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WO 2004/016708 A1

(54) Title: ELECTROLUMINESCENT MATERIALS AND DEVICES

(57) Abstract: An electroluminescent β diketone incorporating a polymer.

Electroluminescent Materials and Devices

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

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

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

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

Typical electroluminescent devices which are commonly referred to as optical light emitting diodes (OLEDS) comprise an anode, normally of an electrically light transmitting material, a layer of a hole transmitting material, a layer of the electroluminescent material, a layer of an electron transmitting material and a metal cathode.

Patent application WO98/58037 describes a range of lanthanide complexes which can be used in electroluminescent devices which have improved properties and give better results. Patent Applications PCT/GB98/01773, PCT/GB99/03619, PCT/GB99/04030, PCT/GB99/04024, PCT/GB99/04028, PCT/GB00/00268 describe electroluminescent complexes, structures and devices using rare earth chelates.

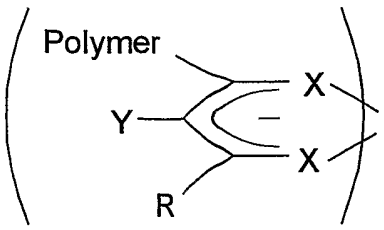
US Patent 5128587 discloses an electroluminescent device which consists of an organometallic complex of rare earth elements of the lanthanide series sandwiched between a transparent electrode of high work function and a second electrode of low work function with a hole conducting layer interposed between the electroluminescent layer and the transparent high work function electrode and an electron conducting layer interposed between the electroluminescent layer and the electron injecting low work function anode. The hole conducting layer and the electron conducting layer are required to improve the working and the efficiency of the device. The hole transporting layer serves to transport holes and to block the electrons, thus preventing electrons from moving into the electrode without recombining with holes. The recombination of carriers therefore mainly takes place in the emitter layer.

We have now invented electroluminescent compounds and devices incorporating them.

According to the invention there is provided electroluminescent compounds of formula $(L\alpha)_nM$ where M is a transition metal, rare earth, lanthanide or an actinide, $L\alpha$ is a β diketone and n is the valence state of M and Lp is a neutral ligand and in which at least one of $L\alpha$ and Lp is substituted by a polymer, an oligomer or a dendrimer.

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

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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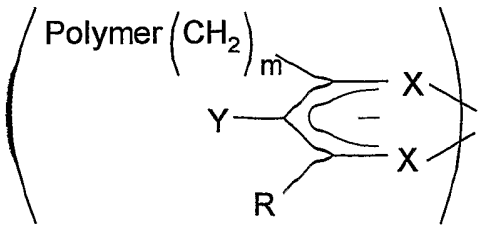

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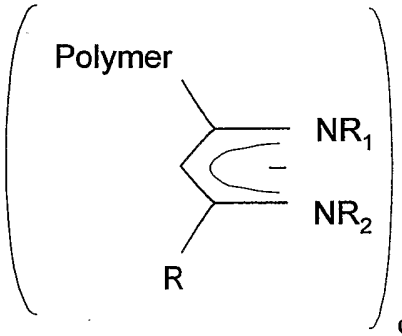
(I) (II)



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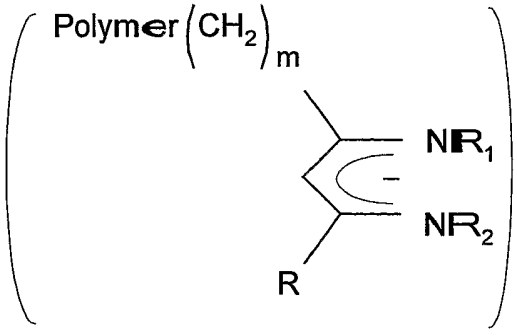
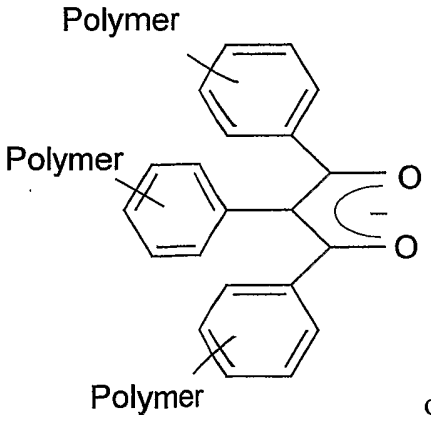


(IIIa) (IIIb)

or through phenyl groups e.g.



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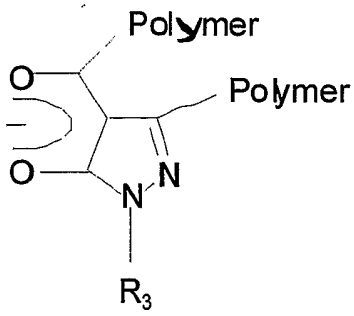
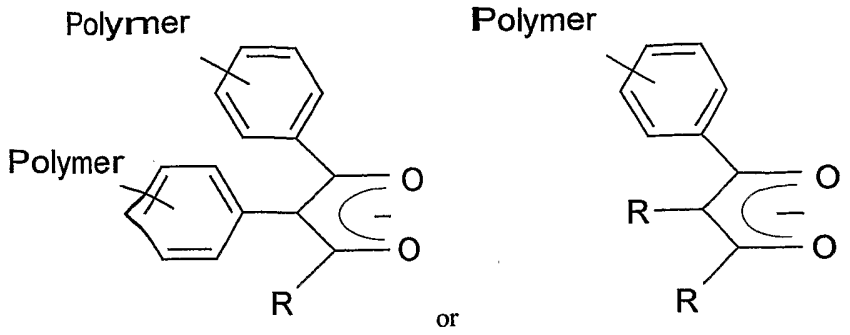


(IIIc) (IIId)

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)) e.g.



(IIIe) (IIIf)

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; X is Se, S or O, Y is R or 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.

R and Y can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer, e.g. styrene "polymer" is an organic polymer and can be linked to R and/or Y to form a ring structure "polymer" and which also includes oligomers and dendrimers, e.g. in which there are four or more repeating units forming a polymer chain, m is an integer preferably from 1 to 5 and R1 and R2 are the same or different R moieties.

Examples of R 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.

Examples of polymers which can be used in the present invention include substituted and unsubstituted polyolefins such as polyethylene, polypropylene, polybutylene, polyvinyl chlorides etc. and their copolymers, substituted and unsubstituted polymers such as polystyrene and their copolymers, polyesters such as polyacrylates, polyurethanes etc. polyethers, polyamines, polysulphonates; examples of oligomers are shown in fig. 19 of the drawings where $2 \leq n < 20$ and examples of dendrimers are shown in figs. 20 and 21 of the drawings; the groups R and Y can also be polymers.

A class of polymers, oligomers or dendrimers which can be used with the present invention are electroluminescent light emitting organic polymers, oligomers or dendrimers. Examples of electroluminescent light emitting organic polymers are the conjugated organic polymers such as any of the conjugated polymers disclosed or referred to in US 5807627, PCT/WO90/13148 and PCT/WO92/03490.

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

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

Any poly(arylenevinylene) including substituted derivatives thereof can be used and the phenylene ring in poly(p-phenylenevinylene) may be replaced by a fused ring

system such as an anthracene or naphthlyene ring and the number of vinylene groups in each polyphenylenevinylene moiety can be increased, e.g. up to 7 or higher.

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

The ligands Lα 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 Lα 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.

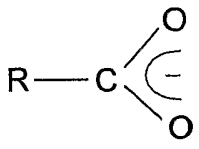
Lp can be monodentate, bidentate or polydentate and there can be one or more ligands Lp.

Preferably M is 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), U(III), $U(VI)O_2$, Tm(III), Th(IV), Ce (III), Ce(IV), Pr(III), Nd(III), Pm(III), Dy(III), Ho(III), Er(III); when M is a transition metal the metal is preferably 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.

Further electroluminescent compounds which can be used in the present invention are of general formula $(L\alpha)_qM_1M_2$ where M_1 is the same as M above, M_2 is a non rare earth metal, $L\alpha$ is a as above and q 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 $(L\alpha)_q$ 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, tantulum, 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.

Some of the different groups $L\alpha$ 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



(IV)

where R is as defined above or the groups L_1, L_2 can be as defined above and $L_{3...}$ etc. are other charged groups.

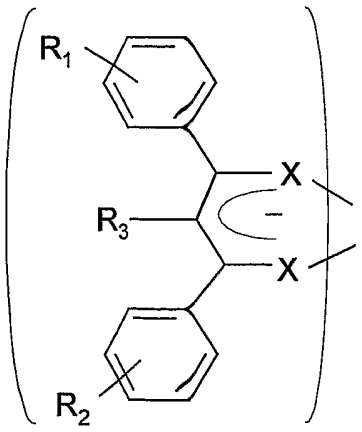
R can also be

where X is O, S, Se or NH.

(V)

A preferred moiety R 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.

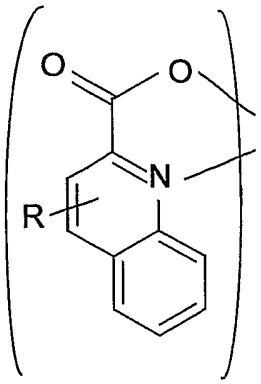
The different groups Lα may be the same or different ligands of formulae



(VI)

where X is O, S, or Se and R_1 and R_2 are the same or different and can be a polymer or can be as R as above.

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



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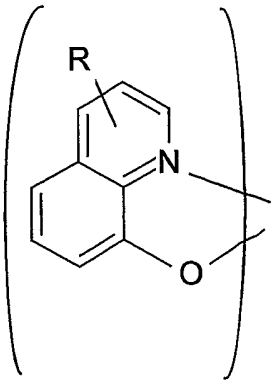
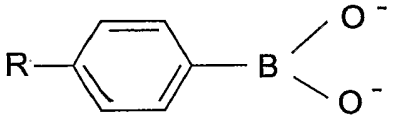


(VII) (VIII)

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



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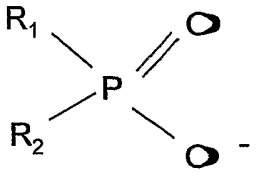
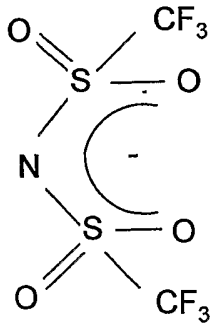


(IX) (X)

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



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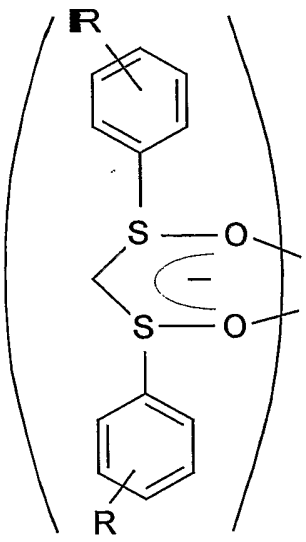
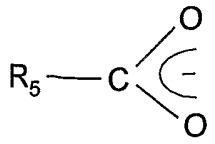


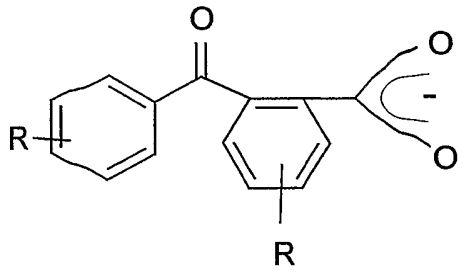
(XI) (XII)

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



(XIII)

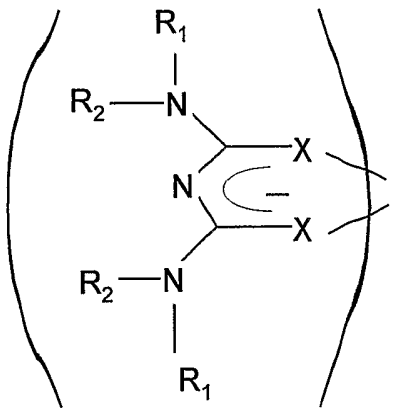
where R_5 is a substituted or unsubstituted aromatic, polycyclic or heterocyclic ring a polypyridyl group, or a polymer, R_5 can also be a 2-ethyl hexyl group so L_n is 2-ethylhexanoate or R_5 can be a chair structure so that L_n is 2-acetyl cyclohexanoate or Lα can be



(XIV)

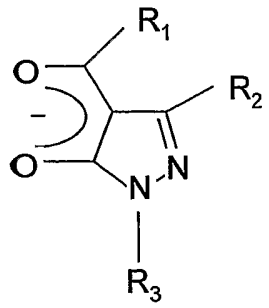
where R is as above, e.g. alkyl, allenyl, amino or a fused ring such as a cyclic or polycyclic ring or a polymer.

The different groups Lα may also be

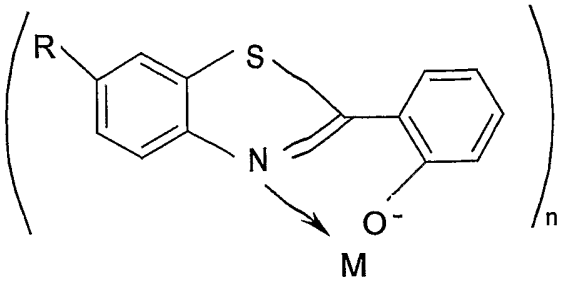


(XV)

or



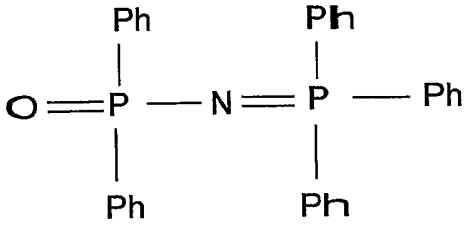
(XVI)



(XVII)

where R, R_1 R_2 and R_3 are as above or one or more of which is an oligomer or a dendrimer.

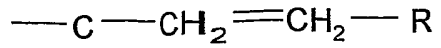
The groups L_P can be selected from



(XVIII)

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. a polymer an oligomer or a dendrimer. 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

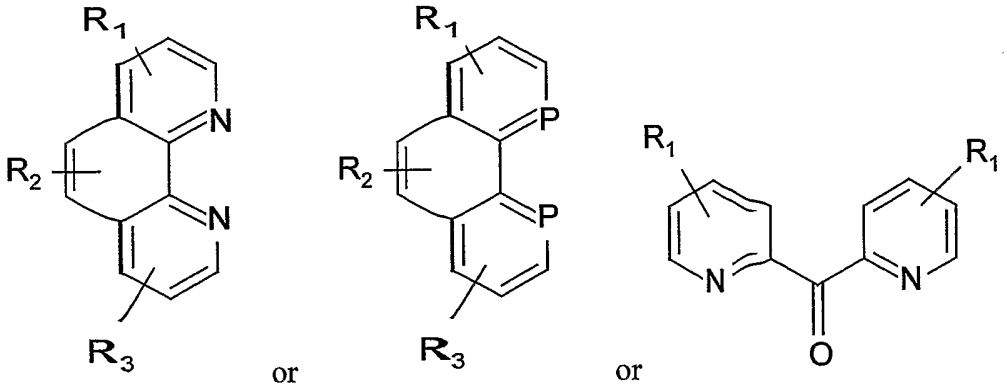
structures and can be copolymerisable with a monomer e.g. styrene. R, R_1, R_2, R_3 and R_4 can also be unsaturated alkylene groups such as vinyl groups or groups



where R is as above or is a polymer an oligomer or a dendrimer.

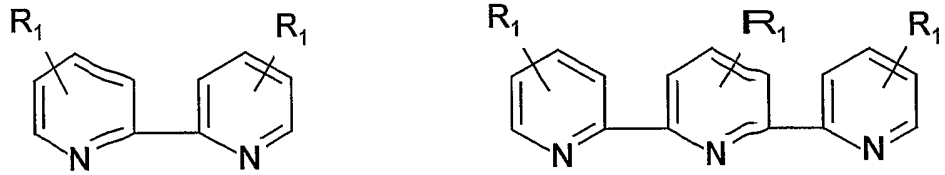
Examples in which the phenyl group in (XVIII) is substituted by a polymer, an oligomer or a dendrimer are shown in Fig. 17a of the drawings.

L_p can also be compounds of formulae



(XVIV) or (XX) or (XXI)

where R_1, R_2 and R_3 can be a polymer an oligomer or a dendrimer or as referred to above, for example bathophen shown in fig. 3 of the drawings in which R is as above or

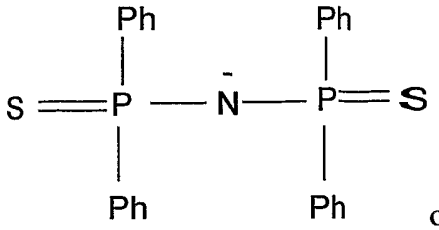


(XXII) (XXIII)

where R_1, R_2 and R_3 are as referred to above or can be a polymer an oligomer or a dendrimer, examples of which are shown in figs. 17b, 17c, 17d 17e and in figs. 18a,

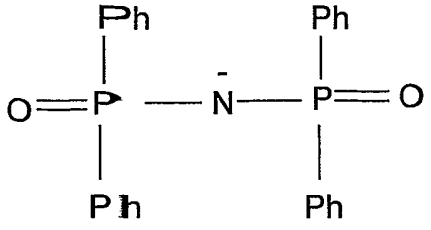
18b and 18c of the drawings where "polymer" can be an oligomer or dendrimer . In fig. 18b one or more of R_1, R_2, R_3, R_4, R_5, and R_6 can be a polymer oligomer or dendrimer.

L_p can also be



(XXIV)

or



(XXV)

where Ph is as above or can be substituted with a polymer an oligomer or a dendrimer.

Other examples of L_p chelates are as shown in figs. 4 and fluorene and fluorene derivatives, e.g. a shown in figs. 5 and compounds of formulae as shown in figs. 6 to 8. Polymer substituted chelates are shown in figs. 17 and 18 of the drawings.

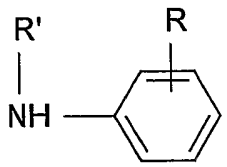
Specific examples of Lα and Lp are tripyridyl and TMHD, and TMHD complexes, α, α', α" tripyridyl, crown ethers, cyclans, cryptans phthalocyanans, porphoryins ethylene diamine tetramine (EDTA), DCTA, DTPA and TTHA. Where TMHD is 2,2,6,6-tetramethyl-3,5-heptanedionato and OPNP is diphenylphosphonimide triphenyl phosphorane. The formulae of the polyamines are shown in fig. 11.

The invention also provides an electroluminescent device which comprises (i) a first electrode, (ii) a layer of a rare earth chelate electroluminescent compound as described above and (iii) a second electrode.

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.

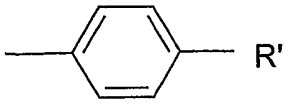
The hole transporting material can be any of the hole transporting materials used in electroluminescent devices.

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



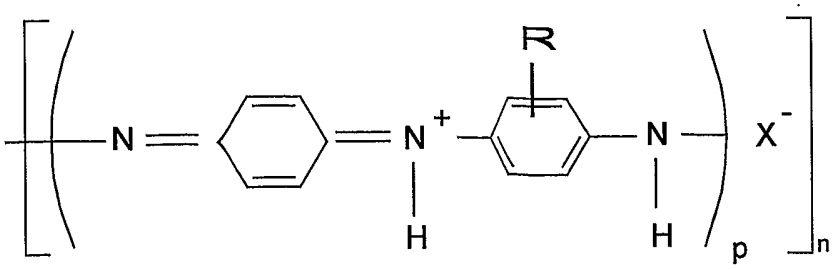
(XXVI)

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



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

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



(XXVII)

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

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

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

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

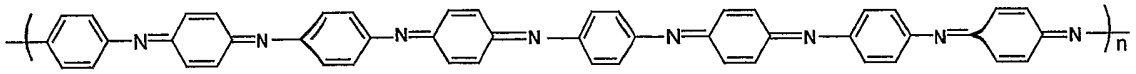
ammonium hydroxide or an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide.

The degree of protonation can be controlled by forming a protonated polyaniline and de-protonating. Methods of preparing polyanilines are described in the article by A. G. MacDiarmid and A. F. Epstein, Faraday Discussions, Chem Soc.88 P3 19 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%, e.g. about 50% for example.

Preferably the polymer is substantially fully deprotonated.

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



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

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

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

Other polymers of an amino substituted aromatic compound which can be used include substituted or unsubstituted polyaminonapthalenes, polyaminoanthracenes,

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

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

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

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

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

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

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

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

The structural formulae of some other hole transporting materials are shown in Figures 12, 13, 14, 15 and 16 of the drawings, where R_1, R_2 and R_3 can be the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoryl methyl groups, halogens such as fluorine or thiophenyl groups; R_1, R_2 and R_3 can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer, e.g. styrene. X is Se, S or O, Y can be hydrogen, substituted or unsubstituted hydrocarbyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorine, fluorocarbons such as trifluoryl methyl groups, halogens such as fluorine or thiophenyl groups or nitrile.

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

Optionally there is a layer of an electron injecting material between the cathode and the electroluminescent 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, $Mx(DBM)_n$ where Mx is a metal and DBM is dibenzoyl methane and n is the valency of Mx, e.g Mx is chromium, a cyano

anthracene such as 9,10 dicyano anthracene, cyano substituted aromatic compounds, tetracyanoquinidodimethane a polystyrene sulphonate or a compound with the structural formulae shown in figures 9 or 10 of the drawings in which the phenyl rings can be substituted with substituents R as defined above. 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.

The hole transporting materials, the electroluminescent material 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, calcium, lithium, magnesium and alloys thereof such as silver/magnesium alloys, rare earth metal alloys etc; aluminium is a preferred metal. A metal fluoride such as an alkali metal, rare earth metal or their alloys can be used as the second electrode for example by having a metal fluoride layer formed on a metal.

The electroluminescent devices of the present invention can be used as both active and passive displays.

Examples

The invention is illustrated in the examples.

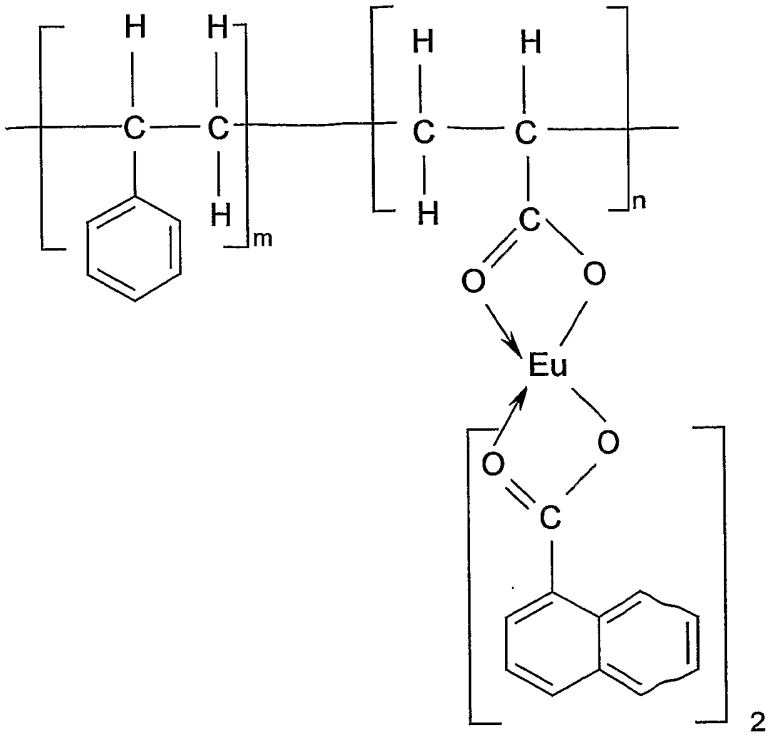
Preparative Methods

1. Europium(III (Naphthylcarboxalate)$_2$(Acrylic acid)$_n$(Styrene)$_m$. (Eu(Naph)$_2$(AA)$_n$ (Styrene)$_m$]

To a mixture of recrystallised naphthoic acid (0.93 g, 5.4 x 10^{-3} moles) in ethanol (20 ml) and distilled acrylic acid (0.19 g, 23 x 10^{-3} moles) in ethanol (10 ml) was added sodium hydroxide (NaOH) (0.32 g, 8.1 x 10^{-3} moles) in water (10ml) and stirred for ten minutes.

Europium chloride ($EuCl_3.6H_2O$) (0.92 g, 2.7 x 10^{-3} moles) in ethanol:water (20 ml, 2:1) was then slowly added to the above mixture and refluxed while stirring for three hours to yield a pale brown colour product [Eu(Naph)$_2$(AA)]. The product was filtered off and washed thoroughly with water, followed by ethanol and vacuum dried for five hours. Yield: 0.8 g (52%). Melting point: > 260 °C.

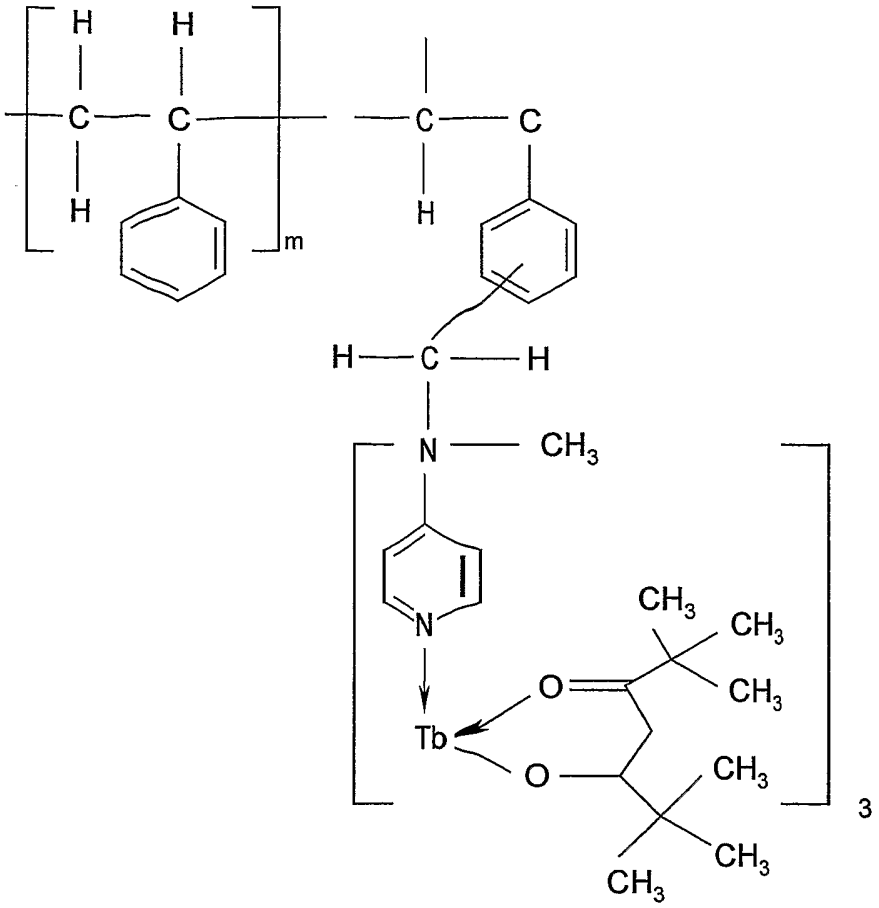
Eu(Naph-COO)$_2$(AA) (0.2 g) was dissolved in methanol (2 ml) and mixed with styrene (4 g). The homogeneous solution was placed in a tube and 1,1'-azobis(cyclohexane carbonitrile) (0.02 g) was added. The solution was degassed by three freeze-thaw cycles under vacuum, then sealed and heated in an oil bath at 60°C. for four hours. The viscous homogeneous solution was then dissolved in tetrahydrofuran (THF) and purified by reprecipitating with methanol, and dried under vacuum for a day. Melting point: 293 °C (Differential Scanning Calorimetry, DSC). The complex had the structure below where m and n had an average value greater than 5.



The photoluminescent spectrum was measured and the results shown in fig. 23.

2. Terbium(III)[tris(2,2,6,6-tetramethyl-3,5-heptanedionate)]$_3$ [Tb(tmhd)$_3$(PS-DMAP)

Dimethylaminopyridine (DMAP) polymer-bound (2% crosslinked poly(styrene), typical DMAP loading 5.5 - 6.6 mmol N/g) (0.5 g) and terbium(III)[tris(2,2,6,6-tetramethyl-3,5-heptanedionate)]$_3$ (0.7 g, 0.99 mmol) were heated together in a boiling mixture of dichloromethane (CH_2Cl_2) and toluene (1:1, 50 ml) for ten minutes. The solution was cooled to room temperature and the orange solid filtered under vacuum and washed with 100 ml of CH_2Cl_2. The solid was dried in a vacuum oven overnight to give a light orange solid with green photoluminescence. Analysis (ICP-AES) shows terbium loading at 9.9 %). The complex had the structure below where m and n had an average value greater than 5.



The photoluminescent spectrum was measured and the results shown in fig. 24.

Photoluminescence data is set out in the table where the colour coordinates are according to the CIE colour chart.

Table

Materials	Colour Coordinates x : y
$Eu(Naph)_2(AA)_n(Styrene)_m$	0.649 : 0.338
$Tb(tmhd)_3(PS\text{-}DMAP)$	0.359 : 0.594

Device Structure

A device of structure shown in figure 22 was fabricated where (1) is an ITO anode, (2) is a hole transporting layer, (3) is the electroluminescent layer, (4) is an electron transmitting layer and (5) is the aluminium cathode.

The device had the structure :-
ITO(100Ω cm^2/PEDOT(170nm)/$Eu(Naph)_2(AA)_n(Styrene)_m$(50 nm)/ BCP(6nm)/Al, where PEDOT is a hole transporting layer of polystyrene doped with poly(3,4-ethylenedioxythiophene) and BCP is an electron transmitting layer (hole blocking layer) of bathocupron.

An ITO coated glass piece (1 x 1cm^2) had a portion etched out with concentrated hydrochloric acid to remove the ITO and was cleaned and dried. The device was fabricated by spin coating the indium tin oxide (ITO) layer in two stages.

The Hole Transporting Layer

Poly(styrene-sulphonate) doped with PEDOT (PEDOT-PSS), as a solution in water, was spin coated on the etched ITO as the first layer. Spin coating conditions for this layer were as follows.

Stage	Spin Speed (rpm)	Time (sec)
1	300	5
2	2000	15

The Emissive Layer

A solution of $Eu(Naph)_2(AA)$ (Styrene)m was prepared in THF (10 mg solid in 5 ml solvent) as above. Spin coating conditions were as follows.

Stage	Spin Speed (rpm)	Time (sec)
1	200	7
2	1500	14

The Hole Blocking Layer

Bathocupron (BCP) was used as a hole-blocker and vacuum evaporated onto the device, followed by aluminium (Al) layer as a top cathode.

The electroluminescent properties of the device of example was measured. The ITO electrode was always connected to the positive terminal. An electric current was passed through the structure and the light emitted was a reddish orange light typical of europium (III) complexes. A plot of current density against voltage is shown in fig. 25.

Claims

1. An electroluminescent compound of formula $(L\alpha)_nM$ where M is a transition metal, rare earth, lanthanide or an actinide, Lα is a β diketone substituted by a polymer, an oligomer or a dendrimer and n is the valence state of M.

2. An electroluminescent compound of formula

where M is a rare earth, transition metal, lanthanide or an actinide, Lα is a β diketone and n is the valence state of M and Lp is a neutral ligand and in which at least one of Lα and Lp is substituted by a polymer, an oligomer or a dendrimer.

3. An electroluminescent compound as claimed in claim 2 or 3 in which the ligands Lα can be the same or different.

4. An electroluminescent compound as claimed in any one of claims 1 to 3 in which Lp can be monodentate, bidentate or polydentate and there are a plurality of ligands Lp which can be the same or different.

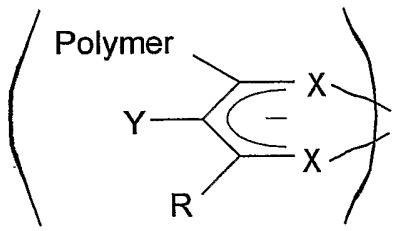
5. An electroluminescent compound as claimed in any one of the preceding claims of formula $(L\alpha)_q (M_1)_r (M_2)_s$ where M_1 is the same as M above, M_2 is M or a non rare earth metal, Lα is as above, r is at least one s is at least one and q is the combined valence state of $r(M_1)$ and $s(M_2)$ and the metals M_1 can be the same or different and the metals M_2 can be the same or different.

6. An electroluminescent compound as claimed in any one of claims 1 to 5 which has the general formula $(L\alpha)_q (M_1)_r (M_2)_s (Lp)$, where Lp is as above and where M_1 is the same as M above, M_2 is M or a non rare earth metal, Lα is a as above, r is at least one, s is at least one and q is the combined valence state of $r(M_1)$ and $s(M_2)$ and the

metals M_1 can be the same or different and the metals M_2 can be the same or different.

7. An electroluminescent compound as claimed in any one of claims 2 to 6 in which Lp has the formula (XVIII) to (XXV) herein or of figures 1 to 8, 17 or 18 of the drawings.

8. An electroluminescent compound as claimed in any one of claims 1 to 7 in which Lα has the formula



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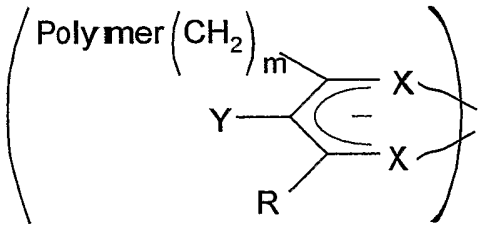
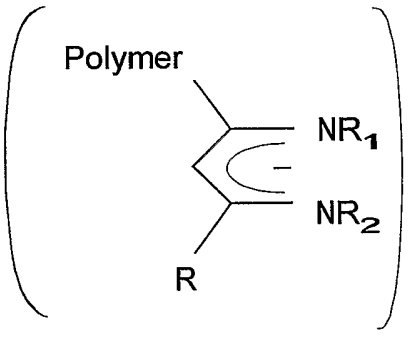


or

(I) (II)



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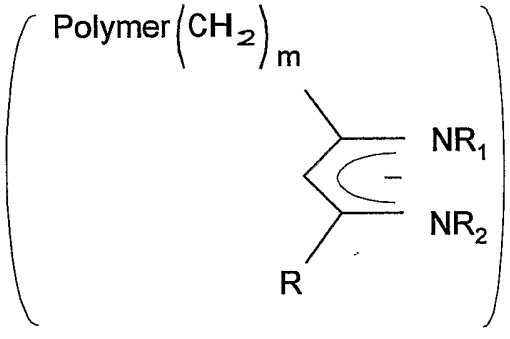
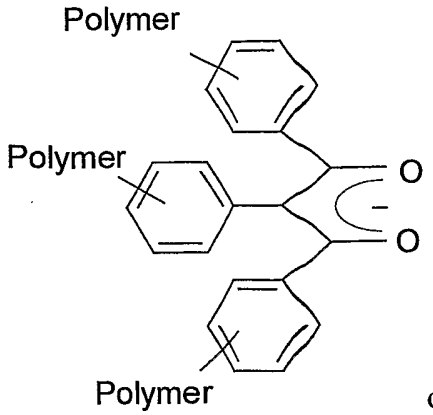


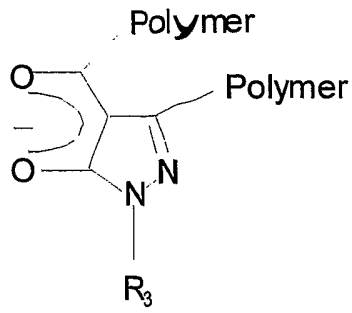
(IIIa) (IIIb)

or

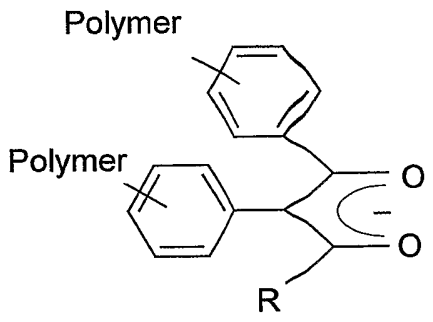


or

(IIIc)

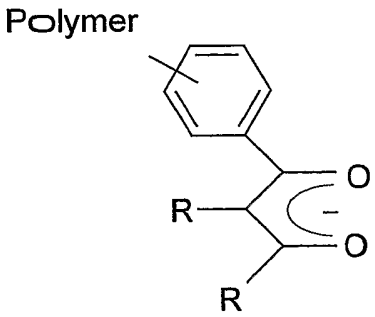


(IIId)



or

(IIIe)



(IIIf)

where the term polymer includes oligomers and dendrimers, 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 X is Se, S or O, Y is R or 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, R and Y can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer, e.g. styrene and the polymer is an organic polymer, oligomers or dendrimer and can be linked to R and/or Y to form a ring

structure m is an integer preferably from 1 to 5 and R_1 and R_2 are the same or different R moieties.

9. An electroluminescent compound as claimed in any one of claims 1 to 8 in which the polymer, oligomer and dendrimer is selected from substituted and unsubstituted polyolefins such as polyethylene, polypropylene, polybutylene, polyvinyl chlorides and their copolymers, substituted and unsubstituted polymers such as polystyrene and their copolymers, polyesters such as polyacrylates, polyurethanes polyethers, polyamines, polysulphonates.

10. An electroluminescent compound as claimed in claim 4 or 5 in which the polymer, oligomer and dendrimer is selected electroluminescent light emitting organic polymers, oligomers and dendrimers.

11. An electroluminescent compound as claimed in claim 10 in which the polymer is selected from poly (p-phenylenevinylene)–PPV and copolymers including PPV.

12. An electroluminescent compound as claimed in claim 10 in which the polymer is selected from poly(2,5 dialkoxyphenylene vinylene) such as poly (2-methoxy-5-(2-methoxypentyloxy-1,4-phenylene vinylene), poly(2-methoxypentyloxy)-1,4-phenylenevinylene), poly(2-methoxy-5-(2-dodecyloxy-1,4-phenylenevinylene) and other poly(2,5 dialkoxyphenylenevinylenes) with at least one of the alkoxy groups being a long chain solubilising alkoxy group, poly fluorenes and oligofluorenes, polyphenylenes and oligophenylenes, polyanthracenes and oligo anthracenes, ploythiophenes and oligothiophenes and copolymers thereof.

13. An electroluminescent compound as claimed in any one of claims 1 to 12 in which the metal M is selected from Sm(III), Eu(II), Eu(III), Tb(III), Dy(III), Yb(III), Lu(III), Gd (III), U(III), $U(VI)O_2$, Tm(III), Th(IV), Ce (III), Ce(IV), Pr(III), Nd(III), Pm(III), Dy(III), Ho(III), Er(III), manganese, iron, ruthenium, osmium, cobalt, nickel,

palladium(II), palladium(IV), platinum(II), platinum(IV), cadmium, chromium. titanium, vanadium, zirconium, tantulum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium.

14. An electroluminescent compound as claimed in any one of claims 5 to 14 in which the metal M_2 is a non rare earth metal selected from 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, tantulum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium.

15. An electroluminescent device which comprises (i) a first electrode, (ii) a layer of electroluminescent compound as claimed in any one of claims 1 to 14 and (iii) a second electrode.

16. An electroluminescent device as claimed in claim 15 in which there is a layer of a hole transmitting material between the first electrode and the electroluminescent layer.

17. An electroluminescent device as claimed in claim 16 in which the hole transmitting material is an aromatic amine complex.

18. An electroluminescent device as claimed in claim 16 in which the hole transmitting material is polyaromatic amine complex.

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

20. An electroluminescent device as claimed in claim 17 in which the hole transmitting material is a film of a compound of formula (XXVI) or (XXVII) herein or as in figures 12 to 16 of the drawings.

21. An electroluminescent device as claimed in claim 17 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.

22. An electroluminescent device as claimed in claim 17 in which the hole transmitting material is a conjugated polymer.

23. An electroluminescent device as claimed in claim 22 in which the conjugated polymer is selected from poly (p-phenylenevinylene)-PPV and copolymers including PPV, poly(2,5 dialkoxyphenylene vinylene), poly (2-methoxy-5-(2-methoxypentyloxy-1,4-phenylene vinylene), poly(2-methoxypentyloxy)–1,4-phenylenevinylene), poly(2-methoxy-5-(2-dodecyloxy- 1,4-phenylenevinylene) and other poly(2,5 dialkoxyphenylenevinylenes) with at least one of the alkoxy groups being a long chain solubilising alkoxy group, poly fluorenes and oligofluorenes, polyphenylenes and oligophenylenes, polyanthracenes and oligo anthracenes, ploythiophenes and oligothiophenes.

24. An electroluminescent device as claimed in any one of claims 16 o 23 in which the electroluminescent compound is mixed with the hole transmitting material.

25. An electroluminescent device as claimed in any one of claims 17 to 24 in which there is a layer of an electron transmitting material between the cathode and the electroluminescent compound layer.

26. An electroluminescent device as claimed in claim 25 in which the electron transmitting material is a metal quinolate.

27. An electroluminescent device as claimed in claim 26 in which the metal quinolate is an aluminium quinolate or lithium quinolate.

28. An electroluminescent device as claimed in claim 25 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.

29. An electroluminescent device as claimed in claim 25 in which the electron transmitting material is a cyano anthracene such as 9,10 dicyano anthracene, a polystyrene sulphonate or a compound of formulae shown in figures 9 or 10 of the drawings.

30. An electroluminescent device as claimed in any one of claims 25 to 29 in which the electron transmitting material is mixed with the electroluminescent compound.

31. An electroluminescent device as claimed in any one of the claims 17 to 30 in which the first electrode is a transparent electricity conducting glass electrode.

32. An electroluminescent device as claimed in any one of the claims 17 to 31 in which the second electrode is selected from aluminium, calcium, lithium, magnesium and alloys thereof and silver/magnesium alloys.

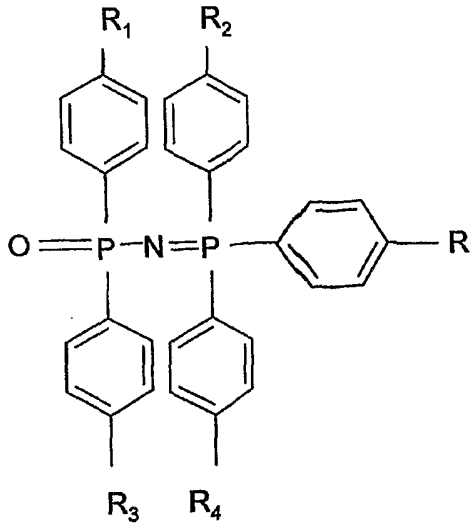


Fig. 1

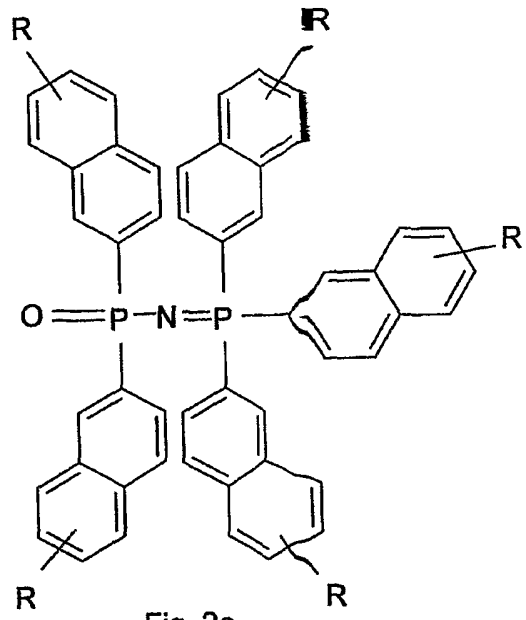


Fig. 2a

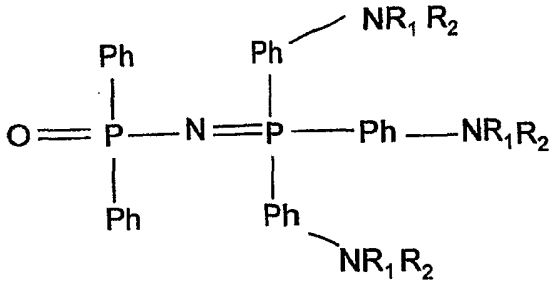


Fig. 2b

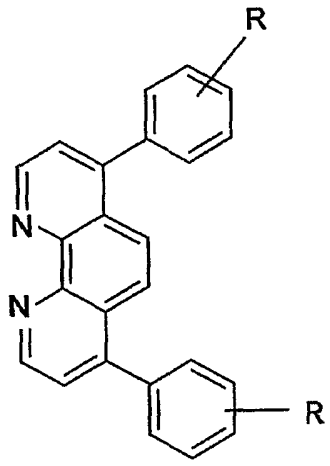


Fig. 3

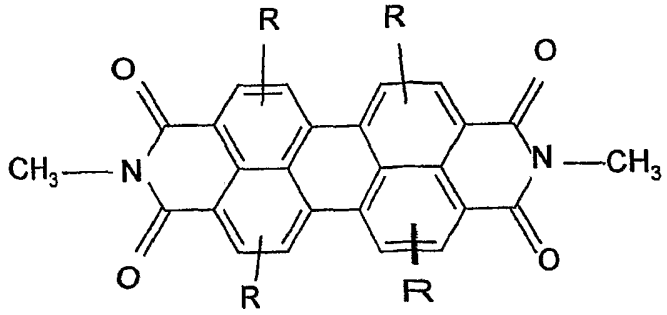


Fig. 4a

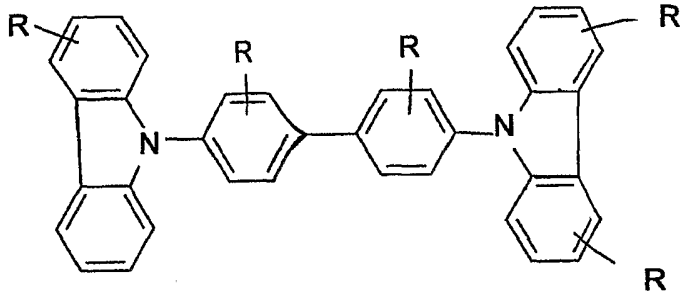


Fig. 4b

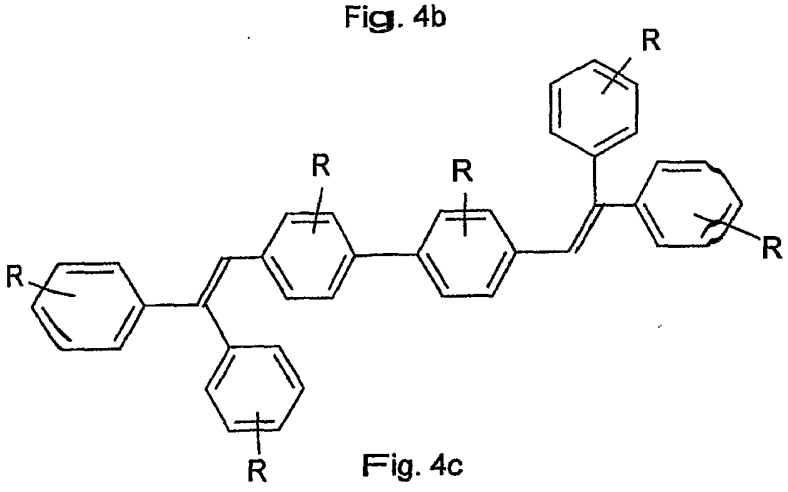


Fig. 4c

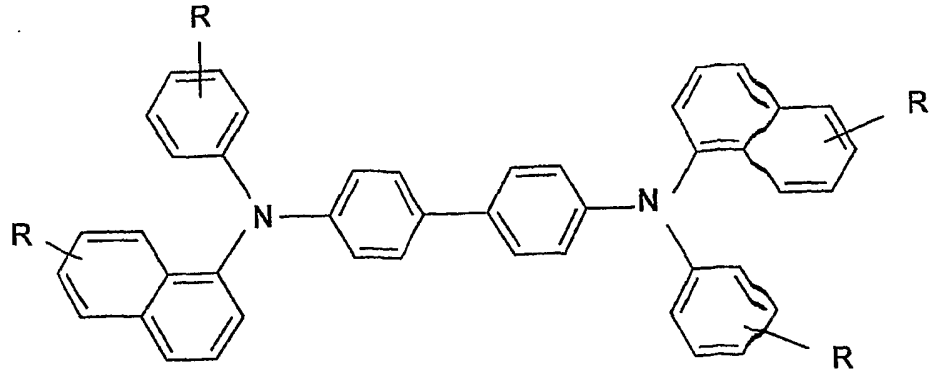


Fig. 4d

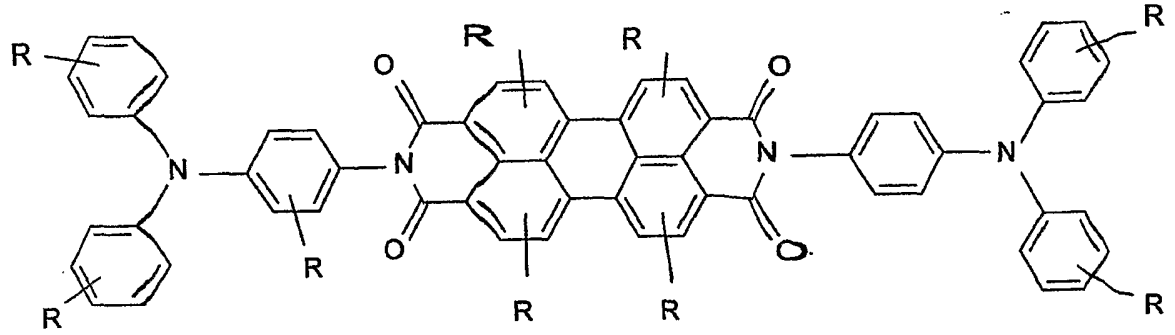


Fig. 4e

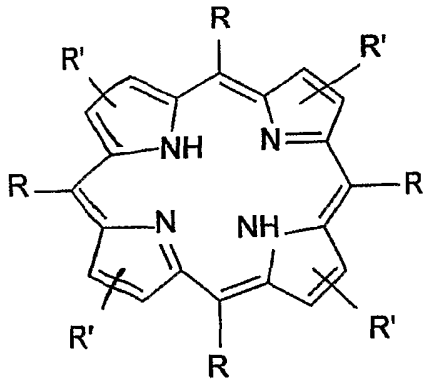


Fig. 4f

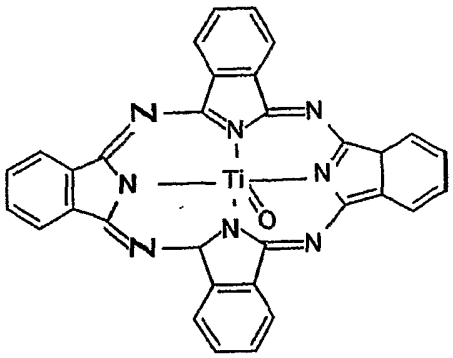


Fig. 4g

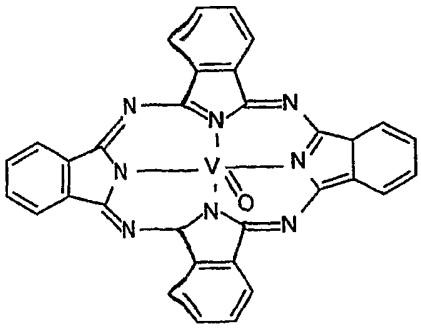


Fig. 4h

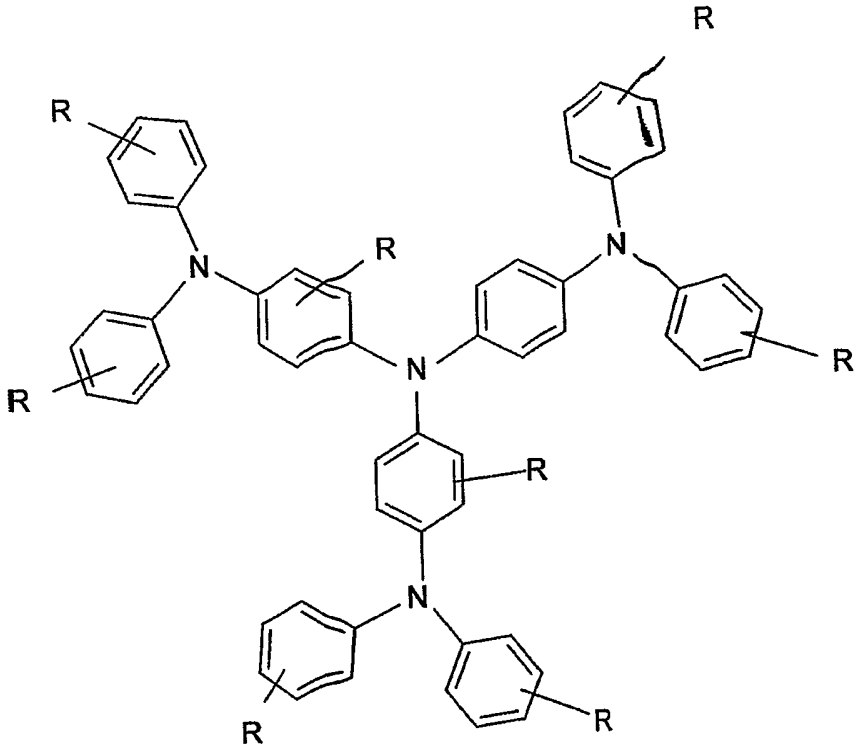


Fig. 4i

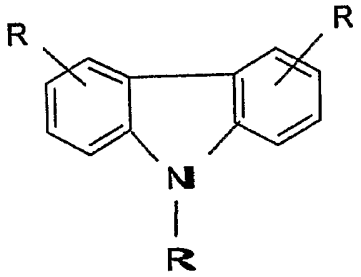


Fig. 4j

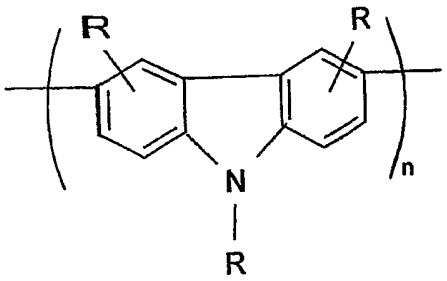


Fig.4k

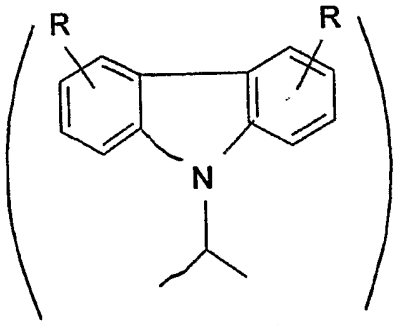


Fig. 4l

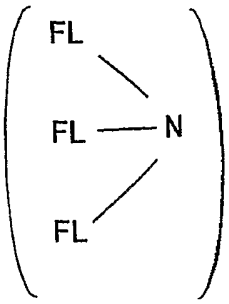


Fig. 5a

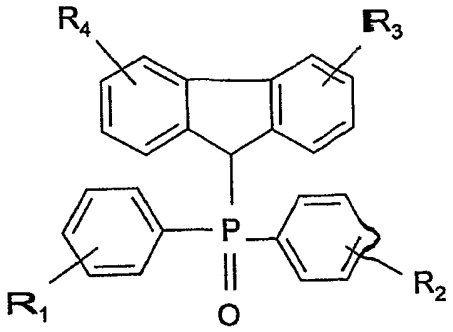


Fig.5b

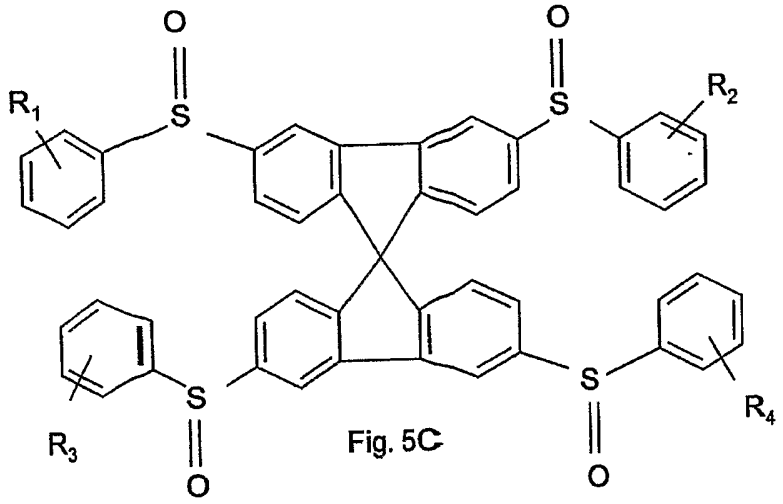


Fig. 5C

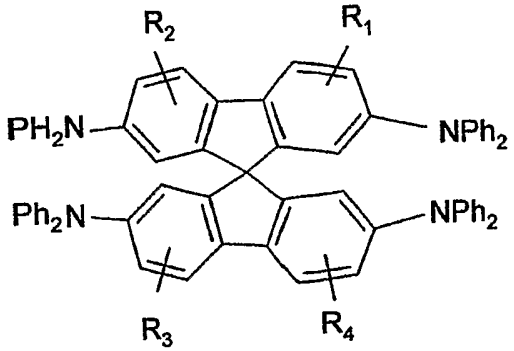


Fig. 5d

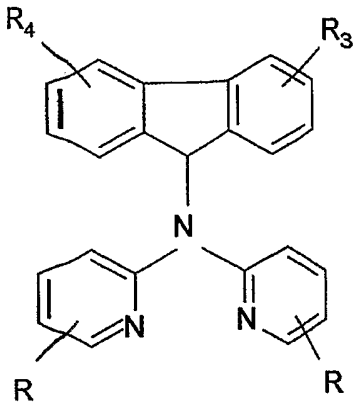


Fig. 5f

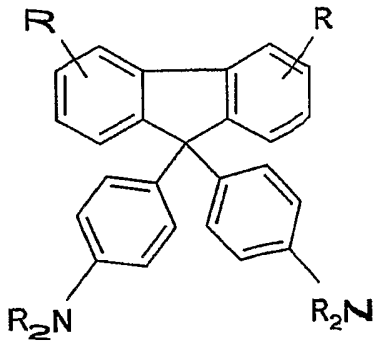


Fig. 5g

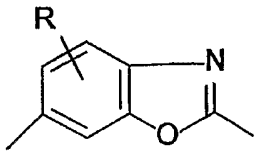


Fig. 6a

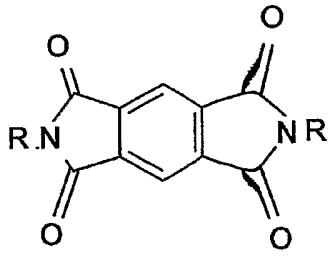


Fig 6b

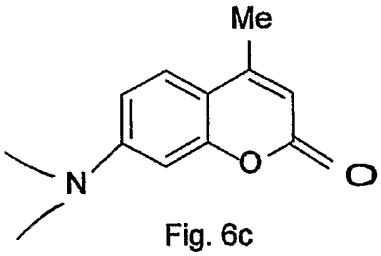


Fig. 6c

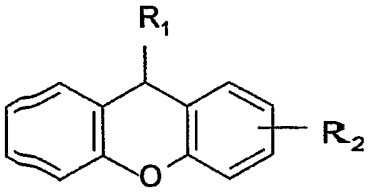


Fig. 6d

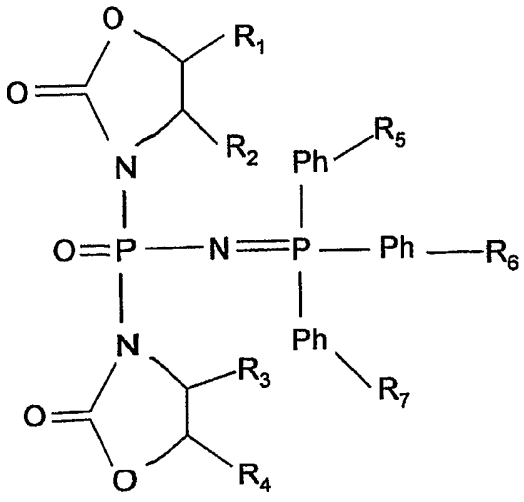


Fig. 6e

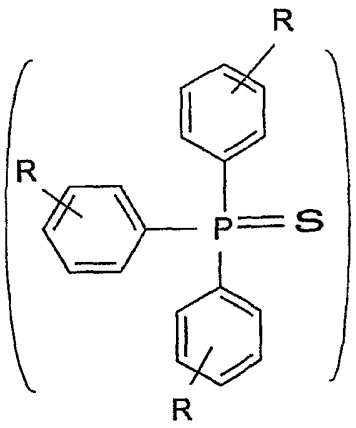


Fig. 7a

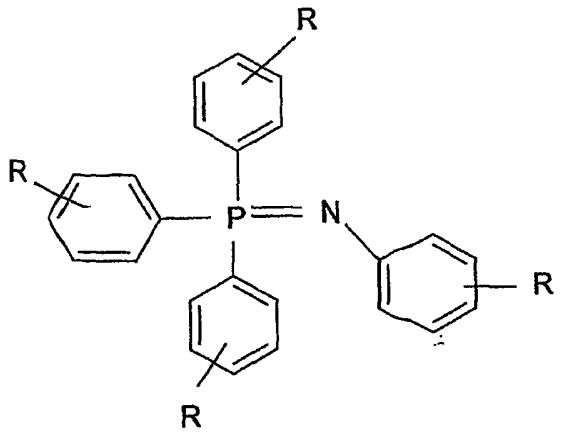
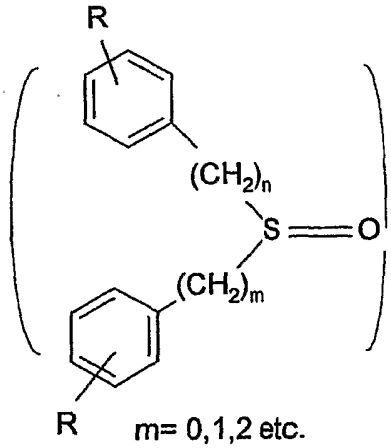


Fig. 7b



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

Fig. 7c

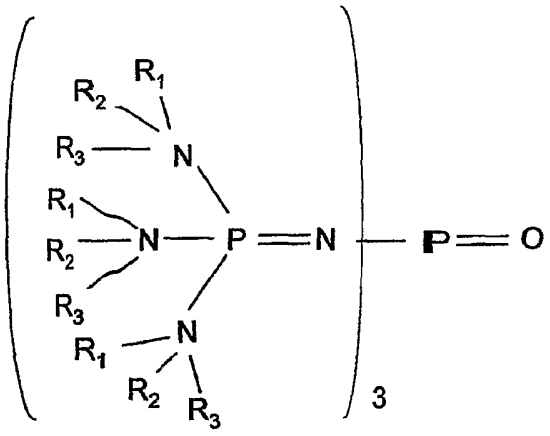
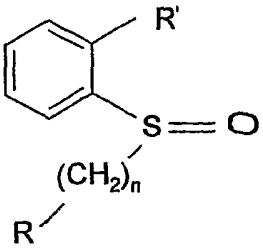
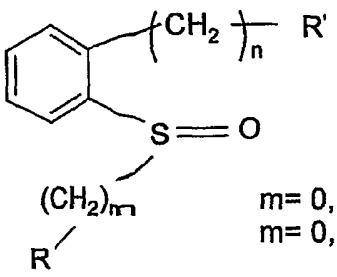


Fig. 7d



n = 0,1,2 etc.

Fig. 7e



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

Fig. 7f

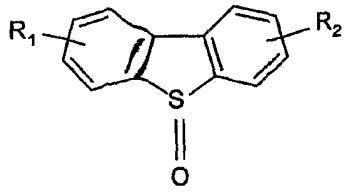


Fig. 8a

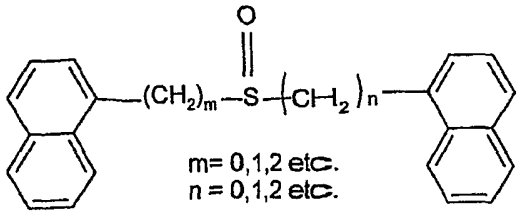


Fig. 8b

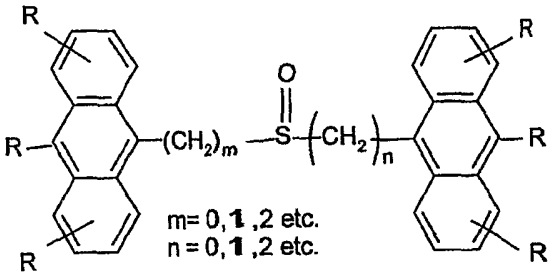


Fig. 8c

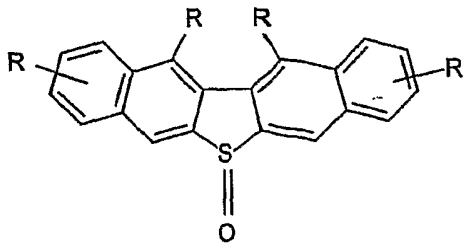


Fig.8d

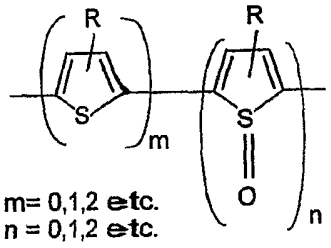


Fig. 8e

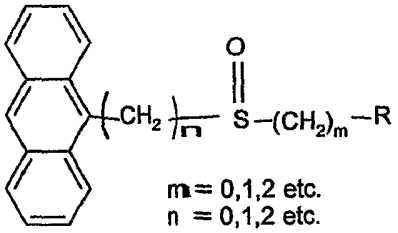


Fig. 8f

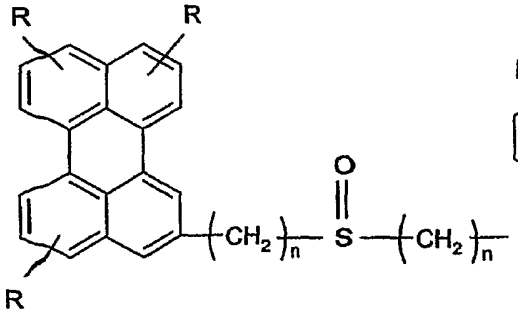


Fig. 8g

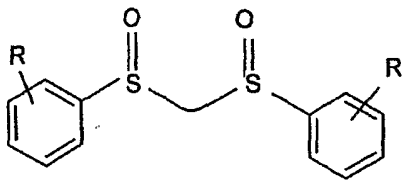
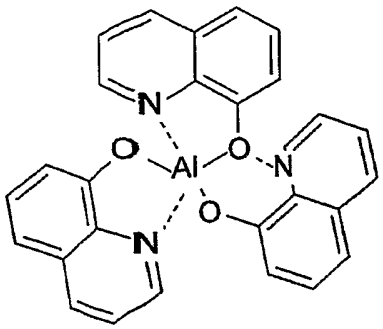


Fig_ 8h



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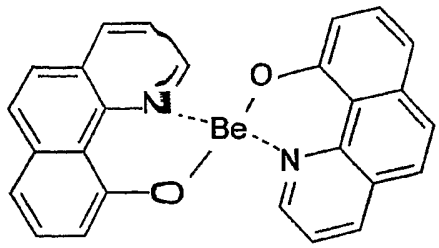

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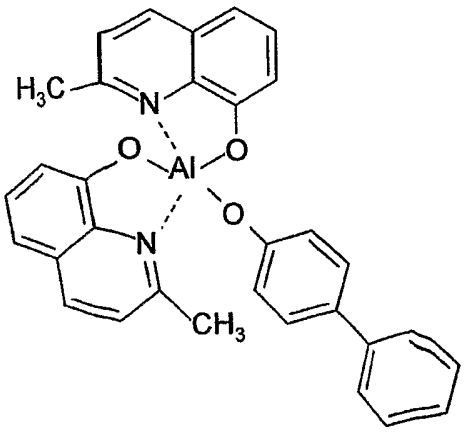

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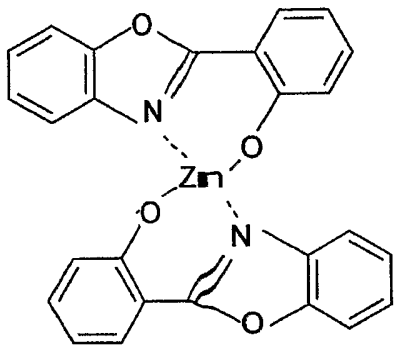
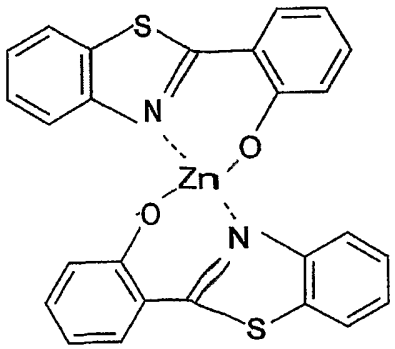


Zn PBO



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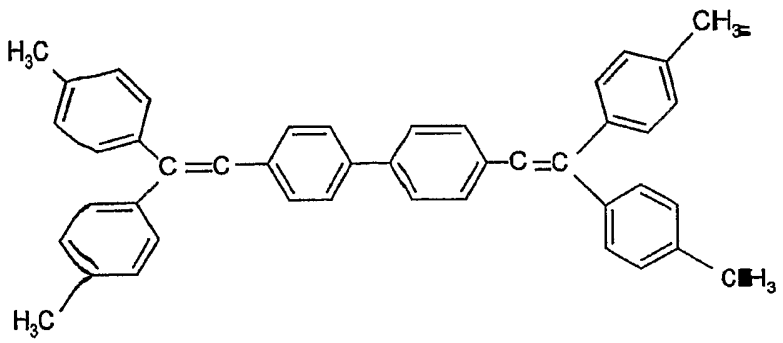
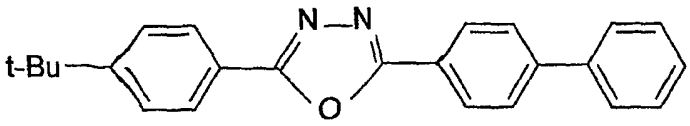
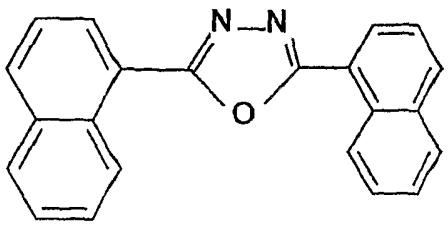


DTVBb1

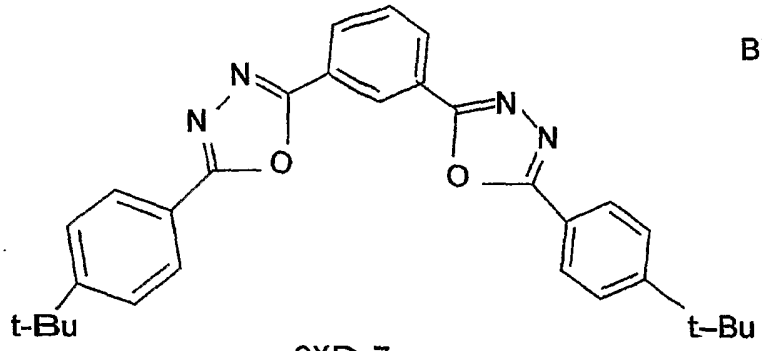
Fig. 9



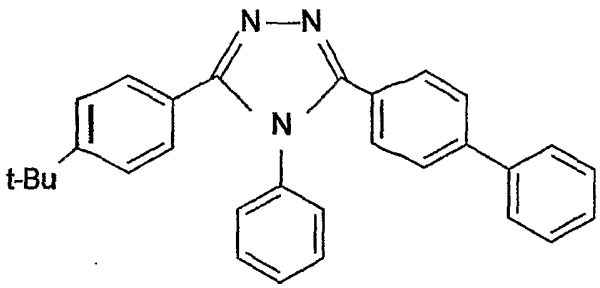
t-Bu-PBD



BND



OXD-7



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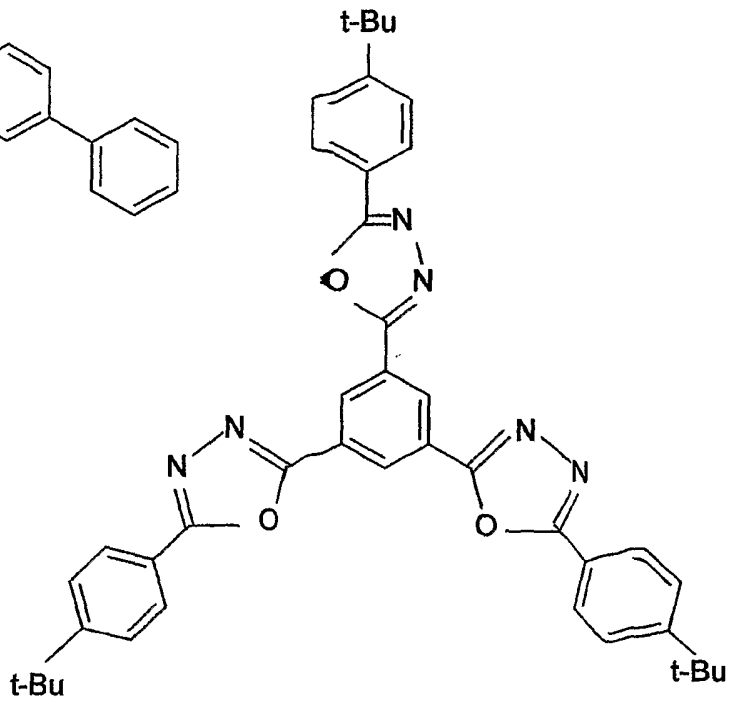
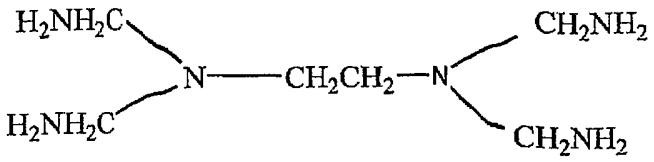
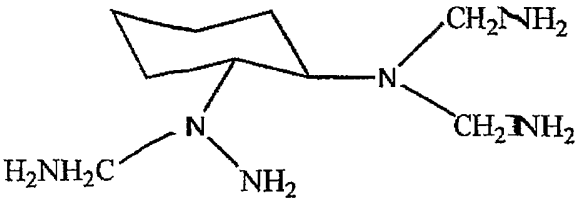


OXD- Star

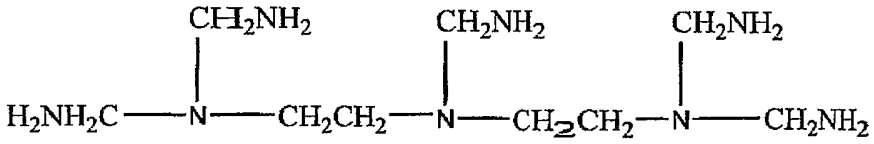
Fig. 10



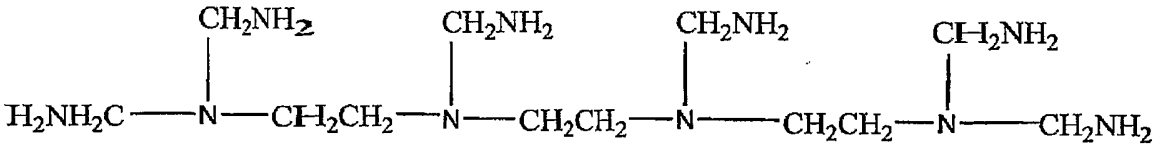
EDTA



DCTA



DTPA



TTHA

Fig. 11

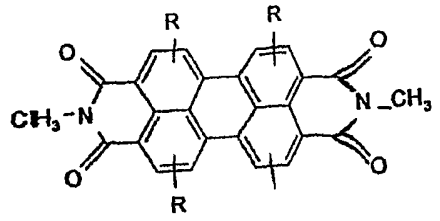


Fig. 12a

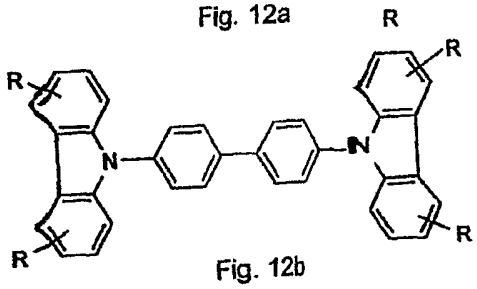


Fig. 12b

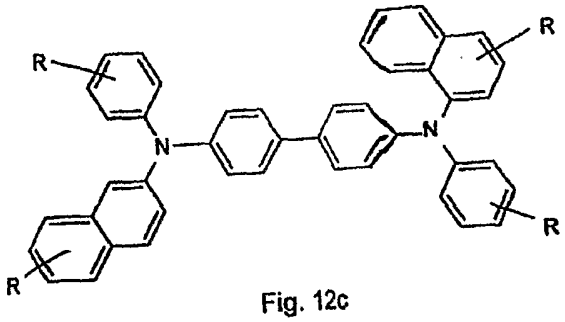


Fig. 12c

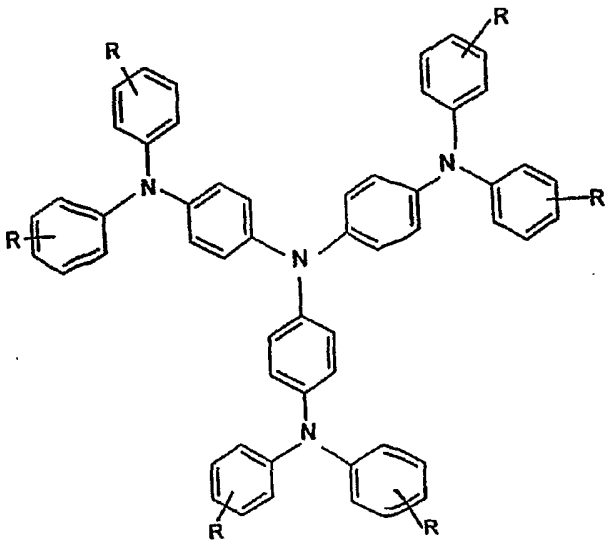


Fig. 12d

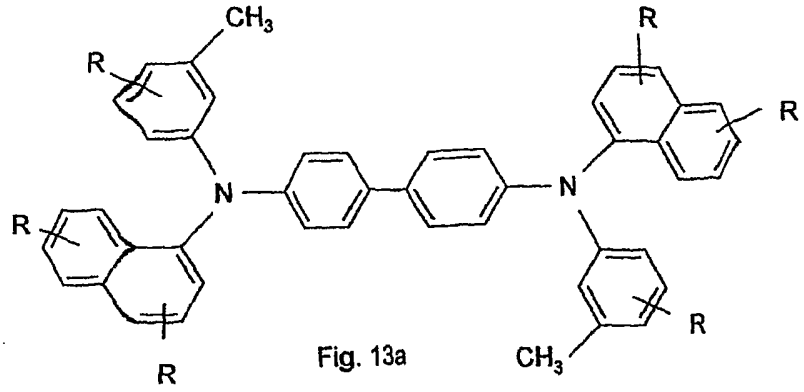


Fig. 13a

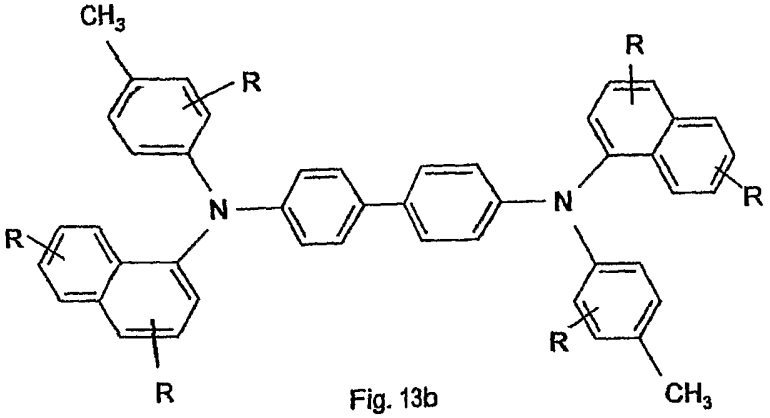


Fig. 13b

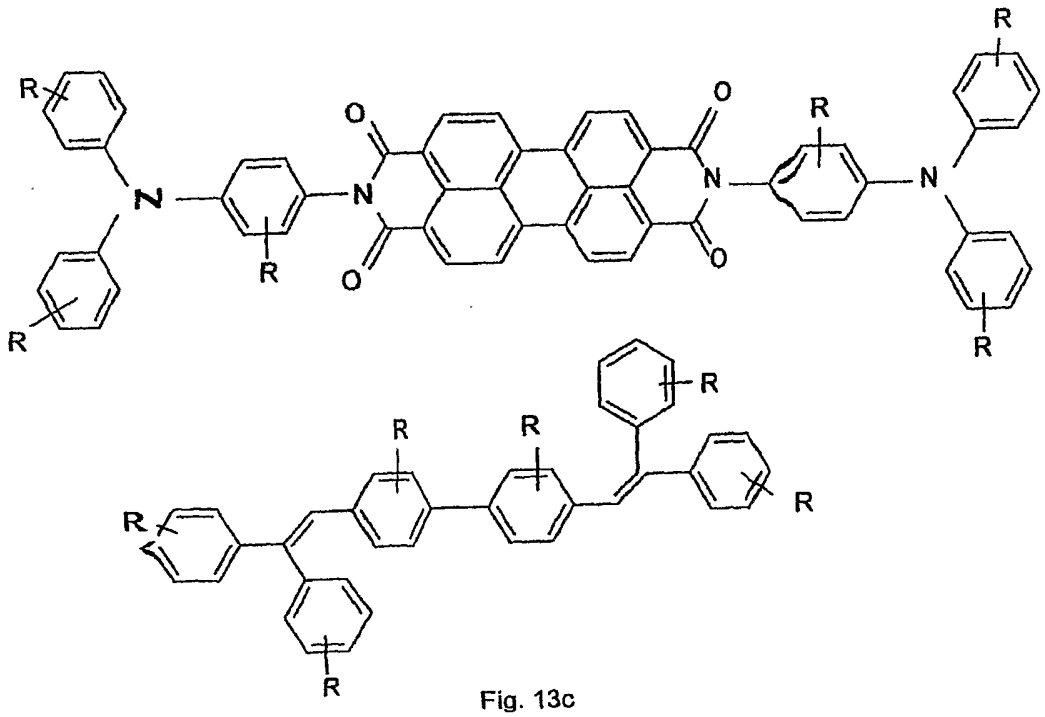


Fig. 13c

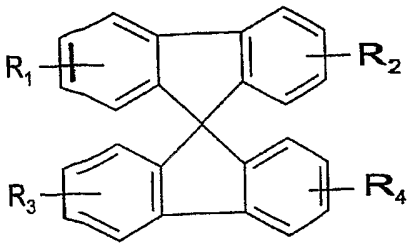


Fig. 14a

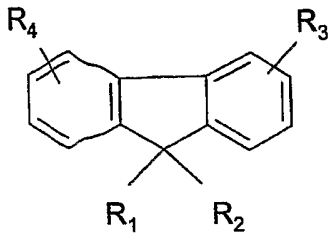
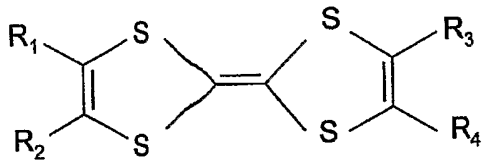


Fig. 14b



or

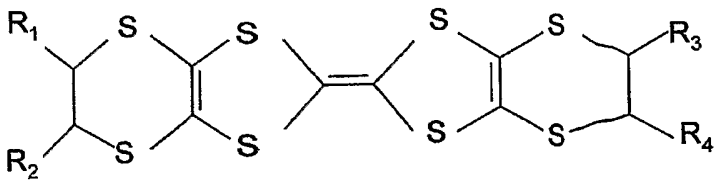


Fig. 14c

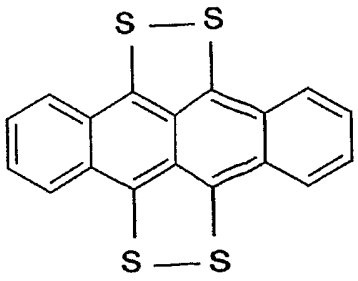
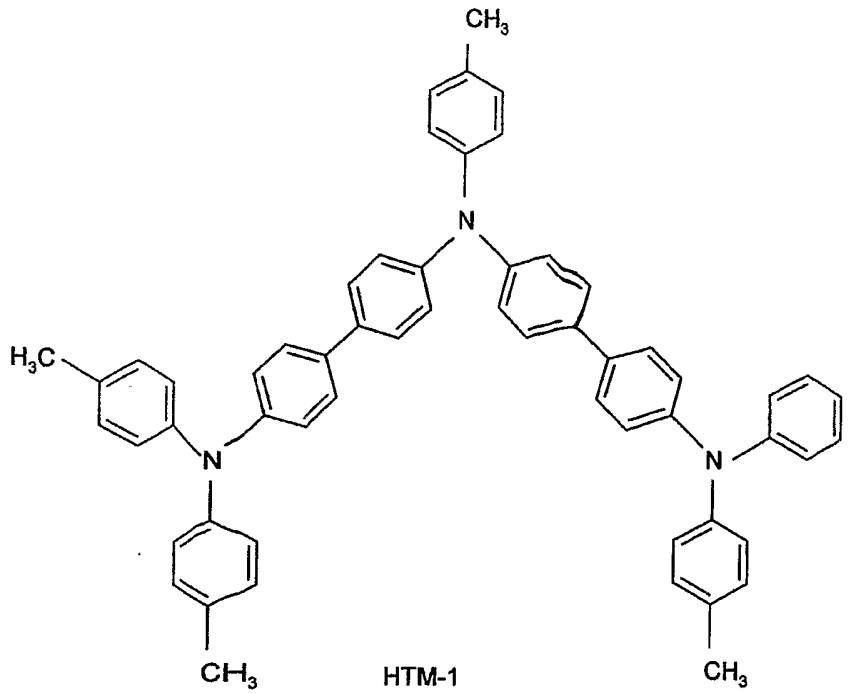
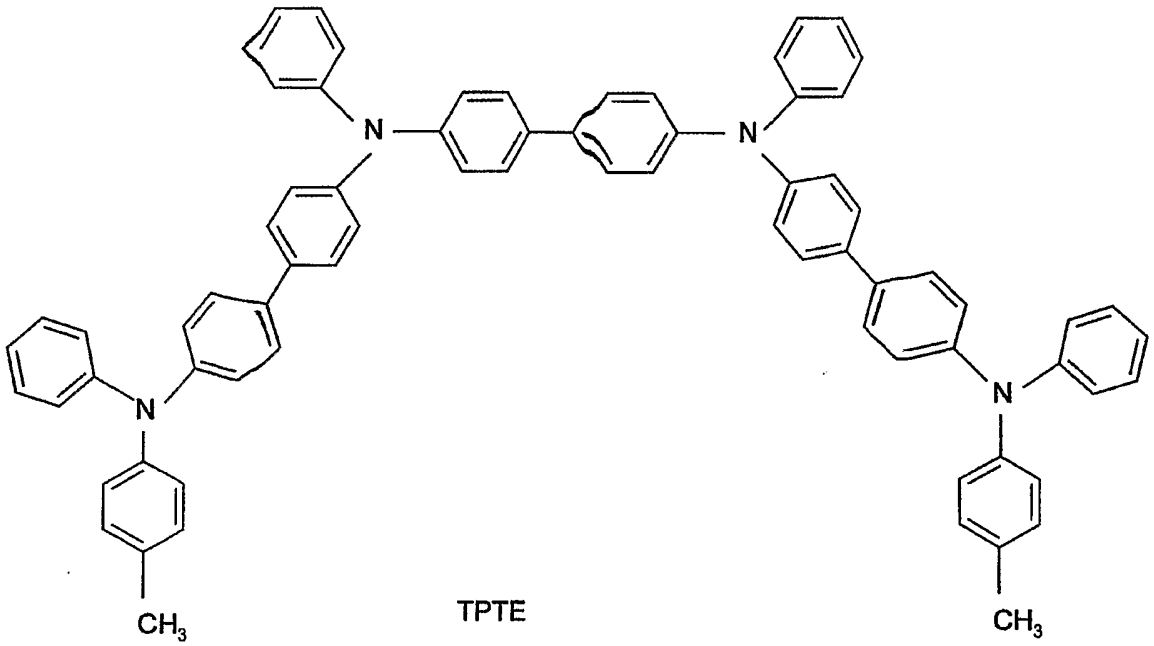


Fig. 14d



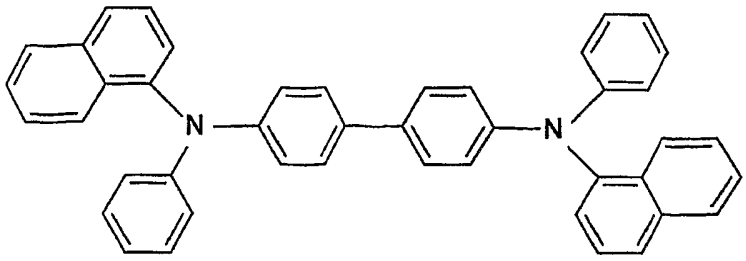
HTM-1

Fig. 15a



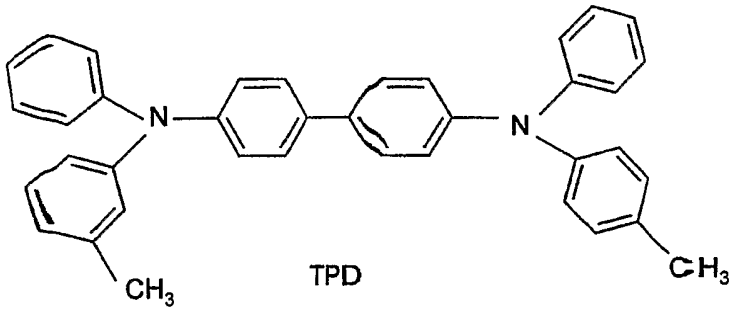
TPTE

Fig. 15b



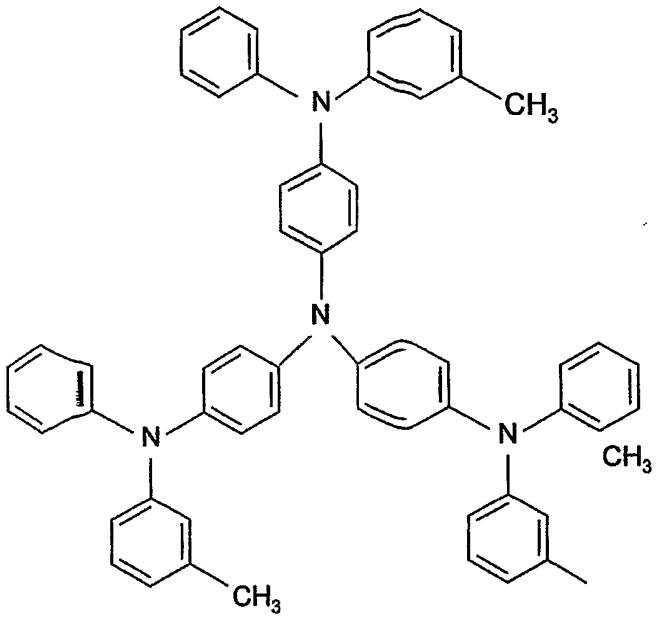
α-NPB

Fig. 16a



TPD

Fig. 16b



mTADATA

Fig. 16c

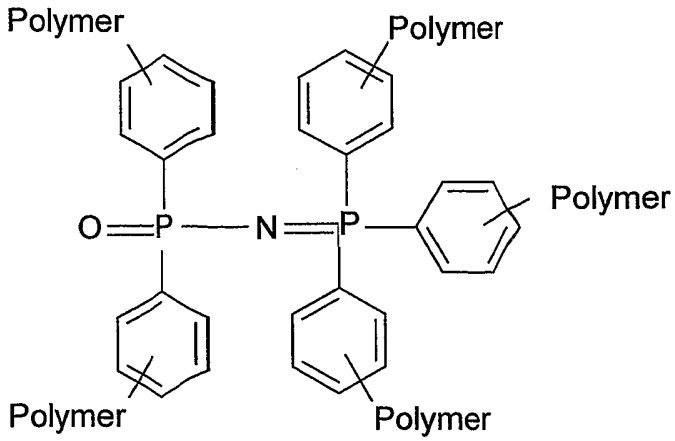


Fig. 17a

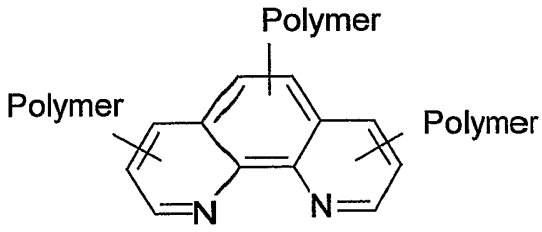


Fig. 17b

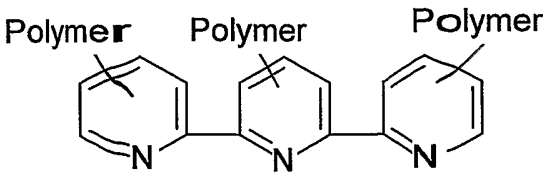


Fig. 17c

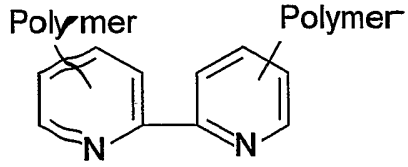


Fig. 17d

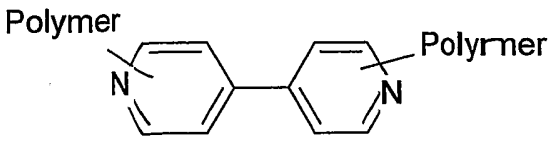


Fig. 17e

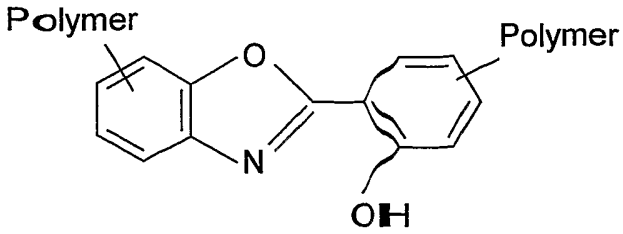


Fig. 18a

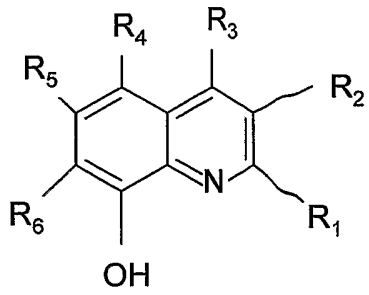


Fig. 18b

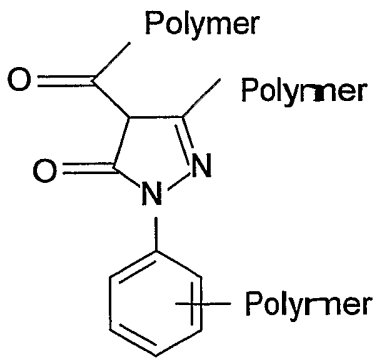


Fig. 18c

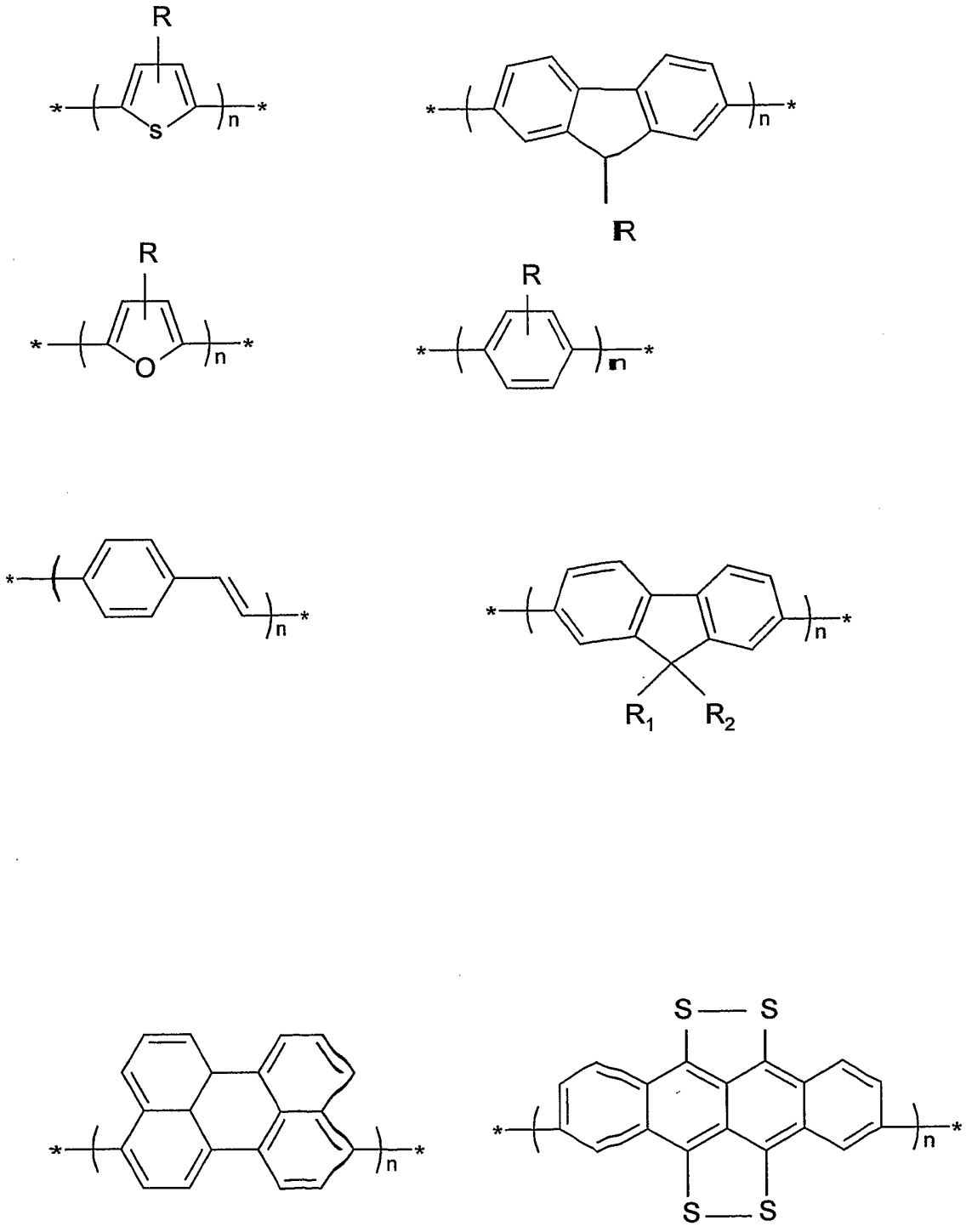


Fig. 19

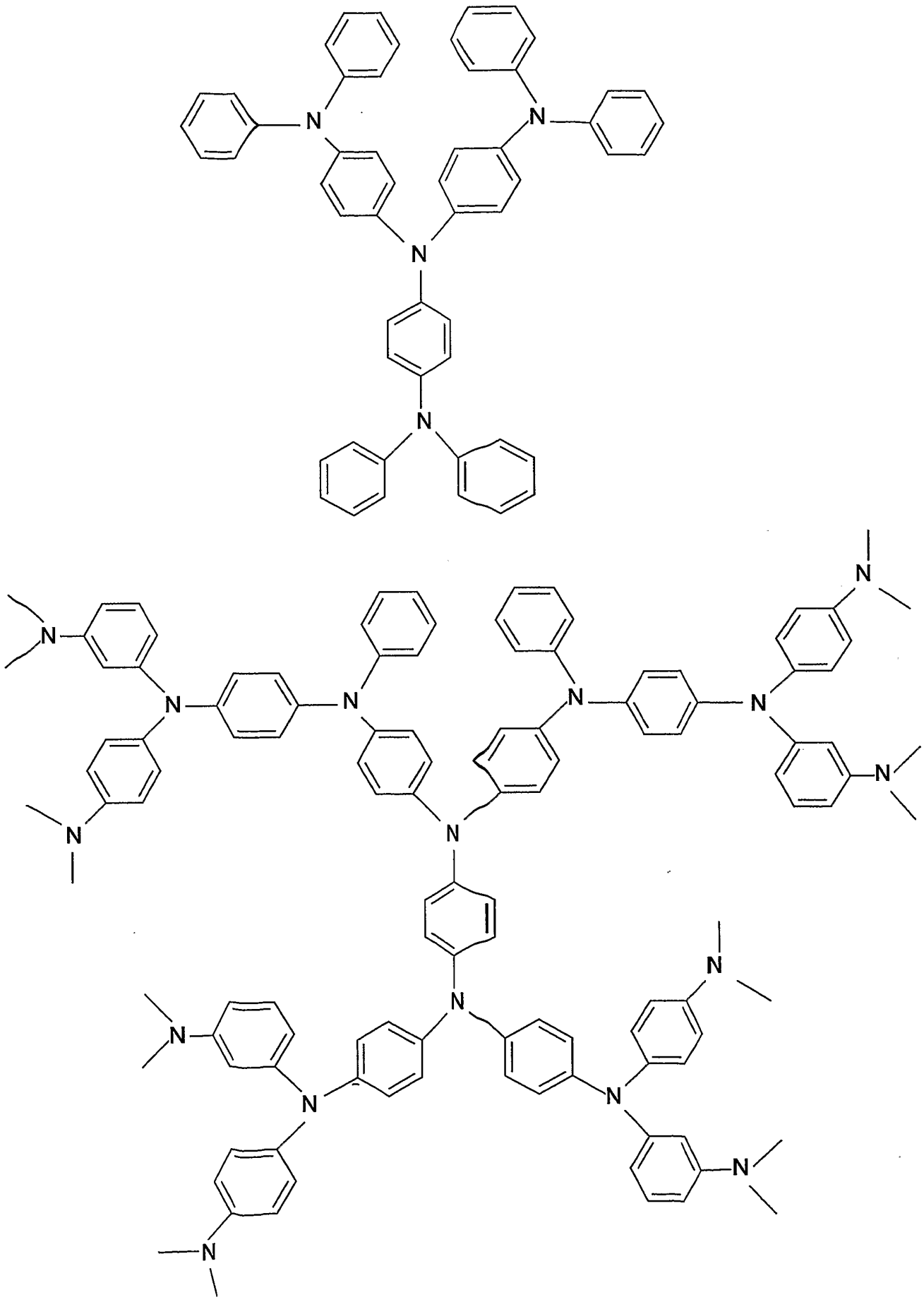


Fig. 20

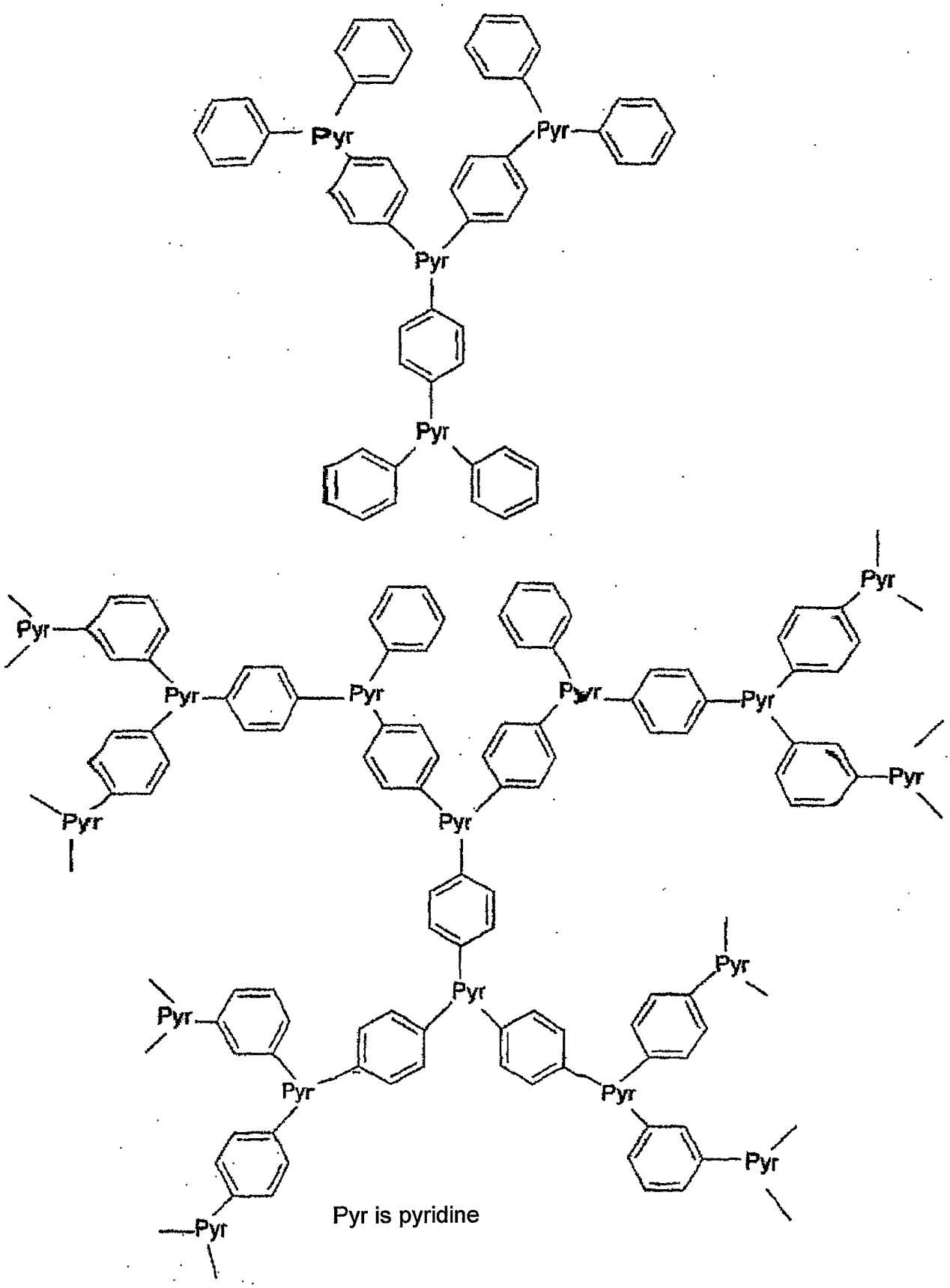


Fig. 21

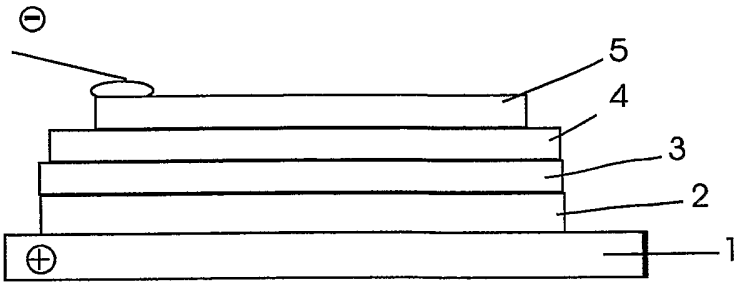
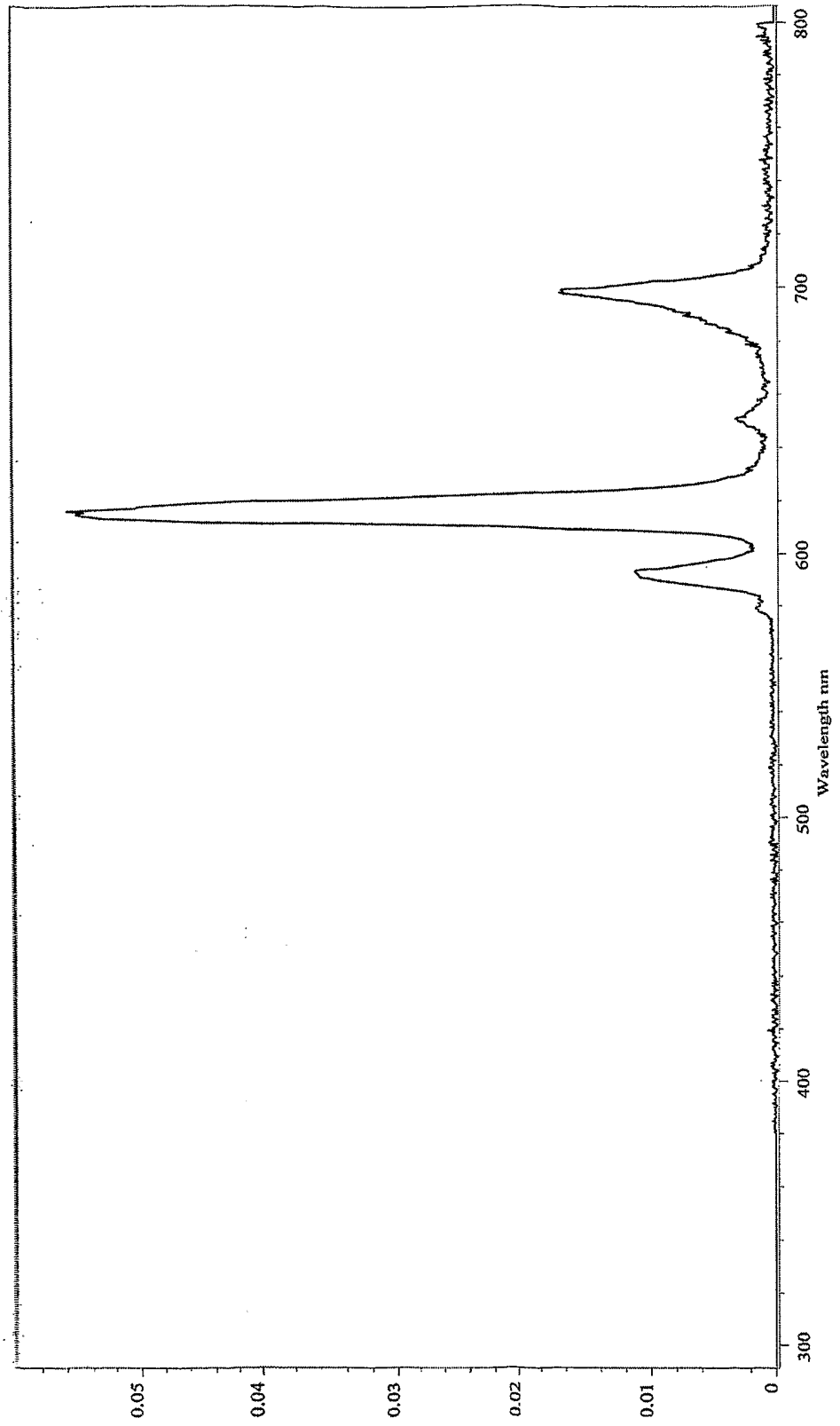


Fig. 22



Photoluminescent Spectrum of $Eu(Naph)_2(AA)_n(Styrene)_m$

Fig. 23

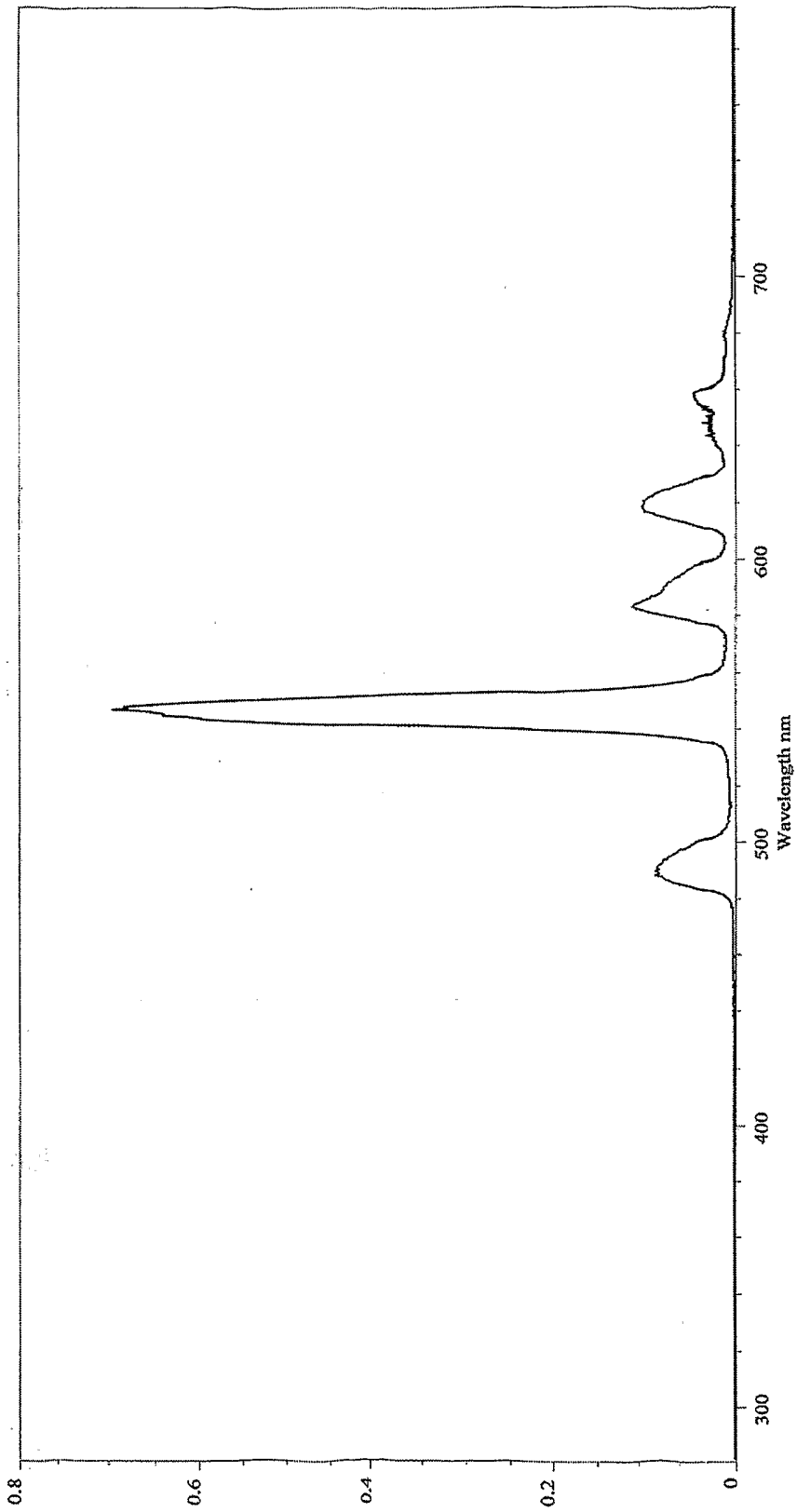

0.8
0.6
0.4
0.2
0
300
400
500
600
700
Wavelength nm
Photoluminescent Spectrum of Tb(tmhd)3(PS-DMAP)

Fig. 24

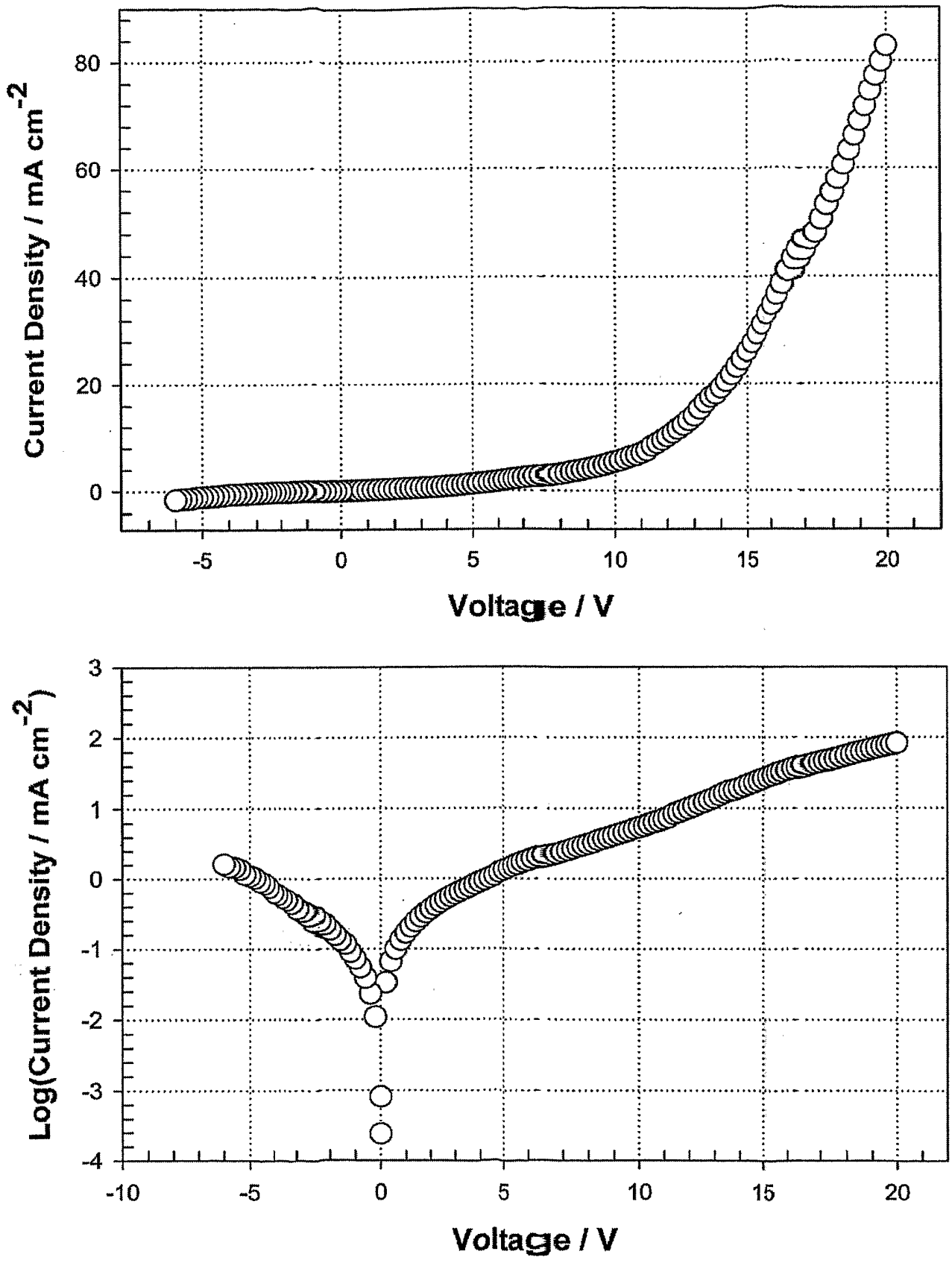

Current Density / mA cm-2
80
60
40
20
0
-5
0
5
10
15
20
Voltage / V
Log(Current Density / mA cm-2)
3
2
1
0
-1
-2
-3
-4
-10
-5
0
5
10
15
20
Voltage / V

Fig. 25

INTERNATIONAL SEARCH REPORT

Internatio Application No
PCT/GB 03/03610

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K11/06 H01L51/20 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)
IPC 7 C09K H01L H05B

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, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LING Q ET AL: "A novel high photoluminescence efficiency polymer incorporated with pendant europium complexes" POLYMER, ELSEVIER SCIENCE PUBLISHERS B.V, GB, vol. 42, no. 10, May 2001 (2001-05), pages 4605-4610, XP004232603 ISSN: 0032-3861 figure 1 ---	1-4, 7-13, 15-32
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 10, 17 November 2000 (2000-11-17) & JP 2000 204364 A (OKI ELECTRIC IND CO LTD), 25 July 2000 (2000-07-25) abstract ---	1-4, 7-13, 15-32

-/--

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

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 January 2004	19/01/2004

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	Lehnert, A

INTERNATIONAL SEARCH REPORT

Internatic Application No
PCT/GB 03/03610

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	ZHAO D ET AL: "ORGANIC LIGHT-EMITTING DIODE USING EU3+ POLYMER COMPLEX AS AN EMITTER" JAPANESE JOURNAL OF APPLIED PHYSICS, PUBLICATION OFFICE JAPANESE JOURNAL OF APPLIED PHYSICS. TOKYO, JP, vol. 1A/B, PART 2, no. 38, 15 January 1999 (1999-01-15), pages L46-L48, XP001086542 ISSN: 0021-4922 the whole document	1-4, 7-13, 15-32
X	WO 02 31896 A (DU PONT) 18 April 2002 (2002-04-18) page 50, line 11 -page 51, line 6; claims	1-4, 7-13, 15-32
P,X	WO 03 022908 A (IGAWA SATOSHI ;CANON KK (JP); KAMATANI JUN (JP); OKADA SHINJIRO (J) 20 March 2003 (2003-03-20) the whole document & US 2003/186080 A1 (KAMATANI ET AL) 2 October 2003 (2003-10-02)	1-4, 7-13, 15-32
P,X	EP 1 316 570 A (KYNAST ULRICH PROF DR ;PASO VERTRIEB CHEM TECHN PRODU (DE)) 4 June 2003 (2003-06-04) the whole document	1-4, 7-13, 15-32
X	EP 0 556 005 A (AMERSHAM INT PLC) 18 August 1993 (1993-08-18) claims 1,10,24; examples	1-4, 7-13, 15-32
X	WO 02 43447 A (KATHIRGAMANATHAN POOPATHY ;ELAM T LTD (GB)) 30 May 2002 (2002-05-30) page 8, line 22 - line 24 page 13, line 16 - line 22; claims	1-4, 7-13, 15-32
X	WO 00 32719 A (KATHIRGAMANATHAN POOPATHY ;SOUTH BANK UNIV ENTPR LTD (GB)) 8 June 2000 (2000-06-08) cited in the application page 4, line 10 - line 17; claim 10	1-4, 7-13, 15-32
X	WO 00 26323 A (KATHIRGAMANATHAN POOPATHY ;SOUTH BANK UNIV ENTPR LTD (GB)) 11 May 2000 (2000-05-11) claim 4	1-4, 7-13, 15-32

-/--

INTERNATIONAL SEARCH REPORT

Internatio Application No
PCT/GB 03/03610

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 98 58037 A (KATHIRGAMANATHAN POOPATHY ;SOUTH BANK UNIV ENTPR LTD (GB)) 23 December 1998 (1998-12-23) cited in the application claims 9,26 ---	1-4, 7-13, 15-32
X	FERY-FORGUES S ET AL: "Ferrocene and Ferrocenyl Derivatives in Luminescent Systems" JOURNAL OF PHOTOCHEMISTRY AND PHOTOBIOLOGY, A: CHEMISTRY, ELSEVIER SEQUOIA, LAUSANNE, CH, vol. 132, 20 April 2000 (2000-04-20), pages 137-159, XP002220496 ISSN: 1010-6030 the whole document ---	1-4, 7-13, 15-32
X	MACHIDA K ET AL: "REDOX BEHAVIOR AND LUMINESCENCE PROPERTY OF EUROPIUM POLYMER COMPLEXES" KIDORUI, NIHON KIDORUI GAKKAI, OSAKA, JP, vol. 18, 1991, pages 70-71, XP000884394 ISSN: 0910-2205 abstract ---	1-4, 7-13, 15-32
A	EP 1 013 740 A (KONISHIROKU PHOTO IND) 28 June 2000 (2000-06-28) paragraph '0101! ---	1-4, 7-13, 15-32
A	US 4 443 380 A (YAMAZOE KATSUHIKO ET AL) 17 April 1984 (1984-04-17) example 51 -----	1-4, 7-13, 15-32

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 03/03610

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 5, 6, 14
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 5, 6, 14

Present claims 5, 6, 14 relate to an electroluminescent device comprising an electroluminescent layer comprising a metal complex with at least two metal atoms as part of the complex.

The claims cover all products having this characteristic, whereas the application provides no support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT.
Binuclear complexes comprising two metals are not sufficiently disclosed within the meaning of Article 5 PCT. Moreover, claims 5, 6, 14 are unclear in the meaning of Article 6 PCT to such an extent that a meaningful seach is not possible, because claims 5, 6 and 14 disclose a compound having two metal atoms whereas claims 1 and 2 which they depend on disclose only compounds having one metal atom.

Consequently, a search has not been carried out for those claims 5, 6, 14 which do not appear to be supported and disclosed.

Present claims 1-4, 7-13, 15-32 relate to an extremely large number of possible products. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the products claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible.

Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the products
prepared in the examples and closely related homologous compounds.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internatic Application No
PCT/GB 03/03610

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
JP 2000204364	A	25-07-2000	NONE		
WO 0231896	A	18-04-2002	AU	1532202 A	22-04-2002
			CA	2423886 A1	18-04-2002
			EP	1364419 A2	26-11-2003
			WO	0231896 A2	18-04-2002
WO 03022908	A	20-03-2003	JP	2003073480 A	12-03-2003
			JP	2003073479 A	12-03-2003
			WO	03022908 A1	20-03-2003
			US	2003186080 A1	02-10-2003
EP 1316570	A	04-06-2003	DE	20119574 U1	02-10-2002
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