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(54) **Title**: EMISSION LAYERS FOR ORGANIC LIGHT EMITTING DIODES AND METHODS FOR THEIR PREPARATION

(57) **Abstract**: A method for producing the emissive layer for an organic light emitting diode comprises dissolving a luminophore-containing compound and an organic conductive material in a common solvent, depositing a thin film of the resulting solution on a substrate and subsequently heat treating the deposited film at a temperature above 100C but below the emissive layer thermal decomposition temperature. The luminophore-containing compound may be a luminophore or a luminophore precursor that is transformable into a luminophore when heated. For example, the luminophore-containing compound may be a soluble ternary coordination compound containing a neutral ligand. The soluble ternary coordination compound is decomposed by heat treatment to form a luminophore; the neutral ligand is completely eliminated from the thin film by the heat treatment. The method allows emission layers to be obtained that contain an insoluble compound as the luminophore.

EMISSION LAYERS FOR ORGANIC LIGHT EMITTING DIODES AND METHODS FOR THEIR PREPARATION

The present invention relates to emission layers for organic light emitting diodes (OLEDs) and, in particular, to methods of preparing them. The invention also relates to OLEDs incorporating emission layers obtained by the methods.

Luminescent thin films are widely used as emissive layers in such devices as organic thin film transistors, organic solar cells and organic light emitting diodes.

OLEDs, where emissive layers are widely used today, are multilayer heterostructures, consisting at least of an emission layer positioned between a cathode and an anode. When an electric current flows through the structure, electrons and holes are caused to move into the emission layer, resulting in electroluminescence. To facilitate the injection of electrons and holes into the emissive layer in an OLED, additional layers of p- and/or n-type conductivity and electron- and/or hole-blocking layers are used. The emission layer and all the other layers of the OLED heterostructure are thin films of typical thickness in the range of 10-500 nm.

The first reported OLED emission layer to exhibit relatively high electroluminescence efficiency at a low switch-on voltage was reported by C.W. Tang and S.A.Vanslyke in Applied Physics Letters, 51, 1987, 913. Their emission layer was composed of tris(8-hydroxyquinolinato)aluminium (Alq_3) and they used triarylamine as a hole-conductive layer.

In 1990, π-conjugated polymers, in particular poly(phenylenevinylene) (PPV), were successfully used as emissive layers - see J.H. Burroughes, D.D.C. Bradley, A.R. Brown *et al.*, Nature, 347, (1990), 539.

Currently, phosphorescent platinum, iridium, rare earth element compounds, fluorescent compounds of aluminium and zinc, organic small molecules and polymer compounds are used as emission layers.

For thin film deposition onto a substrate, the following techniques are commonly used. For soluble compounds, spin-coating may be used which comprises depositing a solution of the compound on a rotating substrate. In a variant, namely dip-coating, the substrate is lowered repeatedly into a solution of the compound and dried between each dipping. For volatile compounds, physical vapor deposition

(PVD) may be used - see “Luminescence: From Theory to Applications”, Edited by Cees Ronda, 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

A method of producing thin films is described in published Russian patent number RU 2469124. The method comprises forming a thin film coating of a soluble luminophore-containing coordination compound, for example luminophore-containing ternary coordination, deposited from solution onto a substrate, and heat treating the resulting thin film. The luminophore-containing ternary complex decomposes to a luminescent coordination compound and a neutral ligand; the neutral ligand is fully removed from the thin film. The method allows thin films of non-volatile and insoluble chemical compounds to be obtained.

In 1989, a process for producing emissive layers by introducing a luminophore into a layer of conductive material was proposed, thus increasing the quantum yield of electroluminescence - see C.W. Tang, S.A. VanSlyke, C.H. Chen, J. Appl. Phys., 65, (1989), 3610. In the described process, Alq_3 was used as the conductive material, and coumarin 540 was used as the luminophore. Deposition of the emission layer was carried out from the gas phase. The homogeneous mixture of luminophore and conductive material was evaporated *in vacuo* and deposited on a cold substrate. The luminophore was uniformly distributed in the conductive material; thus the doping of the luminophore in the conductive material was carried out.

Further methods for producing the emission layer by introducing of the luminophore into conductive material have been widely used, in which the emissive layer coating is carried out from the gas phase or from solution.

For example, J.W. Levell, J.P. Gunning, P.L. Burn, *et al.*, in Org. Electr., 11, (2010), 1561, described obtaining an emission layer by spin-coating of a dichloromethane solution of a mixture of iridium complex (luminophore) and 4,4 '-N, N'-dicarbazolebiphenyl (CBP, a conductive material) in a ratio of 1:5 onto a substrate of glass coated with a layer of indium-tin oxide.

Currently, some of the most widely used conductive materials for the emission layer are poly-N-vinylcarbazole (PVK), N, N'-bis(3-methylphenyl)-N,N'-bis (phenyl)benzidine (TPD), 4,4'-N,N'-dicarbazolebiphenyl (CBP), poly(9,9-dioctyl fluoren-2,7-diyl) (PFO), polyvinyl butyral (PVB) - see R. Bauer, Organic Electronics, vol.9, Issue 5, (2008) 641-648.

The material for the emission layer in which luminophore is doped must meet the following requirements:

- transparency in the visible spectral range;
- ability to form thin films of high quality (low roughness, typically $\leq$ 5% of film thickness);
- high electron and hole conduction (typically $\geq 10^4$ Sm/cm);
- energies of the frontier orbitals (both HOMO and LUMO) higher than those of the luminophore (for effective excitation energy transfer to the luminophore molecules);
- solubility in organic solvent common with doped luminophore or volatility if luminophore is volatile;
- chemical inertness to the adjacent layers;
- UV stability;
- thermal stability (in the mode of operation of the device local overheating may occur).

The present inventors perceive that there is a need to expand the arsenal of methods for producing the emission layer, in particular based on non-volatile and insoluble luminophores, and to increase its conductivity.

In one aspect, the present invention provides a process for producing an emissive layer, comprising providing a solution comprising a luminophore-containing compound and a conductive material, depositing a thin film from the resulting solution on a substrate and subsequently heat treating the film at a temperature above 100 °C, and below the temperature at which the emission layer becomes unstable.

The term "luminophore-containing compound" is used to mean both a luminophore *per se*, a luminophore precursor capable of being converted into a luminophore, and any compound capable of decomposing to form a luminophore.

By the temperature at which the emission layer becomes unstable is meant the temperature above which chemical and/or physical transformation of the emission layer starts (decomposition, polymerization, isomerization, phase transition, etc.).

The inventors have found that heat treatment of the emission layer at temperatures above 100 °C leads to significant improvement of its optoelectronic properties, in particular, increases in the conductivity and decreases in the switch-on voltage. Without wishing to be bound by theory, this effect may be due, for example, to the formation of new bonds between molecules of the luminophore-containing compound and the conductive material (due to the elimination of water molecules or a neutral ligand from the luminophore-containing compound) during thermal treatment of the emission layer.

The permissible heat treatment temperature range is determined in each case depending on the thermal properties of the selected luminophore-containing compound and conductive material combination.

The upper limit of the heat treatment temperature range is determined by the temperature stability of the emission layer.

The choice of substrate for the emission layer deposition depends on the device for which the emission layer is obtained. For OLEDs, for example, a glass plate or polymer film with a deposited anode thin film, and possibly additional conductive layers, may be used as a substrate.

Deposition of a thin film on a substrate can be carried out by any suitable method.

As the luminophore-containing compound in the inventive process, a soluble luminophore itself may be used. Alternatively, a soluble compound which transforms into a luminophore when heated may be used, in particular, a soluble luminophore-containing ternary coordination compound (mixed-ligand complex (MLC)), which is decomposed by heat treatment into the luminophore and a neutral ligand, the neutral ligand being completely removed from the thin film during the heat treatment decomposition step. Thus, the temperature at which removal of the neutral ligand from the MLC occurs should be lower than the temperature of luminophore thermolysis.

Depending on the composition of the luminophore-containing MLC, the ligand removal temperature may be equal to the temperature of the MLC decomposition to the luminophore and the neutral ligand, or the ligand removal temperature may be the temperature of evaporation of the neutral ligand. In either case, by "ligand removal temperature" is meant the temperature at which the complete removal occurs of the neutral ligand from the luminophore-containing MLC.

When a soluble luminophore-containing MLC is used as the luminophore-containing compound, thermal treatment of the emission layer is carried out at the temperature below the stability of the emission layer, but higher than the ligand removal temperature. The neutral ligand and the conductive material are selected so that the neutral ligand, after removal from the MLC, does not interact with the conductive material.

For the purposes of the present invention, the conductive material must have, besides all the previously mentioned properties (high electron and hole conductivity, solubility, film forming properties, transparency and corresponding energy of the frontier orbitals), thermal stability at temperatures above 100 °C. Also, if a luminophore-containing MLC is used as the luminophore-containing compound, the conductive material must possess thermal stability to a temperature at least as great as the neutral ligand removal temperature. Furthermore, the conductive material must be soluble in at least one solvent that also dissolves the luminophore-containing compound.

The present invention allows improvements not only in the characteristics of the emission layer, but also allows emission layers to be produced that are based on insoluble and non-volatile luminophores.

Hence, the invention is able to extend the arsenal of materials for organic light emitting diodes.

Organic light-emitting diodes may be obtained, in which the emission layer is made by the inventive process.

The resulting OLED heterostructure is a multilayer structure consisting of a substrate with a transparent anode layer placed thereon, on which an emission layer is deposited by the inventive method, and a cathode. To improve OLED performance, additional layers of electron and/or hole-conducting and electron- and/or hole-blocking layers may be used.

The invention will now be described by way of example only and without limitation by reference to the drawings, in which:

Figure 1 is a cross-sectional side view of a first step in the manufacture of an OLED showing an anode layer deposited on a substrate;

Figure 2 is a cross-sectional side view showing the partially formed OLED structure of Figure 1 after deposition of a hole-transporting layer;

Figure 3 is a cross-sectional side view showing the partially formed OLED structure of Figure 2 after deposition of an emission layer precursor;

Figure 4 is a cross-sectional side view showing the partially formed OLED structure of Figure 3 after conversion of the emission layer precursor to the final form of the emission layer;

Figure 5 is a cross-sectional side view showing a partially formed OLED structure of Figure 4 after deposition of a blocking layer and/or cathode layer, and

Figure 6 is a cross-sectional side view showing the OLED structure of Figure 5 after deposition of a further substrate layer (encapsulation).

Figures 1 to 6 illustrate schematically a sequence of steps for manufacturing OLEDs in accordance with the present invention.

Figure 1 is a cross-sectional side view of a first manufacturing step, showing an anode layer 102 deposited on a substrate layer 101.

The substrate layer 101 may be made from any material capable of supporting the conductive coating of the anode layer 102 and may be flexible or rigid. Examples include, but are not limited to, plastic, glass, quartz, plastic films, metals, ceramics, polymers or the like. Non-limiting examples of flexible plastic film and plastic include a film or sheet of polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyethersulfone (PES), polyetherimide, polyetheretherketone, polyphenylene sulfide, polyarylate, polyimide, polycarbonate (PC), cellulose triacetate (TAC), and cellulose acetate-propionate. Additionally, the substrate material 101 is transparent or otherwise light transmissive so that the light generated from the OLED material may pass through the device and be visible.

The anode layer 102 may be formed by optionally coating the substrate with a transparent and conductive coating material. For example, and not for limitation, suitable transparent and conductive coating materials for the anode may include indium-tin oxide (ITO), indium-zinc oxide (IZO), and other tin oxides such as, but not limited to, aluminium- or indium-doped zinc oxide, magnesium-indium oxide, nickel-tungsten oxide, metal nitrides, such as but not limited to gallium nitride, and metal selenides, such as but not limited to zinc selenide, and metal sulfides, such as but not limited to zinc sulfide.

ITO-covered glass substrates are commercially available.

Figure 2 is a cross-sectional side view showing the partially formed OLED structure after deposition of a hole-transporting layer 103 on top of the anode layer 102.

The hole-transporting material may include amines, such as but not limited to aromatic tertiary amines. The aromatic tertiary amine may be an arylamine, such as but not limited to a monoarylamine, diarylamine, triarylamine, or a polymeric arylamine. Other polymeric hole-transporting materials include poly(N-vinylcarbazole) (PVK), polythiophenes, polypyrrole, polyaniline, and copolymers such as poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate), often abbreviated to PEDOT:PSS.

Figure 3 is a cross-sectional side view showing the partially formed OLED structure after deposition of emission layer precursor layer 104 on top of hole-transporting layer 103.

Emission layer precursor layer 104 is deposited on the hole-transporting layer 103 by spin-coating a solution of the emission layer precursor mixed with the conducting material. The emission layer precursor and the conducting material are soluble in a common solvent used for the preparation of the spin-coating solution.

Figure 4 is a cross-sectional side view showing the partially formed OLED structure of Figure 3 after heat treatment to convert the emission layer precursor to the emission layer 105.

The partial OLED structure illustrated in Figure 3 is subjected to heat treatment at a temperature of 100°C or higher, the upper limit of the heat treatment temperature being lower than the temperature at which the emission layer is thermally unstable. That is to say, the upper limit of the heat treatment temperature is lower than the temperature at which the luminophore and the conducting material are thermally unstable. The heat treatment may be carried out under reduced pressure and for a duration sufficient to effect full conversion of the emission layer precursor to the emission layer proper. Alternatively, or in addition, the heat treatment may be carried out under an inert atmosphere. In certain circumstances, the heat treatment may be carried out in air. The choice of conditions for the treatment will depend upon the material(s) selected for the luminophore and the conducting material.

Figure 5 is a cross-sectional side view showing the partially formed OLED structure after deposition of a hole-blocking layer 106 on the emission layer 105 and deposition of a cathode layer 107 on the hole-blocking layer 106.

Most organic electroluminescent materials favor injection and transport of holes rather than electrons. Thus, electron-hole recombination tends to occur near the cathode, which can lead to quenching of the excitons produced. In order to prevent the produced excitons or holes from approaching the cathode, a hole-blocking layer is deposited on the emission layer 105. Commonly used hole-blocking materials include tris(8-hydroxyquinolinato)aluminium (Alq3), bathocuproine (BCP), and 3-(4-biphenyl)-4-phenyl-5-tert-butyl-phenyl-1,2,4-triazole (TAZ). Some hole-blocking materials also function as electron-transporting materials layer and hole blocking layer.

So, as an alternative, an electron transport layer may be formed on top of the emission layer 105 prior to depositing the cathode layer. The electron transport layer may be formed of any material known to be useful for this purpose. Such materials help to inject and transport electrons, exhibit high levels of performance, and are readily applied in the form of thin films, for example by spin-coating.

A cathode layer 107 is then deposited on the hole-blocking layer 106. The cathode may be transparent or otherwise light transmissive, opaque, or reflective and can comprise almost any conductive material. Suitable cathode materials have good film-forming properties to ensure good contact with the underlying organic layer, promote electron injection at low voltage, and have good stability. Useful cathode materials often comprise a low work function (<4.0 eV) are metals or metal alloys.

Figure 6 is a cross-sectional side view showing the OLED structure after deposition of a further substrate layer 108.

As indicated above for substrate layer 101, substrate layer 108 may be made from any material capable of supporting the underlying layers, particularly the cathode layer 107, and may be flexible or rigid. Examples include, but are not limited to, plastic, glass, quartz, plastic films, metals, ceramics, polymers or the like. Non-limiting examples of flexible plastic film and plastic include a film or sheet of polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyethersulfone (PES), polyetherimide, polyetheretherketone, polyphenylene sulfide, polyarylate, polyimide, polycarbonate (PC), cellulose triacetate (TAC), and cellulose acetate-propionate. Additionally, the substrate layer 108 may be transparent or otherwise light transmissive, opaque or reflective.

In a further step, not shown, the OLED structure of Figure 6 may be encapsulated to prevent ingress of oxygen and moisture into the OLED structure. Encapsulation also serves to fix the connecting leads for the anode and cathode so that flexure of the leads does not perturb the OLED layers. Typically, an epoxy resin is used as the encapsulant, which may be an epoxy resin that is curable by UV irradiation.

For encapsulation of OLED structures formed on glass substrates, a 'frit'-glass material may be applied at the edge of the glass substrates.

Alternatively, in OLED structures that use flexible substrates, a flexible plastic encapsulant can be used.

Examples

The present invention is further described by reference to the examples below, which are illustrative only and do not in any way limit the scope of the invention.

Testing of the emissive layers was carried out in all of the following examples by inserting them into an OLED structure. The emission layer was deposited, as described above in relation to Figure 4, on a glass substrate (101) covered successively with a thin film anode (indium-tin oxide, ITO (102)) and a thin film of a hole-conducting layer (103). On the top of the emission layer, a thin film of a hole-blocking layer (106) and the cathode (aluminium (107)) were deposited.

As the hole-conducting layer (103) poly(3,4-ethylenedioxy thiophene)poly(styrenesulfonate) (PEDOT:PSS) was used in each example.

As hole-blocking layers, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was used in Example 4, whilst 3-(4-biphenyl)-4-phenyl-5-tert-butyl-phenyl-1,2,4-triazole (TAZ) was used in Examples 1 to 3, 5 and 6.

The choice of hole-blocking layer material was determined by the energy of the highest occupied molecular orbital (HOMO) of the luminophore and hole-blocking material.

For the OLED devices thus obtained, turn-on voltage and current-voltage characteristic in the range of 0-30V were measured. In Table 1 below, current-voltage values at 10 Volts are given.

Example 1. Emission layer - TPD, doped with Tb(pobz)$_3$ (without heat treatment, reference sample)

4 mg of terbium phenoxybenzoate (Tb(pobz)$_3$) as the luminophore-containing compound and 4 mg of N, N'-bis(3-methylphenyl)-N,N'-bis (phenyl)benzidine (TPD) as the conducting material were dissolved in 0.2 ml of a mixture of ethanol and benzene (1:1 by volume). A thin film of the resulting solution was deposited on the substrate by spin-coating (coated on the substrate at a speed of 4500 rpm for 30 seconds). According to analysis by atomic force microscopy (AFM), the resulting emission layer was homogeneous with a roughness of 4.2 nm and a thickness of 100 nm (according to profilometry).

The measurement results shown in Table 1 indicate that the switch-on voltage (U_{on}) of the obtained device was equal to 7V, and the current at a voltage of 10V (I_{10V}) was equal to 0.05 mA/cm^2.

Example 2. Emission layer - TPD, doped with Tb(pobz)$_3$

The emission layer prepared as in Example 1 except that, after deposition onto the substrate, heat treatment was carried out at temperature of 100 °C for 1 hour *in vacuo* (0.01 mmHg).

The resulting emission layer was homogeneous; its roughness was 4.4 nm, and its thickness was 100 nm.

Turn-on voltage of the obtained device was 4V, and the current at a voltage of 10V was 0.2 mA cm^{-2}.

Example 3. Emission layer - TPD, doped with Tb(pobz)$_3$ (obtained from the mixed ligand complex, Tb(pobz)$_3$(Hacim)$_2$)

As the luminophore-containing compound, the ternary complex Tb(pobz)$_3$(Hacim)$_2$ (Hacim = acetylacetone imine) was used, which was prepared as follows.

A suspension of 0.798 g (1 mmol) of $Tb(pobz)_3$ was heated in a solution of 0.198 g (2 mmol) Hacim in a mixture of ethanol and benzene (1:1 by volume) under reflux until complete dissolution. The resulting solution was evaporated using a rotary evaporator and the resulting glassy product was crystallized under vacuum at 60 °C to give ~0.9 g of the ternary complex $Tb(pobz)_3(Hacim)_2$. Its composition was determined by elemental analysis, IR and Raman spectroscopy.

A solution containing 5 mg of $Tb(pobz)_3(Hacim)_2$ as the luminophore-containing compound and 4 mg of TPD as the organic conducting material was prepared in 0.2 ml of solvent (ethanol:benzene = 1:1).

A thin film of the resulting solution was deposited onto a substrate and heat treated as in Example 2.

The resulting film was characterized by IR and Raman spectroscopy, luminescence spectroscopy, atomic force microscopy, scanning electron microscopy.

It was shown that the composition of the film corresponded to TPD doped with $Tb(pobz)_3$; the neutral ligand Hacim was completely removed from the film.

The film thickness was ~100 nm; the film had high homogeneity and low surface roughness (~4 nm).

The turn-on voltage of the obtained device was 3V, and the current at a voltage of 10V was 0.7 mA cm^{-2}.

Example 4. Emission layer - PVK, doped with $Tb(pobz)_3$ (obtained from the mixed ligand complex $Tb(pobz)_3(Hacim)_2$)

Preparation of the emissive layer and the thermal treatment was carried out in the same manner as Example 3, but using poly(N- vinylcarbazole) (PVK) as the organic conductive material.

The composition of the deposited and heat treated film corresponded to PVK doped with $Tb(pobz)_3$; the neutral ligand Hacim was completely removed from the film.

The film thickness was ~100 nm; the film had high homogeneity and low surface roughness (~4 nm).

The turn-on voltage of the obtained device was 5V, and the current at a voltage of 10 V was 0.8 mA cm^{-2}.

Example 5. Emission layer - TPD, doped with $Tb(pobz)_3$ (obtained from the mixed ligand complex $Tb(pobz)_3(MG)(H_2O)_2$)

A suspension of 0.798 g (1 mmol) $Tb(pobz)_3$ was heated in 30 ml of monoglyme (MG, acts as a ligand and as a solvent) at reflux until complete dissolution. The resulting solution was evaporated using a rotary evaporator. The resulting glassy product was crystallized under vacuum at 60 °C to give ~ 0.8 g of the ternary complex $Tb(pobz)_3(MG)(H_2O)_2$.

A solution containing 5 mg of $Tb(pobz)_3(MG)(H_2O)_2$ as the luminophore-containing compound and 4 mg of TPD as the organic conducting material was prepared in 0.2 ml of solvent (ethanol:benzene = 1:1).

A thin film of the resulting solution was spin-coated onto a substrate (dropped on the substrate at a speed of 4500 rpm for 30 seconds). Heat treatment was conducted at a temperature of 150 °C for 3 hours *in vacuo* (0.01 mm Hg).

The thickness of spin-coated and heat treated film was ~100 nm; the film had high homogeneity and a low surface roughness (~4 nm).

The turn-on voltage of the obtained device was 4V, and the current at a voltage of 10 V was 5 mA cm^{-2}.

Example 6. Emission layer - TPD, doped with $Eu(naph)_3$ (obtained from the mixed ligand complex $Eu(naph)_3(MG)_2$)

A suspension of 0.569 g (1 mmol) europium naphthoate ($Eu(naph)_3$) was heated in a solution of 1.736 g (19.3 mmol) monoglyme in 20 ml of ethanol-benzene (1:1 by volume) at reflux for 3 hours. The solution obtained after separation by filtration from undissolved solid (~5 wt. % of the original weight) was slowly evaporated in air. The resulting white microcrystalline product was air dried to give ~0.6 g of the ternary complex $Eu(naph)_3(MG)_2$.

A solution containing 5 mg of $Eu(naph)_3(MG)_2$ as the luminophore-containing compound and 4 mg of TPD as the organic conducting material was prepared in 0.2 ml of solvent (ethanol:benzene = 1:1).

A thin film of the resulting solution was deposited onto a substrate and was subjected to heat treatment as in Example 5.

The turn-on voltage of the obtained device was 6V, and the current at a voltage of 10V was 2.5 mA cm^{-2}.

Table 1 below lists the turn-on voltage, U_{on}, and the current at voltage 10V for each of Examples 1 to 6. Note that Example 1 is a reference example because the emission layer of TPD doped with $Tb(pobz)_3$ was not subjected to any heat treatment.

From Table 1, it can be seen that the emission layers that underwent heat treatment according to the present invention (Examples 2 to 6) showed in an increase in the conductivity of the emission layer, causing an increase in brightness and energy efficiency of electroluminescence in the final OLED device.

Furthermore, the method of the invention allows emission layers to be obtained that contain an insoluble chemical compound as the luminophore because certain insoluble luminophores based on complexes of terbium or europium can be rendered soluble by complexing them with neutral ligands.

Mixed ligand coordination compounds can be formed using other rare earth metals, but terbium and europium are preferred in electroluminescent applications.

Table 1. OLED characteristics

Example	U_{on}, V	I_{10V}, mA/cm^2	Luminophore-containing compound	OLED structure*
1	7	0.05	Tb(pobz)$_3$	ITO/PEDOT:PSS/Tb(pobz)$_3$:TPD/TAZ/Al
2	4	0.2	Tb(pobz)$_3$	ITO/PEDOT:PSS/Tb(pobz)$_3$:TPD/TAZ/Al
3	3	1.2	Tb(pobz)$_3$(Hacim)$_2$	ITO/PEDOT:PSS/Tb(pobz)$_3$:TPD/TAZ/Al
4	5	0.8	Tb(pobz)$_3$(Hacim)$_2$	ITO/PEDOT:PSS/Tb(pobz)$_3$:PVK/BCP/Al
5	4	5	Tb(pobz)$_3$(MG)(H$_2$O)$_2$	ITO/PEDOT:PSS/Tb(pobz)$_3$:TPD/TAZ/Al
6	6	2,5	Eu(naph)$_3$(MG)$_2$	ITO/PEDOT:PSS/Eu(naph)$_3$:TPD/TAZ/Al

*Anode/hole transporting layer/emission layer/hole-blocking layer/cathode

CLAIMS

1. A method for producing a luminescent thin film, comprising:

dissolving a luminophore-containing compound and an organic conductive material in a solvent;

depositing a thin film of the resulting solution on a substrate, and

subjecting the deposited thin film to heat treatment at a temperature above 100 °C and below the temperature at which the emission layer becomes thermally unstable.

2. A method according to claim 1 wherein the luminophore-containing compound is a luminophore, or a luminophore precursor that is transformable into a luminophore, or a compound capable of decomposing to form a luminophore.

3. A method according to claim 1 or claim 2 wherein the luminophore-containing compound is a soluble luminophore-containing ternary coordination compound containing a neutral ligand, said luminophore-containing ternary coordination compound, decomposing during the heat treatment to form a luminophore, said heat treatment being conducted at a temperature above the neutral ligand removal temperature such that the neutral ligand is completely eliminated from the thin film during the heat treatment.

4. The method according to claim 3 wherein the soluble luminophore-containing compound ternary coordination compound is a coordination compound of terbium or europium.

5. The method according to claim 3 wherein the soluble luminophore-containing compound ternary coordination compound is selected from terbium phenoxybenzoate with acetylacetone imine, terbium phenoxybenzoate with monoglyme or europium naphthoate with monoglyme.

6. A method according to any preceding claim wherein the organic conductive material is selected from poly-N-vinylcarbazole (PVK), N, N'-bis(3-methylphenyl)-N,N'-bis(phenyl)benzidine (TPD), 4,4′-bis(N-carbazolyl)-2,2′-biphenyl (CBP), poly(9,9-dioctyl fluoren-2,7-diyl) (PFO), polyvinyl butyral (PVB).

7. A method of manufacturing an organic light emitting diode, comprising:

depositing an emission layer in the form of a luminescent thin film produced according to any one of claims 1 to 6 on a transparent anode layer, and

depositing a cathode layer on the emission layer.

8. A method of manufacturing an organic light emitting diode according to claim 7, comprising depositing the anode layer on a supporting substrate prior to depositing the emission layer.

9. A method of manufacturing an organic light emitting diode according to claim 7, comprising depositing the emission layer on the anode layer of a pre-prepared substrate-anode layer subassembly.

10. A method of manufacturing an organic light emitting diode according to any one of claims 7 to 9 comprising depositing a hole-conducting layer on the anode layer and depositing the emission layer on the hole-conducting layer.

11. A method of manufacturing an organic light emitting diode according to claim 10 wherein the hole-conducting layer comprises at least one of an amine, including an aromatic tertiary amine, poly(N- vinylcarbazole) (PVK), a polythiophene, a polypyrrole, a polyaniline, and poly(3,4-ethylenedioxythiophene)/poly(4-styrene sulfonate) (PEDOT:PSS).

12. A method of manufacturing an organic light emitting diode according to any one of claims 7 to 11 comprising depositing a hole-blocking layer on the emission layer prior to depositing the cathode layer.

13. A method of manufacturing an organic light emitting diode according to claim 12 wherein the hole-blocking layer comprises at least one of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), 3-(4-biphenyl)-4-phenyl-5-tert-butyl-phenyl-1,2,4-triazole (TAZ), tris(8-hydroxyquinolinato)aluminium (Alq3), bathocuproine (BCP), and 3-(4-biphenyl)-4-phenyl-5-tert-butyl-phenyl-1,2,4-triazole (TAZ).

14. A method of manufacturing an organic light emitting diode according to any one of claims 7 to 11 comprising depositing an electron-conducting layer on the emission layer prior to depositing the cathode layer.

15. A method of manufacturing an organic light emitting diode according to claim 14 wherein the electron-conducting layer comprises a metal chelated oxinoid compound.

16. A method of manufacturing an organic light emitting diode according to any one of claims 7 to 15 comprising providing a substrate layer on the cathode layer.

17. A method of manufacturing an organic light emitting diode according to claim 16 wherein at least one of the substrate layers comprises plastic, glass, quartz, plastic film, metals, ceramic, or polymeric material.

18. A method of manufacturing an organic light emitting diode according to claim 17 wherein at least one of the substrate layers comprises a plastic layer of polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyethersulfone (PES), polyetherimide, polyetheretherketone, polyphenylene sulfide, polyarylate, polyimide, polycarbonate (PC), cellulose triacetate (TAC), or cellulose acetate-propionate.

19. A method of manufacturing an organic light emitting diode according to any one of claims 16 to 18, further comprising encapsulating the organic light emitting diode in an encapsulant to prevent ingress of air or moisture.

20. A luminescent thin film prepared by the method of any one of claims 1 to 6.

21. An organic light emitting diode prepared by the method of any one of claims 7 to 19.

22. A method of producing an electroluminescent thin film substantially as described herein.

23. A method of manufacturing an organic light emitting diode substantially as described herein.

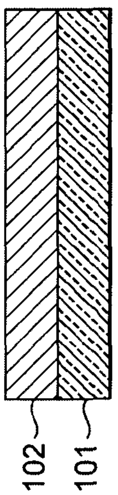

FIG. 1

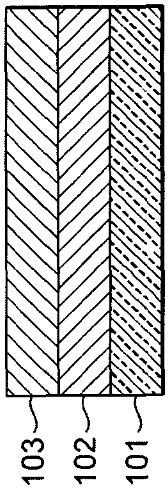

FIG. 2

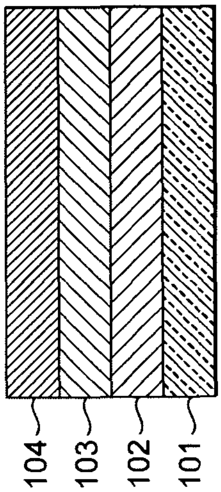

FIG. 3

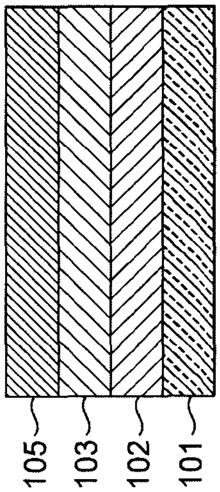

FIG. 4

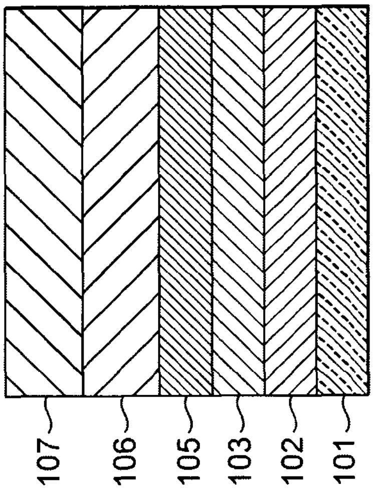

FIG. 5

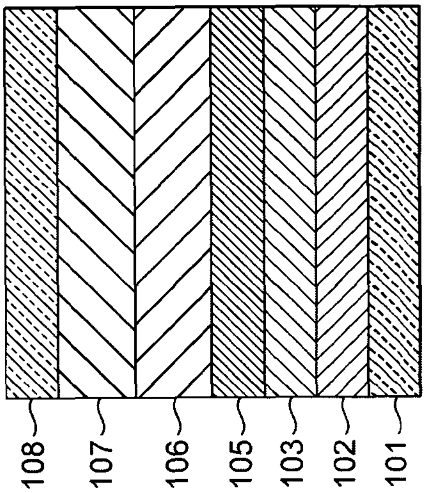

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/RU2014/000435

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L51/54
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/275818 A1 (YERSIN HARTMUT [DE] ET AL) 10 November 2011 (2011-11-10)	1,2, 6-15,17, 20-23
Y	paragraph [0122] - paragraph [0129] paragraphs [0173], [0177], [0179] - paragraph [0184] ----- -/--	16-19

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

☒ See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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Date of the actual completion of the international search 2 February 2015	Date of mailing of the international search report 11/02/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Pusch, Catharina

INTERNATIONAL SEARCH REPORT

International application No
PCT/RU2014/000435

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	US 2013/099658 A1 (TSAI CHIH-HUNG [TW] ET AL) 25 April 2013 (2013-04-25) paragraphs [0018], [0019]; figure 1D -----	16-19
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Information on patent family members

International application No

PCT/RU2014/000435

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