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(54) Title: ELECTROLUMINESCENT DEVICE

(57) Abstract: An electroluminescent device which has an electroluminescent layer formed of a binuclear, trinuclear or polynuclear rare earth organic complex in which the metals are linked through a bridging ligand.

Electroluminescent Device

The present invention relates to electroluminescent devices incorporating electroluminescent materials.

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

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

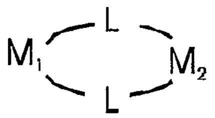
Another compound which has been proposed is aluminium quinolate, but this requires dopants to be used to obtain a range of colours and has a relatively low efficiency.

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

We have now devised electroluminescent devices incorporating other organometallic electroluminescent materials.

According to the invention there is provided an electroluminescent device which comprises sequentially a first electrode, a layer of an electroluminescent compound and second electrode in which the electroluminescent compound is selected from binuclear, trinuclear and polynuclear complexes of rare earth metals.

By binuclear is meant that there are least two metal atoms in the complex, at least one of which is a rare earth metal the other metals can be a rare earth or non rare earth metal one in which the metals are linked by a bridging ligand i.e. of formula



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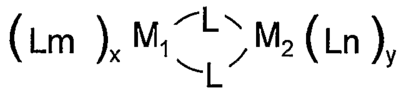
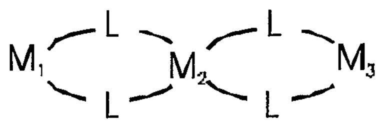


where M_1 is a rare earth metal and M_2 is a rare earth or non rare earth metal Lm and Ln are the same or different organic ligands, x is the valence state of Lm and y is the valence state of Ln and L is a bridging ligand. For example x will be 3 when M_1 is in the III valence state and y will be 2 when M_2 and is in the 2 valence state etc.

By trinuclear is meant there are three metals joined by a bridging ligand one of which metals is a rare earth metal and at least one of which is a non rare earth metal. i.e. of formula



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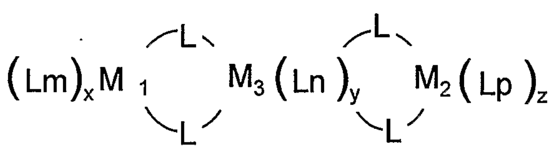

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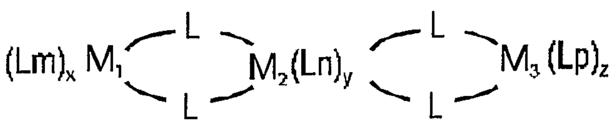

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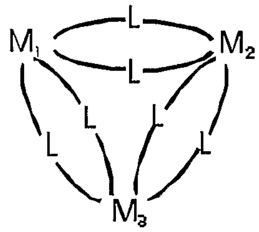

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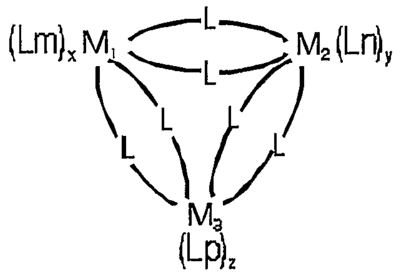


where L is a bridging ligand and at least one of M_1, M_2 and M_3 is a rare earth metal and the other metals can be a rare earth or non rare earth metals. Lm, Ln and Lp are organic ligands and x is the valence state of M_1, y is the valence state of M_2 and z is the valence state of M_3

By polynuclear is meant there are more than three metals joined by bridging ligands and at least one of the metals is a rare earth metal and the other metals can be a rare earth or non rare earth metal.

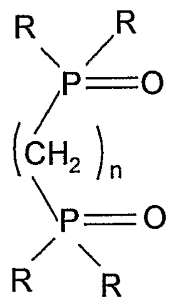
Preferably the rare earth metal is a metal having an unfilled inner shell and the preferred metals are selected from Sm(III), Eu(II), Eu(III), Tb(III), Dy(III), Yb(III), Lu(III), Gd (III), Gd(III) U(III), Tm(III), Ce (III), Pr(III), Nd(III), Pm(III), Dy(III), Ho(III), Er(III), Yb(III) and more preferably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

The non rare earth metal can be any non rare earth metal e.g. 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, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium etc.

For example $(L_1)(L_2)(L_3)(L..)M_1 - L - M_2 (L_1)(L_2)(L_3)(L\ldots)$ where $(L_1)(L_2)(L_3)(L\ldots)$ are the same or different organic complexes.

For example x will be 3 when M_1 is in the III valence state and y will be 2 when M_2 and is in the 2 valence sate.

The bridging ligands L are preferably bidentate or tridentate ligands and are preferably bis or tris phosphane oxide complexes e.g. of formula



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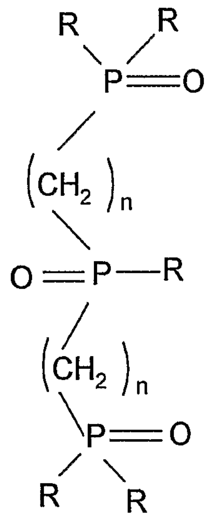
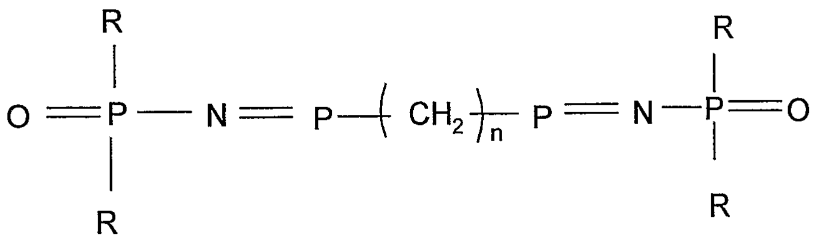


where the groups R which can be the same or different are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoryl methyl groups, halogens such as fluorine or thiophenyl groups, n is preferably 1 to 10 e.g. 1 to 5 or as shown in figs. 17 of the drawings in which Ar are the same or different unsubstituted or substituted aromatic groups.

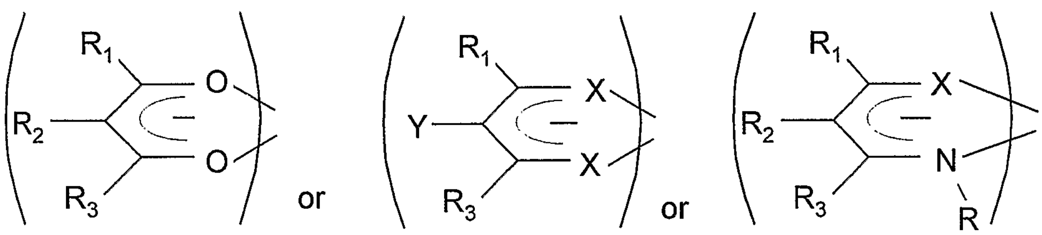
Or bis(diphenylphosphinimino-phosphane oxides e.g. of formula



where R and n are as above. Preferably the groups R are unsubstituted or substituted aromatic groups or as shown in fig. 17.

Examples of other ligands are also shown in fig. 17 of the drawings

The groups Lm, Ln, Lp etc. which can also be the bridging ligands may all be the same or different and can be selected from β diketones such as those of formulae



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.

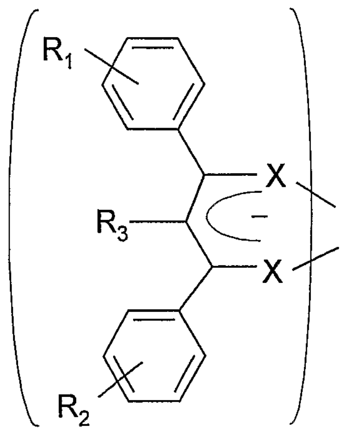
Examples of R_1 and/or R_2 and/or R_3 include aliphatic, aromatic and heterocyclic alkoxy, aryloxy and carboxy groups, substituted and substituted phenyl, fluorophenyl, biphenyl, phenanthrene, anthracene, naphthyl and fluorene groups alkyl groups such as t-butyl, heterocyclic groups such as carbazole.

R_1, R_2 and R_3 can also be

where X is O, S, Se or NH.

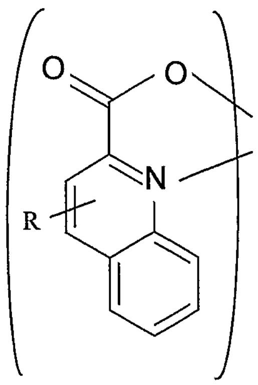
A preferred moiety R_1 is trifluoromethyl CF_3 and examples of such diketones are, banzoyltrifluoroacetone, p-chlorobenzoyltrifluoroacetone, p-bromotrifluoroacetone, p-phenyltrifluoroacetone, 1-naphthoyltrifluoroacetone, 2-naphthoyltrifluoroacetone, 2-phenathoyltrifluoroacetone, 3-phenanthoyltrifluoroacetone,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

The different groups Lm, Ln and Lp may be the same or different ligands of formulae



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

The different groups Lm, Ln and Lp may be the same or different quinolate derivatives such as



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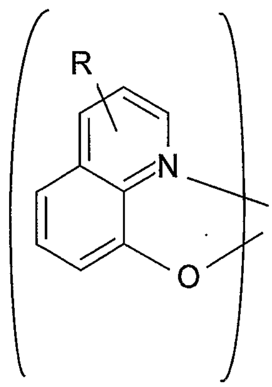
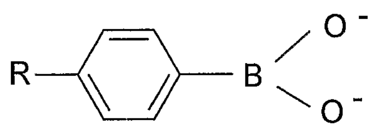
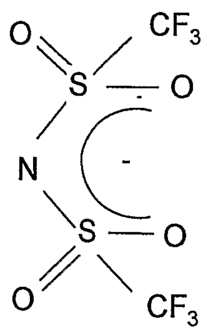


where R is hydrocarbyl, aliphatic, aromatic or heterocyclic carboxy, aryloxy, hydroxy or alkoxy e.g. the 8 hydroxy quinolate derivatives or



where R is as above or H or F or



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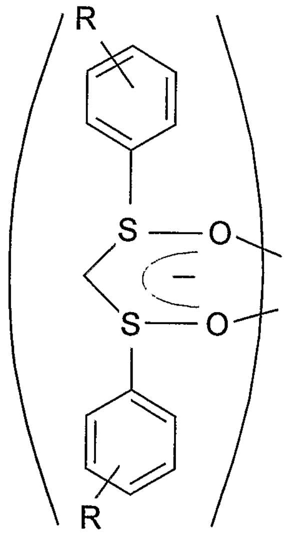
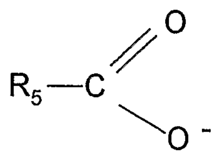
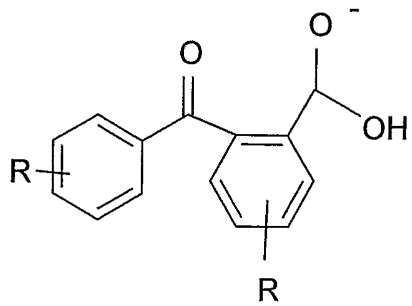


The different groups Lm, Ln and Lp may also be the same or different carboxylate groups

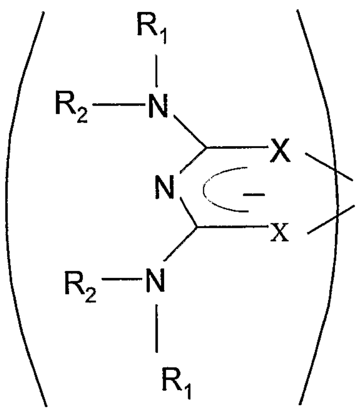


where R_5 is a substituted or unsubstituted aromatic, polycyclic or heterocyclic ring a polypyridyl group, R_5 can also be a 2-ethyl hexyl group so Ln is 2-ethylhexanoate or R_5 can be a chair structure so that Ln is 2-acetyl cyclohexanoate or L can be



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

The different groups Lm, Ln and Lp may also be



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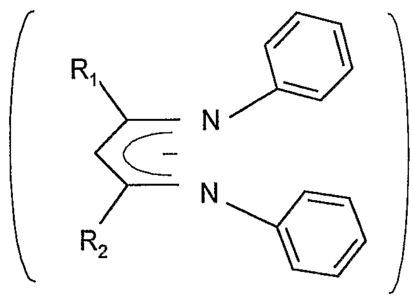

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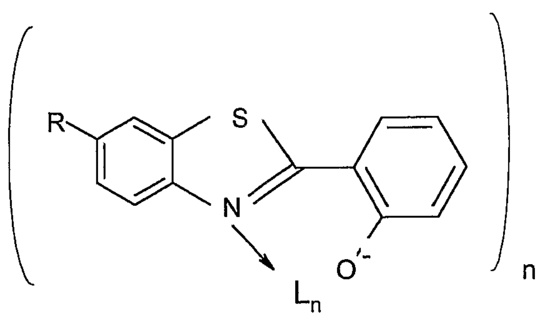


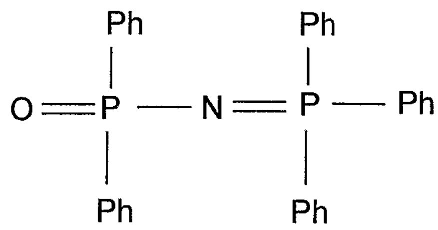
Large or complex molecular structures can be used in which a “cage” or “basket” structure is formed by the ligands Lm and Ln and Lp being condensed together and/or the metal atoms being linked by a hero atom or atoms such as oxygen, nitrogen etc.

For example the groups R, R_1, R_2 and R_3 on the ligands Lm and the groups R , R_1, R_2 and R_3 on the ligands Ln can form a condensed or ring structure e.g. substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures

Examples of such complexes are described in Chem. Abs. Vol 106 page 568, J. Chem. Soc. Dalton Trans 1993 pps 2379 to 2386 and in Inorg. Chem.1994, 33, 1230-1233;

Optionally there can also be a neutral ligand Lq linked to the metal M_1 and/or M_2

The groups Lq can be selected from

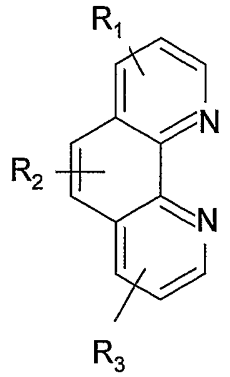


Where each Ph which can be the same or different and can be a phenyl (OPNP) or a substituted phenyl group, other substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic or polyclic group, a substituted or unsubstituted fused aromatic group such as a naphthyl, anthracene, phenanthrene, prylene or pyrene group. The substituents can be an alkyl, aralkyl, alkoxy, aromatic, heterocyclic, polyclic group, and halogen such as fluorine. Examples are given in figs. 1 and 2 of the drawings where R, R_1, R_2, R_4 and R_5 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_4 and R_5 can also 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

$$—C—CH_2=CH_2—R$$

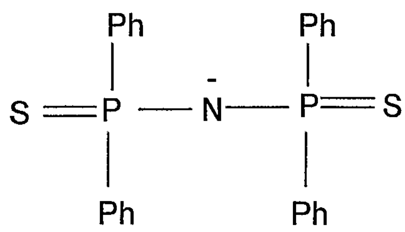
where R is as above.

Lq can also be compounds of formulae



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

Lq can also be



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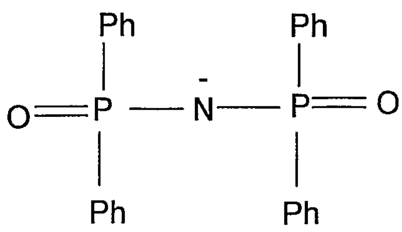


where Ph is as above.

Other examples of Lq 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 as shown in figs. 6 to 8.

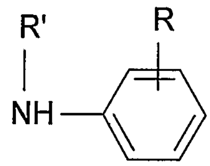
Specific examples of Lq are tripyridyl and TMHD, and TMHD complexes, α, α', α" tripyridyl, crown ethers, cyclans, cryptans phthalocyanans, porphoryins ethylene diamine tetramine (EDTA), DCTA, DTPA and TTHA. Where TMHD is 2,2,6,6-tetramethyl-3,5-heptanedionato and OPNP is diphenylphosphonimide triphenyl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

Preferred complexes of the present invention are shown in figs. 18, 19 and 20 of the drawings where L_3 are the ligands Lm, Ln or Lp.

The first electrode is preferably a transparent substrate which is 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 can be used. Conductive polymers and conductive polymer coated glass or plastics materials can also be used as the substrate.

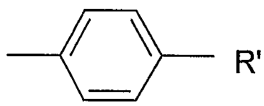
Preferably there is a layer of a hole transporting material between the first electrode and the layer of the electroluminescent material.

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



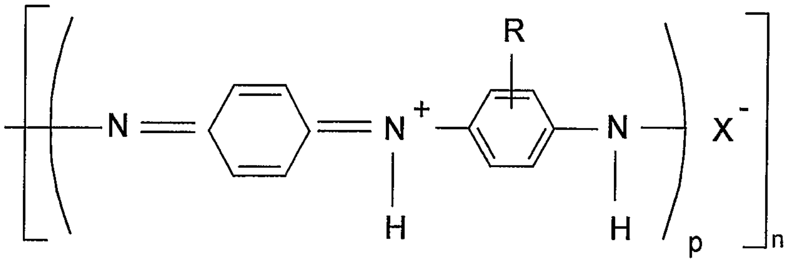
(XXVI)

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 the it can be easily evaporated i.e. the polymer is evaporable.

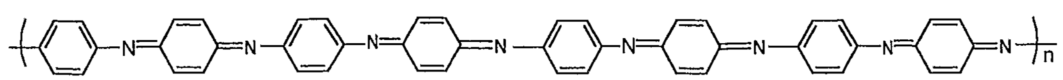
Preferably evaporable deprotonated polymers of unsubstituted or substituted polymer of an amino substituted aromatic compound are used. The de-protonated unsubstituted or substituted polymer of an amino substituted aromatic compound can be formed by deprotonating the polymer by treatment with an alkali 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 P319 1989.

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

Preferably the polymer is substantially fully deprotonated

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



This is referred to as DDPANI

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

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

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

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

The structural formulae of some other hole transporting materials are shown in Figures 11, 12 and 13 to 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 transmitting material between the cathode and the electroluminescent material layer, the electron transmitting material is a material which will transport electrons when an electric current is passed through electron transmitting materials include a metal complex such as a metal quinolate e.g. an aluminium quinolate, lithium quinolate a cyano anthracene such as 9,10 dicyano anthracene, a polystyrene sulphonate and compounds of formulae shown in figs. 9 and 10. Instead of being a separate layer the electron transmitting material can be mixed with the electroluminescent material and co-deposited with it.

In general the thickness of the layers is from 5nm to 500nm.

The second electrode functions as the cathode and can be any low work function metal e.g. aluminium, calcium, lithium, silver/magnesium alloys etc., aluminium is a preferred metal. Lithium fluoride can be used as the second electrode for example by having a lithium fluoride layer formed on a metal.

The hole transporting material can optionally be mixed with the electroluminescent material in a ratio of 5 - 95% of the electroluminescent material to 95 to 5% of the hole transporting compound.

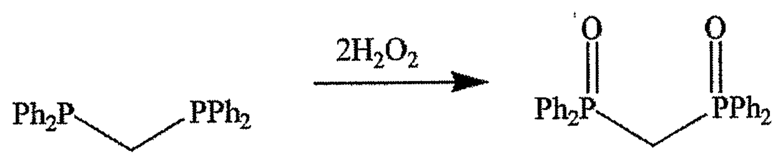
The hole transporting materials, the electroluminescent material and the electron injecting materials can be mixed together to form one layer, which simplifies the construction.

The electroluminescent material can be deposited on the substrate directly by evaporation from a solution of the material in an organic solvent. The solvent which is used will depend on the material but chlorinated hydrocarbons such as dichloromethane, n-methyl pyrrolidone, dimethyl sulphoxide, tetra hydrofuran dimethylformamide etc. are suitable in many cases.

Alternatively the material can be deposited by spin coating from solution or by vacuum deposition from the solid state e.g. by sputtering or any other conventional method can be used.

The invention is illustrated in the following examples in which Examples 1 to 9 show the synthesis of the ligands

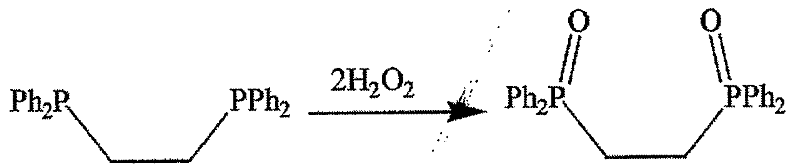
<u>Example 1- Methylene-bis(diphenylphosphbane oxide)</u>



To a solution of Bis(diphenylphospbino)methane (2.0g, 5.2mmol, *Sigma-Aldrich)* in 50mL ethanol was added 2 drops of 0.5M sodium hydroxide solution. Hydrogen peroxide (2.4mL 30%wt solution, 21.0mmol, BDH) was introduced dropwise over 1 minute, the reaction cooled to 5°C and stored for 3 hours. Heating to 60°C afforded complete dissolution of the white precipitate. Addition of deionised water until the cloud-point, followed by storage at 5°C for 12 hours yielded 2.0g (92%) of the desired product (colourless crystals), mp. 182-3°C.

Anal. Cald. for $C_{25}H_{22}O_2P_2$: C, 72.11; H, 5.33

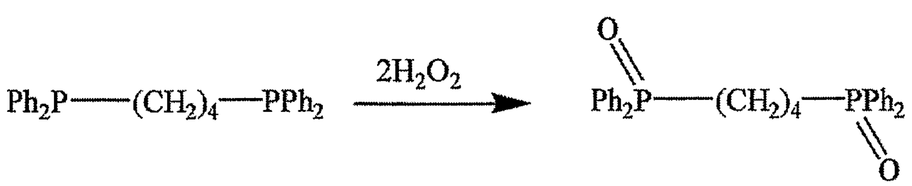
Example 2— Ethylene- 1 ,2-bis(diphenylphosphane oxide)



To a solution of 1,2-Bis(diphenylphosphino)ethane (2.0g. 5.0mmol, *Sigma-Aldrich)* in 50mL ethanol was added 2 drops of 0.5M sodium hydroxide solution. Hydrogen peroxide (2.3mL 30%wt solution, 20.0mmol, BDH) was introduced dropwise over 1 minute, the reaction cooled to 5°C and stored for 3 hours. Heating to 60°C afforded complete dissolution of the white precipitate. Addition of deionised water until the cloud-point, followed by storage at 5°C for 12 hours yielded 1.95g (90%) of the desired product (colourless crystals), mp. 271-3°C.

Anal. Cald. for $C_{26}H_{24}O_2P_2$: C, 72.55; H, 5.62; P, 14.39

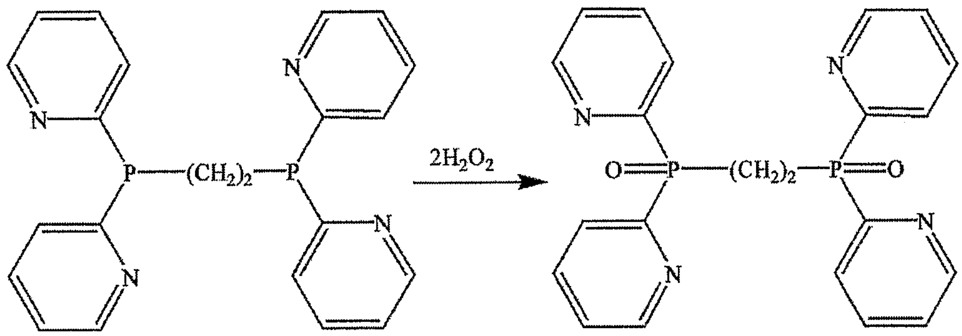
Example 3 Butylene-1,4-bis(diphenylphospane oxide)



To a solution of 1,4-Bis(diphenylphosphino)butane (2.0g. 4.7mmol, *Sigma-Aldrich)* in 50mL ethanol was added 2 drops of 0.5M sodium hydroxide solution. Hydrogen peroxide (2.3mL 30%wt solution, 20.0mmol, BDH) was introduced dropwise over 1 minute, the reaction cooled to 5°C and stored for 3 hours. Heating to 60°C afforded complete dissolution of the white precipitate. Addition of deionised water until the cloud-point, followed by storage at *5°C* for 12 hours yielded 1.80g (84%) of the desired product (colourless crystals), m.p.145°C.

Anal. Cald. for $C_{28}H_{28}0_2P_2$: C, 73.35; H, 6.16

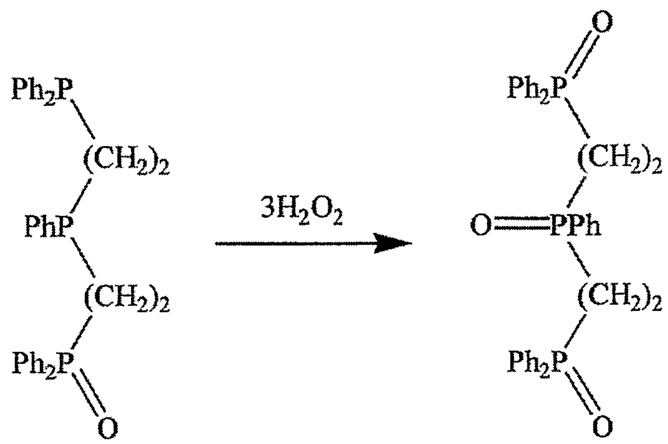
Example 4— Ethylene-1 ,4-bis(dipyridylphosphane oxide)



To a solution of 1,2-Bis(dipyridylphosphino)ethane (0.5g, 1.24mmol) in 50mL ethanol was added 2 drops of 0.5M sodium hydroxide solution. Hydrogen peroxide (0.5mL 30%wt solution, 5mmol, BDH) was introduced dropwise over 1 minute, the reaction cooled to 5°C and stored for 3 hours. Heating to 60°C afforded complete dissolution of the white precipitate. The product (0.5g. 93%) was recrystallised from methanol/water.

Anal. Cald. for $C_{22}H_{20}N_40_2P_2$:C, 60.83; H4.64; N, 12.80

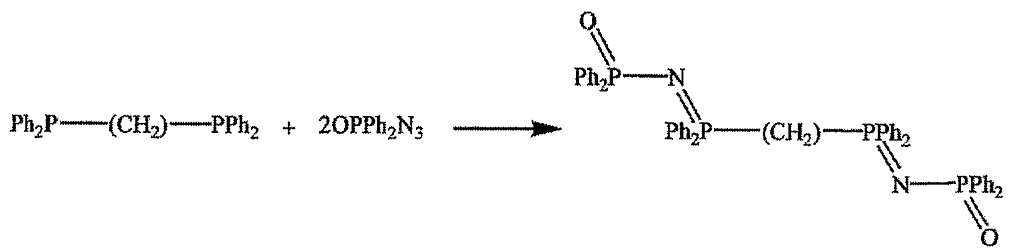
Example 5 — Bis(2-diphenylphosphane oxide-ethyl)phenylphosphane oxide



To a solution of Bis(2-diphenylphosphinoethyl)phenylphosphane (2.0g. 3.74mmol, *Sigma-Aldrich)* in 80mL ethanol was added 2 drops of 0.5M sodium hydroxide solution. Hydrogen peroxide (2.5mL 30%wt solution, 22.0mmol, BDH) was introduced dropwise over 1 minute, the reaction cooled to 5°C and stored for 3 hours. Heating to 60°C afforded complete dissolution of the white precipitate. Addition of deionised water until the cloud-point, followed by storage at 5°C for 12 hours yielded 1 .90g (90%) of the desired product (colourless crystals), mp. 304-5°C.

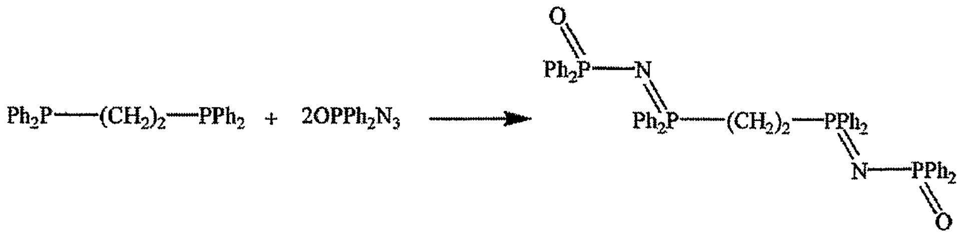
Anal. Cald. for $C_{34}H_{33}0_3P_3$: C, 70.10; H, 5.71

Example 6 - Methylene-bis(diphenylphosphinimino-phosphane oxide)



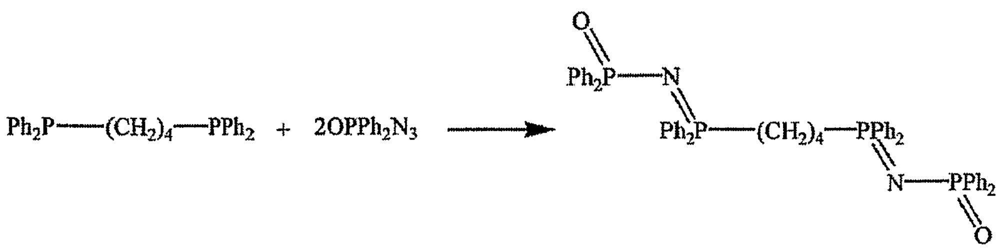
Diethylether (50mL, dried and distilled over sodium) was added to Bis(diphenylphosphino)methane (2.0g. 5.2mmol, *Sigma-Aldrich)* in a three-necked flask equipped with condenser, pressure-equalising dropping funel and under a nitrogen atmosphere. Diphenylazidophosphane (2.78g, 11.0mmol) in dry diethylether (l00mL) was added dropwise over 15 minutes to the suspension. A further 50mL diethylether was used to rinse the pressure-equalising dropping funnel, which was subsequently removed and the reaction refluxed for 3 hours. After stirring for 15 hours at room temperature, a white precipitate (3.0g. 71%) was filtered and washed with diethylether. Recrystallisation from toluene/hexane yielded an analytically pure sample, m.p. 208-9°C. Anal. Cald. for $C_{49}H_{42}N_20_2P_4$: C, 72.23; H, 5.20; N, 3.44

Example 7- Ethylene-1 ,2-bis(diphenylphosphinimino-phosphane oxide)



Diethylether (50mL, dried and distilled over sodium) was added to 1,2-Bis(diphenylphosphino)ethane (4.0g, 10.0mmol, *Sigma-Aldrich)* in a three-necked flask equipped with condenser, pressure-equalising dropping funnel and under a nitrogen atmosphere. Diphenylazidophosphane (6.0g. 25.0mmol) in dry diethylether (l00mL) was added dropwise over 15 minutes to the suspension. A further 50mL diethylether was used to rinse the pressure-equalising dropping funnel, which was subsequently removed and the reaction refluxed for 3 hours. After stirring for 15 hours at room temperature, a white precipitate (7.95g, 96%) was filtered and washed with diethylether. Recrystallisation from ethanol/water yielded an analytically pure sample, m.p. 230°C. Anal. Cald. for $C_{50}H_{44}N_20_2P_4$: C, 72.46; H, 5.35; N, 3.38; P, 14.95.

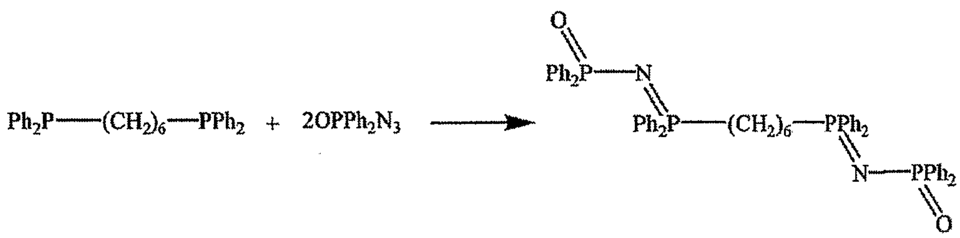
Example 8 Butylene-1,4-bis(diphenylphosphinimo-phosphane oxide)



Diethylether (50mL, dried and distilled over sodium) was added to 1,4-Bis(diphenylphosphino)butane (2.5g, 5.86mmol, *Sigma-Aldrich)* in a three-necked flask equipped with condenser, pressure-equalising dropping funnel and under a nitrogen atmosphere. Diphenylazidophosphane (2.71g. 11.2mmol) in dry diethylether

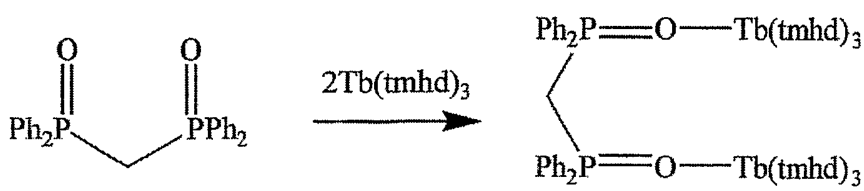
(50mL) was added dropwise over 15 minutes to the suspension. A further 50mL diethylether was used to rinse the pressure-equalising dropping funnel, which was subsequently removed and the reaction refluxed for 3 hours. After stirring for 15 hours at room temperature, a white precipitate (4.27g, 85%) was filtered and washed with diethylether. Recrystallisation from toluene/hexane yielded an analytically pure sample, m.p. 206-7°C. Anal. Cald. for $C_{52}H_{48}N_{2}0_{2}P_{4}$: C, 72.89; H, 5.65; N, 3.27

Example 9- Hexylene-1,6-bis(diphenylphosphinimino-phosphane oxide)



Diethylether (50mL, dried and distilled over sodium) was added to 1,6-Bis(diphenylphosphino)hexane (2.5g, 5.Smmol, *Sigma-Aldrich)* in a three-necked flask equipped with condenser, pressure-equalising dropping funnel and under a nitrogen atmosphere. Diphenylazidophosphane (2.56g, 10.Smmol) in dry diethylether (50mL) was added dropwise over 15 minutes to the suspension. A further 5OmL diethylether was used to rinse the pressure-equalising dropping funnel, which was subsequently removed and the reaction refluxed for 3 hours. After stirring for 15 hours at room temperature, a white precipitate (3.3g, 68%) was filtered and washed with diethylether. Recrystallisalion from toluene/hexane yielded an analytically pure sample, m.p. 245°C. AnaL Cald. for $C_{54}H_{52}N_{2}0_{2}P_{4}$: C, 73.29; H, 5.92; N, 3.16

Example 10 Methylene-bis(diphenylphosphane oxide)-bis-[terbium tris(tetramethylheptanedione)



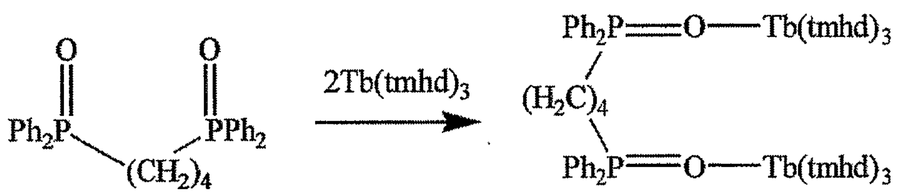
1.18g (2.83mmol) of Methylene-bis(diphenylphosphane oxide) and 4.0g (5.66mmol)

Terbium tris(tetramethylheptanedione) were dissolved in 80mL chloroform. The solution was heated for 1 hour and the solvent removed under vacuum to yield an oily residue. Addition of acetonitrile gave a white precipitate (4.0g. 77%), which was filtered, washed with further acetonitrile and dried under vacuum at 80°C, mp. 195°C.

Anal. Cald. for $C_{91}H_{136}0_{14}P_2Tb_2$:C, 59.60; H, 7.48;P,3.38.

Photoluminescence: $PL_{:eff.}$:0.28cd $m^{-2}\mu mW^{-1}$ @630μW; peak=548nm CIE coordinates x: 0.32, y: 0.61.

Example 11- Butylene-bis(diphenylphosphane oxide)-bis[terbium tris(tetramethylheptanedione)]



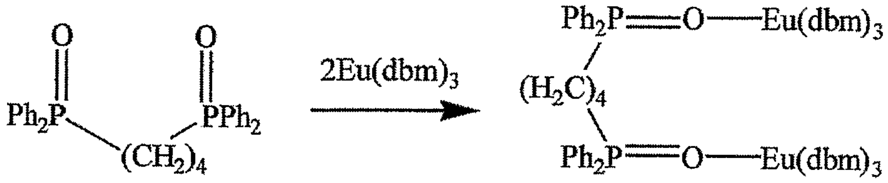
0.50g (1.09mmol) of Butylene-bis(diphenylphosphane oxide) and 1.55g (2.18mmol) Terbium tris(tetramethylheptanedione) were dissolved in 80mL chloroform. The solution was heated for 1 hour and the solvent removed under vacuum to yield an oily residue. Addition of acetonitrile gave a white precipitate (3.Og, 94%), which was filtered, washed with further acetonitrile and dried under vacuum at 80°C, m.p. 212°C. Anal. Cald. for $C_{94}H_{142}0_{14}P_2Tb_2$: C, 60.18; H 7.63; Tn, 16.04

Photoluminescence:

$PL_{:eff.}$:0.25cd $m^{-2}\mu mW^{-1}$ @870μW; peak=545nm CIE coordinates x: 0.31, y: 0.62.

(Terbium tris(tetramethylheptanedione) was prepared from Tetramethyiheptanedione, Terbium (III) chloride and Ammonium hydroxide. It is also available commercially.)

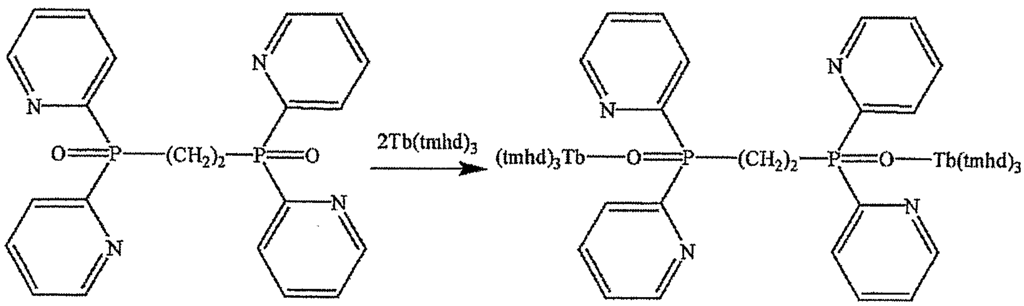
Example 12 Butylene –bis(diphenylphosphane oxide)-bis[europium tris(dibenzoylmethane)]



0.50g (1.09mmol) of Butylene-bis(diphenylphosphane oxide) and 1.79g (2.18mmol) Europium tris(dibenzoylmethane) were dissolved in 80mL chloroform. The solution was heated for 1 hour and the solvent reduced under vacuum to approximately 2mL. Petroleum ether (40-60°C) was added until the cloud point, the reaction cooled to 5°C and stored until a yellow precipitate had formed. This was filtered (2.1g, 92%), washed with petroleum ether (40-60°C) and dried under vacuum at 80°C, mp. 212°C. Anal. Cald. for $C_{118}H_{94}O_{14}P_2Eu_2$:C, 67.43; H, 4.51

Photoluminescence:$PL_{:eff.}$:0.12cd $m^{-2}\mu mW^{-1}$ @800μW; peak=613nm CIE coordinates x: 0.66, y: 0.33.

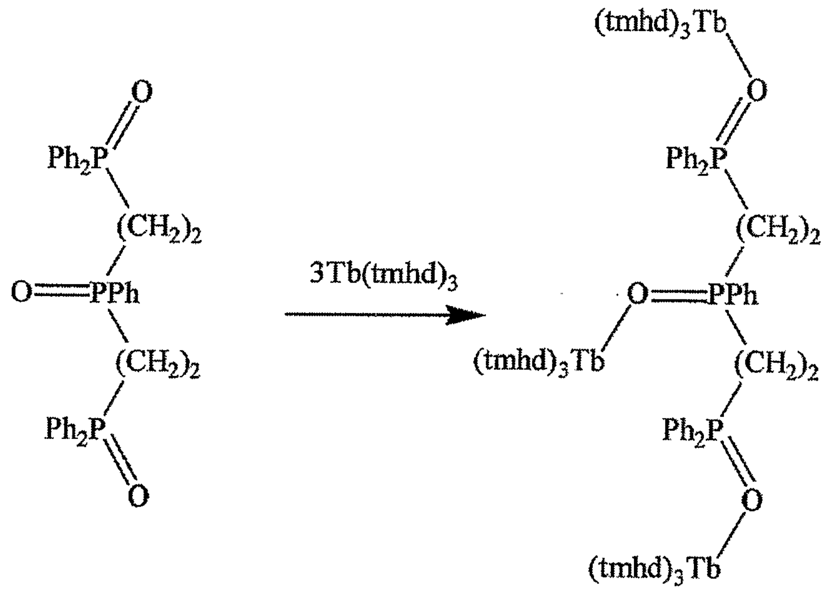
Example 4-Ethylene-bis(dipyridylphosphane oxide)-bis[terbium tris(tetramethylheptanedione)]



0.34g (0.78mmol) of Ethylene-bis(diphenylphosphane oxide) and 1.1 ig (1.57mmol) Terbium tris(tetramethylheptanedione) were dissolved in 60mL chloroform. The solution was heated for 1 hour and the solvent removed under vacuum to yield an oily residue. Acetonitrile was added and the white precipitate was filtered and washed

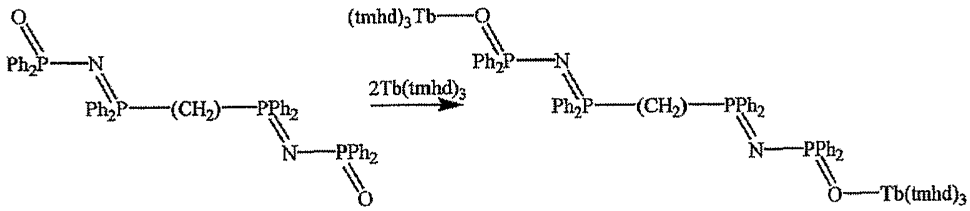
with further acetonitrile. This was recrystallised from toluene/hexane and dried under vacuum at 80°C to give an analytically pure sample (1 .2g, 83%), m.p. 240-241.5 °C. Anal. Cald. for $C_{88}H_{134}N_4O_{14}P_2Tb_2$: C, 57.08; C, 56.97;
Photoluminescence:$PL_{:eff.}$:0.26cd $m^{-2}\mu mW^{-1}$ @880μW; peak=548nm CIE coordinates x: 0.31, y: 0.62.

Example 13



1.0g (1.72mmol) of Bis(2-diphenylphosphane oxide-ethyl)phenylphosphane oxide was dissolved dissolved in 80mL chloroform. 3.65g (5.l5mmol) Terbium tris(tetramethylheptanedione) was dissolved in l20miL acetonitrile. The two solutions were mixed at 60°C and heated for 1 hour. The solvent reduced under vacuum to yield an oily residue. Acetonitrile was added to afford a white precipitate (3.9g. 84%), which was collected and washed with further acetonitrile. An analytical sample was recrystallised from toluene/hexane and dried under vacuum at 80°C, nip. 202-6°C. Anal Cald. for $C_{94}H_{142}0_{14}P_2Tb_2$: C, 60.18; H, 7.63; Tb 16.95
Photoluminescence: $PL_{:eff.}$:0.27cd $m^{-2}\mu mW^{-1}$ @880μW; peak=548nm CIE coordinates x: 0.31, y: 0.62.

Example 14 - Methylene-bis(diphenylphosphinimino-phosphane oxide)-bis~terbium tris(tetramethytheptanedione)]

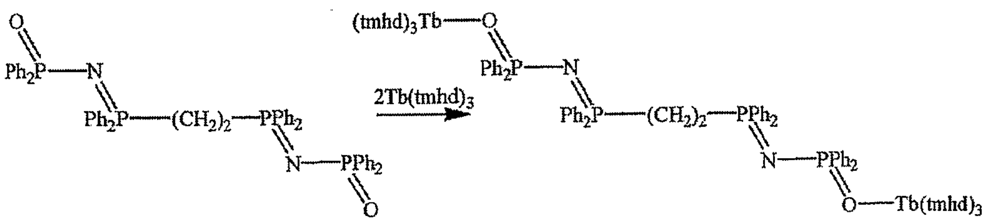


0.57g (0.71 mmol) of Methylene-bis(diphenylphosphinimino-phosphane oxide) and 1.0g (1.4lmmol) Terbium tris(tetramethylheptanedione) were dissolved in 80mL chloroform. The solution was heated for 1 hour and the solvent removed under vacuum to yield an oily residue. Addition of acetonitrile gave a white precipitate (1.4g. 89%), which was filtered, washed with further acetonitrile and dried under vacuum at 80°C, m.p. 275-7°C.

Anal. Cald. for $C_{115}H_{156}N_2O_{14}P_4Tb_2$: C,61.88; H,7.04; N,1.25; P, 5.55; Tb, 14.94

Photoluminescence: $PL_{:eff.}$:0.28cd $m^{-2}\mu mW^{-1}$ @630μW; peak=548nm CIE coordinates x: 0.32, y: 0.61.

Example 15- Ethylene-bis(diphenylphosphinimino-phosphane oxide)-
bis[terbium tris(tetramethylheptanedione)]

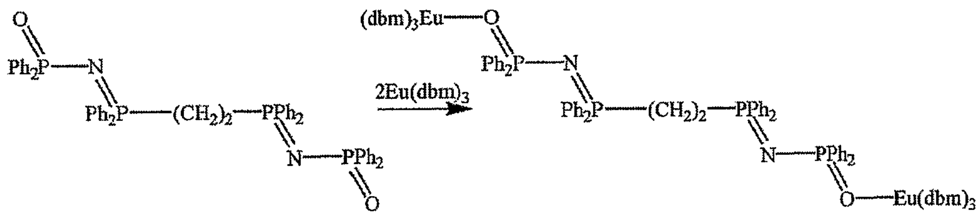


0.585g (0.7lmmol) of Ethylene-bis(diphenylphosphinimino-phosphane oxide) and 1.0g (1.4lmmol) Terbium tris(tetramethylheptanedione) were dissolved in 100mL chloroform. The solution was heated for 1 hour and the solvent removed under vacuum to yield an oily residue. Addition of acetonitrile gave a white precipitate (1.4g. 88%), which was filtered, washed with further acetonitrile and dried under vacuum at 80°C, mp. 240-2°C.

Anal. Cald for for $C_{116}H_{158}N_2O_{14}P_4Tb_2$:C, 62.03; H, 7.09; N, 1.25; P, 5.52; Tb, 14.15

Photoluminescence: $PL_{:eff.}$:0.23cd $m^{-2}\mu mW^{-1}$ @630μW; peak=547nm CIE coordinates x: 0.31, y: 0.62.

Example 16 - Ethylene-bis(diphenylphosphinimino-phosphane oxide)-bis~europium tris(dibenzoyhnethane)]

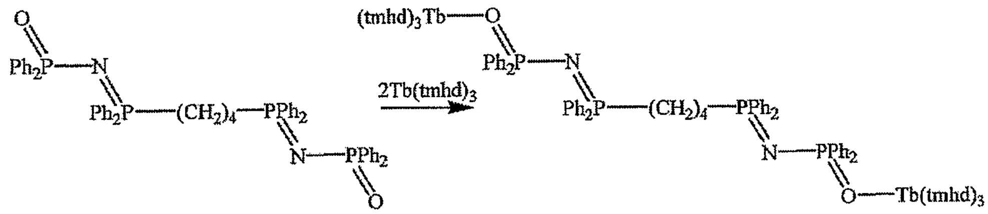


1.01 g (1.22mmol) of Ethylene-bis(diphenylphosphinimino-phosphane oxide) and 2.0g (2.43mmol) Europium tris(dibenzoyhnethane) were dissolved in 50mL dichioromethane. The solution was heated for 1 hour and the solvent removed under vacuum to yield an oily residue. Recrystallisation from toluene/petroleum ether (40-60°C) afforded yellow/orange crystals (2.5g, 83%), which were filtered, washed with further petroleum ether (40-60°C) and dried under vacuum at 80°C, m.p. 236-8°C.

Anal for $C_{140}H_{110}N_2O_{14}P_4Eu_2$ C, 68.02; H, 4.48; N, 1.13; P, 5.01; Eu, 12.29

Photoluminescence: $PL_{:eff.}$:0.0.08cd $m^{-2}\mu mW^{-1}$ @820μW; peak=612nm CIE coordinates x: 0.66, y: 0.33.

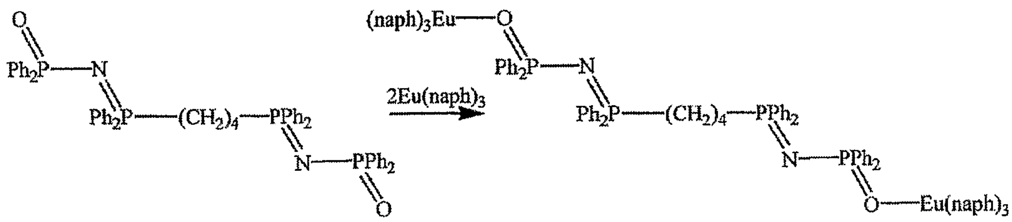
Example 17- Butylene-bis(diphenylphosphinimino-phosphane oxide)-bis~terbium tris(tetramethylheptanedione)]



0.5g (0.58mmol) of Butylene-bis(diphenylphosphinimino-phosphane oxide) and 0.83g (1.17mmol) Terbium tris(tetramethytheptanedione) were dissolved in 80mL chloroform. The solution was heated for 1 hour and the solvent removed under vacuum to yield an oily residue. Addition of acetonitrile gave a white precipitate (0.8g. 60%), which was filtered, washed with further acetonitrile and dried under vacuum at 80°C, m.p. 248-250°C.

Anal Cald. for $C_{118}H_{162}N_2O_{14}P_4Tb_2$ C, 62.32; H, 7.18; N, 1.23; P, 5.45; Tb, 13.98

Example 18 Butylene-bis(diphenylphosphinimino-phosphane oxide)- bis{ europium tris~4,4,4-trifluoro-l-(2-naphthyl)-1 ,3~butanedione}}



0.53g (0.62mmol) of Butylene-bis(diphenylphosphinimino-phosphane oxide) and 1.1 7g (1.24mmol) Europium tris~4,4,4-trifluoro-1-(2-naphthyl)-l,3-butanedione] were dissolved in 100mL dichloromethane. The solution was heated for 1 hour and the solvent reduced to approximately 2mL. Petroleum ether (40-60°C) was added until the cloud point. Storage at 5°C for 3 hours yielded a yellow precipitate (1.0g, 59%). This was filtered, washed with further petroleum ether (40-60°C) and dried under vacuum at 80°C, m.p. 184°C (T_g - 82°C).

Anal. Cald. for $C_{136}H_{96}N_{2}O_{14}F_{15}P_{4}Eu_{2}$:C, 59.36; H, 3.52; N, 1.02

Photoluminescence: $PL_{:eff.}$:0.0.08cd $m^{-2}\mu mW^{-1}$ @820μW; peak=612nm CIE coordinates x: 0.66, y: 0.33.

(Europium tris~4,4,4-trifluoro-I-(2-naphthyl)-I,3-butanedione] was synthesised from Europium (III) chloride, 4,4,4-Trifluoro-1-(2-naphthyl)-1,3-butanedione *(Fluorochem)* and Ammonium hydroxide.)

Example 19 - Electroluminescent Device

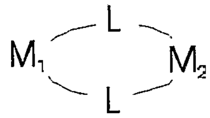
An electroluminescent device was made by depositing sequentially from solution onto a indium tin oxide glass anode layers of DDPANI 8nm; α-NPB; an electroluminescent layer comprising a compound made as in Example 14; aluminium quinolate and an aluminium cathode. The device is shown schematically in fig. 21 where (1) is the ITO anode; (2) is a DDPANI layer; (3) is an α-NPB layer; (4) is the electroluminescent layer comprising a compound made as in Example 14; (5) is an aluminium quinolate layer and (6) is an aluminium cathode.

An electric current was passed between the aluminium cathode and ITO anode and the device emitted a green light with a peak wavelength λ_{max} of 546 nm. The properties were measured and the results shown in figs. 22 and 23. Another device was made replacing the electroluminescent layer with a compound of formula as in Example 16, the device emitted a red length with a peak wavelength λ_{max} of 611nm .

Claims

1. An electroluminescent device which comprises sequentially a first electrode, a layer of an electroluminescent compound and second electrode in which the electroluminescent compound is selected from binuclear, trinuclear and polynuclear complexes of a mixture of rare earth metals and non rare earth metals.

2. An electroluminescent device as claimed in claim 1 in which the electroluminescent compound has the formula



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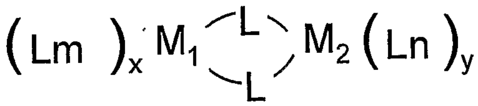
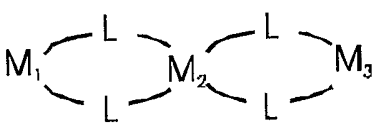


where L is a bridging ligand and where M_1 is one or more rare earth metals and M_2 is one or more non rare earth metals Lm and Ln are the same or different organic ligands, x is the valence state of Lm and y is the valence state of Ln.

3. An electroluminescent device as claimed in claim 1 in which the electroluminescent compound has the formula



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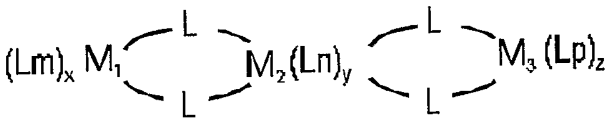

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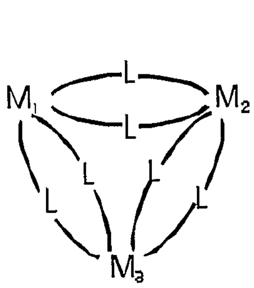

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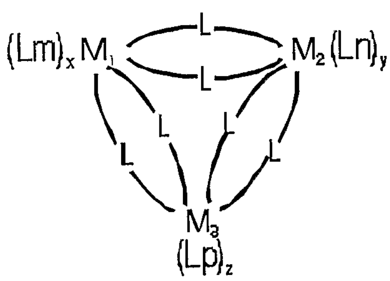
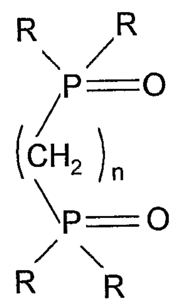


where L is a bridging ligand and where at least one of M_1, M_2 and M_3 is a rare earth metal and at least one of which is a non rare earth metal; Lm, Ln and Lp are organic ligands and x is the valence state of M_1, y is the valence state of M_2 and z is the valence state of M_3

4. An electroluminescent device as claimed in claim 2 or 3 in which the ligand L has the formula

or



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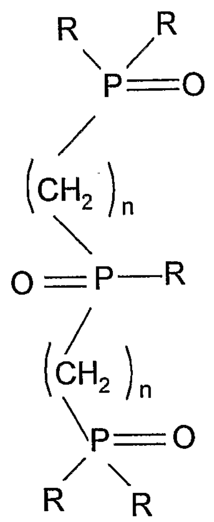
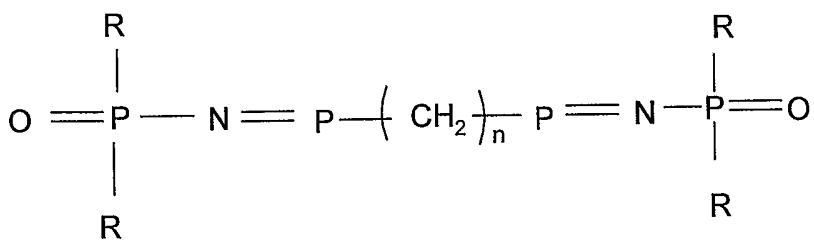




where the groups R which can be the same or different are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoryl methyl groups, halogens such as fluorine or thiophenyl groups and n is from 1 to 10 or as in fig. 17 of the drawings.

5. An electroluminescent device as claimed in any one of claims 1 to 4 in which M_1 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), Er(III), Yb(III) and more preferably Eu(III), Tb(III), Dy(III), Gd (III).

6. An electroluminescent device as claimed in any one of claims 1 to 5 in which 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, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium.

7. An electroluminescent device as claimed in any one of claims 1 to 4 in which the groups Lm and Ln are the same or different and in which the groups Lm and Ln are selected from the groups as specified herein.

8. An electroluminescent device as claimed in any one of the preceding claims in which the groups Lm and Ln are linked together.

9. An electroluminescent device as claimed in claim 7 or 8 in which the groups R, R_1, R_2 and R_3 on the ligands Lm and the groups R , R_1, R_2 and R_3 on the ligands Ln as specified herein are linked together to form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures

10. An electroluminescent device as claimed in any one of the preceding claims in which there is a neutral ligand Lq, as herein specified linked to the metal M_1 and/or M_2 and/or M_3.

11. An electroluminescent device as claimed any one of the preceding claims in which there is a layer of a hole transmitting material between the first electrode and the electroluminescent layer.

12. An electroluminescent device as claimed in claim 11 in which the hole transmitting material is a film of an aromatic amine complex

13. An electroluminescent device as claimed in claim 11 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.

14. An electroluminescent device as claimed in claim 11 in which the hole transmitting material is a film of a compound of formula (II) or (III) herein or as in figure 1, 2, 3, or 4 of the drawings.

15. An electroluminescent device as claimed in any one of claims 1 to 14 in which there is a layer of an electron transmitting material between the cathode and the electroluminescent material layer.

16. An electroluminescent device as claimed in claim 15 in which the electron transmitting material is a metal quinolate.

17. An electroluminescent device as claimed in claim 15 in which the metal quinolate is an aluminium quinolate or lithium quinolate

18. An electroluminescent device as claimed in claim 15 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 fig. 5.

19. An electroluminescent device as claimed in any one of the preceding claims in which the second electrode is selected from aluminium, calcium, lithium, silver/magnesium alloys

20. An electroluminescent device as claimed in claim 19 in which there is a lithium fluoride layer formed on a metal.

21. An electroluminescent device as claimed in any one of the preceding claims in which the electroluminescent compound is as in figs. 18 or 19 of the drawings.

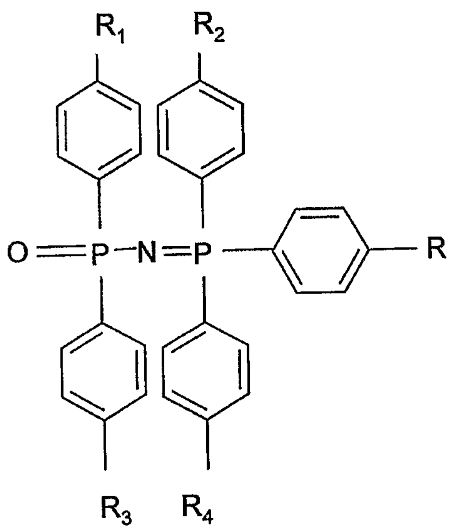


Fig. 1

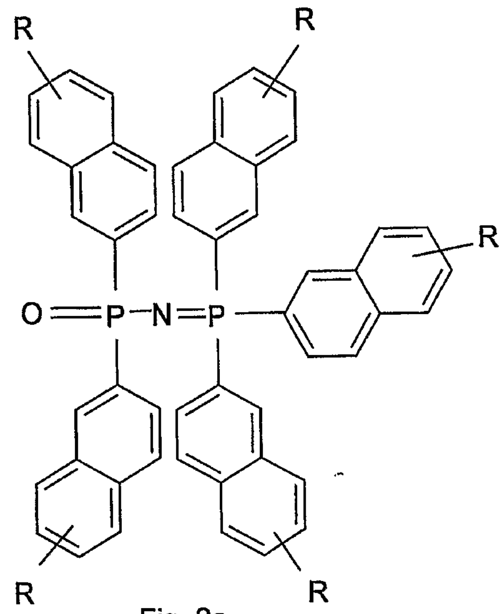


Fig. 2a

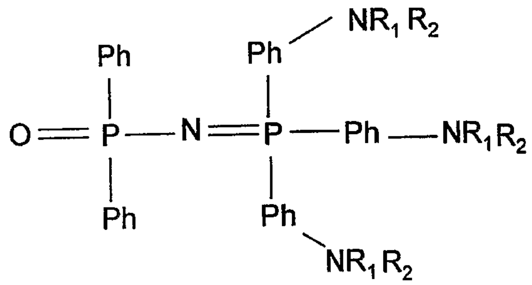


Fig. 2b

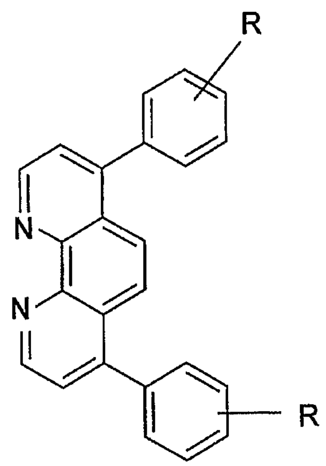


Fig. 3

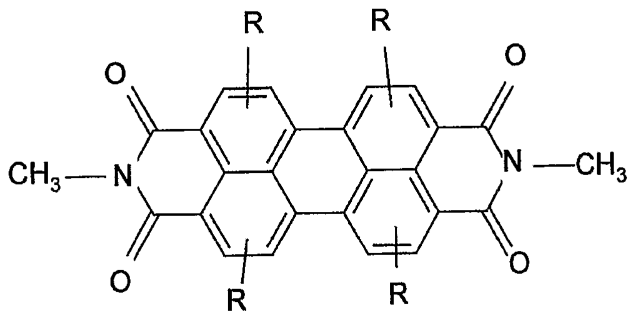


Fig. 4a

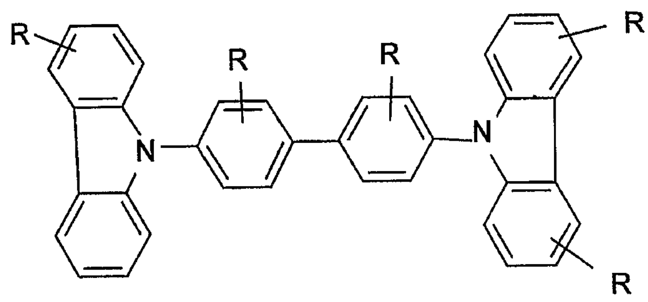


Fig. 4b

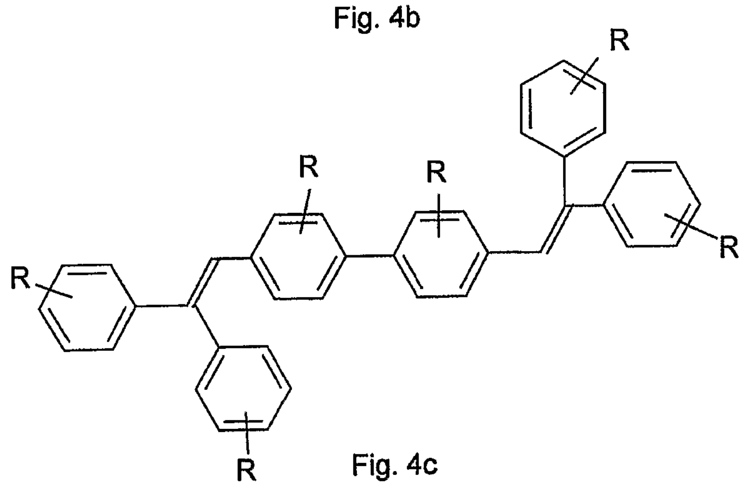


Fig. 4c

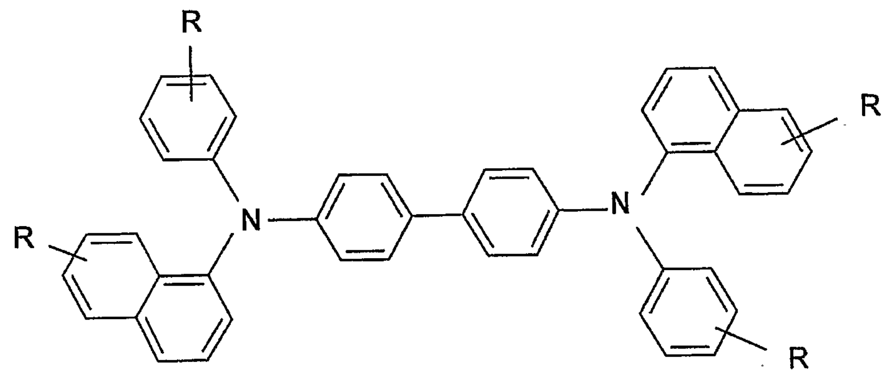


Fig. 4d

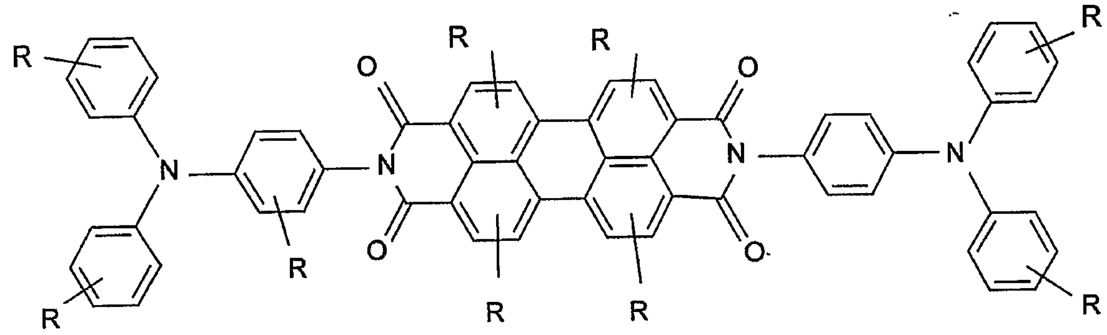


Fig. 4e

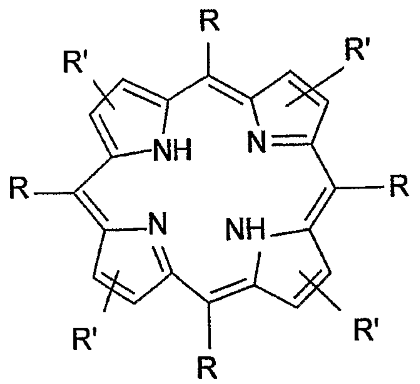


Fig. 4f

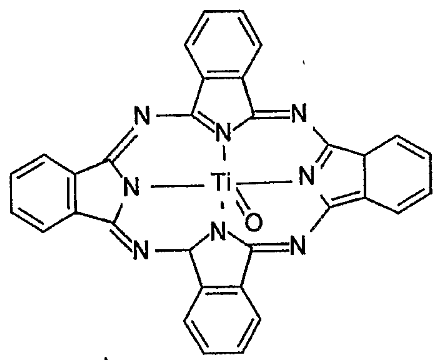


Fig. 4g

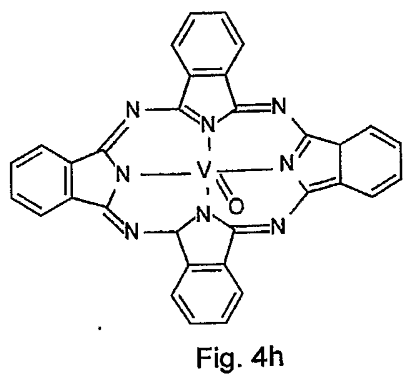


Fig. 4h

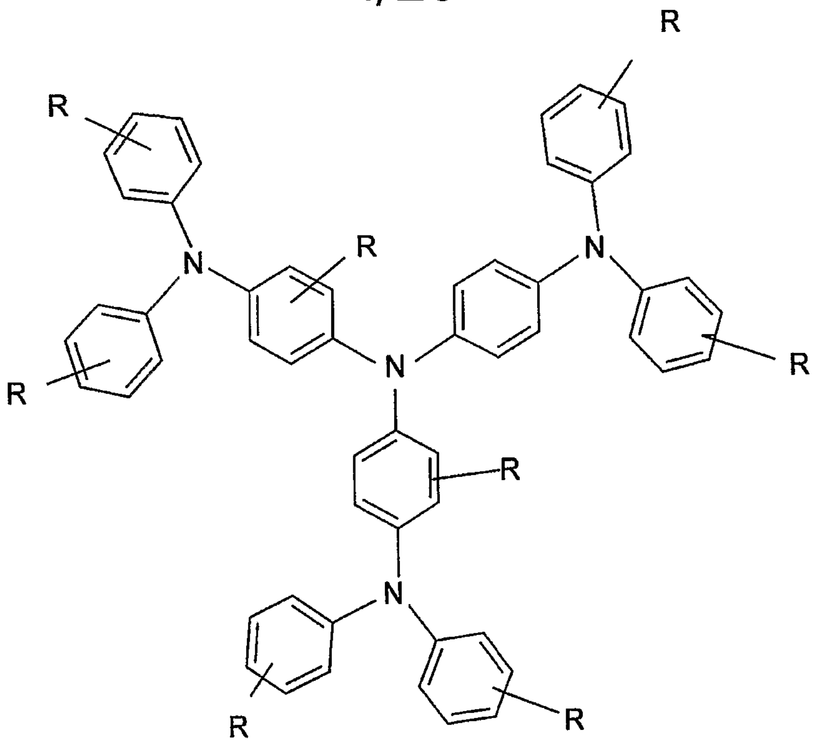


Fig. 4i

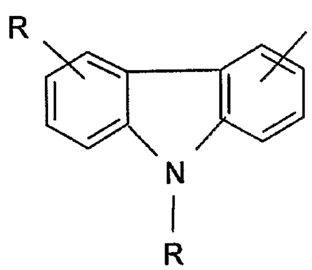


Fig. 4j

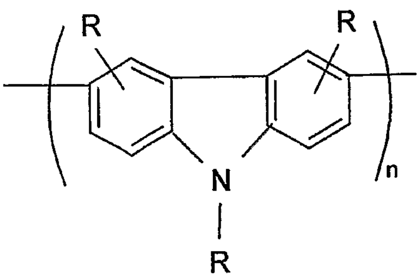


Fig.4k

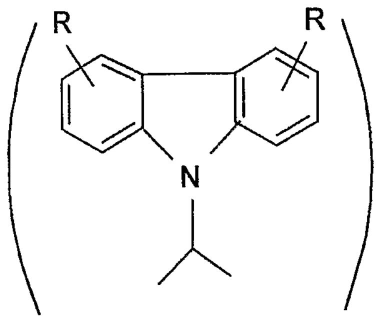


Fig. 4l

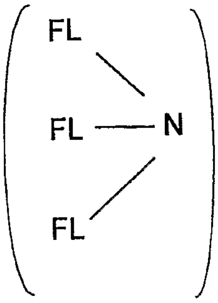


Fig. 5a

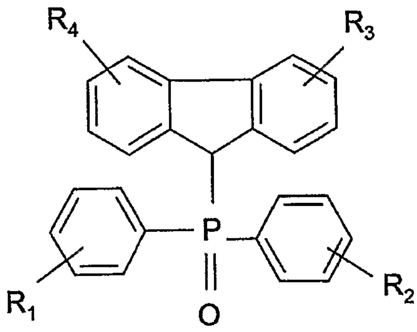


Fig.5b

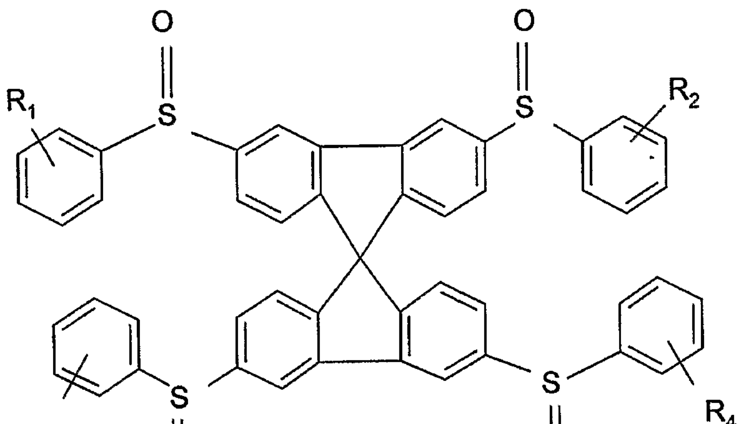


Fig. 5C

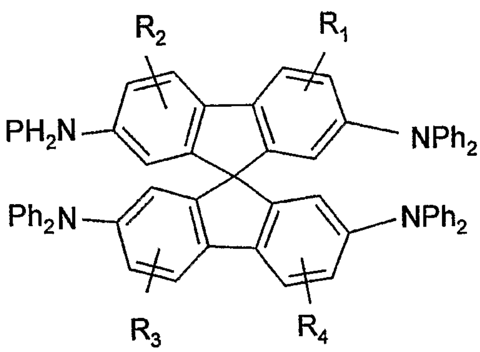


Fig. 5d

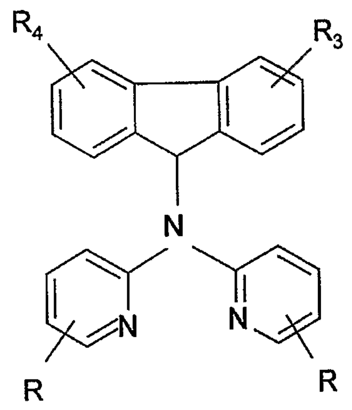


Fig. 5f

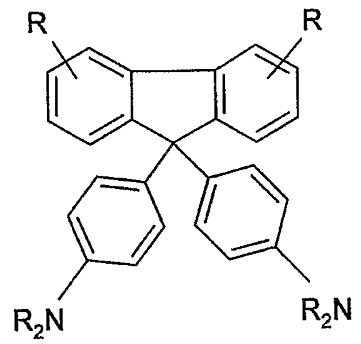


Fig. 5g

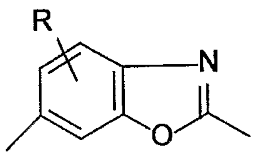


Fig. 6a

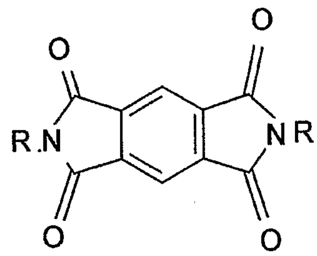


Fig 6b

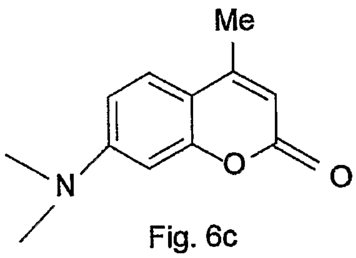


Fig. 6c

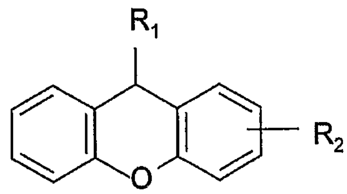


Fig. 6d

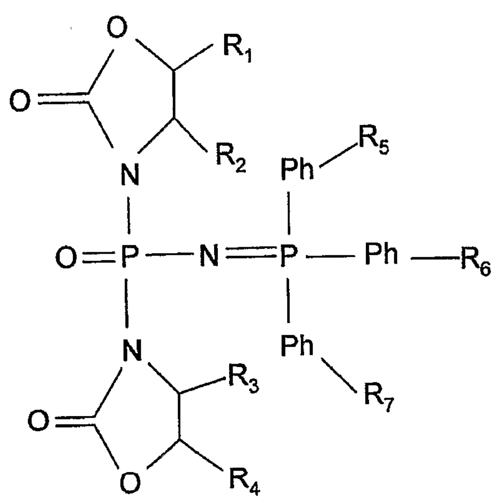


Fig. 6e

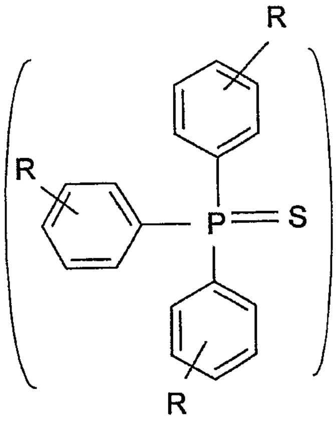


Fig. 7a

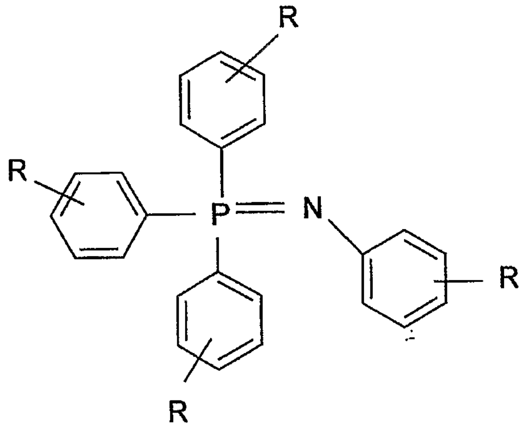


Fig. 7b

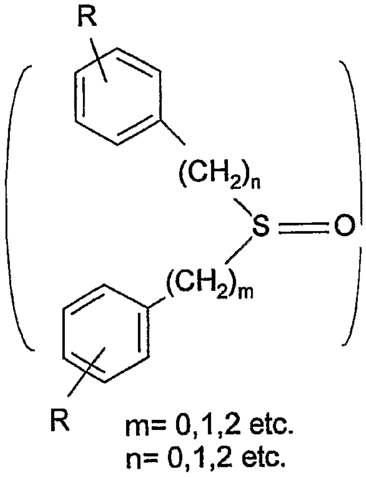


Fig. 7c

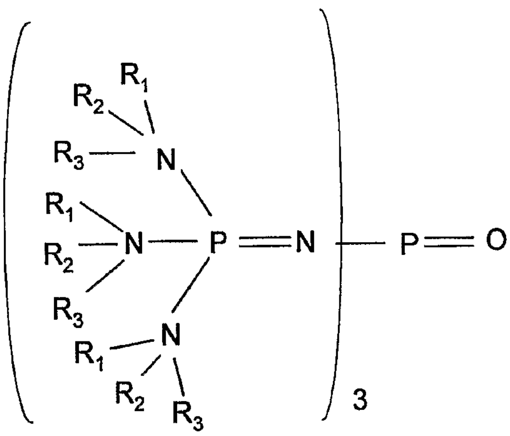


Fig. 7d

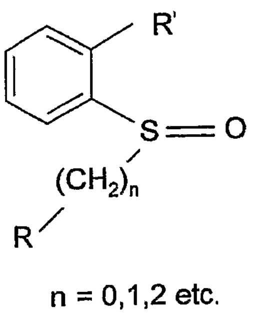


Fig. 7e

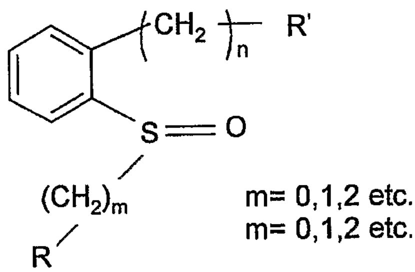


Fig. 7f

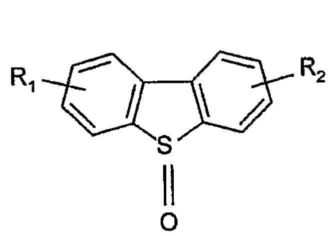


Fig. 8a

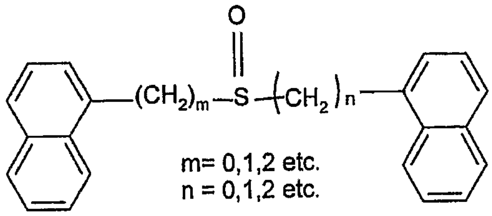


Fig. 8b

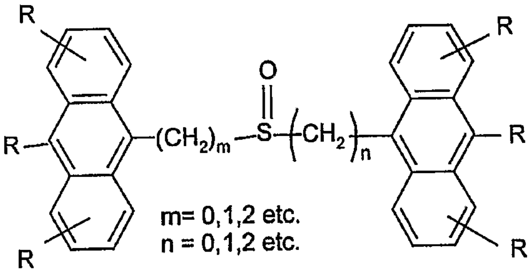


Fig. 8c

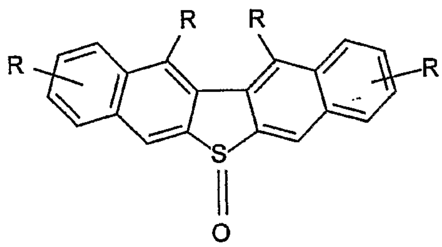


Fig.8d

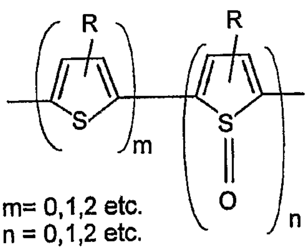


Fig. 8e

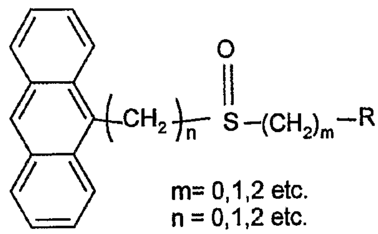


Fig. 8f

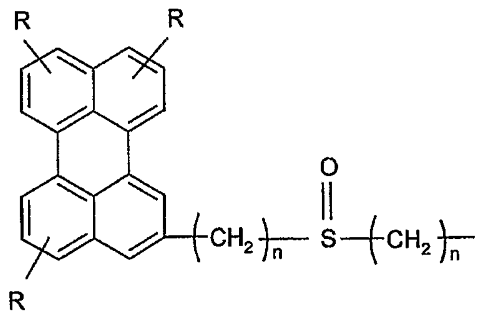


Fig. 8g

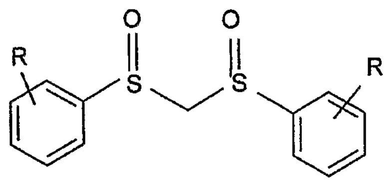
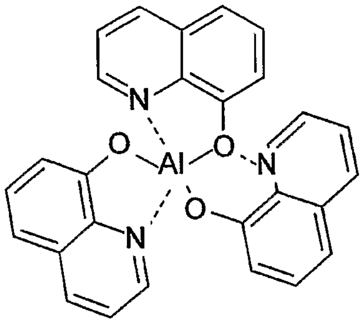
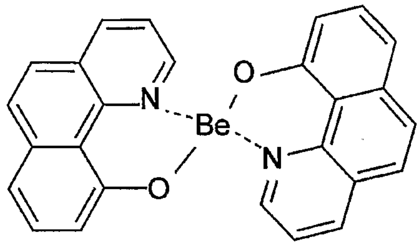


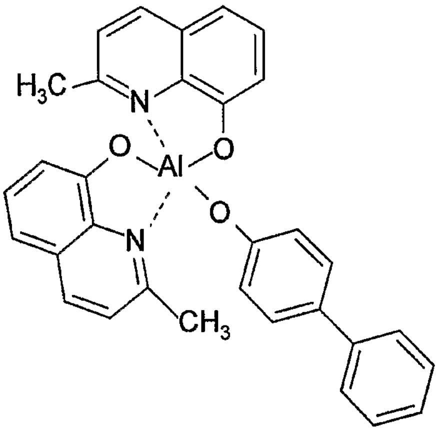
Fig. 8g



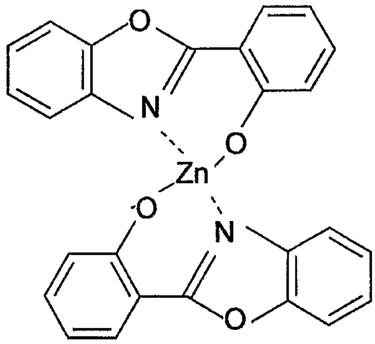
Alq



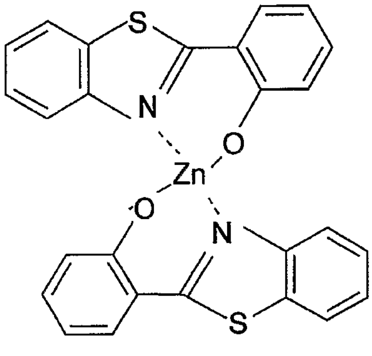
Bebq



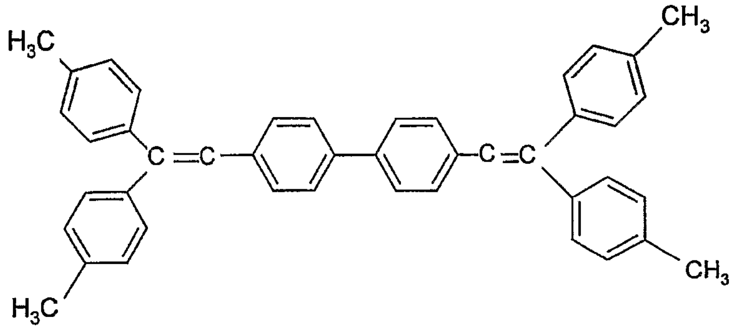
BAlq1



ZnPBO

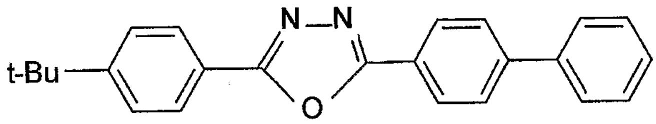


ZnPBT

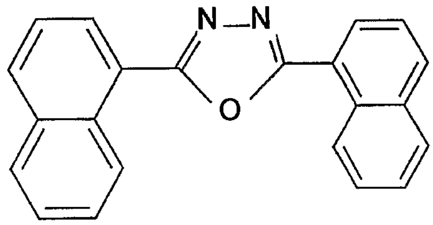


DTVb1

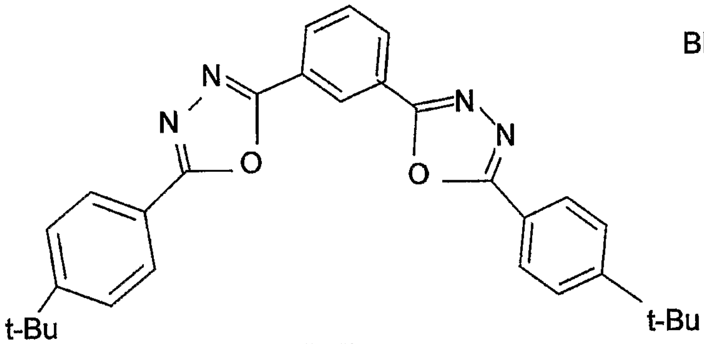
Fig. 9



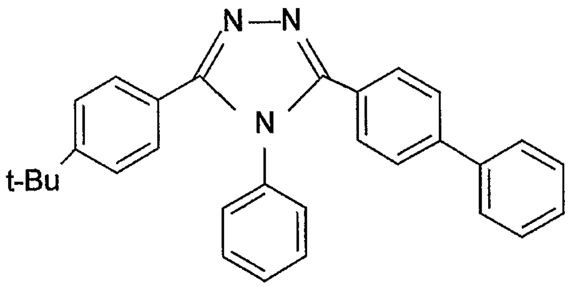
t-Bu-PBD



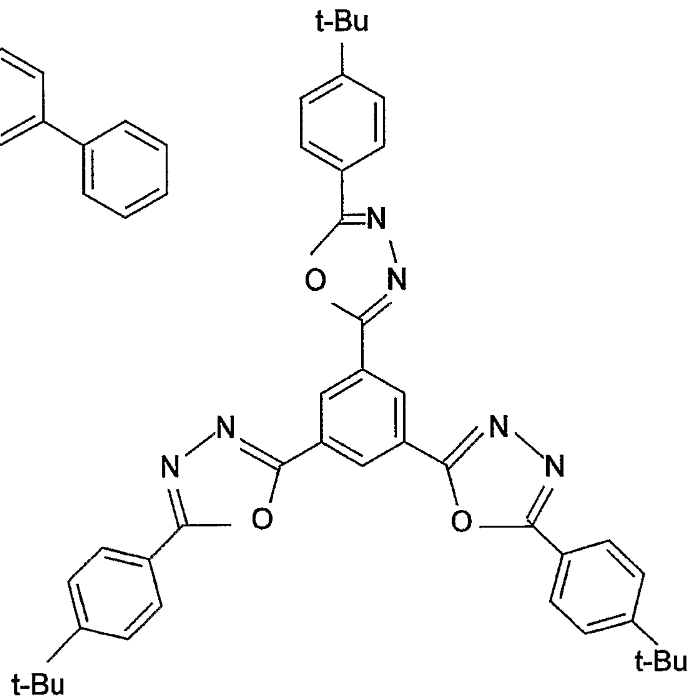
BND



OXD-7

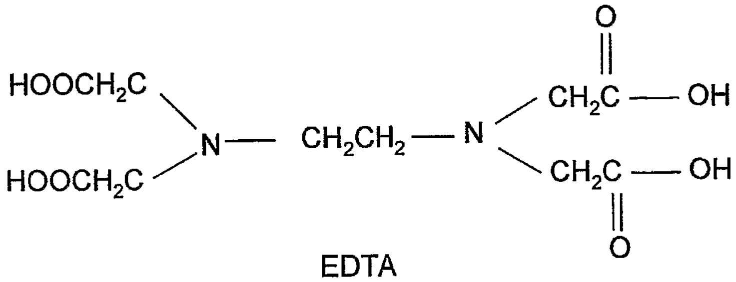


TAZ

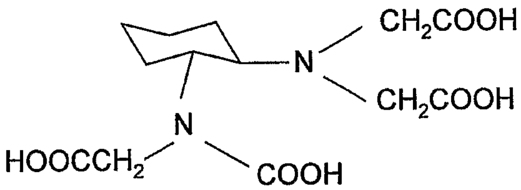


OXD- Star

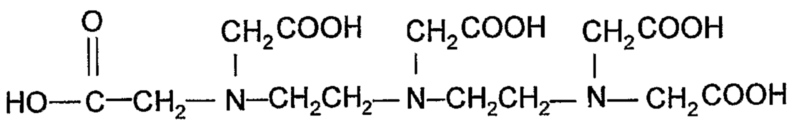
Fig. 10



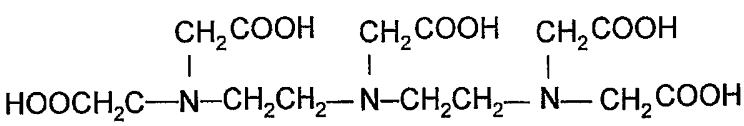
EDTA



DCTA



DTPA



TTHA

Fig. 11

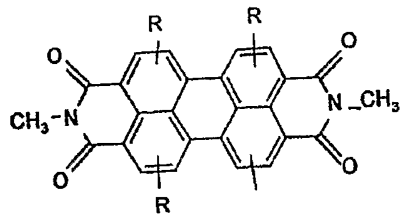


Fig. 12a

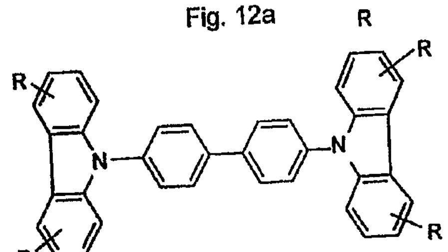


Fig. 12b

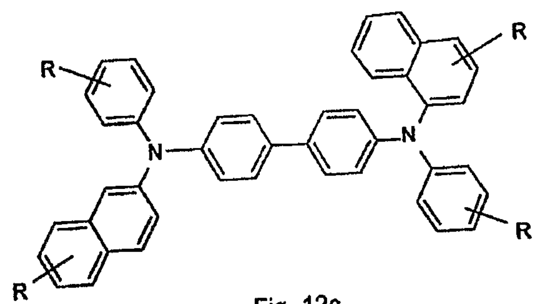


Fig. 12c

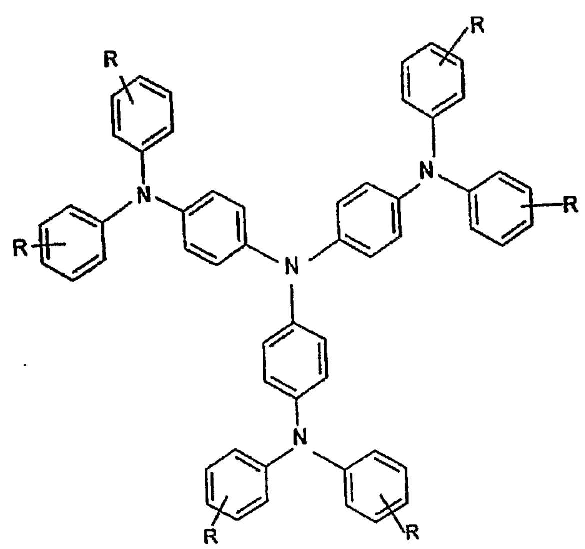


Fig. 12d

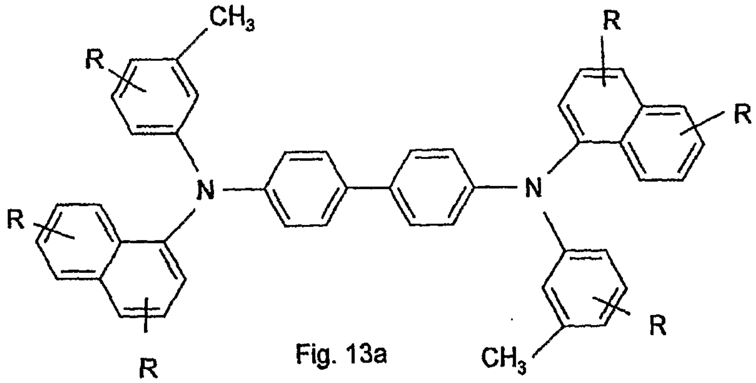


Fig. 13a

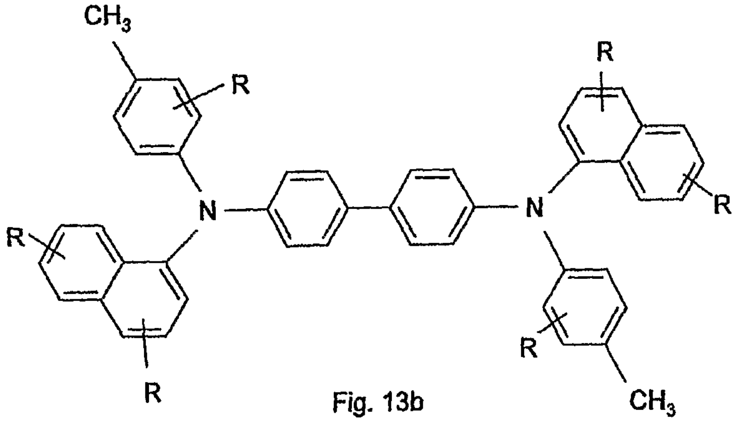


Fig. 13b

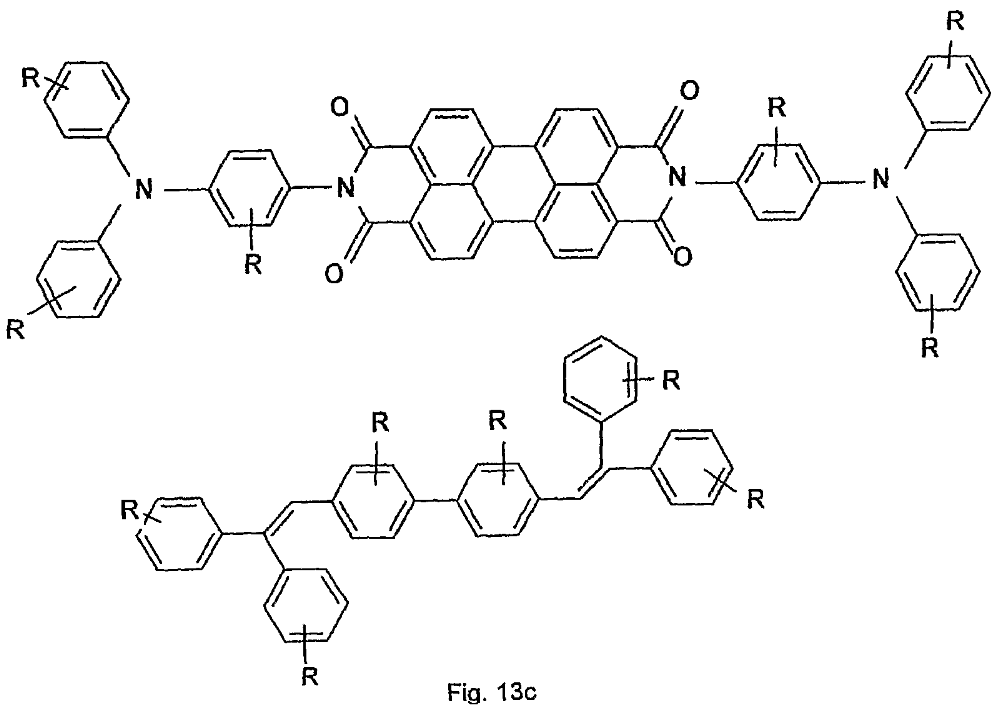


Fig. 13c

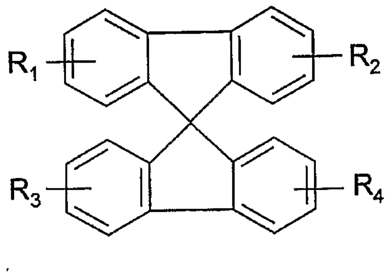


Fig. 14a

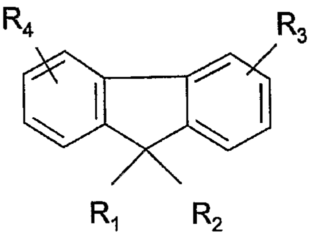


Fig. 14b

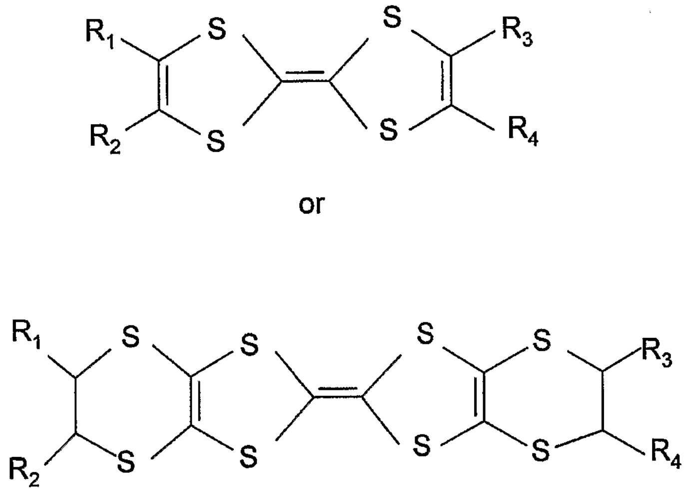


Fig. 14c

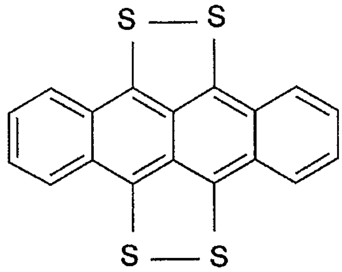
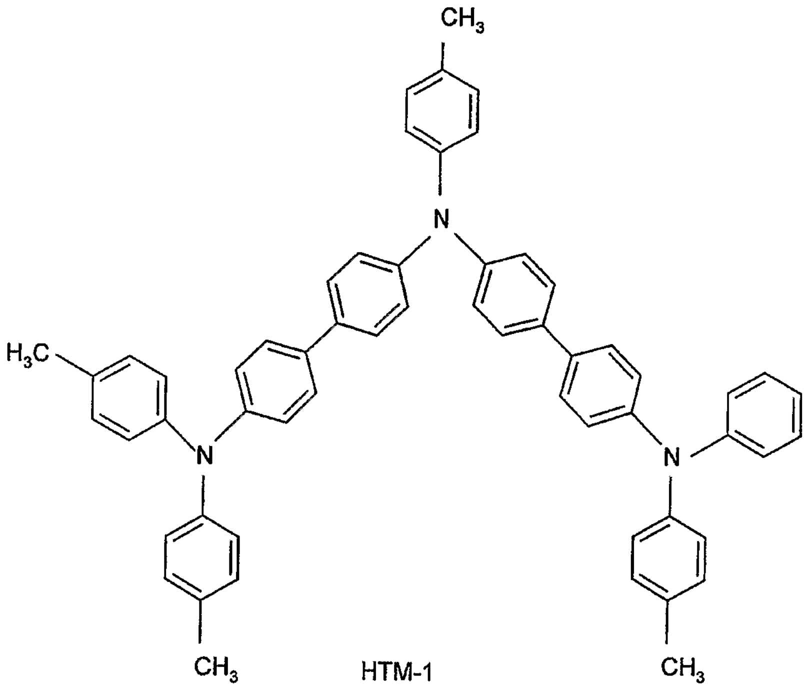
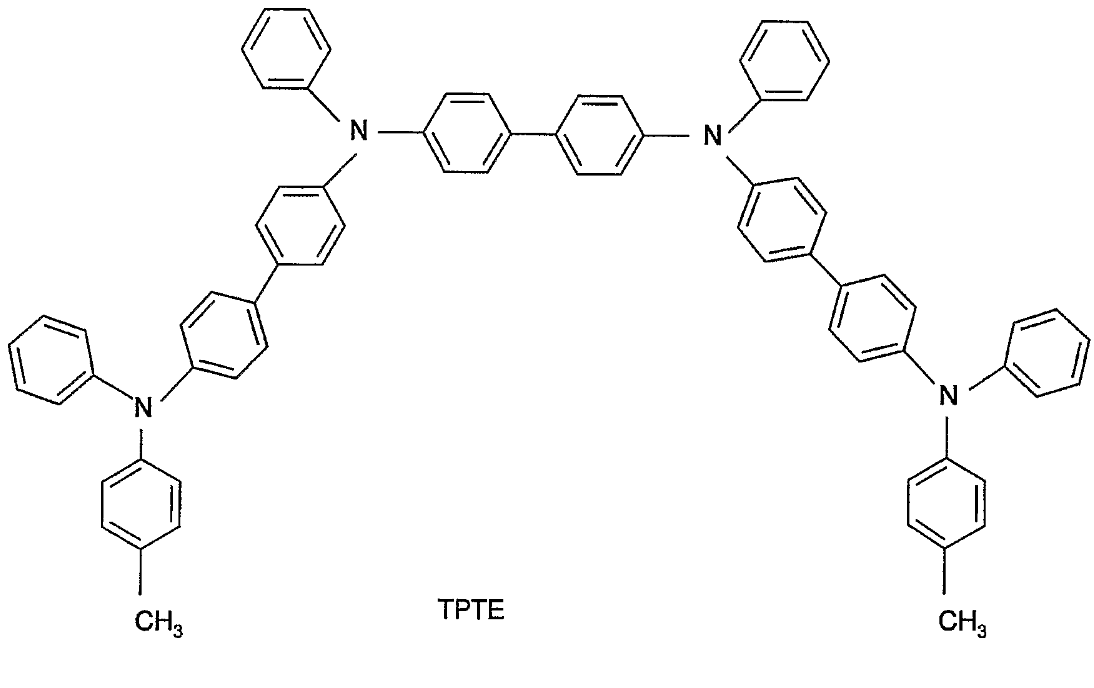


Fig. 14d



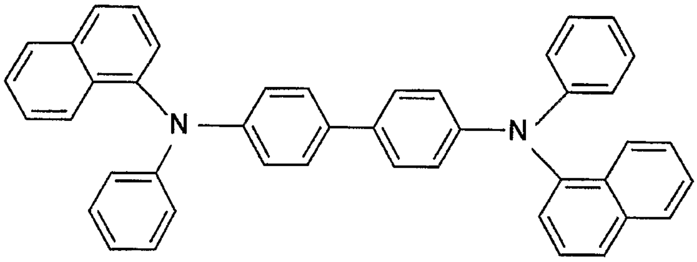
HTM-1

Fig. 15a



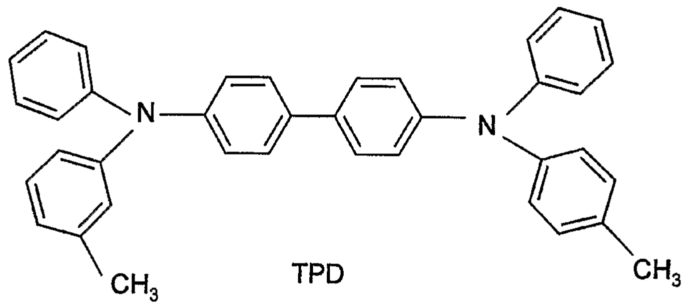
TPTE

Fig. 15b



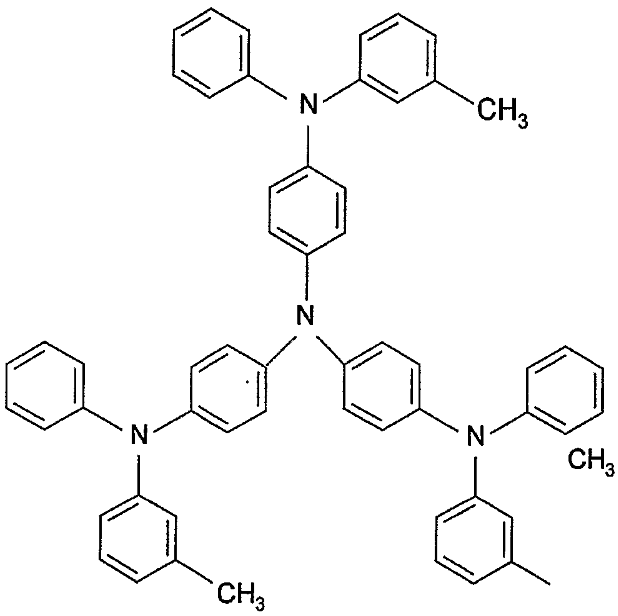
α -NPB

Fig. 16a



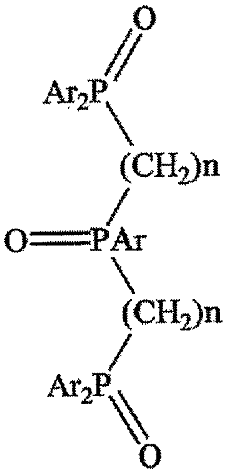
TPD

Fig. 16b

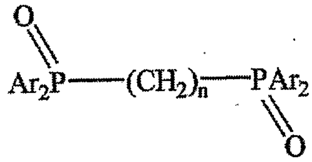


mTADATA

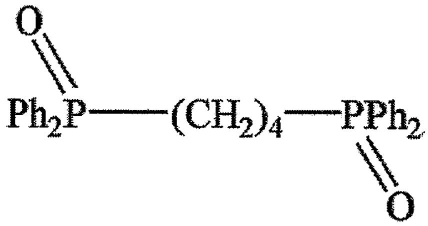
Fig. 16c

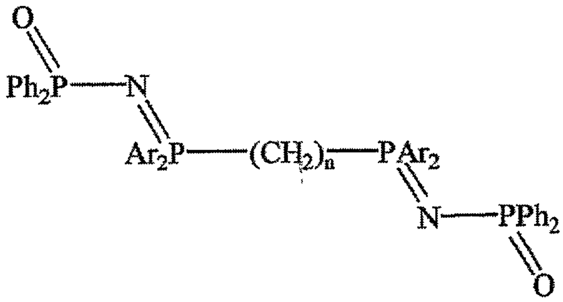


Tris-phosphane oxide

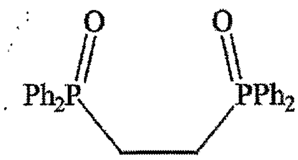


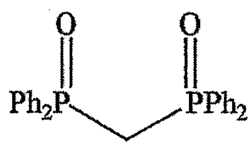
Bis-phosphane oxide

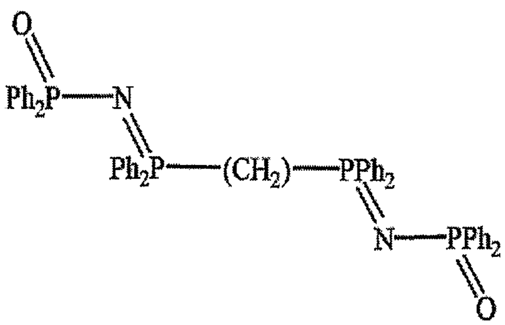




Bis-phosphinimino-phosphane oxide







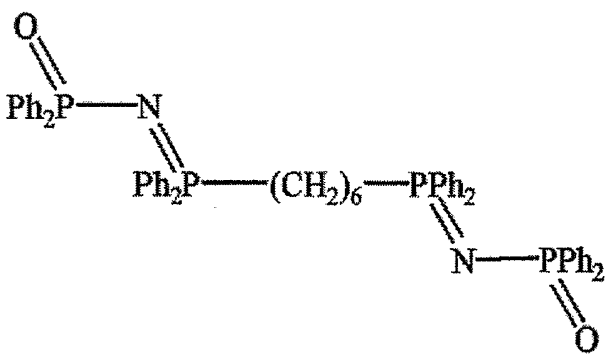


Fig. 17

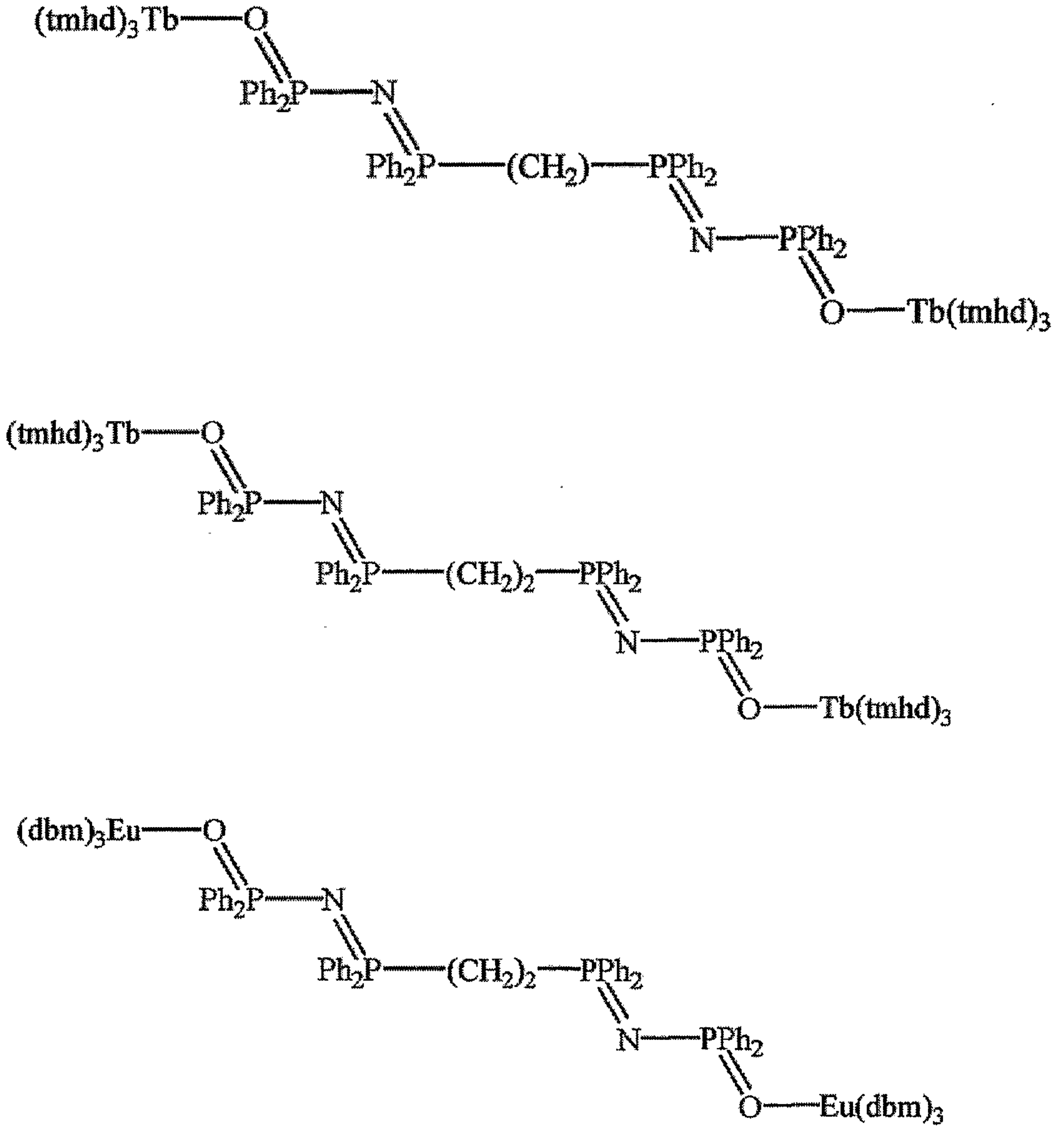
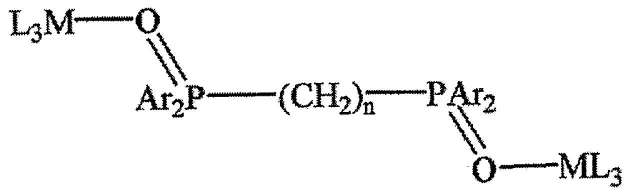
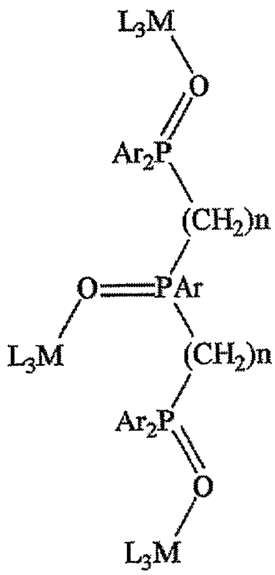


Fig. 18



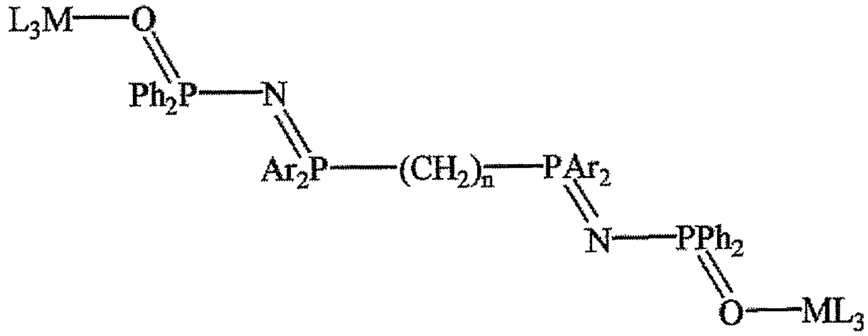
Rare-Earth chelate bis-phosphane oxide complexes

Fig. 19a



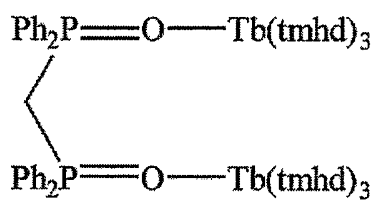
Rare-Earth chelate tris-phosphane oxide complexes

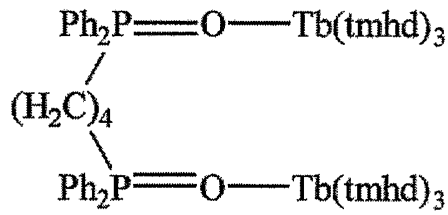
Fig. 19b

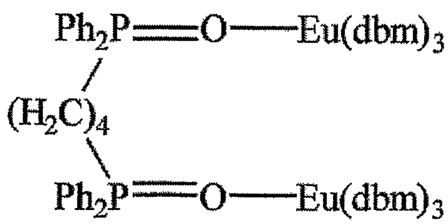


Rare-Earth chelate bis-phosphinimino-phosphane oxide complexes

Fig. 19c


Ph2P=O—Tb(tmhd)3
Ph2P=O—Tb(tmhd)3


Ph2P=O—Tb(tmhd)3
(H2C)4
Ph2P=O—Tb(tmhd)3


Ph2P=O—Eu(dbm)3
(H2C)4
Ph2P=O—Eu(dbm)3

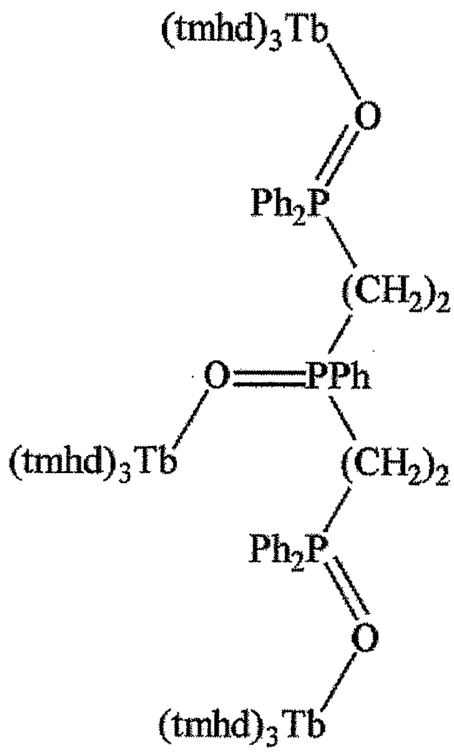

(tmhd)3Tb
O
Ph2P
(CH2)2
O=PPh
(tmhd)3Tb
(CH2)2
Ph2P
O
(tmhd)3Tb

Fig. 20

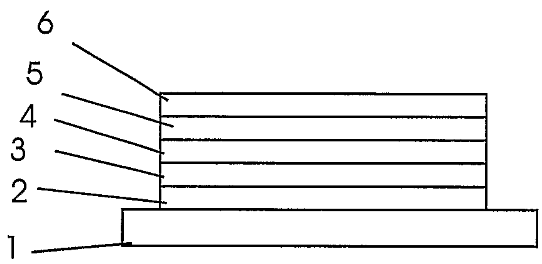


Fig. 21

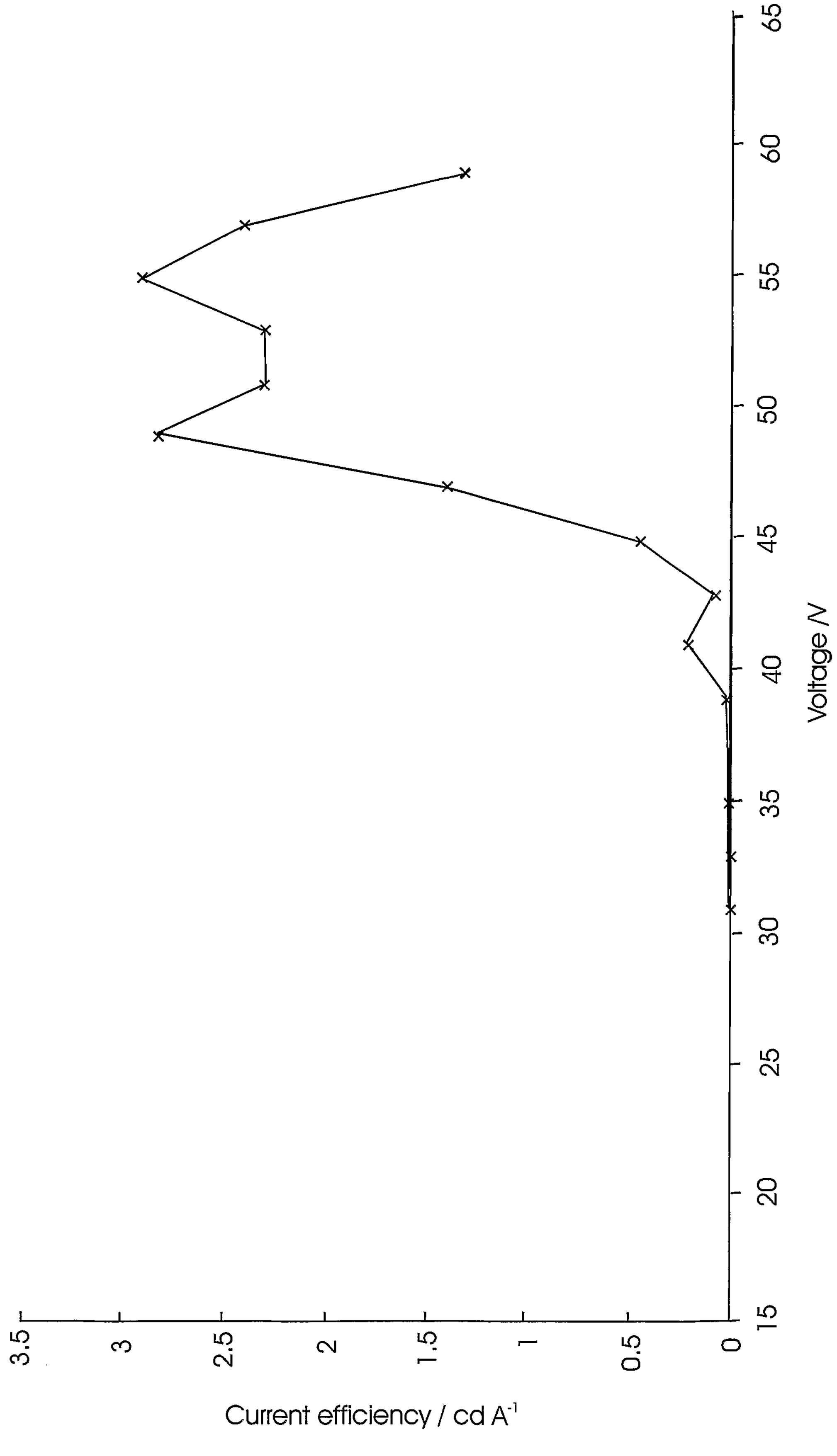

Voltage /V
15
20
25
30
35
40
45
50
55
60
65
Current efficiency / cd A-1
0
0.5
1
1.5
2
2.5
3
3.5

Fig. 22

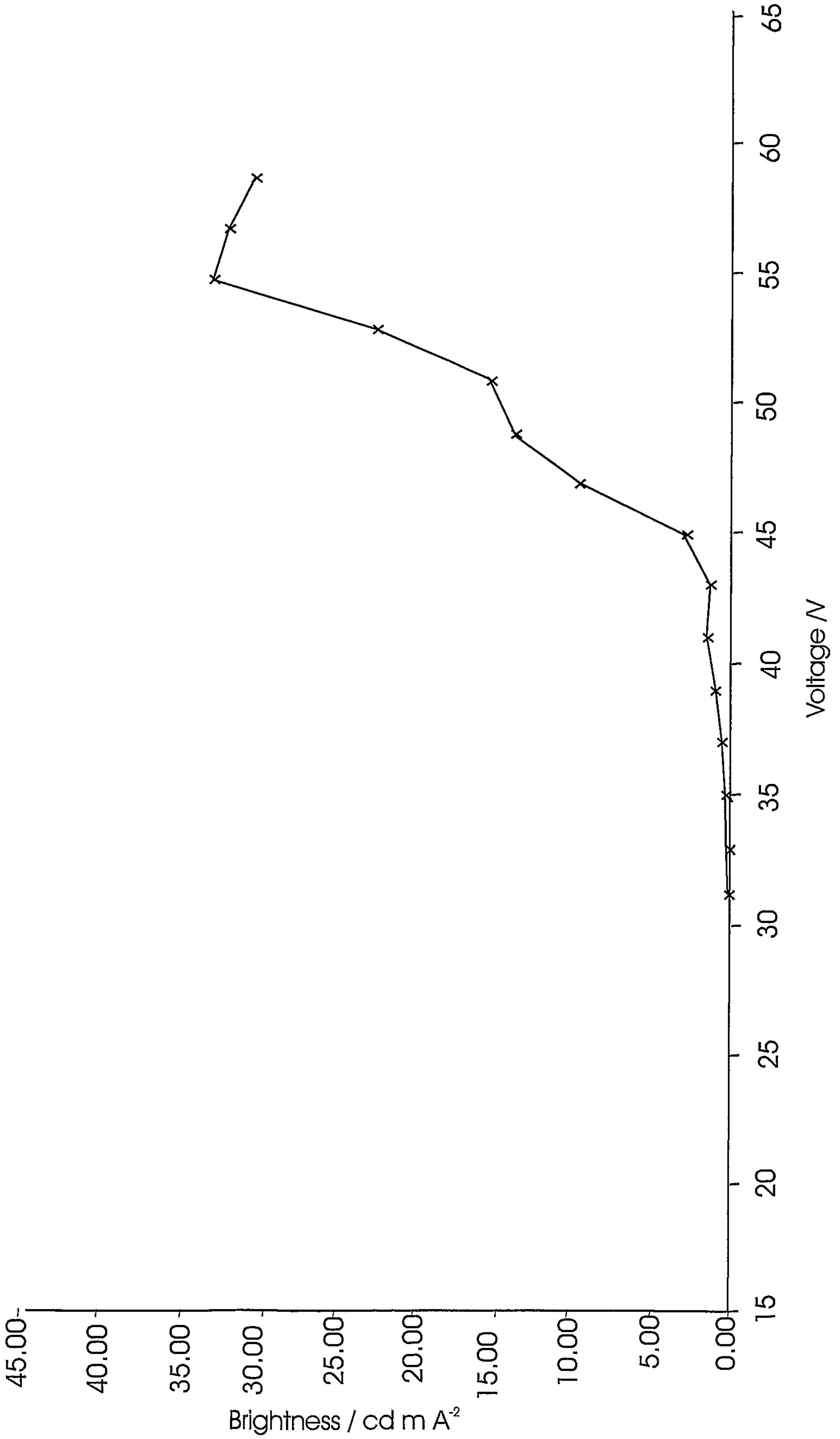

45.00
40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
Brightness / cd m A-2
15
20
25
30
35
40
45
50
55
60
65
Voltage /V

Fig. 23

INTERNATIONAL SEARCH REPORT

PCT/GB 02/03588

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K11/06 H01L51/30 C07F19/00

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 H01L C09K C07F

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, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	Y.CUI, Y. T. QIAN, J. SH. HUANG: "Synthesis, characterization and X-ray structure of three types of triply crotonate-bridged heterometallic zinc(II)-lanthanide(III) complexes" POLYHEDRON, vol. 20, 30 June 2001 (2001-06-30), pages 1795-1802, XP002220494 abstract; figures 1,3,4	1-3,5-9
Y	EP 1 052 661 A (FUJI PHOTO FILM CO LTD) 15 November 2000 (2000-11-15) page 40 -page 54	1-3,6-9

-/--

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

[X] Patent family members are listed in annex.

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"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

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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
13 November 2002	02/12/2002

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	Pusch, C

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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Y	EP 0 744 451 A (AMERSHAM INT PLC) 27 November 1996 (1996-11-27)	1
A	page 5, line 30 -page 9, line 24	4,21
Y	S. R. DRAKE, A. LYONS, D. J. OTWAY, D. J. WILLIAMS: "An Unexpected Product Derived from the Reaction of TbCl3(H2O)6 and ‘Na(hfa)!n: Synthesis, Characterization, and X-ray Structure of{‘Tb2(hfa)(u-O2CCF3)2(H2O)2!2:H2O}" INORGANIC CHEMISTRY, vol. 33, 16 March 1994 (1994-03-16), pages 1230-1233, XP002220495 figures 3,4	2,3,5,7
Y	C. D. HALL, N. W. SHARPE: "Photophysical and Photochemical Studies on the Lanthanide Complexes of Metallocene-Containing Cryptands" JOURNAL OF PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY, vol. 56, 1991, pages 255-265, XP000900063 page 262, line 29 -page 263, line 34; figure 1	1,2,5,6
Y	S. FERY-FORGUES, B. DELAVAUX-NICOT: "Ferrocene and Ferrocenyl Derivatives in Luminescent Systems" JOURNAL OF PHOTOCHEMISTRA AND PHOTOBIOLOGY A: CHEMISTRY, vol. 132, 20 April 2000 (2000-04-20), pages 137-159, XP002220496 figures 4-6,19,20,23	1-3
A	WO 98 58037 A (SOUTH BANK UNIVERSITY ENTERPRISES LTD.) 23 December 1998 (1998-12-23) cited in the application	4,21
Y	page 4 -page 5; example 1	11-13, 15-17,19

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PCT/GB 02/03588

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			AU	8116598 A	04-01-1999
			CN	1260821 T	19-07-2000
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