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**WO 03/006573 A1**

(54) Title: ELECTROLUMINESCENT MATERIALS AND DEVICES

(57) Abstract: An electroluminescent material is a metal complex, preferably aluminium, of a substituted pyrazol-5-one.

## Electroluminescent Materials and Devices

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

5

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  
10 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.

15

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.

20

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.

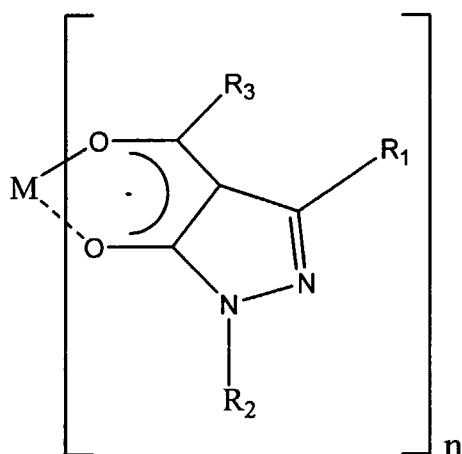
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Hitherto electroluminescent metal complexes have been based on a rare earth, transition metal, lanthanide or an actinide or have been quinolates such as aluminium quinolate.

- 2 -

We have now invented electroluminescent materials which do not include a rare earth, transition metal, lanthanide or an actinide.

According to the invention there is provided an electroluminescent compound which  
 5 has the formula



(I)

10 where M is a metal other than a rare earth, a transition metal, a lanthanide or an actinide; n is the valency of M; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> which may be the same or different are selected from hydrogen, hydrocarbyl groups, substituted and unsubstituted aliphatic groups substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine  
 15 or thiophenyl groups or nitrile; R<sub>1</sub> and R<sub>3</sub> can also be form ring structures and R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> can be copolymerisable with a monomer e.g. styrene.

The invention also provides an electroluminescent device comprising (i) a first electrode, (ii) an electroluminescent layer comprising a layer of a complex of formula  
 20 (I) and (iii) a second electrode.

- 3 -

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.

5

$R_1$  and  $R_2$  can be  $Ph_1$  and  $Ph_2$  and at least one of  $Ph_1$  and  $Ph_2$  is preferably a substituted or unsubstituted aromatic compound and the other moiety 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 trifluoromethyl groups, halogens such as fluorine; substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer e.g. styrene, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine. Examples 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. A preferred group is methyl.

Examples of  $R_3$  are C1 to C5 alkyl groups such as methyl, ethyl, propyl, butyl, pentyl such as  $(CH_2)_3(CH_3)$ , groups and phenyl groups.

M can be any metal compound selected from non rare earth metals e.g. lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, copper, silver, gold, zinc, boron, aluminium, gallium, indium, germanium, tin, antimony, lead, manganese, iron, ruthenium, osmium, cobalt, osmium, rhodium, iridium, nickel, palladium, platinum, cadmium, nickel, chromium and metals of the first, second and third groups of transition metals. etc. which emits light when an electric current is passed through it.

When M is platinum or palladium the complex can be non-stoichiometric i.e. of

- 4 -

formula  $M_xL_y$  where M is the metal and L is the organic ligand. In a stoichiometric complex x will be one and y will be the valence state of the metal, in a non-stoichiometric complex x and y can have different values e.g. x is two and y is three. It is possible that some kind of linked or polymeric structure is formed and/or the metal is present in more than one valence state.

A preferred metal is aluminium and  $R_3$  is preferably a phenyl or substituted phenyl group.

10 Preferably there is a hole transmitting layer deposited on the transparent substrate and the electroluminescent material is deposited on the hole transmitting layer. The hole transmitting 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.

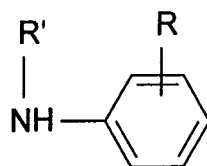
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Hole transmitting layers are used in small molecule based polymer electroluminescent devices and in electroluminescent devices based on rare earth metal complexes and any of the known hole transmitting materials in film form can be used.

20 Hole transmitting layers are used in polymer electroluminescent devices and any of the known hole transmitting materials in film form can be used.

The hole transmitting layer can be made of a film of an aromatic 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

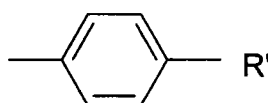
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(II)

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

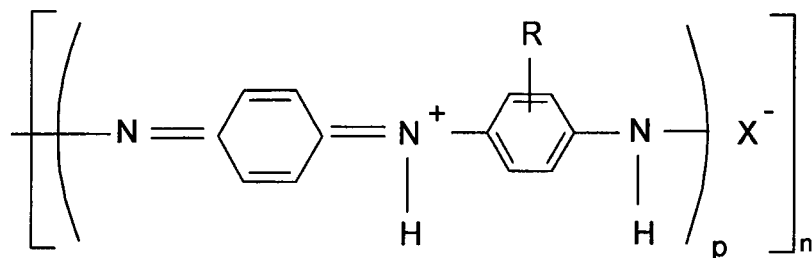
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where R is alkyl or aryl and R' is hydrogen, C1-6 alkyl or aryl with at least one other monomer of formula I above.

10

Polyanilines which can be used in the present invention have the general formula



(III)

where p is from 1 to 10 and n is from 1 to 20, R is as defined above and X is an anion, preferably selected from Cl, Br, SO<sub>4</sub>, BF<sub>4</sub>, PF<sub>6</sub>, H<sub>2</sub>PO<sub>3</sub>, H<sub>2</sub>PO<sub>4</sub>, arylsulphonate, arenedicarboxylate, polystyrenesulphonate, polyacrylate alkylsulphonate, vinylsulphonate, vinylbenzene sulphonate, cellulosesulphonate, camphor sulphonates, cellulose sulphate or a perfluorinated polyanion.

15

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.

5 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 de-protonated it can be easily evaporated i.e. the polymer is evaporable.

10

Preferably evaporable de-protonated 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.

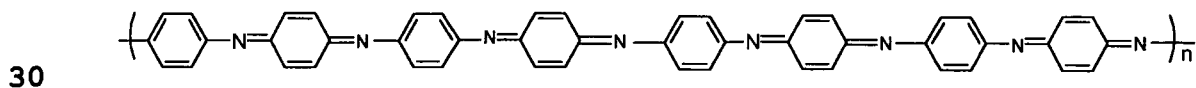
The degree of protonation can be controlled by forming a protonated polyaniline and de-protonating. Methods of preparing polyanilines are described in the article by A. G. MacDiarmid and A. F. Epstein, Faraday Discussions, Chem Soc.88 P319 1989.

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.

25

Preferably the polymer is substantially fully de-protonated

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



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The polyanilines can have conductivities of the order of  $1 \times 10^{-1}$  Siemen  $\text{cm}^{-1}$  or higher.

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

- 10    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.

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

- 20    The polyanilines can be deposited on the first electrode by conventional methods e.g. by vacuum evaporation, spin coating, chemical deposition, direct electrodeposition etc. preferably the thickness of the polyaniline layer is such that the layer is conductive and transparent and can is preferably from 20nm to 200nm. The ployanilines can be doped or undoped, when they are doped they can be dissolved in a  
25    solvent and deposited as a film, when they are undoped they are solids and can be deposited by vacuum evaporation i.e. by sublimation.

- 30    The structural formulae of some other hole transmitting materials are shown in Figures 1, 2, 3, 4 and 5 of the drawings, where R, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> 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<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> 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.

10

Examples of R<sub>1</sub> and/or R<sub>2</sub> and/or R<sub>3</sub> 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.

15

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.

20 Other hole transporting materials which can be used are conjugated polymers.

US Patent 5807627 discloses an electroluminescence device in which there are conjugated polymers in the electroluminescent layer. The conjugated polymers referred to are defined as polymers for which the main chain is either fully conjugated possessing extended pi molecular orbitals along the length of the chain or else is substantially conjugated, but with interruptions to conjugation, either random or regular along the main chain. They can be homopolymers or copolymers.

25 The conjugated polymer used can be any of the conjugated polymers disclosed or referred to in US 5807627, PCT/WO90/13148 and PCT/WO92/03490.

30

The conjugated polymers disclosed 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),  
5 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.

10

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.

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

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

The hole transmitting material and the light emitting metal compound can be mixed to form one layer e.g. in an proportion of 5 to 95% of the hole transmitting material to  
25 95 to 5% of the light emitting metal compound.

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  
30 electron transmitting materials include a metal complex such as a metal quinolate e.g.

- 10 -

an aluminium quinolate, lithium quinolate a cyano anthracene such as 9,10 dicyano anthracene, a polystyrene sulphonate and compounds of formulae shown in Figs. 6 and 7. Other electron transmitting materials which can be used include metal dibenzoyl methanes such as aluminium and scandium dibenzoyl methane, Al or Sc(DBM)<sub>3</sub>. Where the electron transmitting material is electroluminescent it is preferably used in a layer which is too thin to affect the electroluminescent properties of the device. Instead of being a separate layer the electron transmitting material can be mixed with the electroluminescent material to form one layer e.g. in a proportion of 5 to 95% of the electron transmitting material to 95 to 5% of the light emitting metal compound.

The electroluminescent layer can comprise a mixture of the light emitting metal compound with the hole transmitting material and electron transmitting material

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

Alternatively electroluminescent 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.

Preferably the first electrode is 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 transparent conductive layer such as a metal or conductive polymer can be used.

Conductive polymers and conductive polymer coated glass or plastics materials can

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also be used as the substrate.

5 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.

10 The display of the invention may be monochromatic or polychromatic. Electroluminescent rare earth chelate compounds are known which will emit a range of colours e.g. red, green, and blue light and white light and examples are disclosed in Patent Applications WO98/58037 PCT/GB98/01773, PCT/GB99/03619, PCT/GB99/04030, PCT/GB99/04024, PCT/GB99/04028, PCT/GB00/00268 and can be used to form OLEDs emitting those colours. Thus, a full colour display can be formed by arranging three individual backplanes, each emitting a different primary monochrome colour, on different sides of an optical system, from another side of which a combined colour image can be viewed. Alternatively, rare earth chelate electroluminescent compounds emitting different colours can be fabricated so that adjacent diode pixels in groups of three neighbouring pixels produce red, green and blue light. In a further alternative, field sequential colour filters can be fitted to a white light emitting display.

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

25 Preferably, the substrate is of crystalline silicon and the surface of the substrate may be polished or smoothed to produce a flat surface prior to the deposition of electrode, or electroluminescent compound. Alternatively a non-planarised silicon substrate can

30

- 12 -

be coated with a layer of conducting polymer to provide a smooth, flat surface prior to deposition of further materials.

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

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

15

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

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

25

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

As described in WO00/60669 the brightness of light emitted from each pixel is preferably controllable in an analogue manner by adjusting the voltage or current applied by the matrix circuitry or by inputting a digital signal which is converted to an analogue signal in each pixel circuit. The substrate preferably also provides data drivers, data converters and scan drivers for processing information to address the array of pixels so as to create images. When an electroluminescent material is used which emits light of a different colour depending on the applied voltage the colour of each pixel can be controlled by the matrix circuitry.

In one embodiment, each pixel is controlled by a switch comprising a voltage controlled element and a variable resistance element, both of which are conveniently formed by metal-oxide-semiconductor field effect transistors (MOSFETs) or by an active matrix transistor.

#### **Example 1**

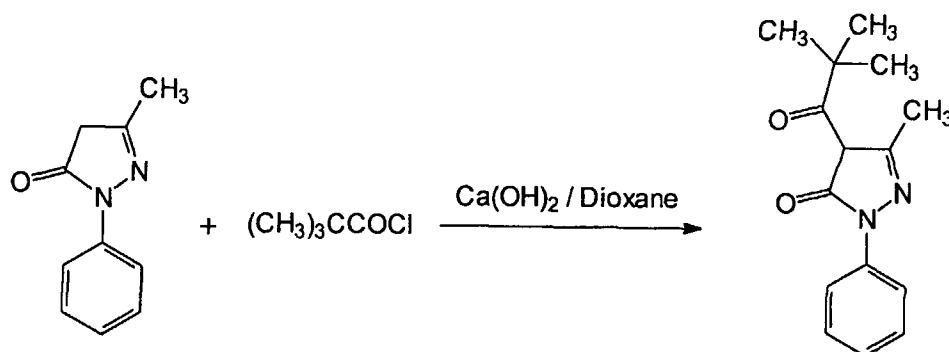
#### **Synthesis of 1-phenyl-3-methyl-4-trimethylacetyl pyrazol-5-one (TMAP) from 1-phenyl-3-methylpyrazol-5-one**

1-phenyl-3-methylpyrazol-5-one (25.0 g) was dissolved with warming in 235.3 ml of dioxane in 500 ml 3-neck quick-fit round bottom flask carrying a reflux condenser, a dropping funnel and stirrer. The solution was cooled to room temperature. 29.4 g of dry calcium hydroxide was added to the solution and stirred. 17.7 ml of trimethylacetyl chloride was added dropwise to the mixture in the flask with vigorous stirring within 15 mm. The mole ratio of pyrazolone and trimethylacetyl chloride is 1:1. The hot reaction mixture was stirred without heating for 40 mm and resultant orange mixture was poured into 1176 ml of chilled 3 M HCl with stirring to decompose the calcium product. The product was extracted into CH<sub>2</sub>Cl<sub>2</sub> and the solvent was evaporated to obtain the crude product. Then the pure product was isolated as reddish-brown solution using column chromatography eluted with diethyl

- 14 -

ether-pet. ether (60-80° C) (3:2). The solvent mixture was evaporated and oily product was kept in refrigerator to solidify. mp 98° C. Elemental analysis of the product. Found: C, 69.47 %; H, 7.00 %; N, 10.69 %. Cal. for (C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>): C, 69.76 %; H, 6.98 %; N, 10.85 %

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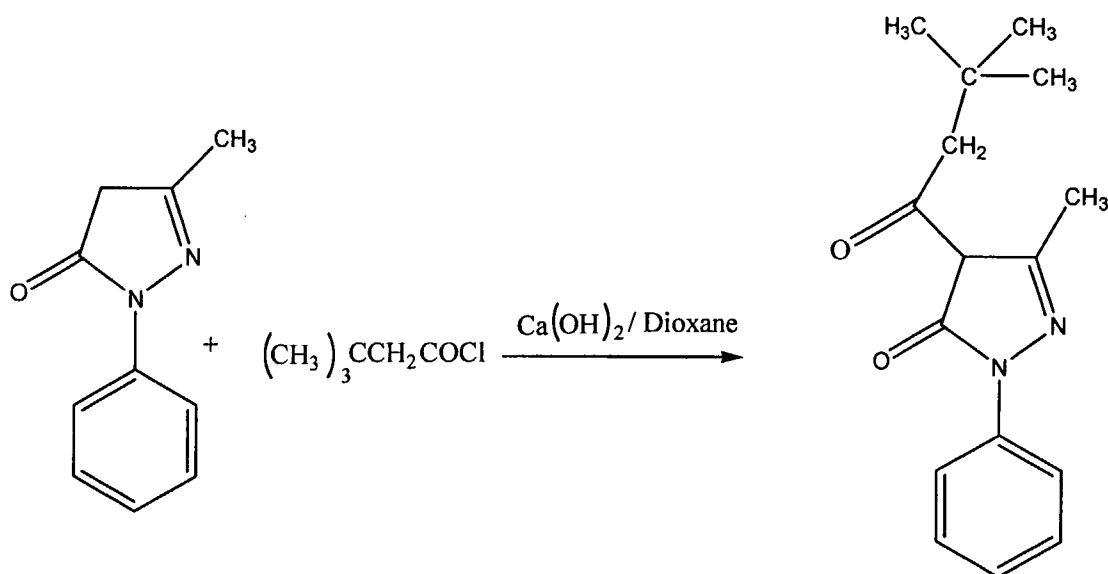
### Example 2

#### 10 **Synthesis of 4-tert-Butyl-3-methyl-1-phenylpyrazol-5-one**

3-Methyl-1-phenylpyrazol-5-one (5 g; 0.029 mole) was placed in a flask equipped with a stirrer and reflux condenser. Dry and distilled dioxane (40 ml) was added by warming and to the clear solution calcium hydroxide (6.4 g; 0.086 mole) was added  
 15 followed by drop wise addition of tert-butylacetyl chloride (4.8 ml; 0.034 mole). The mixture was heated to reflux for 4 hours and then poured into 2M HCl (200 ml) to decompose the calcium complex. A light brown precipitate formed immediately, which was filtered off under suction after refrigerating overnight. The product was washed with water and dried under vacuum at 50 °C. The product was recrystallised  
 20 from methanol to give an off-white crystalline solid, m.p 85-86 °C; 6.8 g (82 %).

## Elemental Analysis

Element	C	H	N
% Theory	70.56	7.40	10.28
5 Found	70.54	7.43	10.26



5

**Example 3 Synthesis of Aluminium(1-phenyl-3-methyl-4-trimethylacetylpyrazol-5-one)<sub>3</sub> Complex  $\text{Al}(\text{TMAP})_3$**

A solution of 1-phenyl-3-methyl-4-trimethylacetylpyrazol-5-one (TMAP) (3.9 mM) in ethanol (15 ml) was stirred and neutralised with sodium hydroxide (NaOH) (3.9 mM in 2 ml  $\text{H}_2\text{O}$ ) solution. To the mixture was added  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (1.3 mM in 2 ml  $\text{H}_2\text{O}$ ) dropwise at room temperature. Then the mixture was stirred for 5 minutes at room temperature and then warmed for another 5 minutes. The crude product, which simultaneously precipitated from the solution, was collected by filtration and washed with water and ethanol. It was dried at  $65^\circ\text{C}$  for 5 hours. mp  $298^\circ\text{C}$ . Elemental analysis of Al complex.

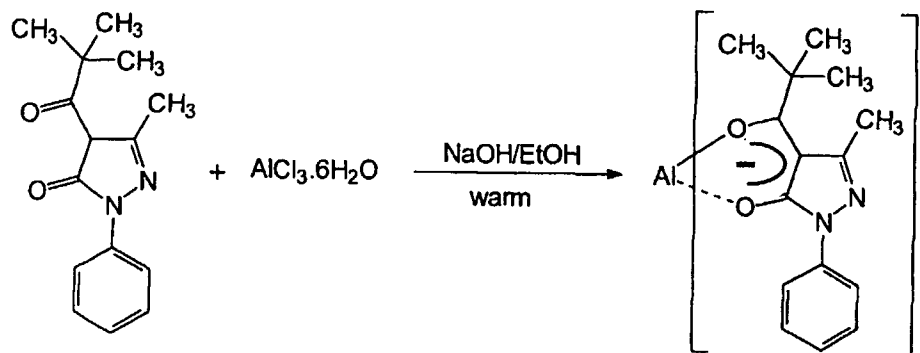
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Found: C, 66.64 %; H, 6.37 %; N, 10.22 %. Cal. for Al (C<sub>45</sub>H<sub>54</sub>N<sub>6</sub>O<sub>6</sub>) complex: C, 67.66 %; H, 6.39 %; N, 10.52 %.



The product is a light-pink colour and showed blue fluorescence.

5

#### Example 4

#### **Synthesis of tris(4-tert-butylacetyl-3-methyl-1-phenylpyrazol-5-one), Al(pyr)<sub>3</sub>**

4-tert-Butylacetyl-3-methyl-1-phenylpyrazol-5-one (2.0g; 0.0074 mole) was dissolved in ethanol (25 ml) and to the stirred solution added aluminium chloride hexahydrate (0.6 g; 0.0025 mole) in water (5 ml). A precipitate formed within 5 minutes. The reaction mixture was stirred at room temperature for 18 hours and filtered off under Suction. The product was washed thoroughly with de-ionised water and ethanol and dried under vacuum at 70 °C for 10 hours, 1.85 g (53 %). M.p 236.5- 237 °C.

15

#### Elemental Analysis

Element	C	H	N	Al
% Theory	68.55	6.83	9.99	3.21
% Found	68.97	6.89	10.01	3.26

#### Thermal analysis:

DSC analysis showed an onset melting point of 231 °C and the peak melting at

20

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236 °C

IR (KBr) spectra showed major absorptions appearing at 2943, 1607, 1488, 1431, 1080 and 753 cm<sup>-1</sup>

The compound showed a blue fluorescence under UV lamp.

5

PL measurement:

PL spectra was measured by Lot Oriel Multispec Model 77400 CCD Camera..

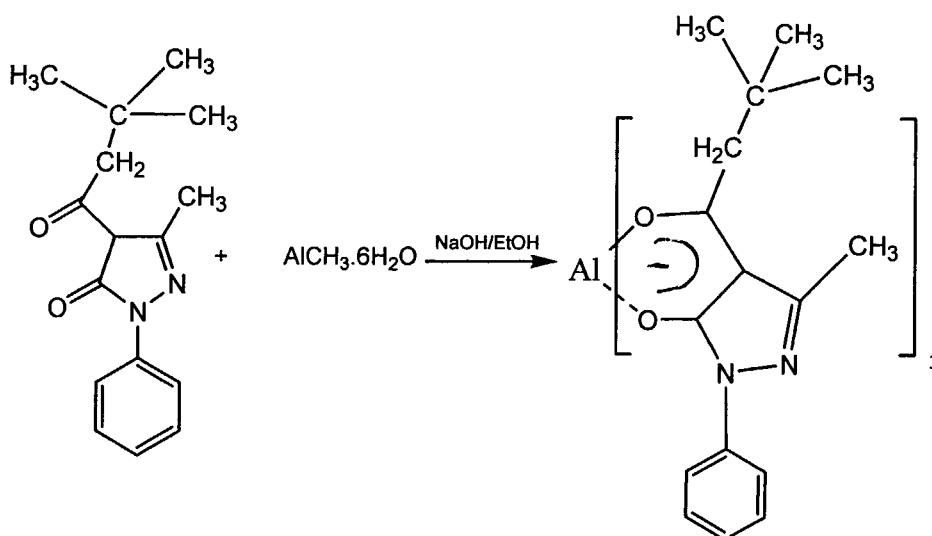
A The measurement was carried out from the powder by spreading the powder on a spectro-sil plate.

10

PL efficiency: 0.034 cd m<sup>-2</sup> μW<sup>-1</sup>

Colour co-ordinates: x 0.19; y 0.21

Peak maximum: 450 nm (FWHM ~ 110 nm).

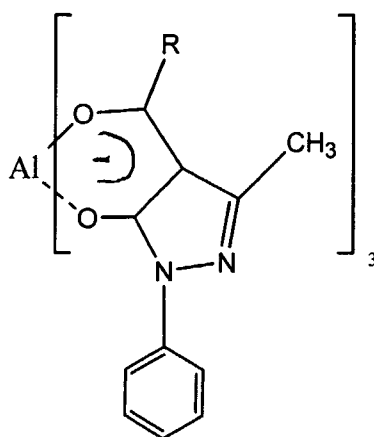


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**Example 5**

By the methods of Examples 1 and 3 the aluminium pyrazolones in below were synthesized.

**5**

where R is as in the Table1.

Table 1

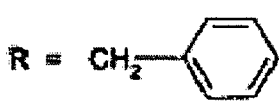
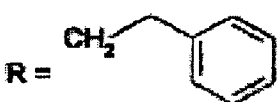
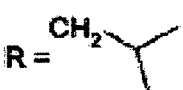
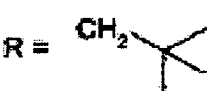
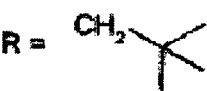

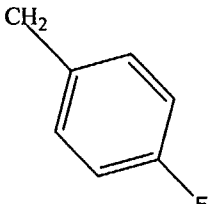
Compound	M.pt.(°C)	PL efficiency cdm <sup>2</sup> μW <sup>-1</sup>	Colour co- ord (x;y)	Comments
R = 	142	0.011	0.24; 0.34	Peak maximum ~500 nm. FWHM ~130 nm
R = 	160	0.009	0.22; 0.25	Peak maximum ~ 460 nm FWHM ~ 110 nm.
R = 	243-244	0.007	0.20; 0.21	Peak maximum ~ 450 nm FWHM ~ 100 nm
R = 	236.5 - 237	0.034 (material was spread on a spectrosil)	0.19; 0.21	
R = 	236 DSC, analysis 236 (peak) 232 (onset)	0.03 (material was spread on a spectrosil)	0.19; 0.21	Peak maximum ~450 nm.
R = CH <sub>3</sub>		0.01	0.21; 0.26	

Table 1 Cont.

Compound	M.pt (°C)	PL efficiency $\text{Cdm}^{-2}\mu\text{W}^{-1}$	Colour co- ord (x;y)	Comments
R=CH <sub>2</sub> CH <sub>3</sub>	182	0.01	0.20;0.21	
R= 		0.009	0.24; 0.31	
R= 		0.011	0.23;0.29	

The PL Efficiencies were measured as in example 4.

## 5 Example 6 Device Fabrication

An ITO coated glass piece (1 x 1cm<sup>2</sup>) had a portion etched out with concentrated hydrochloric acid to remove the ITO and was cleaned and dried. The device was fabricated by sequentially forming on the ITO, by vacuum evaporation, layers comprising:-

ITO(100Ω/ sq. m) /CuPc (2.5mg; ~7.8nm) / TPD (10.4mg; ~44.8 nm)/Al(TMAP)<sub>3</sub> (10.6mg; ~61.6nm) /LiF (0.59mg; ~2.7 nm)/Al

Where ITO is indium titanium oxide coated glass Cu Pc is copper phthalocyanine and TPD is as defined in the specification.

The organic coating on the portion which had been etched with the concentrated hydrochloric acid was wiped with a cotton bud. The coated electrodes were stored in a vacuum desiccator over a molecular sieve and phosphorous pentoxide until they

- 21 -

were loaded into a vacuum coater (Edwards,  $10^{-6}$  torr) and aluminium top contacts made. The active area of the LED's was 0.08 cm by 0.1 cm<sup>2</sup> the devices were then kept in a vacuum desiccator until the electroluminescence studies were performed.

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

10 An electric current was applied across the device and a plot of the current versus voltage is shown in the graph of fig. 8, a plot of brightness against voltage shown in fig. 9, a plot of current efficiency against voltage shown in fig. 10, a plot of power efficiency against voltage shown in fig. 11, the electroluminescence spectrum is shown in fig. 12.

### 15 Example 7

A structure comprising  
ITO(100Ω/ sq. m)/CuPc(3mg;~9.6nm)/β-NPD(2.8mg;~24.4nm)/Al(TMAP)<sub>3</sub> (9.6mg;  
~60.2nm)/LiF(0.6mg;~2.1nm)/Al was fabricated as in example 5 and the  
20 characteristics shown in Fig. 13.

### Example 8

25 A structure comprising  
ITO(100Ω/ sq. m)/α-NPB(30nm)/Al(pyr)<sub>3</sub> (30nm)/Alq<sub>3</sub>(20nm)/Al was fabricated as  
in example 6 where the Al(pyr)<sub>3</sub> and was made as in example 4; the  
electroluminescent spectra at different voltages shown in fig. 14, where

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Voltage/V	Current/mA	Luminance /cdm <sup>-2</sup>	x	y	J/mAcm <sup>-2</sup>	$\eta_i$ /cdA <sup>-1</sup>	$\eta_{EL}$ /lmW <sup>-1</sup>
25.00	0.02	1.70	0.15	0.13	0.30	0.57	0.07
27.00	0.03	1.80	0.15	0.13	0.35	0.51	0.06
29.00	0.04	2.20	0.15	0.13	0.46	0.48	0.05
31.00	0.06	3.70	0.16	0.14	0.76	0.49	0.05
33.00	0.06	3.10	0.16	0.14	0.71	0.44	0.04

The x and y co-ordinates are those on the CIE Colour Chart

5 An electroluminescent spectrum is shown in fig. 15 and the heat flow characteristics using a PerkinElmer Thermal analysis are shown in Fig. 16 in which the heating was from 50 to 300 °C at 40 °C /min and cooling 300 to 50 °C /min.

### Example 9

10 A structure comprising

ITO(10Ω/ sq. m)/CuPc(8nm)/α-NPB(60nm)/Al(pyr)<sub>3</sub>(30nm)/Alq<sub>3</sub>(10nm)/  
LiF(0.7nm)/Al

was fabricated as in example 6 where the Al(pyr)<sub>3</sub> and was made as in example 4 and CuPc is a copper phthalocyanine buffer layer and LiF is lithium fluoride.

15

The electroluminescence characteristics were measured and the results shown in Table 2.

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25

Table 2

Voltage (V)	Current (mA)	Luminance (cd m <sup>-2</sup> )	Colour Co-ordinate		Current Efficiency (cd A <sup>-1</sup> )	Memory ID
			x	y		
7	0.16	0.33	0.16	0.11	0.21	
8	0.52	1.51	0.15	0.10	0.29	
9	1.72	5.48	0.15	0.10	0.32	
11	8.7	28.9	0.15	0.10	0.32	M5
12	13.9	40.7	0.15	0.10	0.29	M6
12.5	16.12	46	0.15	0.10	0.29	
13	19.3	54.1	0.15	0.10	0.28	
13.5	23.5	62.3	0.15	0.10	0.26	
14	27.9	71.6	0.15	0.10	0.26	
14.5	32.3	82	0.15	0.10	0.25	
15	36.2	91.3	0.15	0.10	0.25	
15.5	42.5	100.7	0.15	0.10	0.24	
16	46.5	107.5	0.15	0.10	0.23	M7
16.5	51.3	117.1	0.15	0.10	0.23	
17	57.6	94.31	0.15	0.10	0.16	

The properties are shown in graphical form in Fig. 17

5

#### Example 10

A structure comprising

ITO(10Ω/ sq. m)/CuPc(8nm)/α-NPB(60nm)/Al(DBM)<sub>3</sub>(30nm)/Alq<sub>3</sub>(10nm)/

10 LiF(0.7nm)/Al

was fabricated as in example 6 where the Al(pyr)<sub>3</sub> and was made as in example 4 Al(DBM)<sub>3</sub> is aluminium CuPc is a copper phthalocyanine buffer layer and LiF is lithium fluoride.



The properties are shown in Fig. 18

### **Example 11**

5 A structure comprising

ITO(10Ω/ sq. m)/CuPc(8nm)/α-NPB(60nm)/Al(pyr)<sub>3</sub>(30nm)/Liq(10nm)/

LiF(0.7nm)/Al

was fabricated as in example 6 where the Al(pyr)<sub>3</sub> and was made as in example 4, Liq is lithium quinolate, CuPc is a copper phthalocyanine buffer layer and LiF is lithium

10 fluoride.

The electroluminescence properties are shown in Table 3

Table 3

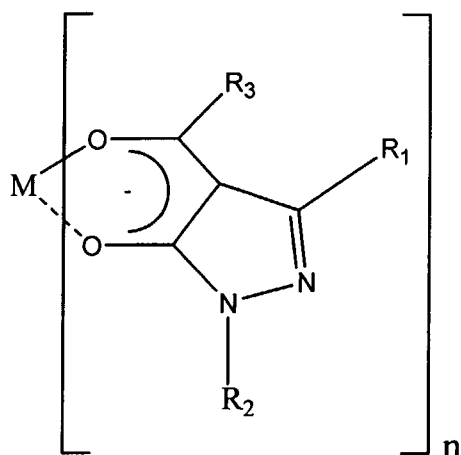
Voltage/V	Current /mA	Luminance /cdm <sup>-2</sup>	x	y	J /mAcm <sup>-2</sup>	η <sub>l</sub> /cdA <sup>-1</sup>	η <sub>EL</sub> /lmW <sup>-1</sup>
9	4.9	0.88	0.15	0.11	61.25	1.44 x 10 <sup>-3</sup>	5.02 x 10 <sup>-4</sup>
10	7.09	1.77	0.15	0.10	88.63	2.00 x 10 <sup>-3</sup>	6.27 x 10 <sup>-4</sup>

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and the relative spectral distribution shown in fig. 19.

## Claims

1. An electroluminescent compound which has the formula



(I)

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where M is a metal other than a rare earth, a transition metal, a lanthanide or an actinide; n is the valency of M; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> which may be the same or different are selected from hydrogen, hydrocarbyl groups, substituted and unsubstituted aliphatic groups substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups or nitrile; R<sub>1</sub> and R<sub>3</sub> can also be form ring structures and R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> can be copolymerisable with a monomer e.g. styrene.

15

2. A compound as claimed in claim 1 in which M is aluminium and R<sub>3</sub> is a phenyl or substituted phenyl group.

3. An electroluminescent device comprising (i) a first electrode, (ii) an electroluminescent layer comprising a layer of a complex of formula (I) and (iii) a second electrode.

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4. An electroluminescent device as claimed in claim 3 in which M is aluminium and R<sub>3</sub> is a phenyl or substituted phenyl group.
5. An electroluminescent device as claimed in claim 3 in which R<sub>3</sub> is a methyl, ethyl, propyl, butyl or a pentyl such as (CH<sub>2</sub>)(CH<sub>3</sub>)<sub>3</sub>, groups.
6. A device as claimed in any one of claims 3 to 5 in which there is a layer of a hole transmitting material between the first electrode and the layer of the electroluminescent complex.
7. A device as claimed in any one of claims 3 to 6 in which there is a layer of an electron transmitting material between the second electrode and the layer of the electroluminescent complex.
8. An electroluminescent device which comprises (i) a first electrode, (ii) a layer of a hole transmitting material, (iii) an electroluminescent layer comprising a complex of general formula (I) herein (iv) a layer of an electron transmitting material and (v) a second electrode.
9. An electroluminescent device as claimed in claim 8 in which the hole transmitting layer is an aromatic amine complex.
10. An electroluminescent device as claimed in claim 9 in which the hole transmitting layer is formed from a poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis (3-methylphenyl) -1,1' -biphenyl -4,4'-diamine (TPD), polyaniline, or a substituted polyaniline.
11. An electroluminescent device as claimed in claim 9 in which the hole transmitting layer has a formula (II) or (III) herein or as in figs. 1 to 5 of the drawings.

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12. An electroluminescent device as claimed in claim 9 in which the hole transmitting layer is a conjugated polymer as herein specified.

13. An electroluminescent device as claimed in claim 12 in which the hole transmitting layer 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.

14. An electroluminescent device as claimed in any one of claims 8 to 13 in which the hole transmitting material and the light emitting metal compound are mixed to form one layer in a proportion of 5 to 95% of the hole transmitting material to 95 to 5% of the light emitting metal compound.

15. An electroluminescent device as claimed in any one of claims 8 to 14 in which the electron transmitting material is a metal quinolate, aluminium or scandium dibenzoyl methane or as in fig. 6 or 7 of the drawings.

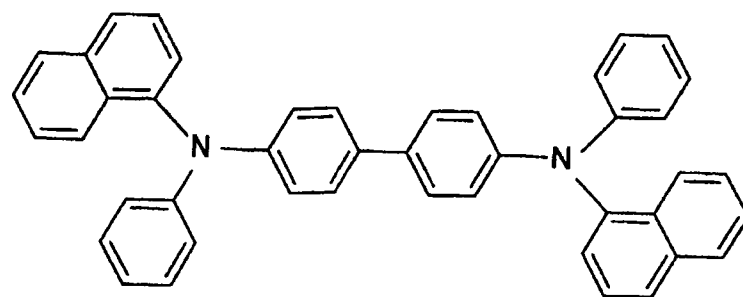
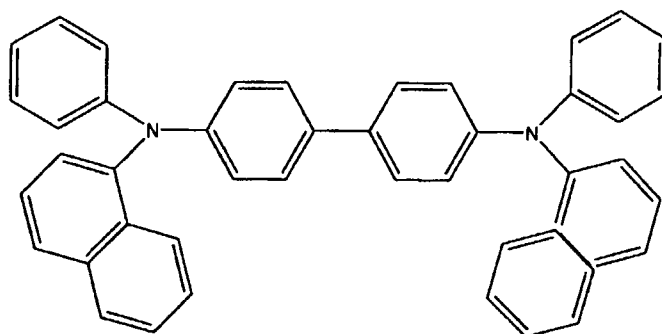
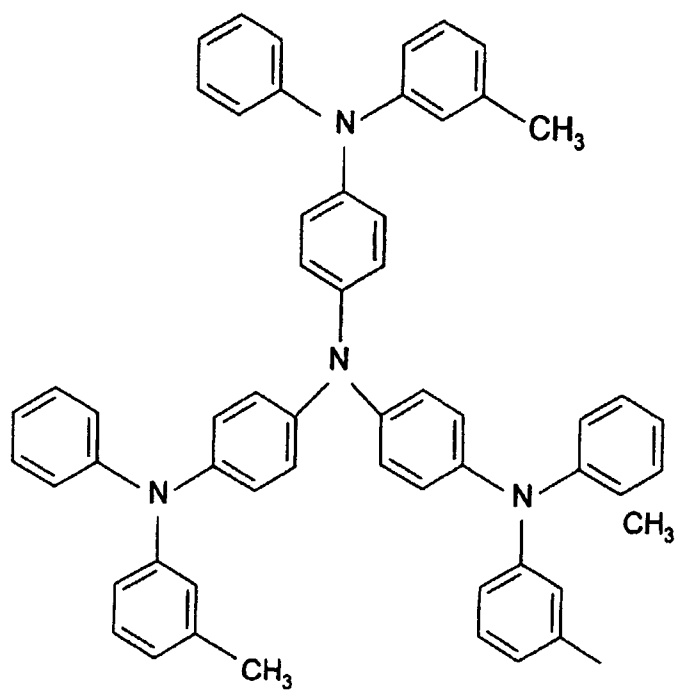
16. An electroluminescent device as claimed in claim 15 in which the metal quinolate is lithium, sodium, potassium, zinc, magnesium or aluminium quinolate.

17. An electroluminescent device as claimed in any one of claims 8 to 16 in which the electron transmitting material and the light emitting metal compound are mixed to form one layer in a proportion of 5 to 95% of the electron transmitting material to 95 to 5% of the light emitting metal compound

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18. An electroluminescent device as claimed in any one of claims 8 to 17 in which the anode and/or cathode is formed on a substrate of crystalline silicon and the surface of the substrate may be polished or smoothed to produce a flat surface prior to the deposition of electrode, or electroluminescent compound.
- 5
19. An electroluminescent device as claimed in any one of claims 8 to 17 in which the anode and/or cathode is formed on a substrate of a non-planarised silicon substrate.
- 10
20. An electroluminescent device as claimed in any one of claims 3 to 19 in which there is a copper phthalocyanine layer on the first electrode and a lithium fluoride layer on the second electrode.

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 $\alpha$  -NPB $\beta$  -NPD

mTADATA

Fig. 1

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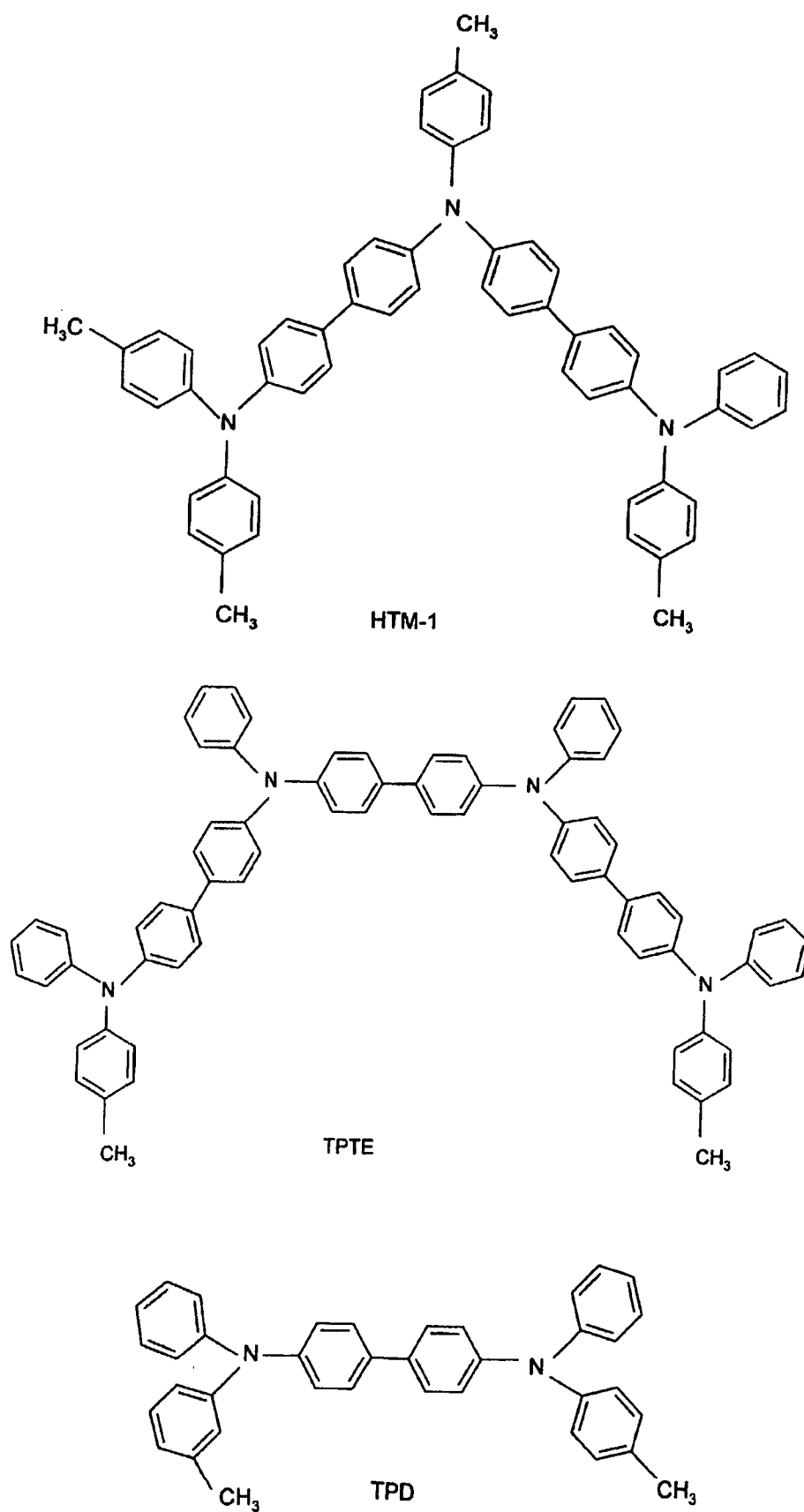


Fig. 2

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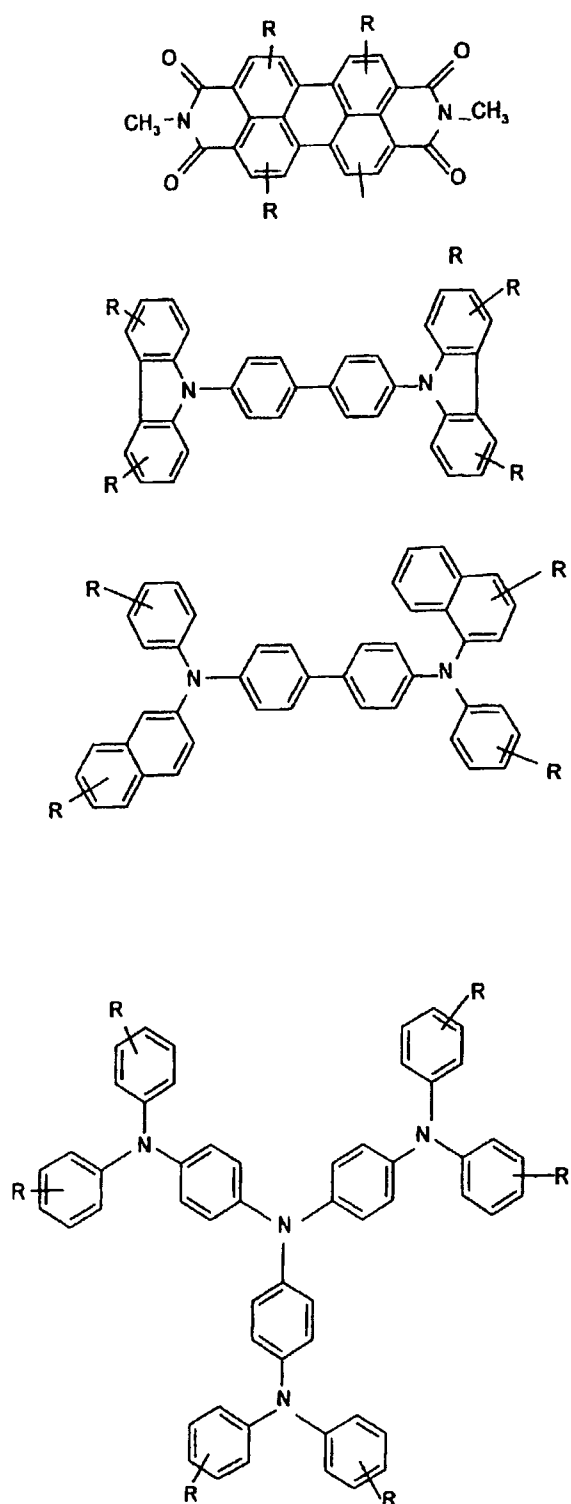


Fig. 3



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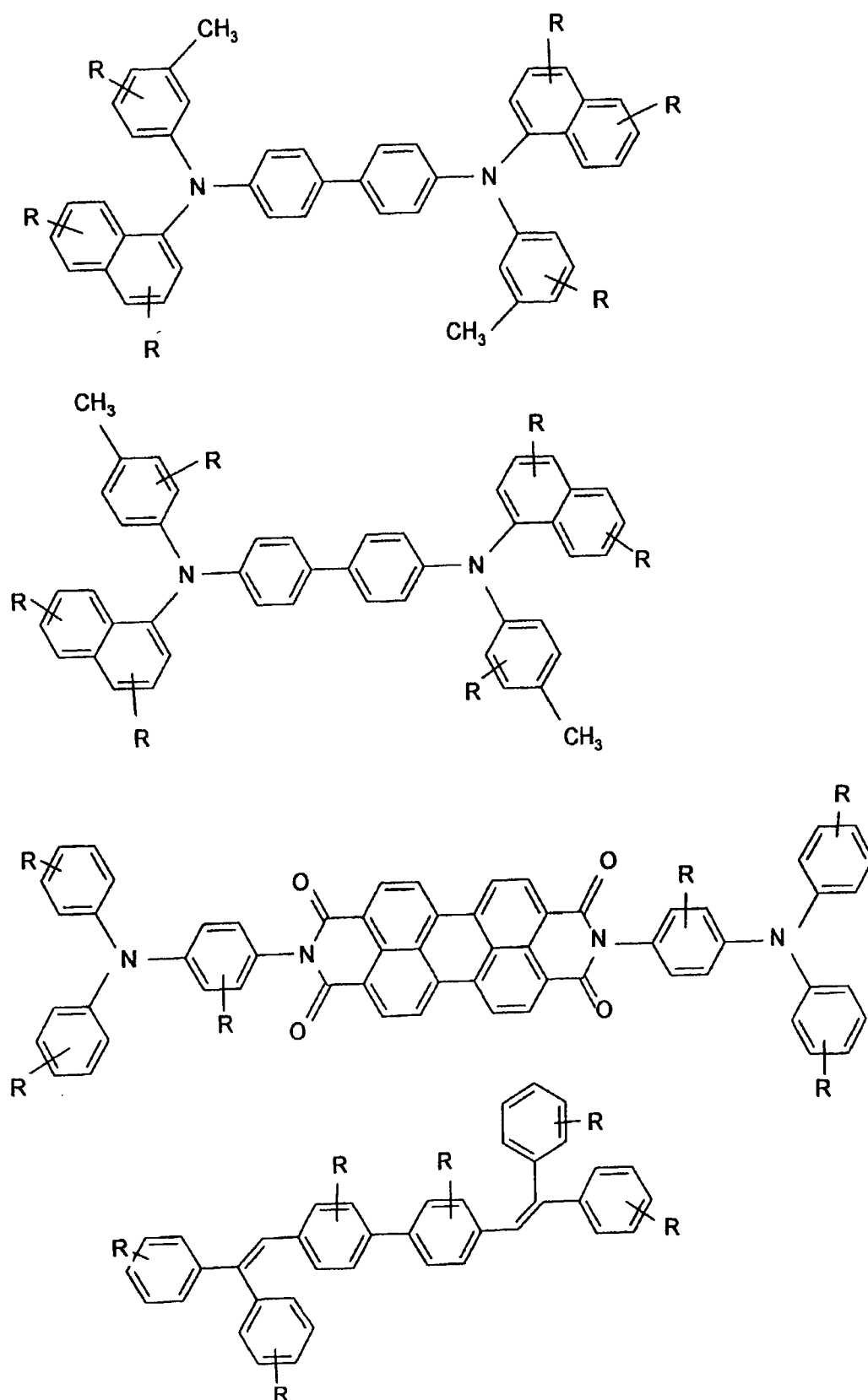
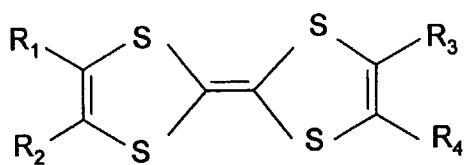
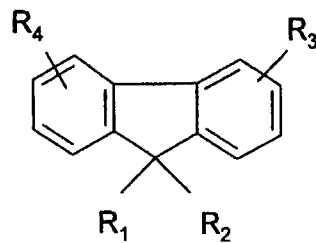
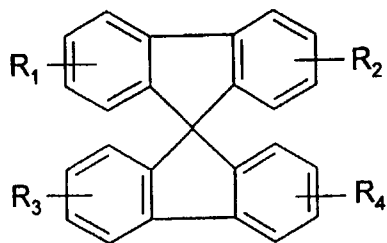


Fig. 4

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or

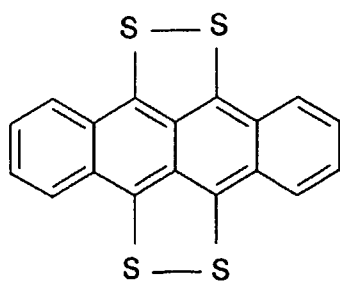
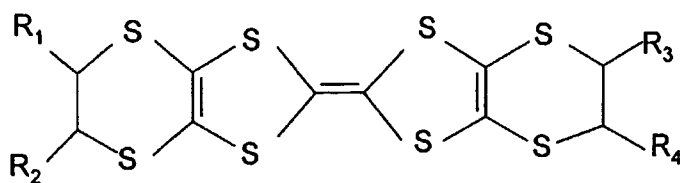
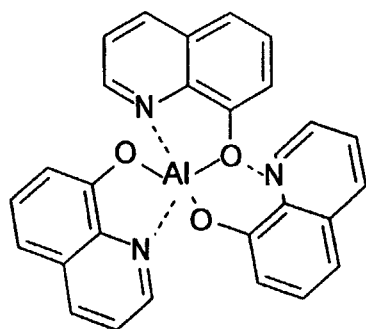
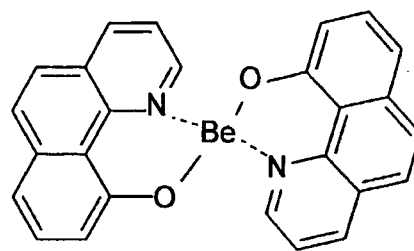


Fig. 5

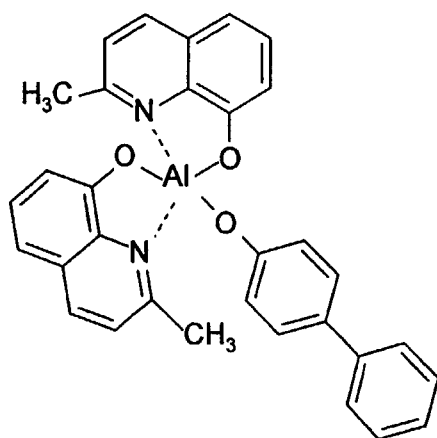
6/19



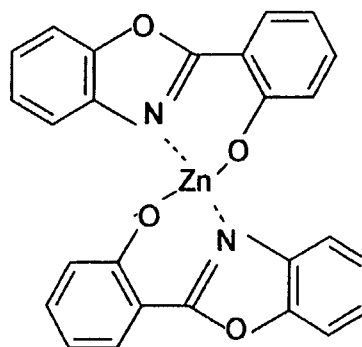
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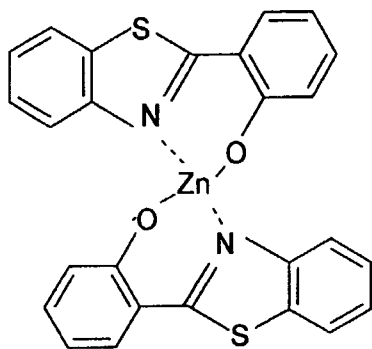
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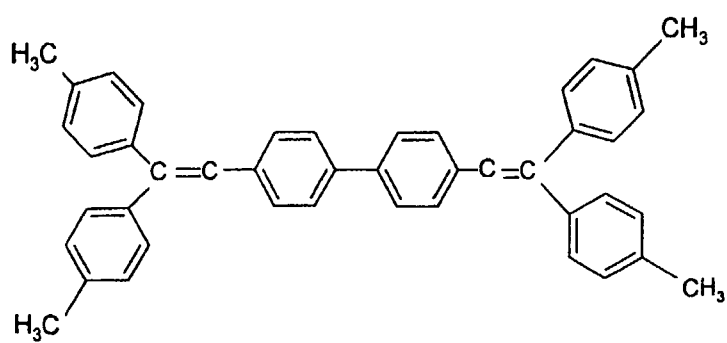
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ZnPBO

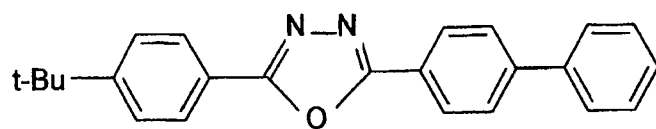


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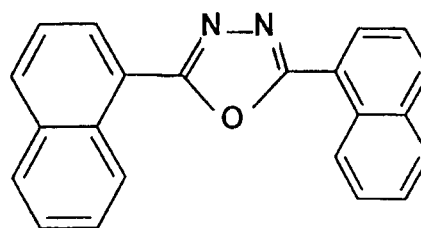


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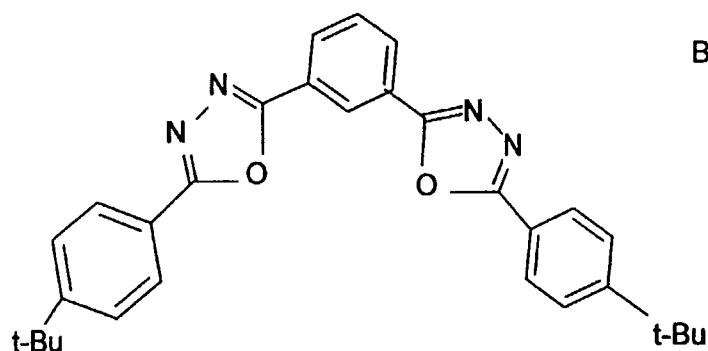
Fig. 6



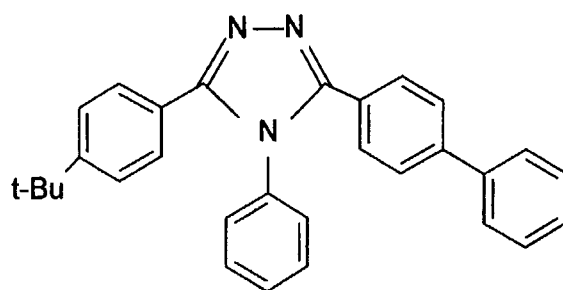
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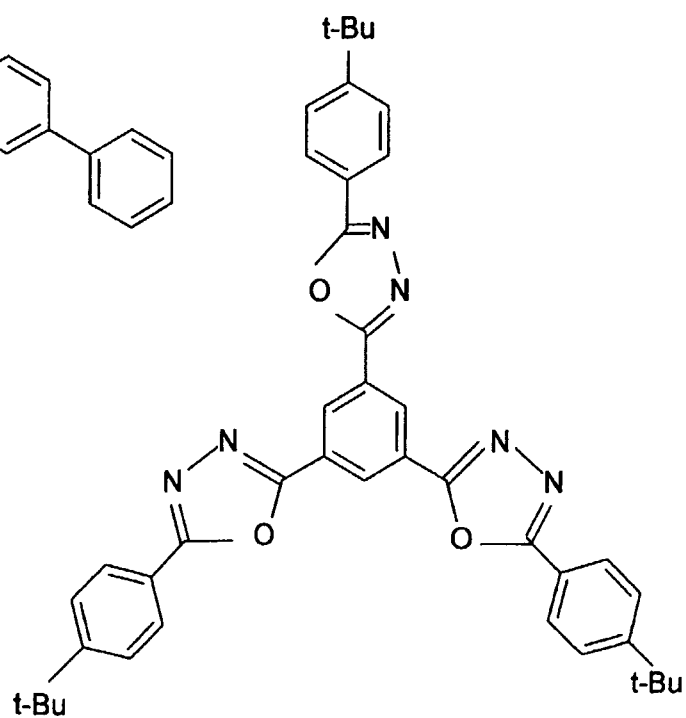
**BND**



OXD-7



TAZ



**OXD- Star**

Fig. 7

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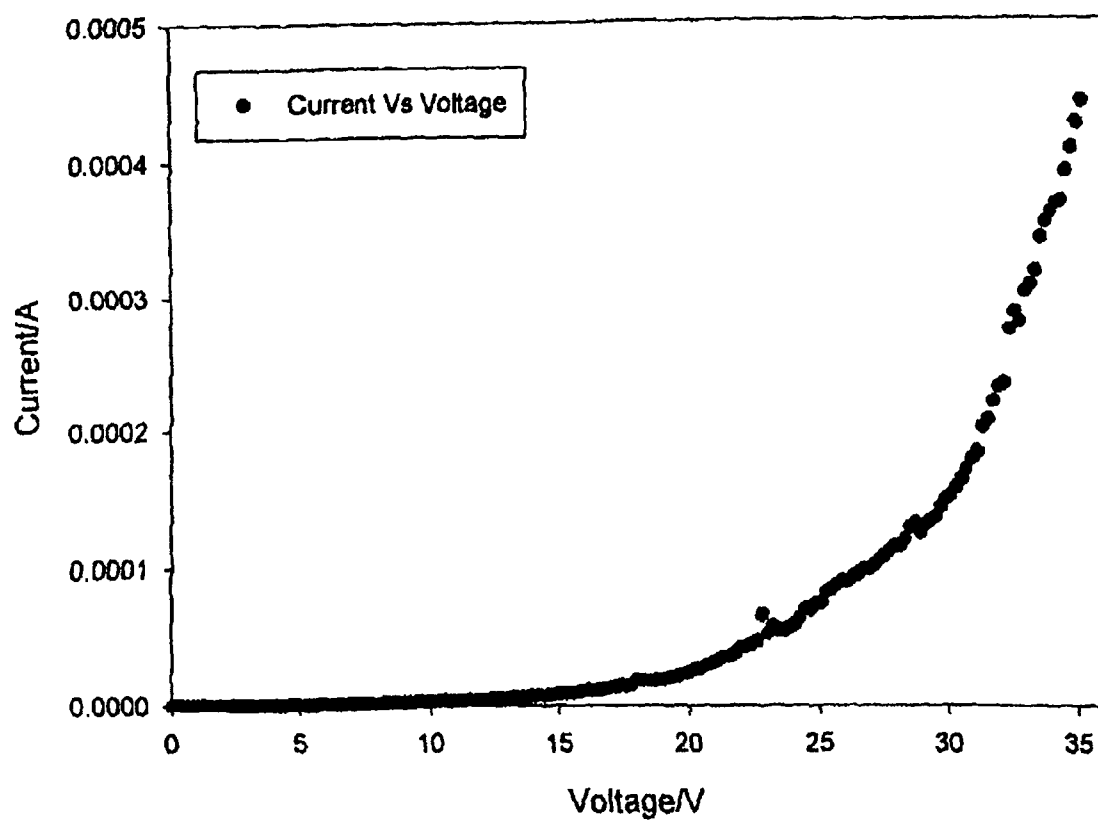


Fig. 8

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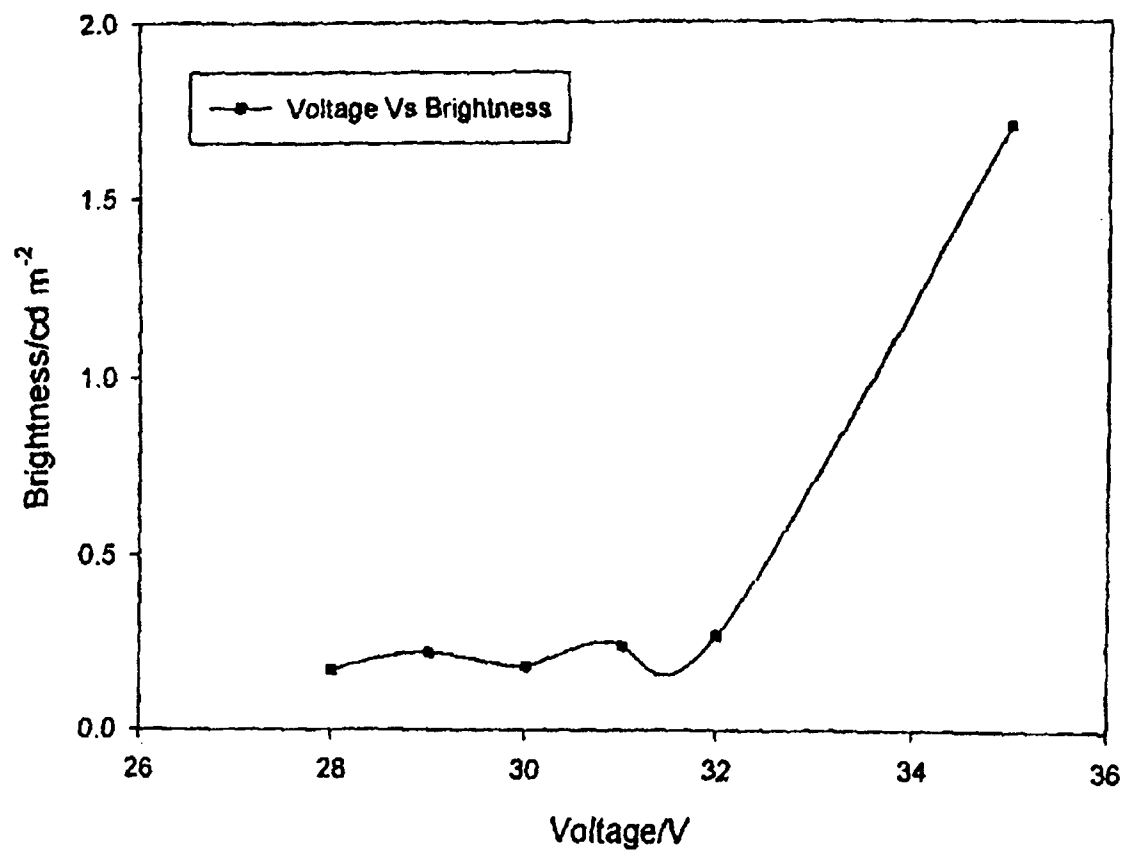


Fig. 9

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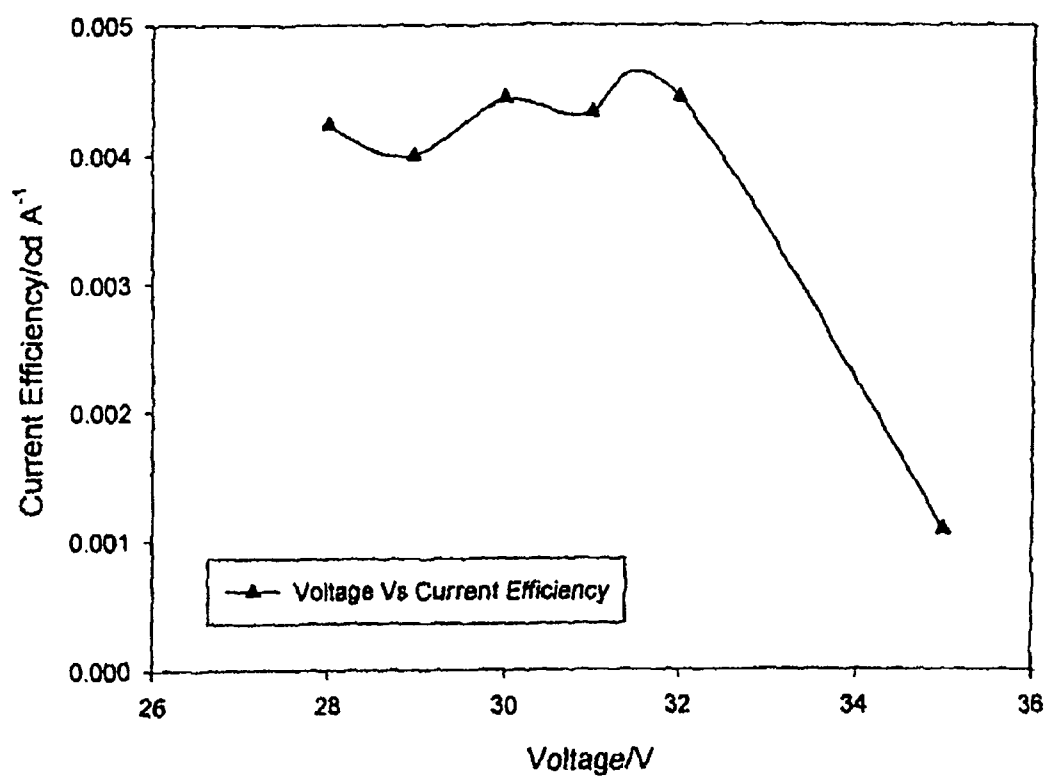


Fig. 10

11/19

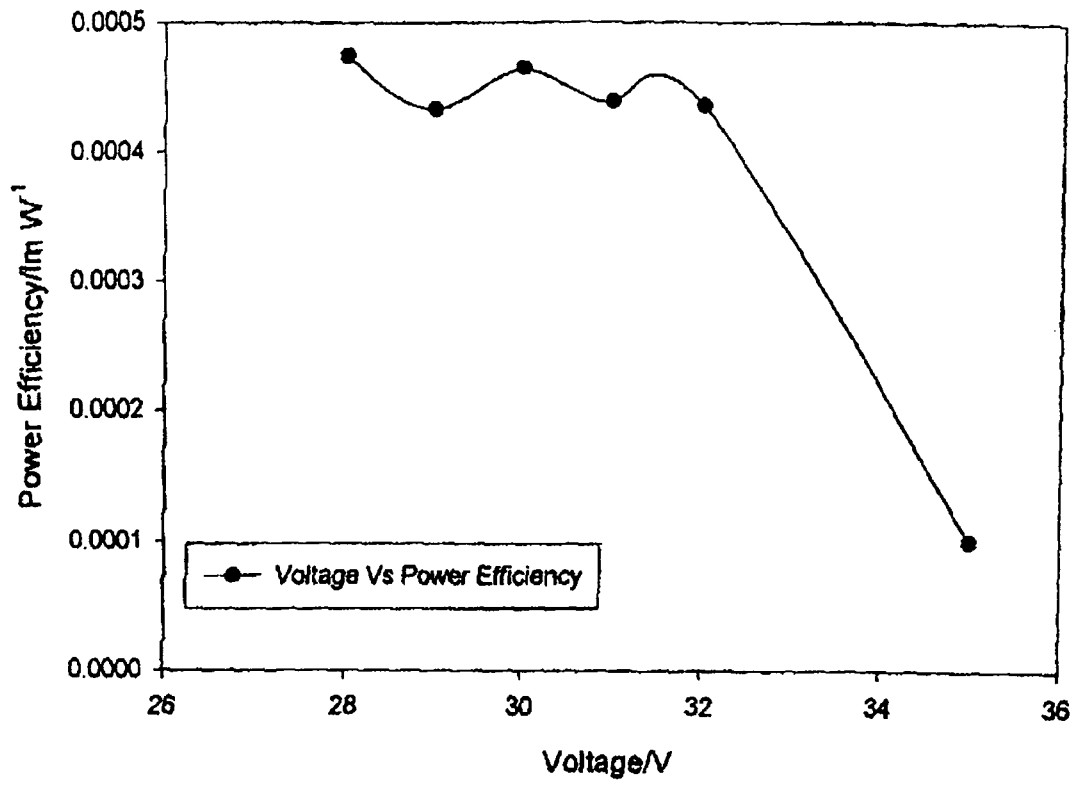


Fig. 11



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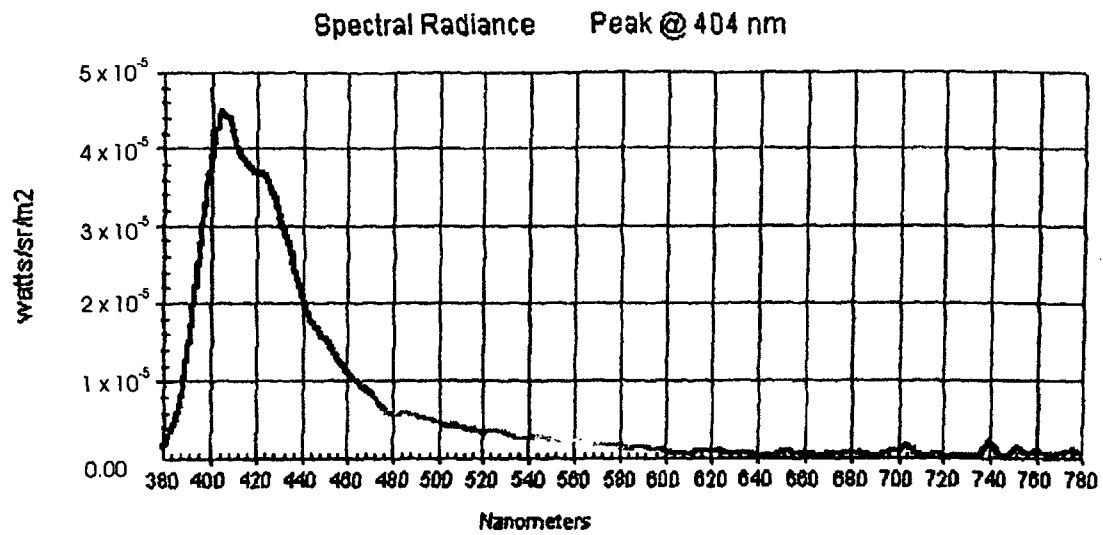


Fig. 12

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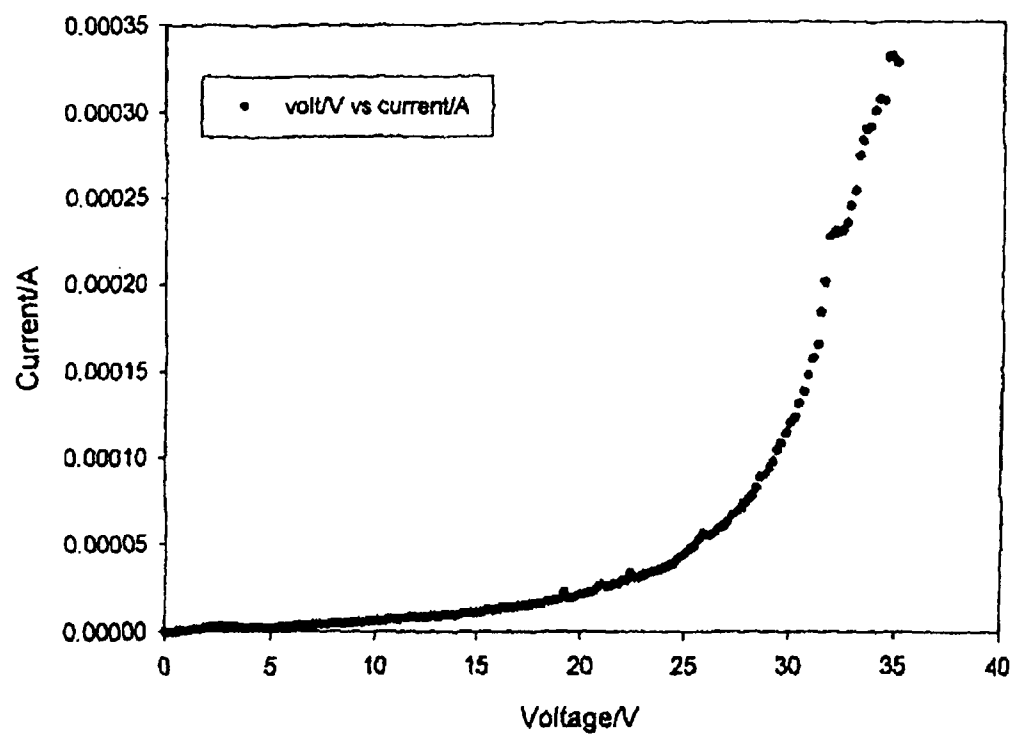


Fig. 13

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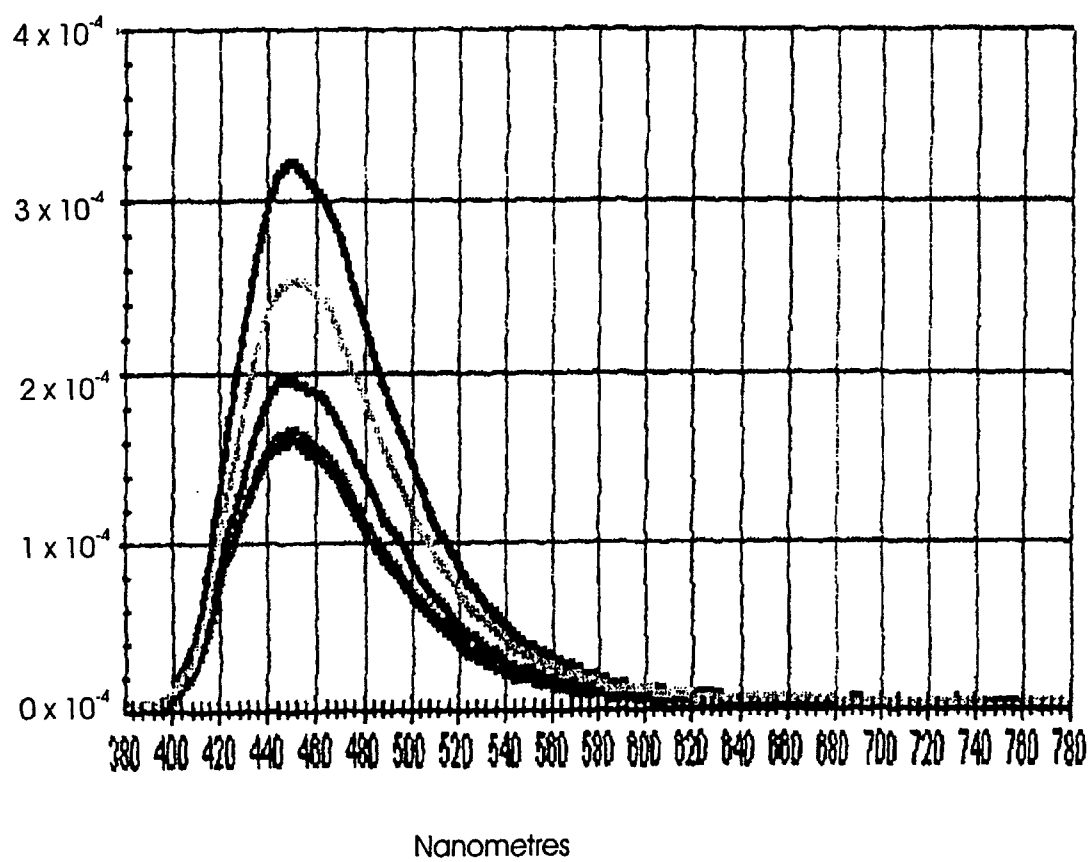


Fig. 14

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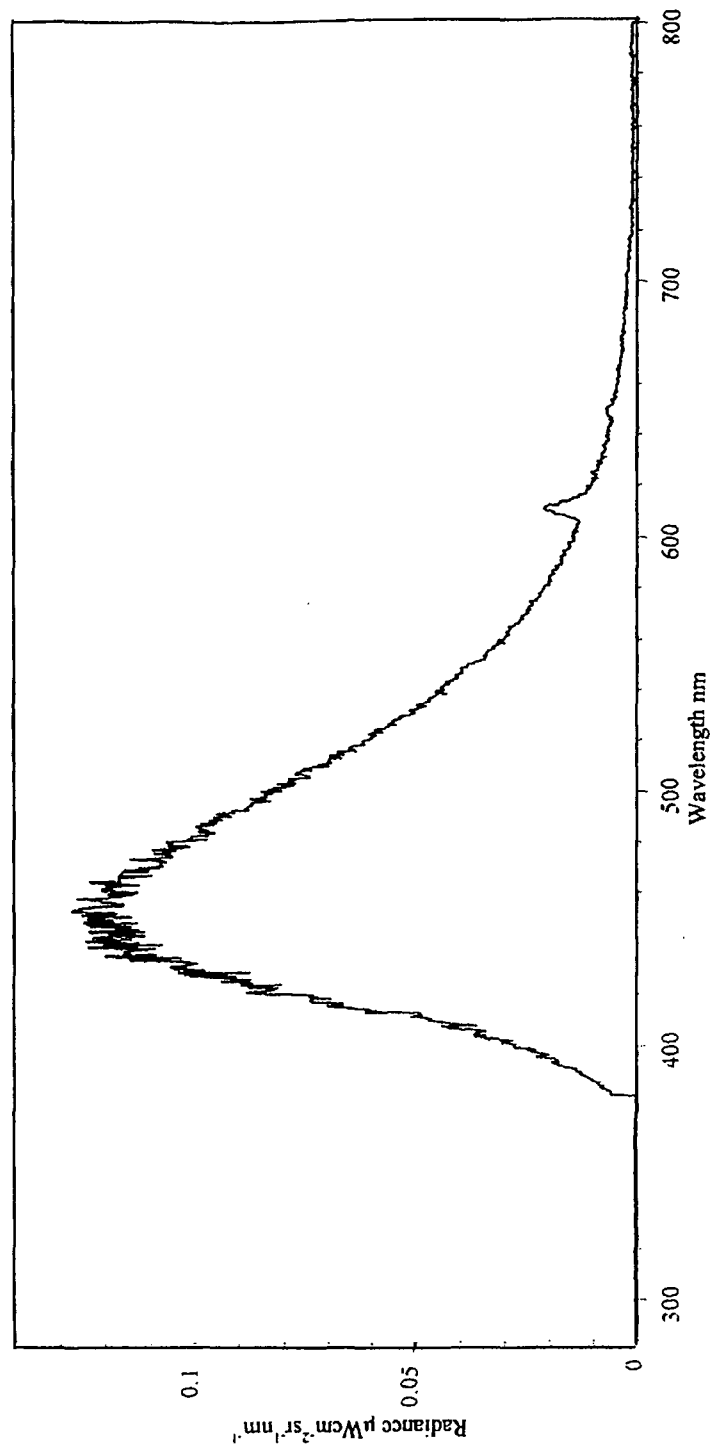


Fig. 15

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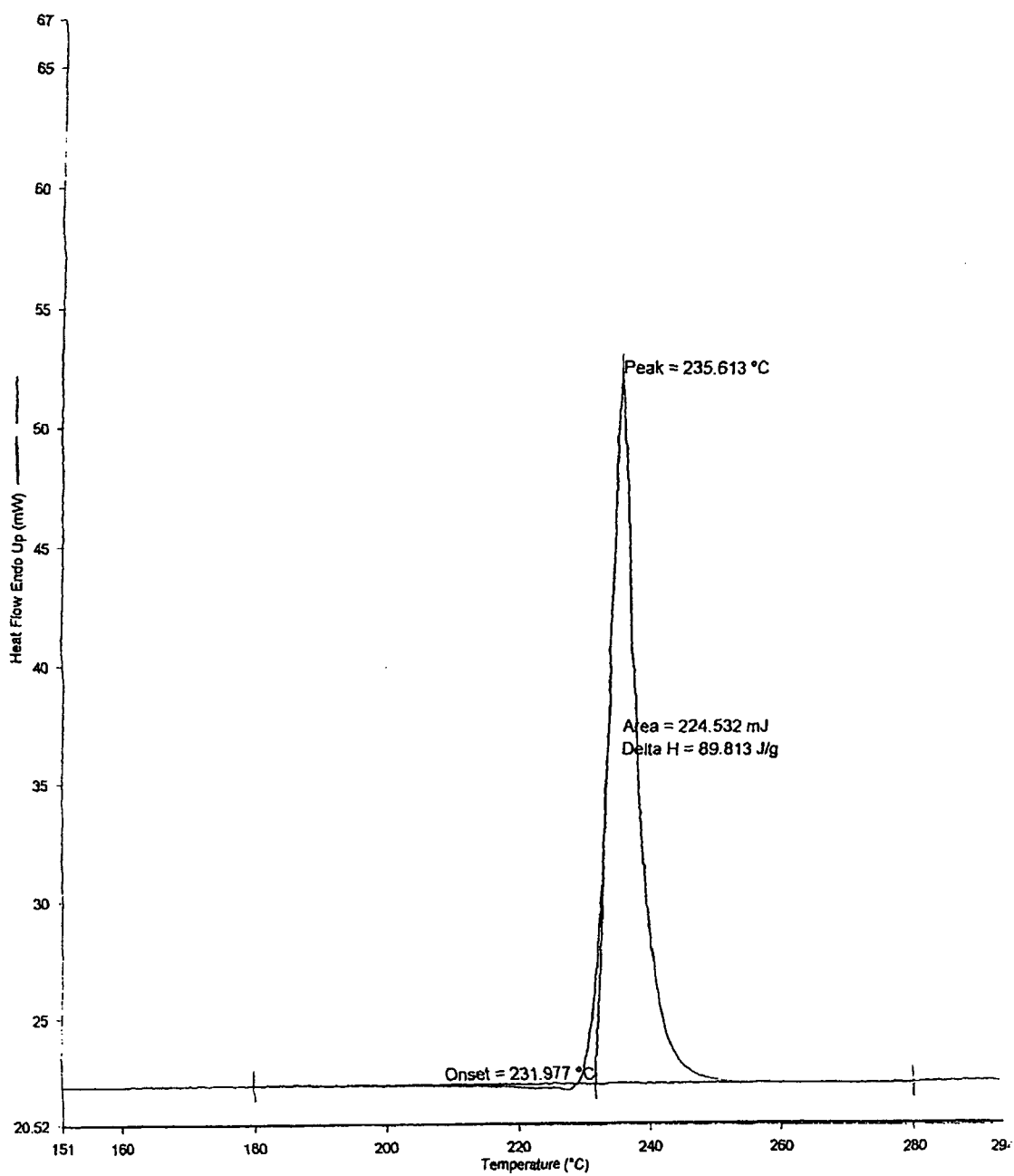


Fig. 16

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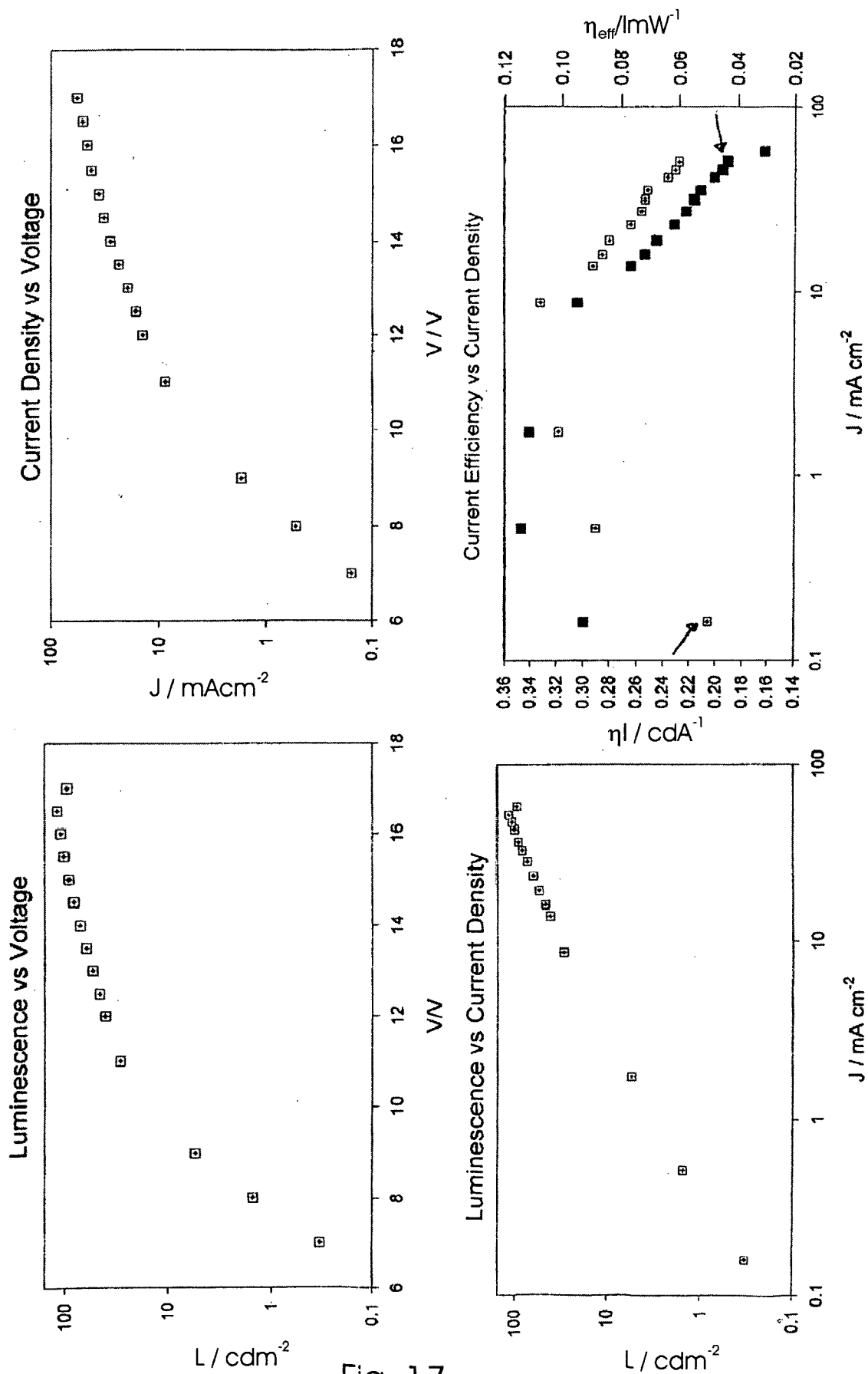


Fig. 17

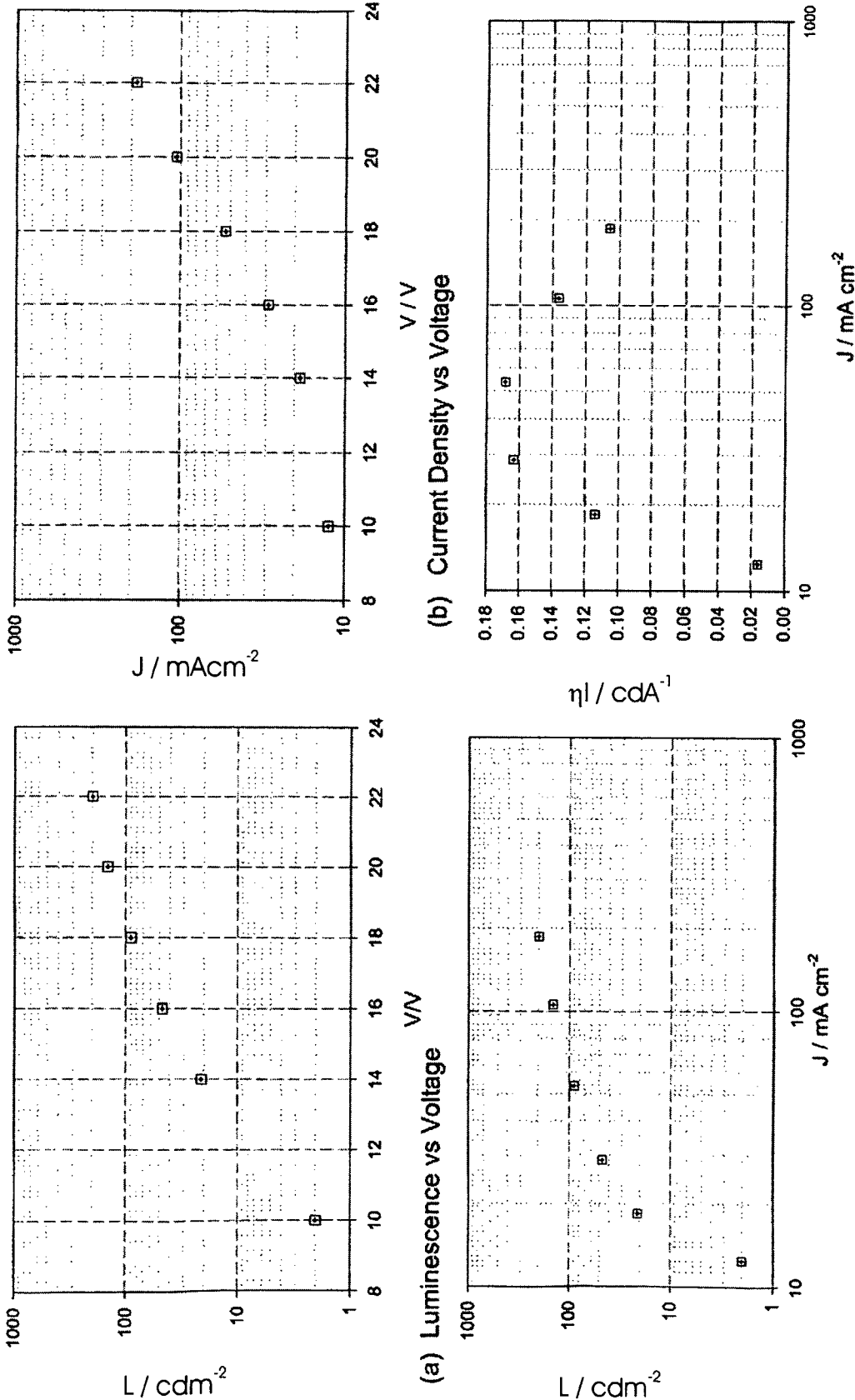


Fig. 18

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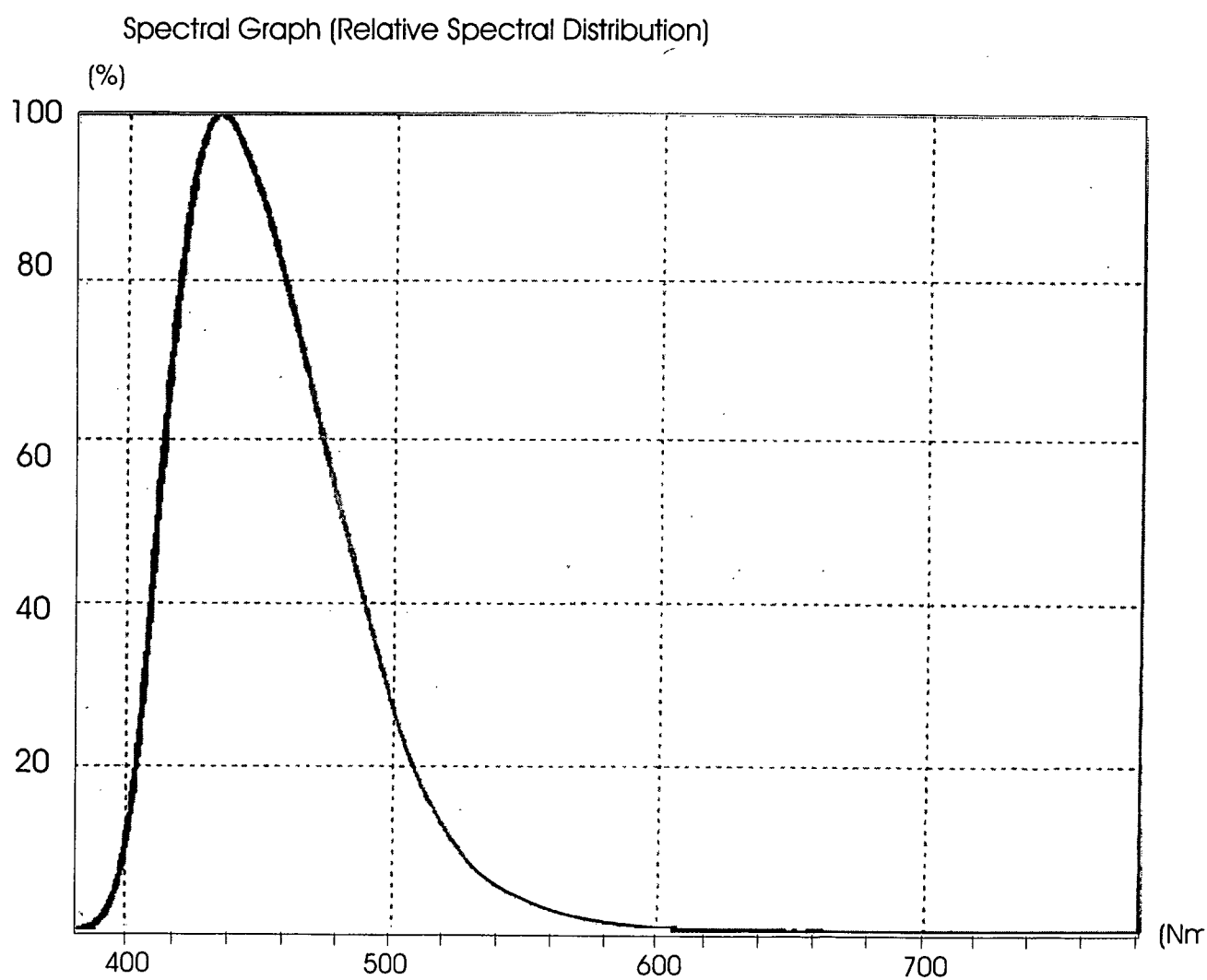


Fig. 19



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/03163

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C09K11/06 H05B33/14

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K H05B H01L

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)

INSPEC, EPO-Internal, WPI Data, PAJ, COMPENDEX, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>MARCHETTI F. ET AL.: "Copper and calcium complexes with anionic O2-donor 4-tert-butylacetyl-3-methyl-1-phenylpyrazol-5-one"</p> <p>J. CHEM. SOC. DALTON TRANS., no. 19, 1998, pages 3325-3333, XP002216363</p> <p>page 3325, column 1</p> <p>figures 1,4</p> <p>page 3331, column 1-2</p> <p>---</p> <p>-/--</p>	1-20

☒ Further documents are listed in the continuation of box C.

☐ 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.

\*G\* document member of the same patent family

Date of the actual completion of the international search

10 October 2002

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Name and mailing address of the ISA

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## INTERNATIONAL SEARCH REPORT

Inter al Application No

PCT/GB 02/03163

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GAO XI-CUN ET AL: "Photoluminescence and electroluminescence of a series of terbium complexes" SYNTHETIC METALS, 12 FEB. 1999, ELSEVIER, SWITZERLAND, vol. 99, no. 2, pages 127-132, XP002216364 ISSN: 0379-6779 figure 2 table 1 ---	1-20
A	GAO D -Q ET AL: "An organic electroluminescent device made from a gadolinium complex" SOLID STATE COMMUNICATIONS, 2001, ELSEVIER, USA, vol. 121, no. 2-3, pages 145-147, XP002216365 ISSN: 0038-1098 the whole document ---	1-20
A	ZHU W ET AL: "Red electroluminescence from a novel europium beta -diketone complex with acylpyrazolone ligand" 2ND INTERNATIONAL CONFERENCE ON ELECTROLUMINESCENCE OF MOLECULAR MATERIALS AND RELATED PHENOMENA, SHEFFIELD, UK, 15-18 MAY 1999, vol. 111-112, pages 445-447, XP002216366 Synthetic Metals, 1 June 2000, Elsevier, Switzerland ISSN: 0379-6779 the whole document ---	1-20
A	MOON D G ET AL: "Efficient single layer organic light emitting diodes based on a terbium pyrazolone complex" SYNTHETIC METALS, 4 SEPT. 2001, ELSEVIER, SWITZERLAND, vol. 123, no. 2, pages 355-357, XP002216367 ISSN: 0379-6779 the whole document ---	1-20
A	PETTINARI C. ET AL.: "Tin(IV) and organotin(IV) derivatives of novel beta-diketones" INORG. CHIM. ACTA, vol. 262, - 1997 pages 33-46, XP002216368 figure 1 tables 1,5 --- -/--	1

## INTERNATIONAL SEARCH REPORT

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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.
A	PETTINARI C. ET AL.: "Tin(IV) and organotin(IV) derivatives of novel beta-diketones" INORG. CHIM. ACTA, vol. 257, - 1997 pages 37-48, XP002216369 figures 1-3 table 1 -----	1
A	PETTINARI C. ET AL.: "Synthesis and characterization of some tin (II) and tin(IV) derivatives of 4-acyl-5-pyrazolones" POLYHEDRON, vol. 13, no. 6-7, - 1994 XP002216370 abstract -----	1

专利名称(译)	电致发光材料和器件		
公开(公告)号	<a href="#">EP1404778A1</a>	公开(公告)日	2004-04-07
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当前申请(专利权)人(译)	MERCK PATENT GMBH		
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优先权	2001016644 2001-07-09 GB		
外部链接	<a href="#">Espacenet</a>		

#### 摘要(译)

电致发光材料是取代的吡唑-5-酮的金属络合物，优选铝。