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0814749.8 13 August 2008 (13.08.2008) GB(71) Applicant (for all designated States except US): **MERCK PATENT GMBH** [DE/DE]; Frankfurter Strasse 250, 64293 Darmstadt (DE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **KATHIRGA-MANATHAN, Poopathy** [GB/GB]; The little Lancaster House, 1 Lancaster Road, North Harrow HA2 7NN (GB). **SURENDRAKUMAR, Sivagnanasumdrum** [GB/GB]; 16 Nolton Place, Edgware, Middlesex HA8 6DL (GB).(74) Common Representative: **MERCK PATENT GMBH**; Frankfurter Strasse 250, 64293 Darmstadt (DE).

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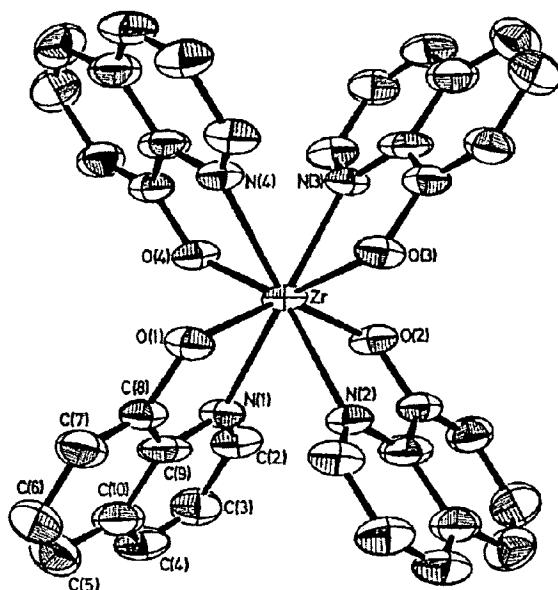
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(54) Title: COMPOUND HAVING ELECTROLUMINESCENT OR ELECTRON TRANSPORT PROPERTIES AND ITS PREPARATION AND USE

Fig. 1

(57) Abstract: A form of zirconium quinolate is disclosed having a monoclinic crystal structure, P21/c space group, unit cell dimensions  $a = 11.22 \text{ \AA}$ ,  $b = 14.67 \text{ \AA}$ ,  $c = 17.21 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 94.816^\circ$ ,  $\gamma = 90^\circ$  and unit cell volume  $2822.7 \text{ \AA}^3$ . It may be made by reacting a zirconium alkoxide with 8-hydroxyquinoline in a solvent comprising tetrahydrofuran, recovering the zirconium quinolate and purifying it by sublimation. It is useful e.g. as a host in an electroluminescent layer of an organic light-emitting diode, and/or in an electron transport layer. After initial purification is by sublimation, it is sublimable substantially without residue and when used as an electron transport layer in an OLED increases the luminance of the OLED and reduces the turn-on voltage compared to either aluminium quinolate or zirconium quinolate made by the earlier chloride route.

## Compound having electroluminescent or electron transport properties and its preparation and use

### FIELD OF THE INVENTION

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This invention relates to a novel compound, to a method for its preparation and to its use in *inter alia* optical light emitting devices e.g. in an electron transport layer or as a host in an electroluminescent layer in the field of flat panel displays and/or in lighting.

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### BACKGROUND TO THE INVENTION

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Kulkarni et al., Chem. Mater. 2004, 16, 4556-4573 (the contents of which are incorporated herein by reference) have reviewed the literature concerning electron transport materials (ETMs) used to enhance the performance of organic light-emitting diodes (OLEDs). In addition to a large number of organic materials, they discuss metal chelates including aluminium quinolate, which they explain remains the most widely studied metal chelate owing to its superior properties such as high EA (~ -3.0 eV; measured by the present applicants as - 2.9 eV) and IP (~ -5.95 eV; measured by the present applicants as about - 5.7 eV), good thermal stability (Tg ~ 172°C) and ready deposition of pinhole-free thin films by vacuum evaporation. Aluminium quinolate remains a preferred material both for use as a host to be doped with various fluorescent materials to provide an electroluminescent layer and for use as an electron transport layer.

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Zirconium quinolate has a particularly advantageous combination of properties for use as an electron transport material and which identify it as being a significant improvement on aluminium quinolate for that use. It has high electron mobility. Its melting point (388°C) is lower than that of aluminium quinolate (414°C). Its lowest unoccupied molecular orbital

(LUMO) is at  $-2.9$  eV and its highest occupied molecular orbital (HOMO) is at  $-5.6$  eV, similar to the values of aluminium quinolate. Furthermore, unexpectedly, it has been found that when incorporated into an electron transport layer it slows loss of luminance of an OLED device at a given current with increase of the time for which the device has been operative (i.e. increases device lifetime), or increases the light output for a given applied voltage, the current efficiency for a given luminance and/or the power efficiency for a given luminance. Embodiments of cells in which the electron transport material is zirconium quinolate can exhibit reduced turn-on voltage and up to four times the lifetime of similar cells in which the electron transport material is aluminium quinolate. It is compatible with aluminium quinolate when aluminium quinolate is used as host in the electroluminescent layer of an OLED, and can therefore be employed by many OLED manufacturers with only small changes to their technology and equipment. It also forms a good electrical and mechanical interface with inorganic electron injection layers e.g. a LiF layer where there is a low likelihood of failure by delamination. As described below, it also gives good results when interfaced with organolithium compounds as electron injection materials e.g. lithium quinolate or a substituted lithium quinolate or lithium Schiff bases. Zirconium quinolate can also be used as a host or as a component of the host material in the electroluminescent layer.

A crystal structure for  $\text{ZrQ}_4\cdot[\text{toluene}]_3$  is reported by Lewis D.F. et al., J. Chem Soc. Chem. Comm., 1974, 1046 and is shown in Fig. 1, the molecules of toluene which form part of the crystal structure being omitted. The authors describe zirconium quinolate having a orthorhombic crystal structure with the space group Fddd and the unit cell parameters  $a = 14.168 \text{ \AA}$ ,  $b = 27.720 \text{ \AA}$ , and  $c = 21.371 \text{ \AA}$ .

## SUMMARY OF THE INVENTION

We have found that different methods of making zirconium quinolate produce forms having different structures and properties.

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Zirconium quinolate made by a previously disclosed method using zirconium chloride as starting material and ethanol as solvent [referred to as Zrq<sub>4</sub>-B or B-form] has an orthorhombic, primitive crystal structure with unit cell dimensions  $a = 8.24 \text{ \AA}$ ,  $b = 17.35 \text{ \AA}$ ,  $c = 19.96 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$  and a unit cell volume of  $2844 \text{ \AA}^3$ . Its structure is shown in Fig. 3.

10

However, zirconium quinolate made from a zirconium alkoxide e.g. zirconium isopropoxide in a solvent comprising tetrahydrofuran is readily purifiable by sublimation and after purification is substantially pure zirconium quinolate having a monoclinic crystal structure, P21/c space group, unit cell dimensions  $a = 11.22 \text{ \AA}$ ,  $b = 14.67 \text{ \AA}$ ,  $c = 17.21 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 94.816^\circ$ ,  $\gamma = 90^\circ$ , unit cell volume  $2822.7 \text{ \AA}^3$  [referred to as Zrq<sub>4</sub>-A or A-form]. Its structure is shown in Fig. 2. The A-form has significantly better sublimation properties (e.g. in embodiments it can sublime without residue) and gives significantly better performance e.g. when used as an electron transport layer in an OLED.

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The invention therefore relates to the monoclinic A-form of zirconium quinolate, to its method of production and to use e.g. electron transport layer in devices.

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The invention further comprises an optical light emitting diode device having a first electrode, a layer comprising monoclinic zirconium quinolate and a second electrode.

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Monoclinic zirconium quinolate may be used as an electron transport material in OLEDs, as an electroluminescent material or as a host material, being dopable as described below. It may also be used in lighting.

- 5 Monoclinic zirconium quinolate, when used to provide an electron transport layer may be n-doped e.g. with lithium, potassium, caesium or another low work function metal. It may be used alone or in admixture with another organic small molecule electron transport material either un-doped or n-doped. It may be used with inorganic electron injection layers e.g. LiF or  
10 with organic small molecule electron injection layers e.g. as described below under the heading "electron injection materials".

- Thus embodiments of the invention may further provide an electroluminescent device having first and second electrodes and between  
15 said electrodes an electroluminescent layer which comprises monoclinic zirconium quinolate which may be doped with a fluorescent dopant, a phosphorescent dopant or an ion fluorescent dopant.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

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- The invention will be further described with reference to the drawings, in which Figs. 1-3 show structures of various forms of zirconium quinolate determined by X-ray crystallography and Figs. 4-8 are performance curves showing how monoclinic zirconium quinolate compares to the orthorhombic  
25 form and to aluminium quinolate.

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## DESCRIPTION OF PREFERRED EMBODIMENTS

### Crystal structure

- 5 The present invention relates to zirconium quinolate having a monoclinic crystal structure, preferably with the space group P21/c.

A particularly preferred embodiment of the present invention is zirconium quinolate having monoclinic crystal structure with space group P21/c,  
10 characterized in that the unit cell dimensions are  $a = 11.2 \pm 0.4 \text{ \AA}$ ,  
 $b = 14.7 \pm 0.4 \text{ \AA}$ ,  $c = 17.2 \pm 0.4 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 95^\circ \pm 1^\circ$ ,  $\gamma = 90^\circ$ , and unit cell volumen  $V = 2823 \pm 5 \text{ \AA}^3$  and very particularly preferably the cell dimensions are  $a = 11.22 \text{ \AA}$ ,  $b = 14.67 \text{ \AA}$ ,  $c = 17.21 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 94.816^\circ$ ,  $\gamma = 90^\circ$ , and unit cell volumen  $V = 2822.7 \text{ \AA}^3$ .

- 15 In another preferred embodiment of the present invention the zirconium quinolate having the monoclinic crystal form as described above has a purity of greater than or equal to 80%, preferably greater than or equal to 85%, particularly preferably greater than or equal to 90%, and very  
20 particularly preferably greater than or equal to 95%.

The term "substantially pure" is used herein to define a purity of greater than or equal to 95%.

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### Preparation of zirconium quinolate

- The present invention also relates to a method of making zirconium quinolate in monoclinic form, which comprises reacting zirconium alkoxide  
30 with 8-hydroxyquinoline in a solvent comprising tetrahydrofuran, recovering the zirconium quinolate and purifying it by sublimation. Preferably the zirconium alkoxide is zirconium isopropoxide.

## Cell structure

The OLEDs of the invention are useful *inter alia* in flat panel displays and in embodiments comprise an anode and a cathode between which is  
5 sandwiched a multiplicity of thin layers including an electroluminescent layer, electron injection and/or transport layer(s), hole injection and/or transport layer(s) and optionally ancillary layers. The layers are in embodiments built up by successive vacuum vapour deposition operations, although it may be convenient to form one or more of the layers e.g. the  
10 hole injection and hole transport layers by other methods e.g. spin coating or ink jet printing.

An OLED device in embodiments comprises a transparent substrate on which are successively formed an anode layer, a hole injector (buffer) layer,  
15 a hole transport layer, an electroluminescent layer, an electron transport layer, an electron injection layer and an anode layer which may in turn be laminated to a second transparent substrate. Top emitting OLED's are also possible in which an aluminium or other metallic substrate carries an ITO  
20 layer, a hole injection layer, a hole transport layer, an electroluminescent layer, an electron transport layer, an electron injection layer and an ITO or other transparent cathode, light being emitted through the cathode. A further possibility is an inverted OLED in which a cathode of aluminium or aluminium alloyed with a low work function metal carries successively an  
25 electron injection layer, an electron transport layer, an electroluminescent layer, a hole transport layer, a hole injection layer and an ITO or other transparent conductive anode, emission of light being through the anode. If desired a hole blocking layer may be inserted e.g. between the electroluminescent layer and the electron transport layer. Based on the disclosure of the present invention any further layer that is known by a  
30 person skilled in the art can be used to build a device without being inventive. One skilled in the art may also establish different device architectures with, e.g., repeating or alternating layers of the same type.

Examples of additional layers are, but are not limited to, electron blocking layer, exciton blocking layer or photoabsorption layer in order to build e.g. a photodiode. Additional layer may also comprise dyes or metal complexes.

5 OLEDs of the invention include small molecule OLEDs, polymer light emitting diodes (p-OLEDs), OLEDs that emit light by fluorescence, OLEDs that emit light by phosphorescence (PHOLEDs) and OLEDs that emit light by ion fluorescence (rare earth complexes) and include single-colour or multi-colour active or passive matrix displays.

10 The OLEDs may be of the active matrix type or of the passive matrix type. A representative active matrix OLED array is described in US-A-5929474 (Huang, Motorola) the contents of which are incorporated herein by reference. That specification describes an active matrix organic light  
15 emitting device array comprising: (a) a semiconductor substrate having an array area defined thereon; (b) a plurality of field effect transistors, each including first and second current carrying terminals and a control terminal, formed in the array area on the semiconductor substrate in rows and columns, each of the rows including a row bus coupled to the first current  
20 carrying terminal of each field effect transistor in the row, and each of the columns including a column bus coupled to the control terminal of each field effect transistor in the column; (c) a planarizing layer of insulating material positioned over the plurality of field effect transistors in the array area and defining a substantially planar surface; (d) a plurality of contact pads formed  
25 on the planar surface of the planarizing layer in the array area in rows and columns, each contact pad of the plurality of contact pads associated with one field effect transistor of the plurality of field effect transistors and coupled to the second current carrying terminal of the associated field effect transistor by a conductor formed through the planar layer; (e) a plurality of  
30 layers of organic material sequentially formed in overlying relationship on the contact pads in the array area so as to define an organic light emitting device on each contact pad with each contact pad operating as a first

terminal of an overlying organic light emitting device; and (f) electrical and light conducting material positioned in overlying relationship over the layers of organic material in the array area and operating as a common second terminal of the organic light emitting devices. Further references describing active matrix devices are EP-A-0717446 (Tang *et al.*, Kodak) and WO 99/65012 (Knapp *et al.*, Philips) the disclosures of which are incorporated herein by reference. Choice of active or passive matrix driving may affect the selection of electrode materials, but need not fundamentally affect the choice of materials for the layers between the electrodes.

### Anode

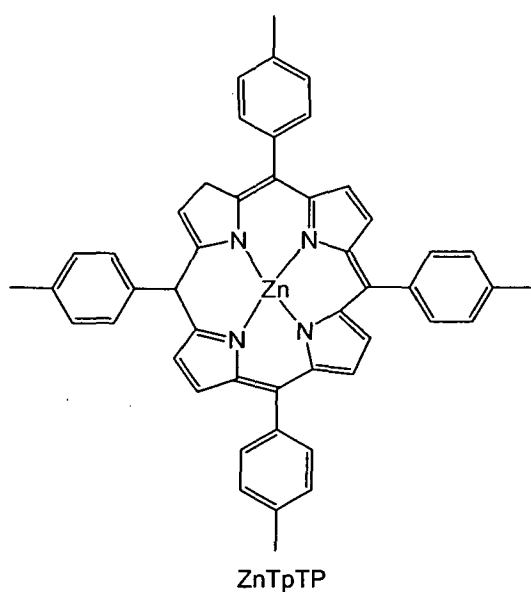
In many embodiments the anode is formed by a layer of tin oxide or indium tin oxide coated onto glass or other transparent substrate. Other materials that may be used include antimony tin oxide and indium zinc oxide. If desired a modified anode may be produced e.g. by subsequently treating the ITO surface with oxygen plasma, and then conditioned as a modified anode by decomposing  $\text{CHF}_3$  gas in a plasma treatment chamber to deposit an ~1-nm-thick layer of  $\text{CF}_x$ . In active matrix embodiments the anode may be a high work function metal or alloy e.g. gold or platinum or may be crystalline, polycrystalline, continuous grain or amorphous silicon which may be p-doped.

### Hole injection materials

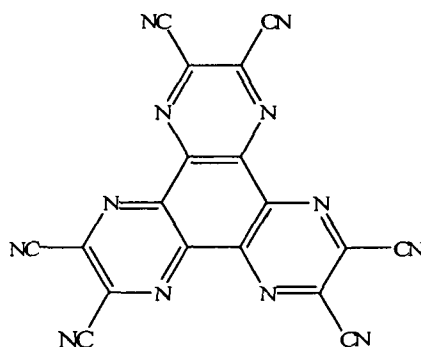
A single layer may be provided between the anode and the electroluminescent material, but in many embodiments there are at least two layers one of which is a hole injection layer (buffer layer) and the other of which is a hole transport layer, the two layer structure offering in some embodiments improved stability and device life (see US-A-4720432 (VanSlyke *et al.*, Kodak). The hole injection layer may serve to improve the

film formation properties of subsequent organic layers and to facilitate the injection of holes into the hole transport layer.

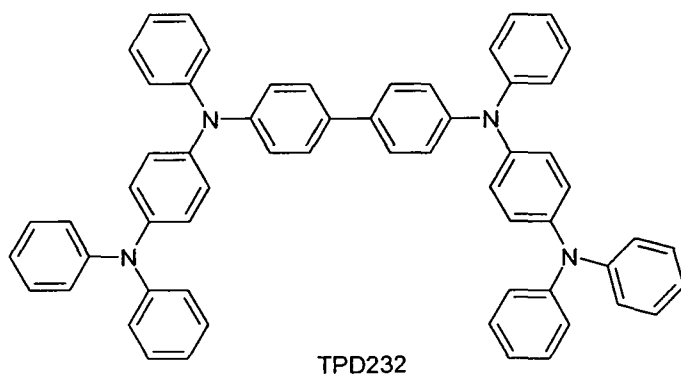
Suitable materials for the hole injection layer which may be of thickness e.g. 0.1 to 200 nm depending on material and cell type include hole-injecting porphyrinic compounds - see US-A-4356429 (Tang, Eastman Kodak) e.g. zinc phthalocyanine copper phthalocyanine and ZnTpTP, whose formula is set out below:

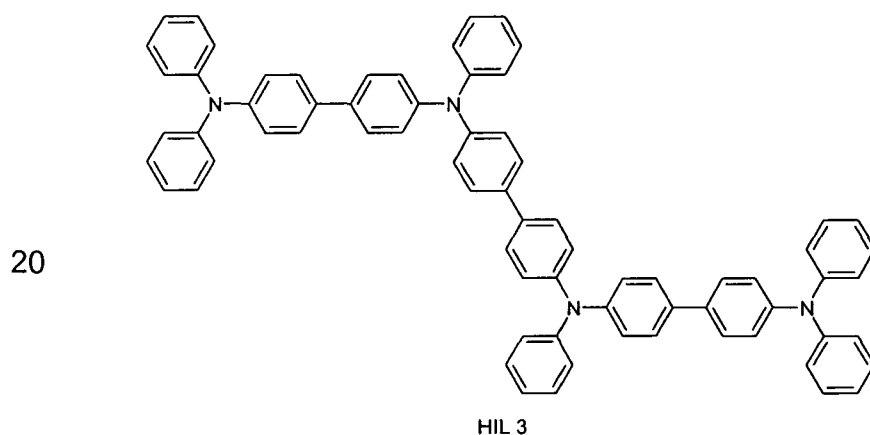
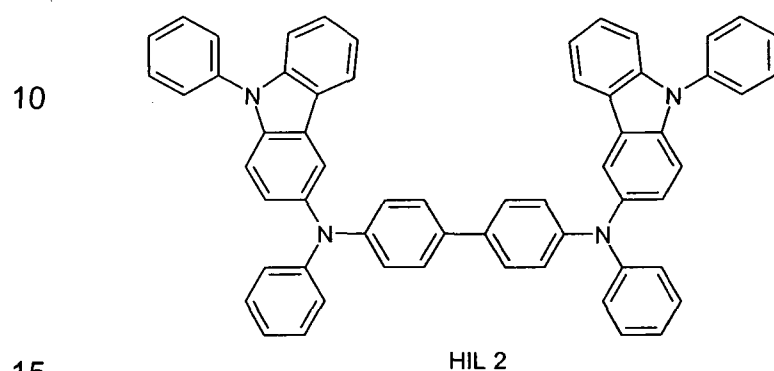
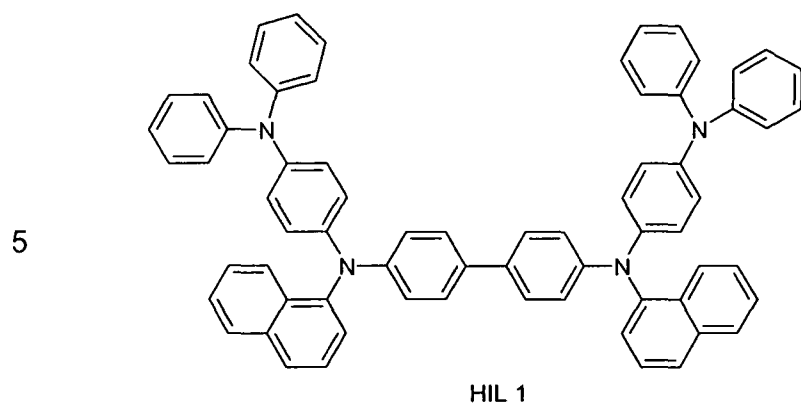


Particularly good device efficiencies, turn/on voltages and/or lifetimes may be obtained where the hole injection layer is ZnTpTP. A further material that may be used is hexacyanohexaazatriphenylene (CHATP) of structure:



The hole injection layer may also be a fluorocarbon-based conductive polymer formed by plasma polymerization of a fluorocarbon gas - see US-A-6208075 (Hung *et al.*; Eastman Kodak), a triarylamine polymer - see EP-A-0891121 (Inoue *et al.*, TDK Corporation) or a phenylenediamine derivative – see EP-A- 1029909 (Kawamura *et al.*, Idemitsu) or the materials described in US-A-6436559 (Ueno, Canon) and 6720573 (Se-Hwan, LG Chemical Co., Ltd.). It may also be a solution-processable hole injecting polymer e.g. PEDOT/PSS (poly-3,4-ethylenedioxythiophene doped with poly(styrenesulfonate) or a block copolymers of PEDOT and a flexible polymer such as a polyether, polysiloxane, polyester, or polyacrylate. Methods of applying such materials include spin coating, printing through a mask and ink jet printing e.g. of a relatively dilute solution where thin hole injection layers are desired. The hole injection material may also be an aromatic amine as described in US 2008/0102311 A1 such as N,N'-diphenyl-N,N'-di(3-tolyl)benzidine (= 4,4'-bis[N-3-methylphenyl]-N-phenylamino)biphenyl, NPD) (US 5061569), N,N'-bis(N,N'-diphenyl-4-aminophenyl)-N,N'-diphenyl-4,4'-diamino-1,1'-biphenyl (TPD 232), and 4,4',4''-tris[3-methylphenyl]phenylamino]-triphenylamine (MTDATA) (JP Heisei 4 (1992) 308688) or an aromatic amine as described in US 7399537 B2 (HIL 1), US 2006/0061265 A1, EP 1661888 B1 (HIL2), and JP 08292586 A (HIL 3).





25 **Hole-transport materials**

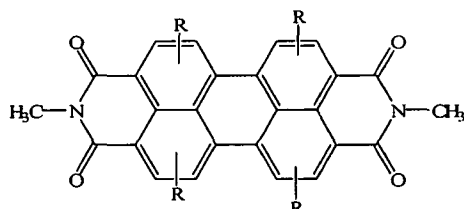
Hole transport layers which may be used are in some embodiments preferably of thickness 20 to 200 nm.

30 One class of hole transport materials comprises polymeric materials that may be deposited as a layer by means of spin coating or ink jet printing. Such polymeric hole-transporting materials include poly(*N*-vinylcarbazole)

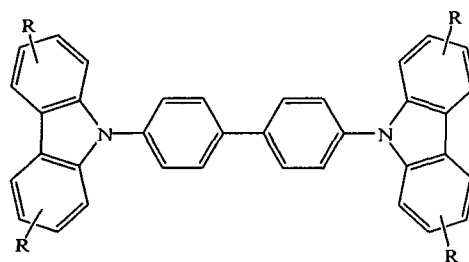
(PVK), polythiophenes, polypyrrole, and polyaniline. Other hole transporting materials are conjugated polymers e.g. poly (p-phenylenevinylene) (PPV) and copolymers including PPV. Other preferred polymers are: poly(2,5 dialkoxyphenylene vinylenes e.g. poly (2-methoxy-5-(2-methoxypentyloxy-1,4-phenylene vinylene), poly(2-methoxypentyloxy)-1,4-phenylenevinylene), poly(2-methoxy-5-(2-dodecyloxy-1,4-phenylenevinylene) and other poly(2,5 dialkoxyphenylenevinylenes) with at least one of the alkoxy groups being a long chain solubilising alkoxy group; polyfluorenes and oligofluorenes; polyphenylenes and oligophenylenes; polyanthracenes and oligoanthracenes; and polythiophenes and oligothiophenes.

A further class of hole transport materials comprises sublimable small molecules. For example, aromatic tertiary amines provide a class of preferred hole-transport materials, e.g. aromatic tertiary amines including at least two aromatic tertiary amine moieties (e.g. those based on biphenyl diamine or of a "starburst" configuration) as described in EP 1162193 B1 , EP 650955 (HTL1), DE 19646119 A1 (HTL2), WO 2006/122630 A1, DE 102008024182.2 (HTL3), EP 1834945 (HTL 4), JP 08053397 A, US 6251531 (HTL5)

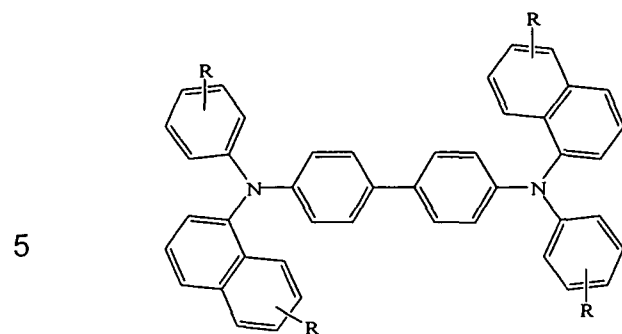
For example, aromatic amines may be used of the general formulae (i)-(xii) below:



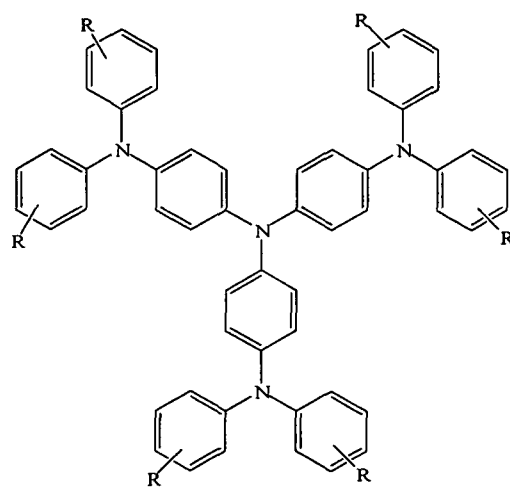
(i);



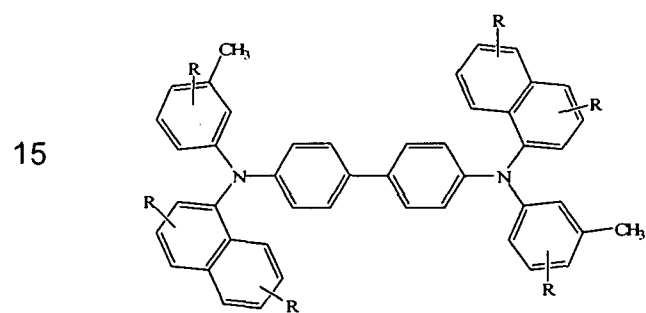
(ii);



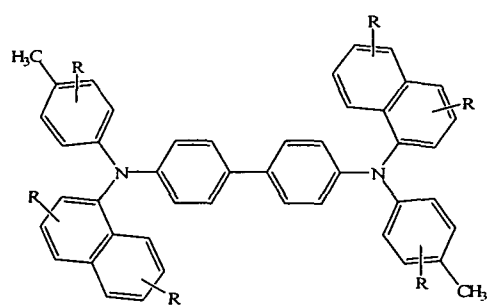
(iii);



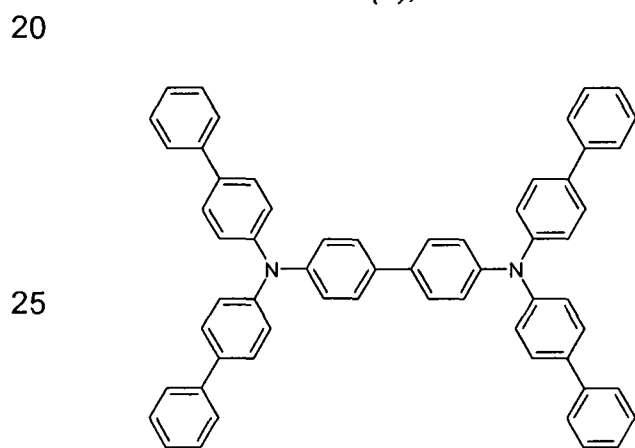
(iv);



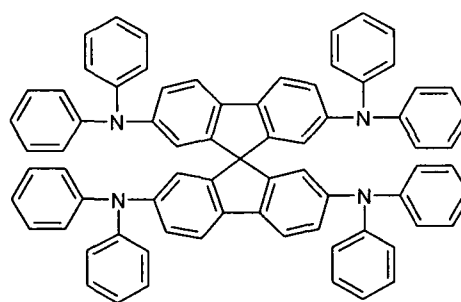
(v);



(vi);

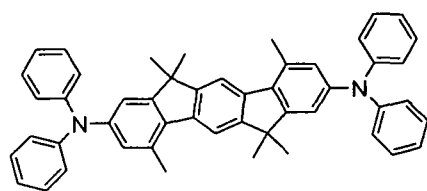


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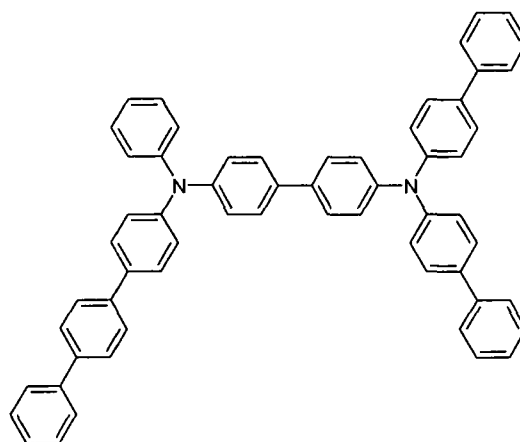


HTL2

(viii)



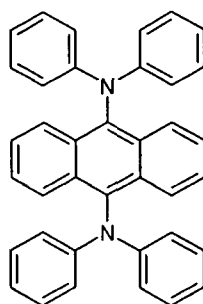
HTL3



HTL4

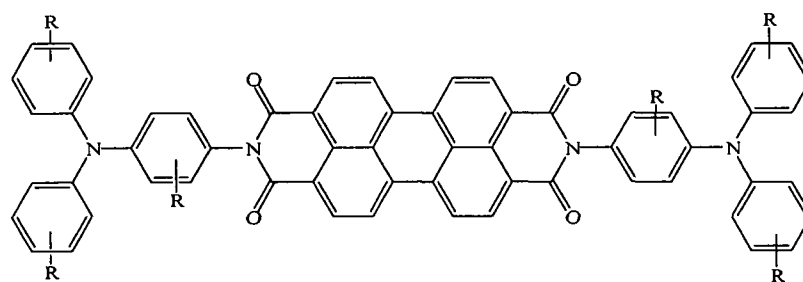
(ix)

(x)



HTL5

(xi)



(xii)

wherein

the groups R in any of the formulae in (i) to (xii) can be the same or different and are selected from hydrogen; substituted and unsubstituted aliphatic groups; substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures; halogens; and thiophenyl groups;

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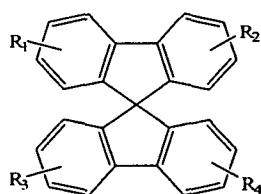
and wherein

in formula (i) the methyl groups may be replaced by C<sub>1</sub> to C<sub>4</sub> alkyl or monocyclic or polycyclic aryl or heteroraryl which may be further substituted e.g. with alkyl, aryl or arylamino.

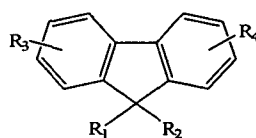
10

Further hole transport materials comprise

15



or



wherein

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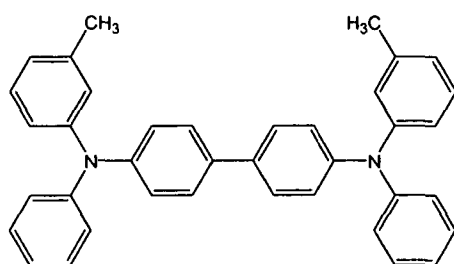
the groups R<sub>1</sub> to R<sub>4</sub> when appearing in either of the above formulae can be the same or different and are selected from hydrogen; substituted and unsubstituted aliphatic groups; substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures; halogens; and thiophenyl groups.

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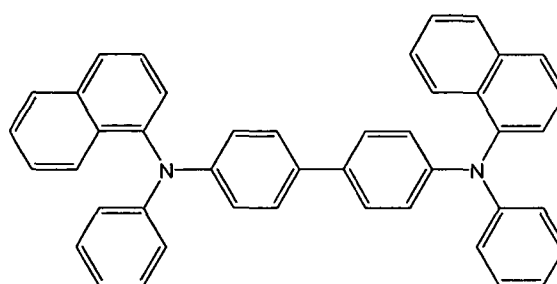
Particular preferred hole-transport materials are aromatic tertiary amines including at least two aromatic tertiary amine moieties (e.g. those based on biphenyl diamine or of a "starburst" configuration) of which the following are representative:

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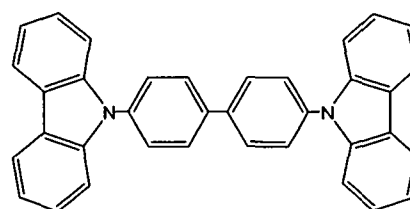
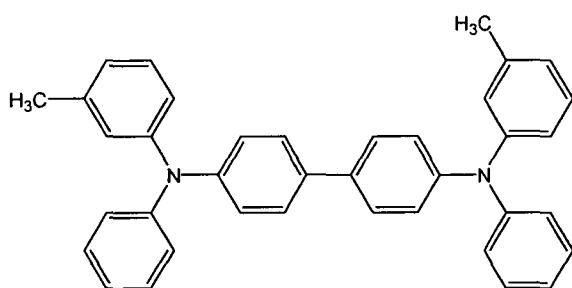
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TPD

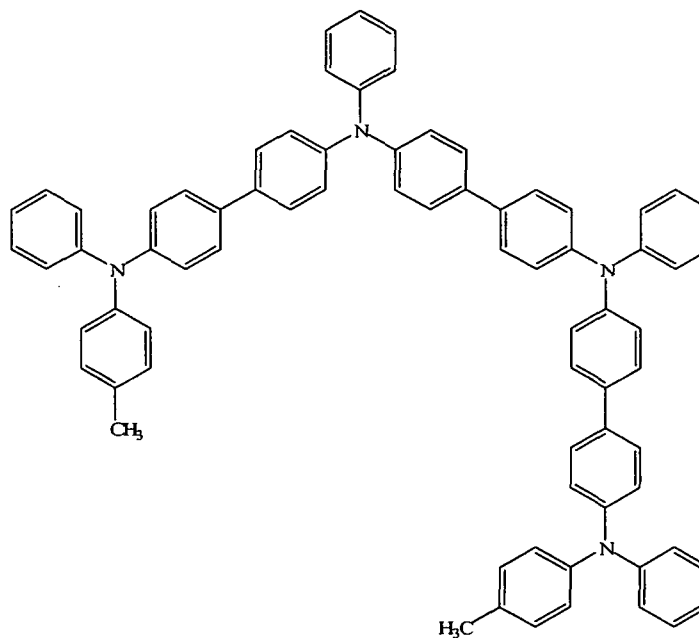
 $T_g$  (°C) 61 $\mu h$  (cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>)  $1 \times 10^{-3}$  $\alpha$ -NPB $T_g$  (°C) 98 $\mu h$  (cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>)  $1 \times 10^{-4}$ 

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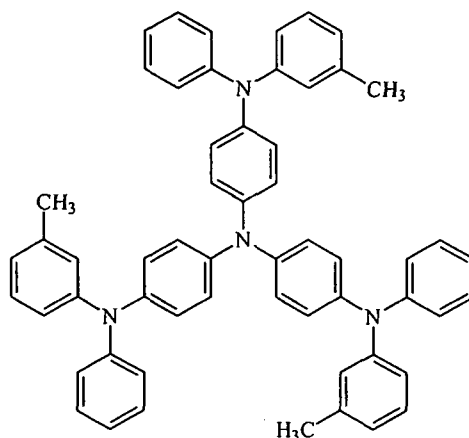


25

m-MTDATA.

 $T_g$  (°C) 75 $\mu h$  (cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>)  $2.7 \times 10^{-5}$ .

30



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10

A further possible material is 4,4',4''-tris(carbazolyl)-triphenylamine (TCTA) which is a hole transport material with a wider band gap than  $\alpha$ -NPB and which can in some embodiments assist in confining excitation to the emissive layer.

15

It further includes spiro-linked molecules which are aromatic amines e.g. spiro-TAD (2,2',7,7'-tetrakis-(diphenylamino)-spiro-9,9'-bifluorene).

A further class of small molecule hole transport materials is disclosed in WO 2006/061594 (Kathirgamanathan *et al*) and is based on diamino dianthracenes. Such compounds include:

20

9-(10-(N-(naphthalen-1-yl)-N-phenylamino)anthracen-9-yl)-N-(naphthalen-1-yl)-N-phenylanthracen-10-amine;

25

9-(10-(N-biphenyl-N-2-*m*-tolylamino)anthracen-9-yl)-N-biphenyl-N-2-*m*-tolylamino-anthracen-10-amine; and

9-(10-(N-phenyl-N-*m*-tolylamino)anthracen-9-yl)-N-phenyl-N-*m*-tolylanthracen-10-amine.

30

The hole transport layer may be p-doped e.g. with an acceptor-type organic molecule e.g. tetrafluorotetracyanoquinodimethane (F<sub>4</sub>-TCNQ) e.g. it may be starburst m-MTDATA doped with F<sub>4</sub>-TCNQ.

## 5      **Electroluminescent materials**

In principle any electroluminescent material may be used, including molecular solids which may be fluorescent dyes e.g. perylene dyes, metal complexes e.g. Alq<sub>3</sub>, so-called "blue" aluminium quinolates of the type Alq<sub>2</sub>L  
10      where q represents a quinolate and L represents a mono-anionic aryloxy ligand e.g. bis(2-methyl-8-quinolinolato)(4-phenyl-phenolato)Al(III), Ir(III)L<sub>3</sub>, rare earth chelates e.g. Tb(III) complexes, dendrimers and oligomers e.g. sexithiophene, or polymeric emissive materials. The electroluminescent layer may comprise as luminescent material a metal quinolate, an iridium,  
15      ruthenium, osmium, rhodium, iridium, palladium or platinum complex, a boron complex or a rare earth complex.

One preferred class of electroluminescent materials comprises host materials doped with one or more dyes or complexes which may be  
20      fluorescent, phosphorescent or ion-phosphorescent (rare earth). The use of monoclinic zirconium quinolate described herein as host material also forms part of the invention and it may provide red and green emitters when doped with appropriate dopants, in embodiments one or more than one dopant. The term "electroluminescent device" includes  
25      electrophosphorescent devices.

Preferably the host is doped with a minor amount of a fluorescent material as a dopant, preferably in an amount of 0.01 to 25% by weight of the doped mixture. As discussed in US-A-4769292 (Tang *et al.*, Kodak), the contents  
30      of which are included by reference, the presence of the fluorescent material permits a choice from amongst a wide latitude of wavelengths of light emission. In particular, as disclosed in US-A-4769292 by blending with the

organo metallic complex a minor amount of a fluorescent material capable of emitting light in response to hole-electron recombination, the hue of the light emitted from the luminescent zone, can be modified. In theory, if a host material and a fluorescent material could be found for blending which have exactly the same affinity for hole-electron recombination, each material should emit light upon injection of holes and electrons in the luminescent zone. The perceived hue of light emission would be the visual integration of both emissions. However, since imposing such a balance of host material and fluorescent materials is limiting, it is preferred to choose the fluorescent material so that it provides the favoured sites for light emission. When only a small proportion of fluorescent material providing favoured sites for light emission is present, peak intensity wavelength emissions typical of the host material can be entirely eliminated in favour of a new peak intensity wavelength emission attributable to the fluorescent material.

While the minimum proportion of fluorescent material sufficient to achieve this effect varies, in no instance is it necessary to employ more than about 10 mole percent fluorescent material, based on host material and seldom is it necessary to employ more than 1 mole percent of the fluorescent material. On the other hand, limiting the fluorescent material present to extremely small amounts, in some embodiments less than about  $10^{-3}$  mole percent, based on the host material, can result in retaining emission at wavelengths characteristic of the host material. Thus, by choosing the proportion of a fluorescent material capable of providing favoured sites for light emission, either a full or partial shifting of emission wavelengths can be realized. This allows the spectral emissions of the EL devices to be selected and balanced to suit the application to be served. In the case of fluorescent dyes, in some embodiments amounts are 0.01 to 5 wt%, for example 2 to 3 wt%. In the case of phosphorescent dyes amounts in some embodiments are 0.1 to 15 wt%. In the case of ion phosphorescent materials amounts in some embodiments are 0.01 to 25 wt% or up to 100 wt%.

Choosing fluorescent materials capable of providing favoured sites for light emission necessarily involves relating the properties of the fluorescent material to those of the host material. The host can be viewed as a collector for injected holes and electrons with the fluorescent material providing the molecular sites for light emission. One important relationship for choosing a fluorescent material capable of modifying the hue of light emission when present in the host is a comparison of the reduction potentials of the two materials. The fluorescent materials demonstrated to shift the wavelength of light emission have exhibited a less negative reduction potential than that of the host. Reduction potentials, measured in electron volts, have been widely reported in the literature along with varied techniques for their measurement. Since it is a comparison of reduction potentials rather than their absolute values which is desired, it is apparent that any accepted technique for reduction potential measurement can be employed, provided both the fluorescent and host reduction potentials are similarly measured. A preferred oxidation and reduction potential measurement techniques is reported by R. J. Cox, Photographic Sensitivity, Academic Press, 1973, Chapter 15.

A second important relationship for choosing a fluorescent material capable of modifying the hue of light emission when present in the host is a comparison of the band-gap potentials of the two materials. The fluorescent materials demonstrated to shift the wavelength of light emission have exhibited a lower band gap potential than that of the host. The band gap potential of a molecule is taken as the potential difference in electron volts (eV) separating its ground state and first singlet state. Band gap potentials and techniques for their measurement have been widely reported in the literature. The band gap potentials herein reported are those measured in electron volts (eV) at an absorption wavelength which is bathochromic to the absorption peak and of a magnitude one tenth that of the magnitude of the absorption peak. Since it is a comparison of band gap potentials rather than their absolute values which is desired, it is apparent that any accepted

technique for band gap measurement can be employed, provided both the fluorescent and host band gaps are similarly measured. One illustrative measurement technique is disclosed by F. Gutman and L. E. Lyons, Organic Semiconductors, Wiley, 1967, Chapter 5.

5

With host materials which are themselves capable of emitting light in the absence of the fluorescent material, it has been observed that suppression of light emission at the wavelengths of emission characteristics of the host alone and enhancement of emission at wavelengths characteristic of the fluorescent material occurs when spectral coupling of the host and fluorescent material is achieved. By "spectral coupling" it is meant that an overlap exists between the wavelengths of emission characteristic of the host alone and the wavelengths of light absorption of the fluorescent material in the absence of the host. Optimal spectral coupling occurs when the emission wavelength of the host is within  $\pm 25$  nm of the maximum absorption of the fluorescent material alone. In practice advantageous spectral coupling can occur with peak emission and absorption wavelengths differing by up to 100 nm or more, depending on the width of the peaks and their hypsochromic and bathochromic slopes. Where less than optimum spectral coupling between the host and fluorescent materials is contemplated, a bathochromic as compared to a hypsochromic displacement of the fluorescent material produces more efficient results.

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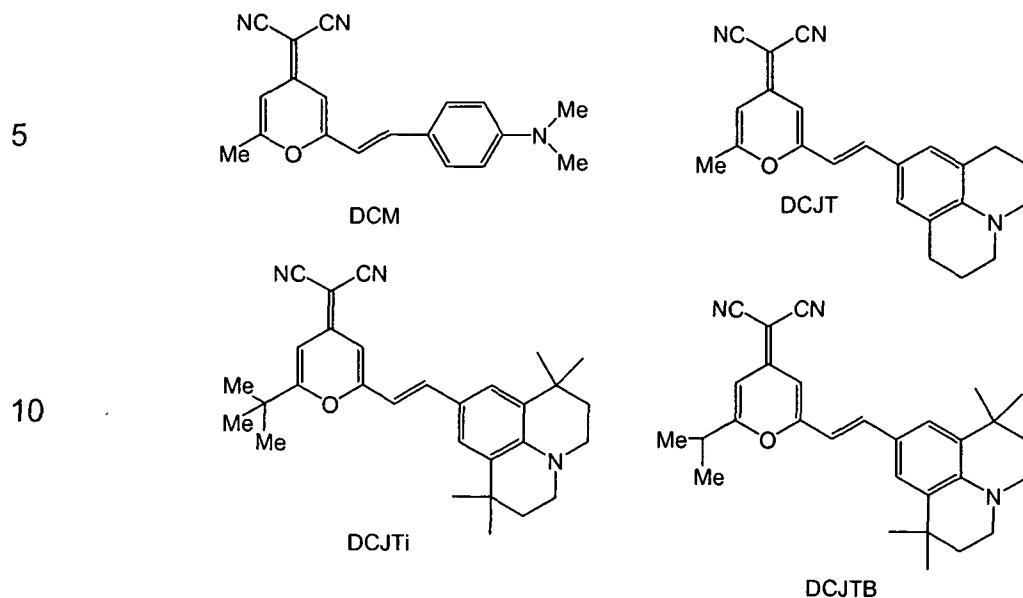
Useful fluorescent materials are those capable of being blended with the host and fabricated into thin films satisfying the thickness ranges described above forming the luminescent zones of the EL devices of this invention. While crystalline organometallic complexes do not lend themselves to thin film formation, the limited amounts of fluorescent materials present in the host permit the use of fluorescent materials which are alone incapable of thin film formation. Preferred fluorescent materials are those which form a common phase with the host. Fluorescent dyes constitute a preferred class of fluorescent materials, since dyes lend themselves to molecular level

- distribution in the host. Although any convenient technique for dispersing the fluorescent dyes in the host can be used preferred fluorescent dyes are those which can be vacuum vapour deposited along with the host materials. One class of host materials comprises metal complexes e.g. metal
- 5 quinolates such as lithium quinolate, aluminium quinolate, titanium quinolate, zirconium quinolate or hafnium quinolate which may be doped with fluorescent materials or dyes as disclosed in patent application WO 2004/058913.
- 10 Common host materials are, for instance, selected from carbazols, ketones, phosphinoxides, sufoxides, bipolar hosts, and oligoarylenes selected from anthracenes, dinaphthyl anthracenes, benzanthracene anthracenes, tetraphenylspirobifluorenes.
- 15 In the case of hosts which comprise quinolates e.g. aluminium quinolate or "blue" quinolates, see e.g. J.C. Deaton *et al.*, Inorg. Chim. Acta (2007), doi:10.1016/j.ica.2007.07.008, the contents of which are incorporated herein by reference:
- 20 Common dopants are, for instance, selected from phosphorescent emitters, diphenylacridine, coumarins, perylene, quinolates, porphoryin, porphines, pyrazalones and derivatives thereof, aryl amines preferably indenofluorene monoamines and -diamines, benzofluorene monoamines and -diamines and dibenzoindenofluorene monoamines and -diamines

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(a) the compounds below, for example, can serve as red dopants:

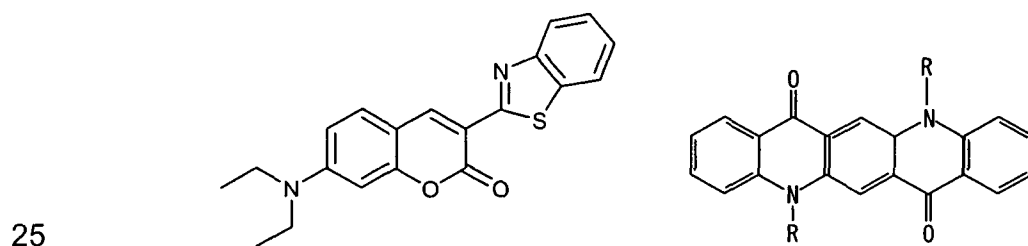


15 wherein

Me is a methyl group

(b) the compounds below, for example can serve as green dopants:

20



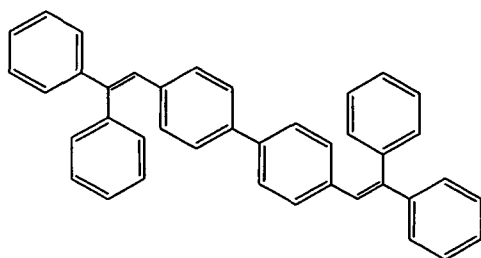
wherein

30 R is C<sub>1</sub> to C<sub>4</sub> alkyl, monocyclic aryl, bicyclic aryl, monocyclic heteroaryl, bicyclic heteroaryl, aralkyl or thienyl, preferably phenyl; and

- (c) for biphenyloxy aluminium bis-quinolate ( $\text{BAIq}_2$ ) or aluminium quinolate the compounds perylene and 9-(10-(N-(naphthalen-8-yl)-N-phenylamino)anthracen-9-yl)-N-(naphthalen-8-yl)-N-phenylanthracen-10-amine can serve as a blue dopants.

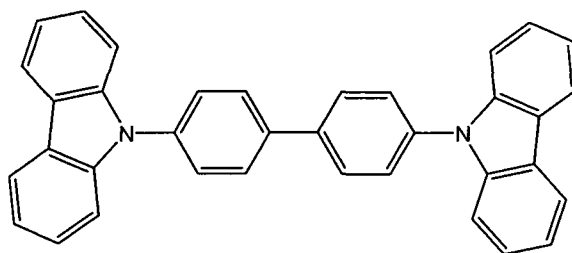
Another preferred class of hosts is small molecules incorporating conjugated aromatic systems with e.g. 4 to 10 aryl or heteroaryl rings which may bear substituents e.g. alkyl (especially methyl), alkoxy and fluoro and which may also be doped with fluorescent materials or dyes.

An example of a system of the above kind is a blue-emitting material based on the following compound (Compound H) as host

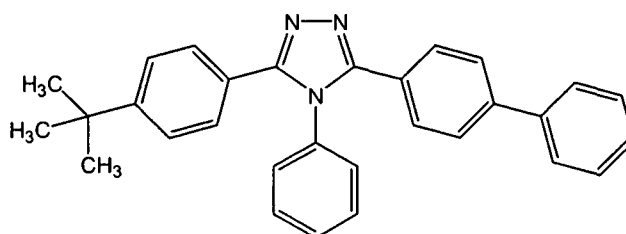


and perylene or 9-(10-(N-(naphthalen-8-yl)-N-phenylamino)anthracen-9-yl)-N-(naphthalen-8-yl)-N-phenylanthracen-10-amine as dopant.

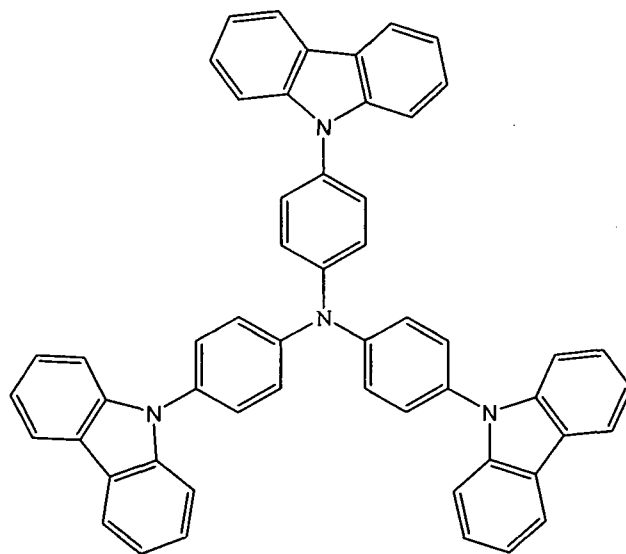
Further examples of host materials which are small aromatic molecules are shown below:



CBP



TAZ

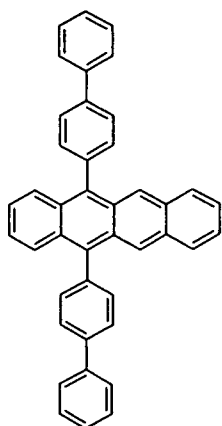


TCTA.

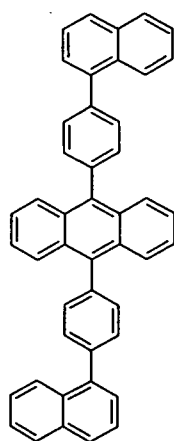
2,9-Bis(2-thiophen-2-yl-vinyl)-[1,10] phenanthroline may, as explained above, may be used as host in the electroluminescent layer or may be present on its own.

Other suitable host materials for fluorescent dopants may be chosen out of the class of oligoarylenes like dinaphthyl anthracenes, benzanthracene-anthracenes as described in WO 2008/145239, tetraphenylspirobifluorenes as described in EP 676461, anthracene based compounds as described in US 2007/0092753, US 2007/0092753, US 2007/0252517, US 2008/0193796, US 2003/0027016, US 7326371, US 2006/043858, and US 2003/0027016. Preferred compounds from these references are the compounds of the following formulae

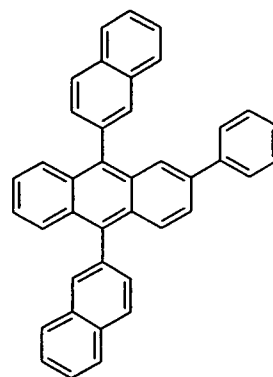
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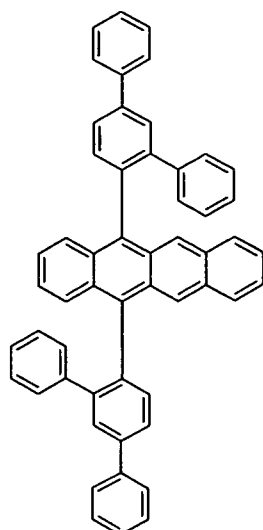
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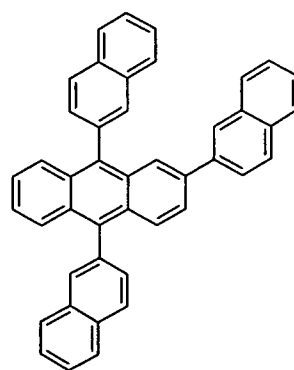
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Blue-emitting materials may be based on an organic host (e.g. a conjugated aromatic compound as indicated above) and diarylamine anthracene compounds disclosed in WO 2006/090098

(Kathirgamanathan *et al.*) as dopants. For example, CBP may be

5 doped with blue-emitting substituted anthracenes *inter alia*

9,10-bis(-4-methylbenzyl)-anthracene,

9,10-bis-(2,4-dimethylbenzyl)-anthracene,

9,10-bis-(2,5-dimethylbenzyl)-anthracene,

1,4-bis-(2,3,5,6-tetramethylbenzyl)-anthracene,

10 9,10-bis-(4-methoxybenzyl)-anthracene,

9,10-bis-(9H-fluoren-9-yl)-anthracene,

2,6-di-*t*-butylanthracene,

2,6-di-*t*-butyl-9,10-bis-(2,5-dimethylbenzyl)-anthracene,

2,6-di-*t*-butyl-9,10-bis-(naphthalene-1-ylmethyl)-anthracene.

15

Other blue emitting materials may be chosen out of indenofluorene monoamines and -diamines as described in WO 2006/122630,

benzofluorene monoamines and -diamines as described in

WO 2008/006449 and dibenzoindenofluorene mono- and diamines as disclosed in WO 2007/140847. The emitters may also be styrylamines

20

as described in DE 2005/058557, US 7250532, or arylamines as described in US 2006/21830, JP 08053397, US 6251531,

EP 1957606, US 2008/ 0113101, and CN 1583691. Preferred

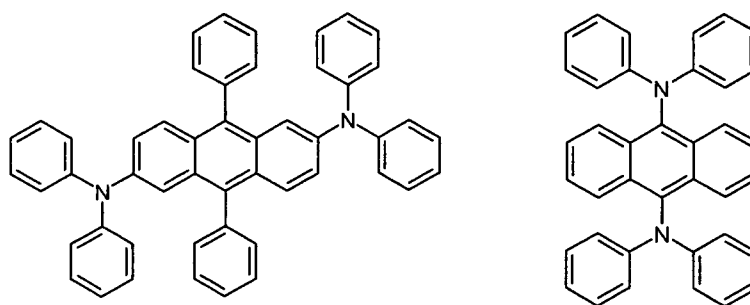
compounds of the cited references are the following compounds

25

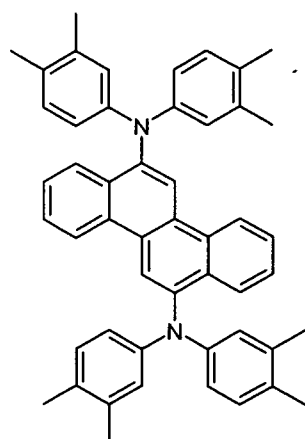
having the formulae

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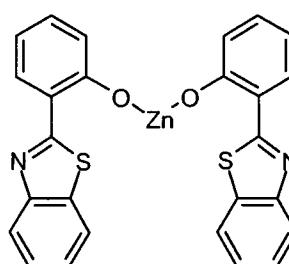
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20

Further blue-emitting materials may use TCTA, or further carbazol derivatives as described in WO 2008/086851, EP 1617710, EP 1617711, EP 1731584, JP 2005/347160, or ketones as described in WO 2004/093207, or be chosen from phoshine oxides and sufoxides as described in WO 2005/003253 or from bipolar host materials as described in WO 2007/137725 or from metal chelates as described in EP 652273, e.g.

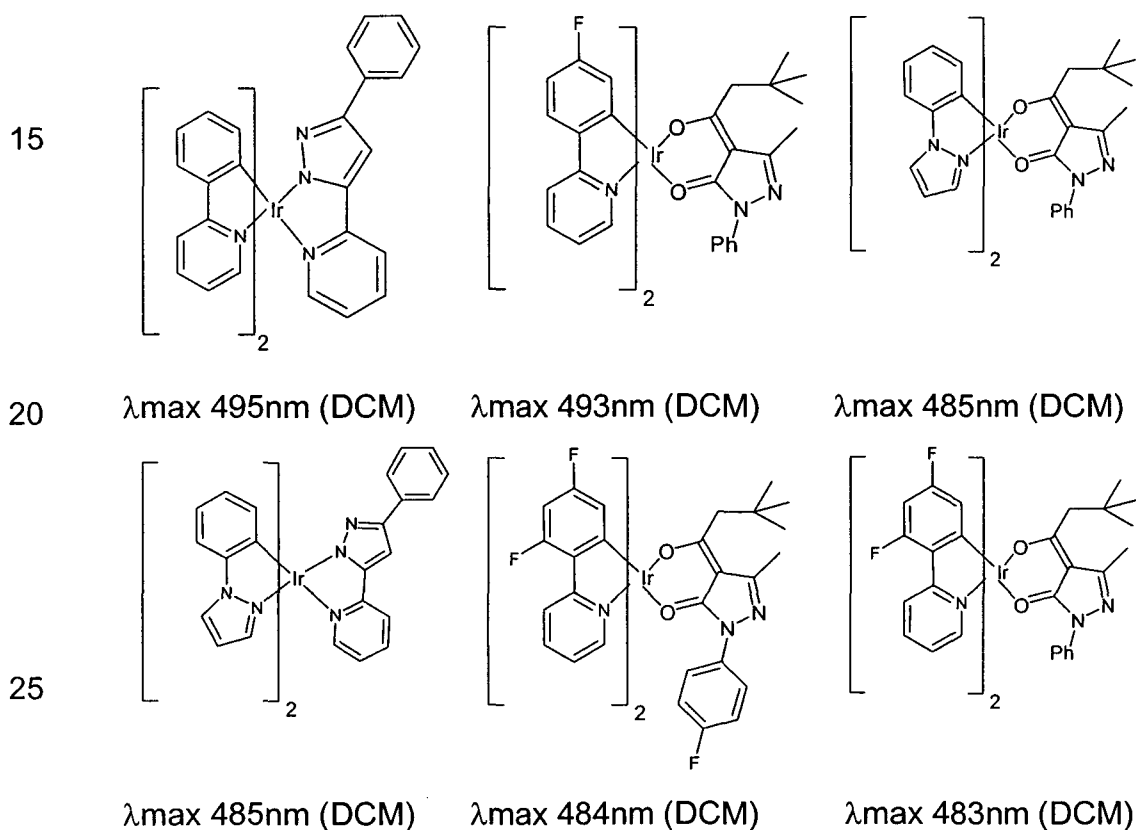
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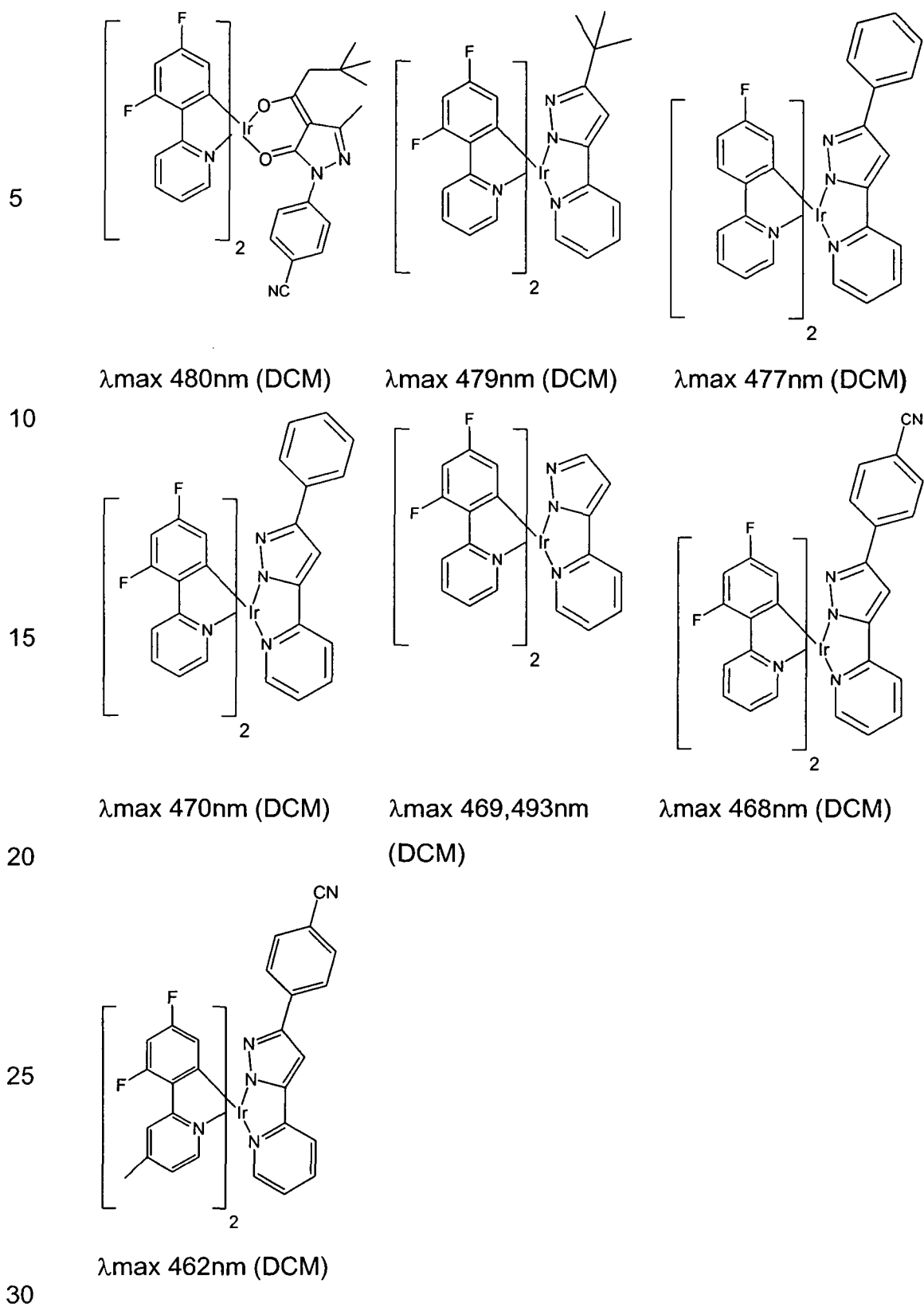
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as hosts and it may be doped with the blue phosphorescent materials set out below, see WO 2005/080526 (Kathirgamanathan *et al.*) or with phosphorescent emitters as described WO 00/70655, WO 01/41512, WO 02/02714, WO 02/15645, EP 1191613, EP 1191612, EP 1191614 and WO 05/033244 or described in US 2007-0087219 A1, US 2009/0061681 A1, US 2009/0061681 A1, US 2001 0053462 A1 or out of Baldo, Thompson *et al* Nature 403 (2000), 750-753 or as described in Adachi *et al* Appl. Phys. Lett. 78 (2001), 1622-24, US 6824895, US 10/729238, US 6835469, US 2001 0053462 A1 :

### Blue Phosphorescent Materials



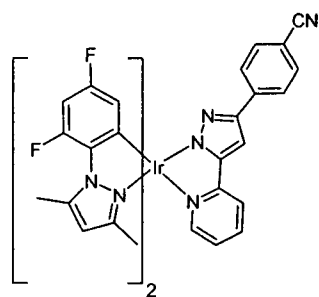
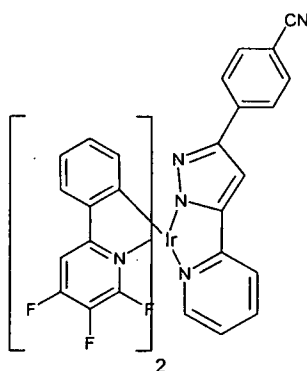
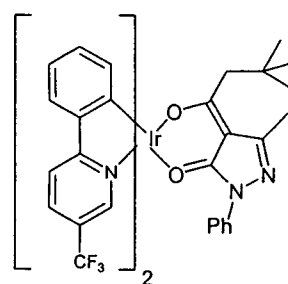


Examples of green phosphorescent materials that may be employed with CBP or TAZ are set out below (see WO 2005/080526):

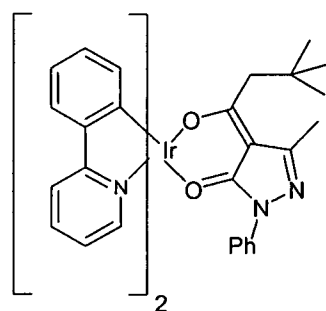
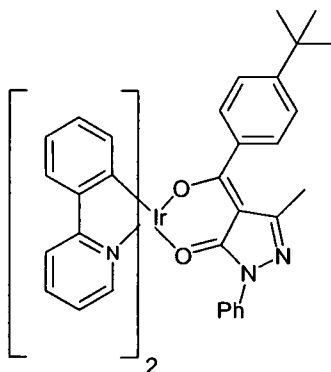
### Green Phosphorescent Materials

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 $\lambda_{\text{max}}$  502nm (DCM)

 $\lambda_{\text{max}}$  509nm (DCM)

 $\lambda_{\text{max}}$  520nm (DCM)

15


 $\lambda_{\text{max}}$  526nm (DCM)

 $\lambda_{\text{max}}$  528nm (DCM)

20

wherein

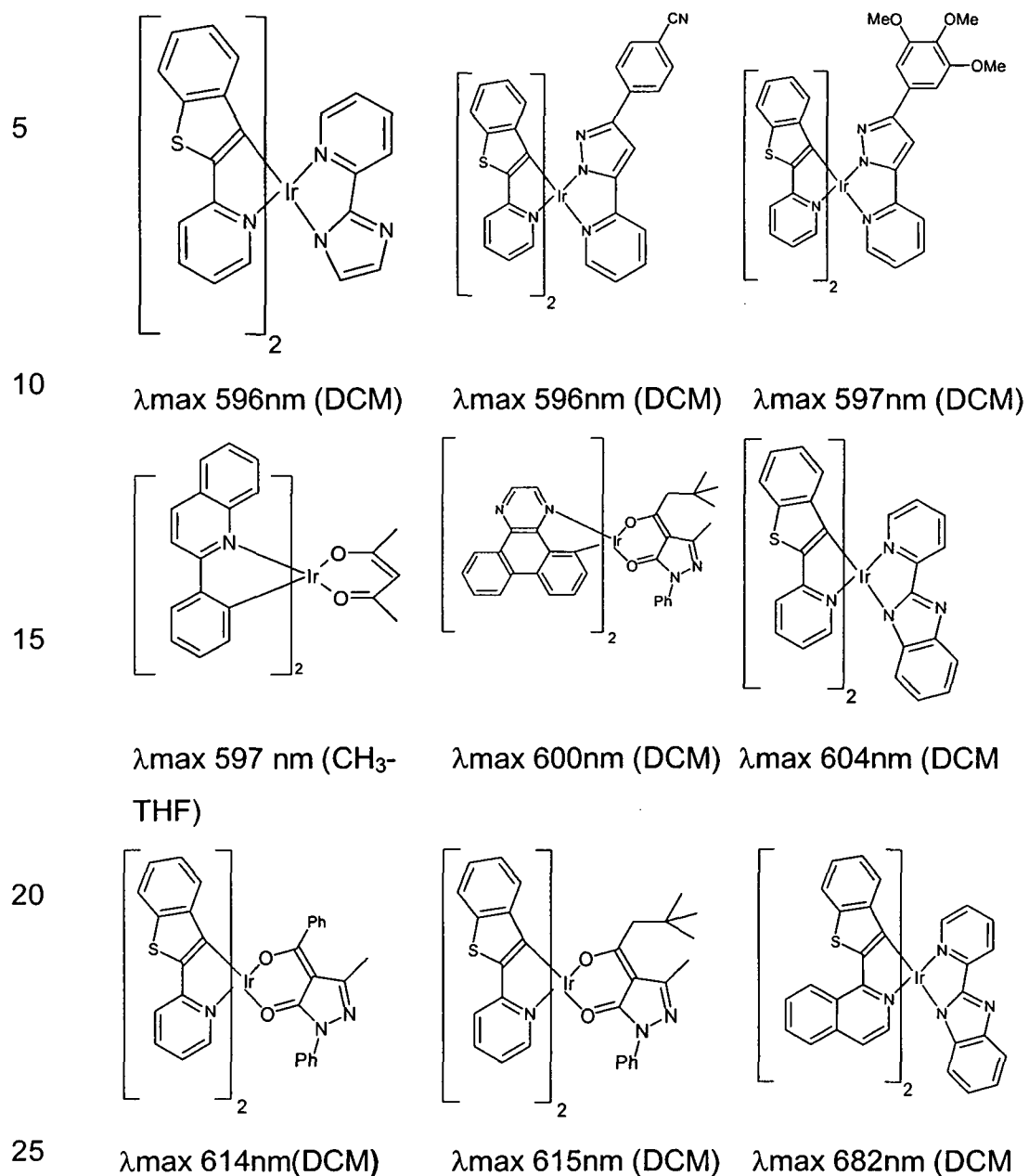
25

Ph is a phenyl group.

Examples of red phosphorescent materials that may be employed with CBP or TAZ are set out below (see WO 2005/080526):

30

# Red Phosphorescent Materials



wherein

Ph is a phenyl group

and wherein Me is a methyl group

As further dopants, fluorescent laser dyes are recognized to be particularly useful fluorescent materials for use in the organic EL devices of this invention. Dopants which can be used include diphenylacridine, coumarins, perylene and their derivatives. Useful fluorescent dopants are disclosed in  
5 US 4769292. One class of preferred dopants is coumarins. The following are illustrative fluorescent coumarin dyes known to be useful as laser dyes:

- FD-1 7-Diethylamino-4-methylcoumarin,
- FD-2 4,6-Dimethyl-7-ethylaminocoumarin,
- 10 FD-3 4-Methylumbelliferone,
- FD-4 3-(2'-Benzothiazolyl)-7-diethylaminocoumarin,
- FD-5 3-(2'-Benzimidazolyl)-7-N,N-diethylaminocoumarin,
- FD-6 7-Amino-3-phenylcoumarin,
- FD-7 3-(2'-N-Methylbenzimidazolyl)-7-N,N-diethylaminocoumarin,
- 15 FD-8 7-Diethylamino-4-trifluoromethylcoumarin,
- FD-9 2,3,5,6-1H,4H-Tetrahydro-8-methylquinolazino[9,9a,1-gh]coumarin,
- FD-10 Cyclopenta[c]julolidino[9,10-3]-11H-pyran-11-one,
- FD-11 7-Amino-4-methylcoumarin,
- FD-12 7-Dimethylaminocyclopenta[c]coumarin,
- 20 FD-13 7-Amino-4-trifluoromethylcoumarin,
- FD-14 7-Dimethylamino-4-trifluoromethylcoumarin,
- FD-15 1,2,4,5,3H,6H,10H-Tetrahydro-8-trifluoromethyl[1]benzopyrano[9,9a,1-gh]quinolizino-10-one,
- FD-16 4-Methyl-7-(sulfomethylamino)coumarin sodium salt,
- 25 FD-17 7-Ethylamino-6-methyl-4-trifluoromethylcoumarin,
- FD-18 7-Dimethylamino-4-methylcoumarin,
- FD-19 1,2,4,5,3H,6H,10H-Tetrahydro-carbethoxy[1]benzopyrano[9,9a,1-gh]quinolizino-10-one,
- FD-20 9-Acetyl-1,2,4,5,3H,6H,10H-tetrahydro[1]benzopyrano[9,9a,1-gh]quinolizino-10-one,
- 30 FD-21 9-Cyano-1,2,4,5,3H,6H,10H-tetrahydro[1]benzopyrano[9,9a,1-gh]quinolizino-10-one,

FD-22 9-(t-Butoxycarbonyl)-1,2,4,5,3H,6H,10H-tetrahyro[1]-benzopyrano-  
[9,9a,1-gh]quinolizino-10-one,

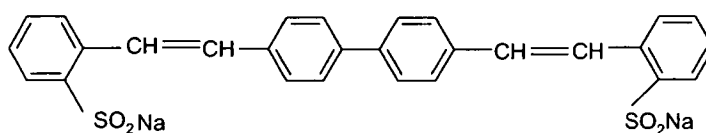
FD-23 4-Methylpiperidino[3,2-g]coumarin,

FD-24 4-Trifluoromethylpiperidino[3,2-g]coumarin,

5 FD-25 9-Carboxy-1,2,4,5,3H,6H,10H-tetrahydro[1]benzopyrano[9,9a,1-  
gh]quinolizino-10-one,

FD-26 N-Ethyl-4-trifluoromethylpiperidino[3,2-g].

10 Other dopants include salts of bis benzene sulphonic acid (require  
deposition by spin-coating rather than sublimation) such as



15 (C)

and perylene and perylene derivatives and dopants. Other dopants are  
dyes such as the fluorescent 4-dicyanomethylene-4H-pyrans and 4-  
dicyanomethylene-4H-thiopyrans, e.g. the fluorescent  
20 dicyanomethylenepyrans and thiopyrans dyes. Useful fluorescent dyes can  
also be selected from among known polymethine dyes, which include the  
cyanines, complex cyanines and merocyanines (i.e. tri-, tetra- and poly-  
nuclear cyanines and merocyanines), oxonols, hemioxonols, styryls,  
merostyryls, and streptocyanines. The cyanine dyes include, joined by a  
25 methine linkage, two basic heterocyclic nuclei, such as azolium or azinium  
nuclei, for example, those derived from pyridinium, quinolinium,  
isoquinolinium, oxazolium, thiazolium, selenazolium, indazolium,  
pyrazolium, pyrrolium, indolium, 3H-indolium, imidazolium, oxadiazolium,  
thiadioxazolium, benzoxazolium, benzothiazolium, benzoselenazolium,  
30 benztellurazolium, benzimidazolium, 3H- or 1H-benzoindolium,  
naphthoxazolium, naphthothiazolium, naphthoselenazolium,  
naphthotellurazolium, carbazolium, pyrrolopyridinium,

phenanthrothiazolium, and acenaphthothiazolium quaternary salts. Other useful classes of fluorescent dyes are 4-oxo-4H-benz-[d,e]anthracenes and pyrylium, thiapyrylium, selenapyrylium, and telluropirylium dyes.

Further blue-emitting materials are disclosed in the following patents,  
5 applications and publications, the contents of which are incorporated herein by reference:

US-A-5141671 (Bryan, Kodak) - Aluminium chelates containing a phenolato ligand and two 8-quinolinolato ligands.

10 WO 00/32717 (Kathirgamanathan) - Lithium quinolate which is vacuum depositable, and other substituted quinolates of lithium where the substituents may be the same or different in the 2,3,4,5,6 and 7 positions and are selected from alky, alkoxy, aryl, aryloxy, sulphonic acids, esters,  
15 carboxylic acids, amino and amido groups or are aromatic, polycyclic or heterocyclic groups.

US 2006/0003089 (Kathirgamanathan) - Lithium quinolate made by reacting a lithium alkyl or alkoxide with 8-hydroxyquinoline in acetonitrile.

20 Misra A. et al U.R.S.I. GA 2005, "Synthesis and characterisation of blue organic electroluminescent bis (2-methyl 8-quinolinolato) (triphenyl Siloxy) aluminium for OLEDs applications"; see the following website:  
[http://www.ursi.org/Proceedings/ProcGA05/pdf/D04.5\(01720\).pdf](http://www.ursi.org/Proceedings/ProcGA05/pdf/D04.5(01720).pdf) - Blue  
25 organic electroluminescent material bis-(2-methyl 8-quinolinolato) (triphenyl siloxy)aluminium (III) vacuum depositable at  $1 \times 10^{-5}$  Torr.

WO 03/006573 (Kathirgamanathan et al) - Metal pyrazolones.

WO 2004/084325 (Kathirgamanathan et al) - Boron complexes.

WO 2005/080526 (Kathitgamanathan et al) - Blue phosphorescent iridium-based complexes.

30 Ma et al., *Chem. Comm.* 1998, 2491-2492 Preparation and crystal structure of a tetranuclear zinc(II) compound  $[Zn_4O(AID)_6]$  with 7-azaindolate as a

bridging ligand. Fabrication of inter alia a single-layer LED by vacuum deposition of this compound ( $< 200\text{ }^{\circ}\text{C}$ ,  $2 \times 10^{-6}$  Torr) onto a glass substrate coated with indium–tin oxide to form a thin homogeneous film was reported.

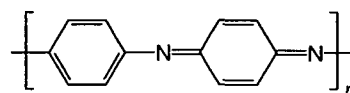
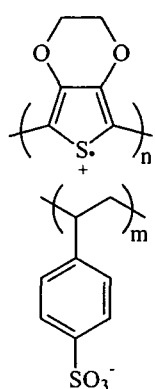
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Further electroluminescent materials which can be used include metal quinolates such as aluminium quinolate, lithium quinolate, titanium quinolate, zirconium quinolate, hafnium quinolate etc..

10 Many further electroluminescent materials that may be used are disclosed in WO 2004/050793 (pyrazolones), WO 2004/058783 (diiridium metal complexes), WO 2006/016193 (dibenzothiophenyl metal complexes) and WO 2006/024878 (thianthrene metal complexes); see also WO 2006/040593 the contents of which are incorporated herein by reference. Rare  
15 earth chelates, in particular may be employed as green and red emitters. Furthermore, there may be used as electroluminescent materials conducting polymers e.g phenylene vinylene polymers, fluorene homopolymers and copolymers, phenylene polymers, as indicated below:

## 20 Conducting Polymers

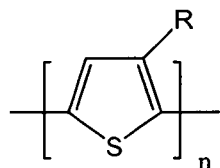
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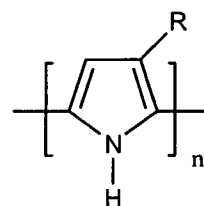
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PEDOT-PSS ( $\sigma = 1\text{ S cm}^{-1}$ )

Polyaniline (PANI) ( $\sigma = 1 - 10\text{ S cm}^{-1}$ )



Polythiophene (PT)  
( $\sigma = 1 - 500 \text{ S cm}^{-1}$ )



Polypyrrole (PPy)  
( $\sigma = 1 - 100 \text{ S cm}^{-1}$ )

Mixed host materials have also been disclosed in the literature and may be used in OLEDs devices according to the invention. Various references disclose additives and mixed hosts for OLED's in an attempt to further improve properties. Jarikov *et al.*, *J. Appl. Phys.*, **100**, 014901 (2006) discloses flat and rigid polycyclic aromatic hydrocarbons (PAHs) as LEL additives e.g. perylene.

Jarikov *et al.* further report *J. Appl. Phys.*, **100**, pp. 094907-094907-7 (2006) perylene derivatives as light-emitting-layer (LEL) additives in organic light-emitting diodes (OLEDs). These molecules readily form emissive aggregates when added to the LEL. Addition of these polycyclic aromatic hydrocarbons increases the half-life ( $t_{50}$ ) of undoped and doped OLEDs by 30 to 150 times e.g. in an Alq<sub>3</sub>+dibenzo[b,k]perylene mixed host. The authors yet further report in *J. Appl. Phys.*, **102**, 104908 (2007) a synergistic effect of a lifetime-extending light-emitting-layer (LEL) additive and improved electron injection and transport in organic light-emitting diodes (OLEDs). Di-(2-naphthyl)perylene (DNP) serves as a LEL additive said to extend the operating lifetime of OLEDs by over two orders of magnitude. Using 2-phenyl-9,10-di(2-naphthyl)anthracene (PADN) as an electron-transport layer (ETL) and a separate layer of 4,7-diphenyl-1,10-phenanthroline (BPhen) as an electron-injection layer (EIL) the authors claimed to have significantly improved electron delivery into the charge recombination zone relative to traditional ETL made of tris(8-

quinolinolate)aluminium (Alq). See also US-A-7175922 (Jarikov *et al*) the disclosure of which is incorporated herein by reference.

5 J.C. Deaton *et al* (*supra*) disclose an  $\alpha$ -NPB host with a "blue" aluminium quinolate as co-host and an iridium dopant. Very good yields were obtained with low concentrations of dopant for phosphorescent devices and it was found that the mixed host device provided increased power efficiency. It was hypothesized that the explanation was a reduction in the energy barrier to inject holes into the emissive layer by mixing the hole-transporting NPB  
10 having an ionization potential of 5.40 eV into the dominantly electron-transporting "blue" aluminium quinolate, having a higher ionization potential of 6.02 eV.

15 US-A-6392250 (Aziz *et al*, the disclosure of which is incorporated herein by reference.) discloses organic light emitting devices comprising a mixed region comprising a mixture of a hole transport material e.g. an aromatic tertiary amine, an electron transport material e.g. a quinolate and a dopant material. For example N,N'-di-1-naphthyl-N,N'-diphenyl-1,1'-biphenyl-1,1'-biphenyl-4,4'-diamine (NPB), and tris (8-hydroxyquinoline) aluminium (Alq<sub>3</sub>)  
20 may be used as the hole transport material and the electron transport material, respectively and N,N'-dimethylquinacridone (DMQ), 5,6,11,12-tetraphenylnaphthacene (Rubrene), and Nile-red dye (available from Aldrich Chemicals of Milwaukee, Wis.) may be used as dopants.

25 US 2002/0074935 (Kwong *et al*) also discloses devices with an emissive layer containing PtOEP or bis(benzothienyl-pyridinato-NAC)Iridium(III) (acetylacetonate) as a dopant and equal proportions of NPB and Alq as host materials. It is explained that the mixed host electroluminescent mixed layer serves to substantially reduce the accumulation of charge that is  
30 normally present at the heterojunction interface of heterostructure devices, thereby reducing organic material decomposition and enhancing device stability and efficiency.

In US 2004/0155238 (Thompson *et al.*) a light emitting layer of the OLED device contains a wide band gap inert host matrix in combination with a charge carrying material and a phosphorescent emitter. The charge carrying compound can transport holes or electrons, and it is selected so that charge carrying material and phosphorescent emitter transport charges of opposite polarity.

M. Furugori *et al.* in US 2003/0141809 disclose phosphorescent devices where a host material is mixed with another hole- or electron transporting material in the light emitting layer. The document discloses that devices utilizing plural host compounds show higher current and higher efficiencies at a given voltage.

T. Igarashi *et al.* in WO 2004/062324 disclose phosphorescent devices with the light emitting layer containing at least one electron transporting compound, at least one hole transporting compound and a phosphorescent dopant.

WO 2006/076092 (Kondakova *et al.*, the contents of which are also incorporated herein by reference) discloses OLED device comprising a cathode, an anode, and located therebetween a light emitting layer (LEL) comprising at least one hole transporting co-host e.g. an aromatic tertiary amine such as 4,4'-Bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB), 4,4'-Bis[N-(1-naphthyl)-N-(2-naphthyl)amino]biphenyl (TNB), 4,4'-Bis[N-(3-methylphenyl)-N-phenylamino-]biphenyl (TPD), 4,4'-Bis-diphenylamino-terphenyl or 2,6,2',6'-tetramethyl-N,N,N',N'-tetraphenyl-benzidine. and at least one electron transporting co-host e.g. a substituted 1,2,4-triazole such as 3-phenyl-4-(1-naphthyl)-5-phenyl-1,2,4-triazole or a substituted 1,3,5-triazine such as 2,4,6-tris(diphenylamino)-1,3,5-triazine, 2,4,6-tricarbazolo-1,3,5-triazine, 2,4,6-tris(N-phenyl-2-naphthylamino)-1,3,5-triazine, 2,4,6-tris(N-phenyl-1-naphthylamino)-1,3,5-triazine and 4,4',6,6'-tetraphenyl-2,2'-bi-1,3,5-triazine together with a phosphorescent emitter, wherein the triplet

energy of each of the co-host materials is greater than the triplet energy of the phosphorescent emitter, and further containing an exciton blocking layer comprising a hole transporting material with triplet energy greater or equal to 2.5 eV adjacent the emitting layer on the anode side, which may be a substituted triarylamine e.g. 4,4',4''-tris[(3-methylphenyl)-phenylamino]triphenylamine (MTDATA), 4,4',4''-tris(N,N-diphenyl-amino)triphenylamine (TDATA), N,N-bis[2,5-dimethyl-4-[(3-methylphenyl)-phenylamino]phenyl]-2,5-dimethyl-N'-(3-methylphenyl)-N'-phenyl-1,4-benzenediamine. The devices are said to exhibit improved efficiency and reduced drive voltage.

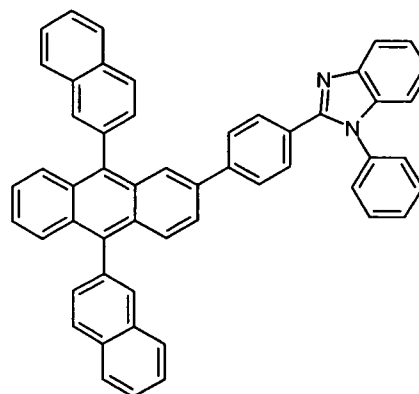
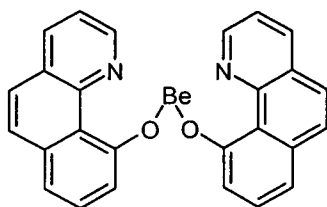
US-A-7045952 (Lu, Universal Display Corporation) discloses an organic light emissive device comprising an emissive region disposed between and electrically connected to an anode and a cathode, wherein the emissive region comprises (i) a first single-host emissive layer, comprising a first host material, and (ii) a mixed-host emissive layer in direct contact with the first single-host emissive layer, wherein the mixed-host emissive layer comprises the first host material, and a second host material, and wherein the first single-host emissive layer and the mixed-host emissive layer each further comprise a phosphorescent emissive material.

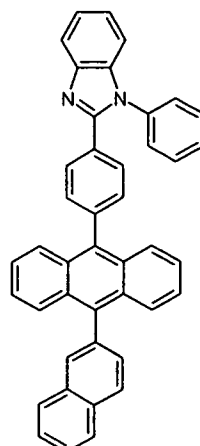
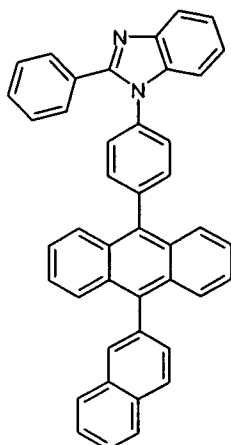
### **Electron transport material**

Monoclinic zirconium quinolate may be the totality, or substantially the totality of the electron transport layer. It may be a mixture of co-deposited materials which is predominantly monoclinic zirconium quinolate. The zirconium quinolate may be doped as described in GB 2006/14847.2, the contents of which are incorporated herein by reference. Suitable dopants include fluorescent or phosphorescent dyes or ion fluorescent materials e.g. as described above in relation to the electroluminescent layer, e.g. in amounts of 0.01 to 25 wt% based on the weight of the doped mixture. Other dopants include metals which can provide high brightness at low voltage.

Additionally or alternatively, the monoclinic zirconium quinolate may be used in admixture with another electron transport material. Such materials may include complexes of metals in the trivalent or pentavalent state which should further increase electron mobility and hence conductivity. The zirconium quinolate may be mixed with a quinolate of a metal of group 1, 2, 3, 13 or 14 of the periodic table, e.g. lithium quinolate or zinc quinolate. The zirconium may also be mixed with at least one further electron transport material, preferably selected from benzimidazoles and quinolates of Li, Al, Ga, Mg, Zn, and Be, particularly preferably lithium quinolate. Additionally the electron transport material may be n-doped e.g. with donor-type organic molecules. Preferably the zirconium quinolate comprises at least 30 wt% of the electron transport layer, more preferably at least 50 wt%.

The electron transport materials may also be chosen out of the benzimidazole class as described in US 5766779, US 5529853, US 6878469, US 20056/147747 and out of EP 1551206, e.g.





### Electron injection material

Any known electron injection material may be used, LiF being used in some embodiments. Other possibilities include BaF<sub>2</sub>, CaF<sub>2</sub> and CsF<sub>2</sub>. A further class of electron injectors comprises sublimable or coatable e.g. spin-coatable small molecules with electron injection properties. Embodiments of a layer of small molecule electron injection material are about 0.3 to 2 nm in thickness, in some particular embodiments about 0.3 nm in thickness and in other embodiments about 0.5 to 1 nm in thickness and preferably has a work function of less than magnesium 3.7 eV, this being regarded for present purposes as a low work function. In some embodiments the electron injection material may be doped with a low work function metal e.g. lithium, potassium or caesium. In the case of a lithium-based small molecule electron injection material, doping may be with metallic lithium.

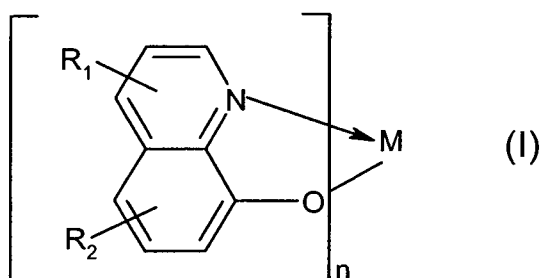
Metal quinolates can lower the work function of the cathode, enable the electroluminescent device to operate at a lower voltage and improve the lifetime and performance of the device. In some embodiments quinolates and derivatives thereof have been found superior to the previously used lithium fluoride. They have significantly lower evaporation temperatures, as is apparent from the table below (q represents quinolate):

| Material | Evaporation Temperature / °C | Vacuum Pressure / Pa    | Evaporation Rate / Å s <sup>-1</sup> |
|----------|------------------------------|-------------------------|--------------------------------------|
| Liq      | 320                          | $\leq 5 \times 10^{-5}$ | 1.0                                  |
| LiF      | 580                          | $\leq 5 \times 10^{-5}$ | 0.1                                  |

5

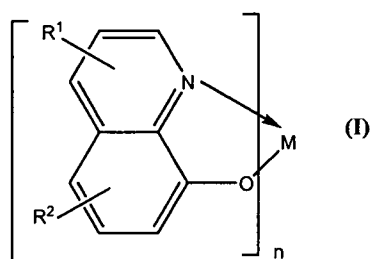
Suitable metal quinolates include the alkali metal quinolates and the alkaline earth quinolates. Preferred quinolates are quinolates of Li, Ga, Mg, Zn, and Be. Preferred metal quinolates have the formula

10



15

20



wherein

25

M is a metal (in embodiments lithium);

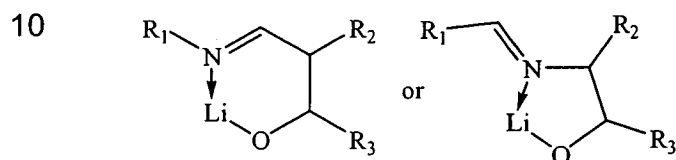
n is the valence state of M when complexed with quinolate;

30

and R<sub>1</sub> and R<sub>2</sub> which may be the same or different are selected from C<sub>1</sub> to C<sub>4</sub> alkyl and substituted or unsubstituted monocyclic or polycyclic aryl or heteroaryl, aralk-(C<sub>1</sub> to C<sub>4</sub>)-yl or aryloxy.

Lithium quinolate and lithium 2-methylquinolate are preferred compounds and are preferably the result of reaction between a lithium alkyl or alkoxide with substituted or unsubstituted 8-hydroxy quinoline in a solvent which comprises acetonitrile. Lithium quinolates made as described above are of high purity and readily sublimable.

The electron injection layer deposited direct onto the cathode may alternatively comprise a compound of the formula



wherein

15

$R_1$  is a 1 to 5 ring aryl (including polycyclic aryl or aryl-substituted polycyclic aryl), aralkyl or heteroaryl group which may be substituted with one or more  $C_1$  to  $C_4$  alkyl or alkoxy substituents;

20

and  $R_2$  and  $R_3$  together form a 1 to 5 ring aryl (including polycyclic or aryl-substituted polycyclic aryl), aralkyl or heteroaryl group which may be substituted with one or more  $C_1$  to  $C_4$  alkyl or alkoxy substituents.

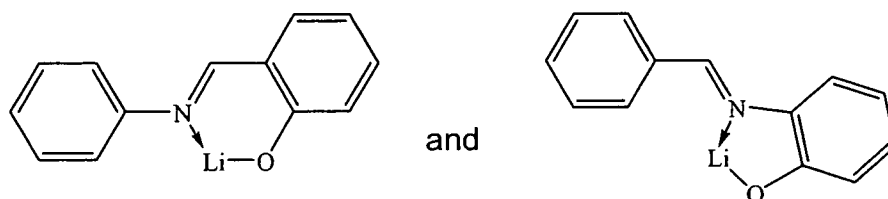
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A compound of the above formula may be used alone or in combination with another electron injection material e.g. a quinolate such as lithium or zirconium quinolate. The Schiff base preferably comprises at least 30 wt% of the electron injection layer, more preferably at least 50 wt%.

30

In the formula set out above,  $R_1$  may be polycyclic aryl e.g. naphthyl, anthracenyl, tetracenyl, pentacenyl or a perylene or pyrene compound or may have up to 5 aromatic rings arranged in a chain e.g. biphenyl. It is

preferably phenyl or substituted phenyl.  $R_2$  and  $R_3$  together may form the same groups as  $R_1$  and are preferably phenyl or substituted phenyl. Where substituents are present they may be methyl, ethyl, propyl or butyl, including t-butyl substituted, or may be methoxy, ethoxy, propoxy or butoxy including t-butoxy substituted. Particular compounds include



Lithium compounds whose formulae are set out above are believed from mass spectrometry (MS) measurements to be capable of forming cluster compounds or oligomers in which 2 to 8 molecules of formula as set out above are associated e.g. in the form of trimeric, tetrameric, hexameric or octomeric oligomers. It is believed that such lithium compounds may in some embodiments associate in trimeric units having a core structure which has alternating Li and O atoms in a 6-membered ring, and that these trimeric units may further associate in pairs. The existence of such structures in lithium quinolate has been detected by crystallography, see Begley *et al.*, Hexakis( $\mu$ -quinolin-8-olato)hexalithium (I): a centrosymmetric doubly stacked trimer, Acta Cryst. (2006), **E62**, m1200-m1202, the disclosure of which is incorporated herein by reference. It is also believed that formation of oligomeric structures of this type imparts a greater covalent character to the Li-O bonds which may be responsible for the volatility of many of the compounds of the invention which enables them to be deposited at relatively low temperatures by vacuum sublimation. However, other structures may also be possible e.g. cubic structures.

### Hole blocking material

5 The devices according to the present invention may also comprise a hole blocking material (HBM). A HBM refers to a material or unit which, if coated adjacent to a hole transporting layer in a multilayer structure, prevents the holes flowing through. Usually it has a lower HOMO as compared to the HOMO level of the hole transport material in the adjacent hole transporting layer.

10 Hole-blocking layers are frequently inserted between the light-emitting layer and the electron-transport layer in devices comprising phosphorescent emitters.

15 Suitable hole-blocking materials are metal complexes (US 2003/0068528), such as, for example, bis(2-methyl-8-quinolinolato)(4-phenylphenolato)aluminium(III) (BAIQ). Fac-tris(1-phenylpyrazolato-N,C2)iridium(III) (Ir(ppz)<sub>3</sub>) is likewise used for this purpose (US 2003/0175553 A1). Phenanthroline derivatives, such as, for example, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (= bathocuproin, BCP), or phthalimides, such as, for example, 2,3,5,6-tetramethylphenyl-1,4-(bisphthalimide) (TMPP), are likewise employed.

20 Suitable hole-blocking materials are described in WO 00/70655 A2, WO 01/41512 and WO 01/93642 A1.

### Electron Blocking material

25 The devices according to the present invention may also comprise an electron blocking material (EBM). An EBM refers to a material or unit which, if coated adjacent to an electron transporting layer in a multilayer structure, prevents the electron flowing through. Usually it has a higher LUMO as compared to the LUMO of the electron transport material in the adjacent  
30 electron transporting layer.

Transition-metal complexes, such as, for example, Ir(ppz)<sub>3</sub> (US 2003/0175553) can be employed as materials for an electron-blocking layer.

## 5      **Exciton blocking material**

The devices according to the present invention may also comprise an exciton blocking material (ExBM). The ExBM refers to a material or unit which, if coated adjacent to an emissive layer in a multilayer structure, prevents the exciton diffuse through. ExBM should have either a higher triplet level or singlet level as compared to the corresponding level of the emissive layer or other adjacent layer.

## **Dyes**

15      The devices according to the present invention may also comprise a dye. A dye can generally be described as an inorganic or organic substance that absorbs light and therefore appears colored.

20      Preferred dyes are selected from the group of acridines, anthraquinones, arylmethanes, diarylmethanes, triarylmethanes, azo-based dyes, cyanines, diazonium-based dyes, nitro-based dyes, nitroso-based dyes, phthalocyanine dyes, quinone-imines, azin-based dyes, eurhodines, safranines, indulines, indamins, indophenoles, oxazines, oxazones, thiazines, thiazoles, xanthenes, fluorenes, pyronines, fluorones, rhodamines, and derivatives thereof.

25

## **Photoabsorption material**

The devices according to the present invention may also comprise a photoabsorbing material. A Photoabsorption material is a dye as mentioned above

30

## Metal complexes

The devices according to the present invention may also comprise a metal complex. The metal of this complex is preferably selected from transition metals, rare earth elements, lanthanides and actinides is also subject of this invention. Preferably the metal is selected from Ir, Ru, Os, Eu, Au, Pt, Cu, Zn, Mo, W, Rh, Pd, or Ag.

## Cathode

The cathode on which there is the layer of electron injection material is in some embodiments a low work function metal. 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 or lithium or cesium deposited on the higher work function metal. The work function of some metals are listed below in Table 1

**Table 1**

| Metal | Work Function eV* |
|-------|-------------------|
| Li    | 2.9               |
| Na    | 2.4               |
| K     | 2.3               |
| Cs    | 1.9               |
| Ba    | 2.5               |
| Ca    | 2.9               |
| Nb    | 2.3               |
| Zr    | 4.05              |
| Mg    | 3.66              |
| Al    | 4.2               |
| Cu    | 4.6               |
| Ag    | 4.64              |

|    |     |
|----|-----|
| Zn | 3.6 |
| Sc | 3.5 |

\* Handbook of Chemistry and Physics

5 In many embodiments, aluminium is used as the cathode either on its own or alloyed with elements such as magnesium or silver, although in some embodiments other cathode materials e.g. calcium, may be employed. In an embodiment the cathode may comprise a first layer of alloy e.g. Li-Ag, Mg-Ag or Al-Mg closer to the electron injection or electron transport layer  
10 and a second layer of pure aluminium further from the electron injection or electron transport layer. In further embodiments the cathode material may be Ag or MgAg or MgIn. Cathode materials may also be on transparent plate materials which may be of glass or may be of plastics which may be rigid or flexible and may be optically transparent As regards plastics  
15 substrates, rigid or flexible transparent plastics materials may be used, preferably materials which are dimensionally stable, impermeable to water (including water vapour) of relatively high glass transition temperature (T<sub>g</sub>). PEN is a preferred material, other materials that may be used including PES, PEEK and PET. The plastics may be coated with a conductive film  
20 and may also have a barrier coating to improve resistance to moisture which may be encountered under working conditions e.g. atmospheric moisture. In yet further embodiments the cathode may be crystalline, polycrystalline, continuous grain or amorphous silicon which may be n-doped.

25

### **Substrate**

The substrate may be rigid or flexible. It may be transparent, translucent, opaque or reflective. The materials used can be glass, plastic, ceramic or  
30 metal foils, where plastic and metal foils are preferably used for flexible substrates. However, semiconductor materials, such as, for example, silicone wafers or printed circuit board (PCB) materials, can also be

employed in order to simplify the generation of conductor tracks. Other substrates can also be employed.

5 The glass used can be, for example, soda-lime glass, Ba- or Sr-containing glass, lead glass, aluminium silicate glass, borosilicate glass, Ba borosilicate glass or quartz.

10 Plastic plates can consist, for example, of polycarbonate resin, acrylic resin, vinyl chloride resin, polyethylene terephthalate resin, polyimide resin, polyester resin, epoxy resin, phenolic resin, silicone resin, fluorine resin, polyether sulfide resin or polysulfone resin.

15 For transparent films, use is made, for example, of polyethylene, ethylene-vinyl acetate copolymers, ethylene-vinyl alcohol copolymers, polypropylene, polystyrene, polymethyl methacrylate, PVC, polyvinyl alcohol, polyvinylbutyral, nylon, polyether ether ketone, polysulfone, polyether sulfone, tetrafluoroethylene-perfluoroalkyl vinyl ether copolymers, polyvinyl fluoride, tetrafluoroethylene-ethylene copolymers, tetrafluoroethylene-hexafluoropropylene copolymers, polychlorotrifluoroethylene, polyvinylidene  
20 fluoride, polyester, polycarbonate, polyurethanes, polyimide or polyether imide.

25 The substrate is provided with a hydrophobic layer. The substrates are preferably transparent.

Other materials than those mentioned here can also be used. Suitable materials are known to the person skilled in the art.

30 It will be appreciated that variations to the foregoing embodiments of the invention can be made while still falling within the scope of the invention. Each feature disclosed in this specification, unless stated otherwise, may be replaced by alternative features serving the same, equivalent or similar

purpose. Thus, unless stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

5 All of the features disclosed in this specification may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. In particular, the preferred features of the invention are applicable to all aspects of the invention and may be used in any combination. Likewise, features described in non-essential combinations may be used separately (not in combination).

10 It will be appreciated that many of the features described above, particularly of the preferred embodiments, are inventive in their own right and not just as part of an embodiment of the present invention. Independent protection may be sought for these features in addition to or alternative to any invention presently claimed.

15 The teaching as disclosed here can be abstracted und combined with other examples disclosed.

Other features of the invention will become apparent in the course of the following descriptions of exemplary embodiments, which are given for  
20 illustration of the invention and are not intended to be limiting thereof.

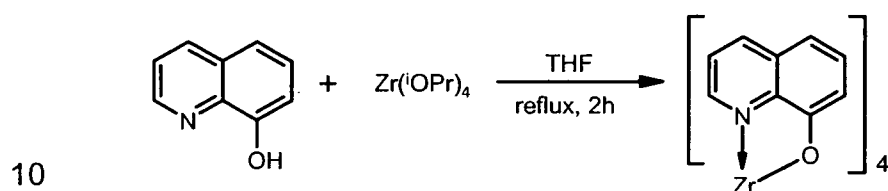
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## Working Examples

### Example 1

#### 5 Preparation of Zirconium tetrakis(8-hydroxyquinolate)- [Zr<sub>4</sub>-A]

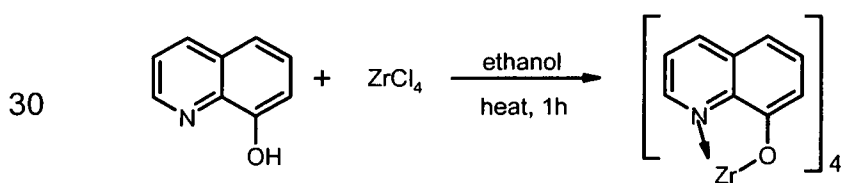


15 8-Hydroxyquinoline, 99+% (Aldrich) (100 g; 0.69 mol) is dissolved in tetrahydrofuran, 99+% (ACS reagent) (400 ml). To the magnetically stirred solution is added zirconium isopropoxide (66.8 g; 0.17 mol) in tetrahydrofuran (175 ml), all at once. A yellow precipitate forms immediately. The reaction mixture is magnetically stirred and refluxed under nitrogen for 2 hours. After cooling the reaction mixture in the refrigerator the product is filtered off under suction, washed with fresh tetrahydrofuran and dried under vacuum at 80°C for 10 hours. Yield 101 g (88%). M.p 388°C (DSC, onset). The product is sublimed to give a sublimation yield of 91%. Overall yield is 81%.

### Example 2

25

#### Preparation of Zirconium tetrakis(8-hydroxyquinolate)- [Zr<sub>4</sub>-B]



Ethanol is dried over potassium hydroxide and distilled before use. To a solution of 8-hydroxyquinoline (100.0 g; 0.69 mol) in ethanol, 95% (700 ml) is carefully added zirconium (IV) chloride (40.2 g; 0.17 mol) in ethanol (200 ml) at 10°C (The solution is cooled in an ice-water bath). After 10 minutes, the solution is warmed to 50°C and piperidine (75 ml; 0.76 mol) is slowly added, during which time a yellow precipitate separates out. The suspension is heated at about 60°C for 2 h, and allowed to cool to room temperature. The precipitate is collected by suction filtration on a Buchner funnel, washed thoroughly with ethanol, tetrahydrofuran and finally with diethyl ether. The product is dried under vacuum at 80°C. Crude yield 106.5 g (93%).

Further purification of the product (65 g) is performed by Soxhlet extraction (65 g) with 1,4-dioxane for 24 h. Concentration of the extract yields a yellow precipitate which is collected on a Buchner funnel and washed with ethanol, (95%; 100 ml). The product is dried under vacuum at 80°C for 8h. Yield, 50 g (77%). M.p., 388°C (DSC, onset). The product is further purified by sublimation to give a sublimed yield of 92%. Overall yield is 66%.

20

### Example 3

Devices with green emission are formed as follows. A pre-etched ITO coated glass piece (10 x 10 cm<sup>2</sup>) is used. The device is fabricated by sequentially forming layers on the ITO, by vacuum evaporation using a Solciet Machine, ULVAC Ltd. Chigacki, Japan. The active area of each pixel is 3 mm by 3 mm. The coated electrodes are encapsulated in an inert atmosphere (nitrogen) with UV-curable adhesive using a glass back plate. Electroluminescence studies are performed with the ITO electrode is always connected to the positive terminal. The current density vs. voltage studies are carried out on a computer controlled Keithly 2400 source meter.

By the method described above devices consisting of an anode layer, buffer layer, hole transport layer, electroluminescent layer (doped material), electron transport layer, electron injection layer and cathode layer are obtained. The layer composition is described in Figs. 5 to 8 and film thicknesses being in nm. The CIE colour coordinates and other characteristics are as illustrated. It will be noted that significantly better performance is obtained with the A-form of zirconium quinolate than with the B-form.

#### Example 4

Diffraction data are collected at 150 K as  $\omega$  scans on a Bruker SMART1000 CCD area detector diffractometer, equipped with an Oxford Cryosystems open-flow nitrogen gas cooler (Cosier, J. & Glazer, A.M. (1986). *J. Appl. Crystallogr.* 19, 105-107) and graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure is solved by direct methods using SHELXS97 (Sheldrick, G. M. (2008). *Acta Crystallogr., Sect. A.* 64, 112-122), developed by iterative cycles of least-squares refinement and difference Fourier synthesis, and refined by full-matrix least-squares on  $F^2$  using SHELXL97 (Sheldrick, G. M. (2008). *Acta Crystallogr., Sect. A.* 64, 112-122). All non-hydrogen atoms are refined anisotropically. Hydrogen atoms are introduced at geometrically calculated positions and refined using a riding model with  $U_{iso}(H) = 1.2U_{eq}(\text{parent atom})$ . The following unit cell parameters are obtained: space group P21/c,  $a = 11.22$  Å,  $b = 14.67$  Å,  $c = 17.21$  Å,  $\alpha = 90^\circ$ ,  $\beta = 94.816^\circ$ ,  $\gamma = 90^\circ$ , and unit cell volumen  $V = 2822.7$  Å<sup>3</sup>.

**CLAIMS**

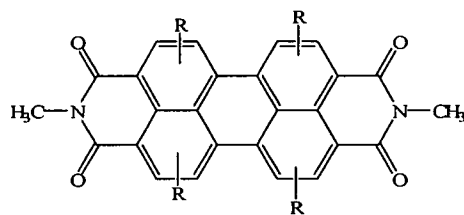
1. Zirconium quinolate having a monoclinic crystal structure.
- 5 2. Zirconium quinolate according to claim 1, characterized in that the space group is P21/c.
3. Zirconium quinolate according to claim 1 or 2, characterized in that the unit cell dimensions are  $a = 11.2 \pm 0.4 \text{ \AA}$ ,  $b = 14.7 \pm 0.4 \text{ \AA}$ ,  
10  $c = 17.2 \pm 0.4 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 95^\circ \pm 1^\circ$ ,  $\gamma = 90^\circ$ , and unit cell volumen  $V = 2823 \pm 5 \text{ \AA}^3$ .
4. Zirconium quinolate of one or more of the claims 1 to 3, characterized in that the unit cell dimensions are  $a = 11.22 \text{ \AA}$ ,  $b = 14.67 \text{ \AA}$ ,  
15  $c = 17.21 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 94.816^\circ$ ,  $\gamma = 90^\circ$ , and unit cell volumen  $V = 2822.7 \text{ \AA}^3$ .
5. Zirconium quinolate of one or more of the claims 1 to 4 characterized in that the purity is greater than or equal to 80%, preferably greater  
20 than or equal to 85%, particularly preferably greater than or equal to 90%, and very particularly preferably greater than or equal to 95%.
6. A method of making zirconium quinolate in monoclinic form, which comprises reacting a zirconium alkoxide with 8-hydroxyquinoline in a  
25 solvent comprising tetrahydrofuran, recovering the zirconium quinolate and purifying it by sublimation.
7. The method of claim 6, characterized in that the zirconium alkoxide is zirconium isopropoxide.
- 30 8. An optical light emitting device having a first electrode, a layer comprising monoclinic zirconium quinolate and a second electrode.

9. A device according to claim 8, having one or more of the following features:

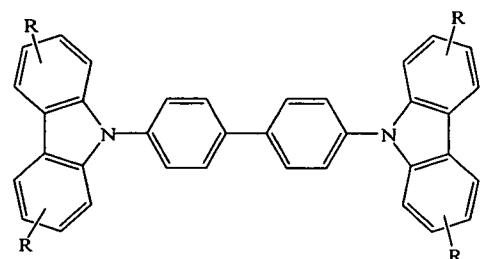
- (a) a hole injection layer comprising a porphyrinic compound;  
(b) a hole injection layer comprising ZnTpTP;  
(c) a hole transport layer comprising an aromatic amine selected from NPD, TPD 232, MTDATA, HIL1, HIL2, HIL3, and CHATP.

10. The device according to claim 8 or 9, having one or more of the following features

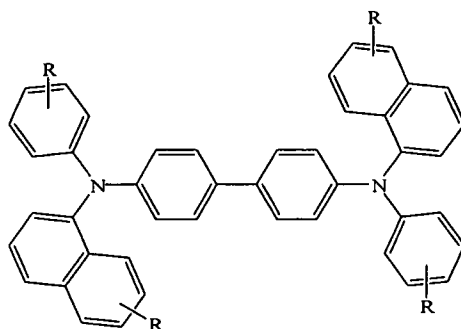
- (a) a hole transport layer comprising an aromatic tertiary amine;  
(b) a hole transport layer comprising any of



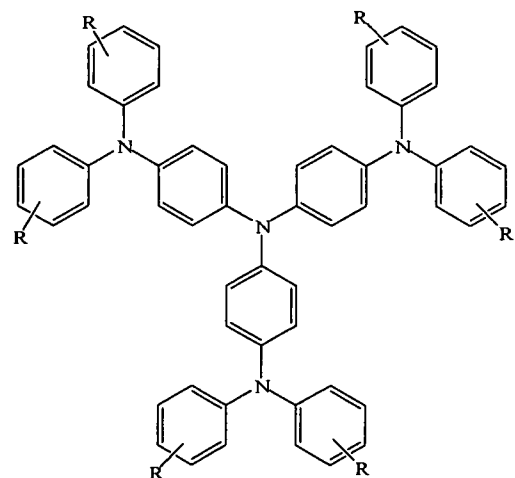
(i);



(ii);

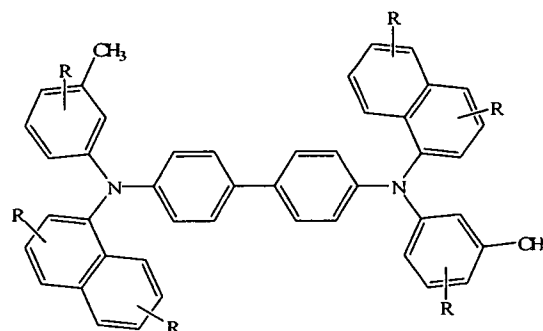


(iii);

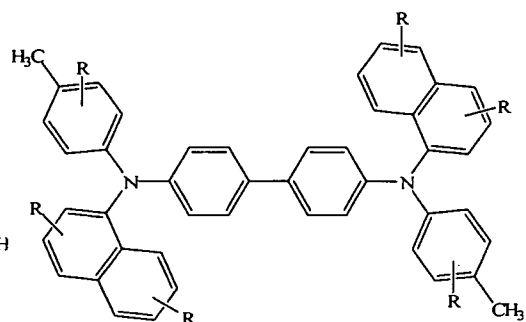


(iv);

5

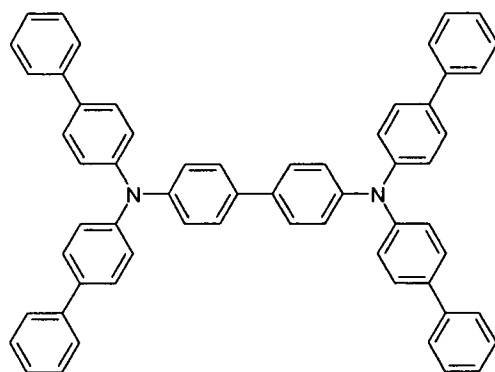


(v);



(vi);

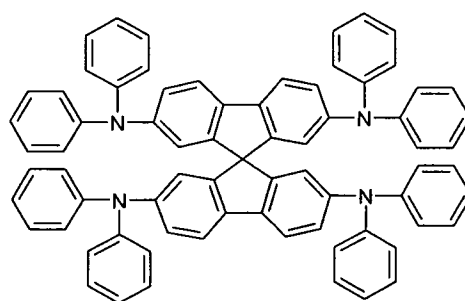
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HTL1

(vii)

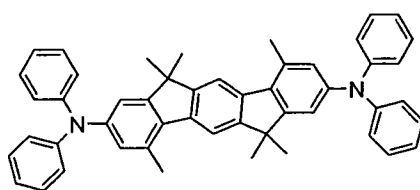
15



HTL2

(viii)

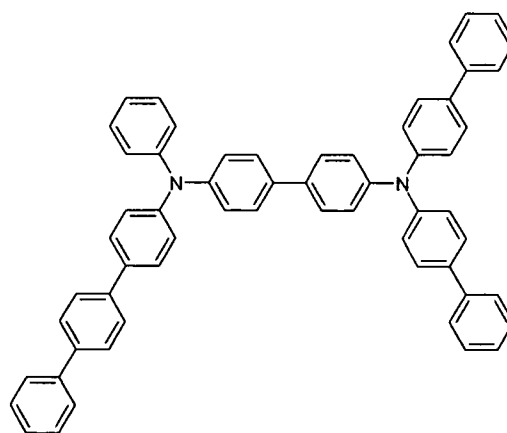
20



HTL3

(ix)

25

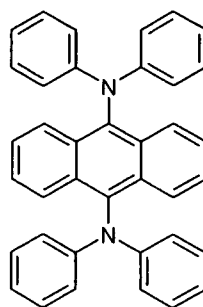


HTL4

(x)

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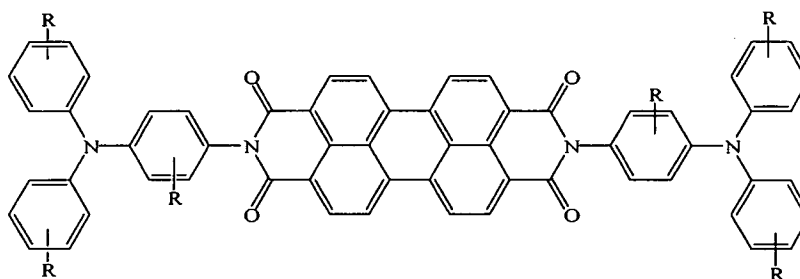
5



HTL5

(xi)

10



15

(xii)

wherein

20

the groups R in any of the formulae in (i) to (xii) can be the same or different and are selected from hydrogen; substituted and unsubstituted aliphatic groups; substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures; halogens; and thiophenyl groups;

25

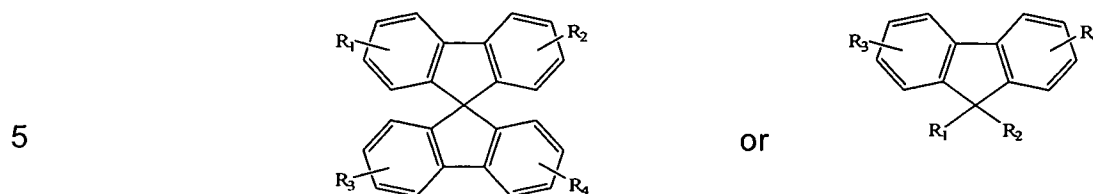
and

wherein

30

in formula (i) the methyl groups may be replaced by C<sub>1</sub> to C<sub>4</sub> alkyl or monocyclic or polycyclic aryl or heteroraryl which may be further substituted e.g. with alkyl, aryl or arylamino.

- (c) the hole transport materials comprises a compound of formula



wherein

- 10 the groups  $R_1$  to  $R_4$  when appearing in either of the above formulae can be the same or different and are selected from hydrogen; substituted and unsubstituted aliphatic groups; substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures; halogens; and thiophenyl groups;

15

- (d) the hole transport layer comprises  $\alpha$ -NPB.

11. The device according to one or more of the claims 8 to 10, characterized in that the electroluminescent layer has one or more of the following features:
- 20

- (a) it comprises a metal or metalloid complex;
- (b) it comprises zirconium quinolate as host material doped with a dopant;
- 25 (c) it comprises monoclinic zirconium quinolate;
- (d) it comprises aluminium quinolate as host material doped with a dopant;
- (e) it comprises an iridium, ruthenium, osmium, rhodium, palladium or platinum complex, a boron complex or a rare
- 30 earth complex;
- (f) it comprises an aromatic tertiary amine as host material doped with a dopant;

- (g) it comprises as a host material selected from carbazols, ketones, phosphinoxides, sufoxides, bipolar hosts, and oligoarylenes selected from anthracenes, dinaphthyl anthracenes, benzanthracene anthracenes, tetraphenylspirobifluorenes.
- (h) it comprises a light-emitting conjugated polymer or copolymer or a dendrimer;
- (i) it comprises monoclinic zirconium quinolate doped with a dopant;
- (j) the dopant is selected from phosphorescent emitters, diphenylacridine, coumarins, perylene, quinolates, porphoryin, porphines, pyrazalones and derivatives thereof, aryl amines preferably indenofluorene monoamines and -diamines, benzofluorene monoamines and -diamines and dibenzoindenofluorene monoamines and -diamines;
- (k) there is up to 10 mole percent fluorescent material, based on moles of organo metallic complex;
- (l) there is up to 1 mole percent fluorescent material, based on moles of organo metallic complex;
- (m) there is less than  $10^{-3}$  mole percent fluorescent material, based on moles of organo metallic complex.
12. The device according to one or more of the claims 8 to 11, characterized in that the electron transport layer comprises monoclinic zirconium quinolate or a composition comprising monoclinic zirconium quinolate and at least one further electron transport material preferably selected from benzimidazoles and quinolates of Li, Al, Ga, Mg, Zn, and Be, particularly preferably lithium quinolate.
13. The device according to one or more of the claims 8 to 12, having an electron injection layer based on metal quinolates, preferably

quinolates of Li, Al, Ga, Mg, Zn, and Be or an inorganic lithium compound or a lithium complex .

- 5           14. The device according to one or more of the claims 8 to 13, which is a flat panel display.
15. The device according to claim 14, which is a passive matrix display.
16. The device according to claim 14 which is an active matrix display.
- 10           17. An imaging member for creation of an electrostatic latent image containing monoclinic zirconium quinolate.
18. A lamp containing electroluminescent material and monoclinic zirconium quinolate as a host or as an electron transport material.
- 15

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25

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Fig. 1

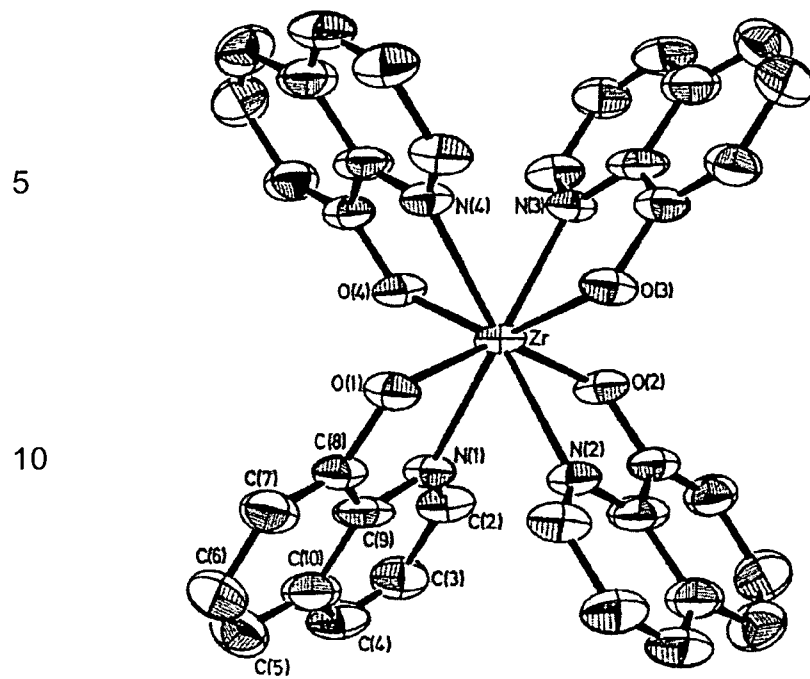


Fig. 2

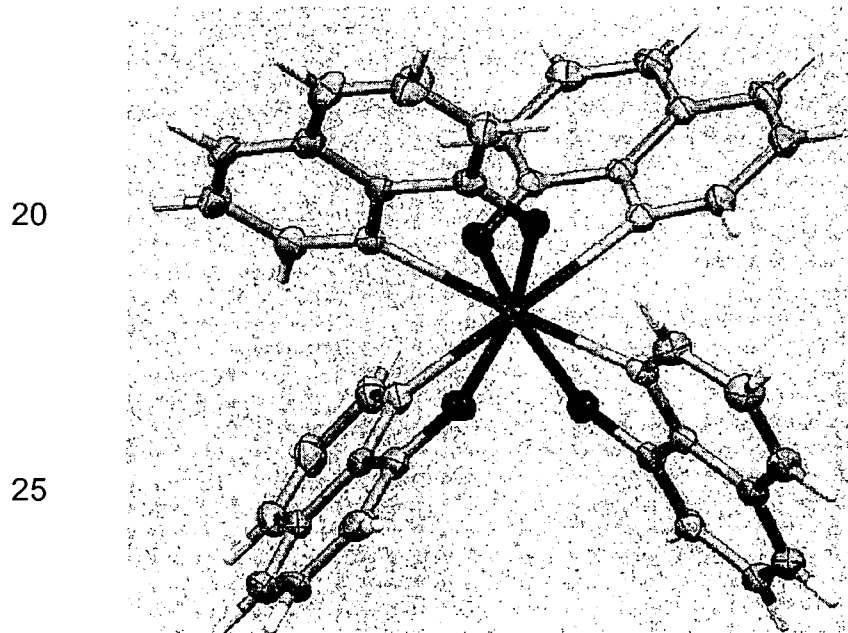


Fig. 3

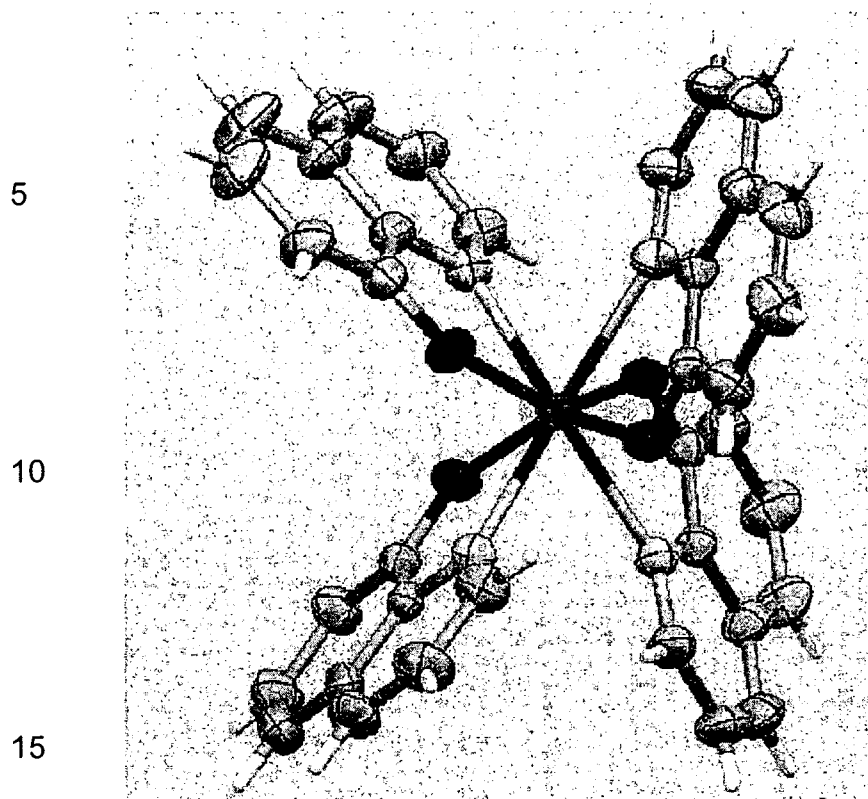


Fig. 4

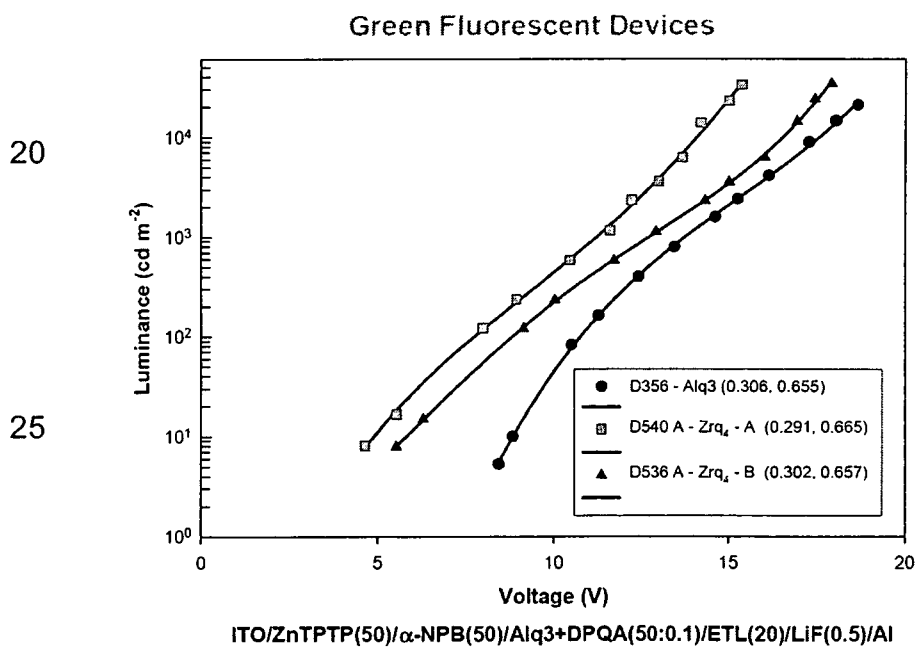


Fig. 5

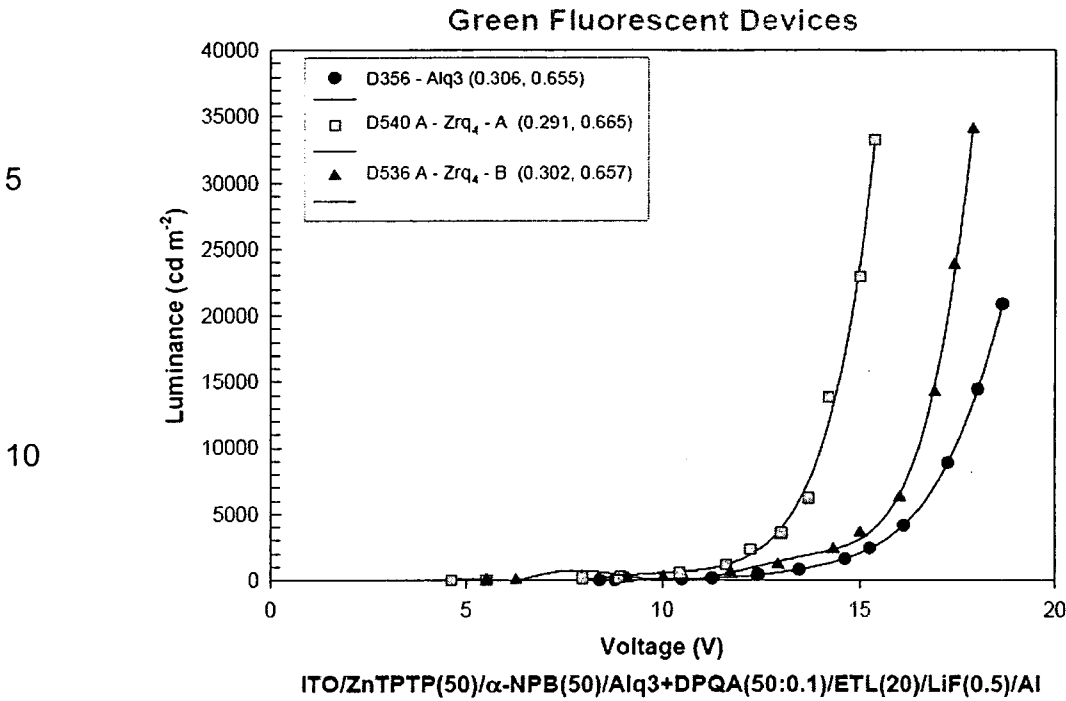


Fig.6

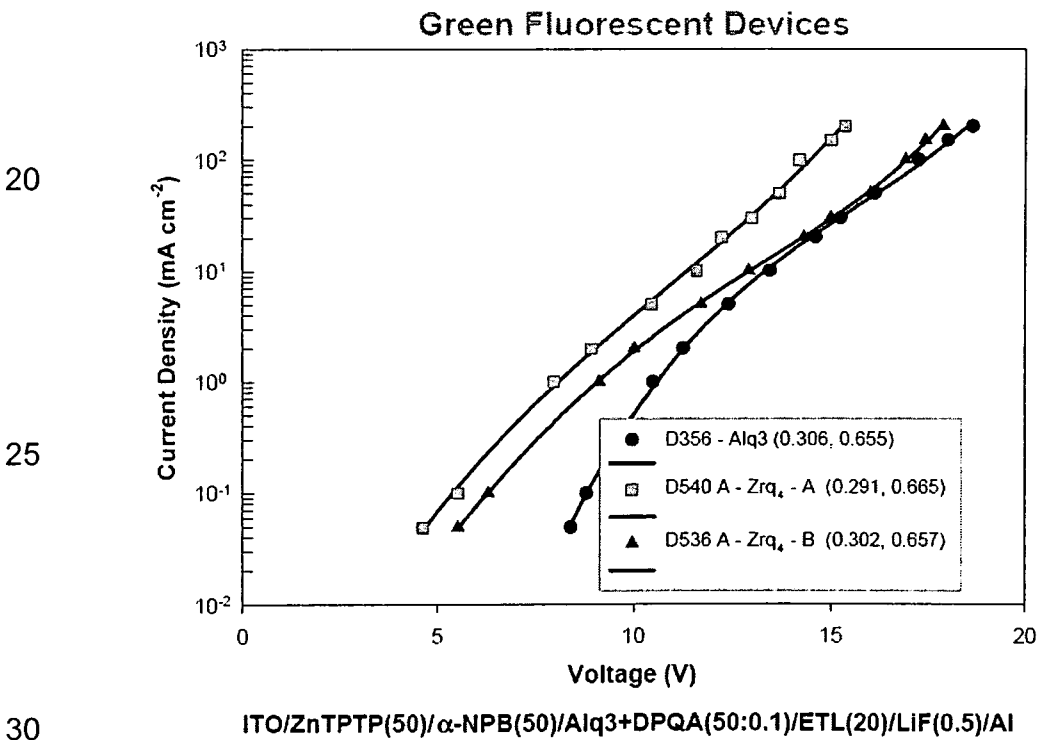


Fig. 7

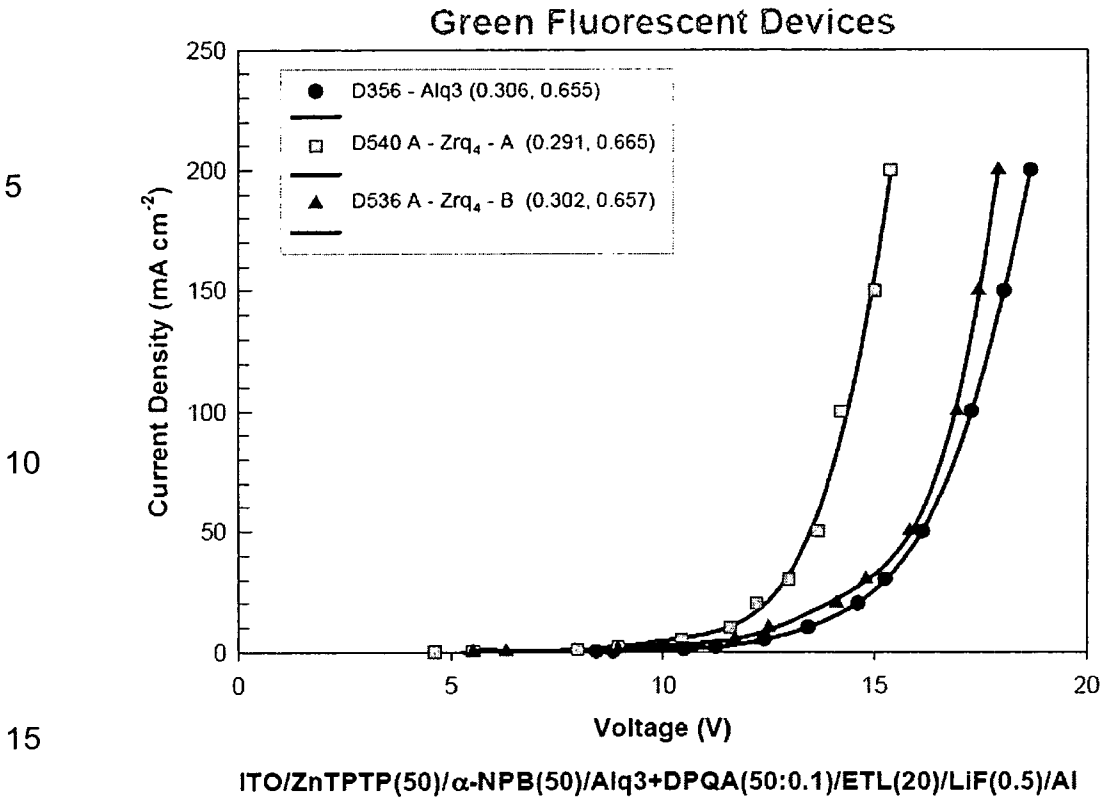
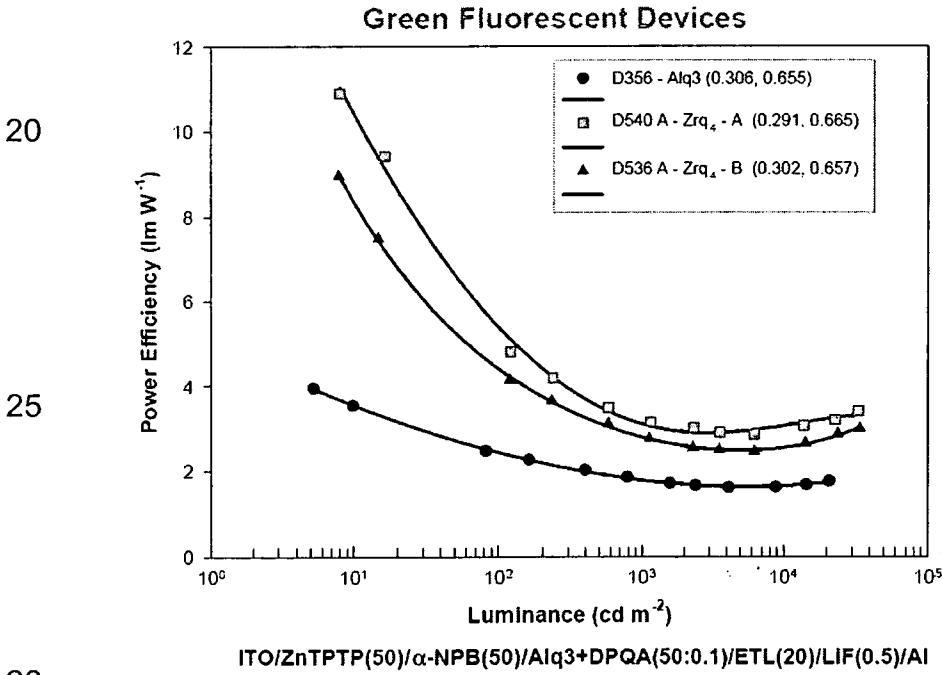


Fig. 8



## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/005523

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K11/06

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)

C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## 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         | claim 1<br>page 2, line 22 - page 3, line 14<br>claim 7<br>page 1, line 6 - line 7                                             | 17                    |
| Y         | WO 2008/078115 A1 (OLED T LTD [GB];<br>KATHIRGAMANATHAN POOPATHY [GB];<br>SURENDRAKUMAR SIVAGNA)<br>3 July 2008 (2008-07-03)   | 17                    |
| A         | claims 11,20,21                                                                                                                | 1-16,18               |
|           | -----<br>-/--                                                                                                                  |                       |



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents:

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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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Date of the actual completion of the international search

27 October 2009

Date of mailing of the international search report

05/11/2009

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040,  
Fax: (+31-70) 340-3016

Authorized officer

Saldamli, Saltuk

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/005523

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                |                       |
|------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| Category*                                            | Citation of document, with indication, where appropriate, of the relevant passages                                                                             | Relevant to claim No. |
| A                                                    | US 2004/247936 A1 (NAKASHIMA HARUE [JP] ET AL) 9 December 2004 (2004-12-09)<br>claim 1<br>examples 3-6                                                         | 1-18                  |
| A                                                    | -----<br>WO 2007/052083 A2 (OLED T LTD [GB]; KATHIRGAMANATHAN POOPATHY [GB]; RAVICHANDRAN SEENIVAS)<br>10 May 2007 (2007-05-10)<br>the whole document<br>----- | 1-18                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2009/005523

| Patent document<br>cited in search report |    | Publication<br>date |    | Patent family<br>member(s) | Publication<br>date |
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|                                           |    |                     | GB | 2423302 A                  | 23-08-2006          |
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|                                           |    |                     | WO | 2004046275 A1              | 03-06-2004          |
| -----                                     |    |                     |    |                            |                     |
| WO 2007052083                             | A2 | 10-05-2007          | EP | 1946392 A2                 | 23-07-2008          |
|                                           |    |                     | JP | 2009515331 T               | 09-04-2009          |
|                                           |    |                     | US | 2009167158 A1              | 02-07-2009          |
| -----                                     |    |                     |    |                            |                     |

|               |                                                                                                    |         |            |
|---------------|----------------------------------------------------------------------------------------------------|---------|------------|
| 专利名称(译)       | 具有电致发光或电子传输性质的化合物及其制备和用途                                                                           |         |            |
| 公开(公告)号       | <a href="#">EP2318474A1</a>                                                                        | 公开(公告)日 | 2011-05-11 |
| 申请号           | EP2009777545                                                                                       | 申请日     | 2009-07-30 |
| 申请(专利权)人(译)   | MERCK PATENT GMBH                                                                                  |         |            |
| 当前申请(专利权)人(译) | MERCK PATENT GMBH                                                                                  |         |            |
| [标]发明人        | KATHIRGAMANATHAN POOPATHY<br>SURENDRAKUMAR SIVAGNANASUNDRAM                                        |         |            |
| 发明人           | KATHIRGAMANATHAN, POOPATHY<br>SURENDRAKUMAR, SIVAGNANASUNDRAM                                      |         |            |
| IPC分类号        | C09K11/06 H01L51/50                                                                                |         |            |
| CPC分类号        | C09K11/06 C09K2211/1029 C09K2211/183 H01L51/0084 H01L51/0085 H01L51/5012 H01L51/5072<br>H01L51/508 |         |            |
| 优先权           | 2008014749 2008-08-13 GB                                                                           |         |            |
| 其他公开文献        | EP2318474B1                                                                                        |         |            |
| 外部链接          | <a href="#">Espacenet</a>                                                                          |         |            |

#### 摘要(译)

公开了一种形式的喹啉锆，其具有单斜晶系结构， $P2_1/c$ 空间群，晶胞尺寸 $a=11.22$ ， $b=14.67$ ， $c=17.21$  $a=90^\circ$ ， $\beta=94.816^\circ$ ， $\gamma=90^\circ$ 和晶胞体积 $2822.7\text{\AA}^3$ 。它可以通过使锆醇盐与8-羟基喹啉在包含四氢呋喃的溶剂中反应，回收喹啉锆并通过升华纯化来制备。它是有用的，例如作为有机发光二极管的电致发光层中的主体，和/或电子传输层中的主体。在初始纯化之后，基本上没有残留物可升华，并且当用作OLED中的电子传输层时，与通过较早氯化物路线制备的喹啉铝或喹啉锆相比，OLED的亮度增加并降低了导通电压。