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(54) **Organic light-emitting diode including an electron transport layer stack comprising different lithium compounds and elemental metal**

Organische Leuchtdiode (OLED) mit einem Elektronentransportschichtstapel mit unterschiedlichen Lithiumverbindungen und elementarem Metall

Diode électroluminescente organique (OLED) comprenant un empilement de couches de transport d'électrons incluant différents composés de lithium et du métal élémentaire

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(56) References cited:
EP-A1- 2 075 858 EP-A1- 2 752 907

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Description

[0001] The present invention relates to an organic light-emitting diode including an electron transport layer stack, and a method of manufacturing the same.

DESCRIPTION OF THE RELATED ART

[0002] Organic light-emitting diodes (OLEDs), which are self-emitting devices, have a wide viewing angle, excellent contrast, quick response, high brightness, excellent driving voltage characteristics, and color reproduction. A typical OLED includes an anode, a hole transport layer (HTL), an emission layer (EML), an electron transport layer (ETL), and a cathode, which are sequentially stacked on a substrate. In this regard, the HTL, the EML, and the ETL are thin films formed from organic compounds.

[0003] EP 2 752 907 A1 refers to an organic light emitting device that includes a first electrode, a second electrode, and two or more light emitting units provided between the first electrode and the second electrode, wherein a charge generation layer is provided between, among the light emitting units, two light emitting units that are adjacent to each other, an electron transport layer is provided between the charge generation layer and the light emitting unit placed closer to the first electrode of the two adjacent light emitting units, and the electron transport layer includes a first electron transport layer doped with an n-type dopant, such as Ca, other elemental metals are also suggested, and a second electron transport layer doped with a metal salt, metal oxide or organic metal salt, such as LiF. Lithium quinolate is also suggested.

[0004] EP 2 075 858 A1 refers to an organic light emitting device includes a first electrode; a second electrode; an emissive layer disposed between the first electrode and the second electrode; a hole injection layer disposed between the first electrode and the emissive layer; and an electron transport layer disposed between the emissive layer and the second electrode. The hole injection layer includes a hole injecting material and a first compound made up of an element selected from the group consisting of Mo, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, and B and an element selected from the group consisting of O, F, S, Cl, Se, Br, and I.

[0005] When a voltage is applied to the anode and the cathode, holes injected from the anode move to the EML, via the HTL, and electrons injected from the cathode move to the EML, via the ETL. The holes and electrons recombine in the EML to generate excitons. When the excitons drop from an excited state to a ground state, light is emitted. The injection and flow of holes and electrons should be balanced, so that an OLED having the above-described structure has excellent efficiency and/or a long lifetime.

SUMMARY

[0006] The following aspects are useful for understanding the invention. It is one object to provide organic light-emitting diode having an increased external quantum efficiency (EQE) of OLEDs, especially for blue emitting OLEDs but also, for example for red, green or white, and/or an increased lifetime, in particular for top and/or bottom emission organic light-emitting diodes (OLED) .

[0007] According to one aspect, there is provided an organic light-emitting diode (OLED) comprising an emission layer and an electron transport layer stack of at least two electron transport layers, wherein a first electron transport layer and a second electron transport layer comprises at least one matrix compound and in addition,

- the at least first electron transport layer comprises a lithium halide or a lithium organic complex; and the at least second electron transport layer comprises an elemental metal selected from the group of lithium, magnesium and/or ytterbium; or
- the at least first electron transport layer comprises an elemental metal selected from the group of lithium, magnesium and/or ytterbium; and the at least second electron transport layer comprises a lithium halide or a lithium organic complex;

wherein the electron transport layer or layers comprising a lithium halide or a lithium organic complex is free of an elemental metal, and the electron transport layer or layers that comprises an elemental metal is free of a metal salt and/or a metal organic complex.

[0008] In the context that the electron transport layer or layers comprising a lithium halide or a lithium organic complex is free of an elemental metal, the term "free of" means that the electron transport layer or layers containing lithium halide/organic complex may comprise impurities of 0.1 wt.-% or less, preferably 0.01 wt.-% or less, and more preferably 0.001 wt.-% or less of a metal dopant and most preferred no metal dopant.

[0009] In the context that the electron transport layer or layers that comprises an elemental metal is free of a metal salt and/or a metal organic complex, the term "free of" means that the electron transport layer or layers containing an

elemental metal may comprise of 5 wt.-% or less of a lithium halide and/or a lithium organic complex, preferably 0.5 wt.-% or less, and more preferably 0.05 wt.-% or less, and even more preferably 0.005 wt.-% or less of a lithium halide and/or a lithium organic complex and most preferred no lithium halide and/or a lithium organic complex.

[0010] According to various aspects, there is provided an organic light-emitting diode, whereby the organic light-emitting diode does not contain a charge generation layer (CGL).

[0011] According to the invention there is provided an organic light-emitting diode comprising an emission layer and an electron transport layer stack of at least two electron transport layers, wherein a first electron transport layer and a second electron transport layer comprises at least one matrix compound, wherein the matrix compound is a phosphine oxide based compound, preferably selected from the group comprising (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide, 3-phenyl-3H-benzo[b]dinaphtho[2,1-d:1',2'-f] phosphine-3-oxide, bis(4-(anthracen-9-yl)phenyl)(phenyl)phosphine oxide and/or phenyl bis(3-(pyren-1-yl)phenyl)phosphine oxide; and in addition,

- the at least first electron transport layer comprises a lithium halide or a lithium organic complex; and the at least second electron transport layer comprises an elemental metal selected from the group of lithium, magnesium and/or yttrium; or
- the at least first electron transport layer comprises an elemental metal selected from the group of lithium, magnesium and/or yttrium; and the at least second electron transport layer comprises a lithium halide or a lithium organic complex;

wherein the electron transport layer or layers comprising a lithium halide or a lithium organic complex is free of an elemental metal, and the electron transport layer or layers that comprises an elemental metal is free of a metal salt and/or a metal organic complex.

[0012] According to various aspects, there is provided an organic light-emitting diode comprising an emission layer and an electron transport layer stack of at least two electron transport layers, wherein a first electron transport layer and a second electron transport layer comprises at least one matrix compound and in addition,

- the at least first electron transport layer comprises a lithium halide or a lithium organic complex, preferably a lithium organic complex; and the at least second electron transport layer comprises an elemental metal selected from the group of yttrium and/or magnesium, preferably yttrium, in view of the stronger doping effect magnesium can be more preferred; or
- the at least first electron transport layer comprises an elemental metal selected from the group of yttrium and/or magnesium, preferably yttrium; and the at least second electron transport layer comprises a lithium halide or a lithium organic complex, preferably a lithium organic complex;

wherein the electron transport layer or layers comprising a lithium halide or a lithium organic complex is free of an elemental metal, and the electron transport layer or layers that comprises an elemental metal is free of a metal salt and/or a metal organic complex.

[0013] According to various aspects, there is provided an organic light-emitting diode comprising an emission layer and an electron transport layer stack of at least two electron transport layers, wherein a first electron transport layer and a second electron transport layer comprises at least one matrix compound and in addition,

- the at least first electron transport layer comprises a lithium organic complex; and the at least second electron transport layer comprises an elemental metal selected from the group of yttrium and/or magnesium, preferably yttrium; or
- the at least first electron transport layer comprises an elemental metal selected from the group of yttrium and/or magnesium, preferably yttrium; and the at least second electron transport layer comprises a lithium organic complex;

wherein the electron transport layer or layers comprising a lithium organic complex is free of an elemental metal, and the electron transport layer or layers that comprises an elemental metal is free of a metal salt and/or a metal organic complex.

[0014] According to various aspects, there is provided an organic light-emitting diode comprising an emission layer and an electron transport layer stack of at least two electron transport layers, wherein a first electron transport layer and a second electron transport layer comprises at least one matrix compound and in addition,

- the at least first electron transport layer comprises a lithium organic complex; and the at least second electron transport layer comprises an elemental metal selected from the group of lithium, yttrium and/or magnesium, preferably magnesium; or

- the at least first electron transport layer comprises an elemental metal selected from the group of lithium, ytterbium and/or magnesium, preferably magnesium; and the at least second electron transport layer comprises a lithium organic complex;

wherein the electron transport layer or layers comprising a lithium organic complex is free of an elemental metal, and the electron transport layer or layers that comprises an elemental metal is free of a metal salt and/or a metal organic complex.

[0015] According to various aspects, there is provided an organic light-emitting diode comprising an emission layer and an electron transport layer stack of at least three electron transport layers, wherein

- at least two electron transport layers comprising a lithium halide or a lithium organic complex; and at least one electron transport layer comprises an elemental metal selected from the group of lithium, magnesium and/or ytterbium; or
- at least two electron transport layers comprising an elemental metal selected from the group of lithium, magnesium and/or ytterbium; and at least one electron transport layer comprises a lithium halide or a lithium organic complex;

wherein for an electron transport layer stack comprising at least two electron transport layers comprising a lithium halide or a lithium organic complex the lithium halide or lithium organic complex of each electron transport layer are selected same or different, and preferably different and more preferred selected the same; and/or wherein for an electron transport layer stack comprising at least two electron transport layers comprising an elemental metal selected from the group of lithium, magnesium and/or ytterbium; the elemental metal selected from the group of lithium, magnesium and/or ytterbium of each electron transport layer are selected same or different, and preferably selected the same.

[0016] According to various aspects, wherein for an electron transport layer stack comprising at least three electron transport layers, at least one or two electron transport layers comprising a lithium organic complex, the lithium organic complex of each electron transport layer are selected same or different, and preferably the same; and the remaining electron transport layers, comprising an elemental metal selected from the group of lithium, magnesium and/or ytterbium, preferably magnesium and/or ytterbium, wherein each electron transport layer comprising an elemental metal, the elemental metal are selected same or different, and preferably the same.

[0017] According to various aspects, wherein for an electron transport layer stack of two electron transport layers the first electron transport layer is arranged closest to an emission layer and the second electron transport layer is arranged closest to a cathode.

[0018] According to various aspects, wherein for an electron transport layer stack of three electron transport layers the first electron transport layer is arranged closest to an emission layer, the second electron layer is sandwiched between the first and the third electron transport layer and the third electron transport layer is arranged closest to a cathode.

[0019] The organic light-emitting diode can be a bottom emission OLED or a top emission OLED.

[0020] For the following defined terms, these definitions shall be applied, unless a different definition is given in the claims or elsewhere in this specification.

[0021] The external quantum efficiency, also named EQE, is measured in percent (%).

[0022] The lifetime, also named LT, between starting brightness and 97 % of the original brightness is measured in hours (h).

[0023] The voltage, also named V, is measured in Volt (V) at 10 milliAmpere per square centimeter (mA/cm²) in bottom emission devices and at 15 mA/cm² for top emission devices.

[0024] The colour space is described by coordinates CIE-x and CIE-y (International Commission on Illumination 1931). For blue emission the CIE-y is of particular importance. A smaller CIE-y denotes a deeper blue color.

[0025] The efficiency of top emission OLEDs is recorded in candela per Ampere, also named cd/A. Candela is a SI base unit of luminous intensity and describes the power emitted by a light source in a particular direction, weighted by the luminosity function (a standardized model of the sensitivity of the human eye to different wavelengths). The human eye is particularly insensitive to deep blue and deep red colors. Therefore, the efficiency measured in cd/A is corrected for the emission color, in the case of blue emission, the CIE-y. For example, a deeper blue OLED would have a lower cd/A efficiency even if the quantum efficiency (photons in compared to photons out) is the same. By dividing the efficiency measured in cd/A by the CIE-y, the efficiency of OLEDs with slightly different shades of blue can be compared. The efficiency, also named Eff., is measured in Candela per Ampere (cd/A) and divided by the CIE-y.

[0026] The highest occupied molecular orbital, also named HOMO, and lowest unoccupied molecular orbital, also named LUMO, are measured in electron volt (eV).

[0027] The term "not the same as" with respect to a lithium halide or a lithium organic complex means that the electron transport layers comprising lithium halide or a lithium organic complex, differs in its containing lithium halide or lithium organic complex.

[0028] The term "not the same as" with respect to elemental metal selected from the group of lithium, magnesium

and/or ytterbium means that the electron transport layers containing elemental lithium, magnesium and/or ytterbium, differs in its containing elemental metal.

[0029] The term "OLED" and "organic light-emitting diode" is simultaneously used and having the same meaning.

[0030] As used herein, "weight percent", "wt.-%", "percent by weight", "% by weight", and variations thereof refer to an elemental metal, a composition, component, substance or agent as the weight of that elemental metal, component, substance or agent of the respective electron transport layer divided by the total weight of the respective electron transport layer thereof and multiplied by 100. It is understood that the total weight percent amount of all elemental metal, components, substances or agents of the respective electron transport layer are selected such that it does not exceed 100 wt.-%.

[0031] All numeric values are herein assumed to be modified by the term "about", whether or not explicitly indicated. As used herein, the term "about" refers to variation in the numerical quantity that can occur. Whether or not modified by the term "about", the claims include equivalents to the quantities.

[0032] It should be noted that, as used in this specification and the appended claims, the singular forms "a", "an", and "the" include plural referents unless the content clearly dictates otherwise.

[0033] The term "free of", "does not contain", "does not comprise" does not exclude impurities. Impurities have no technical effect with respect to the object achieved by the present invention.

[0034] The term "alkyl" refers to straight-chain or branched alkyl groups. The term "1 to 20 carbon atoms" as used herein refers to straight-chain or branched alkyl groups having 1 to 20 carbon atoms. The alkyl groups can be selected from the group comprising methyl, ethyl and the isomers of propyl, butyl or pentyl, such as isopropyl, isobutyl, tert.-butyl, sec.-butyl and/or isopentyl. The term "aryl" refers to aromatic groups for example phenyl or naphthyl.

[0035] Herein, when a first element is referred to as being formed or disposed "on" a second element, the first element can be disposed directly on the second element or one or more other elements may be disposed there between. When a first element is referred to as being formed or disposed "directly on" a second element, no other elements are disposed there between.

[0036] According to various embodiments of the OLED, the electron transport layer stack wherein at least one electron transport layer may be free of a lithium halide or all electron transport layers may be free of a lithium halide.

[0037] According to various embodiments of the OLED the electron transport layer stack may comprise as a lithium compound a lithium organic complex only.

[0038] According to various embodiments of the organic light-emitting diode the amount of the lithium halide or lithium organic complex in an electron transport layer stack, preferably the at least first electron transport layer, is in the range of ≥ 10 mol-% to ≤ 95 mol-%, preferably ≥ 15 mol-% to ≤ 90 mol-% and also preferred ≥ 20 mol-% to ≤ 80 mol-%, based on the corresponding electron transport layer; and/or the amount of the lithium halide or lithium organic complex in an electron transport layer stack of at least three electron transport layers, at least two of the electron transport layers, preferably the at least first electron transport layer and/or the at least third electron transport layer, is in the range of ≥ 10 mol-% to ≤ 95 mol-%, preferably ≥ 15 mol-% to ≤ 90 mol-% and also preferred ≥ 20 mol-% to ≤ 80 mol-%, based on the corresponding electron transport layer.

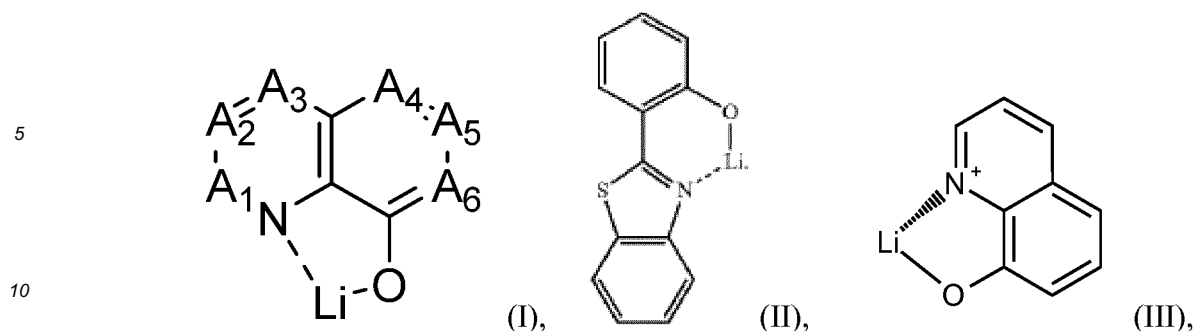
[0039] According to various embodiments of the OLED of the present invention the lithium halide or lithium halide can be selected from the group comprising LiF, LiCl, LiBr and LiI. However, most preferred is LiF.

[0040] According to various embodiments of the organic light-emitting diode comprising an electron transport layer stack, preferably of at least two electron transport layer or three electron transport layer, wherein

- at least one electron transport layer, comprises ≥ 1 wt.-% to ≤ 60 wt.-%, preferably ≥ 2 wt.-% to ≤ 55 wt.-% and also preferred ≥ 5 wt.-% to ≤ 45 wt.-% of an elemental metal selected from the group of lithium, magnesium and/or ytterbium; or
- at least two electron transport layer (161/163) of at least three electron transport layers (161/162/163) comprises ≥ 1 wt.-% to ≤ 60 wt.-%, preferably ≥ 2 wt.-% to ≤ 55 wt.-% and also preferred ≥ 5 wt.-% to ≤ 45 wt.-% of an elemental metal selected from the group of lithium, magnesium and/or ytterbium;

wherein the weight percent of the elemental metal selected from the group of lithium, magnesium and/or ytterbium is based on the total weight of the corresponding electron transport layer.

[0041] According to various embodiments of the organic light-emitting diode (OLED) of the present invention the organic ligand of the lithium organic complex can be a quinolate. Preferably the lithium organic complex is a lithium organic complex of formula I, II or III:



wherein

A1 to A6 are same or independently selected from CH, CR, N, O;

R is same or independently selected from hydrogen, halogen, alkyl or aryl or heteroaryl with 1 to 20 carbon atoms; and more preferred A1 to A6 are CH.

[0042] Quinolates that can be suitable used are disclosed in WO 2013079217 A1.

[0043] According to various embodiments of the organic light-emitting diode (OLED) of the present invention the organic ligand of the lithium organic complex can be a borate based organic ligand, Preferably the lithium organic complex is a lithium tetra(1H-pyrazol-1-yl)borate. Borate based organic ligands that can be suitable used are disclosed in WO 2013079676 A1.

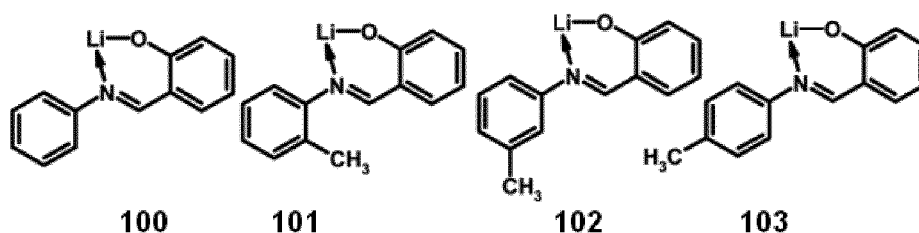
[0044] According to various embodiments of the organic light-emitting diode (OLED) of the present invention the organic ligand of the lithium organic complex can be a phenolate ligand, Preferably the lithium organic complex is a lithium 2-(diphenylphosphoryl)phenolate. Phenolate ligands that can be suitable used are disclosed in WO 2013079678 A1.

[0045] Further, phenolate ligands can be selected from the group of pyridinolate, preferably 2-(diphenylphosphoryl)pyridin-3-olate. Pyridine phenolate ligands that can be suitable used are disclosed in JP 2008195623.

[0046] In addition, phenolate ligands can be selected from the group of imidazol phenolates, preferably 2-(1-phenyl-1H-benzo[d]imidazol-2-yl)phenolate. Imidazol phenolate ligands that can be suitable used are disclosed in JP 2001291593.

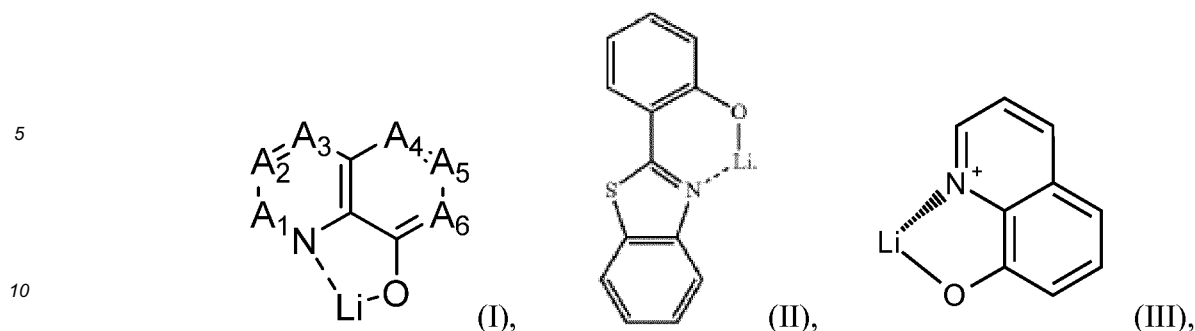
[0047] Also, phenolate ligands can be selected from the group of oxazol phenolates, preferably 2-(benzo[d]oxazol-2-yl)phenolate. Oxazol phenolate ligands that can be suitable used are disclosed in US 20030165711.

[0048] Lithium Schiff base organic complexes can be use. Lithium Schiff base organic complexes that can be suitable used having the structure 100, 101, 102 or 103:



[0049] According to various embodiments of the organic light-emitting diode (OLED) of the present invention the organic ligand of the lithium organic complex is a quinolate, a borate, a phenolate, a pyridinolate or a Schiff base ligand;

- preferably the lithium quinolate complex has the formula I, II or III:

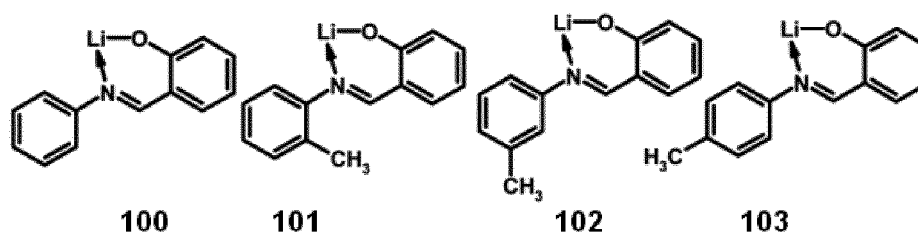


wherein

A1 to A6 are same or independently selected from CH, CR, N, O;

R is same or independently selected from hydrogen, halogen, alkyl or aryl or heteroaryl with 1 to 20 carbon atoms; and more preferred A1 to A6 are CH;

- preferably the borate based organic ligand is a tetra(1H-pyrazol-1-yl)borate;
- preferably the phenolate is a 2-(pyridin-2-yl)phenolate, a 2-(diphenylphosphoryl)phenolate, an imidazol phenolates, or 2-(pyridin-2-yl)phenolate and more preferred 2-(1-phenyl-1H-benzo[d]imidazol-2-yl)phenolate;
- preferably the pyridinolates is a 2-(diphenylphosphoryl)pyridin-3-olate,
- preferably the lithium Schiff base has the structure 100, 101, 102 or 103:



[0050] According to various embodiments of the organic light-emitting diode (OLED) of the present invention the first electron transport layer, the second electron transport layer and/or in case of three electron transport layers the third electron transport layer as well, may comprises at least one matrix compound each.

[0051] According to various embodiments of the organic light-emitting diode (OLED) of the present invention comprising an electron transport layer stack of at least two electron transport layers or at least three electron transport layers, wherein each electron transport layer comprises at least one matrix compound, whereby the matrix compound of the electron transport layers are selected same or different.

[0052] The at least two electron transport layers (161/162) or the at least three electron transport layers (161/162/163) of the inventive organic light-emitting diode (OLED) comprise at least one matrix compound, whereby the matrix compound of the electron transport layers are selected same or different, and wherein the electron matrix compound is selected from a phosphine oxide based compound, preferably (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide and/or phenyl bis (3-(pyren-1-yl)phenyl)phosphine oxide and/or 3-Phenyl-3H-benzo[b]dinaphtho[2,1-d:1',2'-f]phosphine-3-oxide, bis(4-anthracen-9-yl)phenyl)(phenyl)phosphine oxide. Further matrix compounds may be selected from:

- an anthracene based compound or a heteroaryl substituted anthracene based compound, preferably 2-(4-(9,10-di(naphthalen-2-yl)anthracene-2-yl)phenyl)-1-phenyl-1H-benzo[d]imidazole and/or N4,N4"-di(naphthalen-1-yl)-N4,N4"-diphenyl-[1,1':4',1"-terphenyl]-4,4"-diamine; or
- a substituted phenanthroline compound, preferably 2,4,7,9-tetraphenyl-1,10-phenanthroline or 2,9-di(biphenyl-4-yl)-4,7-diphenyl-1,10-phenanthroline.

[0053] According to various embodiments of the organic light-emitting diode (OLED) of the present invention the thicknesses of each electron transport layer, preferably the at least first electron transport layer (161) and the at least second electron transport layer (162) and/or the at least third electron transport layer (163), are same or each independently, in the range of ≥ 0.5 nm to ≤ 95 nm, preferably of ≥ 3 nm to ≤ 80 nm, further preferred of ≥ 5 nm to ≤ 60 nm, also

preferred of ≥ 6 nm to ≤ 40 nm, in addition preferred ≥ 8 nm to ≤ 20 nm and more preferred of ≥ 10 nm to ≤ 18 nm.

[0054] According to various embodiments of the organic light-emitting diode (OLED) the thicknesses of the electron transport layer stack can be in the range of ≥ 25 nm to ≤ 100 nm, preferably of ≥ 30 nm to ≤ 80 nm, further preferred of ≥ 35 nm to ≤ 60 nm, and more preferred of ≥ 36 nm to ≤ 40 nm.

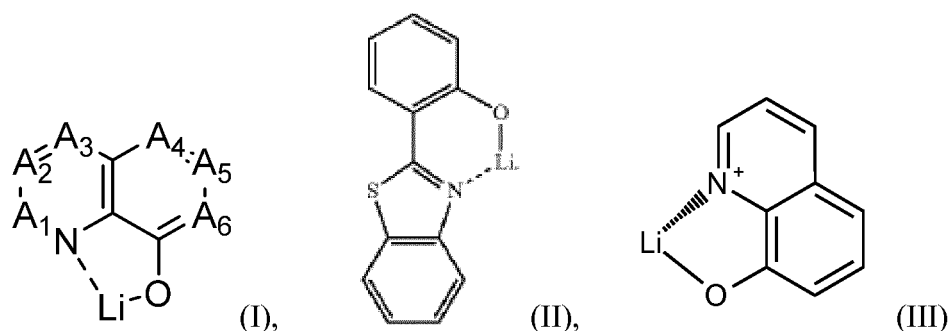
[0055] According to various embodiments of the organic light-emitting diode (OLED) of the present invention the electron transport layer stack has 2 to 4 electron transport layers and more preferred 2 to 3 electron transport layers.

[0056] According to various embodiments of the organic light-emitting diode (OLED) of the present invention the second electron transport layer can be formed directly on the first electron transport layer and an optional third electron transport layer can be formed directly on the second electron transport layer, so that the second electron transport layer is sandwiched between the first and third electron transport layers.

[0057] According to various embodiments of the organic light-emitting diode (OLED) of the present invention:

- at least one electron transport layer or in case of at least three electron transport layers at least two electron transport layer comprise:

a) ≥ 10 wt.-% to ≤ 70 wt.-%, preferably ≥ 20 wt.-% to ≤ 65 wt.-% and also preferred ≥ 50 wt.-% to ≤ 60 wt.-% of a lithium halide, selected from the group comprising a LiF, LiCl, LiBr or LiI, preferably LiF, or of a lithium organic complex of a lithium quinolate, a borate, a phenolate, a pyridinolate or a Schiff base ligand; preferably of a lithium quinolate complex has the formula I, II or III:



wherein

- A1 to A6 are same or independently selected from CH, CR, N, O,
- R is same or independently selected from hydrogen, halogen, alkyl or aryl or heteroaryl with 1 to 20 carbon atoms, and more preferred of a lithium 8-hydroxyquinolate;

b) ≤ 90 wt.-% to ≥ 30 wt.-%, preferably ≤ 80 wt.-% to ≥ 35 wt.-% and also preferred ≤ 50 wt.-% to ≥ 40 wt.-% and also preferred ≤ 50 wt.-% to ≥ 40 wt.-% of a matrix compound of:

- an anthracene based compound or a heteroaryl substituted anthracene based compound, preferably 2-(4-(9,10-di(naphthalen-2-yl)anthracene-2-yl)phenyl)-1-phenyl-1H-benzo[d]imidazole and/or N4,N4"-di(naphthalen-1-yl)-N4,N4"-diphenyl-[1,1':4',1"-terphenyl]-4,4"-diamine; or
 - a phosphine oxide based compound, preferably (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide, 3-phenyl-3H-benzo[b]dinaphtho[2,1-d:1',2'-f]phosphine-3-oxide, bis(4-(anthracen-9-yl)phenyl)(phenyl)phosphine oxide and/or phenyl bis(3-(pyren-1-yl)phenyl)phosphine oxide; or
 - a substituted phenanthroline compound, preferably 2,4,7,9-tetraphenyl-1,10-phenanthroline or 2,9-di(biphenyl-4-yl)-4,7-diphenyl-1,10-phenanthroline;
- whereby more preferred is a phosphine oxide based compound and most preferred is (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide;
- and
- at least one electron transport layer or in case of at least three electron transport layers at least two electron layers comprising:

c) ≥ 1 wt.-% to ≤ 60 wt.-%, preferably ≥ 2 wt.-% to ≤ 55 wt.-% and also preferred ≥ 5 wt.-% to ≤ 45 wt.-% of an elemental metal selected from the group of lithium, magnesium and/or ytterbium, more preferred of an elemental metal magnesium ;

d) ≤ 99 wt.-% to ≥ 40 wt.-%, preferably ≤ 98 wt.-% to ≥ 45 wt.-% and also preferred ≤ 95 wt.-% to ≥ 55 wt.-% of a matrix compound of:

- an anthracene based compound or a heteroaryl substituted anthracene based compound, preferably 2-(4-(9,10-di(naphthalen-2-yl)anthracene-2-yl)phenyl)-1-phenyl-1H-benzo[d]imidazole and/or N4,N4"-di(naphthalen-1-yl)-N4,N4"-diphenyl-[1,1':4',1"-terphenyl]-4,4"-diamine; or
 - a phosphine oxide based compound, preferably (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide, 3-phenyl-3H-benzo[b]dinaphtho[2,1-d:1',2'-f]phosphine-3-oxide, bis(4-(anthracen-9-yl)phenyl)(phenyl)phosphine oxide and/or phenyl bis(3-(pyren-1-yl)phenyl)phosphine oxide; or
 - a substituted phenanthroline compound, preferably 2,4,7,9-tetraphenyl-1,10-phenanthroline or 2,9-di(biphenyl-4-yl)-4,7-diphenyl-1,10-phenanthroline;
- whereby more preferred is a phosphine oxide based compound and most preferred is (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide;
- wherein the weight percent of each component is based on the total weight of the corresponding electron transport layer;
- and wherein one of the at least one matrix compounds is a phosphine oxide based compound.

[0058] According to various embodiments of the OLED of the present invention:

- the at least one, preferably two, lithium organic complex containing electron transport layer (161) comprises of ≥ 50 wt.-% to ≤ 60 wt.-% of a lithium 8-hydroxyquinolate and ≤ 50 wt.-% to ≥ 40 wt.-% of a (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide; and
- the at least one, preferably two, elemental metal containing electron transport layer (162) comprises of ≥ 2 wt.-% to ≤ 45 wt.-% of an elemental metal selected from the group of lithium, magnesium and/or ytterbium, more preferred of an elemental metal magnesium and ≤ 98 wt.-% to ≥ 55 wt.-% of a (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide.

[0059] According to another aspect, there is provided an organic light-emitting diode comprising: a substrate; a first anode electrode formed on the substrate; a second cathode electrode formed on the first anode electrode; and an electron transport layer stack formed between the first anode electrode and the second cathode electrode, comprising or consisting of at least two electron transport layers or at least three electron transport layers.

[0060] According to various embodiments, the organic light-emitting diode (OLED) may further include at least one layer selected from the group consisting of a hole injection layer, a hole transport layer, an emission layer, and a hole blocking layer, formed between the first anode electrode and the electron transport layer.

[0061] According to another aspect, there is provided an organic light-emitting diode comprising in addition: at least one layer selected from the group consisting of a hole injection layer, a hole transport layer, an emission layer, and a hole blocking layer, formed between the first anode electrode and the electron transport layer stack.

[0062] According to various aspects, there is provided an organic light-emitting diode further comprising an electron injection layer formed between the electron transport layer and the second cathode electrode.

[0063] According to various embodiments of the OLED of the present invention, the OLED may not comprise an electron injection layer.

[0064] According to various embodiments of the OLED of the present invention, the OLED may not comprise a charge generation layer.

[0065] According to various embodiments of the OLED of the present invention, the OLED may not comprise an electron injection layer and a charge generation layer.

[0066] According to another aspect, there is provided a method of manufacturing an organic light-emitting diode (OLED), the method using:

- deposition via vacuum thermal evaporation; and/or
- deposition via solution processing, preferably the processing is selected from spin-coating, printing, casting and/or slot-die coating.

[0067] According to various aspects, there is provided a method using:

- at least one or two deposition sources to release the matrix compound, and
- at least one or two deposition sources to release lithium halide or lithium organic complex, and
- at least at least one or two deposition sources to release the elemental metal; the method comprising the steps of forming the electron transport layer stack; whereby

- a first electron transport layer is formed by releasing the matrix compound from at least one deposition source and a lithium halide or a lithium organic complex or an elemental metal is released from at different deposition source;
- onto the first electron transport layer a second electron transport layer is formed by releasing the matrix compound from at least one deposition source and a lithium halide or a lithium organic complex or an elemental metal is released from at different deposition source;
- onto the second electron transport layer a third electron transport layer is formed by releasing the matrix compound from at least one deposition source and a lithium halide or a lithium organic complex or an elemental metal is released from at different deposition source; whereby

at least one electron transport layer comprises a lithium halide or a lithium organic complex and is free of an elemental metal; and at least one electron transport layer comprises an elemental metal and is free of a lithium halide or a lithium organic complex.

[0068] According to various aspects, the method may further include forming on the first anode electrode an emission layer and at least one layer selected from the group consisting of forming a hole injection layer, forming a hole transport layer, or forming a hole blocking layer, between the first anode electrode and the electron transport layer stack.

[0069] According to various aspects, the method may further include the steps for forming an organic light-emitting diode (OLED), wherein

- on a substrate a first anode electrode is formed,
- on the first anode electrode an emission layer is formed,
- on the emission layer an electron transport layer stack is formed, comprising at least two, or at least three electron transport layers, preferably the first electron transport layer is formed on the emission layer and the second electron transport layer or, in case of a third electron transport layer, the third electron transport layer is formed directly on the first electron transport layer,
- on the electron transport layer stack a second cathode electrode is formed,
- optional a hole injection layer, a hole transport layer, and a hole blocking layer, formed in that order between the first anode electrode and the emission layer,
- optional an electron injection layer is formed between the electron transport layer and the second cathode electrode.

[0070] According to various aspects, the method may further include forming an electron injection layer on the electron transport layer stack. However, according to various embodiments of the OLED of the present invention, the OLED may not comprise an electron injection layer and / or a charge generation layer.

[0071] Additional aspects and/or advantages of the invention will be set forth in part in the description which follows and, in part, will be obvious from the description, or may be learned by practice of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0072] These and/or other aspects and advantages of the present invention will become apparent and more readily appreciated from the following description of the exemplary embodiments, taken in conjunction with the accompanying drawings, of which:

- FIG. 1 is a schematic sectional view of an organic light-emitting diode (OLED), according to an exemplary embodiment of the present invention with two electron transport layers;
- FIG. 2 is a schematic sectional view of an OLED, according to an exemplary embodiment of the present invention with three electron transport layers;
- FIG. 3 is a schematic sectional view of an organic light-emitting diode (OLED), according to an exemplary embodiment of the present invention with two electron transport layers;
- FIG. 4 is a schematic sectional view of an OLED, according to an exemplary embodiment of the present invention with three electron transport layers,
- FIG. 5 is a schematic sectional view of an OLED, according to an exemplary embodiment of the present invention with two electron transport layers and having no electron injection layer (EIL).
- FIG. 6 is a schematic sectional view of an OLED, according to an exemplary embodiment of the present invention with three electron transport layers and having no electron injection layer (EIL).

DETAILED DESCRIPTION

[0073] Reference will now be made in detail to the exemplary aspects, examples of which are illustrated in the accompanying drawings, wherein like reference numerals refer to the like elements throughout. The exemplary embodi-

ments are described below, in order to explain the aspects, by referring to the figures.

[0074] Herein, when a first element is referred to as being formed or disposed "on" a second element, the first element can be disposed directly on the second element, or one or more other elements may be disposed there between. When a first element is referred to as being formed or disposed "directly on" a second element, no other elements are disposed there between.

[0075] FIG. 1 is a schematic sectional view of an organic light-emitting diode 100, according to an exemplary embodiment of the present invention. The OLED 100 includes an emission layer 150 and an electron transport layer stack (ETL) 160 comprising a first electron transport layer 161 and a second electron transport layer 162, whereby the second electron transport layer 162 is disposed directly on the first electron transport layer 161.

[0076] FIG. 2 is a schematic sectional view of an organic light-emitting diode 100, according to an exemplary embodiment of the present invention. The OLED 100 includes an emission layer 150 and an electron transport layer stack (ETL) 160 comprising a first electron transport layer 161, a second electron transport layer 162, and a third electron transport layer 163, whereby the second electron transport layer 162 is disposed directly on the first electron transport layer 161 and the third electron transport layer 163 is disposed directly on the first electron transport layer 162.

[0077] FIG. 3 is a schematic sectional view of an organic light-emitting diode 100, according to an exemplary embodiment of the present invention. The OLED 100 includes a substrate 110, a first electrode 120, a hole injection layer (HIL) 130, a hole transport layer (HTL) 140, an emission layer (EML) 150, an electron transport layer (ETL) 160, an electron injection layer (EIL) 180, and a second electrode 190. The electron transport layer (ETL) 160 includes a first electron transport layer 161 including a matrix material and a lithium halide or a lithium organic complex and a second electron transport layer 162 including an elemental metal selected from the group comprising of lithium, magnesium and/or ytterbium. The second electron transport layer 162 is directly formed on the first electron transport layer 161. The first layer 161 may be formed directly on the EML 150.

[0078] FIG. 4 is a schematic sectional view of an organic light-emitting diode 100, according to an exemplary embodiment of the present invention. The OLED 100 includes a substrate 110, a first electrode 120, a hole injection layer (HIL) 130, a hole transport layer (HTL) 140, an emission layer (EML) 150, an electron transport layer (ETL) 160, an electron injection layer (EIL) 180, and a second electrode 190. The electron transport layer (ETL) 160 includes a first electron transport layer 161 and a third electron transport layer 163 including a matrix material and a lithium halide or a lithium organic complex, wherein the lithium halide or the lithium organic complex of the first electron transport layer 161 is not the same as the lithium halide or the lithium organic complex of the third electron transport layer 163; and the second electron transport layer 162 including an elemental metal of lithium, magnesium and/or ytterbium. The second electron transport layer 162 is directly formed on the first electron transport layer 161 and the third electron layer 163 is directly formed on the second electron layer 162. The first layer 161 may be formed directly on the emission layer (EML) 150.

[0079] The substrate 110 may be any substrate that is commonly used in manufacturing of organic light-emitting diodes. If light is emitted through the substrate, the substrate 110 may be a transparent material, for example a glass substrate or a transparent plastic substrate, having excellent mechanical strength, thermal stability, transparency, surface smoothness, ease of handling, and waterproofness. If light is emitted through the top surface, the substrate 110 may be a transparent or non-transparent material, for example a glass substrate, a plastic substrate, a metal substrate or a silicon substrate.

[0080] The first anode electrode 120 may be formed by depositing or sputtering a compound that is used to form the first anode electrode 120. The compound used to form the first anode electrode 120 may be a high work-function compound, so as to facilitate hole injection. If a p-doped HIL is used, the anode material may also be selected from a low work function material (i.e. Aluminum). The first anode electrode 120 may be a transparent or reflective electrode. Transparent conductive compounds, such as indium tin oxide (ITO), indium zinc oxide (IZO), tin-dioxide (SnO_2), and zinc oxide (ZnO), may be used to form the first anode electrode 120. The first anode electrode 120 may also be formed using magnesium (Mg), aluminum (Al), aluminum-lithium (Al-Li), calcium (Ca), magnesium-indium (Mg-In), magnesium-silver (Mg-Ag), silver (Ag), gold (Au), or the like.

[0081] The HIL 130 may be formed on the first anode electrode 120 by vacuum deposition, spin coating, printing, casting, slot-die coating, Langmuir-Blodgett (LB) deposition, or the like. When the HIL 130 is formed using vacuum deposition, the deposition conditions may vary according to the compound that is used to form the HIL 130, and the desired structure and thermal properties of the HIL 130. In general, however, conditions for vacuum deposition may include a deposition temperature of 100° C to 500° C, a pressure of 10^{-8} to 10^{-3} Torr (1 Torr equals 133.322 Pa), and a deposition rate of 0.1 to 10 nm/sec.

[0082] When the HIL 130 is formed using spin coating, printing, coating conditions may vary according to a compound that is used to form the HIL 130, and the desired structure and thermal properties of the HIL 130. For example, the coating conditions may include a coating speed of 2000 rpm to 5000 rpm, and a thermal treatment temperature of 80° C to 200° C. Thermal treatment removes a solvent after the coating is performed.

[0083] The HIL 130 may be formed of any compound that is commonly used to form an HIL. Examples of compounds that may be used to form the HIL 130 include a phthalocyanine compound, such as copper phthalocyanine (CuPc),

4,4',4''-tris (3-methylphenylphenylamino) triphenylamine (m-MTDATA), TDATA, 2T-NATA, polyaniline/dodecylbenzenesulfonic acid (Pani/DBSA), poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) (PEDOT/PSS), polyaniline/camphor sulfonic acid (Pani/CSA), and polyaniline/poly(4-styrenesulfonate) (PANI/PSS).

[0084] The HIL 130 may be a pure layer of p-dopant or may be selected from a hole-transporting matrix compound doped with a p-dopant. Typical examples of known redox doped hole transport materials are: copper phthalocyanine (CuPc), which HOMO level is approximately -5.2 eV, doped with tetrafluoro-tetracyanoquinonodimethane (F4TCNQ), which LUMO level is -5.2 eV; zinc phthalocyanine (ZnPc) (HOMO = -5.2 eV) doped with F4TCNQ; α -NPD (N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine) doped with F4TCNQ. α -NPD doped with 2,2'-(perfluoronaphthalene-2,6-diylidene) dimalononitrile (PD1). α -NPD doped with 2,2',2''-(cyclopropane-1,2,3-triylidene)tris(2-(p-cyanotetrafluorophenyl)acetonitrile) (PD2). Dopant concentrations can be selected from 1 to 20 wt.-%, more preferably from 3 wt.-% to 10 wt.-%.

[0085] The thickness of the HIL 130 may be in the range of 1 nm to 100 nm, and for example, 1 nm to 25 nm. When the thickness of the HIL 130 is within this range, the HIL 130 may have excellent hole injecting characteristics, without a substantial increase in driving voltage.

[0086] The hole transport layer (HTL) 140 may be formed on the HIL 130 by vacuum deposition, spin coating, slot-die coating, printing, casting, Langmuir-Blodgett (LB) deposition, or the like. When the HTL 140 is formed by vacuum deposition or spin coating, the conditions for deposition and coating may be similar to those for the formation of the HIL 130. However, the conditions for the vacuum or solution deposition may vary, according to the compound that is used to form the HTL 140.

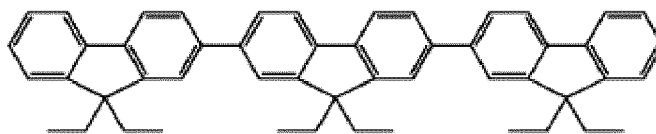
[0087] The HTL 140 may be formed of any compound that is commonly used to form a HTL. Compound that can be suitably used is disclosed for example in Yasuhiko Shirota and Hiroshi Kageyama, Chem. Rev. 2007, 107, 953-1010. Examples of the compound that may be used to form the HTL 140 are: a carbazole derivative, such as N-phenylcarbazole or polyvinylcarbazole; an amine derivative having an aromatic condensation ring, such as N,N'-bis(3-methylphenyl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine (TPD), or N,N'-di(naphthalene-1-yl)-N,N'-diphenyl benzydine (α -NPD); and a triphenylamine-based compound, such as 4,4',4''-tris(N-carbazolyl)triphenylamine (TCTA). Among these compounds, TCTA can transport holes and inhibit excitons from being diffused into the EML.

[0088] The thickness of the HTL 140 may be in the range of 5 nm to 250 nm, preferably, 10 nm to 200 nm, further 20 nm to 190 nm, further 40 nm to 180 nm, further 60 nm to 170 nm, further 80 nm to 160 nm, further 100 nm to 160 nm, further 120 nm to 140 nm. A preferred thickness of the HTL 140 may be 170 nm to 200 nm.

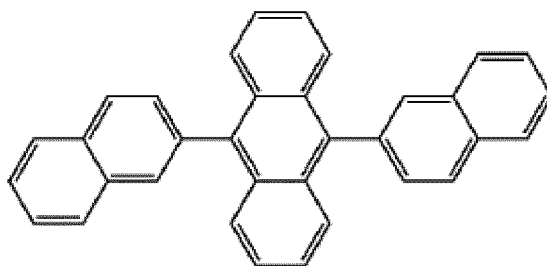
[0089] When the thickness of the HTL 140 is within this range, the HTL 140 may have excellent hole transporting characteristics, without a substantial increase in driving voltage.

[0090] The EML 150 may be formed on the HTL 140 by vacuum deposition, spin coating, slot-die coating, printing, casting, LB, or the like. When the EML 150 is formed using vacuum deposition or spin coating, the conditions for deposition and coating may be similar to those for the formation of the HIL 130. However, the conditions for deposition and coating may vary, according to the compound that is used to form the EML 150.

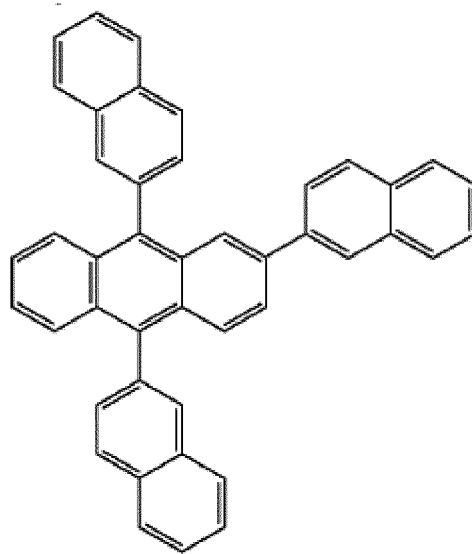
[0091] The emission layer (EML) 150 may be formed of a combination of a host and a dopant. Example of the host are Alq3, 4,4'-N,N'-dicarbazole-biphenyl (CBP), poly(n-vinylcarbazole) (PVK), 9,10-di(naphthalene-2-yl)anthracene (ADN), TCTA, 1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene (TPBI), 3-tert-butyl-9,10-di-2-naphthylanthracene (TBADN), distyrylarylene (DSA), Bis(2-(2-hydroxyphenyl)benzothiazolate)zinc (Zn(BTZ) 2), E3 below, ADN and referred to as Formula 1, Compound 1 below, and Compound 2 below.



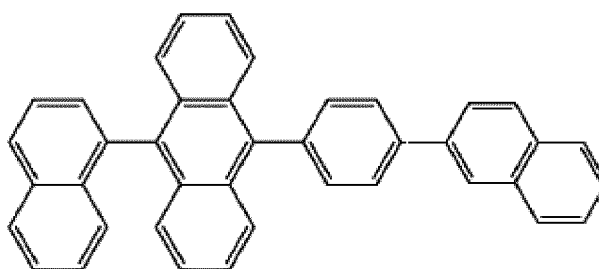
E3



Formula 1 (ADN)



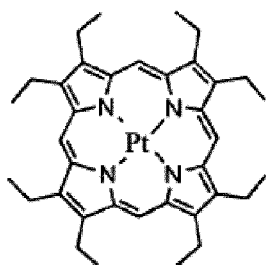
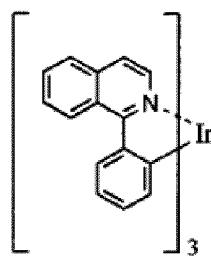
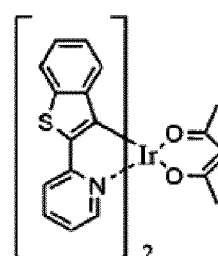
Compound 1



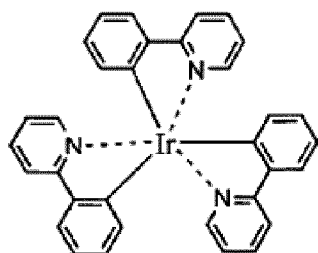
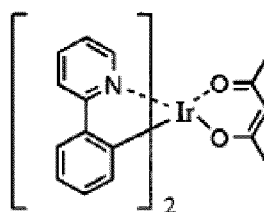
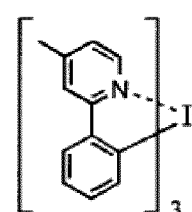
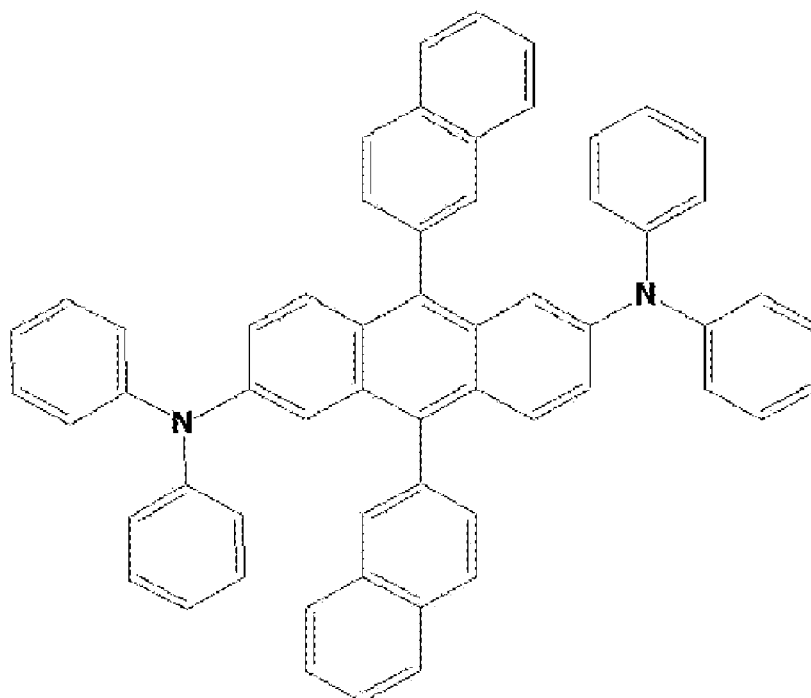
Compound 2

[0092] The dopant may be a phosphorescent or fluorescent emitter. Phosphorescent emitters are preferred due to their higher efficiency

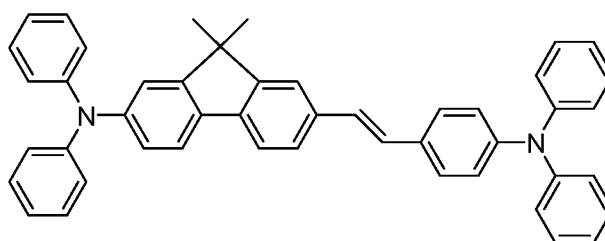
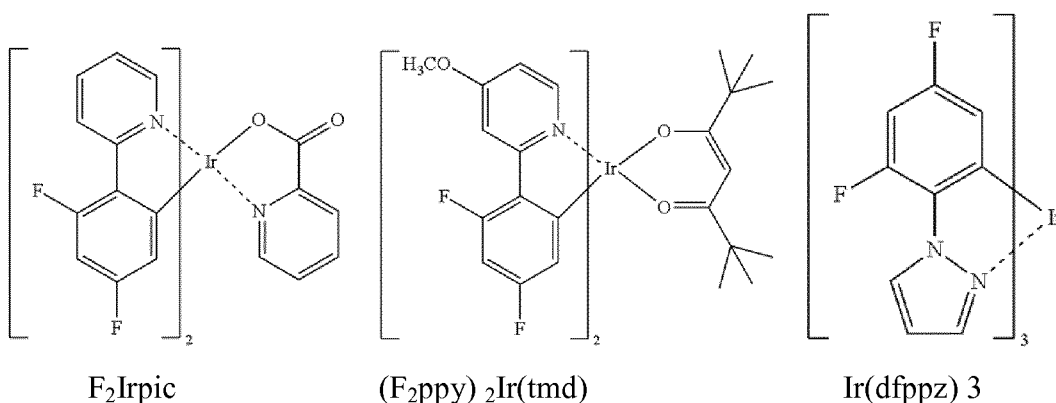
[0093] Examples of a red dopant are PtOEP, Ir(piq) 3, and Btp 2Ir(acac), but are not limited thereto. These compounds are phosphorescent emitters, however, fluorescent red dopants could also be used.

**PtOEP****Ir(piq)₃****Btp₂Ir(acac)**

[0094] Examples of a phosphorescent green dopant are Ir(ppy)₃ (ppy = phenylpyridine), Ir(ppy)₂(acac), Ir(mpyp)₃ are shown below. Compound 3 is an example of a fluorescent green emitter and the structure is shown below.

**Ir(ppy)₃****Ir(ppy)₂(acac)****Ir(mpyp)₃****Compound 3**

[0095] Examples of a phosphorescent blue dopant are F₂Irpic, (F₂ppy)₂Ir(tmd) and Ir(dfppz)₃, ter-fluorene, the structures are shown below. 4,4'-bis(4-diphenyl amino)styryl)biphenyl (DPAVB), 2,5,8,11-tetra-tert-butyl perylene (TBPe), and Compound 4 below are examples of fluorescent blue dopants.



Compound 4

[0096] The amount of the dopant may be in the range of 0.01 to 50 parts by weight, based on 100 parts by weight of the host. The EML 150 may have a thickness of 10 nm to 100 nm, for example, 20 nm to 60 nm. When the thickness of the EML 150 is within this range, the EML 150 may have excellent light emission, without a substantial increase in driving voltage.

[0097] When the EML 150 comprises a phosphorescent dopant, a hole blocking layer (HBL) (not shown) may be formed on the EML 150, by using vacuum deposition, spin coating, slot-die coating, printing, casting, LB deposition, or the like, in order to prevent the diffusion of triplet excitons or holes into the ETL 160. When the HBL is formed using vacuum deposition or spin coating, the conditions for deposition and coating may be similar to those for the formation of the HIL 130. However, the conditions for deposition and coating may vary, according to the compound that is used to form the HBL. Any compound that is commonly used to form a HBL may be used. Examples of compounds for forming the HBL include an oxadiazole derivative, a triazole derivative, and a phenanthroline derivative.

[0098] The HBL may have a thickness of 5 nm to 100 nm, for example, 10 nm to 30 nm. When the thickness of the HBL is within this range, the HBL may have excellent hole-blocking properties, without a substantial increase in driving voltage.

[0099] The ETL 160 may be formed on the EML 150 or on the HBL if the HBL is formed. The ETL 160 includes a first layer 161 including a lithium halide or a lithium organic complex; and the second electron transport layer 162 comprises an elemental metal selected from the group of lithium, magnesium and/or ytterbium; or vice versa.

[0100] The ETL 160 has a stacked structure, preferably of two ETL-layers (161/162), so that injection and transport of electrons may be balanced and holes may be efficiently blocked. In a conventional OLED, since the amounts of electrons and holes vary with time, after driving is initiated, the number of excitons generated in an emission area may be reduced. As a result, a carrier balance may not be maintained, so as to reduce the lifetime of the OLED.

[0101] However, in the ETL 160, the first layer 161 and the second layer 162 may have similar or identical energy levels. Surprisingly, it was found that the lifetime (LT) of the OLED 100 is improved irrespective of HOMO level of the matrix compounds.

[0102] In general the matrix compound for the first electron layer (161) and second electron layer (162) can be identical or different.

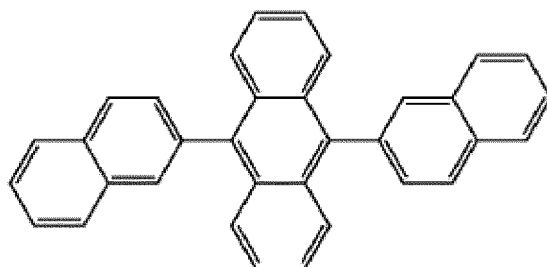
[0103] Matrix compound for the first electron layer (161) and second electron layer (162) are phosphine oxide based compounds, preferably diphenylphosphine oxide, preferably (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide, phenylbis(3-(pyren-1-yl)phenyl)phosphine oxide, 3-phenyl-3H-benzo[b]dinaphtho[2,1-d:1',2'-f]phosphine-3-oxide, bis(4-(anthracen-9-yl)phenyl)(phenyl)phosphine oxide, phenyldi(pyren-1-yl)phosphine oxide.

[0104] Diphenylphosphine oxide compounds that can be used as matrix materials are disclosed in EP 2395571 A1, WO2013079217 A1, EP 13187905, EP13199361 and JP2002063989 A. Other suitable matrix compounds that can be used are phenanthroline compounds, preferably selected from the group comprising of 2,4,7,9-tetraphenyl-1,10-phen-

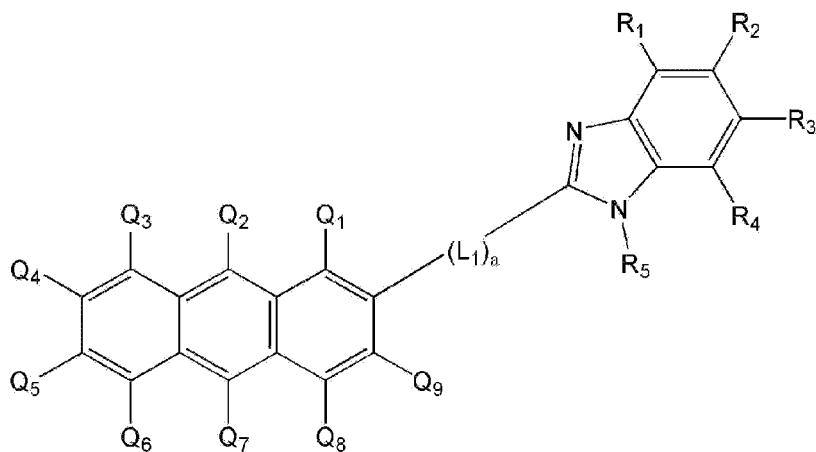
anthroline and 2,9-di(biphenyl-4-yl)-4,7-diphenyl-1,10-phenanthroline. Phenanthroline compounds that can be used as matrix materials are disclosed in EP 1786050 A1.

[0105] Further suitable matrix compounds that can be used are anthracene compounds, preferably 2-(4-(9,10-di(naphthalen-2-yl)anthracene-2-yl)phenyl)-1-phenyl-1H-benzo[d]imidazole. Anthracene compounds that can be used as matrix materials are disclosed in US 6878469 B.

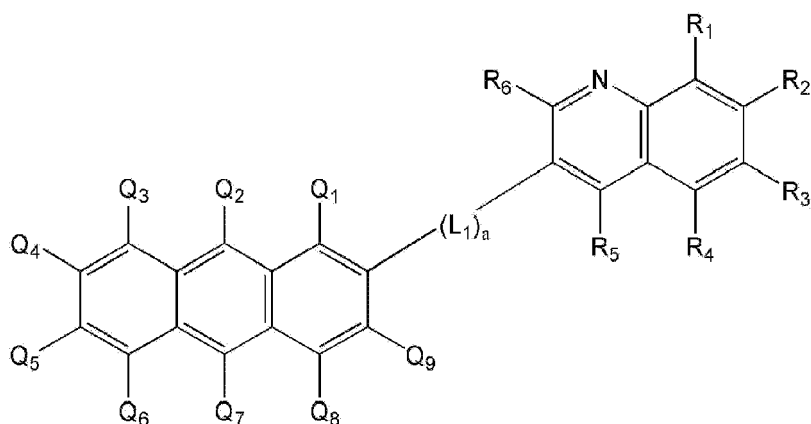
[0106] A matrix compound of the at least one of the matrix compounds of the first electron layer (161) and/or second electron transport layer (162) may be a compound that efficiently transports electrons, and is a phosphine oxide compound. Other matrix compounds may be an anthracene-based compound, or a phenanthroline based compound, preferably a matrix compound mentioned in Table 1. In a non-inventive example, the matrix compound of the first electron layer (161) and/or second electron transport layer (162) may be selected from the group consisting of ADN and referred to as Formula 1, a compound represented by Formula 2, and a compound represented by Formula 3 below:



Formula 1 (ADN)



Formula 2



Formula 3

[0107] In Formulae 2 and 3, R_1 to R_6 are each independently a hydrogen atom, a halogen atom, a hydroxy group, a cyano group, a substituted or unsubstituted C_1 - C_{30} alkyl group, a substituted or unsubstituted C_1 - C_{30} alkoxy group, a substituted or unsubstituted C_1 - C_{30} acyl group, a substituted or unsubstituted C_2 - C_{30} alkenyl group, a substituted or unsubstituted C_2 - C_{30} alkynyl group, a substituted or unsubstituted C_6 - C_{30} aryl group, or a substituted or unsubstituted C_3 - C_{30} heteroaryl group. At least two adjacent R_1 to R_6 groups are optionally bonded to each other, to form a saturated or unsaturated ring. L_1 is a bond, a substituted or unsubstituted C_1 - C_{30} alkylene group, a substituted or unsubstituted C_6 - C_{30} arylene group, or a substituted or unsubstituted C_3 - C_{30} hetero arylene group. Q_1 through Q_9 are each independently a hydrogen atom, a substituted or unsubstituted C_6 - C_{30} aryl group, or a substituted or unsubstituted C_3 - C_{30} hetero aryl group, and "a" is an integer from 1 to 10.

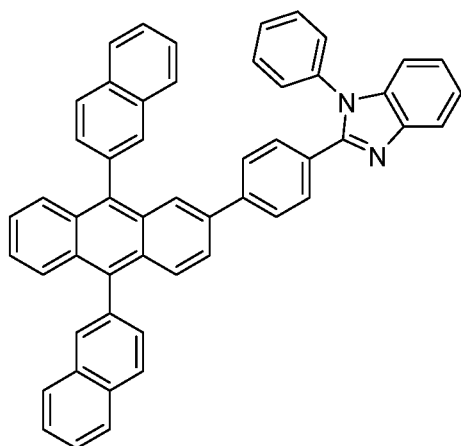
[0108] For example, R_1 to R_6 may be each independently selected from the group consisting of a hydrogen atom, a halogen atom, a hydroxy group, a cyano group, a methyl group, an ethyl group, a propyl group, a butyl group, a methoxy group, an ethoxy group, a propoxy group, a butoxy group, a phenyl group, a naphthyl group, an anthryl group, a pyridinyl group, and a pyrazinyl group.

[0109] In particular, in Formula 2 and/or 3, R_1 to R_4 may each be a hydrogen atom, R_5 may be selected from the group consisting of a halogen atom, a hydroxy group, a cyano group, a methyl group, an ethyl group, a propyl group, a butyl group, a methoxy group, an ethoxy group, a propoxy group, a butoxy group, a phenyl group, a naphthyl group, an anthryl group, a pyridinyl group, and a pyrazinyl group. In addition, in Formula 3, R_1 to R_6 may each be a hydrogen atom.

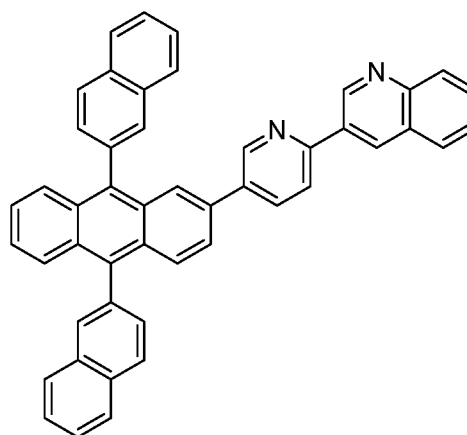
[0110] For example, in Formula 2 and/or 3, Q_1 to Q_9 are each independently a hydrogen atom, a phenyl group, a naphthyl group, an anthryl group, a pyridinyl group, and a pyrazinyl group. In particular, in Formulae 2 and/or 3, Q_1 , Q_3 - Q_6 , Q_8 and Q_9 are hydrogen atoms, and Q_2 and Q_7 may be each independently selected from the group consisting of a phenyl group, a naphthyl group, an anthryl group, a pyridinyl group, and a pyrazinyl group.

[0111] For example, L_1 , in Formula 2 and/or 3, may be selected from the group consisting of a phenylene group, a naphthylene group, an anthrylene group, a pyridinylene group, and a pyrazinylene group. In particular, L_1 may be a phenylene group or a pyridinylene group. For example, "a" may be 1, 2, or, 3.

[0112] In a non-inventive example, the matrix compound may be further selected from Compound 6 or 7 below:



Compound 6

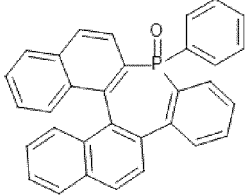
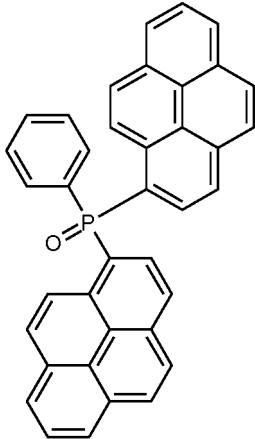
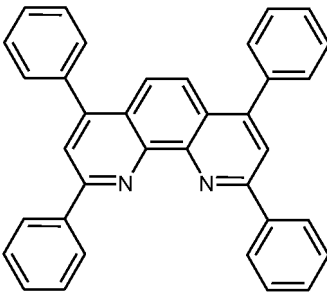
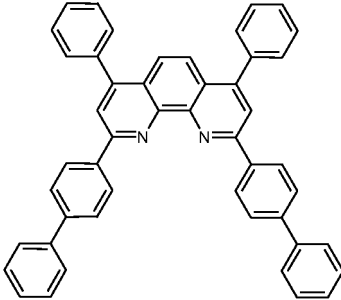


Compound 7.

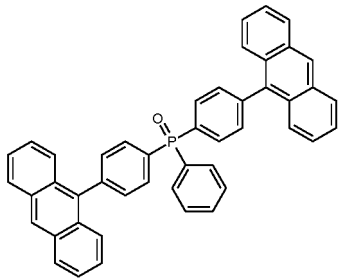
Table 1

Chemical structures of matrix materials that can be suitable used			
Internal name	IUPAC name	Structure	Reference
MX 1	2-(4-(9,10-di(naphthalen-2-yl)anthracen-2-yl)phenyl)-1-phenyl-1H-benzo[d]imidazole		US 6878469 B2
MX 2	(3-(dibenzo[c,h]acridin-7-yl)phenyl) diphenylphosphine oxide		EP 2395571B1, WO2013079217A1
MX 3	Phenylbis(3-(pyren-1-yl)phenyl) phosphine oxide		EP13187905.8

(continued)

Chemical structures of matrix materials that can be suitable used			
Internal name	IUPAC name	Structure	Reference
MX 4	3-Phenyl-3H-benzo[b]dinaphtho[2,1-d:1',2'-f]phosphepine-3-oxide		EP13199361.0
MX 5	Phenyldi(pyren-1-yl)phosphine oxide		JP4876333
MX 6	2,4,7,9-tetraphenyl-1,10-phenanthroline		EP1786050
MX 8	2,9-di(biphenyl-4-yl)-4,7-diphenyl-1,10-phenanthroline		EP1786050

(continued)

Chemical structures of matrix materials that can be suitably used			
Internal name	IUPAC name	Structure	Reference
MX 9	bis(4-(anthracen-9-yl)phenyl)(phenyl) phosphine oxide		EP13187905

[0113] In table 1, matrix compounds MX 2, MX 3, MX 4, MX 5, and MX 9 may be suitably used according to the invention.

[0114] Reduction and oxidation potentials are determined via cyclic voltammetry, using the Ferrocene/Ferrocenium (Fc/Fc^+) redox couple as internal reference. A simple rule is very often used for the conversion of redox potentials into electron affinities and ionization potential: $\text{IP (in eV)} = 4.84 \text{ eV} + e^*E_{\text{ox}}$ (wherein E_{ox} is given in Volt vs. ferrocene/ferrocenium (Fc/Fc^+) and $\text{EA (in eV)} = 4.84 \text{ eV} + e^*E_{\text{red}}$ (E_{red} is given in Volt vs. Fc/Fc^+) respectively (see B.W. D'Andrade, Org. Electron. 6, 11-20 (2005)), e^* is the elemental charge. It is common practice, even if not exactly correct, to use the terms "energy of the HOMO" $E(\text{HOMO})$ and "energy of the LUMO" $E(\text{LUMO})$, respectively, as synonyms for the ionization energy and electron affinity (Koopmans Theorem).

[0115] Table 2 below shows the energy levels of matrix compounds of which MX2, MX3, MX4, and MX9 may be suitably used according to the invention.

Table 2

Reduction and oxidation potential and energy of $E(\text{HOMO})$ and $E(\text{LUMO})$ of matrix materials				
Matrix compound	Oxidation potential vs $\text{Fc}/\text{Fc}^+ / \text{V}$	$E(\text{HOMO}) / \text{eV}$	Reduction potential vs $\text{Fc}/\text{Fc}^+ / \text{V}$	$E(\text{LUMO}) / \text{eV}$
MX1	> 1,6	< -6.45	-2.32	-2.52
MX2	1.26	-6.1	-2.2	-2.64
MX4	> 1,6	< -6.45	-2.62	-2.22
MX3	0.83	-5.67	-2.48	-2.36
MX9			-2.42	-2.42

[0116] The first electron transport layer 161 comprises a lithium halide or a lithium organic complex; and the second electron transport layer 162 comprises an elemental metal selected from the group of lithium, magnesium, and/or ytterbium.

[0117] According to another aspect the first electron transport layer 161 comprises an elemental metal selected from the group of lithium, magnesium and/or ytterbium; and the second electron transport layer 162 comprises a lithium halide or a lithium organic complex.

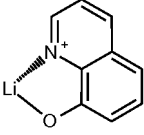
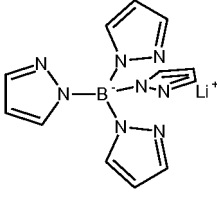
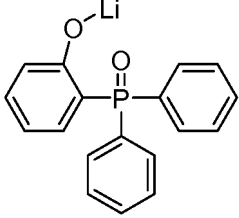
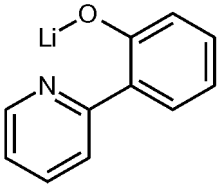
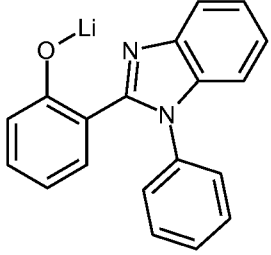
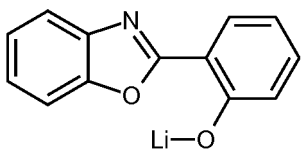
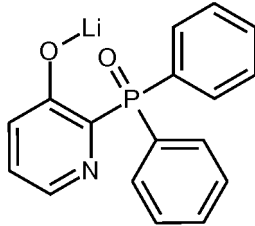
[0118] According to another aspect the first electron transport layer 161 comprises a lithium halide or a lithium organic complex; and the second electron transport layer 162 comprises an elemental metal selected from the group of lithium, magnesium and/or ytterbium; and the third electron transport layer 163 comprises a lithium halide or a lithium organic complex that is the same or differs from the lithium halide or lithium organic complex of the first electron transport layer 161.

[0119] According to another aspect the first electron transport layer 161 comprises an elemental metal selected from the group of lithium, magnesium and/or ytterbium; and the second electron transport layer 162 comprises a lithium halide or a lithium organic complex; and the third electron transport layer 163 comprises an elemental metal selected from the group of lithium, magnesium and/or ytterbium that is the same or differs from the elemental metal selected from the group of lithium, magnesium and/or ytterbium of the first electron transport layer 161.

[0120] Suitable organic ligands to form a lithium organic complex that can be used for the first electron transport layer or the second electron transport layer are disclosed, for example in US 2014/0048792 and Kathirgamanathan, Poopathy; Arkley, Vincent; Surendrakumar, Sivagnanasundram; Chan, Yun F.; Ravichandran, Seenivasagam; Ganeshamurugan,

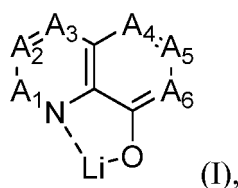
Subramaniam; Kumaraverl, Muttulingam; Antipan-Lara, Juan; Paramaswara, Gnanamolly; Reddy, Vanga R., Digest of Technical Papers - Society for Information Display International Symposium (2010), 41(Bk. 1), 465-468.

Table 3

Lithium organic complex that can be suitable used			
	IUPAC name	Structure	Reference
LiQ	lithium 8-hydroxyquinolate		WO 2013079217 A1
Li-1	lithium tetra(1H-pyrazol-1-yl)borate		WO 2013079676 A1
Li-2	lithium 2-(diphenylphosphoryl)phenolate		WO 2013079678A1
Li-3	lithium 2-(pyridin-2-yl)phenolate		JP2 008195623
Li-4	lithium 2-(1-phenyl-1H-benzo[d]imidazol-2-yl)phenolate		JP 2001291593
Li-5	lithium 2-(benzo[d]oxazol-2-yl)phenolate		US 20030165711
Li-6	lithium 2-(diphenylphosphoryl)pyridin-3-olate		EP 2724388

[0121] The organic ligand of the lithium organic complex of at least one electron transport layer may be selected from the group comprising a quinolate, a borate, a phenolate, a pyridinolate or a Schiff base ligand, or Table 3;

- preferably the lithium quinolate complex has the formula I:

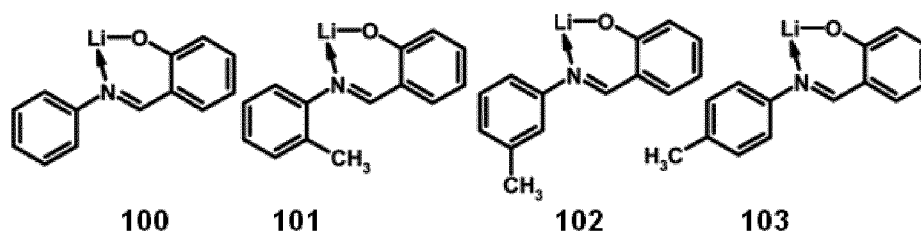


wherein

A1 to A6 are same or independently selected from CH, CR, N, O;

R is same or independently selected from hydrogen, halogen, alkyl or aryl or heteroaryl with 1 to 20 carbon atoms; and more preferred A1 to A6 are CH;

- preferably the borate based organic ligand is a tetra(1H-pyrazol-1-yl)borate;
- preferably the phenolate is a 2-(pyridin-2-yl)phenolate or a 2-(diphenylphosphoryl)phenolate;
- preferably the lithium Schiff base has the structure 100, 101, 102 or 103:



- more preferred the lithium organic complex is selected from a compound of Table 2.

[0122] The lithium halide of at least one electron transport layer may be selected from the group comprising a LiF, LiCl, LiBr or LiI, and preferably LiF.

[0123] The ETL layer stack thickness can be adjusted such that the light out coupling is maximized. Further ETL layer stack thickness can be adjusted for the desired color tuning, for example to achieve a deeper shade of blue, i.e. smaller CIEy.

[0124] The thicknesses of the first electron transport layer 161, second electron transport layer 162 and/or third electron transport layer 163 may be the same or each independently in the range of ≥ 0.5 nm to ≤ 95 nm, preferably of ≥ 3 nm to ≤ 80 nm, further preferred of ≥ 5 nm to ≤ 60 nm, also preferred of ≥ 6 nm to ≤ 40 nm, in addition preferred ≥ 8 nm to ≤ 20 nm and more preferred of ≥ 10 nm to ≤ 18 nm.

[0125] When the thicknesses of the first electron transport layer 161, second electron transport layer 162 and/or third electron transport layer 163 within this range, preferably of ≥ 10 nm to ≤ 18 nm, the electron transport layer stack 160 may effectively inject and transport electrons, without a substantial increase in driving voltage.

[0126] For blue emitting OLEDs, the thickness of the ETL layer stack is 10 to 50 nm, preferably 30 to 40 nm. For red and green emitting OLEDs, the thickness of ETLs is 20 to 100 nm, preferably 20-100 nm and more preferably 30-80 nm. The thickness is selected so as to maximize efficiency of light emission.

[0127] The amount of the lithium organic complex in at least one electron transport layer (161) may be in the range of ≥ 10 mol-% to ≤ 95 mol-%, preferably ≥ 15 mol-% to ≤ 90 mol-% and also preferred ≥ 20 mol-% to ≤ 80 mol-%, based on the first electron transport layer 161.

[0128] The amount of an elemental metal selected from the group of lithium, magnesium, and/or ytterbium in the second electron transport layer 162 may be in the range of ≥ 1 wt.-% to ≤ 60 wt.-%, preferably ≥ 2 wt.-% to ≤ 55 wt.-% and also preferred ≥ 5 wt.-% to ≤ 45 wt.-%, by weight of the second electron transport layer 162.

[0129] The amount of the lithium halide or lithium organic complex in the first electron transport layer 161 may be in the range of ≥ 10 mol-% to ≤ 95 mol-%, preferably ≥ 15 mol-% to ≤ 90 mol-% and also preferred ≥ 20 mol-% to ≤ 80 mol-%, based on the first electron transport layer 161.

[0130] The amount of an elemental metal selected from the group of lithium, magnesium, and/or ytterbium in the second electron transport layer 162 may be in the range of ≥ 10 mol-% to ≤ 90 mol-%, preferably ≥ 20 mol-% to ≤ 85 mol-% and also preferred ≥ 30 mol-% to ≤ 80 mol-%.

[0131] However, the first electron transport layer 161 may comprises the elemental metal and the second electron transport layer 162 may comprises the lithium halide or lithium organic complex.

[0132] The ETL 160 may be formed on the EML 150 by vacuum deposition, spin coating, slot-die coating, printing, casting, or the like. When the ETL 160 is formed by vacuum deposition or spin coating, the deposition and coating conditions may be similar to those for formation of the HIL 130. However, the deposition and coating conditions may vary, according to a compound that is used to form the ETL 160.

[0133] Using vacuum deposition, the first electron transport layer 161 of the ETL 160 may be formed using a first deposition source to deposit a matrix compound, and a second deposition source to deposit a lithium halide or lithium organic complex. The first deposition source and the second deposition source are positioned relative to one another, such that a mixed deposition region of the first electron transport layer 161 is formed directly on the EML 150.

[0134] The second electron transport layer 162 of the ETL 160 may be formed using a first or a third deposition source, for example if the matrix material is different to the ETL 161, and a third or fourth deposition source is used to deposit the elemental metal selected from the group of lithium, magnesium and/or ytterbium.

[0135] The deposition sources are positioned relative to one another, such that a mixed deposition region of the second electron transport layer 162 is formed directly on the first electron transport layer 161.

[0136] The stacking process is more simply and quickly performed, as compared to prior methods. In particular, since a plurality of ETL layers may be almost simultaneously deposited in a single chamber, the chamber may not be required to be exhausted after the formation of each layer.

[0137] The EIL 180, which facilitates injection of electrons from the cathode, may be formed on the ETL 160, preferably directly on the second electron transport layer 162. Examples of materials for forming the EIL 180 include LiF, NaCl, CsF, Li₂O, BaO, Ca, Ba, Yb, Mg which are known in the art. Deposition and coating conditions for forming the EIL 180 are similar to those for formation of the HIL 130, although the deposition and coating conditions may vary, according to a material that is used to form the EIL 180.

[0138] The thickness of the EIL 180 may be in the range of 0.1 nm to 10 nm, for example, in the range of 0.5 nm to 9 nm. When the thickness of the EIL 180 is within this range, the EIL 180 may have satisfactory electron-injecting properties, without a substantial increase in driving voltage.

[0139] The second cathode electrode 190 is formed on the EIL 180 if present. The second cathode electrode 190 may be a cathode, which is an electron-injecting electrode. The second electrode 190 may be formed of a metal, an alloy, an electrically conductive compound, or a mixture thereof. The second electrode 190 may have a low work function. For example, the second electrode 190 may be formed of lithium (Li), magnesium (Mg), aluminum (Al), aluminum (Al)-lithium (Li), calcium (Ca), barium (Ba), ytterbium (Yb), magnesium (Mg)-indium (In), magnesium (Mg)-silver (Ag), or the like. In addition, the second electrode 190 may be formed of a transparent conductive material, such as ITO or IZO.

[0140] The thickness of the cathode electrode 190 may be in the range of 5 nm to 1000 nm, for example, in the range of 10 nm to 100 nm. When the cathode electrode 190 is in the range of 5 nm to 50 nm, the electrode will transparent even if a metal or metal alloy is used.

[0141] Since the layers of the ETL 160 have similar or identical energy levels, the injection and transport of the electrons may be controlled, and the holes may be efficiently blocked. Thus, the OLED 100 may have long lifetime.

[0142] Fig. 5 and 6 is a schematic sectional view of an OLED 200, according to another exemplary embodiment of the present invention. Figs. 3 and 4 differ from Figs. 5 and 6 in that the OLED 200 has no electron injection layer (EIL) 180.

[0143] Referring to Figs. 5 and 6 the OLED 200 includes a substrate 110, a first electrode 120, a HIL 130, a HTL 140, an EML 150, an ETL 160, and a second electrode 190. The ETL stack 160 of Fig. 5 includes a first ETL layer 161 and a second ETL layer 162 and the ETL stack 160 of Fig. 6 includes a first ETL layer 161, a second ETL layer 162 and a third ETL layer 163.

[0144] The electron transport layer stack 160 of Fig. 5 comprises of at least two electron transport layers 161 and 162, wherein a first electron transport layer 161 and a second electron transport layer 162 comprises at least one matrix compound and in addition,

- the first electron transport layer comprises a lithium halide or a lithium organic complex, and
- the second electron transport layer comprises an elemental metal selected from the group of lithium, magnesium and/or ytterbium; wherein the first electron transport layer is arranged closest to an anode and the second electron transport layer is arranged closest to a cathode.

[0145] The electron transport layer stack 160 of Fig. 6 comprises of at least three electron transport layers 161, 162 and 163, wherein a first electron transport layer 161, a second electron transport layer 162 and a third electron transport layer 163 comprises at least one matrix compound and in addition,

- the first electron transport layer 161 and third electron transport layer 163 comprises a lithium halide or a lithium organic complex, and
- the second electron transport layer 162 comprises an elemental metal selected from the group of lithium, magnesium and/or ytterbium; wherein the first electron transport layer 161 is arranged closest to an anode and the third electron transport layer 163 is arranged closest to a cathode.

[0146] The layers of the ETL 161 and 162 or of the ETL 161, 162 and 163 have similar or identical energy level. Further, the OLED 200 have an improved lifetime (LT). The substrate 110, the first electrode 120, the hole injection layer 130, the hole transport layer 140, the emission layer 150, and the electron transport layer 161 and 162 of the OLED 200 of Fig. 5 or the electron transport layer 161, 162 and 163 of the OLED 200 of Fig. 6 are similar to corresponding elements described with reference to Figs. 3 and 4, respectively. Even though the structure of the OLED 200 and the method of manufacturing the OLED 200 are described with reference to Figs. 3 and 4, other methods known in the art can be used. For example, the ETL stack 160 may include three or more ETL layers but two ETL layers of ETL 161 and 162 may be preferred.

[0147] In the description above the method of manufacture an OLED of the present invention is started with a substrate 110 onto which a first anode electrode 120 is formed, on the first anode electrode 120 an emission layer 150 is formed. An electron transport layer stack 160 is formed on the emission layer 150, wherein the first electron transport layer 161 is formed on the emission layer 150 and the second electron transport layer 162 is formed directly on the first electron transport layer 161, on the electron transport layer stack 160, in this case on the second electron transport layer 162, a cathode electrode 190 is formed, optional a hole injection layer 130, and a hole transport layer 140, are formed in that order between the first anode electrode 120 and the electron transport layer stack 160, an optional hole blocking layer is formed between the emission layer and the ETL layer stack, and optionally an electron injection layer 180 is formed between the electron transport layer 160 and the second cathode electrode 190.

[0148] However, the OLED of the present invention can be manufactured also the other way around, starting with the second cathode electrode 190 onto which optionally an electron injection layer 180 is formed. On the second cathode electrode 190 or on the electron injection layer 180, if present, the second electron transport layer 162 is formed and directly on the second electron transport layer 162 the first electron transport layer 161 is formed and so on.

[0149] In case of a three layer electron transport layer stack 160, the second electron layer 162 is formed on the first electron layer 161 and the third electron layer 163 is formed on the second electron layer 162. Then a cathode electrode 190 is formed, optional a hole injection layer 130, and a hole transport layer 140, are formed in that order between the first anode electrode 120 and the electron transport layer stack 160, an optional hole blocking layer is formed between the emission layer and the ETL layer stack, and optionally an electron injection layer 180 is formed between the electron transport layer 160 and the second cathode electrode 190.

[0150] While not shown in Figs. 3 to 6, a sealing layer may further be formed on the second electrodes 190, in order to seal the OLEDs 100, 200. In addition, various other modifications may be applied thereto.

[0151] Hereinafter, one or more exemplary aspects will be described in detail with, reference to the following examples. However, these examples are not intended to limit the purpose and scope of the one or more exemplary aspects.

Examples

General procedure

[0152] For bottom emission devices, a $15\Omega/\text{cm}^2$ glass substrate (available from Corning Co.) with 100 nm ITO was cut to a size of 50 mm x 50 mm x 0.7 mm, ultrasonically cleaned with isopropyl alcohol for 5 minutes and then with pure water for 5 minutes, and cleaned again with UV ozone for 30 minutes, to prepare a first electrode.

[0153] For top emission devices, the anode electrode was formed from 100 nm silver on glass which was prepared by the same methods as described above.

[0154] Then, 80 wt.-% of N4,N4"-di(naphthalen-1-yl)-N4,N4"-diphenyl-[1,1':4',1"-terphenyl]-4,4"-diamine and 20 wt.-% of 2,2',2"-(cyclopropane-1,2,3-triylidene)tris(2-(p-cyanotetrafluorophenyl)acetonitrile) was vacuum deposited on the ITO electrode, to form a HIL having a thickness of 10 nm. Then N4,N4"-di(naphthalen-1-yl)-N4,N4"-diphenyl-[1,1':4',1"-terphenyl]-4,4"-diamine was vacuum deposited on the HIL, to form a HTL having a thickness of 130 nm. 97 wt.-% of ABH113 (Sun Fine Chemicals) as a host and 3 wt.-% of NUBD370 (Sun Fine Chemicals) as a dopant were deposited on the HTL, to form a blue-emitting EML with a thickness of 20 nm.

[0155] Then the ETL-layer stack is formed by depositing the first electron transport layer (ETL 1) including a matrix compound according to Example 1 to Example 21 and comparative examples 2 to 5 by depositing the matrix compound from a first deposition source and the lithium organic complex or lithium halide of from a second deposition source directly on the EML.

[0156] Then the second electron transport layer (ETL 2) including a matrix compound according to Example 1 to

Example 21 and comparative examples 1 to 5 is formed by depositing the matrix compound from a first deposition source, if the same matrix compound is used as in the first electron transport layer, or a third deposition source, if the matrix compound is different from the matrix compound used in the first electron transport layer.

[0157] A lithium organic complex or lithium halide is deposited from a third deposition source directly on the first electron transport layer (ETL 1) and an elemental metal selected from the group of lithium, magnesium and/or ytterbium is deposited from a fourth deposition source directly on the second electron transport layer (ETL 2).

[0158] For an electron transport layer with three electron transport layers (ETL 1, ETL 2 and ETL 3) the corresponding electron transport layer is formed as described above.

[0159] For the comparative examples land 2 only one electron transport layer ETL 2 is formed and for the other comparative examples two electron transport layers of ETL 1 and ETL 2 are formed.

[0160] The wt.-% of the lithium organic complex for the ETL1 as well as for the ETL 2 can be taken from Tables 4 to 10, whereby the wt.-% amount of the matrix compound is added to 100 wt.-% respectively. That means, that the matrix compound of ETL 1 are added in a wt.-% amount such that the given wt.-% of the lithium organic complex for the ETL 1 and the matrix compound of the ETL 1 are in total 100 wt.-%, based on the weight of the ETL 1; and, the matrix compound of ETL 2 are added in a wt.-% amount such that the given wt.-% of the elemental metal selected from the group of lithium, magnesium and/or ytterbium for the ETL2 and the matrix compound of the ETL 2 are in total 100 wt.-%, based on the weight of the ETL 2. Further, the thickness d (in nm) of the ETL 1 and ETL 2 can be taken from Tables 4 to 10. The cathode was evaporated at ultra-high vacuum of 10^{-7} bar. Therefore, a thermal single co-evaporation of one or several metals was performed with a rate of 0, 1 to 10 nm/s (0.01 to 1 Å/s) in order to generate a homogeneous cathode with a thickness of 5 to 1000 nm. For top emission devices, the cathode electrode was formed from 13 nm magnesium (90 vol.-%)-silver (10 vol.-%) alloy, followed by 60 nm N4,N4"-di(naphthalen-1-yl)-N4,N4"-diphenyl-[1,r:4',1"-terphenyl]-4,4"-diamine. For bottom emission devices, the cathode electrode was formed from 100 nm aluminum.

[0161] The OLED stack is protected from ambient conditions by encapsulation of the device with a glass slide. Thereby, a cavity is formed, which includes a getter material for further protection.

[0162] To assess the performance of the inventive examples compared to the prior art, the current efficiency is measured under ambient conditions (20°C). Current voltage measurements are performed using a Keithley 2400 sourcemeter, and recorded in V. At 15 mA/cm², a calibrated spectrometer CAS140 from Instrument Systems is used for measurement of CIE coordinates and brightness in Candela. Lifetime LT of the device is measured at ambient conditions (20°C) and 15 mA/cm², using a Keithley 2400 sourcemeter, and recorded in hours. The brightness of the device is measured using a calibrated photo diode. The lifetime LT is defined as the time till the brightness of the device is reduced to 97 % of its initial value.

[0163] In bottom emission devices, the emission is predominately Lambertian and quantified in percent external quantum efficiency (EQE). To determine the EQE in % the light output of the device is measured using a calibrated photodiode at 10 mA/cm².

[0164] In top emission devices, the emission is forward directed, non-Lambertian and also highly dependent on the mirco-cavity. In order to minimize the effect of the micro-cavity and thus of the emission color on the device performance, the efficiency Eff. is measured in Candela per Ampere (cd/A) and divided by the CIE-y.

Technical Effect of the invention

Bottom emission devices

a) Lifetime and efficiency improvement with two electron transport layers (ETL1 and ETL 2)

[0165] In Table 4 results are shown for top emission devices with two different matrix compounds in the ETL-stack of first electron transport layer (ETL1) and second electron transport layer (ETL 2). An external quantum efficiency (EQE) and lifetime improvement is observed compared to the emission device with one electron transport layer only - Table 4.

Table 4

External quantum efficiency (EQE) and lifetime of bottom emission OLEDs with two ETLs										
	ETL 1	wt.-% Li organic complex ^{*1}	d (ETL1) / nm	ETL 2	wt.-% Li organic complex ^{*1}	wt.-% Metal dopant ^{*2}	d (ETL2) / nm	V at 10 mA/cm ² / V	EQE / %	LT / h
Comp. example 1		none		MX2: Mg		5	36	3.70	4.20	10
Comp. example 2		none		MX2: LiQ: Mg	47.5	5	36	3.79	5.83	12
Example 1	MX2 : LiQ	50	26	MX2: Mg		5	11	4.33	6.25	130
^{*1} = the wt.-% of the matrix compound and the wt.-% of the lithium organic complex are in total 100 wt.-% based on weight of the ETL1 ^{*2} = the wt.-% of the matrix compound and the wt.-% of the elemental metal are in total 100 wt.-% based on weight of the ETL2										

[0166] In the Table 4 above a device data for a single ETL device compared to a device containing two electron transport layers is shown. As can be seen, the lifetime and efficiency are improved for devices with two electron transport layers according to the invention compared to devices with just one electron transport layer (Comparative example 1).

[0167] The lifetime and efficiency are also improved when comparing a single ETL device comprising lithium organic complex and magnesium in the one electron transport layer compared to a device with two electron transport layers where the lithium organic complex is present in the first electron transport layer and magnesium in the second electron transport layer (Comparative example 2).

Table 5

External quantum efficiency (EQE) and lifetime of bottom emission OLEDs with two ETLs									
	ETL 1	wt.-% Li organic complex ^{*1}	d (ETL1) / nm	ETL 2	wt.-% Metal dopant ^{*2}	d (ETL2) / nm	V at 10 mA/cm ² / V	EQE / %	LT / h
Comparative example 3	MX1: LiQ	50	19	MX1: Ca	5	17	3.77	5.48	55
Example 2	MX1: LiQ	50	10	MX1: Mg	5	26	7.20	4.72	130
Example 3	MX2: LiQ	50	26	MX2: Mg	5	11	4.33	6.25	130
Example 4	MX2: LiQ	50	26	MX2: Yb	5	10	4.52	5.79	170
Example 5	MX2: LiQ	50	20	MX2: Li	5	16	4.37	6.15	150

^{*1} = the wt.-% of the matrix compound and the wt.-% of the lithium organic complex are in total 100 wt.-% based on weight of the ETL1

^{*2} = the wt.-% of the matrix compound and the wt.-% of the elemental metal are in total 100 wt.-% based on weight of the ETL2

[0168] In the Table 5 above results for external quantum efficiency and lifetime are shown for devices containing benzimidazole matrix compound MX 1 in the first and second electron transport layer. Example 2 is a non-inventive

example.

[0169] In comparison to comparative example 3, a significant improvement in lifetime is observed when calcium is replaced by magnesium in the second electron transport layer (Example 2). When benzimidazole matrix compound MX 1 is replaced by phosphine oxide matrix compound MX 2 very good lifetime is maintained, and the external quantum efficiency is improved (Example 3 compared to Example 2). Additionally, the voltage is much reduced in Example 3 compared to Example 2. A further increase in lifetime is achieved when magnesium is replaced with lithium and ytterbium (Examples 4 and 5).

Table 6

External quantum efficiency (EQE) and lifetime of bottom emission OLEDs with two ETLs									
	ETL1	wt.-%Li organic complex* ¹	d (ETL1) / nm	ETL 2	wt.-% Metal dopant* ²	d (ETL2) / nm	V at 10 mA/ cm ² / V	EQE / %	LT / h
Example 6	MX2: LiQ	50	26	MX2: Mg	5	11	4.33	6.25	130
Example 7	MX2: LiQ	50	26	MX2: Yb	5	10	4.52	5.79	170
Example 8	MX4: Li-2	60	26	MX4: Mg	5	10	4.52	6.59	150
Example 9	MX9: Li-2	50	21	MX9: Mg	5	15	4.21	5.50	140
Example 10	MX9: Li-2	50	26	MX9: Yb	5	10	4.69	5.42	300
Example 11	MX9: Li-2	50	16	MX9: Yb	5	20	4.47	5.39	220
* ¹ = the wt.-% of the matrix compound and the wt.-% of the lithium organic complex are in total 100 wt.-% based on weight of the ETL1									
* ² = the wt.-% of the matrix compound and the wt.-% of the elemental metal are in total 100 wt.-% based on weight of the ETL2									

[0170] In the Table 6 above a comparison is shown of various phosphine oxide matrix compounds and lithium organic complex Li-2. The lifetime is improved for both magnesium and ytterbium compared to comparative examples 1,2 and 3. As can be seen in Example 10, a lifetime improvement is observed even for a thicker first electron transport layer and a thinner second electron transport layer. As can be seen in Example 11, a lifetime improvement is observed even for a thinner first electron transport layer and a thicker second electron transport layer. The best lifetime in Table 6 is achieved for 26 nm first ETL and 10 nm second ETL, see Example 10. Depending on the matrix compound, an increase in efficiency can also be observed, for example matrix compound MX4 of Example 8 gives higher external quantum efficiency (EQE) than MX2 or MX9.

[0171] In summary, improved lifetime is observed for magnesium, ytterbium and lithium in the second electron transport layer compared to the devices of comparative examples where calcium has been used. For certain combinations of matrix compounds and lithium organic complex, an increase in efficiency has been achieved according to the invention, for example MX2, doped with LiQ, and MX4, doped with Li-2.

[0172] In Table 7 below a bottom-emission device with the same matrix material in the first and second electron transport layer is compared with a device of a first matrix compound in the first electron transport layer and a different second matrix compound in the second electron transport layer.

Table 7

External quantum efficiency (EQE) and lifetime of bottom emission OLEDs with two ETLs									
	ETL 1	wt.-% Li organic complex* ¹	d (ETL1) / nm	ETL 2	wt.-% Metal dopant* ²	d (ETL2) / nm	V at 10 mA/cm ² / V	EQE / %	LT / h
Example 12	MX2: LiQ	50	26	MX2: Mg	5	11	4.33	6.25	130
Example 13	MX3: LiQ	60	20	MX2: Mg	5	16	4.92	5.27	200

*¹ = the wt.-% of the matrix compound and the wt.-% of the lithium organic complex are in total 100 wt.-% based on weight of the ETL1

*² = the wt.-% of the matrix compound and the wt.-% of the elemental metal are in total 100 wt.-% based on weight of the ETL2

[0173] In the Table 7 above results for devices wherein the HOMO level of the first matrix compound is 0.43 eV shallower (shallower means closer to vacuum level) compared to the second matrix compound of Example 13. Additionally, the LUMO level of the first matrix compound is 0.28 eV shallower (closer to vacuum level) than the LUMO of the second matrix compound. The lifetime is increased compared to devices with the same matrix compound in both ETL layers.

[0174] In Table 8 below a comparison of two matrix materials is shown, wherein the first matrix material has a deeper HOMO level than the second matrix material.

Table 8

External quantum efficiency (EQE) and lifetime of bottom emission OLEDs with two ETLs									
	ETL 1	wt.-%Li organic complex* ¹	d (ETL1) / nm	ETL 2	wt.-% Metal dopant* ²	d (ETL2) / nm	V at 10 mA/cm ² / V	EQE / %	LT / h
Example 14	MX4: Li-2	60	20	MX4: Mg	5	16	4.40	6.57	130
Example 15	MX4: Li-2	60	20	MX2: Mg	5	16	4.52	6.36	145

*¹ = the wt.-% of the matrix compound and the wt.-% of the lithium organic complex are in total 100 wt.-% based on weight of the ETL1

*² = the wt.-% of the matrix compound and the wt.-% of the elemental metal are in total 100 wt.-% based on weight of the ETL2

[0175] In the Table 8 above results for bottom emission devices wherein the HOMO level of the first matrix compound of Example 14 is > 0.35 eV deeper (deeper means further away from vacuum level) compared to the second matrix compound of Example 15 is shown. The LUMO level of the first matrix compound is 0.42 eV shallower compared to the LUMO level of the second matrix compound. Again, the lifetime is improved over the device with the same matrix compound in both ETL layers. In summary, a significant lifetime improvement is achieved irrespective of the off-set in HOMO level between the first and second matrix compound.

[0176] In Table 9 below bottom emission devices are compared with various cathode materials of aluminum and silver with a thickness of 100 nm.

Table 9

External quantum efficiency (EQE) and lifetime of bottom emission OLEDs with two ETLs										
	ETL1	wt.-% Lithium organic complex ^{*1}	d (ETL1) / nm	ETL2	wt.-% Metal dopant ^{*2}	d (ETL2) / nm	Cathode	V at 10 mA/cm ² / V	EQE / %	LT / h
Comp. example 4	MX1: LiQ	50	19	MX1: Ca	5	17	Al	3.77	5.48	55
Comp. example 5	MX1: LiQ	50	19	MX1: Ca	5	16	Ag	3.66	4.89	47
Example 16	MX2: LiQ	50	26	MX2: Mg	5	11	Al	4.33	6.25	130
Example 17	MX2: LiQ	50	20	MX2: Mg	5	16	Ag	4.06	5.25	100
^{*1} = the wt.-% of the matrix compound and the wt.-% of the lithium organic complex are in total 100 wt.-% based on weight of the ETL1 ^{*2} = the wt.-% of the matrix compound and the wt.-% of the elemental metal are in total 100 wt.-% based on weight of the ETL2										

[0177] In Table 9 above bottom-emission devices are shown with Al and Ag cathode.

[0178] As can be seen for Comparative Examples 4 and 5, the lifetime with Ag cathode is slightly shorter compared to the Al cathode. When phosphine oxide host matrix MX2 is used in both layers and ETL 2 contains Mg, the lifetime with both Al and Ag cathode is significantly improved over the Comparative Examples 4 and 5.

[0179] Lifetime and efficiency improvement with three electron transport layers (ETL1, ETL 2, and ETL 3).

[0180] In Table 10 below are shown voltages for OLEDs with different thicknesses of ETL2, while keeping the thickness of ETL1 constant.

Table 10

Voltage at 10 mA/cm ² of bottom emission OLEDs with different thicknesses of ETL1 and ETL2							
	ETL1	wt.-% Lithium organic complex ^{*1}	d (ETL1) / nm	ETL2	wt.-% Metal dopant ^{*2}	d (ETL2) / nm	V at 10 mA/cm ² / V
Example 18	MX2: LiQ	50	20	MX2: Mg	5	16	4.09
Example 19	MX2: LiQ	50	20	MX2: Mg	5	56	4.09
Example 20	MX2: LiQ	50	20	MX2: Mg	5	96	4.1
Example 21	MX2: LiQ	50	20	MX2: Mg	5	136	4.09
^{*1} = the wt.-% of the matrix compound and the wt.-% of the lithium organic complex are in total 100 wt.-% based on weight of the ETL1 ^{*2} = the wt.-% of the matrix compound and the wt.-% of the elemental metal are in total 100 wt.-% based on weight of the ETL2							

[0181] As can be seen in Table 10 above, the voltage does not change with the thickness of the electron transport layer containing elemental metal (ETL2). Even when the thickness of ETL2 is increased from 16 to 136 nm, the voltage does not increase (Examples 18 and 21). In manufacturing, this is a very important feature as it allows fine-tuning of the

micro-cavity through optimisation of the layer thickness without loss in conductivity. The micro-cavity influences the emission spectrum and efficiency of an OLED. In devices with an electron transport layer containing elemental metal, the thickness of this layer can be adjusted to optimize the emission spectrum and efficiency without increase in voltage.

Bottom emission devices

b) Lifetime and efficiency improvement with three electron transport layers (ETL 1, ETL 2 and ETL 3)

[0182]

a) A device is fabricated with three ETL layers. ETL 1 (closest to the emission layer) contains a matrix compound and a lithium halide or lithium organic complex. ETL 2 (adjacent to ETL 1) contains a matrix compound and elemental metal, for example Mg or Yb. ETL 3 (adjacent to ETL 2 and closest to the cathode) contains a matrix compound and the same lithium halide or lithium organic complex as used in ETL 1. An Al or Ag cathode is deposited on top. Preferably the same phosphine oxide based matrix compound is used in the three electron transport layers. The external quantum efficiency EQE is > 5.5% and the LT is > 70 h.

b) A device is fabricated with three ETL layers. ETL 1 (closest to the emission layer) contains a matrix compound and an elemental metal, for example Mg or Yb. ETL 2 (adjacent to ETL 1) contains a matrix compound and a lithium halide or lithium organic complex. ETL 3 (adjacent to ETL 2 and closest to the cathode) contains a matrix compound and the same elemental metal as used in ETL 1. An Al or Ag cathode is deposited on top. Preferably the same phosphine oxide based matrix compound is used in the three electron transport layers. The external quantum efficiency EQE is > 5.5% and the LT is > 70 h.

[0183] The double ETL of a first electron transport layer and of a second electron transport layer as well as the triple ETL of a first electron transport layer, a second electron transport layer and a third electron transport layer could also be employed for other emission colors, for example green, red, and white-light emitting devices.

[0184] Another aspect is directed to a device comprising at least one organic light-emitting diode (OLED). A device comprising organic light-emitting diodes is for example a display.

[0185] From the foregoing detailed description and examples, it will be evident that modifications and variations can be made to the compositions and methods of the invention.

Claims

1. An organic light-emitting diode (OLED) (100) comprising an emission layer and an electron transport layer stack (160) of at least two electron transport layers (161/162), wherein a first electron transport layer (161) and a second electron transport layer (162) comprises at least one matrix compound and in addition,

- the at least first electron transport layer (161) comprises a lithium halide or a lithium organic complex; and the at least second electron transport layer (162) comprises an elemental metal selected from the group of lithium, magnesium and/or ytterbium; or

- the at least first electron transport layer (161) comprises an elemental metal selected from the group of lithium, magnesium and/or ytterbium; and the at least second electron transport layer (162) comprises a lithium halide or a lithium organic complex;

wherein the electron transport layer or layers comprising a lithium halide or a lithium organic complex is free of an elemental metal, and the electron transport layer or layers that comprises an elemental metal is free of a metal salt and/or a metal organic complex; wherein the matrix compound is a phosphine oxide based compound.

2. An organic light-emitting diode (OLED) (100) comprising at least three electron transport layers (161/162/163), wherein

- at least two electron transport layers (161/163) comprising a lithium halide or a lithium organic complex; and at least one electron transport layer (162) comprises an elemental metal selected from the group of lithium, magnesium and/or ytterbium; or

- at least two electron transport layers (161/163) comprising an elemental metal selected from the group of lithium, magnesium and/or ytterbium; and at least one electron transport layer (162) comprises a lithium halide or a lithium organic complex;

wherein for an electron transport layer stack (160) comprising at least two electron transport layers (161/163) comprising a lithium halide or a lithium organic complex, the lithium halide or lithium organic complex of each electron transport layer are selected same or different, and more preferred selected the same; and/or

wherein for an electron transport layer stack (160) comprising at least two electron transport layers (161/163) comprising an elemental metal selected from the group of lithium, magnesium and/or ytterbium the elemental metal selected from the group of lithium, magnesium and/or ytterbium of each electron transport layer are selected same or different, and more preferred selected the same; wherein the matrix compound is a phosphine oxide based compound.

3. The OLED (100) comprising the electron transport layer stack (160) according to claim 1 or 2, wherein

- the amount of the lithium halide or lithium organic complex in an electron transport layer, preferably the at least first electron transport layer (161), is in the range of ≥ 10 mol-% to ≤ 95 mol-%, preferably ≥ 15 mol-% to ≤ 90 mol-% and also preferred ≥ 20 mol-% to ≤ 80 mol-%, based on the corresponding electron transport layer (161); and/or

- the amount of the lithium halide or lithium organic complex in an electron transport layer stack (160) of at least three electron transport layers, at least two of the electron transport layers, preferably the at least first electron transport layer (161) and/or the at least third electron transport layer (163), is in the range of ≥ 10 mol-% to ≤ 95 mol-%, preferably ≥ 15 mol-% to ≤ 90 mol-% and also preferred ≥ 20 mol-% to ≤ 80 mol-%, based on the corresponding electron transport layer (161/163).

4. The OLED (100) comprising the electron transport layer stack (160) according to any one of the preceding claim 1 to 3, wherein

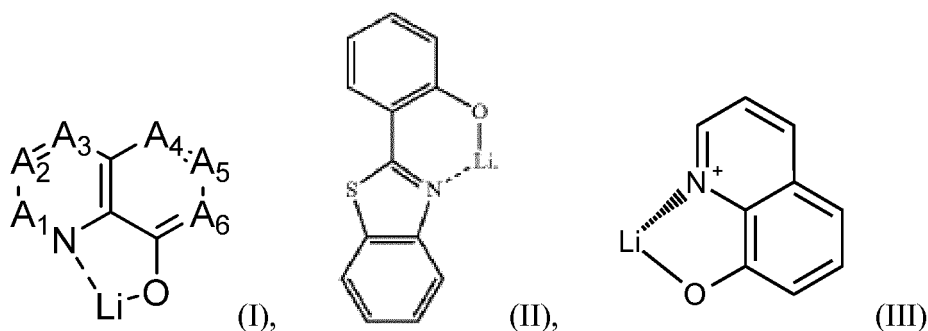
- at least one electron transport layer (161), comprises ≥ 1 wt.-% to ≤ 60 wt.-%, preferably ≥ 2 wt.-% to ≤ 55 wt.-% and also preferred ≥ 5 wt.-% to ≤ 45 wt.-% of an elemental metal selected from the group of lithium, magnesium and/or ytterbium; or

- at least two electron transport layer (161/163) of at least three electron transport layers (161/162/163) comprises ≥ 1 wt.-% to ≤ 60 wt.-%, preferably ≥ 2 wt.-% to ≤ 55 wt.-% and also preferred ≥ 5 wt.-% to ≤ 45 wt.-% of an elemental metal selected from the group of lithium, magnesium and/or ytterbium;

wherein the weight percent of the elemental metal selected from the group of lithium, magnesium and/or ytterbium is based on the total weight of the corresponding electron transport layer.

5. The OLED (100) comprising the electron transport layer stack (160) according to any one of the preceding claims 1 to 4, wherein the lithium halide is selected from a group comprising LiF, LiCl, LiBr or LiJ, and preferably LiF, and the organic ligand of the lithium organic complex is a quinolate, a borate, a phenolate, a pyridinolate or a Schiff base ligand;

- preferably the lithium quinolate complex has the formula I, II or III:

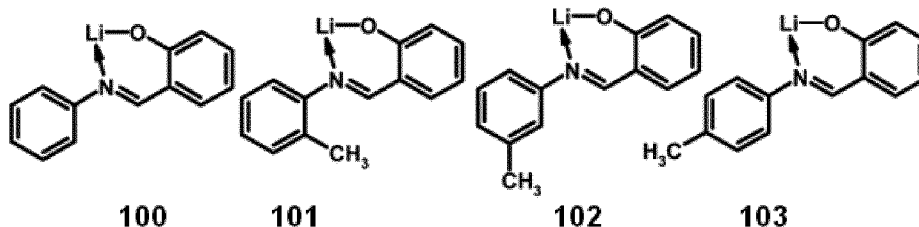


wherein

A1 to A6 are same or independently selected from CH, CR, N, O;

R is same or independently selected from hydrogen, halogen, alkyl or aryl or heteroaryl with 1 to 20 carbon atoms; and more preferred A1 to A6 are CH;

- preferably the borate based organic ligand is a tetra(1H-pyrazol-1-yl)borate;
- preferably the phenolate is a 2-(pyridin-2-yl)phenolate, a 2-(diphenylphosphoryl)phenolate, an imidazol phenolates, or 2-(pyridin-2-yl)phenolate and more preferred 2-(1-phenyl-1H-benzo[d]imidazol-2-yl)phenolate;
- preferably the pyridinolates is a 2-(diphenylphosphoryl)pyridin-3-olate,
- preferably the lithium Schiff base has the structure 100, 101, 102 or 103:



6. The OLED (100) comprising the electron transport layer stack (160) according to any one of the preceding claims 1 to 5, wherein the electron transport layer stack comprises at least two electron transport layers or at least three electron transport layers, and wherein each electron transport layer comprises at least one matrix compound, whereby the matrix compound of the electron transport layers are selected same or different, preferably the same.

7. The OLED (100) comprising the electron transport layer stack (160) according to any one of the preceding claims 1 to 6, wherein the at least two electron transport layers (161/162) or the at least three electron transport layers (161/162/163) comprise at least one matrix compound, whereby the matrix compound of the electron transport layers are selected same or different, and wherein the matrix compound is selected from:

- an anthracene based compound or a heteroaryl substituted anthracene based compound, preferably 2-(4-(9,10-di(naphthalen-2-yl)anthracene-2-yl)phenyl)-1-phenyl-1H-benzo[d]imidazole and/or N4,N4"-di(naphthalen-1-yl)-N4,N4"-diphenyl-[1,1':4',1"-terphenyl]-4,4"-diamine; or
- a phosphine oxide based compound, preferably (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide, 3-phenyl-3H-benzo[b]dinaphtho[2,1-d:1',2'-f] phosphine-3-oxide, bis(4-(anthracen-9-yl)phenyl)(phenyl)phosphine oxide and/or phenyl bis(3-(pyren-1-yl)phenyl)phosphine oxide; or
- a substituted phenanthroline compound, preferably 2,4,7,9-tetraphenyl-1,10-phenanthroline or 2,9-di(biphenyl-4-yl)-4,7-diphenyl-1,10-phenanthroline;

with at least one matrix compound being a phosphine oxide based compound.

8. The OLED (100) comprising the electron transport layer stack (160) according to any one of the preceding claims 1 to 7, wherein the thicknesses of each electron transport layer, preferably the at least first electron transport layer (161) and the at least second electron transport layer (162) and/or the at least third electron transport layer (163), are same or each independently in the range of ≥ 0.5 nm to ≤ 95 nm, preferably of ≥ 3 nm to ≤ 80 nm, further preferred of ≥ 5 nm to ≤ 60 nm, also preferred of ≥ 6 nm to ≤ 40 nm, in addition preferred ≥ 8 nm to ≤ 20 nm and more preferred of ≥ 10 nm to ≤ 18 nm.

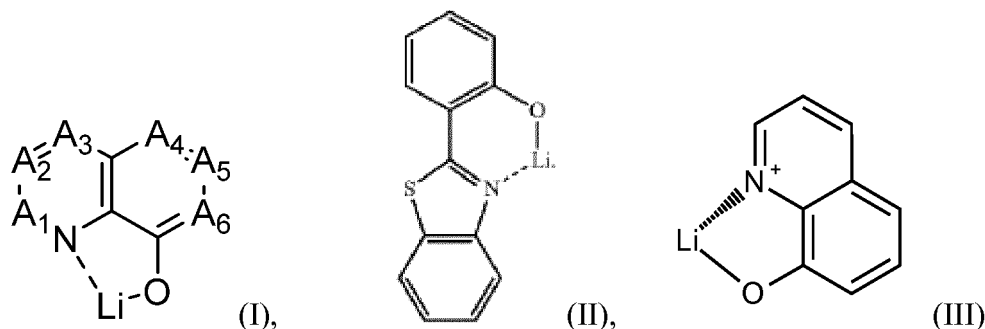
9. The OLED (100) comprising the electron transport layer stack (160) according to any one of the preceding claims 1 to 8, wherein the electron transport layer stack has two to four electron transport layers and more preferred two electron transport layers (162/162) or three electron transport layers (162/162/163) and most preferred two electron transport layers (162/162).

10. The OLED (100) comprising the electron transport layer stack (160) according to any one of the preceding claims 1 to 9, wherein the at least second electron transport layer (162) is formed directly on the at least first electron transport layer (161) and/or the at least third electron transport layer (163) is formed directly on the at least second electron transport layer (162) so that the second electron transport layer (162) is sandwiched between the first electron transport layer (161) and the third electron transport layer (163).

11. The OLED (100) comprising the electron transport layer stack (160) according to any one of the preceding claims 1 to 10, wherein

- at least one electron transport layer (161) or in case of at least three electron transport layers (161/162/163) at least two electron transport layer (161/163) comprise:

a) ≥ 10 wt.-% to ≤ 70 wt.-%, preferably ≥ 20 wt.-% to ≤ 65 wt.-% and also preferred ≥ 50 wt.-% to ≤ 60 wt.-% of a lithium halide, selected from the group comprising a LiF, LiCl, LiBr or LiI, preferably LiF, or of a lithium organic complex, selected from the group comprising a lithium quinolate, a borate, a phenolate, a pyridinolate or a Schiff base ligand; preferably of a lithium quinolate complex has the formula I, II or III:



wherein

- A1 to A6 are same or independently selected from CH, CR, N, O,
- R is same or independently selected from hydrogen, halogen, alkyl or aryl or heteroaryl with 1 to 20 carbon atoms, and more preferred of a lithium 8-hydroxyquinolate;

b) ≤ 90 wt.-% to ≥ 30 wt.-%, preferably ≤ 80 wt.-% to ≥ 35 wt.-% and also preferred ≤ 50 wt.-% to ≥ 40 wt.-% and also preferred ≤ 50 wt.-% to ≥ 40 wt.-% of a matrix compound of:

- an anthracene based compound or a heteroaryl substituted anthracene based compound, preferably 2-(4-(9,10-di(naphthalen-2-yl)anthracene-2-yl)phenyl)-1-phenyl-1H-benzo[d]imidazole and/or N4,N4"-di(naphthalen-1-yl)-N4,N4"-diphenyl-[1,1':4',1"-terphenyl]-4,4"-diamine; or
- a phosphine oxide based compound, preferably (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide, 3-phenyl-3H-benzo[b]dinaphtho[2,1-d:1',2'-f]phosphepine-3-oxide, bis(4-(anthracen-9-yl)phenyl)(phenyl)phosphine oxide and/or phenyl bis(3-(pyren-1-yl)phenyl)phosphine oxide; or
- a substituted phenanthroline compound, preferably 2,4,7,9-tetraphenyl-1,10-phenanthroline or 2,9-di(biphenyl-4-yl)-4,7-diphenyl-1,10-phenanthroline;

whereby more preferred is a phosphine oxide based compound and most preferred is (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide;

and

- at least one electron transport layer (162) or in case of at least three electron transport layers (161/162/163) at least two electron layers (161/163) comprise:

c) ≥ 1 wt.-% to ≤ 60 wt.-%, preferably ≥ 2 wt.-% to ≤ 55 wt.-% and also preferred ≥ 5 wt.-% to ≤ 45 wt.-% of an elemental metal selected from the group of lithium, magnesium and/or ytterbium, more preferred of an elemental metal ytterbium or an elemental metal magnesium and most preferred of an elemental metal magnesium;

d) ≤ 99 wt.-% to ≥ 40 wt.-%, preferably ≤ 98 wt.-% to ≥ 45 wt.-% and also preferred ≤ 95 wt.-% to ≥ 55 wt.-% of a matrix compound of:

- an anthracene based compound or a heteroaryl substituted anthracene based compound, preferably 2-(4-(9,10-di(naphthalen-2-yl)anthracene-2-yl)phenyl)-1-phenyl-1H-benzo[d]imidazole and/or N4,N4"-di(naphthalen-1-yl)-N4,N4"-diphenyl-[1,1':4',1"-terphenyl]-4,4"-diamine; or
- a phosphine oxide based compound, preferably (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide, 3-phenyl-3H-benzo[b]dinaphtho[2,1-d:1',2'-f]phosphepine-3-oxide, bis(4-(anthracen-9-yl)phenyl)(phenyl)phosphine oxide and/or phenyl bis(3-(pyren-1-yl)phenyl)phosphine oxide; or

- a substituted phenanthroline compound, preferably 2,4,7,9-tetraphenyl-1,10-phenanthroline or 2,9-di(biphenyl-4-yl)-4,7-diphenyl-1,10-phenanthroline; whereby more preferred is a phosphine oxide based compound and most preferred is (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide;

wherein the weight percent of each component is based on the total weight of the corresponding electron transport layer,
with at least one matrix compound being a phosphine oxide based compound.

12. The OLED (100) comprising the electron transport layer stack (160) according to any one of the preceding claims 1 to 11, wherein

- the at least one (161), preferably two (161/163), lithium organic complex containing electron transport layer comprises of ≥ 50 wt.-% to ≤ 60 wt.-% of a lithium 8-hydroxyquinolate and ≤ 50 wt.-% to ≥ 40 wt.-% of a (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide; and

- the at least one (162), preferably two (161/163), elemental metal containing electron transport layer comprises of ≥ 2 wt.-% to ≤ 45 wt.-% of an elemental metal selected from the group of lithium, magnesium and/or ytterbium, more preferred of an elemental metal lithium or an elemental metal magnesium and most preferred of an elemental metal ytterbium and ≤ 98 wt.-% to ≥ 55 wt.-% of a (3-(dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphine oxide.

13. A method of manufacturing an organic light-emitting diode (100) according to any one of claims 1 to 12, the method using:

- deposition via vacuum thermal evaporation; and/or
- deposition via solution processing, preferably the processing is selected from spin-coating, casting, printing and/or slot-die coating.

14. A method of manufacturing an organic light-emitting diode (100) according to claim 13, the method using:

- a first or a first and a fourth deposition source to release the matrix compound, and
- a second deposition source to release lithium halide or lithium organic complex, and
- a third deposition source to release the elemental metal; or
- at least one or two deposition sources to release the matrix compound, and
- at least one or two deposition sources to release lithium halide or lithium organic complex, and
the method comprising the steps of forming the electron transport layer stack; whereby
- a first electron transport layer (161) is formed by releasing the matrix compound from at least one deposition source and a lithium halide or a lithium organic complex or an elemental metal is released from at different deposition source;
- onto the first electron transport layer (161) a second electron transport layer (162) is formed by releasing the matrix compound from at least one deposition source and a lithium halide or a lithium organic complex or an elemental metal is released from at different deposition source;
- onto the second electron transport layer (162) a third electron transport layer (163) is formed by releasing the matrix compound from at least one deposition source and a lithium halide or a lithium organic complex or an elemental metal is released from at different deposition source; whereby
at least one electron transport layer comprises a lithium halide or a lithium organic complex and is free of an elemental metal; and at least one electron transport layer comprises an elemental metal and is free of a lithium halide or a lithium organic complex.

15. A device comprising at least one organic light-emitting diode of claims 1 to 12.

Patentansprüche

1. Organische Leuchtdiode (OLED) (100), umfassend eine Emissionsschicht und einen Elektronentransportschichtstapel (160) aus mindestens zwei Elektronentransportschichten (161/162), wobei eine erste Elektronentransportschicht (161) und eine zweite Elektronentransportschicht (162) mindestens eine Matrixverbindung umfassen und zusätzlich,

- die mindestens erste Elektronentransportschicht (161) ein Lithiumhalogenid oder einen organischen Lithiumkomplex umfasst; und die mindestens zweite Elektronentransportschicht (162) ein elementares Metall ausgewählt aus der Gruppe von Lithium, Magnesium und/oder Ytterbium umfasst; oder
- die mindestens erste Elektronentransportschicht (161) ein elementares Metall, ausgewählt aus der Gruppe von Lithium, Magnesium und/oder Ytterbium, umfasst; und die mindestens zweite Elektronentransportschicht (162) ein Lithiumhalogenid oder einen organischen Lithiumkomplex umfasst;

wobei die Elektronentransportschicht oderschichten, die ein Lithiumhalogenid oder einen organischen Lithiumkomplex umfassen, frei von elementarem Metall sind und die Elektronentransportschicht oder -schichten, die ein elementares Metall umfassen, frei von einem Metallsalz und/oder einem organischen Metallkomplex sind; wobei die Matrixverbindung eine auf Phosphinoxid basierende Verbindung ist.

2. Organische Leuchtdiode (OLED) (100), umfassend mindestens drei Elektronentransportschichten (161/162/163), wobei

- mindestens zwei Elektronentransportschichten (161/163), die ein Lithiumhalogenid oder einen organischen Lithiumkomplex umfassen; und mindestens eine Elektronentransportschicht (162) ein elementares Metall umfasst, ausgewählt aus der Gruppe von Lithium, Magnesium und/oder Ytterbium; oder
- mindestens zwei Elektronentransportschichten (161/163), die ein elementares Metall, ausgewählt aus der Gruppe von Lithium, Magnesium und/oder Ytterbium, umfassen; und mindestens eine Elektronentransportschicht (162) ein Lithiumhalogenid oder einen organischen Lithiumkomplex umfasst;

wobei für einen Elektronentransportschichtstapel (160), der mindestens zwei Elektronentransportschichten (161/163) umfasst, die ein Lithiumhalogenid oder einen organischen Lithiumkomplex umfassen, das Lithiumhalogenid oder der organische Lithiumkomplex jeder Elektronentransportschicht gleich oder unterschiedlich ausgewählt sind, und bevorzugter gleich ausgewählt sind; und/oder

wobei für einen Elektronentransportschichtstapel (160), der mindestens zwei Elektronentransportschichten (161/163) umfasst, die ein elementares Metall umfassen, ausgewählt aus der Gruppe von Lithium, Magnesium und/oder Ytterbium, das elementare Metall, das aus der Gruppe von Lithium, Magnesium und/oder Ytterbium ausgewählt ist, jeder Elektronentransportschicht gleich oder unterschiedlich ausgewählt sind, und bevorzugter gleich ausgewählt sind; wobei die Matrixverbindung eine auf Phosphinoxid basierende Verbindung ist.

3. OLED (100), umfassend den Elektronentransportschichtstapel (160) nach Anspruch 1 oder 2, wobei

- die Menge des Lithiumhalogenids oder organischen Lithiumkomplexes in einer Elektronentransportschicht, vorzugsweise der mindestens ersten Elektronentransportschicht (161), im Bereich von ≥ 10 Mol% bis ≤ 95 Mol%, vorzugsweise ≥ 15 Mol% bis ≤ 90 Mol% und auch bevorzugt ≥ 20 Mol% bis ≤ 80 Mol% ist, basierend auf der entsprechenden Elektronentransportschicht (161); und/oder
- die Menge des Lithiumhalogenids oder organischen Lithiumkomplexes in einem Elektronentransportschichtstapel (160) aus mindestens drei Elektronentransportschichten, von mindestens zwei der Elektronentransportschichten, vorzugsweise der mindestens ersten Elektronentransportschicht (161) und/oder der mindestens dritten Elektronentransportschicht (163), im Bereich von ≥ 10 Mol% bis ≤ 95 Mol%, vorzugsweise ≥ 15 Mol% bis ≤ 90 Mol% und auch bevorzugt ≥ 20 Mol% bis ≤ 80 Mol% ist, basierend auf der entsprechenden Elektronentransportschicht (161/163).

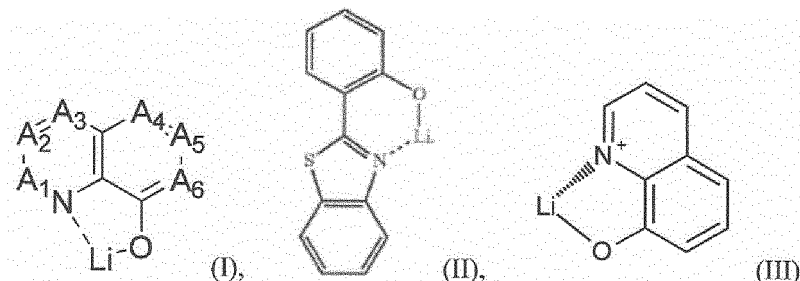
4. OLED (100) umfassend den Elektronentransportschichtstapel (160) nach einem der vorangehenden Ansprüche 1 bis 3, wobei

- mindestens eine Elektronentransportschicht (161) ≥ 1 Gew.-% bis ≤ 60 Gew.-%, vorzugsweise ≥ 2 Gew.-% bis ≤ 55 Gew.-% und auch bevorzugt ≥ 5 Gew.-% bis ≤ 45 Gew.-% eines elementaren Metalls umfasst, ausgewählt aus der Gruppe von Lithium, Magnesium und/oder Ytterbium; oder
- mindestens zwei Elektronentransportschichten (161/163) von mindestens drei Elektronentransportschichten (161/162/163) ≥ 1 Gew.-% bis ≤ 60 Gew.-%, vorzugsweise ≥ 2 Gew.-% bis ≤ 55 Gew.-% und auch bevorzugt ≥ 5 Gew.-% bis ≤ 45 Gew.-% eines elementaren Metalls umfassen, ausgewählt aus der Gruppe von Lithium, Magnesium und/oder Ytterbium;

wobei die Gewichtsprozent des elementaren Metalls, ausgewählt aus der Gruppe von Lithium, Magnesium und/oder Ytterbium, auf dem Gesamtgewicht der entsprechenden Elektronentransportschicht basieren.

5. OLED (100), umfassend den Elektronentransportschichtstapel (160) nach einem der vorangehenden Ansprüche 1 bis 4, wobei das Lithiumhalogenid ausgewählt ist aus der Gruppe umfassend LiF, LiCl, LiBr oder LiI, und vorzugsweise LiF, und der organische Ligand des organischen Lithiumkomplexes ein Chinolat-, ein Borat-, ein Phenolat-, ein Pyridinolat- oder ein Schiff-Base-Ligand ist;

- vorzugsweise der Lithiumchinolatkomplex die Formel I, II oder III hat:

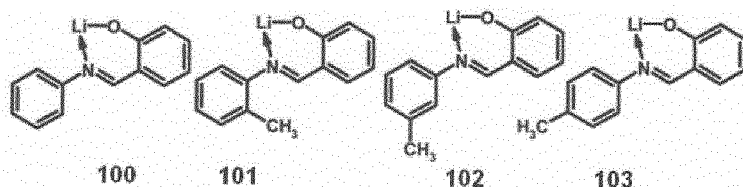


wobei

A1 bis A6 dieselben sind oder unabhängig ausgewählt sind aus CH, CR, N, O;

R dasselbe ist oder unabhängig ausgewählt ist aus Wasserstoff, Halogen, Alkyl oder Aryl oder Heteroaryl mit 1 bis 20 Kohlenstoffatomen; und bevorzugter A1 bis A6 CH sind;

- vorzugsweise der auf Borat basierende organische Ligand ein Tetra(1H-pyrazol-1-yl)borat ist;
- vorzugsweise das Phenolat ein 2-(Pyridin-2-yl)phenolat, ein 2-(Diphenylphosphoryl)phenolat, ein Imidazolphenolat oder 2-(Pyridin-2-yl)phenolat und bevorzugter 2-(1-Phenyl-1H-benzo[d]imidazol-2-yl)phenolat ist;
- vorzugsweise das Pyridinolat ein 2-(Diphenylphosphoryl)pyridin-3-olat ist,
- vorzugsweise die Lithium-Schiff-Base die Struktur 100, 101, 102 oder 103 hat:



6. OLED (100), umfassend den Elektronentransportschichtstapel (160) nach einem der vorangehenden Ansprüche 1 bis 5, wobei der Elektronentransportschichtstapel mindestens zwei Elektronentransportschichten oder mindestens drei Elektronentransportschichten umfasst und wobei jede Elektronentransportschicht mindestens eine Matrixverbindung umfasst, wobei die Matrixverbindung der Elektronentransportschichten gleich oder unterschiedlich ausgewählt ist, vorzugsweise dieselbe ist.

7. OLED (100), umfassend den Elektronentransportschichtstapel (160) nach einem der vorangehenden Ansprüche 1 bis 6, wobei die mindestens zwei Elektronentransportschichten (161/162) oder die mindestens drei Elektronentransportschichten (161/162/163) mindestens eine Matrixverbindung umfassen, wobei die Matrixverbindung der Elektronentransportschichten gleich oder unterschiedlich ausgewählt ist, und wobei die Matrixverbindung ausgewählt ist aus:

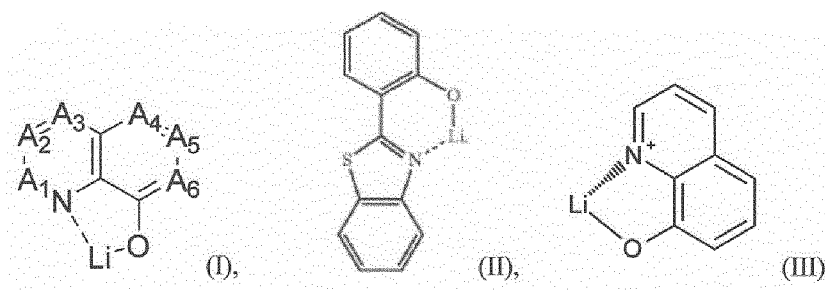
- einer auf Anthracen basierenden Verbindung oder einer auf Heteroaryl-substituiertem Anthracen basierenden Verbindung, vorzugsweise 2-(4-(9,10-Di(naphthalin-2-yl)anthracen-2-yl)phenyl)-1-phenyl-1H-benzo[d]imidazol und/oder N4,N4"-Di(naphthalin-1-yl)-N4,N4"-diphenyl-[1,1':4',1"-terphenyl]-4,4"-diamin; oder
- einer auf Phosphinoxid basierenden Verbindung, vorzugsweise (3-(Dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphinoxid, 3-Phenyl-3H-benzo[b]dinaphtho[2,1-d:1',2'-f]phosphopin-3-oxid, Bis(4-(anthracen-9-yl)phenyl)(phenyl)phosphinoxid und/oder Phenyl bis(3-(pyren-1-yl)phenyl)phosphinoxid; oder
- einer substituierten Phenanthrolinverbindung, vorzugsweise 2,4,7,9-Tetraphenyl-1,10-phenanthrolin oder 2,9-Di(biphenyl-4-yl)-4,7-diphenyl-1,10-phenanthrolin;

wobei wenigstens eine Matrixverbindung eine auf Phosphinoxid basierende Verbindung ist.

8. OLED (100), umfassend den Elektronentransportschichtstapel (160) nach einem der vorangehenden Ansprüche 1 bis 7, wobei die Dicke jeder Elektronentransportschicht, vorzugsweise der mindestens ersten Elektronentransportschicht (161) und der mindestens zweiten Elektronentransportschicht (162) und/oder der mindestens dritten Elektronentransportschicht (163), dieselbe ist oder jeweils unabhängig im Bereich von $\geq 0,5$ nm bis ≤ 95 nm, vorzugsweise von ≥ 3 nm bis ≤ 80 nm, weiter bevorzugt von ≥ 5 nm bis ≤ 60 nm, auch bevorzugt von ≥ 6 nm bis ≤ 40 nm, zusätzlich bevorzugt ≥ 8 nm bis ≤ 20 nm und bevorzugter von ≥ 10 nm bis ≤ 18 nm ist.
9. OLED (100), umfassend den Elektronentransportschichtstapel (160) nach einem der vorangehenden Ansprüche 1 bis 8, wobei der Elektronentransportschichtstapel zwei bis vier Elektronentransportschichten und bevorzugter zwei Elektronentransportschichten (162/162) oder drei Elektronentransportschichten (162/162/163) und äußerst bevorzugt zwei Elektronentransportschichten (162/162) hat.
10. OLED (100), umfassend den Elektronentransportschichtstapel (160) nach einem der vorangehenden Ansprüche 1 bis 9, wobei die mindestens zweite Elektronentransportschicht (162) direkt auf der mindestens ersten Elektronentransportschicht (161) gebildet ist und/oder die mindestens dritte Elektronentransportschicht (163) direkt auf der mindestens zweiten Elektronentransportschicht (162) gebildet ist, sodass die zweite Elektronentransportschicht (162) zwischen der ersten Elektronentransportschicht (161) und der dritten Elektronentransportschicht (163) liegt.
11. OLED (100), umfassend den Elektronentransportschichtstapel (160) nach einem der vorangehenden Ansprüche 1 bis 10, wobei

- mindestens eine Elektronentransportschicht (161) oder im Fall von mindestens drei Elektronentransportschichten (161/162/163) mindestens zwei Elektronentransportschichten (161/163) umfassen:

a) ≥ 10 Gew.-% bis ≤ 70 Gew.-%, vorzugsweise ≥ 20 Gew.-% bis ≤ 65 Gew.-% und auch bevorzugt ≥ 50 Gew.-% bis ≤ 60 Gew.-% eines Lithiumhalogenids, ausgewählt aus der Gruppe umfassend ein LiF, LiCl, LiBr oder LiJ, vorzugsweise LiF, oder eines organischen Lithiumkomplexes, ausgewählt aus der Gruppe umfassend ein Lithiumchinolat, ein Borat, ein Phenolat, ein Pyridinolat oder einen Schiff-Base-Liganden; wobei vorzugsweise ein Lithiumchinolatkomplex die Formel I, II oder III hat:



wobei

- A1 bis A6 dieselben sind oder unabhängig ausgewählt sind aus CH, CR, N, O,
 - R dasselbe ist oder unabhängig ausgewählt ist aus Wasserstoff, Halogen, Alkyl oder Aryl oder Heteroaryl mit 1 bis 20 Kohlenstoffatomen, und bevorzugter eines Lithium 8-Hydroxychinolats;

b) ≤ 90 Gew.-% bis ≥ 30 Gew.-%, vorzugsweise ≤ 80 Gew.-% bis ≥ 35 Gew.-% und auch bevorzugt ≤ 50 Gew.-% bis ≥ 40 Gew.-% und auch bevorzugt ≤ 50 Gew.-% bis ≥ 40 Gew.-% einer Matrixverbindung aus:

- einer Anthracen basierenden Verbindung oder einer Heteroarylsubstituierten Anthracen basierenden Verbindung, vorzugsweise 2-(4-(9,10-Di(naphthalin-2-yl)anthracen-2-yl)phenyl)-1-phenyl-1H-benzo[d]imidazol und/oder N4,N4"-Di(naphthalin-1-yl)-N4,N4"-diphenyl-[1,1':4',1"-terphenyl]-4,4"-diamin; oder
 - einer auf Phosphinoxid basierenden Verbindung, vorzugsweise (3-(Dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphinoxid, 3-Phenyl-3H-benzo[b]dinaphtho[2,1-d:1',2'-f]phosphopin-3-oxid, bis(4-(An-

thracen-9-yl)phenyl)(phenyl)phosphinoxid und/oder Phenyl bis(3-(pyren-1-yl)phenyl)phosphinoxid;
oder
- einer substituierten Phenanthrolinverbindung, vorzugsweise 2,4,7,9-Tetraphenyl-1,10-phenanthrolin
oder 2,9-Di(biphenyl-4-yl)-4,7-diphenyl-1,10-phenanthrolin;

wobei eine auf Phosphin basierende Verbindung bevorzugter ist und (3-(Dibenzo[c,h]acridin-7-yl)phenyl)di-
phenylphosphinoxid äußerst bevorzugt ist;

und

- mindestens eine Elektronentransportschicht (162) oder im Fall von mindestens drei Elektronentransportschich-
ten (161/162/163) mindestens zwei Elektronenschichten (161/163) umfassen:

c) ≥ 1 Gew.-% bis ≤ 60 Gew.-%, vorzugsweise ≥ 2 Gew.-% bis ≤ 55 Gew.-% und auch bevorzugt ≥ 5 Gew.-%
bis ≤ 45 Gew.-% eines elementaren Metalls, ausgewählt aus der Gruppe von Lithium, Magnesium
und/oder Ytterbium, bevorzugter eines elementaren Metalls Ytterbium oder eines elementaren Metalls
Magnesium und äußerst bevorzugt eines elementaren Metalls Magnesium;
d) ≤ 99 Gew.-% bis ≥ 40 Gew.-%, vorzugsweise ≤ 98 Gew.-% bis ≥ 45 Gew.-% und auch bevorzugt ≤ 95
Gew.-% bis ≥ 55 Gew.-% einer Matrixverbindung von:

- einer Anthracen basierenden Verbindung oder einer Heteroarylsubstituierten Anthracen basierenden
Verbindung, vorzugsweise 2-(4-(9,10-Di(naphthalin-2-yl)anthracen-2-yl)phenyl)-1-phenyl-1H-ben-
zo[d]imidazol und/oder N4,N4"-Di(naphthalin-1-yl)-N4,N4"-diphenyl-[1,1':4',1"-terphenyl]-4,4"-diamin;
oder
- einer auf Phosphinoxid basierenden Verbindung, vorzugsweise (3-(Dibenzo[c,h]acridin-7-yl)phe-
nyl)diphenylphosphinoxid, 3-Phenyl-3H-benzo[b]dinaphtho[2,1-d:1',2'-f]phosphopin-3-oxid, Bis(4-(an-
thracen-9-yl)phenyl)(phenyl)phosphinoxid und/oder Phenyl bis(3-(pyren-1-yl)phenyl)phosphinoxid;
oder
- einer substituierten Phenanthrolinverbindung, vorzugsweise 2,4,7,9-Tetraphenyl-1,10-phenanthrolin
oder 2,9-Di(biphenyl-4-yl)-4,7-diphenyl-1,10-phenanthrolin; wobei eine auf Phosphinoxid basierende
Verbindung bevorzugter ist und (3-(Dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphinoxid äußerst be-
vorzugt ist;

wobei die Gewichtsprozent jeder Komponente auf dem Gesamtgewicht der entsprechenden Elektronentrans-
portschicht basieren,

wobei wenigstens eine Matrixverbindung eine auf Phosphinoxid basierende Verbindung ist.

12. OLED (100), umfassend den Elektronentransportschichtstapel (160) nach einem der vorangehenden Ansprüche 1
bis 11, wobei

- die mindestens eine (161), vorzugsweise zwei (161/163), organische Lithiumkomplex enthaltende Elektro-
nentransportschicht ≥ 50 Gew.-% bis ≤ 60 Gew.-% eines Lithium 8-hydroxychinolats und ≤ 50 Gew.-% bis ≥ 40
Gew.-% eines (3-(Dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphinoxids umfasst; und
- die mindestens eine (162), vorzugsweise zwei (161/163), elementares Metall enthaltende Elektronentrans-
portschicht ≥ 2 Gew.-% bis ≤ 45 Gew.-% eines elementaren Metalls umfasst, ausgewählt aus der Gruppe von
Lithium, Magnesium und/oder Ytterbium, bevorzugter eines elementaren Metalls Lithium oder eines elemen-
taren Metalls Magnesium und äußerst bevorzugt eines elementaren Metalls Ytterbium, und ≤ 98 Gew.-% bis $\geq$
55 Gew.-% eines (3-(Dibenzo[c,h]acridin-7-yl)phenyl)diphenylphosphinoxids.

13. Verfahren zur Herstellung einer organischen Leuchtdiode (100) nach einem der Ansprüche 1 bis 12, das Verfahren
verwendend:

- Abscheiden mittels vakuumthermischer Verdampfung; und/oder
- Abscheiden mittels Lösungsbearbeitung, wobei die Bearbeitung vorzugsweise ausgewählt ist aus Rotations-
beschichten, Gießen, Drucken und/oder Schlitzdüsenbeschichtung.

14. Verfahren zur Herstellung einer organischen Leuchtdiode (100) nach Anspruch 13, das Verfahren verwendend:

- eine erste oder eine erste und eine vierte Abscheidungsquelle, um die Matrixverbindung freizusetzen, und

- une seconde Abscheidungsquelle, um Lithiumhalogenid oder einen organischen Lithiumkomplex freizusetzen, und
 - eine dritte Abscheidungsquelle, um das elementare Metall freizusetzen; oder
 - mindestens eine oder zwei Abscheidungsquellen, um die Matrixverbindung freizusetzen, und
 - mindestens eine oder zwei Abscheidungsquellen, um Lithiumhalogenid oder einen organischen Lithiumkomplex freizusetzen, und
- das Verfahren umfassend die Schritte zum Bilden des Elektronentransportschichtstapels; wobei
- eine erste Elektronentransportschicht (161) gebildet wird, indem die Matrixverbindung aus mindestens einer Abscheidungsquelle freigesetzt wird, und ein Lithiumhalogenid oder ein organischer Lithiumkomplex oder ein elementares Metall aus einer anderen Abscheidungsquelle freigesetzt wird;
 - auf der ersten Elektronentransportschicht (161) eine zweite Elektronentransportschicht (162) gebildet wird, indem die Matrixverbindung aus mindestens einer Abscheidungsquelle freigesetzt wird, und ein Lithiumhalogenid oder ein organischer Lithiumkomplex oder ein elementares Metall aus einer anderen Abscheidungsquelle freigesetzt wird;
 - auf der zweiten Elektronentransportschicht (162) eine dritte Elektronentransportschicht (163) gebildet wird, indem die Matrixverbindung aus mindestens einer Abscheidungsquelle freigesetzt wird, und ein Lithiumhalogenid oder ein organischer Lithiumkomplex oder ein elementares Metall aus einer anderen Abscheidungsquelle freigesetzt wird; wobei
- mindestens eine Elektronentransportschicht ein Lithiumhalogenid oder einen organischen Lithiumkomplex umfasst und frei von elementarem Metall ist; und mindestens eine Elektronentransportschicht ein elementares Metall umfasst und frei von einem Lithiumhalogenid oder einem organischen Lithiumkomplex ist.

15. Vorrichtung, umfassend mindestens eine organische Leuchtdiode gemäß den Ansprüchen 1 bis 12.

Revendications

1. Diode électroluminescente organique (OLED) (100) comprenant une couche d'émission et un empilement de couches de transport d'électrons (160) d'au moins deux couches de transport d'électrons (161/162), dans laquelle une première couche de transport d'électrons (161) et une deuxième couche de transport d'électrons (162) comprend au moins un composé matriciel et en outre,

- ladite au moins première couche de transport d'électrons (161) comprend un halogénure de lithium ou un complexe organique de lithium ; et ladite au moins deuxième couche de transport d'électrons (162) comprend un métal élémentaire sélectionné dans le groupe constitué du lithium, du magnésium et/ou de l'ytterbium ; ou
- ladite au moins première couche de transport d'électrons (161) comprend un métal élémentaire sélectionné dans le groupe constitué du lithium, du magnésium et/ou de l'ytterbium ; et ladite au moins deuxième couche de transport d'électrons (162) comprend un halogénure de lithium ou un complexe organique de lithium ;

dans laquelle la couche ou les couches de transport d'électrons comprenant un halogénure de lithium ou un complexe organique de lithium sont exemptes de métal élémentaire, et la couche ou les couches de transport d'électrons comprenant un métal élémentaire sont exemptes de sel métallique et/ou de complexe organique de métal ; dans laquelle le composé matriciel est un composé à base d'oxyde de phosphine.

2. Diode électroluminescente organique (OLED) (100) comprenant au moins trois couches de transport d'électrons (161/162/163), dans laquelle

- au moins deux couches de transport d'électrons (161/163) comprennent un halogénure de lithium ou un complexe organique de lithium ; et au moins une couche de transport d'électrons (162) comprend un métal élémentaire sélectionné dans le groupe constitué du lithium, du magnésium et/ou de l'ytterbium ; ou
- au moins deux couches de transport d'électrons (161/163) comprennent un métal élémentaire sélectionné dans le groupe constitué du lithium, du magnésium et/ou de l'ytterbium ; et au moins une couche de transport d'électrons (162) comprend un halogénure de lithium ou un complexe organique de lithium ;

dans laquelle, pour un empilement de couches de transport d'électrons (160) comprenant au moins deux couches de transport d'électrons (161/163) comprenant un halogénure de lithium ou un complexe organique de lithium, l'halogénure de lithium ou le complexe organique de lithium de chaque couche de transport d'électrons sont sélectionnés.

tionnés de façon à être identique ou différent, et plus préférablement sélectionné de façon à être identique ; et/ou dans laquelle, pour un empilement de couches de transport d'électrons (160) comprenant au moins deux couches de transport d'électrons (161/163) comprenant un métal élémentaire sélectionné dans le groupe constitué du lithium, du magnésium et/ou de l'ytterbium, le métal élémentaire sélectionné dans le groupe constitué du lithium, du magnésium et/ou de l'ytterbium de chaque couche de transport d'électrons est sélectionné de façon à être identique ou différent, et plus préférablement sélectionné de façon à être identique ; dans laquelle le composé matriciel est un composé à base d'oxyde de phosphine.

3. OLED (100) comprenant l'empilement de couches de transport d'électrons (160) selon la revendication 1 ou 2, dans laquelle

- la quantité de l'halogénure de lithium ou du complexe organique de lithium dans une couche de transport d'électrons, préférablement ladite au moins première couche de transport d'électrons (161), est de ≥ 10 %mol à ≤ 95 %mol, préférablement de ≥ 15 %mol à ≤ 90 %mol, et tout aussi préférablement de ≥ 20 %mol à ≤ 80 %mol, relativement à la couche de transport d'électrons correspondante (161) ; et/ou

- la quantité de l'halogénure de lithium ou du complexe organique de lithium dans un empilement de couches de transport d'électrons (160) d'au moins trois couches de transport d'électrons, au moins deux des couches de transport d'électrons, préférablement ladite au moins première couche de transport d'électrons (161) et/ou ladite au moins troisième couche de transport d'électrons (163), est de ≥ 10 %mol à ≤ 95 %mol, préférablement de ≥ 15 %mol à ≤ 90 %mol, et tout aussi préférablement de > 20 %mol à < 80 %mol, relativement à la couche de transport d'électrons correspondante (161/163).

4. OLED (100) comprenant l'empilement de couches de transport d'électrons (160) selon l'une quelconque des revendications précédentes 1 à 3, dans laquelle

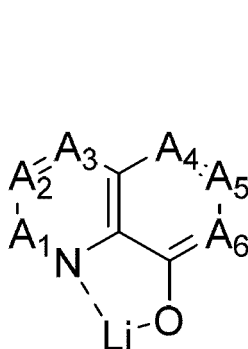
- au moins une couche de transport d'électrons (161) comprend de ≥ 1 % en poids à ≤ 60 % en poids, préférablement de ≥ 2 % en poids à ≤ 55 % en poids, et tout aussi préférablement de ≥ 5 % en poids à < 45 % en poids d'un métal élémentaire sélectionné dans le groupe constitué du lithium, du magnésium et/ou de l'ytterbium ; ou

- au moins deux couches de transport d'électrons (161/163) d'au moins trois couches de transport d'électrons (161/162/163) comprennent de ≥ 1 % en poids à ≤ 60 % en poids, préférablement de ≥ 2 % en poids à ≤ 55 % en poids, et tout aussi préférablement de ≥ 5 % en poids à ≤ 45 % en poids d'un métal élémentaire sélectionné dans le groupe constitué du lithium, du magnésium et/ou de l'ytterbium ;

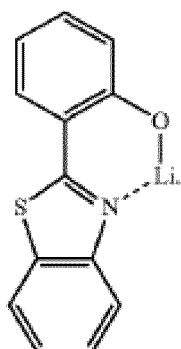
dans laquelle le pourcentage en poids du métal élémentaire sélectionné dans le groupe constitué du lithium, du magnésium et/ou de l'ytterbium est exprimé relativement au poids total de la couche de transport d'électrons correspondante.

5. OLED (100) comprenant l'empilement de couches de transport d'électrons (160) selon l'une quelconque des revendications précédentes 1 à 4, dans laquelle l'halogénure de lithium est sélectionné dans un groupe comprenant LiF, LiCl, LiBr ou LiI, et préférablement LiF, et le ligand organique du complexe organique de lithium est un quinolate, un borate, un phénolate, un pyridinolate ou un ligand de type base de Schiff ;

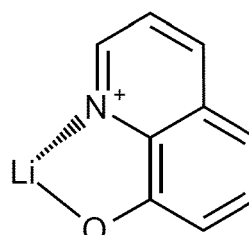
- préférablement, le complexe quinolate de lithium a la formule I, II, ou III ou IV :



(I),



(II),

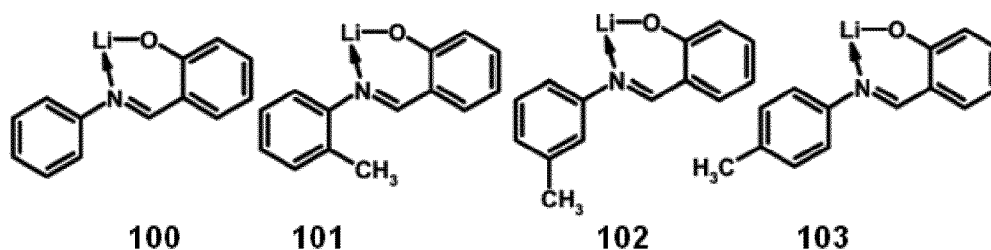


(III)

dans laquelle

les groupes A1 à A6 sont identiques ou sélectionnés indépendamment parmi CH, CR, N, O ;
R est identique ou sélectionné indépendamment parmi un atome d'hydrogène, un atome d'halogène, ou
un groupe alkyle ou aryle ou hétéroaryle comportant 1 à 20 atomes de carbone ; et plus préférablement
les groupes A1 à A6 sont un groupe CH ;

- préférablement, le ligand organique à base de borate est un tétra(1H-pyrazol-1-yl)borate ;
- préférablement, le phénolate est un 2-(pyridin-2-yl)phénolate, un 2-(diphénylphosphoryl)phénolate, un imidazol
phénolate, ou un 2-(pyridin-2-yl)phénolate et plus préférablement le 2-(1-phényl-1H-benzo[d]imidazol-2-
yl)phénolate ;
- préférablement, le pyridinolate est un 2-(diphénylphosphoryl)pyridin-3-olate,
- préférablement la base de Schiff du lithium a la structure 100, 101, 102 ou 103 :



6. OLED (100) comprenant l'empilement de couches de transport d'électrons (160) selon l'une quelconque des re-
vendications précédentes 1 à 5, dans laquelle l'empilement de couches de transport d'électrons comprend au moins
deux couches de transport d'électrons ou au moins trois couches de transport d'électrons, et dans laquelle chaque
couche de transport d'électrons comprend au moins un composé matriciel, le composé matriciel des couches de
transport d'électrons étant sélectionné de façon à être identique ou différent, préférablement identique.
7. OLED (100) comprenant l'empilement de couches de transport d'électrons (160) selon l'une quelconque des re-
vendications précédentes 1 à 6, dans laquelle lesdites au moins deux couches de transport d'électrons (161/162)
ou lesdites au moins trois couches de transport d'électrons (161/162/163) comprennent au moins un composé
matriciel, le composé matriciel des couches de transport d'électrons étant sélectionné de façon à être identique ou
différent, et le composé matriciel étant sélectionné parmi :
 - un composé à base d'anthracène ou un composé à base d'anthracène substitué par un groupe hétéroaryle,
préférablement le 2-(4-(9,10-di(naphtalén-2-yl)anthracène-2-yl)phényl)-1-phényl-1H-benzo[d]imidazole et/ou
la N4,N4''-di(naphtalén-1-yl)-N4,N4''-diphényl[1,1':4',1''-terphényl]-4,4''-diamine ; ou
 - un composé à base d'oxyde de phosphine, préférablement l'oxyde de (3-(dibenzo[c,h]acridin-7-yl)phényl)di-
phénylphosphine, le 3-phényl-3H-benzo[b]dinaphto[2,1-d:1',2'-f]phosphépine-3-oxyde, l'oxyde de bis(4-(an-
thracén-9-yl)phényl)(phényl)phosphine et/ou l'oxyde de phényl-bis(3-(pyrén-1-yl)phényl)phosphine ; ou
 - un composé de phénanthroline substituée, préférablement la 2,4,7,9-tétraphényl-1,10-phénanthroline ou la
2,9-di(biphényl-4-yl)-4,7-diphényl-1,10-phénanthroline ;

dans laquelle au moins un composé matriciel est un composé à base d'oxyde de phosphine.

8. OLED (100) comprenant l'empilement de couches de transport d'électrons (160) selon l'une quelconque des re-
vendications précédentes 1 à 7, dans laquelle les épaisseurs de chaque couche de transport d'électrons, préféra-
blement ladite au moins première couche de transport d'électrons (161) et ladite au moins deuxième couche de
transport d'électrons (162) et/ou ladite au moins troisième couche de transport d'électrons (163), sont identiques
ou chacune indépendamment de $\geq 0,5$ nm à ≤ 95 nm, préférablement de ≥ 3 nm à ≤ 80 nm, encore préférablement
de ≥ 5 nm à ≤ 60 nm, tout aussi préférablement de ≥ 6 nm à ≤ 40 nm, préférablement en outre de ≥ 8 nm à ≤ 20
nm et plus préférablement de ≥ 10 nm à ≤ 18 nm.
9. OLED (100) comprenant l'empilement de couches de transport d'électrons (160) selon l'une quelconque des re-
vendications précédentes 1 à 8, dans laquelle l'empilement de couches de transport d'électrons comporte deux à
quatre couches de transport d'électrons et plus préférablement deux couches de transport d'électrons (162/162)

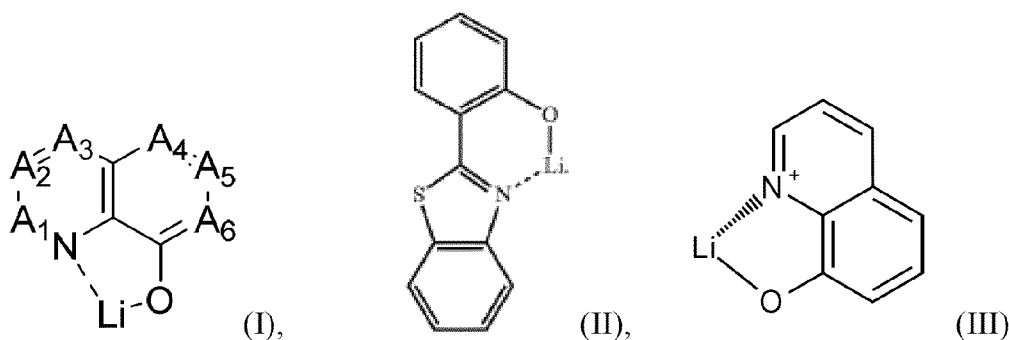
ou trois couches de transport d'électrons (162/162/163) et idéalement deux couches de transport d'électrons (162/162).

10. OLED (100) comprenant l'empilement de couches de transport d'électrons (160) selon l'une quelconque des revendications précédentes 1 à 9, dans laquelle ladite au moins deuxième couche de transport d'électrons (162) est formée directement sur ladite au moins première couche de transport d'électrons (161) et/ou ladite au moins troisième couche de transport d'électrons (163) est formée directement sur ladite au moins deuxième couche de transport d'électrons (162) afin que la deuxième couche de transport d'électrons (162) soit positionnée en sandwich entre la première couche de transport d'électrons (161) et la troisième couche de transport d'électrons (163).

11. OLED (100) comprenant l'empilement de couches de transport d'électrons (160) selon l'une quelconque des revendications précédentes 1 à 10, dans laquelle

- au moins une couche de transport d'électrons (161) ou dans le cas d'au moins trois couches de transport d'électrons (161/162/163) au moins deux couches de transport d'électrons (161/163) comprennent :

a) de ≥ 10 % en poids à ≤ 70 % en poids, préférablement de ≥ 20 % en poids à ≤ 65 % en poids et tout aussi préférablement de ≥ 50 % en poids à ≤ 60 % en poids d'un halogénure de lithium, sélectionné dans le groupe comprenant LiF, LiCl, LiBr or LiI, préférablement LiF, ou d'un complexe organique de lithium, sélectionné dans le groupe comprenant un quinolate de lithium, un borate, un phénolate, un pyridinolate ou un ligand de type base de Schiff ; préférablement d'un complexe de quinolate de lithium ayant la formule I, II ou III :



dans laquelle

- les groupes A1 à A6 sont identiques ou sélectionnés indépendamment parmi CH, CR, N, O ;
 - R est identique ou sélectionné indépendamment parmi un atome d'hydrogène, un atome d'halogène, ou un groupe alkyle ou aryle ou hétéroaryle comportant 1 à 20 atomes de carbone ; et plus préférablement un 8-hydroxyquinolate de lithium ;

b) de ≤ 90 % en poids à ≥ 30 % en poids, préférablement de ≤ 80 % en poids à ≥ 35 % en poids et tout aussi préférablement de ≤ 50 % en poids à ≥ 40 % en poids et tout aussi préférablement de < 50 % en poids à > 40 % en poids d'un composé matriciel constitué de :

- un composé à base d'anthracène ou un composé à base d'anthracène substitué par un groupe hétéroaryle, préférablement le 2-(4-(9,10-di(naphtalén-2-yl)anthracène-2-yl)phényl)-1-phényl-1H-benzo[d]imidazole et/ou la N4,N4''-di(naphtalén-1-yl)-N4,N4''-diphényl[1,1':4',1''-terphényl]-4,4''-diamine ; ou
 - un composé à base d'oxyde de phosphine, préférablement l'oxyde de (3-(dibenzo[c,h]acridin-7-yl)phényl)diphénylphosphine, le 3-phényl-3H-benzo[b]dinaphto[2,1-d:1',2'-f]phosphépine-3-oxyde, l'oxyde de bis(4-(anthracén-9-yl)phényl)(phényl)phosphine et/ou l'oxyde de phényl-bis(3-(pyrén-1-yl)phényl)phosphine ; ou
 - un composé de phénanthroline substituée, préférablement la 2,4,7,9-tétraphényl-1,10-phénanthroline ou la 2,9-di(biphényl-4-yl)-4,7-diphényl-1,10-phénanthroline ; plus préférablement un composé à base d'oxyde de phosphine et idéalement l'oxyde de (3-(dibenzo[c,h]acridin-7-yl)phényl)diphénylphosphine ; et

- au moins une couche de transport d'électrons (162) ou dans le cas d'au moins trois couches de transport d'électrons (161/162/163) au moins deux couches d'électrons (161/163) comprennent :

c) de ≥ 1 % en poids à ≤ 60 % en poids, préférablement de ≥ 2 % en poids à ≤ 55 % en poids et tout aussi préférablement de ≥ 5 % en poids à ≤ 45 % en poids d'un métal élémentaire sélectionné dans le groupe constitué du lithium, du magnésium et/ou de l'ytterbium, plus préférablement d'un métal élémentaire ytterbium ou d'un métal élémentaire magnésium et idéalement d'un métal élémentaire magnésium ;

d) de ≤ 99 % en poids à ≥ 40 % en poids, préférablement de ≤ 98 % en poids à ≥ 45 % en poids et tout aussi préférablement de ≤ 95 % en poids à ≥ 55 % en poids d'un composé matriciel constitué de :

- un composé à base d'anthracène ou un composé à base d'anthracène substitué par un groupe hétéroaryle, préférablement le 2-(4-(9,10-di(naphtalén-2-yl)anthracène-2-yl)phényl)-1-phényl-1H-benzo[d]imidazole et/ou la N4,N4''-di(naphtalén-1-yl)-N4,N4''-diphényl[1,1':4',1''-terphényl]-4,4''-diamine ; ou

- un composé à base d'oxyde de phosphine, préférablement l'oxyde de (3-(dibenzo[c,h]acridin-7-yl)phényl)diphénylphosphine, le 3-phényl-3H-benzo[b]dinaphto[2,1-d:1',2'-f]phosphépène-3-oxyde, l'oxyde de bis(4-(anthracén-9-yl)phényl)(phényl)phosphine et/ou l'oxyde de phényl-bis(3-(pyrén-1-yl)phényl)phosphine ; ou

- un composé de phénanthroline substituée, préférablement la 2,4,7,9-tétraphényl-1,10-phénanthroline ou la 2,9-di(biphényl-4-yl)-4,7-diphényl-1,10-phénanthroline ;

plus préférablement un composé à base d'oxyde de phosphine et idéalement l'oxyde de (3-(dibenzo[c,h]acridin-7-yl)phényl)diphénylphosphine ;

dans laquelle le pourcentage en poids de chaque constituant est exprimé relativement au poids total de la couche de transport d'électrons correspondante,

dans laquelle au moins un composé matriciel est un composé à base d'oxyde de phosphine.

12. OLED (100) comprenant l'empilement de couches de transport d'électrons (160) selon l'une quelconque des revendications précédentes 1 à 11, dans laquelle

- ladite au moins une (161), préférablement lesdites au moins deux (161/163) couches de transport d'électrons contenant le complexe organique de lithium se composent de ≥ 50 % en poids à ≤ 60 % en poids d'un 8-hydroxyquinolate de lithium et de ≤ 50 % en poids à ≥ 40 % en poids d'un oxyde de (3-(dibenzo[c,h]acridin-7-yl)phényl)diphénylphosphine ; et

- ladite au moins une (162), préférablement lesdites au moins deux (161/163) couches de transport d'électrons contenant un métal élémentaire se composent de ≥ 2 % en poids à ≤ 45 % en poids d'un métal élémentaire sélectionné dans le groupe constitué du lithium, du magnésium et/ou de l'ytterbium, plus préférablement d'un métal élémentaire lithium ou d'un métal élémentaire magnésium et idéalement d'un métal élémentaire ytterbium et de ≤ 98 % en poids à ≥ 55 % en poids d'un oxyde de (3-(dibenzo[c,h]acridin-7-yl)phényl)diphénylphosphine.

13. Procédé de fabrication d'une diode électroluminescente organique (100) selon l'une quelconque des revendications 1 à 12, le procédé utilisant :

- un dépôt par évaporation thermique sous vide ; et/ou

- un dépôt par transformation en solution, la transformation étant préférablement sélectionnée parmi le revêtement par centrifugation, la coulée, l'impression, et/ou le revêtement avec un système d'enduction à filière plate.

14. Procédé de fabrication d'une diode électroluminescente organique (100) selon la revendication 13, le procédé utilisant :

- une première ou une première et une quatrième source de dépôt pour libérer le composé matriciel, et

- une deuxième source de dépôt pour libérer un halogénure de lithium ou un complexe organique de lithium, et

- une troisième source de dépôt pour libérer le métal élémentaire ; ou

- au moins une ou deux sources de dépôt pour libérer le composé matriciel, et

- au moins une ou deux sources de dépôt pour libérer un halogénure de lithium ou un complexe organique de lithium, et

le procédé comprenant les étapes de formation de l'empilement de couches de transport d'électrons ; dans lequel

- une première couche de transport d'électrons (161) est formée par libération du composé matriciel à partir

d'au moins une source de dépôt et un halogénure de lithium ou un complexe organique de lithium ou un métal élémentaire est libéré à partir d'une différente source de dépôt ;

- sur la première couche de transport d'électrons (161) est formée une deuxième couche de transport d'électrons (162) par libération du composé matriciel à partir d'au moins une source de dépôt et un halogénure de lithium

ou un complexe organique de lithium ou un métal élémentaire est libéré à partir d'une différente source de dépôt ;

- sur la deuxième couche de transport d'électrons (162) est formée une troisième couche de transport d'électrons (163) par libération du composé matriciel à partir d'au moins une source de dépôt et un halogénure de lithium

ou un complexe organique de lithium ou un métal élémentaire est libéré à partir d'une différente source de

dépôt ; dans lequel

au moins une couche de transport d'électrons comprend un halogénure de lithium ou un complexe organique de lithium et est exempte de métal élémentaire ; et au moins une couche de transport d'électrons comprend

un métal élémentaire et est exempte d'halogénure de lithium ou de complexe organique de lithium.

15. Dispositif comprenant au moins une diode électroluminescente organique selon les revendications 1 à 12.

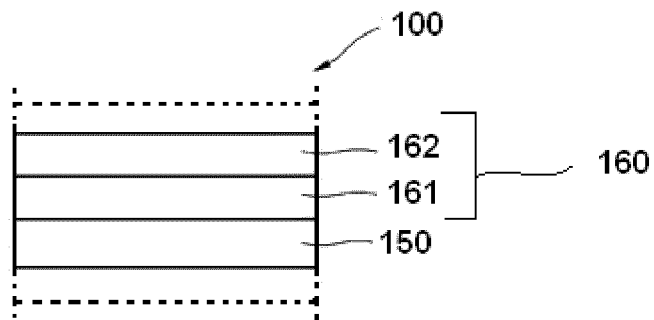


Fig. 1

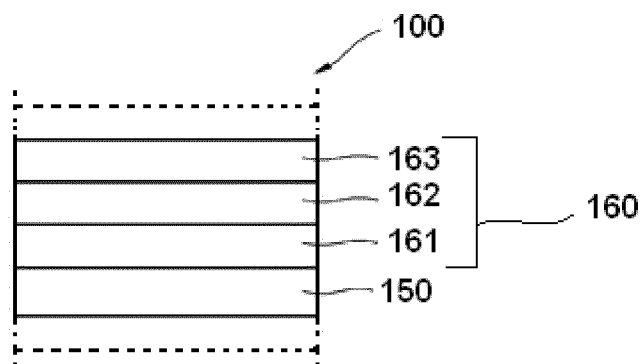


Fig. 2

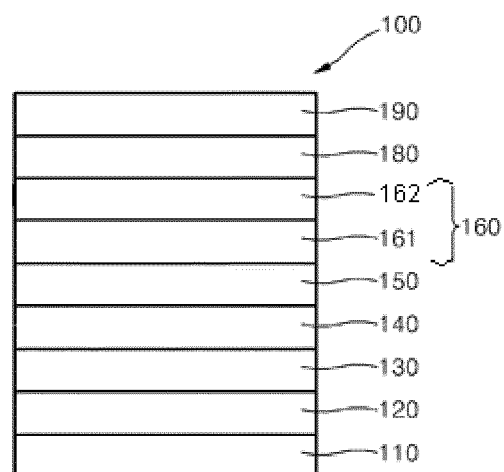


Fig. 3

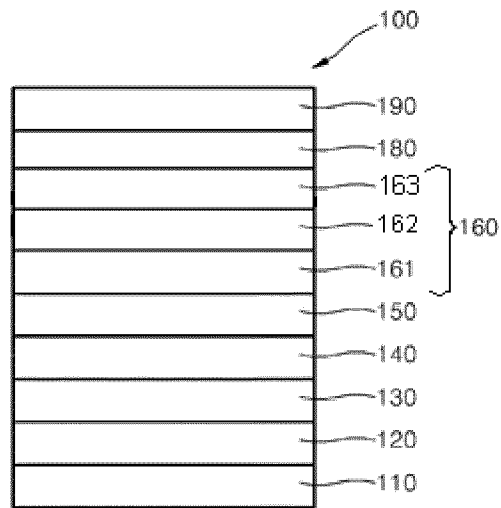


Fig. 4

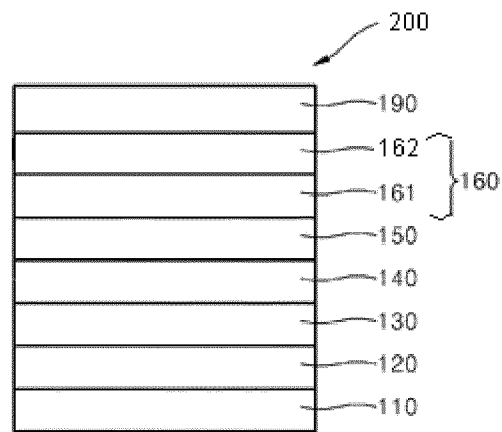


Fig. 5

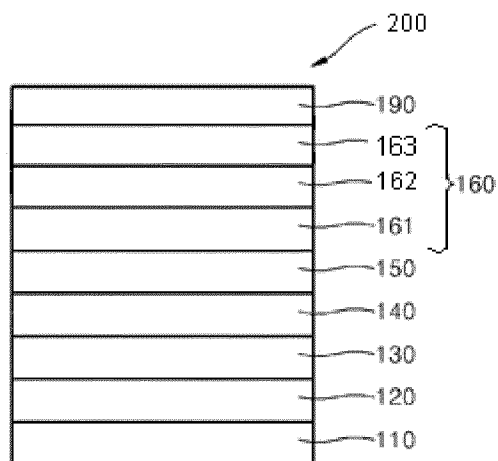


Fig. 6

REFERENCES CITED IN THE DESCRIPTION

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专利名称(译)	有机发光二极管包括含有不同锂化合物和元素金属的电子传输层叠层		
公开(公告)号	EP2999019B1	公开(公告)日	2019-06-12
申请号	EP2014185560	申请日	2014-09-19
[标]申请(专利权)人(译)	诺瓦莱德公开股份有限公司		
申请(专利权)人(译)	Novaled公司GMBH		
当前申请(专利权)人(译)	Novaled公司GMBH		
[标]发明人	WALLIKEWITZ BODO ROTHER CARSTEN		
发明人	WALLIKEWITZ, BODO ROTHER, CARSTEN		
IPC分类号	H01L51/52 H01L51/54		
CPC分类号	H01L51/5076 H01L51/508 H01L51/5088		
其他公开文献	EP2999019A1		
外部链接	Espacenet		

摘要(译)

有机发光二极管技术领域本发明涉及一种有机发光二极管 (100 , OLED) , 其包括发光层 (150) 和至少两个电子传输层 (161,162) 的电子传输层堆叠, 其中第一电子传输层 (161) 和第二电子传输层 (162) 包含至少一种基质化合物, 此外, - 至少第一电子传输层 (161) 包含卤化锂或锂有机络合物; 所述至少第二电子传输层 (162) 包含选自锂, 镁和/或铯的元素金属; 或者 - 至少第一电子传输层 (161) 包含选自锂, 镁和/或铯的元素金属; 所述至少第二电子传输层 (162) 包含卤化锂或锂有机络合物; 其中包含卤化锂或锂有机配合物的电子传输层不含元素金属, 并且包含元素金属的电子传输层不含金属盐和/或金属有机配合物。

