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(54) Title: PLATINUM(II) TETRADENTATE O-N-C-N COMPLEXES FOR ORGANIC LIGHT-EMITTING DIODE APPLICATIONS

(57) Abstract: Described are novel platinum (II) containing organometallic materials. These materials show green to orange emissions with high emission quantum efficiencies. Using the materials as emitting materials; pure green emitting organic light-emitting diodes can be fabricated. Since the novel platinum (II) containing organometallic materials are soluble in common solvents, solution process methods such as spin coating and printing can be used for device fabrication.

PLATINUM(II) TETRADENTATE O-N-C-N COMPLEXES FOR ORGANIC LIGHT-EMITTING DIODE APPLICATIONS

Cross-Reference to Related Applications

This application claims priority to provisional application Serial No. 61/366,359, filed on July 21, 2010, which is incorporated herein by reference.

Technical Field

Described are a class of new organometallic materials and their usage in organic light-emitting diode (OLED) and polymer light emitting diode (PLED).The organometallic materials show good emission quantum efficiency and soluble in common organic solvents. Making use these materials, high efficiency single color and white OLED (WOLED) can be fabricated by various techniques including vacuum deposition, spin coating or printing methods.

Background

In 1965 Edward F. Gurnee and Fernandez Reet Teoste first observed and studied organic electroluminescence (U. S. patent 3,172,862). Later on, Tang in Eastman Kodak disclosed double-layer structure OLED (organic light emitting diode, US 4,356,429; Appl. Phys. Lett. 1987, 51, 12, 913). This diode was based on employing a multilayer structure including an emissive electron-transporting layer (fabricated from Alq_3 (q = deprotonated 8-hydroxyquinolinyl)) and a hole-transport layer of suitable organic materials. Afterward, research on materials used in OLED becomes a hot research topic. OLED possesses many advantages such as: low operating voltage; ultra thin; self emitting; good device efficiency; high contrast and high resolution which suggest the possible use of OLED in flat panel displays and lighting.

There are two classes of emitting materials for OLED application: fluorescent and phosphorescent materials. Phosphorescent materials become the major trend for emitting materials development since 75 % excitons produced from OLED are in triplet, only 25 % excitons are in singlet. It means the maximum device efficiency for phosphorescent materials are 3 times higher than fluorescent materials.

Platinum is one of the transition metals from emissive complexes with organic ligands, which have high emission quantum efficiency and good thermal stability. With these advantages, platinum(II) complexes were used as emitting materials in high performance OELDs.(Applied Physics Letters (2007), 91(6) 063508; Chemistry-A European Journal (2010), 16(1), 233-247) Among the platinum complexes used in OLED applications, pure green emitting materials with stable chemical structure are rare.

For the stability of the platinum(II) complexes, the binding energy between the ligand and platinum(II) center gets higher when the number of coordination positions in the ligand increases; that is, the binding energy between the ligand and platinum(II) center is the highest in tetradentate ligand platinum(II) complexes. Moreover, the addition of extra atom(s) between the aromatic coordination position to break the conjugation of the ligand may weaken the stability of the ligand and eventually weaken the stability of the complexes. Green emitting platinum(II) materials with bidentate ligands, tridentate ligand or tetradentate ligand with extra atom(s) between the aromatic coordination position to break the conjugation is not as good as a conjugated tetradentate ligand system.

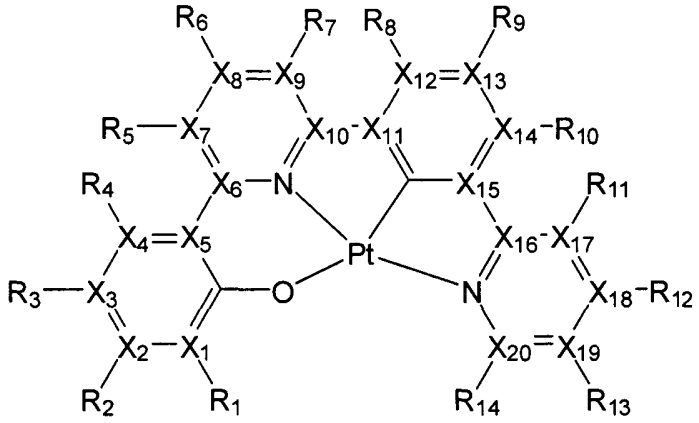
However, most of the conjugated tetradentate ligand systems are not able to have pure green emitting materials due to their intrinsic properties such as the band gaps are limited by the MLCT transitions and the emission spectra are vibronically structured. (see US 6,653,654; US 7,361,415; US 7,691,495). For these reasons, stable green emitting platinum(II) material is difficult to develop.

Summary

Despite the above-mentioned problems, described herein are new platinum(II) complex systems, which have stable chemical structure, high emission quantum efficiency and pure green emission which are used as green emitting material in OLED. By changing the substitutes in the tetradentate ligand, the emission color of the platinum can also tune back to yellow or orange color. Making use of the yellow or orange emitting materials in the series, white OLED (WOLED) can also be fabricated by complementary colors mixing approach. Besides, as some of the complexes show strong excimer emission, single emitting component WOLED can be fabricated from these complexes by combining the monomer and excimer emission of one complex.

Since most of the platinum(II) complexes used for OLED application are only slightly soluble in common solvent, solution process methods such as spin coating and printing (including inkjet printing, roll to roll printing, etc.) cannot be applied. Materials described herein overcome this drawback, as all of the platinum(II) complexes described herein are soluble in common solvents, solution process methods can be applied for low cost and large area fabrication.

This invention concerns platinum(II) based emitting materials having chemical structure of structure I, their preparation and application in organic light-emitting diode(OLED) and polymer light-emitting diode(PLED).



Structure I

wherein R_1–R_{14} are independently hydrogen, halogen, hydroxyl, an unsubstituted alkyl, a substituted alkyl, cycloalkyl, an unsubstituted aryl, a substituted aryl, acyl, alkoxy, acyloxy, amino, nitro, acylamino, aralkyl, cyano, carboxyl, thio, styryl, aminocarbonyl, carbamoyl, aryloxycarbonyl, phenoxycarbonyl, or an alkoxycarbonyl group. Each R_1–R_{14} can independently form 5 – 8 member ring(s) with adjacent R group(s). X_1 – X_{20} are independently boron, carbon, nitrogen, oxygen, or silicon.

For the purposes of the present application, unless otherwise specified, the terms halogen, alkyl, cycloalkyl, aryl, acyl, alkoxy and heterocyclic aromatic system or heterocyclic aromatic group may have the following meanings:

The halogen or halo used herein includes fluorine, chlorine, bromine and iodine, preferably F, Cl, Br, particularly preferably F or Cl, most preferably F.

The aryl group, aryl moiety or aromatic system as used herein includes aryl having from 6 to 30 carbon atoms, preferably from 6 to 20 carbon atoms, more preferably from 6 to 8 carbon atoms and is made up of an aromatic ring or a plurality of fused aromatic rings. Suitable aryls are, for example, phenyl, naphthyl, acenaphthenyl, acenaphthylenyl, anthracenyl, fluorenyl, phenalenyl, phenanthrenyl. This aryl can be unsubstituted (i.e. all carbon atoms which are capable of substitution bear hydrogen atoms) or be substituted on one, more than one or all substitutable positions of the aryl. Suitable substituents are, for example, halogen, preferably F, Br or Cl, alkyl radicals, preferably alkyl radicals having from 1 to 20, 1 to 10, or 1 to 8 carbon atoms, particularly preferably methyl, ethyl, i-propyl or t-butyl, aryl radicals, preferably C_6-aryl radicals or fluorenyl, which may once again be substituted or unsubstituted, heteroaryl radicals, preferably heteroaryl radicals containing at least one nitrogen atom, particularly preferably pyridyl radicals, alkenyl radicals, preferably alkenyl radicals which have one double bond, particularly preferably alkenyl radicals having a double bond and from 1 to 8 carbon atoms. The aryl radicals very particularly preferably bear substituents selected from the group consisting of F and t-butyl. Preference is given to the aryl radical or the aryl group being a C_6-aryl

radical which may optionally be substituted by at least one of the abovementioned substituents. The C_6-aryl radical particularly preferably bears none, one or two of the abovementioned substituents. The C_6-aryl radical is very particularly preferably an unsubstituted phenyl radical or substituted phenyl, such as biphenyl, phenyl substituted by two t-butyl, preferably at meta positions. The aryl or aryl moiety as used herein is preferably phenyl, which may be unsubstituted or substituted by the abovementioned substituents, preferably halogen, alkyl or aryl.

The alkyl or alkyl moiety used herein includes alkyl having from 1 to 20 carbon atoms, preferably from 1 to 10 carbon atoms, particularly preferably from 1 to 6 carbon atoms. This alkyl can be branched or unbranched and may be interrupted by one or more heteroatoms, preferably N, O or S. Furthermore, this alkyl may be substituted by one or more of the substituents mentioned in respect of the aryl groups. It is likewise possible for the alkyl radical to bear one or more aryl groups. All the mentioned aryl groups are suitable for this purpose. The alkyl radicals are particularly preferably selected from the group consisting of methyl, ethyl, i-propyl, n-propyl, i-butyl, n-butyl, t-butyl, sec-butyl, i-pentyl, n-pentyl, sec-pentyl, neopentyl, n-hexyl, i-hexyl and sec-hexyl. Very particular preference is given to t-butyl, C_4H_9, C_6H_{13}.

The cycloalkyl as used herein contemplates cyclic alkyl radicals. Preferred cycloalkyl groups are those containing 3 to 7 carbon atoms and includes cyclopropyl, cyclopentyl, cyclohexyl, and the like. Additionally, the cycloalkyl group may be optionally substituted with one or more substituents selected from halo, alkyl group, such as t-butyl, C_4H_9, C_6H_{13}.

The acyl as used herein is an alkyl group as used herein that is attached to the CO group with a single bond.

The alkoxy as used herei is an alkyl group as used herein linked to oxygen.

The heterocyclic aromatic system or heterocyclic aromatic group as used herein is understood to relate to aromatic, C_{3-8} cyclic groups further containing one oxygen or sulfur atom or one to four nitrogen atoms, or a combination of one oxygen or sulfur atom with up to two nitrogen atoms, and their substituted as well as benzo- and pyrido-fused derivatives, for example, connected via one of the ring-forming carbon atoms. Said heterocyclic aromatic system or heterocyclic aromatic group may be substituted by one or more of the substituents mentioned in respect of the aryl groups.

In some embodiments, heteroaryl groups can be five- and six-membered aromatic heterocyclic systems carrying 0, 1, or 2 substituents above, which can be the same as or different from one another. Representative examples of heteroaryl groups include, but are not limited to, unsubstituted and mono- or di-substituted derivatives of furan, benzofuran, thiophene, benzothiophene, pyrrole, pyridine, indole, oxazole, benzoxazole, isoxazole, benzisoxazole, thiazole, benzothiazole, isothiazole, imidazole,

benzimidazole, pyrazole, indazole, tetrazole, quionoline, isoquinoline, pyridazine, pyrimidine, purine and pyrazine, furazan, 1,2,3-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, triazole, benzotriazole, pteridine, phenoxazole, oxadiazole, benzopyrazole, quinolizine, cinnoline, phthalazine, quinazoline, and quinoxaline. In some embodiments, the substituents are halo, hydroxy, cyano, O-C_{1-6}-alkyl, C_{1-6}-alkyl, hydroxy- C_{1-6}-alkyl, and amino- C_{1-6}-alkyl.

Brief Description of Drawings

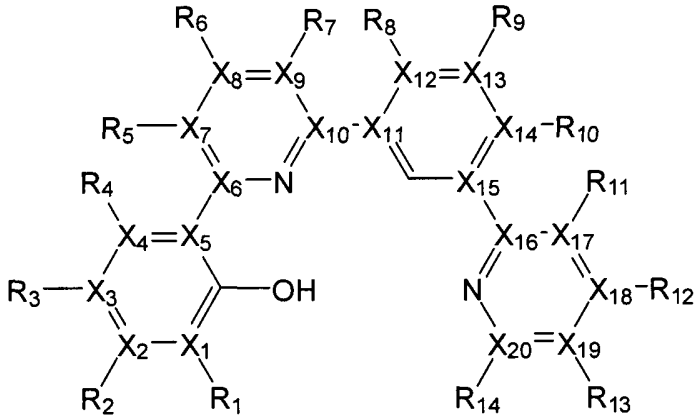
Figure 1: Synthetic scheme for ligand with structure II.

Figure 2: Synthetic scheme for ligand with structure I.

Detailed Description

The organometallic complexes with chemical structure of Structure I are referred to cyclometallated complexes. The platinum center in Structure I is in the +2 oxidation state and has a square planar geometry.

The coordination sites of the platinum center are occupied by a tetradentate ligand. The tetradentate ligand coordinates to the platinum center through a metal-oxygen bond, a nitrogen donor bond, a metal-carbon bond and a nitrogen donor bond in a sequence of O, N, C, N (ONCN ligand). The metal-oxygen bond is a bond between deprotonated phenol or substituted phenol and platinum, the nitrogen donors are from an N-heterocyclic group such as pyridine and / or isoquinoline groups, and the metal-carbon bond is formed by benzene or substituted benzene and platinum. The chemical structure of the tetradentate ligands in current invention can be represented by Structure II:



Structure II

wherein R_1–R_{14} are independently hydrogen, halogen, hydroxyl, an unsubstituted alkyl, a substituted alkyl, cycloalkyl, an unsubstituted aryl, a substituted aryl, acyl, alkoxy, acyloxy, amino, nitro, acylamino, aralkyl, cyano, carboxyl, thio, styryl,

aminocarbonyl, carbamoyl, aryloxycarbonyl, phenoxycarbonyl, or an alkoxycarbonyl group. Each R_1–R_{14} can independently form 5 – 8 member ring(s) (such as substituted or unsubstituted aryl, substituted or unsubstituted cycloalkyl ring) with adjacent R group(s). X_1 – X_{20} are independently boron, carbon, nitrogen, oxygen, or silicon.

In one embodiment, in both Structure I and II, each R_1–R_{14} is independently hydrogen, halogen (such as fluorine, chlorine bromine, and iodine), hydroxyl, an unsubstituted alkyl containing from 1 to 10 carbon atoms, a substituted alkyl containing from 1 to 20 carbon atoms, cycloalkyl containing from 1 to 20 carbon atoms, an unsubstituted aryl containing from 1 to 20 carbon atoms, a substituted aryl containing from 1 to 20 carbon atoms, acyl containing from 1 to 20 carbon atoms, alkoxy containing from 1 to 20 carbon atoms, acyloxy containing from 1 to 20 carbon atoms, amino, nitro, acylamino containing from 1 to 20 carbon atoms, aralkyl containing from 1 to 20 carbon atoms, cyano, carboxyl containing from 1 to 20 carbon atoms, thio, styryl, aminocarbonyl containing from 1 to 20 carbon atoms, carbamoyl containing from 1 to 20 carbon atoms, aryloxycarbonyl containing from 1 to 20 carbon atoms, phenoxycarbonyl containing from 1 to 20 carbon atoms, or an alkoxycarbonyl group containing from 1 to 20 carbon atoms.

In another embodiment, the total number of carbon atoms provided by the R_1–R_{14} groups is from 1 to 40. In another embodiment, the total number of carbon atoms provided by the R_1–R_{14} groups is from 2 to 30.

In another embodiment, R_1= halogen, alkyl, R_3= alkyl, R_4=halogen, R_6= alkyl, aryl substituted by alkyl or aryl, R_8= halogen, R_9= alkyl, aryl substituted by aryl, R_{10}= halogen, X_{14} = heteroatom, preferably N, O or S, X_{13} = heteroatom, preferably N, O or S, and/or X_{17} = heteroatom, preferably N, O or S. In another embodiment, R_2 together with R_3 form an aryl or cycloalkyl, R_{12} together with R_{13} form an aryl or cycloalkyl.

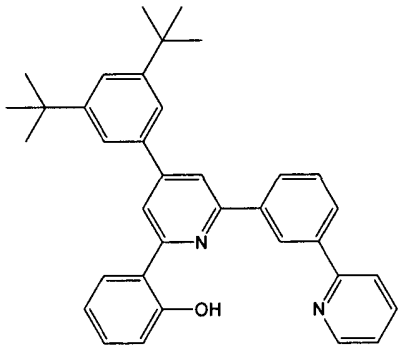
In another embodiment, R_1= F, t-butyl, R_3= t-butyl, R_4=F, R_6= biphenyl, t-butyl, bisubstituted phenyl, R_8= F, R_9= biphenyl, t-butyl, R_{10}= F, X_{14} = N, X_{13} = N, and/or X_{17} = N. In another embodiment, R_2 together with R_3 form a phenyl, R_{12} together with R_{13} form a phenyl.

The tetradentate ligand can be prepared by a series of reactions depicted in Figure 1. For brevity and simplicity, aromatic ring systems A, B, C, and D as shown are unsubstituted (that is, R_1–R_{14} as shown are hydrogen). However, although not shown in Figure 1, but as indicated in Structures I and II, R_1–R_{14} can be other than hydrogen.

Aromatic system C, which contains a precursor group for coupling reaction(F_1) and a precursor group for pyridine ring formation reaction(F_4) or a precursor group for making F_4(F_3), is coupled with a nitrogen containing heterocyclic aromatic system

D, which contains a precursor group for pyridine ring formation reaction(F_2), through metal coupling. If the aromatic system C contains F_3, it will then be transformed to F_4 by functional group transformation reaction. The resultant products are then reacted with aromatic system A, which can contain a methoxy group and a precursor group for pyridine ring formation(F_6) by pyridine ring formation reaction. (If aromatic system A with F_6 is not commercially available, a functional group transformation reaction can be performed to transform the precursor group for making F_5(F_6) to F_6.) Finally, the methoxy group is transformed to hydroxyl group by demethylation reaction.

Specific examples of the ONCN ligand are shown but not restricted to below:



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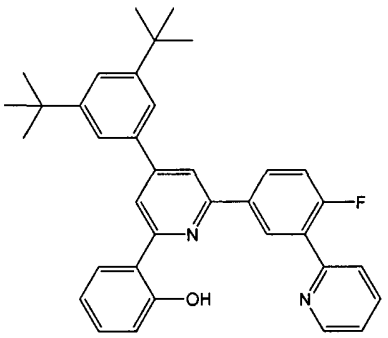

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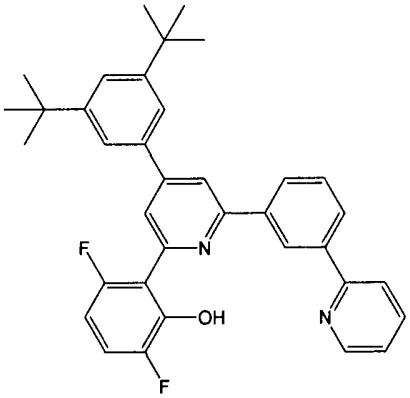

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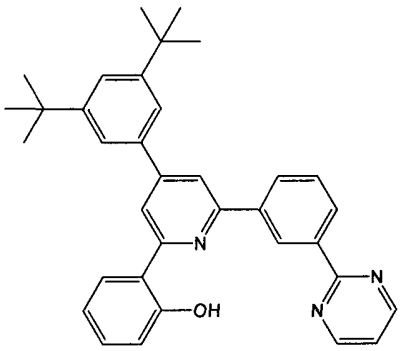

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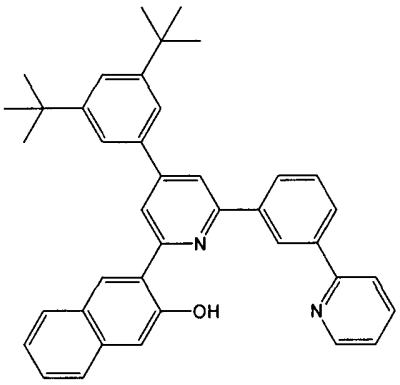

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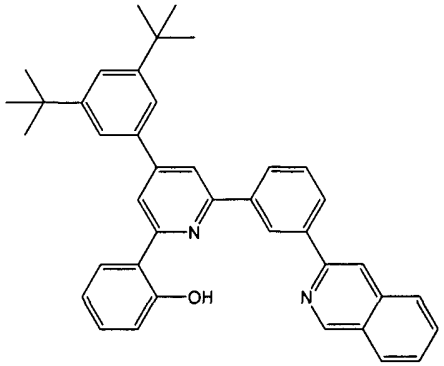

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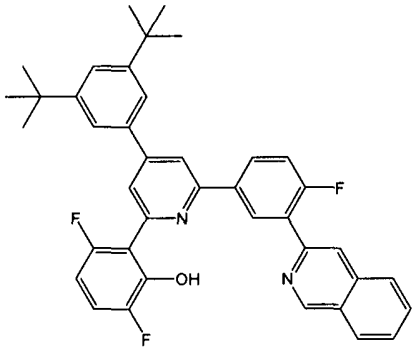

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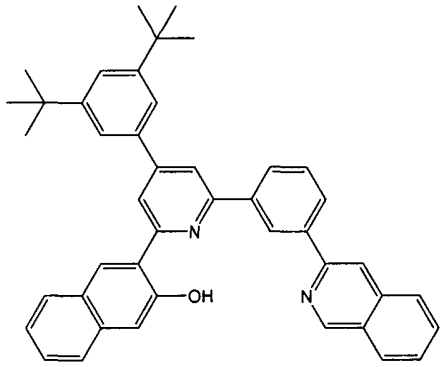

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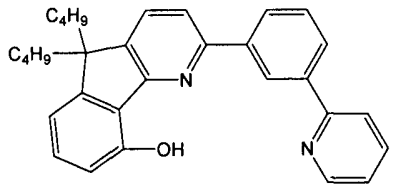

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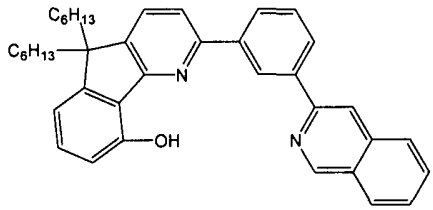

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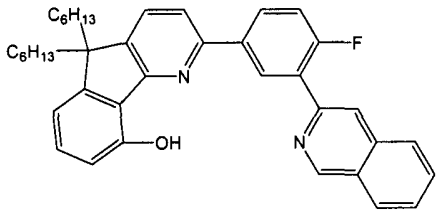

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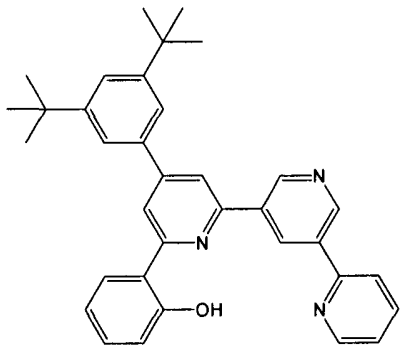

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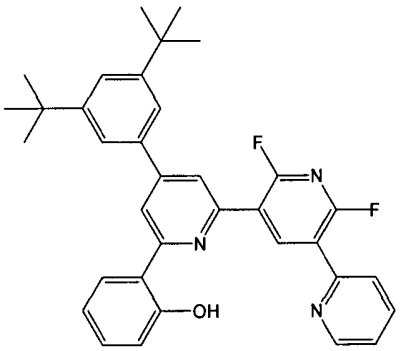

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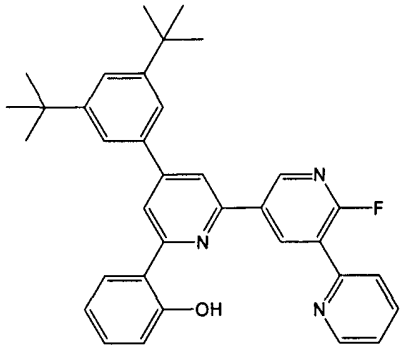

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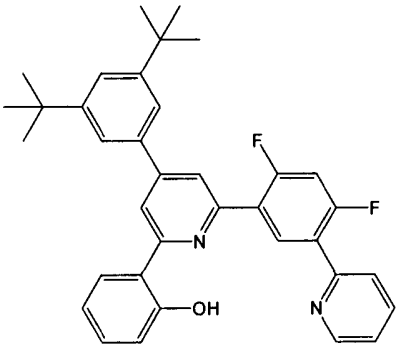

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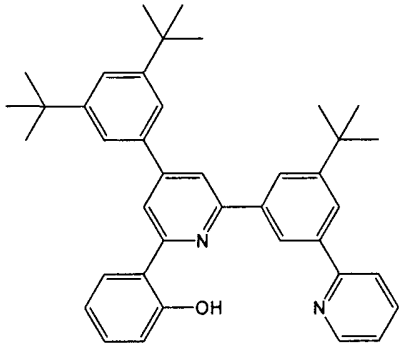

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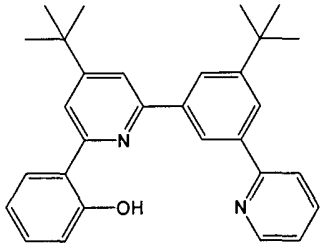

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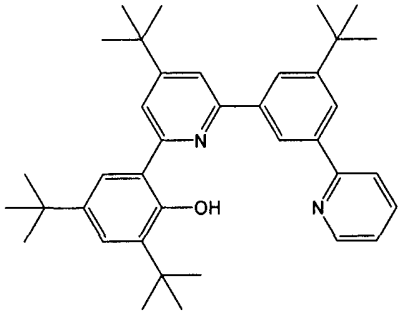

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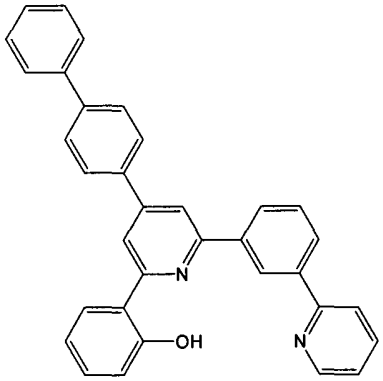

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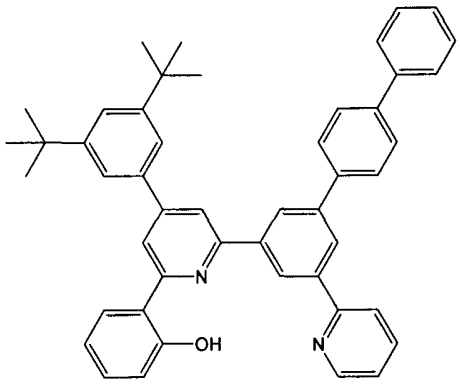
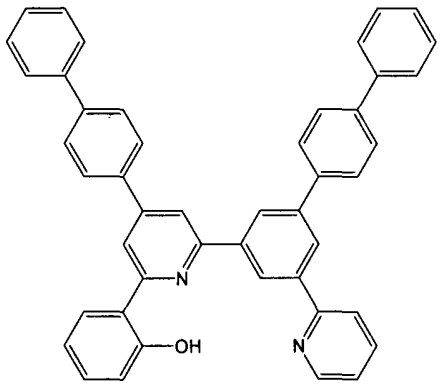
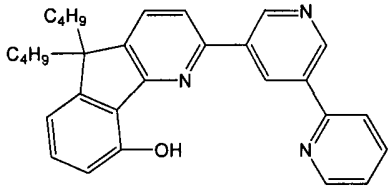
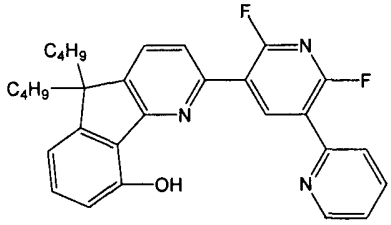
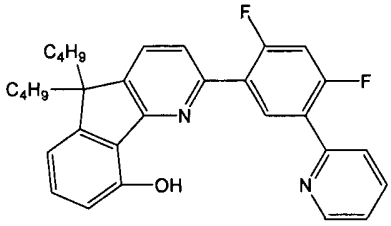
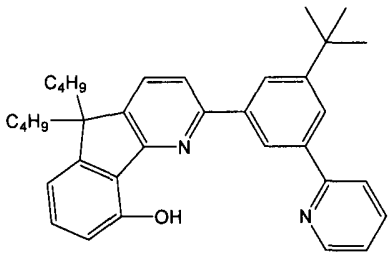
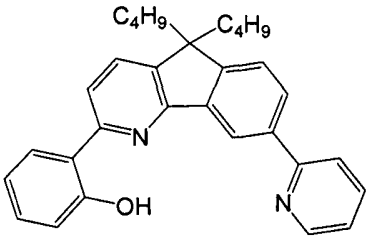
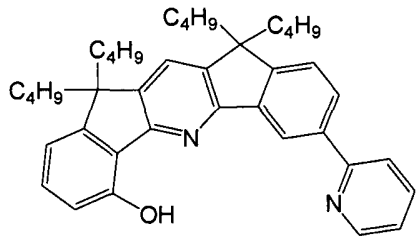


Ligand 220

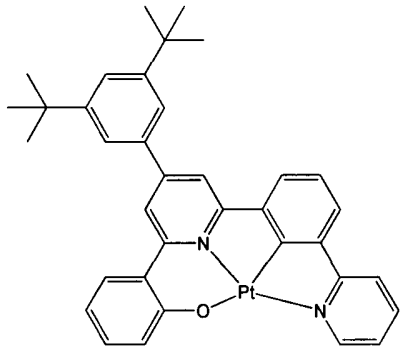
 Ligand 221	 Ligand 222
 Ligand 223	 Ligand 224
 Ligand 225	 Ligand 226
 Ligand 227	

The platinum(II) complexes in current invention (represented by Structure I) can be prepared a series of reactions depicted in Figure 2.

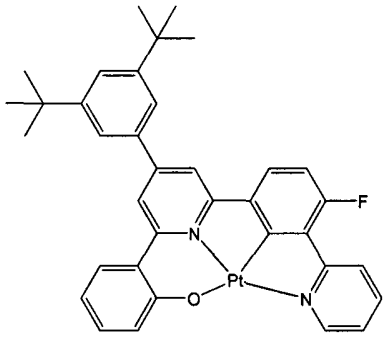
A ligand with structure II is reacted with a platinum compound, such as potassium tetrachloroplatinate, in a suitable solvent(s) (such as acetic acid or mixture

of acetic acid and chloroform) at a suitable temperature (such as refluxing acetic acid). Platinum compounds include platinum salts, especially those containing platinum(II).

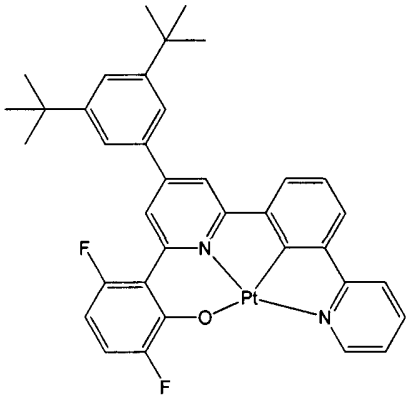
Specific examples of the platinum(II) complexes are shown but not restricted to below:



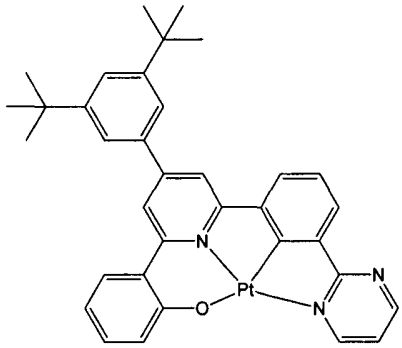
Complex 101



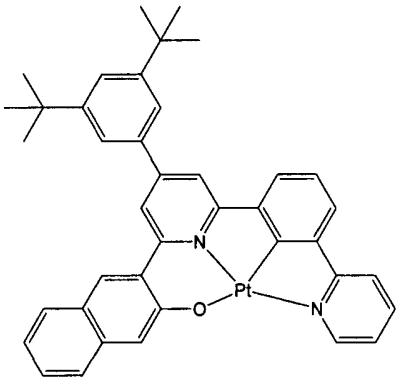
Complex 102



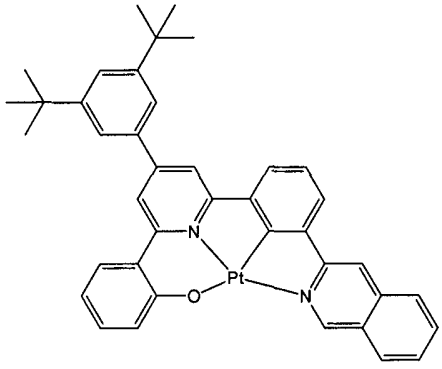
Complex 103



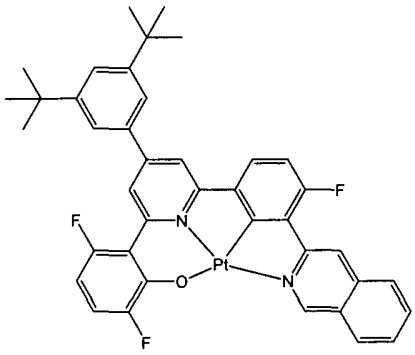
Complex 104



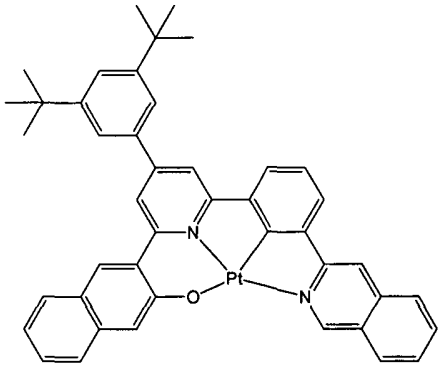
Complex 105



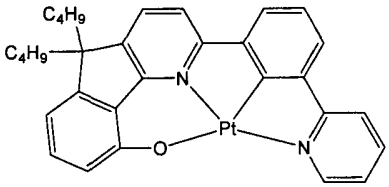
Complex 106



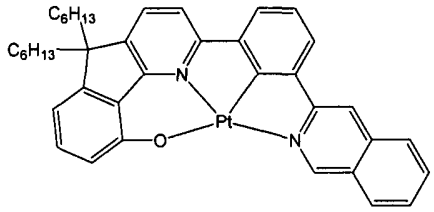
Complex 107



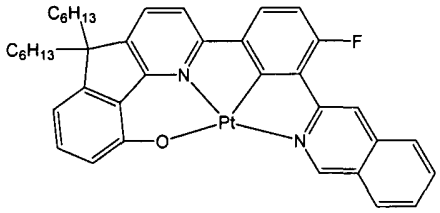
Complex 108



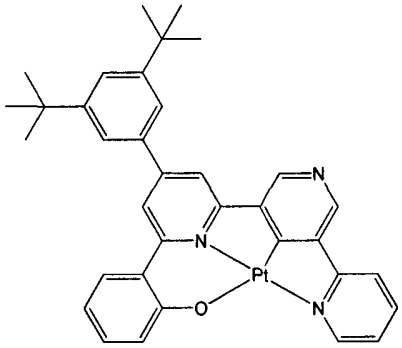
Complex 109



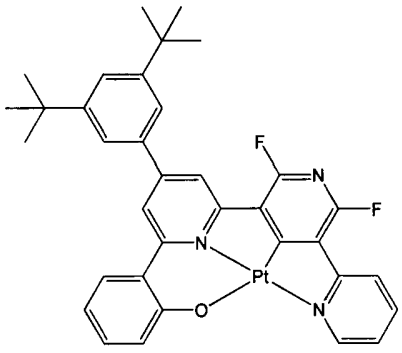
Complex 110



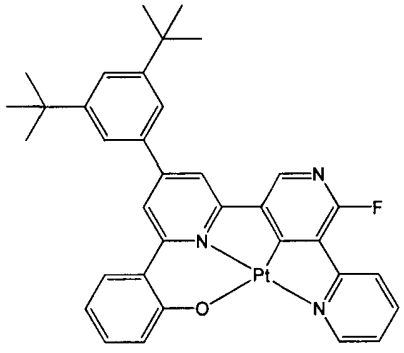
Complex 111



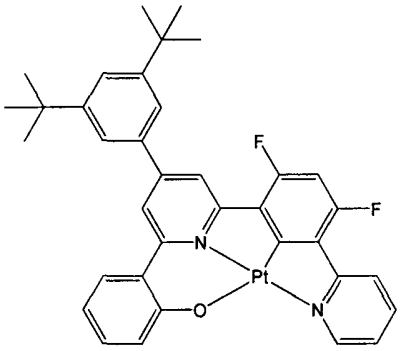
Complex 112



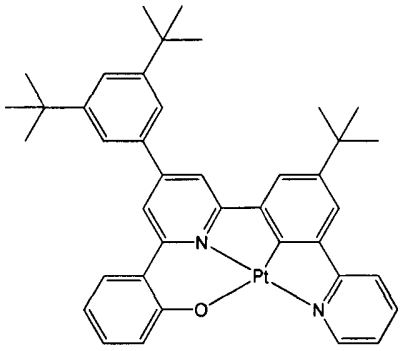
Complex 213



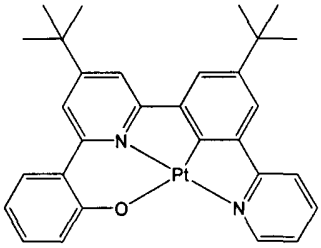
Complex 214



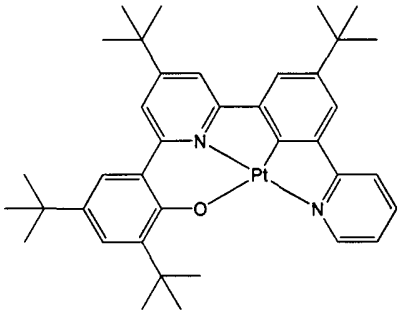
Complex 215



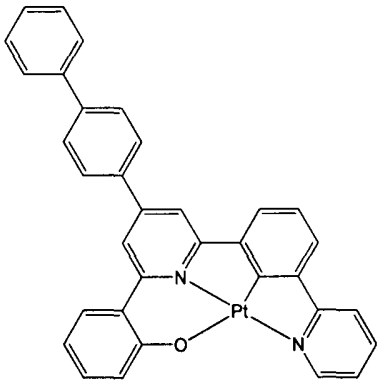
Complex 216



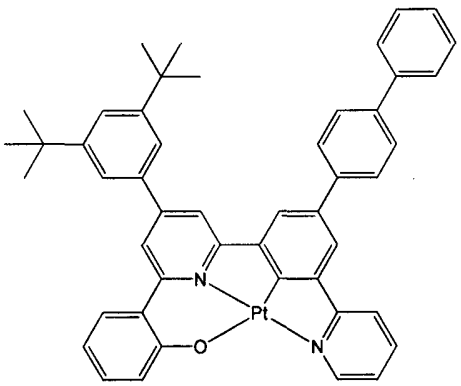
Complex 217



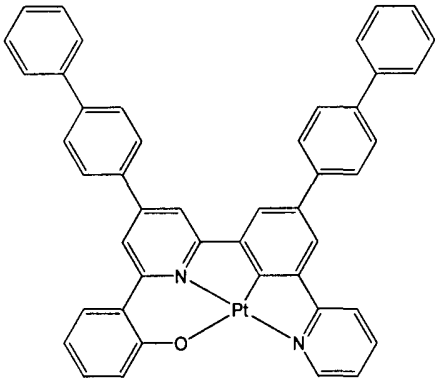
Complex 218



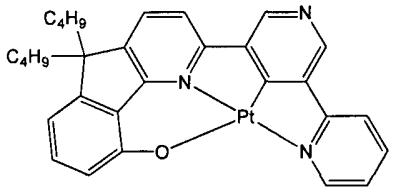
Complex 219



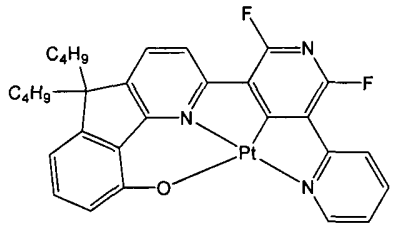
Complex 220



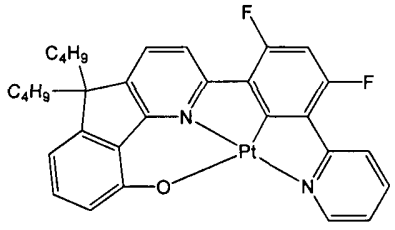
Complex 221



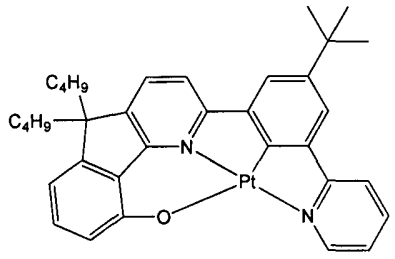
Complex 222



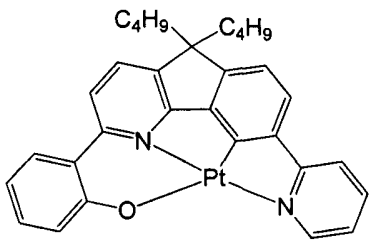
Complex 223



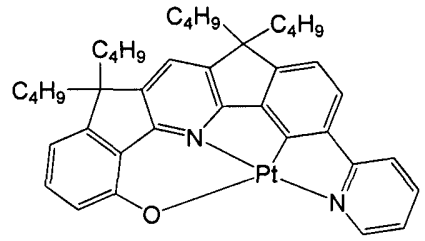
Complex 224



Complex 225



Complex 226



Complex 227

Making use of the complexes with Structure I, thermal deposition and solution process OLED can be fabricated. Below are examples for the preparation, physical properties and electroluminescent data for the platinum(II) complexes as described herein. The examples are set forth to aid in an understanding of the invention 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.

Unless otherwise indicated in the following examples and elsewhere in the specification and claims, all parts and percentages are by weight, all temperatures are in degrees Centigrade, and pressure is at or near atmospheric pressure.

Other than in the operating examples, or where otherwise indicated, all numbers, values and/or expressions referring to quantities of ingredients, reaction conditions, etc., used in the specification and claims are to be understood as modified in all instances by the term "about."

With respect to any figure or numerical range for a given characteristic, a figure or a parameter from one range may be combined with another figure or a parameter

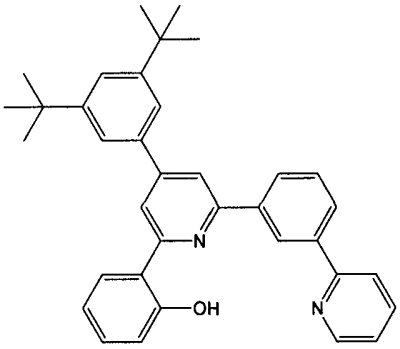
from a different range for the same characteristic to generate a numerical range.

Example 401

General preparation method for ligand with chemical structure of Structure II: Refer to Figure 1, aromatic system C, which contains a precursor group for coupling reaction(F_1) and a precursor group for pyridine ring formation reaction(F_4) or a precursor group for making F_4(F_3), is coupled with a nitrogen containing heterocyclic aromatic system D, which contains a precursor group for pyridine ring formation reaction(F_2), through metal coupling. If the aromatic system C contains F_3, it will then be transformed to F_4 by functional group transformation reaction. The resultant products is then reacted with aromatic system A, which contains a methoxy group and a precursor group for pyridine ring formation(F_6) by pyridine ring formation reaction. (If aromatic system A with F_6 is not commercially available, a functional group transformation reaction will be performed to transform the precursor group for making F_5(F_6) to F_6.) Finally, the methoxy group is transformed to hydroxyl group by demethylation reaction.

Example 402

Preparation of Ligand 201

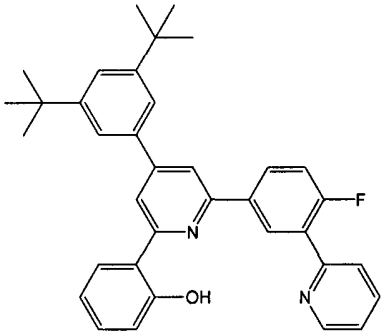


Ligand 201 was prepared by the procedures in Example 401 with:
A: benzene; C: benzene; D: pyridine; F_1: boronic acid; F_2: triflate; F_3: acetyl; F_4: 1-(2-oxoethyl)-pyridinium iodide; F_5: acetyl; F_6: 3-[3,5-bis(*tert*-butyl)phenyl]-2-Propenal; coupling reaction: Suzuki reaction; functional group transformation 1: pyridinium salt formation reaction; functional group transformation 2: alpha beta unsaturated ketone formation reaction; pyridine ring formation: reaction in the presence of ammonium acetate and methanol; demethylation: melting pyridine hydrogen chloride. Yield: 72%. ^{1}H NMR (500 MHz, $CDCl_3$): 1.43 (s, 18H), 6.98 (t, J = 8.1 Hz, 1H), 7.08 (d, J = 8.6 Hz, 1H), 7.26–7.28 (m, 1H), 7.36 (t, J = 8.4 Hz, 1H), 7.53 (s, 2H), 7.60 (s, 1H), 7.67 (t, J = 7.8 Hz, 1H), 7.82 (t, J = 7.2 Hz, 1H), 7.85 (d, J = 7.4 Hz, 1H), 7.90 (s, 1H), 7.95 (d, J = 8.1 Hz, 1H), 8.04 (s, 1H), 8.07 (d, J = 8.4 Hz,

1H), 8.13 (d, J = 7.8 Hz, 1H), 8.59 (s, 1H), 8.73 (d, J = 7.4 Hz, 1H), 14.84 (s, 1H). MS(EI, +ve): 513 (M^+).

Example 403

Preparation of Ligand 202

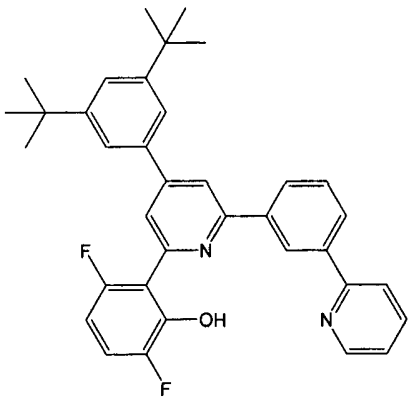


Ligand 202 was prepared by the procedures in Example 401 with:

A: benzene; C: fluorobenzene; D: pyridine; F_1: boronic acid; F_2: triflate; F_3: acetyl; F_4: 1-(2-oxoethyl)-pyridinium iodide; F_5: acetyl; F_6: 3-[3,5-bis(*tert*-butyl)phenyl]-2-Propenal; coupling reaction: Suzuki reaction; functional group transformation 1: pyridinium salt formation reaction; functional group transformation 2: alpha beta unsaturated ketone formation reaction; pyridine ring formation: reaction in the presence of ammonium acetate and methanol; demethylation: melting pyridine hydrogen chloride. Yield: 60%. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.42 (s, 18H, ^{t}Bu), 6.97 (t, J = 8.1 Hz, 1H), 7.07 (d, J = 7.1 Hz, 1H), 7.28–7.31 (m, 1H), 7.33–7.37 (m, 2H), 7.51 (s, 2H), 7.59 (s, 1H), 7.78–7.82 (m, 1H), 7.85–7.87 (m, 2H), 7.93 (d, J = 6.6 Hz, 1H), 8.02 (s, 1H), 8.04–8.08 (m, 1H), 8.55–8.58 (m, 1H), 8.75–8.77 (m, 1H), 15.02 (s, 1H, -OH).

Example 404

Preparation of Ligand 203

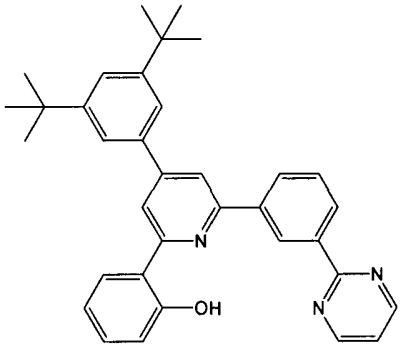


Ligand 203 was prepared by the procedures in Example 401 with:

A: *para*difluorobenzene; C: benzene; D: pyridine; F_1: boronic acid; F_2: triflate; F_3: acetyl; F_4: 1-(2-oxoethyl)-pyridinium iodide; F_5: acetyl; F_6: 3-[3,5-bis(*tert*-butyl)phenyl]- 2-Propenal; coupling reaction: Suzuki reaction; functional group transformation 1: pyridinium salt formation reaction; functional group transformation 2: alpha beta unsaturated ketone formation reaction; pyridine ring formation: reaction in the presence of ammonium acetate and methanol; demethylation: melting pyridine hydrogen chloride. Yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.43 (s, 18H, ^{t}Bu), 6.96–7.01 (m, 1H), 7.28–7.31 (m, 1H), 7.43–7.46 (m, 1H), 7.51 (s, 2H), 7.61 (s, 1H), 7.67 (t, J = 7.8 Hz, 1H), 7.82–7.86 (m, 2H), 7.93 (s, 1H), 7.96 (s, 1H), 8.06 (d, J = 7.1 Hz, 1H), 8.14 (d, J = 7.8 Hz, 1H), 8.57 (s, 1H), 8.73 (d, J = 3.8 Hz, 1H), 15.02 (s, 1H, -OH). ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -123.5, -132.5.

Example 405

Preparation of Ligand 204

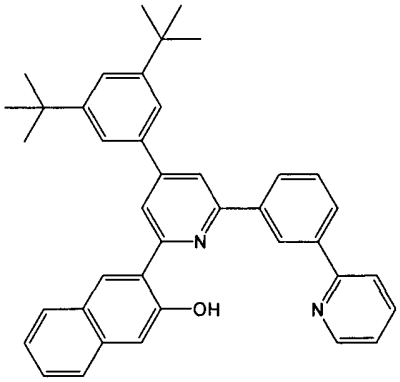


Ligand 204 was prepared by the procedures in Example 401 with:

A: benzene; C: benzene; D: pyrimidine; F_1: boronic acid; F_2: bromide; F_3: acetyl; F_4: 1-(2-oxoethyl)-pyridinium iodide; F_5: acetyl; F_6: 3-[3,5-bis(*tert*-butyl)phenyl]-2-Propenal; coupling reaction: Suzuki reaction; functional group transformation 1: pyridinium salt formation reaction; functional group transformation 2: alpha beta unsaturated ketone formation reaction; pyridine ring formation: reaction in the presence of ammonium acetate and methanol; demethylation: melting pyridine hydrogen chloride. Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.43 (s, 18H, ^{t}Bu), 6.97 (t, J = 7.1 Hz, 1H), 7.09 (d, J = 8.2 Hz, 1H), 7.22–7.25 (m, 1H), 7.36 (t, J = 8.3 Hz, 1H), 7.53 (s, 2H), 7.60 (s, 1H), 7.69 (t, J = 7.8 Hz, 1H), 7.93–7.96 (m, 2H), 8.04 (s, 1H), 8.16 (d, J = 7.7 Hz, 1H), 8.58 (d, J = 7.9 Hz, 1H), 8.86 (d, J = 7.9 Hz, 2H), 9.06 (s, 1H), 14.82 (s, 1H, -OH).

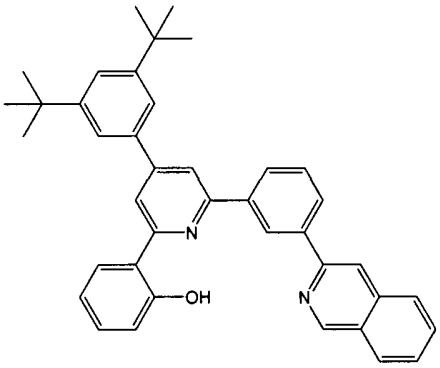
Example 406

Preparation of Ligand 205



Ligand 205 was prepared by the procedures in Example 401 with:
A: naphthalene; C: benzene; D: pyridine; F_1: boronic acid; F_2: triflate; F_3: acetyl; F_4: 1-(2-oxoethyl)-pyridinium iodide; F_5: acetyl; F_6: 3-[3,5-bis(*tert*-butyl)phenyl]-2-Propenal; coupling reaction: Suzuki reaction; functional group transformation 1: pyridinium salt formation reaction; functional group transformation 2: alpha beta unsaturated ketone formation reaction; pyridine ring formation: reaction in the presence of ammonium acetate and methanol; demethylation: melting pyridine hydrogen chloride. Yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.45 (s, 18H, ^{t}Bu), 7.27–7.32 (m, 2H), 7.42 (s, 1H), 7.47 (t, J = 6.9 Hz, 1H), 7.56 (s, 2H), 7.63 (s, 1H), 7.70 (t, J = 7.7 Hz, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.82–7.88 (m, 3H), 7.96 (s, 1H), 8.12 (d, J = 6.9 Hz, 1H), 8.17 (d, J = 7.8 Hz, 1H), 8.23 (s, 1H), 8.47 (s, 1H), 8.62 (s, 1H), 8.76 (d, J = 4.0 Hz, 1H), 14.52 (s, 1H, -OH).

Example 407
Preparation of Ligand 206

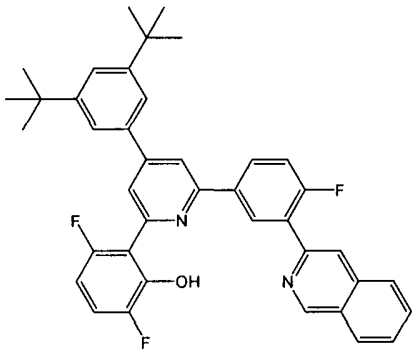


Ligand 206 was prepared by the procedures in Example 401 with:
A: benzene; C: benzene; D: isoquinoline; F_1: boronic acid; F_2: triflate; F_3: acetyl; F_4: 1-(2-oxoethyl)-pyridinium iodide; F_5: acetyl; F_6: 3-[3,5-bis(*tert*-butyl)phenyl]-2-Propenal; coupling reaction: Suzuki reaction; functional group transformation 1: pyridinium salt formation reaction; functional group transformation 2: alpha beta unsaturated ketone formation reaction; pyridine ring formation: reaction in the

presence of ammonium acetate and methanol; demethylation: melting pyridine hydrogen chloride. Yield: 77%.^{1}H NMR (500 MHz, $CDCl_3$): 1.44 (s, 18H), 6.98 (t, J = 8.1 Hz, 1H), 7.09 (d, J = 8.6 Hz, 1H), 7.35 (t, J = 8.4 Hz, 1H), 7.55 (s, 2H), 7.60–7.73 (m, 4H), 7.92–8.09 (m, 6H), 8.19 (s, 1H), 8.27 (d, J = 7.8 Hz, 1H), 8.72 (s, 1H), 9.38 (s, 1H), 14.88 (s, 1H). MS(EI, +ve): 563 (M^+).

Example 408

Preparation of Ligand 207

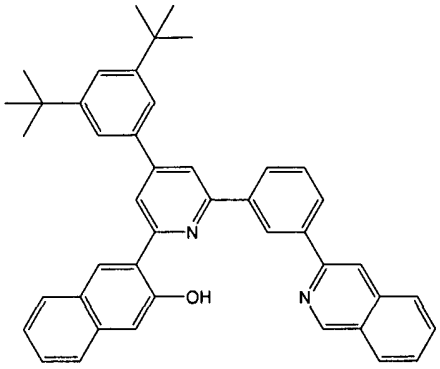


Ligand 207 was prepared by the procedures in Example 401 with:

A: *para*difluorobenzene; C: fluorobenzene; D: isoquinoline; F_1: boronic acid; F_2: triflate; F_3: acetyl; F_4: 1-(2-oxoethyl)-pyridinium iodide; F_5: acetyl; F_6: 3-[3,5-bis(*tert*-butyl)phenyl]- 2-Propenal; coupling reaction: Suzuki reaction; functional group transformation 1: pyridinium salt formation reaction; functional group transformation 2: alpha beta unsaturated ketone formation reaction; pyridine ring formation: reaction in the presence of ammonium acetate and methanol; demethylation: melting pyridine hydrogen chloride. Yield: 60%.^{1}H NMR (500 MHz, $CDCl_3$): 1.43 (s, 18H), 6.95–7.01 (m, 1H), 7.09 (d, J = 8.6 Hz, 1H), 7.36–7.45 (m, 2H), 7.51 (s, 2H), 7.61 (s, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.75 (t, J = 7.4 Hz, 1H), 7.91–8.06 (m, 5H), 8.28 (s, 1H), 8.75 (m, 1H), 9.38 (s, 1H), 15.02 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): -114.93, -123.42, -132.54. MS(EI, +ve): 617 (M^+).

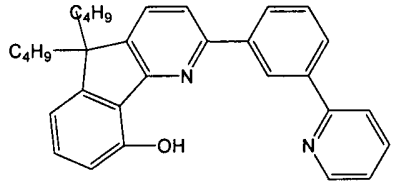
Example 409

Preparation of Ligand 208



Ligand 208 was prepared by the procedures in Example 401 with:
A: naphthalene; C: benzene; D: isoquinoline; F_1: boronic acid; F_2: triflate; F_3: acetyl; F_4: 1-(2-oxoethyl)-pyridinium iodide; F_5: acetyl; F_6: 3-[3,5-bis(*tert*-butyl)phenyl]-2-Propenal; coupling reaction: Suzuki reaction; functional group transformation 1: pyridinium salt formation reaction; functional group transformation 2: alpha beta unsaturated ketone formation reaction; pyridine ring formation: reaction in the presence of ammonium acetate and methanol; demethylation: melting pyridine hydrogen chloride. Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.46 (s, 18H, ^{t}Bu), 7.32 (t, J = 7.1 Hz, 1H), 7.43 (s, 1H), 7.44 (t, J = 7.1 Hz, 1H), 7.58 (s, 2H), 7.62–7.64 (m, 2H), 7.70–7.75 (m, 3H), 7.87 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 8.00 (s, 1H), 8.03 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 7.9 Hz, 1H), 8.21 (s, 1H), 8.24 (s, 1H), 8.29 (d, J = 7.9 Hz, 1H), 8.48 (s, 1H), 8.75 (s, 1H), 9.39 (s, 1H), 14.49 (s, 1H, -OH).

Example 410
Preparation of Ligand 209

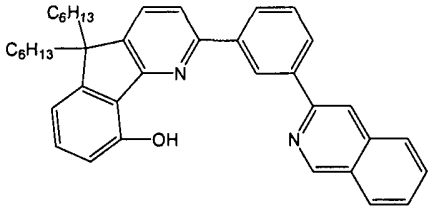


Ligand 209 was prepared by the procedures in Example 401 with:
A: 1-Indanone; C: benzene; D: pyridine; F_1: boronic acid; F_2: triflate; F_3: nil; F_4: acetyl; F_5: proton; F_6: *N*,*N*-dimethylethenamine; coupling reaction: Suzuki reaction; functional group transformation 1: nil; functional group transformation 2: reaction with dimethylacetamide; pyridine ring formation: a) reaction in the presence of potassium *tert*-butoxide and THF b) remove THF and reaction in the presence of ammonium acetate and methanol c) addition of butyl chains by reaction with 1-bromobutane in the presence of potassium *tert*-butoxide; demethylation: melting pyridine hydrogen chloride. Yield: 65%. ^{1}H NMR (500 MHz, $CDCl_3$): 0.70–0.73 (m, 10H), 1.09–1.16 (m, 4H), 1.97–2.03 (m, 4H), 6.90–6.94 (m, 2H), 7.28–7.29 (m, 1H),

7.33 (t, J = 7.8 Hz, 1H), 7.62 (t, J = 7.7 Hz, 1H), 7.70–7.71 (m, 2H), 7.80 (t, J = 8.5 Hz), 7.85 (d, J = 7.9 Hz, 1H), 8.06–8.11 (m, 2H), 8.65 (s, 1H), 8.75 (d, J = 4.7 Hz, 1H), 9.52 (s, br, 1H). MS(EI, +ve): 449 [M^+].

Example 411

Preparation of Ligand 210

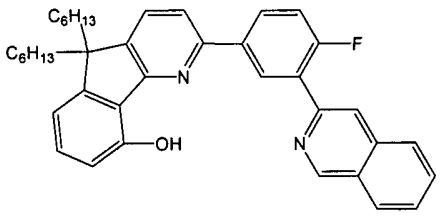


Ligand 210 was prepared by the procedures in Example 401 with:

A: 1-Indanone; C: benzene; D: isoquinoline; F_1: boronic acid; F_2: triflate; F_3: nil; F_4: acetyl; F_5: proton; F_6: *N,N*-dimethylethenamine; coupling reaction: Suzuki reaction; functional group transformation 1: nil; functional group transformation 2: reaction with dimethylacetamide; pyridine ring formation: a) reaction in the presence of potassium *tert*-butoxide and THF b) remove THF and reaction in the presence of ammonium acetate and methanol c) addition of hexyl chains by reaction with 1-bromohexane in the presence of potassium *tert*-butoxide; demethylation: melting pyridine hydrogen chloride. Yield: 73%.^{1}H NMR (500 MHz, $CDCl_3$): 0.72–0.80 (m, 10H), 1.05–1.17 (m, 12H), 1.95–2.05 (m, 4H), 6.92–6.95 (m, 2H), 7.34 (t, J = 7.8 Hz, 1H), 7.60 (t, J = 7.0 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.71–7.77 (m, 3H), 7.91 (d, J = 8.1 Hz, 1H), 8.01 (d, J = 7.9 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.18 (s, 1H), 8.21 (d, J = 7.9 Hz, 1H), 8.79 (s, 1H), 9.38 (s, 1H), 9.54 (s, br, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2): 13.98, 22.54, 24.02, 29.66, 31.48, 39.70, 54.32, 113.17, 114.25, 116.70, 117.98, 124.36, 125.57, 127.02, 127.18, 127.52, 127.57, 127.89, 129.28, 130.57, 130.91, 130.99, 136.66, 139.57, 140.14, 142.09, 151.04, 152.47, 152.53, 154.44, 155.14, 161.25. MS(EI, +ve): 555 [M^+].

Example 412

Preparation of Ligand 211



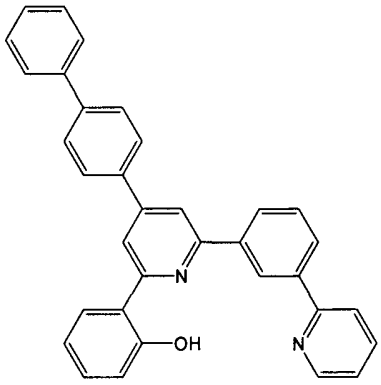
Ligand 211 was prepared by the procedures in Example 401 with:

A: 1-Indanone; C: fluorobenzene; D: isoquinoline; F_1: boronic acid; F_2: triflate; F_3: nil;

F_4: acetyl; F_5: proton; F_6: *N*,*N*-dimethylethenamine; coupling reaction: Suzuki reaction; functional group transformation 1: nil; functional group transformation 2: reaction with dimethylacetamide; pyridine ring formation: a) reaction in the presence of potassium *tert*-butoxide and THF b) remove THF and reaction in the presence of ammonium acetate and methanol c) addition of hexyl chains by reaction with 1-bromohexane in the presence of potassium *tert*-butoxide; demethylation: melting pyridine hydrogen chloride. Yield: 44%.^{1}H NMR (500 MHz, $CDCl_3$): 0.71–0.80 (m, 10H), 1.08–1.18 (m, 12H), 1.92–2.01 (m, 4H), 6.89–6.93 (m, 2H), 7.30–7.37 (m, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.70 (m, 2H), 7.75 (t, J = 7.5 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 8.09–8.12 (m, 1H)

Example 413

Preparation of Ligand 219



Ligand 219 was prepared by the procedures in Example 401 with:

A: benzene; C: benzene; D: pyridine; F_1: boronic acid; F_2: triflate; F_3: acetyl; F_4: 1-(2-oxoethyl)-pyridinium iodide; F_5: acetyl; F_6: 4,4'-biphenyl-2-Propenal; coupling reaction: Suzuki reaction; functional group transformation 1: pyridinium salt formation reaction; functional group transformation 2: alpha beta unsaturated ketone formation reaction; pyridine ring formation: reaction in the presence of ammonium acetate and methanol; demethylation: melting pyridine hydrogen chloride. Yield: 72%. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 6.99 (t, J = 8.2 Hz, 1H), 7.05 (d, J = 8.3 Hz, 1H), 7.29–7.32 (m, 1H), 7.32–7.38 (m, 1H), 7.40–7.43 (m, 1H), 7.49–7.52 (m, 2H), 7.67–7.72 (m, 3H), 7.81–7.86 (m, 3H), 7.89–7.93 (m, 3H), 8.03 (d, J = 8.1 Hz, 1H), 8.04 (s, 1H), 8.08–8.10 (m, 1H), 8.16–8.18 (m, 1H), 8.19 (s, 1H), 8.69 (s, 1H), 8.72–8.74 (m, 1H).

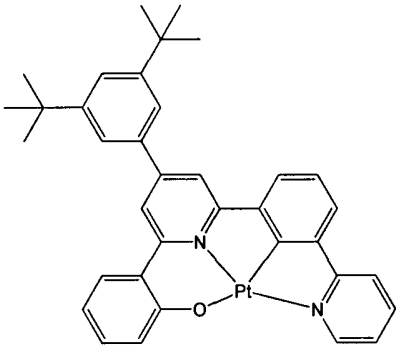
Example 414

General preparation method for complexes with Structure I:

Refer the Figure 2, ligand with Structure II is reacted with potassium

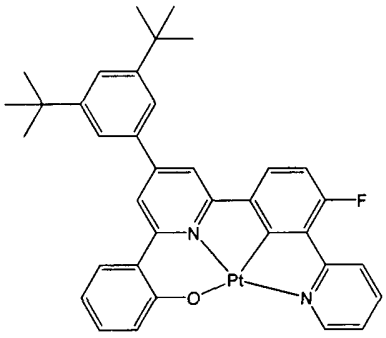
tetrachloroplatinate in the mixture of acetic acid and chloroform at 118 °C for 24 hours. The product is purified by column chromatography.

Example 415
Preparation of Complex 101



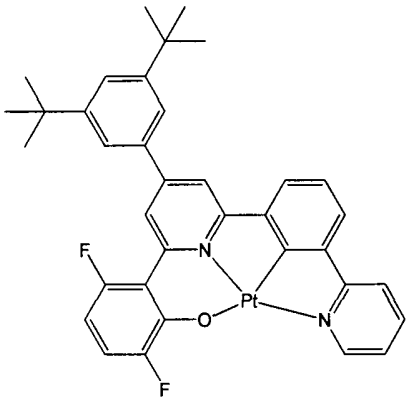
Complex 101 was prepared by Example 410 using Ligand 201. Yield: 80 %. ^{1}H NMR (500 MHz, CD_2Cl_2): 1.47 (s, 18H), 6.74 (t, J = 6.8 Hz, 1H), 7.24–7.29 (m, 2H),7.32–7.40 (m, 2H), 7.57 (d, J = 7.5 Hz, 1H), 7.66–7.69 (m, 4H), 7.78 (d, J = 8.9 Hz, 1H), 7.83 (s, 1H), 7.97 (t, J = 7.9 Hz, 1H), 8.17 (d, J = 8.5 Hz, 1H), 8.37 (s, 1H), 8.99 (d, J = 6.8 Hz, 1H). MS(FAB, +ve): 706 (M^+).

Example 416
Preparation of Complex 102



Complex 102 was prepared by Example 410 using Ligand 202. Yield: 70 %. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.49 (s, 18H, ^{t}Bu), 6.76–6.80 (m, 1H), 6.88–6.93 (m, 1H), 7.36–7.43 (m, 3H), 7.60 (s, 2H), 7.61–7.65 (m, 3H), 7.69 (s,1H), 7.98–8.01 (m, 2H), 8.14 (d, J = 7.3 Hz, 1H), 8.33 (s, 1H), 9.08 (d, J = 6.8 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -113.2.

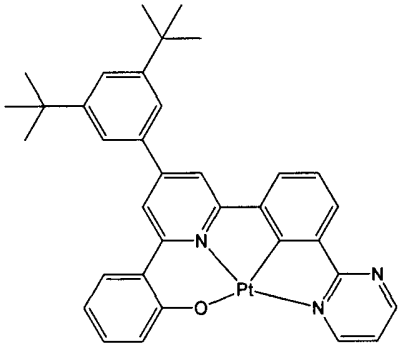
Example 417
Preparation of Complex 103



Complex 103 was prepared by Example 410 using Ligand 203. Yield: 80 %. ^{1}H NMR (500 MHz, DMF, 25 °C): δ = 1.43 (s, 18H, ^{t}Bu), 7.36–7.41 (m, 1H), 7.52 (t, J = 6.0 Hz, 1H), 7.69 (s, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.91 (s, 1H), 8.11–8.15 (m, 2H), 8.22 (t, J = 7.8 Hz, 1H), 8.29 (d, J = 8.1 Hz, 1H), 8.40 (s, 1H), 8.43 (s, 1H), 8.54 (s, 1H), 9.00 (d, J = 5.7 Hz, 1H). ^{19}F NMR (376 MHz, DMF, 25 °C): δ = -126.6, -129.3.

Example 418

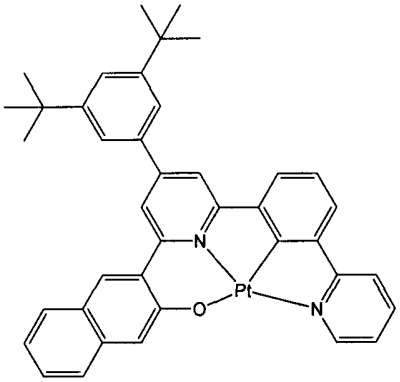
Preparation of complex 104



Complex 104 was prepared by Example 410 using Ligand 204. Yield: 80 % .^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 1.50 (s, 18H, ^{t}Bu), 6.74 (t, J = 6.9 Hz, 1H), 7.15 (s, 1H), 7.21–7.26 (m, 2H), 7.36 (t, J = 6.5 Hz, 1H), 7.67–7.71 (m, 6H), 8.12 (d, J = 7.8 Hz, 1H), 8.30 (s, 1H), 8.86 (s, 1H), 9.04 (m, 1H).

Example 419

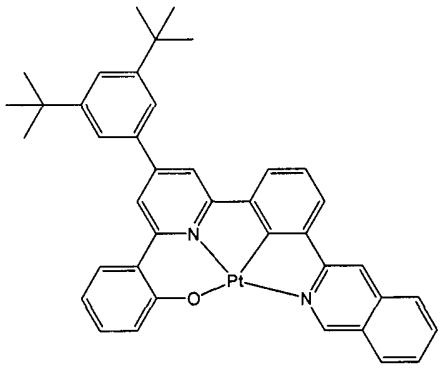
Preparation of complex 105



Complex 105 was prepared by Example 410 using Ligand 205. Yield: 60 %. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 1.48 (s, 18H, ^{t}Bu), 7.13 (t, J = 7.0 Hz, 1H), 7.30 (t, J = 7.4 Hz, 1H), 7.37–7.43 (m, 2H), 7.58–7.64 (m, 3H), 7.6–7.71 (m, 4H), 7.80–7.84 (m, 2H), 7.93 (s, 1H), 8.03 (t, J = 7.7 Hz, 1H), 8.54 (s, 1H), 8.69 (s, 1H), 9.0–9.04 (m, 1H).

Example 420

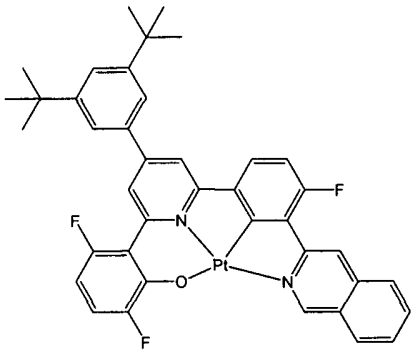
Preparation of Complex 106



Complex 106 was prepared by Example 410 using Ligand 206. Yield: 80 %. ^{1}H NMR (500 MHz, CD_2Cl_2): 1.48 (s, 18H), 6.74 (t, J = 6.8 Hz, 1H), 7.28–7.42 (m, 3H), 7.60–7.70 (m, 6H), 7.80–7.90 (m, 3H), 8.03 (s, 1H), 8.13–8.17 (m, 2H), 8.35 (s, 1H), 9.65 (s, 1H). MS(FAB, +ve): 756 (M^+).

Example 421

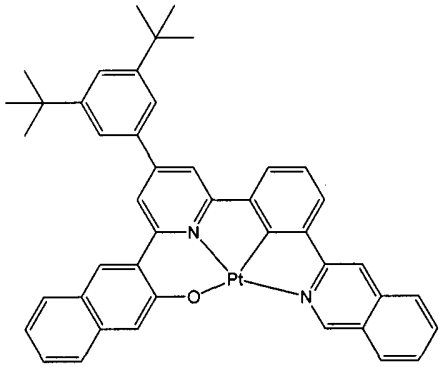
Preparation of Complex 107



Complex 107 was prepared by Example 410 using Ligand 207. Yield: 65 %. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.49 (s, 18H, ^{t}Bu), 6.68–6.73 (m, 1H), 6.82–6.87 (m, 1H), 7.28–7.29 (m, 1H), 7.34–7.36 (m, 1H), 7.39 (s, 1H), 7.56 (s, 2H), 7.62–7.66 (m, 2H), 7.75–7.82(m, 2H), 7.95–8.01 (m, 3H), 9.32 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = -113.8, -126.3, -129.7.

Example 422

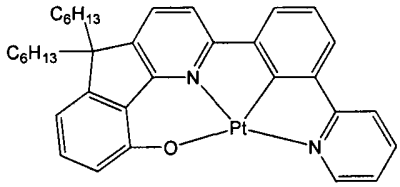
Preparation of Complex 108



Complex 108 was prepared by Example 410 using Ligand 208. Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.54 (s, 18H, ^{t}Bu), 6.88–6.93 (m, 2H), 7.01 (t, J = 7.5 Hz, 1H), 7.06–7.11 (m, 2H), 7.16–7.21 (m, 3H), 7.30 (t, J = 6.7 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.59–7.63 (m, 4H), 7.72 (s, 1H), 8.01 (d, J = 8.1 Hz, 1H), 8.58 (s, 1H), 8.68 (s, 1H), 8.80 (s, 1H).

Example 423

Preparation of Complex 109

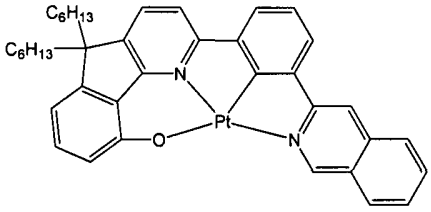


Complex 109 was prepared by Example 410 using Ligand 209. Yield: 65 %.^{1}H NMR (500 MHz, CD_2Cl_2): 0.69–0.80 (m, 10H), 1.10–1.18 (m, 4H), 2.00–2.15 (m, 4H), 6.75

(d, J = 7.1 Hz, 1H), 7.19 (d, J = 8.4 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 6.0 Hz, 1H), 7.49–7.53 (m, 2H), 7.57 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.92 (t, J = 7.7 Hz, 1H), 7.96 (d, J = 7.7 Hz, 1H), 9.12 (d, J = 5.3 Hz, 1H). MS(FAB, +ve): 642 [M^+].

Example 424

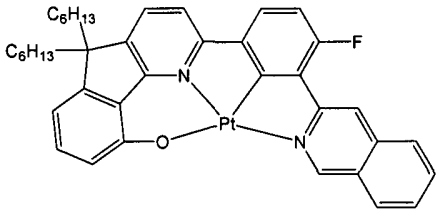
Preparation of Complex 110



Complex 110 was prepared by Example 410 using Ligand 210. Yield: 70 %. ^{1}H NMR (500 MHz, CD_2Cl_2): 0.76–0.85 (m, 10H), 1.03–1.19 (m, 12H), 2.01–2.13 (m, 4H), 6.74 (d, J = 7.0 Hz, 1H), 7.16 (d, J = 7.2 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H), 7.52–7.63 (m, 5H), 7.77–7.80 (m, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 8.08 (s, 1H, 8.14 (d, J = 7.9 Hz, 1H), 9.74 (s, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2): 13.72, 22.52, 24.05, 29.67, 31.49, 39.91, 55.38, 108.18, 113.77, 116.10, 119.30, 122.32, 122.54, 122.62, 125.70, 126.85, 127.68, 127.98, 128.60, 129.09, 132.51, 132.84, 136.64, 140.91, 141.41, 143.53, 153.74, 153.88, 154.50, 157.73, 160.81, 160.89, 162.73. MS(FAB, +ve): 748 [M^+].

Example 425

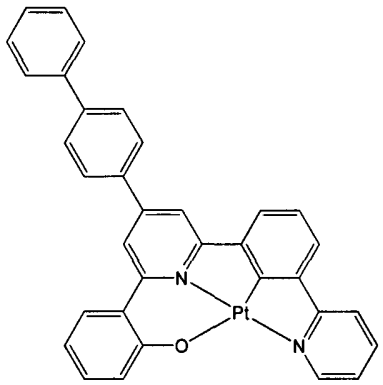
Preparation of Complex 111



Complex 111 was prepared by Example 410 using Ligand 211. Yield: 80 %.^{1}H NMR (500 MHz, $CDCl_3$): 0.68–0.77 (m, 10H), 1.02–1.12 (m, 12H), 2.00–2.07 (m, 4H), 6.71 (d, J = 7.0 Hz, 1H), 7.00 (dd, J = 8.4 Hz, $^3J_{F\text{-}H}$ = 11.9 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.62 (dd, J = 8.3 Hz, $^4J_{F\text{-}H}$ = 3.9 Hz, 1H), 7.71 (t, J = 8.6 Hz, 1H), 7.87 (t, J = 8.6 Hz, 1H), 7.90 (d, J = 7.7 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 8.18 (d, J = 8.1 Hz, 1H), 8.43 (s, 1H), 9.84 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): -114.17. MS(FAB, +ve): 766 [M^+].

Example 426

Preparation of Complex 219



Complex 219 was prepared by Example 410 using Ligand 219. Yield: 60 %. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 6.75 (t, J = 8.1 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 8.4 Hz, 1H), 7.36–7.46 (m, 3H), 7.51–7.58 (m, 2H), 7.65 (d, J = 7.6 Hz, 1H), 7.73–7.79 (m, 3H), 7.84 (d, J = 8.3 Hz, 2H), 7.88 (s, 1H), 7.96–8.00 (m, 3H), 8.18 (d, J = 7.4 Hz, 1H), 8.42 (s, 1H), 8.95 (d, J = 4.8 Hz, 1H).

Example 427

Photophysical properties for Complex 101 – Complex 112

	Absorption λ_{max} (molar extinction coefficient)	Emission λ_{max} (dichloromethane solution)	Solution quantum Yield
Complex 101	242 (37400); 285 (38400); 372 (13800); 437 (sh) 5600	502	0.76
Complex 102	242 (4.19), 253 (4.07), 284 (4.45), 301 (3.52), 363 (1.71), 400 (1.14), 424 (0.86)	511	0.83
Complex 103	242 (3.65), 287 (3.88), 370 (1.59), 425 (0.73)	526	0.71
Complex 106	248 (5.72), 285 (5.30), 300 (5.23), 381 (1.79), 419 (0.92), 494 (0.26)	528	0.17
Complex 107	248 (4.20), 259 (4.24), 284 (3.84), 296 (3.92), 380 (1.65), 441 (0.32)	534	0.61
Complex 108	292 (56100); 303 (49500);	523	0.60

	369 (25600); 403 (10600); 445 (sh) (2400)		
Complex 109	252 (6.45), 288 (5.36), 374 (1.52), 398 (1.49), 530 (0.18)	661	0.019
Complex 110	254 (39800); 354 (15400); 390 (12700); 424 (sh) (8186)	496	0.63
Complex 111	255 (55300); 275 (47900); 293 (35600); 364 (20800); 398 (16300); 427 (sh) (5900)	528	0.38
Complex 112	273 (56900); 290 (41800); 357 (21800); 393 (17400); 415 (sh) (9400)	517	0.47

Example 428

General thermal deposition OLED fabrication method.

On an anode coated transparent substrate, hole transporting layer(s), emitting layer(s), electron transporting layer(s), electron injection layer and a metal cathode were deposited sequentially under a high vacuum environment (pressure < 1 x 10^{-6} torr).

Example 429

A device fabricated with example 428 wherein the hole transporting layers are 10 nm of N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine(NPB) and 30nm of 4,4',4" -tris(carbazol-9-yl)triphenylamine(TCTA), the emitting layer is 30 nm of complex 101 doped TCTA layer (2.8% complex 101), the electron transporting layer is 30 nm of 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline(BCP), the electron injection layer is 1 nm of lithium fluoride and the metal cathode is 100 nm of aluminum.

Example 430

A device fabricated with Example 428 wherein the hole transporting layer is 40 nm of NPB, the emitting layer is 20 nm of complex 106 doped 4,4'-Bis(carbazol-9-yl)biphenyl(CBP) layer (4.4% complex 106), the electron transporting layers are 15 nm of BCP and 30 nm of Tris(8-hydroxy-quinolinato)aluminium (Alq), the electron injection layer is 1 nm of

lithium fluoride and the metal cathode is 100 nm of aluminum.

Example 431

A device fabricated with Example 428 wherein the hole transporting layer is 40 nm of NPB, the emitting layer is 20 nm of complex 110 doped 1,3-Bis(carbazol-9-yl)benzene(mCP) layer (4.9% complex 110), the electron transporting layer is 30 nm of BCP, the electron injection layer is 1 nm of lithium fluoride and the metal cathode is 100 nm of aluminum.

Example 432

A device fabricated with Example 428 wherein the hole transporting layer is 40 nm of NPB, the emitting layers are 20 nm of complex 110 doped CBP(2.6% complex 110) and 20 nm complex 107 doped 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi; 2.9% complex 107) layers, the electron transporting layer is 30 nm of BCP, the electron injection layer is 1 nm of lithium fluoride and the metal cathode is 100 nm of aluminum.

Example 433

A device fabricated with Example 428 wherein the hole transporting layer is 40 nm of NPB, the emitting layers are 20 nm of complex 101 doped mCP(3.1% complex 101) and 20 nm complex 101 doped CBP(3.5% complex 101) layers, the electron transporting layer is 30 nm of BCP, the electron injection layer is 1 nm of lithium fluoride and the metal cathode is 100 nm of aluminum.

Example 434

A device fabricated with Example 428 wherein the hole transporting layer is 40 nm of NPB, the emitting layers are 20 nm of complex 101 doped TCTA(1.3% complex 101), 10 nm complex 101 doped CBP(1.2% complex 101) and 20 nm complex 101 doped TPBi(1.5% complex 101) layers, the electron transporting layer is 30 nm of BCP, the electron injection layer is 1 nm of lithium fluoride and the metal cathode is 100 nm of aluminum.

Example 435

A device fabricated with Example 428 wherein the hole transporting layer is 40 nm of NPB, the emitting layers are 20 nm of complex 101 doped TCTA(1.1% complex 101) and 20 nm complex 101 doped TPBi(1.2% complex 101) layers, the electron transporting layer is 30 nm of BCP, the electron injection layer is 1 nm of lithium fluoride and the metal cathode is 100 nm of aluminum.

Example 436

A device fabricated with Example 428 wherein the hole transporting layer is 40 nm of NPB, the emitting layer is 100 nm of complex 101 doped CBP(1.1% complex 101) layer, the electron transporting layer is 30 nm of BCP, the electron injection layer is 1 nm of lithium fluoride and the metal cathode is 100 nm of aluminum.

Example 439

Fabrication of single emitter WOLED.

A single emitter WOLED fabricated with Example 428 wherein the hole transporting layer is 40 nm of NPB, the emitting layer is 30 nm of complex 224 doped mCP(9% complex 224) layer, the electron transporting layer is 40 nm of BAlQ, the electron injection layer is 0.5 nm of lithium fluoride and the metal cathode is 80 nm of aluminum.

Example 437

The performances for the devices in above examples are shown below:

Example	EL λ_{max}	CIE	Efficiency$_{max}$ cd/A@ current density mA/cm^2
429	512	0.31, 0.61	7.59/ 3.53
430	543	0.39, 0.58	20.7/ 1.05
431			10.5/ 0.76
432	524	0.34, 0.56	11.9/ 0.15
433	516	0.31, 0.59	10.7/ 1.91
434	508	0.26, 0.63	17.3/ 7.0
435	512	0.26, 0.64	12.6/ 1.14
436	512	0.26, 0.64	22.2/0.58
439	483, 619	0.37, 0.43	36.4/0.021

Example 438

Solution process OLED fabrication.

A layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PPS) (~ 40 nm) was deposition on indium tin oxide (ITO) glass by spin coating and dried in an oven. 5 % complex 101 in PVK was dissolved in chlorobenzene in 20 mg/ mL ratio. The 5 % complex 101 doped PVK was spin coated on the top of PEDOT:PPS layer and dried in an oven (~80 nm). 10 nm of BCP, 30 nm of Alq, 1 nm LiF and 100 nm of Al layers were sequentially deposited on top of the polymer layer by thermal deposition (pressure < 1 x 10^{-6} torr). This device has CIE,

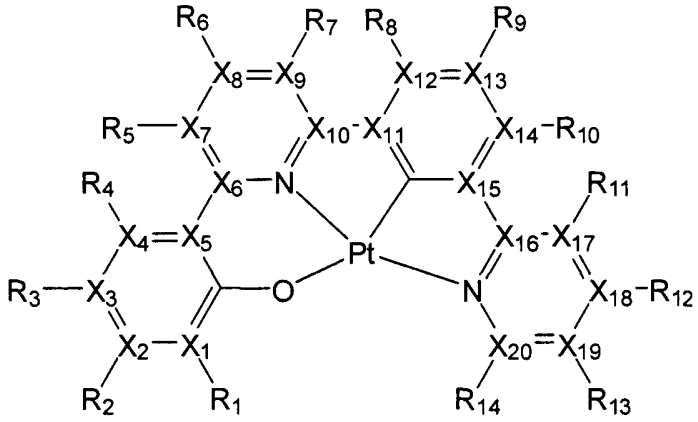
brightness$_{max}$ and efficiency$_{max}$ of (0.31, 0.61), 17,800 cdm^{-2} and 10.9 cdA^{-1} respectively.

While the invention has been explained in relation to certain embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

Claims

What is claimed is:

1. An organometallic complex having a chemical structure of structure I:

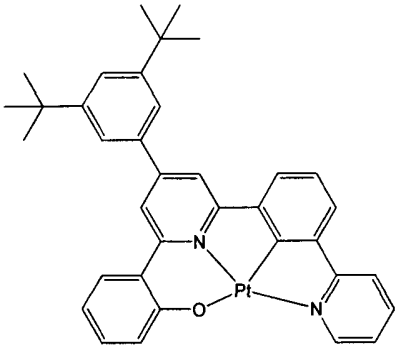


Structure I

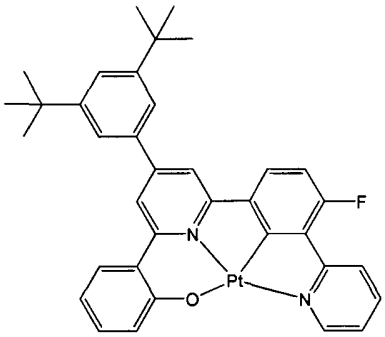
wherein R_1–R_{14} are independently hydrogen, halogen, hydroxyl, an unsubstituted alkyl, a substituted alkyl, cycloalkyl, an unsubstituted aryl, a substituted aryl, acyl, alkoxy, acyloxy, amino, nitro, acylamino, aralkyl, cyano, carboxyl, thio, styryl, aminocarbonyl, carbamoyl, aryloxycarbonyl, phenoxycarbonyl, or an alkoxycarbonyl group, each R_1–R_{14} may independently form 5 – 8 member ring(s) with adjacent R group(s), X_1 – X_{20} are independently boron, carbon, nitrogen, oxygen, or silicon.

2. The organometallic complex of claim 1, wherein R_1= halogen or alkyl having from 1 to 20 carbon atoms, R_3= alkyl having from 1 to 20 carbon atoms, R_4=halogen, R_6= alkyl having from 1 to 20 carbon atoms, or aryl having from 6 to 30 carbon atoms substituted by alkyl having from 1 to 20 carbon atoms or aryl having from 6 to 30 carbon atoms, R_8= halogen, R_9= alkyl having from 1 to 20 carbon atoms, or aryl having from 6 to 30 carbon atoms substituted by aryl having from 6 to 30 carbon atoms, R_{10}= halogen, X_{14} = heteroatom, X_{13} = heteroatom, X_{17} = heteroatom, each R_1–R_{14} may independently form an aryl having from 6 to 8 carbon atoms or cycloalkyl containing 3 to 7 carbon atoms with adjacent R group(s).

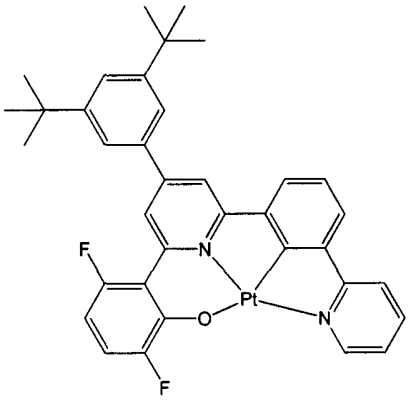
3. The organometallic complex of claim 1 which is one of:



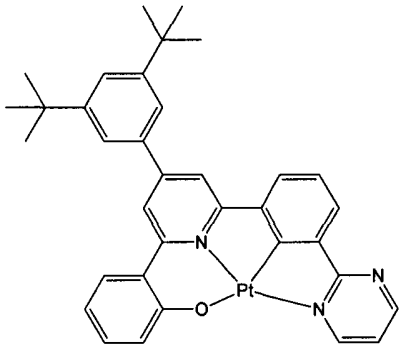
Complex 101



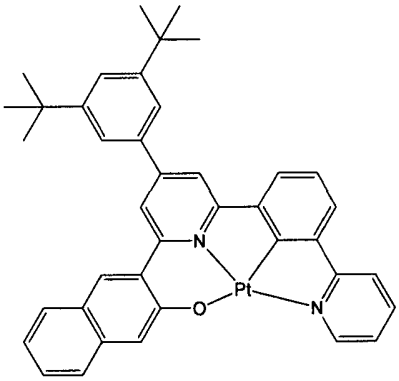
Complex 102



Complex 103



Complex 104



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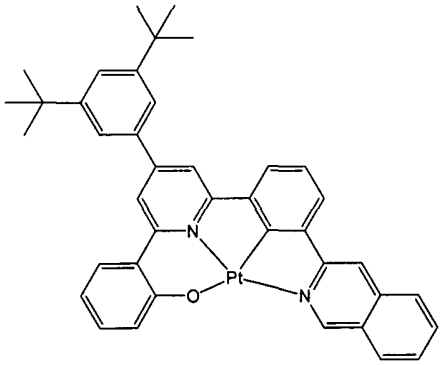
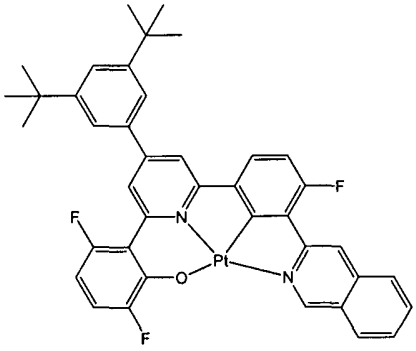
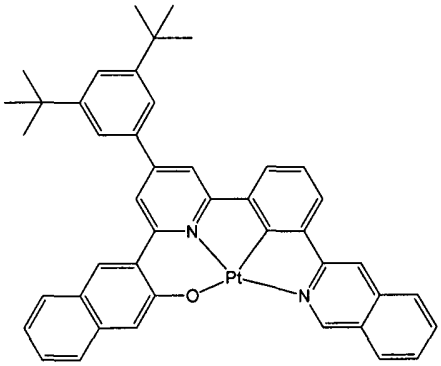


Complex 106



Complex 107



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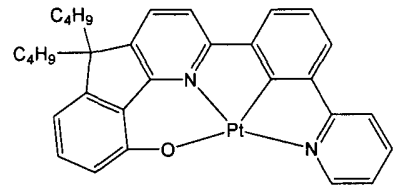
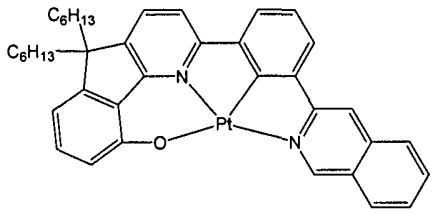
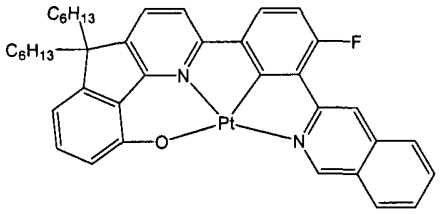
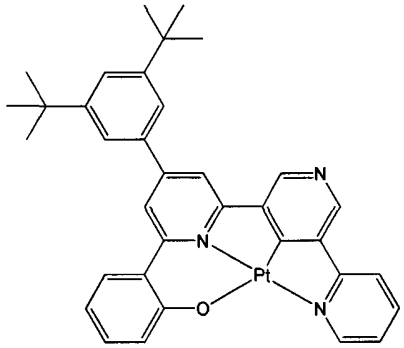
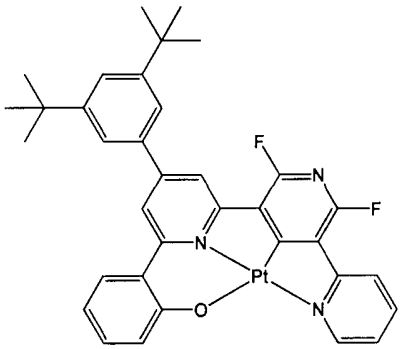
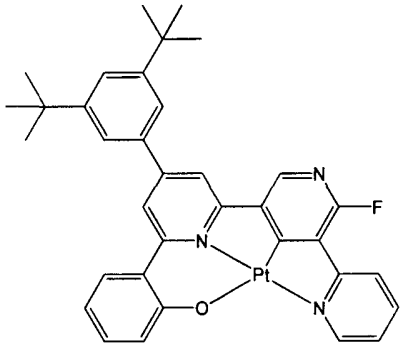
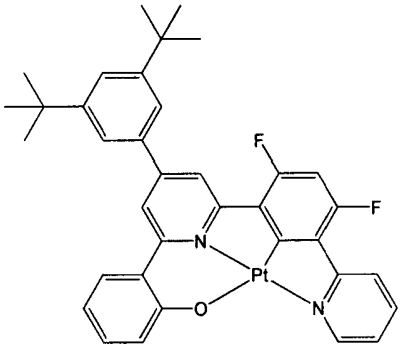
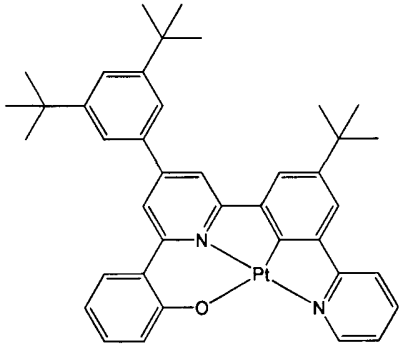
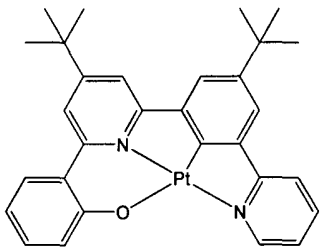
 Complex 109	 Complex 110
 Complex 111	 Complex 112
 Complex 213	 Complex 214
 Complex 215	 Complex 216



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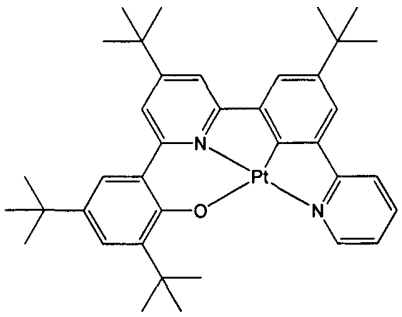

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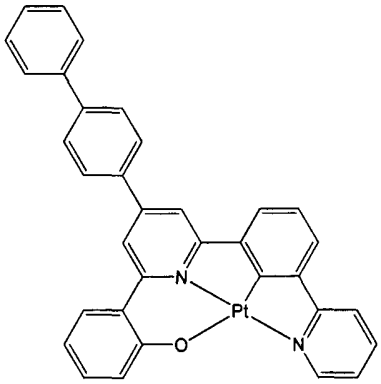

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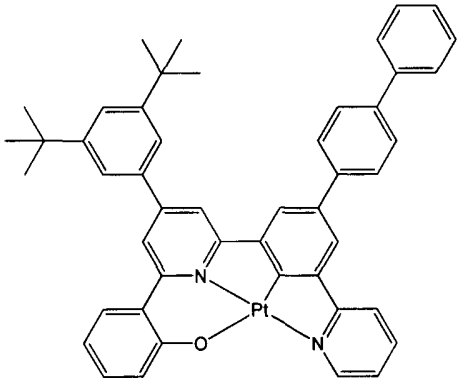
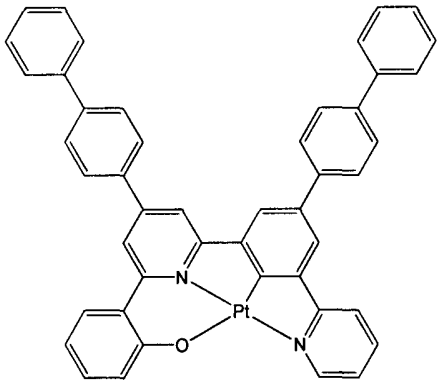
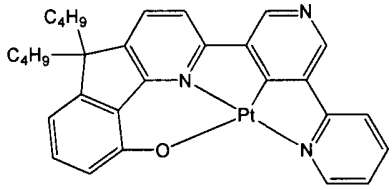


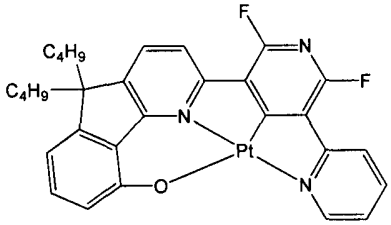
Complex 220



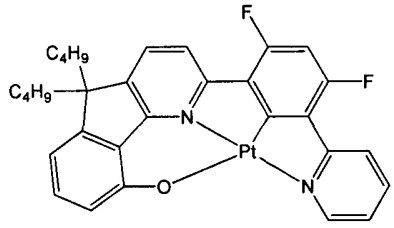
Complex 221



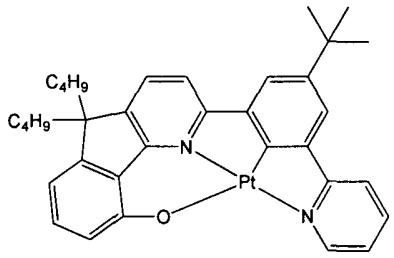
Complex 222



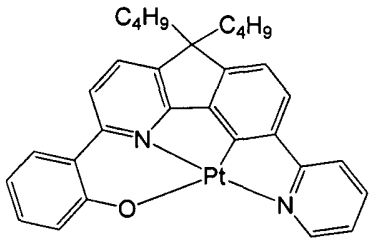
Complex 223



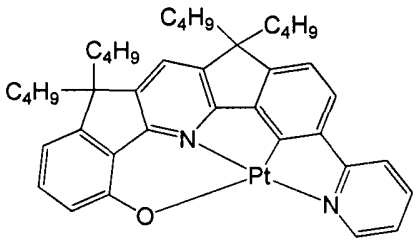
Complex 224



Complex 225



Complex 226



Complex 227

4. An organic light-emitting diode or polymer light-emitting diode comprising one or more organometallic complex described in any one of claims 1 to 3 as a light-emitting material(s).

5. An organic light-emitting diode or polymer light-emitting diode of claim 4, wherein the organic light-emitting diode is fabricated by thermal deposition, by spin coating or by printing.

6. An organic light-emitting diode or polymer light-emitting diode of any one of claims 4-5, wherein it emits a single color emission originating from the organometallic complex.

7. An organic light-emitting diode or polymer light-emitting diode of any one of claims 4-5, wherein it emits a green color with the x-coordinate of CIE ≤ 0.31 and y-coordinate of the CIE ≥ 0.59.

8. An organic light-emitting diode or polymer light-emitting diode of any one of claims 4-5, wherein it emits white emission which all the emission components come from the organometallic the complex.

9. An organic light-emitting diode or polymer light-emitting diode of any one of claims 4-5, wherein it emits a white emission which is combining emission from the

organometallic complex and one or more different emission component(s) from another emitting material(s).

10. A method to prepare the organometallic complex of any one of claims 1 to 3, comprising:

coupling a first aromatic system with a nitrogen containing heterocyclic aromatic system to form an intermediate;

reacting the intermediate with a second aromatic system to form a ligand; and

reacting the ligand with a platinum compound to form said organometallic complex.

11. The method of claim 10, wherein the second aromatic system comprises a methoxy group and a precursor group for pyridine ring formation.

12. The method of claim 11, further comprising demethylating the ligand before reacting the ligand with the platinum compound.

13. The method of claim 10, wherein the platinum compound is potassium tetrachloroplatinate.

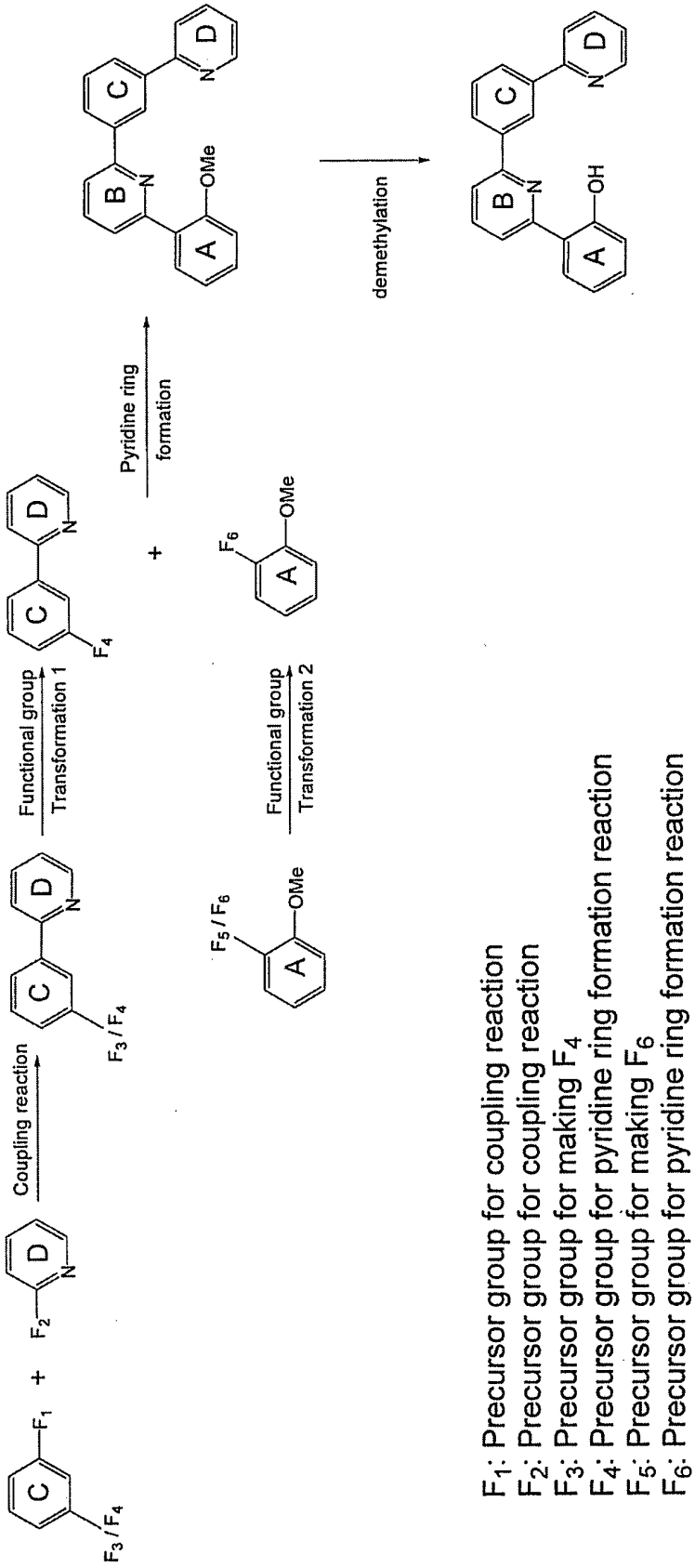

Coupling reaction
Functional group Transformation 1
Functional group Transformation 2
Pyridine ring formation
demethylation
F1: Precursor group for coupling reaction
F2: Precursor group for coupling reaction
F3: Precursor group for making F4
F4: Precursor group for pyridine ring formation reaction
F5: Precursor group for making F6
F6: Precursor group for pyridine ring formation reaction

Figure 1

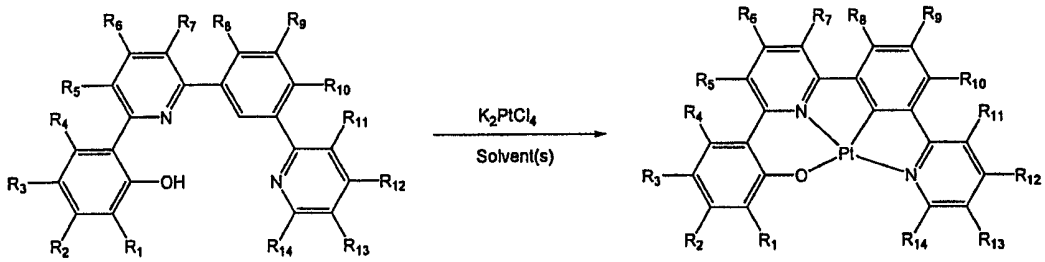

R6
R7
R8
R9
R5
R10
R4
N
R11
R3
OH
N
R12
R2
R1
R14
R13
K2PtCl4
Solvent(s)
Pt
O

Figure 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2011/001184

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C07F 17, C09K 11, H01L 51

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)

CNPAT, CNKI, WPI, EPODOC, REGISTRY, CAPLUS(STN)

PLATINUM, PT, PLATINIC, +PLATINATE?, +PYRIDINE?, +PYRIDINIUM?, +QUINOLINE, OLED?, DIODE?, SEARCH ACCORDING TO THE STRUCTURES OF THE COMPLEXES IN CLAIM 1

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1683804 A2 (TAKASAGO INT CORP), 26 July 2006 (26.07.2006), see the whole document	1-13
A	WO 2005068074 A2 (CIBA SC HOLDING AG), 28 July 2005 (28.07.2005), see the whole document	1-13

☐ 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

"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 Sep 2011(13.09.2011)	**27 Oct. 2011 (27.10.2011)**
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer CHANG, Xiaoyu Telephone No. (86-10)62084403

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A. CLASSIFICATION OF SUBJECT MATTER

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

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