



US006830831B2

(12) **United States Patent**
O'Neill et al.

(10) **Patent No.:** **US 6,830,831 B2**
(45) **Date of Patent:** **Dec. 14, 2004**

(54) **LIGHT EMITTER FOR A DISPLAY**

(75) Inventors: **Mary O'Neill**, Hull (GB); **Stephen Malcolm Kelly**, East Yorkshire (GB); **Adam Edward Alexander Contoret**, Bradley Stoke (GB); **Gary James Richards**, Oxford (GB)

(73) Assignee: **University of Hull**, North Humberside (GB)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **10/187,402**

(22) Filed: **Jul. 1, 2002**

(65) **Prior Publication Data**

US 2003/0099862 A1 May 29, 2003

Related U.S. Application Data

(63) Continuation-in-part of application No. 09/898,518, filed on Jul. 3, 2001, now abandoned.

(30) **Foreign Application Priority Data**

Jun. 29, 2001 (GB) 0115984

(51) **Int. Cl.**⁷ **H05B 33/00**

(52) **U.S. Cl.** **428/690**; 428/1.2; 428/917; 313/504; 313/506; 313/112; 257/89; 257/90; 257/98; 427/66

(58) **Field of Search** 428/690, 917, 428/1.2, 195; 313/504, 506, 112; 257/89, 90, 98; 427/66

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,707,544 A * 1/1998 Kelly 252/299.01
6,201,087 B1 * 3/2001 Herr et al. 526/268
6,489,044 B1 * 12/2002 Chen et al. 428/690
2002/0158574 A1 * 10/2002 Wolk et al. 313/504
2003/0018097 A1 * 1/2003 O'Neill et al. 522/1
2003/0099785 A1 * 5/2003 O'Neill et al. 428/1.26
2003/0119936 A1 * 6/2003 O'Neill et al. 522/168

FOREIGN PATENT DOCUMENTS

EP 1011154 A1 * 6/2000

OTHER PUBLICATIONS

Chemical Materials, (2002), vol. 14, p. 1477-1487.*
Proceedings of SPIE (1999), 3635 (Liquid Crystal Materials, Devices, and Applications VII), p. 38-47.*
Molecular Crystal Liquid Crystal, (1999), vol. 332, pp. 439-446.*
Chemical Materials (2001), vol. 13, pp. 694-703.*
Journal of Materials Chemistry, (1999), vol. 9, pp. 2985-2989.*
Journal of Applied Physics, (Jan. 2000), vol. 87, No. 1, pp. 274-279.*
Molecular Crystal and Liquid Crystal, (2001), vol. 364, pp. 511-518.*
Synthetic Metals, (Mar. 15, 2001), vol. 121, pp. 1645-1646.*
Chemical Materials, (1995), vol. 7, pp. 1568-1575.*
Advanced Materials, (2000), vol. 12, No. 13, pp. 971-974.*
Peregrine Orr Jackson and Mary O'Neill, Warren Lee Duffy, Paul Hindmarsh, Stephen Malcom 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. Contoret, Simon R. Farrar, Mary O'Neill and J.Edward Nicholls. Gary James Richards. Stephen Malcom Kelly, and Gareth James Owen. "The Photopolymerization and Cross-Linking of Electroluminescent Liquid Crystals Containing Mothacrylate 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

Primary Examiner—Dawn Garrett

(74) *Attorney, Agent, or Firm*—Martin Fleit; Paul D. Bianco; Fleit Kain Gibbons Gutman Bongini & Bianco P.L.

(57) **ABSTRACT**

There is provided a light emitter for a display comprising a photoalignment layer; and photoaligned on said photoalignment layer, a light emitting polymer. Also provided are methods for forming the light emitter and the use of the light emitter in displays, backlights, electronic apparatus and security viewers.

61 Claims, 12 Drawing Sheets

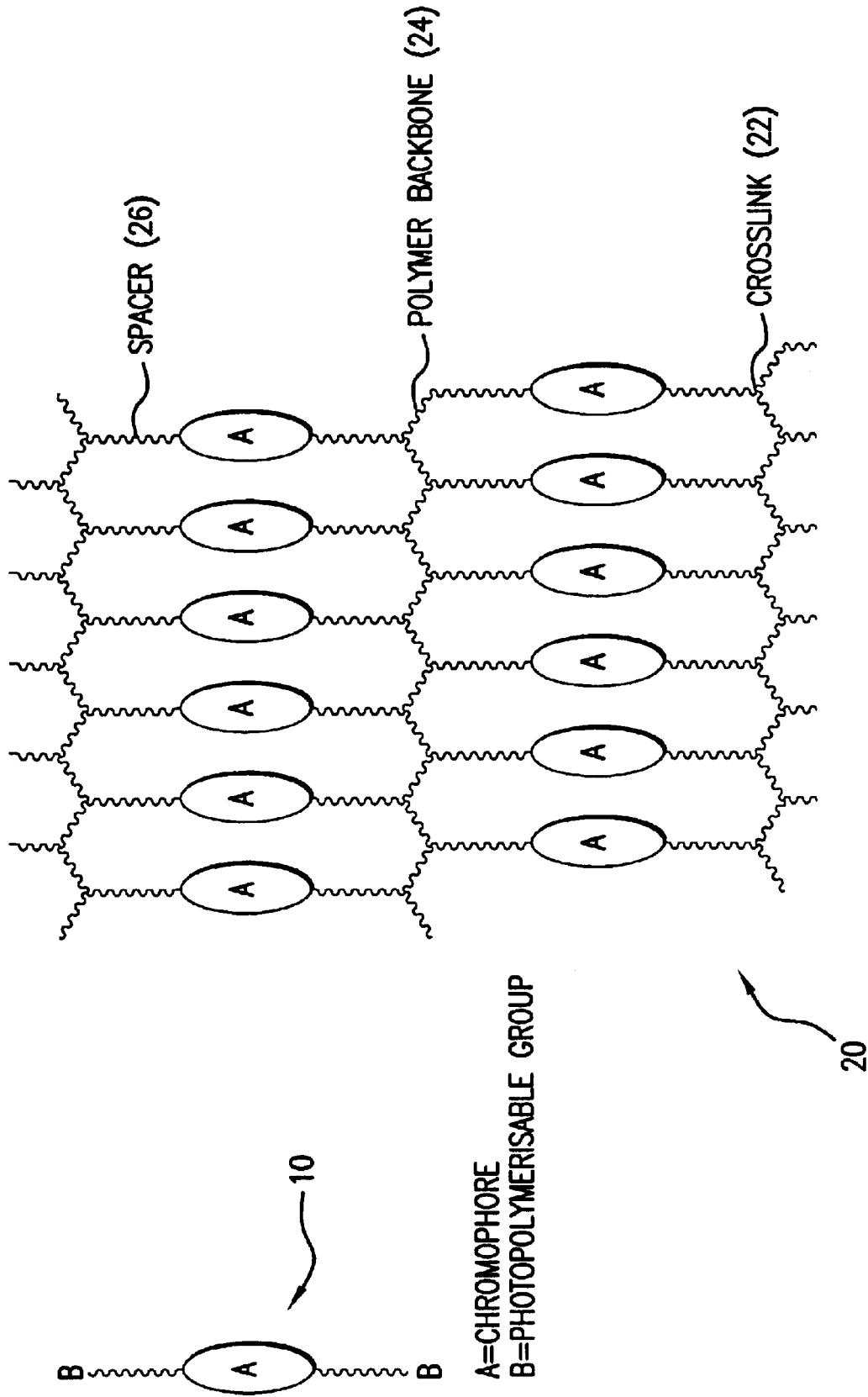


FIG. 1

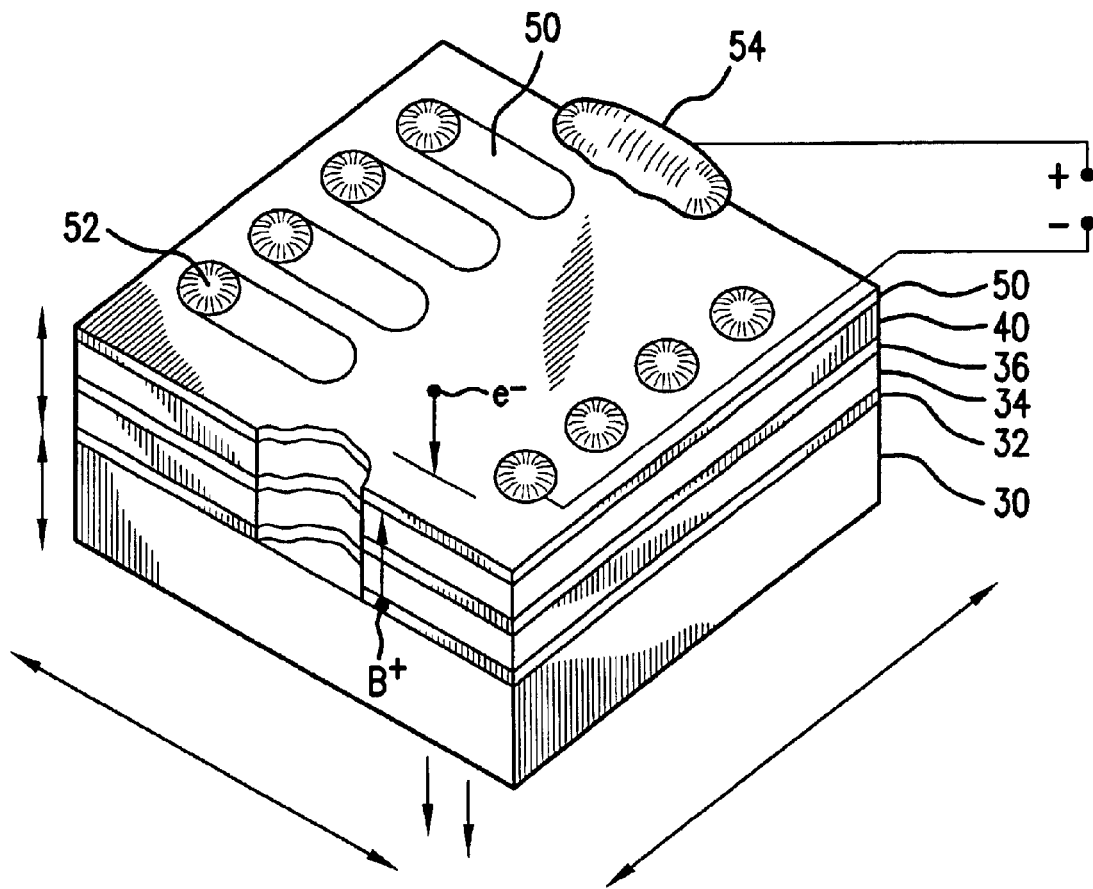


FIG. 2

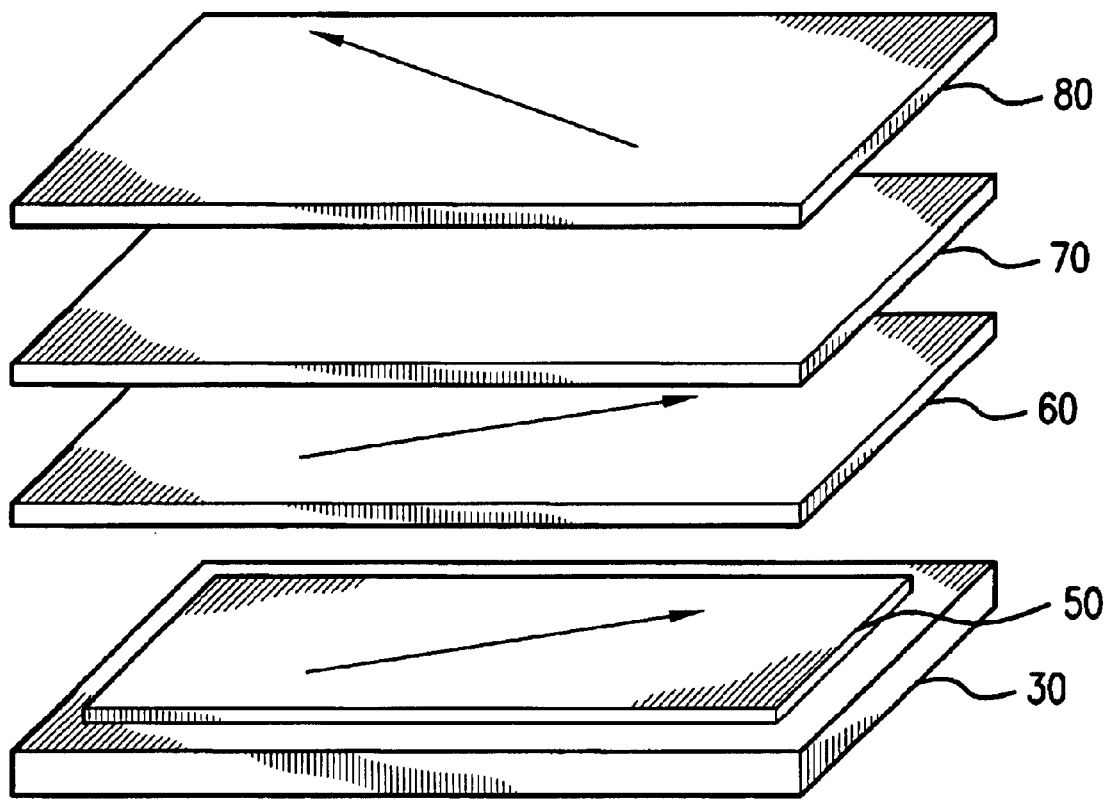


FIG. 3

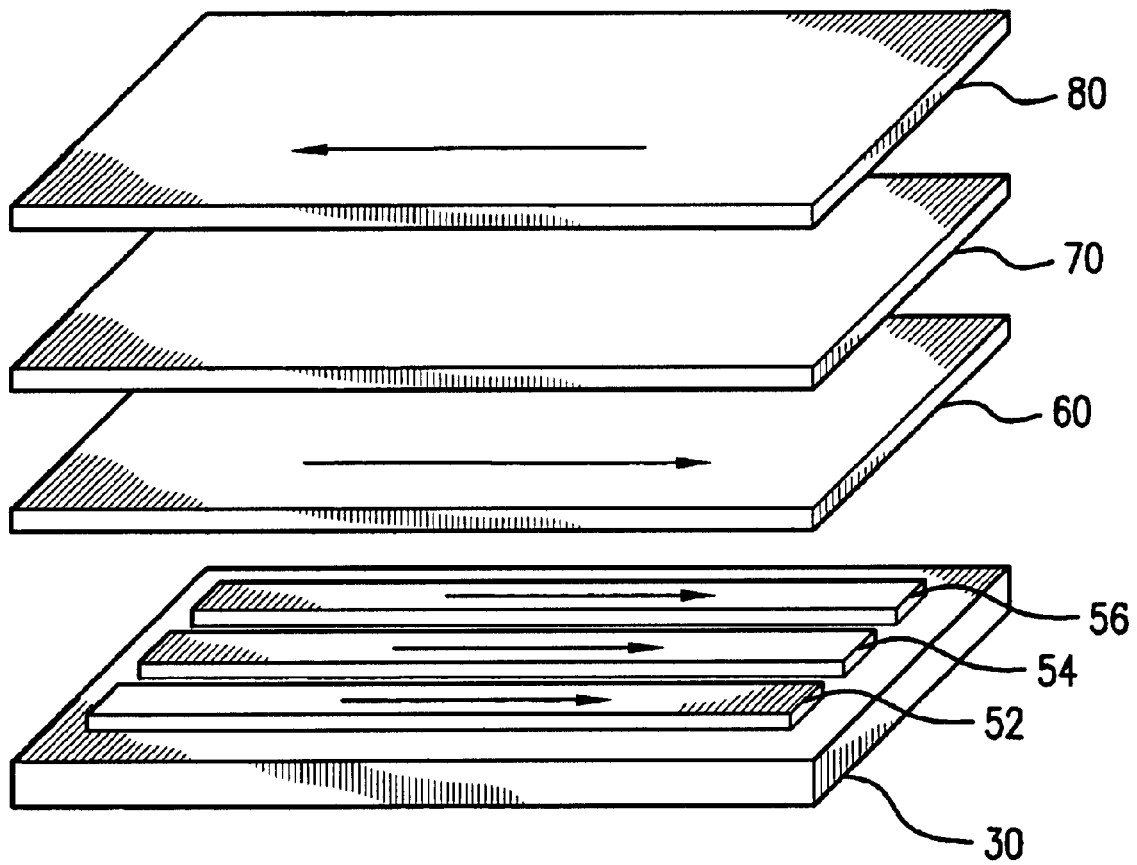
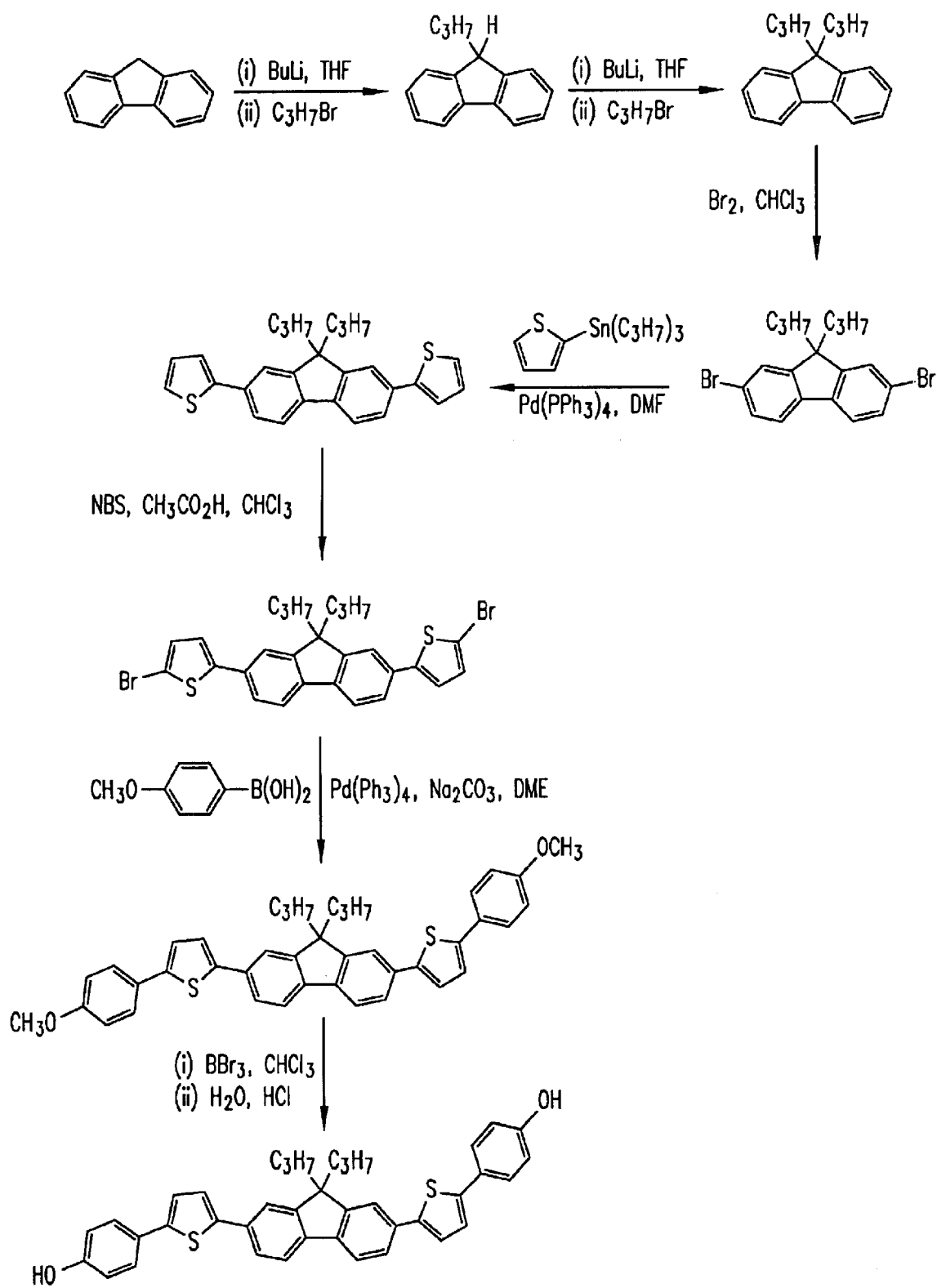
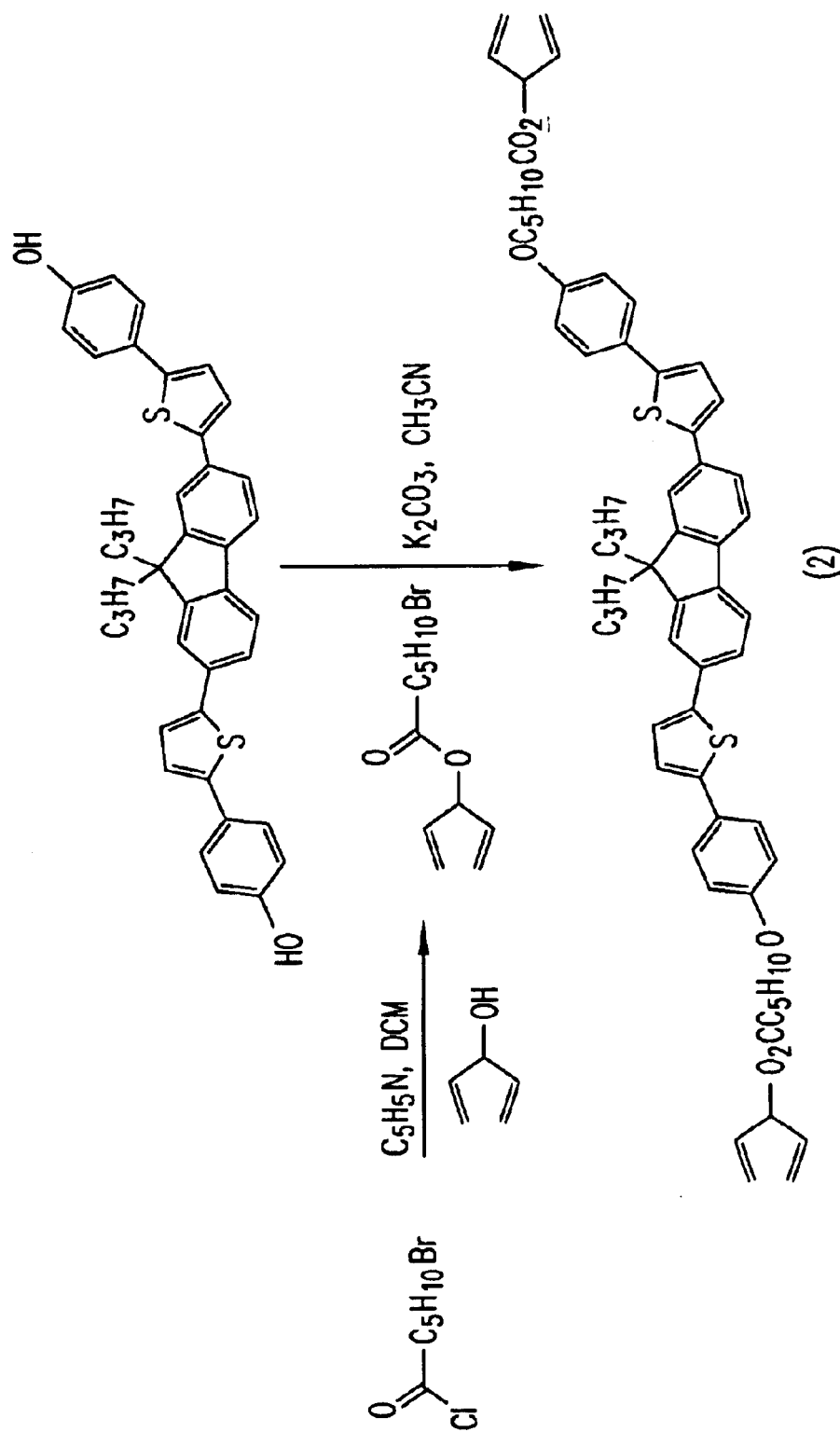


FIG.4



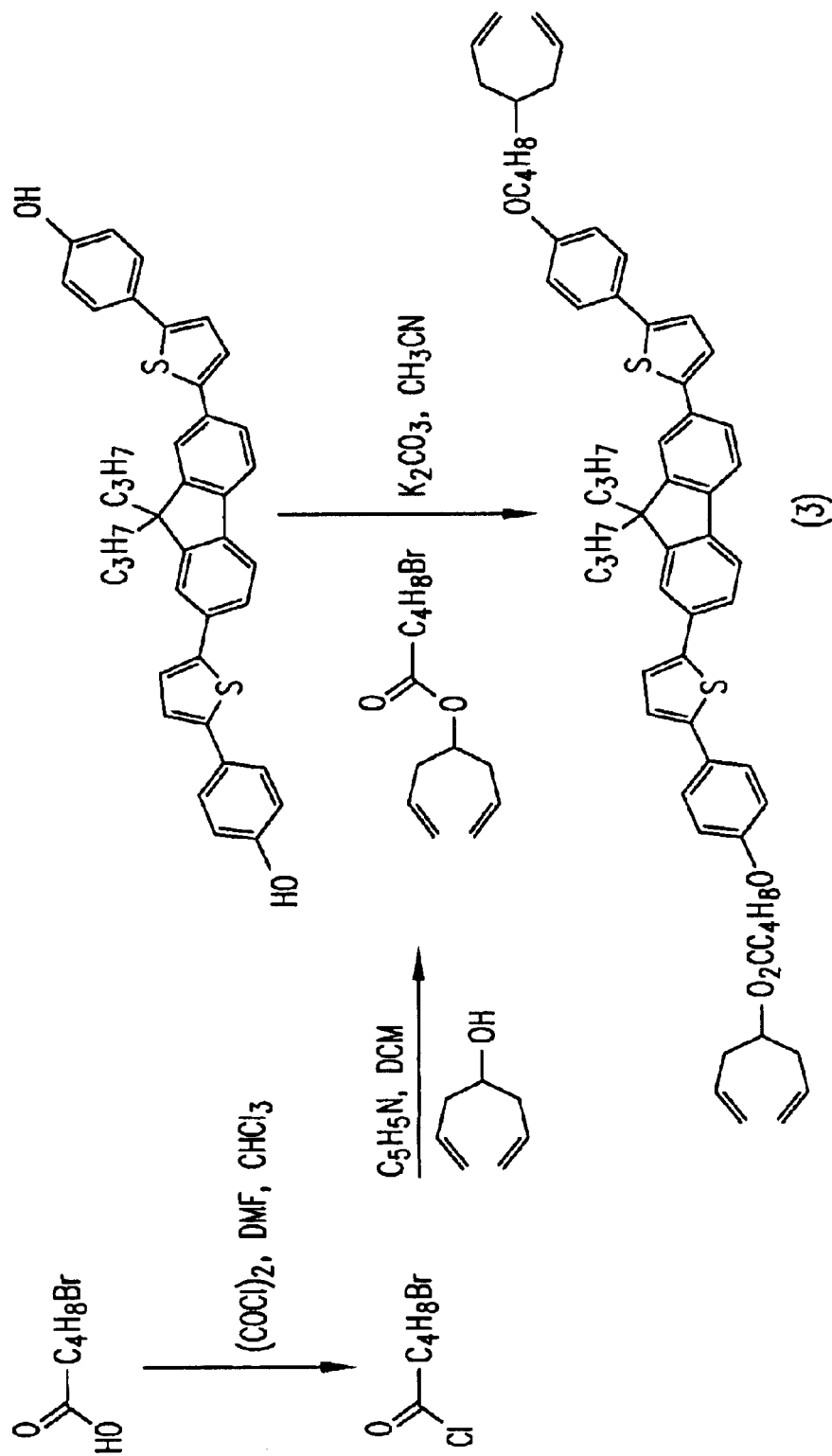
SCHEME 1

FIG. 5

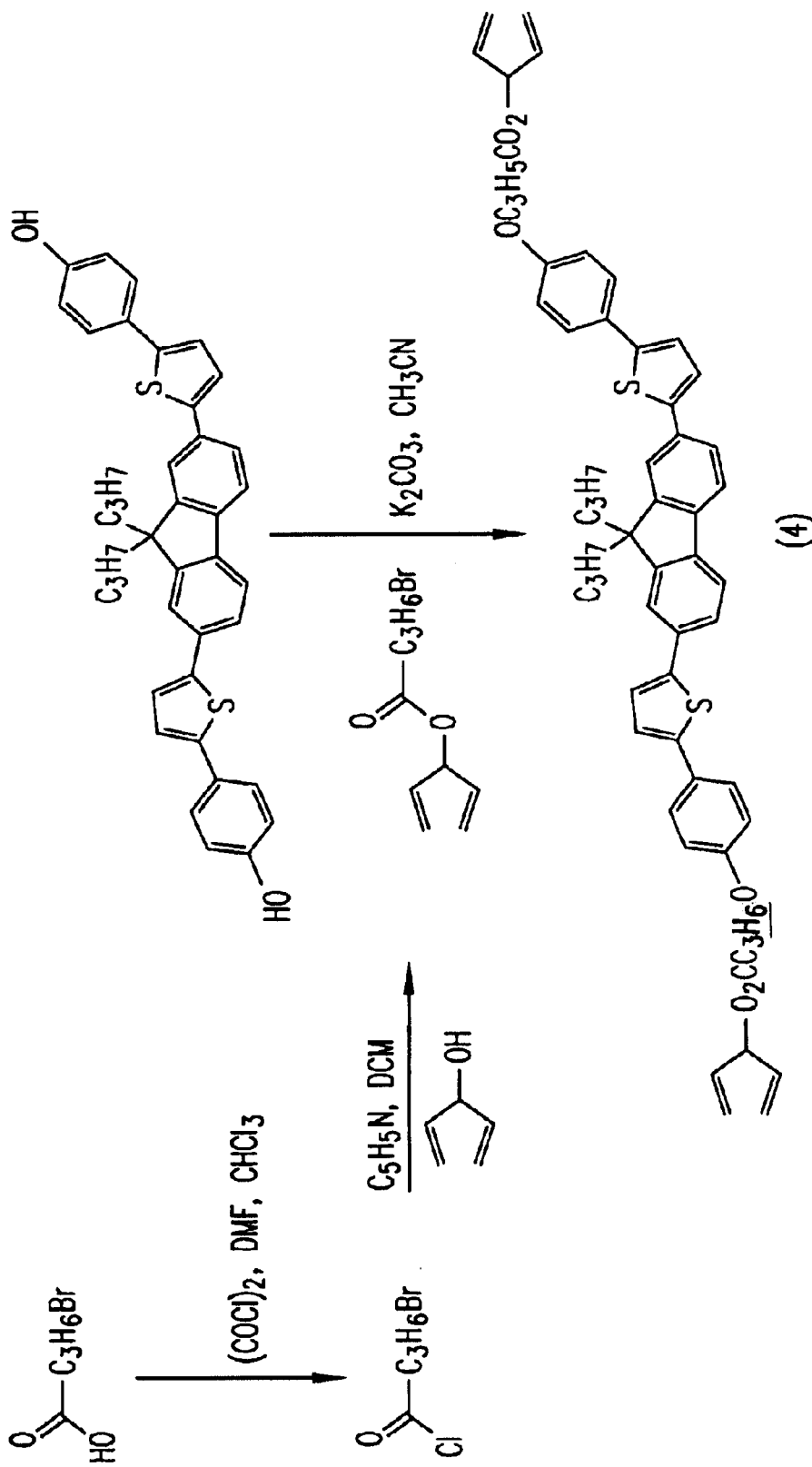


SCHEME 2

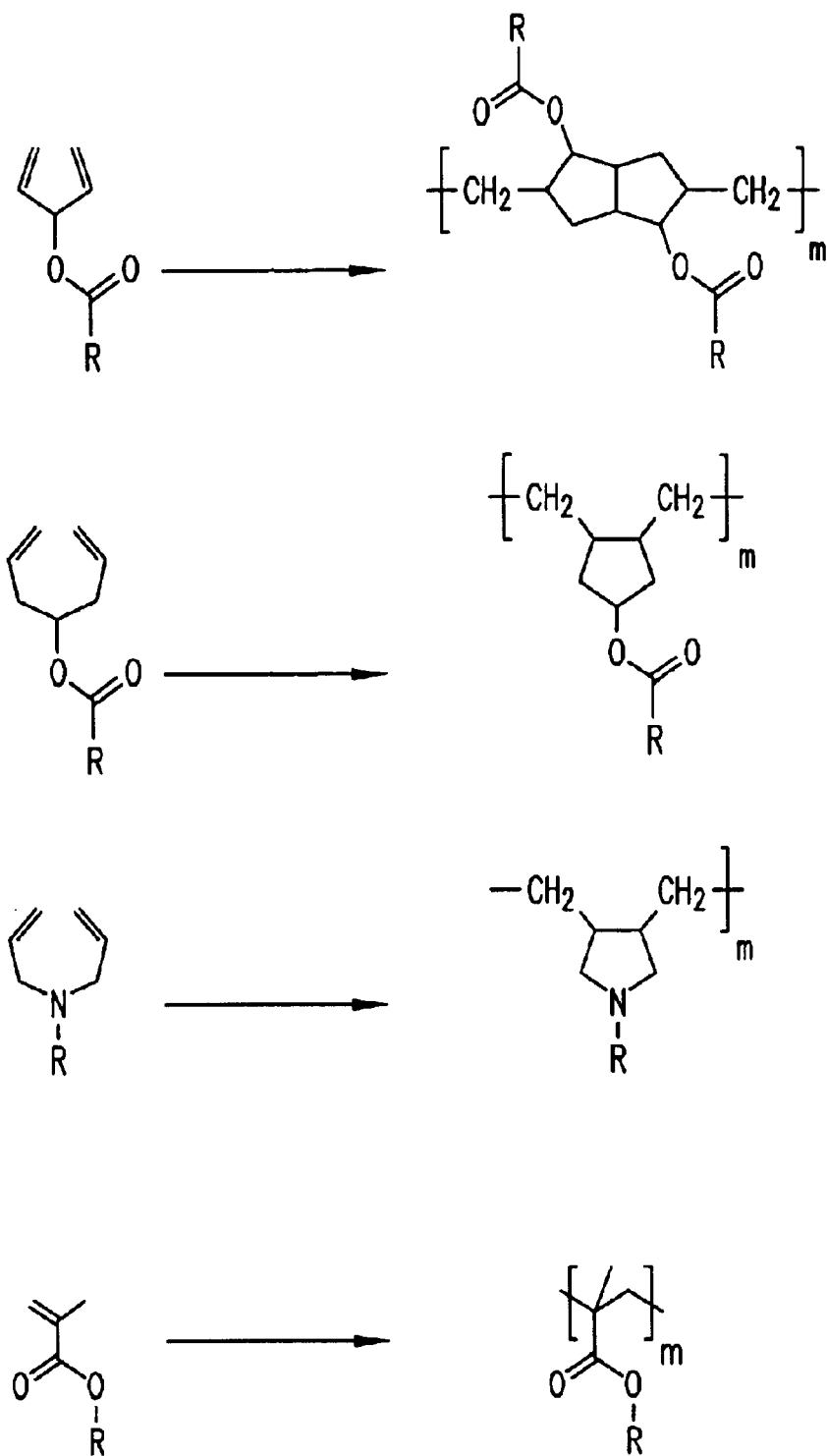
FIG. 6



SCHEME 3
FIG. 7

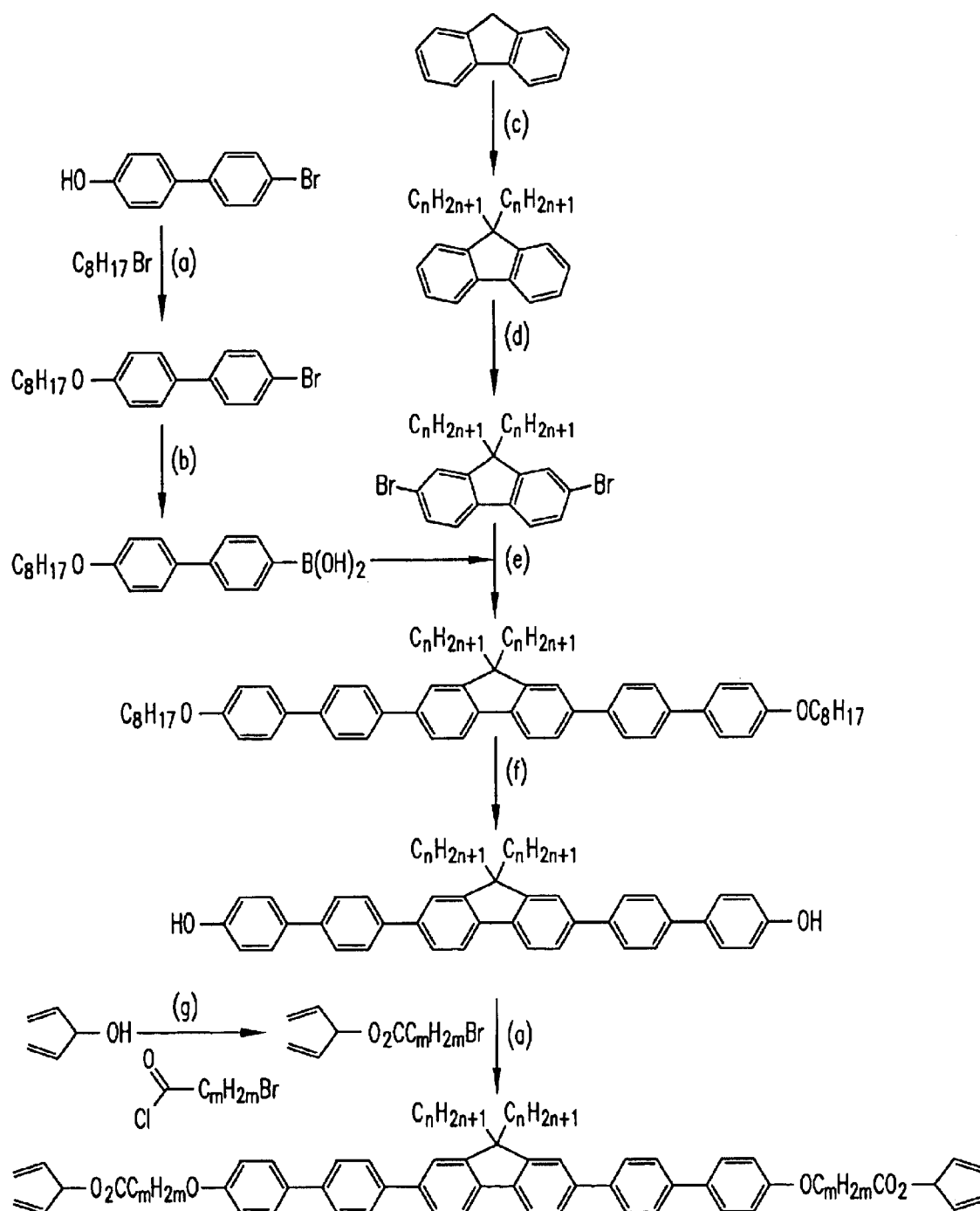


SCHEME 4
FIG. 8



SCHEME 6

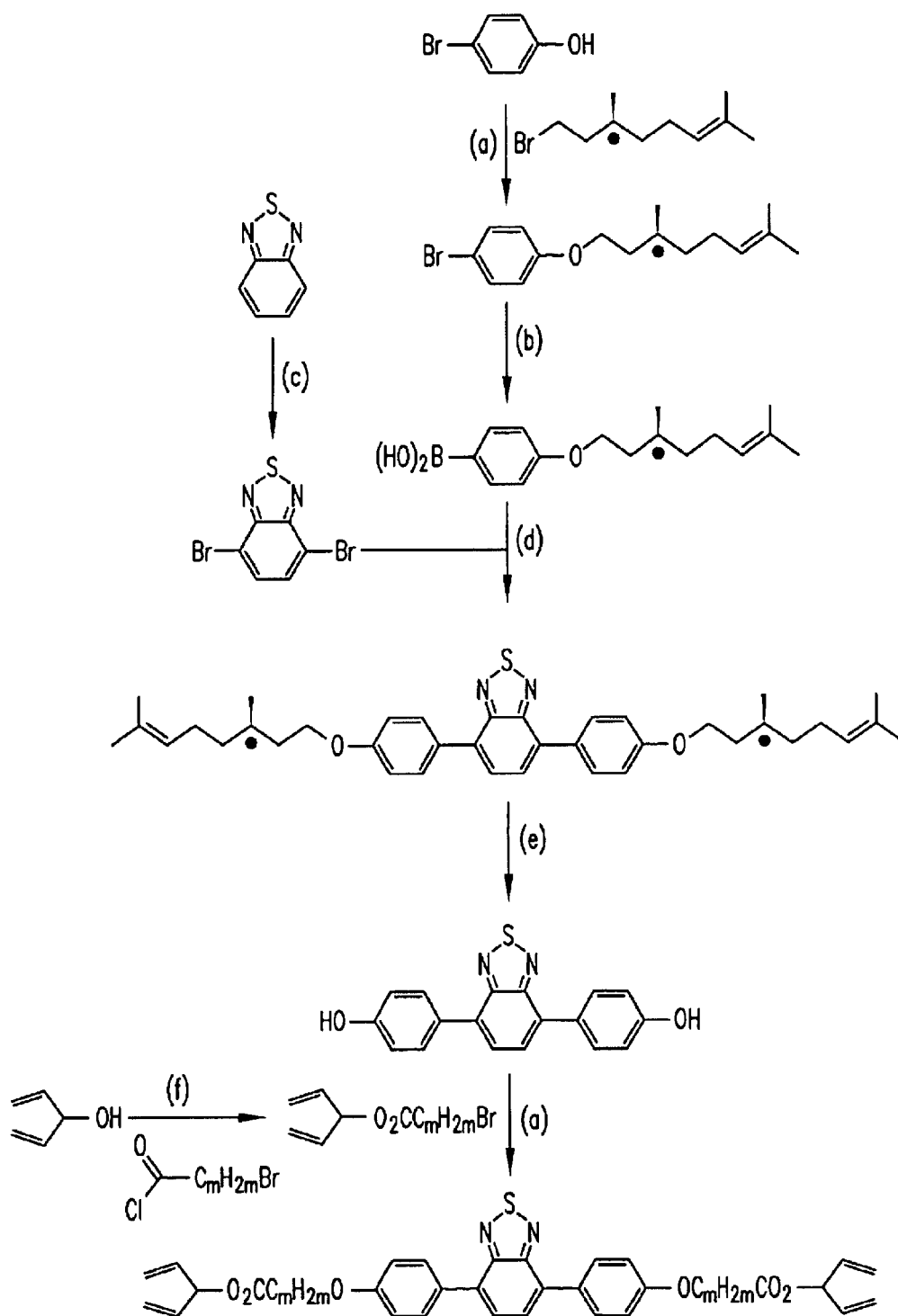
FIG. 10



Reagents: (a) (a) K_2CO_3 , $CH_3CO_2C_2H_5$; (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) $Pd(Ph_3)_4$, Na_2CO_3 , H_2O , DME; (f) (i) BBr_3 , $CHCl_3$ (ii) HCl_{aq} ;
 (f) pyridine, CH_2Cl_2

SCHEME 7

FIG. 11



Reagents: (a) K_2CO_3 , CH_3CO_2H ; (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 .

SCHEME 8
FIG. 12

1

LIGHT EMITTER FOR A DISPLAY

This application is a continuation-in-part of Ser. No. 09/898,518 filed Jul. 3, 2001, now abandoned, and claims priority from GB Application No. 0115984.7 filed Jun. 29, 2001.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a light emitter for a display for use in electronic products and a method of forming the light emitter and display.

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.

Conventional displays comprise twisted nematic liquid crystal displays (TN-LCDs) with active matrix addressing and super-twisted nematic liquid crystal displays (STN-LCDs) with multiplex addressing. These however require intense back lighting which presents a heavy drain on power. The low intrinsic brightness of LCDs is believed to be due to high losses of light caused by the absorbing polarizers and filters which can result in external transmission efficiencies of as low as 4%.

SUMMARY OF THE INVENTION

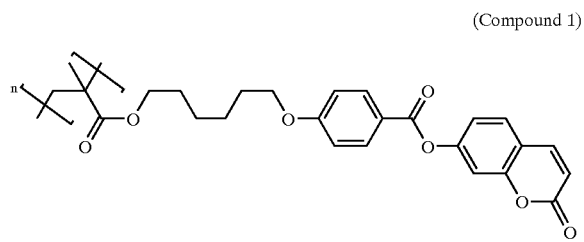
The Applicants have now devised a new kind of light emitter for a display which offers the prospect of lower power consumption and/or higher brightness. The display utilises an alternative light source which can in embodiments be used instead of the conventional polarizers and/or back light. The alternative light source comprises a light emitting polymer or polymer network aligned on a photoalignment layer. The combination of this alternative lighting source with existing LCD technology offers the possibility of low-cost, bright, portable displays with the benefits of simple manufacturing and enhanced power efficiency.

According to one aspect of the present invention there is provided a light emitter for a display comprising a photoalignment layer; and aligned on said photoalignment layer, a light emitting polymer.

The photoalignment layer is comprised of materials that photoalign (e.g. by cross-linking) to form anisotropic layers when polarised light (e.g. UV) is applied.

The photoalignment layer 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 unsaturated organic chains, including e.g. aliphatic, amine or ether linkages.

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



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.

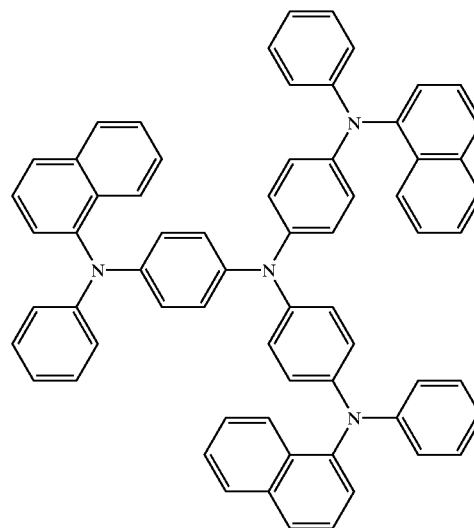
2

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.

The photoalignment layer may also be doped with a hole transport compound, that is to say a compound which enables hole transport within the photoalignment layer such as a triarylamine. Examples of suitable triarylaminines include those described in C. H. Chen, J. Shi, C. W. Tang, *Macromol Symp.* [1997] 125, 1.

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

(Compound 2)



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

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

3

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 light 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 organic chains (e.g. unsaturated), 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^{\bullet} is a radicalised endgroup which is capable of reacting with

4

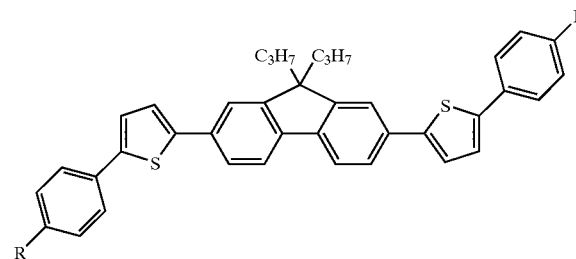
another B endgroup (particularly to form a cyclic entity). The B^{\bullet} radicalised endgroup suitably comprises a bound radical such that the polymerisation process may be sterically controlled.

Suitable endgroups include dienes such as 1,4, 1,5 and 1,6 dienes. The diene functionalities may be separated by aliphatic linkages, but other inert linkages including ether and amine linkages may also be employed.

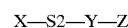
Methacrylate endgroups have been found to be less suitable than dienes because the high reactivity of the radicals formed after the photoinitiation step can result in a correspondingly high photodegradation rate. By contrast, it has been found that the photodegradation rate of light emitting polymers 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:



and wherein

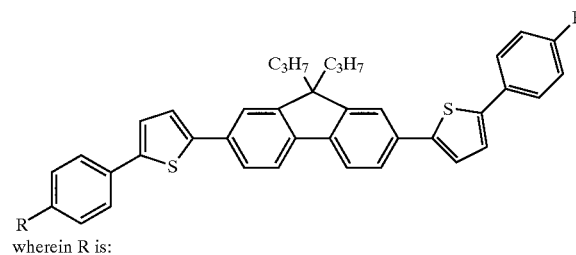
$X=O$, CH_2 or NH and preferably $X=O$;

S_2 =linear or branched alkyl or alkenyl chain optionally including a heteroatom (e.g. O, S or NH) and preferably S_2 =a linear alkyl chain;

$Y=O$, CO_2 or S and preferably $Y=CO_2$; and

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

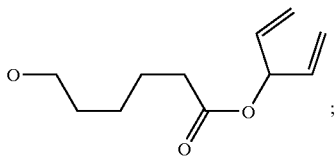
Exemplary reactive mesogens have the general formula:



wherein R is:

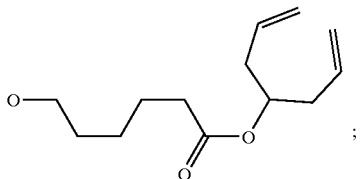
5

-continued



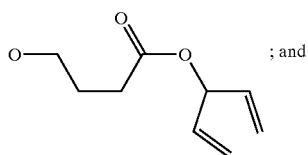
(Compound 3)

5



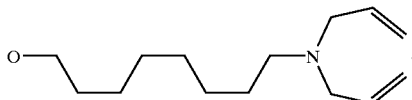
(Compound 4)

10



(Compound 5)

15



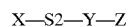
(Compound 6)

25

An exemplary reactive mesogen has the formula:

6

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



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;

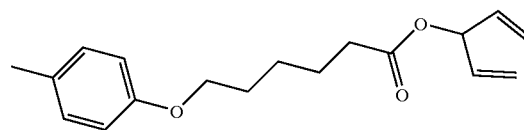
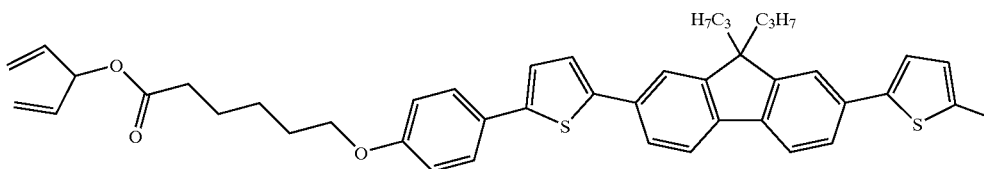
Y=O, CO₂ or S and preferably Y=CO₂; and

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

Suitably, R is as for any of Compounds 3 to 6, as shown above.

A particular class of exemplary reactive mesogens has the formula:

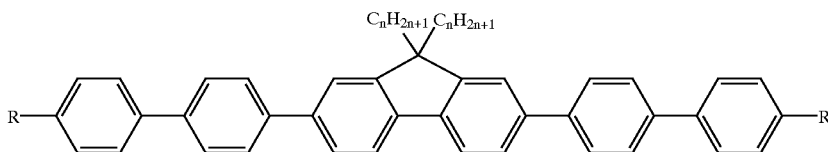
(Compound 3)



All of Compounds 3 to 6 exhibit a nematic phase with a clearing point (N-I) between 79 and 120° C.

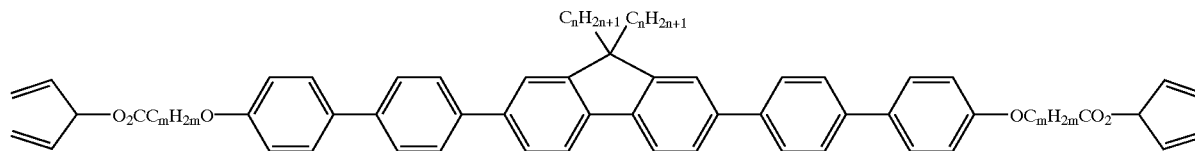
55

Other suitable exemplary reactive mesogens have the general formula:



7

8



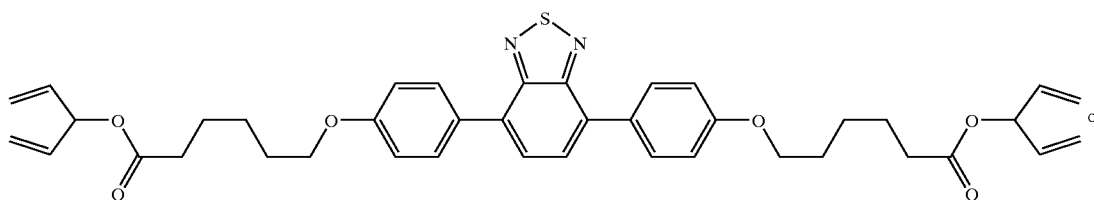
wherein:

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

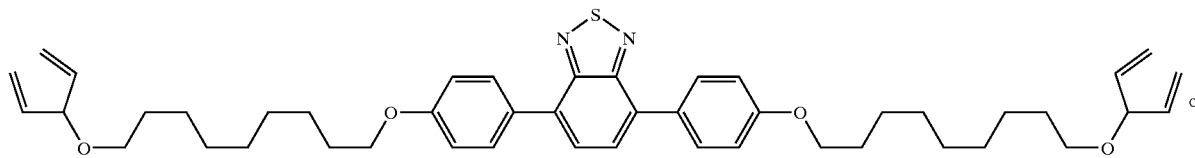
10 Suitably, R is as for any of Compounds 3 to 6, as shown above.

Particular exemplary reactive mesogens of this type have the formula:

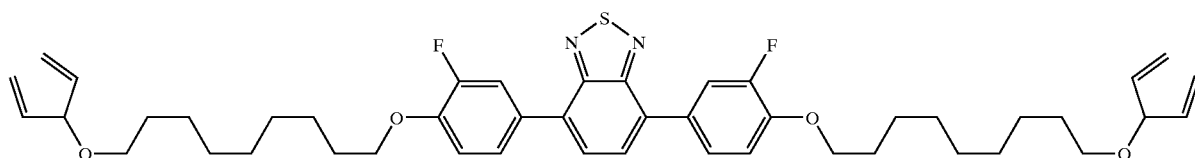
(Compound 16)



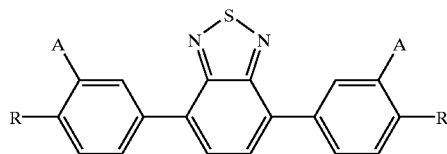
(Compound 17)



(Compound 18)

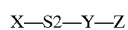


Still further suitable exemplary reactive mesogens have the general formula:



wherein A=H or F

and wherein, as above, R has the general formula:



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.

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

Further steps may be conducted prior to the polymerization process including doping of the reactive mesogen. The dopant may in aspects comprise a further reactive monomer capable of co-polymerization with the reactive mesogen.

Further steps also 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 mechanical stretching, rubbing, and Langmuir-Blodgett deposition. Mechanical alignment methods can however lead to structural degradation. The use of rubbed polyimide is a suitable method for aligning the light emitting polymer especially in the liquid crystal state. 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-

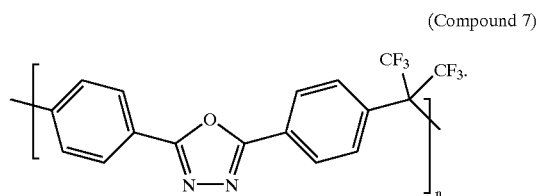
ropy to the alignment layer and hence a preferred in-plane orientation to the overlying light emitting polymer (e.g. in liquid crystal form).

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 photalignment materials and methods.

The emitter herein may include additional layers such as 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:



Pixelation of the light emitter may be achieved by selective photopatterning to produce red, green and blue pixels as desired. The pixels are typically rectangular in shape. The pixels typically have a size of from 1 to 50 μm . For microdisplays the pixel size is likely to be from 1 to 50 μm , preferably from 5 to 15 μm , such as from 8 to 10 μm . For other displays, larger pixel sizes e.g. 300 μm are more suitable.

In one preferred aspect, the pixels are arranged for polarized light emission. Suitably, the pixels are of the same color but have their polarization direction in different orientations. To the naked eye this would look one color, but when viewed through a polarizer some pixels would be bright and others less bright thereby giving an impression of 3D viewing when viewed with glasses having a different polarization for each eye.

The layers may also be doped with photoactive dyes. In aspects, the dye comprises a dichroic or pleochroic 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 and reflective 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.

According to another aspect of the present invention there is provided a backlight for a display comprising a power input; and 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.

According to yet another aspect of the present invention 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 electronic apparatus including a drive means therefor. The display is suitable for use in consumer electronic goods such as mobile telephones, hand-held computers, watches and clocks and games machines.

According to yet another aspect of the claimed invention 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.

According to yet another aspect of the claimed invention there is provided a 3D viewer (e.g. in kit form) comprising a light emitter as described herein in which the pixels are arranged for polarized emission wherein the alignment of polarisation axis of each pixel is different; and a viewer having polarization characteristics aligned with those of the pixels.

According to yet another aspect of the claimed invention there is provided a method of forming a light emitter for a display comprising forming a photoalignment layer; and aligning a light emitting polymer on said photoalignment layer.

According to yet another aspect of the claimed invention there is provided a method of forming a multicolor emitter comprising applying a first color light emitter 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 12 show reaction schemes 1 to 8, 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 μm, 25 cm×0.46 cm, ODS Microsorb column, methanol, >99%) and by gel-permeation chromatography [GPC] (5 μm, 30 cm×0.75 cm, 2×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 Mw 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 μm). 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-ware 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, 10 M 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, 2.5 M 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-(tributylstanyl)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 (2H, 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.

13

2,7-bis(5-Bromothien-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-bromothien-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.

14

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

The 1,3-pentadiene monomer (Compound 3) 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 4: 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 4) 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.

15

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

The 1,3-pentadiene homologue (Compound 5) 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,

16

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 6: 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 6) 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-diallylaminooctyl ester.

4-Toluene-sulphonyl chloride (12.5 g, 0.066 mol) was added slowly to a stirred solution of 8-diallylaminooctan-1-ol (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-Diallylaminooctyloxy)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-diallylaminooctyl 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), 180 (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 7: poly(phenylene-1,3,4-oxadiazole-phenylene-hexafluoropropylene)

The electron-transporting polymer (Compound 7) 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, 2.5 M 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 cm^3) was added and the resultant mixture stirred for 1 h. The product was extracted into diethyl ether ($3\times 300\text{ cm}^3$). The combined organic layers were washed with water (300 cm^3), dried (MgSO_4), 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. $134\text{--}136^{\circ}\text{C}$).

$^1\text{H NMR}$ (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 $\nu_{\text{max}}/\text{cm}^{-1}$: 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-octyloxybiphenyl-4'-yl boronic acid (5.00 g , 0.0153 mol), 20% sodium carbonate solution (100 cm^3) and 1,2-dimethoxyethane (150 cm^3). The reaction mixture was heated under reflux overnight. Water (300 cm^3) was added to the cooled reaction mixture and the product extracted into DCM ($3\times 300\text{ cm}^3$). The combined organic extracts were washed with brine ($2\times 150\text{ cm}^3$), dried (MgSO_4), 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).

$^1\text{H NMR}$ (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 $\nu_{\text{max}}/\text{cm}^{-1}$: 3024, 2921, 2853, 1609, 1501, 1463, 1251, 808. MS m/z : 782 (M^+), 669, 514, 485, 279, 145, 121, 107, 83, 71. CHN

hexane (30:70) as the eluent and recrystallisation from ethanol to yield a white powder (0.83 g , 40%, m.pt. $>300^{\circ}\text{C}$).

$^1\text{H NMR}$ (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 $\nu_{\text{max}}/\text{cm}^{-1}$: 1608, 1500, 1463, 1244, 1173, 811. MS m/z : 558 (M^+), 529, 514, 313, 279, 257, 115, 77, 65.

Compound 8: 9,9-Diethyl-2,7-bis{4-[5-(1-vinylallyloxycarbonyl)pentoxy]biphenyl-4'-yl}fluorene:

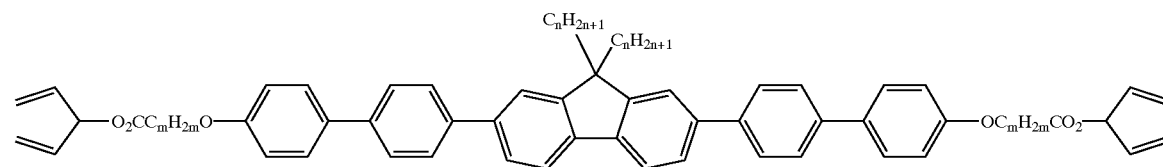
Compound 8 was synthesised as follows:

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 cm^3) was heated under reflux overnight. The cooled reaction mixture was added to water (500 cm^3) and then extracted with DCM ($3\times 50\text{ cm}^3$). The combined organic extracts were washed with water (250 cm^3), dried (MgSO_4) 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%).

$^1\text{H NMR}$ (CDCl_3) 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 $\nu_{\text{max}}/\text{cm}^{-1}$: 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 9–15:

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



	n	m
Compound 9	3	5
Compound 10	4	5
Compound 11	5	5
Compound 12	6	5
Compound 13	8	5
Compound 14	8	7
Compound 15	8	11

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 cm^3 , 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 cm^3). 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

Compound 16:

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

Compound 16 was synthesised as depicted in Reaction Scheme 8. Full details of each step follows:

4,7-Dibromo-2,1,3-benzothiazole:

Bromine (52.8 g , 0.33 mol) was added to a solution of 2,1,3-benzothiazole (8.1 g , 0.032 mol) in hydrobromic acid (47%, 100 cm^3) and the resultant solution was heated under reflux for 2.5 h. The cooled reaction mixture reaction mixture was filtered and the solid product washed with water (200 cm^3) 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:

2.5 M 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-benzothiazole:

A mixture of tetrakis(triphenylphosphine)palladium(0) (0.8 g, 0.70×10⁻³ mol), 4,7-dibromo-2,1,3-benzothiazole (2) (2 g, 6.75×10⁻³ mol), 4-[(S)-3,7-dimethyloct-6-enyloxy]phenyl boronic acid (4.66g, 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-benzothiazole:

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-benzothiazole (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-allyloxycarbonyl]pentyloxy}phenyl)-2,1,3-benzothiazole:

A mixture of 2,5-bis(4-hydroxyphenyl)-2,1,3-benzothiazole (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 17 and 18 are preparable by an analogous process.

Thin Film Polymerisation and Evaluation

Thin films of Compounds 3 to 6 and Compounds 9 to 15 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 15Ω) 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 3 to 6) 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 4) 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 3 and 5) but the increase of PL intensity after polymerization is less for Compound 4. 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 3 and 5) are homologues and differ only in the length of the flexible alkoxy-spacer part of the end-groups. The PL spectrum of Compound 5 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 5 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 5. The diallylamine monomer Compound 6 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 3) 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 polymerization 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 3) 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 3 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 3). Half of the layer of Compound 3 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 3 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 7), 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 3). 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 ($12 \text{ mm} \times 12 \text{ mm} \times 1 \text{ mm}$) 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 ($\sim 2 \text{ mm}$) of polyimide 34 along opposite edges of the substrate then covered with a polyethylene dioxthiophene/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 1 and 2 was spun from a 0.5% solution in cyclopentanone forming an alignment layer 40 of thickness $\sim 20 \text{ nm}$. 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 3 was then spun cast from a chloroform solution forming a film of $\sim 10 \text{ nm}$ 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 $02^\circ \text{ C}/\text{min}$ 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 3 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 10^9 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 Polarcot 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 $100 \mu\text{m}$ 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 3 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 Tri-color 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 3 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 3 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 50mJ 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 ($D\sim 6.5$) and obtained PL polarization ratios of 8:1.

Electroluminescence Characteristics

Devices made with compound 3 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 3 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 2. 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:

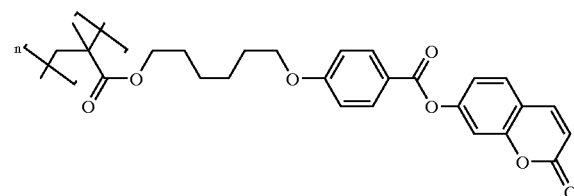
1. A light emitter comprising:
 - a photoalignment layer; and
 - a light emitting polymer aligned on the photoalignment layer,
 wherein the photoalignment layer comprises a chromophore attached to a sidechain polymer backbone by a flexible spacer entity.

2. A light emitter according to claim 1, wherein the chromophore is selected from the group consisting of cinnamates, coumarins and any derivatives thereof and any mixtures thereof.

3. A light emitter according to claim 2, wherein the chromophore is selected from the group consisting of 6-hydroxycoumarins, 7-hydroxycoumarins and any derivatives thereof and any mixtures thereof.

4. A light emitter according to claim 3, wherein the photoalignment layer comprises the 7-hydroxycoumarin compound having the formula:

(Compound 1)



5. A light emitter according to claim 1, wherein the flexible spacer comprises an unsaturated organic chain.

6. A light emitter according to claim 5, wherein the unsaturated organic chain is selected from the group consisting of aliphatic, amine and ether linkages.

7. A light emitter comprising:

- a photoalignment layer; and
- a light emitting polymer aligned on the photoalignment layer,

wherein the photoalignment layer includes a copolymer incorporating both linear rod-like hole-transporting and photoactive side chains.

8. A light emitter comprising:

- a photoalignment layer; and
- a light emitting polymer aligned on the photoalignment layer,

wherein the light emitting polymer comprises from 5 to 50 monomeric units.

9. A light emitter comprising:

- a photoalignment layer; and
- a light emitting polymer aligned on the photoalignment layer,

wherein the light emitting polymer comprises uniaxially aligned chromophores.

10. A light emitter comprising:

- a photoalignment layer; and
- a light emitting polymer aligned on the photoalignment layer, wherein the light emitting polymer has a polarization ratio of greater than 10.

11. A light emitter comprising:

- a photoalignment layer; and
- a light emitting polymer aligned on the photoalignment layer,

wherein the light emitting polymer forms an insoluble, cross-linked network.

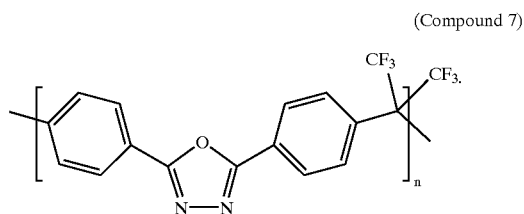
12. A light emitter comprising:

- a photoalignment layer;
- a light emitting polymer aligned on the photoalignment layer; and

an electron-transporting polymer layer.

13. A light emitter according to claim 12, comprising an electron transporting polymer of the formula:

27



14. A light emitter comprising:
a photoalignment layer; and
a light emitting polymer aligned on the photoalignment layer in pixellated form.
15. A light emitter according to claim 14, comprising pixels arranged for polarized emission.
16. A light emitter comprising:
a photoalignment layer and a light emitting polymer aligned on said photoalignment layer,
wherein the light emitter is in pixellated form with pixels arranged for polarized emission and the pixels are of the same color but have their polarization direction in different orientations.
17. A light emitter according to claim 16, additionally comprising a photoactive dye as a dopant.
18. A multicolor light emitter comprising:
a photoalignment layer and a light emitting polymer aligned on said photoalignment layer,
wherein the light emitter is in pixellated form with pixels having arrangements or sequences of different pixel colors.
19. A multicolor light emitter according to claim 18, comprising stripes of red, green and blue pixels having the same polarization state.
20. A multicolor light emitter according to claim 18, comprising red, green and blue pixels having the same or different alignment.
21. A display comprising:
a screen and a light emitter wherein the screen comprises a plastic polymer selected from the group consisting of polyethylene, polyethylene terephthalate and any mixtures thereof; and
wherein the light emitter comprises a photoalignment layer and a light emitting polymer aligned on the photoalignment layer.
22. The display of claim 21, wherein the screen is curved.
23. A security viewer comprising:
a photoalignment layer;
a light emitting polymer aligned on the photoalignment layer, wherein the pixels are arranged for polarized emission; and
viewing means having a different polarization for each eye.
24. A method of forming a light emitter comprising:
forming a photoalignment layer; and forming the light emitting polymer on the photoalignment layer by an in situ polymerization process such that the light emitting polymer is aligned.
25. A method according to claim 24, wherein reactive monomer components are deposited on the photoalignment layer by a spin-coating process.
26. A method according to claim 24, wherein the in situ polymerization process involves photopolymerization.
27. The method of claim 24, wherein the light emitting polymer is formed from a reactive mesogen and a reactive monomer capable of co-polymerization with the reactive mesogen.

28

28. The method of claim 27, wherein the reactive mesogen has a molecular weight of from 400 to 2,000.
29. The method of claim 27, wherein the light emitting polymer has a molecular weight of above 4,000.
30. The method of claim 27, wherein the light emitting polymer is formed from 5 to 50 monomeric units.
31. A method of forming a light emitter comprising:
forming a photoalignment layer;
aligning a light emitting polymer on the photoalignment layer, and
applying an electron-transporting polymer layer.
32. A method of forming a multicolor emitter, the method comprising:
forming a photoalignment layer;
aligning a light emitting polymer on the photoalignment layer,
applying a first color light emitter 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.
33. A method of forming a light emitter comprising:
forming a photoalignment layer;
forming a light emitting polymer on the photoalignment layer; and
aligning the light emitting polymer on the photoalignment layer,
wherein the light emitting polymer is formed from a reactive mesogen and a reactive monomer capable of co-polymerization with the reactive mesogen.
34. The method of claim 33, wherein the reactive mesogen has a molecular weight of from 400 to 2,000.
35. The method of claim 33, wherein the light emitting polymer has a molecular weight of above 4,000.
36. The method of claim 33, wherein the light emitting polymer is formed from 5 to 50 monomeric units.
37. A method of forming a light emitter comprising:
forming a photoalignment layer;
forming a first light emitting polymer on the photoalignment layer;
patterning the first light emitting polymer; and
forming a second light emitting polymer on the photoalignment layer,
wherein the first light emitting polymer and the second light emitting polymer are aligned by the photoalignment layer.
38. The method of claim 37, further comprising:
patterning the second light emitting polymer; and
forming a third light emitting polymer on the photoalignment layer,
wherein the third light emitting polymer is aligned by the photoalignment layer.
39. The method of claim 37, wherein the first, second and third light emitting polymers emit different colors of light.
40. The method of claim 39, wherein the different colors of light are selected from the group consisting of red, blue and green.
41. The method of claim 37, wherein
the first light emitting polymer includes a first chromophore;
the second light emitting polymer includes a second chromophore different from the first chromophore.

29

42. The method of claim 37,
 wherein the first light emitting polymer and the second
 light emitting polymer are each formed from a reactive
 mesogen and a reactive monomer capable of
 co-polymerization with the reactive mesogen. 5
43. A light emitter comprising:
 a photoalignment layer; and
 a light emitting polymer on the photoalignment layer, the
 light emitting polymer being formed from a reactive 10
 mesogen and a reactive monomer capable of
 co-polymerization with the reactive mesogen,
 wherein the light emitting polymer is aligned by the
 photoalignment layer.
44. The emitter of claim 43, wherein the reactive mesogen 15
 has a molecular weight of from 400 to 2,000.
45. The emitter of claim 43, wherein the light emitting
 polymer has a molecular weight of above 4,000.
46. The emitter of claim 43, wherein the light emitting
 polymer is formed from 5 to 50 monomeric units. 20
47. A light emitter comprising:
 a photoalignment layer;
 a first light emitting polymer on the photoalignment layer;
 and
 a second light emitting polymer on the photoalignment 25
 layer,
 wherein the first light emitting polymer and the second
 light emitting polymer are aligned by the photoalign-
 ment layer; and
 wherein the first light emitting polymer is patterned. 30
48. The emitter of claim 47, further comprising:
 a third light emitting polymer on the photoalignment
 layer,
 wherein the second light emitting polymer is patterned; 35
 and
 wherein the third light emitting polymer is aligned by the
 photoalignment layer.
49. The emitter of claim 47, wherein the first, second and
 third light emitting polymers emit different colors of light. 40
50. The emitter of claim 49, wherein the different colors
 of light are selected from the group consisting of red, blue
 and green.
51. The emitter of claim 47, wherein 45
 the first light emitting polymer includes a first chro-
 mophore; and
 the second light emitting polymer includes a second
 chromophore different from the first chromophore.

30

52. The emitter of claim 47,
 wherein the first light emitting polymer and the second
 light emitting polymer are each formed from a reactive
 mesogen and a reactive monomer capable of
 co-polymerization with the reactive mesogen.
53. A light emitter comprising:
 a photoalignment layer; and
 a light emitting polymer aligned on the photoalignment
 layer,
 wherein the photoalignment layer is formed from a
 co-polymer incorporating side chains.
54. The emitter of claim 53, wherein the side chains
 include both linear rod-like hole-transporting side chains
 and photoactive side chains.
55. A method of forming a light emitter comprising:
 forming a photoalignment layer;
 depositing a polymerizable material including a reactive
 mesogen on the photoalignment layer;
 doping the polymerizable material with at least one reac-
 tive monomer capable of co-polymerization with the
 reactive mesogen; and
 polymerizing the polymerizable material and the at least
 one reactive monomer to form a light emitting layer.
56. The method of claim 55, wherein the at least one
 reactive monomer includes two or more reactive monomers.
57. The method of claim 56, wherein each reactive
 monomer of two or more reactive monomers are doped into
 different areas of the polymerizable material so as to form
 different colored pixels when polymerized.
58. A light emitter comprising:
 a photoalignment layer; and
 an aligned polymer light emitting layer on the photoalign-
 ment layer, the polymer light emitting layer including
 at least one reactive monomer co-polymerized with a
 reactive mesogen.
59. The emitter of claim 58, wherein the at least one
 reactive monomer includes two or more reactive monomers.
60. The emitter of claim 59, wherein each reactive mono-
 mer of two or more reactive monomers are located in
 different areas of the aligned polymer light emitting layer so
 as to form different colored pixels. 45
61. The emitter of claim 60, wherein the different areas
 correspond to different colored pixels.

* * * * *