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Electroluminescent segmented liquid crystalline trimers

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The synthesis and liquid crystal behaviour of light-emitting trimeric liquid crystals consisting of three mesomorphic moieties connected by aliphatic spacers are reported. The combination of an aromatic light-emitting central core and two cholestanyl (dihydrocholesteryl) groups induces a helical liquid crystalline phase with circularly polarised photoluminescence and electroluminescence. These segmented trimers are designed to possess a high glass transition temperature below which the structure of liquid crystalline phases can be fixed. The effects of odd and even spacers, spacer length and the presence of large lateral substituents on the liquid crystal behaviour and the glass transition temperature of these trimers were studied. Electroluminescence from a segmented liquid crystalline trimer is reported for the first time.

Keywords: electroluminescence; LC trimer

1. Introduction

Liquid crystals (LCs) are a new class of organic semiconductor for use in organic light-emitting diodes (OLEDs) (*1, 2*), organic field-effect transistors (OFETs) (*3, 4*) and photovoltaics (*5, 6*). Non-polymerisable nematic and smectic liquid crystals can be used in these devices as long as they form a glassy liquid crystalline state above room temperature (*7–25*). The glass transition temperature should be considerably higher than room temperature to avoid crystallisation during device operation. Non-polymerisable chiral nematic compounds in the glassy state can also be used for organic lasers (*26, 27*) and circularly polarised photoluminescence (PL) and electroluminescence (EL) (*28*) for applications in optical information displays, processing and storage. Segmented liquid crystalline dimers and trimers represent a new approach to semiconducting and light-emitting LCs with a high glass transition temperature. The mesomorphic behaviour and structure/property relationships of a diverse range of liquid crystalline symmetrical and unsymmetrical dimers and trimers consisting of aromatic cores connected by aliphatic spacer groups and incorporating aliphatic chains in terminal positions on the aromatic cores have been extensively studied (*29–35*). Most segmented dimers exhibit a nematic phase and have been investigated as models for the corresponding oligomers and polymers, to study odd–even effects as a function of molecular shape and conformation (*29–35*). A large variety of dimers incorporating large optically-active aliphatic groups, such as the cholesteryl and dihydrocholesteryl moieties, have been prepared in order to study their mesomorphic nature and to induce helical phases, such as chiral nematic (N*), smectic C (SmC*) and smectic A phases (SmA*) (*36–46*). Trimeric LCs, in which the molecular structure consists of three aromatic and/or aliphatic cores, have been investigated to a much lesser degree than dimeric LCs. However, trimers incorporating cholesterol can also exhibit liquid crystalline phases with high transition temperatures as well as the glassy state at elevated transition temperatures (*47*). Optically-responsive groups, such as azo moieties, have been incorporated in dimers incorporating cholesteryl groups to use them as optical switches (*48–50*). The presence of two cholesteryl groups in trimers incorporating a non-mesomorphic core in the centre of the molecular structure has been used to induce smectic phases (*51*). Polarised fluorescence was observed from a mechanically sheared smectic trimer. Optically-active dimers incorporating cholesteryl groups have also been used for use in flexolectric LCDs (*52*). Several dimeric and trimeric reactive mesogens, optically-active liquid crystalline mixtures thereof and the highly-crosslinked polymer networks formed from them by photochemical polymerisation have also been reported (*53–55*).

It has been shown that for a homologous series of trimeric LCs, the clearing temperatures and entropy changes exhibit an odd–even effect in relation to the odd–even number of methylene groups in the spacers that connect the three mesogenic groups. Strong odd–even effects were observed as a function of spacer

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length for chiral trimeric LCs consisting of a central biphenyl unit and two dihydrocholesteryl groups, in which three mesogenic cores were linked by two flexible spacers (see Figure 1) (*47*). In the case of an even–even molecule, in which two identical even spacers are used to connect the three mesogenic units, the long structural axis of all three mesogenic units are parallel. In an odd–odd molecular conformation, the long axes of only the two outside mesogenic units are parallel whereas the long axis of the inner mesogen is positioned in a different orientation. In the case of an even–odd molecule, the central mesogen and only one of the outside mesogens are parallel, whereas the other one of the outside mesogenic groups has a different orientation. These different conformations have an influence on the ordering of the liquid crystalline phase. An even–even conformation of the mesogenic cores results in a poorer ordering in the nematic phase compared to an even-odd conformation (*47*). This was indicated by lower $\Delta S/R$ values for compounds with an even–even conformation.

The chiral nematic glass used originally to demonstrate highly-efficient emission of circularly polarised light exhibited a low glass transition temperature (29°C) just above room temperature (*28*). We now report the synthesis of the photoluminescent and electroluminescent liquid crystalline trimers with the same luminescent core designed to exhibit a high glass transition temperature. The trimeric LCs incorporate two cholestanyl (dihydrocholesteryl) groups attached to the luminescent aromatic core by two flexible aliphatic spacers in order to induce chiral liquid crystalline phases, with a high glass transition temperature, capable of circularly polarised photoluminescence and electroluminescence. The presence of the two optically-active cholestanyl groups should suppress the tendency to crystallise due to a combination of steric molecular interactions and a high degree of assymmetry as well as inducing a very high viscosity essential for glass formation. These structures are not ideal for electroluminescence or the emission of circularly polarised light with a high contrast ratio, but they should serve to demonstrate proof of principle for electroluminescence from liquid crystalline trimers.

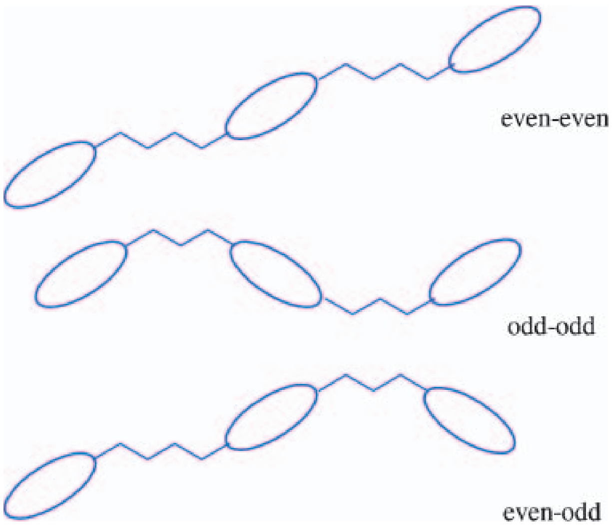


Figure 1. The idealised molecular shapes of even–even, odd–odd and even–odd trimeric LCs (*47*).

2. Experimental

Instrumentation

All commercially available starting materials, reagents and solvents were used as supplied, unless otherwise stated, and were obtained from Aldrich, Strem Chem Inc, Acros or Lancaster Synthesis. Tetrahydrofuran was pre-dried with sodium wire and then distilled over sodium wire under nitrogen with benzophenone indicator, when required and was not stored. All reactions were carried out using a dry nitrogen atmosphere unless water was present as solvent or reagent and the temperatures were measured externally. For compounds with RMM $<800\,\mathrm{g\,mol^{-1}}$ mass spectra were recorded using a gas chromatography/mass spectrometer (GC/MS)-QP5050A Schimadzu with electron impact (EI) at a source temperature of 200°C. For compounds with RMM $>800\,\mathrm{g\,mol^{-1}}$ mass spectra were analysed using a Bruker, reflex IV, matrix-assisted laser desorption/ionisation (MALDI), time of flight (TOF) MS. A 384-well microlitre plate format was used with a scout target. Samples were dissolved in DCM with HABA [2-(4-hydroxyphenylazo)benzoic acid] matrix (1:10, respectively). IR spectra were recorded using a Perkin-Elmer Paragon 1000 Fourier transform-infrared (FT-IR) spectrometer. ^{1}H NMR spectra were recorded using a JEOL Lambda 400 spectrometer and an internal standard of tetramethylsilane (TMS) was used. Aluminium-backed TLC plates coated with silica gel (60 F254 Merck) were used to measure the progress of reactions. GC was carried out using a Chromopack CP3800 gas chromatogaph equipped with a 10 m CP-SIL 5CB column. Purification of intermediates and final products was mainly accomplished by gravity column chromatography, using silica gel (40–63 μm, 60 Å) obtained from Fluorochem. The melting point and liquid crystal transition temperatures of the solids prepared were measured using a Linkam 350 hot-stage and control unit in conjunction with a Nikon

E400 polarising microscope. The transition temperatures of all of the final products were confirmed using a Perkin-Elmer DSC-7 differential scanning calprimeter in conjunction with a TAC 7/3 instrument controller, using the peak measurement for the reported value of the transition temperatures. Half Cp extrapolation was used to determine the value of the glass transition temperature (T_g). Thin layer chromatography (TLC), gas–liquid cromatography (GLC) and elemental analysis, using a Fisons EA 1108 CHN, were employed to measure the purity of the reaction intermediates and final compounds.

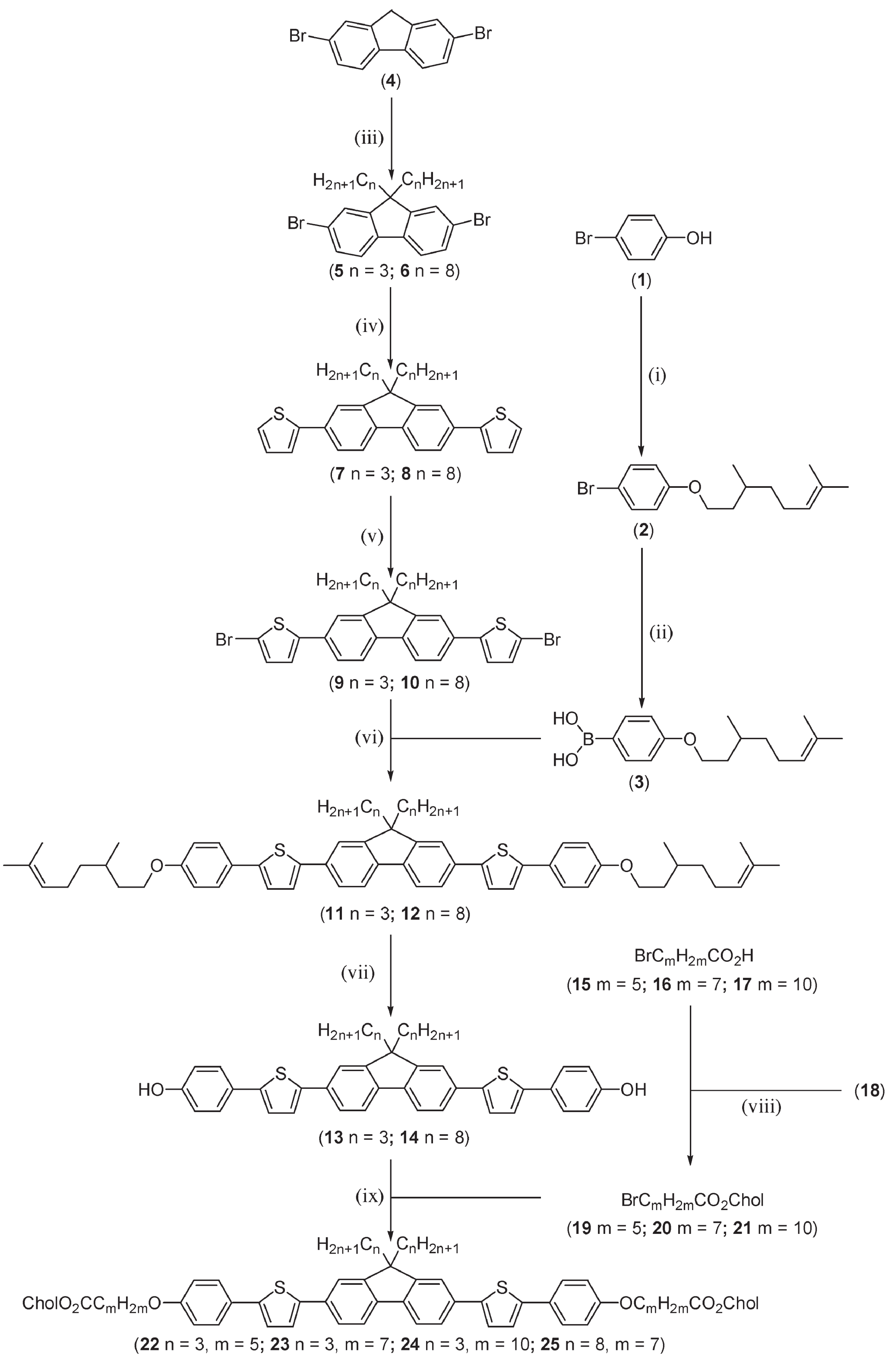
The photocurrent TOF method was used to obtain the hole mobility. A glass/ITO/film/ITO/glass cell structure was used. Capillary flow of the trimer **24** at isotropic temperature was found to be very slow as the results of high viscosity. Hence, the cells were filled by vacuum-assisted movement of trimer **24** in the isotropic phase and then sealed. The thickness, *l*, of the thin films was about 3 µm. The samples were heated to the isotropic phase before testing and measurements were taken on cooling. An optical pulse from a N_2 laser (Laser Science VSL-337ND, 337 nm) incident on the thin film creates a thin sheet of electron–hole pairs next to the contact. A uniform electric field, $E=3.3\times10^4\,\mathrm{V\,cm^{-1}}$, was applied across the organic layer of trimer **24** and the transit time, τ, was obtained from the intercept of the photocurrent plateau and tail, plotted on a logarithmic scale. The carrier mobility, μ, was obtained from the equation $\mu=l/E\tau$ (*21*).

X-ray diffraction (XRD) experiments were performed on a MAR345 diffractometer with a two-demensional image plate detector (Cu K_α radiation, graphite monochromator, $\lambda=1.54$ Å). The samples were aligned in a magnetic field. Spacings were calculated by applying Bragg's Law: $2d\sin\theta=n\lambda$, where *d* is the spacing, θ is half the diffraction angle and *n* is an integer. Integrated diffractograms are shown as a function of the scattering vector: $q\equiv2\pi n/d=4\pi\sin\theta/\lambda$ (*21*).

OLEDs were fabricated on a glass substrate (25 mm × 45 mm × 1 mm) covered with an ITO transparent anode and a poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) aqueous dispersion (PEDOT/PSS, Baytron P VP AI 4083, H.C. Starck) EL grade layer (thickness 45 nm) deposited by spin coating. The PSS/PEDOT layer was baked at 50°C for 5 min and subsequently at 165°C for 10 min in order to cure the layer and remove volatile components. Thin films of the mixtures of light-emitting trimer **34** were prepared by spin coating from a 1 wt% solution in toluene followed by baking at 140°C. A hole-blocking layer (12 nm) of tri(phenyl-2-benzimidazolyl)benzene (TPBi) was deposited on top of the emission layer of trimer **34** by vapour deposition using a vacuum of 10^{-6} mbar. Layers of lithium fluoride (0.6 nm) and aluminium (83 nm) were sequentially deposited in the same chamber as a combined cathode. EL was measured using a Labview-controlled Agilent E3631A DC power supply with Minolta LS100 luminance meter and Avaspec2048 fibre spectrometer. The PL quantum efficiency (QE) was measured using a literature method (*56*).

Synthesis

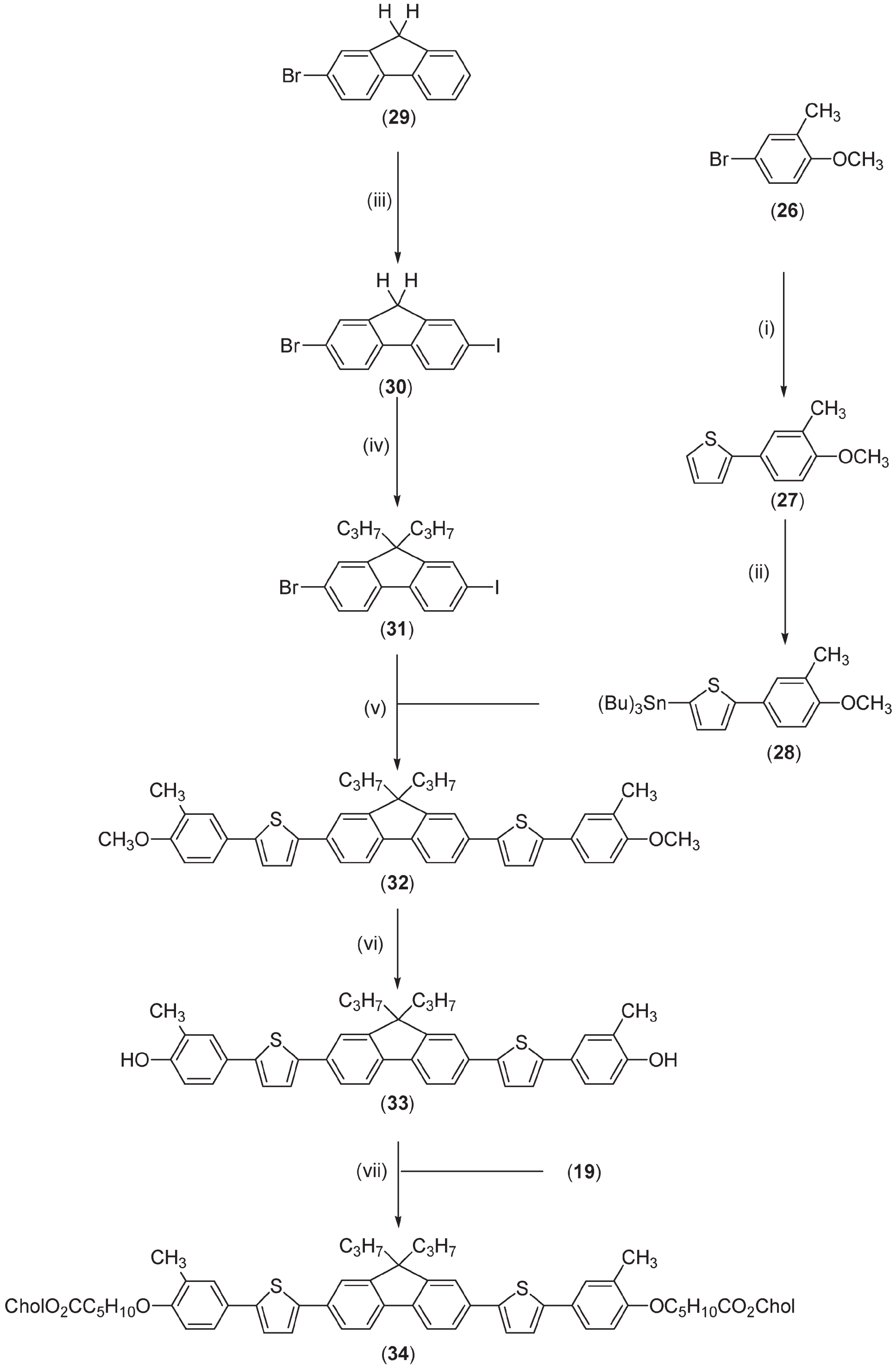
Trimers **22–25** were synthesised using the reactions shown in Scheme 1. The branched-chain (*S*)-(+)-citronellyl was used instead of the methoxy and octyloxy chains used previously (*6, 12*) in the synthesis of the intermediate diphenols (**13** and **14**) in order to improve the solubility of the reaction intermediates in the organic solvents used in the preceding steps. Commercially available 4-bromophenol and (*S*)-(+)-citronellyl bromide were reacted together in a Williamson ether reaction (*57*) to produce the aryl bromide (**2**), which was converted into the corresponding phenyl boronic acid (**3**) in the usual way (*58*) Commercially available 2,7-dibromofluorene (**4**) was alkylated twice in the 9-position with propyl bromide or octyl bromide and potassium *tert*-butoxide in DMF (*59*) to produce the dibromide (**5** and **6**). Conversion of the dibromides (**5** and **6**) into the dithiophenes (**7** and **8**) was achieved by reaction with the 2-(tributylstannyl)thiophene in a Stille reaction (*60*). The dithiophenes (**7** and **8**) were then selectively brominated in position 5 on the thiophene rings to yield the dibromides (**9** and **10**) using NBS (*61*). A Suzuki aryl–aryl coupling reaction (*58*) between the dibromides (**9** and **10**) and the phenyl boronic acid (**3**) yielded the diethers (**11** and **12**) with six aromatic rings in the molecular core. Deprotection of the dioctyloxy-substituted compounds (**11** and **12**) using boron tribromide produced the bisphenols (**13** and **14**) (*62*). Esterification of commercially available cholestan-3β-ol (**18**) with 6-bromohexanoic acid (**15**), 8-bromoheptanoic acid (**16**) or 11-bromoundecanoic acid (**17**) using DCC and DMAP (*63*) afforded cholestan-3β-yl 6-bromohexanoate (**19**), cholestan-3β-yl 7-bromoheptanoate (**20**) or cholestan-3β-yl 11-bromoundecanoate (**21**), respectively. Reaction of the 9,9-dipropyl-substituted bisphenol (**13**) with the bromoalkanes (**19–21**), utilising the Williamson-ether synthesis (*57*), afforded the optically-active trimers (**22–24**) with two propyl chains at the 9-position of the fluorene moiety. Reaction of the 9,9-octyl-substituted bisphenol (**14**) with the bromoalkane (**20**), utilising the



Scheme 1. Reagents and conditions: (i) (*S*)-(+)-citronellyl bromide, K_2CO_3, butanone; (ii) (a) *n*-BuLi, THF, (b) $B(OCH_3)_3$, (c) H_3O^+; (iii) tributylammonium bromide, 50% NaOH (aq.), toluene, 1-bromoalkane (n=3 or 8); (iv) 2-(tributylstannyl)-thiophene, $Pd(PPh_3)_4$, DMF; (v) *N*-bromosuccinimide, acetic acid, $CHCl_3$; (vi) Na_2CO_3 (aq.), $Pd(PPh_3)_4$, toluene; (vii) (a) BBr_3, CH_2Cl_2, (b) H_2O (ice); (viii) 11-bromoalkanoic acid (m=5, 7 or 10), DCC, DMAP, CH_2Cl_2; (ix) K_2CO_3, DMF.

Williamson-ether synthesis (*57*), afforded the optically-active trimer (**25**).

Trimer **34** was synthesised using the reactions shown in Scheme 2. The bromoanisole (**26**) was converted to the thiophene (**27**) by a Stille reaction (*60*). The thiophene (**27**) was then converted into the Stille reagent (**28**) by reaction with *n*-BuLi in THF at −78°C followed by addition of tri-*n*-butyltin chloride



Scheme 2. (i) 2-(tributylstannyl)thiophene, $Pd(PPh_3)_4$, DMF; (ii) (a) *n*-BuLi, THF, (b) $Sn(C_4H_9)_3Cl$; (iii) I_2, periodic acid, CH_3CO_2H, H_2SO_4, H_2O; (iv) tributylammonium bromide, 50% NaOH (aq.), 1-bromopropane, toluene; (v) $Pd(PPh_3)_4$, DMF; (vi) (a) BBr_3, CH_2Cl_2, (b) H_2O (ice); (vii) K_2CO_3, butanone.

(*60*). Iodination of commercially available 2-bromofluorene (**29**) using periodic acid and iodine in sulfuric acid and acetic acid (*64*) produced 2-bromo-7-iodofluorene (**30**). A double alkylation of the fluorene (**30**) in position 9 using 1-bromopropane, sodium hydroxide and tetra-*n*-butylammonium bromide (*59*) in toluene afforded compound (**31**). A Stille aryl–aryl cross-coupling reaction (*60*) between the dibromide (**31**) and the thiophene Stille reagent (**28**) yielded the diether (**32**). Deprotection of the methoxy-substituted compound (**32**) using boron tribromide produced the bisphenol (**33**) (*62*). Reaction of the bisphenol (**33**) with the bromoalkane (**19**), utilising the Williamson-ether synthesis (*57*), afforded the optically-active trimer (**34**).

Experimental details

1-Bromo-4-[(S)-3,7-dimethyloct-6-enyloxy]benzene (2).

A mixture of 4-bromophenol (**1**) (30.0 g, 0.1734 mol), (*S*)-(+)-citronellyl bromide (45.6 g, 0.2081 mol) and potassium carbonate (47.9 g, 0.3468 mol) in butanone (400 cm^3) was heated under reflux for 24 h. The cooled reaction mixture was filtered and the filtrate concentrated under reduced pressure. The crude product was purified by fractional distillation to yield a colourless oil. Yield 43.0 g, 79.8%. B.p. 160–162°C at 1.0 mbar Hg. Purity >99% (GC). ^{1}H NMR ($CDCl_3$) δ_H: 0.94 (3H, d), 1.16–1.44 (2H, m), 1.53–1.59 (2H, m), 1.60 (3H, s), 1.68 (3H, s), 1.79–1.86 (1H, m), 1.94–2.05 (2H, m), 3.92–3.97 (2H, m), 5.10 (1H, t), 6.75 (2H, d, J=9.0 Hz), 7.35 (2H, d, J=9.0 Hz). IR ν_{max} (cm^{-1}): 3085, 2952, 2928, 2850, 1602, 1504, 1457, 1268, 1209, 859, 800. MS *m*/*z*: 312, 310 (M$^+$), 293, 277, 227, 187, 174, 138, 123, 109, 95, 83, 69 (M100). Combustion analysis: expected, C 61.74%, H 7.45%; obtained, C 61.74%, H 7.71%.

4-[(S)-3,7-Dimethyloct-6-enyloxy]phenyl boronic acid (3).

A solution of *n*-BuLi in hexanes (59.2 cm^3, 2.5M, 0.12 mol) was added dropwise to a cooled (−78°C) solution of 1-bromo-4-[(*S*)-3,7-dimethyloct-6-enyloxy] benzene (**2**) (40.0 g, 0.1286 mol) in THF (dry, 350 cm^3). The resultant solution was stirred at this temperature for 1 h and then trimethyl borate (26.8 g, 0.2572 mol) was added dropwise to the mixture. After completion of the addition the reaction mixture was stirred overnight. Hydrochloric acid (20%, 250 cm^3) was added and the resultant mixture was stirred for 1 h and then extracted into diethyl ether (2 × 400 cm^3). The ethereal extracts were washed with water (2 × 400 cm^3) and dried ($MgSO_4$). After filtration the solvent was removed under reduced pressure to yield a waxy solid. Yield 27.7 g, 78%. M.p. 42–44°C. ^{1}H NMR ($(CD_3)_2SO$) δ_H: 0.91 (3H, d), 1.13–1.40 (2H, m), 1.45–1.53 (2H, m), 1.56 (3H, s), 1.64 (3H, s), 1.72–1.78 (1H, m), 1.89–2.03 (2H, m), 3.91–4.04 (2H, m), 5.09 (1H, t), 6.90 (2H, d, J=8.4 Hz), 7.78 (2H, d, J=8.4 Hz), 2 × –OH not detected. IR ν_{max} (cm^{-1}): 3150–3550, 3056, 2971, 2933, 2852, 1610, 1556, 1456, 1385, 1311, 1252, 1179, 972, 826.

2,7-Dibromo-9,9-dipropylfluorene (5).

A 50% aqueous solution of NaOH (70 cm^3) was added to a mixture of 2,7-dibromofluorene (**4**) (10.0 g, 0.0309 mol) and TBAB (0.50 g, 0.0015 mol) in toluene (70 cm^3). 1-Bromopropane (8.73 g, 0.0710 mol) in toluene (10 cm^3) was then added dropwise at room temperature (RT) and the reaction was stirred vigorously overnight at 60°C. The reaction mixture was cooled to RT and water was added (200 cm^3). Toluene (300 cm^3) was added, the aqueous layer separated off and the residual organic layer washed with water (200 cm^3), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified by gravity column chromatography (silica gel, hexane, 100%) and recrystallised from ethanol to yield a white crystalline solid. Yield 7.62 g, 60%. M.p. 139–140°C. Purity >99% (GC).^{1}H NMR ($CDCl_3$) δ_H: 0.58–0.71 (10H, m), 1.88–1.92 (4H, m), 7.43–7.45 (4H, m), 7.50 (2H, d, J=7.6 Hz). IR ν_{max} (cm^{-1}): 3083, 2955, 2932, 2873, 2855, 1600, 1573, 1452, 1416, 1110, 1050, 1006, 879, 800, 771, 735. MS *m*/*z* (EI): 410, 408, 406 (M$^+$), 368, 365, 323, 284, 271, 269, 189, 176 (M100), 150, 108, 88, 77, 63. Combustion analysis: expected, C 55.91%, H 4.94%; obtained, C 55.94%, H 4.89%.

2,7-Bis(thien-2-yl)-9,9-dipropylfluorene (7).

A mixture of 2,7-dibromo-9,9-dipropylfluorene (**5**) (25.0 g, 0.0610 mol), 2-(tributylstannyl)thiophene (52.3 g, 0.1402 mol) and tetrakis(triphenylphosphine)-palladium(0) (1.41 g, 0.0012 mol) in DMF (400 cm^3) was heated at 90°C for 24 h. The mixture was allowed to cool to RT and the solution was treated with a saturated potassium fluoride solution (100 cm^3) to destroy the tin side products. DCM (500 cm^3) was added and the resultant solution washed with brine (4 × 200 cm^3), dried ($MgSO_4$), filtered and concentrated under reduced pressure. Catalyst residues were removed by passing the crude product though a short column containing silica gel (DCM:hexane, 50:50). The product was recrystallised from a DCM and ethanol mixture, filtered and washed with cold ethanol (2 × 50 cm^3) to yield a light green crystalline solid. Yield 18.1 g, 71.8%. M.p. 174–176°C. ^{1}H NMR (CDCl$_3$) δ_H: 0.69–0.73 (10H, m), 1.99–2.03 (4H, m), 7.11 (2H, dd, J=3.6, 5.1 Hz), 7.29 (2H, dd, J=1.2, 5.2 Hz), 7.38 (2H, dd, J=1.1, 3.6 Hz), 7.57 (2H, d, J=1.5 Hz), 7.60 (2H, dd, J=1.5, 7.9 Hz), 7.67 (2H, d, J=7.9 Hz). IR ν_{max} (cm^{-1}): 3068, 2956, 2927, 2870, 1608, 1525, 1460, 1376, 1276, 1207, 1055, 872, 853, 816, 748. MS (m/z): 414 (M$^+$, M100), 371, 342, 329, 308, 297, 207, 185, 165, 84, 71.

2,7-Bis(5-bromothien-2-yl)-9,9-dipropylfluorene (9).

N-Bromosuccinimide (11.1 g, 0.0623 mol, recrystallised from water) was added slowly to a stirred solution of 2,7-bis(thien-2-yl)-9,9-dipropylfluorene (**7**) (12.0 g, 0.0290 mol) in chloroform (120 cm^3) and glacial acetic acid (120 cm^3). The solution was heated under reflux and the progress of the reaction was carefully monitored by TLC analysis to avoid further bromination. After 1 h the reaction mixture was washed with a sodium hydrogensulfite solution (5%, 100 cm^3) and chloroform (200 cm^3) was added. The organic layer was washed with water (2 × 200 cm^3), dried (MgSO$_4$), filtered and concentrated under reduced pressure. The crude product was recrystallised from a DCM and ethanol mixture to yield a green crystalline solid. Yield 13.4 g, 80.7%. M.p. 170°C. ^{1}H NMR (CDCl$_3$) δ_H: 0.68–0.71 (10H, m), 1.96–2.00 (4H, m), 7.06 (2H, d, J=3.9 Hz), 7.11 (2H, d, J=3.9 Hz), 7.46 (2H, d, J=1.4 Hz), 7.49 (2H, dd, J=1.7, 7.9 Hz), 7.66 (2H, d, J=7.7 Hz). IR ν_{max} (cm^{-1}): 3060, 2999, 2958, 2852, 1598, 1490, 1438, 1290, 1202, 1063, 867, 816, 788. MS (m/z): 576, 574, 572 (M$^+$, M100), 500, 487, 452, 450, 419, 377, 286, 282, 188, 126, 101, 82, 69 Combustion analysis: expected, C 56.65%, H 4.23%, S 11.20%; obtained, C 56.60%, H 4.19%, S 11.43%.

2,7-Bis(5-{4-[(S)-3,7-dimethyloct-6-enyloxy]phenyl} thien-2-yl)-9,9-dipropylfluorene (11).

Tetrakis(triphenylphosphine)palladium(0) (1.21 g, 1.05 × 10^{-3} mol) was added to a stirred solution of 4-[(*S*)-3,7-dimethyloct-6-enyloxy]phenyl boronic acid (**3**) (7.21 g, 0.0261 mol), 2,7-*bis*(5-bromothien-2-yl)-9,9-dipropylfluorene (**9**) (6.00 g, 0.0105 mol) and a 20% aqueous sodium carbonate solution (3.32 g, 0.0314 mol) in toluene (250 cm^3) at RT. The reaction mixture was heated under reflux for 48 h. Toluene (100 cm^3) was added and the organic layer was washed with water (150 cm^3). The combined organic extracts were dried (MgSO$_4$), filtered and concentrated under reduced pressure. The crude product was purified by gravity column chromatography (silica gel, DCM:hexane, 20:80) to yield a green crystalline solid. Yield 4.00 g, 43.7%. Transition temperatures (/=°C): T_g 23 Cr 123 N* 122 I. ^{1}H NMR (CDCl$_3$) δ_H: 0.68–0.78 (10H, m), 0.97 (6H, d), 1.21–1.46 (4H, m), 1.46–1.62 (4H, m), 1.62 (6H, s), 1.70 (6H, s), 1.82–1.90 (2H, m), 1.96–2.09 (8H, m), 4.01–4.08 (4H, m), 5.12 (2H, t), 6.93 (4H, d, J=8.7 Hz), 7.20 (2H, d, J=3.6 Hz), 7.34 (2H, d, J=3.6 Hz), 7.57 (4H, d, J=8.7 Hz), 7.58 (2H, d, J=1.6 Hz), 7.60 (2H, dd, J=1.6, 7.8 Hz), 7.67 (2H, d, J=7.8 Hz). IR ν_{max} (cm^{-1}): 3060, 2962, 2860, 1609, 1512, 1473, 1381, 1282, 1250, 1178, 1114, 1062, 1025, 830, 798. MS *m/z* (EI): 875 (M$^+$), 737, 598, 526, 349, 299, 263, 195, 149, 97, 83, 69 (M100). Combustion analysis: expected, C 80.96%, H 8.06%, S 7.33%; obtained, C 81.11%, H 8.20%, S 7.12%.

2,7-Bis[5-(4-hydroxyphenyl)thien-2-yl]-9,9-dipropylfluorene (13).

Boron tribromide (0.78 cm^3, 0.0082 mol) in DCM (10 cm^3) was added dropwise to a cooled (0°C) stirred solution of 2,7-bis(5-{4-[(*S*)-3,7-dimethyloct-6-enyloxy]phenyl]thien-2-yl)-9,9-dipropylfluorene (**11**) (2.40 g, 0.0027 mol) in chloroform (120 cm^3). The reaction mixture was stirred at RT overnight, then poured onto an ice/water mixture (200 g) and stirred for 30 min. The product was extracted into ethyl acetate (2 × 200 cm^3). The combined organic layers were washed with water (2 × 100 cm^3), dried (MgSO$_4$), filtered and concentrated under reduced pressure. The crude product was purified by gravity column chromatography (silica gel, ethyl acetate:hexane, 30:70) to yield a green powder. Yield 1.15 g, 70%. M.p. 264–267°C (literature, 277°C (*12*)). ^{1}H NMR (CDCl$_3$): δ_H 0.70–0.78 (10H, m), 2.00–2.05 (4H, m), 4.95 (2H, s, –OH), 6.87 (4H, d, J=8.7 Hz), 7.20 (2H, d, J=3.6 Hz), 7.33 (2H, d, J=3.6 Hz), 7.55 (4H, d, J=8.7 Hz), 7.57 (2H, d, J=1.6 Hz), 7.60 (2H, dd, J=1.7, 7.9 Hz), 7.68 (2H, d, J=7.9 Hz). IR ν_{max} (cm^{-1}): 3100–3500, 3100, 2956, 2925, 2853, 1610, 1545, 1502, 1473, 1455, 1376, 1242, 1174, 1106, 880, 831, 798. MS *m/z* (EI): 598 (M$^+$), 526, 513, 299, 263 (M100), 248, 171, 149, 122, 105, 97, 77, 71.

Cholestan-3β-yl 11-bromoundecanoate (21).

DCC (2.64 g, 0.0128 mol) was added to a stirred solution of 11-bromoundecanoic acid (**17**) (3.40 g, 0.0128 mol), cholestan-3*β*-ol (**18**) (4.97 g, 0.0128 mol) and DMAP (1.56 g, 0.0128 mol) in DCM (150 cm^3) at RT. The reaction mixture was stirred overnight. The byproduct, dicyclohexylurea (DCU), was filtered off, and the target compound concentrated under reduced pressure and purified by gravity column chromatography (silica gel, DCM:hexane, 50:50) to yield a white powder. Yield 5.00g, 61.3%. M.p. 69°C. ^{1}H NMR (CDCl$_3$) δ_H: 0.65 (3H, s), 0.82 (3H, s), 0.85 (3H, d), 0.87 (3H, d), 0.90 (3H, d), 1.00–2.00 (47H, m), 2.23 (2H, t), 3.42 (2H, t), 4.61–4.69 (1H, m). IR ν_{max} (cm^{-1}): 2914, 2849, 1732, 1470, 1387, 1376, 1281, 1246, 1217, 1186, 1008, 720. MS *m*/*z* (EI): 636, 634 (M$^+$), 616, 614, 481, 370, 355, 215 (M100), 201, 173, 147, 121, 107, 95, 81, 55, 43. Combustion analysis: expected, C 71.78%, H 10.62%; obtained, C 72.00%, H 10.92%. $[\alpha]_d^{25} = +8.18°$.

2,7-Bis(5-{4-[10-cholestan-3β-yl-oxycarbonyl)decyloxy]phenyl}thien-2-yl)-9,9-dipropylfluorene (24).

A mixture of 2,7-bis[5-(4-hydroxyphenyl)thien-2-yl]-9,9-dipropylfluorene (**13**) (0.15 g, 2.51×10^{-4} mol), cholestan-3β-yl 11-bromoundecanoate (**21**) (0.37 g, 5.77×10^{-4} mol) and potassium carbonate (0.10 g, 7.53×10^{-4} mol) in DMF (10 cm^3) was heated at 90°C for 48 h. The reaction mixture was cooled to RT and the precipitate was filtered and washed with water (2 × 20 cm^3), hydrochloric acid (10%, 20 cm^3), water (2 × 20 cm^3) and ethanol (2 × 20 cm^3). The crude product was recrystallised from a DCM and ethanol mixture to yield a green powder. Yield 0.20 g, 46.5%. ^{1}H NMR (CDCl$_3$) δ_H: 0.65 (6H, s), 0.68–0.76 (10H, m), 0.82 (6H, s), 0.85 (6H, d), 0.87 (6H, d), 0.90 (6H, d), 1.00–2.00 (94H, m), 2.00–2.08 (4H, m), 2.23 (4H, t), 3.99 (4H, t), 4.62–4.70 (2H, m), 6.93 (4H, d, *J*=8.7 Hz), 7.23 (2H, d, *J*=3.6 Hz), 7.36 (2H, d, *J*=3.6 Hz), 7.58 (4H, d, *J*=8.7 Hz), 7.62 (2H, d, *J*=1.6 Hz), 7.64 (2H, dd, *J*=1.7, 7.9 Hz), 7.71 (2H, d, *J*=7.9 Hz). IR ν_{max} (cm^{-1}): 3072, 2930, 2853, 1732, 1607, 1541, 1511, 1472, 1287, 1249, 1177, 1112, 1009, 828, 795. MS *m*/*z* (MALDI): 1709 (M$^+$). Combustion analysis: expected, C 80.84%, H 9.79%, S 3.75%; obtained, C 80.88%, H 10.03%, S 3.74%. $[\alpha]_d^{25} = +8.25$.

2-(4-Methoxy-3-methylphenyl)thiophene (27).

Tetrakis(triphenylphosphine)palladium(0) (2.88 g, 2.48×10^{-3} mol) was added to a heated (90°C) solution of 4-bromo-2-methylanisole (**26**) (10.00 g, 0.0498 mol), tributyl(thiophen-2-yl)stannane (18.54 g, 0.0498 mol) and DMF (160 cm^3). The mixture was stirred overnight for 16 h, allowed to cool, poured into water (200 cm^3), and the crude product extracted into diethyl ether (3 × 200 cm^3). The combined organic extracts were washed with saturated KF solution (200 cm^3), brine (200 cm^3), dried (MgSO$_4$), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography (silica gel, DCM:hexane, 1:1) to yield a colourless liquid. Yield 7.82 g, 77%. Purity >99% (GC). ^{1}H NMR (CDCl$_3$) δ_H: 2.41 (3H, s), 3.84 (3H, s), 6.78 (1H, dd, *J*=8.4, 2.8 Hz), 6.83 (1H, d, *J*=2.8 Hz), 7.01 (1H, dd, *J*=3.5, 1.1 Hz), 7.08 (1H, dd, *J*=5.2, 3.4 Hz), 7.31 (1H, dd, *J*=5, 1.1 Hz), 7.34 (1H, d, *J*=8.4 Hz). IR ν_{max} (cm^{-1}): 3071, 2999, 2955, 2834, 1607, 1570, 1537, 1494, 1464, 1435, 1414, 1379, 1350, 1295, 1259, 1239, 1163, 1123, 1045, 963, 847, 809, 697, 580, 452. MS *m*/*z* (EI): 204 (M$^+$), 189, 173, 167, 149 (M 100), 128, 104, 84, 57. Combustion analysis: expected, C 70.55%, H 5.92%, S 15.70%; obtained, C 70.33%, H 6.09%, S 15.53%.

Tributyl[5-(4-methoxy-3-methylphenyl)thiophen-2-yl]stannane (28).

A solution of *n*-BuLi in hexanes (11.84 cm^3, 2.5M) was added dropwise to a cooled (−78°C) solution of 2-(4-methoxy-3-methylphenyl)thiophene (**27**) (5.04 g, 0.0247 mol) in THF (50 cm^3). The mixture was stirred for 1 h, maintaining the temperature, followed by the dropwise addition of tributyltin chloride (11.24 g, 0.0345 mol). The mixture was allowed to warm to RT and stirred overnight. The crude product was extracted into diethyl ether (2 × 100 cm^3), the combined organic extracts washed with water (100 cm^3), dried (MgSO$_4$), filtered and concentrated under reduced pressure. No further purification was carried out. Purity >68% (GC). MS *m*/*z* (EI): 493 (M$^+$), 491, 437, 436, 435, 381, 379, 325, 324, 323, 217, 173, 158, 128, 57.

2-Bromo-7-iodofluorene (30).

A solution of 2-bromofluorene (**29**) (25.00 g, 0.1000 mol), glacial AcOH (250 cm^3), concentrated sulfuric acid (3 cm^3) and water (20 cm^3) was heated (75°C) for 10 min; dehydrated periodic acid (4.56 g, 0.0200 mol) and pulverised I$_2$ (10.20 g, 0.0400 mol) were then added. After 2 h the deep purple reaction mixture became yellow in colour. Glacial AcOH (100 cm^3) was added to the cooled reaction mixture, which was further diluted with sodium metabisulfite solution (2.5 g, 20 cm^3, water). The resultant yellow precipitate was filtered off, washed with MeOH (3 × 250 cm^3), NaOH (5% aq. solution, 3 × 250 cm^3) and water (3 × 250 cm^3). The product was then recrystallised from EtOH/DCM to yield a white crystalline solid. Yield 24.45 g, 69%. M.p. 185°C. Purity >99% (GC). ^{1}H NMR (CDCl$_3$) δ_H: 3.84 (2H, s), 7.48 (1H, d, *J*=8.2 Hz), 7.50 (1H, dd, *J*=1.7, 8.2 Hz), 7.60 (1H, d, *J*=8.2 Hz), 7.66 (1H, d, *J*=1.1 Hz), 7.69 (1H, dd, *J*=1.7, 8.2 Hz) 7.87 (1H, d, *J*=1.1 Hz). IR ν_{max} (cm^{-1}) 3068, 1600, 1580, 1486, 1450, 1412, 1140, 1055, 1002, 814, 760. MS *m*/*z* (EI): 372, 370 (M$^+$, M100), 291, 243, 163, 146, 123, 82, 63.

Combustion analysis: expected, C 42.08%, H 2.17%; obtained, C 41.80%, H 1.90%.

2-Bromo-7-iodo-9,9-dipropylfluorene (31).

A mixture of NaOH (65.00 g), water (130 cm^3), 2-bromo-7-iodofluorene (**30**) (20.00 g, 0.0540 mol), 1-bromopropane (19.94 g, 0.1620 mol), toluene (130 cm^3), and TBAB (0.80 g) was heated under reflux with vigorous stirring overnight. The reaction was allowed to cool and the product extracted into diethyl ether (3×250 cm^3). The combined organic extracts were washed with HCl_{aq} (10%, 500 cm^3), water (3×250 cm^3), dried ($MgSO_4$), filtered and concentrated under reduced pressure. Purification was carried out via column chromatography (silica gel, hexane) and recrystallisation from EtOH to yield a pale yellow waxy solid. Yield 12.05 g, 49%. M.p. 140–142°C [literature 136–139°C, EtOH, (*6*)]. Purity >99% (GC). ^{1}H NMR ($CDCl_3$) δ_H: 0.65 (10H, m), 1.89 (4H, quint), 7.40–7.51 (4H, m), 7.64 (2H, d, J=7.4 Hz). IR ν_{max} (cm^{-1}): 2946, 2925, 2866, 2839, 1884, 1734, 1593, 1569, 1454, 1445, 1413, 1394, 1377, 1270, 1239, 1131, 1108, 1050, 1003, 930, 874, 809, 754, 742, 668, 659, 494, 424. MS *m/z* (EI): 457, 455 (M^+, M 100), 453 413, 408, 371, 332, 317, 304, 284, 269, 256, 248, 228, 219, 205, 189, 176, 163, 150, 101, 88, 75, 57. Combustion analysis: expected, C 50.14%, H 4.43%; obtained, C 50.29%, H 4.42%.

2,7-Bis[5-(4-methoxy-3-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (32).

Tetrakis(triphenylphosphine)palladium(0) (0.44 g, 3.81×10^{-4} mol) was added to a heated (90°C) solution of 2-bromo-7-iodo-9,9-dipropylfluorene (**31**) (1.75 g, 0.0038 mol), tributyl[5-(4-methoxy-3-methylphenyl)thiophen-2-yl]stannane (**28**) (7.59 g, 0.0154 mol) and DMF (50 cm^3). The mixture was stirred overnight, 16 h, allowed to cool, poured into water (300 cm^3), and the crude product extracted into diethyl ether (3×200 cm^3). The combined organic extracts were washed with saturated aqueous KF (200 cm^3), brine (2×250 cm^3), dried ($MgSO_4$), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography (silica gel, DCM:hexane, 2:1) and recrystallisation from DCM/EtOH to yield a pale yellow crystalline solid. Yield 1.68 g, 67%. Transition temperatures (°C): Cr 157 N (125) I. ^{1}H NMR ($CDCl_3$) δ_H: 0.74 (6H, t), 0.81–0.88 (4H, m), 2.02 (4H, t), 2.49 (6H, s), 3.85 (6H, s), 6.78–6.84 (6H, m), 7.00 (2H, d, J=4.5 Hz), 7.40 (2H, d, J=8.4 Hz), 7.59–7.72 (4H, m). IR ν_{max} (cm^{-1}): 2955, 2834, 1604, 1566, 1492, 1467, 1294, 1242, 1160, 1121, 1049, 865, 802, 721, 582, 451. MS *m/z* (EI): 654 (M^+), 537, 536, 494, 407, 406, 391, 368, 298, 247, 203, 152, 115.

2,7-Bis[5-(4-hydroxy-3-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (33).

Boron tribromide (2.58 g, 0.0103 mol) was added dropwise to a cooled (0°C) solution of bis-2,7-[5-(4-methoxy-3-methylphenyl)thiophen-2-yl]-9,9-dipropylfluorene (**32**) (1.50 g, 0.0023 mol) in DCM (10 cm^3). The reaction mixture was allowed to warm to RT and stirred overnight, poured into ice (300 cm^3) and stirred for 1 h. The organic layer was separated and the aqueous layer washed with DCM (3×200 cm^3). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Purification was carried out *via* column chromatography (silica gel, hexane:ethyl acetate, 2:1) to yield a pale yellow crystalline solid. Yield 1.23 g, 85%. M.p. 171°C. ^{1}H NMR ($CDCl_3$) δ_H: 0.69–0.75 (10H, m), 2.02 (4H, t), 2.46 (6H, s), 4.74 (2H, s), 6.71–6.78 (6H, m), 7.00 (2H, d, J=3.7 Hz), 7.29–7.37 (4H, m), 7.58–7.69 (4H, m). IR ν_{max} (cm^{-1}): 3306, 2952, 1603, 1577, 1454, 1289, 1239, 1161, 1005, 966, 862, 802, 654, 577, 451. MS *m/z* (EI): 626 (M^+), 555, 554, 378, 357, 356, 313, 278, 277, 187, 186 (M 100).

2,7-Bis(5-{4-[5(cholestan-3β-yl-oxycarbonyl)pentyloxy] 3-methylphenyl}thien-2-yl)-9,9-dipropylfluorene (34).

A mixture of bis-2,7-[5-(4-hydroxy-3-methylphenyl) thiophen-2-yl]-9,9-dipropylfluorene (**33**) (0.20 g, 3.05×10^{-4} mol), K_2CO_3 (0.15 g, 0.0011 mol), cholestan-3β-yl 6-bromohexanoate (**19**) (0.40 g, 7.02×10^{-4} mol) and butanone (10 cm^3) was heated under reflux overnight. The cooled reaction mixture was concentrated under reduced pressure and the crude product was purified *via* column chromatography (silica gel, hexane:ethyl acetate, 4:1) and recrystallisation from DCM/EtOH to yield a yellow crystalline solid. Yield 0.38 g, 72%. Transition temperatures (°C): T_g 60 Cr 124 N* 160 I. ^{1}H NMR ($CDCl_3$) δ_H: 0.65 (6H, s), 0.70–0.74 (4H, m), 0.82–0.91 (30H, m), 0.97–1.40 (40H, m), 1.97 (34H, m), 2.01 (4H, t), 2.27, (4H, m), 2.49 (6H, s), 3.99 (4H, t), 4.66–4.74 (2H, m), 6.75–6.83 (6H, m), 7.00 (2H, d, J=3.7 Hz), 7.34–7.37 (4H, m), 7.57–7.69 (4H, m). IR ν_{max} (cm^{-1}): 2931, 1730, 1604, 1469, 1240, 1172, 1045, 796. MS *m/z* (MALDI): 1596 (M^+, M 100), 1574, 1472, 1408, 1407, 1406, 1405, 1388, 1387, 1386, 1350, 1349, 1348, 1347, 1320, 1319. Combustion analysis: expected, C 80.50%, H 9.47%, S 4.02%, obtained, C 80.63%, H 9.64%, S 3.85%.

Mesomorphic behaviour

The mesomorphic behaviour of the trimers (**22**–**25** and **34**) were investigated between crossed polarisers using optical microscopy. The trimers (**22**, **23**, **25** and **34**) with an odd number of methylene units in the flexible aliphatic spacers between the aliphatic cholestanyl groups and the aromatic core only exhibit an enantiotropic chiral nematic (N*) phase. Above the chiral nematic–isotropic (N*–I) temperature the optical texture appears black and no birefringence is observed. Nematic droplets are then observed just below the clearing point upon slow cooling from the isotropic phase, which is a characteristic feature of a nematic phase or a chiral nematic phase (see Figure 2). These droplets then coalesce to form the planar Grandjean texture of the chiral nematic phase (see Figure 3). The pseudo focal-conic texture of the chiral nematic phase can be sheared to a Grandjean texture (see Figures 4 and 5, respectively).

Trimer **24** also exhibits chiral nematic drops on cooling from the isotropic phase (see Figure 6) then the planar Grandjean texture of the chiral nematic phase (see Figure 7) on further cooling. This mesophase texture then transforms itself into the Schlieren texture of the chiral smectic C (SmC*) phase on cooling below the SmC*–N* transition, as shown in Figure 8.

The LC transition temperatures and glass transition temperature (T_g) of the trimers (**22**–**25** and **34**) were confirmed by DSC and good agreement (≈1–2°C) with those values determined by optical microscopy was obtained (see Table 1). These values were determined twice on heating and cooling cycles on the same sample. The values obtained on separate samples of the same compounds were reproducible

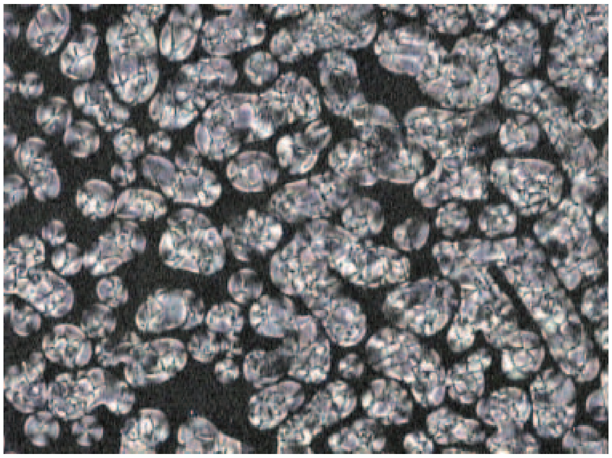


Figure 2. Droplet texture of trimer **34** formed by slow cooling (1°C min^{-1}) from the isotropic liquid (black) to the onset of the chiral nematic phase (bright droplets) at ~157°C.

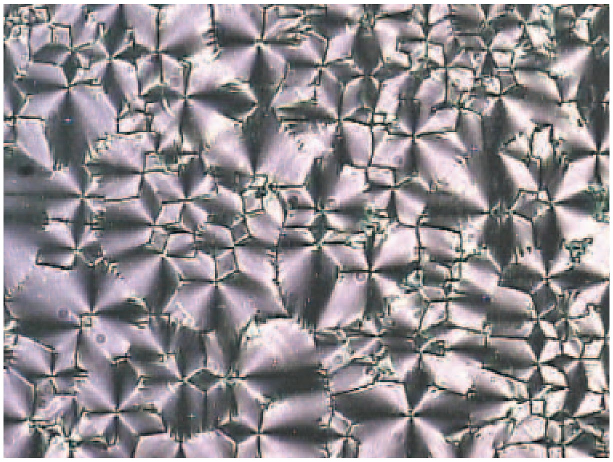


Figure 3. The pseudo focal-conic texture of the chiral nematic phase of trimer **34** formed upon cooling (1°C min^{-1}) at 120°C.

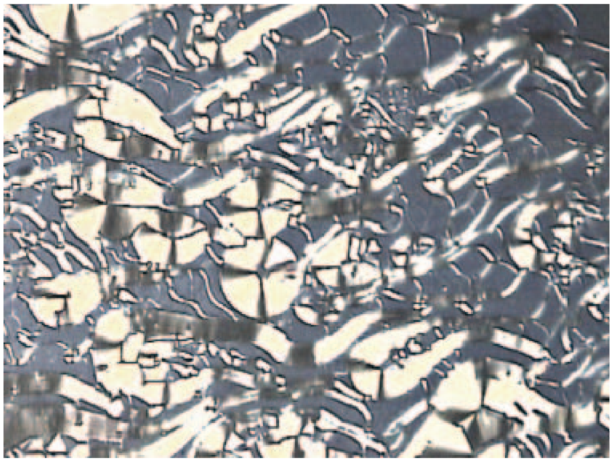


Figure 4. The pseudo focal-conic fan and Grandjean texture of the N* phase of trimer **34** formed after shearing the pseudo focal-conic texture shown in Figure 3.

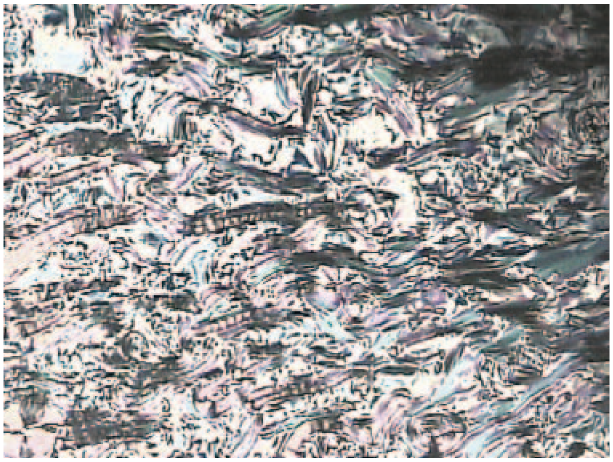


Figure 5. The finger-print texture of the chiral nematic phase of trimer **34** formed in separate regions to the pseudo focal-conic fan texture seen in Figure 3.

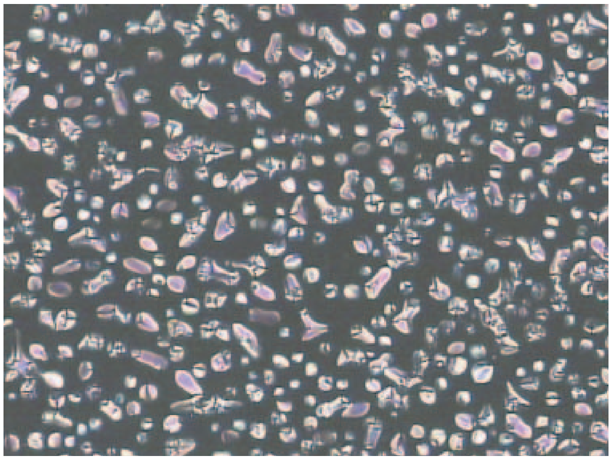


Figure 6. Droplet texture of trimer **24** formed by slow cooling (1°C min^{-1}) from the isotropic liquid (black) to the onset of the chiral nematic phase (bright droplets) at ~161°C.

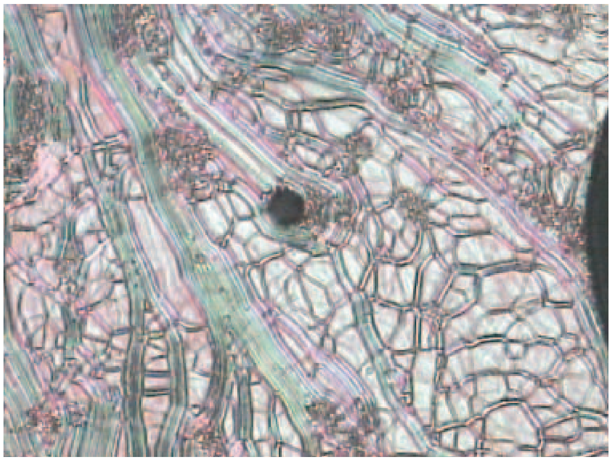


Figure 7. The Grandjean texture of the chiral nematic phase of trimer **24** formed upon cooling (1°C min^{-1}) at 144°C.

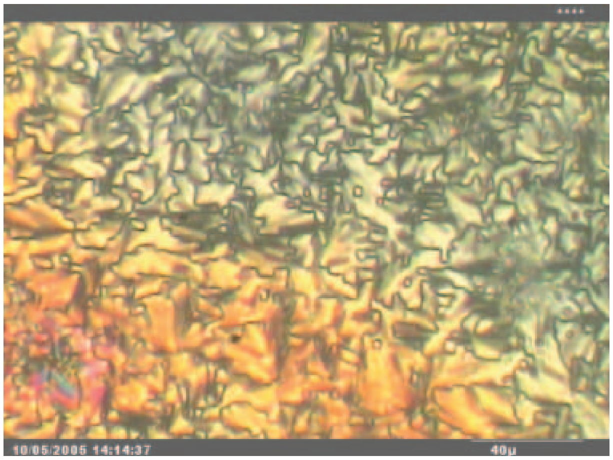


Figure 8. The Schlieren texture of the SmC* phase of trimer **24** formed upon cooling (1°C min^{-1}) at 132°C.

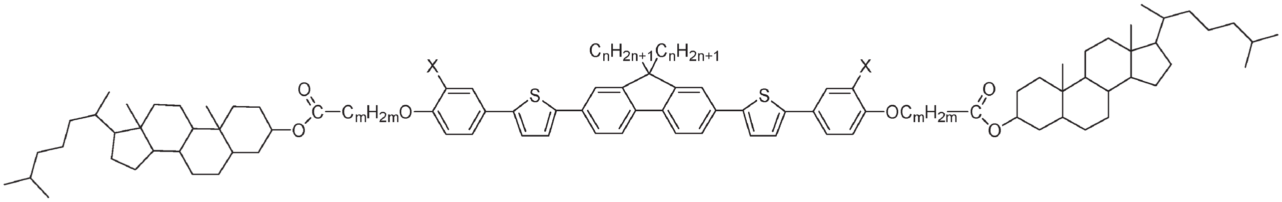
and usually very little thermal degradation was observed even at relatively high temperatures. The base line of the spectra is relatively flat and sharp transition peaks are observed.

3. Results and discussion

Mesomorphic properties

The trimers (**22**, **23**, **25** and **34**) with an odd number of methylene units in the spacers between the mesomorphic groups only exhibit an enantiotropic N* phase and no smectic phases. The melting and clearing points of trimers **22**–**24** (n=3; m=5, 7 and 10) decrease with increasing length of the spacer groups. The reduction in the liquid crystalline transition temperatures is due to dilution of the aromatic cores by an increasing concentration of flexible aliphatic chains with low melting points. Odd–even effects are also a contributory factor (*47*). The melting and clearing points of trimer **25** (n=8; m=7) with two

Table 1. The liquid crystalline transition temperatures (°C) of the trimers (**22**–**25** and **34**) of the general structure shown below.



Compound	n	m	X	T_g		Cr		SmC*		N*		I
22	3	5	H		–	•	211		–	•	225	•
23	3	7	H			•	190		–	•	201	•
24	3	10	H	•	60	•	65	•	136	•	161	•
25	8	7	H	•	44	•	85		–	•	146	•
34	3	5	CH_3	•	60	•	124		–	•	160	•

octyl chains in the 9-position on the fluorene moiety are significantly lower (by 105°C and 55°C, respectively) than those of the corresponding trimer (**23**; n=3; m=7) with two propyl chains in the same position. This is due to steric effects attributable to the longer chains, which increase the intermolecular distance and thereby reduce the intermolecular forces of attraction. The liquid crystalline transition temperatures of the trimer **34** (n=3; m=5; X=CH_3) with two methyl substituents in lateral positions on the fluorene moiety are also significantly lower (by 87°C and 65°C, respectively) than the melting and clearing points of the corresponding trimer (**22**; n=3; m=5; X=H) with two hydrogen atoms in the same position. This behaviour is also caused by steric effects attributable to the presence of large substituents in a lateral position in the aromatic molecular core, which increase the intermolecular distance and thereby reduce the intermolecular forces of attraction (*14*).

Trimer **24** exhibits both a SmC* phase, which is unusual for trimeric liquid crystals, and a N* phase. This mesomorphic behaviour is confirmed by optical microscopy, DSC and XRD. A fairly sharp glass transition at approximately 50°C on the second heating in the DSC trace of trimer **24** is indicative of the chemical purity of the sample and the monodispersity of its molecular weight. A small enthalpic peak is observed at 65°C, which is due to melting of the solid to form a SmC* mesophase. At room temperature trimer **24** exists as a glassy smectic liquid crystal and no crystallisation is observed on the cooling and heating scans. A larger enthalpy peak is observed at 136°C at the SmC*–N* transition with a high clearing point (N*–I=161°C). XRD studies of trimer **24** confirm the presence of the tilted layer structure of a SmC* phase (see Figure 9). The sharp peak observed when the scattering wavevector **Q** is 2.9 nm^{-1} signifies a highly ordered system, which is typical of the layered structure of the SmC phase (see Figure 9). As shown in Figure 1, the even–even conformation of the molecular structure results in a parallel orientation of the long molecular axes of the three mesogenic units. Therefore, if the terminal mesogenic units are flat and have a long length-to-breadth ratio, as is the case with the cholestanyl (dihydrocholesteryl) groups, then the terminal aliphatic cores may stack on top of each other in a kind of well-ordered microphase separation (*47*). Also, the presence of a large number of methylene groups in the flexible spacer between the aromatic core and the cholestanyl group decouple the influence of the aromatic core from the terminal groups and therefore the behaviour of the stacking becomes less influenced by the aromatic core and more so by the large and bulky cholestanyl groups. Therefore, the presence of two aliphatic and optically-active cholestanyl groups connected by long even aliphatic spacers to the mesomorphic aromatic core of the trimer (**24**) leads to the formation of a SmC* phase and a relatively high glass transition temperature. The chiral nematic clearing point of trimer **24** (n=3; m=10) with an even–even spacer configuration is lower than those of the corresponding trimers (**22**; n=3; m=5) and (**23**; n=3; m=7) with an odd–odd spacer configuration. This is also consistent with previous observations (*47*).

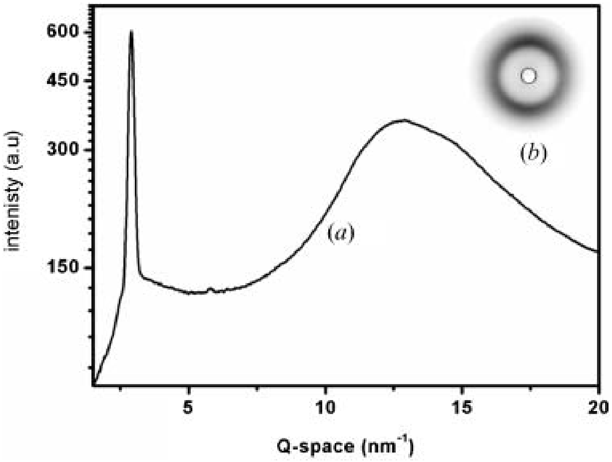


Figure 9. Integrated intensity of the X-ray diffraction pattern of trimer **24** in the SmC* phase as a function of the scattering wavevector, **Q**.

Physical properties

The UV/visible absorbance and photoluminescence (PL) spectra of trimer **34** in solution are shown in Figure 10. Trimer **34** absorbs in the ultraviolet and emits blue-green light in photoluminescence. This is consistent with the behaviour of related nematic

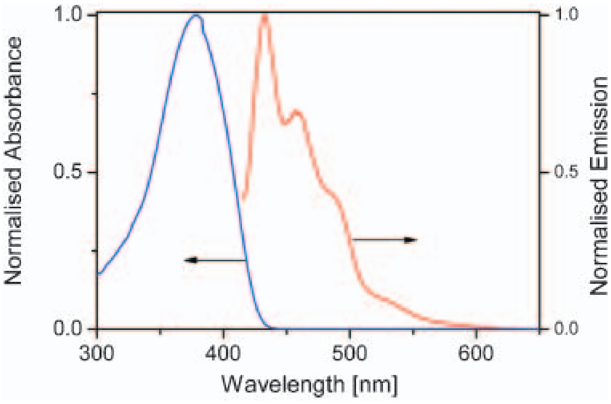


Figure 10. UV/visible absorption spectrum (blue) and PL spectrum (red) of trimer **34** in a toluene solution.

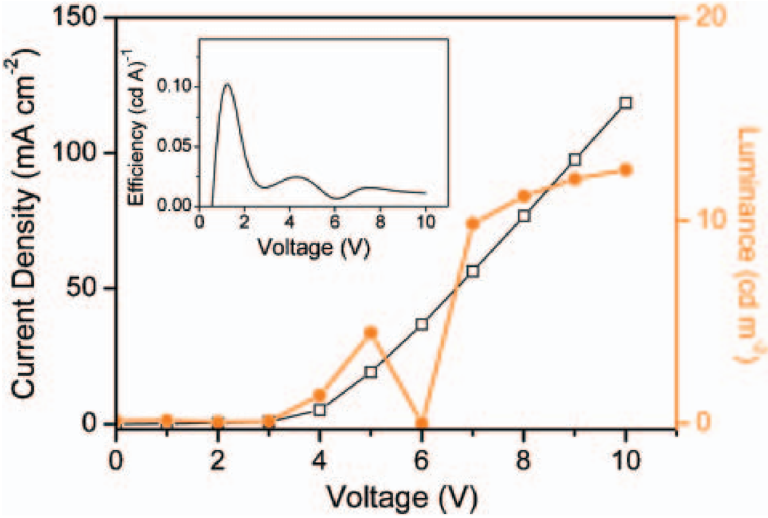


Figure 11. Current–voltage (◆) and luminance–voltage (●) characteristics of the OLED incorporating trimer **34** as the emission layer. The inset shows the efficacy as a function of voltage.

liquid crystals with the same aromatic core with two straight or branched alkoxy chains attached to it instead of the cholestanyl groups (*1, 28*).

As expected, an OLED incorporating trimer **34** as the emission layer also exhibits blue-green electroluminescence, as shown in Figure 11. The CIE (1931) coordinates are x=0.228, y=0.248 at 10 V. Unfortunately, the luminescence efficiency (0.027 cd A^{-1} at 4.5 V), the current density (120 mA cm^2 at 10 V) and the brightness (12.5 cd m^{-2} at 10 V) are low, as also shown in Figure 11. These values are consistent with the low hole carrier mobility ($\mu_h = 1.75 \times 10^{-6}\,cm^2\,s^{-1}\,V^{-1}$) of the SmC* phase at room temperature of the closely related trimer (**24**) with an almost identical structure determined by standard TOF measurements (*11, 21*). The charge transport of the nematic phase of similar liquid crystals with the same aromatic molecular core, but much shorter aliphatic chains, can be several orders of magnitude greater ($\mu_h \sim 1.75 \times 10^{-3}\,cm^2\,s^{-1}\,V^{-1}$) (*21, 28*). The charge carrier mobility should be greater in a smectic phase than that in the nematic phase of a similar material (*8*). Therefore, the very large aliphatic cholestanyl components of the trimer clearly reduce the mean free path of charges flowing through the smectic phase of trimer **24**. Although the performance of OLEDs incorporating trimer **34** is poor, and not good enough for the generation of electrically-pumped emission of circularly polarised light, it is comparable with that of the first OLEDs made incorporating liquid crystalline glasses with this luminescent core (*1*) and serves to demonstrate proof of principle for electroluminescence from segmented liquid crystalline trimers. Subsequent work improved the performance of such OLEDs by orders of magnitude (*2*).

4. Conclusions

The combination of a large aromatic core connected by flexible aliphatic spacers to cholestanyl (dihydrocholesteryl) groups in segmented liquid crystalline trimers leads to the induction of a high glass transition temperature and the formation of the optically-active chiral nematic and smectic C phases. Electroluminescence from a segmented liquid crystalline trimer is observed for the first time, but the high aliphatic content of the trimers leads to a low charge carrier mobility and poor performance in OLEDs.

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References

(1) Contoret A.E.A.; Farrar S.R.; Jackson P.O.; May L.; O'Neill M.; Nicholls J.E.; Richards G.J.; Kelly S.M. *Adv. Mater.* **2000**, *12*, 971–974.
(2) Contoret A.E.A.; Aldred M.P.; Vlachos P.; Farrar S.R.; Tsoi W.C.; O'Neill M.; Kelly S.M. *Adv. Mater.* **2005**, *17*, 1368–1372.
(3) Redecker M.; Bradley D.D.C.; Inbasekaran M.; Woo E.P. *Appl. Phys. Lett.* **1998**, *74*, 1400.
(4) Sirringhaus H.; Wilson R.J.; Friend R.H.; Inbasekaran M.; Wu W.; Woo E.P.; Grell M.; Bradley D.D.C. *Appl. Phys. Lett.* **2005**, *77*, 406–408.

(5) Carrasco-Orozco M.; Tsoi W.C.; O'Neill M.; Aldred M.P.; Vlachos P.; Kelly S.M. *Adv. Mater.* **2006**, *18*, 1754–1758.

(6) Tsoi W.C.; O'Neill M.; Aldred M.P.; Kitney S.P.; Hegde M.; Vlachos P.; Kelly S.M. *Chem. Mater.* **2007**, *19*, 5475–5484.

(7) O'Neill M.; Kelly S.M. *Adv. Mater.* **2003**, *15*, 1135–1146.

(8) Funahashi M.; Hanna J.-I. *Appl. Phys. Lett.* **1998**, *73*, 3733–3735; Funahashi, M.; Hanna, J.-I. *Mol. Cryst. liq. Cryst*. **1999**, *331*, 509–516; Maeda, H.; Funahashi, M.; Hanna, J.-I. *Mol. Cryst. liq. Cryst*. **2001**, *366*, 369–376.

(9) Méry S.; Haristoy D.; Nicoud J.-F.; Guillon D.; Diele S.; Monobe H.; Shimizu Y. *J. Mater. Chem.* **2002**, *12*, 37–41.

(10) Strohriegel P.; Hanft D.; Jandke M.; Pfeuffer T. *Mater. Res. Soc. Symp. Proc.* **2002**, *709*, 31–42.

(11) Farrar S.R.; Contoret A.E.A.; O'Neill M.; Nicholls J.E.; Richards G.J.; Kelly S.M. *Phys. Rev. B*. **2002**, *66*, 125107–1–5.

(12) Contoret A.E.A.; Farrar S.R.; O'Neill M.; Nicholls J.E.; Richards G.J.; Kelly S.M.; Hall A.W. *Chem. Mater.* **2002**, *14*, 1477–1487.

(13) Vlachos P.; Kelly S.M.; Mansoor B.; O'Neill M. *Chem. Commun.* **2002**, 874–875.

(14) Aldred M.P.; Eastwood A.J.; Kelly S.M.; Vlachos P.; Contoret A.E.A.; Farrar S.R.; Mansoor B.; O'Neill M.; Tsoi W.C. *Chem. Mater.* **2004**, *16*, 4928–4936.

(15) Aldred M.P.; Vlachos P.; Dong D.; Kitney S.P.; Tsoi W.C.; O'Neill M.; Kelly S.M. *Liq. Cryst.* **2005**, *32*, 951–965.

(16) Woon K.L.; O'Neill M.; Vlachos P.; Aldred M.P.; Kelly S.M. *Liq. Cryst.* **2005**, *32*, 1191–1194.

(17) Aldred M.P.; Eastwood A.J.; Kitney S.P.; Richards G.J.; Vlachos P.; Kelly S.M.; O'Neill M. *Liq. Cryst.* **2005**, *32*, 1251–1264.

(18) Vlachos P.; Mansoor B.; Aldred M.P.; O'Neill M.; Kelly S.M. *Chem. Commun.* **2005**, 2921–2923.

(19) Aldred M.P.; Contoret A.E.A.; Devine P.; Farrar S.R.; Hudson R.; Kelly S.M.; Koch G.C.; O'Neill M.; Tsoi W.C.; Woon K.L., et al. *Mater. Res. Soc. Symp. Proc.* **2005**, *871E*, I10.7.1–5.

(20) Woon K.L.; Contoret A.E.A.; Farrar S.R.; Liedtke A.; O'Neill M.; Vlachos P.; Aldred M.P.; Kelly S.M. *J. SID* **2006**, *14*, 1–7.

(21) Woon K.L.; Aldred M.P.; Vlachos P.; Mehl G.H.; Stirner T.; Kelly S.M.; O'Neill M. *Chem. Mater.* **2006**, *18*, 2311–2317.

(22) Tsutsui T.; Lin C.P.; Saito S.; Chen S.H.; Shi H.; Mastrangelo J.C. *Mater. Res. Soc. Symp. Proc.* **1996**, *425*, 225–231.

(23) Jandke M.; Hanft D.; Strohriegel P.; Whitehead K.; Grell M.; Bradley D.D.C. *Proc. SPIE* **2001**, *4105*, 338–347.

(24) Culligan S.W.; Geng Y.H.; Chen S.H.; Klubeck K.; Vaeth K.M.; Tang C.W. *Adv. Mater.* **2003**, *15*, 1176–1180.

(25) Geng Y.H.; Culligan S.W.; Trajkovska A.; Wallace J.U.; Chen S.H. *Chem. Mater.* **2003**, *15*, 542–549.

(26) Kopp V.I.; Fan B.; Vithana H.K.M.; Genack A.Z. *Opt. Lett.* **1998**, *21*, 1707–1709.

(27) Chen S.H.; Katsis D.; Schmid A.W.; Mastrangelo J.C.; Tsutsui T.; Blanton T.N. *Nature* **1999**, *397*, 506–508.

(28) Woon K.L.; O'Neill M.; Richards G.J.; Aldred M.P.; Kelly S.M.; Fox A.M. *Adv. Mater.* **2003**, *15*, 1555–1558.

(29) Vorländer D. *Z. phys. Chem.* **1927**, *126*, 449.

(30) Rault J.; Liebert L.; Strzelecki L. *Bull. Soc. Chim. Fr.* **1975**, 1175–1178.

(31) Hogan J.L.; Imrie C.T.; Luckhurst G.R. *Mol. Cryst. liq. Cryst.* **1988**, *3*, 645–650.

(32) Imrie C.T. *Liq. Cryst.* **1989**, *6*, 391–396.

(33) Imrie C.T.; Luckhurst G.R. In *Handbook of Liquid Crystals,* Vol. 2B; Demus D., Goodby J.W., Gray G.W., Spiess H.-W., Vill V. (Eds), Chaper 10, Wiley-VCH: Weinheim, 1998.

(34) Imrie C.T. *Struct. Bonding* **1999**, *95*, 149–192.

(35) Imrie C.T.; Henderson P.A. *Curr. Opinion Colloid Interface Sci.* **2002**, *7*, 298–311.

(36) Ennulat R.D.; Brown A.J. *Mol. Cryst. liq. Cryst.* **1971**, *12*, 367–378.

(37) Elser W.; Pohlmann J.L.W.; Boyd P.R. *Mol. Cryst. liq. Cryst.* **1971**, *15*, 175–182.

(38) Pohlmann J.L.W.; Elser W.; Boyd P.R. *Mol. Cryst. liq. Cryst.* **1973**, *20*, 87–97.

(39) Sisido M.; Takeuchi K.; Imanishi Y. *J. phys. Chem.* **1984**, *88*, 2893–2898.

(40) Koden M.; Miyake S.; Takenaka S.; Kusabayashi S. *J. phys. Chem.* **1984**, *88*, 2387–2390.

(41) Yelamaggad C.V.; Srikrishna A.; Shankar Rao D.S.; Prassad S.K. *Liq. Cryst.* **1999**, *26*, 1547–1554.

(42) Yelamaggad C.V.; Nagamani S.A.; Hiremath U.S.; Nair G.G. *Liq. Cryst.* **2001**, *28*, 1009–1015.

(43) Yelamaggad C.V.; Mathews M.; Fujita T.; Iyi N. *Liq. Cryst.* **2003**, *30*, 1079–1087.

(44) Cha S.W.; Jin J.-I.; Laguerre M.; Acard M.F.; Hardoiun F. *Liq. Cryst.* **1999**, *26*, 1325–1337.

(45) Cha S.W.; Jin J.-I.; Acard M.F.; Hardoiun F. *Liq. Cryst.* **2002**, *29*, 755–763.

(46) Marcelis A.T.M.; Koudijs A.; Karczemarzyk Z.; Sudhölter E.J.R. *Liq. Cryst.* **2003**, *30*, 1357–1364; Marcelis, A.T.M.; Koudijs, A.; Sudhölter, E.J.R. *Liq. Cryst*. **2000**, *27*, 1515–1523.

(47) Marcelis A.T.M.; Koudijs A.; Sudhölter E.J.R. *Liq. Cryst.* **1995**, *18*, 851–855.

(48) Mallia V.A.; Tamaoki N. *Chem. Mater.* **2003**, *15*, 3237–3239; Mallia, V.A.; Tamaoki, N. *Chem. Soc. Rev*. **2004**, *33*, 76–84.

(49) Tamaoki N.; Aoki Y.; Moriyama M.; Kidowaki M. *Chem. Mater.* **2003**, *15*, 719–726.

(50) Wu C. *Mater. Lett.* **2007**, *61*, 1380–1383.

(51) Sentman A.C.; Gin D.L. *Adv. Mater.* **2001**, *13*, 1398–1401.

(52) Musgrave B.; Lehman P.; Coles H.J. *Liq. Cryst.* **1999**, *28*, 1235–1249.

(53) Pfeuffer T.; Hanft D.; Strohriegl P. *Liq. Cryst.* **2002**, *29*, 1555–1564.

(54) Ribera D.; Mantecon A.; Serra A. *Macromol. Chem. Phys.* **2001**, *202*, 1658–1671.

(55) Hölter D.; Frey H.; Mülhaupt R.; Klee J.E. *Adv. Mater.* **1988**, *10*, 864–868; Hölter, D.; Frey, H.; Mülhaupt, R.; Klee, J.E. *Macromolecules* **1996**, *29*, 7003–7011.

(56) deMello J.C.; Friend R.H. *Adv. Mater.* **1997**, *9*, 230–222.

(57) Williamson W. *Justus Liebigs Ann. Chem.* **1851**, *77*, 37.

(58) Suzuki A. *Pure appl. Chem.* **1994**, *66*, 213–222; Suzuki, A. *J. organometallic Chem*. **1999**, *576*, 147–168.

(59) Ranger M.; Rondeau D.; Leclerc M. *Macromolecules* **1997**, *30*, 7686–7691.
(60) Stille J.K. *Angew. Chem. Int. Ed.* **1986**, *25*, 504–519.
(61) Kellog R.M.; Schlapp A.P.; Harper E.T.; Wynberg H. *J. org. Chem.* **1968**, *33*, 2902–2909.
(62) McOmie J.F.; Watts M.L.; West D.E. *Tetrahedron* **1968**, *24*, 2289–2292.
(63) Miyaura N.; Suzuki A. *J. Chem. Soc., Chem. Commun.* **1979**, 866–867.
(64) Kelley C.J.; Ghiorgis A.; Kauffman M. *J. Chem. Res. (S)* **1997**, 446–447.