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(54) **ELECTROLUMINESCENT MATERIALS AND DEVICES**

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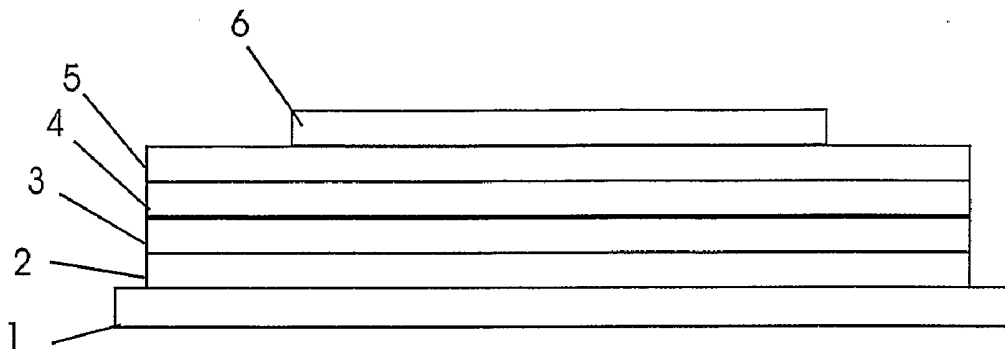
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(57) **ABSTRACT**

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



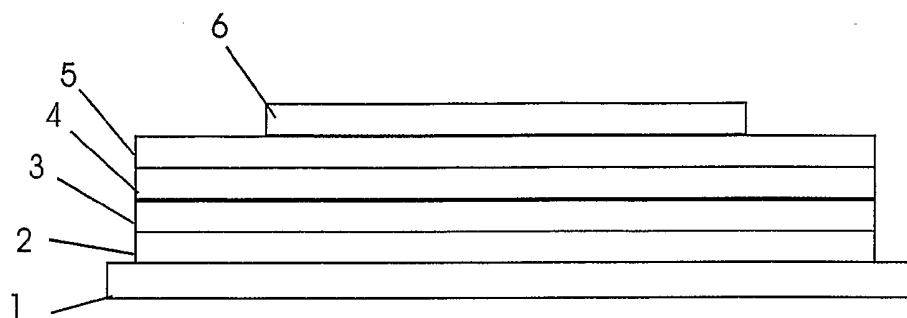
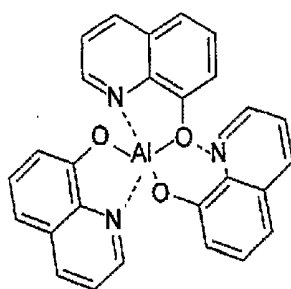
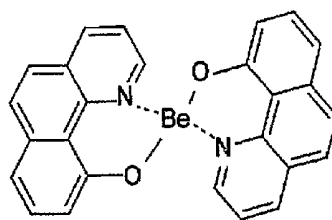


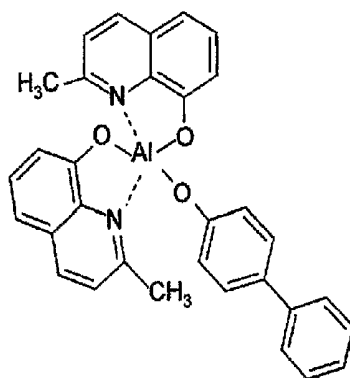
Fig. 1



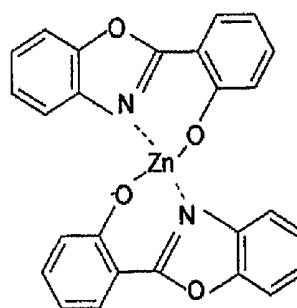
Alq



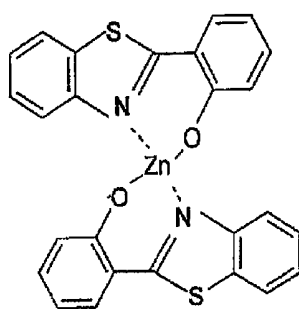
Beq



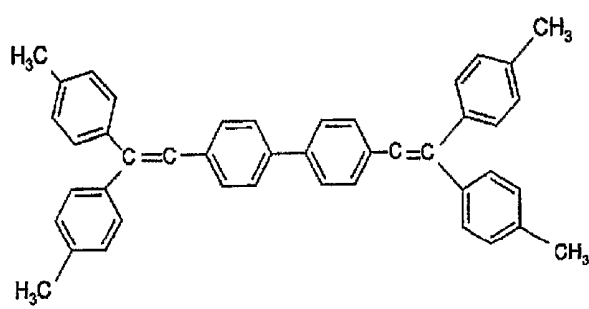
BAlq1



ZnPBO



ZnPBT



DTVb1

Fig. 2

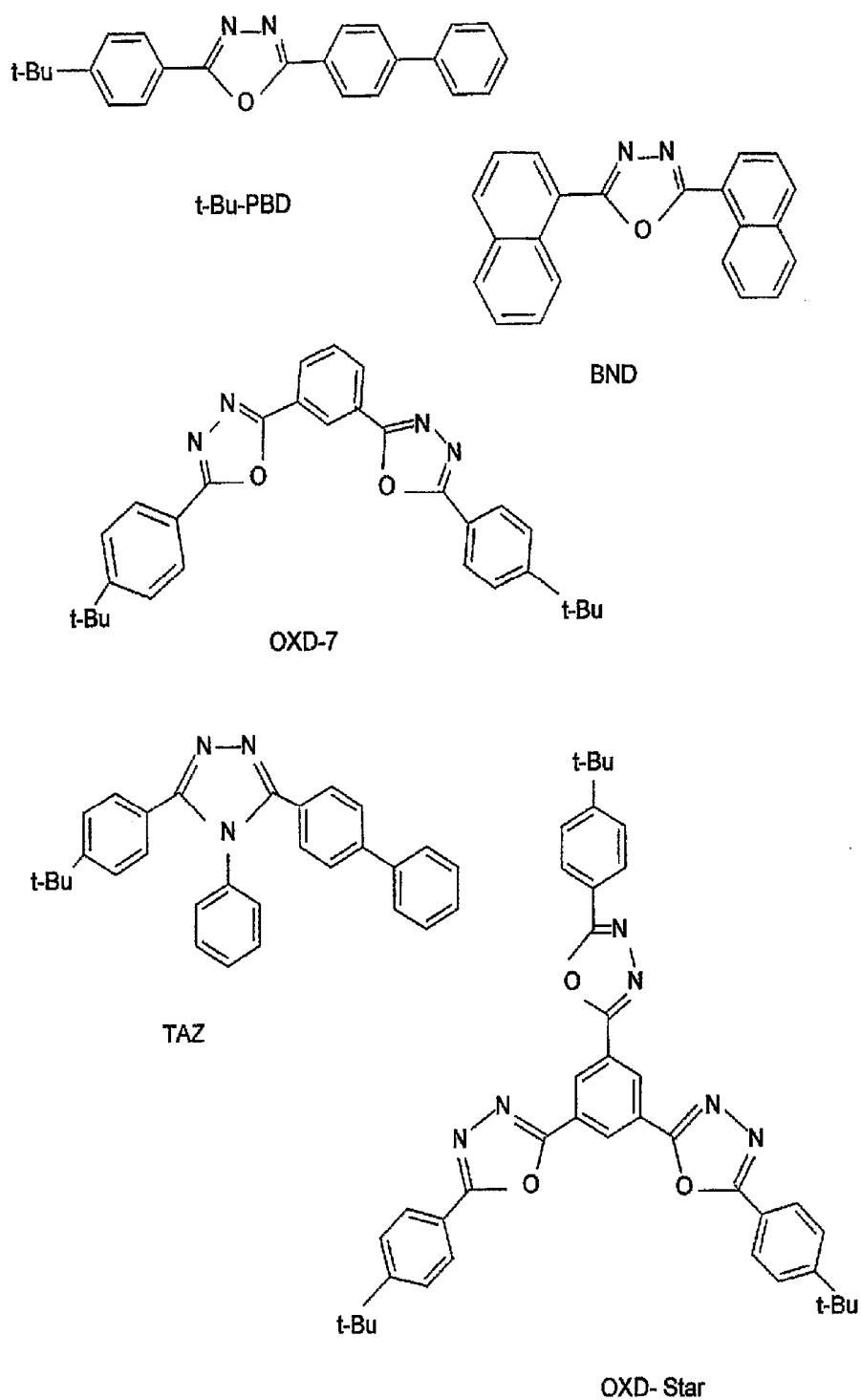
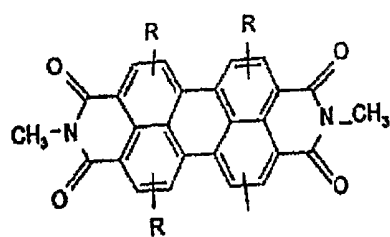
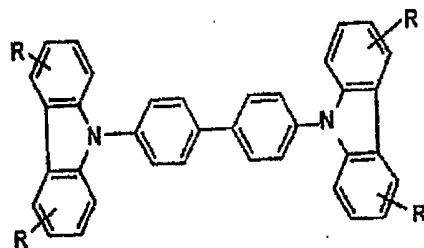


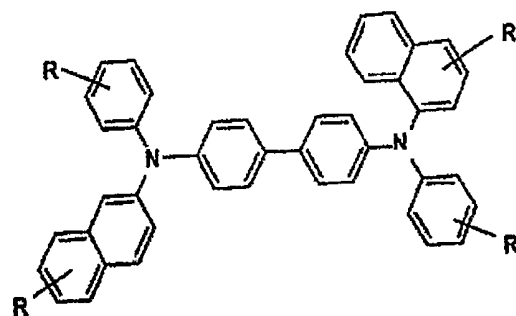
Fig. 3



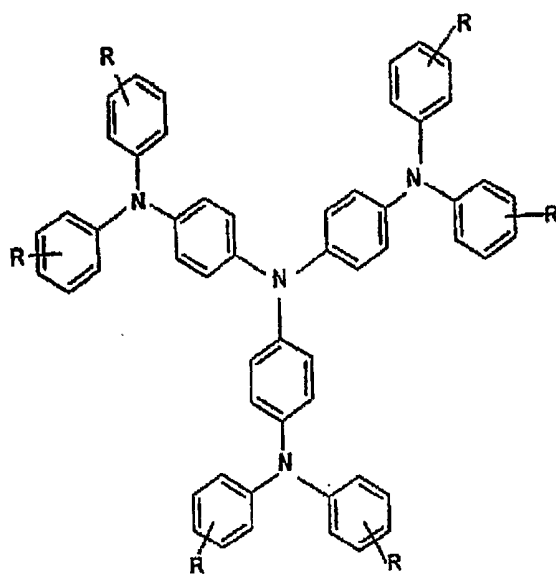
4a



4b



4c



4d

Fig. 4

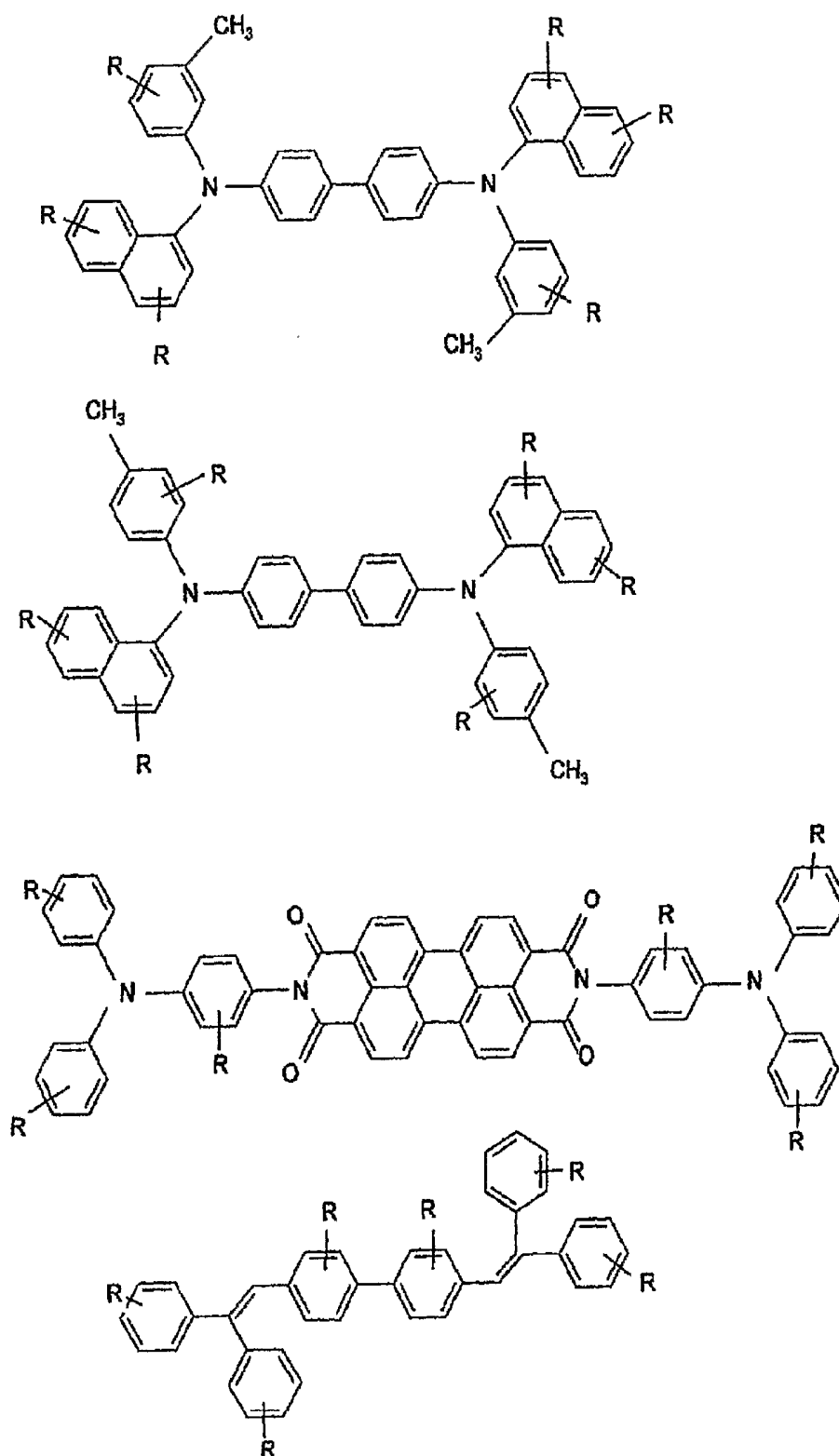


Fig. 5

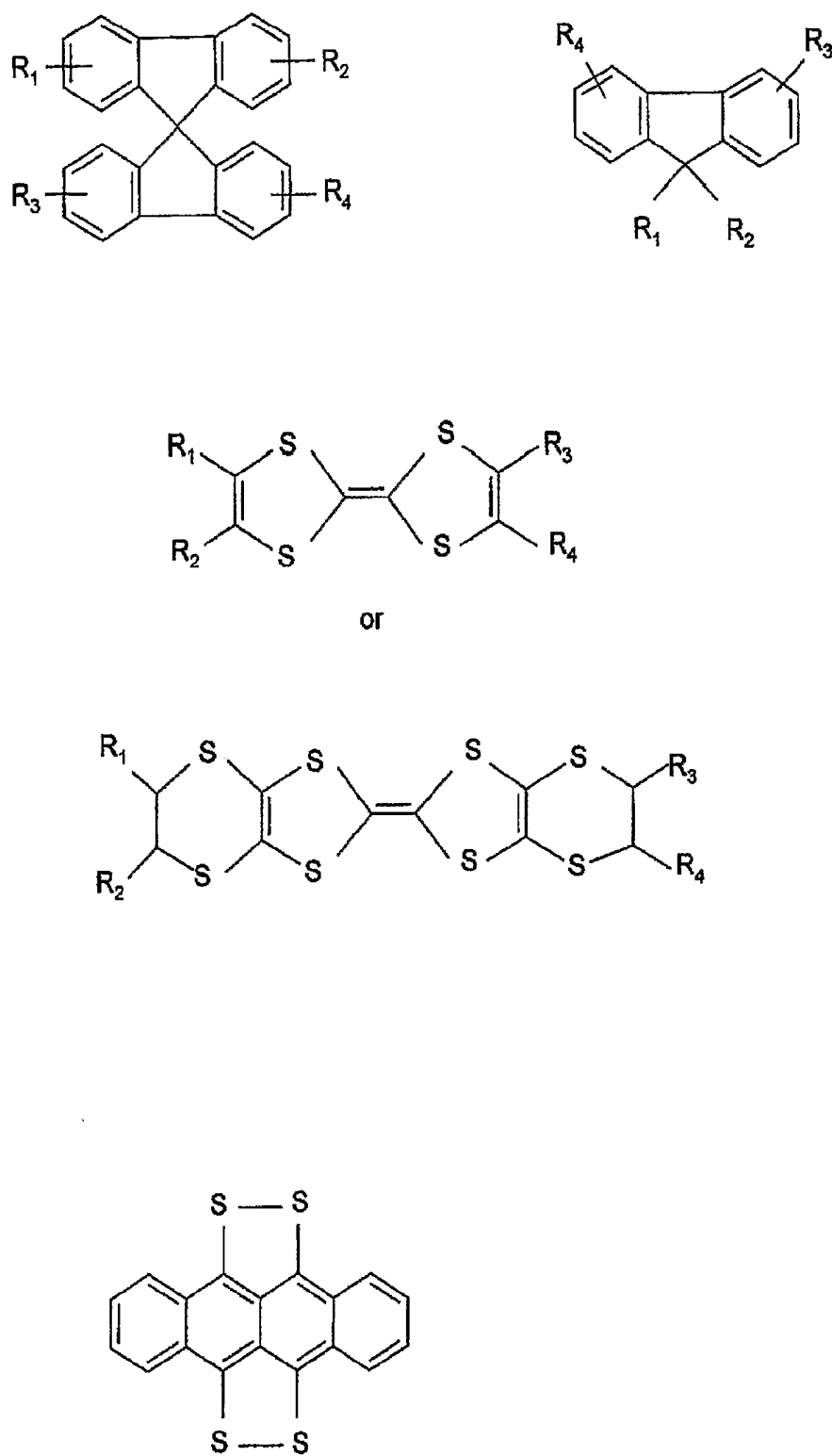


Fig. 6

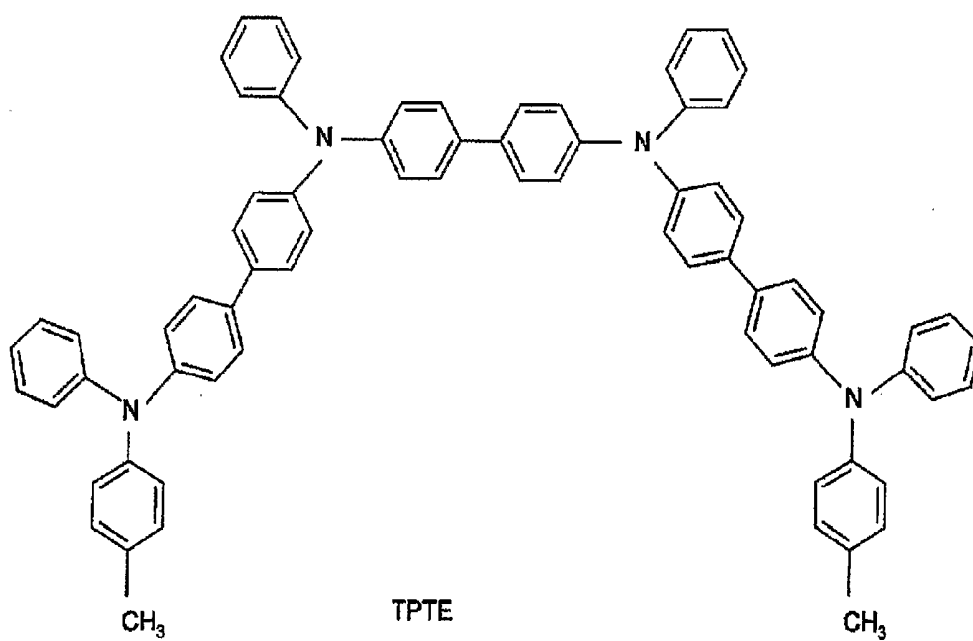
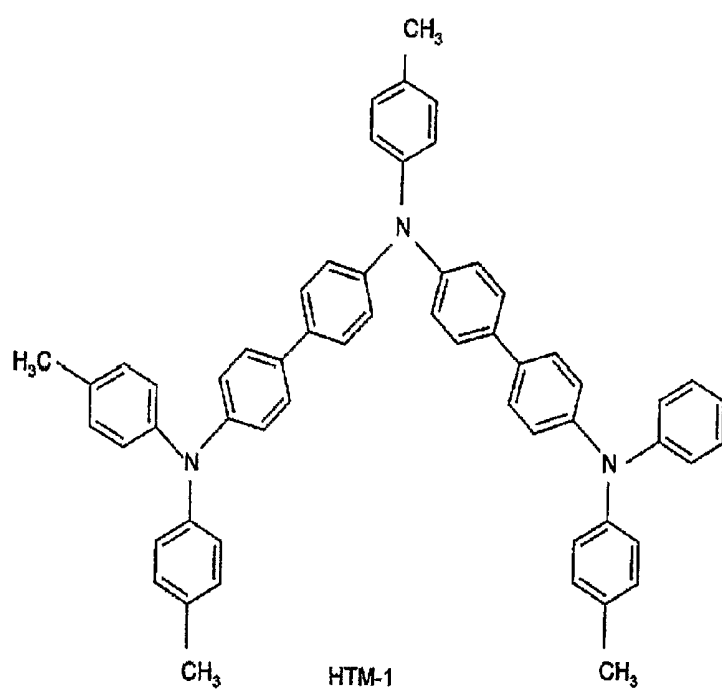
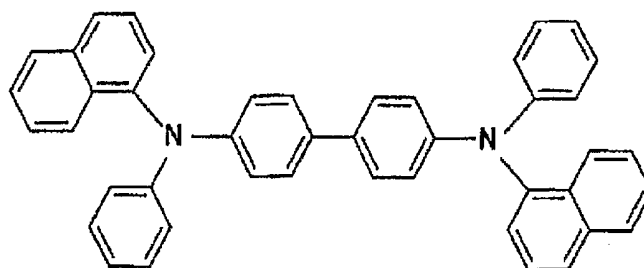
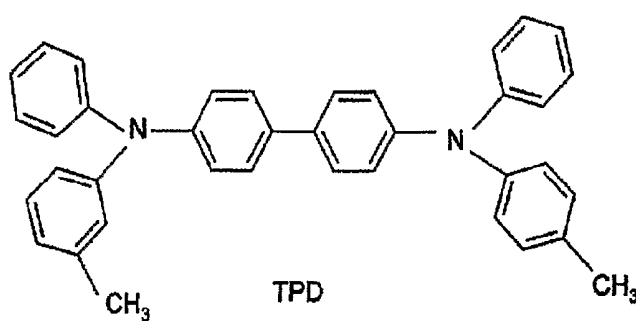


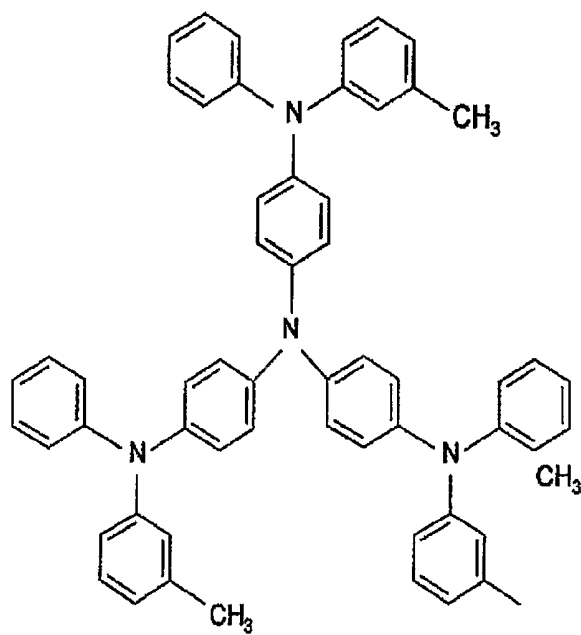
Fig. 7



$\alpha$ -NPB



TPD



mTADATA

Fig. 8

ITO/ $\alpha$ -NPB (42 nm)/K : H (20 : 1) (26 nm)//Zr<sub>q</sub>4 (17 nm)/LiF (0.3 nm)/Al

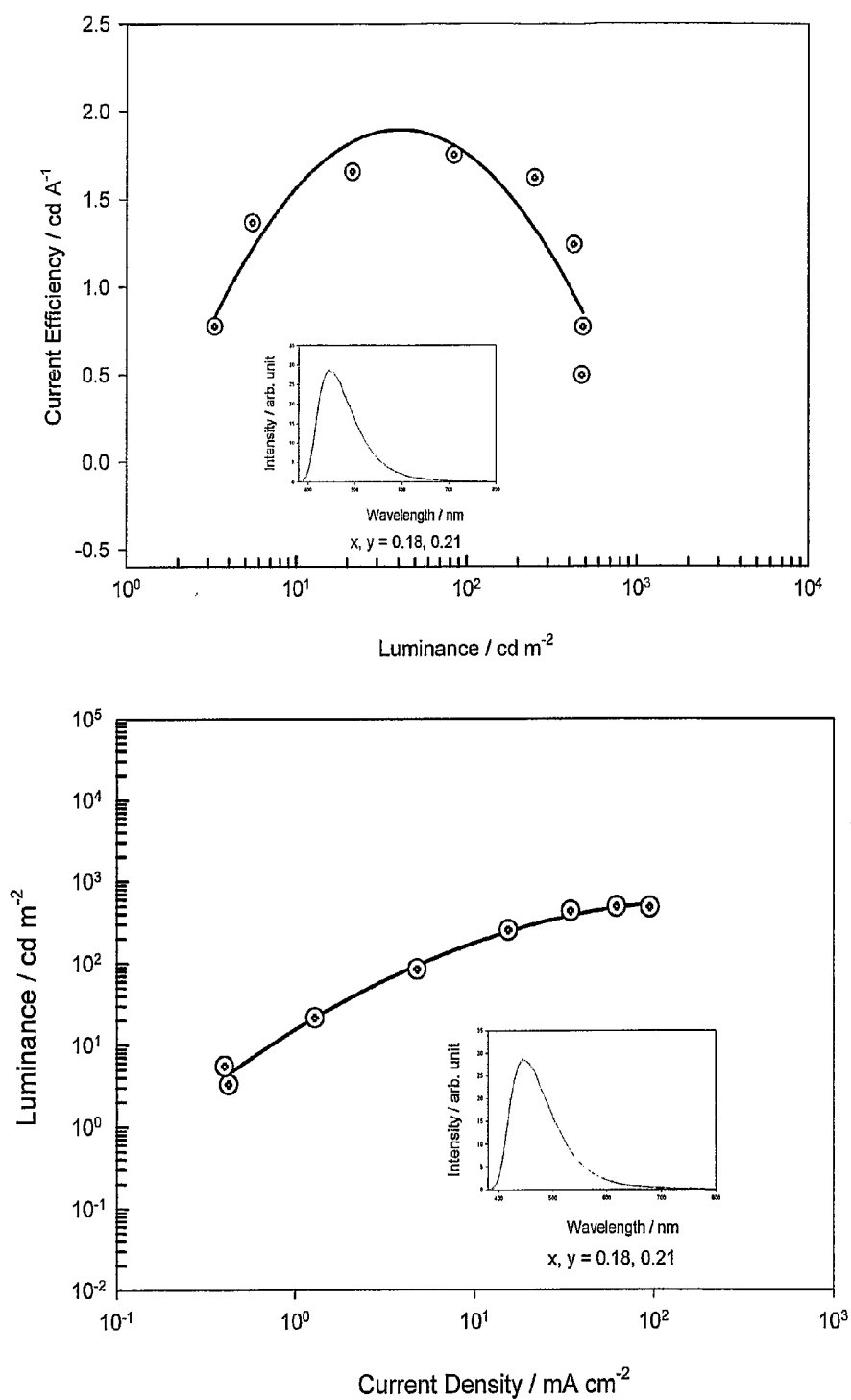


Fig. 9

ITO/ $\alpha$ -NPB (42 nm)/K : H (20 : 1) (26 nm)//Zr<sub>q</sub> (17 nm)/LiF (0.3 nm)/Al

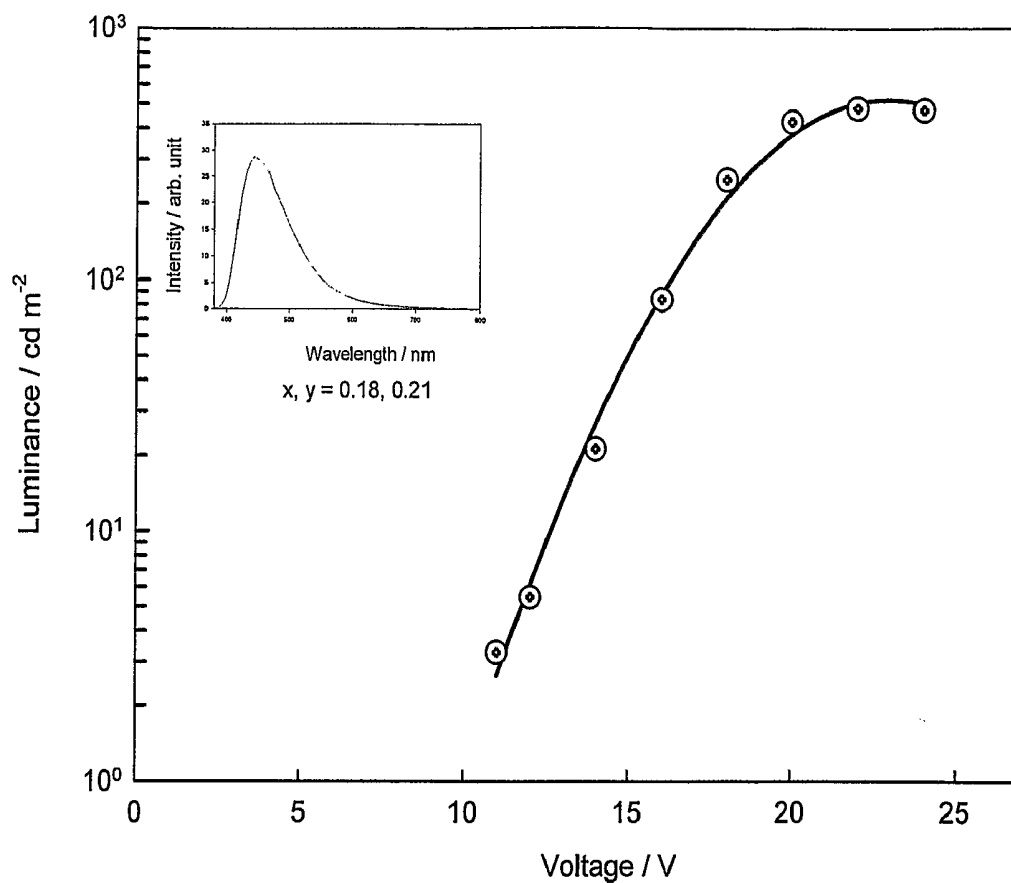


Fig. 10

ITO/ $\alpha$ -NPB (40 nm)/L : H (20 : 2) (27 nm)//Zr<sub>q</sub> (17 nm)/LiF (0.3 nm)/Al

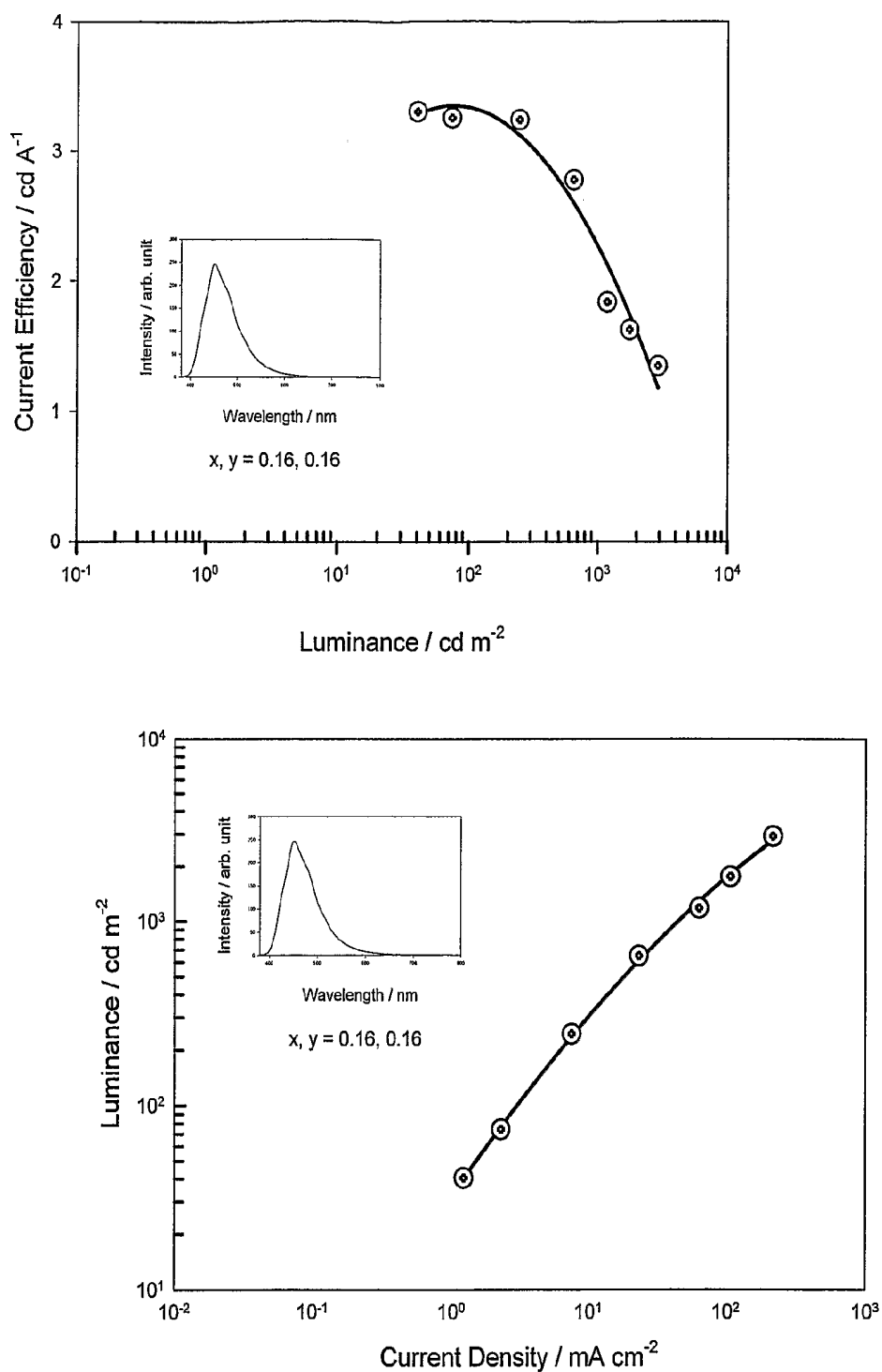


Fig. 11

ITO/ $\alpha$ -NPB (40 nm)/L : H (20 : 2) (27 nm)//Zr<sub>q</sub>4 (17 nm)/LiF (0.3 nm)/Al

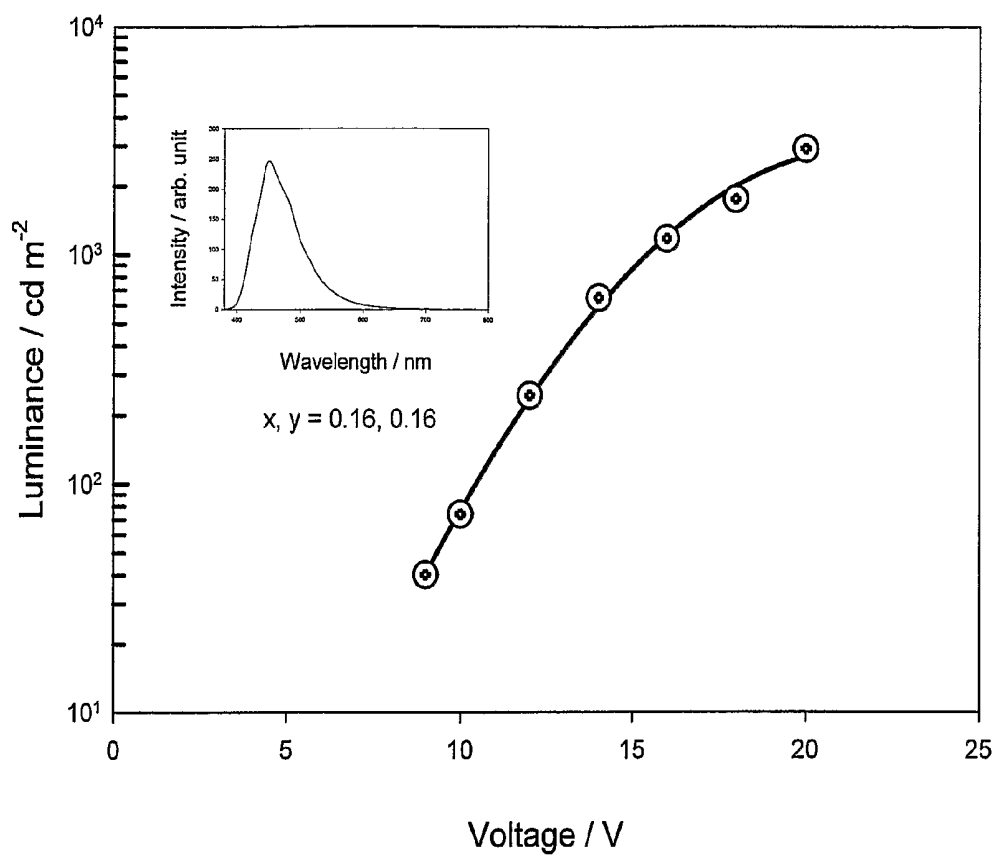


Fig. 12

# ELECTROLUMINESCENT MATERIALS AND DEVICES

[0001] The present invention relates to electroluminescent compositions and to electroluminescent devices.

[0002] 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.

[0003] 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.

[0004] 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.

[0005] 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.

[0006] U.S. Pat. No. 5,128,587 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.

[0007] 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.

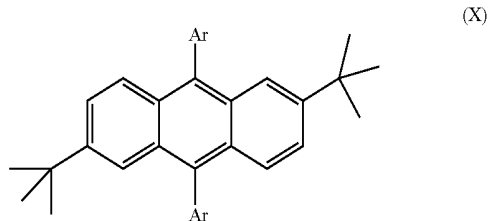
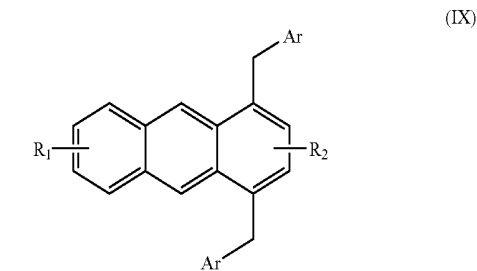
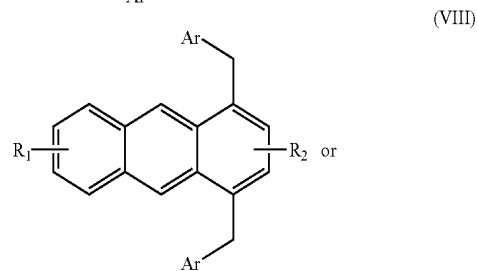
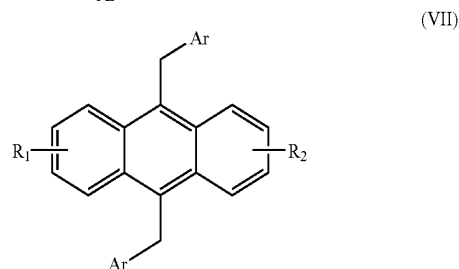
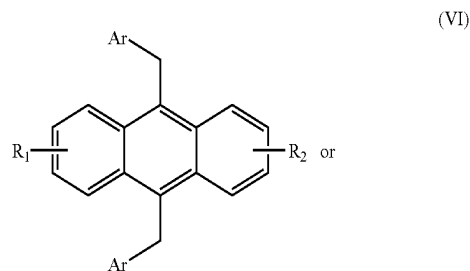
[0008] We have now found that an electroluminescent composition that comprises a host material doped with an aromatic substituted anthracene compound has improved properties.

[0009] 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.

[0010] The invention also provides an electroluminescent device which comprises (i) a first electrode, (ii) a layer of an electroluminescent composition comprising a dopant which

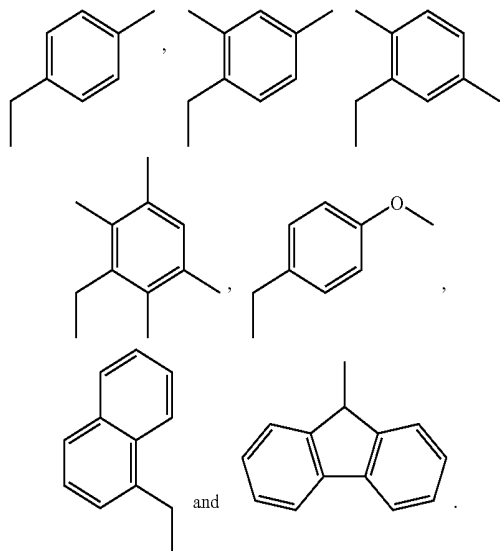
is an aromatic substituted anthracene compound mixed with a host material and (iii) a second electrode.

[0011] Preferably the aromatic substituted anthracene compound has the formula



where Ar is an aromatic or a substituted aromatic group, a substituted or unsubstituted polyatomic group such as anthracene or naphthalene and R<sub>1</sub> and R<sub>2</sub> 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 trifluoromethyl groups, halogens such as fluorine or thiophenyl groups.

[0012] Examples of groups Ar are



[0013] 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.

[0014] Preferably the host material is an electroluminescent compound.

[0015] As discussed in U.S. Pat. No. 4,769,292, 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.

[0016] 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.

[0017] 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.

[0018] 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.

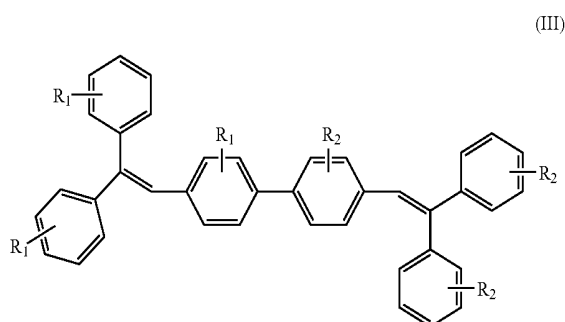
[0019] Where a host material is chosen, which is itself capable of emitting light in the absence of the aromatic substituted anthracene compounds, it has been observed that suppression of light emission at the wavelengths of emission characteristics of the host material alone and enhancement of emission 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.

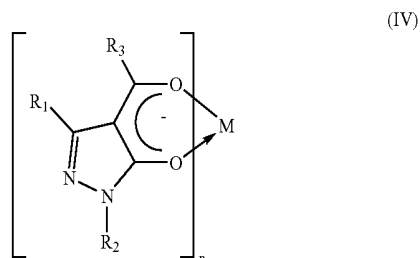
[0020] Although the foregoing discussion has been undertaken by reference to host materials which are known themselves to emit light in response to hole and electron injection, in fact light emission by the host material itself can entirely cease where light emission by the aromatic substituted anthracene 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.

[0021] 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.

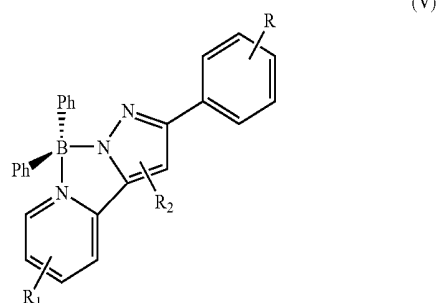
[0022] Preferred host materials are conjugated aromatic compounds of formula:



where  $R_1$  and  $R_2$  are as above;  
or compounds of formula



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 trifluoromethyl groups, halogens such as fluorine or thiophenyl groups or nitrile;  $R_1$ ,  $R_2$  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



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 trifluoromethyl 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 trifluoromethyl groups, halogens such as fluorine or thiophenyl groups or nitrile.

[0023] 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.

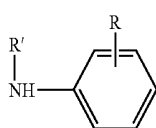
[0024] Preferably the layer of the electroluminescent composition is a thin film of less than 1  $\mu\text{m}$  in thickness.

[0025] 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.

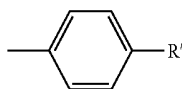
[0026] The hole transporting material can be any of the hole transporting materials used in electroluminescent devices.

[0027] 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



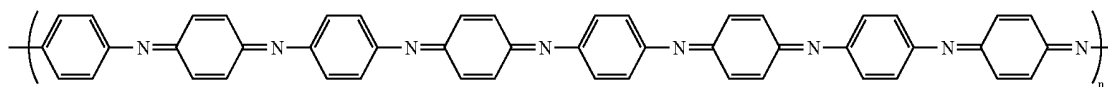
(I)

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

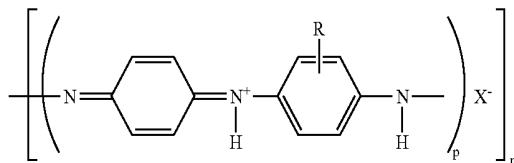


where R is alkyl or aryl and R' is hydrogen, C1-6 alkyl or aryl with at least one other monomer of formula (I) above.

[0028] 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<sub>4</sub>, BF<sub>4</sub>, PF<sub>6</sub>, H<sub>2</sub>PO<sub>3</sub>, H<sub>2</sub>PO<sub>4</sub>, arylsulphonate, arenedicarboxylate, polystyrenesulphonate, polyacrylate alkylsulphonate, vinylsulphonate, vinylbenzene sulphonate, cellulose

sulphonate, camphor sulphonates, cellulose sulphate or a perfluorinated polyanion.

[0029] 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.

[0030] 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.

[0031] 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.

[0032] 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 P 37 789.

[0033] 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%.

[0034] Preferably the polymer is substantially fully deprotonated.

[0035] A polyaniline can be formed of octamer units i.e. p is four, e.g.

[0036] The polyanilines can have conductivities of the order of  $1 \times 10^{-1}$  Siemen cm<sup>-1</sup> or higher.

[0037] The aromatic rings can be unsubstituted or substituted e.g. by a C1 to 20 alkyl group such as ethyl.

[0038] 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.

[0039] Other polymers of an amino substituted aromatic compound which can be used include substituted or unsubstituted polyaminonaphthalenes, polyaminoanthracenes, polyaminophenanthrenes, etc. and polymers of any other condensed polyaromatic compound. Polyaminoanthracenes and methods of making them are disclosed in U.S. Pat. No. 6,153,726. The aromatic rings can be unsubstituted or substituted e.g. by a group R as defined above.

[0040] 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 U.S. Pat. No. 5,807,627, PCT/WO90/13148 and PCT/WO92/03490.

[0041] 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 dialkoxyphenylenevinylene)s 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.

[0042] 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.

[0043] 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 naphthylene ring and the number of vinylene groups in each polyphenylenevinylene moiety can be increased e.g. up to 7 or higher.

[0044] The conjugated polymers can be made by the methods disclosed in U.S. Pat. No. 5807627, PCT/WO90/13148 and PCT/WO92/03490.

[0045] The thickness of the hole transporting layer is preferably 20 nm to 200 nm.

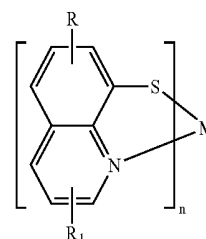
[0046] The polymers of an amino substituted aromatic compound such as polyanilines referred to above can also be used as buffer layers with or in conjunction with other hole transporting materials.

[0047] The structural formulae of some other hole transporting materials are shown in FIGS. 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.

[0048] 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.

[0049] 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, tetracyanoquinodimethane a polystyrene sulphonate or a compound with the structural formulae shown in FIGS. 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.

[0050] 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.

[0051] Instead of being a separate layer the electron injecting material can be mixed with the electroluminescent composition and co-deposited with it.

[0052] Optionally the hole transporting material can be mixed with the electroluminescent composition and co-deposited with it.

[0053] The hole transporting materials, the electroluminescent composition and the electron injecting materials can be mixed together to form one layer, which simplifies the construction.

[0054] 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.

[0055] 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.

[0056] 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

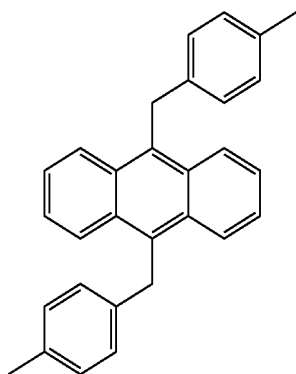
[0057] This is a general synthesis for these compounds. In each separate example a different benzyl halide compound is used, but the synthesis process is the same.

[0058] Anthracene (8.0 g, 44.9 mmol), Zinc dust (2.35 g, 35.9 mmol) and the benzyl chloride (94 mmol) were stirred in carbon disulphide (150 ml) and refluxed for 30 h. The reaction was cooled to room temperature and the solvent was removed by distillation. The residue was extracted into hot toluene (200 ml) and filtered under vacuum to remove excess zinc. On cooling. The toluene solution yielded a light yellow crystalline product which was recrystallised from hot toluene. filtered and dried in a vacuum oven.

## Example 1

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

[0059]



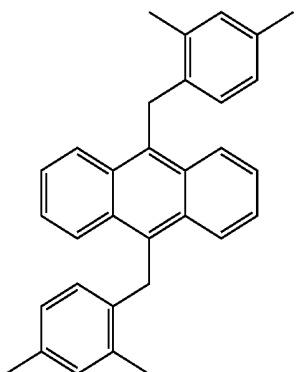
(XI)

[0060] 4-Methylbenzylchloride was used as the starting material

## Example 2

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

[0061]



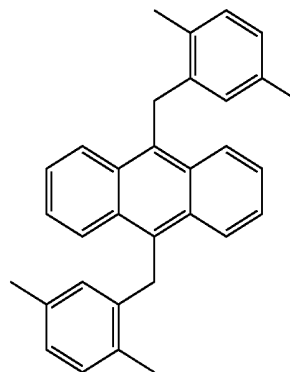
(XII)

[0062] 2,4-Dimethylbenzyl chloride was used as the starting material.

## Example 3

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

[0063]



(XIII)

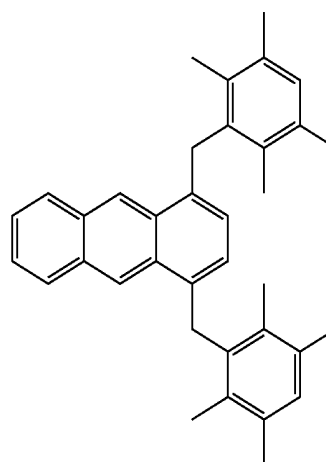
[0064] 2,5-Dimethylbenzyl chloride was used as the starting material.

## Example 4

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

(D)

[0065]



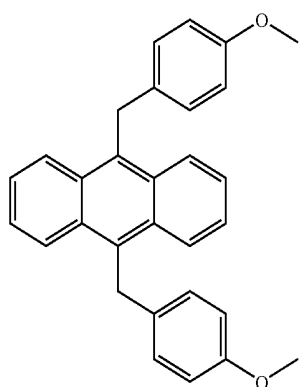
(XIV)

[0066] 2,3,5,6-tetramethylbenzyl chloride was used as the starting material.

## Example 5

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

[0067]



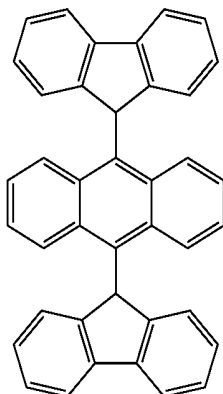
(XV)

[0068] 4-Methoxybenzyl chloride was used as the starting material.

## Example 6

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

[0069]



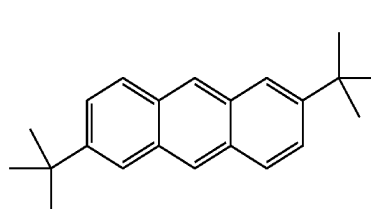
(XVI)

[0070] 9-Bromofluorene was used as the starting material.

## Example 7

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

[0071]



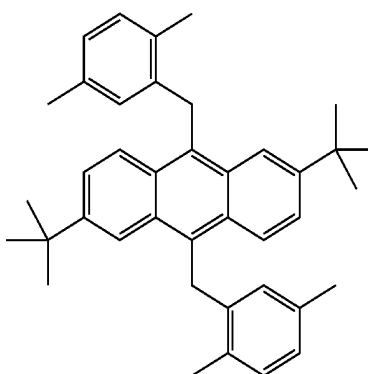
(XVII)

[0072] Anthracene (7.13 g, 40 mmol) and tert-Butanol (10.8 g, 120 mmol) were refluxed for 15 h in trifluoroacetic acid (40 ml). The mixture was cooled and poured into water (250 ml). The solid that formed was filtered under vacuum, washed with water and dried. The solid was recrystallised 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)

[0073]



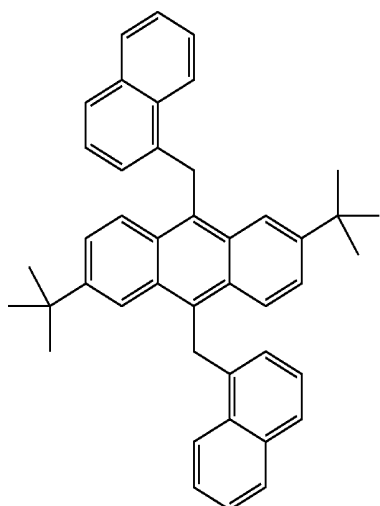
(XVIII)

[0074] 2,6-Di-tert-butyl-anthracene (3.0 g, 10.3 mmol), Zinc dust (0.54 g, 8.3 mmol) and 2,5-Dimethylbenzyl chloride (3.35 g, 21.7 mmol) were stirred in carbon disulphide (50 ml) and refluxed for 30 h. The reaction was cooled to room temperature and the solvent was removed by distillation. The residue was extracted into hot toluene (50 ml) and filtered under vacuum to remove excess zinc. On cooling, the toluene solution yielded a colourless crystalline product which was recrystallised 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-1-ylmethyl-anthracene (H)

[0075]



(XIX)

[0076] 2,6-Di-tert-butyl-anthracene (2.9 g, 10 mmol), Zinc dust (0.52 g, 8 mmol) and 1-(chloromethyl)naphthalene (3.7 g, 20.9 mmol) were stirred in carbon disulphide (50 ml) and refluxed for 30 h. The reaction was cooled to room temperature and the solvent was removed by distillation. The residue was extracted into hot toluene (50 ml) and filtered under vacuum to remove excess zinc. On cooling, the toluene solution yielded a colourless crystalline product which was recrystallised from hot toluene filtered and dried in a vacuum oven. M.p. 285° C.

Electroluminescent Devices

## Example 10

[0077] A pre-etched ITO coated glass piece (10×10 cm<sup>2</sup>) 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. Chigasaki, Japan. The active area of each pixel was 3 mm by 3 mm, the device is shown in FIG. 1 and the layers comprised:

[0078] (1) ITO/(2)α-NPB (42 nm)/(3) K:H (20:1) (26 nm)/(4) Zr<sub>q</sub> (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, Zr<sub>q</sub> is zirconium quinolate and K and H are as defined below.

[0079] 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<sup>-6</sup> torr) and aluminium top contacts made. The devices were then kept in a vacuum desiccator until the electroluminescence studies were performed.

[0080] 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.

[0081] An electric current was applied across the device and the performance shown in FIGS. 9 and 10.

## Example 11

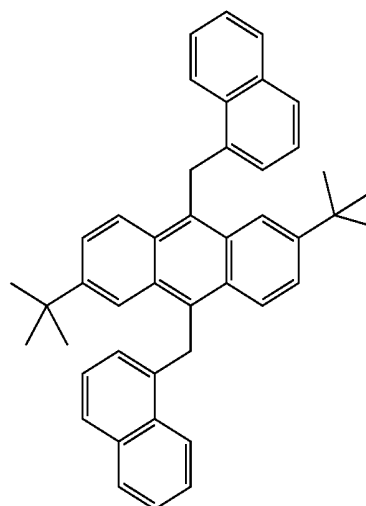
[0082] A device was formed as in example 10 with the structure:

[0083] (1) ITO/α-NPB (40 nm)/(2) L:H (20:2) (27 nm)/(3) Zr<sub>q</sub> (17 nm)/(4) LiF (0.3 nm)/(5) Al.

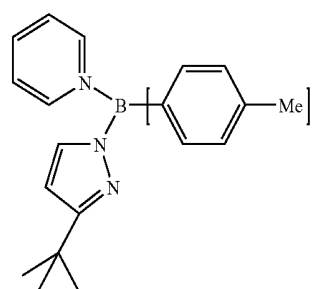
where H and L are as shown below

[0084] The performance is shown in FIGS. 11 and 12.

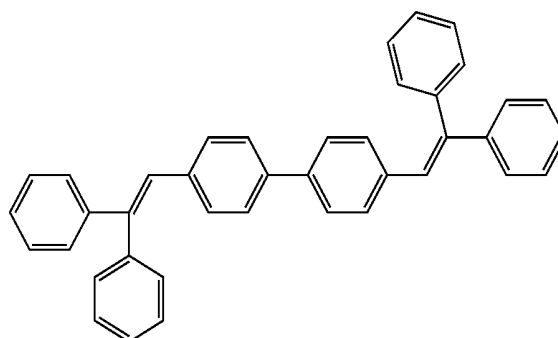
[0085] Compounds used in devices



H



K

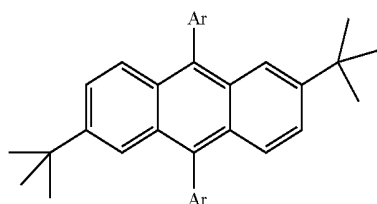
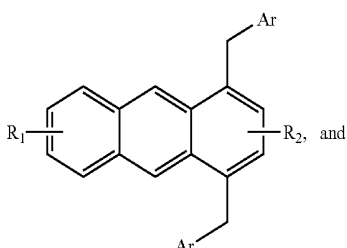
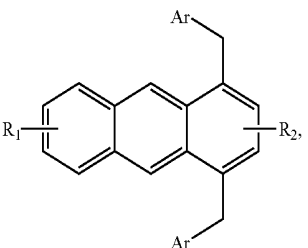
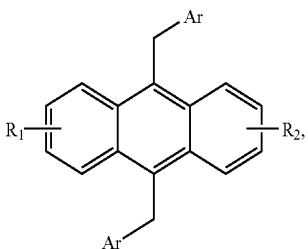
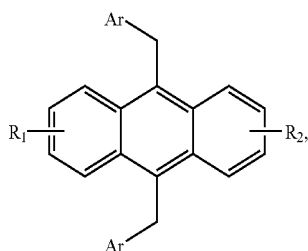


L

1.-40. (canceled)

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

42. The composition of claim 41, wherein the aromatic substituted anthracene compound has a general chemical formula selected from the group consisting of:



wherein Ar is an aromatic or substituted aromatic group and  $R_1$  and  $R_2$ , which may be the same or different, are independently selected from the group consisting of hydrogen; substituted and unsubstituted aliphatic groups; substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures; fluorocarbons; halogens; and thiophenyl groups.

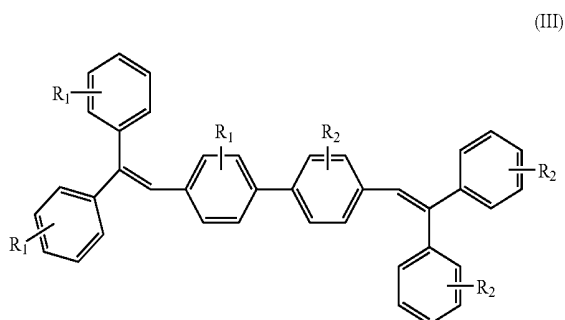
43. The composition of claim 41, wherein the anthracene compound is selected from the group consisting of:

- 9,10-bis-(2,4-dimethylbenzyl)-anthracene;
- 9,10-bis-(2,5-dimethylbenzyl)-anthracene;
- 1,4-bis-(2,3,5,6-tetramethylbenzyl)-anthracene;
- 9,10-bis-(4-methoxybenzyl)-anthracene;
- 9,10-bis-(9H-fluoren-9-yl)-anthracene;
- 2,6-di-*t*-butyl-9,10-bis-(2,5-dimethylbenzyl)-anthracene; and
- 2,6-di-*t*-butyl-9,10-bis-naphthalen-1-ylmethul-anthracene.

44. The composition of claim 41, wherein the composition contains about  $10^{-3}$  to 10 mole percent of the aromatic substituted anthracene compound, based on the moles of host material in the composition.

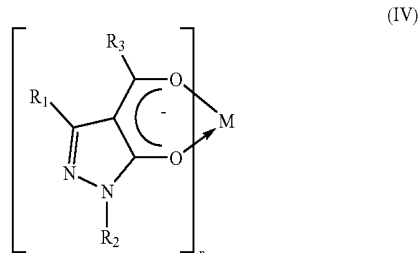
45. The composition of claim 41, wherein the host material is selected from the group consisting of:

- (a) aromatic compounds having the general chemical formula:



wherein  $R_1$  and  $R_2$ , which may be the same or different, are independently selected from the group consisting of hydrogen; substitute and unsubstituted aliphatic groups; substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures; fluorocarbons; halogens; and thiophenyl groups;

- (b) compounds having the general chemical formula:



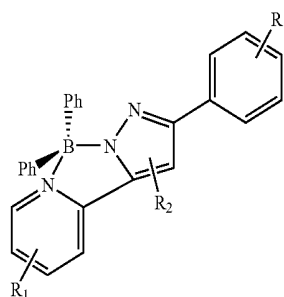
where:

M is a metal;

n is the valence of M;

$R_1$ ,  $R_2$  and  $R_3$ , which may be the same or different, are independently selected from the group consisting of hydrogen; hydrocarbyl groups; substituted and unsubstituted aliphatic groups; substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures; fluorocarbons; halogens; thiophenyl groups; and nitrile; alternatively  $R_1$  and  $R_3$  can form ring structures, and  $R_1$ ,  $R_2$  and  $R_3$  can be copolymerisable with a monomer, and,

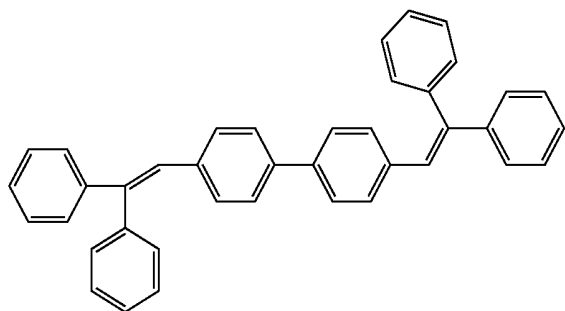
(c) compounds having the general chemical formula:



(V)

where Ph is an unsubstituted or substituted phenyl group in which the substituents can be the same or different and are independently selected from hydrogen, substituted and unsubstituted aliphatic groups; substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures; fluorocarbon; halogens; and thiophenyl groups;  $R$ ,  $R_1$  and  $R_2$  are selected from the group consisting of hydrogen, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures; fluorine; fluorbons; halogens; thiophenyl groups; and nitrile.

46. The composition of claim 41, wherein the host comprises a material having the chemical formula



L

47. An electroluminescent device which comprises (i) a first electrode; (ii) a second electrode; and (iii) a layer of an electroluminescent composition as claimed in claim 41 located between said first and second electrodes.

48. An electroluminescent device according to claim 47 wherein the layer of the electroluminescent composition is a film of less than about 1  $\mu\text{m}$  in thickness.

49. An electroluminescent device as claimed in claim 47 further wherein a layer of a hole transiting material is located between the first electrode and the electroluminescent layer, and wherein the hole transmitting material comprises a material selected from the group consisting of

- (a) an aromatic amine selected from the group consisting of  $\alpha$ -NBP, TPD, mTADATA, and other polyaromatic amines;
- (b) a film of a polymer selected from poly(vinylcarbazole); N5N'-diphenyl-N,N'-bis (3-methylphenyl)-1,1'-biphenyl 4,4'-diamine (TPD); polyaniline; substituted polyanilines; polythiophenes; substituted polythiophenes; polysilanes; and substituted polysilanes;
- (c) a copolymer of aniline; a copolymer of aniline with o-anisidine, m-sulphanilic acid or o-aminophenol; and a copolymer of o-toluidine with o-aminophenol, o-ethylaniline, o-phenylene diamine or with an amino anthracene; and,

- (d) a conjugated polymer selected from the group consisting of poly(p-phenylenevinylene)-PPV and copolymers; 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); other poly(2,5 dialkoxyphenylenevinylene)s wherein at least one of the alkoxy groups is a long chain solubilising alkoxy group; poly fluorenes; oligofluorenes; polyphenylenes; oligophenylenes; polyanthracenes; oligo anthracenes; polythiophenes; and oligothiophenes.

50. An electroluminescent device according to claim 47, further wherein a layer of an electron transmitting material is located between the cathode and the electroluminescent compound layer, and the electron transmitting layer comprises a material selected from the group consisting of:

- (a) a metal quinolate;
- (b) a metal thioxinate;
- (c) a material having the general chemical formula  $\text{Mx}(\text{DBM})_n$  where Mx is a metal, DBM is dibenzoyl methane and n is the valency of Mx;
- (d) a cyano anthracene; and,
- (e) Beq, ZnPBO, ZnPBT, DTVb1, t-BuPVD, BND, OXD-7, TAZ and OXD-Star.

51. An electroluminescent device according to claim 50 wherein the electron transmitting layer comprises a material selected from the group consisting of aluminum quinolate, zirconium quinolate, lithium quinolate, zinc thioxinate, cadmium thioxinate, gallium thioxinate and indium thioxinate.

52. An electroluminescent device according to claim 50 wherein the electron transmitting layer comprises a material selected from the group consisting of 9,10 dicyano anthracene and polystyrene sulphonate.

|                |                                                                     |         |            |
|----------------|---------------------------------------------------------------------|---------|------------|
| 专利名称(译)        | 电致发光材料和器件                                                           |         |            |
| 公开(公告)号        | <a href="#">US20070252108A1</a>                                     | 公开(公告)日 | 2007-11-01 |
| 申请号            | US11/659919                                                         | 申请日     | 2005-08-12 |
| [标]申请(专利权)人(译) | KATHIRGAMANATHAN POOPATHY                                           |         |            |
| 申请(专利权)人(译)    | KATHIRGAMANATHAN POOPATHY                                           |         |            |
| 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         | C07C15/28 C09K11/06 H05B33/14 H01L51/0052 H01L51/5012 C09K2211/1011 |         |            |
| 优先权            | 2004017927 2004-08-12 GB                                            |         |            |
| 外部链接           | <a href="#">Espacenet</a> <a href="#">USPTO</a>                     |         |            |

#### 摘要(译)

电致发光组合合物包含掺杂剂，该掺杂剂是与主体材料混合的芳族取代的蒽化合物。

