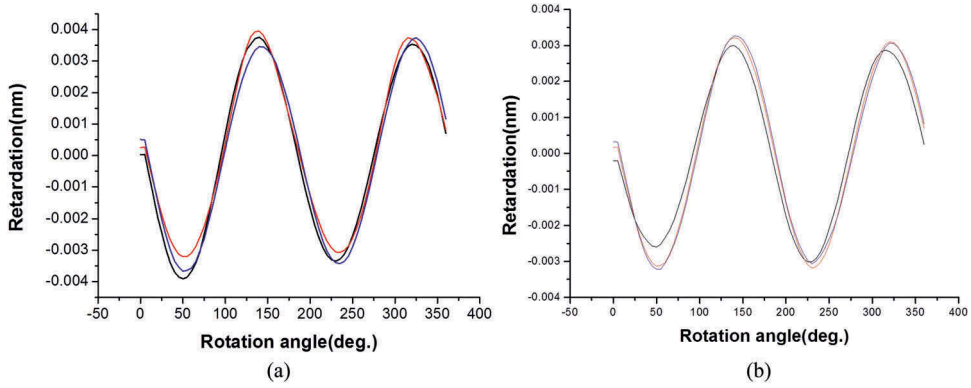


Figure 7. Photo-elastic modulator measurement results of films of compounds **12** and **23** (5 wt.% 1,1,2,2-tetrachloroethane) after UV curing. (a) **12** (0.22 µm thickness), (b) **23** (0.20 µm thickness).

compounds were characterised using proton and carbon NMR, mass spectroscopy and elemental analysis. $T_{Cr\text{-}N}$ was 111°C for **9**, 105°C for **10**, 147°C for **11**, 104°C for **12**, 83°C for **23** and 103°C for **24**. Curing began at approximately 200°C. Due to the asymmetry of molecule, prepared high-birefringent rod-shape

Table 1. Birefringence (Δn) of UV-cured films of compounds **9**–**12, 23**–**24** and LC 242 calculated from retardation and thickness relationships.

Compound	LC film thickness (μm)	Retardation (nm)	□*n*
9	0.21	67	0.32
10	0.20	69	0.35
11	0.21	77	0.37
12	0.22	86	0.39
23	0.21	80	0.38
24	0.23	93	0.40
LC 242	0.23	56	0.24

Retardation = $\Delta n \cdot d$.

reactive liquid crystals showed high solubility in general coating solvents such as toluene, xylene, 1,2-dichlorobenzene and 1,1,2,2-tetrachloroethane [32]. Accordingly, films were manufactured using these six compounds and a control LC 242 compound, and their birefringence values were measured. From measurement results, the Δn value of the control LC 242 was 0.24, while the newly-synthesised compounds with triple bonds showed higher Δn values of 0.32–0.40.

Acknowledgments

This work was supported by the Technology Innovation Industrial Program funded by the Ministry of Trade, Industry and Energy [10052667, Korea] and the National Research Council of Science and Technology for Creative Convergence Research Project under the Contract No. SKM1509 and KRICT Project No. KK-1602-D00.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the Technology Innovation Industrial Program funded by the Ministry of Trade, Industry and Energy [10052667, Korea] and the National Research Council of Science and Technology for Creative Convergence Research Project under the Contract No. SKM1509 and KRICT Project No. KK-1602-D00.

References

[1] Seed AJ, Tietz JI, Gipson RM, et al. Low molar mass thieno 3,2-b and thieno 2,3-b thiophenes in liquid crystal materials science: recent synthetic approaches. Liq Cryst. 2015;42(5–6):918–927.

[2] Okano K, Tsutsumi O, Shishido A, et al. Azotolane liquid-crystalline polymers: huge change in birefringence by photoinduced alignment change. J Am Chem Soc. 2006;128(48):15368–15369.

[3] Zhang H, Yu Z, Wan X, et al. Effects of molecular weight on liquid-crystalline behaviour of a mesogen-jacketed crystal polymer synthesized by atom transfer radical polymerization. Polymer. 2002;43:2357–2361.

[4] Kim J, Jung YJ, Ka J-W, et al. Mesomorphic phase transition behaviour of photopolymerisable liquid crystalline triphenylene ether compounds. Liq Cryst. 2009;36(12):1451–1457.

[5] Nichinori N. Design of polyimides for liquid crystal alignment films. Polym Adv Technol. 2000;11:404–412.

[6] Guan X-L, Zhang L-Y, Zhang Z-L, et al. Synthesis and properties of novel liquid crystalline materials with super high birefringence: styrene monomers bearing diacetylenes, naphthyl, and nitrogen-containing groups. Tetrahedron. 2009;65:3728–3732.

[7] Li XF, Tan N, Pivnenko M, et al. High-birefringence nematic liquid crystal for broadband THz applications. Liq Cryst. 2016;43(7):955–962.

[8] Xu S, Li Y, Liu Y, et al. Fast-response liquid crystal microlens. Micromachines. 2014;5:300–324.

[9] Tsai Y-J, Larouche S, Tyler T, et al. Arbitrary birefringent metamaterials for holographic optics at λ = 1.55 μm. Opt Express. 2013;21:26620–26630.

[10] Arakawa Y, Kuwahara H, Sakajiri K, et al. Highly birefringent polymer films from the photo-crosslinking polymerisation of bistolane-based methacrylate monomers. Liq Cryst. 2015;42(10):1419–1427.

[11] Wu ST. High Δn liquid crystals for displays and optical communications. SID Symp Dig Tech Pap. 2001;32:954–957.

[12] Cross GJ, Seed AJ, Toyne KJ, et al. Synthesis, transition temperatures, and optical properties of compounds with simple phenyl units linked by double bond, triple bond, ester or propiolate linkages. J Mater Chem. 2000;10:1555–1563.

[13] Seed AJ, Toyne KJ, Goodby JW, et al. Synthesis, transition temperatures, and optical properties of various 2,6-disubstituted naphthalenes and related 1-benzothiophenes with butylsulfanyl and cyano or isothiocyanato terminal groups. J Mater Chem. 2000;10:2069–2080.

[14] Wu S-T, Cox RJ. Optical and electro-optic properties of cyanotolanes and cyanostilbenes: potential infrared liquid crystals. J Appl Phys. 1988;64:821–826.

[15] Rego JA, Kumar S, Dmochowski IJ, et al. Synthesis and characterization of fluorescent, low-symmetry triphenylene discotic liquid crystals: tailoring of mesomorphic and optical properties. Chem Mater. 1996;8:1402–1409.

[16] Iino H, Hanna J-I. Liquid crystalline organic semiconductors for organic transistor applications. Polym J. 2017;49:23–30.

[17] VanMeter JP, Klanderman BH. Low-melting liquid crystalline phenyl 4-benzoyloxy benzoates. J Am Chem Soc. 1973;95:626–627.

[18] Bae JW, Song KG. FTIR spectroscopic studies of molecular arrangements of reactive mesogen mixtures. Polym Korea. 2015;39(4):690–696.

[19] Guo J, Wu H, Chen F, et al. Fabrication of multi-pitched photonic structure in cholesteric liquid crystals based on a polymer template with helical structure. J Mater Chem. 2010;20:4094–4102.

[20] Mulani KB, Ganjave NV, Chavan NN. Synthesis and characterization of triad based rigid mesogenic diols derived from hydroquinone and 4-hydroxybenzoic acid. Indian J Chem. 2014;53:591–596.

[21] Mulani K, Momin M, Ganjave N, et al. Thermotropic liquid crystalline polyesters derived from bis-(4-hydroxybenzoyloxy)-2-methyl-1,4-benzene and aliphatic dicarboxylic acid chlorides. Bull Mater Sci. 2015;38(5):1301–1308.
[22] Zhao KQ, Wang BQ, Hu P, et al. Synthesis of new triphenylene-containing discotic liquid crystals and the influence of fluorophilic effect and molecular symmetry on mesomorphism. Chin J Chem. 2005;23(6):767–774.
[23] McGlacken GP, Fairlamb IJS. Palladium-catalysed cross-coupling and related processes: some interesting observations that have been exploited in synthetic chemistry. Eun J Org Chem. 2009;24:4011–4029.
[24] McIlroy SP, Cló E, Nikolajsen L, et al. Two-photon photosensitized production of singlet oxygen: sensitizers with phenylene-ethynylene-based chromophores. J Org Chem. 2005;70(4):1134–1146.
[25] Bovonsombat P, Leykajarakul J, Khan C, et al. Regioselective iodination of phenol and analogues using *N*-iodosuccinimide and *p*-toluenesulfonic acid. Tetrahedron Lett. 2009;50:2664–2667.
[26] Zhu Y-F, Guan X-L, Shen Z, et al. Competition and promotion between two different liquid-crystalline building blocks: mesogen-jacketed liquid-crystalline polymers and triphenylene discotic liquid crystals. Macromolecules. 2012;45:3346–3355.
[27] Xu J, Okada H, Onnagawa H, et al. Liquid crystal system as molecular machinery: investigation of dynamic impedance matching between molecular core and terminal groups using rotor-bearing model. Jpn J Appl. 2000;39:1801–1807.
[28] Li X, Yang C, Wang Q, et al. Enhanced birefringence for metallic nanoparticle doped liquid crystals. Opt Commun. 2013;286:224–227.
[29] Hu L, Xuan L, Cao Z, et al. A liquid crystal atmospheric turbulence simulator. Opt Express. 2006;14:11911–11918.
[30] Mu Q, Cao Z, Hu L, et al. Adaptive optics imaging system based on a high-resolution liquid crystal on silicon device. Opt Express. 2006;14:8013–8018.
[31] Lee M, Bae JW, Kim A, et al. Alignments of reactive mesogen using rubbed glass substrates. Polym Korea. 2014;39(1):174–179.
[32] Pinal R. Effect of molecular symmetry on melting temperature and solubility. Org Biomol Chem. 2004;2:2692–2699.