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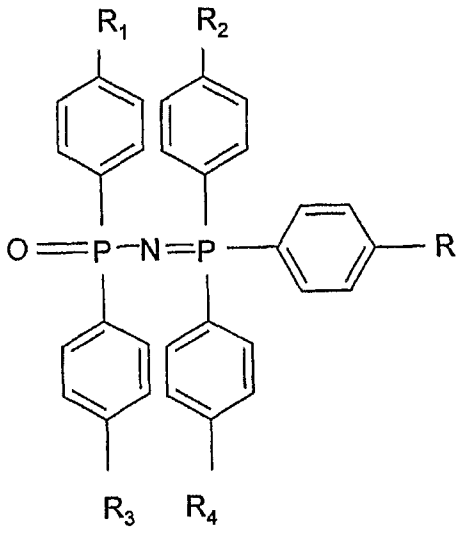
(54) **Title:** ELECTROLUMINESCENT MATERIALS AND DEVICES



(57) **Abstract:** Lithium quinolate is a host material for organometallic electroluminescent materials to form an electroluminescent layer in an electroluminescent device.

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ELECTROLUMINESCENT MATERIALS AND DEVICES

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

Materials that emit light when an electric current is passed through them are well known and used in a wide range of display applications. 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 electroluminescent compound which has been proposed is aluminium quinolate, but it 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 transition metal and lanthanide complexes which can be used in electroluminescent devices which have improved properties and give better results. Patent Applications PCT/GB98/01773, PCT/GB99/03619, PCT/GB99/04030, PCT/GB99/04024, PCT/GB99/04028 and 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.

In order to enhance the performance of electroluminescent organo metallic complexes the electroluminescent organo metallic complex can be mixed with a host material and we have now devised an improved electroluminescent material using a metal quinolate as the host material.

According to the invention there is provided an electroluminescent composition which comprises a mixture of a substituted or unsubstituted metal quinolate and an electroluminescent organo metallic complex.

The invention also provides an electroluminescent device which comprises (i) a first electrode, (ii) a layer of an electroluminescent composition comprising a mixture of a substituted or unsubstituted metal quinolate and an electroluminescent organo metallic complex and (iii) a second electrode.

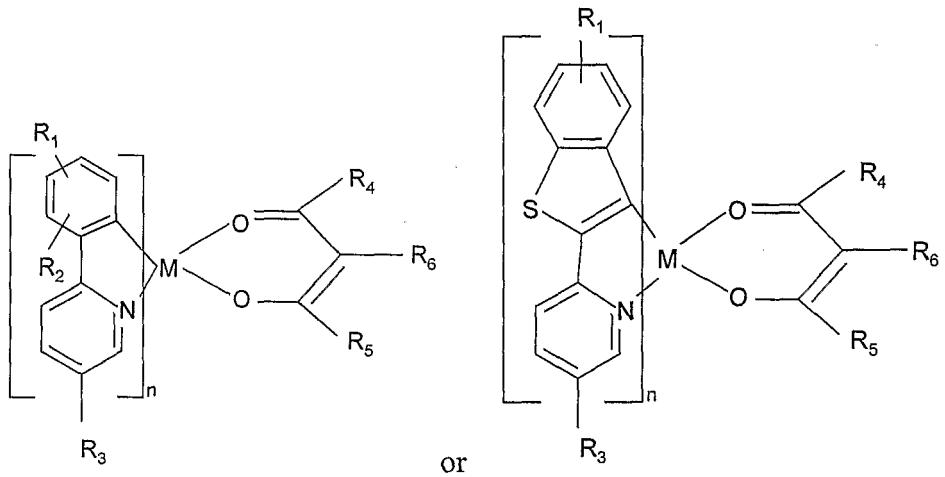
The metal forming the metal quinolate can be selected from sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, copper (I), copper (II), silver, gold, zinc, cadmium, boron, aluminium, gallium, indium, germanium, tin (II), tin (IV), antimony (II), antimony (IV), lead (II), lead (IV) and metals of the first, second and third groups of transition metals in different valence states e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium(II), palladium(IV), platinum(II), platinum(IV), cadmium, chromium. titanium, vanadium, zirconium, tantalum, niobium molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium and the preferred metals are lithium, aluminium, titanium, zirconium, hafnium, vanadium, niobium or tantalum; lithium quinolate is the most preferred metal.

Some metal quinolates are electroluminescent materials and, in particular lithium quinolate is a known electroluminescent material and WO 00/32717 discloses a lithium quinolate which is made by the reaction of n-butyl lithium with 8-hydroxy quinoline in an acetonitrile solvent and which emits light in the blue region of the spectrum.

Provided the light emitting band gap of the electroluminescent organo metallic complex is wider than the band gap of the light emitting excited singlet state of the metal quinolate host material and the light emitting band gap of the electroluminescent organo metallic complex material is within the excited singlet state of the metal quinolate host material the metal quinolate makes no contribution to the colour of the light emitted by the mixture of the electroluminescent organo metallic complex and lithium quinolate.

Preferably the HOMO-LUMO gap of the organo metallic complex is within the HOMO-LUMO gap of the metal quinolate.

One type of preferred organo metallic complexes are the ruthenium, rhodium, palladium, osmium, iridium or platinum iridium complexes and, in particular, iridium complexes :-



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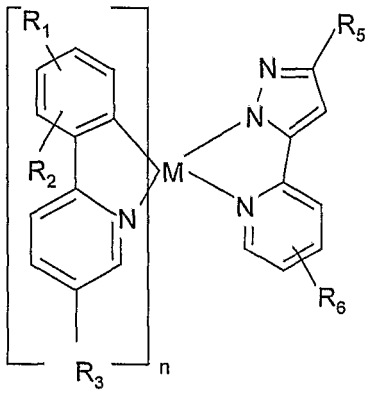

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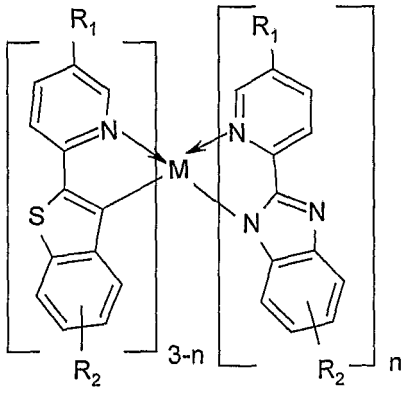

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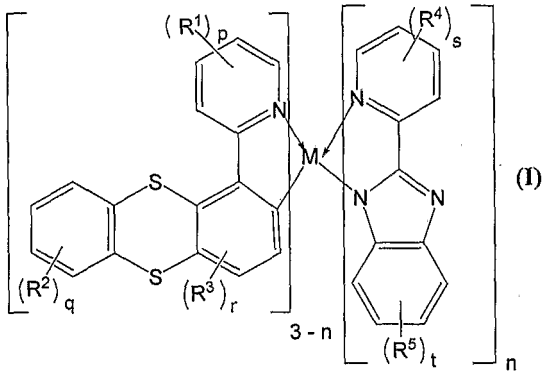

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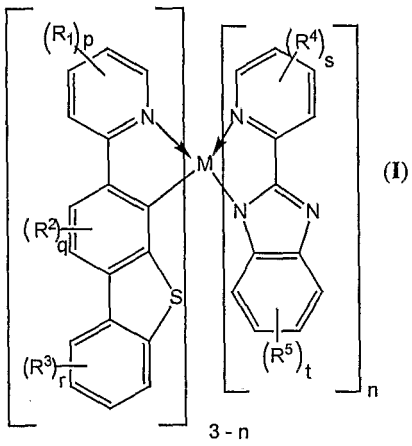
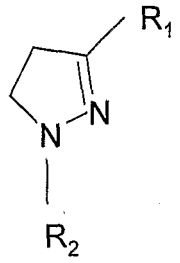


(VI)

wherein M is ruthenium, rhodium, palladium, osmium, iridium or platinum; n is 1 or 2; R^1 - R^5 which may be the same or different are selected from substituted and unsubstituted hydrocarbyl groups; substituted and unsubstituted monocyclic and polycyclic heterocyclic groups; substituted and unsubstituted hydrocarbyloxy or carboxy groups; fluorocarbyl groups; halogen; nitrile; nitro; amino; alkylamino; dialkylamino; arylamino; diarylamino; *N*-alkylamido, *N*-arylamido, sulfonyl and thiophenyl; and R^2 and R^3 can additionally be alkylsilyl or arylsilyl; p, s and t independently are 0, 1, 2 or 3; subject to the proviso that where any of p, s and t is 2 or 3 only one of them can be other than saturated hydrocarbyl or halogen; q and r independently are 0, 1 or 2, subject to the proviso that when q or r is 2, only one of

them can be other than saturated hydrocarbyl or halogen where R_1, R_2, R_3 , R_4, R_5 and R_6 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, and where R_4, and R_5 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, or or R_5 and R_6 form a



Group and M is ruthenium, rhodium, palladium, osmium, iridium or platinum and n+2 is the valency of M. Preferably M is iridium.

Other preferred organo metallic complexes are of formula $M(L)_n$ and $MO(L)_{n-2}$ where M is a metal in a valency state n of greater than 3 and L is an organic ligand, the ligands L can be the same or different, e.g. $M(L_1)$ (L_2) (L_3) (L_4)... or $MO(L_1)$ (L_2)....

Preferably the metal M is a transition metal such as titanium, zirconium or hafnium in the four valency state or vanadium, niobium or tantalum in the five valency state and in particular is zirconium quinolate.

Patent Application WO 2004/058913, the contents of which are included by reference, discloses doped zirconium quinolates which can be used in the present invention.

Preferably the electroluminescent compound is doped with a minor amount of a fluorescent material as a dopant, preferably in an amount of 5 to 15% of the doped mixture.

As discussed in US 4769292, the contents of which are included by reference, the presence of the fluorescent material permits a choice from among a wide latitude of wavelengths of light emission.

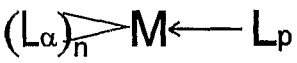
Useful fluorescent materials are those capable of being blended with the organo metallic complex and fabricated into thin films satisfying the thickness ranges described above forming the luminescent zones of the EL devices of this invention. While crystalline organo metallic complexes do not lend themselves to thin film formation, the limited amounts of fluorescent materials present in the organo metallic complex materials permits the use of fluorescent materials which are alone incapable of thin film formation. Preferred fluorescent materials are those which form a common phase with the organo metallic complex material. Fluorescent dyes constitute a preferred class of fluorescent materials, since dyes lend themselves to molecular level distribution in the organo metallic complex. Although any convenient technique for dispersing the fluorescent dyes in the organo metallic complexes can be undertaken, preferred fluorescent dyes are those which can be vacuum vapour deposited along with the organo metallic complex materials. Assuming other criteria, noted above, are satisfied, fluorescent laser dyes are recognized to be particularly useful fluorescent materials for use in the organic EL devices of this invention. Dopants which can be used include diphenylacridine, coumarins, perylene and their derivatives.

Useful fluorescent dopants are disclosed in US 4769292.

The organometallic complex can be mixed with a dopant and co-deposited with it, preferably by dissolving the dopant and the organometallic complex in the solvent and spin coating the mixed solution.

Other electroluminescent compounds which can be used as the electroluminescent material in the present invention are of general formula $(L\alpha)_nM$ where M is a rare earth, lanthanide or an actinide, $L\alpha$ is an organic complex and n is the valence state of M.

Further organic electroluminescent compounds which can be used in the present invention are of formula



where $L\alpha$ and Lp are organic ligands, M is a rare earth, transition metal, lanthanide or an actinide and n is the valence state of the metal M. The ligands $L\alpha$ can be the same or different and there can be a plurality of ligands Lp which can be the same or different.

For example, $(L_1)(L_2)(L_3)(L..)M(Lp)$ where M is a rare earth, transition metal, lanthanide or an actinide and $(L_1)(L_2)(L_3)(L...)$ are the same or different organic complexes and (Lp) is a neutral ligand. The total charge of the ligands $(L_1)(L_2)(L_3)(L..)$ is equal to the valence state of the metal M. Where there are 3 groups $L\alpha$ which corresponds to the III valence state of M the complex has the formula $(L_1)(L_2)(L_3)M$ (Lp) and the different groups $(L_1)(L_2)(L_3)$ may be the same or different.

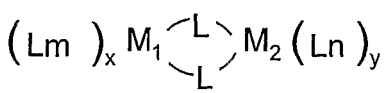
Lp can be monodentate, bidentate or polydentate and there can be one or more ligands Lp.

Preferably M is a metal ion having an unfilled inner shell and the preferred metals are selected from Sm(III), Eu(II), Eu(III), Tb(III), Dy(III), Yb(III), Lu(III), Gd (III), Gd(III) U(III), Tm(III), Ce (III), Pr(III), Nd(III), Pm(III), Dy(III), Ho(III), Er(III), Yb(III) and more preferably Eu(III), Tb(III), Dy(III), Gd (III), Er (III), Yt(III).

Further organic electroluminescent compounds which can be used in the present invention are of general formula $(L\alpha)_nM_1M_2$ where M_1 is the same as M above, M_2 is a non rare earth metal, $L\alpha$ is as above and n is the combined valence state of M_1 and M_2. The complex can also comprise one or more neutral ligands Lp so the complex has the general formula $(L\alpha)_n$ M_1 M_2 (Lp), where Lp is as above. The metal M_2 can be any metal which is not a rare earth, transition metal, lanthanide or an actinide. Examples of metals which can be used include lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, copper (I), copper (II), silver, gold, zinc, cadmium, boron, aluminium, gallium, indium, germanium, tin (II), tin (IV), antimony (II), antimony (IV), lead (II), lead (IV) and metals of the first, second and third groups of transition metals in different valence states e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium(II), palladium(IV), platinum(II), platinum(IV), cadmium, chromium. titanium, vanadium, zirconium, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium.

For example $(L_1)(L_2)(L_3)(L..)M$ (Lp) where M is a rare earth, transition metal, lanthanide or an actinide and $(L_1)(L_2)(L_3)(L...)$ and (Lp) are the same or different organic complexes.

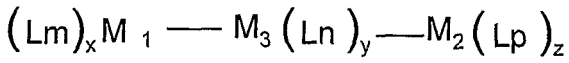
Further organometallic complexes which can be used in the present invention are binuclear, trinuclear and polynuclear organometallic complexes e.g. of formula $(Lm)_x M_1 \leftarrow M_2(Ln)_y$ e.g.



where L is a bridging ligand and where M_1 is a rare earth metal and M_2 is M_1 or a non rare earth metal, Lm and Ln are the same or different organic ligands Lα as defined above, x is the valence state of M_1 and y is the valence state of M_2.

In these complexes there can be a metal to metal bond or there can be one or more bridging ligands between M_1 and M_2 and the groups Lm and Ln can be the same or different.

By trinuclear is meant there are three rare earth metals joined by a metal to metal bond i.e. of formula



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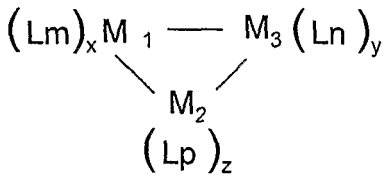
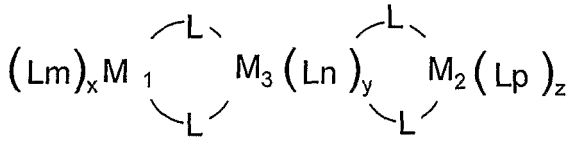


where M_1, M_2 and M_3 are the same or different rare earth metals and Lm, Ln and Lp are organic ligands Lα and x is the valence state of M_1, y is the valence state of M_2 and z is the valence state of M_3. Lp can be the same as Lm and Ln or different.

The rare earth metals and the non rare earth metals can be joined together by a metal to metal bond and/or via an intermediate bridging atom, ligand or molecular group.

For example the metals can be linked by bridging ligands e.g.



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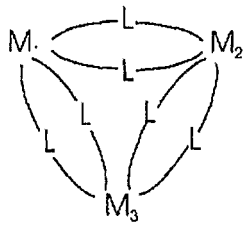

where L is a bridging ligand.

By polynuclear is meant there are more than three metals joined by metal to metal bonds and/or via intermediate ligands

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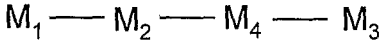

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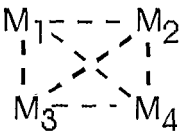

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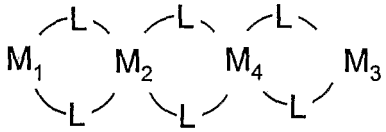
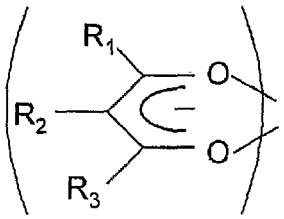


where M_1, M_2, M_3 and M_4 are rare earth metals and L is a bridging ligand.

Preferably Lα is selected from α diketones such as those of formulae



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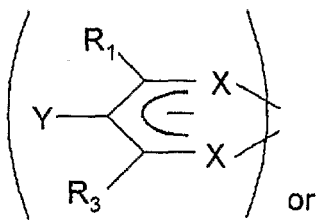

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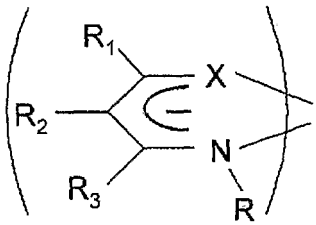
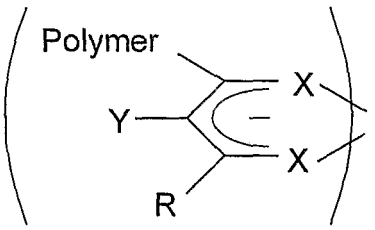


(VII) (VIII) (XIX)

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.

The beta diketones can be polymer substituted beta diketones and in the polymer, oligomer or dendrimer substituted β diketone the substituents group can be directly linked to the diketone or can be linked through one or more - CH_2 groups i.e.



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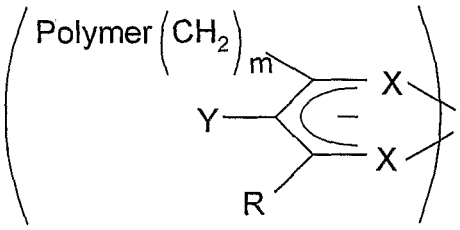

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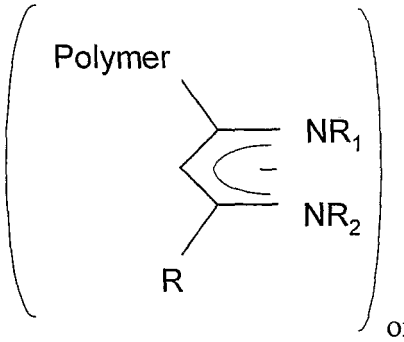

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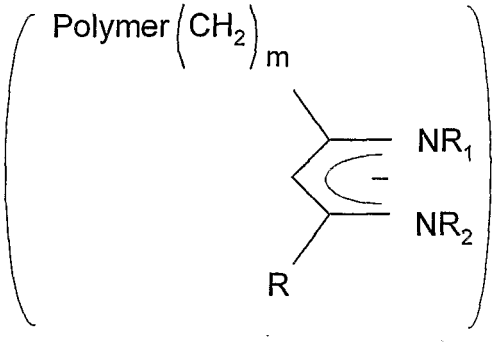
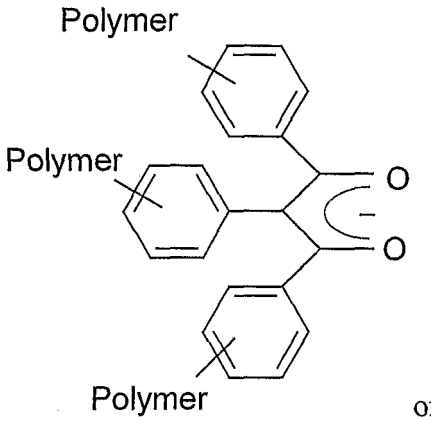


(XII) (XIII)

or through phenyl groups e.g.



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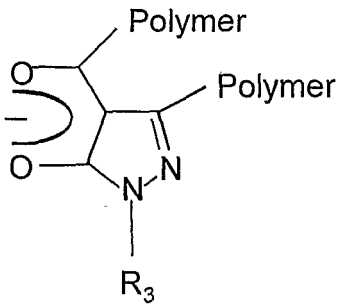
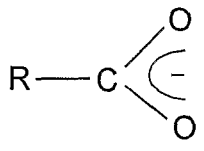


(XIV) (XV)

where "polymer" can be a polymer, an oligomer or a dendrimer, (there can be one or two substituted phenyl groups as well as three as shown in (IIIc)) and where R is 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 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.

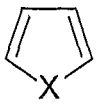
Some of the different groups Lα may also be the same or different charged groups such as carboxylate groups so that the group L_1 can be as defined above and the groups L_2, $L_{3...}$ can be charged groups such as



(XVI)

where R is R_1 as defined above or the groups L_1, L_2 can be as defined above and L_3... etc. are other charged groups.

R_1, R_2 and R_3 can also be

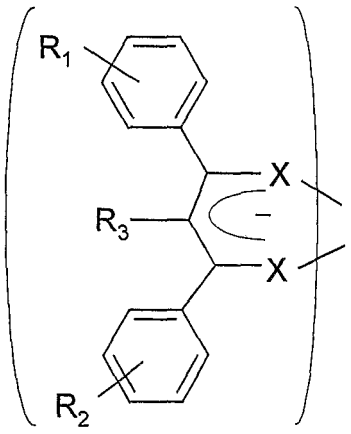


where X is O, S, Se or NH.

(XVII)

A preferred moiety R_1 is trifluoromethyl CF_3 and examples of such diketones are, banzoyltrifluoroacetone, p-chlorobenzoyltrifluoroacetone, p-bromotrifluoroacetone, p-phenyltrifluoroacetone, 1-naphthoyltrifluoroacetone, 2-naphthoyltrifluoroacetone, 2-phenathoyltrifluoroacetone, 3-phenanthoyltrifluoroacetone, 9-anthroyltrifluoroacetonetrifluoroacetone, cinnamoyltrifluoroacetone, and 2-thenoyltrifluoroacetone.

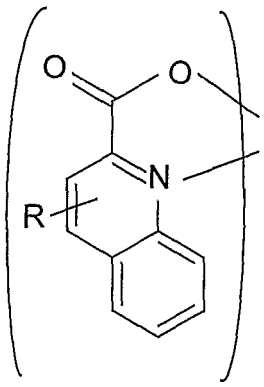
The different groups Lα may be the same or different ligands of formulae



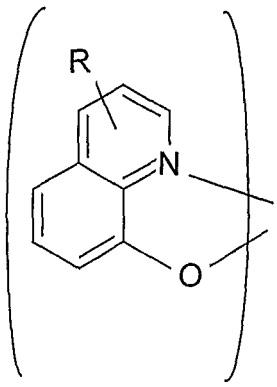
(XVIII)

where X is O, S, or Se and R_1 R_2 and R_3 are as above.

The different groups Lα may be the same or different quinolate derivatives such as

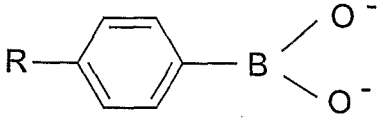


or

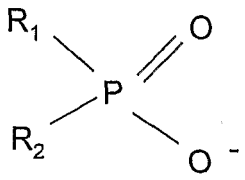


(XIX) (XX)

where R is hydrocarbyl, aliphatic, aromatic or heterocyclic carboxy, aryloxy, hydroxy or alkoxy e.g. the 8 hydroxy quinolate derivatives or

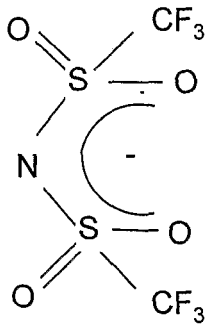


or

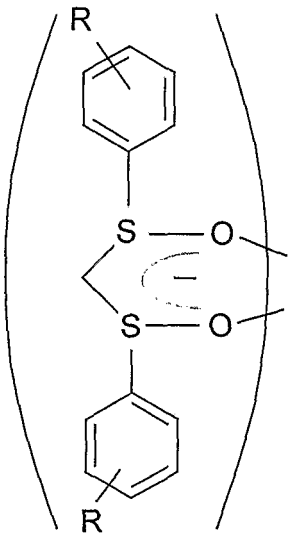


(XXI) (XXII)

where R, R_1, and R_2 are as above or are H or F e.g. R_1 and R_2 are alkyl or alkoxy groups

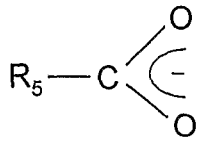


or



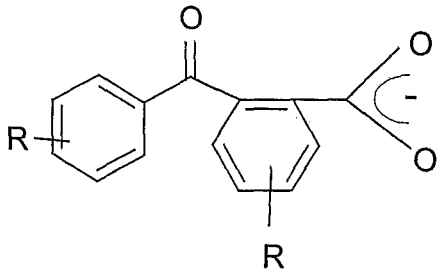
(XXIII) (XXIV)

As stated above the different groups Lα may also be the same or different carboxylate groups e.g.



(XXV)

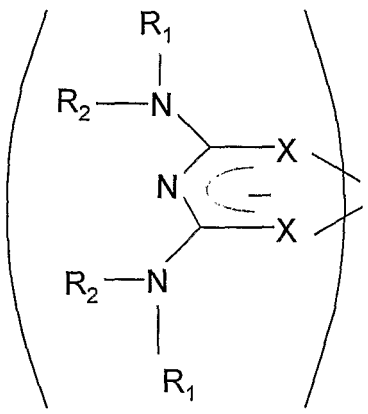
where R_5 is a substituted or unsubstituted aromatic, polycyclic or heterocyclic ring a polypyridyl group, R_5 can also be a 2-ethyl hexyl group so L_n is 2-ethylhexanoate or R_5 can be a chair structure so that L_n is 2-acetyl cyclohexanoate or Lα can be



(XXVI)

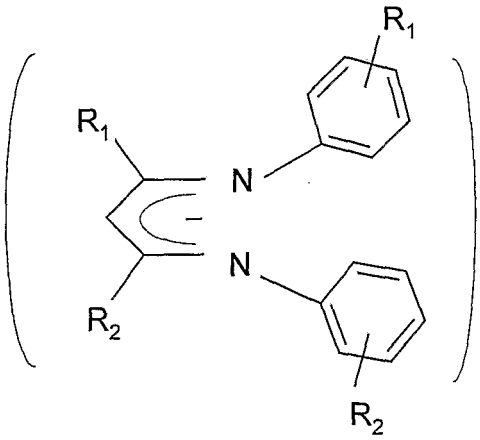
where R is as above e.g. alkyl, allenyl, amino or a fused ring such as a cyclic or polycyclic ring.

The different groups Lα may also be



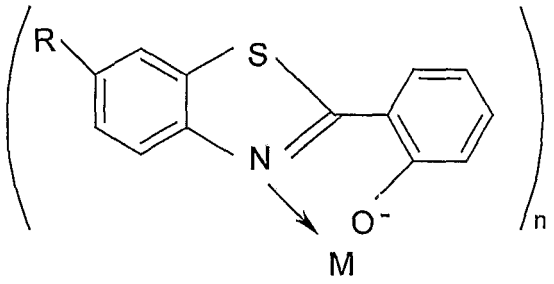
or

(XXVII)



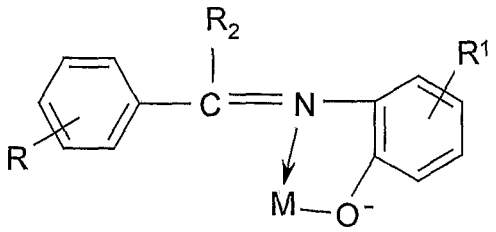
or

(XXVIII)



or

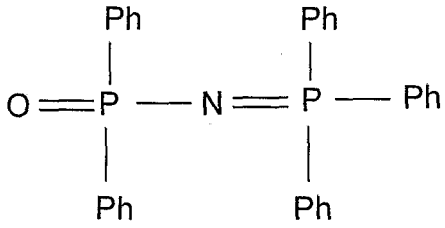
(XXIX)



(XXX)

where R, R_1 and R_2 are as above.

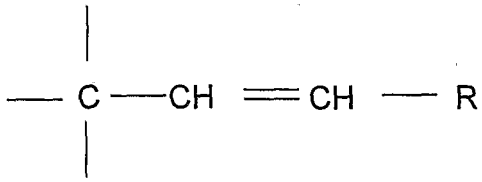
The groups L_P can be selected from



(XXXI)

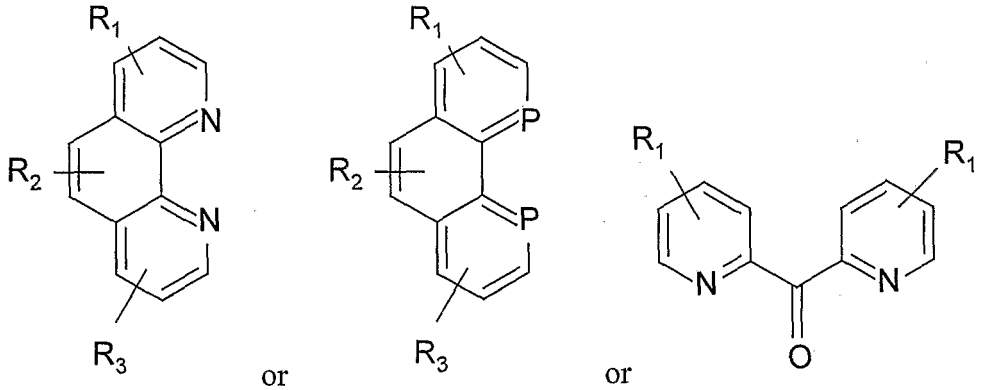
where each Ph which can be the same or different and can be a phenyl (OPNP) or a substituted phenyl group, other substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic or polycyclic group, a substituted or unsubstituted fused aromatic group such as a naphthyl, anthracene, phenanthrene or pyrene group. The substituents can be for example an alkyl, aralkyl, alkoxy, aromatic, heterocyclic, polycyclic group, halogen such as fluorine, cyano, amino, substituted amino etc. Examples are given in figs. 1 and 2 of the drawings where R,

R_1, R_2, R_3 and R_4 can be the same or different and are selected from hydrogen, hydrocarbyl 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, R_2, R_3 and R_4 can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer e.g. styrene. R, R_1, R_2, R_3 and R_4 can also be unsaturated alkylene groups such as vinyl groups or groups



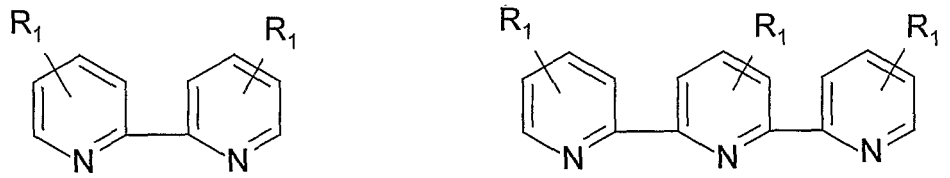
where R is as above.

L_p can also be compounds of formulae



(XXXII) or (XXXIII) or (XXXIV)

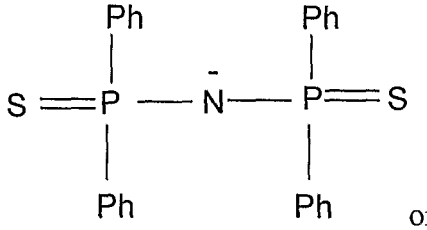
where R_1, R_2 and R_3 are as referred to above, for example bathophen shown in fig. 3 of the drawings in which R is as above or



(XXXV) (XXXVI)

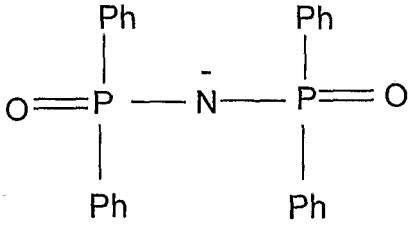
where R_1, R_2 and R_3 are as referred to above.

L_p can also be



(XXXVII)

or



(XXXVIII)

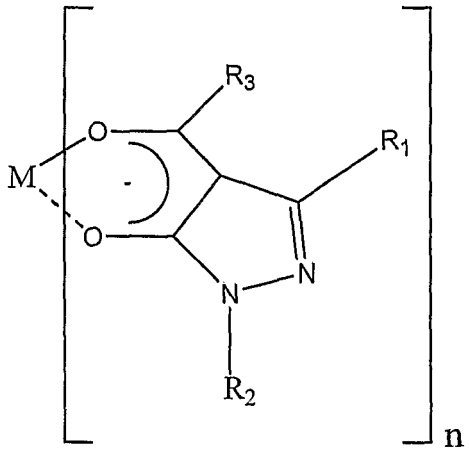
where Ph is as above.

Other examples of L_p chelates are as shown in fig. 4 and fluorene and fluorene derivatives e.g. as shown in fig. 5 and compounds of formulae as shown in figs. 6 to 8.

Specific examples of Lα and Lp are tripyridyl and TMHD, and TMHD complexes, α, α′, α′′ tripyridyl, crown ethers, cyclans, cryptans phthalocyanans, porphoryins ethylene diamine tetramine (EDTA), DCTA, DTPA and TTHA, where TMHD is 2,2,6,6-tetramethyl-3,5-heptanedionato and OPNP is diphenylphosphonimide triphenyl phosphorane. The formulae of the polyamines are shown in fig. 9.

Other organic electroluminescent materials which can be used include metal quinolates such as lithium quinolate, and non rare earth metal complexes such as aluminium, magnesium, zinc and scandium complexes such as complexes of β-diketones e.g. Tris -(1,3-diphenyl-1-3-propanedione) (DBM) and suitable metal complexes are $Al(DBM)_3$, $Zn(DBM)_2$ and $Mg(DBM)_2$., $Sc(DBM)_3$ etc.

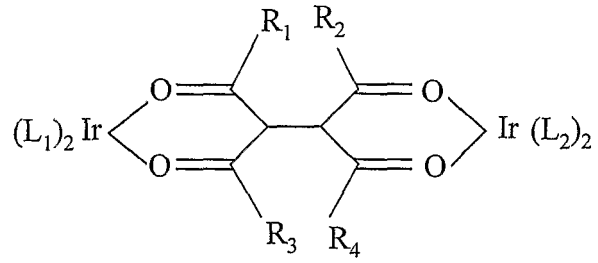
Other organic electroluminescent materials which can be used include the metal complexes of formula



(XXXIX)

where M is a metal other than a rare earth, a transition metal, a lanthanide or an actinide; 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. Preferably M is aluminium and R_3 is a phenyl or substituted phenyl group.

Other organic electroluminescent materials which can be used include electroluminescent diiridium compounds of formula

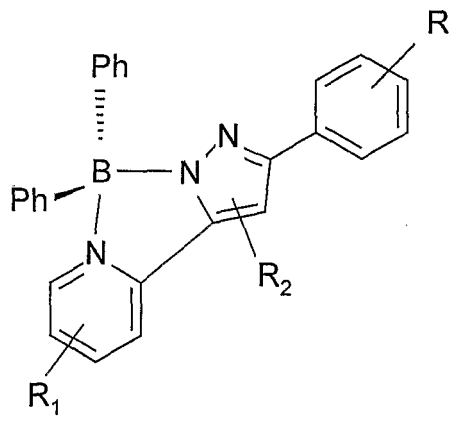


(XXXX)

where R_1, R_2, R_3 and R_4 can be the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups; preferably R_1, R_2, R_3 and R_4 are selected from 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 and L_1 and L_2 are the same or different organic ligands and more preferably L_1 and L_2 are selected from phenyl pyridine and substituted phenylpryidines.

Other electroluminescent compounds which can be used are of formula



(XXXXI)

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.

Further electroluminescent materials which can be used include metal quinolates such as aluminium quinolate, lithium quinolate, zirconium quinolate etc. and metal quinolates doped with fluorescent materials or dies as disclosed in patent application WO/2004/058913.

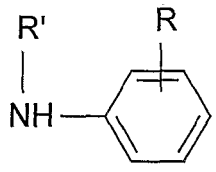
The metal quinolate host and the electroluminescent material must be different.

The thickness of the layer of the electroluminescent material is preferably from 10 – 250 nm, more preferably 20 – 75 nm.

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

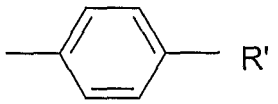
The hole transporting material can be any of the hole transporting materials used in electroluminescent devices.

The hole transporting material can be an amine complex such as α-NBP, 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 and substituted polysilanes etc. Examples of polyanilines are polymers of:



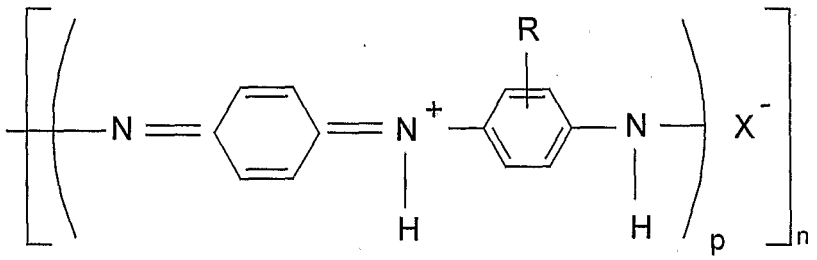
(XXXXII)

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 II above.

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



(XXXXIII)

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 alkylsulphonate, vinylsulphonate, vinylbenzene sulphonate, cellulose sulphonate, camphor sulphonate, 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 be easily evaporated, i.e. the polymer is evaporable.

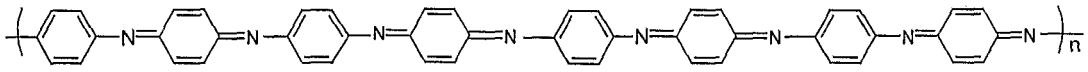
Preferably evaporable deprotonated polymers of unsubstituted or substituted polymers of an amino substituted aromatic compound are used. The deprotonated unsubstituted or substituted polymer of an amino substituted aromatic compound can be formed by deprotonating the polymer by treatment with an alkali 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 deprotonating. Methods of preparing polyanilines are described in the article by A. G. MacDiarmid and A. F. Epstein, Faraday Discussions, Chem Soc.88 P319, 1989.

The conductivity of the polyaniline is dependent on the degree of protonation with the maximum conductivity being when the degree of protonation is between 40 and 60%, for example 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 6153726. 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, WO90/13148 and 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, polyfluorenes and oligofluorenes, polyphenylenes and oligophenylenes, polyanthracenes and oligoanthracenes, polythiophenes and oligothiophenes.

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

In polyfluorene, the fluorene 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 an anthracene or naphthalene ring and the number of vinylene groups in each poly(phenylenevinylene) moiety can be increased, e.g. up to 7 or higher.

The conjugated polymers can be made by the methods disclosed in US 5807627, WO90/13148 and 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 e.g. between the anode and the hole transporting layer. Other buffer layers can be formed of phthalocyanines such as copper phthalocyanine.

The structural formulae of some other hole transporting materials are shown in Figures 12, 13, 14, 15 and 16 of the drawings, where R, R^1, R^2, R^3 and R^4 can be the same or different and are selected from hydrogen, substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbon groups such as trifluoromethyl, halogens such as fluorine or thiophenyl groups; R, R^1, R^2, R^3 and R^4 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 hydrocarboxyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbon groups such as trifluoromethyl, halogens such as fluorine, thiophenyl or nitrile groups.

Examples of R and/or R^1 and/or R^2 and/or R^3 and/or R^4 include aliphatic, aromatic and heterocyclic groups, alkoxy, aryloxy and carboxy groups, substituted and

unsubstituted phenyl, fluorophenyl, biphenyl, naphthyl, fluorenyl, anthracenyl and phenanthrenyl groups, alkyl groups such as t-butyl, and heterocyclic groups such as carbazole.

Optionally there is a layer of an electron injecting material between the anode and the electroluminescent material layer. The electron injecting material is a material which will transport electrons when an electric current is passed through. Electron injecting materials include a metal complex such as a metal quinolate, e.g. an aluminium quinolate, lithium quinolate, zirconium quinolate (Zrq_4), a cyanoanthracene such as 9,10dicyanoanthracene, cyano substituted aromatic compounds, tetracyanoquinodimethane, a polystyrene sulphonate or a compound with the structural formulae shown in figures 10 or 11 of the drawings or $Mx(DBM)_n$ where Mx is a metal and DBM is dibenzoyl methane and n is the valency of Mx e.g. Mx is aluminium or chromium. A Schiff base can also be used in place of the DBM moiety.

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

Optionally the hole transporting material can be mixed with the electroluminescent material and co-deposited with it and the electron injecting materials and the electroluminescent materials can be mixed. The hole transporting materials, the electroluminescent materials and the electron injecting materials can be mixed together to form one layer, which simplifies the construction.

The first electrode 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, e.g. aluminium, barium, calcium, lithium, rare earth metals, transition metals, 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 e.g. lithium fluoride or 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 iridium or other metal complex can be mixed with a host material.

The devices of the present invention can be used as displays in video displays, mobile telephones, portable computers and any other application where an electronically controlled visual image is used. The devices of the present invention can be used in both active and passive applications of such displays.

In known electroluminescent devices either one or both electrodes can be formed of silicon and the electroluminescent material and intervening layers of hole transporting and electron transporting materials can be formed as pixels on the silicon substrate. Preferably each pixel comprises at least one layer of an electroluminescent material and a (at least semi-) transparent electrode in contact with the organic layer on a side thereof remote from the substrate.

Preferably, the substrate is of crystalline silicon and the surface of the substrate may be polished or smoothed to produce a flat surface prior to the deposition of electrode, or electroluminescent compound. Alternatively a non-planarised silicon substrate can be coated with a layer of conducting polymer to provide a smooth, flat surface prior to deposition of further materials.

In one embodiment, each pixel comprises a metal electrode in contact with the substrate. Depending on the relative work functions of the metal and transparent electrodes, either may serve as the anode with the other constituting the cathode.

When the silicon substrate is the cathode an indium tin oxide coated glass can act as the anode and light is emitted through the anode. When the silicon substrate acts as the anode, the cathode can be formed of a transparent electrode which has a suitable work function; for example by an indium zinc oxide coated glass in which the indium zinc oxide has a low work function. The anode can have a transparent coating of a metal formed on it to give a suitable work function. These devices are sometimes referred to as top emitting devices or back emitting devices.

The metal electrode may consist of a plurality of metal layers; for example a higher work function metal such as aluminium deposited on the substrate and a lower work function metal such as calcium deposited on the higher work function metal. In another example, a further layer of conducting polymer lies on top of a stable metal such as aluminium.

Preferably, the electrode also acts as a mirror behind each pixel and is either deposited on, or sunk into, the planarised surface of the substrate. However, there may alternatively be a light absorbing black layer adjacent to the substrate.

In still another embodiment, selective regions of a bottom conducting polymer layer are made non-conducting by exposure to a suitable aqueous solution allowing formation of arrays of conducting pixel pads which serve as the bottom contacts of the pixel electrodes.

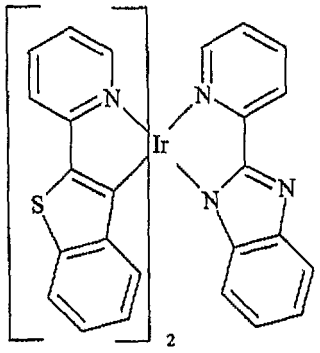
Device construction

An electroluminescent device was prepared by sequentially depositing layers of the component layers on an ITO coated glass substrate.

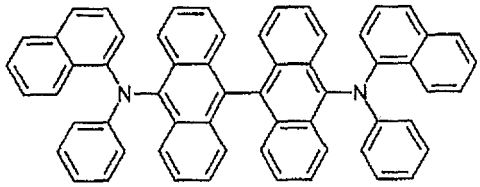
To form the device a pre-etched ITO coated glass piece (10 x 10cm^2) was used. The device was fabricated by sequentially forming the layers on the ITO, by vacuum evaporation using a Solciet Machine, ULVAC Ltd. Chigacki, Japan; the active area

of each pixel was 3mm by 3mm.

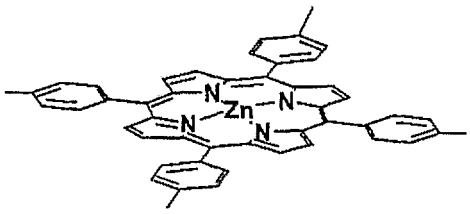
The mixed layers were formed by depositing the two materials simultaneously onto the substrate. In the examples compounds X, Y and Z are



Compound X



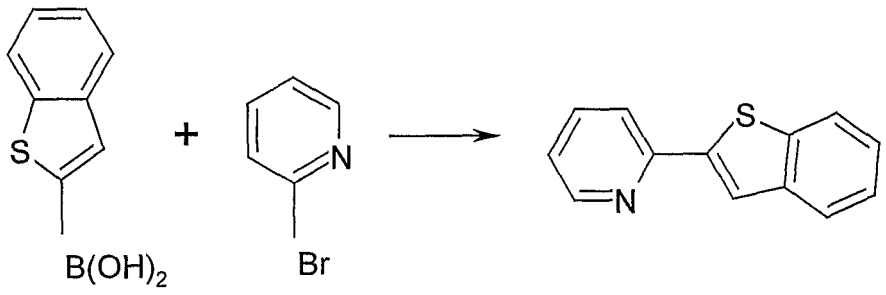
Compound Y



Zn TpTP

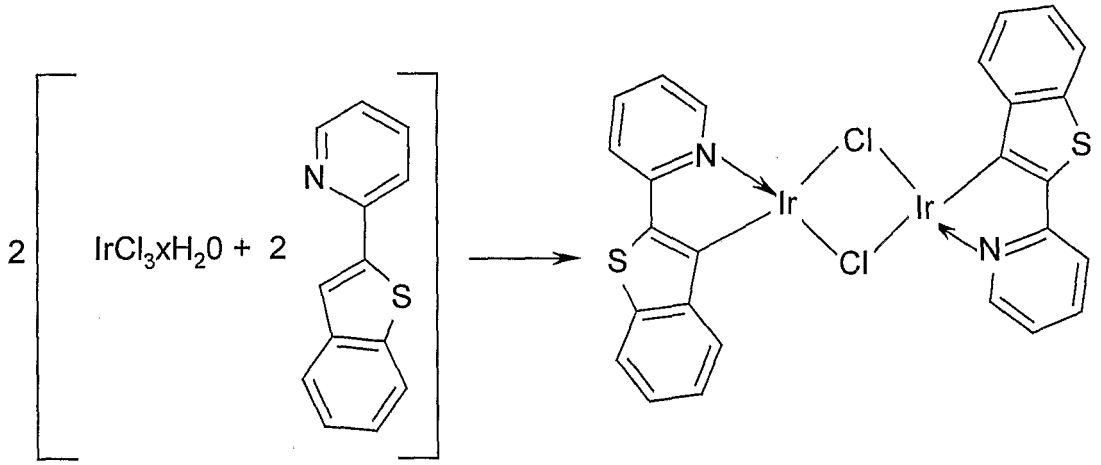
Example 1

2-Benzo[b] thiophen-2-yL-pyridine



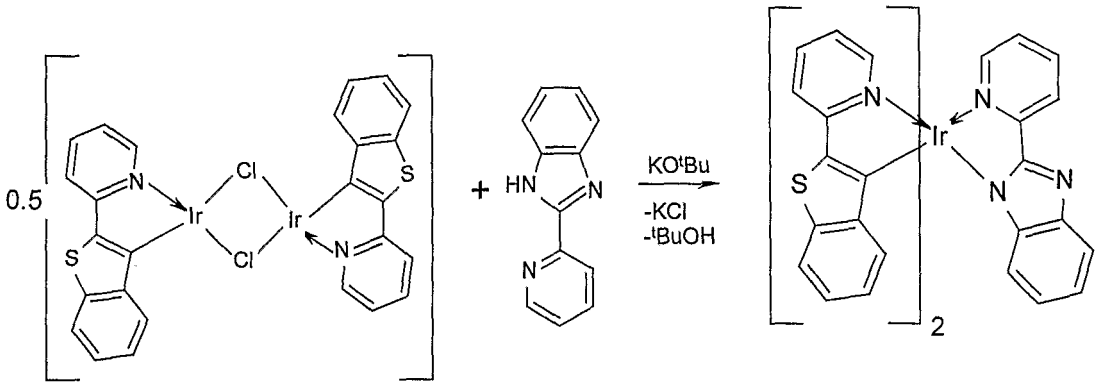
A two-necked 250mL round-bottomed flask fitted with a reflux condenser (with gas inlet) and a rubber septum was flushed with argon before 2-bromopyridine (2.57mL, 27mmol) and ethyleneglycol dimethylether (80mL, dry and degassed) were introduced. Tetrakis(triphenylphosphine) palladium (1.0g, 0.87mmol) was added and the solution stirred at room temperature for 10 minutes. Benzothiophene-2-boronic acid (5.0g, 28.1 mmol) was then added, followed by anhydrous sodium bicarbonate (8.4g. 100mmol) and water (50mL, degassed). The septum was replaced with a glass stopper and the reaction mixture was heated at 80°C for 16 hours, cooled to room temperature and the volatiles removed *in vacuo*. Organics were extracted with ethyl acetate (3 x 100mL), washed with brine and dried over magnesium sulphate. Removal of the organics yielded a pale yellow solid. Recrystallisation from ethanol yielded a colourless solid (3.9g, 68%, two crops), m.p. 124-6°C

Tetrakis [2-benzo][b]thiophen-2-yl-pyridine-C^2, N'](μ-chloro) dilridium



Iridium trichioride hydrate (0.97g, 3.24mmol) was combined with 2-benzo[b]thiophen-2-yl-pyridine (2.05g, 9.7mmol), dissolved in a mixture of 2-ethoxyethanol (70mL, dried and distilled over $MgSO_4$, degassed) and water (20mL, degassed), and refluxed for 24 hours. The solution was cooled to room temperature and the orange precipitate collected on a glass sinter. The precipitate was washed with ethanol (60mL, 95%), acetone (60mL), and hexane. This was dried and used without further purification. Yield (1.5g. 71%)

Bis thiophen-2-yl-pyridine-C^2, N']-2-(2-pyridyl)benzimidazole iridium



Potassium *tert-butoxide* (1.1 2g, 10 mmol) and 2-(2-pyridyl)benzimidazole (1.95 g, 10mmol) were added to a 200mL Schienk tube under an inert atmosphere. 2-Ethoxyethanol (dried and distilled over magnesium sulphate, 100mL) was added and the resultant solution stirred at ambient temperature for 10 minutes. Tetrakis[2-benzo[b]thiophen-2-yl-pyridine-C^2, N'](μ-chloro) diiridium (6.0g, 4.62mmol) was added and the mixture refluxed under an inert atmosphere for 16 hours. On cooling to room temperature, an orange/red solid separated out. The solid was collected by filtration and washed with ethanol (3 x 100mL) and diethyl ether (100mL). After drying *in vacuo* the material was purified by soxhlet extraction with ethyl acetate for 24 hours. Further purification was achieved by high-vacuum sublimation (3 x 10^{-7} Torr, 400°C). Yield (6.6g, 89%, pre-sublimation)

Elemental Analysis:

Calc.: C, 56.56; H, 3.00, N, 8.68

Found: C, 56.41; H, 2.91; N, 8.64

Example 2

A device was fabricated of structure

ITO(110nm)/CuPc(10nm)/α-NPB(60nm)/Liq:Compound X (30:2)nm /BCP(6nm) / Zrq_4 (30nm)/LiF (0.5nm)/Al

where Compound X is thiophen-2-yl-pyridine-C^2, N']-2-(2-pyridyl)benzimidazole iridium synthesised as above, CuPc is a copper phthalocyanine buffer layer, α-NPB is as in fig. 16a, Liq is lithium quinolate, BCP is bathocupron, Zrq_4 is zirconium quinolate and LiF is lithium fluoride.

The coated electrodes were stored in a vacuum desiccator over a molecular sieve and phosphorous pentoxide until they were loaded into a vacuum coater Solciet Machine,ULVAC Ltd. Chigacki, Japan; the active area of each pixel was 3mm by

3mm, 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.

The electroluminescent properties were measured and the results are shown in figs. 17, 18 and 19.

Example 3

A device was constructed as in Example 2 which had the structure ITO(110nm)/Compound Y(10nm)/α-NPB(60nm)/Liq:Compound X (30:2)nm / Zrq_4 (30nm)/LiF (0.5nm)/Al

An electric current was passed through the device as in Example 2 and the properties of the emitted light measured and the results are shown in figs. 20 to 22 of the drawings.

Example 4

A device was constructed as in Example 2 which had the structure ITO(110nm)/ZnTpTP(10nm)/α-NPB(60nm)/Liq:Compound X (30:2)nm / Zrq_4 (30nm)/LiF (0.5nm)/Al

An electric current was passed through the device as in Example 1 and the properties of the emitted light measured and the results are shown in figs. 23 to 25 of the drawings.

Example 5

A device was constructed as in Example 2 which had the structure ITO(110nm)/Compound Y(10nm)/α-NPB(60nm)/Liq:Compound X (30:2)nm/ 30nm) /LiF (0.5nm)/Al

An electric current was passed through the device as in Example 1 and the properties of the emitted light measured and the results are shown in figs. 26 to 28 of the drawings.

Example 6

A device was constructed as in Example 2 which had the structure ITO(110nm)/ZnTpTP(10nm)/α-NPB(60nm)/Liq:Compound X (30:2)nm / Liq (30nm)/LiF (0.5nm)/Al

An electric current was passed through the device as in Example 2 and the properties of the emitted light measured and the results are shown in figs. 29 to 31 of the drawings.

CLAIMS

1. An electroluminescent composition which comprises a mixture of a substituted or unsubstituted metal quinolate and an electroluminescent organo metallic complex.

2. An electroluminescent device which comprises (i) a first electrode, (ii) a layer of an electroluminescent composition comprising a mixture of a substituted or unsubstituted lithium quinolate and an electroluminescent organo metallic complex and (iii) a second electrode.

3. An electroluminescent composition or device as claimed in claims 1 or 2 in which the metal is lithium, aluminium, titanium, zirconium, hafnium, vanadium, niobium or tantalum.

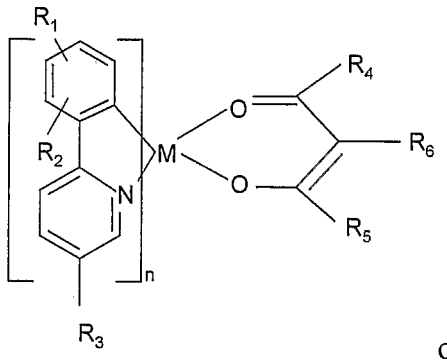
4. An electroluminescent composition or device as claimed in any one of claims 1 to 3 in which the wave length of the emitted light is longer than the wave length which would be emitted by the metal quinolate alone.

5. An electroluminescent composition or device as claimed in any one of claims 1 to 4 in which the HOMO-LUMO gap of the organo metallic complex is within the HOMO-LUMO gap of the metal quinolate.

6. An electroluminescent composition or device as claimed in any one of claims 1 to 5 in which the metal quinolate is lithium quinolate made by the reaction of n-butyl lithium with 8-hydroxy quinoline in an acetonitrile solvent.

7. An electroluminescent composition or device as claimed in any one of claims 1 to 6 in which the organo metallic complex is a ruthenium, rhodium, palladium, osmium, iridium or platinum complex.

8. An electroluminescent composition or device as claimed in claim 7 in which the complex is of formula:-



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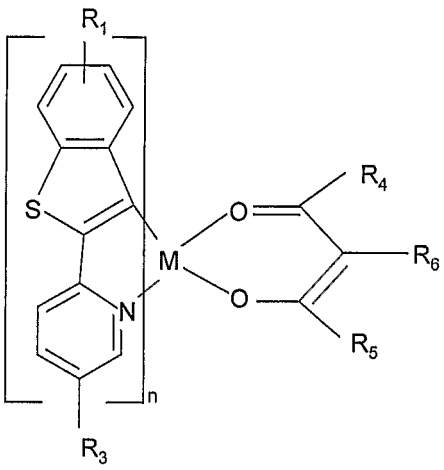
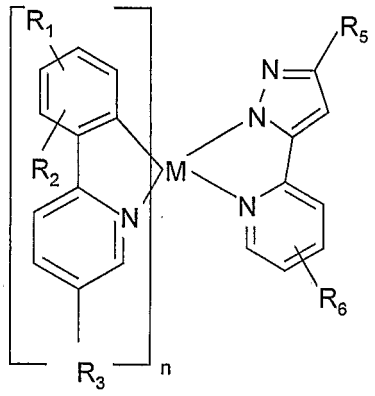
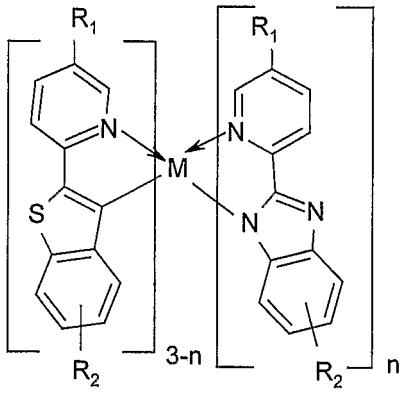
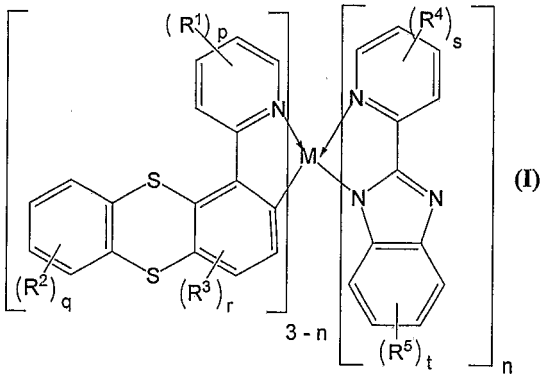


(I) (II)

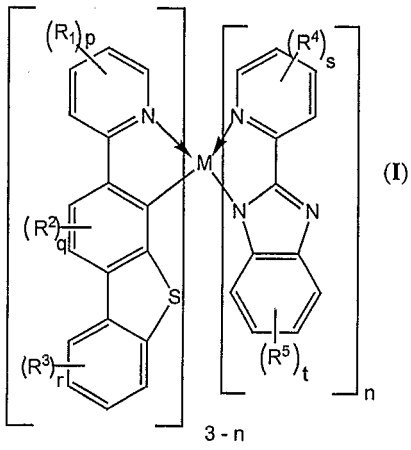




(III) (IV)



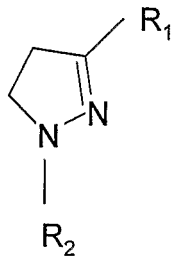
(I)



(I)

(V) (VI)

wherein M is ruthenium, rhodium, palladium, osmium, iridium or platinum; n is 1 or 2; R^1 - R^5 which may be the same or different are selected from substituted and unsubstituted hydrocarbyl groups; substituted and unsubstituted monocyclic and polycyclic heterocyclic groups; substituted and unsubstituted hydrocarbyloxy or carboxy groups; fluorocarbyl groups; halogen; nitrile; nitro; amino; alkylamino; dialkylamino; arylamino; diarylamino; *N*-alkylamido, *N*-arylamido, sulfonyl and thiophenyl; and R^2 and R^3 can additionally be alkylsilyl or arylsilyl; p, s and t independently are 0, 1, 2 or 3; subject to the proviso that where any of p, s and t is 2 or 3 only one of them can be other than saturated hydrocarbyl or halogen; q and r independently are 0, 1 or 2, subject to the proviso that when q or r is 2, only one of them can be other than saturated hydrocarbyl or halogen where R_1, R_2, R_3 , R_4, R_5 and R_6 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, and where R_4, and R_5 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 or R_5 and R_6 form a



Group and M is ruthenium, rhodium, palladium, osmium, iridium or platinum and n+2 is the valency of M.

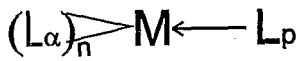
9. An electroluminescent composition or device as claimed in claim 8 in which the metal is iridium.

10. An electroluminescent composition or device as claimed in any one of claims 1 to 6 in which the organo metallic complex is of formula $M(L)_n$ and $MO(L)_{n-2}$ where M is a metal in a valency state n of greater than 3 and L is an organic ligand; the ligands L can be the same or different, e.g. $M(L_1)$ (L_2) (L_3) (L_4)... or $MO(L_1)$ (L_2)....

11. An electroluminescent composition or device as claimed in claim 10 in which the metal M is titanium, zirconium or hafnium in the four valency state or vanadium, niobium or tantalum in the five valency state.

12. An electroluminescent composition or device as claimed in claim 11 in which the organo metal complex is zirconium quinolate.

13. An electroluminescent composition or device as claimed in any one of claims 1 to 6 in which the electroluminescent material is an organo metallic complex of formula



where Lα and Lp are organic ligands, M is a rare earth, transition metal, lanthanide or an actinide and n is the valence state of the metal M and in which the ligands Lα are the same or different.

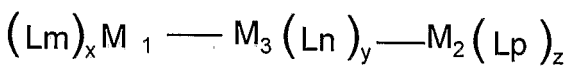
14. An electroluminescent composition or device as claimed in claim 13 in which there are a plurality of ligands Lp which can be the same or different.

15. An electroluminescent composition or device as claimed in any one of claims 1 to 6 in which the electroluminescent material is an organo metallic complex of formula $(L_n)_nM_1M_2$ or $(L_n)_n M_1M_2 (L_p)$, where L_n is Lα, L_p is a neutral ligand M_1 is a rare earth, transition metal, lanthanide or an actinide, M_2 is a non rare earth metal and n is the combined valence state of M_1 and M_2.

16. An electroluminescent composition or device as claimed in any one of claims 1 to 6 in which the electroluminescent material is a binuclear, trinuclear or polynuclear organometallic complex of formula

$(Lm)_x M_1 \leftarrow M_2(Ln)_y$ or

where L is a bridging ligand and where M_1 is a rare earth metal and M_2 is M_1 or a non rare earth metal, Lm and Ln are the same or different organic ligands Lα as defined above, x is the valence state of M_1 and y is the valence state of M_2 or



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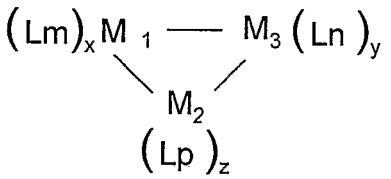
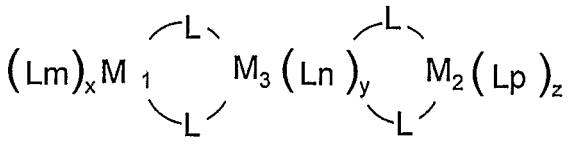


where M_1, M_2 and M_3 are the same or different rare earth metals and Lm, Ln and Lp are organic ligands Lα and x is the valence state of M_1, y is the valence state of M_2 and z is the valence state of M_3 and Lp can be the same as Lm and Ln or different or



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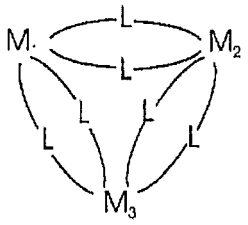

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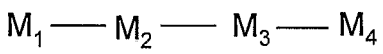

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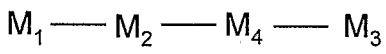

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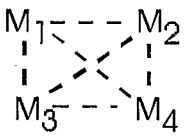

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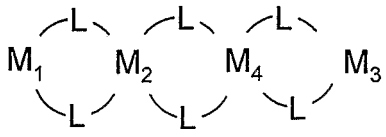


where M_4 is M_1 and L is a bridging ligand and in which the rare earth metals and the non rare earth metals can be joined together by a metal to metal bond and/or via an

intermediate bridging atom, ligand or molecular group or in which there are more than three metals joined by metal to metal bonds and/or via intermediate ligands.

17. An electroluminescent composition or device as claimed in claims 15 or 16 in which the non rare earth metal M_2 is selected from lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, copper, silver, gold, zinc, cadmium, boron, aluminium, gallium, indium, germanium, tin, antimony, lead, and metals of the first, second and third groups of transition metals e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium, platinum, cadmium, chromium, titanium, vanadium, zirconium, tantulum, molybdenum, rhodium, iridium, titanium, niobium, scandium, and yttrium.

18. An electroluminescent composition or device as claimed in any one of claims 13 to 15 in which Lα has the formula (VII) to (XXX) herein.

19. An electroluminescent composition or device as claimed in any one of claims 13 to 15 in which Lp has the formula of figs. 1 to 8 of the accompanying drawings or of formula (XXXI) to (XXXVIII) herein.

20. An electroluminescent composition or device as claimed in any one of claims 5 to 17 in which the said rare earth, transition metal, lanthanide or an actinide is selected from Sm(III), Eu(II), Eu(III), Tb(III), Dy(III), Yb(III), Lu(III), Gd (III), Gd(III) U(III), Tm(III), Ce (III), Pr(III), Nd(III), Pm(III), Dy(III), Ho(III) and Er(III).

21. An electroluminescent device as claimed in any one claims 1 to 6 in which the electroluminescent material is a metal quinolate of formula Mq_n where M is a metal, n is the valency of the metal and q is a substituted or unsubstituted quinolate ion but is not the same as the metal quinolate host.

22. An electroluminescent composition or device as claimed in claim 21 in which the metal M is lithium, aluminium, titanium, zirconium, hafnium, vanadium, niobium or tantalum.

23. An electroluminescent composition or device as claimed in any one of claims 1 to 6 in which the electroluminescent material is an electroluminescent non rare earth metal complex.

24. An electroluminescent composition or device as claimed in claim 23 in which the electroluminescent material is an aluminium, magnesium, zinc or scandium complex.

25. An electroluminescent composition or device as claimed in claim 24 in which the electroluminescent material is a β-diketone complex.

26. An electroluminescent composition or device as claimed in claim 25 in which the electroluminescent material is $Al(DBM)_3$, $Zn(DBM)_2$ and $Mg(DBM)_{2.}$, $Sc(DBM)_3$ where (DBM) is Tris -(1,3-diphenyl-1-3-propanedione).

27. An electroluminescent composition or device as claimed in any one of claims 1 to 6 in which the electroluminescent material is a compound of formula (XXXIX), to (XXXXI) herein.

28. An electroluminescent composition or device as claimed in any one of claims 1 to 6 in which the electroluminescent compound is doped with a minor amount of a fluorescent material as a dopant, preferably in an amount of 5 to 15% of the doped mixture.

29. An electroluminescent composition or device as claimed in any one of claims 1 to 28 in which there is a layer of a hole transmitting material between the first electrode and the electroluminescent layer.

30. An electroluminescent composition or device as claimed in claim 29, in which the hole transmitting material is an aromatic amine complex.

31. The device of claim 29 in which the hole transmitting material is a polyaromatic amine complex.

32. The device of claim 29 in which the hole transmitting material is a film of a polymer selected from α-NPB, 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.

33. The device of claim 29, in which the hole transmitting material is a film of a compound of formula (XXXXII) or (XXXXIII) herein or as in figures 14 to 16 of the drawings.

34. The device of claim 29, 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.

35. The device of claim 29 in which the hole transmitting material is a conjugated polymer.

36. The device of claim 34, 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, polyfluorenes and oligofluorenes, polyphenylenes and oligophenylenes, polyanthracenes and oligo anthracenes, polythiophenes and oligothiophenes.

37. The device of any of claims 29 to 36, in which the electroluminescent compound is in admixture with the hole transmitting material.

38. The device of any of claims 14 to 23, in which there is a layer of an electron transmitting material between the cathode and the electroluminescent compound layer.

39. The device of claim 38 in which the electron transmitting material is a metal quinolate.

40. The device of claim 39, in which the metal quinolate is an aluminium quinolate, zirconium quinolate or lithium quinolate.

41. The device of claim 38, 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.

42. The device of claim 31, in which the electron transmitting material is a cyanoanthracene such as 9,10-dicyanoanthracene, a polystyrene sulphonate or a compound of formulae shown in figures 10 or 11 of the drawings.

43. The device of any of claims 38 to 42, in which the electron transmitting material is in admixture with the electroluminescent compound.

44. The device of any of claims 28 to 43, in which the first electrode is a transparent electrically conducting glass electrode.

45. The device of any of claims 28 to 44, in which the second electrode is selected from aluminium, barium, rare earth metals, transition metals, calcium, lithium, magnesium and alloys thereof and silver/magnesium alloys.

46. The device of any of claims 28 to 45, wherein the second electrode is selected from a metal having a metal fluoride layer formed on it.

47. The device of claim 46, wherein the metal fluoride is a lithium fluoride or rare earth fluoride.

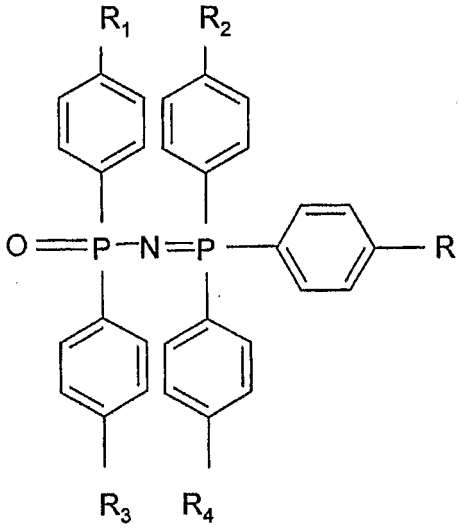


Fig. 1

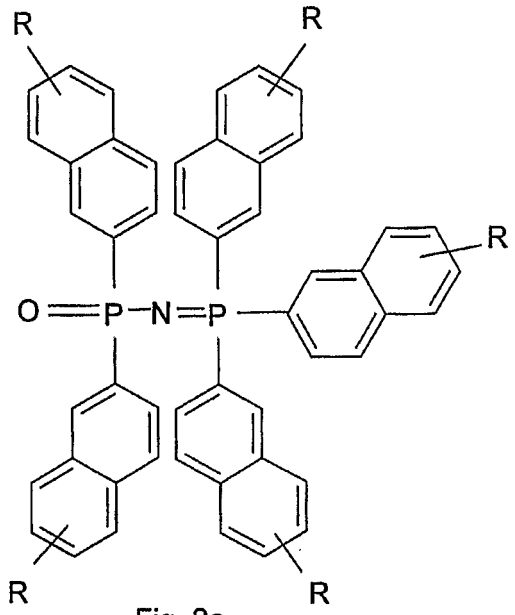


Fig. 2a

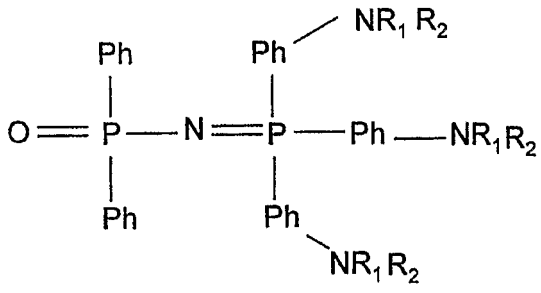


Fig. 2b

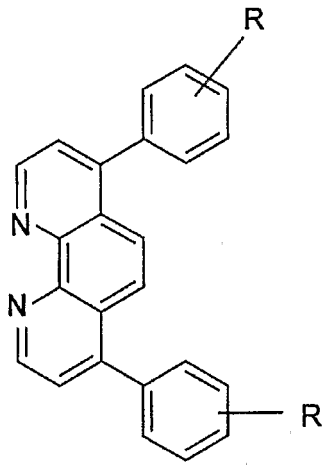


Fig. 3

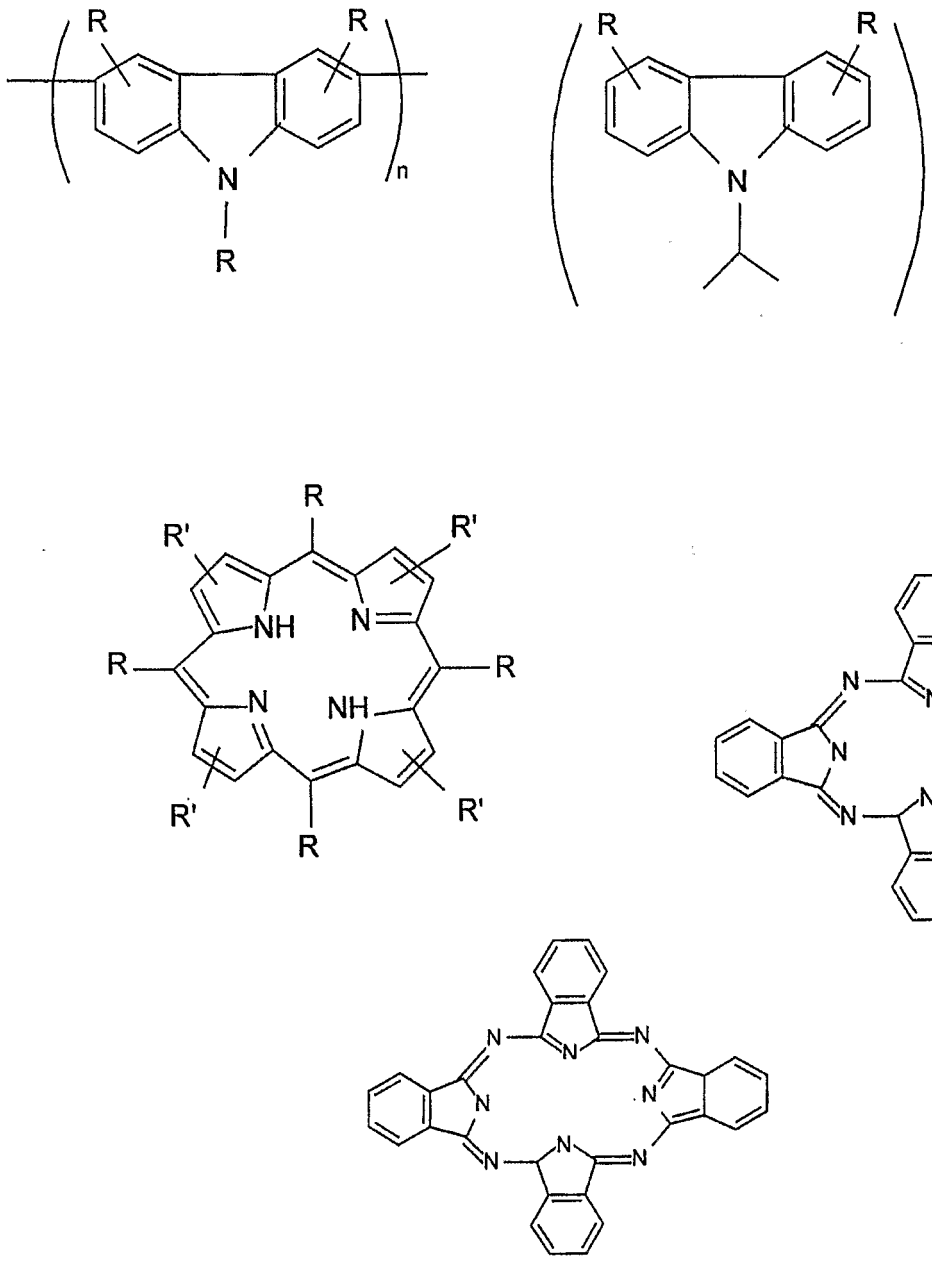


Fig. 4a

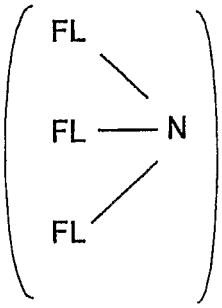


Fig. 5a

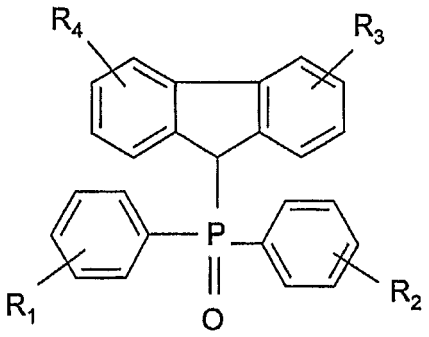


Fig.5b

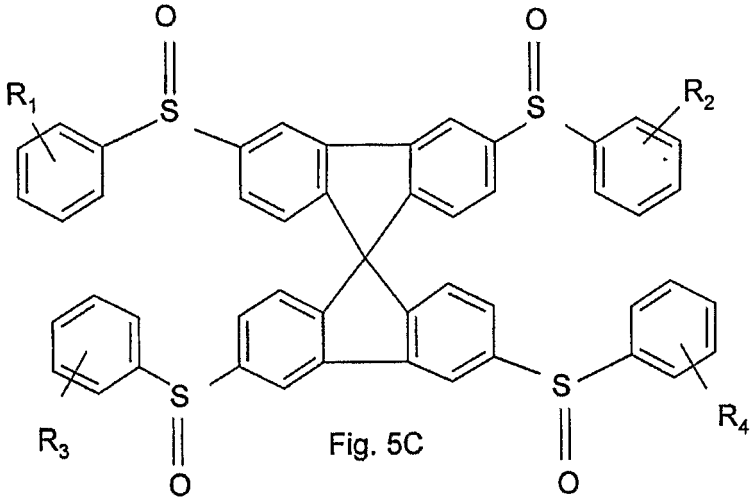


Fig. 5C

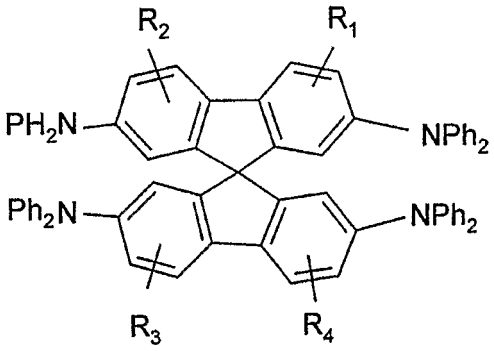


Fig. 5d

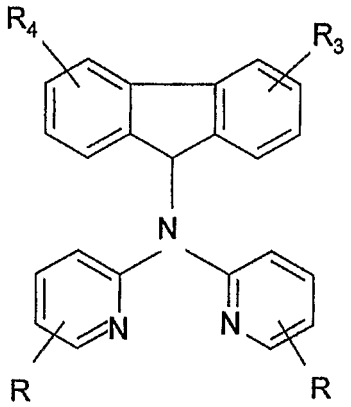


Fig. 5f

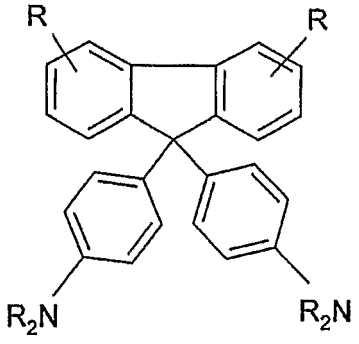


Fig. 5g

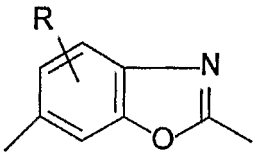


Fig. 6a

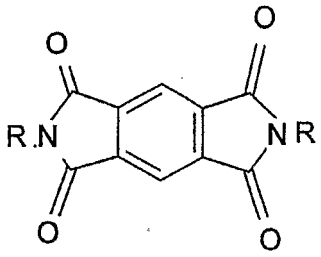


Fig 6b

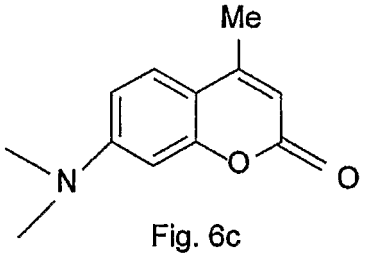


Fig. 6c

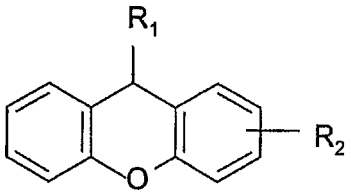


Fig. 6d

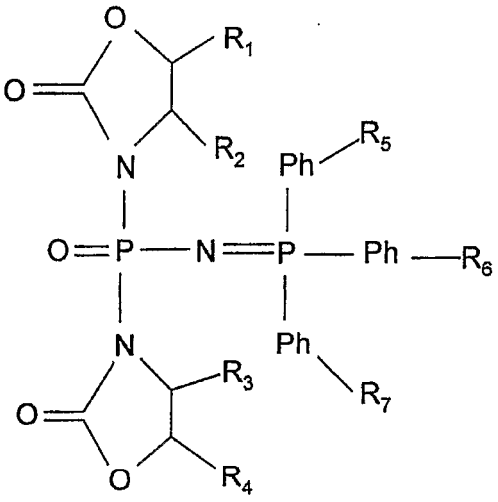


Fig. 6e

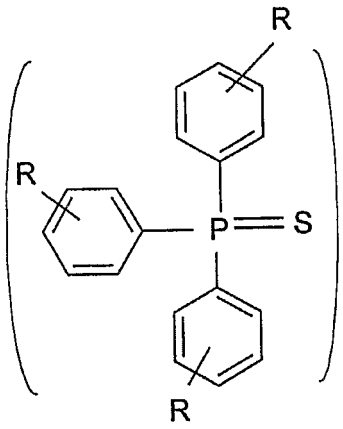


Fig. 7a

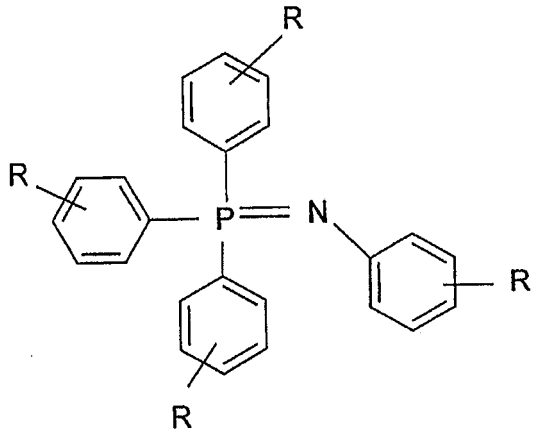
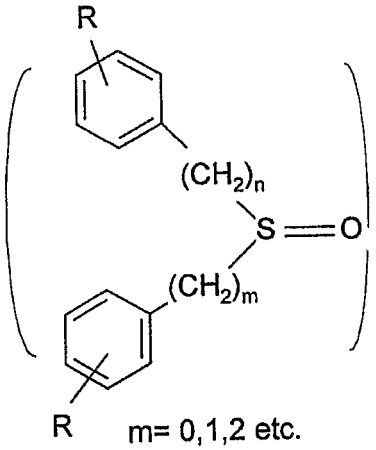


Fig. 7b



m= 0,1,2 etc.
n= 0,1,2 etc.

Fig. 7c

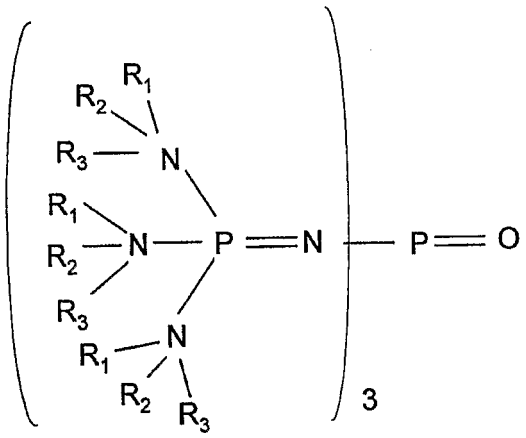
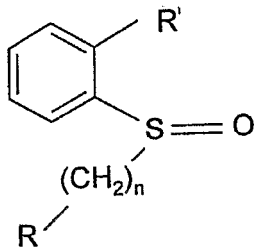
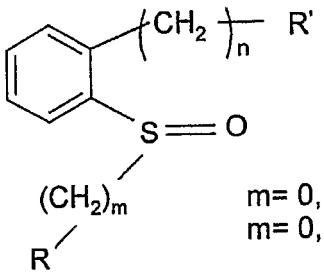


Fig. 7d



n = 0,1,2 etc.

Fig. 7e



m= 0,1,2 etc.
m= 0,1,2 etc.

Fig. 7f

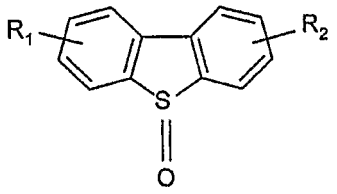


Fig. 8a

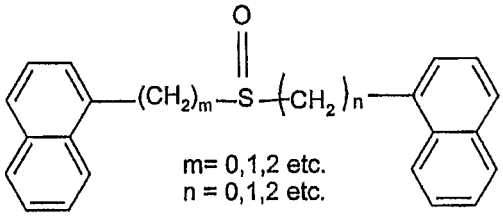


Fig. 8b

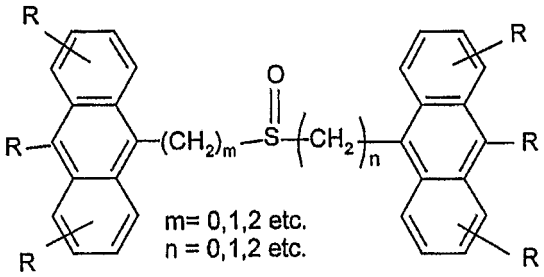


Fig. 8c

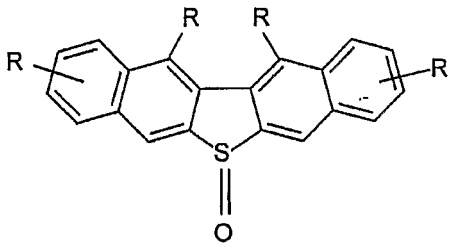


Fig.8d

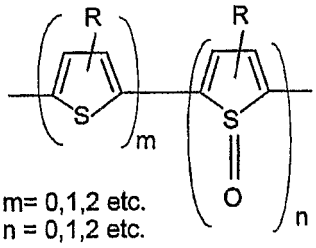


Fig. 8e

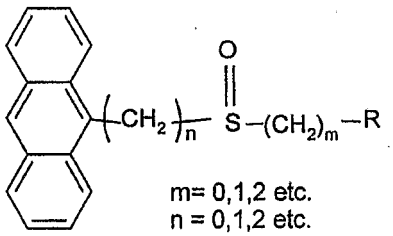


Fig. 8f

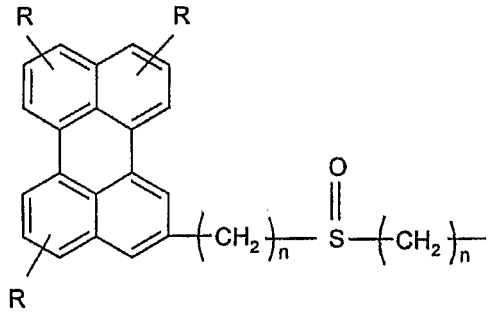


Fig. 8g

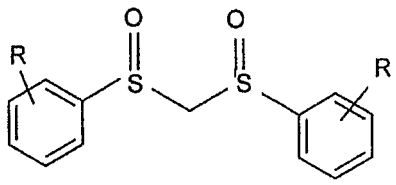
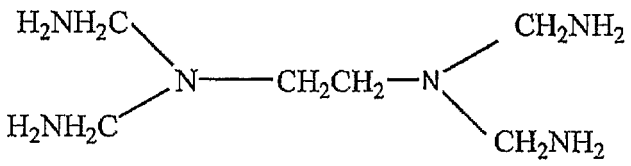


Fig. 8h



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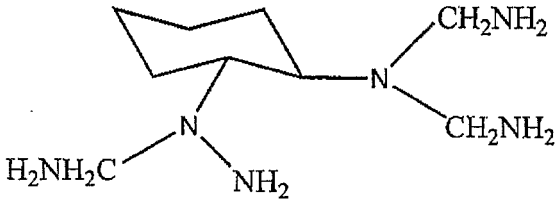

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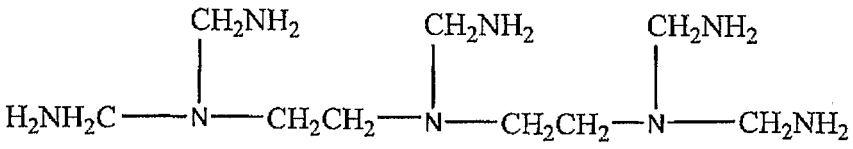

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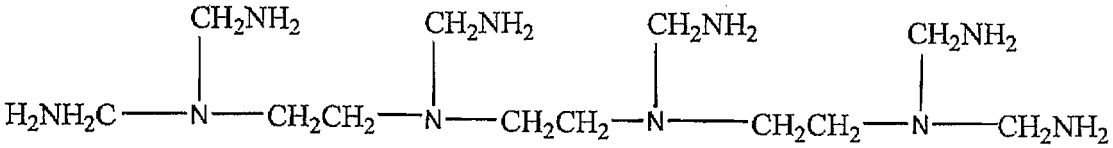
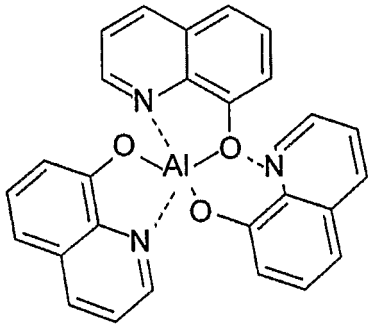


TTHA

Fig. 9



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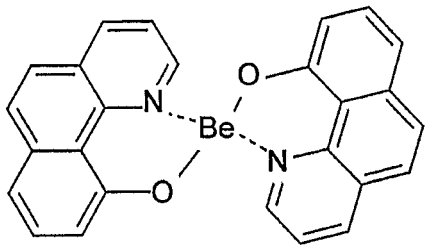

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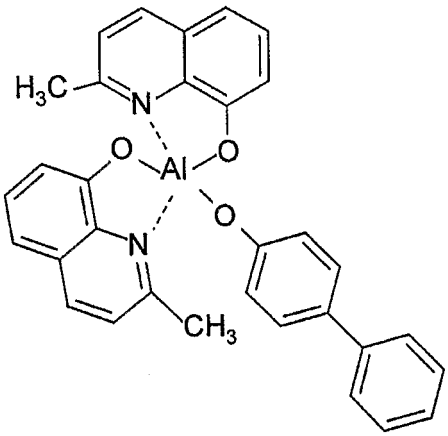
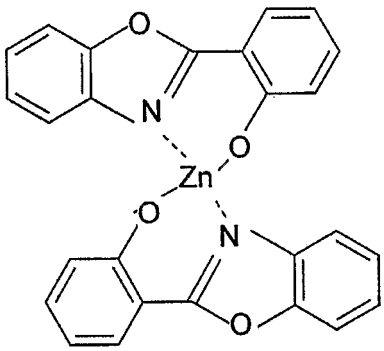
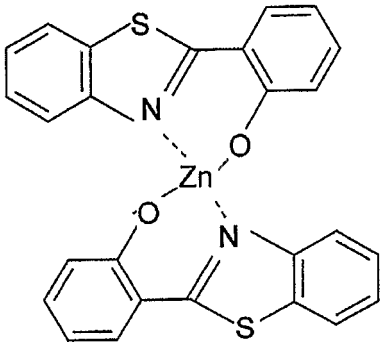


BAlq1



ZnPBO



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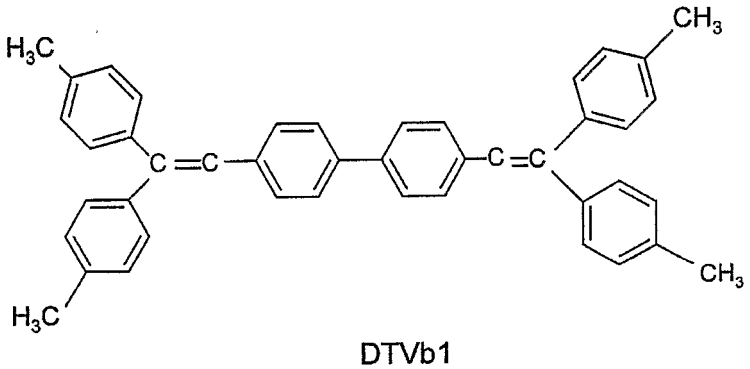
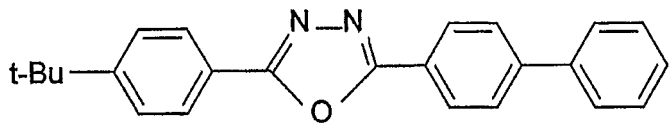
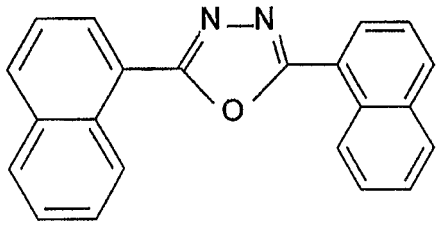


DTVb1

Fig. 10



t-Bu-PBD



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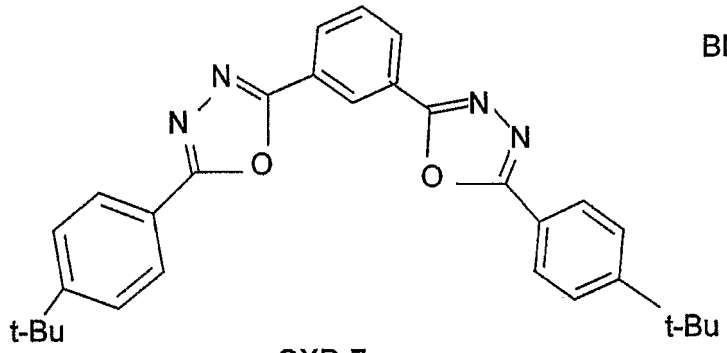
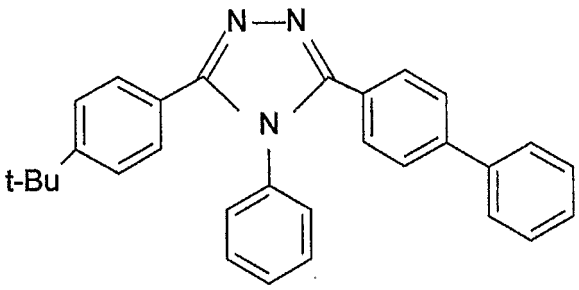
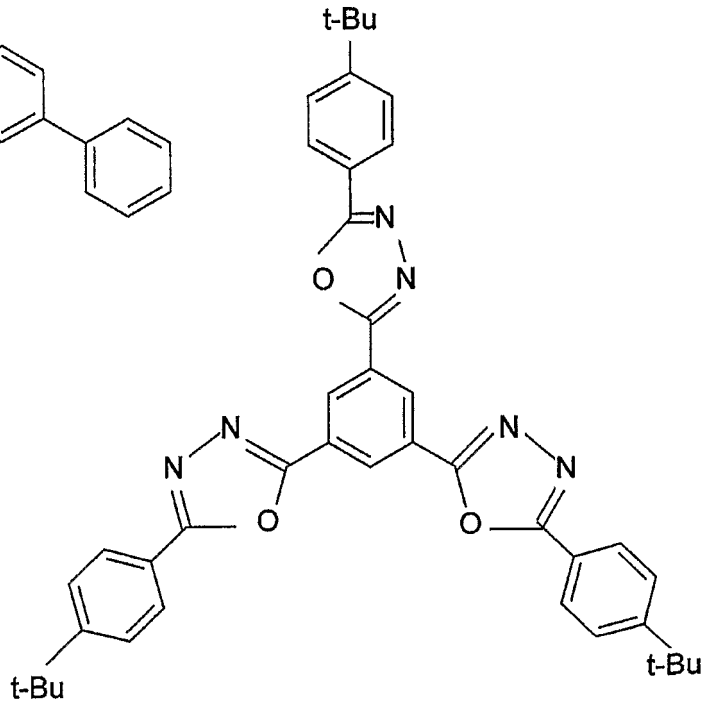


OXD-7



TAZ



OXD- Star

Fig. 11

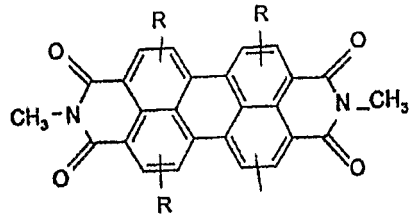


Fig. 12a

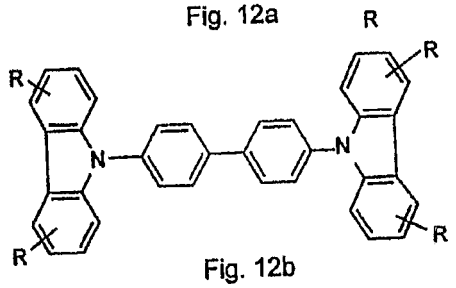


Fig. 12b

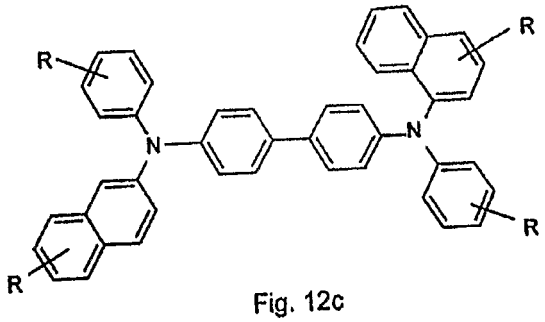


Fig. 12c

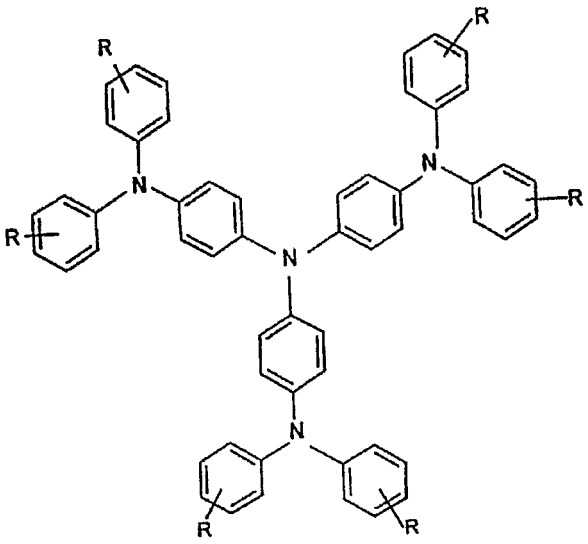


Fig. 12d

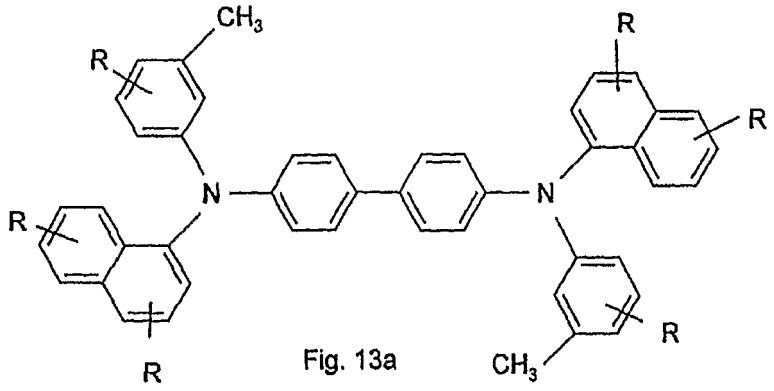


Fig. 13a

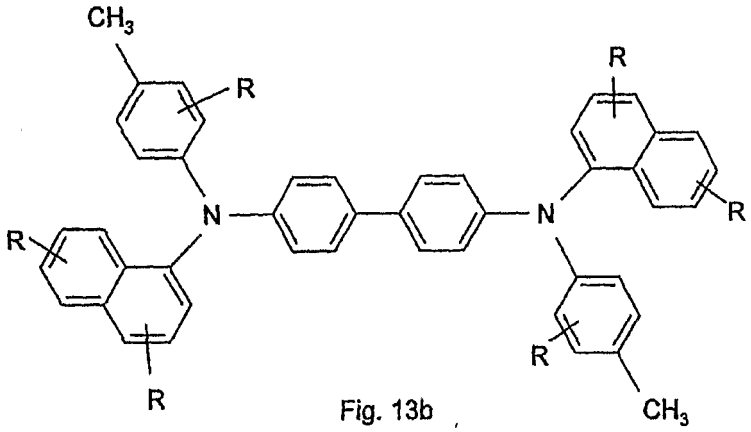


Fig. 13b

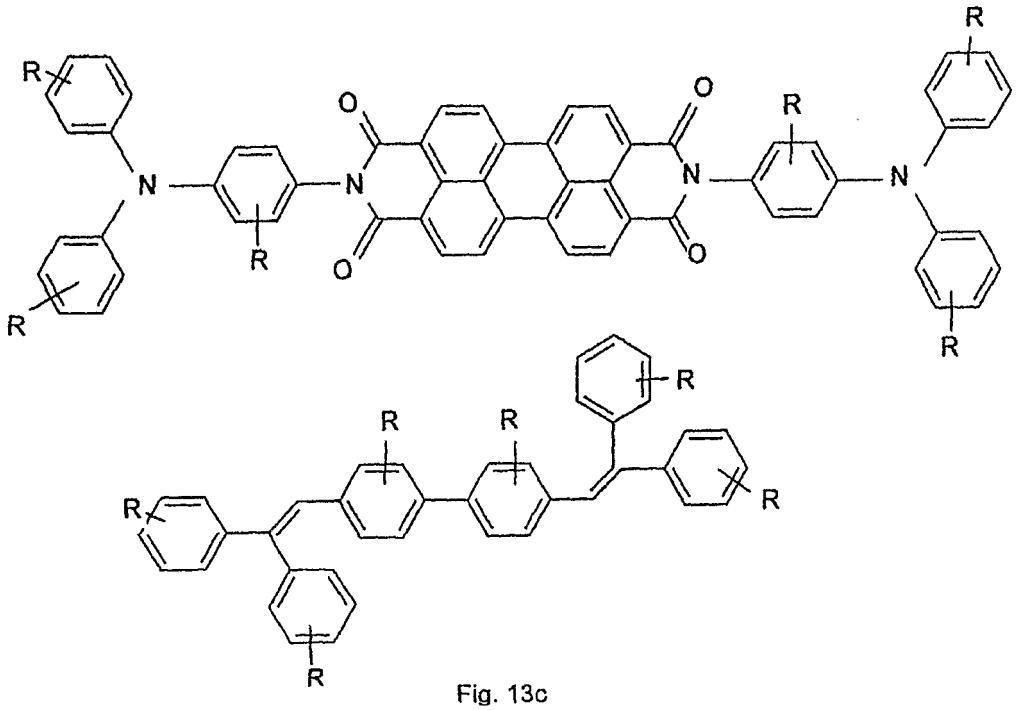


Fig. 13c

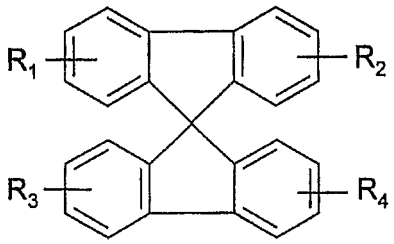


Fig. 14a

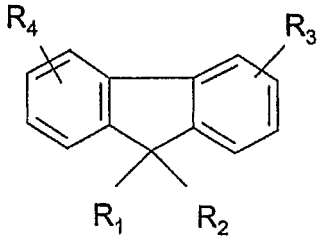
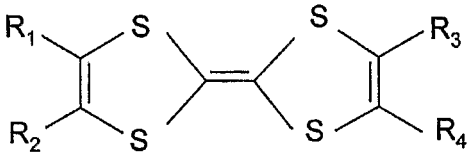


Fig. 14b



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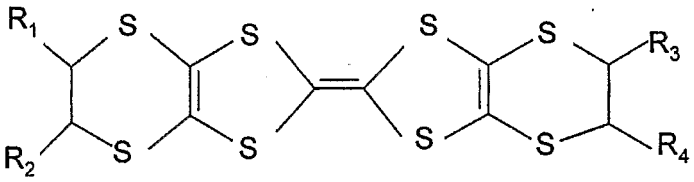


Fig. 14c

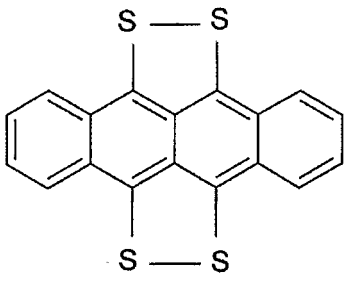
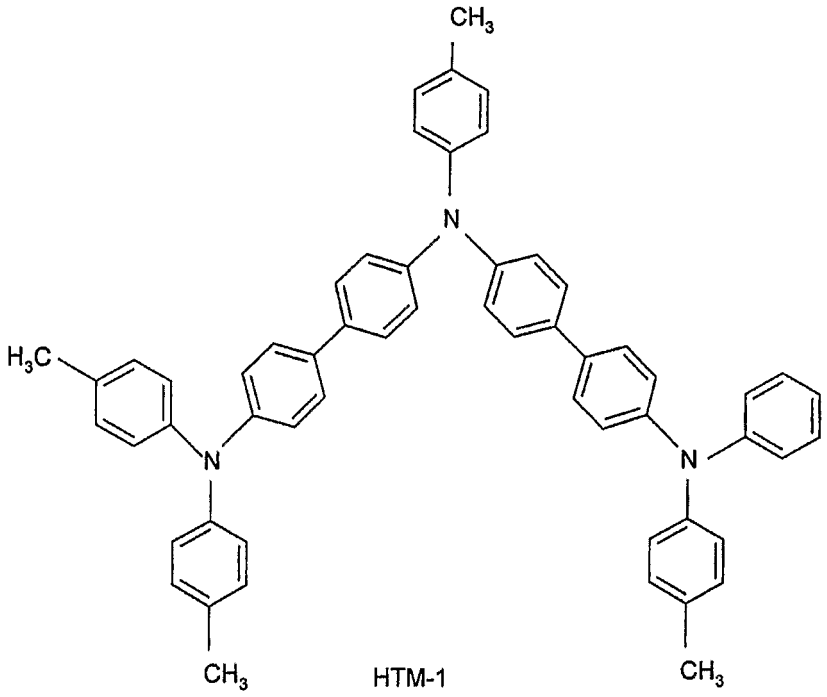
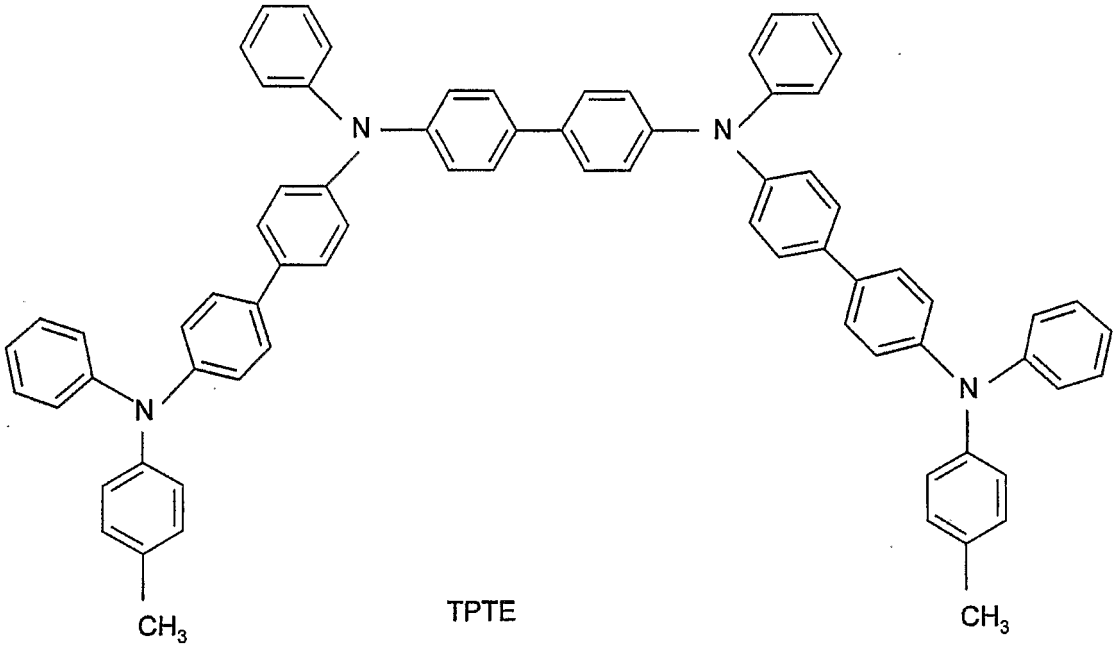


Fig. 14d



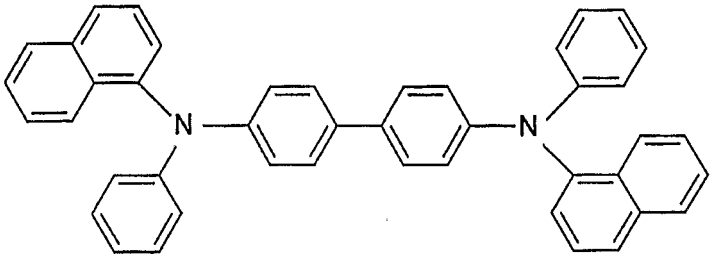
HTM-1

Fig. 15a



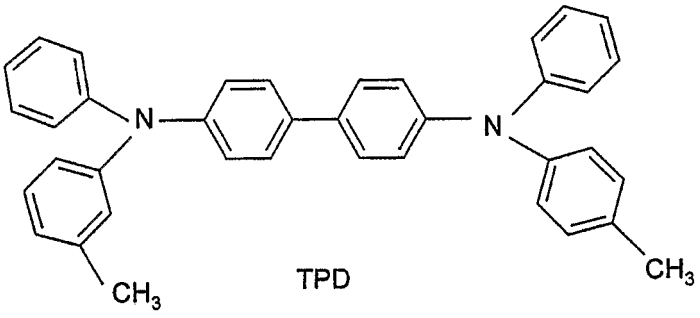
TPTE

Fig. 15b



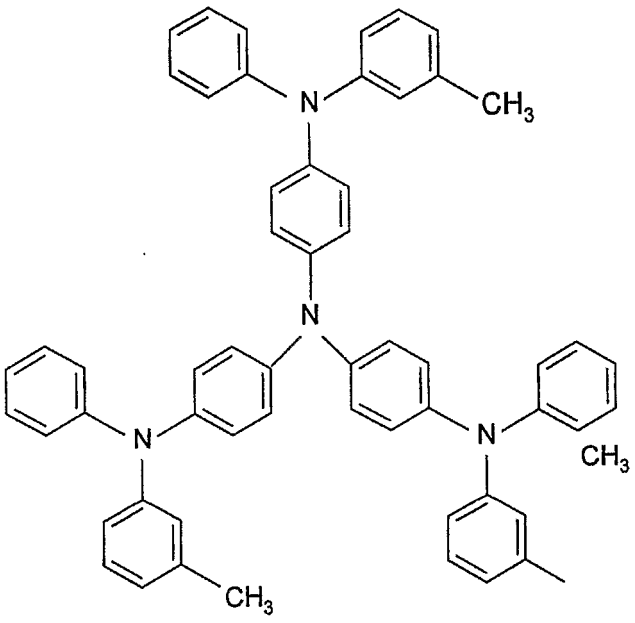
α -NPB

Fig. 16a



TPD

Fig. 16b



mTADATA

Fig. 16c

ITO (110 nm)/CuPc (10 nm)/α-NPB (60 nm)/Liq : Compound X (30 : 2 nm)/BCP (6 nm)/Zrq_4 (30 nm)/LiF (0.5 nm)/Al

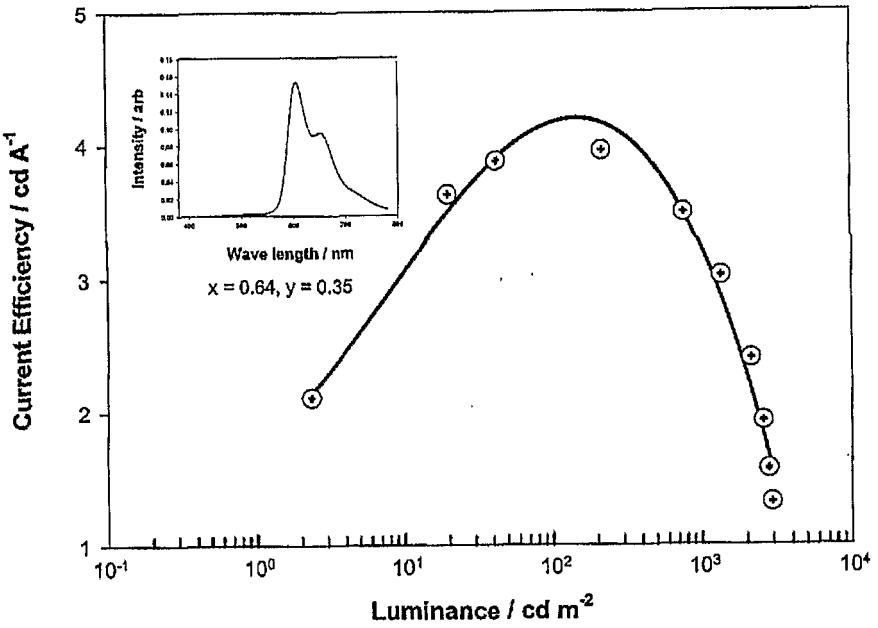


Fig. 17

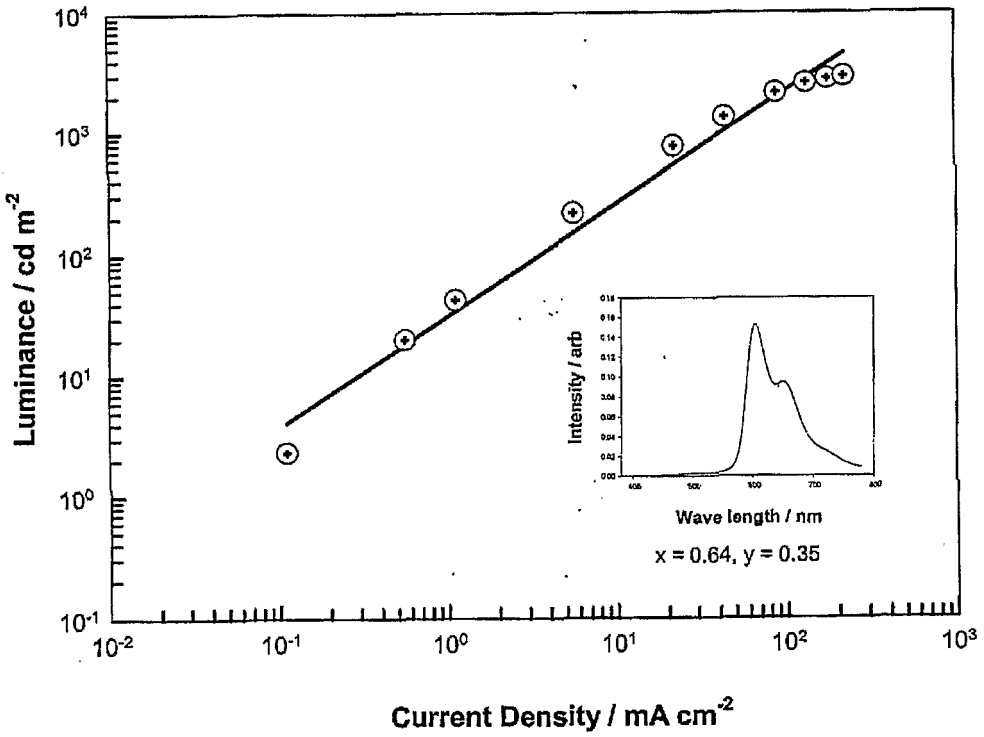


Fig. 18

ITO (110 nm)/CuPc (10 nm)/α-NPB (60 nm)/Liq : Compound X (30 : 2 nm)/BCP (6 nm)/Zrq_4 (30 nm)/LiF (0.5 nm)/Al

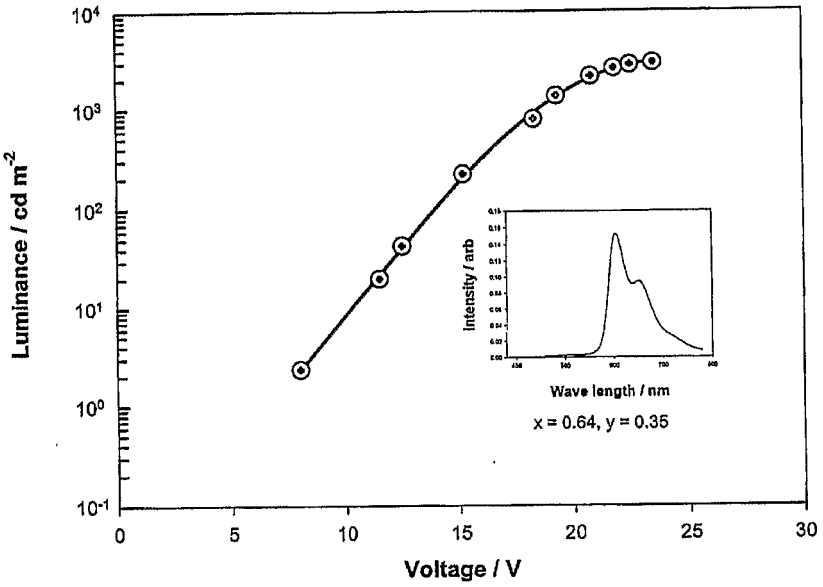
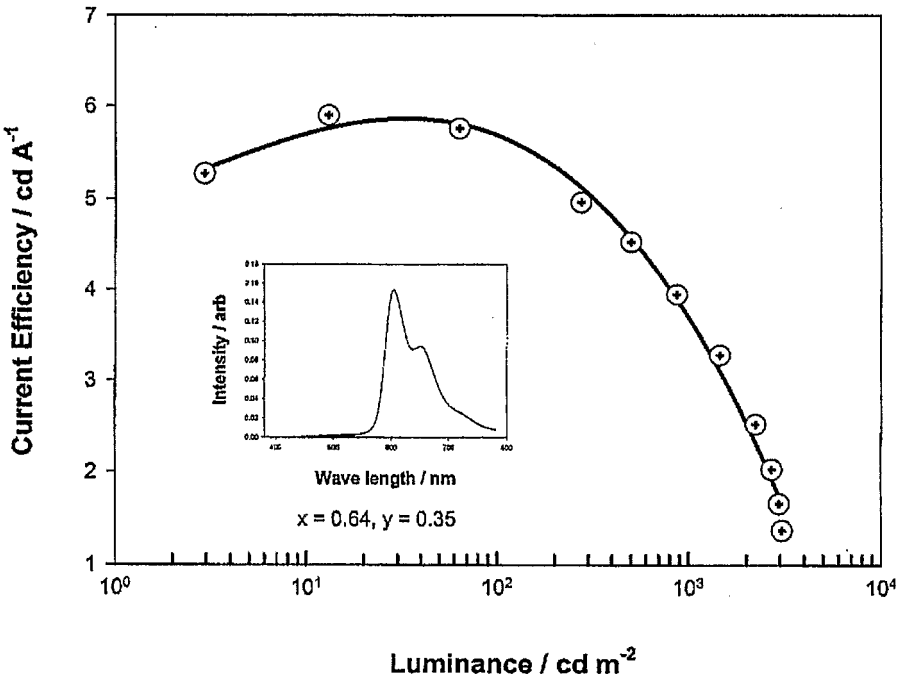


Fig. 19

ITO (110 nm)/Compound Y (10 nm)/α-NPB (60 nm)/Liq : Compound X (30 : 2 nm)/Zrq_4 (30 nm)/LiF (0.5 nm)/Al



Fig, 20

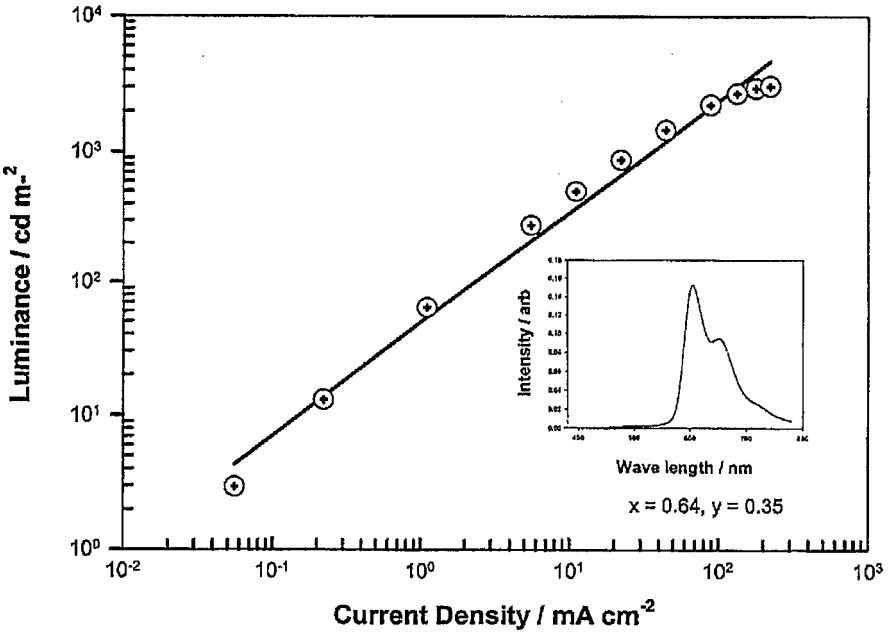


Fig. 21

ITO (110 nm)/Compound Y (10 nm)/α-NPB (60 nm)/Liq : Compound X (30 : 2 nm)/Zrq_4 (30 nm)/LiF (0.5 nm)/Al

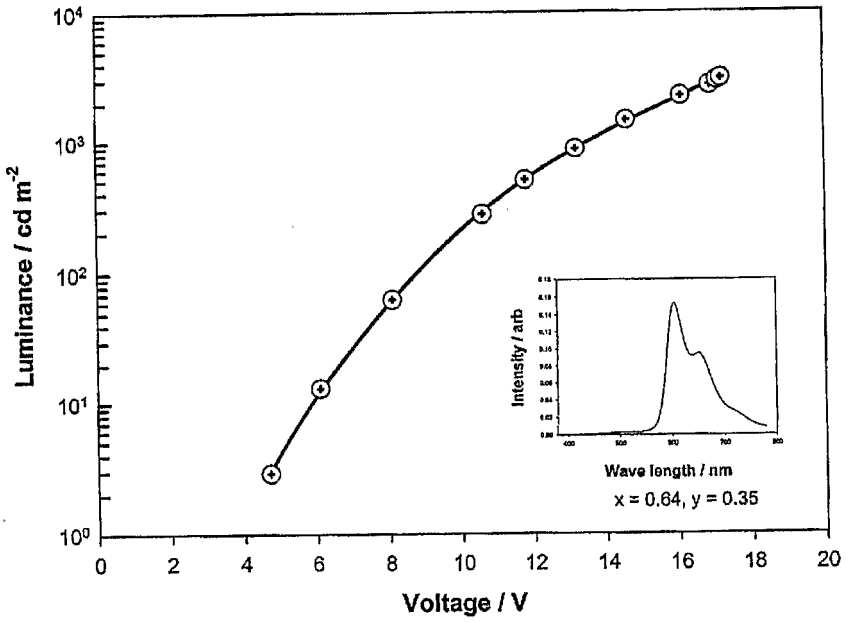


Fig. 22

ITO (110 nm)/ZnTpTP (10 nm)/α-NPB (60 nm)/Liq : Compound X (30 : 2 nm)/Zrq_4 (30 nm)/LiF (0.5 nm)/Al

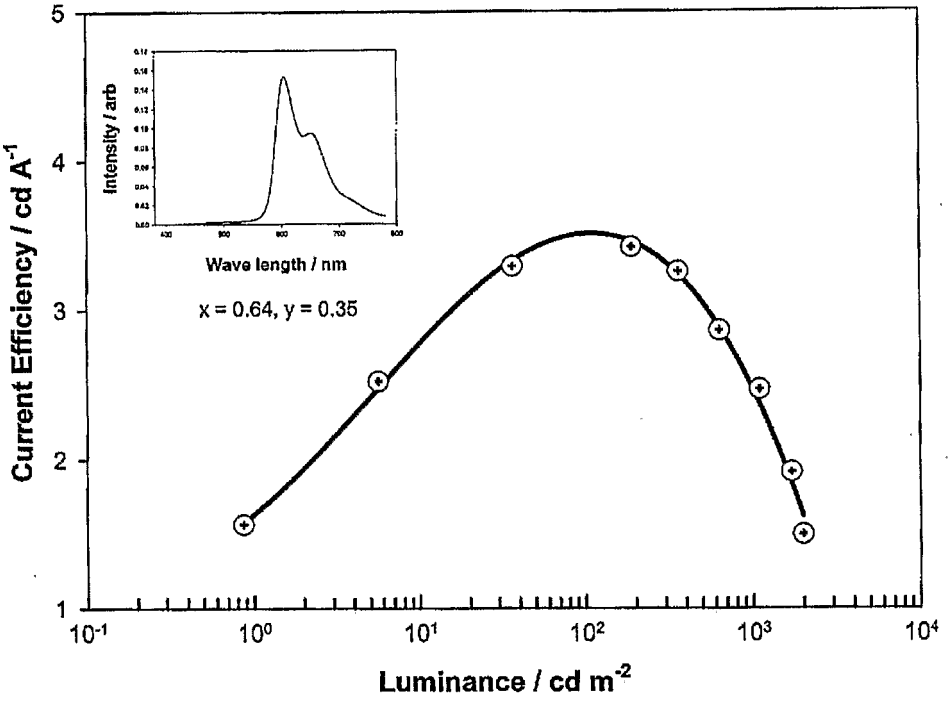


Fig. 23

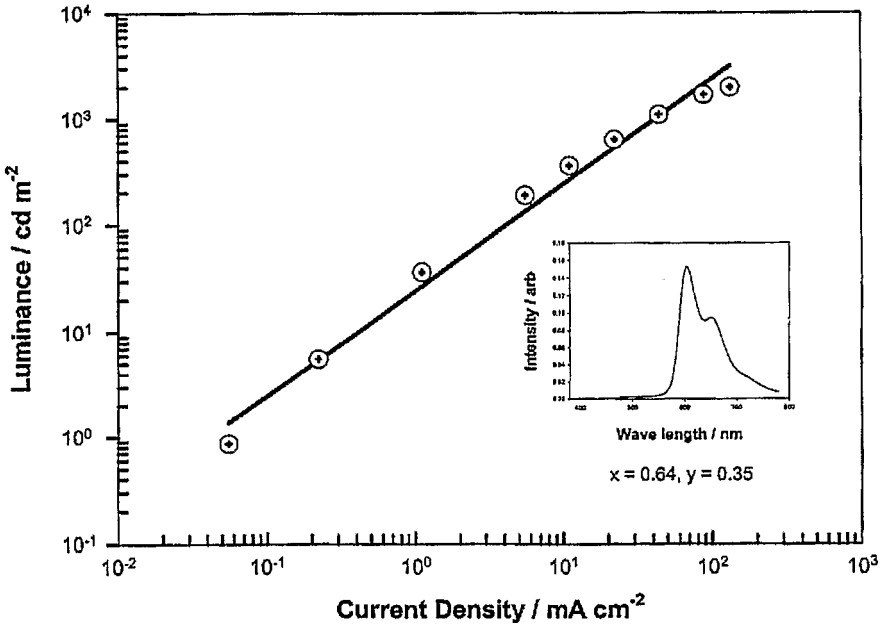


Fig. 24

ITO (110 nm)/ZnTpTP (10 nm)/α-NPB (60 nm)/Liq : Compound X (30 : 2 nm)/Zrq_4 (30 nm)/LiF (0.5 nm)/Al

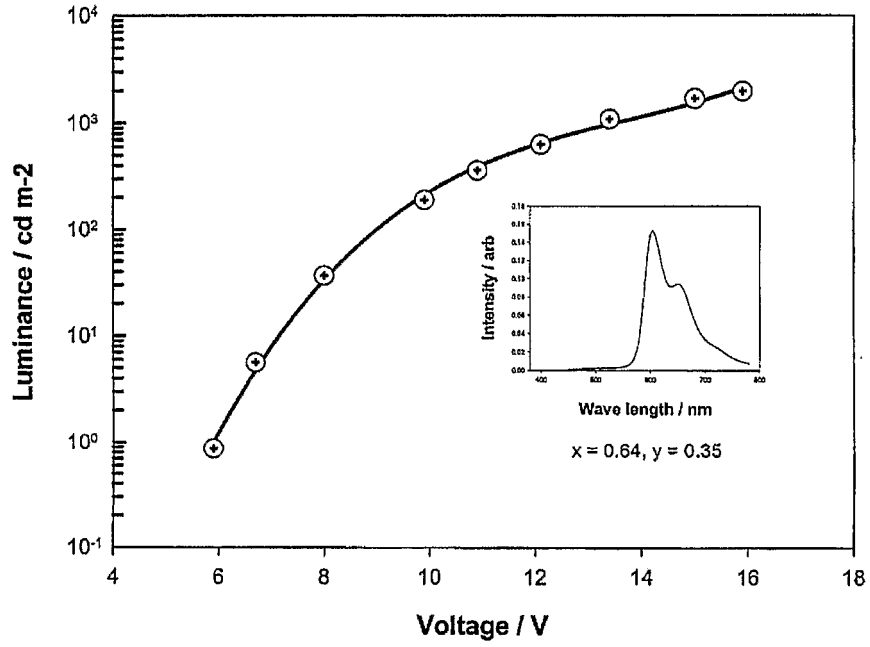


Fig. 25

ITO (110 nm)/Compound Y (10 nm)/α-NPB (60 nm)/Liq : Compound X (3(
: 2 nm)/Liq (30 nm)/LiF (0.5 nm)/Al

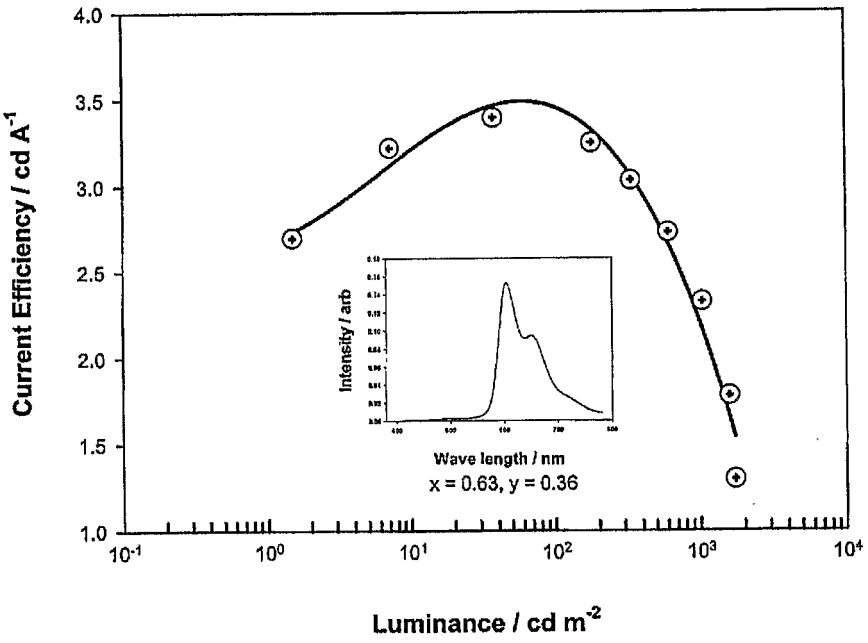


Fig. 26

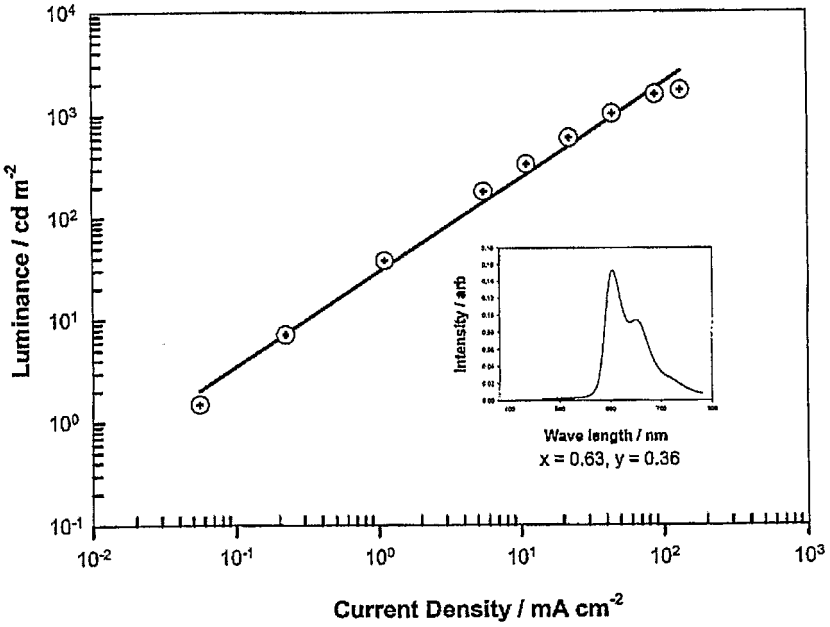


Fig. 27

ITO (110 nm)/Compound Y (10 nm)/α-NPB (60 nm)/Liq : Compound X (30 : 2 nm)/Liq (30 nm)/LiF (0.5 nm)/Al

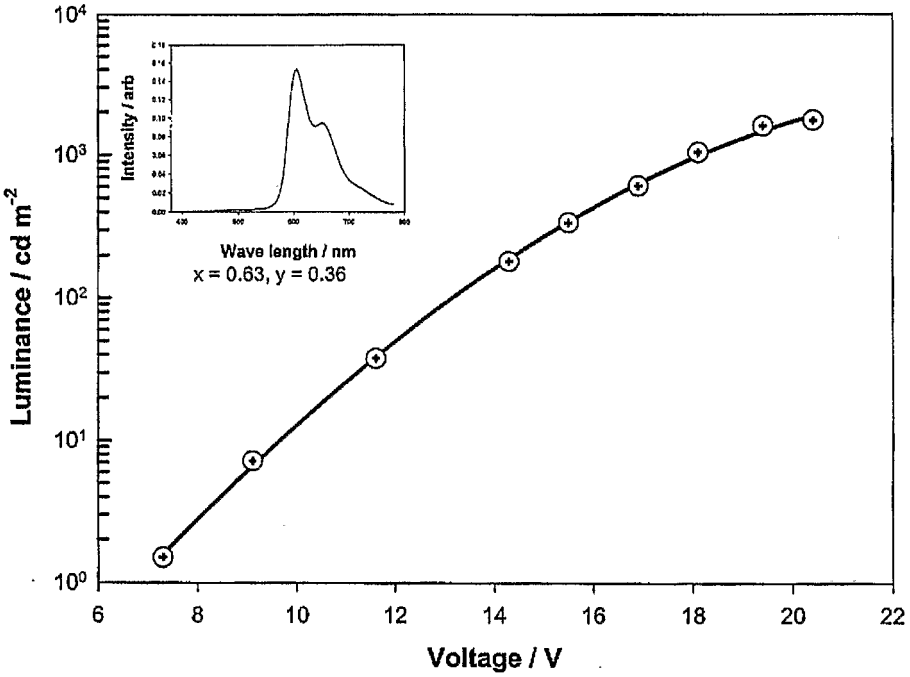


Fig. 28

ITO (110 nm)/ZnTpTp (10 nm)/α-NPB (60 nm)/Liq : Compound X (30 : 2 nm)/Liq (30 nm)/LiF (0.5 nm)/Al

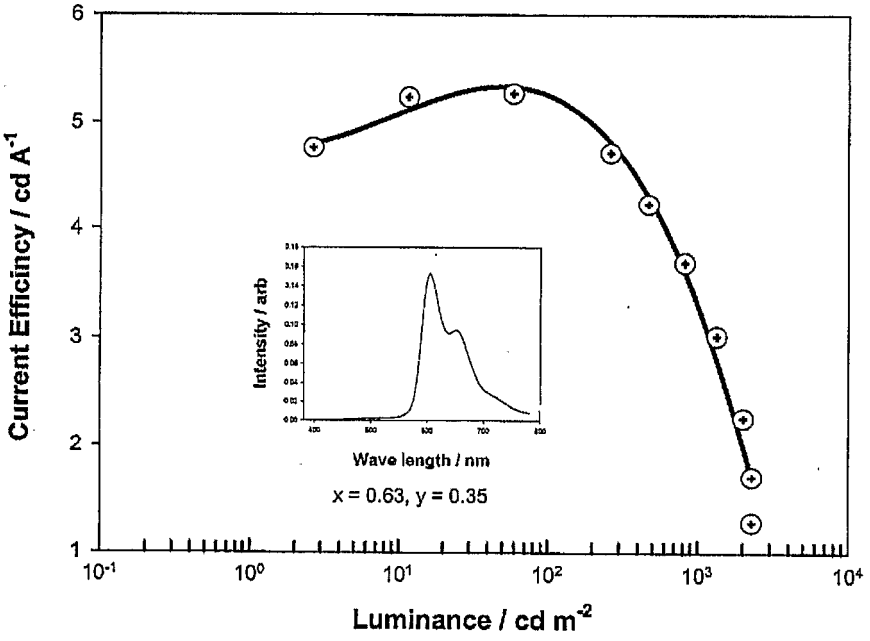


Fig. 29

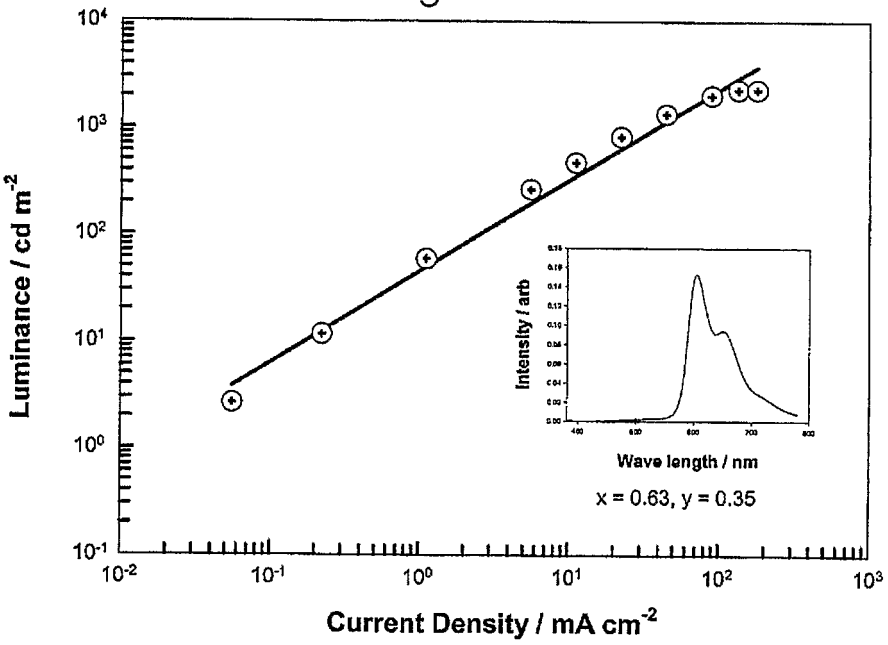


Fig. 30

ITO (110 nm)/ZnTpTp (10 nm)/α-NPB (60 nm)/Liq : Compound X (30 : 2 nm)/Liq (30 nm)/LiF (0.5 nm)/Al

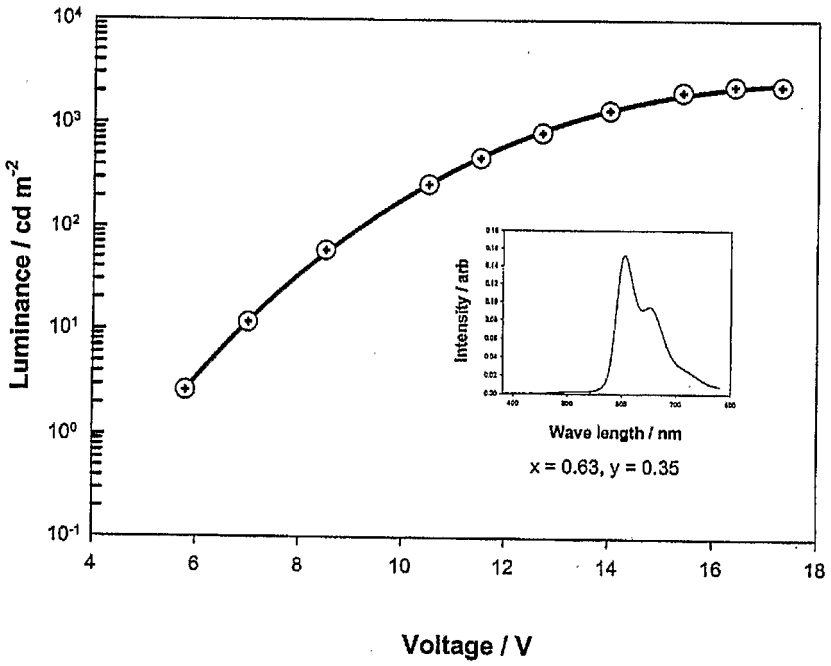


Fig. 31

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2006/000441

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/06 H05B33/14

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)
H05B C09K

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, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/046107 A (ELAM-T LIMITED; KATHIRGAMANATHAN, POOPATHY) 5 June 2003 (2003-06-05) page 2, lines 1-7 page 3, line 16 - page 14, line 20 claims 1,4,5,7-39	1-47
X	WO 2004/084325 A (ELAM-T LIMITED; KATHIRGAMANATHAN, POOPATHY; KIRKHAM, MATTHEW, SAMUEL;) 30 September 2004 (2004-09-30) compounds IA, A, B, C, D, E, G claims 13-31	25-27, 29-47

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

[X] See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 April 2006	18/05/2006

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

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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2006/000441

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2004/008554 A (ELAM-LIMITED; KATHIRGAMANATHAN, POOPATHY; ANTIPAN-LARA, JUAN; PARTHEEP) 22 January 2004 (2004-01-22) page 5, line 28 - page 14, line 15 examples 1,4 compound C claims 3-14	5,7-10, 13-21, 23,25
X	US 2001/019782 A1 (IGARASHI TATSUYA ET AL) 6 September 2001 (2001-09-06) the whole document	8,9
X	PATENT ABSTRACTS OF JAPAN vol. 2003, no. 11, 5 November 2003 (2003-11-05) & JP 2003 192691 A (MITSUBISHI CHEMICALS CORP), 9 July 2003 (2003-07-09) abstract	8,9

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2006/000441

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		EP 1458834 A1	22-09-2004
		JP 2005510838 T	21-04-2005
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WO 2004084325 A	30-09-2004	EP 1620905 A1	01-02-2006
WO 2004008554 A	22-01-2004	AU 2003281003 A1	02-02-2004
US 2001019782 A1	06-09-2001	NONE	
JP 2003192691 A	09-07-2003	NONE	

专利名称(译)	电致发光材料和器件		
公开(公告)号	EP1848786A1	公开(公告)日	2007-10-31
申请号	EP2006709679	申请日	2006-02-09
[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 GANESHAMURUGAN SUBRAMANIAM KUMARAVERL MUTTULINGAM PARTHEEPAN ARUMUGAM PARAMASWARA GNANAMOLY		
发明人	KATHIRGAMANATHAN, POOPATHY GANESHAMURUGAN, SUBRAMANIAM KUMARAVERL, MUTTULINGAM PARTHEEPAN, ARUMUGAM PARAMASWARA, GNANAMOLY		
IPC分类号	C09K11/06 H05B33/14 H01L51/00 H01L51/50		
CPC分类号	C09K11/06 C09K2211/1033 C09K2211/1037 C09K2211/1051 C09K2211/1059 C09K2211/181 C09K2211/183 C09K2211/185 H01L51/0058 H01L51/006 H01L51/0077 H01L51/0078 H01L51/0085 H01L51/5012 H01L51/5016 H05B33/14		
优先权	2005003393 2005-02-18 GB		
其他公开文献	EP1848786B1		
外部链接	Espacenet		

摘要(译)

喹啉锂是有机金属电致发光材料的主体材料，以在电致发光器件中形成电致发光层。