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(54) Title: ELECTROLUMINESCENT MATERIALS AND DEVICES

(57) Abstract: An electroluminescent composition comprises a dopant which is an aromatic substituted anthracene compound mixed with a host material.

Electroluminescent Materials and Devices

The present invention relates to electroluminescent compositions and to electroluminescent devices.

Materials which emit light when an electric current is passed through them are well known and used in a wide range of display applications. Liquid crystal devices and devices which are based on inorganic semiconductor systems are widely used; however these suffer from the disadvantages of high energy consumption, high cost of manufacture, low quantum efficiency and the inability to make flat panel displays.

Organic polymers have been proposed as useful in electroluminescent devices, but it is not possible to obtain pure colours; they are expensive to make and have a relatively low efficiency.

Another compound which has been proposed is aluminium quinolate, but this requires dopants to be used to obtain a range of colours and has a relatively low efficiency.

Patent application WO98/58037 describes a range of lanthanide complexes which can be used in electroluminescent devices which have improved properties and give better results. Patent Applications PCT/GB98/01773, PCT/GB99/0367, PCT/GB99/04030, PCT/GB99/04024, PCT/GB99/04028, PCT/GB00/00268 describe electroluminescent complexes, structures and devices using rare earth chelates.

US Patent 5128587 discloses an electroluminescent device which consists of an organometallic complex of rare earth elements of the lanthanide series sandwiched between a transparent electrode of high work function and a second electrode of low

work function with a hole conducting layer interposed between the electroluminescent layer and the transparent high work function electrode and an electron conducting layer interposed between the electroluminescent layer and the electron injecting low work function anode. The hole conducting layer and the electron conducting layer are required to improve the working and the efficiency of the device. The hole transporting layer serves to transport holes and to block the electrons, thus preventing electrons from moving into the electrode without recombining with holes. The recombination of carriers therefore mainly takes place in the emitter layer.

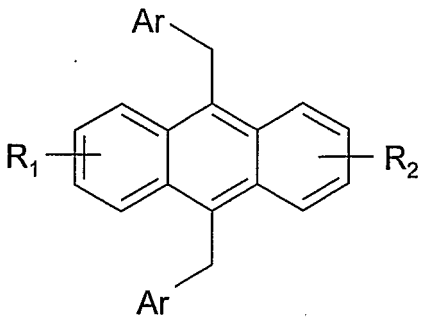
It is known that anthracene is an electroluminescent composition and can emit light in the blue region of the spectrum, but its performance has not been adequate to enable it to be used in electroluminescent devices.

We have now found that an electroluminescent composition that comprises a host material doped with an aromatic substituted anthracene compound has improved properties.

According to the invention there is provided an electroluminescent composition comprising a dopant which is an aromatic substituted anthracene compound mixed with a host material.

The invention also provides an electroluminescent device which comprises (i) a first electrode, (ii) a layer of an electroluminescent composition comprising a dopant which is an aromatic substituted anthracene compound mixed with a host material and (iii) a second electrode.

Preferably the aromatic substituted anthracene compound has the formula



(VI)

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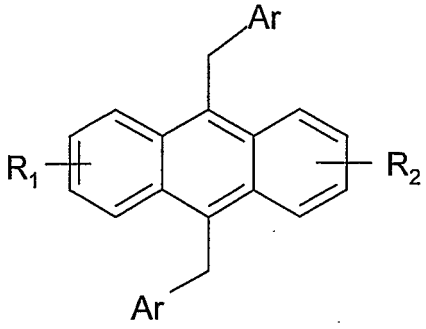

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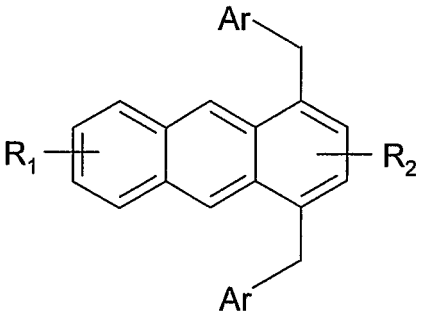

(VIII)

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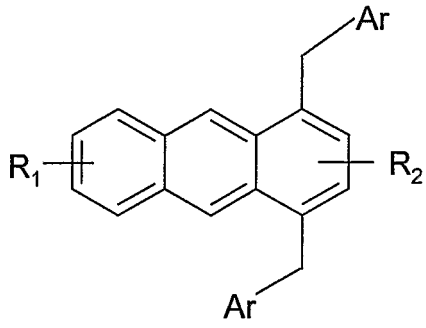

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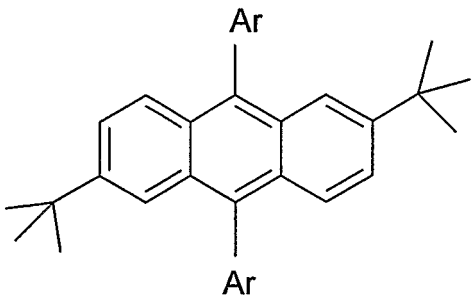
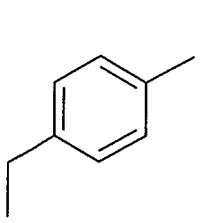


(X)

where Ar is an aromatic or a substituted aromatic group, a substituted or unsubstituted polyaromatic group such as anthracene or naphthalene and R_1 and R_2 are the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoryl methyl groups, halogens such as fluorine or thiophenyl groups.

Examples of groups Ar are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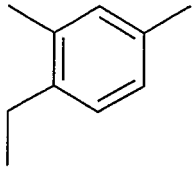
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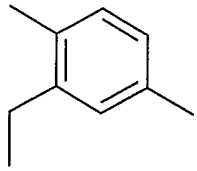
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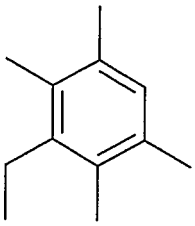
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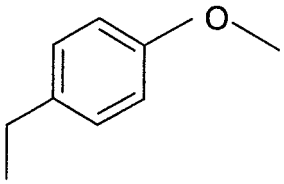
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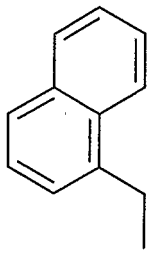
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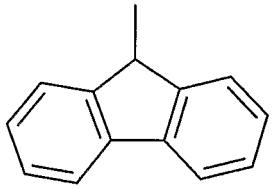
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The host material should have a bandgap which is wider than that of the aromatic substituted aromatic compound and the upper band level is higher than the upper band level of the aromatic substituted aromatic compound and the lower band level is lower than the lower band level of the aromatic substituted aromatic compound.

Preferably the host material is an electroluminescent compound.

As discussed in US 4769292, in theory, if the host material and the aromatic substituted anthracene could be found for blending which have exactly the same affinity for hole-electron recombination, each material should emit light upon injection of holes and electrons into the luminescent zone. The perceived hue of light emission would be the visual integration of both emissions.

Since imposing such a balance of the host material and aromatic substituted anthracene compounds is highly limiting, it is preferred to choose the aromatic substituted anthracene compound so that it provides the favoured sites for light emission. When only a small proportion of aromatic substituted anthracene compounds providing favoured sites for light emission are present, peak intensity wavelength emissions typical of the host material can be entirely eliminated in favour

of a new peak intensity wavelength emission attributable to the aromatic substituted anthracene compound. While the minimum proportion of aromatic substituted anthracene compounds sufficient to achieve this effect varies by the specific choice of host material and aromatic substituted anthracene compounds, in no instance is it necessary to employ more than about 10 mole percent aromatic substituted anthracene compound based on moles of host material and seldom is it necessary to employ more than 1 mole percent of the aromatic substituted anthracene compound. On the other hand, for any host material capable of emitting light in the absence of aromatic substituted anthracene compounds, limiting the aromatic substituted anthracene compounds present to extremely small amounts, typically less than about 10^{-3} mole percent, based on host material, can result in retaining emission at wavelengths characteristic of the host material. Thus, by choosing the proportion of aromatic substituted anthracene compounds capable of providing favoured sites for light emission, either a full or partial shifting of emission wavelengths can be realized. This allows the spectral emissions of the EL devices of this invention to be selected and balanced to suit the application to be served.

Choosing aromatic substituted anthracene compounds capable of providing favoured sites for light emission, necessarily involves relating the properties of the aromatic substituted anthracene compounds to those of the host material. The host material can be viewed as a collector for injected holes and electrons with the aromatic substituted anthracene compounds providing the molecular sites for light emission. One important relationship for choosing aromatic substituted anthracene compounds capable of modifying the hue of light emission when present in a host material is a comparison of the reduction potentials of the two materials. The aromatic substituted anthracene compounds demonstrated to shift the wavelength of light emission have exhibited a less negative reduction potential than that of the host material. Reduction potentials, measured in electron volts, have been widely reported in the literature along with varied techniques for their measurement. Since it is a comparison of reduction potentials rather than their absolute values which is desired, it is apparent

that any accepted technique for reduction potential measurement can be employed, provided both the fluorescent and host material reduction potentials are similarly measured. A preferred oxidation and reduction potential measurement technique is reported by R. J. Cox, Photographic Sensitivity, Academic Press, 773, Chapter 15.

A second important relationship for choosing aromatic substituted anthracene compounds capable of modifying the hue of light emission when present in a host material is a comparison of the bandgap potentials of the two materials. The aromatic substituted anthracene compounds demonstrated to shift the wavelength of light emission have exhibited a lower bandgap potential than that of the host material. The bandgap potential of a molecule is taken as the potential difference in electron volts (eV) separating its ground state and first singlet state. Bandgap potentials and techniques for their measurement have been widely reported in the literature. The bandgap potentials herein reported are those measured in electron volts (eV) at an absorption wavelength which is bathochromic to the absorption peak and of a magnitude one tenth that of the magnitude of the absorption peak. Since it is a comparison of bandgap potentials rather than their absolute values which is desired, it is apparent that any accepted technique for bandgap measurement can be employed, provided both the fluorescent and host material band gaps are similarly measured. One illustrative measurement technique is disclosed by F. Gutman and L. E. Lyons, Organic Semiconductors, Wiley, 767, Chapter 5.

Where a host material is chosen, which is itself capable of emitting light in the absence of the aromatic substituted anthracene compounds, it has been observed that suppression of light emission at the wavelengths of emission characteristics of the host material alone and enhancement of emission at wavelengths characteristic of the aromatic substituted anthracene compounds occurs when spectral coupling of the host material and aromatic substituted anthracene compounds is achieved. By spectral coupling it is meant that an overlap exists between the wavelengths of emission characteristic of the host material alone and the wavelengths of light absorption of the

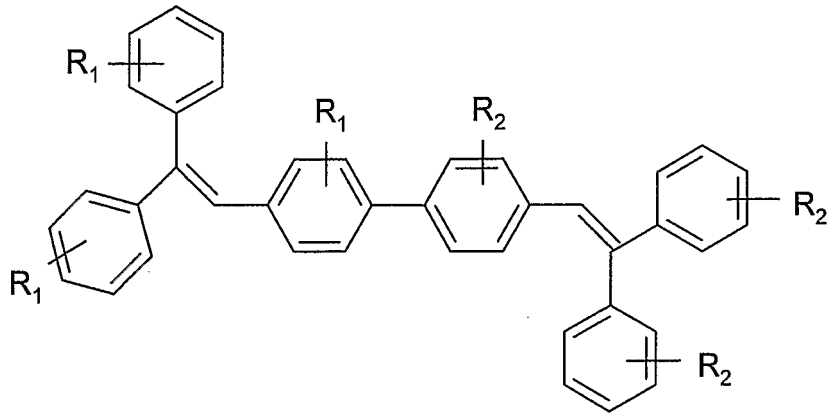
aromatic substituted anthracene compounds in the absence of the host material. Optimal spectral coupling occurs when the wavelength of maximum light emitted by said host material in the absence of said substituted anthracene compound is within 25 nm of the wavelength of maximum light absorption by said substituted anthracene compound alone. In practice advantageous spectral coupling can occur with peak emission and absorption wavelengths differing by up to 100 nm or more, depending on the width of the peaks and their hypsochromic and bathochromic slopes. Where less than optimum spectral coupling between the host material and aromatic substituted anthracene compounds is contemplated, a bathochromic as compared to a hypsochromic displacement of the aromatic substituted anthracene compounds produces more efficient results.

Although the foregoing discussion has been undertaken by reference to host materials which are known themselves to emit light in response to hole and electron injection, in fact light emission by the host material itself can entirely cease where light emission by the aromatic substituted anthracene compounds is favoured by any one or a combination of the various relationships noted above. It is appreciated that shifting the role of light emission to the aromatic substituted anthracene compounds allows a still broader range of choices of host materials. For example, one fundamental requirement of a material chosen to emit light is that it must exhibit a low extinction coefficient for light of the wavelength it emits to avoid internal absorption. The present invention permits use of host materials which are capable of sustaining the injection of holes and electrons, but are themselves incapable of efficiently emitting light.

Useful aromatic substituted anthracene compounds are those capable of being blended with the host material and fabricated into thin films satisfying the thickness ranges described above forming the luminescent zones of the electroluminescent devices of this invention. While crystalline host materials do not lend themselves to thin film formation, the limited amounts of aromatic substituted anthracene

compounds present in the host material permits the use of aromatic substituted anthracene compounds which are alone incapable of thin film formation. Preferred aromatic substituted anthracene compounds are those which form a common phase with the host material.

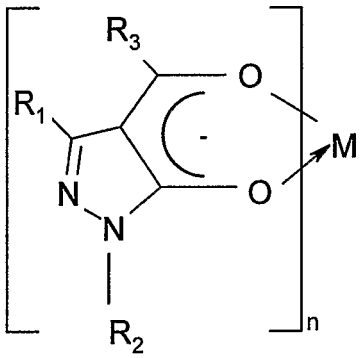
Preferred host materials are conjugated aromatic compounds of formula :-



(III)

where R_1 and R_2 are as above;

or compounds of formula

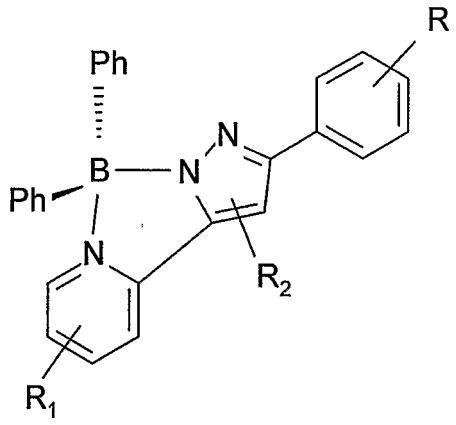


(IV)

where M is a metal; n is the valency of M; R_1, R_2 and R_3 which may be the same or different are selected from hydrogen, hydrocarbyl groups, substituted and unsubstituted aliphatic groups substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoryl methyl groups,

halogens such as fluorine or thiophenyl groups or nitrile; R_1, and R_3 can also be in the form of ring structures and R_1, R_2 and R_3 can be copolymerisable with a monomer, e.g. styrene;

or compounds of formula



(V)

where Ph is an unsubstituted or substituted phenyl group where the substituents can be the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoryl methyl groups, halogens such as fluorine or thiophenyl groups; R, R_1 and R_2 can be hydrogen or substituted or unsubstituted hydrocarbyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorine, fluorocarbons such as trifluoryl methyl groups, halogens such as fluorine or thiophenyl groups or nitrile.

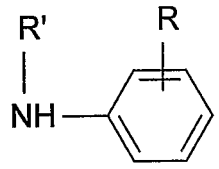
Examples of R and/or R_1 and/or R_2 and/or R_3 include aliphatic, aromatic and heterocyclic alkoxy, aryloxy and carboxy groups, substituted and substituted phenyl, fluorophenyl, biphenyl, phenanthrene, anthracene, naphthyl and fluorene groups alkyl groups such as t-butyl, heterocyclic groups such as carbazole.

Preferably the layer of the electroluminescent composition is a thin film of less than 1 μm in thickness.

In the electroluminescent device of the invention the first electrode can function as the cathode and the second electrode can function as the anode and preferably there is a layer of a hole transporting material between the anode and the layer of the electroluminescent compound.

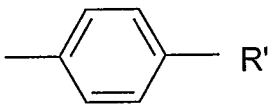
The hole transporting material can be any of the hole transporting materials used in electroluminescent devices.

The hole transporting material can be an amine complex such as poly (vinylcarbazole), N, N'-diphenyl-N, N'-bis (3-methylphenyl) -1,1' -biphenyl -4,4'-diamine (TPD), an unsubstituted or substituted polymer of an amino substituted aromatic compound, a polyaniline, substituted polyanilines, polythiophenes, substituted polythiophenes, polysilanes etc. Examples of polyanilines are polymers of



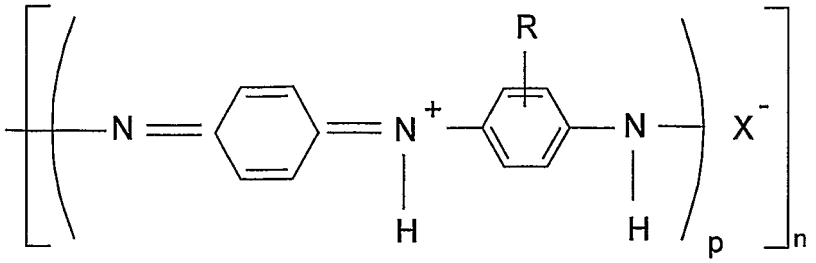
(I)

where R is in the ortho – or meta-position and is hydrogen, C1-18 alkyl, C1-6 alkoxy, amino, chloro, bromo, hydroxy or the group



where R is alky or aryl and R' is hydrogen, C1-6 alkyl or aryl with at least one other monomer of formula (I) above.

Or the hole transporting material can be a polyaniline. Polyanilines which can be used in the present invention have the general formula



(II)

where p is from 1 to 10 and n is from 1 to 20, R is as defined above and X is an anion, preferably selected from Cl, Br, SO_4, BF_4, PF_6, H_2PO_3, H_2PO_4, arylsulphonate, arenedicarboxylate, polystyrenesulphonate, polyacrylate alkysulphonate, vinylsulphonate, vinylbenzene sulphonate, cellulose sulphonate, camphor sulphonates, cellulose sulphate or a perfluorinated polyanion.

Examples of arylsulphonates are p-toluenesulphonate, benzenesulphonate, 9,10-anthraquinone-sulphonate and anthracenesulphonate, an example of an arenedicarboxylate is phthalate and an example of arenecarboxylate is benzoate.

We have found that protonated polymers of the unsubstituted or substituted polymer of an amino substituted aromatic compound such as a polyaniline are difficult to evaporate or cannot be evaporated, however we have surprisingly found that if the unsubstituted or substituted polymer of an amino substituted aromatic compound is deprotonated then it can easily be evaporated i.e. the polymer is evaporable.

Preferably evaporable deprotonated polymers of unsubstituted or a substituted polymer of an amino substituted aromatic compound are used. The de-protonated unsubstituted or substituted polymer of an amino substituted aromatic compound can be formed by deprotonating the polymer by treatment with an alkali such as

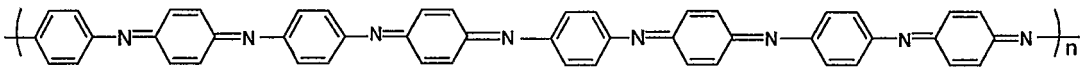
ammonium hydroxide or an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide.

The degree of protonation can be controlled by forming a protonated polyaniline and de-protonating. Methods of preparing polyanilines are described in the article by A. G. MacDiarmid and A. F. Epstein, Faraday Discussions, Chem Soc.88 P37 789.

The conductivity of the polyaniline is dependant on the degree of protonation with the maximum conductivity being when the degree of protonation is between 40 and 60% e.g. about 50%.

Preferably the polymer is substantially fully deprotonated.

A polyaniline can be formed of octamer units i.e. p is four, e.g.



The polyanilines can have conductivities of the order of 1 x 10^{-1} Siemen cm^{-1} or higher.

The aromatic rings can be unsubstituted or substituted e.g. by a C1 to 20 alkyl group such as ethyl.

The polyaniline can be a copolymer of aniline and preferred copolymers are the copolymers of aniline with o-anisidine, m-sulphanilic acid or o-aminophenol, or o-toluidine with o-aminophenol, o-ethylaniline, o-phenylene diamine or with amino anthracenes.

Other polymers of an amino substituted aromatic compound which can be used include substituted or unsubstituted polyaminonapthalenes, polyaminoanthracenes, polyaminophenanthrenes, etc. and polymers of any other condensed polyaromatic compound. Polyaminoanthracenes and methods of making them are disclosed in US Patent 6,153,726. The aromatic rings can be unsubstituted or substituted e.g. by a group R as defined above.

Other hole transporting materials are conjugated polymers and the conjugated polymers which can be used can be any of the conjugated polymers disclosed or referred to in US 5807627, PCT/WO90/13148 and PCT/WO92/03490.

The preferred conjugated polymers are poly (p-phenylenevinylene)-PPV and copolymers including PPV. Other preferred polymers are poly(2,5 dialkoxyphenylene vinylene) such as poly (2-methoxy-5-(2-methoxypentyloxy-1,4-phenylene vinylene), poly(2-methoxypentyloxy)-1,4-phenylenevinylene), poly(2-methoxy-5-(2-dodecyloxy-1,4-phenylenevinylene) and other poly(2,5 dialkoxyphenylenevinylenes) with at least one of the alkoxy groups being a long chain solubilising alkoxy group, poly fluorenes and oligofluorenes, polyphenylenes and oligophenylenes, polyanthracenes and oligo anthracenes, ploythiophenes and oligothiophenes.

In PPV the phenylene ring may optionally carry one or more substituents e.g. each independently selected from alkyl, preferably methyl, alkoxy, preferably methoxy or ethoxy.

Any poly(arylenevinylene) including substituted derivatives thereof can be used and the phenylene ring in poly(p-phenylenevinylene) may be replaced by a fused ring system such as anthracene or naphthlyene ring and the number of vinylene groups in each polyphenylenevinylene moiety can be increased e.g. up to 7 or higher.

The conjugated polymers can be made by the methods disclosed in US 5807627, PCT/WO90/13148 and PCT/WO92/03490.

The thickness of the hole transporting layer is preferably 20nm to 200nm.

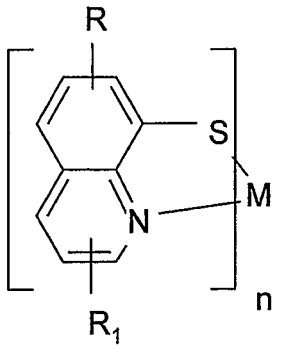
The polymers of an amino substituted aromatic compound such as polyanilines referred to above can also be used as buffer layers with or in conjunction with other hole transporting materials.

The structural formulae of some other hole transporting materials are shown in Figures 4, 5, 6, 7 and 8 of the drawings, where R_1, R_2 and R_3 can be the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoryl methyl groups, halogens such as fluorine or thiophenyl groups; R_1, R_2 and R_3 can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer e.g. styrene. X is Se, S or O, Y can be hydrogen, substituted or unsubstituted hydrocarbyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorine, fluorocarbons such as trifluoryl methyl groups, halogens such as fluorine or thiophenyl groups or nitrile.

Examples of R_1 and/or R_2 and/or R_3 include aliphatic, aromatic and heterocyclic alkoxy, aryloxy and carboxy groups, substituted and substituted phenyl, fluorophenyl, biphenyl, phenanthrene, anthracene, naphthyl and fluorene groups alkyl groups such as t-butyl, heterocyclic groups such as carbazole.

Optionally there is a layer of an electron injecting material between the cathode and the electroluminescent composition layer; the electron injecting material is a material which will transport electrons when an electric current is passed through electron

injecting materials and include a metal complex such as a metal quinolate e.g. an aluminium quinolate, lithium quinolate, zirconium quinolate; a compound of formula $Mx(DBM)_n$ where Mx is a metal and DBM is dibenzoyl methane and n is the valency of Mx, e.g. Mx is chromium. The electron injecting material can also be a cyano anthracene such as 9,10 dicyano anthracene, cyano substituted aromatic compounds, tetracyanoquinidodimethane a polystyrene sulphonate or a compound with the structural formulae shown in figures 2 or 3 of the drawings in which the phenyl rings can be substituted with substituents R as defined above; or a metal thioxinate of formula



(VI)

where M is a metal, preferably zinc, cadmium, gallium and indium; n is the valency of M; R and R_1 which can be the same or different are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoryl methyl groups, halogens such as fluorine; thiophenyl groups; cyano group; substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aliphatic groups as described in patent application PCT/GB2005/002579.

The electron injecting material layer should have a thickness so that the holes form the anode and the electrons from the cathode combine in the electroluminescent layer.

Instead of being a separate layer the electron injecting material can be mixed with the electroluminescent composition and co-deposited with it.

Optionally the hole transporting material can be mixed with the electroluminescent composition and co-deposited with it.

The hole transporting materials, the electroluminescent composition and the electron injecting materials can be mixed together to form one layer, which simplifies the construction.

The anode is preferably a transparent substrate such as a conductive glass or plastic material which acts as the anode. Preferred substrates are conductive glasses such as indium tin oxide coated glass, but any glass which is conductive or has a conductive layer such as a metal or conductive polymer can be used. Conductive polymers and conductive polymer coated glass or plastics materials can also be used as the substrate.

The cathode is preferably a low work function metal and preferably is comprised of a metal other than an alkali metal having a work function of less than 4 eV e.g. aluminium, calcium, lithium, magnesium and alloys thereof such as silver/magnesium alloys, rare earth metal alloys etc.; aluminium is a preferred metal. A metal fluoride such as an alkali metal, rare earth metal or their alloys can be used as the second electrode, for example by having a metal fluoride layer formed on a metal.

The invention is illustrated in the Examples in which examples 1-9 show the synthesis of the aromatic substituted anthracene compounds.

Examples

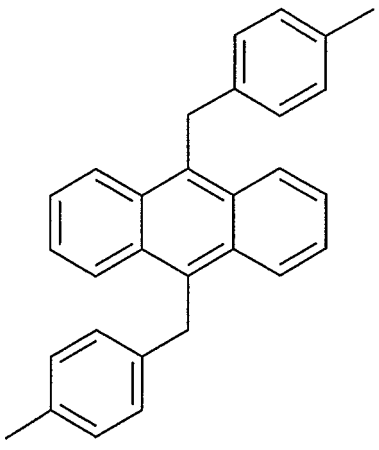
Synthesis for 9,10-Dibenzylanthracene Compounds

This is a general synthesis for these compounds. In each separate example a different benzyl halide compound is used, but the synthesis process is the same.

Anthracene (8.0g, 44.9mmol), Zinc dust (2.35g, 35.9mmol) and the benzyl chloride (94mmol) were stirred in carbon disulphide (150ml) and refluxed for 30h. The reaction was cooled to room temperature and the solvent was removed by distillation. The residue was extracted into hot toluene (200ml) and filtered under vacuum to remove excess zinc. On cooling. The toluene solution yielded a light yellow crystalline product which was recrystalised from hot toluene. filtered and dried in a vacuum oven.

Example 1

For 9,10 –Bis(4-methyl-benzyl)-anthracene (A)

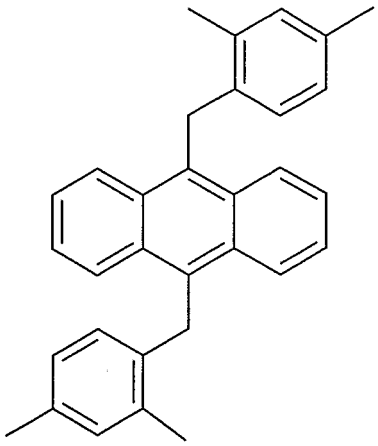


(XI)

4-Methylbenzylchloride was used as the starting material

Example 2

For 9,10-Bis-(2,4-dimethyl-benzyl)-anthracene (B)

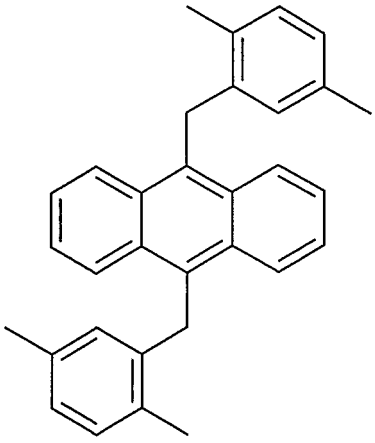


(XII)

2,4-Dimethylbenzyl chloride was used as the starting material.

Example 3

For 9,10-Bis-(2,5-dimethyl-benzyl)-anthracene (C)

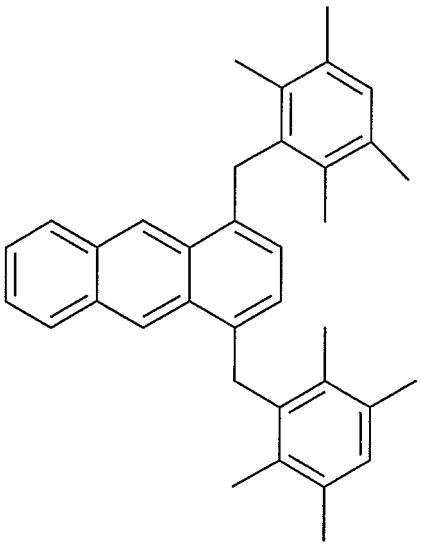


(XIII)

2,5-Dimethylbenzyl chloride was used as the starting material.

Example 4

For 1,4-Bis-(2,3,5,6-tetramethyl-benzyl)-anthracene (D)

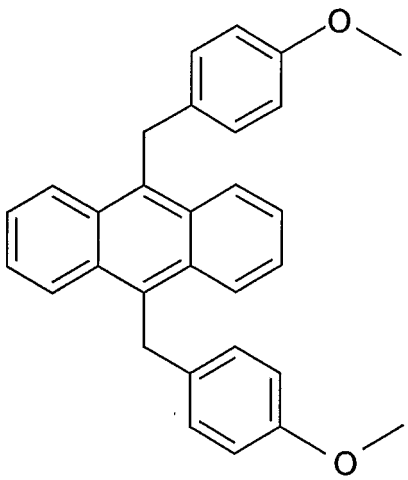


(XIV)

2,3,5,6-tetrameyhylbenzyl chloride was used as the starting material.

Example 5

For 9,10-Bis-(4-methoxy-benzyl)-anthracene (E)

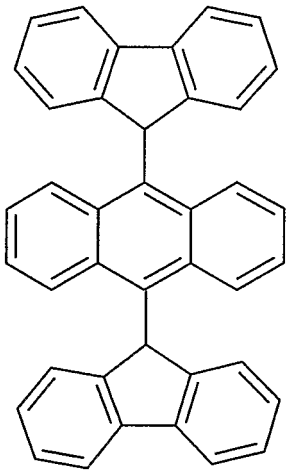


(XV)

4-Methoxybenzyl chloride was used as the starting material.

Example 6

For 9,10-Bis-(9H-fluoren-9-yl)-anthracene (F)

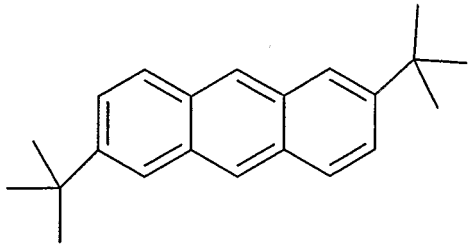


(XVI)

9-Bromofluorene was used as the starting material.

Example 7

Preparation of 2,6-Di-tert-butyl-anthracene



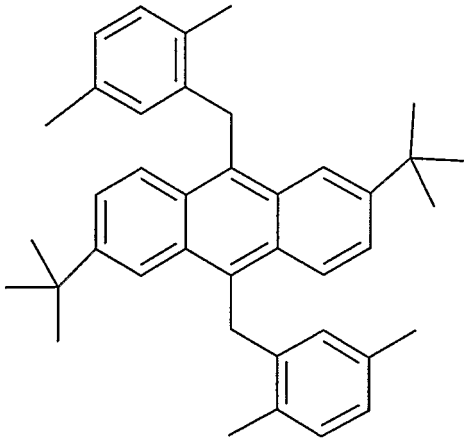
(XVII)

Anthracene (7.13g. 40mmol) and *tert*-Butanol (10.8g, 120mmol) were refluxed for 15h in trifluroacetic acid (40ml). The mixture was cooled and poured into water (250ml). The solid that formed was filtered under vacuum, washed with water and dried. The solid was recrystalised from hot hexane to yield a colourless crystalline

solid. M.p. 249-253°C.

Example 8

Preparation of 2,6-Di-tert-butyl-9,10-bis-(2,5-dimethyl-benzyl)-anthracene (G)

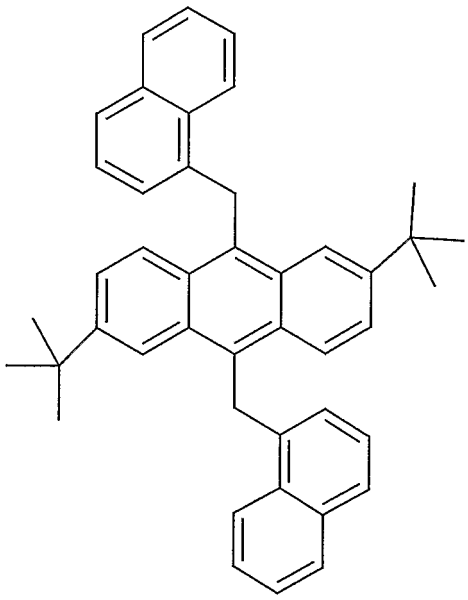


(XVIII)

2,6-Di-tert-butyl-anthracene (3.0g, 10.3mmol), Zinc dust (0.54g, 8.3mmol) and 2,5-Dimethylbenzyl chloride (3.35g, 21.7mmol) were stirred in carbon disulphide (50ml) and refluxed for 30h. The reaction was cooled to room temperature and the solvent was removed by distillation. The residue was extracted into hot toluene (50ml) and filtered under vacuum to remove excess zinc. On cooling, the toluene solution yielded a colourless crystalline product which was recrystalised from hot toluene, filtered and dried in a vacuum oven. M.p. 273-275°C.

Example 9

Preparation of 2,6-Di-tert-butyl-9,10-bis-naphthalen-I -ylmethyl-anthracene (H)



(XIX)

2,6-Di-tert-butyl-anthracene (2.9g, 10mmol), Zinc dust (0.52g, 8mmol) and 1-(chloromethyl)naphthalene (3.7g, 20.9mmol) were stirred in carbon disulphide (50ml) and refluxed for 30h. The reaction was cooled to room temperature and the solvent was removed by distillation. The residue was extracted into hot toluene (50ml) and filtered under vacuum to remove excess zinc. On cooling. The toluene solution yielded a colourless crystalline product which was recrystalised from hot toluene filtered and dried in a vacuum oven. M.p. 285°C.

Electroluminescent Devices

Example 10

A pre-etched ITO coated glass piece (10 x 10cm^2) was used. The device was fabricated by sequentially forming on the ITO, by vacuum evaporation the

compositions forming the layers comprising the electroluminescent device. The layers were deposited using a Solciet Machine, ULVAC Ltd. Chigacki, Japan. The active area of each pixel was 3mm by 3mm, the device is shown in fig. 1 and the layers comprised:-

(1) ITO/ (2) α-NPB (42 nm)/ (3) K:H (20 : 1) (26 nm)/ (4) Zrq_4 (17 nm)/ (5) LiF (0.3 nm)/ (6) Al.

Where ITO is indium tin oxide coated glass, α-NPB is shown in the fig. 8 of the drawings, Zrq_4 is zirconium quinolate and K and H are as defined below.

The coated electrodes were stored in a vacuum desiccator over a molecular sieve and phosphorous pentoxide until they were loaded into a vacuum coater (Edwards, 10^{-6} torr) and aluminium top contacts made. The devices were then kept in a vacuum desiccator until the electroluminescence studies were performed.

The ITO electrode was always connected to the positive terminal. The current vs. voltage studies were carried out on a computer controlled Keithly 2400 source meter.

An electric current was applied across the device and the performance shown in figs. 9 and 10.

Example 11

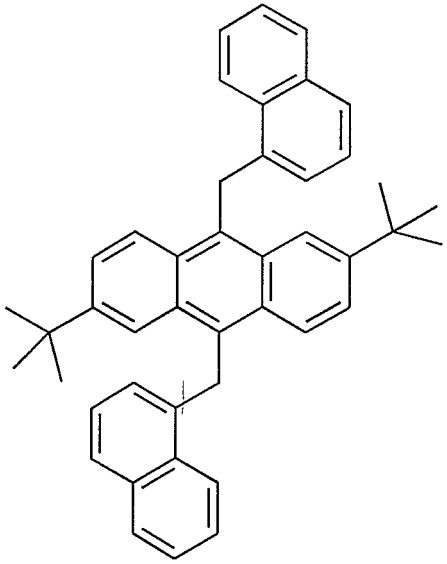
A device was formed as in example 10 with the structure:-

(1) ITO/α-NPB (40 nm)/(2) L : H (20 : 2) (27 nm)/(3) Zrq_4 (17 nm)/(4) LiF (0.3 nm)/ (5) Al.

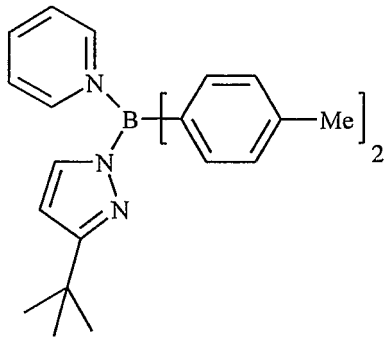
where H and L are as shown below

The performance is shown in figs. 11 and 12.

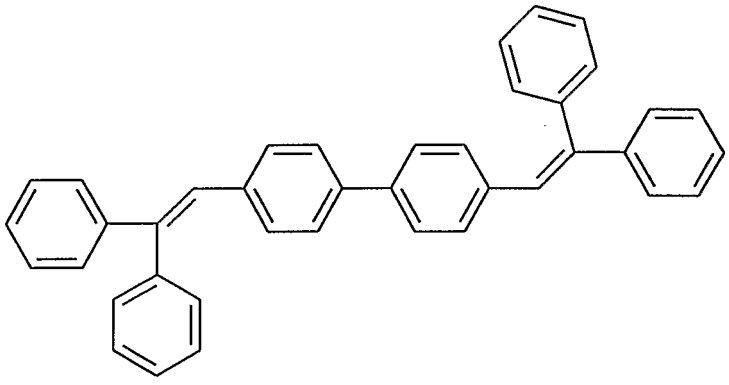
Compounds used in devices



H



K



L

Claims

1. An electroluminescent composition comprising a dopant which is an aromatic substituted anthracene compound mixed with a host material..

2. An electroluminescent composition as claimed in claim 1 in which the aromatic substituted anthracene compound has the formula (VI) to (XIX) herein.

3. An electroluminescent composition as claimed in claims 1 or 2 in which there is up to 10 mole percent aromatic substituted anthracene compounds, based on moles of host material.

4. An electroluminescent composition as claimed in claims 1 or 2 in which there is up to 1 mole percent aromatic substituted anthracene compounds, based on moles of host material.

5. An electroluminescent composition as claimed in claims 1 or 2 in which there is less than 10^{-3} mole percent aromatic substituted anthracene compounds, based on moles of host material.

6. An electroluminescent composition as claimed in claims 1 or 2 in which there is 10^{-3} to 10 mole percent, aromatic substituted anthracene compounds, based on moles of host material.

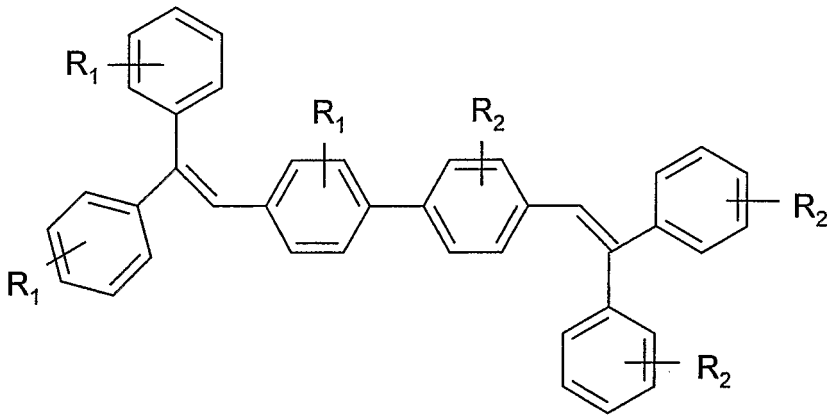
7. An electroluminescent composition as claimed in any one of claims 1 to 6 in which the aromatic substituted anthracene compound has a bandgap no greater than that of said host material and a reduction potential less negative than that of said host material.

8. An electroluminescent composition as claimed in any one of claims 1 to 7 in which said host material is capable of emitting light of a first wavelength in the absence of

said aromatic substituted anthracene compound and the aromatic substituted anthracene compound is capable of absorbing light at the first wavelength.

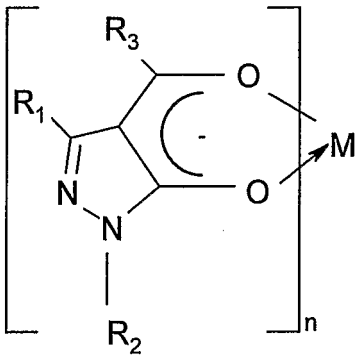
9. An electroluminescent composition as claimed in any one of claims 1 to 8 in which the wavelength of maximum light emitted by said host material in the absence of said substituted anthracene compound is within 25 nm of the wavelength of maximum light absorption by said substituted anthracene compound.

10. An electroluminescent composition as claimed in any one of the preceding claims in which the host material is selected from aromatic compounds of formula



(III)

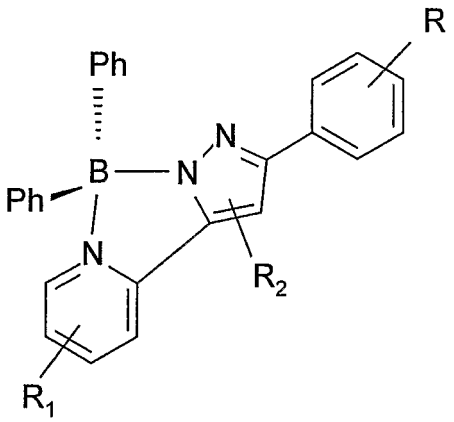
where R_1 and R_2 are as above or compounds of formula



(IV)

where M is a metal; n is the valency of M; R_1, R_2 and R_3 which may be the same or different are selected from hydrogen, hydrocarbyl groups, substituted and

unsubstituted aliphatic groups substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoryl methyl groups, halogens such as fluorine or thiophenyl groups or nitrile; R_1, and R_3 can also be form ring structures and R_1, R_2 and R_3 can be copolymerisable with a monomer, e.g. styrene; or compounds of formula



(V)

where Ph is an unsubstituted or substituted phenyl group where the substituents can be the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoryl methyl groups, halogens such as fluorine or thiophenyl groups; R, R_1 and R_2 can be hydrogen or substituted or unsubstituted hydrocarbyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorine, fluorocarbons such as trifluoryl methyl groups, halogens such as fluorine or thiophenyl groups or nitrile.

11. An electroluminescent device which comprises (i) a first electrode, (ii) a layer of electroluminescent composition as claimed in any one of claims 1 to 10 and (iii) a second electrode.

12. An electroluminescent device as claimed in claim 11 in which the layer of the electroluminescent composition is a thin film of less than 1 μm in thickness.

13. An electroluminescent device as claimed in claims 11 or 12 in which there is a layer of a hole transmitting material between the first electrode and the electroluminescent layer.

14. An electroluminescent device as claimed in claim 13 in which the hole transmitting material is an aromatic amine complex.

15. An electroluminescent device as claimed in claim 13 in which the hole transmitting material is a polyaromatic amine complex.

16. An electroluminescent device as claimed in claim 13 in which the hole transmitting material is a film of a polymer selected from poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis (3-methylphenyl) -1,1' -biphenyl -4,4'-diamine (TPD), polyaniline, substituted polyanilines, polythiophenes, substituted polythiophenes, polysilanes and substituted polysilanes.

17. An electroluminescent device as claimed in claim 13 in which the hole transmitting material is a film of a compound of formula (I) or (II) herein or as in figures 4 to 8 of the drawings.

18. An electroluminescent device as claimed in claim 13 in which the hole transmitting material is a copolymer of aniline, a copolymer of aniline with o-anisidine, m-sulphanilic acid or o-aminophenol, or o-toluidine with o-aminophenol, o-ethylaniline, o-phenylene diamine or with an amino anthracene.

19. An electroluminescent device as claimed in claim 13 in which the hole transmitting material is a conjugated polymer.

20. An electroluminescent device as claimed in claim 19 in which the conjugated polymer is selected from poly (p-phenylenevinylene)-PPV and copolymers including PPV, poly(2,5 dialkoxyphenylene vinylene), poly (2-methoxy-5-(2-methoxypentyloxy-1,4-phenylene vinylene), poly(2-methoxypentyloxy)-1,4-phenylenevinylene), poly(2-methoxy-5-(2-dodecyloxy-1,4-phenylenevinylene) and other poly(2,5 dialkoxyphenylenevinylenes) with at least one of the alkoxy groups being a long chain solubilising alkoxy group, poly fluorenes and oligofluorenes, polyphenylenes and oligophenylenes, polyanthracenes and oligo anthracenes, ploythiophenes and oligothiophenes.

21. An electroluminescent device as claimed in any one of claims 13 to 20 in which the electroluminescent compound is mixed with the hole transmitting material.

22. An electroluminescent device as claimed in any one of claims 11 to 21 in which there is a layer of an electron transmitting material between the cathode and the electroluminescent compound layer.

23. An electroluminescent device as claimed in claim 22 in which the electron transmitting material is a metal quinolate or a metal thioxinate.

24. An electroluminescent device as claimed in claim 23 in which the metal quinolate is an aluminium quinolate, zirconium quinolate or lithium quinolate and the metal thioxinate is zinc thioxinate, cadmium thioxinate, gallium thioxinate or indium thioxinate.

25. An electroluminescent device as claimed in claim 22 in which the electron transmitting material is of formula $Mx(DBM)_n$ where Mx is a metal and DBM is dibenzoyl methane and n is the valency of Mx.

26. An electroluminescent device as claimed in claim 22 in which the electron transmitting material is a cyano anthracene such as 9,10 dicyano anthracene, a polystyrene sulphonate or a compound of formulae shown in figures 2 or 3 of the drawings.

27. An electroluminescent device as claimed in any one of claims 22 to 26 in which the electron transmitting material is mixed with the electroluminescent compound.

28. An electroluminescent device as claimed in any one of claims 11 to 27 in which the first electrode is a transparent electricity conducting glass electrode.

29. An electroluminescent device as claimed in any one of claims 11 to 28 in which the second electrode is comprised of a metal other than an alkali metal having a work function of less than 4 eV.

30. An electroluminescent device as claimed in any one of claims 11 to 28 in which the second electrode is selected from aluminium, calcium, lithium, magnesium and alloys thereof and silver/magnesium alloys.

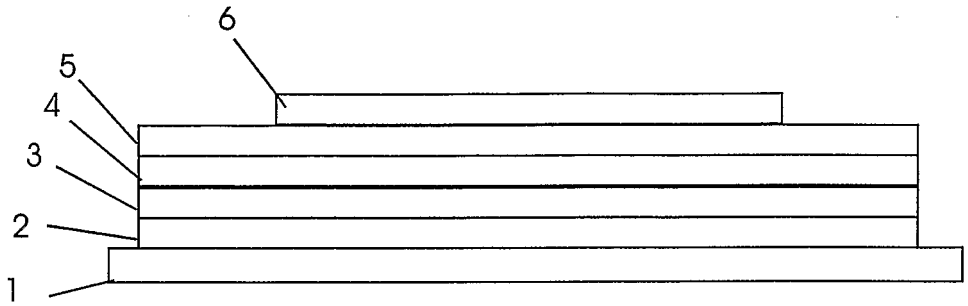
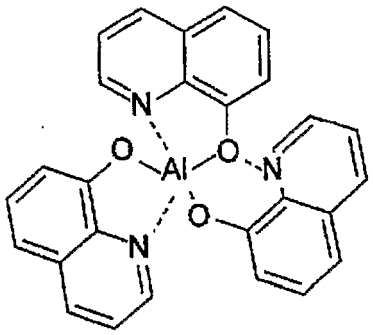
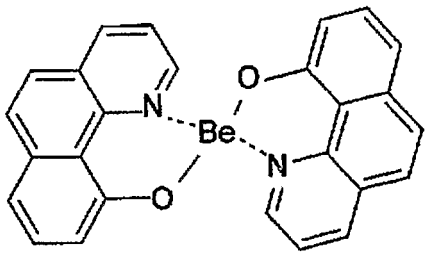


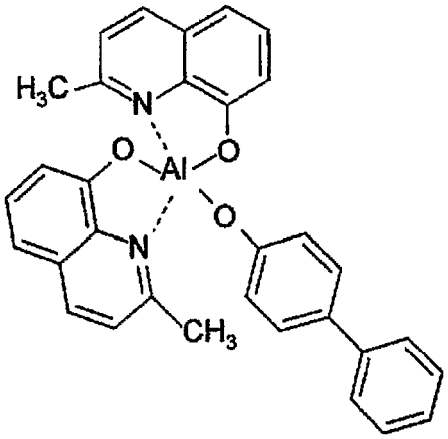
Fig. 1



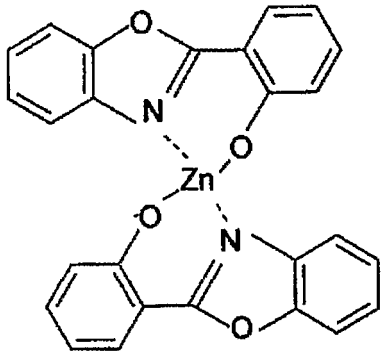
Alq



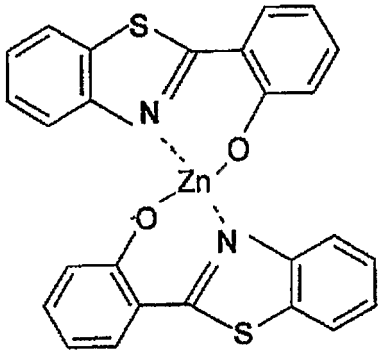
Bebq



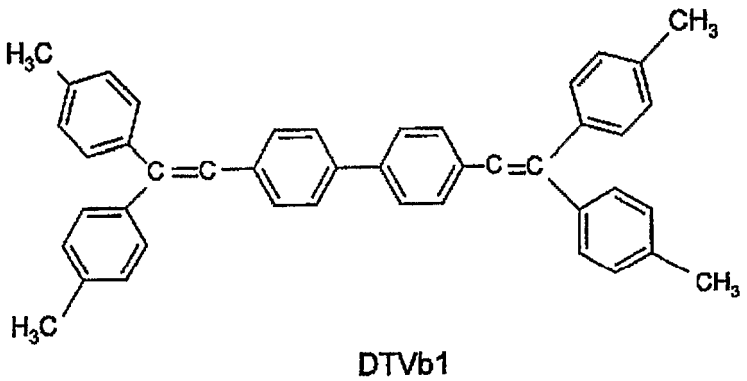
BAlq1



ZnPBO

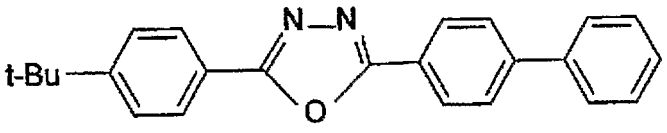


ZnPBT

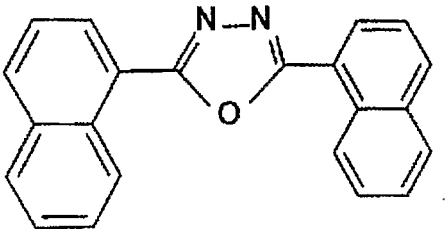


DTVb1

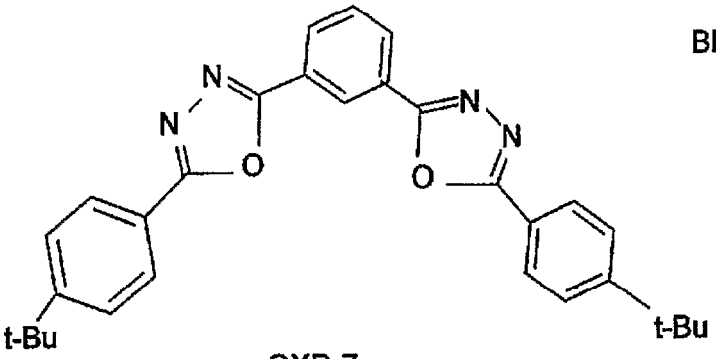
Fig. 2



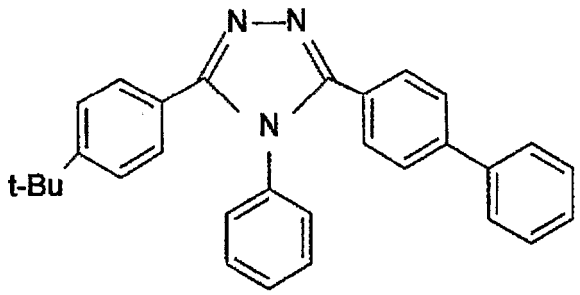
t-Bu-PBD



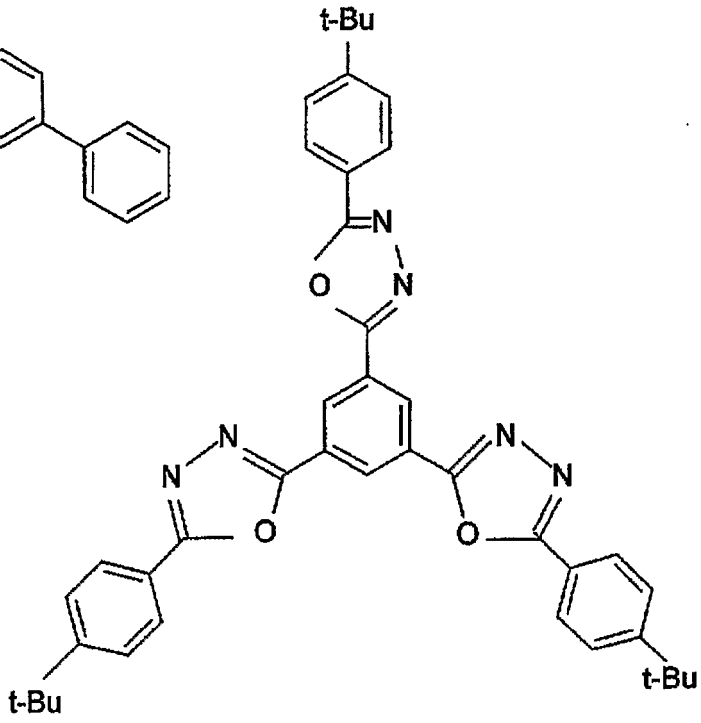
BND



OXD-7

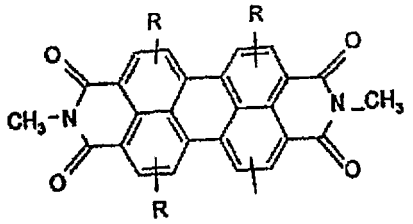


TAZ

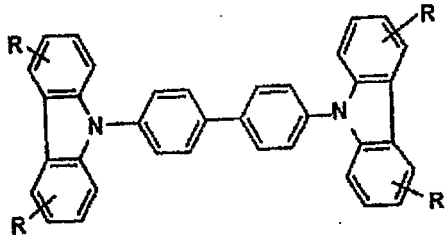


OXD- Star

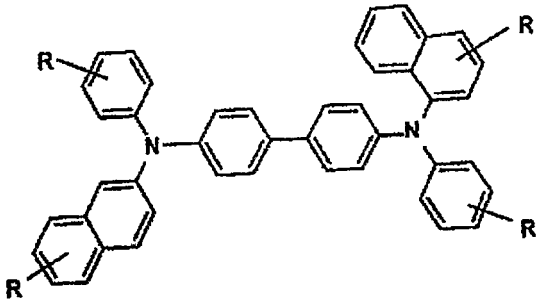
Fig. 3



4a



4b



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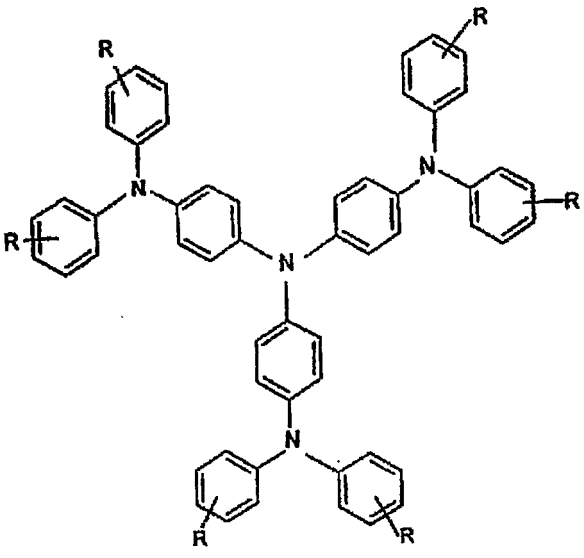


4d

Fig. 4

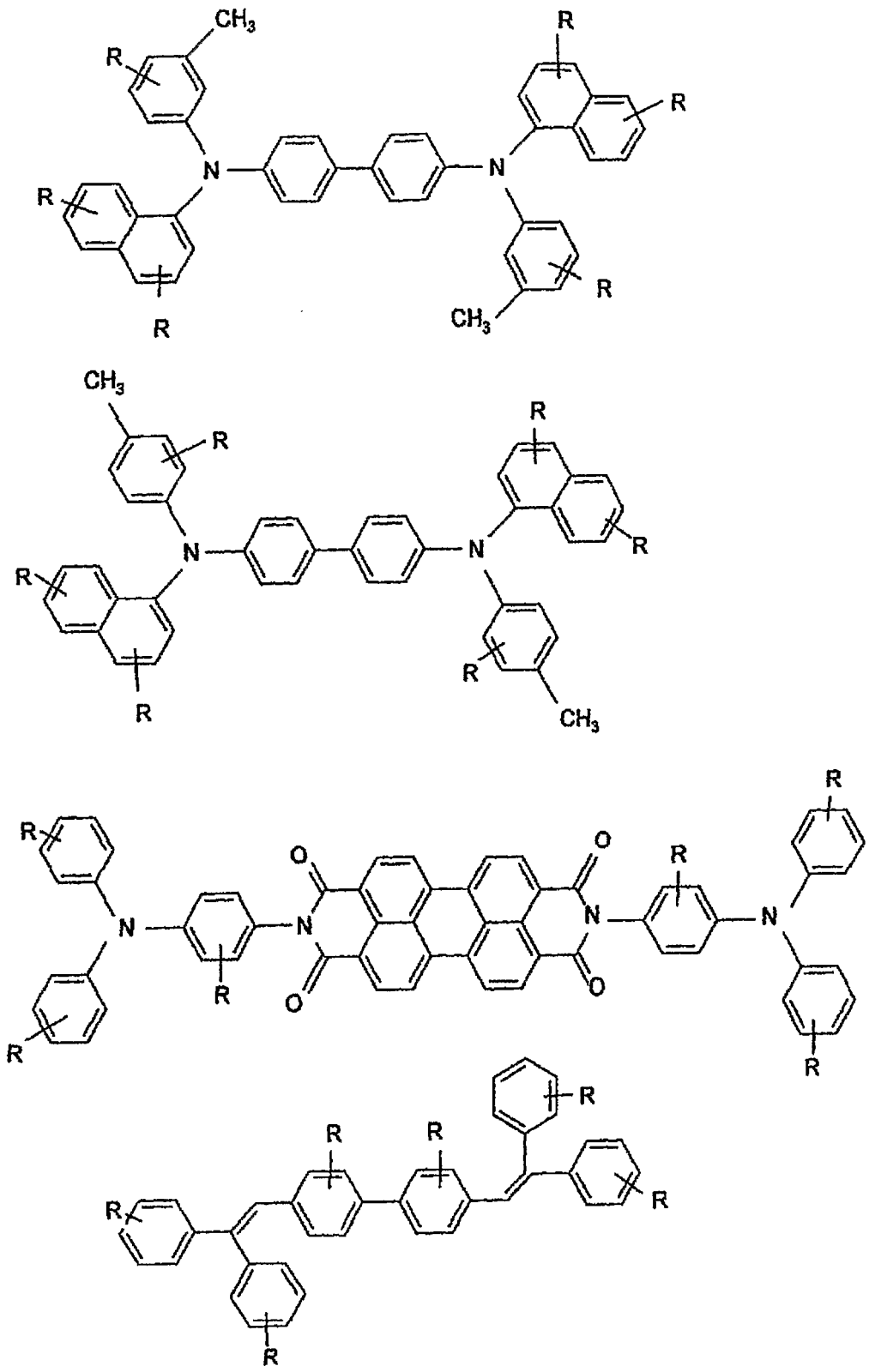
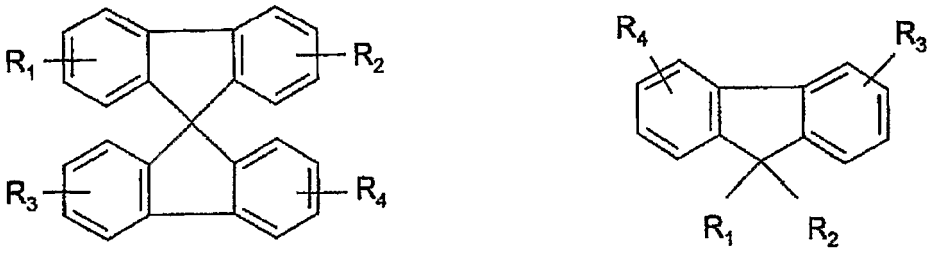
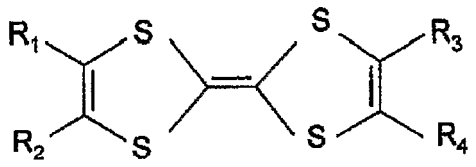
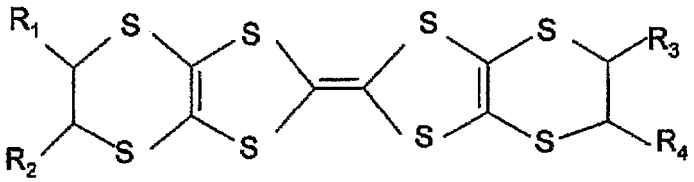


Fig. 5





or



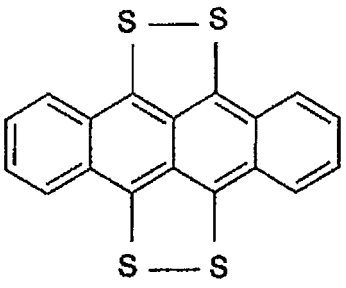
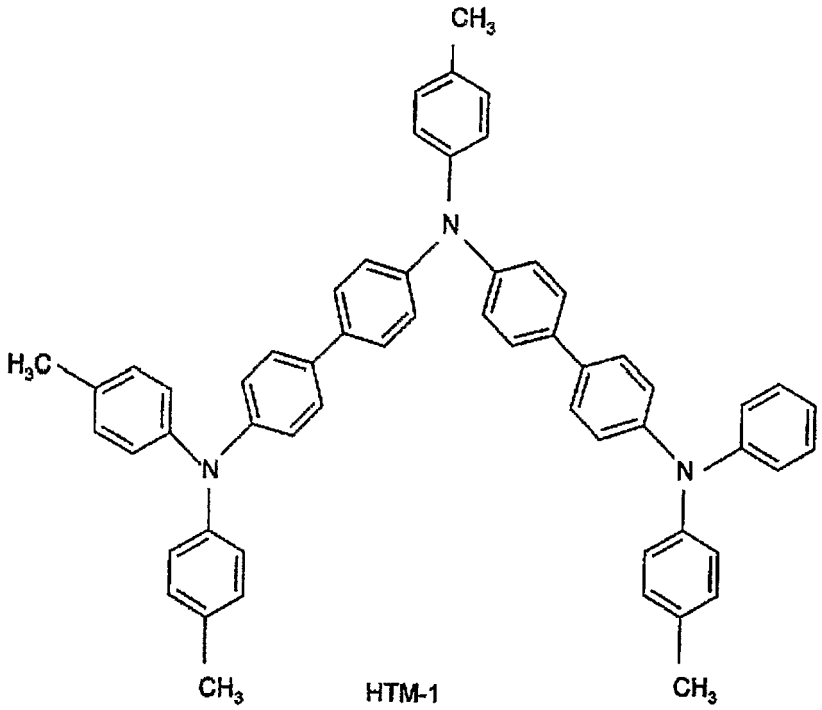
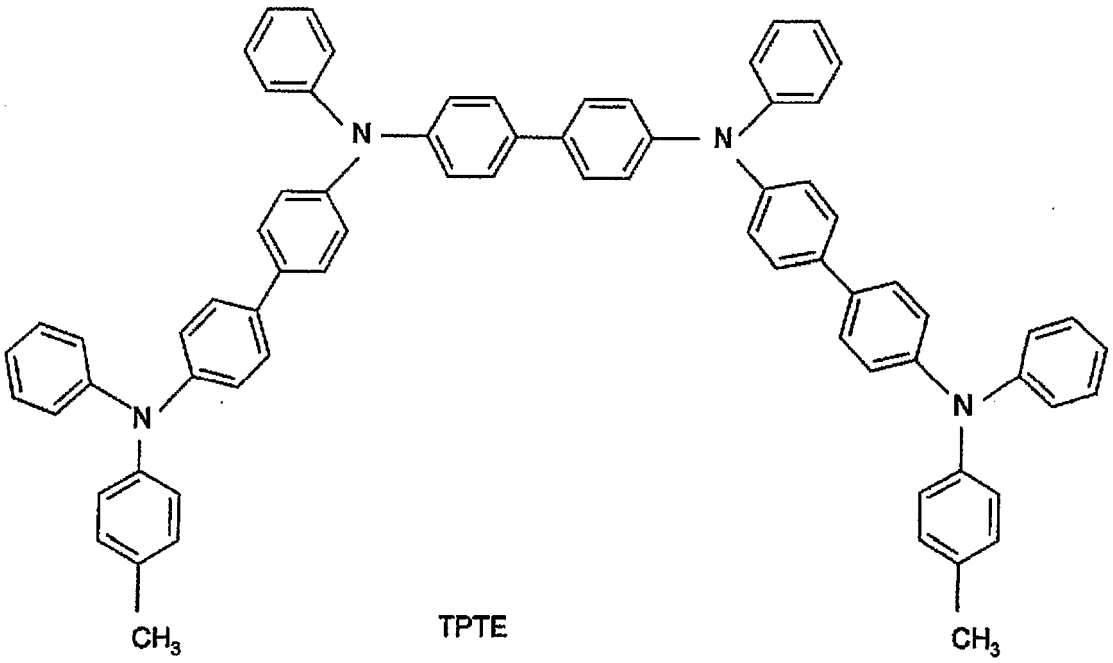


Fig. 6

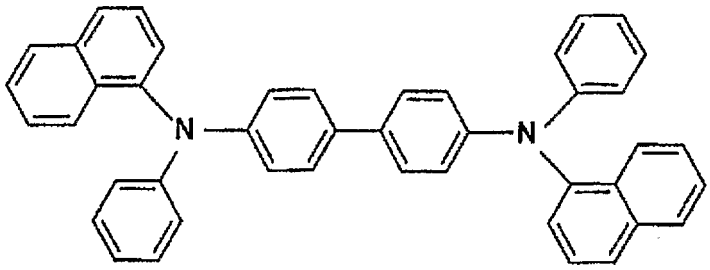


HTM-1

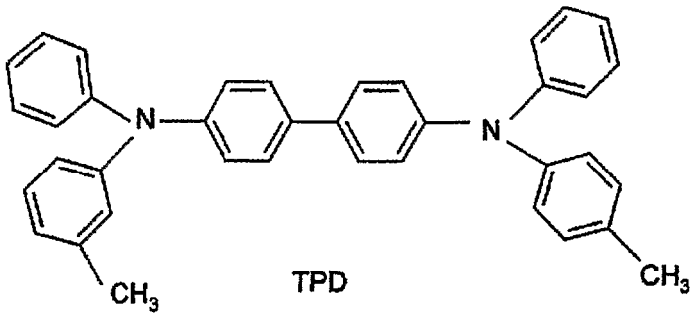


TPTE

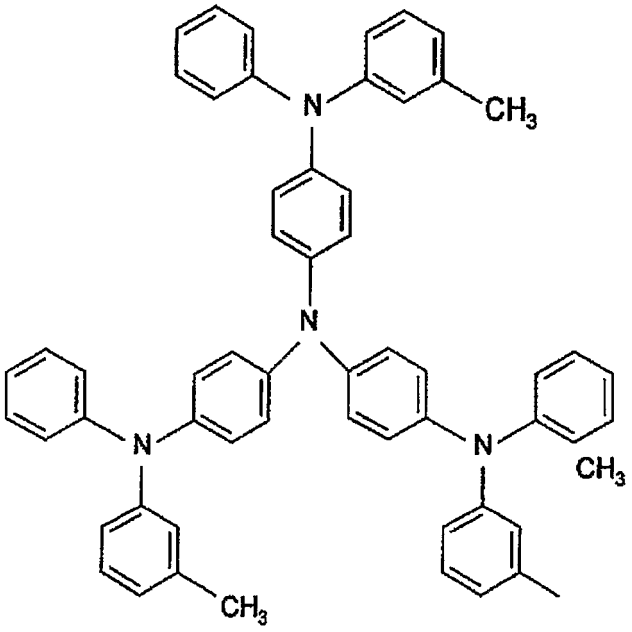
Fig. 7



α -NPB



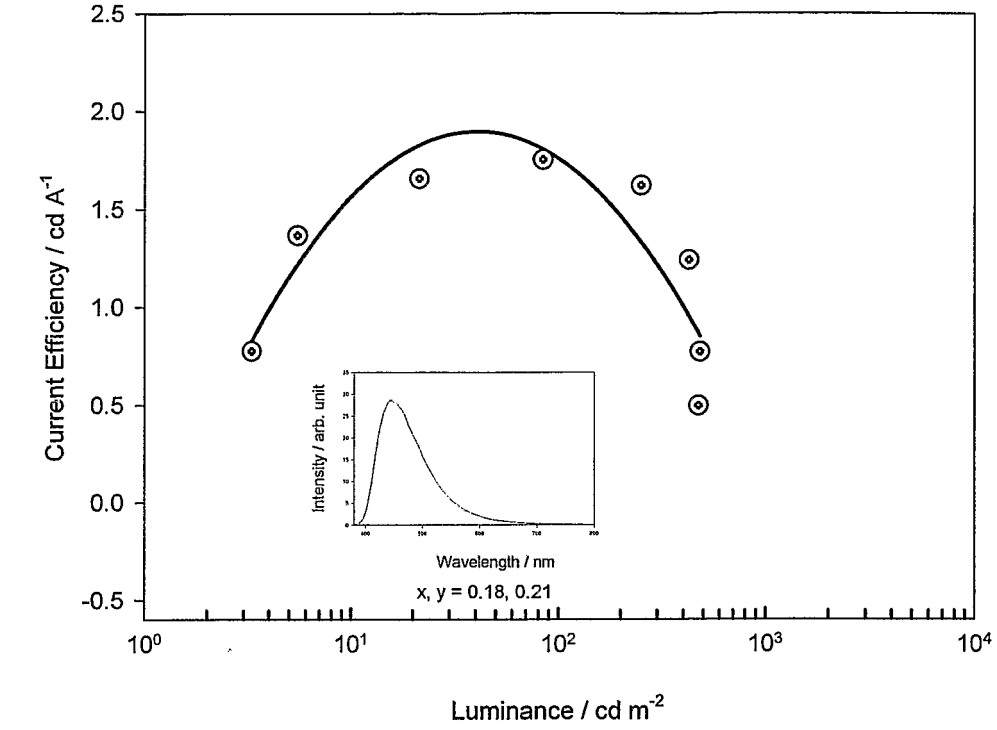
TPD



mTADATA

Fig. 8

ITO/α-NPB (42 nm)/K : H (20 : 1) (26 nm)//Zrq_4 (17 nm)/LiF (0.3 nm)/Al



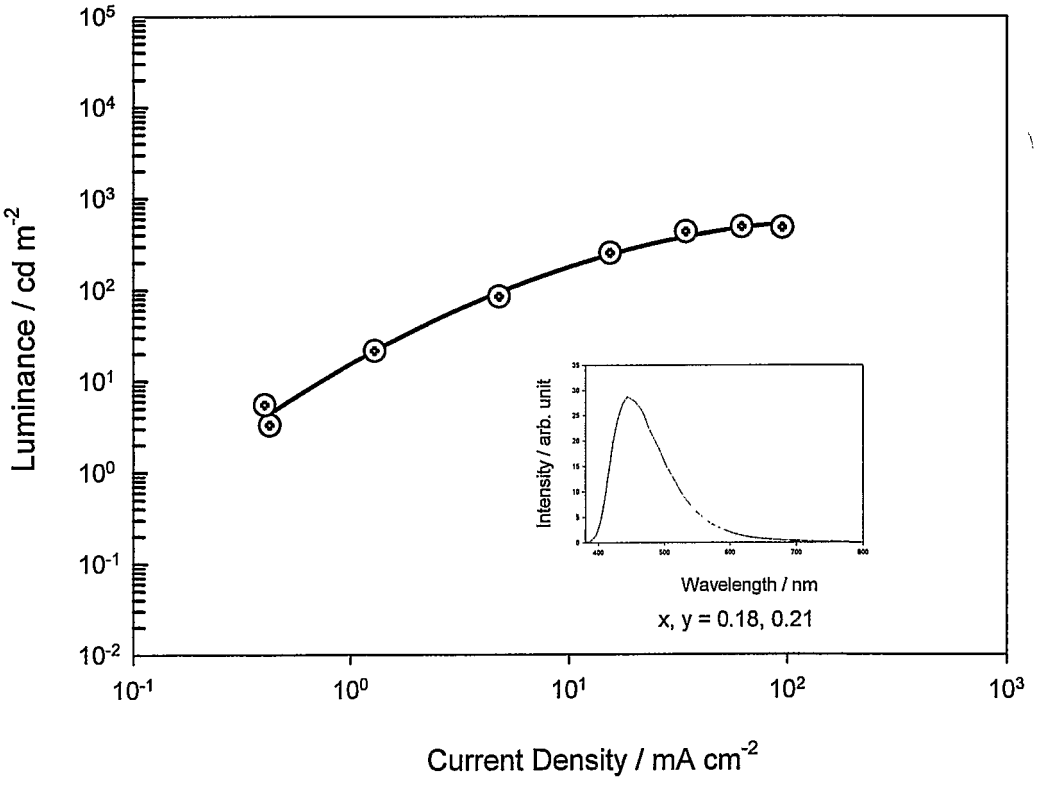


Fig. 9

ITO/α-NPB (42 nm)/K : H (20 : 1) (26 nm)//Zrq_4 (17 nm)/LiF (0.3 nm)/Al

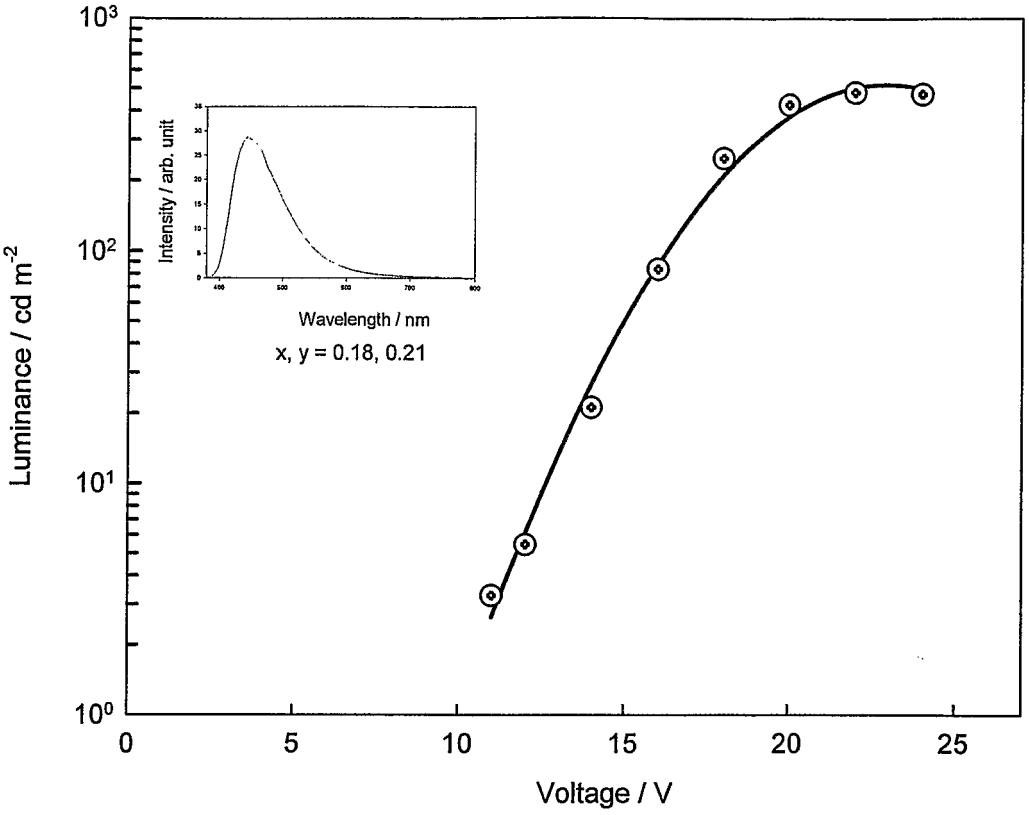
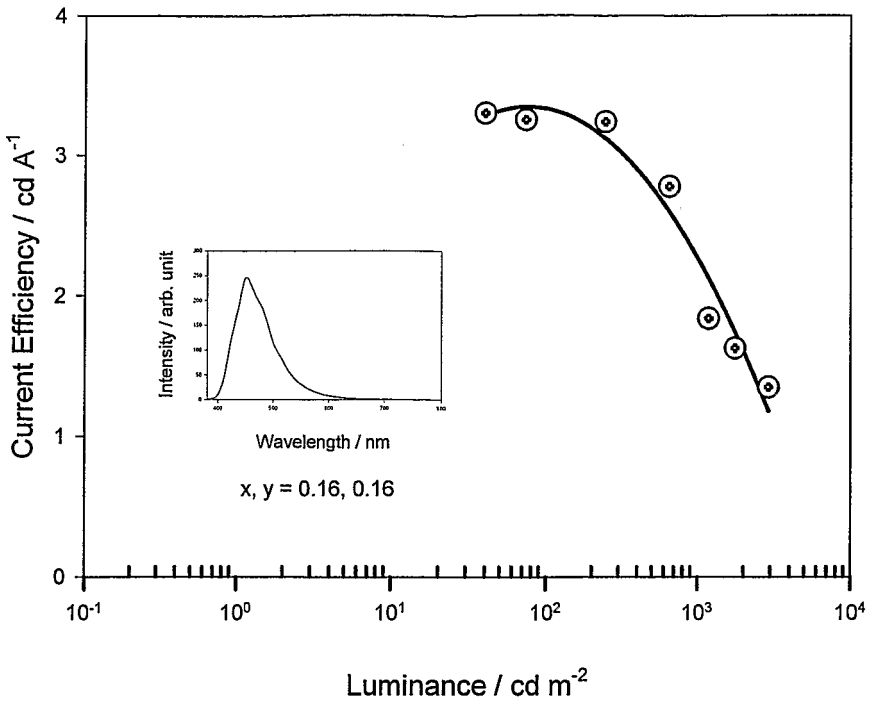


Fig. 10

ITO/α-NPB (40 nm)/L : H (20 : 2) (27 nm)//Zrq_4 (17 nm)/LiF (0.3 nm)/Al



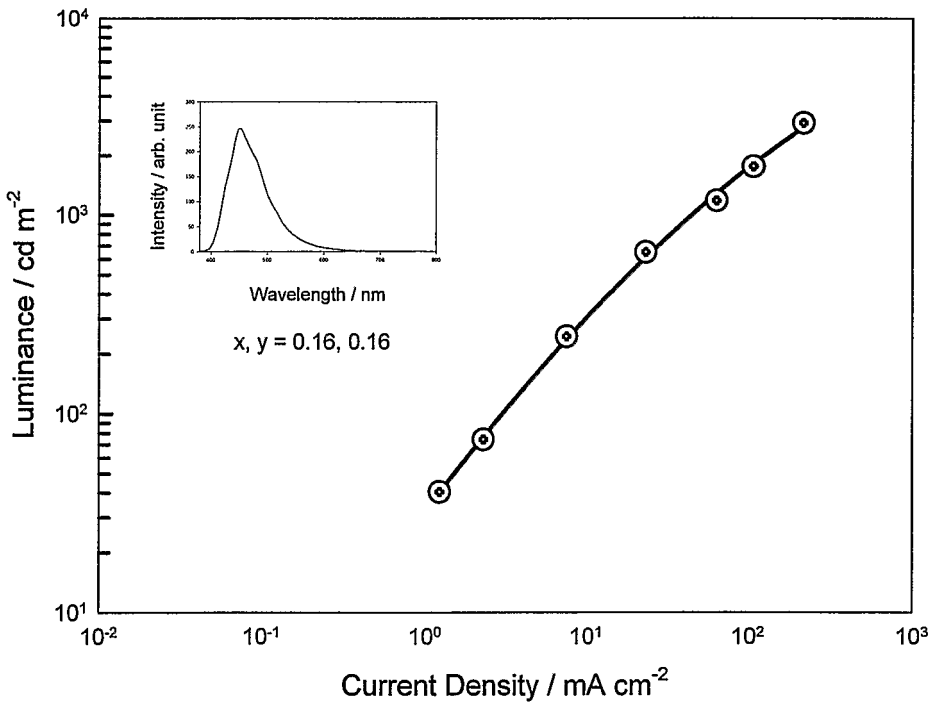


Fig. 11

ITO/α-NPB (40 nm)/L : H (20 : 2) (27 nm)//Zrq_4 (17 nm)/LiF (0.3 nm)/Al

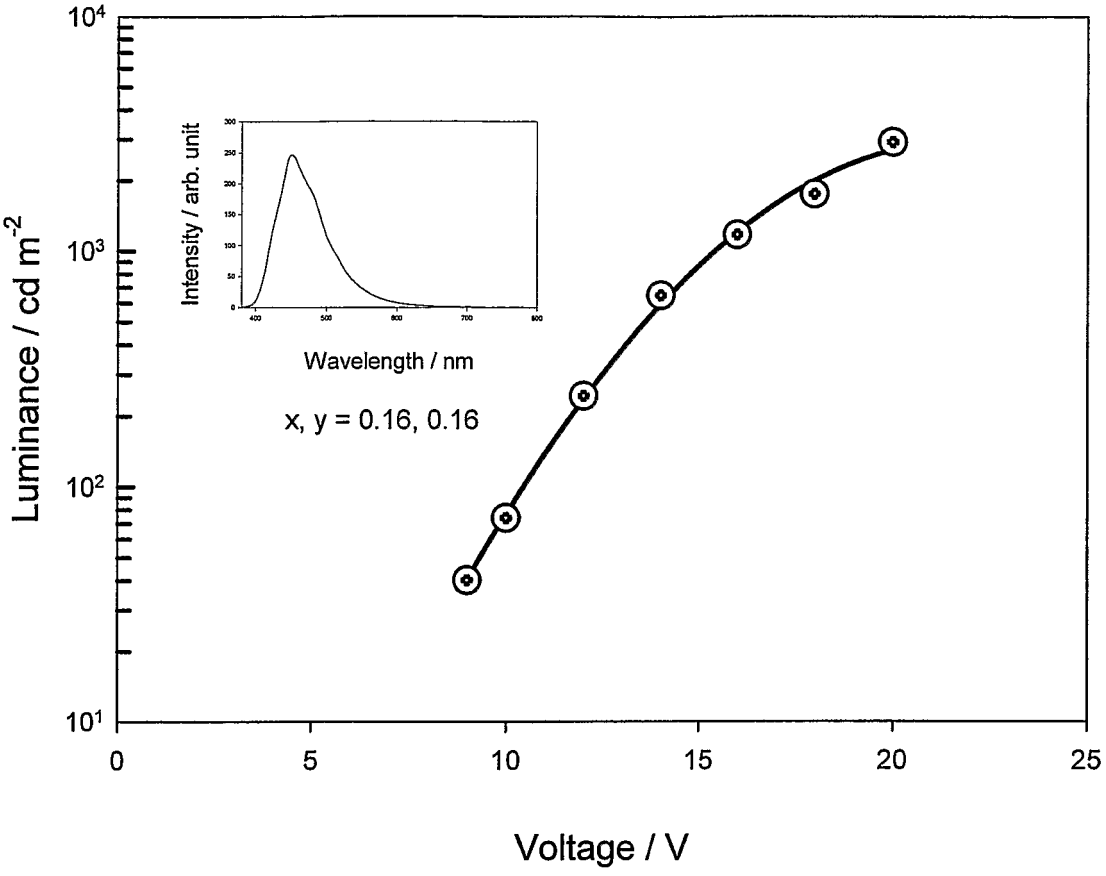


Fig. 12

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2005/003173

A. CLASSIFICATION OF SUBJECT MATTER
C09K11/06 C07C15/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 281 381 A (EASTMAN KODAK COMPANY; EASTMAN KODAK COMPANY) 7 September 1988 (1988-09-07) cited in the application page 1, lines 7-20 page 3, lines 31-36 page 6, line 47 - page 7, line 50 page 28, line 65 - page 29, line 9 claim 1 ----- -/--	1-30

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
24 November 2005	02/12/2005

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Vanier, C

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2005/003173

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 182 183 A (IDEMITSU KOSAN CO., LTD) 27 February 2002 (2002-02-27) paragraphs '0004!, '0005! paragraphs '0009!, '0023! paragraphs '0026!, '0027! paragraphs '0042!, '0043!, '0047! paragraphs '0051! - '0053! paragraph '0060! claims 1,5-8	1-30
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A	page 3, line 12 - page 4, line 9 page 5, line 19 - page 6, line 22 page 7, line 29 - page 8, line 18 figures 4c,9,13c claims 16-32	1-30

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB2005/003173

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		EP 1578756 A1	28-09-2005

专利名称(译)	电致发光材料和器件		
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申请号	EP2005797974	申请日	2005-08-12
[标]申请(专利权)人(译)	OLED - T有限公司		
申请(专利权)人(译)	OLED-T有限公司		
当前申请(专利权)人(译)	MERCK PATENT GMBH		
[标]发明人	KATHIRGAMANATHAN POOPATHY		
发明人	KATHIRGAMANATHAN, POOPATHY		
IPC分类号	C09K11/06 C07C15/28 H05B33/14		
CPC分类号	C09K11/06 C07C15/28 C09K2211/1011 H01L51/0052 H01L51/5012 H05B33/14		
优先权	2004017927 2004-08-12 GB		
其他公开文献	EP1786885B1		
外部链接	Espacenet		

摘要(译)

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