



(11) **EP 1 499 624 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:  
**06.01.2016 Bulletin 2016/01**

(51) Int Cl.:  
**C07D 471/04<sup>(2006.01)</sup> C07D 213/38<sup>(2006.01)</sup>**  
**H01L 51/30<sup>(2006.01)</sup>**

(21) Application number: **03714623.0**

(86) International application number:  
**PCT/CN2003/000221**

(22) Date of filing: **27.03.2003**

(87) International publication number:  
**WO 2003/093283 (13.11.2003 Gazette 2003/46)**

(54) **ELECTROLUMINESCENT MATERIALS**

ELEKTROLUMINESZIERENDE MATERIALIEN

MATERIAUX ELECTROLUMINESCENTS

(84) Designated Contracting States:  
**DE FR GB**

(30) Priority: **01.05.2002 US 137272**

(43) Date of publication of application:  
**26.01.2005 Bulletin 2005/04**

(73) Proprietor: **The University of Hong Kong  
Hong Kong (CN)**

(72) Inventor: **CHE, Chiming  
Parkway Court,  
4 Park Road,  
Hong Kong (CN)**

(74) Representative: **Ahner, Philippe et al  
BREVALEX  
95, rue d'Amsterdam  
75378 Paris Cedex 8 (FR)**

(56) References cited:

- **CAPDEVIELLE ET AL:** "Electroactive polymers exchanging transition metal ions; synthesis of new monomers and polymers based on 6,6'-bis (2- hydroxyphenyl)bipyridine complexes" **NEW JOURNAL OF CHEMISTRY, CNRS-GAUTHIER-VILLARS, MONTROUGE, FR, vol. 18, no. 4, April 1994 (1994-04), pages 519-524, XP002121132 ISSN: 1144-0546**
- **LIN Y-Y ET AL:** "Structural, photophysical and electrophosphorescent properties of platinum(II) complexes supported by etradentate N2O2 chelates" **CHEMISTRY - A EUROPEAN JOURNAL, VCH PUBLISHERS, US, vol. 9, no. 6, 2003, pages 1263-1272, XP002980393 ISSN: 0947-6539**
- **CHEMICAL ABSTRACTS, 2001, Columbus, Ohio, US; abstract no. 135:152935, TSUKADAN. ETAL.:** 'Synthesis and crystal structure of tristed dinuclear eta3-allylpalladium complexes containing tetradentate nitrogen ligands' **XP008065241**
- **CHEMICAL ABSTRACTS, 2000, Columbus, Ohio, US; abstract no. 134:50644, MAMULA OLIMPIA ET AL.:** 'Predetermined chirality at metal centers of various coordination geometries: a chiral cleft ligand for tetrahedral (T-4), square-planar(SP-4), trigonal-bipyramide(TB-5), square-pyramidal (SPY-5) and octahedral(OC-6) complexes' **XP008065255**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**EP 1 499 624 B1**

**Description****Field of the Invention**

5 [0001] The present invention relates to light-emitting materials, which can be deposited as a thin layer by vacuum deposition, and which can be used as effective dopants in organic light-emitting devices (OLEDs).

**Background of the Invention**

10 [0002] The progress of light-emitting diode (LED) over the past two decades has primarily focused on inorganic types because early development in organic light-emitting devices (OLEDs) resulted in poor fabrication and packaging, and short lifetimes. Today, gallium arsenide-based LEDs in the market are commonly available with efficiencies in some spectral regions exceeding conventional filtered fluorescent lamps. However, in the development of light-emitting materials for display technology, inorganic semi-conductor materials are not compatible for large-area assembled displays.

15 [0003] Pope *et al.* at New York University demonstrated organic electroluminescence in the 1960s based on anthracene materials (J. Chem. Phys. 38, 2042, (1963)). Much progress have been made since the discovery of the tris(8-hydroxyquinolato)aluminum (Alq<sub>3</sub>) based thin film device by C. W. Tang *et al.* at Kodak (Appl. Phys. Lett. 51, 913, (1987)). These contributed largely to the continuous discovery of new and improved electroluminescent materials. From small fluorescent molecules to conjugated polymers, many OLEDs have been shown to exhibit sufficient brightness, remarkable efficiencies, good operating lifetimes and desirable ranges of color emission.

20 [0004] Organic light-emitting devices containing metal complexes are of particular interest because of their unusual chemical and electronic properties. Some compounds bearing heavy metals exhibit potential advantages for OLEDs owing to their high internal quantum efficiencies. Conventionally, fluorescent materials are employed as dopants in emissive hosts. Singlet excitons (maximum theoretical internal quantum efficiency = 25 %) are formed after recombination of hole and electron to emit electroluminescence via dipole-dipole interaction through Förster mechanism (US Patent 6,310,360). Whereas, for heavy metal complexes, strong spin-orbit coupling can lead to singlet-triplet state mixing, which can result in high-efficiency electrophosphorescence in OLEDs (theoretical internal quantum efficiency up to 100 %) (Nature, 395, 151, (1998); Synthetic Metals, 93, 245, (1998); Appl. Phys Lett. 77, 904, (2000)).

25 [0005] However, some phosphorescent materials have intrinsic disadvantages, such as saturation of emission sites due to excessively long lifetimes as well as triplet-triplet annihilation and concentration quenching arising from strong intermolecular interactions at high doping levels (Phys. Rev. B. 60, 14422, (1999)).

30 [0006] For example, quadridentate azomethine-zinc complexes have been used as blue light emitters in organic light-emitting devices, which exhibit maximum luminance of approximately 1000 cd/m<sup>2</sup> only (Jpn. J. Appl. Phys., 32, L511 (1993); US Patent 5,432,014).

35 [0007] Azomethine-aluminum/gallium complexes have been employed in OLEDs as emissive materials. The current density of the device containing azomethine-gallium complex is 1 mA/cm<sup>2</sup> at 10 V and the electroluminescence is greenish blue (US Patent 6,316,130).

40 [0008] The Article by P.Capdevielle *et al.* "Electroactive polymers exchanging transition metal ions; synthesis of new monomers and polymers based on 6,6'-bis(2-hydroxyethyl)bipyridine complexes", New J. Chem. 1994, 18, 519 - 524, discloses Nickel or Copper complexes of a 6,6'-bis(2-hydroxyethyl)bipyridine ligand (LH2) and the preparation of film layers from polymers of said complexes without any host material. Said document remains silent with respect to the use of these polymeric layers in any kind of light-emitting device for producing electroluminescence.

45 [0009] It is therefore desirable to develop emissive dopant materials that can permit efficient energy transfer between the host and dopant in OLEDs, while causing little or no self-quenching even at sufficiently high doping concentrations.

**Summary of the Invention**

[0010] Examples of objects of the present invention in embodiments thereof include:

50 The main objective of this invention is to prepare organic light-emitting devices (OLEDs) doped with new light-emitting materials. The devices exhibit low turn-on voltages and high luminance and efficiencies

[0011] Said objective is achieved, according to the invention by the organic light-emitting device of Claim 1.

55 [0012] Preferred embodiment of the light-emitting device according to the invention are disclosed in dependent claims 2 to 5.

[0013] An object of the present invention is to provide thermally stable, moisture-resistant metal-chelated materials that can be deposited as a thin layer of known thickness by a vapor deposition process.

[0014] Further, the present invention concerns the design of high luminous dopants, which can be used at low con-

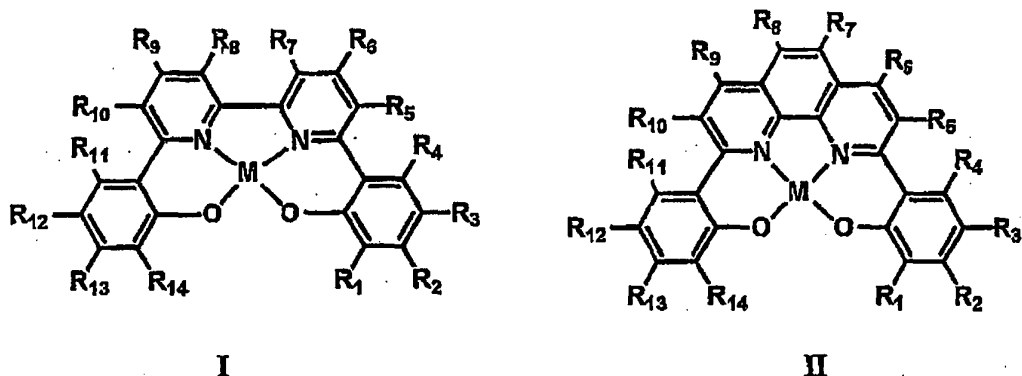
centration levels in light-emitting devices.

[0015] Light-emitting materials derived from quadridentate ONNO-type ligands, and a Group 10 metal (including platinum) were prepared as illustrated by formula I and II:

5

10

15



20

wherein M represents Group 10 metal (including platinum) and R<sub>1</sub>-R<sub>14</sub> are each independently selected from the group consisting of hydrogen; halogen; alkyl; substituted alkyl; aryl; substituted aryl, with substituents selected from the group consisting of halogen, lower alkyl and recognized donor and acceptor groups.

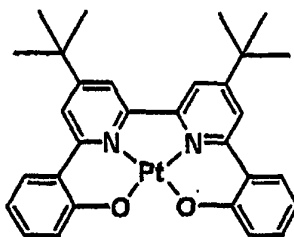
25

[0016] Embodiments of the present invention includes, but is not limited to, OLEDs comprising heterostructures for producing electroluminescence which contain anode (ITO glass substance), hole transport layer (NPB ( $\alpha$ -naphthylphenylbiphenyl amine)), matrix emissive layer [host material (beryllium bis(2-(2'-hydroxyphenyl)pyridine) (Bepp<sub>2</sub>)) with different concentration of dopants as illustrated by formula I and II herein], charge transport layer (lithium fluoride) and cathode (aluminum metal).

[0017] The preferred embodiment as an effective dopant in the OLEDs herein is:

30

35



40

[0018] The present invention provides new materials for applications as emissive dopants in electroluminescent devices. The invention includes the synthetic methods for these novel complexes plus their use as light-emitting materials. The devices of the present invention can be applied to field of display, light-emitter, display board for sign lamp, or light source for liquid crystal display.

[0019] Thus, new emissive molecules as represented by Formula I are disclosed in claim 6, and new emissive molecules as represented by Formula II are disclosed in claim 7.

45

[0020] A method for the preparation of a new light-emitting material having a structure represented by Formula I is disclosed in claim 8, and a method for the preparation of a new light-emitting material having a structure represented by Formula II is disclosed in claim 9.

### Brief Description of the Figures

50

[0021]

- Figure 1. Absorption spectra of complexes **1b** & **2b** in CH<sub>2</sub>Cl<sub>2</sub>  
 Figure 2. Emission spectra of complex **1b** in CH<sub>2</sub>Cl<sub>2</sub> and as thin film at 298 K  
 Figure 3. Emission spectra of complex **2b** in CH<sub>2</sub>Cl<sub>2</sub> and as thin film at 298 K  
 Figure 4. TGA thermograms of complexes **1b** and **2b** under nitrogen and air  
 Figure 5. Schematic diagram of OLED in present invention  
 Figure 6a. Electroluminescent spectrum of Device **A** containing complex **1b** (doping level 0.3 wt%)

55

- Figure 6b. Current density-voltage-luminance curve of Device **A** containing complex **1b** (doping level 0.3 wt%)  
 Figure 7a. Electroluminescent spectrum of Device **B** containing complex **1b** (doping level 1.0 wt%)  
 Figure 7b. Current density-voltage-luminance curve of Device **B** containing complex **1b** (doping level 1.0 wt%)  
 Figure 8. Electroluminescent spectrum of Device **C** containing complex **1b** (doping level 2.0 wt%)

5

### Detailed Description of the Invention

[0022] The inventions are generally related to syntheses, spectral characterization, phosphorescence, light-emitting properties of the new light-emitting materials, and their applications in OLEDs. The examples are set forth to aid in an understanding of the inventions but are not intended to, and should not be interpreted to, limit in any way the invention as set forth in the claims which follow thereafter.

[0023] The examples given illustrate the synthetic methods of ligands **1a** and **2a**, and the platinum complexes **1b** and **2b**. The quadridentate ONNO-type ligands **1a** and **2a** were prepared by modification of a literature procedure (J. Chem. Soc., Perkin Trans. 2, 863, (1998)). Another example of the preparation of ONNO-type ligands has been reported (US Patent 6,177,419).

15

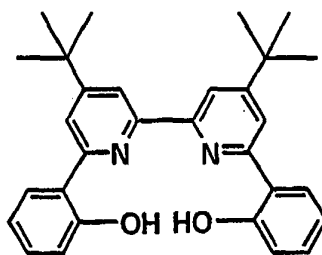
### EXAMPLE 1

#### Synthesis of **1a**

20

#### [0024]

25



30

**1a**

[0025] A mixture of 6,6'-bis(2-methoxyphenyl)-4,4'-bis(*tert*-butyl)-2,2'-bipyridine (1 g) in hydrobromic acid (47 %, 20 mL) was refluxed for 12 hours. This was cooled to room temperature and was neutralized with an aqueous saturated Na<sub>2</sub>CO<sub>3</sub> solution at room temperature. The organic product was extracted with chloroform and the extracts were washed with deionized water (50 mL × 2), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and a solid residue was obtained by removal of solvent. Crystalline product of **1a** was obtained by recrystallization from a methanol/dichloromethane solution. EI-MS (*m/z*): 452 [*M*]<sup>+</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 14.45 (2H, s, OH), 8.16 (2H, d, *J* = 1.4 Hz, ArH), 7.97 (2H, d, *J* = 1.3 Hz, ArH), 7.90 (2H, dd, *J* = 8.0 Hz, *J* = 1.4 Hz, ArH), 7.34 (2H, td, *J* = 8.4 Hz, *J* = 1.5 Hz, ArH), 7.07 (2H, dd, *J* = 8.2 Hz, *J* = 1.6 Hz, ArH), 6.96 (2H, td, *J* = 8.1 Hz, *J* = 1.2 Hz, ArH), 1.47 (18H, s, <sup>t</sup>Bu). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 163.3, 159.7, 157.5, 152.2, 131.5, 126.5, 119.2, 118.9, 118.4, 116.4, 35.6, 30.6.

35

40

### EXAMPLE 2

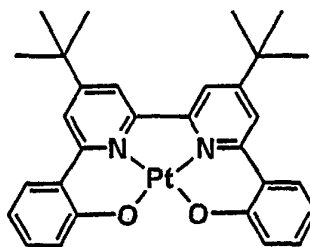
45

#### Synthesis of **1b**

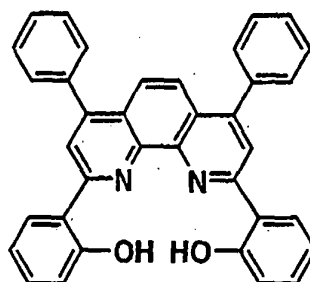
#### [0026]

50

55

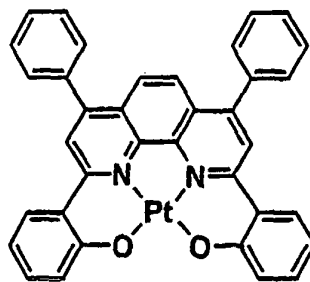
**1b**

**[0027]** The synthetic method of metal complex **1b** is described. A mixture of NaOMe (0.014 g, 0.25 mmol) and the ligand **1a** (0.113 g, 0.25 mmol) in methanol (20 mL) was stirred for 2 hours. An acetonitrile solution (20 mL) of Pt(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> (0.25 mmol) was added to the methanolic suspension, which was refluxed for 24 hours. The resulting suspension was filtered and concentrated to about 5 mL. Upon addition of diethyl ether, a brown-yellow solid was obtained. The crude product was recrystallized by diffusion of diethyl ether into a dichloromethane solution to afford yellow crystals. FAB-MS (m/z): 645 [M]<sup>+</sup>, 1292 (2M<sup>+</sup> + 2), 1938 (3M<sup>+</sup> + 3). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 8.32 (d, 2H, J = 1.41 Hz ArH), 8.01 (d, 2H, J = 7.25 Hz, ArH), 7.85 (d, 2H, J = 1.68 Hz, ArH), 7.48 (dd, 2H, J = 7.38 Hz, J = 1.13 Hz, ArH), 7.38 (td, 2H, J = 5.35, 1.61 Hz, ArH), 6.79 (td, 2H, J = 5.40, 1.35 Hz, ArH), 1.54 (s, 18H, <sup>t</sup>Bu). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 162.745, 159.105, 155.291, 149.851, 131.269, 128.005, 124.060, 120.465, 120.402, 116.302, 116.148, 30.402, 29.715. FTIR(KBr, cm<sup>-1</sup>): 3086 w, 2953 m, 1612 w, 1528 s, 1351 s, 1034 m, 885 w, 723 m

**EXAMPLE 3**Synthesis of **2a****[0028]****2a**

**[0029]** In a 100 mL round-bottom flask equipped with a reflux condenser, 2,9-bis(2-methoxyphenyl)-4,7-diphenyl-1,10-phenanthroline (finely ground, 2 g, 3.7 mmol) and pyridinium hydrochloride (4.23 g, 37 mmol) were mixed. The mixture was heated under nitrogen flow to 210 °C for 36 hours. After cooling, water (30 mL) was added and the aqueous solution was extracted with chloroform (3 × 30 mL). Combined organic extracts were washed with saturated sodium bicarbonate solution (5 × 30 mL) and water (3 × 30 mL), dried over anhydrous magnesium sulfate and evaporated to give a bright yellow solid. Chromatography over silica gel using n-hexane: dichloromethane (1:2) as eluent afforded 0.99 g of a yellow solid. FAB-MS (m/z): 517 [M+H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 14.69 (2H, s, OH), 8.52 (2H, s, ArH), 8.41 (2H, dd, J = 8.0, 1.3 Hz, ArH), 7.90 (2H, s, ArH), 7.71 (4H, d, J = 7.4 Hz), 7.64 (6H, m, ArH), 7.43 (2H, td, J = 7.7, 1.5 Hz, ArH), 7.10 (2H, dd, J = 7.4 Hz, 1.3 Hz, ArH), 7.04 (2H, td, J = 7.5, 1.3 Hz, ArH). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>): δ = 160.5, 157.7, 150.3, 142.8, 137.8, 132.2, 129.6, 128.9, 128.8, 127.1, 125.7, 123.7, 120.6, 119.4, 119.2, 118.9.

**EXAMPLE 4**Synthesis of **2b****[0030]**

**2b**

**[0031]**  $K_2PtCl_4$  (0.08 g, 0.19 mmol) and **2a** (0.1 g, 0.19 mmol) were refluxed in glacial acetic acid (10 mL) for 2 days. After cooling, the resulting suspension was collected by filtration, washed with acetic acid and water successively and then dried under vacuum to afford a brown solid. The crude product was purified by chromatography on a silica gel column with dichloromethane as eluent. The product was recrystallized by slow evaporation of a dichloromethane solution to afford red crystals. FAB-MS:  $m/z = 710 [M+H]^+$ .  $^1H$  NMR (270 MHz, DMSO- $d_6$ ) 8.81 (2H, s, ArH), 8.56 (2H, d,  $J = 8.9$  Hz, ArH), 8.01 (2H, s, ArH), 7.86 (4H, m, ArH), 7.71 (6H, dd,  $J = 4.9, 2.0$  Hz, ArH), 7.44 (2H, t,  $J = 7.4$  Hz, ArH), 7.24 (2H, d,  $J = 8.2$  Hz, ArH), 6.80 (2H, t,  $J = 7.6$  Hz, ArH).

**[0032]** The spectral characteristics of the platinum complexes **1b** and **2b** according to this invention are shown in Table 1. For complex **1b**, strong absorption bands at 250-350 nm ( $\epsilon = 38400$ -17500  $dm^3mol^{-1}cm^{-1}$ ) and a moderately intense absorption band at  $\lambda_{max}$  398 nm ( $\epsilon = 10800$   $dm^3mol^{-1}cm^{-1}$ ) are observed (Figure 1). In addition, a broad absorption band can be found at ca. 480 nm (2800  $dm^3mol^{-1}cm^{-1}$ ). For complex **2b** (Figure 1), several vibronic transitions at 291-375 nm ( $\epsilon = 39200$  to 24700  $dm^3mol^{-1}cm^{-1}$ ) and a broad band at 504 nm ( $\epsilon = 7200$   $dm^3mol^{-1}cm^{-1}$ ) are observed in  $CH_2Cl_2$ .

Table 1. UV/vis absorption data of **1b** and **2b** in  $CH_2Cl_2$ 

Complexes	$\lambda_{max}$ / nm ( $\epsilon / 10^4 \times dm^3mol^{-1}cm^{-1}$ )
<b>1b</b>	255 (3.80), 315 (1.75), 400 (0.82), 480 (0.25), 505 (0.22)
<b>2b</b>	291 (3.92), 315 (3.40), 325 (3.23), 352 (2.58), 375 (2.47), 420 (0.52), 488 (0.67), 504 (0.72)

**[0033]** The photoluminescence (PL) of the platinum complexes **1b** and **2b** in solution and as thin film are summarized in Table 2. In Figure 2, the 298 K structureless emission of complex **1b** are observed at 595 and 599 nm in  $CH_2Cl_2$  and as thin film respectively. The PL properties of complex **2b** in solution and as thin film are shown in Figure 3. The emission maximum of **2b** in thin film is shifted by 1704  $cm^{-1}$  compared to that in solution. Meanwhile, complexes **1b** and **2b** exhibit lifetimes of 1.9 and 5.3  $\mu s$  in  $CH_2Cl_2$  and luminescent quantum yields of 0.1 and 0.6 (with  $Ru(bpy)_3Cl_2$  as reference standard) respectively.

Table 2. PL properties of complexes **1b** and **2b** in solution and as thin film

Complexes (Measuring medium / Temperature)	Emission (Maximum / nm)	Lifetime ( $\mu s$ )	Quantum yield
<b>1b</b> ( $CH_2Cl_2$ / 298 K)	595	1.9	0.1
<b>1b</b> (Thin Film / 298 K)	599	/	/
<b>2b</b> ( $CH_2Cl_2$ / 298 K)	586	5.3	0.6
<b>2b</b> (Thin Film / 298 K)	651	/	/
concentration = $1 \times 10^{-5} mol dm^{-3}$			

**[0034]** The TGA thermograms of complexes **1b** and **2b** are shown in Figure 4. Both the complexes demonstrate high thermal stabilities in nitrogen and air at heating rate of 15  $^\circ C/min$ . Complex **2b** is stable up to 536  $^\circ C$  in nitrogen and 379  $^\circ C$  in air. The on-set temperatures of **1b** are at 438  $^\circ C$  in nitrogen and 382  $^\circ C$  in air. These observations reveal that these light-emitting materials can be sublimed and stable at vacuum deposition conditions in preparation of OLEDs.

**[0035]** An electroluminescent device according to this invention is schematically illustrated in Figure 5. As examples of the present invention, OLEDs with configurations of ITO / NPB ( $\alpha$ -naphthylphenylbiphenyl amine) (500  $\text{\AA}$ ) / [0.3 wt% (device **A**), 1 wt% (device **B**), or 2 wt% (device **C**) of complex **1b**]:Bepp<sub>2</sub> (400  $\text{\AA}$ ) / LiF (15  $\text{\AA}$ ) / A1 (2000  $\text{\AA}$ ) were prepared.

The fabrication of device **A** (0.3 wt% of **1b**) follows:

#### EXAMPLE 5

5 **[0036]** The device **A** was assembled as follows: indium tin oxide (ITO) electrode with sheet resistance of 20Ω/square on glass substrate, a hole transport material NPB ( $\alpha$ -naphthylphenylbiphenyl amine) with thickness of 500 Å, an emitting layer made of mixture of 0.3 wt.% complex **1b** and blue luminescent material Bepp<sub>2</sub> (beryllium bis(2-(2'-hydroxyphenyl)pyridine) with 400 Å thickness, an enhanced charge transport layer LiF with thickness of 15 Å, and aluminum layer with 2000 Å thickness. The metal and organic layers were laminated in sequence under  $5 \times 10^{-6}$  mbar without breaking vacuum between different vacuum deposition processes. The layers were deposited at rates of 2 or 5 Å per second. The emissive area of the device as defined by overlapping area of cathode and anode was  $3 \times 3$  mm<sup>2</sup>. The ITO coated glass slides were cleaned with organic solvents (acetone-isopropanol-methanol), deionized water, followed by ultra-violet-ozone cleaner. EL spectra and current density-voltage-luminance characteristics of the devices were measured with a spectrophotometer and a computer-controlled direct-current power supply respectively at room temperature.

10  
15 **[0037]** For these examples, the device external efficiencies increase when the doping concentration levels of complex **1b** were adjusted from 2 to 0.3 wt%. The specific examples are further illustrated as follows:

#### EXAMPLE 6

20 **[0038]** The performances of device **A** with 0.3 wt% doping level of complex **1b** are shown in Figures 6a and 6b. Two intense EL emissions at 453 and 540 nm are observed when the device was driven under forward bias. The current density-voltage-luminance characteristics curves of device **A** are also shown. The turn-on voltage is approximately 6-7 V. The maximum efficiency of the device was 4.1 cd/A at luminance of 2849 cd/m<sup>2</sup>. The maximum luminance of 9325 cd/m<sup>2</sup> was obtained at driving voltage of 10 V. The EL color of device **A** is yellow (CIE coordinates:  $x = 0.33$ ,  $y = 0.47$ ).

#### EXAMPLE 7

25  
30 **[0039]** The performances of device **B** with 1.0 wt% doping level of complex **1b** are shown in Figures 7a and 7b. The device exhibits an intense EL emission peak at 546 nm and a weak emission at 457 nm. The onset voltage of device **B** was approximately at 6-7 V. The efficiency and maximum luminance were 1.9 cd/A at luminance of 1927 cd/m<sup>2</sup> and 6563 cd/m<sup>2</sup> at driving voltage of 9.5 V respectively. The EL color of device **B** is yellow (CIE coordinates:  $x = 0.39$ ,  $y = 0.54$ ).

#### EXAMPLE 8

35 **[0040]** Device **C** with 2.0 wt% doping level of complex **1b** exhibits an intense EL emission peak at 548 nm with an extremely weak emission at around 450 nm (Figure 8); EL efficiency of 1.5 cd/A was detected. Luminance of 6450 cd/m<sup>2</sup> was observed at driving voltage of 12 V.

**[0041]** The EL color of device C is yellow (CIE coordinates:  $x = 0.42$ ,  $y = 0.56$ ).

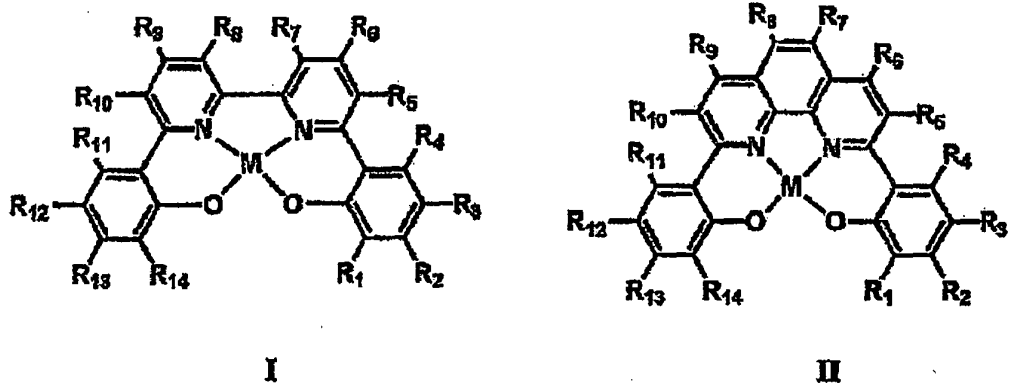
40 **[0042]** Typically, doping level of greater than 5 % is reported to achieve dopant emission in organic or polymeric light-emitting devices. In this invention, the OLEDs show virtually complete emission of complex **1b** when the doping level is around 2% and the efficiencies of devices increase from 1.5 to 4.1 cd/A when the doping levels of complex are decreased from 2.0 to 0.3 wt%.

#### 45 Claims

1. An organic light-emitting device containing a heterostructure for producing electroluminescence, an emissive layer, comprising at least a host material and an emissive molecule, present as a dopant in said host material, wherein the said emissive molecule has a chemical structure represented by Formula I and II:

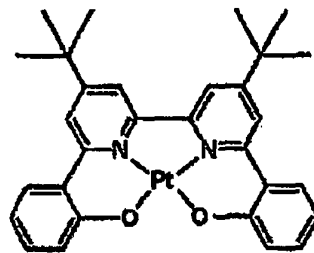
50

55



wherein M represents a Group 10 metal, including platinum, and  $R_1$ - $R_{14}$  are each independently selected from the group consisting of hydrogen; halogen; alkyl; substituted alkyl; aryl; substituted aryl; the substituents of said substituted alkyl or aryl groups being selected from the group consisting of halogens.

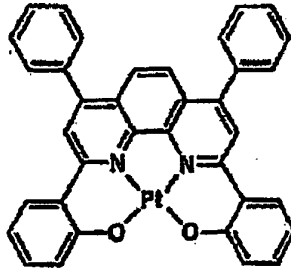
2. The organic light-emitting device of claim 1, wherein said emissive molecule is present as a dopant in said host material in low concentration, including 0.3 to 2.0 weight % based on weight of host material.
3. The organic light-emitting device of claim 1 that produces electroluminescence of yellow color.
4. The organic light-emitting device of claim 1, wherein said the host material is beryllium bis(2-(2'-hydroxyphenyl)pyridine) ( $\text{Bepp}_2$ ).
5. The organic light-emitting device of claim 1, wherein the said host material and said emissive molecule can be deposited as a thin layer by method of sublimation or vacuum deposition or vapor deposition or spin-coating or other methods.
6. The emissive molecule as represented by Formula I in accordance with claim 1, wherein the  $R_1$ - $R_5$ ,  $R_7$ - $R_8$  and  $R_{10}$ - $R_{14}$  groups are hydrogen atoms,  $R_6$  and  $R_9$  groups are *tert*-butyl groups, and M is platinum, namely:



7. The emissive molecule as represented by Formula II in accordance with claim 1, wherein the  $R_1$ - $R_5$ ,  $R_7$ - $R_8$  and  $R_{10}$ - $R_{14}$  groups are hydrogen atoms,  $R_6$  and  $R_9$  groups are phenyl groups, and M is platinum, namely:



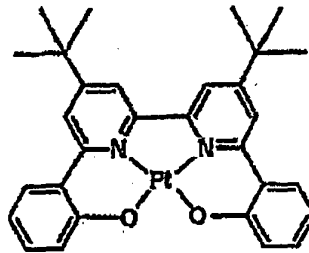
5



10

8. A method for the preparation of a light emitting material having a structure represented by Formula (I), claim 1, wherein the  $R_1$ - $R_5$ ,  $R_7$ - $R_8$  and  $R_{10}$ - $R_{14}$  groups are hydrogen atoms,  $R_6$  and  $R_9$  groups are *tert*-butyl groups, and M is platinum, namely:

15



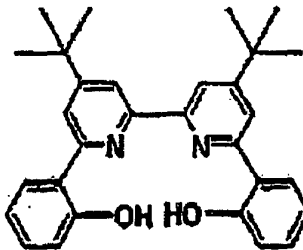
20

25

wherein said method comprises the steps of:

- demethylation of 6,6'-bis(2-methoxyphenyl)-4,4'-bis(*tert*-butyl)-2,2'-bipyridine by hydrobromic acid to prepare a ligand of Formula 1a:

30



35

40

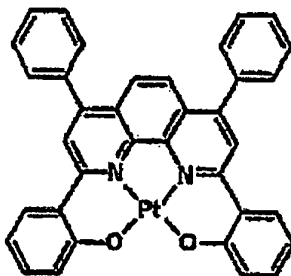
1a

- coordination of the ligand of Formula 1a by reacting the ligand with  $Pt(CH_3CN)_2Cl_2$ ; whereby the material of Formula (I) is obtained.

45

9. A method for the preparation of a light emitting material having a structure represented by Formula (II), claim 1, wherein the  $R_1$ - $R_5$ ,  $R_7$ - $R_8$  and  $R_{10}$ - $R_{14}$  groups are hydrogen atoms,  $R_6$  and  $R_9$  groups are phenyl groups, and M is platinum, namely:

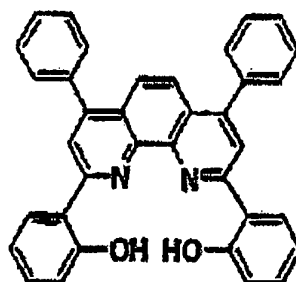
50



55

wherein said method comprises the steps of:

- demethylation of 2,9-bis(2-methoxyphenyl)-4,7-diphenyl-1,10-phenanthroline by pyridinium hydrochloride to prepare a ligand of Formula 2a:

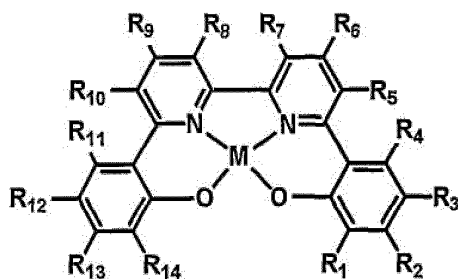


2a

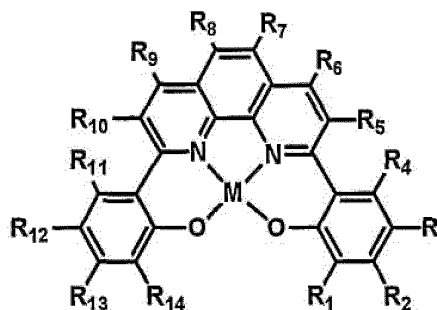
- coordination of the ligand of Formula 2a by reacting the ligand with  $K_2PtCl_4$ ; whereby the material of Formula (II) is obtained.

### Patentansprüche

1. Organische lichtemittierende Vorrichtung, enthaltend eine Heterostruktur zum Erzeugen von Elektrolumineszenz, eine emittierende Schicht, umfassend wenigstens ein Wirtsmaterial und ein emittierendes Molekül, das als ein Dotierstoff in dem Wirtsmaterial vorhanden ist, wobei das emittierende Molekül eine chemische Struktur aufweist, die durch Formel I und II wiedergegeben ist:



I



II

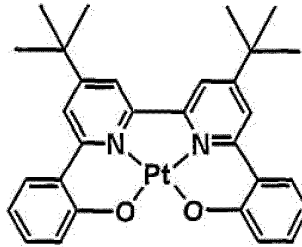
wobei M ein Metall der Gruppe 10, einschließlich Platin, bedeutet und  $R_1$ - $R_{14}$  jeweils unabhängig ausgewählt sind aus der Gruppe bestehend aus Wasserstoff; Halogen; Alkyl; substituiertem Alkyl; Aryl; substituiertem Aryl; wobei die Substituenten der substituierten Alkyl- oder Arylgruppen aus der Gruppe bestehend aus Halogenen ausgewählt sind.

2. Organische lichtemittierende Vorrichtung nach Anspruch 1, wobei das emittierende Molekül als ein Dotierstoff in dem Wirtsmaterial in niedriger Konzentration vorhanden ist, die 0,3 bis 2,0 Gew.-%, bezogen auf das Gewicht des Wirtsmaterials, einschließt.
3. Organische lichtemittierende Vorrichtung nach Anspruch 1, welche eine Elektrolumineszenz mit gelber Farbe erzeugt.
4. Organische lichtemittierende Vorrichtung nach Anspruch 1, wobei das Wirtsmaterial Beryllium-bis(2-(2'-hydroxyphenyl)pyridin) ( $Bepp_2$ ) ist.

5. Organische lichtemittierende Vorrichtung nach Anspruch 1, wobei das Wirtsmaterial und das emittierende Molekül durch ein Sublimationsverfahren oder Vakuumabscheidung oder Dampfabscheidung oder Schleuderbeschichtung oder andere Verfahren als eine dünne Schicht abgeschieden werden kann.

6. Emittierendes Molekül, wie es durch Formel I gemäß Anspruch 1 wiedergegeben ist, wobei die R<sub>1</sub>-R<sub>5</sub>-, R<sub>7</sub>-R<sub>8</sub>- und R<sub>10</sub>-R<sub>14</sub>-Gruppen Wasserstoffatome sind, die R<sub>6</sub>- und R<sub>9</sub>-Gruppen *tert*-Butylgruppen sind, und M Platin ist, nämlich:

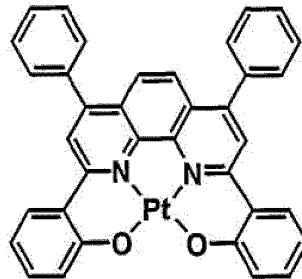
10



15

7. Emittierendes Molekül, wie es durch Formel II gemäß Anspruch 1 wiedergegeben ist, wobei die R<sub>1</sub>-R<sub>5</sub>-, R<sub>7</sub>-R<sub>8</sub>- und R<sub>10</sub>-R<sub>14</sub>-Gruppen Wasserstoffatome sind, die R<sub>6</sub>- und R<sub>9</sub>-Gruppen Phenylgruppen sind, und M Platin ist, nämlich:

20

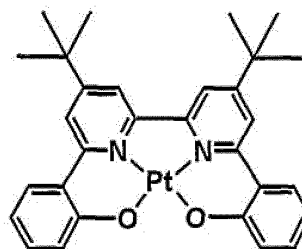


25

30

8. Verfahren zur Herstellung eines lichtemittierenden Materials mit einer Struktur, die durch Formel (I), Anspruch 1 wiedergegeben ist, wobei R<sub>1</sub>-R<sub>5</sub>-, R<sub>7</sub>-R<sub>8</sub>- und R<sub>10</sub>-R<sub>14</sub>-Gruppen Wasserstoffatome sind, die R<sub>6</sub>- und R<sub>9</sub>-Gruppen *tert*-Butylgruppen sind, und M Platin ist, nämlich:

35



40

45

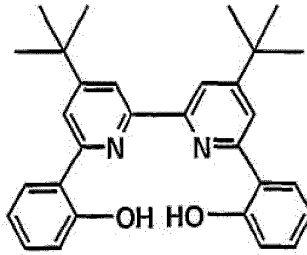
wobei das Verfahren die Schritte umfasst:

- Demethylierung von 6,6'-Bis(2-methoxyphenyl)-4,4'-bis(*tert*-butyl)-2,2'-bipyridin durch Bromwasserstoffsäure, um einen Liganden der Formel 1a herzustellen:

50

55

5



10

1a

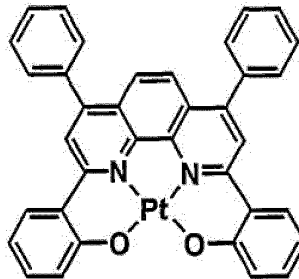
- Koordinierung des Liganden der Formel 1a durch Umsetzen des Liganden mit  $\text{Pt}(\text{CH}_3\text{CN})_2\text{Cl}_2$ ;

15

wodurch das Material der Formel (I) erhalten wird.

9. Verfahren zur Herstellung eines lichtemittierenden Materials mit einer Struktur, die durch Formel (II), Anspruch 1 wiedergegeben ist, wobei die  $\text{R}_1$ - $\text{R}_5$ -,  $\text{R}_7$ - $\text{R}_8$ - und  $\text{R}_{10}$ - $\text{R}_{14}$ -Gruppen Wasserstoffatome sind, die  $\text{R}_6$ - und  $\text{R}_9$ -Gruppen Phenylgruppen sind, und M Platin ist, nämlich:

20



25

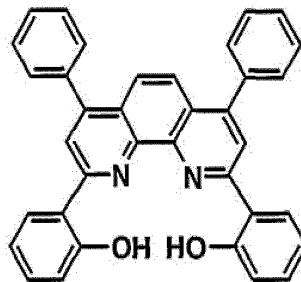
30

wobei das Verfahren die Schritte umfasst:

- Demethylierung von 2,9-Bis(2-methoxyphenyl)-4,7-diphenyl-1,10-phenanthrolin durch Pyridinium-hydrochlorid, um einen Liganden der Formel 2a herzustellen:

35

40



45

2a

50

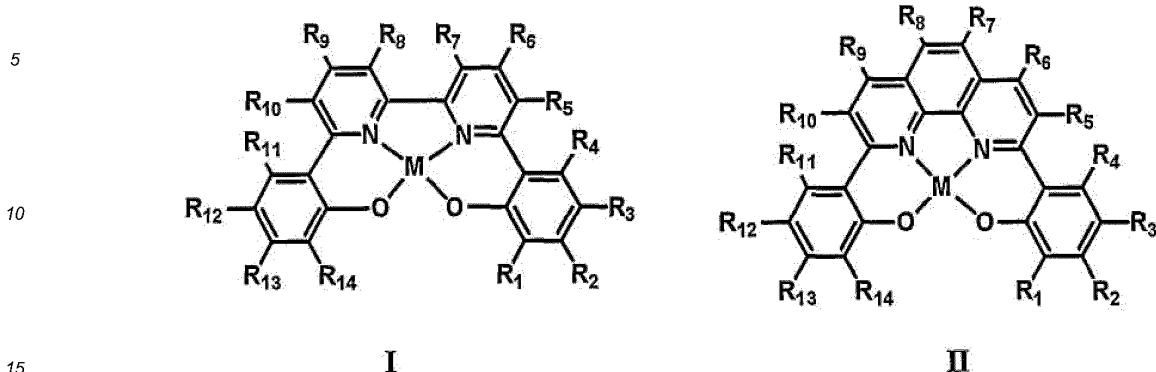
- Koordinierung des Liganden der Formel 2a durch Umsetzen des Liganden mit  $\text{K}_2\text{PtCl}_4$ ; wodurch das Material der Formel (II) erhalten wird.

### Revendications

55

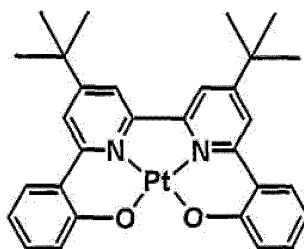
1. Dispositif électroluminescent organique contenant une hétérostructure pour produire de l'électroluminescence, une couche émissive, comprenant au moins une matière hôte et une molécule émissive, présente en tant que dopant dans ladite matière hôte, dans lequel ladite molécule émissive a une structure chimique représentée par les formules

I et II :



20 dans lesquelles M représente un métal du groupe 10, incluant le platine, et  $R_1$  à  $R_{14}$  sont chacun indépendamment choisis dans le groupe constitué par l'hydrogène ; un halogène ; un alkyle ; un alkyle substitué ; un aryle ; un aryle substitué ; les substituants desdits groupes alkyle ou aryle substitués étant choisis dans le groupe constitué par les halogènes.

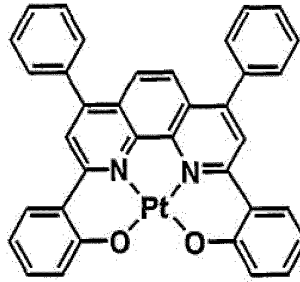
- 25
- 30
- 35
- 40
2. Dispositif électroluminescent organique selon la revendication 1, dans lequel ladite molécule émissive est présente en tant que dopant dans ladite matière hôte à une faible concentration, incluant 0,3 à 2,0 % en poids par rapport au poids de la matière hôte.
  3. Dispositif électroluminescent organique selon la revendication 1, qui produit une électroluminescence de couleur jaune.
  4. Dispositif électroluminescent organique selon la revendication 1, dans lequel ladite matière hôte est la béryllium bis(2-(2'-hydroxyphényl)pyridine) ( $\text{Bepp}_2$ ).
  5. Dispositif électroluminescent organique selon la revendication 1, dans lequel ladite matière hôte et ladite molécule émissive peuvent être déposées sous la forme d'une couche mince par un procédé de sublimation ou de dépôt sous vide ou de dépôt en phase vapeur ou d'enduction centrifuge ou par d'autres procédés.
  6. Molécule émissive telle que représentée par la Formule I selon la revendication 1, dans laquelle les groupes  $R_1$  à  $R_5$ ,  $R_7$ - $R_8$  et  $R_{10}$  à  $R_{14}$  sont des atomes d'hydrogène, les groupes  $R_6$  et  $R_9$  sont des groupes *tert*-butyles, et M est du platine, à savoir :



- 50
7. Molécule émissive telle que représentée par la Formule II selon la revendication 1, dans laquelle les groupes  $R_1$  à  $R_5$ ,  $R_7$ - $R_8$  et  $R_{10}$  à  $R_{14}$  sont des atomes d'hydrogène, les groupes  $R_6$  et  $R_9$  sont des groupes phényles, et M est du platine, à savoir :

55

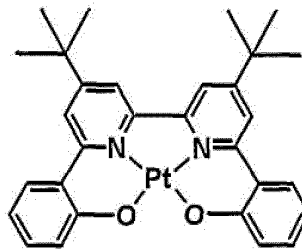
5



10

8. Procédé pour la préparation d'une matière électroluminescente ayant une structure représentée par la Formule (I), revendication 1, dans lequel les groupes  $R_1$  à  $R_5$ ,  $R_7$ - $R_8$  et  $R_{10}$  à  $R_{14}$  sont des atomes d'hydrogène, les groupes  $R_6$  et  $R_9$  sont des groupes *tert*-butyles, et M est du platine, à savoir :

15



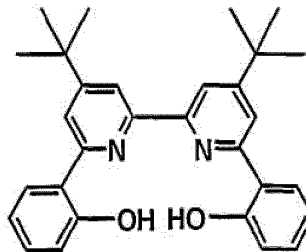
20

25

dans lequel ledit procédé comprend les étapes de :

- déméthylation de la 6,6'-bis(2-méthoxyphényl)-4,4'-bis(*tert*-butyl)-2,2'-bipyridine par de l'acide bromhydrique pour préparer un ligand de Formule la :

30



35

40

1a

- coordination du ligand de Formule la en faisant réagir le ligand avec  $Pt(CH_3CN)_2Cl_2$  ;

45

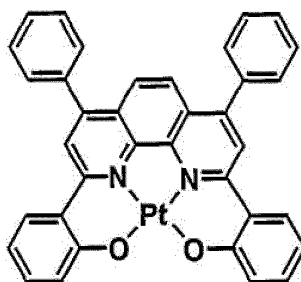
de sorte que la matière de Formule (I) est obtenue.

9. Procédé pour la préparation d'une matière électroluminescente ayant une structure représentée par la Formule (II), revendication 1, dans lequel les groupes  $R_1$  à  $R_5$ ,  $R_7$ - $R_8$  et  $R_{10}$  à  $R_{14}$  sont des atomes d'hydrogène, les groupes  $R_6$  et  $R_9$  sont des groupes phényles, et M est du platine, à savoir :

50

55

5



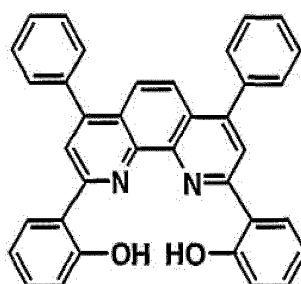
10

dans lequel ledit procédé comprend les étapes de :

15

- déméthylation de la 2,9-bis(2-méthoxyphényl)-4,7-diphényl-1,10-phénanthroline par du chlorhydrate de pyridinium pour préparer un ligand de Formule 2a :

20



25

**2a**

30

- coordination du ligand de Formule 2a en faisant réagir le ligand avec  $K_2PtCl_4$  ;

de sorte que la matière de Formule (II) est obtenue.

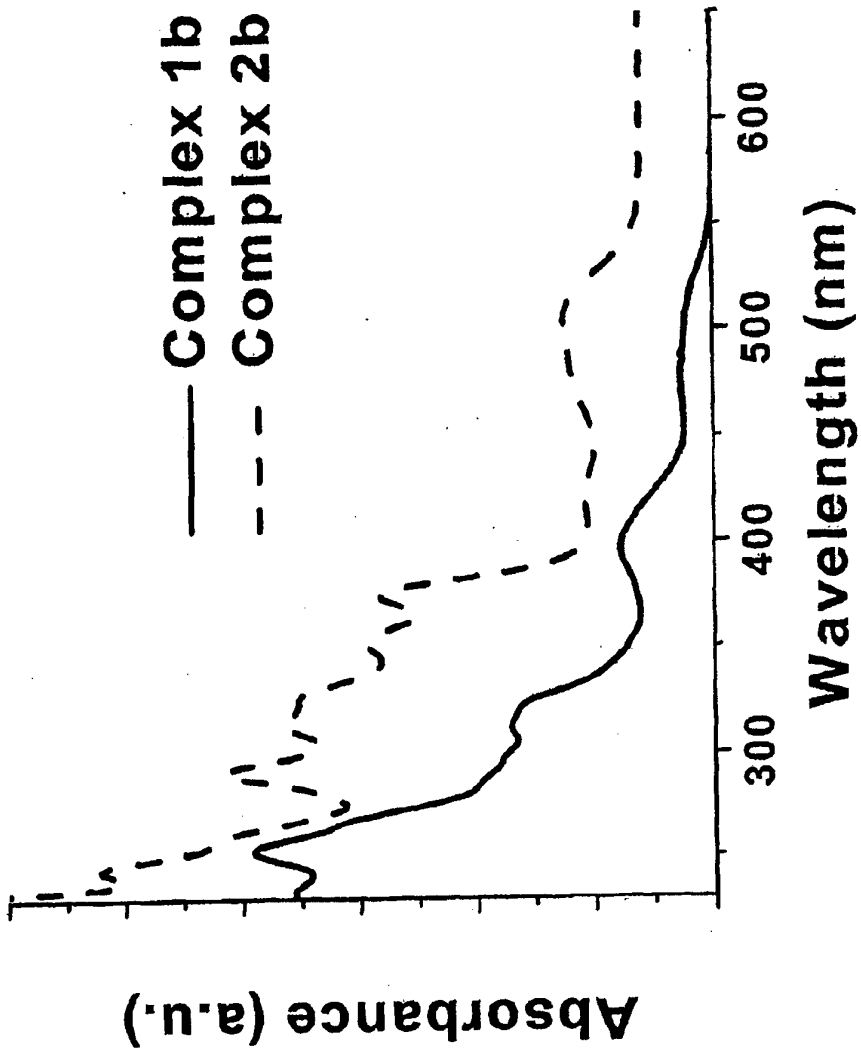
35

40

45

50

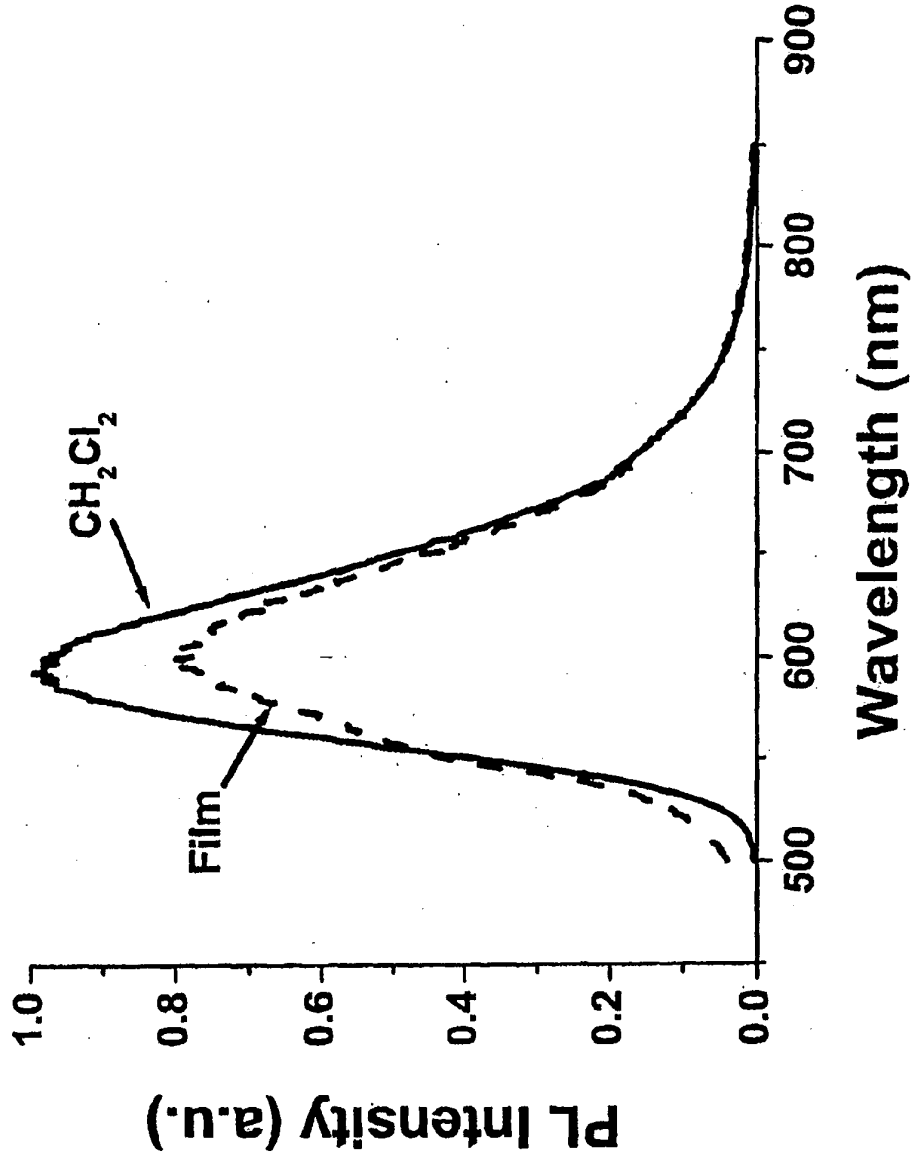
55



Absorption spectra of complexes 1b & 2b in  $\text{CH}_2\text{Cl}_2$

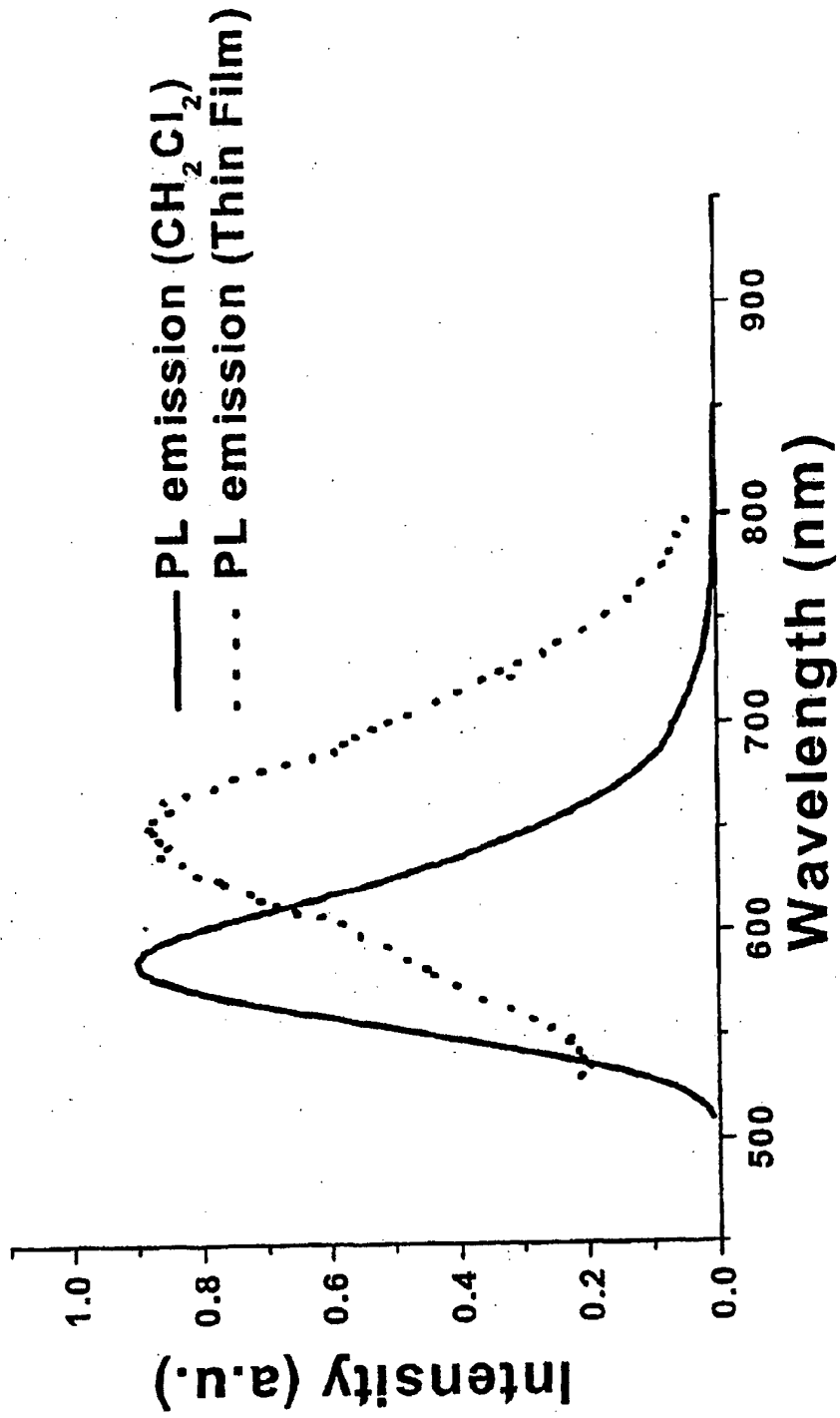
FIG. 1





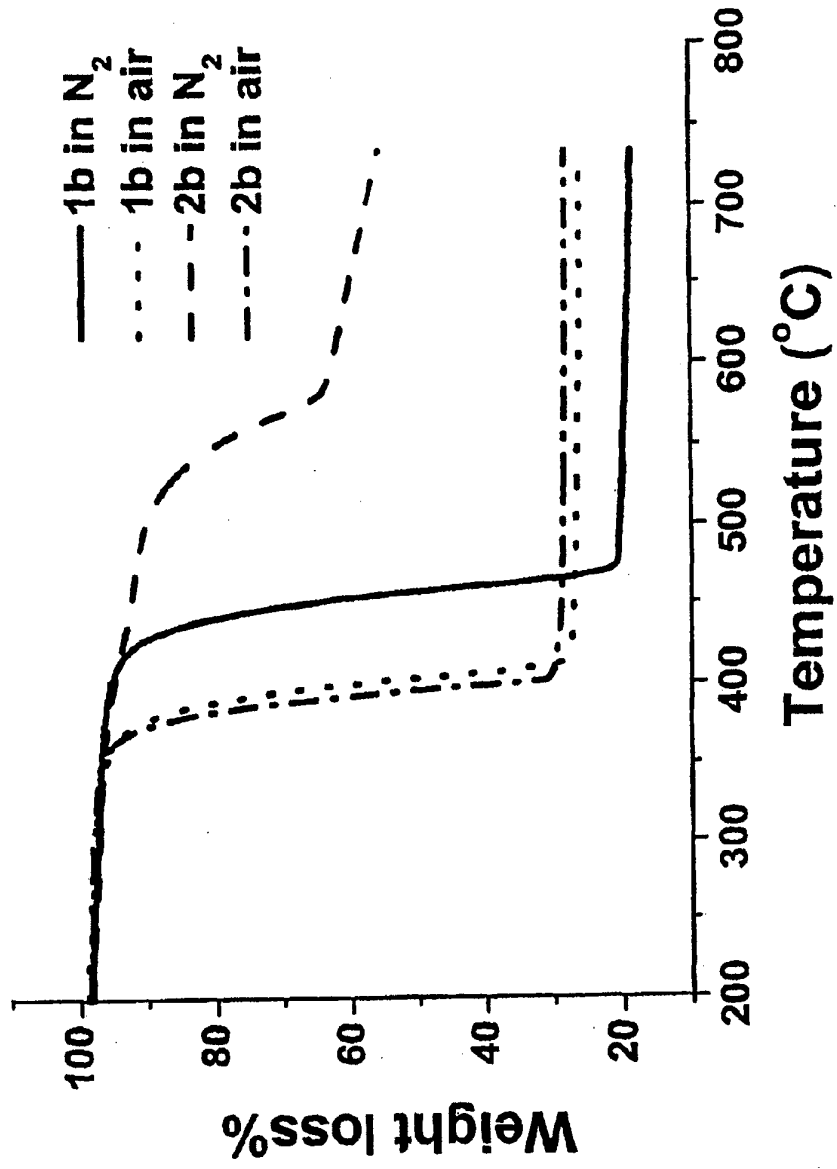
Emission spectra of complex 1b in  $\text{CH}_2\text{Cl}_2$  and as thin film at 298 K

FIG. 2



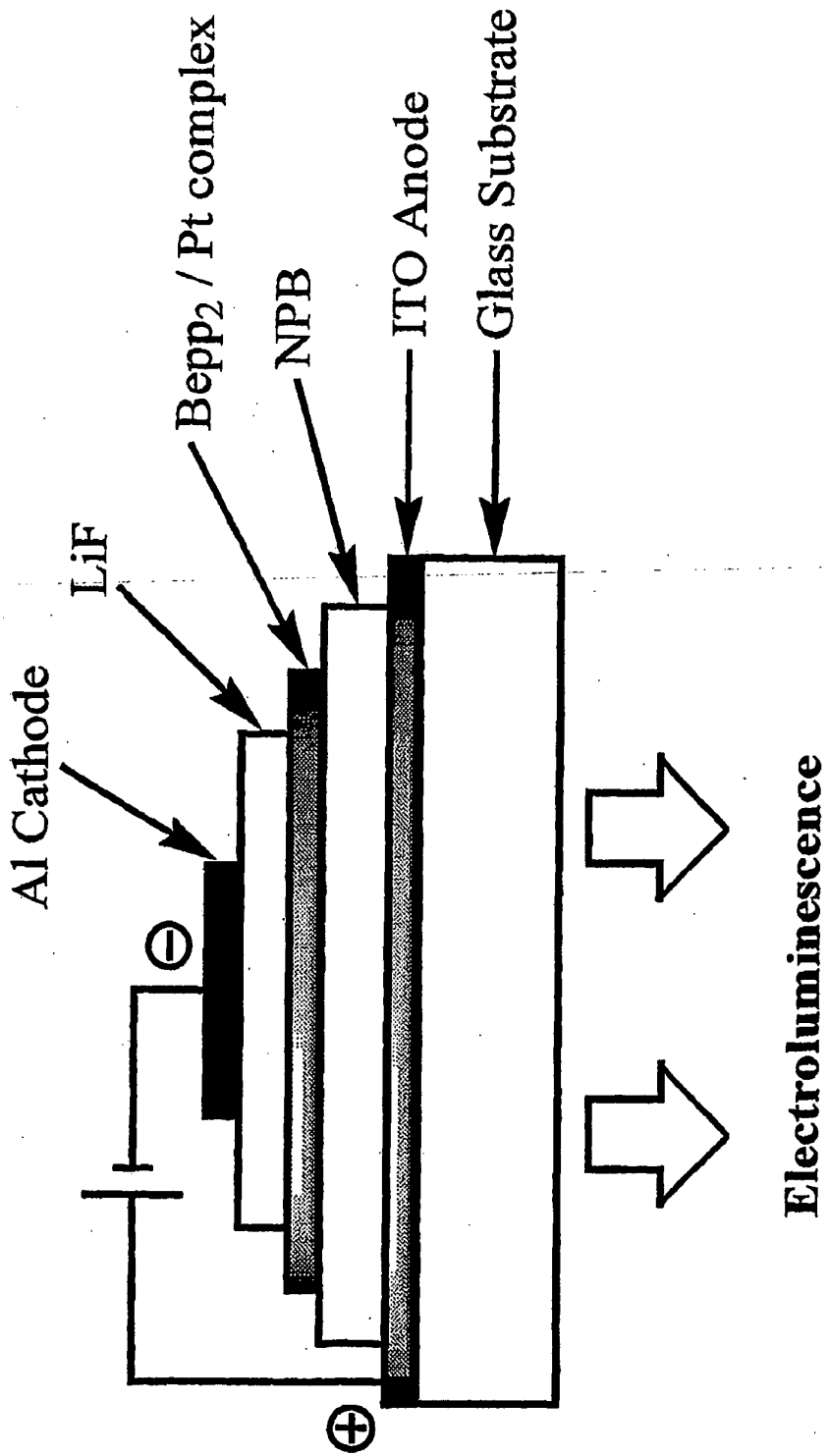
Emission spectra of complex 2b in  $\text{CH}_2\text{Cl}_2$  and as thin film at 298 K

FIG. 3



TGA thermograms of complexes 1b and 2b under nitrogen and air

FIG. 4



Schematic diagram of OLED in present invention

FIG. 5

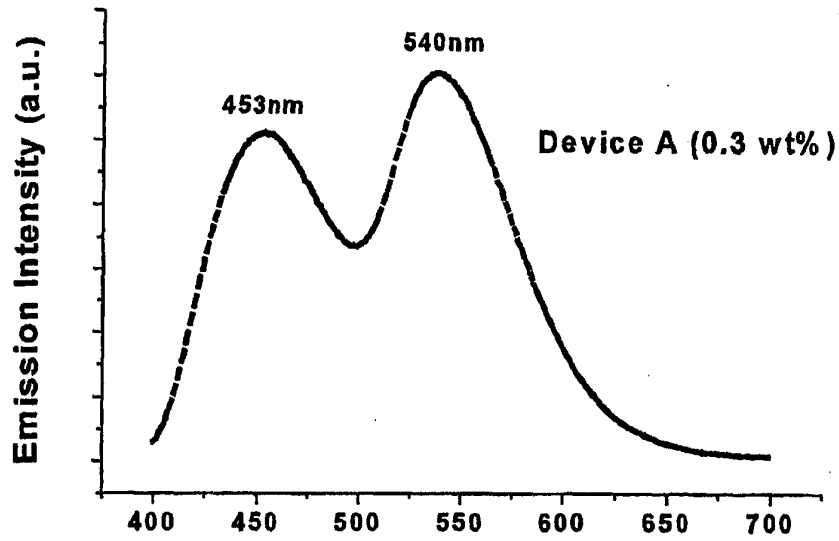


Figure 6a. Electroluminescent spectrum of Device A containing complex 1b (doping level 0.3 wt%)

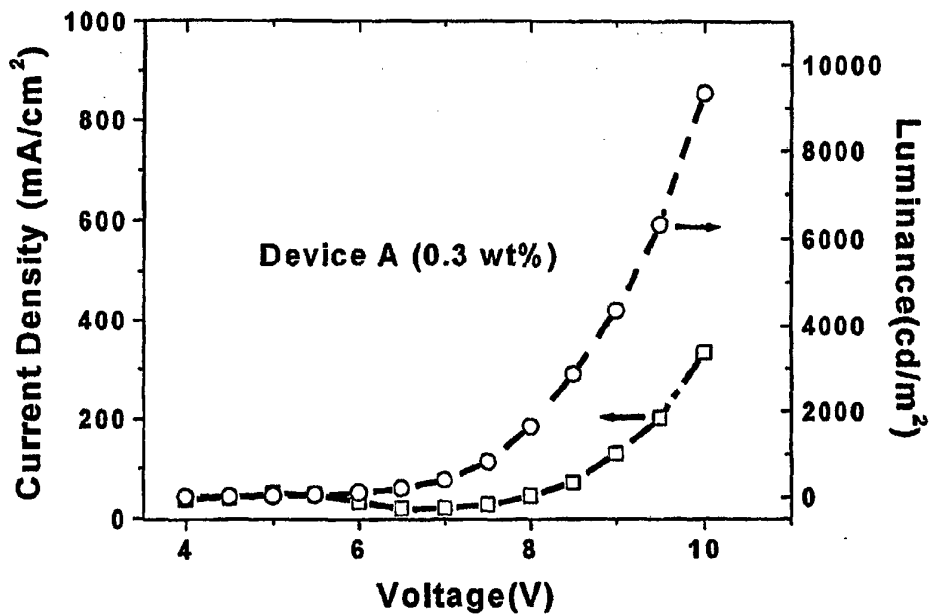


Figure 6b. Current density-voltage-luminance curve of Device A containing complex 1b (doping level 0.3 wt%)

FIG. 6

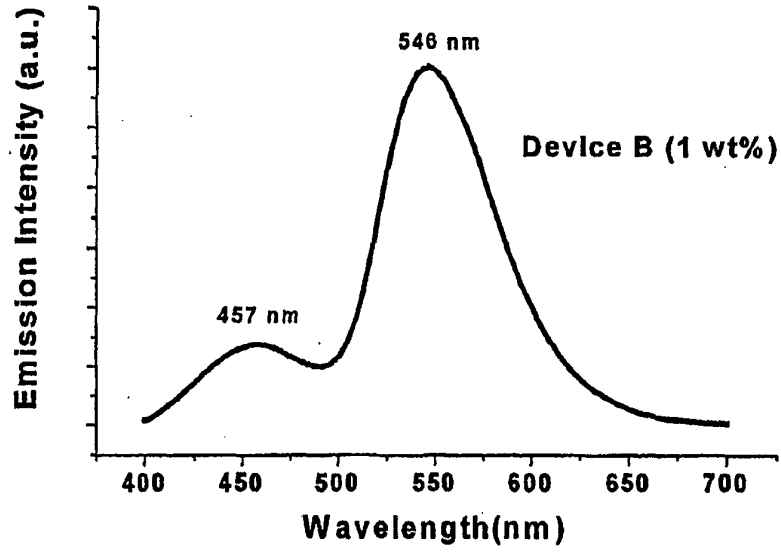


Figure 7a. Electroluminescent spectrum of Device B containing complex 1b (doping level 1.0 wt%)

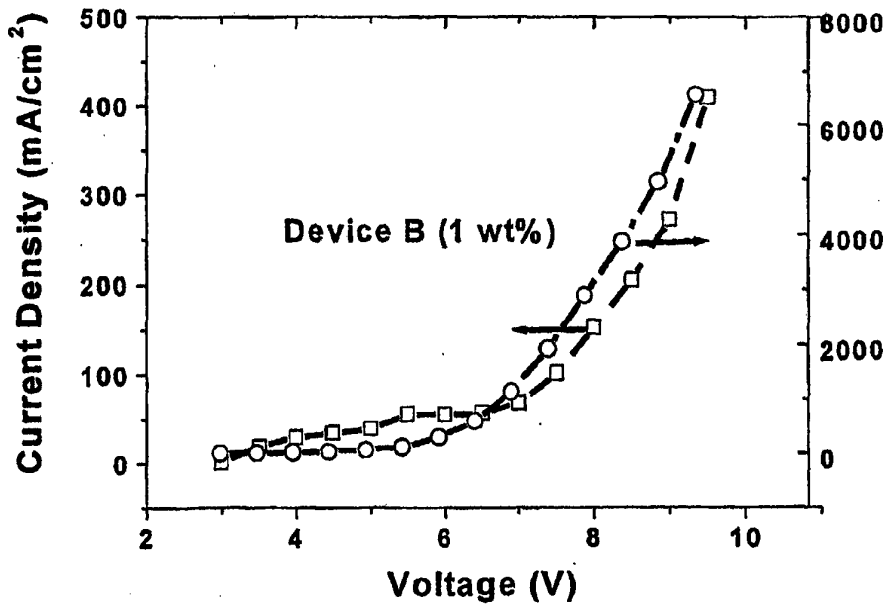
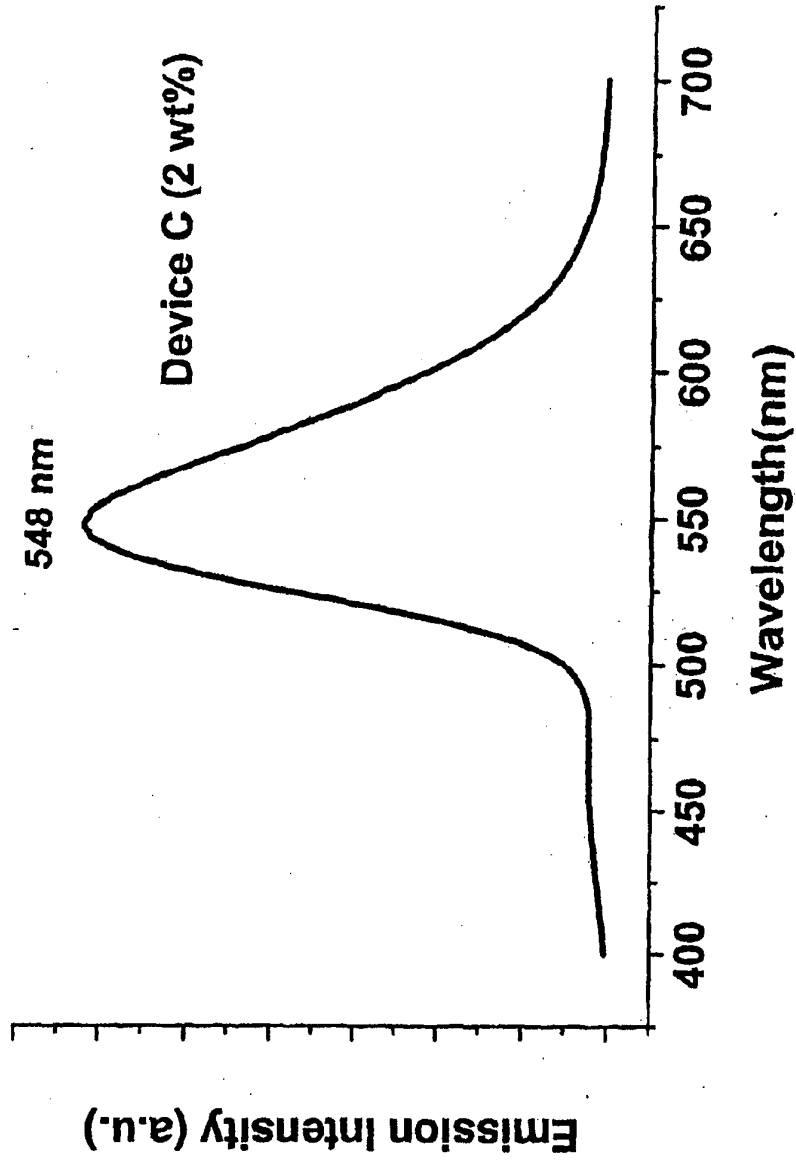


Figure 7b. Current density-voltage-luminance curve of Device B containing complex 1b (doping level 1.0 wt%)

FIG. 7



Electroluminescent spectrum of Device C containing complex 1b (doping level 2.0 wt%)

FIG. 8

**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- US 6310360 B [0004]
- US 5432014 A [0006]
- US 6316130 B [0007]
- US 6177419 B [0023]

**Non-patent literature cited in the description**

- *J. Chem. Phys.*, 1963, vol. 38, 2042 [0003]
- *Appl. Phys. Lett.*, 1987, vol. 51, 913 [0003]
- *Nature*, 1998, vol. 395, 151 [0004]
- *Synthetic Metals*, 1998, vol. 93, 245 [0004]
- *Appl. Phys Lett.*, 2000, vol. 77, 904 [0004]
- *Phys. Rev. B.*, 1999, vol. 60, 14422 [0005]
- *Jpn. J. Appl. Phys.*, 1993, vol. 32, L511 [0006]
- **P.CAPDEVIELLE et al.** Electroactive polymers exchanging transition metal ions; synthesis of new monomers and polymers based on 6,6'-bis(2-hydroxyethyl)bipyridine complexes. *New J. Chem.*, 1994, vol. 18, 519-524 [0008]
- *J. Chem. Soc., Perkin Trans. 2*, 1998, 863 [0023]