

U.S. PATENT DOCUMENTS

5,929,194	A *	7/1999	Woo et al.	528/229
5,998,045	A *	12/1999	Chen et al.	428/690
6,001,277	A *	12/1999	Ichimura et al.	252/299.4
RE36,625	E *	3/2000	Herr et al.	526/245
6,201,087	B1 *	3/2001	Herr et al.	526/268
6,218,061	B1 *	4/2001	Hanna et al.	430/58.05
6,309,901	B1 *	10/2001	Tahon et al.	438/29
6,406,825	B1 *	6/2002	Sakimura et al.	430/67
6,559,256	B1 *	5/2003	Holmes et al.	526/260
6,649,230	B1 *	11/2003	Seiberle et al.	428/1.2
6,649,283	B1 *	11/2003	Lupo et al.	428/690
6,670,213	B1 *	12/2003	Halls et al.	438/52
6,830,831	B1 *	12/2004	O'Neill et al.	428/690
6,939,587	B1 *	9/2005	Kumar et al.	427/510

OTHER PUBLICATIONS

Whitehead et al., Highly polarized blue electroluminescence from homogeneously aligned films of poly(9,9-dioctylfluorene), May 15, 2000, Applied Physics Letters, vol. 76, No. 20, pp. 2946-2948.*

Meisel et al., "Influence of the dopant concentration on the morphology of hole-transporting alignment layers based on a polyimide matrix", 2002, Polymer, vol. 43, pp. 5235-5242.*

JPO website English Machine Translation of JP 11-236391, Aug. 1999, Katsumi et al.*

WO 99/15576, Buchecker et al., Apr. 1, 1999.*

Peregrine Orr Jackson and Mary O'Neill, Warren Lee Duffy, Paul Hindmarsh, Stephen Malcolm Kelly, and Gareth James Owen, "An Investigation of the Role of Cross-Linking and Photodegradation of Side-Chain Coumarin Polymers in the Photoalignment of Liquid Crystals", Journal 2001 American Chemical Society, Published on Web Jan. 30, 2001, Chem. Matter No. 2,2001, vol. 13, 694-703. USA.

Adam E.A. Contorer, Simon R. Farrar, Mary O'Neill and J.Edward Nicholls, Gary James Richards, Stephen Malcolm Kelly, and Gareth James Owen. "The Photopolymerization and Cross-Linking of Electroluminescent Liquid Crystals Containing Methacrylate and Diene Photopolymerizable End Groups for Multilayer Organic Light-Emitting Diodes". Journal 2001 American Chemical Society, Published on Web Mar. 20, 2002. Chem. Matter No. 4,2002, vol. 14, 1477-1487, USA.

* cited by examiner

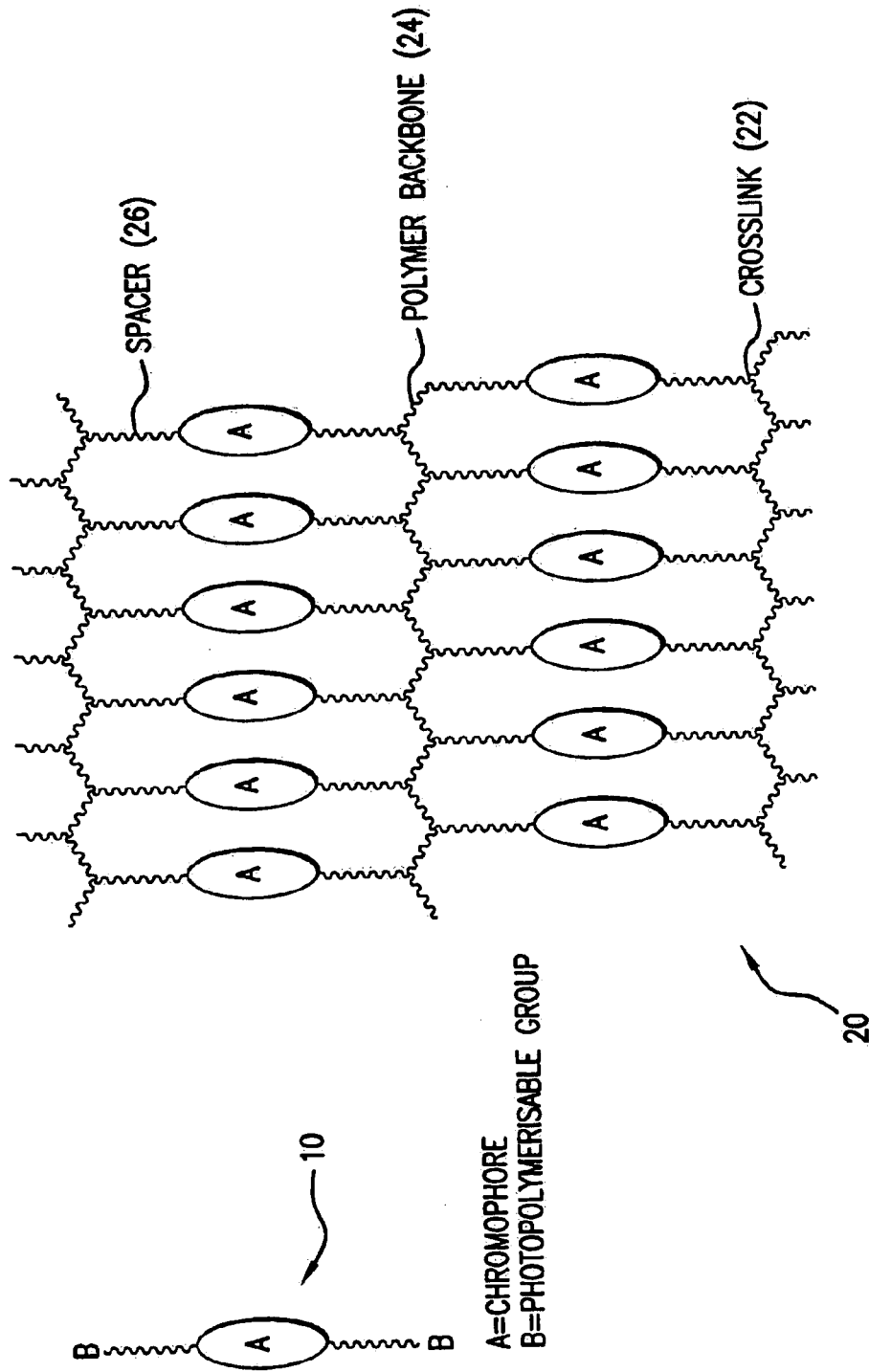


Figure 1

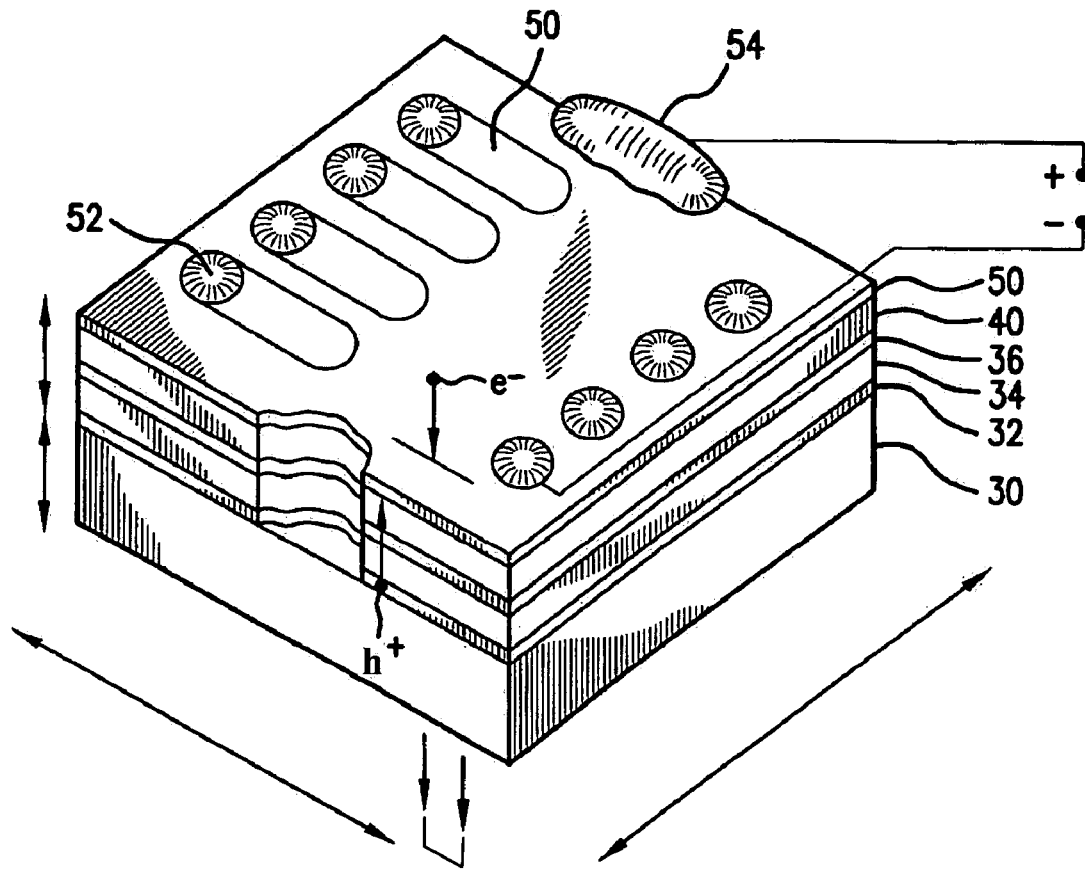


Figure 2

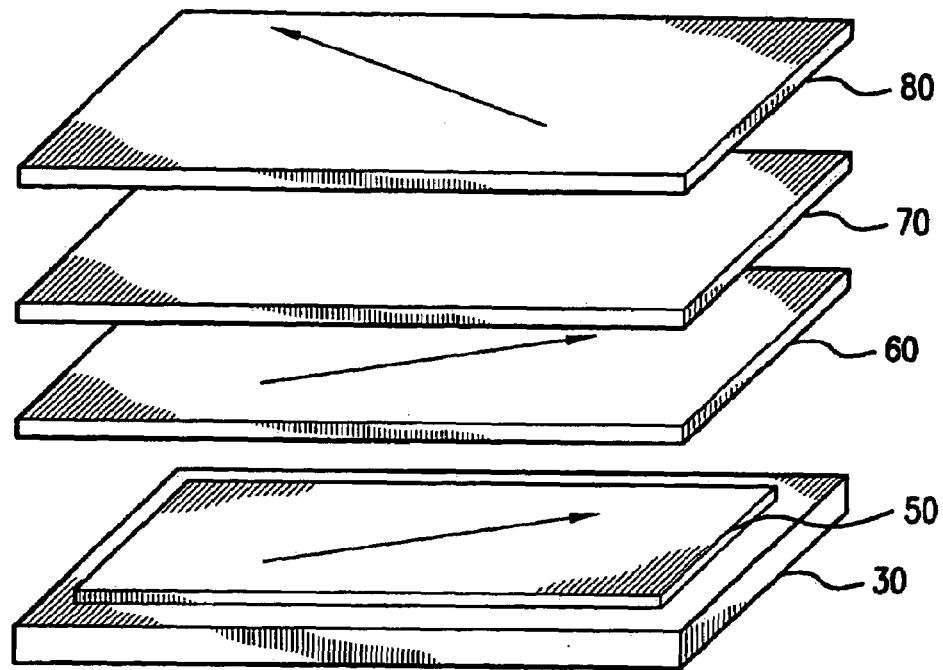


Figure 3

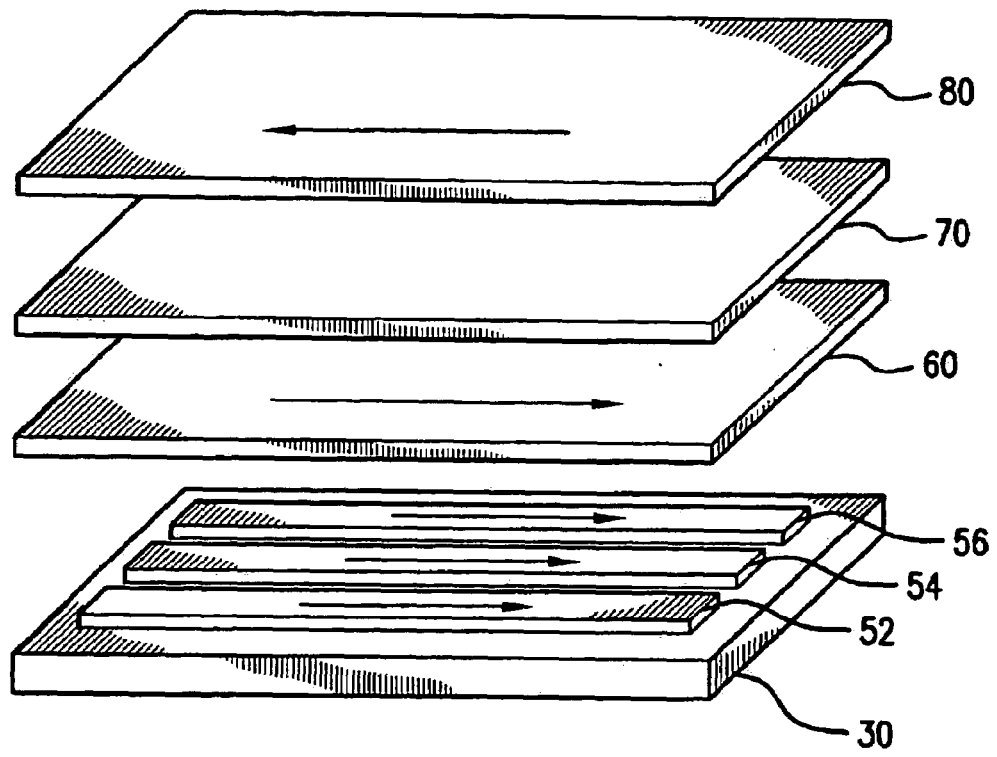


Figure 4

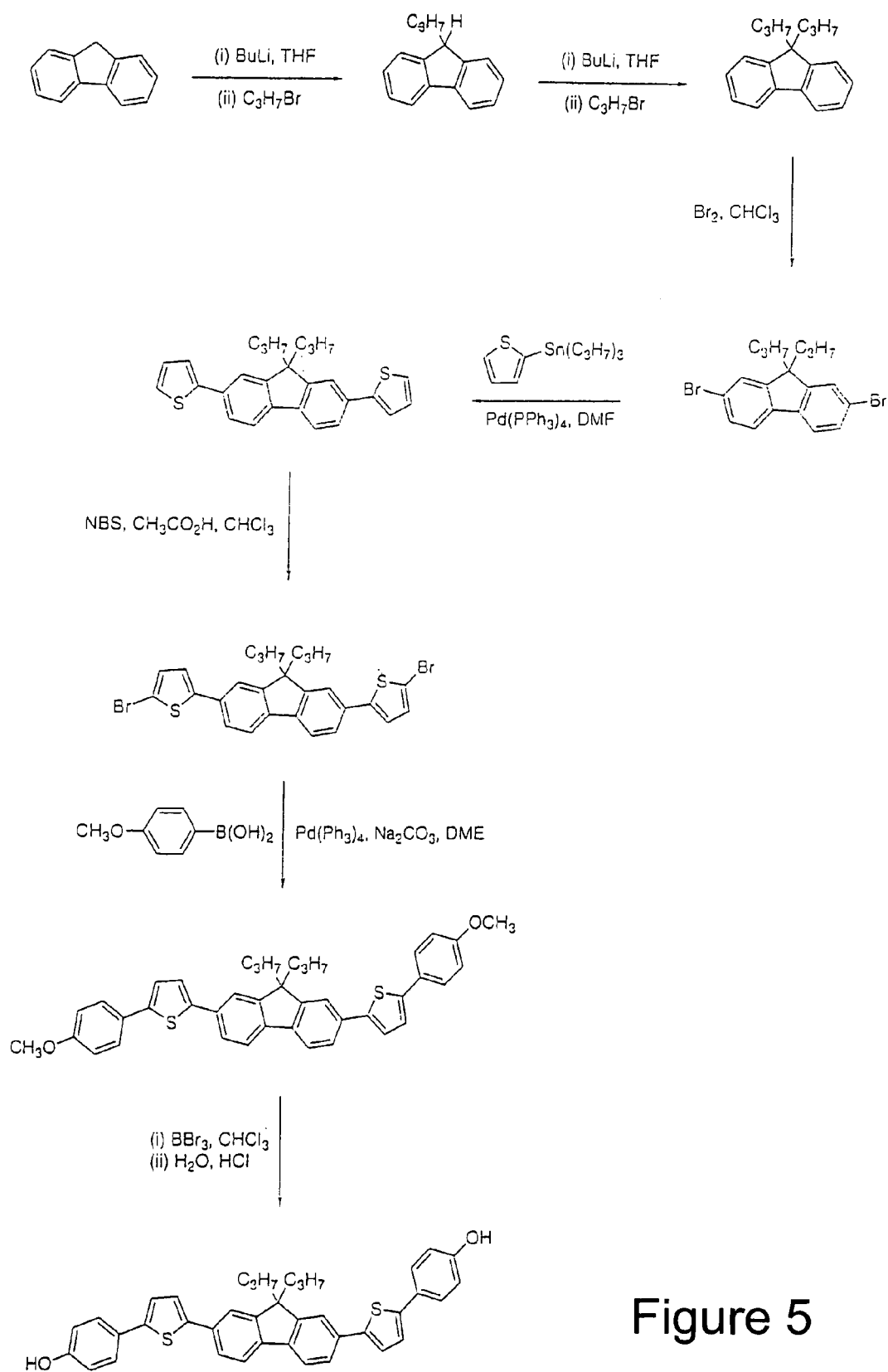


Figure 5

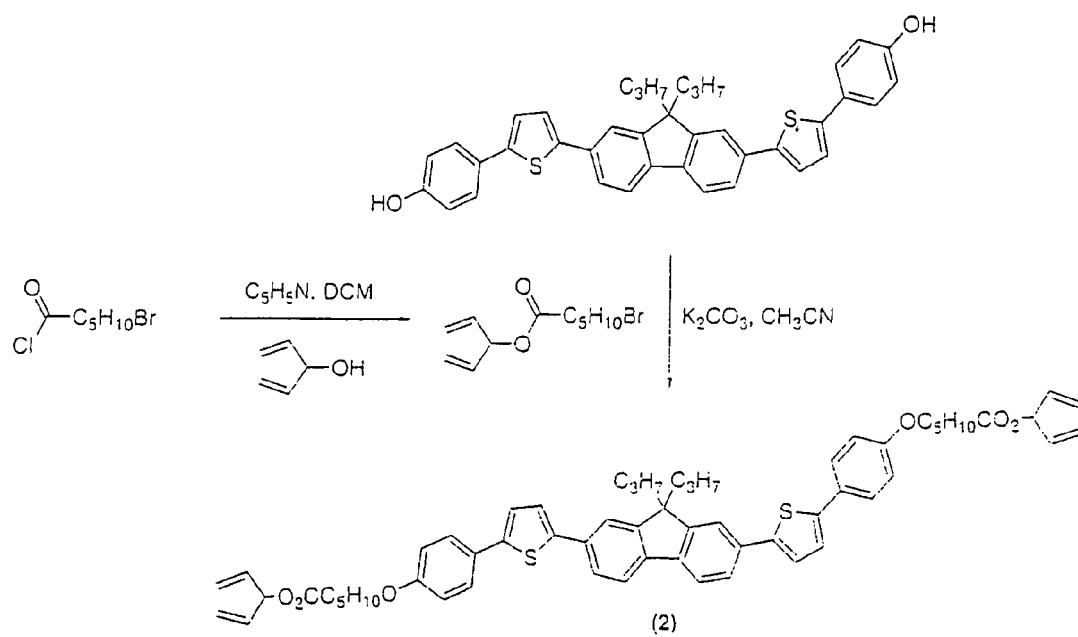


Figure 6

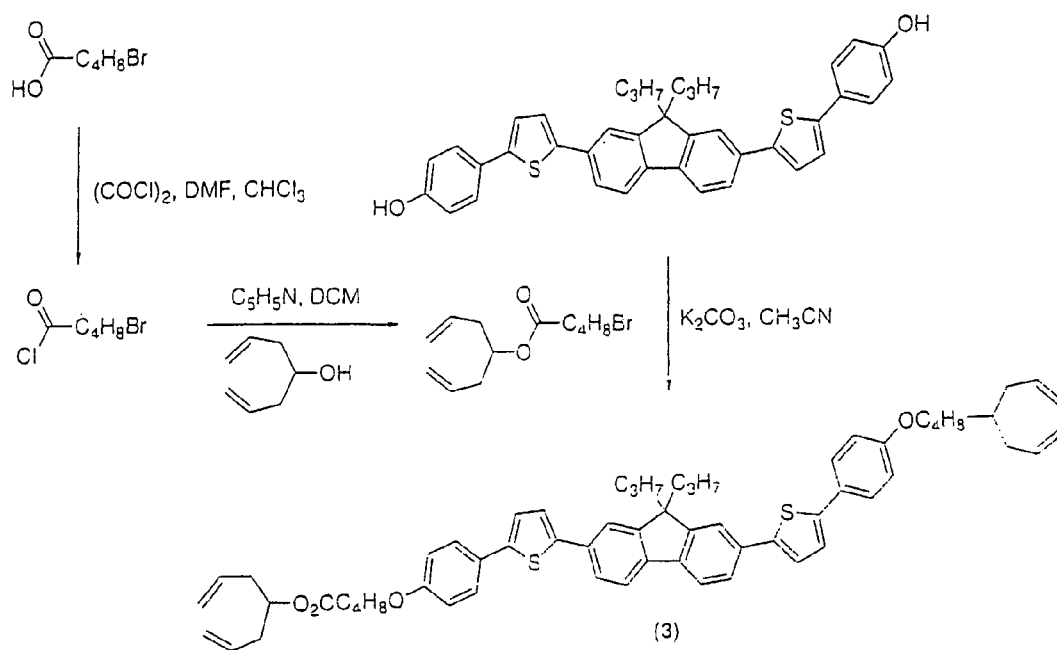


Figure 7

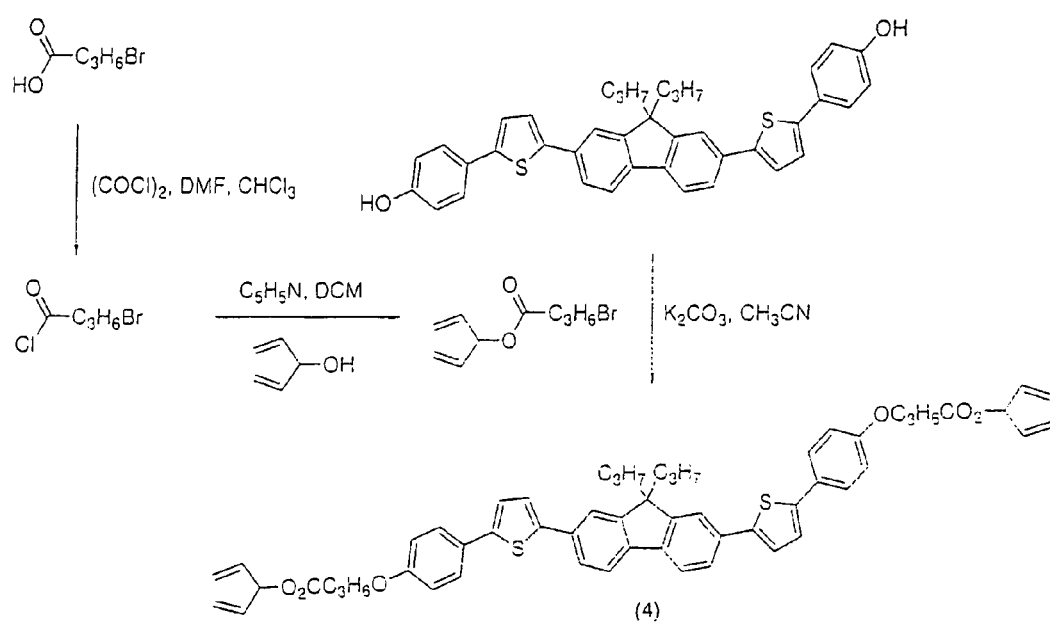


Figure 8

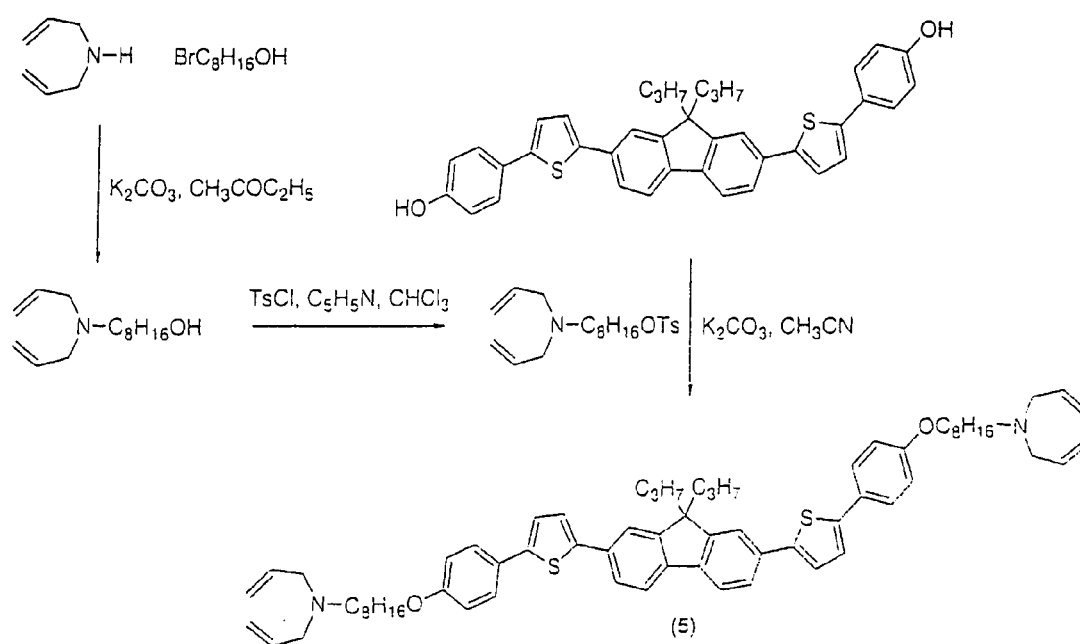


Figure 9

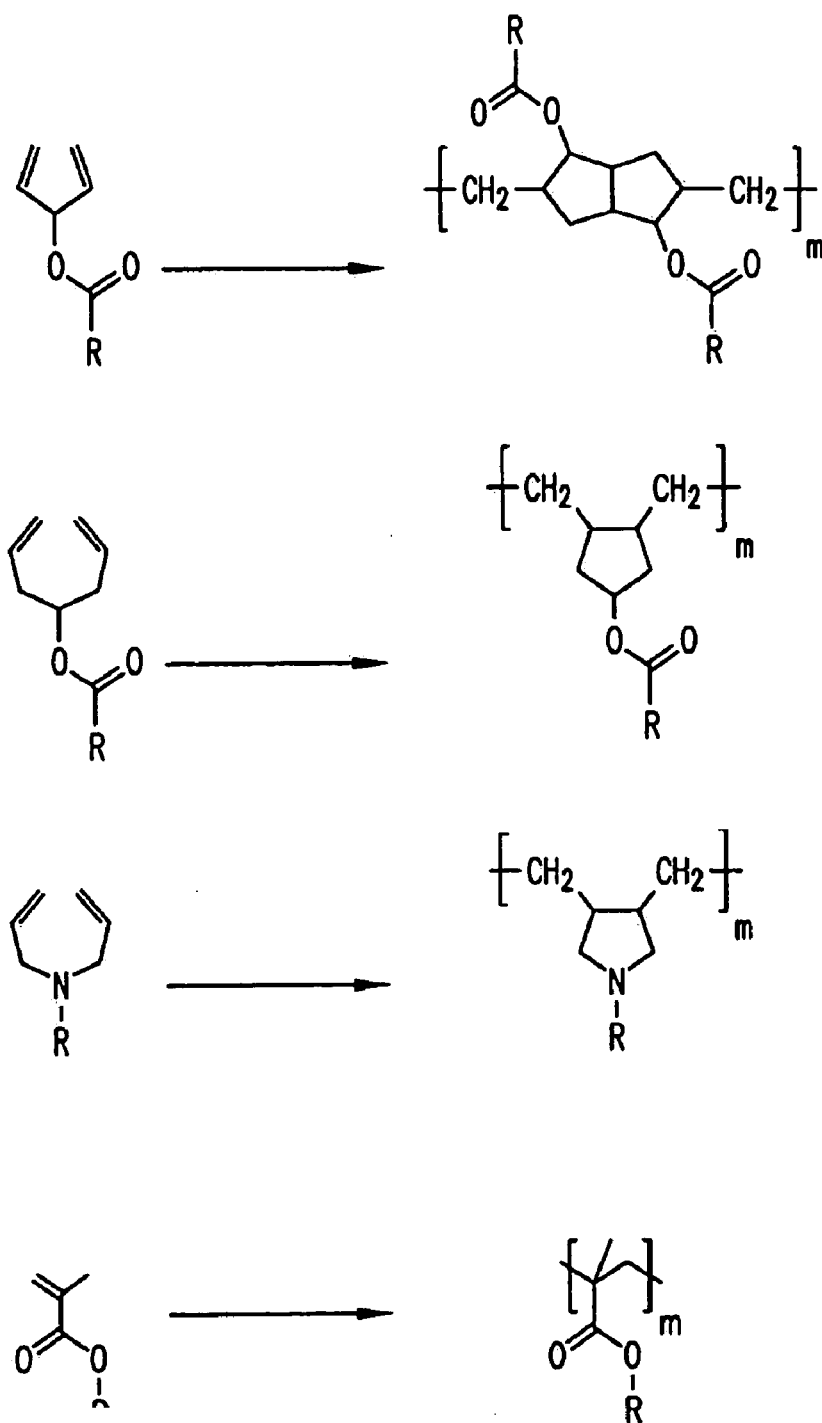
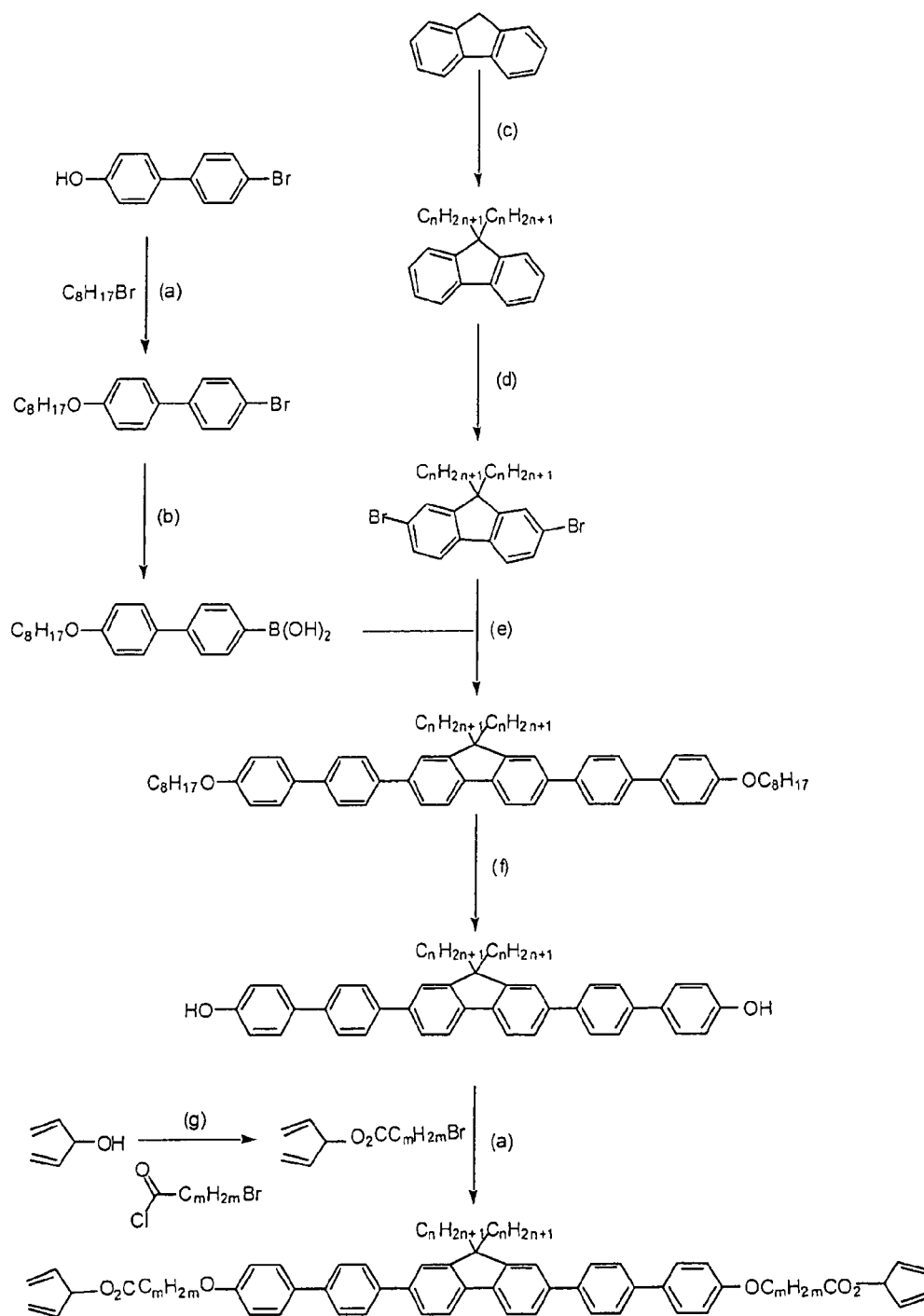
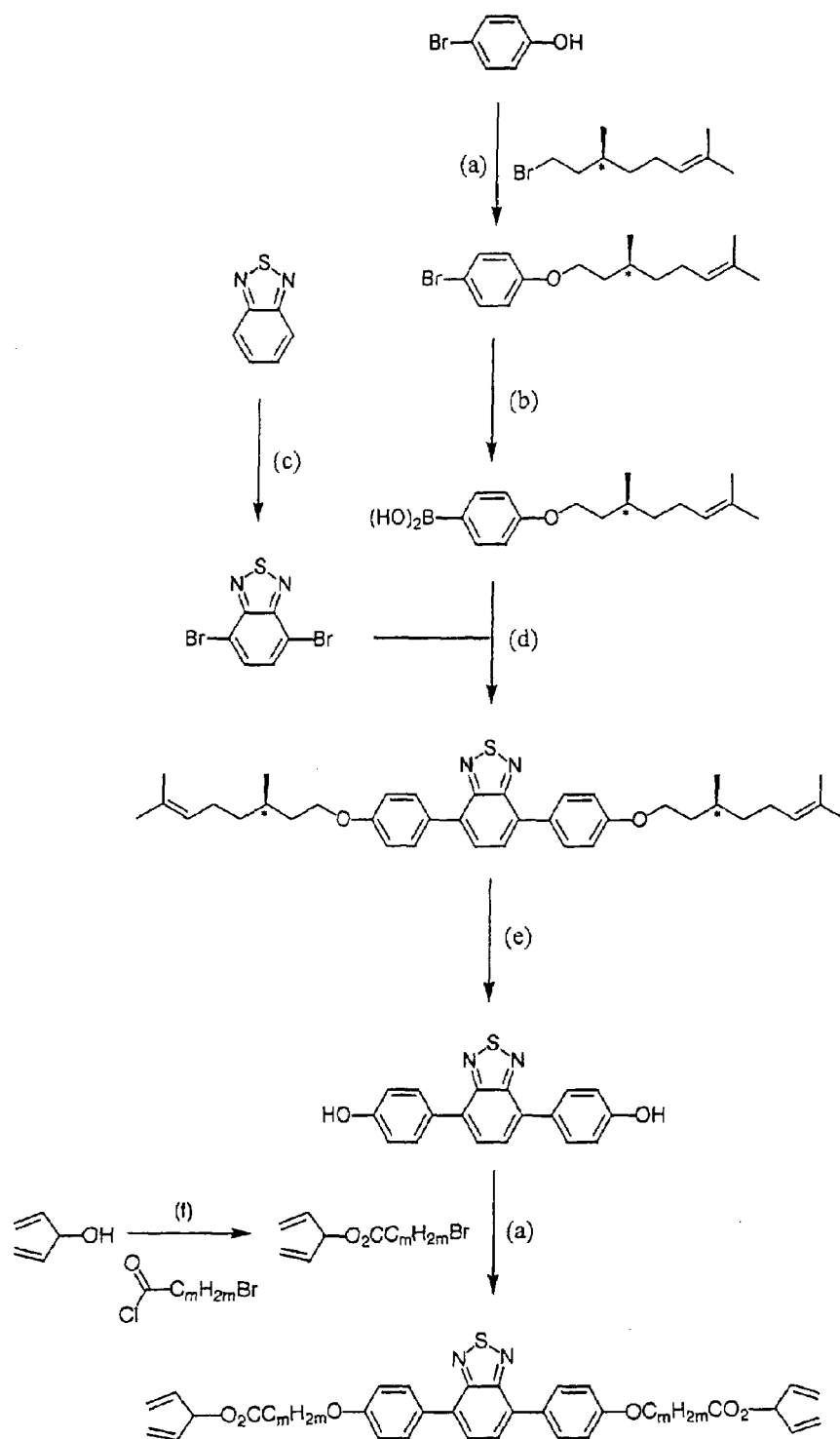


Figure 10



Reagents: (a) K_2CO_3 , $CH_3COOC_2H_5$; (b) (i) $BuLi$, THF (ii) $B(OCH_3)_3$ (iii) HCl_{aq} ; (c) (i) $BuLi$, THF (ii) $C_nH_{2n+1}Br$; (d) Br_2 , $CHCl_3$; (e) $Pd(PPh_3)_4$, Na_2CO_3 , H_2O , DME; (f) (i) BBR_3 , $CHCl_3$ (ii) HCl_{aq} ; (g) pyridine, CH_2Cl_2

Figure 11



Reagents: (a) (a) K_2CO_3 , $CH_3COC_2H_5$; (b) (i) $BuLi$, THF (ii) $B(OCH_3)_3$ (iii) HCl_{aq} ; (c) Br_2 , HBr_{aq} ; (d) $Pd(Ph_3)_4$, Na_2CO_3 , H_2O , DME; (e) (i) BBr_3 , $CHCl_3$ (ii) HCl_{aq} ; (f) pyridine, CH_2Cl_2 .

Figure 12

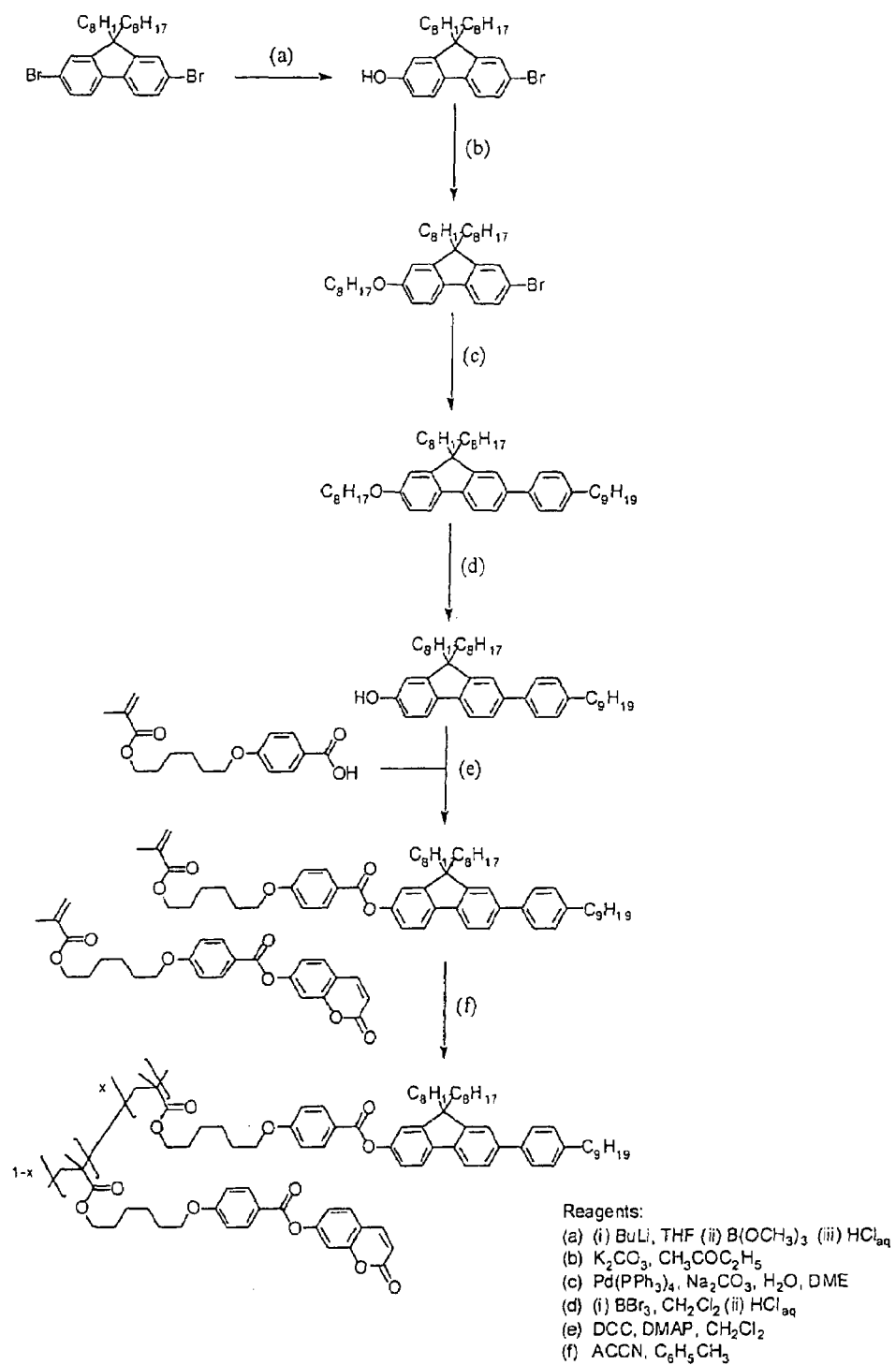
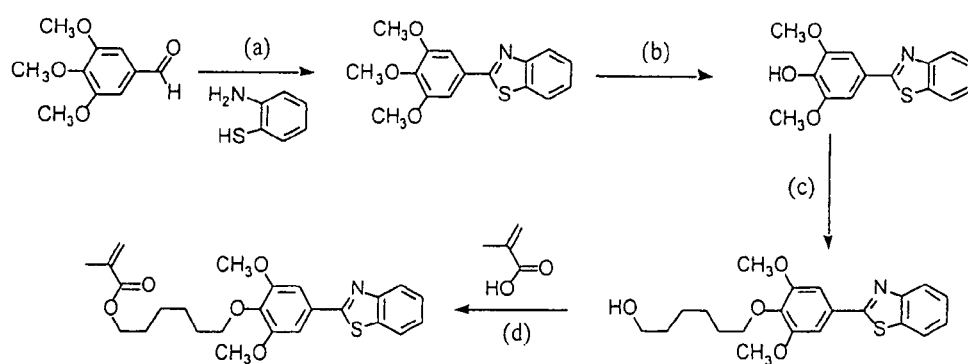


Figure 13



- (a) DMSO
(b) AlCl_3 , CS_2
(b) NaOH , H_2O , KI , CH_3OH
(c) PTS , $\text{C}_6\text{H}_5\text{CH}_3$, hydroquinone

Figure 14

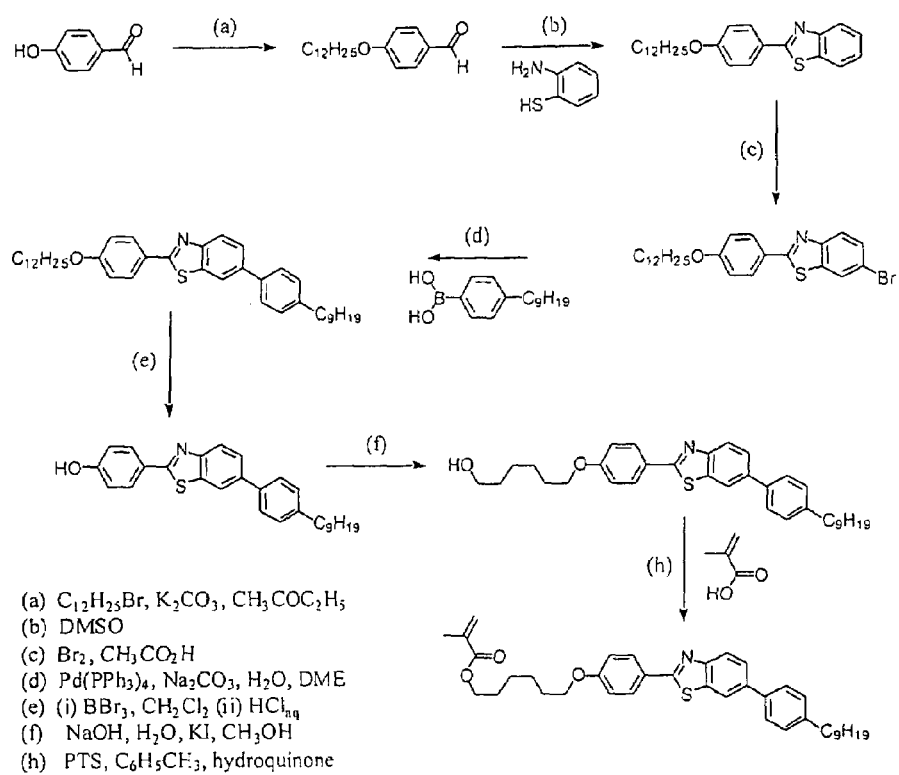


Figure 15

LIQUID CRYSTAL ALIGNMENT LAYER

This application is a continuation-in-part of Ser. No. 09/898,749 filed Jul. 3, 2001 now abandoned and claims priority from GB Application No. 0115987.0 filed Jun. 29, 2001.

BACKGROUND OF THE INVENTION**1. Field of the Invention**

The present invention relates to a liquid crystal alignment layer suitable for use in displays for electronic products and a method of forming the liquid crystal alignment layer and displays.

2. Prior Art

Modern consumer electronics require cheap, high-contrast displays with good power efficiency and low drive voltages. Particular applications include displays for mobile phones and hand-held computers. Liquid crystal displays are often used for this purpose and light emitting polymers displays are also of interest for this purpose.

SUMMARY OF THE INVENTION

Conventional liquid crystal displays (LCD) comprise a liquid crystal alignment layer for aligning the liquid crystal. The alignment layer is typically made of an electrical insulator. Light emitting displays (e.g. made by the in situ polymerization of reactive mesogens) also require alignment such as by the use of aligning materials (e.g. polyimide) which, if as is usual, are insulating can impair the efficiency of the device. The Applicants have now found that a number of benefits may be achieved by enhancing the electrical conductivity of the alignment layer by the inclusion of a transport material therein.

In one aspect, enhancing the electrical conductivity of the alignment layer can reduce adverse residual dc effects in liquid crystal display cells. These arise as a result of poorly balanced dc drive schemes that leave a small charge in the cell, which can induce image sticking e.g. in active matrix-addressed LCDs. The adverse effects are more frequently observed in ferroelectric liquid crystal (FLC) cells where dc imbalance is more likely to occur. The presence of a conducting alignment layer enables residual dc to discharge, thereby reducing the adverse affects.

In another aspect, in FLC cells the switching of the spontaneous polarisation charge produces significant charge within the cell. This charge tends to counter the effect of any electric field applied to align the liquid crystal molecules therein and thereby adversely reduce or eliminate any bistability in the display cell. The presence of a conducting alignment layer tends to reduce this adverse effect.

In a further aspect, where an electroluminescent material is used as the light emitting backlight of the LCD, the electrical conductivity of the alignment layer has been found to enhance the electroluminescence of the material used as the backlight for the LCD.

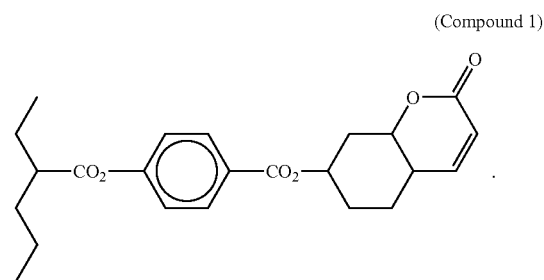
The Applicants have found that including (e.g. by doping) a transport material into the alignment layer produces the desired enhancement in electrical conductivity thereof, but that when used in liquid crystal cells the transport material can tend to migrate into the liquid crystal. This migration reduces the resistivity of the liquid crystal, which then undesirably draws more current. In the case of active matrix addressed displays, the RC time constant of the liquid crystal can also be undesirably reduced. The Applicants have found that these potential negatives can be ameliorated by chemically binding the transport material to the alignment layer.

According to one aspect of the present invention there is provided a liquid crystal alignment layer comprising an alignment layer; and chemically bound to said alignment layer, a transport material.

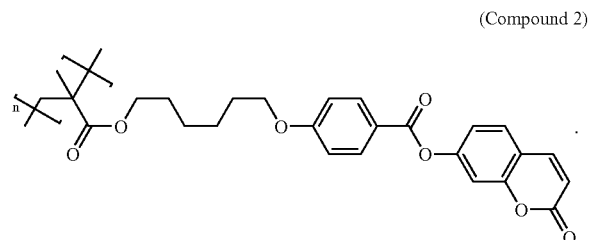
In one aspect, the alignment layer is a photoalignment layer, that is to say an alignment layer comprised of materials that photoalign (e.g. by cross-linking or ablation) to form anisotropic layers when polarised light (e.g. UV) is applied.

Suitable photoalignment layers typically comprises a chromophore attached to a sidechain polymer backbone by a flexible spacer entity. Suitable chromophores include cinnamates or coumarins, including derivatives of 6 or 7-hydroxycoumarins. Suitable flexible spacers comprise organic chains (e.g. unsaturated), including e.g. aliphatic, amine or ether linkages.

A typical sidechain photoalignment polymer containing coumarin as the photoreactive group has the formula:



An exemplary photoalignment layer comprises the 7-hydroxycoumarin compound having the formula:



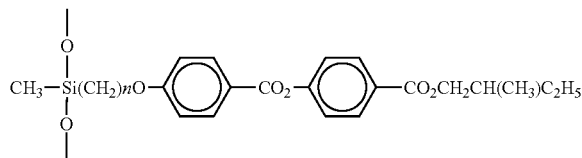
3

Other suitable materials for use in photoalignment layers are described in M. O'Neill and S. M. Kelly, *J. Phys. D. Appl. Phys.* [2000], 33, R67.

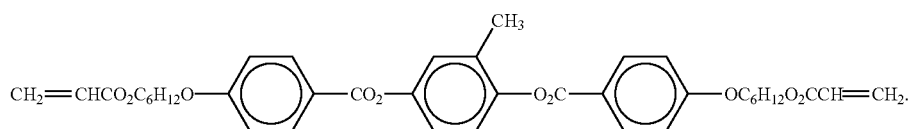
In aspects, the photoalignment layer is photocurable. This allows for flexibility in the angle at which the light emitting polymer (e.g. as a liquid crystal) is alignable and thus flexibility in its polarization characteristics.

In another aspect, the alignment layer is a polyimide layer. The layer may be formed by dissolving polyamic acid in cyclopentanone or another aggressive solvent and then coat-

4



In a further aspect, the alignment layer comprises a reactive liquid crystal formed from a reactive mesogen. A particular reactive mesogen has the formula:



(Compound 4)

ing onto a substrate followed by heating. The polyimide layer is largely insoluble in most conventional solvents.

When subjected to high energy (short wavelength e.g. 360 nm) UV light polyimide is degraded. Where plane polarised UV light is employed the polyimide may be degraded in one direction only to provide a unidirectionally aligned layer which may be used to align liquid crystals.

The polyimide layer may be in the form of a rubbed polyimide layer.

In a further aspect, nylon (e.g. in the form of rubbed nylon) may be used as the alignment layer, typically in the form of a thin film (e.g. <100 nm film thickness). Nylon is particularly useful for aligning ferroelectric liquid crystals.

Suitable nylon layers may be formed by dissolving Nylon 6 (say 0.1–1% by weight) in a solvent such as formic acid, m-cresol or 2-chloroethanol. This is then applied to a substrate (e.g. by spin-coating) followed by heating to drive off the solvent and leave a thin nylon film that can then be rubbed to cause alignment thereof.

In a further aspect, the alignment layer comprises a cross-linked polymer layer formed by deposition of a curable reactive monomer/oligomer onto a surface followed by photo or thermal cross-linking thereof. The cross-linked polymer layer is typically rubbed to obtain the necessary alignment. It is also possible that it could be treated with polarised UV light to create alignment.

Suitable oligomers include acrylated polyurethane and acrylated polyesters. A particular oligomer is that commercially available from Ciba Geigy under the trade name Ebecryl. Photo or thermal initiators may also be employed to initiate the cross-linking of the polymer layer.

In a further aspect, the alignment layer comprises a side chain liquid crystal polymer. A particular polymer of this type comprises the formula:

25

The reactive liquid crystal is typically formed by coating onto a substrate, drying and curing within the liquid crystal phase to form an anisotropic polymer film. In these cases the liquid crystal polymer or reactive mesogen is coated onto a conventional alignment layer. The subsequent coating is typically used to impart some special property such as a different surface energy.

In a further aspect, the alignment layer comprises a grating structure. Such grating structures are for example, employed in the Zenithal (trade name) bistable device (ZBD). Typical grating structures comprise thick alignment films having ribbed structures. The films are generally formed from UV cured material.

The alignment layer comprises a transport material chemically bound to said alignment layer. The transport material acts such as to increase the electrical conductivity of the alignment layer. The alignment layer is typically an electrical insulator in the absence of the transport material.

The transport material may be an ion, hole or electron transport compound. By transport material it is meant a material that is capable of transporting the named species through an otherwise electrically insulating material.

Suitable ion transport compounds include mono- and di-reactive ion transport materials.

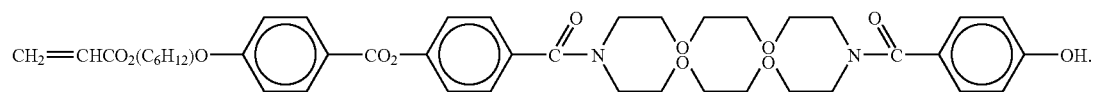
An exemplary mono-reactive ion transport material has the formula:

65

5

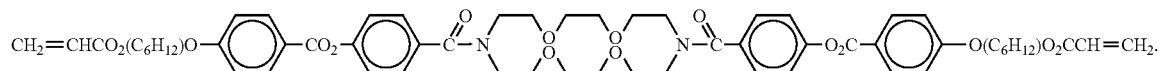
6

(Compound 5)



An exemplary di-reactive ion transport material has the formula:

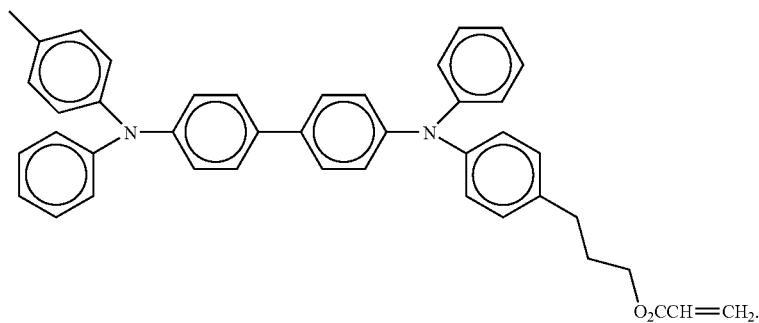
(Compound 6)



Suitable hole transport compounds include triarylamine. 20
Examples of suitable triarylamines include those described
in C. H. Chen, J. Shi, C. W. Tang, *Macromol Symp.* [1997]
125, 1.

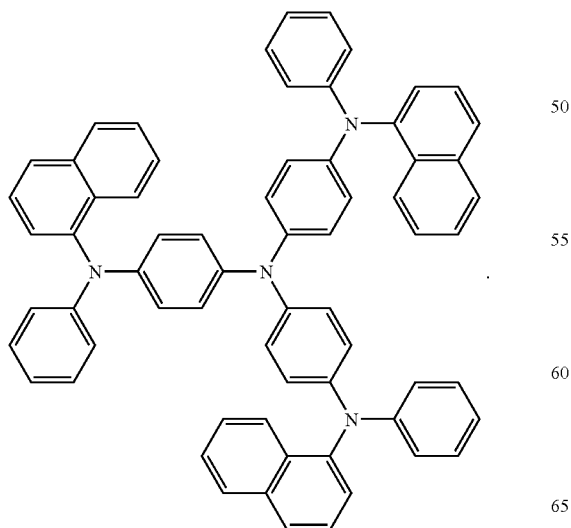
One exemplary hole transport compound has the formula:

(Compound 7)



Another exemplary hole transport compound is 4,4',4''-
tris[N-(1-naphthyl)-N-phenyl-amino]triphenylamine which
has the formula:

(Compound 8) 45



65

In aspects, the hole transport compound has a tetrahedral (pyramidal) shape which acts such as to controllably disrupt the alignment characteristics of the layer in a limited manner.

In one aspect, the photoalignment layer includes a copolymer incorporating both linear rod-like hole-transporting and photoactive side chains.

The alignment layer and transport material thereof are chemically bound. In one aspect, the alignment polymer is in the form of a cross-linked polymer network with the transport material as a bound component thereof.

According to another aspect of the present invention there is provided a liquid crystal cell comprising an inert substrate; and present on said inert substrate, a liquid crystal alignment layer as described hereinbefore.

The alignment layer is typically formed on an inert substrate such as a glass or plastic substrate. Indium tin oxide (ITO) coated glass is a preferred substrate. The layer may be applied to the substrate by any suitable coating method. Spin-coating is a preferred coating method herein.

The coating thickness is typically in the range from 10 to 500 nm, particularly 20 to 200 nm.

According to other aspects of the present invention there are provided methods for making liquid crystal display cells. In aspects, the chemical bond between the alignment layer and transport material may be formed by reacting the constituents together prior to applying the layer to a substrate, or the bond may be formed by an in situ reaction on a substrate. The reaction (e.g. a co-polymerisation) may in aspects be heat or UV light initiated with known photo or thermal initiator compounds being employed as necessary.

According to another aspect of the present invention there is provided a liquid crystal display comprising a driver for driving the display; and a liquid crystal cell as described herein before. The liquid crystal display is suitably in the form of a ferroelectric liquid crystal (FLC) display.

In a particular aspect herein, the alignment layer is a photoalignment layer having a light emitting polymer aligned thereon. In this aspect, the transport material is preferably a hole and/or an electron transport compound. Compound 8 is a preferred hole transport compound for this application.

Suitably, the light emitting polymer is a polymer having a light emitting chromophore. Suitable chromophores include fluorene, vinylenebenzene, anthracene and perylene. Useful chromophores are described in A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem. Int. Ed. Eng.* [1998], 37, 402.

Suitably, the light emitting polymer is a liquid crystal which can be aligned to emit polarised light. A suitable class of polymers is based on fluorene.

In one aspect, the light emitting polymer comprises an organic light emitting diode (OLED) such as described in S. M. Kelly, *Flat Panel Displays: Advanced Organic Materials*, RSC Materials Monograph, ed. J. A. Connor, [2000]; C. H. Chen, J. Shi, C. W. Tang, *Macromol Symp.* [1997] 125, 1; R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, W. R. Salaneck, *Nature* [1999] 397, 121; M. Grell, D. D. C. Bradley, *Adv. Mater.* [1999] 11, 895; N. C. Greenman, R. H. Friend *Solid State Phys.* [1995] 49, 1.

OLEDs may be configured to provide polarized electroluminescence.

The reactive mesogen (monomer) typically has a molecular weight of from 400 to 2,000. Lower molecular weight monomers are preferred because their viscosity is also lower leading to enhanced spin coating characteristics and shorter

annealing times which aids processing. The light emitting polymer typically has a molecular weight of above 4,000, typically 4,000 to 15,000.

The light emitting polymer typically comprises from 5 to 50, preferably from 10 to 30 monomeric units.

The light emitting polymer is aligned on the photoalignment layer. Suitably, the photoaligned polymer comprises uniaxially aligned chromophores. Typically polarization ratios of 30 to 40 are required, but with the use of a clean up polarizer ratios of 10 or more can be adequate for display uses.

In aspects, the light emitting polymer is formed by a polymerization process. Suitable processes involve the polymerization of reactive mesogens (e.g. in liquid crystal form) via photo-polymerization or thermal polymerization of suitable end-groups of the mesogens. In preferred aspects, the polymerization process results in cross-linking e.g. to form an insoluble, cross-linked network.

The polymerization process can in a preferred aspect be conducted in situ after deposition of the reactive mesogens on the photoalignment layer by any suitable deposition process including a spin-coating process.

In a preferred polymerization process, the light emitting polymer is formed by photopolymerization of reactive mesogens having photoactive end-groups.

Suitable reactive mesogens have the following general structure:



wherein

A is a chromophore;

S is a spacer; and

B is an endgroup which is susceptible to radical photopolymerisation.

The polymerisation typically results in a light emitting polymer comprising arrangements of chromophores (e.g. uniaxially aligned) spaced by a crosslinked polymer backbone. The process is shown schematically in FIG. 1 from which it may be seen that the polymerisation of reactive monomer 10 results in the formation of crosslinked polymer network 20 comprising crosslink 22, polymer backbone 24 and spacer 26 elements.

Suitable chromophore (A) groups have been described previously.

Suitable spacer (S) groups comprise unsaturated organic chains, including e.g. flexible aliphatic, amine or ether linkages. Aliphatic spacers are preferred. The presence of spacer groups aids the solubility and lowers the melting point of the light emitting polymer which assists the spin coating thereof.

Suitable endgroups are susceptible to photopolymerization (e.g. by a process using UV radiation, generally unpolarized). Preferably, the polymerization involves cyclopolymerization (i.e. the radical polymerization step results in formation of a cyclic entity).

A typical polymerization process involves exposure of a reactive mesogen of general formula 1 to UV radiation to form an initial radical having the general formula as shown below:



wherein A, S and B are as defined previously and B. is a radicalised endgroup which is capable of reacting with another B endgroup (particularly to form a cyclic entity). The B. radicalised endgroup suitably comprises a bound radical such that the polymerisation process may be sterically controlled.

Suitable endgroups include dienes such as 1,4, 1,5 and 1,6 dienes. The diene functionalities may be separated by ali-

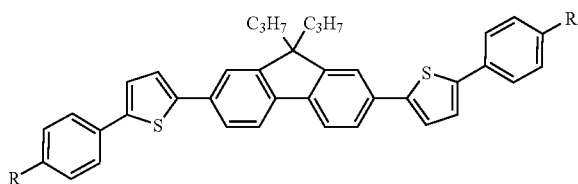
9

phatic linkages, but other inert linkages including ether and amine linkages may also be employed.

Methacrylate endgroups have been found to be less suitable than dienes because the high reactivity of the radicals formed after the photoinitiation step can result in a correspondingly high photodegradation rate. By contrast, it has been found that the photodegradation rate of light emitting polymers formed from dienes is much lower. The use of methacrylate endgroups also does not result in cyclopolymerization.

Where the endgroups are dienes the reaction typically involves cyclopolymerization by a sequential intramolecular and intermolecular propagation: A ring structure is formed first by reaction of the free radical with the second double bond of the diene group. A double ring is obtained by the cyclopolymerization which provides a particularly rigid backbone. The reaction is in general, sterically controlled.

Suitable reactive mesogens have the general formula:



wherein R has the general formula: X-S2-Y-Z

and wherein

X=O, CH₂ or NH and preferably X=O;

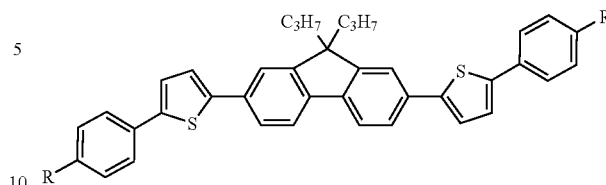
S2=linear or branched alkyl or alkenyl chain optionally including a heteroatom (e.g. O, S or NH) and preferably S2=a linear alkyl chain;

Y=O, CO₂ or S and preferably Y=CO₂; and

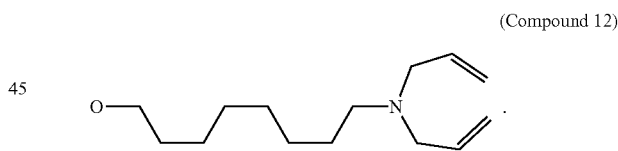
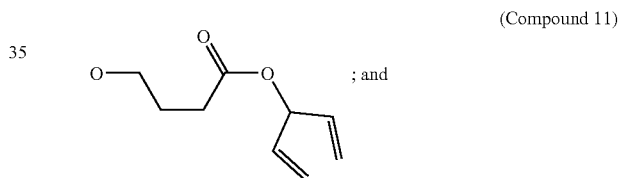
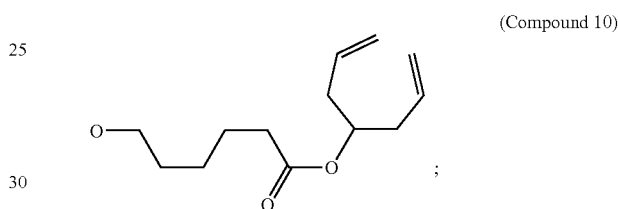
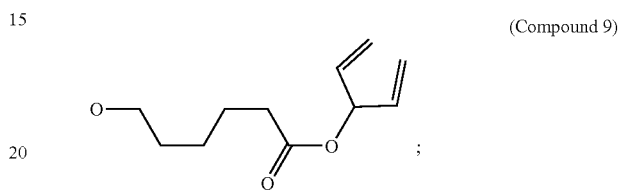
Z=a diene (end-group) and preferably Z=a 1,4, 1,5 or 1,6 diene.

10

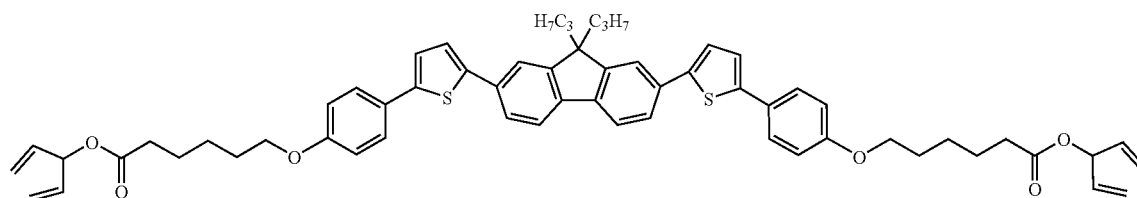
Exemplary reactive mesogens have the general formula:



wherein R is selected from:

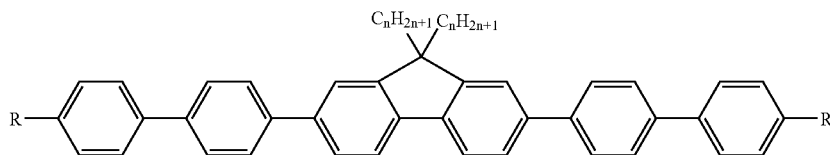


An exemplary reactive mesogen has the formula:



All of Compounds 9 to 12 exhibit a nematic phase with a clearing point (N-I) between 79 and 120° C.

Other suitable exemplary reactive mesogens have the general formula:



wherein n is from 2 to 10, preferably from 3 to 8 and
wherein, as above, R has the general formula: X-2-Y-Z ¹⁵

and wherein

X=O, CH₂ or NH and preferably X=O;

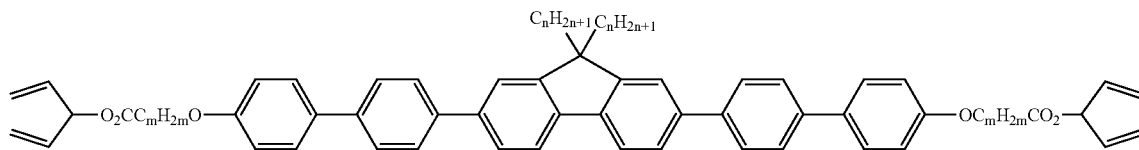
S2=linear or branched alkyl or alkenyl chain optionally
including a heteroatom (e.g. O, S or NH) and preferably
S2=a linear alkyl chain; ²⁰

Y=O, CO₂ or S and preferably Y=CO₂; and

Z=a diene (end-group) and preferably Z=a 1,4, 1,5 or 1,6
diene. ²⁵

Suitably, R is as for any of Compounds 9 to 12, as shown
above.

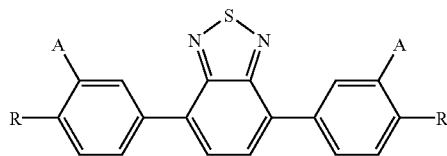
A particular class of exemplary reactive mesogens has the
formula:



wherein:

n is from 2 to 10, preferably from 3 to 8; and
m is from 4 to 12, preferably from 5 to 11.

Still further suitable exemplary reactive mesogens have
the general formula:



wherein A=H or F

and wherein, as above, R has the general formula: X-S2-Y-Z

and wherein ⁴⁰

X=O, CH₂ or NH and preferably X=O;

S2=linear or branched alkyl or alkenyl chain optionally
including a heteroatom (e.g. O, S or NH) and preferably
S2=a linear alkyl chain; ⁴⁵

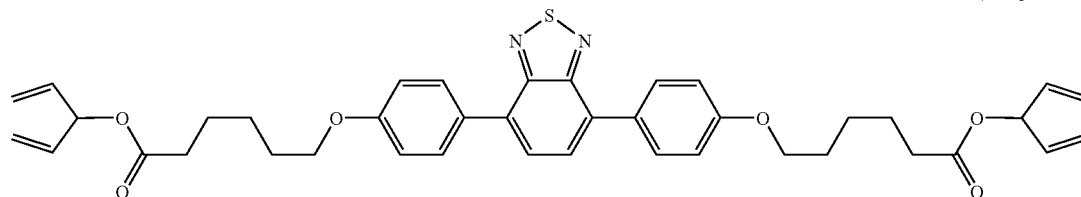
Y=O, CO₂ or S and preferably Y=CO₂; and

Z=a diene (end-group) and preferably Z=a 1,4, 1,5 or 1,6
diene. ⁵⁰

Suitably, R is as for any of Compounds 9 to 12, as shown
above.

Particular exemplary reactive mesogens of this type have
the formula:

(Compound 22)



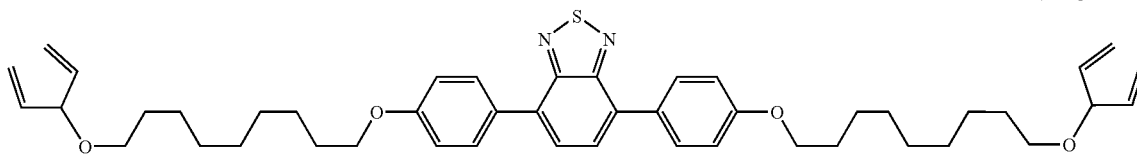
or

13

14

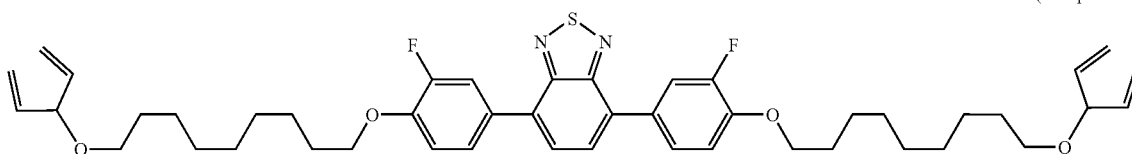
-continued

(Compound 23)



or

(Compound 24)



In aspects, the preferred photopolymerization process can be conducted at room temperature, thereby minimizing any possible thermal degradation of the reaction mesogen or polymer entities. Photopolymerization is also preferable to thermal polymerization because it allows subsequent sub-

Further steps may be conducted subsequent to the polymerization process including doping and the addition of other layers (as described in more detail below).

The light emitting polymer may be aligned by a range of methods including the use of polyimide. However, standard polyimide alignment layers are insulators, giving rise to low charge injection for OLEDs.

The susceptibility to damage of the alignment layer during the alignment process can be reduced by the use of a non-contact photoalignment method. In such methods, illumination with polarized light introduces a surface anisot-

ropy to the alignment layer and hence a preferred in-plane orientation to the overlying light emitting polymer (e.g. in liquid crystal form).

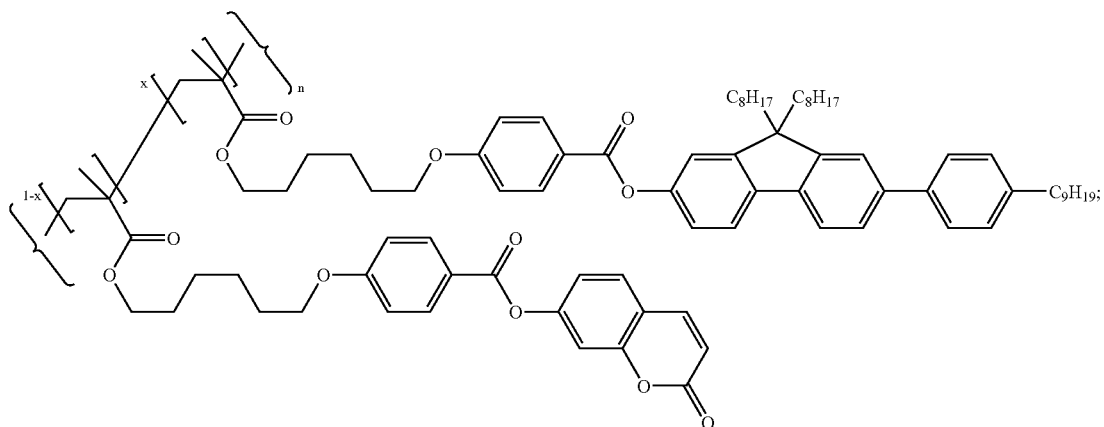
The aligned light emitting polymer is in one aspect in the form of an insoluble nematic polymer network. Cross-linking has been found to improve the photoluminescence properties.

M. O'Neill, S. M. Kelly *J. Appl. Phys. D* [2000] 33, R67 provides a review of photoalignment materials and methods.

In one particular aspect, herein a transport material (suitably comprising a methacrylate end-group) is co-polymerised with a known alignment layer (e.g. a coumarin alignment layer, such as one comprising Compound 2) to form a transporting (e.g. hole transporting) alignment copolymer layer.

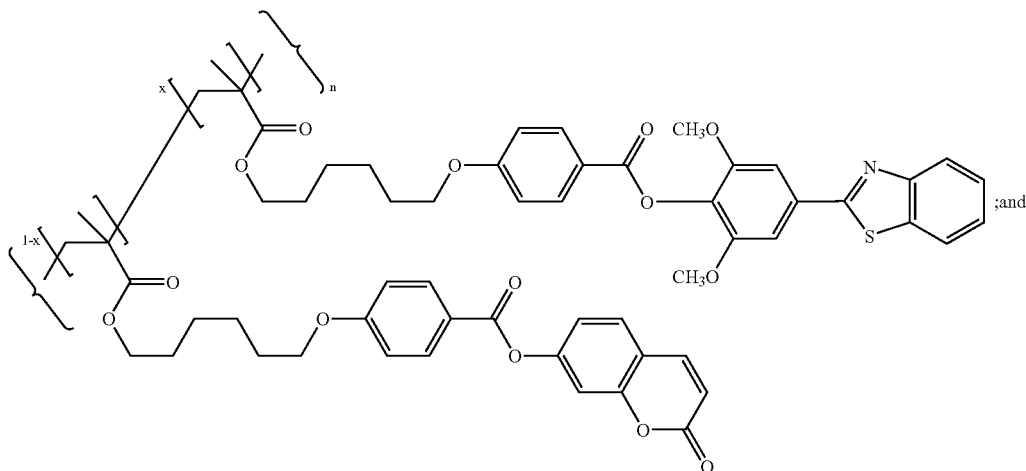
Particular examples of such copolymers include:

(Compound 25)

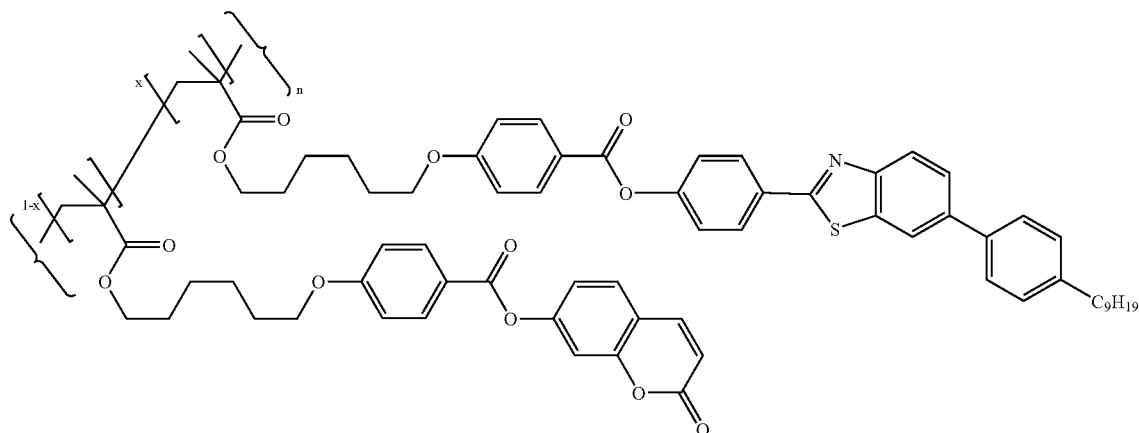


-continued

(Compound 26)



(Compound 27)



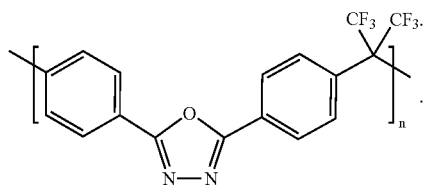
40

wherein, for each of Compounds 25 to 27, $0 < x < 1$ (i.e. x is greater than 0 and less than 1) and n is from 5 to 500, preferably from 10 to 30.

The emitter herein may comprise additional layers such as additional carrier transport layers. The presence of an electron-transporting polymer layer (e.g. comprising an oxadiazole ring) has been found to increase electroluminescence.

An exemplary electron transporting polymer has the formula:

(Compound 13)



Pixellation of the light emitter may be achieved by selective photopatterning to produce red, green and blue pixels as desired. The pixels typically have a size of from 1 to 500 μm . In microdisplays, the pixels have a size of from 1 to 50 μm , preferably from 5 to 15 μm , such as from 8 to

10 μm . In other displays, the pixel size is typically larger with a size of about 300 μm being typical.

The layers may also be doped with photoactive dyes. In aspects, the dye comprises a dichroic or pleachroic dye. Examples include anthraquinone dyes or tetralines, including those described in S. M. Kelly, Flat Panel Displays: Advanced Organic Materials, RSC Materials Monograph, ed. J. A. Connor, [2000]. Different dopant types can be used to obtain different pixel colors.

Pixel color can also be influenced by the choice of chromophore with different chromophores having more suitability as red, green or blue pixels, for example using suitably modified anthraquinone dyes.

Multicolor emitters are envisaged herein comprising arrangements or sequences of different pixel colors.

One suitable multicolor emitter comprises stripes of red, green and blue pixels having the same polarization state. This may be used as a sequential color backlight for a display which allows the sequential flashing of red, green and blue lights. Such backlights can be used in transmissive FLC displays where the FLC acts as a shutter for the flashing colored lights.

Another suitable multicolor emitter comprises a full color pixelated display in which the component pixels thereof have the same or different alignment.

Suitable multicolor emitters may be formed by a sequential "coat, selective cure, wash off" process in which a first

color emitter is applied to the aligned layer by a suitable coating process (e.g. spin coating). The coated first color emitter is then selectively cured only where pixels of that color are required. The residue (of uncured first color emitter) is then washed off. A second color emitter is then applied to the aligned layer, cured only where pixels of that color are required and the residue washed off. If desired, a third color may be applied by repeating the process for the third color.

The above process may be used to form a pixelated display such as for use in a color emissive display. This process is simpler than traditional printing (e.g. ink jet) methods of forming such displays.

In one aspect there is provided a backlight for a display comprising a power input; and a photoalignment layer comprising a light emitter as described hereinbefore.

The backlight may be arranged for use with a liquid crystal display. In aspects, the backlight may be monochrome or multicolor.

In one aspect there is provided a display comprising a screen; and a light emitter or backlight as described hereinbefore.

The screen may have any suitable shape or configuration including flat or curved and may comprise any suitable material such as glass or a plastic polymer.

The light source of the present invention has been found to be particularly suitable for use with screens comprising plastic polymers such as polyethylene or polyethylene terephthalate (PET).

The display is suitable for use in consumer electronic goods such as mobile telephones, hand-held computers, watches, clocks and games machines.

In one aspect there is provided a security viewer (e.g. in kit form) comprising a light emitter as described herein in which the pixels are arranged for polarized emission; and view glasses having a different polarization for each eye.

In one aspect there is provided a method of forming a light emitter for a display comprising forming a photoalignment layer herein; and aligning a light emitting polymer on said photoalignment layer.

In one aspect there is provided a method of forming a multicolor emitter comprising applying a first color light emitter is applied to the photoalignment layer; selectively curing said first color light emitter only where that color is required; washing off any residue of uncured first color emitter; and repeating the process for a second and any subsequent light color emitters.

All references herein are incorporated by reference in their entirety.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of systems according to the invention will now be described with reference to the accompanying experimental detail and drawings in which:

FIG. 1 is a schematic representation of a polymerization process herein;

FIG. 2 is a representation of a display device in accord with the present invention;

FIG. 3 is a representation of a backlight in accord with the present invention; and

FIG. 4 is a representation of a polarised sequential light emitting backlight in accord with the present invention.

FIGS. 5 to 15 show reaction schemes 1 to 11, respectively.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

General Experimental Details

Fluorene, 2-(tributylstanyl)thiophene, 4-(methoxyphenyl)boronic acid and the dienes were purchased from Aldrich and used as received. Reagent grade solvents were dried and purified as follows. N,N-Dimethylformamide (DMF) was dried over anhydrous P₂O₅ and purified by distillation. Butanone and methanol were distilled and stored over 5 Å molecular sieves. Triethylamine was distilled over potassium hydroxide pellets and then stored over 5 Å molecular sieves. Dichloromethane was dried by distillation over phosphorus pentoxide and then stored over 5 Å molecular sieves. Chloroform was alumina-filtered to remove any residual ethanol and then stored over 5 Å molecular sieves. ¹H nuclear magnetic resonance (NMR) spectra were obtained using a JOEL JMN-GX270 FT nuclear resonance spectrometer. Infra-red (IR) spectra were recorded using a Perkin Elmer 783 infra-red spectrophotometer. Mass spectral data were obtained using a Finnegan MAT 1020 automated GC/MS. The purity of the reaction intermediates was checked using a CHROMPACK CP 9001 capillary gas chromatograph fitted with a 10 m CP-SIL 5CB capillary column. The purity of the final products was determined by high-performance liquid chromatography [HPLC] (5 μ m, 25 cm \times 0.46 cm, ODS Microsorb column, methanol, >99%) and by gel-permeation chromatography [GPC] (5 μ m, 30 cm \times 0.75 cm, 2 \times mixed D PL columns, calibrated using polystyrene standards [molecular weights=1000-4305000], toluene; no monomer present). The polymers were found to exhibit moderate to high M_w values (10,000-30,000) and acceptable M_w/M_n values (1.5-3). The liquid crystalline transition temperatures were determined using an Olympus BH-2 polarising light microscope together with a Mettler FP52 heating stage and a Mettler FP5 temperature control unit. The thermal analysis of the photopolymerisable monomers (Compounds 3 to 6) and the mainchain polymer (Compound 7) was carried out by a Perkin-Elmer Perkin-Elmer DSC 7 differential scanning calorimeter in conjunction with a TAC 7/3 instrument controller. Purification of intermediates and products was mainly accomplished by column chromatography using silica gel 60 (200-400 mesh) or aluminium oxide (Activated, Brockman 1, ~150 mesh). Dry flash column chromatography was carried out using silica gel H (Fluka, 5-40 μ m). Electroluminescent materials were further purified by passing through a column consisting of a layer of basic alumina, a thin layer of activated charcoal, a layer of neutral alumina and a layer of Hi-Flo filter aid using DCM as an eluent. This was followed by recrystallisation from an ethanol-DCM mixture. At this stage, all glass-wear was thoroughly cleaned by rinsing with chromic acid followed by distilled water and then drying in an oven at 100° C. for 45 minutes. Purity of final products was normally confirmed by elemental analysis using a Fisons EA 1108 CHN apparatus.

Key intermediate 1: 2,7-bis[5-(4-hydroxyphenyl)thien-2-yl]-9,9-dipropylfluorene was synthesised as shown in Reaction Scheme 1. Full details each step are now given:

9-Propylfluorene: A solution of n-Butyllithium (18.0 cm³, 10M solution in hexanes, 0.18 mol) was added slowly to a solution of fluorene (30.0 g, 0.18 mol) in THF (350 cm³) at -50° C. The solution was stirred for 1 h at -75° C. and 1-bromopropane (23.0 g, 0.19 mol) was added slowly. The solution was allowed to warm to RT and then stirred for a further 1 h. Dilute hydrochloric acid (100 cm³, 20%) and water (100 cm³) were added and the product extracted into

diethyl ether (3×150 cm³). The ethereal extracts were dried (MgSO₄) and concentrated to a pale yellow oil (37.5 g, yield 100%). Purity 100% (GC).

¹H NMR (CD₂Cl₂) δ: 7.75 (2H, dd), 7.52 (2H, m), 7.32 (4H, m), 3.98 (1H, t), 1.95 (2H, m), 1.19 (2H, m), 0.85 (3H, t). IR (KBr pellet cm⁻¹): 3070 (m), 2962 (s), 1450 (s), 1296 (w), 1189 (w), 1030 (w), 938 (w), 739 (s). MS (m/z): 208 (M⁺), 178, 165 (M100), 139.

9,9-Dipropylfluorene: A solution of n-Butyllithium (29.0 cm³, 2.5M solution in hexanes, 0.073 mol) was added slowly to a solution of 9-propylfluorene (15.0 g, 0.072 mol) in THF at -50° C. The solution was stirred for 1 h at -75° C., 1-bromopropane (10.0 g, 0.092 mol) was added slowly and the temperature raised to RT after completion of the addition. After 18 h, dilute hydrochloric acid (20%, 100 cm³) and water (100 cm³) were added and the product extracted into diethyl ether (2 □100 cm³). The ethereal extracts were dried (MgSO₄) and concentrated to a pale brown oil which crystallised overnight at RT. The product was purified by recrystallisation from methanol to yield a white crystalline solid (14.5 g, yield 80%) mp 47–49° C. (Lit. 49–50° C. ¹⁹). Purity 100% (GC).

¹H NMR (CDCl₃) δ: 7.68 (2H, m), 7.31 (6H, m), 1.95 (4H, t), 0.65 (10H, m). IR (KBr pellet cm⁻¹): 3068 (m), 2961 (s), 1449 (s), 1293 (w), 1106 (w), 1027 (w), 775 (m), 736 (s), 637 (m). MS (m/z): 250 (M⁺), 207 (M100), 191, 179, 165.

2,7-Dibromo-9,9-dipropylfluorene: Bromine (10.0 g, 0.063 mol) was added to a stirred solution of 9,9-dipropylfluorene (7.0 g, 0.028 mol) in chloroform (25 cm³) and the solution purged with dry N₂ for 0.5 h. Chloroform (50 cm³) was added and the solution washed with saturated sodium bisulphite solution (75 cm³), water (75 cm³), dried (MgSO₄) and concentrated to a pale yellow powder (11.3 g, yield 98%) mp 134–137° C.

¹H NMR (CDCl₃) δ: 7.51 (2H, d), 7.45 (4H, m), 1.90 (4H, t), 0.66 (10H, m). IR (KBr pellet cm⁻¹): 2954 (s), 1574 (w), 1451 (s), 1416 (m), 1270 (w), 1238 (w), 1111 (w), 1057 (s), 1006 (w), 931 (w), 878 (m), 808 (s), 749 (m). MS (m/z): 409 (M⁺), 365, 336, 323, 284, 269, 256, 248, 202, 189, 176 (M100), 163.

2,7-bis(Thien-2-yl)-9,9-dipropylfluorene: A mixture of 2,7-dibromo-9,9-dipropylfluorene (6.0 g, 0.015 mol), 2-(tributylstannyl)thiophene (13.0 g, 0.035 mol) and tetrakis (triphenylphosphine)-palladium (0) (0.3 g, 2.6×10⁻⁴ mol) in DMF (30 cm³) was heated at 90° C. for 24 h. DCM (200 cm³) was added to the cooled reaction mixture and the solution washed with dilute hydrochloric acid (2□150 cm³, 20%), water (100 cm³), dried (MgSO₄) and concentrated onto silica gel for purification by column chromatography [silica gel, DCM:hexane 1:1]. The compound was purified by recrystallisation from DCM: ethanol to yield light green crystals (4.3 g, yield 6 9%), mp 165–170° C. Purity 100% (GC).

¹H NMR (CDCl₃) δ: 7.67 (2H, d), 7.60 (2H, dd), 7.57 (2 h, d), 7.39 (2H, dd), 7.29 (2H, dd), 7.11 (2H, dd), 2.01 (4H, m), 0.70 (10H, m). IR (KBr pellet cm⁻¹): 2962 (m), 2934 (m), 2872 (m), 1467 (m), 1276 (w), 1210 (m), 1052 (w), 853 (m), 817 (s), 691 (s). MS (m/z): 414 (M⁺, M100), 371, 342, 329, 297, 207, 165.

2,7-bis(5-Bromothiien-2-yl)-9,9-dipropylfluorene: N-Bromosuccinimide (2.1 g, 0.012 mol freshly purified by recrystallisation from water) was added slowly to a stirred solution of 2,7-bis(thien-2-yl)-9,9-dipropylfluorene (2.3 g, 5.55×10⁻³ mol) in chloroform (25.0 cm³) and glacial acetic acid (25.0 cm³). The solution was heated under reflux for 1 h, DCM (100 cm³) added to the cooled reaction mixture, washed with water (100 cm³), HCl (150 cm³, 20%), saturated aqueous sodium bisulphite solution (50 cm³), and dried (MgSO₄).

The solvent was removed in vacuo and the product purified by recrystallisation from an ethanol-DCM mixture to yield yellow-green crystals (2.74 g, yield 86%). mp 160–165° C.

¹H NMR (CDCl₃) δ: 7.66 (2H, d), 7.49 (2H, dd), 7.46 (2H, d), 7.12 (2H, d), 7.05 (2H, d), 1.98 (4H, t), 0.69 (10H, m). IR (KBr pellet cm⁻¹): 3481 (w), 2956 (s), 1468 (s), 1444 (m), 1206 (w), 1011 (w), 963 (w), 822 (m), 791 (s), 474 (w). MS (m/z): 572 (M⁺), 529, 500, 487, 448, 433, 420, 407, 375, 250, 126.

2,7-bis[5-(4-Methoxyphenyl)thien-2-yl]-9,9-dipropylfluorene: A mixture of 2,7-bis(5-bromothiien-2-yl)-9,9-dipropylfluorene (2.7 g, 4.7×10⁻³ mol), 4-(methoxyphenyl)boronic acid (2.15 g, 0.014 mol), tetrakis (triphenylphosphine)palladium (0) (0.33 g, 2.9×10⁻⁴ mol), sodium carbonate (3.0 g, 0.029 mol) and water (20 cm³) in DME (100 cm³) was heated under reflux for 24 h. More 4-(methoxyphenyl)boronic acid (1.0 g, 6.5×10⁻³ mol) was added to the cooled reaction mixture, which was then heated under reflux for a further 24 h. DMF (20 cm³) was added and the solution heated at 110° C. for 24 h, cooled and dilute hydrochloric acid (100 cm³, 20%) added. The cooled reaction mixture was extracted with diethyl ether (230 cm³) and the combined ethereal extracts washed with water (100 cm³), dried (MgSO₄), and concentrated onto silica gel to be purified by column chromatography [silica gel, DCM:hexane 1:1] and recrystallisation from an ethanol-DCM mixture to yield a green crystalline solid (1.86 g, yield 63%), Cr—N, 235° C.; N—I, 265° C.

¹H NMR (CD₂Cl₂) δ: 7.71 (2H, dd), 7.61 (8H, m), 7.37 (2H, d), 7.24 (2H, d), 6.95 (4H, d), 3.84 (6H, s), 2.06 (4H, m), 0.71 (10H, m). IR (KBr pellet cm⁻¹): 2961 (w), 1610 (m), 1561 (m), 1511 (s), 1474 (s), 1441 (m), 1281 (m), 1242 (s), 1170 (s), 1103 (m), 829 (m), 790 (s). MS (m/z): 584 (M⁺-C₃H₇), 569, 555, 539, 525, 511, 468, 313, 277 (M100), 248, 234. Elemental analysis. Calculated: wt % C=78.56%, H, 6.11%, S, 10.23%. Found: C, 78.64%, H, 6.14%, S, 10.25%.

2,7-bis[5-(4-Hydroxyphenyl)thien-2-yl]-9,9-dipropylfluorene: A 1M solution of boron tribromide in chloroform (9 cm³, 9.0 mmol) was added dropwise to a stirred solution of 2,7-bis[5-(4-methoxyphenyl)thien-2-yl]-9,9-dipropylfluorene (1.3 g, 2.1×10⁻³ mol) at 0° C. The temperature was allowed to rise to RT overnight and the solution added to ice-water (200 cm³) with vigorous stirring. The product was extracted into diethyl ether (220 cm³), washed with aqueous sodium carbonate (2M, 150 cm³), dried (MgSO₄) and purified by column chromatography [silica gel DCM:diethyl ether:ethanol 40:4:1] to yield a green solid (1.2 g, yield 96%), Cr—I, 277° C.; N—I, 259° C.

¹H NMR (d-acetone) δ: 8.56 (2H, s), 7.83 (2H, dd), 7.79 (2H, d), 7.68 (2H, dd), 7.57 (4H, dd), 7.50 (2H, dd), 7.31 (2H, dd), 6.91 (4H, dd), 2.15 (4H, m), 0.69 (10H, m). IR (KBr pellet cm⁻¹): 3443 (s, broad), 2961 (m), 1610 (m), 1512 (m), 1474 (m), 1243 (m), 1174 (m), 1110 (w), 831 (m), 799 (s). MS (m/z): 598 (M⁺), 526, 419 (M100), 337.

Compound 9: 2,7-bis(5-{4-[5-(1-Vinyl-allyloxycarbonyl)pentyl]oxy}phenyl)thien-2-yl)-9,9-dipropylfluorene: The 1,3-pentadiene monomer (Compound 9) was synthesised as depicted in Reaction Scheme 2. Full details of each step are now given:

1,4-Pentadien-3-yl 6-bromohexanoate: A solution of 6-bromohexanoyl chloride (3.2 g, 0.026 mol) in DCM (30 cm³) was added dropwise to a solution of 1,4-pentadien-3-ol (2.0 g, 0.024 mol) and triethylamine (2.4 g, 0.024 mol) in DCM (30 cm³). The mixture was stirred for 1 h and washed with dilute hydrochloric acid (20%, 50 cm³), saturated potassium carbonate solution (50 cm³), water (50 cm³) then dried (MgSO₄) and concentrated to a brown oil. The product

was purified by dry flash chromatography [silica gel, DCM] to yield a pale yellow oil (4.7 g, yield 75%). Purity >95% (GC).

¹H NMR (CDCl₃) δ: 5.82 (2H, m), 5.72 (1H, m), 5.30 (2H, d), 5.27 (2H, d), 3.42 (2H, t), 2.37 (2H, t), 1.93 (2H, m), 1.72 (2H, m), 1.54 (2H, m). IR (KBr pellet cm⁻¹): 3095 (w), 1744 (s), 1418 (w), 1371 (w), 12521 (m), 1185 (s), 983 (m), 934 (m).

MS (m/z): 261 (M⁺), 177, 67.

2,7-bis(5-{4-[5-(1-Vinyl-allyloxycarbonyl)pentyl]oxy}phenyl)thien-2-yl)-9,9-dipropylfluorene: A mixture of 2,7-bis[5-(4-hydroxyphenyl)thien-2-yl]-9,9-dipropylfluorene (0.6 g, 1.0 × 10⁻³ mol), 1,4-pentadien-3-yl 5-bromohexanoate (0.7 g, 2.7 × 10⁻³ mol) and potassium carbonate (0.5 g, 3.6 × 10⁻³ mol) in acetonitrile (25 cm³) was heated at 50° C. for 18 h. The mixture was then heated under reflux conditions for a further 20 h. Excess potassium carbonate was filtered off and precipitated product rinsed through with DCM (230 cm³). The solution was concentrated onto silica gel for purification by column chromatography [silica gel, DCM:hexane 1:1 gradients to DCM] and recrystallisation from a DCM-ethanol mixture to yield a green-yellow solid (0.4 g, yield 40%), Cr—N, 92° C.; N—I, 108° C.

¹H NMR (CD₂Cl₂) δ: 7.69 (2H, d), 7.58 (8H, m), 7.35 (2H, d), 7.22 (2H, d), 6.91 (4H, d), 5.83 (4H, m), 5.68 (2H, m), 5.29 (2H, t), 5.25 (2H, t), 5.21 (2H, t), 5.19 (2H, t), 3.99 (4H, t), 2.37 (4H, t), 2.04 (4H, m), 1.80 (4H, quint), 1.70 (4H, quint), 1.51 (4H, quint) 0.69 (10H, m). IR (KBr pellet cm⁻¹): 2936 (m), 2873 (m), 1738 (s), 1608 (m), 1511 (m), 1473 (s), 1282 (m), 1249 (s), 1177 (s), 1110 (m), 982 (m), 928 (m), 829 (m), 798 (s). APCI-MS (m/z): 958 (M⁺), 892 (M100). Elemental analysis. Calculated: wt % C=76.37, wt % H=6.93, wt % S=6.68. Found: wt % C=75.93, wt % H=6.95, wt % S=6.69.

Compound 10: 2,7-bis(5-{4-[5-(1-Allylbut-3-enyloxycarbonyl)pentyl]oxy}phenyl)thien-2-yl)-9,9-dipropylfluorene:

The 1,3-heptadiene monomer (Compound 10) was synthesised as depicted in reaction Scheme 3. Full details of each step are now given:

1,6-Heptadien-5-yl 5-bromopentanoate: 5-Bromopentanoyl chloride (3.0 g, 0.015 mol) was added dropwise to 1,6-heptadien-4-ol (1.5 g, 0.013 mol) and triethylamine (1.4 g, 0.014 mol) in DCM (25 cm³). The mixture was stirred for 2 h and washed with dilute hydrochloric acid (20%, 50 cm³), saturated aqueous potassium carbonate solution (50 cm³), water (50 cm³) then dried (MgSO₄) and concentrated to a brown oil. The product was purified by dry flash chromatography [silica gel, DCM] to yield a pale yellow oil (1.7 g, yield 48%). Purity >92% (GC).

¹H NMR (CDCl₃) δ: 5.74 (2H, m), 5.08 (4H, m), 4.99 (1H, m), 3.41 (2H, t), 2.31 (6H, m), 1.88 (2H, m), 1.76 (2H, m). IR (Film cm⁻¹): 2952 (m), 1882 (w), 1734 (s), 1654 (m) 1563 (w), 1438 (m), 1255 (m), 1196 (s), 996 (m), 920 (s). MS (m/z): 275 (M⁺), 245, 219, 191, 183, 163 (M100), 135, 95, 79.

2,7-bis(5-{4-[5-(1-Allylbut-3-enyloxycarbonyl)pentyl]oxy}phenyl)thien-2-yl)-9,9-dipropylfluorene: A mixture of 2,7-bis[5-(4-hydroxyphenyl)thien-2-yl]-9,9-dipropylfluorene (0.3 g, 1.0 × 10⁻³ mol), 1,6-heptadienyl 6-bromohexanoate (0.7 g, 2.7 × 10⁻³ mol) and potassium carbonate (0.5 g, 3.6 × 10⁻³ mol) in acetonitrile (25 cm³) was heated under reflux for 20 h. Excess potassium carbonate was filtered off and precipitated product rinsed through with DCM (230 cm³). The solution was concentrated onto silica gel for purification by column chromatography [silica gel, DCM:hexane 1:1 gradients to DCM] and recrystallisation from a DCM-ethanol mixture to yield a green-yellow solid (0.21 g, yield 21%), Cr—I, 97° C., N—I, 94° C.

¹H NMR (CDCl₃) δ: 7.68 (2H, d), 7.60 (2H, dd), 7.58 (2H, d), 7.57 (2H, d), 7.33 (2H, d), 7.20 (2H, d), 6.91 (2H, d), 5.75 (4H, m), 5.08 (8H, m), 5.00 (2H, quint), 4.00 (4H, t), 2.33 (12H, m), 2.02 (4H, t), 1.82 (4H, quint), 1.71 (4H, quint), 1.53 (4H, m), 0.72 (10H, m). IR (KBr pellet cm⁻¹): 3443 (s), 2955 (s), 1734 (s), 1643 (w), 1609 (m), 1512 (m), 1473 (s), 1249 (s), 1178 (s), 996 (m), 918 (m), 829 (m), 799 (s). APCI-MS (m/z): 1015 (M⁺, M100), 921. Elemental analysis. Calculated: wt % C, 76.89, wt % H=7.35, wt % S=6.32%. Found: wt % C=76.96, wt % H=7.42, wt % S=6.23.

Compound 11: 2,7-bis(5-{4-[3-(1-Vinylallyloxycarbonyl)propyl]oxy}phenyl)thien-2-yl)-9,9-dipropylfluorene

The 1,3-pentadiene homologue (Compound 11) was synthesised as depicted in reaction Scheme 4. Full details of each step are now given:

4-Bromobutanoyl chloride: Oxalyl chloride (15.2 g, 0.12 mol) was added dropwise to a stirred solution of 4-bromobutanoic acid (10.0 g, 0.060 mol) and DMF (few drops) in chloroform (30 cm³). The solution was stirred overnight under anhydrous conditions and concentrated to a pale brown oil which was filtered to remove solid impurities (11.0 g, yield 99%).

1,4-Pentadien-3-yl 4-bromobutanoate: 4-Bromobutanoyl chloride (3.0 g, 0.016 mol) was added dropwise to a solution of 1,4-pentadien-3-ol (1.3 g, 0.015 mol) and triethylamine (1.5 g, 0.015 mol) in DCM (30 cm³). The solution was stirred for 2 h and washed with dilute hydrochloric acid (20%, 50 cm³), saturated potassium carbonate solution (50 cm³), water (50 cm³) then dried (MgSO₄) and concentrated to a pale brown oil. The product was purified by dry flash chromatography [silica gel, DCM] to yield a pale yellow oil (1.8 g, yield 51%). Purity >85% (GC; decomposition on column).

¹H NMR (CDCl₃) δ: 5.83 (2H, m), 5.72 (1H, m), 5.27 (4H, m), 3.47 (2H, t), 2.55 (2H, t), 2.19 (2H, quint). IR (KBr pellet cm⁻¹): 3096 (w), 2973 (w), 1740 (s), 1647 (w), 1419 (m), 1376 (m), 1198 (s), 1131 (s), 987 (s), 932 (s), 557 (w). MS (m/z): 217, 166, 152, 149, 125, 110, 84, 67 (M100).

2,7-bis(5-{4-[3-(1-Vinylallyloxycarbonyl)propyl]oxy}phenyl)thien-2-yl)-9,9-dipropylfluorene: A mixture of 2,7-bis[5-(4-hydroxyphenyl)thien-2-yl]-9,9-dipropylfluorene (0.25 g, 4.2 × 10⁻⁴ mol), 1,4-pentadien-3-yl 4-bromobutanoate (0.40 g, 1.7 × 10⁻³ mol) and potassium carbonate (0.20 g, 1.4 × 10⁻³ mol) in DMF (10 cm³) was heated under reflux for 4 h. The cooled solution was filtered, rinsed through with DCM (3 × 20 cm³) and concentrated to a pale green oil which was purified by column chromatography [silica gel, DCM:hexane 2:1] followed by recrystallisation from ethanol:DCM to yield a green-yellow powder (0.20 g, yield 53%), Cr—N, 92° C.; N—I, 116° C.

¹H NMR (CDCl₃) δ: 7.61 (10H, m), 7.33 (2H, d), 7.20 (2H, d), 6.92 (4H, d), 5.85 (4H, m), 5.74 (2H, m), 5.32 (4H, d, J=17 Hz), 5.24 (4H, d, J=10 Hz), 4.06 (4H, t), 2.56 (4H, t), 2.16 (4H, quint), 2.05 (4H, t), 0.72 (10H, m). IR (KBr pellet cm⁻¹): 3449 (m), 2960 (m), 1738 (s), 1609 (m), 1512 (m), 1473 (s), 1380 (w), 1249 (s), 1174 (s), 1051 (m), 936 (m), 830 (m), 799 (s). APCI-MS (m/z): 903 (M⁺), 837 (M100), 772. Elemental analysis. Calculated: wt % C=75.80, wt % H=6.47, wt % S=7.10. Found: wt % C=76.13, wt % H=6.48%, wt % S=6.91.

Compound 12: 2,7-bis{5-[4-(8-Diallylaminoctyloxy)phenyl]thien-2-yl}-9,9-dipropylfluorene

The method of preparation of the N,N-diallylamine monomer (Compound 12) is shown in reaction Scheme 5. Full details of each step are now given:

8-Diallylaminooctan-1-ol. A mixture of 8-bromooctan-1-ol (10.0 g, 0.048 mol), diallylamine (4.85 g, 0.050 mol) and potassium carbonate (7.0 g, 0.051 mol) in butanone (100

cm³) was heated under reflux for 18 h. Excess potassium carbonate was filtered off and the solution concentrated to a colourless oil. The product was purified by dry flash chromatography [silica gel, DCM:ethanol 4:1]. (10.0 g, yield 93%)

¹H NMR (CDCl₃) δ: 5.86 (2H, d), 5.14 (4H, m), 3.71 (4H, quart), 3.63 (4H, t), 3.09 (4H, d), 1.56 (4H, m), 1.45 (2H, quint), 1.30 (6H, m). IR (KBr pellet cm⁻¹): 3344 (s), 2936 (s), 1453 (w), 1054 (m), 998 (m), 921 (m). MS (m/z): 225 (M⁺), 198, 184, 166, 152, 138, 124, 110 (M100), 81.

Toluene-4-sulphonic acid 8-diallylaminoethyl ester. 4-Toluene-sulphonyl chloride (12.5 g, 0.066 mol) was added slowly to a stirred solution of 8-diallylaminoethanol (10.0 g, 0.044 mol) and pyridine (7.0 g, 0.088 mol) in chloroform (100 cm³) at 0° C. After 24 h, water (100 cm³) was added and the solution washed with dilute hydrochloric acid (20%, 100 cm³), sodium carbonate solution (100 cm³), water (100 cm³), dried (MgSO₄) and concentrated to a yellow oil which was purified by column chromatography [silica gel, 4% diethyl ether in hexane eluting to DCM:ethanol 10:1] to yield the desired product (6.7 g, yield 40%).

¹H NMR (CDCl₃) δ: 7.78 (2H, d), 7.34 (2H, d), 5.84 (2H, m), 5.13 (4H, m), 4.01 (2H, t), 3.41 (4H, d), 2.45 (3H, s), 2.39 (2H, t), 1.63 (2H, quint), 1.42 (2H, quint), 1.30 (2H, quint), 1.23 (6H, m). IR (KBr pellet cm⁻¹): 3454 (w), 2957 (m), 1453 (s), 1402 (m), 1287 (m), 1159 (w), 1061 (m), 914 (w), 878 (m), 808 (s), 448 (m). MS (m/z): 380 (M⁺), 364, 352, 338, 224, 110 (M100), 91, 79, 66.

2,7-bis[5-[4-(8-Diallylaminoethoxy)phenyl]-thien-2-yl]-9,9-dipropylfluorene: A mixture of 2,7-bis[5-(4-hydroxyphenyl)thien-2-yl]-9,9-dipropylfluorene (0.5 g, 8.4×10⁻⁴ mol), toluene-4-sulphonic acid-8-diallylaminoethyl ester (0.8 g, 2.1×10⁻³ mol) and potassium carbonate (0.3 g, 2.2×10⁻³ mol) in butanone (30 cm³) was heated under reflux for 24 h. Excess potassium carbonate was filtered off and rinsed with DCM (3×30 cm³). The solution was concentrated onto silica gel for purification by column chromatography [silica gel, DCM:hexane 2:1 eluting to DCM:ethanol 4:1]. The product was obtained as a yellow-green glass (0.35 g, yield 41%), N—I, 95° C.

¹H NMR (CDCl₃) δ: 7.67 (2H, d), 7.58 (8H, m), 7.34 (2H, d), 7.20 (2H, d), 6.92 (4H, d), 5.94 (4H, m), 5.25 (8H, m), 3.99 (4H, t), 3.22 (8H, d), 2.02 (4H, t), 1.80 (4H, quint), 1.56 (4H, quint), 1.47 (4H, quint), 1.35 (12H, m), 0.71 (10H, m). IR (KBr pellet cm⁻¹): 3437 (s), (2934 (s), 1609 (s), 1512 (s), 1472 (s), 1283 (m), 1249 (s), 1179 (s), 1031 (w), 918 (w), 829 (m), 798 (s). APCI-MS (m/z): 1014 (M⁺, M100), 973. Elemental analysis. Calculated: wt % C=79.40, wt % H=8.35, wt % N=2.76, wt % S, 6.33. Found: wt % C=79.33, wt % H=8.29, wt % N=2.88, wt % S=6.17.

Compound 13: poly(phenylene-1,3,4-oxadiazole-phenylene-hexafluoropropylene)

The electron-transporting polymer (Compound 13) was prepared according to a literature method described in Li, X. -C.; Kraft, A.; Cervini, R.; Spencer, G. C. W.; Cacialli, F.; Friend, R. H.; Gruener, J.; Holmes, A. B.; de Mello, J. C.; Moratti, S. C. *Mat. Res. Symp. Proc.* 1996, 413 13.

In more detail the preparation details were as follows: A solution of 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (2.54 g, 6.48×10⁻³ mol) and hydrazine sulphate (0.84 g, 6.48×10⁻³ mol) in Eaton's reagent (25 cm³) was heated under reflux for 18 h. The cooled solution was added to brine (300 cm³) and the product extracted into chloroform (8×200 cm³). The organic extracts were combined, dried (MgSO₄) and the solvent removed under reduced pressure to yield the crude product which was purified by dissolving in a minimum volume of chloroform and precipitating by dropwise addition to methanol (1000 cm³). The precipitate was filtered off and washed with hot water before being dried in

vacuo. The precipitation was repeated a further three times washing with methanol each time. The product was then dissolved in chloroform and passed through a microfilter (0.45 μm). The pure product was then precipitated in methanol (500 cm³) and the methanol removed under reduced pressure to yield a white fibrous solid which was dried in vacuo. Yield 1.26 g (50%).

¹H NMR (CDCl₃) δ_H: 8.19 (4H/repeat unit, d), 7.61 (4H/repeat unit, d). IR ν_{max}/cm⁻¹: 3488 (m), 1621 (m), 1553 (m), 1502 (s), 1421 (m), 1329 (m), 1255 (s), 1211 (s), 1176 (s), 1140 (s), 1073 (m), 1020 (m), 969 (m), 929 (m), 840 (m), 751 (m), 723 (s). GPC: M_w:M_n=258211:101054.

An alternative electron-transport copolymer is prepared according to the method described in Xiao-Chang Li et al J. Chem. Soc. Chem. Commun., 1995, 2211.

In more detail the preparation details were as follows: Terephthaloyl chloride (0.50 g, 2.46×10⁻³ mol) was added to hydrazine hydrate (50 cm³) at room temperature and the mixture stirred for 2 h. The precipitate was filtered off, washed with water (100 cm³) and dried in vacuo. The crude hydrazide (0.25 g, 1.3×10⁻³ mol), 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (2.50 g, 6.4×10⁻³ mol) and hydrazine sulphate (0.66 g, 5.2×10⁻³ mol) were added to Eaton's reagent and the resultant mixture heated at 100° C. for 24 h. The reaction mixture was added to water (300 cm³) and the product extracted into chloroform (3×300 cm³). The organic extracts were combined, dried (MgSO₄) and the solvent removed in vacuo before re-dissolving the product in the minimum volume of chloroform. The solution was added dropwise to methanol (900 cm³) to give a white precipitate which was filtered off and dried in vacuo. The precipitation was repeated twice before dissolving the product in chloroform and passing through a microfilter (0.45 μm) into methanol (500 cm³). The methanol was removed under reduced pressure and the product dried in vacuo. Yield 1.1 g (41%)

¹H NMR (CDCl₃) δ_H: 8.18 (dd, 4H/repeat unit), 7.60 (dd, 4H/repeat unit). IR ν_{max}/cm⁻¹: 3411 (w), 2366 (w), 1501 (m), 1261 (s), 1211 (s), 1176 (s), 1140 (m), 1072 (m), 1021 (w), 968 (m), 931 (w), 840 (m), 722 (m). GPC: M_w:M_n=20572:8320.

Key intermediate 2: 9,9-diethyl-2,7-bis(4-hydroxybiphenyl-4'-yl)fluorene was synthesised as shown in Reaction Scheme 7. Full details of each step are now given:

9-Ethylfluorene: A solution of n-butyllithium (79.52 cm³, 0.2168 mol, 2.5M in hexane) was added slowly to a solution of fluorene (30.00 g, 0.1807 mol) in THF (300 cm³) at -70° C. The solution was stirred for 1 hour at -75° C. and 1-bromoethane (17.59 cm³, 0.2349 mol) was added slowly. The solution was allowed to warm to room temperature and then stirred overnight. Dilute hydrochloric acid (200 ml, 20%) was added to the reaction mixture and stirred for a further 10 minutes. Water (250 cm³) was added and the product extracted into diethyl ether (3×300 cm³). The combined organic extracts were dried (MgSO₄) and the solvent removed on a rotary evaporator. The resulting oil was purified by distillation to yield a pale yellow oil (25.00 g, 71%, b.pt. -150° C. @ 1 mbar Hg).

¹H NMR (DMSO) δ: 7.70 (2H, m), 7.50 (2H, m), 7.30 (4H, m), 4.00 (1H, t), 2.02 (2H, quart), 0.31 (3H, t). IR ν_{max}/cm⁻¹: 3072 (m), 2971, 1618, 1453, 1380, 1187, 759, 734. MS m/z: 170 (M⁺), 94, 82, 69.

9,9-Diethylfluorene: A solution of n-butyllithium (77.34 cm³, 0.1934 mol, 2.5M in hexane) was added slowly to a solution of 9-ethylfluorene (25.00 g, 0.1289 mol) in THF (250 cm³) at -70° C. The solution was stirred for 1 hour at -75° C. and 1-bromoethane (17.59 cm³, 0.1934 mol) was added slowly. The solution was allowed to warm to room temperature and then stirred overnight. Dilute hydrochloric acid (200 cm³, 20%) was added to the reaction mixture and

stirred for a further 10 minutes. Water (250 cm³) was added and the product extracted into diethyl ether (3×300 cm³). The combined organic extracts were dried (MgSO₄) and the solvent removed on a rotary evaporator. The resulting oil was cooled to room temperature and recrystallised with ethanol to yield white crystals (19.50 g, 68%, m.pt. 60–62° C.).

¹H NMR (DMSO) δ: 7.76 (2H, m), 7.51 (2H, m), 7.35 (4H, m), 1.51 (4H, quart), 0.30 (6H, t), IR ν_{max}/cm^{-1} : 3069, 2972, 1612, 1448, 1310, 761, 736. MS m/z: 222 (M⁺), 193, 152, 94, 82, 75.

2,7-Dibromo-9,9-diethylfluorene: Bromine (13.47 cm³, 0.2568 mol) was added to a stirred solution of 9,9-diethylfluorene (19.00 g, 0.0856 mol) in DCM (250 cm³). The HBr gas evolved was passed through a scrubbing solution of NaOH (1.5M). The reaction mixture was stirred for 4 hours. The reaction mixture was washed with sodium metabisulphite solution and extracted into diethyl ether (3×300 cm³). The combined organic extracts were dried and the solvent removed on a rotary evaporator. The crude product was recrystallised from ethanol to yield a white crystalline solid (20.00 g, 61%, m.pt. 152–154° C.).

¹H NMR (DMSO) δ: 7.52 (2H, m), 7.45 (4H, m), 1.99 (4H, quart), 0.31 (6H, t), IR ν_{max}/cm^{-1} : 2966, 1599, 1453, 1418, 1058, 772, 734. MS m/z: 380 (M⁺), 351, 272, 220, 189, 176, 165, 94, 87, 75.

4-Bromo-4'-octyloxybiphenyl: A mixture of 4-bromo-4'-hydroxybiphenyl (50.00 g, 0.2008 mol), 1-bromooctane (50.38 g, 0.2610 mol), potassium carbonate (47.11 g, 0.3414 mol) and butanone (500 cm³) was heated under reflux overnight. The cooled mixture was filtered and the solvent removed on a rotary evaporator. The crude solid was recrystallised from ethanol to yield a white crystalline solid (47.30 g, 66%, m.pt. 120° C.).

¹H NMR (DMSO) δ: 7.46 (6H, m), 6.95 (2H, m), 3.99 (2H, t), 1.80 (2H, quint), 1.38 (10H, m), 0.88 (3H, t), IR ν_{max}/cm^{-1} : 2927, 2860, 1608, 1481, 1290, 1259, 844. MS m/z: 362 (M⁺), 250, 221, 195, 182, 152, 139, 115, 89, 76, 69.

4-Octyloxybiphenyl-4'-yl boronic acid: A solution of n-butyllithium (50.97 cm³, 0.1274 mol, 2.5M in hexane) was added dropwise to a cooled (–78° C.) stirred solution of 4-bromo-4'-octyloxybiphenyl (40.00 g, 0.1108 mol) in THF (400 cm³). After 1 h, trimethyl borate (23.05 g, 0.2216 mol) was added dropwise to the reaction mixture maintaining a temperature of –78° C. The reaction mixture was allowed to warm to room temperature overnight. 20% hydrochloric acid (350 cm³) was added and the resultant mixture stirred for 1 h. The product was extracted into diethyl ether (3×300 cm³). The combined organic layers were washed with water (300 cm³), dried (MgSO₄), filtered and the filtrate evaporated down under partially reduced pressure. The crude product was stirred with hexane for 30 minutes and filtered off to yield a white powder (26.20 g, 73%, m.pt. 134–136° C.).

¹H NMR (DMSO) δ: 8.04 (2H, s), 7.84 (2H, m), 7.57 (4H, m), 7.00 (2H, m), 3.99 (2H, t), 1.74 (2H, quint), 1.35 (10H, m), 0.85 (3H, t), IR ν_{max}/cm^{-1} : 2933, 2860, 1608, 1473, 1286, 1258, 818. MS m/z: 326 (M⁺), 214, 196, 186, 170, 157, 128, 115, 77, 63

9,9-Diethyl-2,7-bis(4-octyloxybiphenyl-4'-yl)fluorene:

Tetrakis(triphenylphosphine)palladium(0) (0.70 g, 0.0006 mol) was added to a stirred solution of 2,7-dibromo-9,9-diethylfluorene (4) (2.33 g, 0.0061 mol), 4-octyloxybiphe-

nyl-4'-yl boronic acid (5.00 g, 0.0153 mol), 20% sodium carbonate solution (100 cm³) and 1,2-dimethoxyethane (150 cm³). The reaction mixture was heated under reflux overnight. Water (300 cm³) was added to the cooled reaction mixture and the product extracted into DCM (3×300 cm³). The combined organic extracts were washed with brine (2×150 cm³), dried (MgSO₄), filtered and the filtrate evaporated down under partially reduced pressure. The residue was purified by column chromatography on silica gel using DCM and hexane (30:70) as eluent and recrystallisation from ethanol and DCM to yield a white crystalline solid (3.10 g, 65%, m.pt. 146° C.).

¹H NMR (DMSO) δ: 7.77 (6H, m), 7.63 (12H, m), 7.00 (4H, m), 4.01 (4H, t), 2.13 (4H, quart), 1.82 (4H, quint), 1.40 (20H, m), 0.89 (6H, t), 0.43 (6H, t), IR ν_{max}/cm^{-1} : 3024, 2921, 2853, 1609, 1501, 1463, 1251, 808. MS m/z: 782 (M⁺), 669, 514, 485, 279, 145, 121, 107, 83, 71. CHN analysis: % Expected C (87.42%), H (8.49%). % Found C (87.66%), H (8.56%).

9,9-Diethyl-2,7-bis(4-hydroxybiphenyl-4'-yl)fluorene: Boron tribromide (99.9%, 1.05 cm³, 0.0111 mol) in DCM (10 ml) was added dropwise to a cooled (0° C.) stirred solution of 9,9-diethyl-2,7-bis(4-octyloxybiphenyl-4'-yl)fluorene (2.90 g, 0.0037 mol) in DCM (100 cm³). The reaction mixture was stirred at room temperature overnight, then poured onto an ice/water mixture (50 g) and stirred (30 minutes). The crude product was purified by column chromatography on silica gel with a mixture of ethyl acetate and hexane (30:70) as the eluent and recrystallisation from ethanol to yield a white powder (0.83 g, 40%, m.pt.>300° C.).

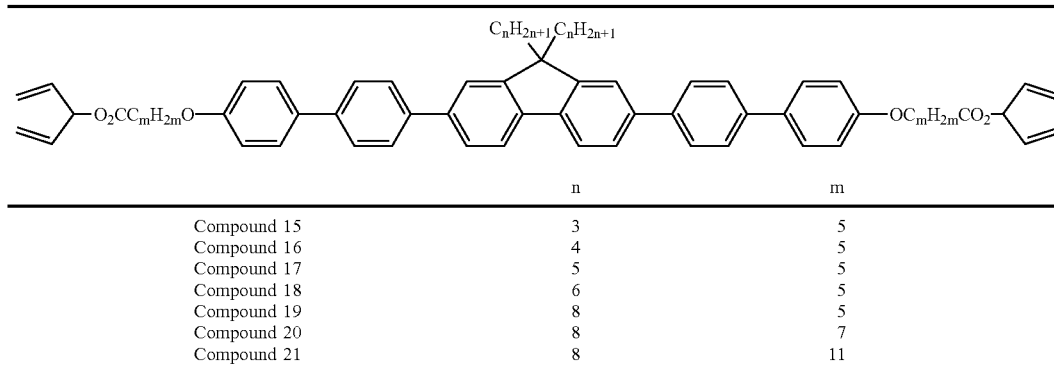
¹H NMR (DMSO) δ: 9.09 (2H, OH), 7.77 (6H, m), 7.64 (8H, m), 7.51 (4H, m), 6.94 (4H, m), 1.19 (4H, m), 0.42 (6H, t), IR ν_{max}/cm^{-1} : 1608, 1500, 1463, 1244, 1173, 811. MS m/z: 558 (M⁺), 529, 514, 313, 279, 257, 115, 77, 65.

Compound 14: 9,9-Diethyl-2,7-bis{4-[5-(1-vinyl-allyloxy-carbonyl)pentyloxy]biphenyl-4'-yl}fluorene: Compound 14 was synthesised as follows:

A mixture of 9,9-diethyl-2,7-bis(4-hydroxybiphenyl-4'-yl)fluorene (0.83 g, 0.0015 mol), 1,4-pentadienyl-3-yl 6-bromohexanoate (0.97 g, 0.0037 mol), potassium carbonate (0.62 g, 0.0045 mol) and DMF (25 cm³) was heated under reflux overnight. The cooled reaction mixture was added to water (500 cm³) and then extracted with DCM (3×50 cm³). The combined organic extracts were washed with water (250 cm³), dried (MgSO₄) and the filtrate evaporated down under partially reduced pressure. The crude product was purified by column chromatography using silica gel using a mixture of DCM and hexane (80:20) as the eluent and recrystallisation from DCM and ethanol to yield a white crystalline solid (0.2 g, 22%).

¹H NMR (CDCl₃) δ: 7.78 (6H, m), 7.62 (12H, m), 7.00 (4H, m), 5.85 (4H, m), 5.74 (4H, m), 5.27 (4H, m), 4.03 (4H, t), 2.42 (4H, t), 2.14 (4H, quart), 1.85 (4H, m), 1.74 (4H, m), 1.25 (4H, q), 0.43 (3H, t), IR ν_{max}/cm^{-1} : 3028, 2922, 2870, 1734, 1606, 1500, 1464, 1246, 1176, 812. CHN analysis: % Expected C (82.32%), H (7.24%). % Found C (81.59%), H (6.93%).

Compounds 15–21: Compounds 15 to 21, comprising the 2,7-bis{ω-[5-(1-vinyl-allyloxy-carbonyl) alkoxy]-4'-biphenyl]-9,9-dialkylfluorenes compounds of Table 1 were prepared analogously to Compound 8.



Compound 22: 4,7-bis{4-[(S)-3,7-Dimethyl-oct-6-enyloxy]phenyl}-2,1,3-benzothiadiazole

Compound 22 was synthesised as depicted in Reaction Scheme 8. Full details of each step follows:

4,7-Dibromo-2,1,3-benzothiadiazole: Bromine (52.8 g, 0.33 mol) was added to a solution of 2,1,3-benzothiadiazole (8.1 g, 0.032 mol) in hydrobromic acid (47%, 100 cm³) and the resultant solution was heated under reflux for 2.5 h. The cooled reaction mixture was filtered and the solid product washed with water (200 cm³) and sucked dry. The raw product was purified by recrystallisation from ethanol to yield 21.0 g (65%) of the desired product.

1-Bromo-4-[(S)-3,7-dimethyloct-6-enyloxy]benzene: A mixture of 4-bromophenol (34.6 g, 0.20 mol), (S)-(+)-citronellal bromide (50 g, 0.023 mol) and potassium carbonate (45 g, 0.33 mol) in butanone (500 cm³) was heated under reflux overnight. The cooled reaction mixture was filtered and the filtrate concentrated under reduced pressure. The crude product was purified by fractional distillation to yield 42.3 g (68.2%) of the desired product.

4-[(S)-3,7-Dimethyloct-6-enyloxy]phenyl boronic acid: 2.5M n-Butyllithium in hexanes (49.3 cm³, 0.12 mol) was added dropwise to a cooled (-78° C.) solution of 1-bromo-4-[(S)-3,7-dimethyloct-6-enyloxy]benzene (35 g, 0.11 mol) in tetrahydrofuran (350 cm³). The resultant solution was stirred at this temperature for 1 h and then trimethyl borate (23.8 g, 0.23 mol) was added dropwise to the mixture while maintaining the temperature at -78° C. 20% hydrochloric acid (250 cm³) was added and the resultant mixture was stirred for 1 h and then extracted into diethyl ether (2×200 cm³). The combined organic layers were washed with water (2×100 cm³) and dried (MgSO₄). After filtration the solvent was removed under reduce pressure to yield 20.35 g (65%) of the desired product.

4,7-bis{4-[(S)-3,7-Dimethyl-oct-6-enyloxy]phenyl}-2,1,3-benzothiadiazole: A mixture of tetrakis(triphenylphosphine)palladium(0) (0.8 g, 0.70×10⁻³ mol), 4,7-dibromo-2,1,3-benzothiadiazole (2) (2 g, 6.75×10⁻³ mol), 4-[(S)-3,7-dimethyloct-6-enyloxy]phenyl boronic acid (4.66 g, 1.70×10⁻² mol), 2M sodium carbonate solution (50 cm³) and 1,2-dimethoxyethane (150 cm³). The reaction mixture was heated under reflux overnight. The cooled reaction mixture was extracted with dichloromethane (2×150 cm³) and the combined organic layers were washed with brine (2×100 cm³) and dried (MgSO₄). After filtration the solvent was removed under reduced pressure and the residue was purified by column chromatography [silica gel, dichloromethane: hexane 1:4] followed by recrystallisation from ethanol to yield 3.2 g (79.5%) of the desired product.

4,7-bis(4-Hydroxyphenyl)-2,1,3-benzothiadiazole: Boron tribromide (1.51 cm³, 1.61×10⁻² mol) was added dropwise

to a cooled (0° C.) stirred solution of 2,5-bis{4-[(S)-3,7-dimethyl-oct-6-enyloxy]phenyl}-2,1,3-benzothiadiazole (4.0 g, 7.40×10⁻³ mol) in dichloromethane (100 cm³). The reaction mixture was stirred at room temperature overnight, then poured onto an ice/water mixture (200 g) and stirred (30 min). The desired product was precipitated and it was filtered off and sucked dry to yield 1.23 g (71.5%) of the desired product.

4,7-bis(4-{5-[1-Vinyl-allyloxy]carbonyl}pentyloxy)phenyl)-2,1,3-benzothiadiazole: A mixture of 2,5-bis(4-hydroxyphenyl)-2,1,3-benzothiadiazole (0.3 g, 0.93×10⁻³ mol), 1,4-pentadien-3-yl 5-bromopentanoate (0.61 g, 2.34×10⁻³ mol) and potassium carbonate (0.38 g, 2.79×10⁻³ mol) in N,N-dimethylformaldehyde (30 cm³) was heated (80° C.) overnight. The cooled reaction mixture was filtered and the filtrate concentrated under reduce pressure. The crude product was purified by column chromatography [silica gel, ethyl acetate:hexane 1:5] followed by recrystallisation from ethanol to yield 0.39 g (61.8%) of the desired product.

Compounds 23 and 24 are preparable by an analogous process.

Compound 25: Poly(4-[6-(methacryloyloxy)hexyloxy]benzoic acid 9,9-dioctyl-2-(4-nonylphenyl)fluoren-7-yl ester 4-[6-(methacryloyloxy)hexyloxy]benzoic acid 2-oxo-2H-chromen-7-yl ester:

Compound 25 was prepared as shown in Reaction Scheme 9. Full details of each step are as follows:

2-Bromo-9,9-dioctyl-7-hydroxyfluorene: 2.5M n-butyllithium in hexanes (20.0 cm³, 0.05 mol) was added dropwise to a solution of 2,7-dibromo-9,9-dioctylfluorene (20.0 g, 0.0364 mol) and tetrahydrofuran (300 cm³) maintaining a temperature of -70° C. After stirring for 1 h, trimethylborate (9.45 g, 0.09 mol) was added dropwise. After allowing the solution to reach RT, 20% hydrochloric acid (100 cm³) was added and the solution stirred for a further 1.5 h. The product was extracted into diethyl ether (2×100 cm³) and the combined extracts washed with water (2×100 cm³), dried (MgSO₄) and concentrated to a pale yellow oil. Diethyl ether (200 cm³) and hydrogen peroxide (30%, 100 cm³) were added and the solution heated under gentle reflux for 2.5 h with vigorous stirring. The ether layer was separated off and the aqueous layer extracted into diethyl ether (3×50 cm³). The combined organic layers were washed with saturated sodium metabisulphite solution (2×100 cm³), dried (MgSO₄), filtered and evaporated down under slightly reduced pressure to a pale yellow oil, which was purified by column chromatography [silica gel, dichloromethane:hex-

ane:ethanol 50:50:1] and recrystallisation from hexane to yield a white crystalline solid (yield 7.80 g, 45%), GC: 99%, mpt 110° C.

¹H NMR (CDCl₃) δ_H: 0.62 (6H, t), 0.82 (4H, m), 1.1 (20H, m), 1.86 (4H, t), 4.70 (1H, s), 6.77 (2H, m), 7.43 (2H, d), 7.50 (2H, d), IR ν_{max}/cm⁻¹: 3471, 3388, 2927.6, 2849, 1611, 1452, 1234, 1180, 816, 528. MS m/z: 486, 484 (M⁺), 422, 211, 197, 122.

2-Bromo-9,9-dioctyl-7-octyloxyfluorene: A mixture of 2-bromo-9,9-dioctyl-7-hydroxyfluorene (6.00 g, 0.0124 mol), 1-bromooctane (3.104 g, 0.0161 mol), potassium carbonate (3.41 g, 0.0247 mol) and butanone (100 cm³) was heated under reflux overnight. The cooled mixture was filtered and evaporated down under reduced pressure. The crude product was purified by column chromatography [silica gel, dichloromethane: hexane: 1:1] and then used without further purification (yield 5.04 g, 68.3%), GC: 99%.

¹H NMR (CDCl₃) δ_H: 0.6 (6H, t), 0.82 (4H, m), 0.89 (6H), 1.2 (25H, m), 1.49 (4H, sext), 1.85 (4H, m), 4.0 (2H, t), 6.85 (2H, m), 7.42 (2H, m), 7.53 (2H, d) MS m/z: 598, 596 (M⁺), 519, 404, 292, 194.

9,9-Dioctyl-2-(4-nonylphenyl)-7-octyloxyfluorene: A mixture of tetrakis(triphenylphosphine)palladium(0) (0.5 g, 4.64×10⁻⁴ mol), 2-bromo-9,9-dioctyl-7-octyloxyfluorene (5.04 g, 0.00844 mol), 4-nonylphenylboronic acid (2.30 g, 0.00929 mol), 20% aqueous sodium carbonate solution (40 cm³) and N,N-dimethylformamide (150 cm³) was heated under reflux overnight. The reaction mixture was filtered and extracted into diethyl ether (2×100 cm³). The combined organic layers were washed with water (2×100 cm³), dried (MgSO₄), filtered and the solvent removed under partially reduced pressure. The residue was purified by column chromatography [silica gel, dichloromethane: hexane: 30:70] (yield 3.65 g, 60.0%).

¹H NMR (CDCl₃) δ_H: 0.66 (4H, t), 0.85 (14H, dt), 1.11 (20H, m), 1.3 (23H, t), 1.5 (2H, quint), 1.65 (2H, quint), 1.87 (6H, m), 2.65 (2H, t), 4.2 (2H, t), 6.87 (2H, d), 7.26 (2H, d), 7.55 (6H, m). MS m/z: 720 (M⁺), 608, 283.

9,9-Dioctyl-2-hydroxy-7-(4-Nonylphenyl)fluorene: A 1 M solution of boron tribromide in dichloromethane, (0.55 cm³, 0.00581 mol) was added dropwise to a stirred solution of 9,9-dioctyl-2-(4-nonylphenyl)-7-octyloxyfluorene (2.79 g, 0.00388 mol) and dichloromethane (100 cm³) at 0° C. The temperature was allowed to rise to RT overnight and the solution added to ice-water (200 cm³) with vigorous stirring. The product was extracted into diethyl ether (2×200 cm³). The combined organic extracts were washed with saturated aqueous sodium carbonate solution (150 cm³), dried (MgSO₄), filtered and the solvent removed under reduced pressure. The residue was purified by column chromatography [silica gel, dichloromethane:hexane: 20:80] (yield 2.2 g, 93.4%).

¹H NMR (CDCl₃) δ_H: 0.66 (4H, t), 0.84 (9H, m), 1.10 (20H, m), 1.30 (12H, d), 1.65 (2H, quint), 1.94 (4H, m), 2.65 (2H, t), 4.79 (1H, s), 6.80 (2H, m), 7.26 (2H, d), 7.56 (6H, m). IR ν_{max}/cm⁻¹: 2900, 2850, 1450, 1250, 750. MS (m/z): 602 (M⁺), 495, 406, 283.

4-[6-(Methylacryloyloxy)hexyloxy]benzoic acid 9,9-dioctyl-2-(4-nonylphenyl)fluoren-7-yl ester: A solution of N,N-dicyclohexylcarbodiimide (0.34 g, 0.0017 mol) in dichloromethane (20 cm³) was added to a solution of 9,9-dioctyl-2-hydroxy-7-(4-nonylphenyl)fluorene (1.0 g, 0.0017 mol), 4-[6-(methylacryloyloxy)hexyloxy]benzoic acid (0.5 g, 0.0017 mol), 4-(N,N-dimethyl)pyridine (0.2 g, 0.0017 mol) and dichloromethane (10 cm³) at room temperature. The reaction mixture was stirred overnight, filtered and the filtrate evaporated down under reduced pressure. The crude product was purified by column chromatography [silica gel, dichloromethane:hexane:60:40] (yield 0.15 g, 10.1%).

¹H NMR (CDCl₃) δ_H: 0.69 (3H, s), 0.85 (9H, m), 1.13 (26H, quint), 1.3 (24H, d), 1.58 (2H, d), 1.95 (4H, quint), 2.1 (3H, s), 2.66 (2H, t), 5.77 (1H, t), 6.38 (1H, s), 7.1 (2H, d), 7.23 (6H, d), 7.56 (4H, m), 7.69 (2H, m). IR ν_{max}/cm⁻¹: 2900, 2850, 1720, 1450, 1150, 800. MS m/z: 789 (M100), 681, 677.

Poly(4-[6-(methylacryloyloxy)hexyloxy]benzoic acid 9,9-dioctyl-2-(4-nonylphenyl)fluoren-7-yl ester 4-[6-(methylacryloyloxy)hexyloxy]benzoic acid 2-oxo-2H-chromen-7-yl ester: A solution of 4-[6-(methylacryloyloxy)hexyloxy]benzoic acid 9,9-dioctyl-2-(4-nonylphenyl)fluoren-7-yl ester (0.10 g, 1.11×10⁻⁴ mol), 4-[6-(methylacryloyloxy)hexyloxy]benzoic acid 2-oxo-2H-chromen-7-yl ester (0.10 g, 2.22×10⁻⁴ mol), 1,1'-azobis(cyclohexanecarbonitrile) (0.05 g) and toluene (10 cm³) was heated under reflux overnight. The reaction mixture was evaporated down and the residue taken up in a minimum of dichloromethane. The resultant solution was poured into methanol (100 cm³) and the resultant precipitate filtered off and dried by suction. This procedure was repeated several times before drying the product under vacuum to yield the desired copolymer.

Compound 26: Poly 2-Methylacrylic acid 6-(4-benzothiazol-2-yl)-2,6-dimethoxyphenoxy]hexyl ester 4-[6-(methylacryloyloxy)hexyloxy]benzoic acid 2-oxo-2H-chromen-7-yl ester

Compound 26 was prepared by copolymerisation of 2-Methylacrylic acid 6-(4-benzothiazol-2-yl)-2,6-dimethoxyphenoxy]hexyl ester with 4-[6-(methylacryloyloxy)hexyloxy]benzoic acid 2-oxo-2H-chromen-7-yl ester in a method analogous to the copolymerisation step of Compound 25.

The initial reaction steps are shown in Reaction Scheme 10 and full details are provided below.

2-(3,4,5-Trimethoxyphenyl)benzothiazole: A solution of 3,4,5-trimethoxybenzaldehyde (19.7 g, 0.1 mol), 2-aminobenzenethiol (11.2 cm³, 0.105 mol) and dimethylsulfoxide acid (75 cm³) was heated under reflux for 24 hours. The cooled solution was added to water and extracted into ethyl acetate (3×50 cm³). The combined organic layers were dried (MgSO₄), filtered and the filtrate evaporated down under reduced pressure. The solid residue was recrystallised from ethyl acetate to give 25.5 g (85.0%) of the desired product, mpt. 135° C.

¹H NMR (CDCl₃) δ_H: 3.83 (3H, s), 3.95 (6H, s), 7.33 (2H, s), 7.41 (1H, td), 7.51 (1H, td), 7.99 (1H, d), 8.02 (1H, d). Elemental analysis: Calculated: C, 63.77, H, 5.02, N, 4.65, S, 10.64; Found: C, 63.54; H, 5.02; N, 4.65, S, 10.70%.

2-(4-Hydroxy-3,5-dimethoxyphenyl)benzothiazole: A solution of 2-(3,4,5-trimethoxyphenyl)benzothiazole (4.0 g), aluminium trichloride (4.0 g) and carbon disulphide (75 cm³) was stirred at room temperature overnight. The reaction mixture was poured onto 20% hydrochloric acid (500 cm³) and extracted with ethyl acetate (3×50 cm³). The combined organic extracts were washed with water (2×250 cm³), dried (MgSO₄), filtered and the filtrate evaporated down under reduced pressure. The solid residue was recrystallised from ethyl acetate to give 3.0 g (75.0%) of the desired product.

¹H NMR (CDCl₃) δ_H: 3.97 (6H, s), 7.33 (2H, s), 7.35 (1H, td), 7.47 (1H, td), 7.86 (1H, d), 8.03 (1H, d).

6-[4-(Benzothiazol-2-yl)-3,5-dimethoxyphenoxy]hexan-1-ol: A solution of sodium hydroxide (0.4 g, 0.01 mol) in water (10 cm³) was added dropwise to a solution of 2-(4-hydroxy-3,5-dimethoxyphenyl)benzothiazole (1.20 g, 0.0042 mol) in methanol (100 cm³). The 6-bromohexanol (1.00 g, 0.0055 mol) was then added dropwise, followed by the potassium iodide (0.06 g, 0.0037 mol) in one portion. The reaction mixture was heated under reflux overnight and the poured onto a mixture of water (100 cm³) and 10% hydrochloric acid (20 cm³). The resultant white precipitate

was filtered off, pressed dry and recrystallised from ethanol to yield 1.1 g (67.9%) of the desired alcohol.

¹H NMR (CDCl₃) δ_H: 1.2–1.68 (8H, m), 1.72–1.87 (2H, t), 3.62–3.70 (2 H, t), 3.90–4.0 (6H, s), 5.28–5.32 (1H, s), 7.33 (2H, s), 7.37–7.39 (1H, dd), 7.43–7.51 (1H, dd), 7.83–7.90 (1H, d), 8.01–8.08 (1H, d). IR ν_{max}/cm⁻¹: 3450, 2920, 2368, 1609, 1451, 1360, 1257, 807. MS m/z: 387 (M⁺), 287 (M100), 272, 241, 212, 172, 140, 115, 83, 69. Elemental analysis: Calculated: C, 65.09; H, 6.50; N, 3.61, S, 8.28;

Found:

2-Methylacrylic acid 6-(4-benzothiazol-2-yl-2,6-dimethoxyphenoxy)hexyl ester: A solution of 6-(4-benzothiazol-2-yl-2,6-dimethoxy-phenoxy)hexan-1-ol (1.10 g, 0.0038 mol), methacrylic acid (1.30 g, 0.015 mol) of p-toluenesulfonic acid (0.10 g, 0.0005 mol), hydroquinone (0.10 g, 0.0009 mol) and toluene (50 cm³) was heated under reflux for 48 hours in a Dean and Stark apparatus to remove water continuously and then allowed to cool. The solvent was removed under reduced pressure and the residue dissolved into diethyl ether (100 cm³). The resultant solution was washed with water (20 cm³), dried (Na₂SO₄), filtered and then evaporated down under slightly reduced pressure. The residue was recrystallised from methanol to yield 1.16 g (67.1%) of the desired product. A small amount of 2,6-di-tert-butyl-4-methylphenol was added to act as an inhibitor to prevent spontaneous polymerisation.

¹H NMR (CDCl₃) δ_H: 1.26–1.30 (8H, m), 1.68–1.83 (2H, t), 1.95–2.00 (3H, s), 4.01 (6H, s), 4.15–4.20 (2H, t), 5.66–5.70 (1H, d), 6.23–6.28 (1H, d), 7.33 (2H, s), 7.37–7.40 (1H, dd), 7.45–7.52 (1H, dd), 7.86–7.91 (1H, d), 8.05–8.10 (1H, d). IR ν_{max}/cm⁻¹: 3440, 2920, 2370, 1610, 1450, 1350, 1257, 812. MS m/z: 455 (M⁺), 401, 306, 287 (M100), 272, 244, 201, 173, 144, 108, 86, 69. Elemental analysis:

Calculated: C, 65.91; H, 6.42; N, 3.07, S, 7.04. Found:

Compound 27: Poly 2-Methylacrylic acid 6-(4-benzothiazol-2-yl-2,6-dimethoxyphenoxy)hexyl ester 2-Methylacrylic acid 6-[4-[6-(4-nonylphenyl)benzothiazol-2-yl]phenoxy]hexyl ester

Compound 27 was prepared by copolymerisation of 2-Methylacrylic acid 6-(4-benzothiazol-2-yl-2,6-dimethoxyphenoxy)hexyl ester with 2-Methylacrylic acid 6-[4-[6-(4-nonylphenyl)benzothiazol-2-yl]phenoxy]hexyl ester in a method analogous to the copolymerisation step of Compound 25.

The initial reaction steps are shown in Reaction Scheme 11 and full details are provided below.

4-Dodecyloxybenzaldehyde: A mixture of 1-bromododecane (43.5 g, 0.22 mol), 4-hydroxybenzaldehyde (25 g, 0.20 mol), potassium carbonate (69 g, 0.5 mol) and butanone (500 cm³) was heated under reflux for 24 hours. The cooled solution was filtered and the filtrate evaporated down under reduced pressure. The crude product was then distilled at 142° C.@0.6 mmHg, to give a liquid, which crystallised on cooling to yield 39.2 g (67.6%) of a white solid.

¹H NMR (CDCl₃) δ_H: 0.85–0.91 (3H, t), 1.20–1.50 (18H, m), 1.76–1.85 (2H, quin), 4.00–4.20 (2H, t), 6.90–7.00 (2H, d), 7.80–7.90 (2H, d), 9.90–9.92 (1H, s), IR ν_{max}/cm⁻¹: 3440, 2918, 1610, 1261, 968, 834. MS m/z: 290 (M⁺), 201, 163, 135, 123(M100), 105, 97, 85, 71. Elemental analysis: Calculated: C, 78.57, H, 10.41;

Found: C, 78.28, H, 10.70%.

2-(4-Dodecyloxyphenyl)benzothiazole: A solution of 4-dodecyloxybenzaldehyde (37.12 g, 0.128 mol), 2-aminobenzenethiol (16 g, 0.128 mol) and dimethylsulfoxide acid (200 cm³) was heated under reflux for 24 hours. The cooled solution was added to water and extracted into dichloromethane (3×50 cm³). The combined organic layers

were dried (MgSO₄), filtered and the filtrate evaporated down under reduced pressure. The solid residue was recrystallised from ethanol to give 23.1 g (45.7%) of the desired product.

¹H NMR (CDCl₃) δ_H: 0.85–0.91 (3H, t), 1.20–1.40 (14H, m), 1.42–1.52 (2H, quin), 1.60 (2H, s), 1.78–1.86 (2H, quin), 4.00–4.08 (2H, t), 6.96–7.04 (2H, d), 7.32–7.40 (1H, dd), 7.44–7.52 (1H, d), 7.85–7.93 (1H, dd), 8.00–8.05 (2H, d), 8.10 (1H, d). IR ν_{max}/cm⁻¹: 3440, 2918, 2360, 1610, 1261, 968, 834. MS m/z: 395(M⁺), 228, 227(M100), 198, 149, 105, 97, 77, 69. Elemental analysis: Calculated: C, 75.90, H-8.41, N, 3.54, S, 8.11; Found: C, 73.19, H, 8.69, N-3.55, S, 8.29%.

6-Bromo-2-(4-dodecyloxyphenyl)benzothiazole: Bromine was added dropwise to a solution of 2-(4-dodecyloxyphenyl)benzothiazole (20 g, 0.059 mol) and acetic acid (1,000 cm³). The reaction mixture was then heated for a further 6 h. The cooled reaction mixture was then added to aqueous sodium metabisulphite solution (1,000 cm³). The product was extracted using diethyl ether (3×100 cm³). The combined organic layers are washed with concentrated sodium carbonate solution (2×100 cm³) and then with water (1×100 cm³), dried (MgSO₄), filtered and then evaporated down under partially reduced pressure. The crude product was purified using column chromatography, using a 50:50 mixture of dichloromethane/hexane an eluent to yield 2.7 g (9.6%) of the desired product.

¹H NMR (CDCl₃) δ_H: 0.85–0.91 (3H, t), 1.20–1.40 (16H, m), 1.42–1.52 (2H, quin), 1.78–1.86 (2H, quin), 4.0–4.05 (2H, t), 6.96–7.01 (2H, d), 7.53–7.60 (1H, dd), 7.84–7.88 (1H, d), 7.97–8.00 (2H, d), 8.02 (1H, d). IR ν_{max}/cm⁻¹: 3440, 2918, 2360, 1610, 1261, 968, 834. MS m/z: 475, 473 (M⁺), 395, 305(M100), 227, 197, 149, 111, 97, 83, 69. Elemental analysis: Calculated: C, 63.28; H, 6.80; N, 2.95, S, 6.76; Found: C, 63.54; H, 6.99; N, 2.95, S, 6.85%.

2-(4-Dodecyloxyphenyl)-6-(4-nonylphenyl)benzothiazole: A mixture of tetrakis(triphenylphosphine)palladium(0) (0.30 g, 0.26×10⁻³ mol), 6-bromo-2-(4-dodecyloxyphenyl)benzothiazole (2.50 g, 5.27×10⁻³ mol), 4-nonylbenzene boronic acid (1.57 g, 6.33×10⁻³ mol), 2M sodium carbonate solution (25 cm³) and 1,2-dimethoxyethane (100 cm³). The reaction mixture was heated under reflux overnight. The cooled reaction mixture was extracted with dichloromethane (2×100 cm³) and the combined organic layers were washed with brine (2×100 cm³) and dried (MgSO₄). After filtration the solvent was removed under reduced pressure and the residue was purified by column chromatography [silica gel, dichloromethane: hexane 1:1] followed by recrystallisation from ethanol to yield 2.35 g (74.5%) of the desired product.

2-(4-Hydroxyphenyl)-6-(4-nonylphenyl)benzothiazole: Boron tribromide (0.53 cm³, 5.65×10⁻³ mol) was added dropwise to a cooled (0° C.) stirred solution of 2-(4-dodecyloxyphenyl)-6-(4-nonylphenyl)benzothiazole (2.25 g, 3.76×10⁻³ mol) in dichloromethane (100 cm³). The reaction mixture was stirred at room temperature overnight, then poured onto an ice/water mixture (200 g) and stirred (30 min). The reaction mixture was extracted with dichloromethane (2×75 cm³) and the combined organic layers were washed with brine (2×100 cm³) and dried (MgSO₄). After filtration the solvent was removed under reduced pressure and the residue was purified by column chromatography [silica gel, ethyl acetate:hexane 1:1] followed by recrystallisation from ethyl acetate to yield 1.25 g (77.3%) of the desired product.

6-[4-[6-(4-Nonylphenyl)benzothiazol-2-yl]phenoxy]hexan-1-ol: A solution of sodium hydroxide (0.08 g, 0.0020 mol) in water (20 cm³) was added dropwise to a solution of 4-[6-(4-nonylphenyl)benzothiazol-2-yl]phenol (0.42 g, 0.0010 mol) in methanol (50 cm³). The 6-bromo-hexanol (0.18 g, 0.001 mol) was then added dropwise,

followed by the potassium iodide (0.02 g, 0.00125 mol) in one portion. The reaction mixture was heated under reflux overnight and the poured onto a mixture of water (100 cm³) and 10% hydrochloric acid (20 cm³). The resultant precipitate was filtered off and recrystallised from ethanol to yield 0.31 g (62%) of the pure compound.

¹H NMR (CDCl₃) δ_H: 0.85–0.91 (3H, t), 1.20–1.40 (16H, m), 1.60–1.80 (6H, m), 2.60–2.70 (2H, t), 3.65–3.80 (2H, tt), 4.00–4.08 (2H, t), 6.50–6.60 (1H, s), 6.90–7.00 (2H, d), 7.20–7.28 (1H, d), 7.30–7.32 (1H, d), 7.53–7.60 (2H, d), 7.65–7.74 (1H, dd), 7.95–8.02 (2H, d), 8.03–8.10 (2H, d). IR ν_{max}/cm⁻¹: 3402, 2920, 2368, 1609, 1451, 1257, 807, 521. MS m/z: 529 (M⁺), 429, 329, 316(M100), 287, 197, 158, 139, 91, 77, 69. Elemental analysis: Calculated: C, 77.08; H, 8.18; N, 2.64, S, 6.05; Found: C, 74.50; H, 7.14; N, 3.15, S, 6.57%.

2-Methacrylic acid 6-{4-[6-(4-nonylphenyl)benzothiazol-2-yl]phenoxy}hexyl ester: A solution of 6-{4-[6-(4-nonylphenyl)benzothiazol-2-yl]phenoxy}hexan-1-ol (0.3 g, 0.0006 mol), methacrylic acid (0.2 g, 0.0023 mol), p-toluenesulfonic acid (0.015 g, 0.0008 mol), hydroquinone (0.015 g, 0.0002 mol) and toluene (50 cm³) was heated under reflux for 48 hours in a Dean and Stark apparatus to remove water continuously and then allowed to cool. The solvent was removed under reduced pressure and the residue dissolved into diethyl ether (50 cm³). The resultant solution was washed with water (20 cm³), dried (Na₂SO₄), filtered and then evaporated down under slightly reduced pressure. The residue was recrystallised from methanol to yield 0.05 g (14.7%) of the desired product. A small amount of 2,6-di-tert-butyl-4-methylphenol was added to act as an inhibitor to prevent self polymerisation.

¹H NMR (CDCl₃) δ_H: 0.80–0.90 (3H, t), 1.10–1.40 (16H, m), 1.45–1.80 (6H, m), 1.95–2.00 (3H, s), 2.68–2.72 (2H, t), 4.05–4.10 (2H, tt), 4.15–4.22 (2H, t), 5.65–5.71 (1H, s), 5.68–5.72 (1H, s), 6.20–6.24 (1H, s), 6.92–7.00 (2H, d), 7.25–7.28 (2H, d), 7.29–7.31 (1H, d), 7.55–7.60 (1H, d), 7.68–7.72 (1H, dd), 7.99–8.03 (2H, d), 8.04–8.08 (2H, d). IR ν_{max}/cm⁻¹: 2920, 2370, 1602, 1454, 1257, 806. MS m/z: 597 (M⁺), 544, 497, 429 (M100), 316, 287, 197, 158, 105, 97, 69. Elemental analysis:

Calculated: C, 76.34; H, 7.92; N, 2.34, S, 5.36; Found: C, 76.12; H, 8.82; N, 1.48, S, 3.16%.

Thin Film Polymerisation and Evaluation

Thin films of Compounds 9 to 12 and Compounds 15 to 21 were prepared by spin casting from a 0.5%–2% M solution in chloroform onto quartz substrates. All sample processing was carried out in a dry nitrogen filled glove box to avoid oxygen and water contamination. The samples were subsequently baked at 50° C. for 30 minutes, heated to 90° C. and then cooled at a rate of 0.2° C. to room temperature to form a nematic glass. Polarised microscopy showed that no change was observed in the films over several months at room temperature. The films were polymerized in a nitrogen filled chamber using light from an Argon Ion laser. Most of the polymerization studies were carried out at 300 nm with a constant intensity of 100 MWcm⁻² and the total fluence varied according to the exposure time. No photoinitiator was used. Temperature dependent polymerization studies were carried out in a Linkham model LTS 350 hot-stage driven by a TP 93 controller under flowing nitrogen gas. A solubility test was used to find the optimum fluence: different regions of the film were exposed to UV irradiation with different fluences and the film was subsequently washed in chloroform for 30 s. The unpolymerized and partially polymerized regions of the film were washed away and PL from the remaining regions was observed on excitation with an expanded beam from the Argon Ion laser. Optical absorbance measurements were made using a Unicam 5625

UV-VIS spectrophotometer. PL and EL were measured in a chamber filled with dry nitrogen gas using a photodiode array (Ocean Optics S2000) with a spectral range from 200 nm to 850 nm and a resolution of 2 nm. Films were deposited onto CaF₂ substrates for Fourier Transform infrared measurements, which were carried out on a Perkin Elmer Paragon 1000 Spectrometer. Indium tin oxide (ITO) coated glass substrates, (Merck 15 Ω/Q) were used for EL devices. These were cleaned using an Argon plasma.²⁰ A PDOT (EL-grade, Bayer) layer of thickness 45 nm±10% was spin-cast onto the substrate and baked at 165° C. for 30 minutes. This formed a hole-transporting film. One or more organic films of thickness ≈45 nm were subsequently deposited by spin-casting and crosslinked as discussed below. Film thicknesses were measured using a Dektak surface profiler. Aluminum was selectively evaporated onto the films at a pressure less than 1×10⁻⁵ torr using a shadow mask to form the cathode.

Photopolymerisation Details

The optimum fluences required in order to polymerize the diene monomers (Compounds 9 to 12) efficiently with a minimum of photodegradation, were found to be 100 Jcm⁻², 20 Jcm⁻², 100 Jcm⁻² and 300 Jcm⁻² respectively, using the solubility test. As Scheme 6 shows, the 1,6-heptadiene monomer (e.g. Compound 10) forms a network with a repeat unit containing a single ring. Its polymerization rate is equal to that of the 1,4-pentadiene monomer (e.g. Compounds 9 and 11) but the increase of PL intensity after polymerization is less for Compound 10. This may be because of the increased flexibility of the C₇ ring in the backbone of the crosslinked material. The 1,4-pentadiene diene monomers (Compounds 9 and 11) are homologues and differ only in the length of the flexible alkoxy-spacer part of the end-groups. The PL spectrum of Compound 11 with the shorter spacer is significantly different to all other materials before exposure suggesting a different conformation. The higher fluence required to polymerize the 1,4-pentadiene monomer Compound 11 implies that the polymerization rate is dependent on the spacer length: the freedom of motion of the photopolymerizable end-group is reduced, because of the shorter aliphatic spacer in Compound 11. The diallylamine monomer Compound 12 has a significantly different structure to the dienes. It is much more photosensitive than the other diene monomers because of the activation by the electron rich nitrogen atom. Scheme 6 also shows (by way of comparison) that when a methacrylate monomer is employed the polymerization step does not involve the formation of a ring.

Photopolymerization Characteristics

The absorbance and PL spectra of 1,4-pentadiene monomer (Compound 9) were measured before and after exposure with the optimum UV fluence of 100 J cm⁻². The latter measurements were repeated after washing in chloroform for 30 s. The absorbance spectra of the unexposed and exposed films are almost identical and the total absorbance decreases by 15% after washing indicating that only a small amount of the material is removed. This confirms conclusively that a predominantly insoluble network is formed.

The UV irradiation was carried out in the nematic glass phases at room temperature at 300 nm. The excitation of the fluorene chromophore is minimal at this wavelength and the absorbance is extremely low. The experiment was repeated using a wavelength of 350 nm near the absorbance peak. Although the number of absorbed photons is far greater at 350 nm, a similar fluence is required to form an insoluble network. Furthermore excitation at 350 nm results in some photodegradation. UV photopolymerization was also carried out at 300 nm at temperatures of 50° C., 65° C. and 80° C. all in the nematic phase. It was anticipated that the poly-

merization rate would increase, when the photoreactive mesogens were irradiated in the more mobile nematic phase. However, the fluence required to form the crosslinked network was independent of temperature, within the resolution of our solubility test. Furthermore, the integrated PL intensity from the crosslinked network decreases with temperature indicating a temperature dependent photodegradation.

Bilayer Electroluminescent Devices

Bilayer electroluminescent devices were prepared by spin-casting the 1,4-pentadiene monomer (Compound 9) onto a hole-transporting PEDT layer. The diene functioned as the light-emitting and electron-transporting material in the stable nematic glassy state. Equivalent devices using cross-linked networks formed from Compound 9 by photopolymerisation with UV were also fabricated on the same substrate under identical conditions and the EL properties of both types of devices evaluated and compared. The fabrication of such bilayer OLEDs is facilitated by the fact that the hole-transporting PEDT layer is insoluble in the organic solvent used to deposit the electroluminescent and electron-transporting reactive mesogen (Compound 9). Half of the layer of Compound 9 was photopolymerized using optimum conditions and the other half was left unexposed so that EL devices incorporating either the nematic glass or the cross-linked polymer network could be directly compared on the same substrate under identical conditions. Aluminum cathodes were deposited onto both the cross-linked and non cross-linked regions. Polarized electroluminescent devices were prepared by the polymerization of uniformly aligned Compound 9 achieved by depositing it onto a photoalignment layer doped with a hole transporting molecule. In these devices external quantum efficiencies of 1.4% were obtained for electroluminescence at 80 cd m^{-2} . Three layer devices were also prepared by spin-casting an electron transporting polymer (Compound 13), which shows a broad featureless blue emission, on top of the crosslinked nematic polymer network. In the case of both the three layer and bilayer devices the luminescence originates from the cross-linked polymer network of the 1,4-pentadiene monomer (Compound 9). The increased brightness of the three-layer device may result from an improved balance of electron and hole injection and/or from a shift of the recombination region away from the absorbing cathode.

Multilayer Device

A multilayer device configuration was implemented as illustrated in FIG. 2. A glass substrate **30** (12 mm×12 mm×1 mm) coated with a layer of indium tin oxide **32** (ITO) was cleaned via oxygen plasma etching. Scanning electron microscopy revealed an improvement in the surface smoothness by using this process which also results in a beneficial lowering of the ITO work function. The ITO was coated with two strips (~2 mm) of polyimide **34** along opposite edges of the substrate then covered with a polyethylene dioxythiophene/polystyrene sulfonate (PEDT/PSS) EL-grade layer **36** of thickness $45 \pm 5 \text{ nm}$ deposited by spin-coating. The layer **36** was baked at 165° C. for 30 min in order to cure the PEDT/PSS and remove any volatile contaminants. The doped polymer blend of Compounds 2 and 8 was spun from a 0.5% solution in cyclopentanone forming an alignment layer **40** of thickness ~20 nm. This formed the hole-injecting aligning interface after exposure to linearly polarized CV from an argon ion laser tuned to 300 nm. A liquid-crystalline luminescent layer **50** of Compound 9 was then spun cast from a chloroform solution forming a film of ~10 nm thickness. A further bake at 50° C. for 30 min was employed to drive off any residual solvent. The sample was heated to 100° C. and slowly cooled at 02° C./min to room temperature to achieve macroscopic alignment of chromophores in

the nematic glass phase. Irradiation with UV light at 300 nm from an argon ion laser was used to induce crosslinking of the photoactive end-groups of the Compound 9 to form an insoluble and intractable layer. No photoinitiator was used hence minimizing continued photoreaction during the device lifetime. Aluminium electrodes **50** were vapor-deposited under a vacuum of 10° mbar or better and silver paste dots **52** applied for electrical contact. A silver paste contact **54** was also applied for contact with the indium tin oxide base electrode. This entire fabrication process was carried out under dry nitrogen of purity greater than 99.99%. Film thickness was measured using a Dektak ST surface profiler.

The samples were mounted for testing within a nitrogen-filled chamber with spring-loaded probes. The polyimide strips form a protective layer preventing the spring-loaded test probes from pushing through the various layers. Optical absorbance measurements were taken using a Unicam UV-vis spectrometer with a polarizer (Ealing Polarcoat 105 UV-vis code 23-2363) in the beam. The spectrometer's polarization bias was taken into account and dichroic ratios were obtained by comparing maxima at around 370–380 nm.

Luminescence/voltage measurements were taken using a photomultiplier tube (EMI 6097B with S11 type photocathode) and Keithley 196 multimeter with computer control. Polarized EL measurements were taken using a photodiode array (Ocean Optics S2000, 200–850 nm bandwidth 2 nm resolution) and polarizer as described above. The polarization bias of the spectrometer was eliminated by use of an input fiber (fused silica 100 μm diameter) ensuring complete depolarisation of light into the instrument.

Monochrome Backlight

FIG. 3 shows a schematic representation of a polarised light monochrome backlight used to illuminate a twisted nematic liquid crystal display. The arrows indicate the polarisation direction. An inert substrate **30** (e.g. glass coated with a layer of indium tin oxide (ITO) as in FIG. 2) is provided with a layer **50** of a polarised light emitting polymer (e.g. comprising Compound 9 as in FIG. 2). The assembly further includes a clean up polariser **60** comprising a high transmission low polarisation efficiency polariser; a twisted nematic liquid crystal display **70**; and a front polariser **80**. It will be appreciated that the light emitting polymer layer **50** acts as a light source for the liquid crystal display **70**.

Polarised Light Sequential Tricolor Backlight

FIG. 3 schematic of a polarised light sequential red, green and blue light emitting backlight used to illuminate a fast liquid crystal display (ferroelectric display). The arrows indicate the polarisation direction. An inert substrate **30** (e.g. glass coated with a layer of indium tin oxide (ITO) as in FIG. 2) is respectively provided with red **52**, green **54** and blue **56** striped layers of a polarised light emitting polymer (e.g. comprising Compound 9 as in FIG. 2 and a suitable dye molecule as a dopant). The assembly further includes a clean up polariser **60** comprising a high transmission low polarisation efficiency polariser; a fast (ferroelectric) liquid crystal display **70**; and a front polariser **80**. It will be appreciated that the striped light emitting polymer layer **52**, **54**, **56** acts as a light source for the fast liquid crystal display **70**. The sequential emission of the RGB stripes corresponds with the appropriate colour image on the fast liquid crystal display. Thus, a colour display is seen.

Alignment Characteristics

The PL polarization ratio ($PL_{\parallel}/PL_{\perp}$) of the aligned polymer formed from Compound 9 in its nematic glass phase can be taken as a measure of the alignment quality. Optimum

alignment is obtained with the undoped alignment layer for an incident fluence of 50 mJ cm^{-2} . The alignment quality deteriorates when higher fluences are used. This is expected because there are competing LC-surface interactions giving parallel and perpendicular alignment respectively. When the dopant concentration is 40% or higher there is a detrimental effect on alignment. However with concentrations up to 30% the polarization ratio of emitted light is not severely effected although higher fluences are required to obtain optimum alignment. The EL intensity reaches its peak for the ~50% mixture. A 30% mixture offers a good compromise in balancing the output luminescence intensity and polarization ratio. From these conditions and using the 30% doped layer we have observed strong optical dichroism in the absorbance (D~6.5) and obtained PL polarization ratios of 8:1.

Electroluminescence Characteristics

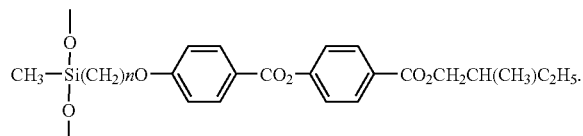
Devices made with Compound 9 in the nematic glassy state showed poor EL polarization ratios because the low glass transition temperature compromised the alignment stability. Much better performance was achieved when compound 9 was crosslinked.

A brightness of 60 cd m^{-2} (measured without polarizer) was obtained at a drive voltage of 11V. The threshold voltage, EL polarization ratio and intensity all depend on the composition of the alignment layer. A luminance of 90 cd m^{-2} was obtained from a 50% doped device but with a reduction in the EL polarization ratio. Conversely a polarized EL ratio of 11:1 is found from a 20% doped device but with lower brightness. A threshold voltage of 2V is found for the device with a hole-transporting layer with 100% of the dopant comprising compound 8. Clearly a photo-alignment polymer optimised for both alignment and hole-transporting properties would improve device performance. This could be achieved using a co-polymer incorporating both linear rod-like hole-transporting and photoactive side chains.

What is claimed is:

1. A liquid crystal alignment layer comprising an alignment layer; and chemically bound to said alignment layer, a transport material, wherein said alignment layer is an electrically insulating alignment layer in the absence of the transport material; wherein the alignment layer is an electrically conducting alignment layer with the transport material; and wherein the alignment layer comprises a side chain liquid crystal polymer having the formula:

(Compound 3)



2. A liquid crystal alignment layer according to claim 1, wherein the alignment layer comprises a grating structure.

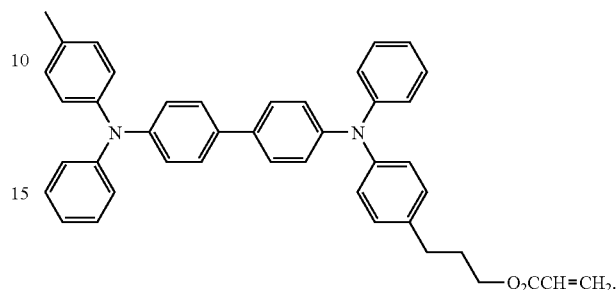
3. A liquid crystal alignment layer according to claim 1, wherein the transport material is selected from the group consisting of an ion transport compound, a hole transport compound, an electron transport compound and any mixtures thereof.

4. A liquid crystal alignment layer according to claim 3, wherein the ion transport compound is selected from the group consisting of mono-reactive ion transport materials, di-reactive ion transport materials and any mixtures thereof.

5. A liquid crystal alignment layer according to claim 3, wherein the ion transport compound is a hole transport compound.

6. A liquid crystal alignment layer according to claim 5, wherein the hole transport compound is a triarylamine.

7. A liquid crystal alignment layer according to claim 6, wherein the triarylamine is:



8. A liquid crystal cell comprising an inert substrate; and on said inert substrate, a liquid crystal alignment layer according to claim 1.

9. A liquid crystal cell according to claim 8, wherein the inert substrate is selected from the group consisting of glass and plastic substrates.

10. A liquid crystal cell according to claim 9, wherein the inert substrate is an indium tin oxide (ITO) coated glass substrate.

11. A liquid crystal alignment layer according to claim 1, wherein the layer has a thickness of from 10 to 500 nm.

12. Method of forming a liquid crystal cell according to claim 11, comprising reacting the constituents of the alignment layer and the transport material to form a chemical bond therebetween; and subsequently applying the layer to the substrate.

13. Method of forming a liquid crystal cell according to claim 11, comprising applying the constituents of the alignment layer and the transport material to the substrate; and subsequently reacting said constituents in situ to form a chemical bond therebetween.

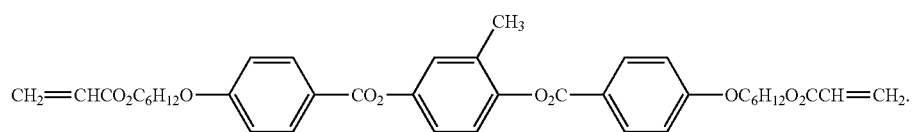
14. A liquid crystal display comprising a driver for driving the display; and a liquid crystal cell according to claim 11.

15. A liquid crystal display according to claim 14, in the form of a ferroelectric liquid crystal (FLC) display.

16. A liquid crystal alignment layer according to claim 1, wherein the transport material is a rod-like transporting side chain.

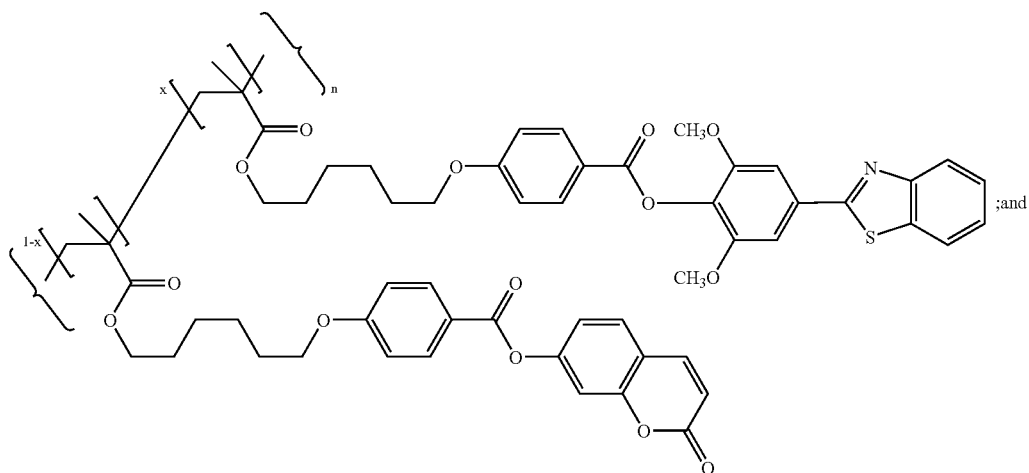
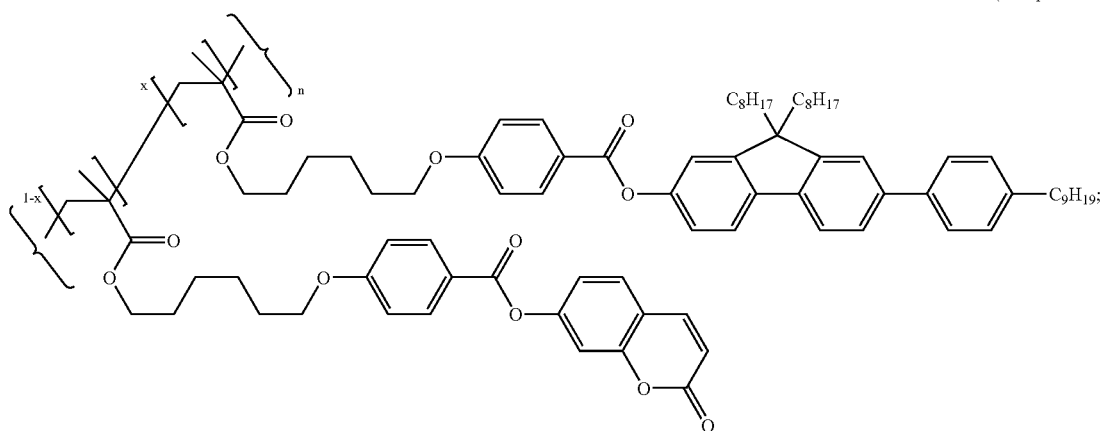
17. A liquid crystal alignment layer according to claim 1, further comprising a light emissive material on the alignment layer.

18. A liquid crystal alignment layer comprising an alignment layer; and chemically bound to said alignment layer, a transport material, wherein said alignment layer is an electrically insulating alignment layer in the absence of the transport material; wherein the alignment layer is an electrically conducting alignment layer with the transport material; and wherein the alignment layer comprises a reactive liquid crystal obtained from a reactive mesogen having the formula:



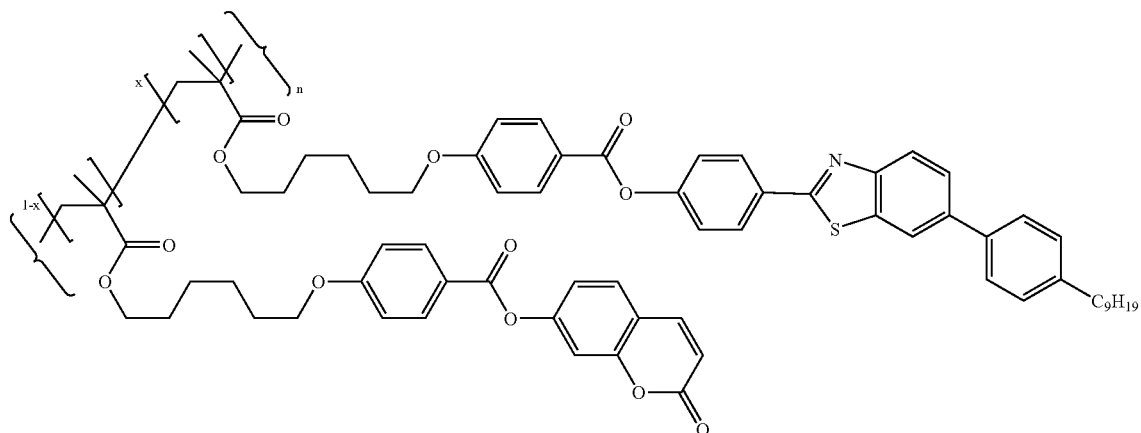
19. A liquid crystal alignment layer comprising an alignment layer; and chemically bound to said alignment layer, a transport material, wherein the alignment layer and the transport material are comprised as a co-polymer obtained

10 by co-polymerising a coumarin alignment layer with a transport material comprising a methacrylate end-group, wherein the co-polymer is selected from the group consisting of:



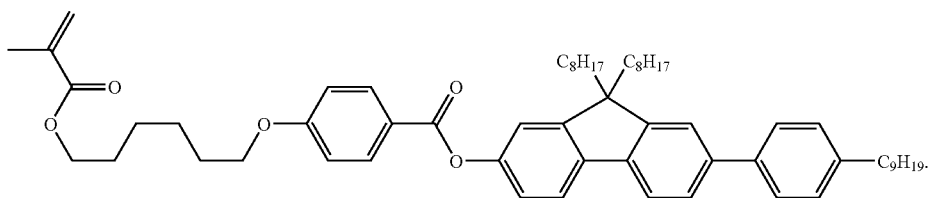
-continued

(Compound 27)



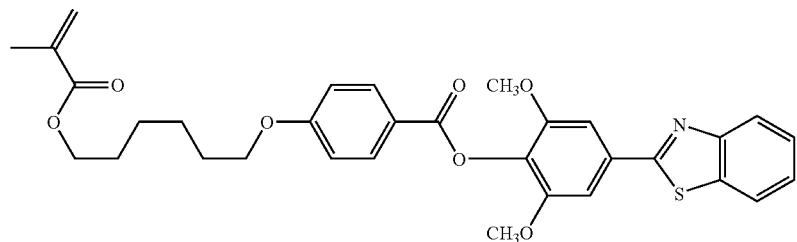
wherein, x is greater than 0 and less than 1; and n is from 5 to 500.

20. A transporting-alignment layer, comprising: a transporting-alignment copolymer layer formed from an alignment material and a transport material, wherein the alignment material is a photoalignment material, wherein the transport material is selected from the group consisting of ion transport compounds, hole transport compounds, electron transport compounds, and a mixture thereof, wherein the transport material is a hole transport compound, and wherein the hole transport compound, prior to copolymerization, is:



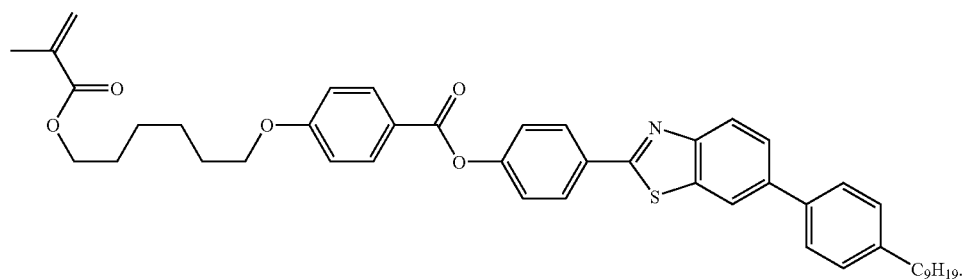
21. A transporting-alignment layer, comprising: a transporting-alignment copolymer layer formed from an alignment material and a transport material, wherein the alignment material is a photoalignment material, wherein the

transport material is selected from the group consisting of ion transport compounds, hole transport compounds, electron transport compounds, and a mixture thereof, wherein the transport material is a hole transport compound, wherein the hole transport compound, prior to copolymerization, is:



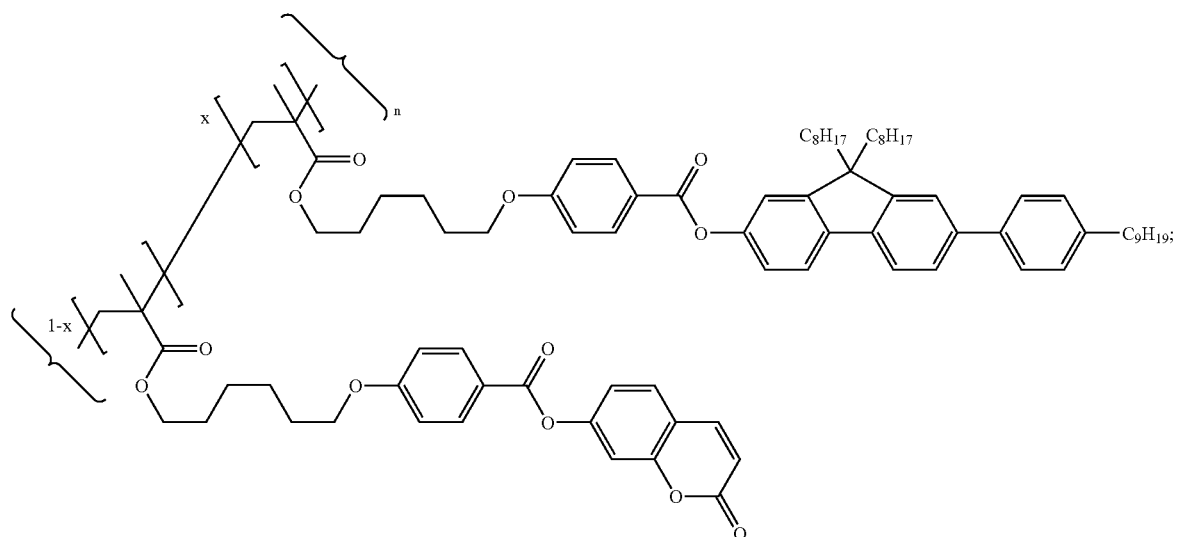
43

22. A transporting-alignment layer, comprising: a transporting-alignment copolymer layer formed from an alignment material and a transport material, wherein the alignment material is a photoalignment material, wherein the transport material is selected from the group consisting of ion transport compounds, hole transport compounds, electron transport compounds, and a mixture thereof, wherein the transport material is a hole transport compound, wherein the hole transport compound, prior to copolymerization, is:



30

23. A transporting-alignment layer, comprising: a transporting-alignment copolymer layer formed from an alignment material and a transport material, wherein the alignment material is a photoalignment material, wherein the co-polymer is:



65

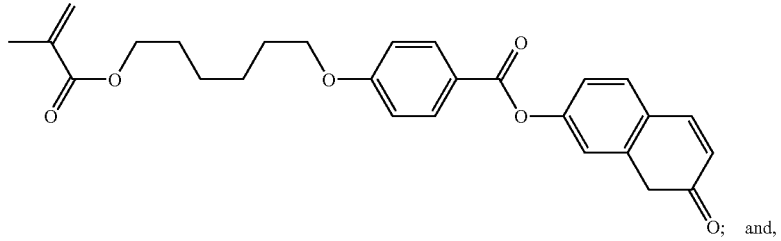
47

wherein, x is greater than 0 and less than 1; and n is from 5 to 500.

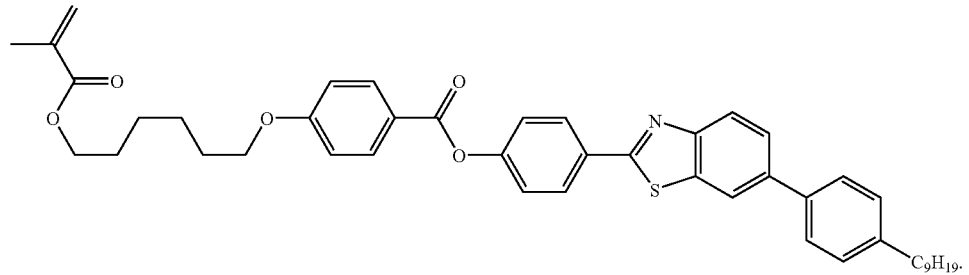
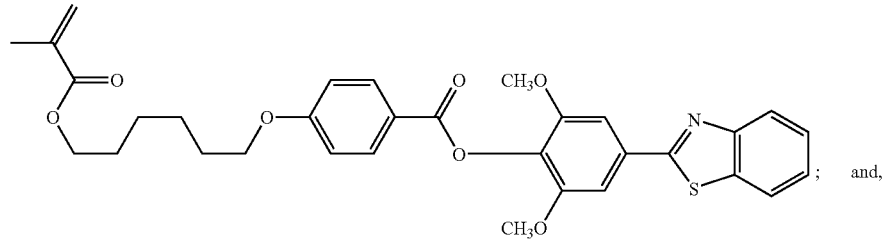
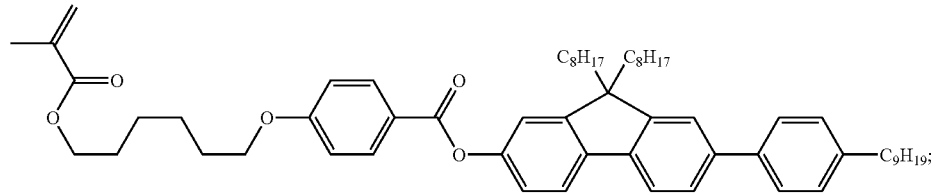
26. A backlight or display device, comprising a transporting-alignment layer, comprising: a copolymer formed from

48

an alignment material and a transport material, wherein the alignment material is a photoalignment material and the transport material is a hole transport material, wherein the photoalignment material, prior to copolymerization, is:



the hole transport material, prior to copolymerization, is selected from the group consisting of:



* * * * *